

# Report

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## Future diesel-like renewable fuels - A literature review



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## ABSTRACT

IFP Energies Nouvelles was commissioned by Concawe to identify novel sustainable liquid fuels pathways by 2030 for heavy duty trucks applications. The study consists of an extensive literature review to address three main topics: (1) the overall fuel production pathways from the resources, the processes, and the renewable components; (2) renewable fuels performances through engine tests and blending behavior; and (3) life cycle and techno-economic assessment of selected pathways. The work is combined with interview sessions of relevant stakeholders involved in fuel production or use.

The study contributed to shed light on opportunities and limitations related to the development of novel renewable diesel-like fuel. Three main constraints were identified for the development of novel fuel production pathways. First, the availability of sustainable feedstock in the 2030 horizon; second, some dedicated fuel conversion processes are potentially mature for certain routes while other require important investments and time to be developed which may not be compatible with the 2030 timeframe; finally, along with the large number of renewable products identified, an evaluation of their “drop-in” capabilities was performed. This evaluation remains partial for most of the compounds, except for the well-known conventional renewable products, i.e. fatty acid methyl esters and paraffinic fuels (e.g. hydrotreated vegetable oil alike). This evaluation includes their overall compatibility with current fuel specifications or more globally their impact on engine/vehicle hardware and emissions.

Two main routes were considered.

First, paraffins and FAME were excluded to identify other sustainable components. This led to highlight dioxolane derivatives and two ethers (di-n-pentylether and dibutoxymethane). It was concluded that while such oxygenated compounds are promising and related to recent research and development studies, they suffer from important shortages including the availability of key reactants. However, encouraging developments were identified and these could contribute to accelerate the development of such pathways in the future beyond the 2030 timeframe.

Second, this work focused on parafins and esters to assess and discuss the advantages or drawbacks of the related production pathways. The latter included hydrotreatment, gasification combined with Fischer Tropsch, esterification, fermentation and e-fuel. The study concludes that fuels arising from these energy pathways could lead to significant CO<sub>2</sub> emissions reductions thanks to the resources and processes characteristics but also a high blending potential with respect to the EN590 specification. The main identified constraints are the density or the cold flow properties for increasing the incorporation of such renewable components.

Also included is an evaluation of the production potential of renewable parafins and esters assuming the mobilisation of locally produced European sustainable biomass, leading to a range between 57 and 88 Mtoe by 2030, or between 24% and 37% of the

expected energy demand for middle distillates in the transport sector<sup>1</sup> (low or high mobilization scenario<sup>2</sup> with energy pathways already at industrial scale and expected to become mature by 2030; this evaluation only considers the use of advanced biomass and does not include current mainstream biofuels from food and feed crops (often called “1<sup>st</sup> generation biofuels”)). These values must be seen as a maximum theoretical potential, pending the development and upscaling of the technologies, the mobilisation of biomass to biorefineries, the necessary investments and development of a profitable business, etc. This maximum theoretical production potential is however highly unlikely to be reached in 2030, as it would require massive investments to be realized in technologies which today do not exist at industrial scale, without waiting for demonstration of a First-Of-A-Kind. Competitions will certainly be present between heavy duty transport and aviation or maritime sectors due to ambitious decarbonation targets by 2050.

Findings of this study were shared with 15 stakeholders involved either in fuel production, fuel logistics, engine manufacturing, fleet operation or representing public authorities. Their views mostly highlight the significant role that renewable liquid fuels will have to play to contribute to the decarbonization of the commercial transport sector in the short term and for the next decades. In this context, this work contributes to assess the strengths and weaknesses related to existing and potential future liquid fuel energy pathways.

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<sup>1</sup> The energy demand for middle distillates in the transport sector in 2030 is expected to be 241 Mtoe, including demand of diesel fuel for heavy-duty vehicles, for passenger cars and demand of Jet fuel for aviation. This report focuses on diesel-like fuels for heavy-duty vehicles only, but considering that similar feedstock are used to produce all distillates for the transport sector, the maximum theoretical potential production is compared to the overall demand for distillates in the transport sector.

<sup>2</sup> According to the report “Sustainable biomass availability in the EU, to 2050” from Imperial College London, between 208 and 344 Mt/y of sustainable biomass is locally available in Europe, which is the scenario considered in this study (resp. low and high mobilization scenarios). On top of that, 48 Mt of biomass can be imported to Europe and 130 Mt of this biomass could be used by other bioenergy applications (such as power generation). These two items were not considered in this work.

## KEYWORDS

Renewable diesel-like fuel, low-carbon pathways, heavy-duty, literature review, oxygenated diesel fuels.

## INTERNET

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## SUMMARY

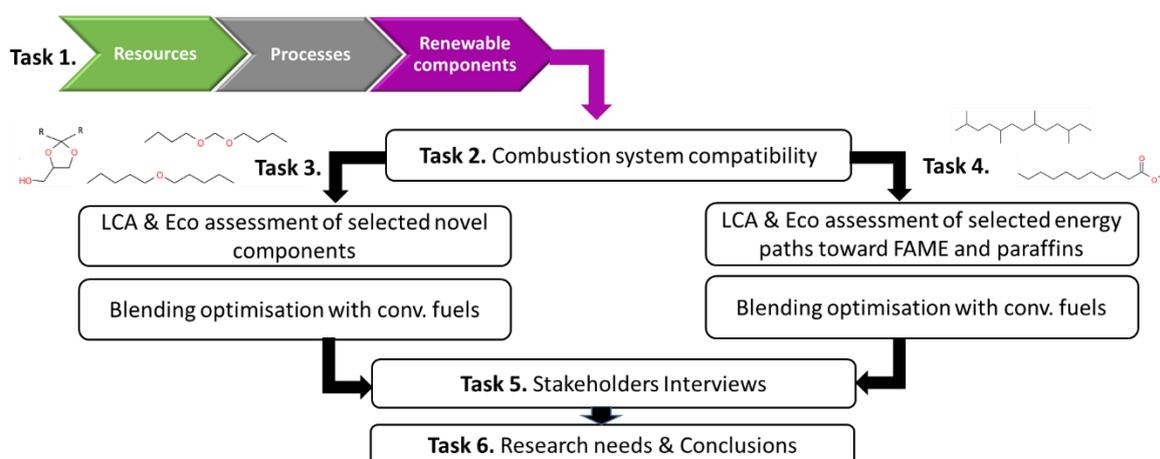
### Objective

Considering the large contribution of internal combustion engines (ICEs) for commercial transportation, the development of alternative fuels is essential to decarbonize the sector with immediate and long term effects. Long-distance transport will still significantly rely on ICE in the next 10 years. In order to decarbonize these vehicles, the use of low-carbon fuels is essential.

In this work, Concawe's ambition is to gather, review and analyze scientific publications and international reviews/reports regarding the development of low-carbon, sustainable diesel-like fuels, with a focus on heavy duty fleets which will be present by 2030 and that could be used without any significant update of the engine hardware.

### Methodology

Six tasks were addressed and discussed in this report as illustrated below.



A brief description is provided below:

- (1) Resources, processes, and fuels review:  
It aims at identifying and gathering all relevant information in the literature related to each step including resources type, process maturity and fuel components physical-chemical properties.
- (2) Combustion system compatibility:  
Literature review focusing on the use of the products identified in Task (1) to illustrate the related impacts in terms of engine hardware and emissions.
- (3) Limitations and opportunities for novel fuel components:  
Literature review on published life-cycle analysis and economic assessment, when available, of selected fuel production pathways and blending potential with conventional fuels.
- (4) Limitations and opportunities for paraffins and fatty acids methyl esters (FAME):  
Literature review on published life-cycle analysis and economic assessment, when available, of selected fuel production pathways for FAME and paraffins and blending potential with conventional fuels.

## (5) Interview sessions:

15 stakeholders representing fuel producers and users, regarding key questions related to alternative fuels development, are interviewed on the main literature findings.

## (6) Conclusion and research needs:

Conclude on the main findings and summarize the key enablers or obstacles identified for the different fuel pathways.

## Results

**Task 1 Resources/processes/components**

The table below provides a synthesis of the potential renewable diesel-like fuel pathways. The most relevant products include: dioxolane derivatives, alkanes, esters and selected ethers. For each type of product, the potential compatibility with current specifications according to this work is provided. Corresponding resources and potential processes are also listed with the corresponding ranking depending on the resources challenges, processes technology readiness level (TRL) and components blending compatibility with current diesel specifications.

Ranking	Components		Resources (most advanced)	Processes (most mature)
Top 4	<b>Dioxolane derivatives</b> (2-(heptan-3-yl)-4,5-dimethyl-1,3-dioxolane, etc.)	● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Fermentation
	<b>Alkanes</b> (n-decane, etc.)	● ● ● ●	Agricultural & forestry residues Industrial residues (biomass)	Thermochemical process
	<b>Esters</b> (single esters such as methyl laurate, etc.)	● ● ● ●	Agricultural & forestry residues Industrial residues (biomass)	Transesterification
	<b>Ethers (excluding OME<sub>x</sub> &amp; dioxolane derivatives)</b> (dipentyl ether, isoamyl ether, etc.)	● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Fermentation
Others	<b>Ketones</b> (4-methylacetophenone, 3-octanone, etc.)	● ● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Pyrolysis
	<b>OME<sub>x</sub></b>	● ● ● ● ●	Industrial off-gases Atmospheric CO <sub>2</sub> + renewable energy	E-fuels/solar fuel
	<b>Light alcohols</b> (ethanol, methanol, pentanol, etc.)	● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Fermentation

Legend:

●	: suitable for blending in D, FAME, or HVO
●	: challenging
●	: very challenging
●	: not suitable

●	: suitable
●	: challenging

●	: high TRL
●	: intermediate TRL

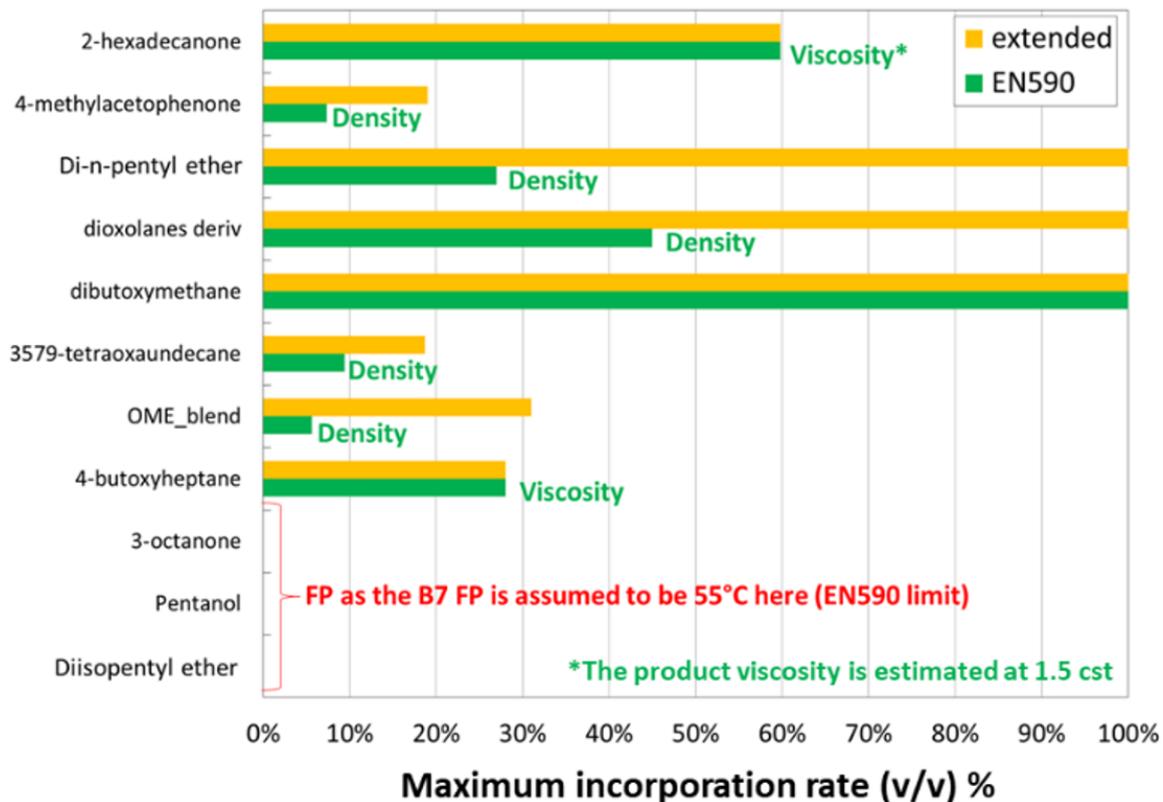
**Task 2 Combustion system compatibility (NB: “blending in D” stands for “blending in Diesel”)**

Engine test results were identified for many components having renewable production pathways, and one of the key findings was that most of the products contribute to decreased particulate matter emissions but can also lead to an increase in nitrogen oxides emissions when certain oxygenated products are used. These observations shed light on the fact that in order to take advantage of novel fuel formulations, engine optimization may be required and this is not necessarily considered for every component in the literature. In addition, hardware compatibility remains mostly unknown due to very limited data on important fuel properties such as material compatibility, oxidation stability or cold flow properties. Limited data were identified on these aspects but more information would certainly help eliminate fuel candidates if data showed that a major vehicle upgrade, and thus investment, was required, also leading to non-compatibility with the legacy fleet.

### **Task 3**    **Limitations and opportunities for novel fuel components**

Oxygenates through dioxolane derivatives, dibutoxymethane and di-n-pentylether were assessed first regarding LCA and TEA data available in the literature. However, while some opportunities were identified for these pathways regarding for example the development of new catalysts, the review also highlighted the lack of data and important limitations regarding the availability of key reactants. It was concluded that it would be unlikely that these compounds would be produced at scale in the 2030 timeframe. Despite these limitations, more recent data found for several pathways would suggest that ongoing research activities could lead to a renewed interest in these compounds.

These renewable fuel candidates were then evaluated based on their blending properties considering cetane number, flash point, viscosity and density. The objective was to determine to which extent these products could enable to either maximize the renewable content of a hypothetical fuel combining: B7, B100, paraffinic fuel (PF) and the renewable fuel candidate, or simply facilitate the incorporation of the product into a market B7 fuel. A dedicated internal IFPEN code was used in order to explore the different blends and the multiple combinations of hypotheses (e.g. specifications, target for optimization, etc). This enabled to demonstrate that almost every renewable component mixed with B100 and PF could potentially comply with EN590 regarding the four cited properties. Another interesting feature of the approach was related to the possibility to identify synergies between the renewable products and one of the current renewable market fuels (i.e. B100 or PF). That supported for example the use of FAME products to counterbalance certain low density products. More generally, certain physical chemical characteristics in B100 and HVO, such as the density, balance each other out contributing to increase the overall renewable content. Finally, the study highlighted the high potential of certain products for a high incorporation rate into B7 (>20 vol.%) considering again EN590 boundaries. This is for example illustrated below for 11 key components and considering either the EN590 boundaries for Cetane number, viscosity, density and flash point (FP) or “extended specifications” where EN590, EN15940 and EN14214 boundaries are combined.



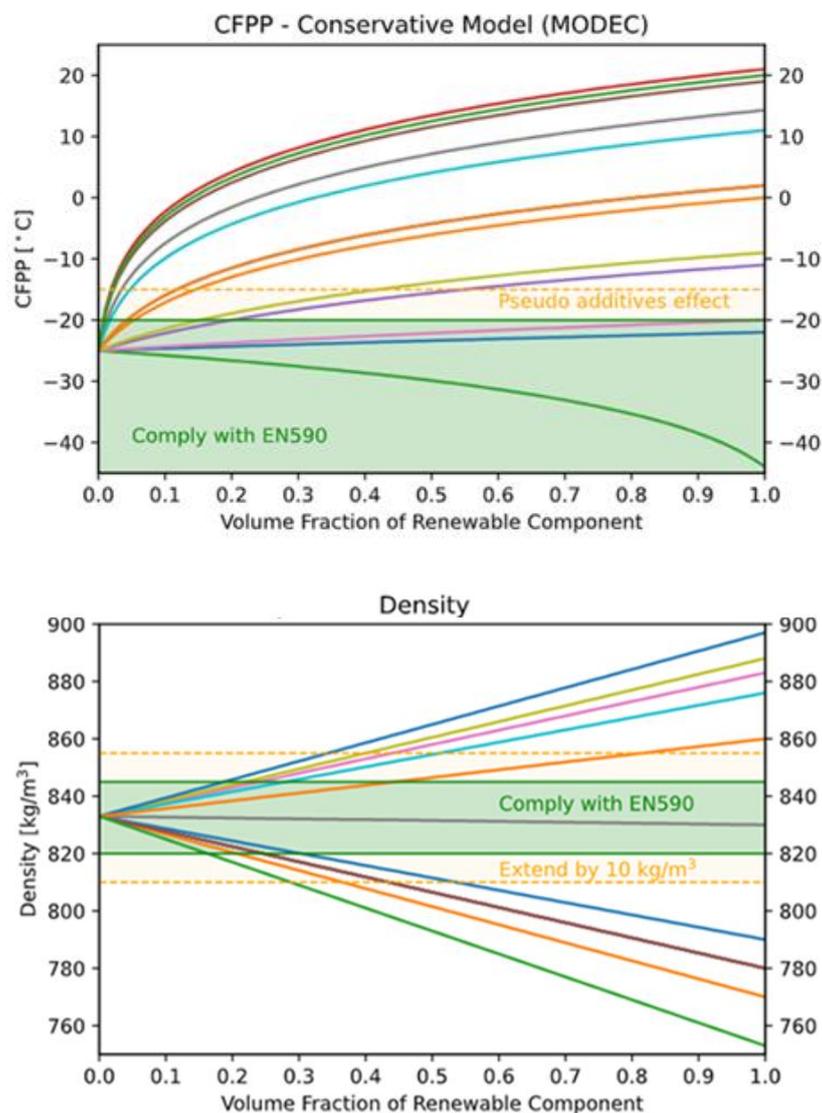
Plot of the maximum incorporation rate for each renewable component in mixture with B7 considering both EN590 (green) and extended specifications (yellow) for the optimization constraints. Property that limits the renewable component incorporation is highlighted for the EN590 case study.

The bar plot indicates the maximum incorporation for both constraints. In addition, the property that limits the renewable component incorporation is written in green for the EN590 case study. The results demonstrate that a few components can be incorporated to a large extent to current B7 conventional fuel once we consider these four key properties. Interestingly, the most limiting parameter is density with respect to EN590. The last three components, 3-octanone, pentanol and diisopentyl ether (DIPE), are however mostly limited by their low FP. A higher hypothesis for the reference fuel B7 FP would enable to incorporate these components but this property would certainly remain the limiting parameter.

#### Task 4 Limitations and opportunities for paraffins and FAME production pathways

In this task, paraffins and esters were considered to assess the advantages and limitations of the related production pathways. The latter included hydrotreatment, gasification combined with Fischer-Tropsch, esterification, fermentation and e-fuel. A lack of environmental and economic assessment was identified in certain cases including hydrotreatment from lignocellulose or alcohol to diesel fermentation pathways. Otherwise the study concludes that fuels arising from these energy pathways could lead to significant CO<sub>2</sub> emissions reductions thanks to the resources and processes characteristics.

Following the same approach as for task 3, paraffins and esters identified and their chemical variability from the different energy pathways were used to evaluate the blending potential with respect to the EN590 specification. A high blending rate potential is reported in many cases and the main identified constraints are the density or the cold flow properties. The use of additives can however improve the blending rate for the latter. To illustrate these findings, the two figures below summarize the blending behavior for several FAME and paraffinic products (each line refers to a specific energy pathway). A conservative model is used to predict blending properties.



Estimated evolution of CFPP (top) and density (bottom) with the incorporation ratio for all the renewable diesel products used in the present work, with indications of EN590 boundaries (min 820 - max 845 kg/m<sup>3</sup> and Class F, -20 °C for CFPP). Legends are not provided in the figure but they could be identified by checking the property of pure products (i.e., the values at 100% incorporation ratio). The orange lines and areas demonstrate the effect of extending the EN590 boundary, which is arbitrarily chosen as 10 kg/m<sup>3</sup> extension of both upper and lower bound for density. For CFPP, a 5 °C reduction is considered for the blend and whose effect on maximum blending ratio is equivalent to 5 °C increase in EN590 limit.

CFPP increases rapidly at low blending ratio limiting significantly the biocomponent concentration. A hypothetical additive effect (5°C) mostly increases the incorporation rate for low CFPP products. Therefore, adjusting the standards for CFPP may be difficult. Instead, focusing on improving the cold flow properties of renewable diesel products through various means is potentially an important lever for maximizing the use of sustainable products.

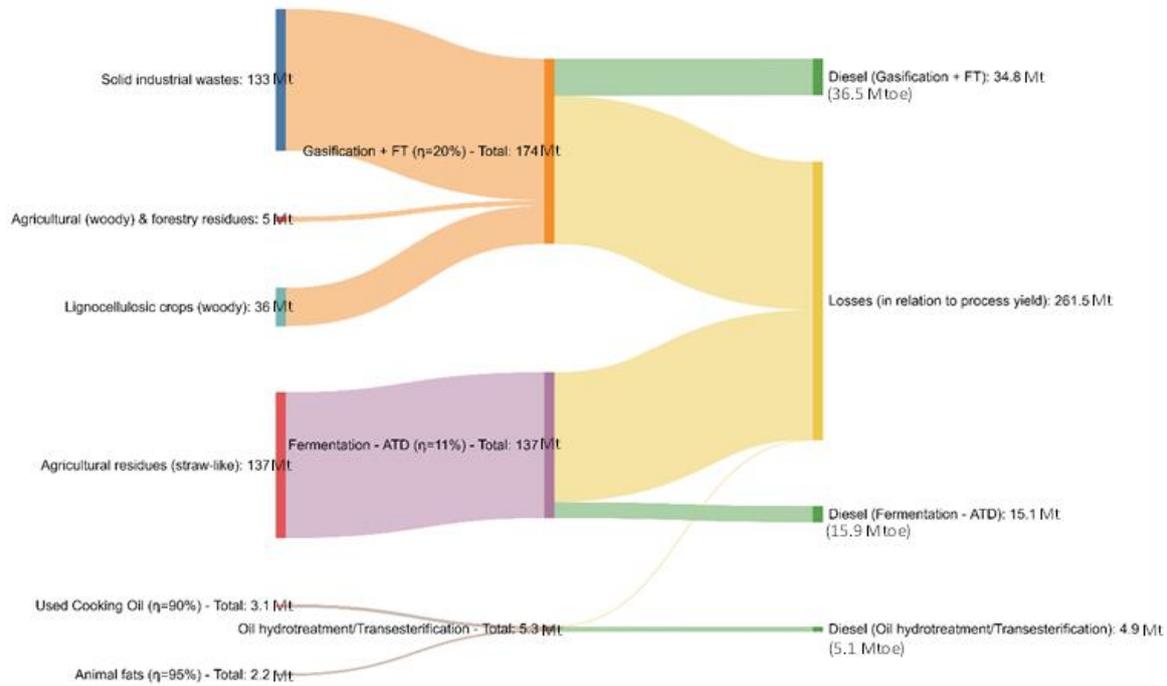
Regarding the density, only one product identified is fully compatible with EN590 range. Other components either cross the upper or lower boundary. Their maximum blending ratios complying with EN590 range from 15% to about 45%. As density follows a linear mixing rule, the effect of relaxing EN590 boundaries could be well predicted. Extending the EN590 density limits by  $\pm 10 \text{ kg/m}^3$  (arbitrarily chosen for demonstration only) could lead to increase in the maximum blending ratio by about 15-25% (best case by 35%).

The use of these components also include important limitations related to the resources or the fuel uses. Indeed, considering most mature technologies (i.e. technologies already at industrial scale today or expected to become at industrial scale by 2030), this study indicates that these energy pathways lead to a production potential of renewable parafins and esters ranging between 57 and 88 Mtoe by 2030, or between 24% and 37% of the expected energy demand for middle distillates in the transport sector<sup>3</sup> (low and high advanced biomass mobilization scenario<sup>4</sup> with energy pathways at industrial scale today and expected to become mature by 2030; this evaluation only considers the use of advanced feedstock (part of Annex IX in the Renewable Energy Directive) and does not include current mainstream biofuels from food and feed crops (often called “1<sup>st</sup> generation biofuels”). These values must be seen as a maximum theoretical potential, pending the development and upscaling of the technologies, the mobilisation of biomass to biorefineries, the necessary investments and development of a profitable business, etc. This maximum production potential is however highly unlikely to be reached in 2030, as it would require massive investments to be realized on very short term in technologies which today do not exist at industrial scale. The figure below illustrates in the case of the low mobilization scenario the share of each energy pathway identified.

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<sup>3</sup> The energy demand for middle distillates in the transport sector in 2030 is expected to be 241 Mtoe, including demand of diesel fuel for heavy-duty vehicles, for passenger cars and demand of Jet fuel for aviation. This report focuses on diesel-like fuels for heavy-duty vehicles only, but considering that similar feedstock are used to produce all distillates for the transport sector, the maximum theoretical potential production is compared to the overall demand for distillates in the transport sector.

<sup>4</sup> According to the report “Sustainable biomass availability in the EU, to 2050” from Imperial College London, between 208 and 344 Mt/y of sustainable biomass is locally available in Europe, which is the scenario considered in this study (resp. low and high mobilization scenarios). On top of that, 48 Mt of biomass can be imported to Europe and 130 Mt of this biomass could be used by other bioenergy applications (such as power generation). These two items are not studied in this work.

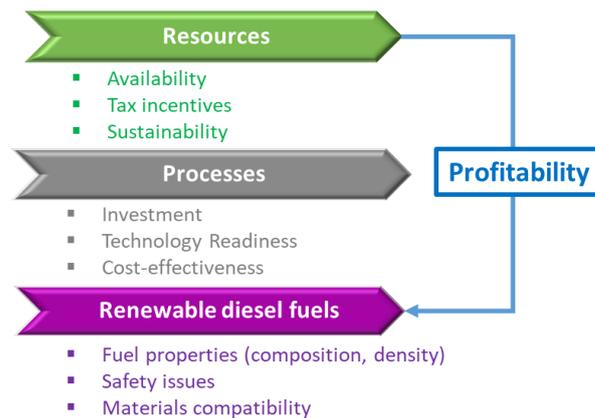


Finally, competition for similar feedstocks will certainly be present between heavy duty transport and aviation or maritime sectors due to significant decarbonization targets by 2050 for all these sectors which might use similar energy pathways.

**Task 5 Interview sessions**

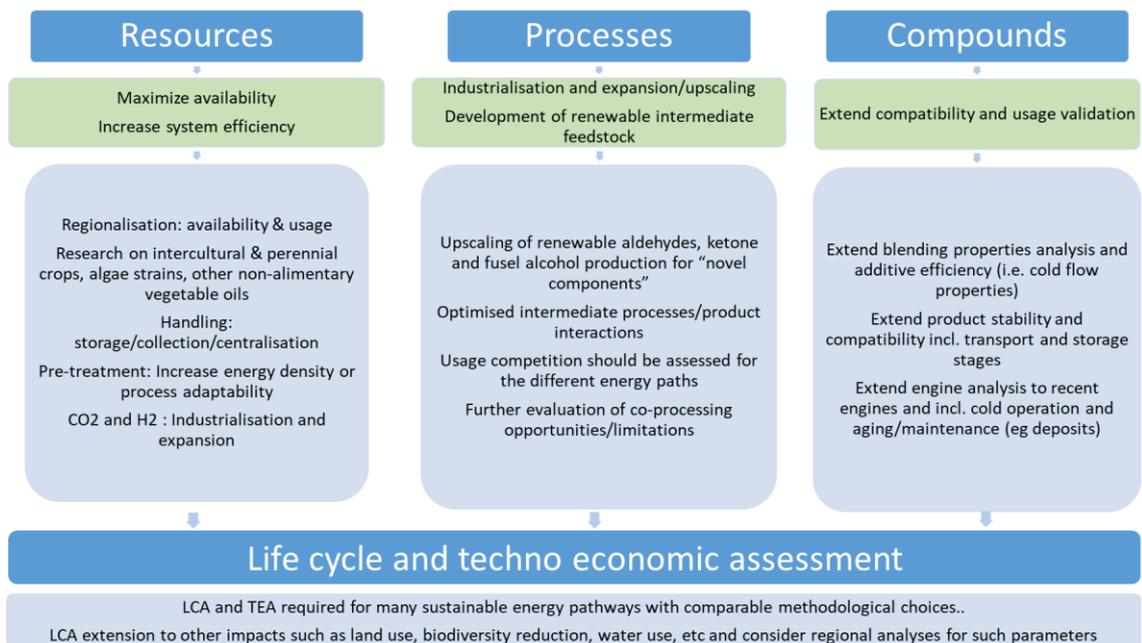
These findings were shared with 15 stakeholders involved either in fuel production, fuel logistics, engine manufacturing, fleet operation or representing public authorities.

Their answers highlighted the significant role that renewable liquid fuels will have to play to contribute to the decarbonization of the commercial transport sector in the short term and for the next decades. Related challenges were highlighted to maximize the chance of success of any novel fuel or simply to develop the current ones. In this context, the key ideas identified are listed below for the resources, processes and renewable diesel-like fuels. Among these specific items, the profitability of any sustainable fuel pathway is a major parameter mentioned.



**Task 6 Conclusion and research needs**

The literature research led to identify several sustainable energy pathways. They can produce novel components including for example ethers or dioxolane derivatives as well as FAME or paraffins. Among these pathways, several research and development needs have been highlighted and are summarized below.



Each step of the energy pathways is considered. First the resources require mostly a high mobilisation and an efficient use. Second, the processes are mostly related to industrialisation/upscaling needs. The transformation step also require additional development to produce sustainable intermediate feedstocks. Third, the sustainable diesel-like compounds are associated to a few research needs including a better characterisation of blending properties with conventional products to maximise their use. Another key requirement is the evaluation of the compatibility with existing fleet or with current fuel logistic. This would enable a safe operation with limited impacts on emissions or systems durability. Finally, LCA and TEA are also related to important developments. Comparable methodologies for environmental evaluation is required. The GHG emissions is well documented but limited information exist for other impacts such as land use, impact on biodiversity or water requirement.

## 1. INTRODUCTION

Commercial transportation is primarily powered by internal combustion engines (ICE). The development of alternative fuels is essential to decarbonize the sector with immediate and long term effect. Although electrification for long-distance is proposed, it is still challenging considering the large weight of batteries, the logistic considerations including the current lack of charging infrastructure. Therefore, long-distance transport will still significantly rely on ICE in the next 10 years. In order to decarbonize these vehicles, the use of low-carbon fuels is essential.

However, there is no obvious option for the next 5 - 10 years as several low carbon fuels strategies exist. Moreover, several barriers must be overcome to make them at scale and meet the ambitious transport-related climate targets.

First, it must be considered that adding a new fuel requires compatibility with existing powertrains and future ones. Combustion, after-treatment efficiency, hardware compatibility and durability are key parameters. Ideal fuels would enable a high blending rate with conventional fuels and possibly up to 100% ("drop-in" fuel) and would not require adaptations to the vehicle's settings or hardware. The powertrain is not the only constraint as the fuel must also be compatible with existing logistics facilities to ensure a safe and efficient use across different geographic areas. Today, as an example, paraffinic compounds are drop-in for market diesel fuel and they can be blended up to 30-50% and comply with EN590.

Second, the objective is to decarbonize the sector which means that the fuel must be produced in a sustainable and scalable way from renewable resources. The feedstock type and availability, production cost, production capacity, logistics and life-cycle greenhouse gases emissions are key parameters to consider. This implies great complexity since many combinations of options can be considered today. As an example, one possible choice would be to produce a sustainable fuel with properties similar to a conventional fuel to limit the engine hardware change. For diesel engines, Hydrotreated Vegetable Oil (HVO) falls into this category as it replicates a specific diesel cut (paraffinic diesel). Another option is to extend the fuel/engine compatibility to different fuel compounds, currently not used in conventional diesel fuel, with no to limited hardware change. In that case, options such as heavy alcohols, furan derivatives or ethers could be considered.

Finally, cooperation in the development or modification of existing fuel/renewable fuel specifications is also important to shorten the time required to update or create novel fuel standards.

The development of optimised low-carbon diesel-like fuels must be addressed considering every cited item above.

In this work, Concawe's ambition is to gather, review and analyze scientific publications and international reviews/reports regarding the development of low-carbon, sustainable diesel-like fuels, with a focus on heavy duty fleets which will be present by 2030 and that could be used without any significant update of the engine hardware.

In order to perform such a literature review, six tasks were addressed and discussed in this report. A brief description is provided below:

(1) Resources, processes, and fuels review:

This task aims at identifying and gathering all relevant information in the literature related to each item mentioned above in order to evaluate their interest and the TRL (Technology Readiness Level, indicating the research to industry technology maturity) of the different fuel production pathways. This includes the physical-chemical properties but also storage and logistics considerations.

(2) Combustion system compatibility:

In this section, IFPEN will continue the literature review focusing on the use of the products identified in Task (1) in order to illustrate the related impacts in terms of engine hardware and emissions.

(3) Limitations and opportunities for novel fuel components:

Literature review on published life-cycle analysis and economic assessment, when available, of selected fuel production pathways and blending potential with conventional fuels.

(4) Limitations and opportunities for paraffins and fatty acids methyl esters (FAME):

Literature review on published life-cycle analysis and economic assessment, when available, of selected fuel production pathways for FAME and paraffins and blending potential with conventional fuels.

(5) Interview sessions:

The development of novel fuels should consider the current stakeholders opinion and strategy. This section will shed the light on the feedbacks from 15 stakeholders, representing fuel producers and users, regarding key questions related to alternative fuels development.

(6) Conclusion and research needs:

Conclude on the main findings and summarize the key enablers or obstacles identified for the different fuel pathways. This section will also include a discussion on the research needs that would enable a further development of the most relevant fuel pathways.

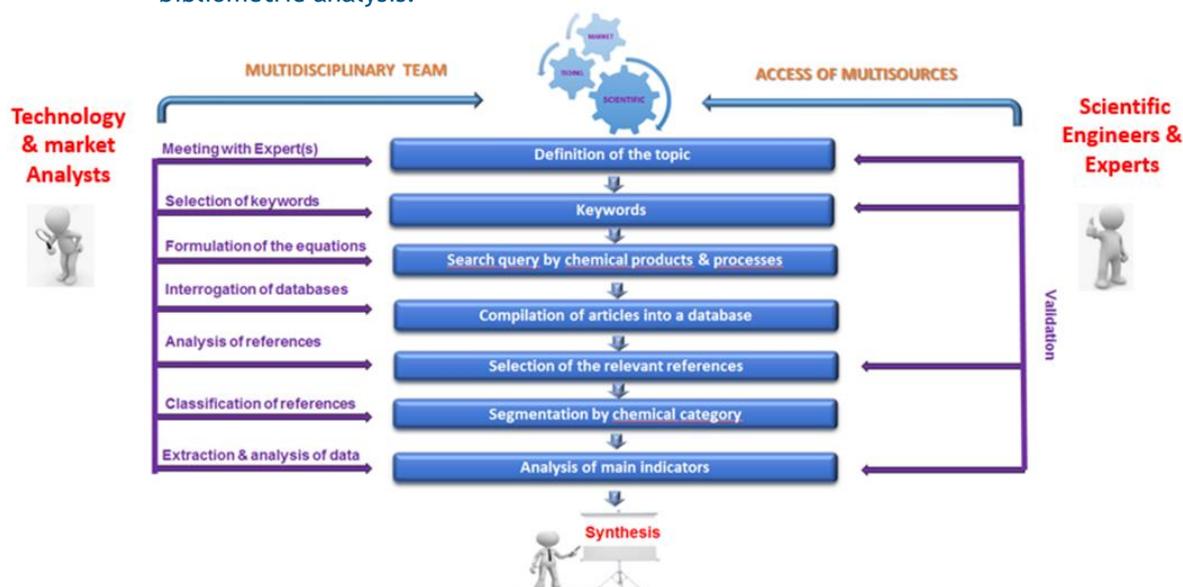
To address these different tasks, the literature review method is first described in this report.

## 2. SCIENTIFIC LITERATURE DATABASE

Sustainable diesel-like renewable fuels have been extensively studied in the past, resulting in a significant number of scientific publications, international reviews, and conference proceedings. A literature review was conducted accordingly with the aim to establish the state-of-the-art for future low carbon fuel options compatible with a current HD diesel truck engine technology.

Having access to multidisciplinary databases (including SCOPUS, thematic journals, books, etc.), IFPEN applied its global methodology combining information specialists' skills with Research and Development fuel expertise engineers to select and extract the relevant technical references. A bibliometric analysis was also carried out using the Intellixir processing and visualization tool to categorize the documents. The literature review covered the period from 2015 onwards.

Figure 1 illustrates the methodological process of the document search and bibliometric analysis.



**Figure 1** Global methodology followed to identify relevant scientific literature

Search queries per task and component were applied to identify documents covering the full scope of the study. Details for each task are given hereafter. Although the queries and analyses were performed with particular care, it can neither be excluded that some academic articles that conceptually fall within the set of interest were missed nor that this data set contains academic articles that fall outside the scope of this literature review.

### 2.1. TASK 1: RESOURCES, PROCESSES AND FUELS REVIEW

WP1 focused on the resources, industrial processes enabling the production of diesel-like renewable fuels, and the resulting potential fuels. Accordingly, this task aimed at identifying and gathering all relevant information in the literature related to each fuel candidate in order to evaluate their interest and the TRL of the different fuel production pathways.

Firstly, a non-exhaustive list of sustainable diesel-like renewable fuels was considered in building search queries, and each fuel candidate was classified by

chemical family. A specific attention was paid to the products which are shown in the table hereunder. Several fuel candidates may be present in similar processes, or may necessitate similar resources.

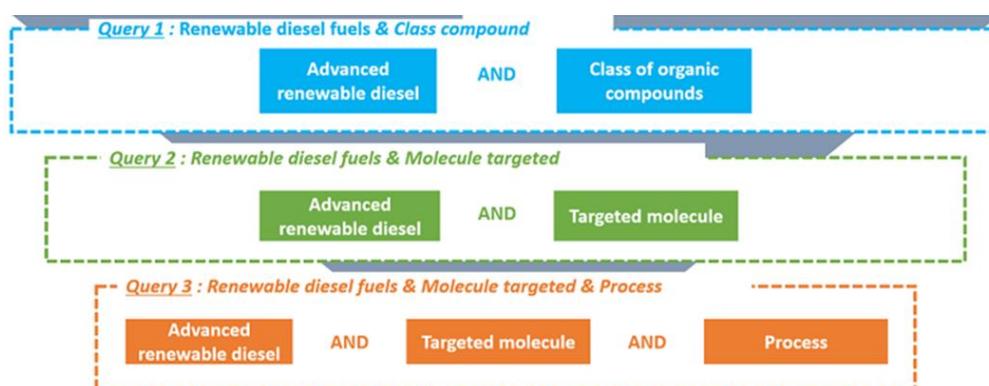
**Table 1** Non-exhaustive list of sustainable diesel-like renewable fuels considered in building search queries and classified by chemical family

Sustainable diesel-like products	Sustainable diesel-like products
<b>Esters</b>	<b>Alcohols</b>
Ex: B7, FAME (Fatty acid methyl esters/FAME, B100)	Ex: octanol, pentanol
<b>Alkanes &amp; Paraffins</b>	<b>Ethers</b>
<b>HVO</b>	<i>Linear ethers</i>
<b>Paraffins</b>	Ex: polyoxymethylene ether (OMeX/POME)
<b>Alkanes</b>	<i>Furan (cyclic ethers)</i>
Linear alkanes	Ex: methyltetrahydrofuran (MTHF), dioxolane
Ex: farnesane, undecane	
Cyclic alkanes	
Ex: Oligo-cyclopropane	
<b>Terpene derivatives</b>	
<b>R33</b>	

For each molecule, the first step consisted into formulating the concepts with the following adapted keywords:

- Advanced renewable diesel,
- Class of organic compounds,
- Targeted sustainable diesel-like products,
- Processes.

This was achieved through the definition of three series of Boolean search queries and using relevant keywords and synonyms specific to each product as shown below.



**Figure 2** Methodology applied to generate the database

This approach enabled IFPEN to identify the number of references being either cited through more general keywords such as the class of organic compounds or in combination with a specific upgrading process. Table 2 shows the global analysis performed including the output from the different queries. Query 1 refers to the values in bold for each class of components. Query 2 refers to each specified component. Query 3 corresponds to the output from the column “Volumetry with process”. The volumetry refers to the number of references identified matching the query. For Query 3, the corresponding filters for upgrading steps are detailed in the last column. The retrieved documents from Query 3 account for approximately 50% or more of the global query. This supports the term used for the upgrading processes and suggests that further analyses of the database may be required. In addition, most of the listed components from Query 2 compared to Query 1 are accounting for most of the class of organic compounds. FAME is an exception here as B7, B100 or specific FAME components are not frequently cited in the literature. The hypothesis was accordingly made that the term FAME might be more frequent.

**Table 2** Sustainable diesel-like products publication volumetry and detailed processes

Products	Volumetry	Volumetry with process	Processes described
<b>FAME</b>	<b>6 888</b>	<b>5302</b>	(process or processes or synthesis or production or transesterif* or (trans PRE/I esterif*) or "trans-esterification" or "trans-esterificated" or "trans-esterified" or "trans-esterifying" or "trans-esterify")
B7	121	53	
B100	384	174	
Fatty acid fusel esters	2	2	
<b>Alkanes &amp; Paraffins</b>			( process or processes or synthesis or production or hydrotreat* or hydrodeoxygen* or (hydro W11 deoxygen*) or hydroisom* or (hydro W11 isom*) or deoxygenat*)
HVO	122	105	
Paraffins	235	130	(process or processes or synthesis or production or (fischer W12 tropesch) OR gtl OR btl OR ( gas OR biomass) W12 liquid))
<b>Alkanes</b>	<b>30</b>	<b>20</b>	(process or processes or synthesis or production)
<i>Linear alkanes</i>			
Farnesane (Trimethyldecane)	9	4	
Undecane	3	2	
5-ethyl-4-propylnonane	1	1	
<i>Cyclic alkanes</i>			
Oligo-cyclopropane	5	4	
Bicyclopentane	0	0	
Bicyclohexane	0	0	
<b>Terpene derivatives</b>	<b>37</b>	<b>24</b>	
<b>R33</b>	<b>3</b>	<b>0</b>	(process or processes or synthesis or production)
<b>Alcohols</b>	<b>7289</b>	<b>5820</b>	( process or processes or synthesis or production or ferment* or ziegler)
Octanol	67	23	
Pentanol	125	30	
Methanol	4090	3571	
ED95	2	2	
Fatty alcohols	72	61	
<b>Ethers</b>	<b>705</b>	<b>417</b>	(process or processes or synthesis or production or etheri* or williamson)
<i>Linear ethers</i>			
DME or POME	117	81	
ETBE	47	37	
MTBE	52	41	
DME	108	61	
DEE	118	31	
DMBE	22	9	
4-butylheptane	2	2	
Fatty alkyl ether	2	1	
Ether-ester lactate derivatives	0	0	
<i>Furan (cyclic ethers)</i>			
MTHF	37	30	
Dioxolane	6	5	
Dioxetane	2	2	

Finally, in order to identify other targeted molecules or processes that may not have been considered in the queries, experts in fuel/engine compatibility analyzed the data and extracted specific articles.

## 2.2. TASK 2: FUEL/ENGINE CO-OPTIMIZATION

The literature review focused on the use and impacts of the sustainable diesel-like products on heavy duty engines. The literature analysis was carried out by organic compound classes (i.e. esters, alkanes, alcohols, ethers, ketones) and selected scientific references were analyzed based on the citations and relevance.

This task relies on the same approach as the previous one. The literature focuses on articles published after 2014 using SCOPUS database. The first step consisted in combining adapted keywords:

- Describing the class of organic compounds,
- Dealing with internal combustion engine

Focusing on fuel/engine adequacy including combustion optimization, after-treatment, hardware compatibility, corrosion/clogging, etc. The search query is detailed Figure 3.

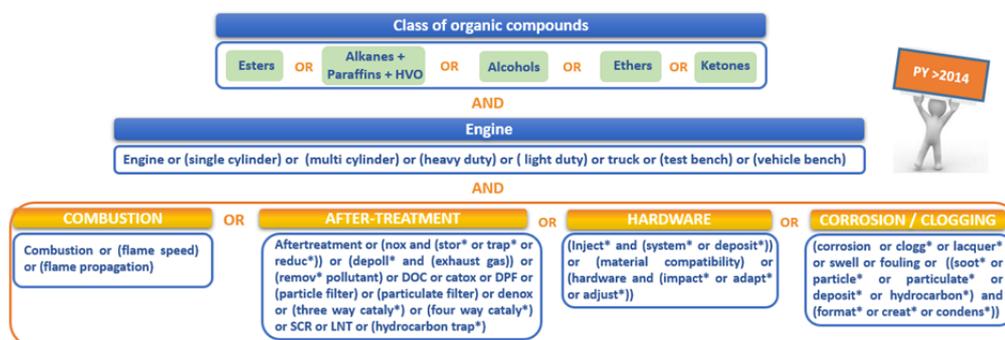


Figure 3 Methodology applied to generate the data set for task 2

Table 3 shows the number of references obtained per class of organic compounds and engine impact category. A bibliometric analysis was carried out to better understand the trends in publication. A final set of most relevant articles was selected out of the database for further analyses.

Table 3 Number of references per class of organic compounds and effect category.

	ESTERS	ALKANES	ALCOHOLS	ETHERS	KETONES
Family + engine	2 477	212	2 054	373	42
Family + engine + <b>Combustion</b>	999	79	761	195	16
Family + engine + <b>Aftertreatment</b>	288	34	184	56	3
Family + engine + <b>Hardware</b>	77	10	39	10	0
Family + engine + <b>Corrosion, Fouling</b>	84	16	56	12	1

### 2.3. TASK 3: ECONOMIC AND LIFE CYCLE ANALYSIS ASSESSMENT

Task 3 focused on the literature dealing with life cycle and technoeconomic assessment (LCA and TEA) of selected fuel production pathways. Components were identified from task 1 and 2.

In Work Package 3, the identification of relevant literature was carried out in two steps. The first one consisted into defining:

- TEA related keywords with the data set obtained from task 1 with query 2.
- LCA related keywords with the data set obtained from task 1 with query 2.

A selection of publications dealing with organic compounds was made from these search results.

A second step consisted in finding keywords describing the selected molecules to combine them with keywords dealing with LCA or TEA. The detailed search query is shown in Figure 4. A selection of relevant documents was carried out and the final data set was analyzed.

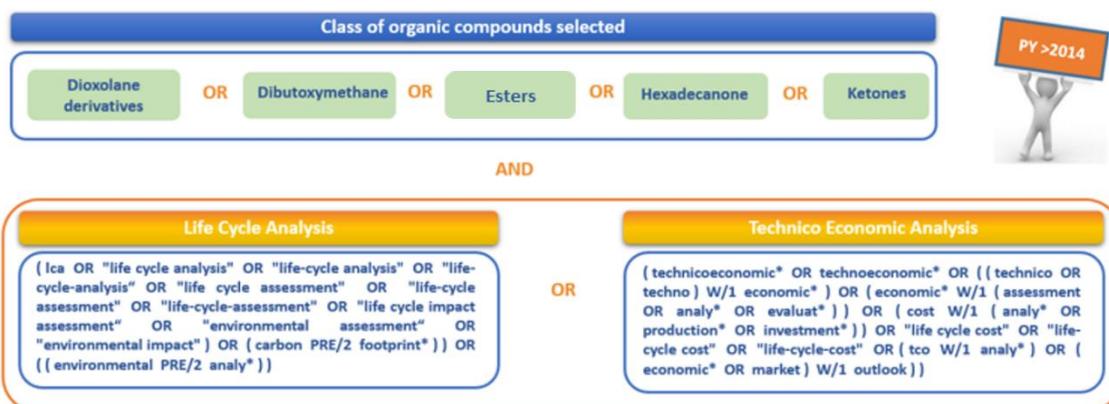


Figure 4 Detailed search query for task 3

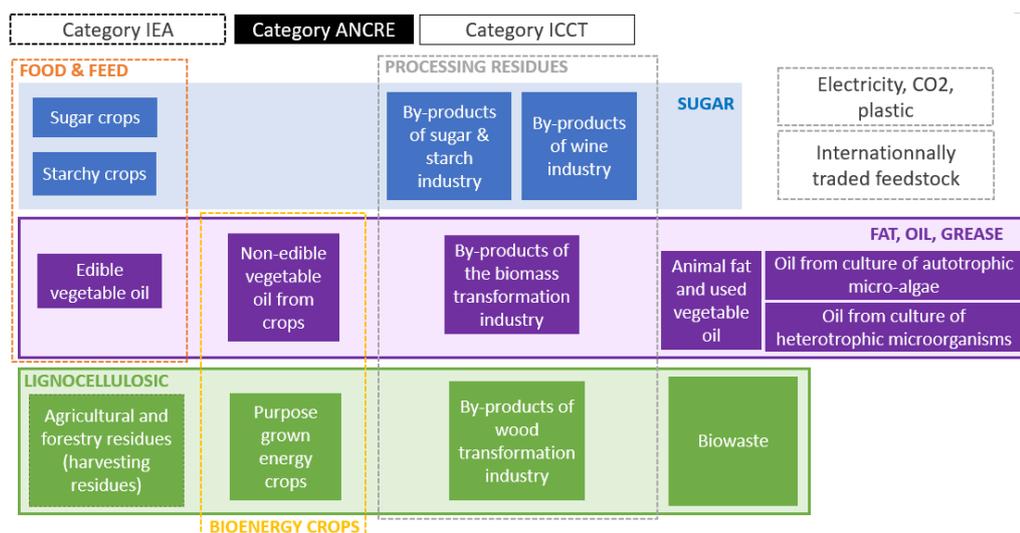
### 3. RESOURCES, PROCESSES AND PRODUCTS REVIEW

#### 3.1. RESOURCES

This study starts with a discussion on the main characteristics and challenges regarding the resources that can be converted to renewable fuels. Six documents were used to collect relevant data:

- The Role of Renewable Transport Fuels in Decarbonizing **Road Transport** Production Technologies and Costs from the International energy agency (IEA) [1]
- The potential of liquid biofuels in reducing **ship** emissions [2]
- Directive (EU) 2018/2001 of the European parliament and of the council of December 2018 on the promotion of the use of energy from renewable sources [3]
- JEC Well-to-Tank report v5. Well-to-Wheels analysis of future **automotive fuels** and powertrains in the European context [4]
- Opportunities and challenges for broadening biomass feedstock in Europe [5]
- Biofuel roadmap for the **aeronautics** industry from ANCRE [6]

As we look into the different references, two main findings are emerging: (1) A great diversity of biomass exists. In the REDII alone [3], more than twenty different resources are quoted; (2) There is no consensus on how to regroup biomass as shown in Figure 5. Some categories are linked to the composition of the biomass, as “Lignocellulosic”, while some are linked to the origin of the biomass or their use, as “Food & Feed”.



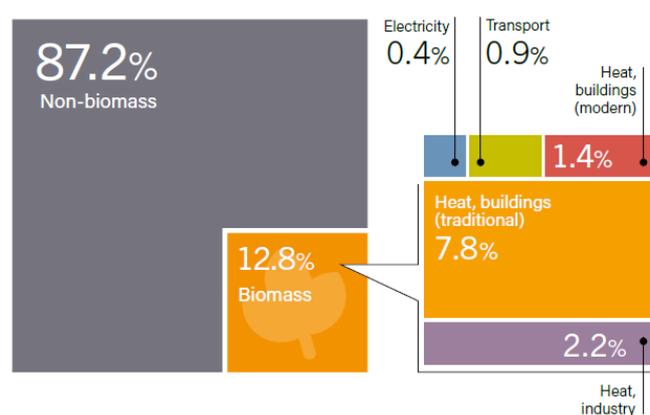
**Figure 5** Categorisation of the resources in ANCRE, IEA and ICCT reports [1, 2, 6]. To be consistent throughout this study, REDII categories are considered as the reference. It corresponds to:

- Conventional feedstock: biomass that could be used in the food & feed sector

- Advanced feedstock: quoted in the Annex IX part A of the REDII [3] and further detailed in this document as:
  - Agricultural & forestry residues
  - Industrial residues
  - Woody and grassy energy crops
  - Algae & micro-organism
- Others: quoted in the ANNEX IX, part B, i.e. Used Cooking Oil (UCO) and animal fat

Some processes require specific types of biomass as input for a given output. Sugar is used to produce ethanol through fermentation, while fats and oils are feedstocks to produce diesel-like fuel through esterification. Thus, the availability of each type of biomass is a key issue for the development of biofuel and is the subject of this section, in terms of cost, technology readiness, sustainability and available quantity.

This question can be addressed qualitatively and quantitatively. ANCRE [6] and ICCT [2] define grades (good, average or poor) to compare the availability of different types of biomass. Quantitative aspects are shared for several aspects including the available/necessary quantity. The quantity of biomass is then given either in terms of mass [2] or energy with the lower heating value (LHV) [1, 6]. Moreover, two approaches are observed: quantification of the demand [6] or the supply [1, 2]. As arable land is unequally distributed across continents, IEA estimates that 26 % of the total global supply potential is exportable biomass [1]. The figures given of biomass supply, for instance in the Figure 4 of the document from IEA, are given for all energy use. It must be highlighted that transport represents only a minor part of the biomass used for an energy purpose, as shown in Figure 6.



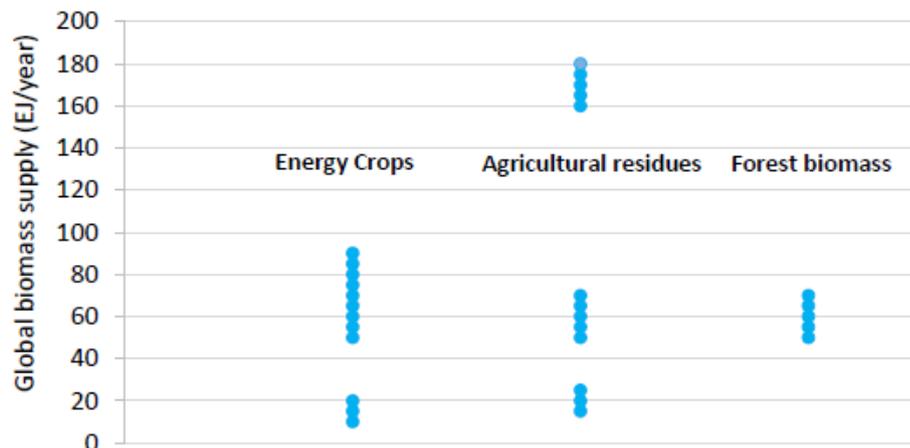
Note: Totals may not add up due to rounding.

**Figure 6** Usage competition for biomass in the energy sector [7].

It is one of the reasons why the prospective evaluation of biomass availability is a difficult exercise. The estimates are calculated with models based on several assumptions including:

- the usage competition,
- the yield and the available plantation area,
- the sustainable amount of residues that can be recovered,
- the food demand.

Consequently, the estimates vary greatly from one study to another as shown in Figure 7. They also vary depending on the type of biomass, each type facing different challenges that can affect their availability. These challenges are detailed in the following sections.



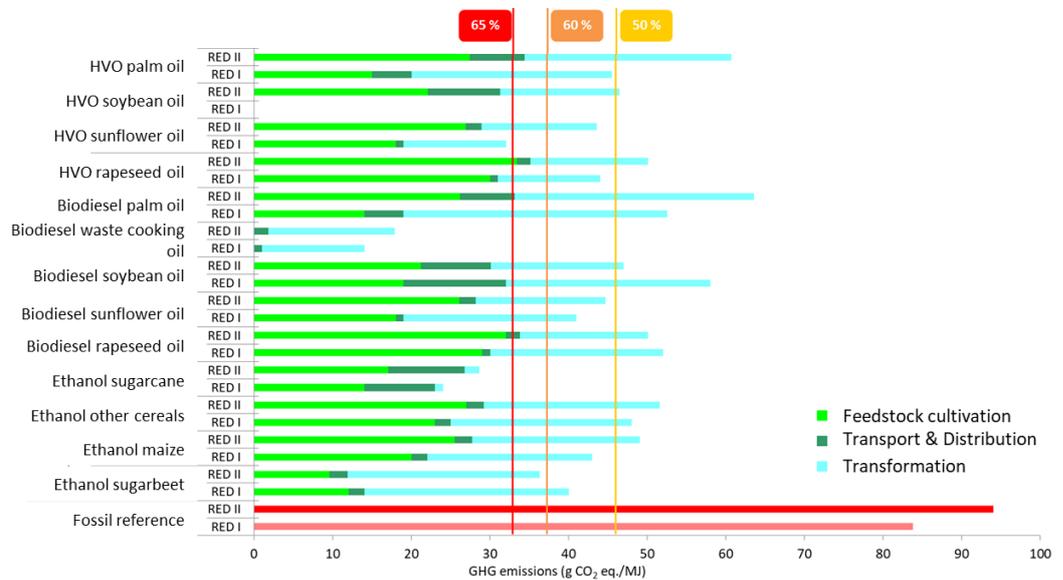
**Figure 7** Summary of global biomass energy supply potential estimates in 2030. Each blue point represents the estimate of one study.

### 3.1.1. Conventional biomass

Conventional biomass are well known, and their value chains are well established. But they face two main sustainability challenges:

- Food security concern: using conventional biomass to produce fuel enters in competition with using it for food or feed. Their cultivation can thus cause indirect land-use change. Indirect land-use change occurs when the cultivation of crops for biofuels displaces the traditional production of crops for food and feed purposes, that was cultivated in the field now used for biofuel production. For this reason, the use of this kind of biomass is capped by the REDII, [3] i.e. it may not account for more than 7% of final energy consumption in the transport sector (road and rail) in a Member State.
- Reaching the greenhouse gases (GHGs) reduction requirement of the REDII [3]: on Figure 8 GHG emissions of conventional biobased fuels compared to the fossil reference. Source: IFPEN composition
- it can be seen that for most of the conventional pathways to produce biofuel, the 65% reduction is not reached. Feedstock cultivation contributes more or less to half of the GHG emissions, and rapeseed oil cultivation even reaches the 65% reduction limit alone.

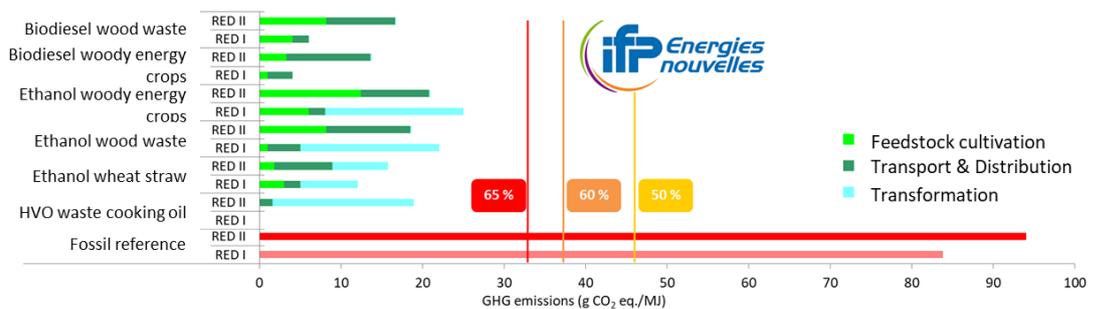
Other continents are still relying on these resources but in Europe, the amount of usable conventional biomass is capped by the RED II, i.e. conventional biobased fuel can only account at most to 7% of the final energy consumption in the transport sector (road and rail) in a Member State. Thus, its development potential is limited.



**Figure 8** GHG emissions of conventional biobased fuels compared to the fossil reference. Source: IFPEN composition

### 3.1.2. Advanced biomass

Contrary to conventional biobased fuels, advanced biobased fuels, i.e. produced from advanced biomass, are promoted by the REDII [3]. In 2030, they must represent at least 3,5% of the final energy consumption in the transport sector (road and rail) in a Member State. They have a greater potential for GHG reduction than conventional biobased fuels, as shown in Figure 9.



**Figure 9** GHG emissions of advanced biobased fuels compared to the fossil reference. Source: IFPEN composition

#### 3.1.2.1. Agricultural & forestry residues

Straw, corn stover, bagasse are examples of biomass included in this subcategory. Agricultural and forestry residues have both great potential for availability and sustainability. In fact, as they are not the main reason for the biomass exploitation, they are not held responsible for land use change, contrary to crops. Moreover it is stated in the REDII that « no emissions shall be allocated to wastes and residues » [3]. Their collection enables the avoidance of burning of residues in open field fires and thus the associated GHG emissions and other local pollutants, but sustainable harvesting rates (which depends on the climate, type of soil, type of crops...) of residues must be respected to avoid soil carbon loss [1-3, 5, 6].

However, there are still some techno-economic challenges to overcome. The associated agricultural machineries and processes have lower technology readiness than conventional biomass [2]. The collection can be quite costly, notably when they are harvested on steep slopes or soft soil [5]. Then the storage in good condition can also be difficult, leading to dry matter losses by the development of fungus or moss [5]. The pre-treatment of this kind of biomass, compared to starchy or fatty material, is more costly as the energy content is less accessible [2]. And finally, they can also be used in other industrial sectors: livestock bedding or feed [1] or other energy use (heat and power).

### 3.1.2.2. Industrial residues

Sawdust and black liquor are examples of biomass included in this subcategory. As for agricultural and forestry residues, industrial residues have a great sustainability potential, as they do not lead to land use change and are not allocated emissions for their production. However, attention must be given to the status of industrial by-product to avoid distortive effect or even fraud on markets for waste and residues [3, 6]. Industrial residues have a limited availability potential, as « it appears that industrial wastes or recovered wood are already used as much as possible » [3].

Once again, as for agricultural and forestry residues, industrial residues face technical challenges for their collection, storage [6] and pre-treatment [2]. They are economically attractive, but can be used in other industrial sectors: production of paper pulp [5, 6], other energy use.

Woody and grassy energy crops

Poplar, willow, ryegrass, and miscanthus are examples of biomass included in this subcategory.

On the one hand, growing energy crops can have benefic effect on the environment. If grown on marginal land, it can restore the soil quality [1], and growing perennial crops enables the soil to store more carbon and living biomass (no till, bigger stems, roots not removed during harvest) than growing annual crops [3, 5]. Moreover, energy crops have a higher land productivity and need less fertilization than conventional crops [1, 5]. On the other hand, growing energy crops can displace food production [1], cause conflict over land and damage biodiversity [2, 5].

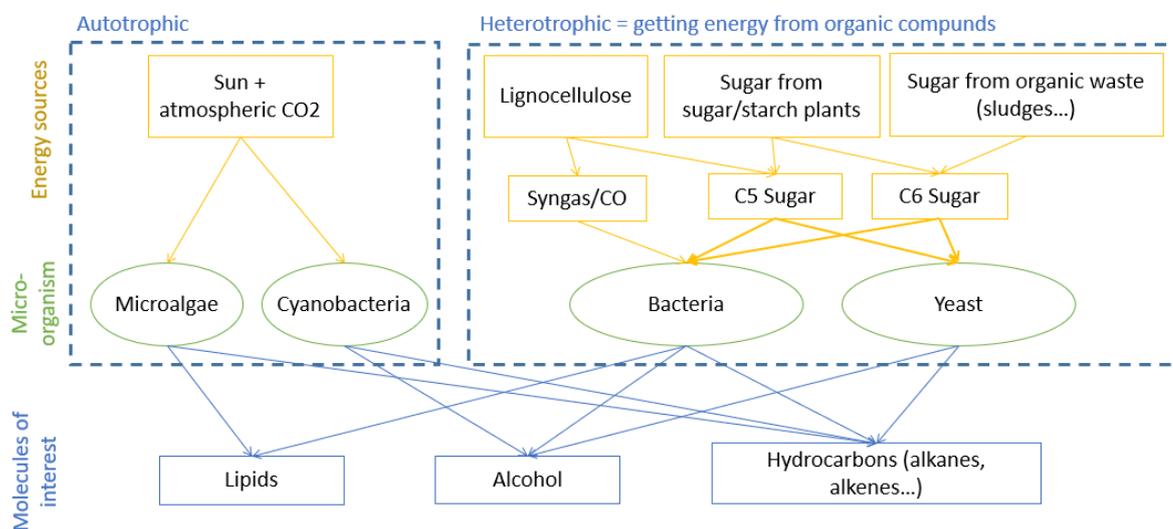
Some improvement of knowledge of energy crops is still necessary to optimize the time of harvest, the machinery, etc. Concerning economic challenges, estimates show that energy crops are one of the most costly biomass (>USD 8 per GJ) [1]. Moreover, growing energy crops means using land over long periods of time (around 15 years) and the first harvest is only after 2 to 4 years [1, 6], which can hold back farmers from investing in energy crops.

### 3.1.2.3. Algae & micro-organism

As shown in Figure 10, there are two types of micro-organism; autotrophic and heterotrophic. The technology readiness level of heterotrophic micro-organism is even lower than autotrophic micro-organism. For both types, several technological challenges still have to be overcome to scale-up the cultivation systems (oxygen inhibition, competing species contamination, costly separation and purification step) [3, 6]. As an example, industrial mobilization of algae and the biobased jet-fuel production is not seen as conceivable before 2040 [6]. For now, notably because of the energy consuming steps that are harvesting and drying [1], meeting the GHG reduction requirement of the REDII is also a challenge for algae biofuels [3].

Using algae and micro-organism still has some advantages. Their cultivation do not lead to land use change [6] and their yield are much higher than the yield of conventional crops [1]. Moreover, if they use wastewater as an input, they do not enter in competition over water and nutrients [1].

However, algae and micro-organism are not just used to produce biobased fuel. They can also be used to produce cosmetics or even food [1].



**Figure 10** Presentation of algae and micro-organism

### 3.1.3. Used cooking oil and animal fats

The amount of UCO and animal fat- based biofuels is capped by the RED II, i.e. biobased fuels produced with UCO and animal fat can only account at most to 1,7% of the final energy consumption in the transport sector (road and rail) in a Member State. This cap is aimed at limiting fraud, e.g. in 2014 500kt of palm oil were imported from Asia as UCO [3].

UCO and animal fat do not lead to land use change and are not allocated emissions for their production. Moreover, they are normally cheap but they could be economically attractive if the demand exceeds the local availability [1].

However, using them to produce fuel for road transportation faces two major obstacles:

- The implementation of collection programs, that can be costly [2, 6],
- Competition with the aviation sector [6]. The ICAO will make the incorporation of bio-fuel mandatory to reach thresholds and will increase competition even more.

Fossil waste sources are not included in the REDII [3] but nonetheless discussed below.

### 3.1.4. Waste plastic

In the selected reference documents, the availability of waste plastic is not quantified. However, non-recyclable plastics are easily accessible at the exit of the sorting centres [6]. The ANCRE report also warns about the cost of pre-treatment (grinding, washing...), that can go up to 100€/tonnes in case of heavy metals contamination for instance [6]. The use of waste plastic is governed by the EU waste management law, and the waste hierarchy must be followed. The recovery of waste for other purpose, such as the production of biobased fuel, is allowed only if prevention, reuse, and recycling are not possible. This will certainly limit drastically the plastic quantities available for fuel production.

### 3.1.5. Steel industry & chemical industry off-gases

For now, coke oven gas, blast furnace gas, oxygen converter gas, etc are flared or used for heat and power [1]. But they can also be used as feedstock for Fischer-Tropsch or gas fermentation [1]. Their availability is graded as average (renewable electricity and CO<sub>2</sub>) in ICCT [2].

### 3.1.6. Atmospheric carbon dioxide

Among the negative emissions technologies, direct air capture (DAC) powered by renewable energies aims at lowering atmospheric concentrations of CO<sub>2</sub>, a greenhouse gas (GHG). DAC has several advantages compared to highly concentrated CO<sub>2</sub> sources such as industry off-gases: limited contaminants, not limited to a certain area and can in principle be at large scale. However, financial, energy and material requirements are the main uncertainties related to the development of this system. The low CO<sub>2</sub> concentration is also an important parameter contributing to increase the energy demand and to reach similar purity than on concentrated sources. These different aspects were recently discussed in the literature [8, 9]. A few examples of DAC-related companies and projects targeting fuel production can be listed: Highly Innovative Fuels<sup>1</sup>, Nordic Electrofuel<sup>2</sup>, Prometheus Fuels<sup>3</sup>.

### 3.1.7. Conclusions on the resources

Table 4 summarizes the main considered feedstocks and their related challenges. Out of the eight feedstocks, three are considered as positive by 2030: agricultural and forestry residues, industrial biomass residues and woody and grassy energy crops. They are all taking advantage of regulation incentives and a potentially high sustainability. Resources that will have to face a major constraint are listed in the challenging category in orange. Atmospheric CO<sub>2</sub> combined with renewable energy is considered as challenging for a large scale use considering the very high cost foreseen without strong incentives. UCO and animal fats are capped by regulation and the associated product logistic may limit their global availability. Industrial off gases are limited in terms of availability and a potentially non virtuous use if the activity promotes industrial activities requiring conventional fossil-based feedstock by any means. Plastic should be mentioned as a potential waste from petroleum industry by 2030. This is supported by the processes development ongoing to upgrade this material. However, plastic use may be limited for different reasons. As an example, the EU waste management law states that prevention, reuse, and recycling should be considered first. The waste hierarchy must be followed. In addition, plastic composition variability including impurities can affect the conversion process.

In red are listed the resources that are facing regulatory limitations or several constraints. This is for example the case for photosynthetic organisms which may enable the development of new energy pathways but overall GHG emissions and cost are key issues. In addition, conventional feedstocks are well established and used today but the regulations aim at limiting their incorporation with more and more stringent constraints.

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<sup>1</sup> <https://nordicelectrofuel.no/>

<sup>2</sup> <https://www.hif.cl/en>

<sup>3</sup> <https://www.prometheusfuels.com/>

Resources	Regulation	Availability	Sustainability	Cost	Classification
Agricultural & forestry residues	Incentive	High	High	Low	H2030 positive
Industrial residues (biomass)	Incentive	Limited	High	Low	H2030 positive
Woody & grassy energy crops	Incentive	High	High <sup>2</sup>	Intermediate	H2030 positive
Atmospheric CO <sub>2</sub> + renewable energy		High	Very High	Very High	
UCO & animal fat	Capped	Limited	High	Intermediate	
Industrial off-gases	Lower GHG reduction potential than the biomass fractions of residues	Limited	Intermediate	Intermediate	
Plastic		Unknown but probably limited <sup>4</sup>	Intermediate (High if bioplastics)	Intermediate	
Photosynthetic organisms (micro/macro algae)	Criteria for GHG reduction difficult to achieve	Potentially High	Limited <sup>3</sup>	High	May be different for specific cases such as IHI process
Conventional feedstock <sup>1</sup>	<ul style="list-style-type: none"> <li>• Competition with food industry</li> <li>• Criteria for GHG reduction difficult to achieve</li> </ul>	High	Limited	High (cereals & Lipids)	

**Table 4** Summary of resources categories, related challenges enabling their classification as a potential supported feedstock in 2030. 1 The different feedstock are considered similarly (e.g. palm and other vegetable oils) as they all are limited by regulation (even if not at the same level). 2 If grown on a land where it will not be in competition with food production and will not harm biodiversity (ex: marginal land). 3 It depends a lot on the types of algae. There are a lot of challenges in terms of global energy balance. 4 It is difficult to forecast toward 2030. The total output of waste plastic in landfill in Europe is 3 700 kt/year [10]so it would require small refining units all over Europe to manage this.

### 3.2. PROCESS DEVELOPPEMENT

#### 3.2.1. Industrially-mature processes and emerging processes

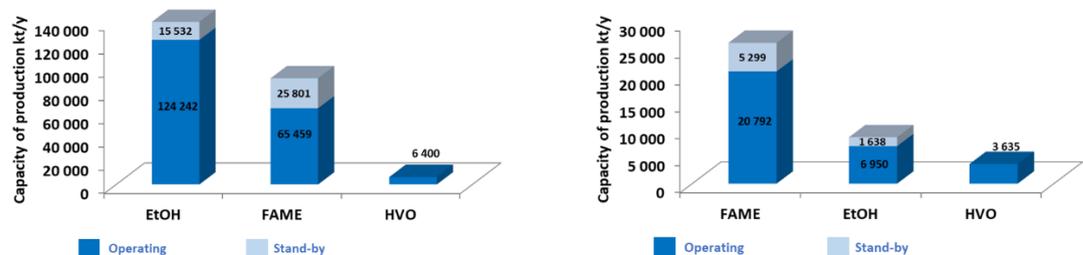
This section will briefly consider the different pathways towards the production of renewable diesel-like fuels that are either already available or close to industrial scale. Public communications will be the main considered references for this section as the relevant data is already widely accessible.

High TRL biofuel pathways for diesel production include today:

- Hydrotreatment of Vegetable oil also named esters or fatty acids (HVO/HEFA) or hydrotreatment of specific feedstocks such as tall oil or lipid wastes. This leads to paraffinic drop-in hydrocarbons
- Transesterification of vegetable oil or lipid waste leading to fatty acid methyl esters (FAME)
- Fischer-Tropsch (FT) from coal and natural gas leading to paraffinic components.

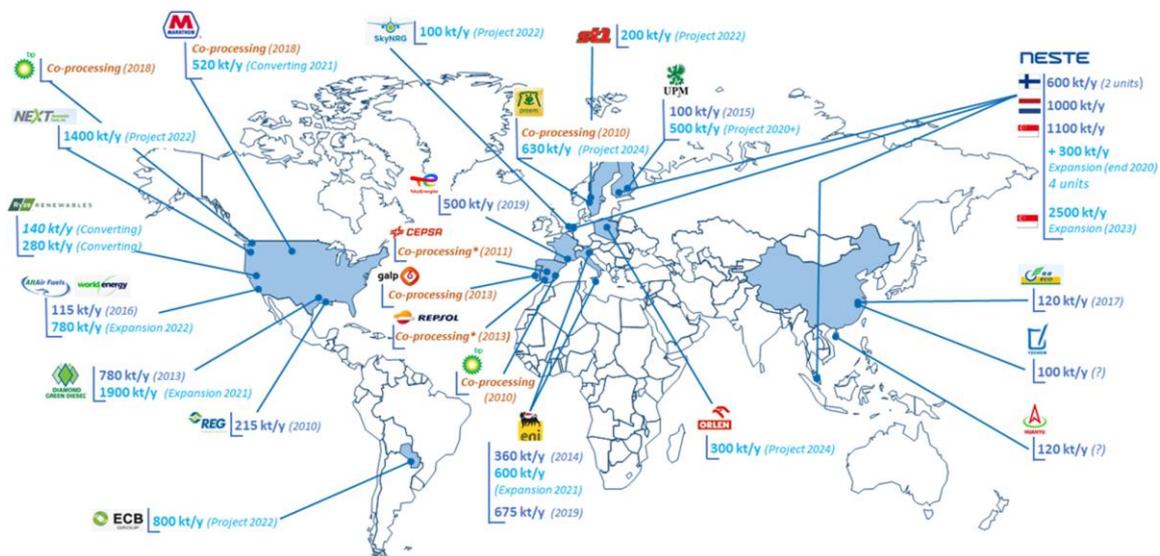
Figure 11 illustrates the world and European biofuel production capacities. This highlights first that worldwide the fermentation pathway to ethanol production is the main route. However, it leads mostly today to gasoline type of fuel. For diesel application, FAME is the most developed option taking advantage of well established processes and incentives. About 70% of the global capacity is being operated. HVO

currently is a limited pathway but is growing related to multiple announcements worldwide.



**Figure 11** World (left) and European (right) production capacity for the main available biofuels today [11]

Figure 12 provides additional details for the HVO production capacity worldwide. It emphasizes established facilities, the use of coprocessing as well as the projects related to potential future HVO developments. The worldwide production capacity, estimated at 6400 kT/year in 2020 could be almost multiplied by three considering expansions and new facilities projects. Since April 2020, 19 companies have announced additional revamping/expansion projects or new biorefineries contributing to further expand the potential role of HVO in the coming years. This includes for example in Europe SCA, STL, PREEM in Sweden, TotalEnergies in France, REPSOL in Spain, UPM in Finland and ORLEN in Poland [12]. All these projects could add about 3000 kT/year of HVO production capacity within the next few years.



**Figure 12** HVO world production capacity (blue) including coprocessing (orange) and projects (cyan). Last update April 2020. Source: IFPEN composition.

In addition to these industrially mature options, emerging routes should also be mentioned. These pathways can be divided into three categories:

- Biological pathway
  - Mostly based on enzymatic hydrolysis step followed by a fermentation step.

- Thermochemical pathways
  - Biomass, wastes or plastics direct liquefaction. This can include a catalyst or specific thermodynamic conditions with different solvents (subcritical or supercritical solvents)
  - Biomass, wastes or plastics indirect liquefaction. A dedicated gasification process is developed followed by syngas conversion through FT for example.
- Electrofuels (e-fuels)
  - Using ideally water electrolysis and air carbon capture to produce hydrocarbons. The main building blocks are demonstrated but the full chain is not. The process is far from being economic.

A few examples of the most advanced technologies for diesel production are listed below.

At the pre-industrial scale, TRL 7 - 8, can be listed:

- Biomass gasification with FT. The closest process to industrialization with RedRock/Fulcrum pre-commercial units under construction in USA with BioTfuel demonstration, Velocys Microchannel FT (UK project)
- Catalytic Pyrolysis and hydrolysis which are more suitable for gasoline and aromatics (Anellotech in USA or GTI)
- Plastic to fuel: Total Grandpuits/Plastic Energy.
- Fermented Hydroprocessed Sugar - SIP Amyris - which looks dedicated to high value products such as sweeteners, beauty & personal care (Biossance, Neossance), cannabinoids, flavor & fragrances, or very specific military fuels such as JP10 type (high density cruising missile fuel) with a niche market.

The following industrialised mature technology pathways, for which the industrial feasibility is estimated as being possible by 2030, will be further described within this section: (1) Transesterification, (2) triglycerides hydrotreatment, (3) fermentation, (4) gasification + Fischer-Tropsch and (5) e-fuel. Available literature dedicated to processes having a lower technical readiness are discussed in the section 3.2.2.

### 3.2.2. Developing processes

This section considers the different pathways towards the production of renewable diesel-like fuels that are currently at intermediate or low TRL (TRL < 7) according to the literature research. The data is limited to literature data dating from 2015 onwards. However, reference to earlier publications might be made when relevant. For each process, the general characteristics and current advantages and limitations are described.

#### 3.2.2.1. Hydrodeoxygenation upgrading of bio-oil or lignin

The approach for the treatment of lignin or bio-oil is the hydrodeoxygenation (HDO) through the combination of oxygen removal with C-C coupling reactions. For this, the depolymerised aromatic rings are hydrogenated, and oxygen is removed. Aromatic alkylation with alcohols, and coupling is carried out to improve carbon size into diesel and jet fuels, for which the reaction temperature is critical to determine the promotion of the earlier or later reaction [13-17]. C-C cracking is also cited as an alternative to jet fuel production [18]. Some research has been

made over the combination of the cracking and alkylation stages [19]. Most publications propose the optimisation for C<sub>5</sub>-C<sub>15</sub> jet fuel like products [20]. The ratio of C<sub>8</sub>-C<sub>15</sub> cycloalkanes in the final product is near 70 %. Some studies focused on the integration of microwave pyrolysis techniques [21]. The literature indicates a negative effect of sugars in the lignin conversion, suggesting the importance of separating the substrate before reactions [22]. Research in this field relates mainly to the improvement of catalyst efficiency at low cost, through the optimisation of combined metal compounds. Some of the difficulties rely on the avoidance of coke formation [17], sulphur contamination, catalyst deactivation, and water poisoning [23].

#### 3.2.2.2. Glycerol processing

Glycerol is a by-product in the production of biodiesel by conventional esterification and represents near 10 % wt of the production. Glycerol products are composed of near 80 % wt pure glycerol, 10 % wt water, 10 % wt sodium chloride and less than 1 % methanol. Despite the apparent interest in optimizing glycerol processing, it should be considered that the expansion in glycerol production is limited by the production of biofuel itself and it is commercialised by other industries. However, many research works evaluate possible economical solutions for upgrading glycerol into higher value products [24, 25]. Some of the processes proposed to produce fuel-like compounds are Transesterification, Esterification, Acetylation and Hydrogenation. Each of them is briefly discussed below:

- **Glycerol transesterification**

The transesterification of glycerol is commonly carried out through methanol and cosolvents (as di-ethyl-ether, DEE, or tetrahydrofuran, THF) to produce ester biofuels. The transesterification process has a reduced conversion rate compared to esterification, and it encounters hindrance by saponification of the fatty acids, slowing the reaction [26].

- **Glycerol Etherification**

Another known pathway is the etherification of glycerol with isobutene, methanol, or with tert-Butyl alcohol (TBA) [24, 27, 28]. This process has a high selectivity (90 % mol), and most research works concentrate on its optimization over heterogeneous or homogeneous catalysts, where the former are most advantageous. The resulting glycerol esters are namely di-tert-Butyl glycerol ethers (DTBGs) and tri-tert-Butyl glycerol ether (TTBG).

- **Glycerol acetylation**

The products of glycerol acetylation are usually referred to as acetin. Acetylation can be carried out by phenyl acetaldehyde, C<sub>4-8</sub> aldehydes, or ketone, using a distillation series or a reactive distillation. This pathway produces diolaxanes (dioxolane, Dioxane / 1,3 Dioxylanes) and additive Solketal [29-32].

- **Glycerol hydrogenation**

The hydroprocessing pathway includes a three-step hydrogenation, dehydration, and hydrogenation processes [25, 33, 34]. The glycerol reaction with hydrogen to form propylene glycol (PG) and water, via consecutive dehydration and hydrogenation, has been patented and commercialised as a BASF production [35]. The final product, Tri Propylene Glycol Methyl Ether (TPGME), is a highly

oxygenated molecule mainly composed of a series of ether bonds. The process has been reported to present over 40% conversion and 70% selectivity.

### 3.2.2.3. **Supercritical and superheated transterifications**

Supercritical and superheated transterification are two main processes in development that aim to counteract transterification drawbacks. Of these, supercritical transterification seems most promising or mature [17, 26]. Several technologies are available according to the solvent used, for example: methanol, ethanol, methyl acetate, dimethyl acetate, methyl tertiary-butyl ether. The supercritical conditions apply to the solvent, most usually methanol, for which the supercritical temperature and pressure are 239.2°C and 8.09 MPa, respectively [36]. The product of the supercritical reaction is Fatty acids or FAME and a by-product of glycerol family, dependant on the reactant. An interesting application could be the supercritical transterification of algae, as it avoids mass drying and lipid extraction, main hindrance in algae processing and upgrading [17, 26, 37].

The advantages of supercritical processes over conventional methods include faster reaction times (minutes), catalyst-free operation, simultaneous triglyceride transterification and free fatty acid esterification, reduced processing steps and higher purity of final product. These might compensate for the higher pressure and temperature required. Under supercritical conditions methanol's mass density, solubility and mass transfer characteristics change lead to a reduced polarity that facilitates triglyceride's solubility in methanol.

To date, biodiesel production using supercritical method requires an excessive proportion of reactants to achieve the complete conversion of oil to biodiesel. To make the process efficient and less reactant consuming, a reactant recovery is required. The technique has advanced in recent years, but it requires further optimization, upscaling, and economic analysis.

### 3.2.2.4. **Lignocellulose Fermentation**

One commercialised pathway is the production of farnesane by idol condensation. Farnesane is the commercial name for isoparaffin 2,6,10-trimethyldodecane, and can be hydroprocessed for renewable jet fuel production [38]. Yeast used for fermentation have been developed by Amyris, and the Direct Sugar to Biocarbon process is coproduced with TotalEnergies. However, to date its commercialisation is mainly destined to other higher value products. Other routes described below have been proposed to produce Diesel-like fuels from fermentation of lignocellulose:

- **Idol condensation to dioxolanes**

In addition to glycerol acetylation, Idol condensation (2-tridencanone) is another pathway to the production of alkyl dioxolane, through acidic conditions. This method has also been used to produce gasoline fuels and diesel additives. The biosynthetic approach allows increasing scales to industry relevant production. The produced dioxolanes inherit the ketone's characteristic high cetane property. Part of the process development is the branching engineering to ensure low freezing point. Another aspect that is of research concern is the elimination of water during the formation of dioxolane, as it represents a low energy pathway to deoxygenating, hence reducing H<sub>2</sub> consumption [39, 40].

- **Ketone bioderived processing to alkanes**

Two pathways to the production of drop-in C<sub>8</sub>-C<sub>15</sub> alkanes have been proposed in the literature. One is the 2-step reduction process, and the other a hydrogenation pathway [41, 42]. The resulting alkanes are reported to have cetane number (CN) between 40 and 45.

For the reduction pathway, short chain acids go through a ketonisation and subsequent condensation to form C<sub>8</sub>-C<sub>15</sub> enones. These will be partly reduced and hydrodeoxygenated to yield together C<sub>8</sub>-C<sub>15</sub> alkanes. These alkanes show a CN ranging between 40 to 50, well suited to Diesel usage. The second pathway is the esterification of alcohol and ketones obtained through the reduction of C<sub>2</sub>/C<sub>4</sub> acids. The process was modeled incorporating previously demonstrated stages but no demonstration plant are identified.

- **Ketone processing to ethers**

Esterification of ketones with ethanol or butanol has also been recognised as a way of producing C<sub>4</sub>-C<sub>8</sub> ethers and C<sub>5</sub>-C<sub>11</sub> ethers, leading to high cetane value (50 and above) products [39, 40, 43]. Because of the high cetane value, the reduced processing and avoidance of oxygen removal steps, this production processes could be of higher interest. However, high value of ethanol and availability of renewable butanol could be a hindrance to such process.

- **Butyric acid processing**

Butyric acid is a platform compound that can be used to produce Diesel-like products. Several pathways have been identified to produce butyric acid. The most relevant is the production from *Clostridium butyricum* fermentation. However, today's production remains low and process development would be required to enhance diesel fuel production through this pathway. Recent research focuses on the improvement of butyric acid fermentation through bacterial engineered methods [44, 45]. Two pathways to diesel-like compounds from butyric acid have been identified in the literature.

- Ketonisation and hydrotreatment

5-ethyl-4-propylnonane is an interesting compound for Diesel blends. It is produced by upgrading of butyric acid through ketonization, condensation and subsequent hydrodeoxygenation [46, 47]. The proposed method evaluated by Luo et al. [44] indicates a high selectivity (above 80 %) for individual conversion steps, and more than 80 % of the carbon in the acid feed is captured, with 60 % purity of the target C<sub>14</sub> hydrocarbon.

- Reductive esterification

Another method for processing butyric acid consists of a reductive esterification. First, butyric acid undergoes simultaneous reduction and ketonisation stages. The reduction pathway leads to n-butanol, while ketonisation of butyric acid produces 4-heptanol [41, 47, 48]. These subproducts go through a reductive esterification stage, and

final distillation. Target product n-butoxyheptane is produced at a 20 % wt yield. The by-products are n-heptane (36 % wt), n-butyl ether (11 % wt). The main advantage of the process is the continuous solvent-free catalytic process. The method also avoids hydrogenations steps present in conventional n-butoxyheptane production pathways.

#### 3.2.2.5. Furan platform to alkanes

Furanic components are produced through the hydrolysis and dehydration of lignocellulose resources. Several pathways exist for the upgrading of the furanic platform. Some of these compounds, as cyclopentanone and 2-Methylfuran, present high RON values and have been studied for integration into the gasoline pool. Furanic compounds are characterised by short chains and oxygen concentration, thus their transformation into diesel-compatible compounds requires several steps of chain growth and oxygen extraction: Depolymerisation, carbon chain extension over acid and base catalysts, oxygen removal, hydrogen reduction [49]. Due to the extensive processes implied, the subject of most literature research is the improvement of the process efficiency and cost reduction (e.g. hydrogen consumption). Moreover, many processes require other platform chemicals as simple ketones and mono-alcohols. Catalyst cost and lifetime are also of concern. For example, the development of low-cost metal catalysts is a pathway towards optimization. However, many pathways have the advantage of producing drop-in alkanes that do not require the definition of specific regulations before integration into diesel blend.

- **Alkylation-Hydrodeoxygenation**

Several methods for the hydroalkylation-alkylation of 2-methylfuran and furfural are proposed. Studies evaluate the impact of catalytic material and operating conditions on the efficiency of the process [92-96]. Materials as Ni/H-ZSM-5, Pb/NbOPO<sub>4</sub>, LF resin and protonated titanate nanotube have been presented.

Aldol condensation pathway has also been studied for different species combination, as are the furan condensation of ethanal, pentanal, or biomass-derived 4-oxopentanal with 2-methylfuran; or the 5-Hydroxymethylfurfural (HMF) condensation with acetone. Final compounds specification depends on the furanic species and aldol employed. Results agree with a total hydrocarbon yield of 89 to 94 % wt. over the Alkylation-Hydrodeoxygenation process. The product is then hydrogenised to hydrocarbon, where most of the product (~75 % wt.) comprises alkanes as the major components. In the literature the products of 6-butylundecane, and of tridecane and pentadecane are specified.

- **Solvent-free esterification**

The solvent free catalytic reaction of furfural and glycol have been proposed by Wegenhart et al. [50]. The method has the advantage of requiring low temperature, from ambient to 100 °C, and not being inhibited by the presence of water impurities. The product is that of 2-(furan-2-yl)-1,3-dioxan-5-ol and (2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol.

### 3.2.2.6. Hydrogenation for the processing of algae biomass

Another pathway that has been proposed is that of the acid catalytic cracking of long-chain algae derived branched hydrocarbons, followed by subsequent acid alkylation and hydrogenation [51]. The cracking process might be hydrocracking but it is not specified in the literature. A high efficiency, above 90 %, has been reported in laboratory studies for each of the steps. The main products are alkenes of C<sub>8</sub>-C<sub>15</sub>. This process is at research level, and aims at improving catalyst conditions and materials, as most are rare metals. Moreover, this process demands high temperature, and is subject to risks of coking. The product will possibly comprise partial low chain compounds not suitable for diesel fuels.

### 3.2.2.7. Enzymatic processes for the processing of fatty acids

- **Fatty Alkyl Ethers (FAE)**

The process for developing Fatty Alkyl Ethers (FAE) is in the progress of laboratory research. The process is expected to produce FAE through the etherification of widely used fatty acids and fusel alcohols. Laboratory study has indicated that the variation of terminal groups enables the optimisation of compound yield, and hence fuel properties. Further study of synthesis directly from triglycerides or fatty acids, and large-scale chemistry operation is expected [52, 53].

- **Fatty Acids Fusel Esters (FAFE)**

The production of Fatty Acids Fusel Esters (FAFE) is expected to be possible through the enzymatic catalysis of fusel alcohol (isobutanol, 3-methyl-1-butanol, and (S)-(-)-2-methyl-1-butanol), with glyceryl trioleate using *Aspergillus oryzae*. The process is expected to be of low-cost, and FAFE to have high cetane value and good cold properties [54].

Under laboratory tests conditions the process achieves more than 97 % wt. conversion to FAFE. The process remains to be evaluated under large scale, and the study of its economic viability has not been reported to date [55].

- **Fatty Acid Diester**

Fatty Acid Diesters have been proposed as a renewable compound for diesel fuels. The proposed process is that of the enzymatic catalysis of renewable HMF-derived 5-Bis(hydroxymethyl)furan and fatty acids reactants, with 2-Methyltetrahydrofuran solvent, under CaL-B (Novozym 435) catalysis [56].

### 3.2.2.8. Di-n-butyl ether production

The pathways that have been identified for the production of Di-n-butyl ether are the esterification or dehydration of n-Butanol [57-59]. Either of these processes could be integrated as a by-process within the production of ethanol, butanol and acetone. The production is restrained by the production of biobutanol itself, for which the production is today limited, and partly in competition with ethanol production.

### 3.2.2.9. Methyl Decanoate

Methyl decanoate is produced through the esterification reaction of decanoic acid with methanol through batch or continuous reactive distillation columns [60]. The production is mainly limited by the availability of decanoic acid, a valuable

compound, for which the renewable production is currently limited. Therefore, enhancing methyl decanoate production would be subject to the improvement and development of decanoic acid production pathways. Recently, a process identified to produce decanoic acid is the metabolic engineering treatment of glycerol [61].

#### 3.2.2.10. 1-octanol

Current researches on 1-octanol production routes are developed through the microbial treatment of biomass. Latest published studies indicate a production of 1.3 g per litre of resource, which accounts for a relatively low yield. Another process is the coupled dehydration and hydroxygenation, through Ru catalyst, thus increasing the yield to 73 % wt. octanol yield, and 54 % wt. in one pot yield [62-65].

#### 3.2.2.11. 2-Nonanol

The conventional pathway for producing 2-nonanol is of hydroformylation. A process of non-Kolbe electrolysis of a biogenic acid containing a 3-hydroxy backbone has been recently proposed. The resource is derivable from glucose or xylose waste-streams. Under optimised conditions, anodic decarboxylation of 3-HDA allows a near full conversion and over 95% total yield after 30 minutes [66]. Other studies have evaluated a similar method over a 3-hydroxy-fatty acid dimer (i.e. HAA) [67]. It is expected that the process' viability will depend on the price and technical industrialisations of electrolyser production and usage.

#### 3.2.2.12. Di-n-pentyl ether (DNPE)

Two different processes were identified for the production of DNPE [68]. The first is a process of reaction, separation and recycle, and the second a catalyst distillation. Water is the only side product of the processes. Pentanol production is a prerequisite to both processes. Options are specific fermentation processes having scattered literature reviews [69], or the hydroforming of syngas (CO and H<sub>2</sub>) with dehydrogenated n-butane. Consequent n-pentanal produced is then hydrogenated to n-pentanol [70].

#### 3.2.2.13. Dibutoxymethane (DBM)

Two different processes were identified for the production of dibutoxymethane. The first is a condensation reaction from butanol and formaldehyde. The process is done through a reaction vessel under sulfuric acid and sodium hydroxide, followed by a distillation, and recycling of butanol/dibutoxymethane mixture for improved yield rate [71] (US2010/0076226). The second identified process is the catalytic transformation of CO<sub>2</sub> and H<sub>2</sub> with butanol, into butoxymethanol and subsequent catalytic treatment into dibutoxymethane. This is an eFuel production pathway. The process could also be optimised into a single catalytic stage. The process is similar to dimetoxymethane production [72]. Both processes require butanol as one of the main input components.

#### 3.2.2.14. Electrofuels / E-Fuels

Several products can be obtained from electric hydrogen production and CO<sub>2</sub> upgrading including paraffinic fuels or alcohols such as methanol. Methanol can also be a chemical feedstock to produce both classical fuels via methanol-to-fuel, but also oxymethylene ether (OME) and dimethyl ether (DME) as well as dimethyl carbonate and methyl formate. Polyoxymethylene ethers (OMEx) are among the most discussed sustainable fuels in the literature as they rely on methanation of CO<sub>2</sub>, a process having less technical challenges than RWGS. Several methods exist to produce OMEx from carbon dioxide and hydrogen using renewable energy, and some pathways are in the stage of demonstration scale [73].

Of these, the most mature method for the production of OME<sub>3-5</sub> is through the reacting of methanol with a formaldehyde source (either trioxane or

paraformaldehyde) to enhance chain elongation. To ensure production is made from renewable resources, study by Damyanov et al. [74] proposed the production of methanol and formaldehyde from hemicellulose fermentation. The OME<sub>x</sub> production process is characterised by a large excess of formaldehyde, which is required to obtain a significant chain growth [75]. Moreover, the presence of water in the system compromises these chain elongation reactions. Another challenge is the optimisation of the separation steps on the pathway to the target product. The process presents a low efficiency, multi-step process and multi-purification, making it costly and limiting the product yield. Currently, this pathway is the most mature available. However, because of these issues, other processes have been developed aiming at increasing the efficiency.

**OME<sub>1</sub> Production via the direct oxidation of methanol:** The process enables to decrease the number of process steps and thus increase efficiency and productivity. It also has the advantage of not requiring noble metal catalyst systems.

**One Step Synthesis of OME<sub>1</sub> From the Direct Hydrogenation of CO<sub>2</sub> with H<sub>2</sub>:** The process presents a higher sustainability, and further reduces the number of steps required to produce oxymethylene ether. To carry out the direct hydrogenation, molecular catalyst systems have been developed and are subject of recent optimizations.

### 3.2.3. Conclusions on production pathways

Renewable diesel production relies mostly today on two pathways: hydrotreated vegetable oil to HVO/HEFA and transesterification of triglycerides to FAME. These represent about 100 000 kt/year of production capacity. Amongst them, HVO production capacity will probably increase due to many announcements of biorefineries development or extension. These well established pathways may also compete in the near future with biological, thermochemical and e-fuel routes. These processes will likely be developed during the next decade but it remains difficult to evaluate their real contribution to diesel-like fuel production by then. Indeed, developing new refineries requires years of development and investments adding a significant delay into the development of novel fuel production pathways. In addition, the mobility sector may be facing important transitions which could favour certain pathways.

A wide variety of pathways for the processing of renewable feedstock are currently under research and development stages. Of these, the upgrading of by-products from conventional biofuel (as bio-oil and glycerol) production into conventional alkanes, has attracted most research, as it takes advantage of already developed processes and upgrading of currently available by-products. However, these processes require several steps of oxygen removal and hydro-processing, making the processes complex and costly. To avoid these issues, the partial hydrogenation has been evaluated as a way of reducing cost.

The upgrading of fermentation products is of interest and literature indicates that several alternative compounds of high CN value can be produced. For this, the synergy of bioengineering (e.g. bacteria fermentation) and process design is a pathway to simplifying the overall process and targeting specific molecules. Moreover, the resulting non-alkanes compounds might be of interest because of their higher CN; especially if they enable reduced process complexity. However, most solutions require the simultaneous optimisation and development of both the bio- or enzymatic processing of the resource, as well as the processing of the resulting short carbon chain into a diesel-like compound.

The production of higher alcohols and their derivatives currently faces great challenges, constrained by the biosynthesis through microbial enzymatic treatment, and maintenance of algae matter. Alternative techniques are in the state of research but are hindered by the requirement of specific compounds, not readily available. Similar constraints are possibly present in the production processes of methyl decanoate, di-n-butyl ether, butyric acid derived 5-ethyl-4-propylnonane and n-butoxymethane. Possible promising solutions could be the processing of fatty alkyl ethers, for which some production stages are readily in mature conditions. However, research work is in early stage.

Processes considered as essential to produce renewable fuels have been classified considering their Technology Readiness Level (TRL) by 2030 (see Table 5). These processes are considered as the main building blocks but are not the only ones to generate relevant products. In green, at least five key steps have been identified as available by 2030 or already available: transesterification, triglycerides hydrotreatment, fermentation, gasification with Fischer-Tropsch and pyrolysis to produce bio-oil. In orange, three steps have been identified as being at intermediate TRL by 2030. They are hydrothermal conversion + upgrading, fast pyrolysis bio-oil upgrading and e-fuel/solar fuel. The upgrading part is the most challenging both for hydrothermal conversion and fast pyrolysis due to the necessity of dealing with highly oxygenated products or specific contaminants. Finally, in red are listed options considered still at low TRL by 2030. They are bioengineering such as the use of photosynthetic organisms (not many outcomes are seen), glycerol pathway (very specific but mentioned in the literature) and furanic platform mainly focusing on upgrading lignocellulosic biomass.

**Table 5** Processes classification by 2030. <sup>1</sup>Bio-oil can be used in replacement of Heavy Fuel Oil or gas in heavy applications but cannot replace conventional Diesel. Bio-oil can be co-processed to a limited extent as it is thermally unstable and does not blend with hydrocarbons (unstable mixtures). <sup>2</sup>Mainly hydrotreatment upgrading to obtain biofuel is an issue. <sup>3</sup>Reverse Water-Gas Shift (RWGS) reaction is a necessary step to this process, and is not mature yet; a pilot plant is planned to be set up in 2024 but it is unknown whether it will available at industrial scale by 2030.

Resources	Regulation	Availability
Transesterification	High TRL	Green
Thermochemical process		
Fermentation		
Gasification + FT		
Pyrolysis (to bio-oil <sup>1</sup> )		
Hydrothermal conversion + upgrading	Intermediate TRL	Yellow
Fast pyrolysis bio-oil upgrading <sup>2</sup>		
E-fuel/solar fuel <sup>3</sup>		
Photosynthetic organisms	Low TRL	Red
Non-photosynthetic organisms (microalgae, bacteria, fungus)		
Glycerol pathway		
Superheated/supercritical		
Furanic platform		

### 3.3. RENEWABLE DIESEL FUELS

This section covers the third step of the literature review consisting into identifying the main components considered as potential renewable diesel-like fuel products. Three items are discussed to complete the overview of the available pathways according to the literature: (1) the fuel specifications which define the fuel formulation area; (2) products that cited in the literature as potential diesel-like components; and (3) an approach to select relevant components for the market by 2030 based on the available specifications.

#### 3.3.1. European fuel standards for diesel engine

The European diesel-like fuel specifications include five main references:

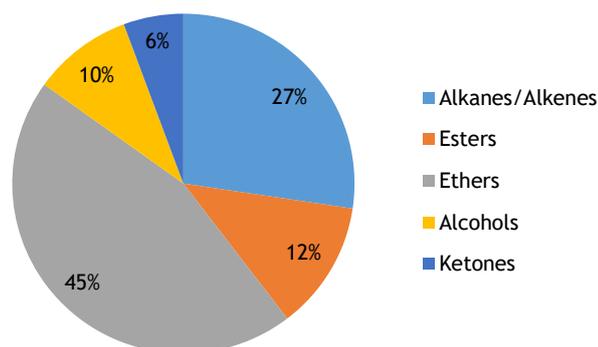
- EN 590 establishes specifications for biodiesel/diesel fuel blends up to 7% v/v of FAME (B0, B7 and R33).
- EN 14214 establishes specifications for fatty acid methyl esters (FAME) for diesel engines. B100 that meets this standard could be used unblended in a diesel engine (if the engine is adapted to operate on B100) or blended with diesel fuel in accordance with EN 590 or other applicable standards.
- EN 16734 establishes specifications for biodiesel/diesel blends up to 10% v/v of FAME. B10 that meets this standard could be used in a compatible diesel engine.

- EN 16709 establishes specifications for high FAME diesel fuel blends. B20 and B30 blends that meet this standard could be used by adapted captive fleets.
- EN 15940 establishes specifications for paraffinic diesel fuel covering hydrotreated paraffinic renewable diesel fuel (HVO) and synthetic Fischer-Tropsch products XTL (e.g. GTL, BTL, Coal-to-Liquid (CTL), e-Diesel) that could be used in a diesel engine or blended with diesel fuel in accordance with EN 590 or other applicable standards.

In addition, ED95, a fuel for modified diesel engines containing 95% ethanol and additives has been developed. The corresponding European regulation EC n° 582/2011 establishes specifications for this fuel. The listed specifications are provided in Appendix 1.

### 3.3.2. Products summary

The analysis of the scientific literature enabled the identification of more than 100 components that are claimed as potential renewable diesel-like components. Different classes of organic components are identified comprising mostly ethers and alkanes or alkenes (see Figure 13).



**Figure 13** Distribution by compounds categories of molecules identified through the scientific literature analysis

In addition to pure compounds, the literature review also highlights the use of straight vegetable oils (SVO) as a potential renewable fuel for compression ignition applications. The main properties are given in the Figure 14 below.

**Table 6** Straight vegetable oils properties compared to fossil fuels [76]

Feedstock	Density kg /m <sup>3</sup> at 15°C	Kinematic viscosity (cS)	Cetane Number	HHV MJ/kg	Flash point °C	Carbon residue %wt	Iodine value gI <sub>2</sub> /g	Pour point (°C)	Sulphur Wt.%
Diesel (SONABHY)	820 to 890	1.6 to 5.9 <sup>a</sup>	> 50	> 45.0	> 61	< 0.15	-	-	< 1.0
DDO (SONABHY)	835 to 950	5.9 to 15 <sup>a</sup>	> 40	> 44.70	> 66	< 0.2	-	<15	< 1.5
Fuel-oil 180 (SONABHY)	920 to 990	< 180 <sup>c</sup>	> 30	> 43.00	> 66	< 12	-	<15	< 3
Biodiesel (EN14214)	860 to 900	3.5-5.0 <sup>b</sup>	> 51	-	120	0.3	120	-	1
Babassu	946	30 <sup>a</sup>	38	-	150	-	16	-	-
Castor	955	251 <sup>b</sup>	42	37.4	-	-	83-86	-	-
Coconut	918	27 <sup>b</sup>	40-42	37.1	-	-	8-11	-	0.01
Corn	910	31-35 <sup>a</sup>	38	39.5	277	0.24	103-128	-40	0.01
Cottonseed	915	34 <sup>b</sup>	42	38.7-39.5	234	0.24	103-115	-15	0.01
Crambe	905	54 <sup>a</sup>	45	40.5	274	0.23	-	-12	-
Jatropha	940	34 <sup>b</sup>	39	38.8	225	-	82-98	-	0.01
Linseed	924	26-27 <sup>a</sup>	35	39.3-39.5	241	0.22	180	-15	-
Mahua	960	25 <sup>b</sup>	-	36	232	-	58-70	-	-
Neem	919	50 <sup>b</sup>	-	-	-	-	65-80	-	-
Palm	918	40 <sup>a</sup> -45 <sup>b</sup>	42	39.5	267	0.23	48-58	-	0.01
Peanut	903	40 <sup>b</sup>	42	39.8	271	0.24	84-100	-7	0.01
Rapeseed	912	35-37 <sup>a</sup>	41	39.7	246	0.3	105	-32	0.01
Sesame	913	36 <sup>b</sup>	40-42	39.4	260	0.24	103-116	-9	0.01
Soybean	914	29 <sup>b</sup> -33 <sup>a</sup>	38	39.6	254	0.25	128-143	-12	0.01
Safflower	914	31 <sup>a</sup>	41	39.5	260	0.25	145	-7	-
Sunflower	916	34 <sup>a</sup> -36 <sup>b</sup>	37	39.6	274	0.27	125-140	-15	0.01

<sup>a</sup> kinematic viscosity at 37.8°C; <sup>b</sup> kinematic viscosity at 40°C; <sup>c</sup> kinematic viscosity at 50°C

The higher molecular weight of such components will certainly imply that the distillation properties do not fall within the boundaries of EN590. In addition, the products have a rather high viscosity and a low cetane number, which may require additivation to address. These limitations will contribute to constant their use in current engines for the transport sector unless the fuel specifications are extended and engine operability thoroughly demonstrated.

### 3.3.3. Conclusions on identified renewable diesel-like products

The objective of this section is to summarize and highlight the components that could be the most promising for a use by 2030 considering current specifications. Molecules identified in the literature can be categorised according to three criteria:

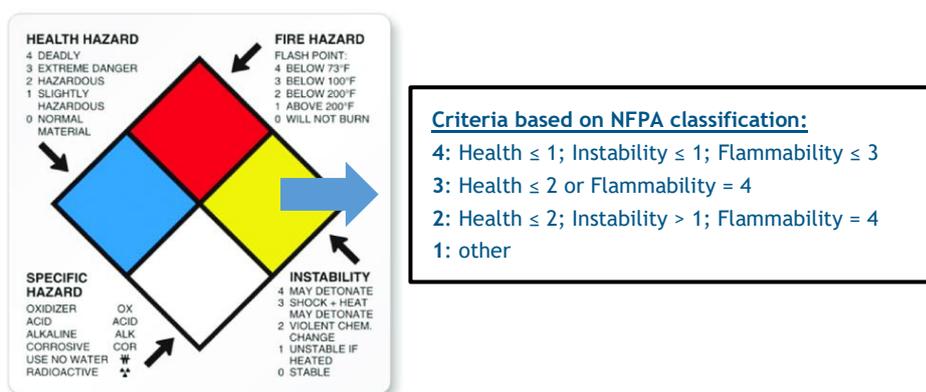
- Key physical chemical properties are met - meaning that the product could be considered as a drop-in fuel.
- Health & Environment score
- Logistic compatibility

Key quantitative properties in relation to European diesel fuels standards were considered to be:

- **Density at 15°C and viscosity at 40°C.** These two properties refer to hardware limitations within the vehicle including for example the fuel pumping system and the injection.
- **Flash point** to ensure a safe use of the product with current facilities and systems.
- **Melting point** as a reference property for cold flow behaviour of the product. The property is selected instead of the cloud point for example as the latter is not accessible for all the products.

- **Initial boiling point** to account for the product volatility.
- **Cetane number** to maintain good engine performances through a satisfactory auto-ignition delay.

Regarding health and environment, the NFPA classification was considered as a reference. *Figure 14* shows the corresponding classification as well as the criteria used in this study. For example, the best case for an identified renewable diesel-like compound would be a classification of 4 which corresponds to limited risks.



**Figure 14** Health & Environment toxicity criteria definition [77]

Finally, qualitative properties have been added to complete the overview of the products evaluation. They include miscibility in hydrocarbons, material compatibility and oxidation stability. For each of them, four levels have been defined:

- ++: good
- +: fair
- -: bad
- Ø: unknown

These qualitative properties were considered to extend the database however for most of the components, these properties could not be directly assessed.

The different components were classified according to four levels defined below:

- Suitable (drop-in)
- Challenging (limited incorporation)
- Very challenging (very limited incorporation ~5 %)
- Not suitable due to a very limited incorporation rate

Table 7 summarizes the corresponding boundaries for each property. The classification of a compound as green, yellow, red, or dark is based on the lowest score of one of these seven properties.

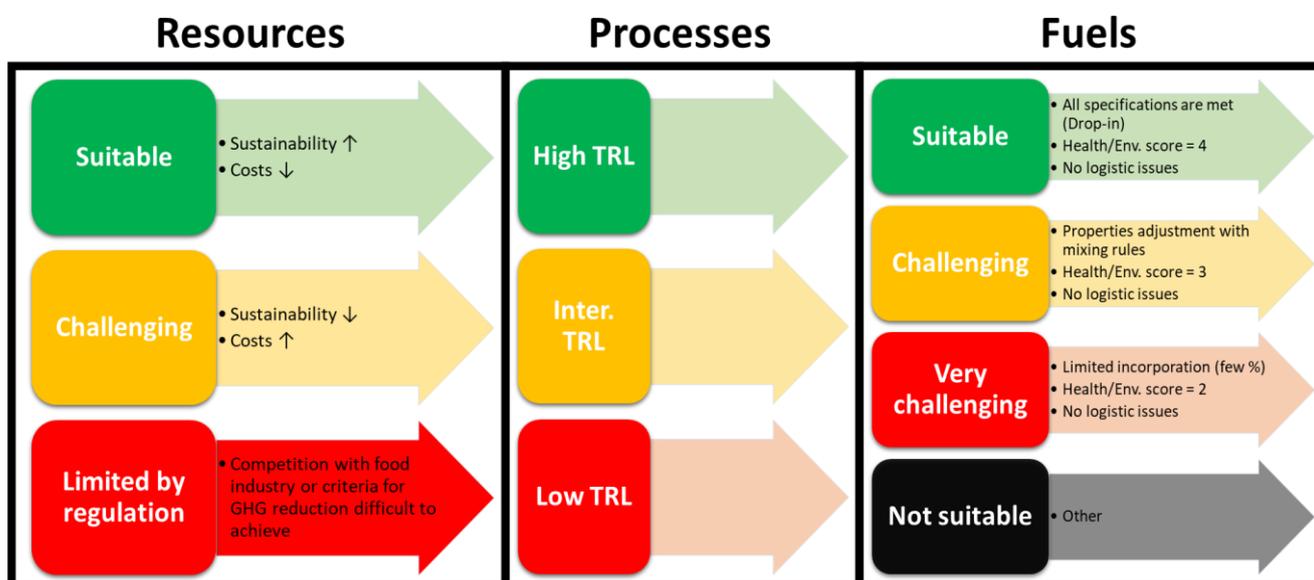
**Table 7** Quantitative properties selection methodology. <sup>1</sup>Concatenation of diesel fuel specifications EN590, EN14214 and EN15940. <sup>2</sup>Defined based on the fact that FAME with MP <0°C are integrated today up to 10%. <sup>3</sup>Lower density acceptable for incorporation of about 10% compound in a base fuel with a density of 830 kg/m<sup>3</sup>. <sup>4</sup>To avoid miscibility issues (water). <sup>5</sup>Compound with CN<30 limits its incorporation in the mixture. <sup>6</sup>Non-linear property that cannot be improved easily / Very limited incorporation (< 5%). <sup>7</sup>It is allowed to add up to 5% of compounds boiling beyond 360°C.

	Property	Density	Cetane Number	Viscosity at 40 °C	Flash Point	Melting Point	Initial Boiling Point	Health & Env. toxicity
	Unit	Kg/m <sup>3</sup>	[-]	[mm <sup>2</sup> /s]	[°C]	[°C]	[°C]	[-]
<b>Suitable</b> (drop-in)		[765-900] <sup>1</sup>	≥ 51 <sup>1</sup>	[2-5] <sup>1</sup>	≥ 55 <sup>1</sup>	≤ 0 <sup>2</sup>	≤ 250	4
<b>Challenging</b> (limited incorporation)		other	[30-51[	< 2	[45-55[	]0-40]	]250-350]	3
<b>Very challenging</b> (very limited incorporation -5 %)		< 730 <sup>3</sup> or > 1000 <sup>4</sup>	[15-30] <sup>5</sup>	> 5	[30-45] <sup>6</sup>	> 40	]350-375]	2
<b>Not suitable</b> (cannot be used for Diesel-like blends)		-	< 15	-	< 30 <sup>6</sup>	-	> 375 <sup>7</sup>	1

A full table is provided in Appendix 2 to illustrate the classification of the identified products.

### 3.4. SUMMARY

This first task including reviewing the resources, processes and potential renewable diesel-fuel like components is summarised in this section. The overall classification methodology for the resources, the processes and the renewable diesel-like fuels is illustrated Figure 15.

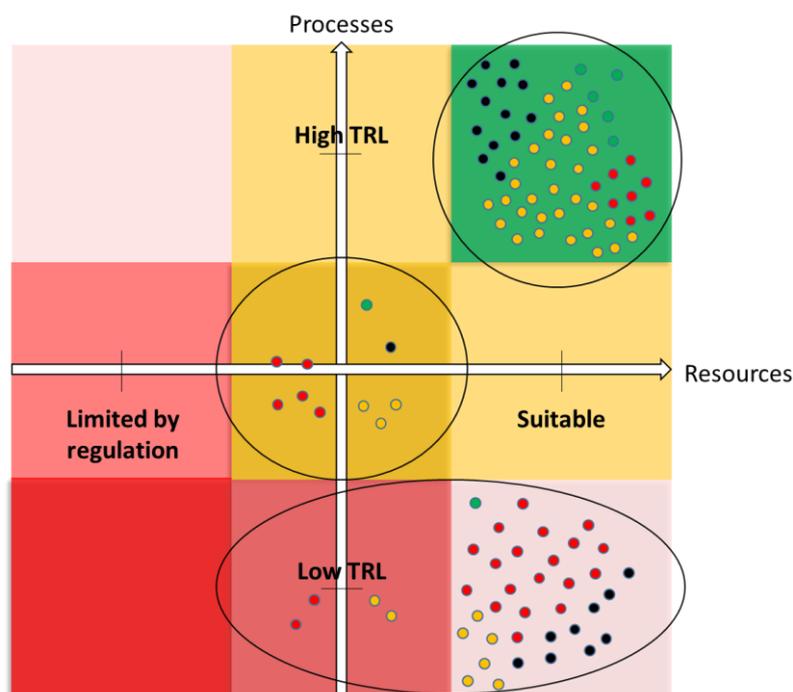


**Figure 15** Overall classification methodology for the resources, the processes and the renewable diesel-like fuels based on criteria defined in section 3. The colours correspond to the classification level.

Products mapping of has been carried out (see Figure 16) to identify fuel pathways that could be of interest. This leads to:

- 58 compounds identified with processes “high TRL” and resources “suitable”
- 10 compounds identified with processes “intermediate TRL” and resources “challenging”
- 39 compounds identified with processes “low TRL” (glycerol & furanic derivatives, esters, heavy alcohols, ketones)

It should be emphasised that while a product could be theoretically obtained through different combinations of resources and processes, only the best one in terms of TRL and resources availability is considered here.



**Figure 16** Products mapping considering the classification level of resources (x-axis) and processes (y-axis) used to produce identified renewable diesel-like fuels. Each box corresponds to a category (e.g. green box refers to the processes “high TRL” and the resources “suitable”, orange box refers to the processes “intermediate TRL” and the resources “challenging”, red box refers to the processes “low TRL” and resources “limited by regulation”, etc.). Each point represents an identified product (colour refers to classification level defined in section 3.3.3).

This approach enabled to define different categories for the identified components (“R” refers to resources, “P” to processes and “F” to fuel):

- **R <suitable> and P <high TRL> and F <suitable>**: bicyclohexyl, 6-butylundecane, 5-butylnonane, farnesane, di-n-pentylether correspond to selection criteria and are considered as promising candidates for future Diesel-like renewable fuels.
- **R<suitable> and P<high TRL> and F<challenging>**: **36 compounds** were identified including alkanes (e.g. farnesane, n-decane), esters (e.g. methyl laurate, methyl oleate), ethers (e.g. di-n-pentyl ether, di-isopentyl ether), dioxolane derivatives (e.g. 4,5-dimethyl-2-(pentan-3-yl)-1,3-dioxolane), fatty acid ethyl esters (FAEE) and ketones (e.g. 3-octanone).
- **R<suitable> and P<high TRL> and F<very challenging>**: **8 compounds** including pinene, limonene, methyl stearate, 2,4-dimethyl-2-undecyl-1,3-dioxolane, n-butanol, pentanol, 2-hexadecanone and 2,2,5,5-tetramethyl-3-hexanone need to be further investigated and may be relevant.
- **R<challenging> and P<intermediate TRL> and F<suitable>**: only **dibutoxymethane** corresponds to selection criteria and is considered as promising candidates for future Diesel-like renewable fuels.

- R<challenging> and P<intermediate TRL> and F<challenging>: light oxymethylene ethers (OME<sub>x<3></sub>) were identified.
- R<challenging> and P<intermediate TRL> and F<very challenging>: heavier oxymethylene ethers (OME<sub>x≥3</sub>) were identified in this category.

Table 8 provides a synthesis of the potential renewable diesel-like fuel pathways. The most relevant products include: dioxolane derivatives, alkanes, esters and selected ethers.

**Table 8** Overview of the potential renewable diesel-like fuel pathways by type of product. For each type of product, the potential compatibility with current specifications is illustrated as defined in section 3.3.3. Corresponding resources and potential processes are also listed with the corresponding colours according to sections 3.1.7 and 3.2.3.

Ranking	Components		Resources (most advanced)	Processes (most mature)	
Top 4	<b>Dioxolane derivatives</b> (2-(heptan-3-yl)-4,5-dimethyl-1,3-dioxolane, etc.)	● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Fermentation	● ●
	<b>Alkanes</b> (n-decane, etc.)	● ● ● ●	Agricultural & forestry residues Industrial residues (biomass)		Thermochemical process
	<b>Esters</b> (single esters such as methyl laurate, etc.)	● ● ● ●	Agricultural & forestry residues Industrial residues (biomass)	Transesterification	● ●
	<b>Ethers (excluding OME<sub>x</sub> &amp; dioxolane derivatives)</b> (dipentyl ether, isoamyl ether, etc.)	● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Fermentation	● ● ●
Others	<b>Ketones</b> (4-methylacetophenone, 3-octanone, etc.)	● ● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Pyrolysis	● ● ● ●
	<b>OME<sub>x</sub></b>	● ● ● ● ●	Industrial off-gases Atmospheric CO <sub>2</sub> + renewable energy	E-fuelsolar fuel	● ● ● ● ●
	<b>Light alcohols</b> (ethanol, methanol, pentanol, etc.)	● ● ●	Agricultural & forestry residues Industrial residues (biomass) Woody & grassy energy crops	Fermentation	● ● ●

Legend:

- : suitable for blending in D, FAME, or HVO
- : challenging
- : very challenging
- : not suitable

- : suitable
- : challenging

- : high TRL
- : intermediate TRL

## 4. FUEL AND ENGINE CO-OPTIMISATION

Identification of renewable diesel-like fuel pathways has highlighted the component diversity as well as some limitations regarding the fuel compatibility with existing specifications. .

This section presents the literature review on diesel-like compounds' suitability for engine usage, and considers their properties, combustion and engine-out emissions impact, material and aftertreatment compatibility. The research has been extended to most cited species or families found in the literature having demonstrated some favourable combustion or emissions results, beyond those considered as relevant according to the resource, process and property criteria listed in the previous section. The review is organised by chemical families: Ethers, Dioxolanes, Long-chain alcohols, Ketones, Esters and Paraffinic compounds. For some of these compounds, data before 2015 is proposed when no relevant more recent data could be identified.

### 4.1. ETHERS

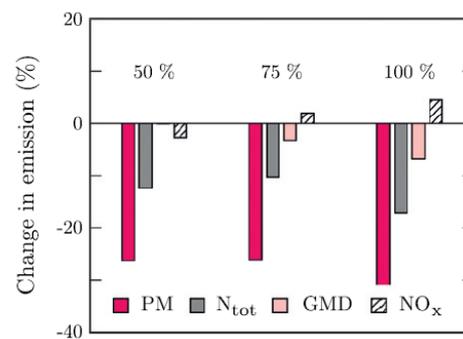
Ethers for which resource availability and process development are acceptable, and compatibility properties were suitable are limited to Dibutoxymethane (DBM), Di-n-pentyl ether (DNPE), di-isopentyl ether (DIPE), and long chain oxymethyl-ether OME<sub>x</sub>.

#### 4.1.1. Dibutoxymethane (DBM)

Recent and previous research on DBM have confirmed its compatibility with engine applications, with respect to fluid properties, fuel miscibility, and hardware compatibility [54, 71, 78-80]. Studies have evaluated blends from 5 to 75 vol.% in conventional Diesel fuel. However, literature research does not indicate any recent publication on the use of DBM on engine tests. Engine studies available date up to 2013. Research by Bertola et al. [81] and Happonen et al. [80] over several oxygenated fuels indicated that DBM is a potential additive for Diesel fuels, capable of improving NO<sub>x</sub> and particles trade-off. Experimental results have highlighted the potential to reduce particle emissions thanks mainly to the presence of oxygen in the fuel's composition and, as a second order parameter, by the higher CN. Combustion noise can also be improved.

#### 4.1.2. Di-n-pentyl ether (DNPE)

From 2015 literature on DNPE is limited to the development of production pathways and blend properties [80, 82, 83]. DNPE is characterised by a high CN of 111 and low freezing temperature, hence a good cold operation behaviour. Its density is slightly below the EN590 standard (781 kg/m<sup>3</sup>). However, very limited engine testing is available for this compound. Results over a 20 vol.% blend of DNPE in HVO have been presented by Happonen et al. [80] (see Figure 17) and indicate the potential to reduce particle matter by 25 to 30%, and particle number ( $N_{tot}$ ) by 10-17%, on an off-road engine, and this independently of the engine load. The changes on NO<sub>x</sub> emissions are within 5% variation, showing a limited reduction at low load, and limited increase at full load. Similar results have been reported by Marchionna et al.[70].

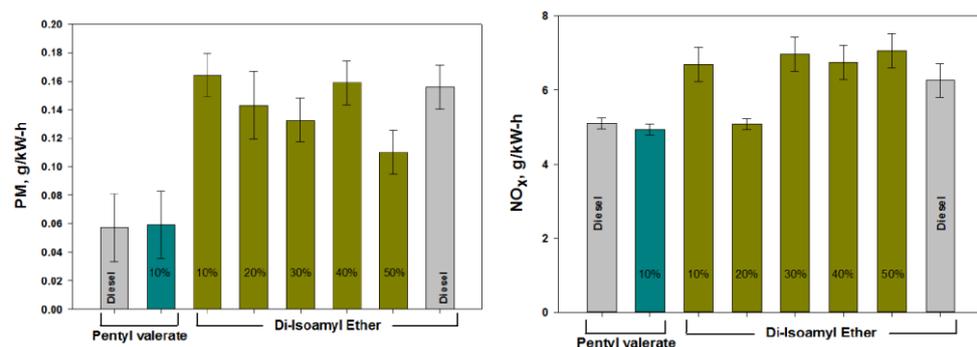


**Figure 17** Impact of 20 % DNPE mixed with HVO fuel at 50 %, 75 % and 100 % load on a commercial six-cylinder off-road common rail diesel engine. PM: particle matter, N<sub>tot</sub>: total particle number [80].

#### 4.1.3. Di-isopentyl ether (DIPE)

No recent literature is available on the use of Di-isopentyl ether (DIPE) on Diesel engine applications. Work by McCormick et al. [83] indicates that this component has good fluid properties for Diesel applications, with highlight on the high CN of 96 and density slightly below EN590 range (778 kg/m<sup>3</sup>). Analysis on oxidation stability indicated no peroxide formation in a 12 weeks aging test. Dedicated hardware compatibility results have not been published for DIPE.

Engine test results at blending rates of 10 to 60 vol.% of DIPE showed no impact over particle matter or NO<sub>x</sub> emissions, except for a NO<sub>x</sub> reduction at 20 vol.% (see Figure 18). Publication by Burton et al. [84] showed acceptable fuel properties for a blend at 30 vol.%, while providing a 30% soot reduction at constant EGR rate. Hence, demonstrating the potential to improve the typical NO<sub>x</sub> to particulatettrade-off, and permit additional EGR is allowed. Under no calibration modifications, the impact on efficiency and NO<sub>x</sub> emissions remains negligible.



**Figure 18** Impact of di-isopentyl ether blends on PM and NO<sub>x</sub> emissions, 4-cylinder, turbocharged, 4.5L John Deere PowerTech Plus common rail, direct injection diesel engine.

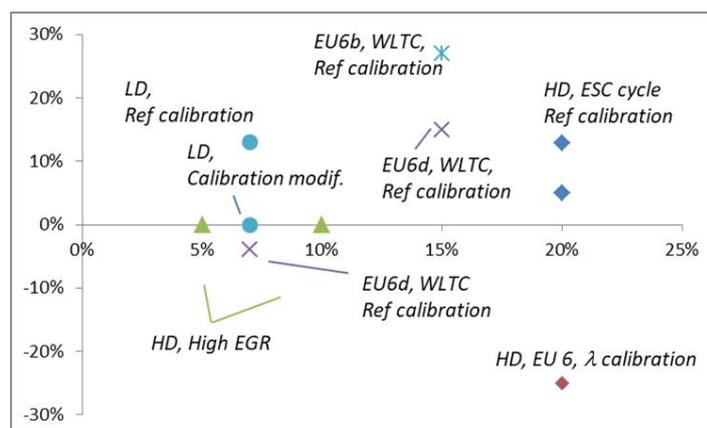
#### 4.1.4. Polyoxymethylene ether (OMeX)

More than 15 relevant publications have been registered listing significant information on fuel properties, compatibility and emissions impact. Several researches [85-88] have indicated the need to adapt elastomers to ensure compatibility, this even at low concentrations levels, 5 vol.% [89]. Elastomers

fluoro-elastomer (FKM) and nitrile butadiene rubber (NBR) are not compatible with the use of OME<sub>x</sub>. A possible replaceable elastomer is Perfluorinated rubber (FFKM), a higher cost material than conventionally used materials. Ethylene propylene diene rubber (EPDM) also shows good compatibility with pure OME<sub>x</sub> fuel, but it is not tolerant to Diesel fuels.

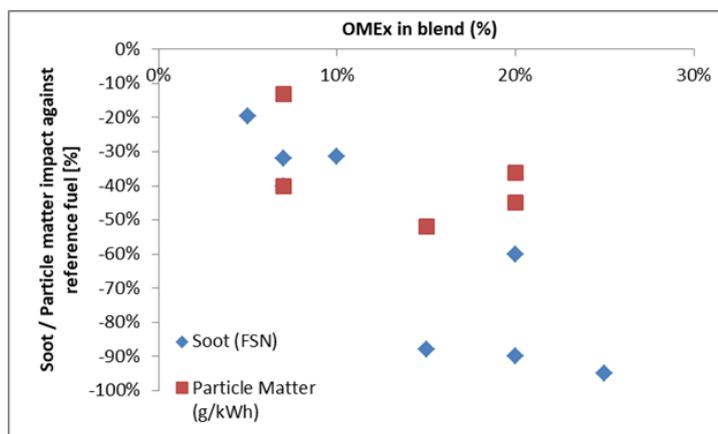
Data indicates that the use of OME<sub>x</sub> remains challenging because of its high density, low viscosity and reduced lower heating value. OME<sub>x</sub> has a high oxygen concentration per volume among potential advanced fuels explaining its inherent low energy density. Literature indicates that blending up to 30 vol.% is feasible within the suitable blending frame [90]. Higher concentration will possibly require adapted nozzle geometry or loss of performance [91-93]. Most literature indicates that OME<sub>x</sub> blends facilitate an increase of the brake efficiency. This is explained by different factors: OME<sub>x</sub>'s high CN, leading to improved combustion timing and faster combustion, and also by the increased spray gas entrainment [94, 95]. Despite these properties, lower combustion efficiency has been observed in cases where the advanced combustion increases negative work with cylinder pressure increase before top dead centre [95].

The impact upon engine out emissions is strongly dependent on the test conditions. Most literature reviews are based on light-duty vehicles [96-99], and it could be expected that similar tendencies are to be found on heavy duty applications. An increase in NO<sub>x</sub> emissions is mainly observed for tests where calibration has not been adjusted. Moreover, tendencies vary within -2 to +27% [100]. The main reason for this tendency is the LHV of OME<sub>x</sub>, that results in a stronger electronic control unit torque request, usually associated to reduced EGR. Figure 19 illustrates the results variability according to the literature, with a higher concentration of results indicating a 10 to 30% increase. These results are comparable amongst light duty and heavy duty applications [101].



**Figure 19** Impact of OME<sub>x</sub> blend volume over NO<sub>x</sub> emissions with respect to Diesel EN590 fuel, depending on OME<sub>x</sub> blend rate. LD: light duty. HD: heavy duty

Results obtained by Härtl et al. [86] for an heavy duty Euro VI engine with a lambda calibration, for which EGR is adapted to oxygenated fuels, indicate that appropriate calibration could improve NO<sub>x</sub> emissions. In this case a 25% NO<sub>x</sub> emissions reduction is observed. Figure 20 illustrates literature data on the impact of OME<sub>x</sub> blend over particle emissions, highlighting a linear reduction as oxygenated blending rate increases [90, 102, 103].



**Figure 20** Soot and particle matter variation with respect to reference Diesel fuel against OMEx concentration

The impact of OMEx fuels on non-regulated emissions has also been studied. Oxygenated fuels tend to increase polyaromatic and aldehyde emissions and facilitate particle oxidation [104, 105]. To explain PAH emission increases with oxygenates, Pellegrini et al. suggests that the oxidation catalyst might have a slightly lower catalytic activity with oxygenated fuels [105]. Soluble and insoluble organic fractions (SOF and IOF) are reduced with the OMEx blends [106].

Concerning the after-treatment system, it has been reported that a faster tail-end of combustion and reduced maximum heat release enabled the for advancing combustion timing. This can result in lower engine out temperature, retarding the activation of the aftertreatment system [107]. Consequently, a reduction in the SCR and catalyst efficiency has been reported by Pellegrini, L., et al. [105] and Rösel G., et al. [108]. Moreover, adapted calibration at increased EGR can result in low NOx emissions [108, 109]. Engine optimization as the increase of air-fuel ratio and cylinder pressure can even contribute to reach levels equivalent to Diesel fuel [110]. Limited data has been found on the impact of OMEx blends over engine's performance. Only one study has reported a reduction of 3 to 4% of full load response [105]. Recent research focuses on engine optimization for 100% OMEx. That is, high EGR and stoichiometric operation under EU6 NOx limits. However, results indicate high unburned hydrocarbons (UHC), CO, volatile organic components (VOC) including formaldehyde and methane [111].

#### 4.1.5. Tert butyl glycerol ether (TBGE)

Several publications evaluate the impact of glycerol derivatives over Diesel combustion engines [112-122], with blends ranging from 2 to 5 vol.% in conventional Diesel, and 10 to 20 vol.% in Biodiesel. The interest of glycerol derivatives resides mainly in the improvement of cold properties and viscosity of biodiesel. However, works by Melero et al. [118] indicate that oxidation stability could be reduced at 20 vol.% in biodiesel. The study of several glycerol derivatives by Jaecker et al. [119] indicates that TBGE provides the best NOx -Particles trade-off. The evaluation of TBGE on engine out emissions indicates a reduction of 15 to 30% (10-15% and 20% blend, respectively) [119-122] of particle matter under same calibration, and a 45 to 80% reduction (10 and 20% blend, respectively) where calibration has been optimised for the fuel blend [121]. The impact on NOx emissions is reduced and varies within -3 to +6% of the reference fuels considering the different studies available. Unburned hydrocarbons (HC) and carbon dioxide (CO) emissions both increase by 7 and 15%, respectively, with 10 vol.% of TBGE. Carbonyls emissions have also been reported to increase [122].

#### 4.1.6. Diethylene glycol ethyl ether (DEGEE)

DEGEE (or DEGEEM) is a compound that has been of interest from earlier research [121, 123-125] up to more recent date [85]. The advantage of DEGEE resides in its capacity to reduce particle emissions, thanks to its high O/C and H/C ratio, with intermediate chain oxygen branching. Research has indicated DEGEE capacity of reducing cold filterability plugging point (CFPP), with a limited cloud point (CP) increase of 1 °C per 10 vol.% blend. However, the main limitation for the utilization of DEGEE is the non-miscibility observed from 15 % vol blends, reduced to 10 vol.% limit at 0 °C [126].

#### 4.1.7. 4-butoxyheptane

Research and development of 4-butoxyheptane is limited to publications by CoOptima research group. These indicate that 4-butoxyheptane's high CN and good cold properties are well adapted to diesel combustion. However, a low viscosity (0.8 mm<sup>2</sup>/s) and slightly low density (791 kg/m<sup>3</sup>) could limit its blending ratio. Moreover, blend properties up to 30 vol.% are available. Works by Huq et al. [41] and Fiorini et al. [71] indicate a good material compatibility up to 30 vol.%, with increased silicone swelling when used as a pure compound. Large property and compatibility analyses indicate that at 20 vol.% blend in Diesel lubricity improver would be required. Oxidation stability is also limited and would require additivation. No combustion tests are available.

#### 4.1.8. 3,5,7,9-Tetraoxaundecane

This fuel has been listed as a possible renewable compound by Fiorini et al. [71] It is characterised by a relatively low density (783 kg/m<sup>3</sup>); high CN (70), and low viscosity (0.5 mm<sup>2</sup>/s). No blend properties or engine tests are available for this fuel.

### 4.2. DIOXOLANES

There is no information on the combustion characteristics, engine-out emissions or hardware and after-treatment compatibility of relevant dioxolane compounds for diesel application. Works on dioxolanes refer mainly to short branch 1,3-dioxolane [127]. Study by Song et al. [128] compared the impact of linear compounds mono and di-glyme, against ring structure oxygenate 1,3-dioxolane, and observed that oxygen introduction through linear structure is the most efficient in reducing soot emissions. The air bore oxygen concentration is the second most beneficial parameter, while ring compound oxygen has the least potential. The results indicate a reduced particle mitigation potential for dioxolane compounds as compared to other linear oxygenated. However, negative effect over NO<sub>x</sub> emissions is lower for dioxolane against glycol ethers. NO<sub>x</sub> emissions are greatly increased by intake oxygen, being a first-degree parameter over fuel-borne oxygen.

### 4.3. ALCOHOLS

Several studies evaluate the impact of n-pentanol or heavier alcohols on combustion behaviour of naturally aspirated engines or constant speed applications [129, 130]. Limited data is available on light or heavy-duty transportation engines. N-pentanol is characterised by a very challenging CN of 20 and rather low density and flashpoint (814 kg/m<sup>3</sup> and 49 °C, respectively). Several studies [131-134] agree on the reduction of the torque efficiency up to 14 %, lower NO<sub>x</sub> emissions by 5 to 20 %, and increased HC emissions from 5 % to doubled. The reduced efficiency and improved NO<sub>x</sub> emissions are possibly a consequence of the low CN. Longer alcohol hydrocarbon chains may contribute to approach more suitable CN property but can also impact other properties including the spray characteristics.

The use of short alcohol chains including methanol and ethanol is also discussed in the literature for compression ignition application [135]. Both of these alcohols require additivitation to promote ignition and to ensure correct lubricity. Their use is only possible in specific engines which is mostly related today to an increase in compression ratio, a special injection system and a catalyst to control aldehyde emissions.

#### 4.4. **KETONES**

According to literature, ketones are challenging to very challenging compounds to be used in diesel blends. This is mainly because of their low viscosity, and unsuitable flash point or melting point. 2-hexadecanone has a high melting point of 48 °C, and 2,2,5,5-tetramethyl-3-hexanone a low flash point (39.6 °C) and CN (19). Tests on 3-heptanone and 5-nonanone did not indicate a clear advantage over other compounds [136]. More suitable compounds are 4-methylacetophenone and 3-octanone, however their integration could be limited by their viscosity, density, and flash point. No combustion tests were found for the selected ketones. Study by Kass et al. [137] evaluated the impact of ketones on elastomer swelling and detected that they produced a 30 % expansion and softening of a large variety of elastomers: Fluorocarbon, Fluorosilicone, Silicone, Neoprene, SBR, Epichlorohydrin, ECO, OZO, HNBR, and NBR. Only elastomers EPDM and Polyurethane are compatible with ketones, of which EPDM is incompatible with diesel fuel.

#### 4.5. **ESTERS**

Most studies on ester renewable fuels refer to the analysis of different biodiesels with respect to their resource, or their impact on properties and combustion characteristics. Esters are known for having a reduced oxidation stability, improved with use of antioxidants as butylated hydroxytoluene (BHT) or tert-butylhydroquinone (TBHQ). The results over NO<sub>x</sub> emissions are highly variable indicating possible reduction of 30 % to an increase of 50 % as compared to reference diesel fuel. However, the impact on particulate matter is consistent, and a reduction between 20 to 75 % has been observed, with little impact of the ether composition or bio-resource [138, 139]. Engine-out HC emissions are reduced from 10 to 40 %, and CO emissions tend to increase. Nevertheless, there is a negligible impact on vehicle CO emissions [140-142]. Similar tendencies have been found for selected compounds methyl decanoate and hexyl hexanoate, most advantageous type of ester fuels with respect to their melting and boiling point and viscosity [84]. Study by Kugelmeier et al. [143] on corrosion of metal, for different ratio of biodiesel blends show that FAME do not affect carbon steel, stainless steel and aluminium significantly. However, copper parts displayed reduced compatibility, where corrosion attack and consequent mass loss were improved as FAME blend ratio is increased.

#### 4.6. **PARAFFINIC AND OLEFINIC COMPOUNDS**

Alkane and alkene compounds are usually found in petroleum diesel. Several studies, aiming at the selection of appropriate surrogate, evaluate the impact of some of the selected alkanes and cyclic organic compounds on the combustion and emission behaviour [144]. These studies have observed that the blend's properties, as CN, density, volatility, distillation and carbon and hydrogen content, are the dominating parameters affecting combustion behaviour and emissions, above the specific paraffinic and olefinic compounds and their concentrations. Luning et al. [145] observed that the CN and the density are the dominant fuel properties affecting combustion timing and heat release rate. Within the diesel-like paraffinic hydrocarbon, the second-degree parameters are the distillation, LHV and C/H ratio [146, 147]. Density and volatility are the dominant parameters affecting spray

penetration, while viscosity is an important but not dominant parameter [148]. Spray penetration will have a significant role over local stoichiometric ratio and surface wetting, affecting unburned HC and particle emissions.

The alkane and alkenes effect on combustion and emissions will depend mainly on the blend's properties, with a significant impact determined by the dilution of the total aromatic content. More specifically, in the literature, engine tests of alkane and alkene compounds are usually related to the general analysis of paraffinic fuels, GTL, FT, HVO, and farnesane, and their impact on emissions and after-treatment efficiency. These data are briefly reported below.

#### 4.6.1. Fisher-Tropsh Diesel fuel

FT diesel is a mix of n and iso-paraffins of carbon chains between C<sub>10</sub> and C<sub>25</sub>, and with almost no aromatic content. Consequently, FT is characterised by a high cetane and low density (near 770 kg/m<sup>3</sup>) [149, 150]. Publication have identified the potential emission reduction, namely particles. Nevertheless, a trade-off between NO<sub>x</sub> and particle emissions persists. Study by Rodriguez-Fernandez et al. [138, 151] over a 4-cylinder engine with a diesel oxidation catalyst (DOC) and a diesel particle filter (DPF) suggest that particle composition allows for improved after-treatment reactivity due to the reduced particle surface area, and higher surface to mass ratio.

#### 4.6.2. Farnesane

Farnesane has properties that are suitable for conventional diesel blending. Several studies have evaluated the combustion and emission impact of Farnesane over engine-out, specific calibration, and vehicle, no calibration modified usages [149, 152-157]. Results indicate a reduction in particle emissions varying between 20 to 70 %, depending on the application and usage. NO<sub>x</sub> emissions are not modified or reduced, and a variable impact on HC and CO emissions has been reported. Increase of unburnt emissions has been related to a reduced DOC efficiency.

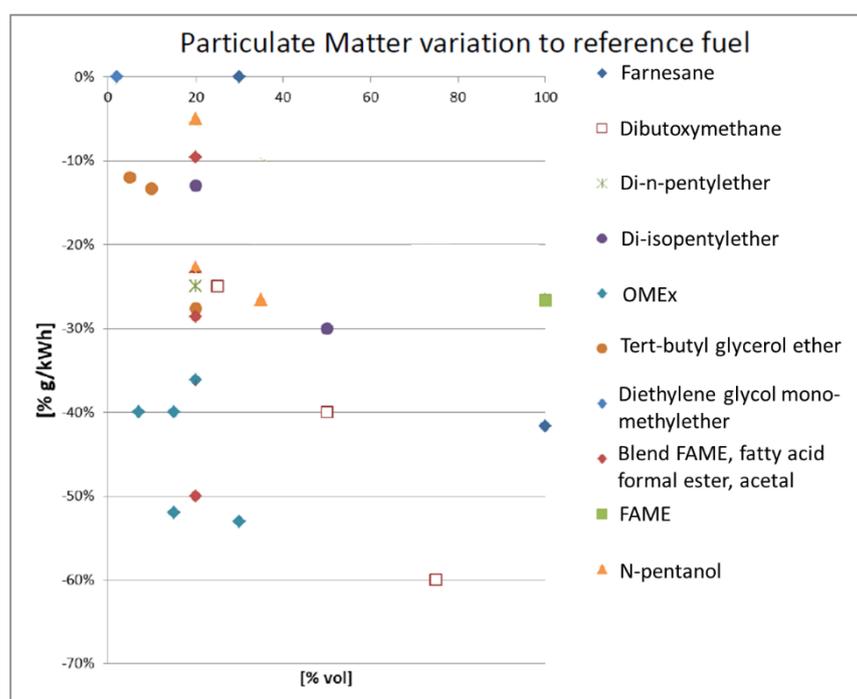
#### 4.6.3. Hydrotreated Vegetable Oil (HVO)

Many literature data is available on the impact of HVO over engine and vehicle applications [138, 141, 142, 158-161]. Studies indicate a reduction of engine-out particle emissions [162], but a negligible impact on aftertreatment particle number [158]. HVO concentration has a negligible impact on Vehicle NO<sub>x</sub> emissions according to tests on EU6d SCR or NT, under WLTC or RDE road driving conditions. Stronger variations are observed for other technologies [161]. Exception is observed for the case of an application with SCR aftertreatment system and under WLTC warm operation, where NO<sub>x</sub> emissions increase up to 150 %. The SCR strategy could be related to this effect. Moreover, results on same vehicle under -7°C start conditions presented a mean 5% increase. A reduction of HC and CO emissions is also reported (e. Nonregulated emissions N<sub>2</sub>O or NH<sub>3</sub> are not impacted [158]). Moreover, combustion with 100% HVO indicates a 4 to 8% CO<sub>2</sub> reduction.

### 4.7. CONCLUSIONS ON DIESEL-LIKE RENEWABLE COMPONENT ENGINE TESTING

This section provided an overview of the renewable diesel-like components impact on engine performances. Two main topics were discussed: (1) the overall operation of renewable components with engine operation (blending ratio, impact on emissions); (2) the specific hardware compatibility including material compatibility or impact on aftertreatment system.

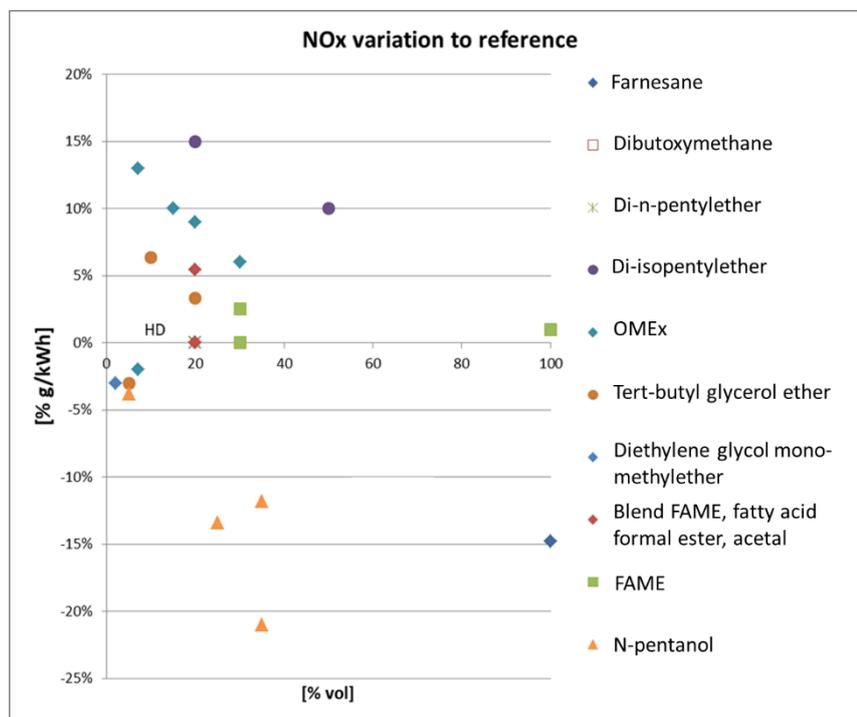
Regarding the operability of renewable components, most of them have been studied at various blending ratios, of at least 20 vol.%, without indicating incompatibility other than of elastomers for some of the families. Most of the renewable compounds identified are characterised by a significant oxygen content making them prone to particle emissions reduction. Of the several fuels analysed, OME<sub>x</sub>, Methyl decanoate and Hexyl decanoate present highest potential. Chemical structures having reduced C-C bonds is a favourable characteristic, as the case of OME<sub>x</sub> fuels. In order to illustrate these comments, Figure 21 shows engine-out particulate matter emissions as compared to a reference fuel considered in the different studies and for different compound blend ratios. Engine-out measurement are performed under non-optimised setting for this comparison.



**Figure 21** Engine-out soot emissions as compared to reference fuel for different compound blend ratios. Measurement engine-out under non-optimised engine settings.

Engine-out temperature and particle morphology are the main parameters affecting regeneration [138]. Literature indicates that the lower particle diameter is associated with higher specific surface and hence higher reactivity. Fuels having reduced aromatic compounds or having oxygenates can be related to reduced particle sizes. Moreover, the presence of oxygenated functionalities also facilitates the oxidation [163]. These tendencies have been confirmed by a comparison of particle reactivity with Biodiesel, Diesel, HVO, GTL: Biodiesel soot emissions present highest reactivity, followed by GTL. Diesel and farnesane present similar oxidation reactivity [154].

These observations for particulate matter reduction contrasts with the ones for nitrogen oxides. Indeed, results indicate a tendency for renewable oxygenated fuels to aggravate NO<sub>x</sub> emissions (see Figure 22), by up to 15% for most cases. Impact is strongest for OME<sub>x</sub> and DIPE. Paraffinic compounds do not display the same behaviour as illustrated for Farnesane. Specific calibration would be recommended to avoid such impacts of oxygenates.



**Figure 22** Engine-out NO<sub>x</sub> emissions as compared to reference fuel for different compound blend ratios. Measurement engine-out under unmodified settings.

These two results tend to support the impact of renewable component on aftertreatment system operation. Several studies have confirmed a reduced conversion over DOC after-treatment for oxygenated fuels as biodiesel, RME and OME<sub>x</sub> [105, 108, 152, 164]. Some of the publications list the lower exhaust temperature and higher EGR rates as factors affecting the catalytic abatement. Study by Piqueras et al. indicates a possible increased selectivity to medium-heavy HC and light alkanes, that are less concentrated at engine-out for oxygenated fuels [164]. The final vehicle emissions respond to a compromise between reduced engine-out emissions, and the composition's impact on catalytic efficiency and exhaust gas temperature.

Literature did not focus on unregulated emissions; however, some observations are available in the literature. No negative impact on formaldehyde, NH<sub>3</sub> or N<sub>2</sub>O has been observed with use of HVO as drop-in fuel [158]. Studies on the use of OME<sub>x</sub> fuels shows that formaldehyde emissions are generally not affected. However, some specific operating conditions, as late injection strategy for catalyst warm up, can result in high formaldehyde emissions [155]. Studies indicates that higher EGR rates, typically applied on optimised parameters for oxygenated blends, induced lower combustion temperature that increase formaldehyde formation [110]. Moreover, optimised settings for high OME<sub>x</sub> blending rates can lead to near stoichiometry conditions, and high methane and formaldehyde emissions [165]. Another study has observed higher PAH engine-out [105]. Carbonyl emissions increase from 20 to 100 %, at 20 vol.%, has also been reported for tert-butyl-glycerol ethers [121].

Regarding specific hardware compatibility, the first important property to discuss is the material compatibility including elastomers and metals. Most molecules identified in this review have diesel-like elastomer compatibility. Table 9 lists compatibility and non-compatibility for the different elastomers and families found in the literature [88, 89, 137, 143, 166]. In general, a good compatibility is observed over most chemical families. Limitations have been observed for ketones and glycol methyl ethers, against fluor elastomers, Epichlorohydrin, OZO, and NBR. OMEx fuels present a strong incompatibility with most elastomers, and of the materials studied, only Fluorosilicone offers a compatibility to both Diesel and OMEx fuels.

**Table 9** Elastomer compatibility with most of the identified diesel-like components chemical classes. Green indicates diesel-like behaviour, red represents incompatibility, white indicates absence of literature data. Comments regarding the incompatibility are added into the cells once they are available. [137, 141, 166].

	Diesel	Biodiesel	Renewable Diesel	Alkanes	Cyclo alkane	Alcohol	Acid esters	Ketone	Glycol methyl ether	OMEX
Fluorocarbon								Swell, hardness reduction		
Fluorosilicone								Swell		
Silicone	Swell									
Neoprene	Swell, hardness							Swell, hardness	Swell, hardness	
SBR										
Polyurethane										
Epichlorohydrin, ECO							30% vol			
OZO										
EPDM										
HNBR										
NBR								2-nonanone	Static seal only	

Literature on metal compatibility and risk of corrosion is scattered for the renewable fuels here investigated. Exception can be listed for biofuels, for which a good metal compatibility is observed [143].

To conclude, despite the multiple publication found in the field, limited data is available for overall hardware compatibility considering the diversity of renewable diesel-like components. This includes for example corrosion tendency, oxidation stability, aftertreatment efficiency on cold start and unregulated emissions.

## 5. LIMITATIONS AND OPPORTUNITIES FOR NOVEL FUEL COMPONENTS

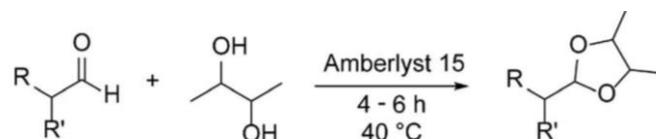
### 5.1. ECONOMIC AND LCA ASSESSMENT

The objective of this section is to identify relevant life cycle and techno economic assessment (LCA and TEA) data for selected renewable diesel-like fuel pathways. The same approach than for the previous tasks was applied (see section 2). Selected fuel pathways include the production of dioxolane derivatives, dibutoxymethane and DNPE. These three molecules were amongst the most suitable products for blending with renewable base fuels or conventional B7. They also refer to resources or processes that were not considered respectively as unsuitable or low TRL. The following sections will review the available data in the literature for these three fuel production pathways.

#### 5.1.1. Dioxolane derivatives

##### 5.1.1.1. Production processes

The chemical reactions involved and the catalyst required to produce dioxolane derivatives are described by Staples et al. [167]. Figure 23 illustrates the typical reaction involved. Chemical feedstocks include a di-ol and a ketone. Da Silva et al. also consider a similar route but use instead glycerol and acetone are used to produce dioxolane.



**Figure 23** Dioxolane formation reaction including a di-ol and a ketone

More specifically, Da Silva et al. aimed at producing solketal [168], a dioxolane derivative used as fuel additive either as a viscosity improver or to reach better cold flow performances compared to biodiesel [118]. The product is however not compatible with a large incorporation into diesel fuel due to a rather low molecular weight. Optimal dioxolane derivatives for diesel application require long hydrocarbon chains for R and R' fragments illustrated in Figure 23. The ketone or aldehyde origin may contribute to reach that objective.

Glycerol would be an accessible product as it is a co-product of biodiesel production and extensive research is done on the potential valorization routes [169]. Butanediols are alternative products and could be produced from second generation bioethanol synthesis step as illustrated by Rosales-Calderon and Arantes [170]. However, butanediols have a high cost and other uses including paints, plastics production, and solvents.

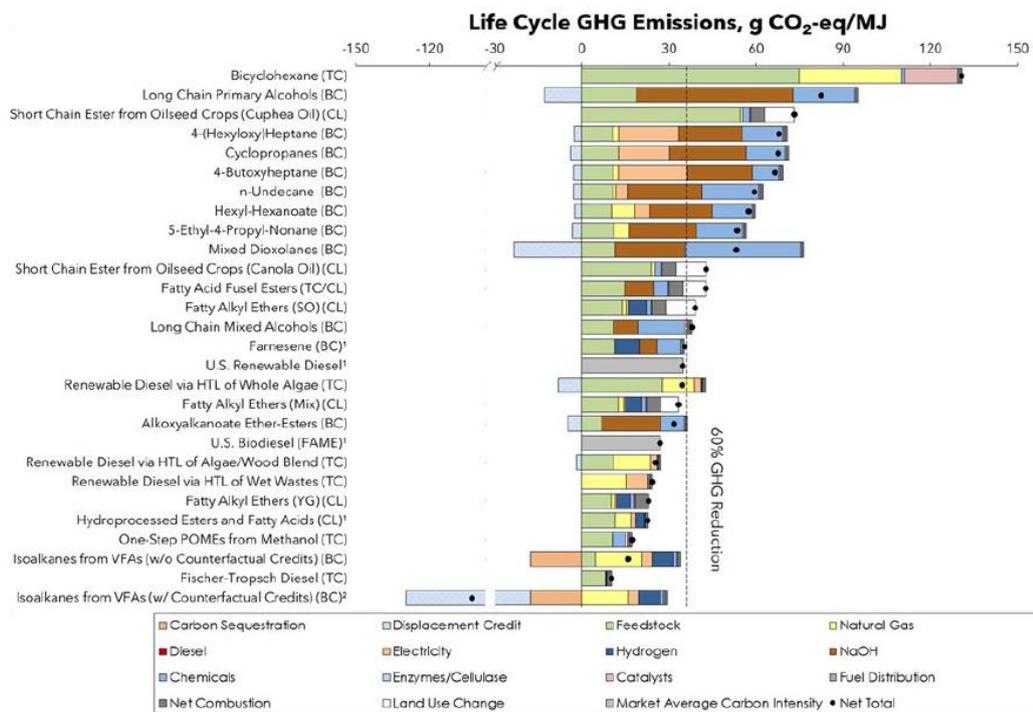
Ketone production can be obtained with existing processes through for example the Acetone-Butanol-Ethanol (ABE) process. Methyl ketones alternatives are of particular interest [171]. However, they are today intermediate components for jet fuel production. Their use may thus be in competition with this market.

Limited data exist on mixed dioxolanes production even if a few scientific references were identified regarding solketal production. Correa et al. proposed for example a review of the different research activities for solketal production [169].

The authors mostly highlight the important research performed on the different syntheses available with several catalysts or reactor types but also report that limited literature exist regarding the large industrial scale production. This work however provides interesting insights into the dioxolane production which relies on two steps: reaction and separation. It is emphasised that the separation step is considered as the most impactful both from an environmental and economic point of view. This is indeed an energy intensive step as the reaction itself has a low equilibrium constant. Different approaches are reported in the literature including the use of an excess of one reactant or the use of membrane is mentioned. It is however interesting to note that the associated literature is rather recent and the proposed methods relying on continuous process to improve soketal production could also be relevant for biofuel production.

#### 5.1.1.2. **LCA review**

Dioxolane derivatives were evaluated within the co-optima project in addition to many other fuel production pathways. Figure 24 illustrates the different fuel pathways considered and their environmental impact through carbon dioxide emissions. The results indicate that the reduction threshold of the REDII is exceeded mostly due to the production step through the use of “chemicals”. It is however unclear what this statement refers to in this study. An important information shared though is the type of process considered which is biochemical fermentation of corn stover to ethanol and 2,3-butanediol with catalytic upgrading.



<sup>1</sup> GHG emissions of these pathways are from either an earlier study or average of market fuels.  
<sup>2</sup> The negative GHG emissions from the "Isoalkanes from Volatile Fatty Acids" pathway are because of the credits from avoided emissions from landfill of the food waste feedstock.

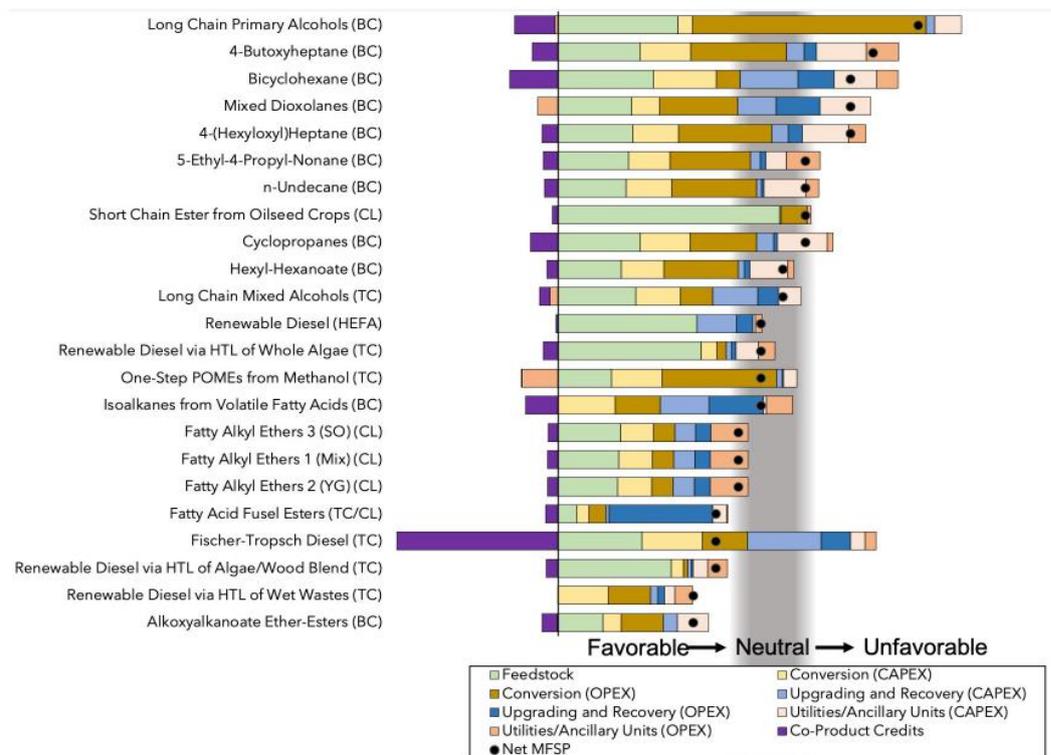
**Figure 24** Life cycle GHG emissions for a selection of candidates evaluated by Co-optima project. The colours represent the contribution from feedstock and process inputs. SO refers to soybean and YG is yellow grease and Mix is a blend of soybean oil and yellow grease. [172]

Another study provide LCA data for dioxolane through solketal production. Aghbashlo et al. normalised and aggregated results for LCA [173]. Their result suggest that solketal production pathway is not relevant compared to fossil-based fuel as the solketal score is either similar or about six times greater than fossil pathway. However, a detailed LCA analysis at a midpoint level could reveal benefits from producing biobased dioxolane rather than fossil fuel, not visible with this type of aggregated results.

To conclude, LCA of dioxolane derivatives with clear assumptions, using biobased reactants and calculating the results also at a midpoint level is still required. This conclusions is also highlighted by Correa et al. [174].

5.1.1.3. **TEA review**

Techno economic assessment of dioxolane derivatives is also limited in the literature but relies again on the recent study proposed by the co-optima project. Figure 25 shows the economic impact of the different fuel production pathways selected in the co-optima project. Again, the mixed dioxolanes pathway is reported as unfavourable. Most constraining steps are the upgrading and recovery as well as utilities. These results are however neither yet supported by a full description of the method employed nor by the numbers for the different analyses.



**Figure 25** Economic evaluation of the different fuel production pathways selected in the co-optima project. CAPEX = capital expense, OPEX = operating expense, HTL = hydrothermal liquefaction, POME = polyoxymethylene ether, SO = soybean oil, YG = yellow grease, and mix is a blend of soybean oil and yellow grease. [172]

Two additional studies were identified to further discuss the economic impact of dioxolanes, through solketal production [168, 175]. Their respective results are illustrated Table 10. Surprisingly the breakeven price is six times greater for Da Silva et al. The results discussion is limited as both studies do not provide similar methodology or hypotheses details. For example, Da Silva reports the detailed analysis of the annual operating costs and both glycerol and acetone represent about 17% of the total cost (~ 2.9 \$/kg). This actual price is higher than the breakeven price reported by Al Saadi highlighting large discrepancies and potentially unrealistic numbers in one of the TEA study. Al Saadi focuses the analysis on the comparison of three solketal process options and less on the common techno economic assessment of the overall production. Cost breakdown would be for example required to support any comparison with other studies. This suggests a strong bias in their study but which could not be confirmed in this review. In addition, it should be mentioned that Da Silva's results were also reported by Correa et al. [169] but with a production cost of 1229 \$/ton (~ 1\$/kg). The differences identified are not explained so far and would require further investigations.

**Table 10** Economic evaluation of dioxolanes through solketal production for two studies from Da Silva et al. [168] and Al-Saadi et al. [175]

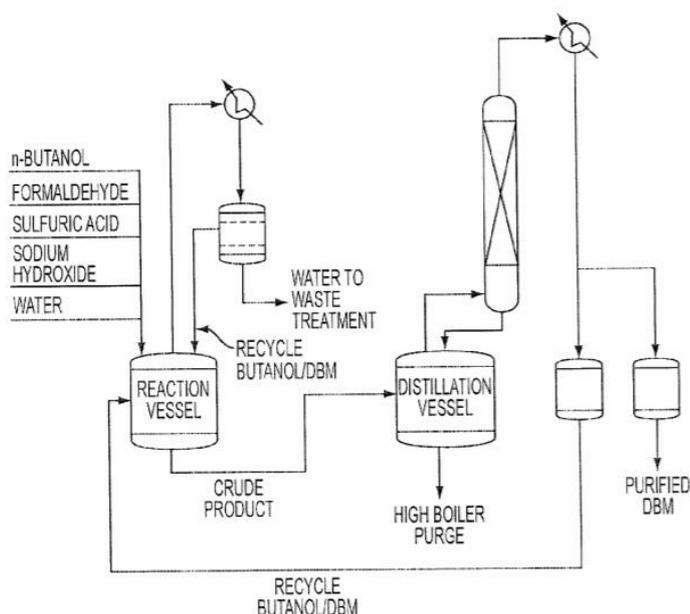
	<i>Da silva et al.</i> <b>[168]</b>	<i>Al-Saadi et al.</i> <b>[175]</b>
Production rate (10 <sup>6</sup> t/yr)	0,7	0,1
Total Investment cost (\$)	14 450 000	~30 000 000
Operating cost (\$)	5 467 000	25-30 000 000
Breakeven price	12,29 \$/kg	-2 \$/kg

To conclude, it is difficult to assess clearly the TEA impact of dioxolane derivatives but the identified literature confirms that the topic has been considered either for mixed dioxolanes or for solketal production which would be an asset for further studies. In addition, the reported analyses strongly emphasize the impact of process optimization through different reactor types (continuously stirred or plug flow for example) and different catalysts. Both aspects could significantly affect the profitability of the fuel production pathway. Finally, it should be highlighted that the references identified were published over the last four years suggesting ongoing research activities.

## 5.1.2. Dibutoxymethane

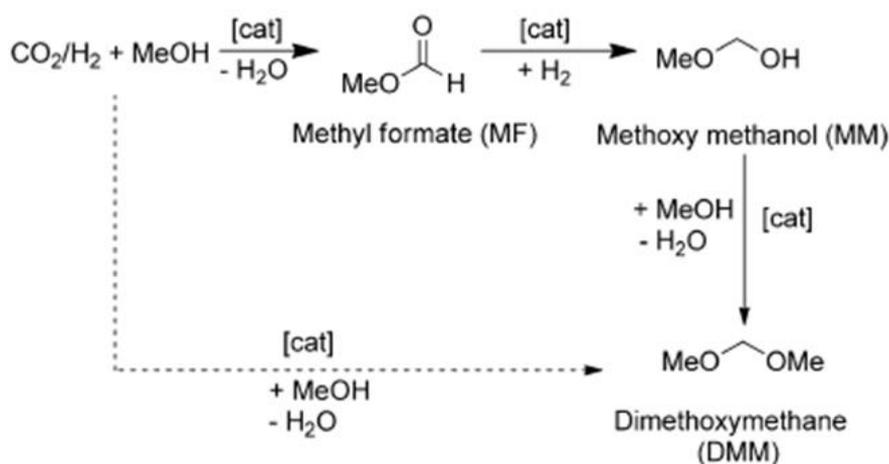
### 5.1.2.1. Production processes

Dibutoxymethane (DBM) production is presented in the literature as a potential e-fuel route. Colemant et al. reports in a patent a way to produce DBM through a condensation reaction between formaldehyde and butanol under acidic conditions [176]. Figure 26 illustrates the process flow diagram provided for a batch production of DBM.



**Figure 26** Process flow diagram provided for a batch production of dibuthoxymethane [176]

Schieweck et al. reports another approach relying on the use of a cobalt catalyst system involving an alcohol substrate,  $\text{CO}_2$  and  $\text{H}_2$  [72]. Figure 27 illustrates the approach for dimethoxymethane (DMM) production. The use of butanol instead of methanol would lead to DBM and the approach has been successfully tested by the authors.

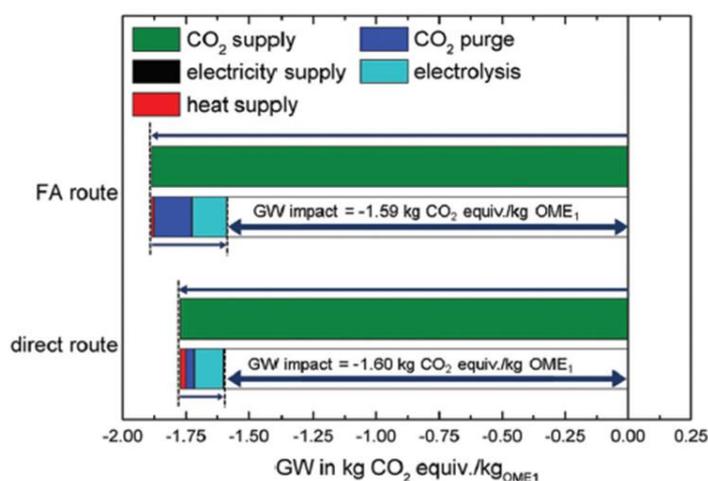


**Figure 27** Reaction pathway for the catalytic formation of dimethoxymethane utilizing  $\text{CO}_2/\text{H}_2$  and methanol [72]

Both specific processes are thus demonstrated at laboratory scale for DBM production but further work is required to scale-up and no literature could be identified on that matter.

### 5.1.2.2. LCA review

No reference could be identified for the LCA of DBM. To provide some insights into the LCA of e-fuel type of processes, the work from Deutz et al. is discussed [75]. Figure 28 shows the best-case scenario LCA in terms of global warming impact (in CO<sub>2</sub> equivalent per kg of OME<sub>1</sub>). This best-case refers to carbon capture from atmosphere and water electrolysis using electricity from renewable energies. Two routes are considered: (1) the Formaldehyde route (FA) and; (2) a “direct route” involving a catalytic process with CO<sub>2</sub> and H<sub>2</sub> as inputs.



**Figure 28** Best-case scenario LCA in terms of global warming impact (in CO<sub>2</sub> equivalent per kg of OME<sub>1</sub>)

This analysis demonstrates that for this ideal case, both routes have a negative cradle-to-gate emissions for producing OME<sub>1</sub>. This is related to the negative impacts of the CO<sub>2</sub> supply.

It seems promising and this is in line with point of view for the co-optima project (See Figure 24). The real impact for such fuel production pathways highly depends on assumptions made regarding the electricity for electrolysis and feedstock for heat production.

Considering the two fuel production pathways mentioned above, LCA impact will mostly be related to butanol production. Schubert et al. reviewed the different light alcohols production pathways and reported for butanol three potential routes: (1) Fermentation but with an important limitation as butanol is an inhibitor for the fermentation. This is already developed through the ABE fermentation process but butanol yield is rather low and product separation is challenging. This first process is thus mature. (2) Catalytic conversion of ethanol. This process is at laboratory scale; (3) Catalytic conversion of syngas. This leads to the production of butanol along with other alcohols, hence not developed as a pathway for the production of butanol as a single component. This third pathway should be investigated in order to support the production of DBM. The two other pathways rely to some extent on a fermentation step in addition to the catalytic conversion mentioned previously which would degrade significantly the overall potential of CO<sub>2</sub> reduction for the process.

Upscaling of renewable butanol routes is a major challenge to achieve the production of a full e-fuel like DBM.

### 5.1.2.3. TEA review

No literature could be identified for DBM TEA. The only comments are related to the main feedstocks butanol, CO<sub>2</sub> capture and renewable H<sub>2</sub>.

First Butanol production costs is ranging from 0.49 to 4.79 €/kg depending on the resource (corn stover or glucose respectively). Butanol also face several usages including solvents production which would certainly be of interest if the compound had to be used to fuel production.

Second, renewable hydrogen price is ranging from 2 to 20 €/kg according to Maggio et al. [177]. The variability is associated to the assumptions and working parameters for the different concatenated sources. The production scale appeared to be most dominant one.

Finally, for the CO<sub>2</sub> production, current technologies rely on direct air capture (DAC) and from concentrated sources. DAC is today the most expensive technology (~0.5€/kg) and only available at small scale. This price is expected to decrease significantly along with process scale up [178].

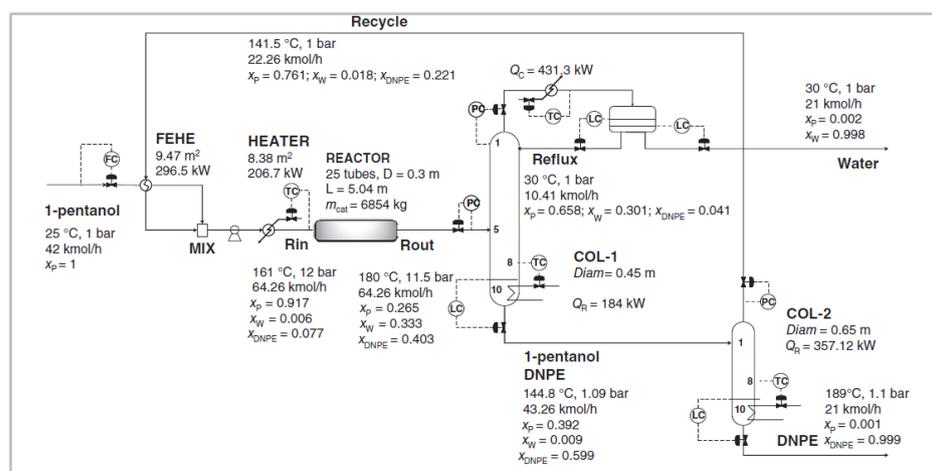
### 5.1.3. DNPE

#### 5.1.3.1. Production processes

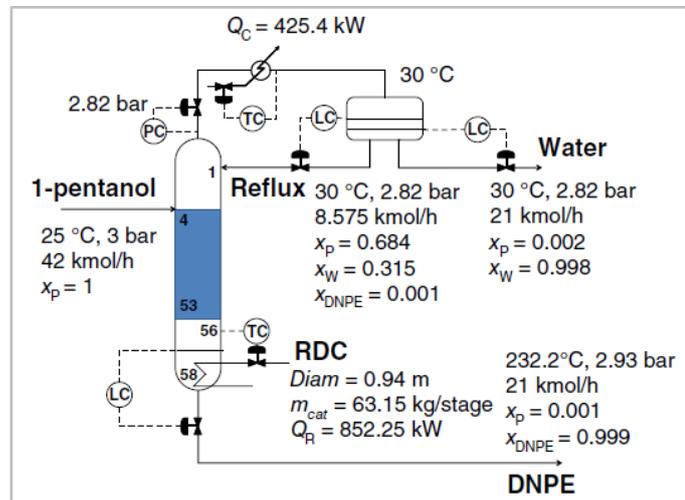
Two types of processes were recently compared in the literature for di-n-pentylether [68]. The first one refers to reaction separation recycling and the second to catalytic distillation. Both flowsheets are illustrated Figure 29. 1-pentanol is the main reactant required to operate.

The former process is performed in a plug-flow reactor. The recycling step is required due to a limited equilibrium reaction which prevents complete pentanol conversion. The latter represents a more advanced technology combining the reaction and separation steps in the same unit. This is possible as DNPE is the middle boiling component in the water/1-pentanol/DNPE mixture.

a.



b.



**Figure 29** Flowsheet and control of a DNPE plant through (a) reaction-separation-recycle and (b) catalytic distillation [68]

The authors highlight the fact the reaction-separation-recycle process may be slightly more attractive than catalytic distillation due to the possibility to operate closer to optimised conditions for the different units.

The main required reactant is 1-pentanol which can be procured from the catalytic conversion of syngas [179] or bioengineering [180]. Pentanol isomers are also accessible through fermentation pathways such as the one described by Olson et al. [181]. Finally, n-butane can be used to produce 1-pentanol by dehydrogenation to n-butene and conversion to 1-pentanol [70]. This process is also non-existent in the recent literature and it should also be mentioned that the availability of sustainable n-butane is also of concern. As an example, Jiang et al. recently investigated at laboratory scale a novel catalytic approach based on Levulinic acid conversion to n-butane [69].

#### 5.1.3.2. LCA and TEA reviews

Both environmental and techno economic assessment are lacking for the production of DNPE. Bildea et al. provide an overview of the key economical performance indicators for the two processes and the main information are provided Figure 30 [68]. This analysis clearly emphasize a low energy requirement ( $\approx 1 \text{ MJ/kg}$ ) for the production processes reaction-separation-recycle and catalytic distillation.

Key performance indicator	R-S-R process	Catalytic distillation
Total investment costs, TIC (k\$)	842.02	816.34
Total operating costs, TOC (k\$ yr <sup>-1</sup> )	200.7	251.2
Total annual costs, TAC (k\$ yr <sup>-1</sup> )	481.4	523.3
Specific production cost (\$ ton <sup>-1</sup> DNPE)	18.2	19.7
Energy requirements (kWh ton <sup>-1</sup> DNPE)	225	256.6

Note: The following economic figures were reported for the membrane reactor in Pera-Titus *et al.*,<sup>13</sup> OPEX includes: 25.4 M\$ yr<sup>-1</sup> for membranes, 13.3 M\$ yr<sup>-1</sup> for refrigeration, 1.3 M\$ yr<sup>-1</sup> for cooling water, and 3.8 M\$ yr<sup>-1</sup> for steam, and 0.2 M\$ yr<sup>-1</sup> for the catalyst. The equipment costs (CAPEX) are evaluated at 9.0 M\$, with 7.7 M\$ being ascribed to the membrane reactor.

**Figure 30** Key economical performance indicators for DNPE plant through (a) reaction-separation-recycle and (b) catalytic distillation processes [68]

However, the production cost of 1-pentanol is not reported limiting again the discussion.

This third product appears clearly as the most challenging of the three analysed regarding the available data in the literature. It seems to rely on promising processes being low cost and low energy demand but important work is needed regarding the reactant production.

#### 5.1.4. Conclusions on LCA and TEA for renewable products

This section focused on LCA and TEA data available in the literature for selected pathways. FAME and paraffinic fuels were not considered due to their well known impact today. In this context, a systematic approach was followed to identify a few relevant pathways regarding their potential compatibility with diesel fuel specifications, engine hardware or potential development through existing processing steps. This led to select oxygenates with dioxolane derivatives, dibutoxymethane and di-n-pentylether.

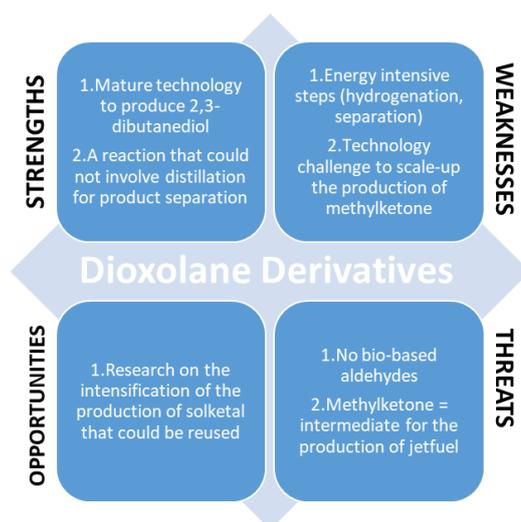
The first observation here is that limited literature could be identified for these three pathways. Dioxolane derivatives development could rely to some extent to the existing studies for processes development or LCA/TEA analyses for solketal. However, for the two other pathways, the data are not sufficiently available to review different options and thus provide a relevant analysis.

This analysis contributed to identify important limitations for these pathways including for example important shortages for key reactants availability. Encouraging developments were also identified through less energy intensive separation steps or catalysts developments. These research were in addition published over the last few years and a focus is made on the necessity to develop renewable pathways for solvents production. This suggests that ongoing research and development activities could contribute to facilitate future renewable fuel production.

### 5.1.5. Summary

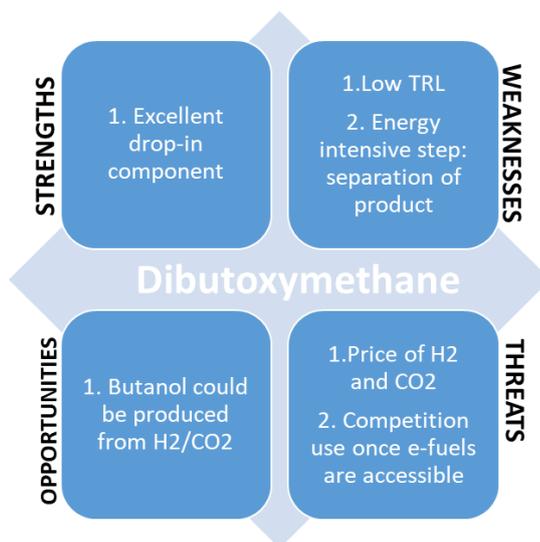
To summarize the main findings of this section, a SWOT (Strength, Weaknesses, Opportunities, Threats) analysis is proposed for each fuel production pathway.

Figure 31 shows the SWOT for dioxolanes derivatives. The main strengths that could be identified are related to the processes either for the production of di-ol reactant or the dioxolane production itself. The latter could rely on a different separation step than distillation, a very energy intensive step. However, the overall process is also the weakness of the dioxolane route as it is related globally to energy intensive steps through hydrogenation and distillation which is easier to perform than the alternatives such as membrane assisted separation. The main opportunity relies on the available studies for solketal, a dioxolane derivative considered as a fuel additive. Solketal is not fully compatible with diesel specifications but the chemical reactions involved in the production are similar to the dioxolane route. Finally, the identified threats are the lack of bio-sourced reactants and the potential competition with other applications.



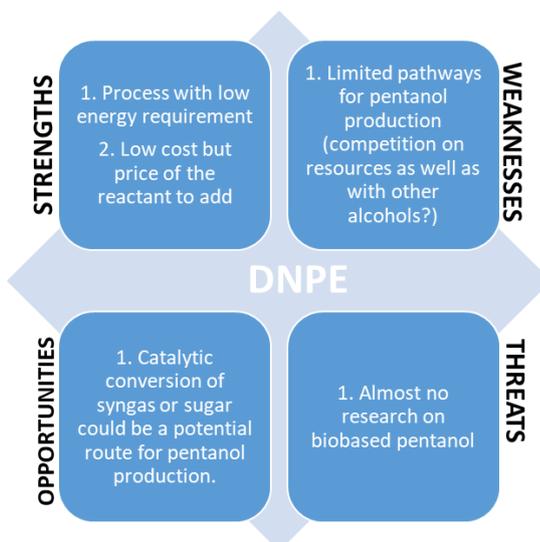
**Figure 31** SWOT analysis for dioxolane derivatives production path

Figure 32 illustrates the SWOT analysis for DBM. The main strength refers to the properties of DBM as it is amongst the most compatible products identified based on the considered physical chemical properties section 685. The main weaknesses refer to the low TRL of the overall production process as well as the required combination of e-fuel type of process with fermentation to obtain 1-butanol. Catalytic 1-Butanol production from  $H_2$  and  $CO_2$  is considered in the literature and could be an interesting opportunity to develop a novel pathway toward light alcohol production. Finally, the main threats are the price the overall e-fuel pathway and the high competition with other applications once renewable hydrogen or e-fuels are available.



**Figure 32** SWOT analysis for DBM production pathway

Figure 33 shows the SWOT analysis for DNPE. The main strength highlighted in the literature is the low energy requirement of the process and a potentially low cost even if the reactant price is not assessed. Weakness of this fuel production pathway is the limited availability of renewable pentanol production even if several options are investigated in the literature. The main opportunity for DNPE relies in the development of catalytic conversion of syngas or sugar to alcohols but this is also the main threat as the research on this topic is limited.



**Figure 33** SWOT analysis for DNPE production pathway

## 5.2. BLENDING OPTIMIZATION

Previous sections demonstrate that renewable components can be quite diverse and present certain benefits regarding particulate matter emissions and limitations while being used in an engine. If any of these blends succeed in being formulated at industrial scale, the product formulation strategy would require to match the EN590 specification which will probably remain similar by 2030. In addition, the ultimate goal is to maximise the renewable content of the blend meaning that several constraints exist regarding the physical chemical properties of the formulated product. In order to evaluate these aspects, the following section aims at identifying the optimised incorporation strategy of selected renewable components. Two main constraints will be considered: (1) Fuel specifications; (2) key physical chemical properties with density, viscosity, cetane number and flash point.

### 5.2.1.1. Optimised incorporation strategy of renewable components

#### 5.2.1.1.1. Base fuels definition

Selected renewable components with unsuitable properties have been investigated in mixture with three market fuels:

- B7 (EN 590)
- B100 (EN 14214)
- HVO (EN 15940)

For each of the four considered fuel properties, specifications for each market fuel were used as reference (see Table 11). An extended reference fuel was also considered and consisted into the less constraining properties of each specification and the average for the density and the viscosity.

**Table 11** Hypotheses for calculations

		EN 14214	EN 590	EN 15940	Extended
Property	Unit	<i>B100</i>	<i>B0 → B7</i>	<i>Paraf. fuels Class A (HVO, XTL)</i>	-
Cetane number	-	51.0	51.0	70.0	51.0
Density at 15 °C	kg/m <sup>3</sup>	880	833	783	833
Flash point	°C	101	55.0	55.0	55
Viscosity at 40 °C	mm <sup>2</sup> /s	4.3	3.3	3.5	3.5

This task was performed on selected species. The selection was based on the identified limitations of each pure component. Indeed, the first part of the review enabled to classify each component into four categories based on their physical chemical properties (see section 3.3.3). Table 12 summarizes products classified as challenging or very challenging for a potential incorporation into conventional diesel fuel. These products are then considered in this study as potential blending chemicals into conventional fuels.

**Table 12** List of selected products based on the identified limitations of each pure component. Colours in the first column refer to product classification as challenging or very challenging for a potential incorporation into conventional diesel fuel as defined in section 3.3.3.

Alkanes/alkenes C <sub>5</sub> to C <sub>19</sub> (cyclic, branched and linear)	
	<i>Standard (cyclic or paraffins)</i>
	<i>Paraffins</i>
2	n-undecane
3	6-Methylundecane
5	n-decane
6	n-dodecane
7	3-ethyldecane
8	n-tridecane
10	n-tetradecane
11	n-pentadecane
12	2-methyltetradecane
13	n-hexadecane
14	n-heptadecane
15	3,3,5-trimethyldecane
16	7-butyltridecane
17	n-octadecane
18	n-eicosane
	<i>Cyclic</i>
19	Decalin
22	n-Butylcyclohexane
	<i>Olefines</i>
24	Limonene
<b>Esters (fatty esters, fusel)</b>	
	<i>Conventional esters (FAME)</i>
33	Methyl linoleate
<b>Ethers</b>	
	<i>Linear ethers</i>
45	Di-Isopentyl ether (DIPE)
	<i>OMEx</i>
68	4-butoxyheptane
69	OME mix
71	3,5,7,9-Tetraoxaundecane
	<i>Dioxolanes derivatives</i>
79	4,5-dimethyl-2-(pentan-3-yl)-1,3-dioxolane
81	4,5-dimethyl-2-pentyl-1,3-dioxolane
84	2,4-dimethyl-2-undecyl-1,3-dioxolane
<b>Alcohols</b>	
	<i>C5-</i>
94	Pentanol

Ketones	
101	4-methylacetophenone
102	2-hexadecanone
103	3-octanone

The use of fully paraffinic fuels or B100 is already accessible for certain applications and this is supported by the corresponding specifications (EN15940 and EN14214). This work does not aim at considering these products as a potential new blending component but more as a potential base fuel. Consequently, a focus will be made in this work on the blending properties of other classes of molecules including ethers, alcohols, ketones or dioxolanes derivatives. This led to consider 17 components shown in Table 13. It should be highlighted that only an OME mix is considered instead of pure OME<sub>x</sub> products.

**Table 13** List of selected components based on the identified limitations of each pure component. Colours in the first column refer to product classification for a potential incorporation into conventional diesel fuel as defined in section 3.3.3. Corresponding resources and potential processes are also listed with the corresponding colours according to sections 3.1.7 and 3.2.3.

Products	Resources	Processes
<b>Ethers</b>		
<i>Linear ethers</i>		
44	Di-n-pentyl ether (DNPE, DPE)	
45	Di-isopentyl ether (DIPE)	
<i>Dioxolanes derivatives</i>		
79	4,5-dimethyl-2-(pentan-3-yl)-1,3-dioxolane	
80	2-(heptan-3-yl)-4,5-dimethyl-1,3-dioxolane	
81	4,5-dimethyl-2-pentyl-1,3-dioxolane	
82	2-heptyl-4,5-dimethyl-1,3-dioxolane	
83	2,4,5-trimethyl-2-undecyl-1,3-dioxolane	
84	2,4-dimethyl-2-undecyl-1,3-dioxolane	
85	2-methyl-2-undecyl-1,3-dioxolane	
<b>Alcohols</b>		
<i>C5-</i>		
94	Pentanol	
<b>Ketones</b>		
101	4-methylacetophenone	
102	2-hexadecanone	
103	3-octanone	
<b>OMEx or similar</b>		
68	4-butoxyheptane	
69	OME mix	
71	3,5,5,7,9-Tetraoxaundecane	

#### 5.2.1.1.2. Blending rules

Blending rules are required in order to establish the final fuel properties. These can be quite challenging once the property does not match a linear blending rule. In this study, linear blending rules are considered for density and cetane number. The latter is known to be non-linear but based on the moderate CN value of the identified components and the rather low limit of the specification, the bias is expected to be limited. Each of the considered blending rules is presented below.

- **Density**

The evaluation of a mixture density at a given temperature requires:

- Densities of the various base components, which must be given at the relevant temperature
- Percentages by volume (%vol) of each of the mixture components

$$\rho_{mix}(15\text{ }^{\circ}\text{C}) = \sum_{i=1}^n v_i \rho_i(15\text{ }^{\circ}\text{C})$$

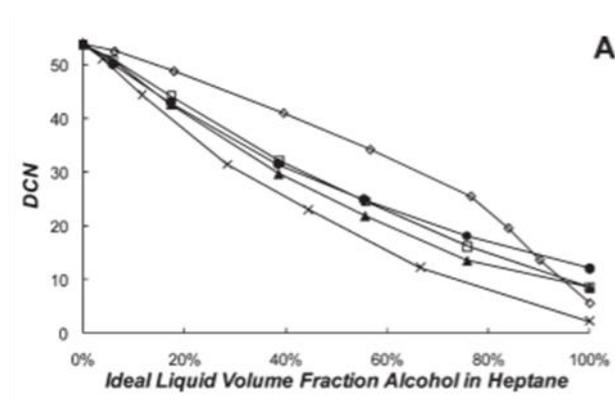
Where  $n$  is the number of components in the mixture and  $v_i$  is the volume fraction of component  $i$ .

- **Cetane number**

When available, it should be mentioned that data from literature was considered for each component in order to identify the maximum blending rate. This is of interest as in certain cases the blending rule can be non-linear. An example is provided Figure 34 for alcohols into an alkane. When no data could be found a linear blending rule was considered.

$$CN_{mix} = \sum_{i=1}^n v_i CN_i$$

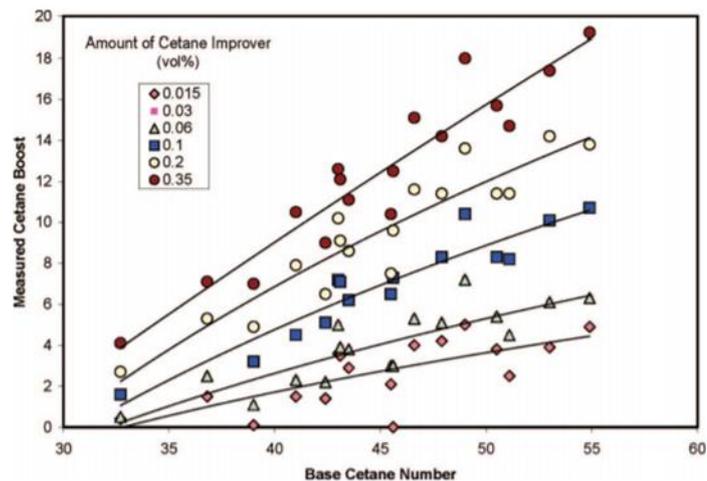
Where  $n$  is the number of components in the mixture and  $v_i$  is the volume fraction of component  $i$ .



(●) 1-butanol, (□) 2-butanol, (▲) iso-butanol, (◇) t-butanol, and (×) ethanol.

**Figure 34** CN of alcohol/n-heptane mixtures [182]

In addition, the use of additives was considered as it is quite common to improve this property. The data from Ghosh and al. [183] is used as a reference for evaluating the boosting effect through additivation. Figure 35 illustrates the impact of a common cetane improver, 2-ethylhexylnitrate, on different base fuels.



**Figure 35** Plot of cetane boost as a function of the CN of the base fuel [183]. Cetane boost is defined as the difference in CN of the diesel fuel with and without the improver. The figure shows that the higher the CN of the base fuel, the higher the cetane boost for the same amount of improver.

- **Flash point**

Flash point (FP) requires a non-linear blending rule. Indeed, the lighter fraction has a strong influence as it brings more volatile components to the ignitable mixture. Among the different correlations available for evaluating the flash point, the use of mixing index (MI) is presented within the ASTM procedure. Table 14 reports the MI from ASTM. The principle of this method is to replace the flash points with volume weighted index values:

- From *MI* of each base, mixture *MI* can be obtained according to its volume composition

$$MI_{mix} = \sum_{i=1}^n v_i MI_i$$

Where  $n$  is the number of components in the mixture and  $v_i$  is the volume fraction of component  $i$ .

- From this mixing index, FP can be obtained according to its volume composition

**Table 14** Flash point mixing index from ASTM chart

Flash point	Mixing index						
40	636,2	71	77,0	102	13,8	133	3,3
41	589,8	72	72,4	103	13,1	134	3,1
42	542,6	73	68,2	104	12,5	135	3,0
43	507,8	74	64,2	105	11,9	136	2,9
44	471,6	75	60,5	106	11,3	137	2,8
45	438,2	76	57,0	107	10,8	138	2,7
46	407,4	77	53,7	108	10,3	139	2,5
47	378,6	78	50,7	109	9,8	140	2,5
48	352,6	79	47,8	110	9,3	141	2,3
49	328,3	80	45,1	111	8,9	142	2,2
50	305,9	81	42,6	112	8,5	143	2,2
51	285,1	82	40,2	113	8,1	144	2,1
52	265,9	83	38,0	114	7,7	145	2,0
53	248,0	84	35,9	115	7,4	146	1,9
54	231,5	85	34,0	116	7	147	1,8
55	216,2	86	32,1	117	6,7	148	1,8
56	202,0	87	30,4	118	6,4	149	1,7
57	188,8	88	28,8	119	6,1	150	1,6
58	176,6	89	27,3	120	5,8		
59	165,2	90	25,8	121	5,6		
60	154,7	91	24,5	122	5,3		
61	144,9	92	23,2	123	5,1		
62	135,7	93	22,0	124	4,8		
63	127,2	94	20,8	125	4,5		
64	119,3	95	19,8	126	4,4		
65	111,9	96	18,8	127	4,2		
66	105,0	97	17,8	128	4,1		
67	98,6	98	16,9	129	3,9		
68	92,6	99	16,1	130	3,7		
69	87,1	100	15,3	131	3,6		
70	81,8	101	14,5	132	3,4		

This method was selected as the molecules considered in this study have a FP ranging from 40 to 150°C which is consistent with the method validation range. Example of additional validation data with this method are given in Appendix 3.

It should be highlighted that among the components that were not selected, several have either a very low (e.g. C<4 ethers) or rather high FP (e.g. SVO). If the former or the later were to be considered with conventional diesel fuel, a strong non-linear blending rule would be expected. The lack of experimental data or numerical work for such extreme components would certainly require additional work to model the blending behaviour. In addition, these extreme components would certainly fail

outside of the current FP fuel specification. This could lead to consider blending both extreme products.

- **Viscosity**

Accurate viscosity prediction for binary mixtures of two components with a large difference in viscosity remains a challenging task because viscosity blending curves may show a large degree of non-linearity. Indeed, the fluid base has a predominant weight which gives the mixture a much lower viscosity than calculated by volume weighting. Viscosity blending equations are commonly used in petroleum industry. One of the best known is the double-logarithmic equation of Refutas [184]. The Refutas equation calculates the viscosity  $\mu_{12}$ , of the binary blend from viscosities and weight fractions of the components by introducing the so-called viscosity mixing index (ASTM D7152):

$$A_i = 14.534 \ln[\ln(\mu_i + 0.8)] + 10.975 \quad (i = 1,2)$$

Where  $x_i$  is the weight fraction,  $\mu_i$  is the kinematic viscosity of the  $i$ th component in the blend. Then, the blend viscosity is calculated as:

$$\mu_{12} = \exp \left[ \exp \left( \frac{A_{12} - 10.975}{14.534} \right) \right] - 0.8$$

Where  $A_{12}$  is the average viscosity mixing index:

$$A_{12} = x_1 A_1 + x_2 A_2$$

Examples of validation data with the mixing index method are given in Appendix 4.

#### 5.2.1.2. Renewable fuel blends optimization results

The optimization of the fuel blend composition is performed using an in-house python script. The code has three main functionalities: (i) Calculation of blend properties, (ii) Visualization of standard-compliant blend compositions, and (iii) Blend optimization.

Firstly, the code calculates blend properties based on the volume fractions and properties of the components using suitable mixing rules. Linear mixing rule is used for density and cetane number. The mixing index method is used for flash point. The kinematic viscosity of a blend is calculated based on the binary mixing rule proposed by Refutas (see section 5.2.1.1.2) but extended to unlimited number of components.

Secondly, the code could find mixture compositions where the properties of the blend comply with selected one or more standards. The visualization is made through ternary plots, which are only applicable for ternary blends. The "gnuplot" package is used for plotting.

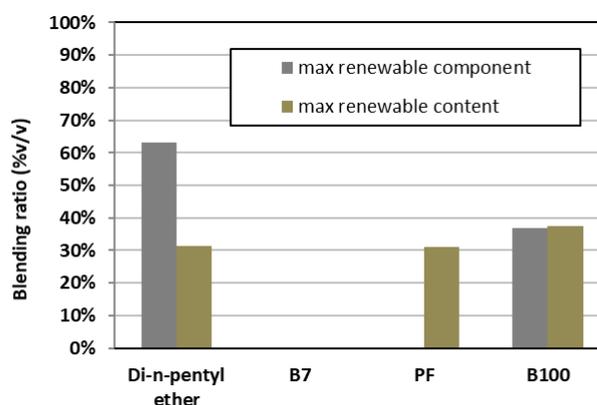
Finally, the blend optimization functionality finds the optimal combination of fractions for a certain target (e.g., maximizing cetane number, maximizing share of sustainable fuels, etc.) while complying with the standards at the same time. The optimization is done using the Sequential Least Squares Programming (SLSQP) algorithm implemented in the "scipy" package.

Two approaches were considered to optimize the 17 components identified:

- **Optimizing the renewable content**

The blend of B7, B100, PF and the renewable component are optimised to maximize either the renewable component concentration or the overall renewable content (B100+PF+renewable component). For these optimizations, the EN590 is considered as the reference but extended specifications are also evaluated. The later correspond to the concatenation of the three main fuel specifications available today. Again, the blends are optimised in order to remain within the EN590 boundaries for the four key properties considered: CN, FP, Density and viscosity.

As an example, a result for di-n-pentyl ether is provided Figure 36.



**Figure 36** Plot of optimised blends with di-n-pentyl ether as renewable component in mixture with B7, B100 and paraffinic fuel (PF). Optimization is performed either to maximize di-n-pentyl ether or the overall renewable content. Grey bars refer to the optimized blend maximizing di-n-pentyl ether and green bars refer to the overall renewable content optimization. Both optimizations consider EN590 boundaries.

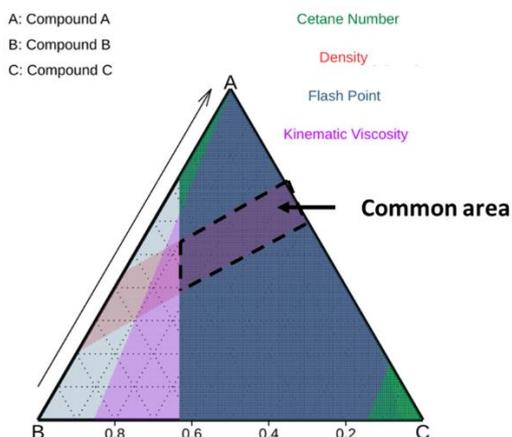
These results indicate that DNPE can be added up to 63% (v/v) when the base fuel is B100. Regarding the maximum renewable content evaluation, the converged blend is:

- Di-n-pentylether, PF, B100 [31-31-38] % (v/v)

This highlight the fact that conventional B7 can be totally removed and the blend can reach 100% renewable components.

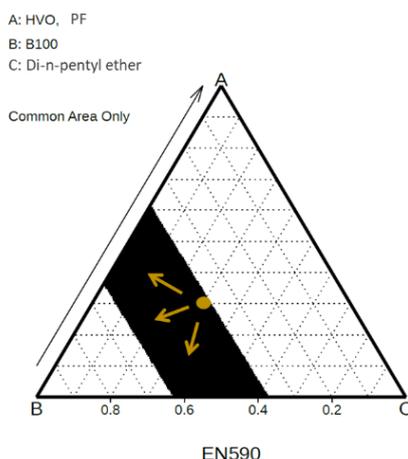
- **Ternary plots**

Ternary diagrams were developed to identify the range of incorporation rate considering the four key properties: cetane, viscosity, flash point and density independently first and then simultaneously. This enables to visualize the compatible blends with the considered specification (see Figure 37).



**Figure 37** Illustration of the ternary diagram developed to overlap the different blend properties and the selected specifications. Four properties are considered: Cetane number, density, flash point and kinematic viscosity. The common area is illustrated with the dashed line and will be reported in black in the next figures.

Figure 38 shows an example of results for DNPE where the “common area” refers to the black area. This corresponds to the EN590 boundaries for CN, viscosity, flash point and density. As an illustration, the yellow dot within the black area corresponds to the optimised blend mentioned above. Consequently, the ternary diagram illustrates the fact that there exists a wide range of blends that can be fully renewable.



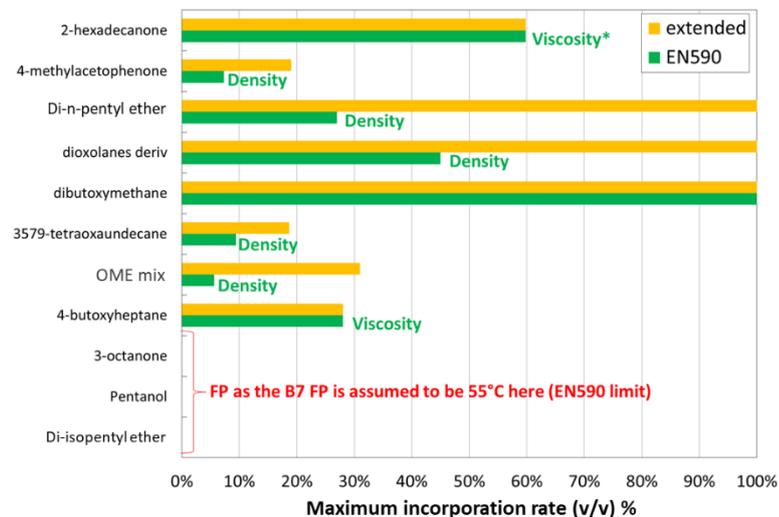
**Figure 38** Ternary diagram with di-n-pentyl ether as renewable component in mixture with HVO and B100. Black area includes all mixtures that meet the EN590 boundaries for CN, viscosity, flash point and density.

#### 5.2.1.2.1. Renewable content optimization

- **Renewable component optimization with B7**

The 17 components were evaluated considering both EN590 and extended specifications for the optimization constraints. Figure 39 shows the obtained results. The bar plot indicates the maximum incorporation for both constraints. In addition, the property that limits the renewable component incorporation is written in green for the EN590 case study. The results demonstrate that a few

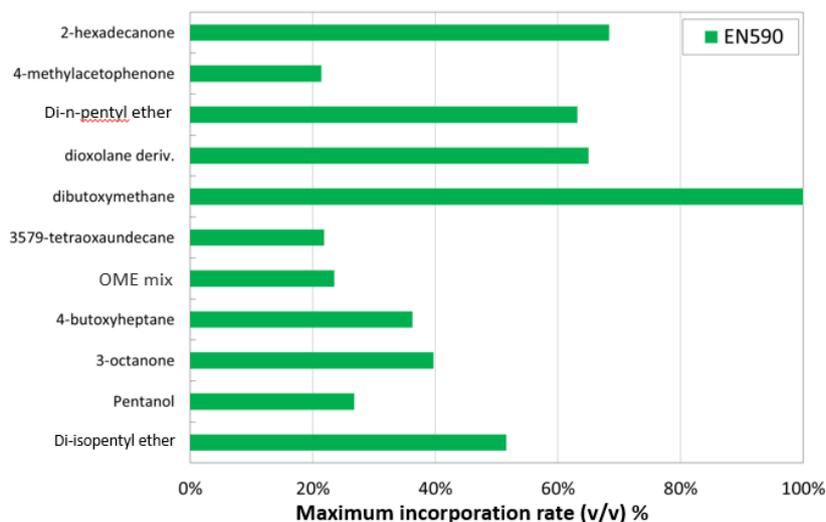
components can be incorporated to a large extent to current B7 conventional fuel once we consider these four key properties. Interestingly, the most limiting parameter is density with respect to EN590. The last three components, 3-octanone, pentanol and DIPE, are however mostly limited by their low FP. A higher hypothesis for the reference fuel B7 FP would enable to incorporate these components but this property would certainly remain the limiting parameter.



**Figure 39** Plot of the maximum incorporation rate for each renewable component in mixture with B7 considering both EN590 (green) and extended specifications (yellow) for the optimization constraints. Property that limits the renewable component incorporation is highlighted for the EN590 case study. \*The viscosity of the product could not be assessed. Its value is estimated at 1.5 cSt.

- **Renewable component optimization with B7/PF/B100**

An evaluation of the maximum incorporation rate of each renewable component has been performed considering again the EN590 specifications and the three base fuels simultaneously as a constraint. Figure 40 shows the results and highlights again the limiting property in this condition. Density is again a limiting parameter and viscosity is also of interest in this context. All the components can be added to at least 20%. The details for each component are available in Appendix 5. These results highlight that B7 is globally not necessary to increase the incorporation rate of the renewable components. With their opposite properties, PF and B100 blends, enable to counterbalance several negative effects of the final optimised fuel including the density.



**Figure 40** Plot of the maximum incorporation rate for each renewable component in mixture with B7/PF/B100 considering EN590 boundaries.

\* The viscosity of the product could not be evaluated. Its value is estimated at 1.5 cSt for 2-hexadecanone and 0.5 cSt for 3,5,7,9-tetraoxaundecane.

Three categories were identified according to the maximum renewable component ratio within a mixture of B7, PF, B100 (Figure 41): (1) > 50 vol.% incorporation rate for the renewable component ;(2) from 30 to 50 vol.% incorporation rate; (3); < 30 vol.%. The potential synergy with one or the other base fuels is also highlighted with this analysis. Indeed, B100 seems to be related to the higher blending rates due to its high density compare to PF.

**Figure 41** Results summary - renewable component addition to B7/PF/B100. The considered properties are the cetane number, kinematic viscosity, density and flash point.

\*The renewable component optimization does not involve the addition of B7 except for one dioxolane.

> 50% (v/v)	[ 30 ; 50]% (v/v)	< 30% (v/v)
<ul style="list-style-type: none"> <li>•Dimethoxybutane: up to 100%</li> <li>•2-hexadecanone: up to 68% (v/v) in mixture with B100</li> <li>•Di-n-pentyl ether: up to 63% (v/v) in mixture with B100</li> <li>•Di-isopentyl ether: up to 51% (v/v) with B100</li> <li>•Dioxolanes derivatives*: from 62 to 80% (v/v)</li> </ul>	<ul style="list-style-type: none"> <li>•3-octanone: up to 40% (v/v) in mixture with PF and B100</li> <li>•4-butoxyheptane: up to 36% (v/v) in mixture with PF and B100</li> </ul>	<ul style="list-style-type: none"> <li>•Pentanol: up to 27% (v/v) in mixture with PF and B100</li> <li>•OME mix: up to 24% (v/v) in mixture with PF</li> <li>•3,5,7,9-tetraoxaundecane: up to 22% (v/v) in mixture with PF and B100</li> <li>•4-methylacetophenone: up to 21% (v/v) in mixture with PF and B100</li> </ul>

It should be emphasised again that the optimization strategies performed in this study led to B7 free blends. Only one dioxolane derivative requires a small amount of B7 to be fully compatible with the four targeted properties. It seems possible to formulate 100% renewable blends according to the constraints of this study.

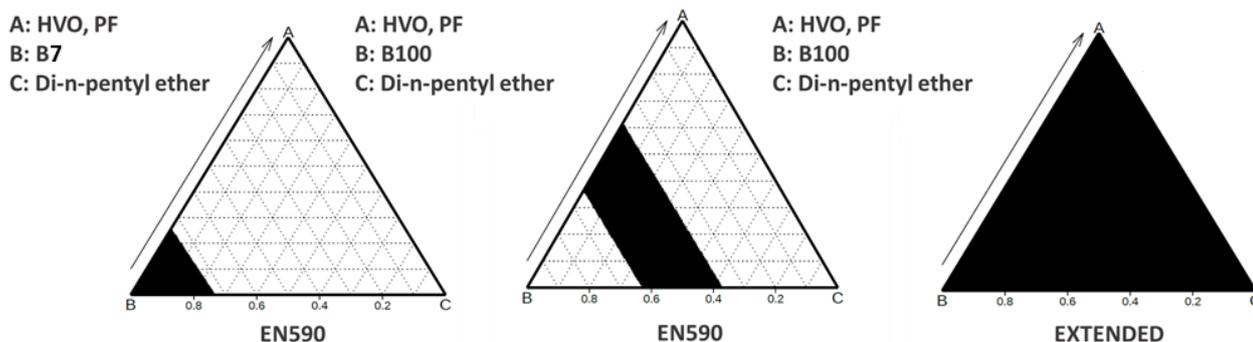
Finally, in addition to the 17 components identified as relevant for this task, every components mentioned in Table 12 were evaluated following a similar approach than the one proposed in this section (see Appendix 5). While this is beyond the scope of the study, it enables to confirm the key properties that limit the incorporation of renewable components within the three considered base fuels (B100, PF and B7). In addition, to provide a full overview of the available literature for these components, when any suitable information regarding miscibility, material compatibility, oxidation stability, emissions and incorporation limits into a base diesel fuel could be identified, it is also reported in the corresponding appendix.

#### 5.2.1.2.2. Ternary plot analysis

As previously discussed, the use of ternary diagram enables to better highlight the blending potential of the identified renewable components. The approach makes it possible to also consider different reference fuels or different specifications. This section will enable to further discuss the case where B7 can be totally removed from the blend. Three hypotheses were tested to evaluate the blending potential of the different renewable components:

- PF+B7+renewable component with EN590 specifications referring to a potential use case for future diesel fuels by 2030.
- PF+B100+renewable component with EN590 specifications referring again to a potential use case.
- PF+B100+renewable component with extended specifications to demonstrate the full potential of the blends once the three specifications are actually concatenated.

Results are provided in Figure 42 for di-n-pentyl ether as an example. Figures for every component are available in Appendix 6.

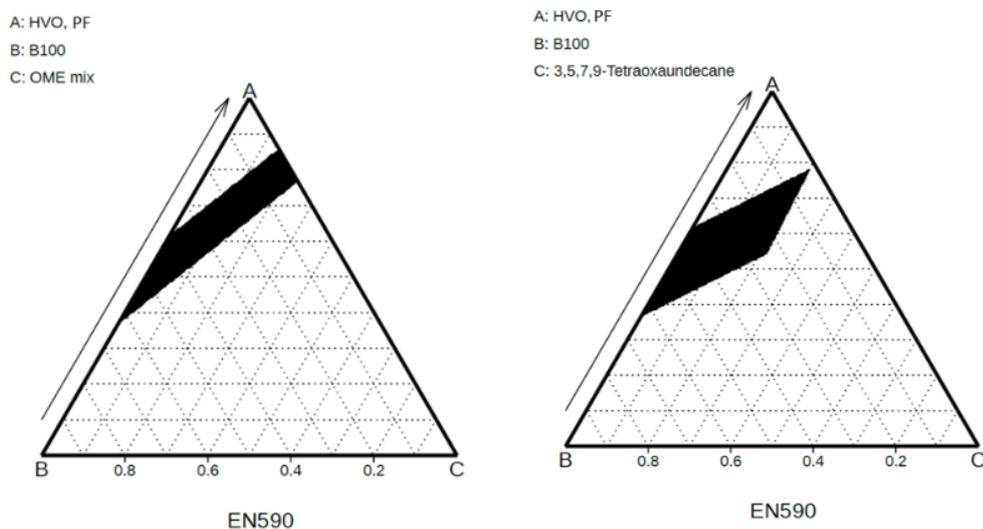


**Figure 42** Ternary diagrams di-n-pentyl ether as renewable component in mixture with B7, HVO and B100. Black area includes all mixtures that meet the EN590 boundaries and extended boundaries for CN, viscosity, flash point and density.

Different observations can be made thanks to this approach.

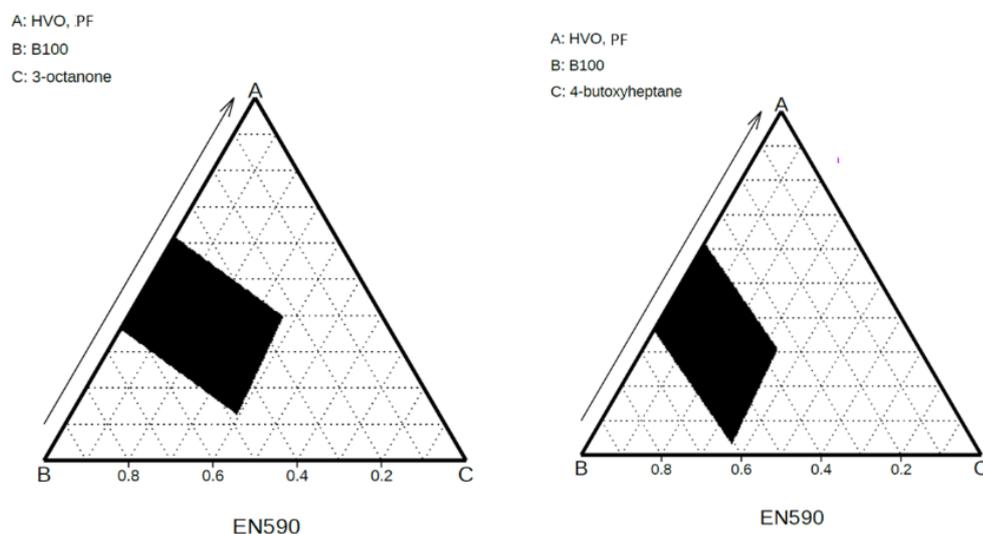
First of all, the most promising components in terms of incorporation rates with PF+B7 with EN590 are the dibutoxymethane, 2-hexadecanone, DPNE and dioxolane derivatives.

Then, synergetic effects between the renewable components and the base fuel are clearly illustrated. Figure 43 for example demonstrates that OME mix and 2,5,7,9-tetraoxaundecane are requiring a large amount of paraffinic fuels to be incorporated.



**Figure 43** Ternary diagrams for OME mix and 2,5,7,9-tetraoxaundecane as renewable component in mixture with HVO and B100. Black area includes all mixtures that meet the EN590 boundaries for CN, viscosity, flash point and density.

Third, certain products require a blend of B100 and PF to be incorporated. This is the case for example of 3-octanone and 4-butoxyheptane (see Figure 44).



**Figure 44** Ternary diagrams for 3-octanone and 4-butoxyheptane as renewable component in mixture with HVO and B100. Black area includes all mixtures that meet the EN590 boundaries for CN, viscosity, flash point and density.

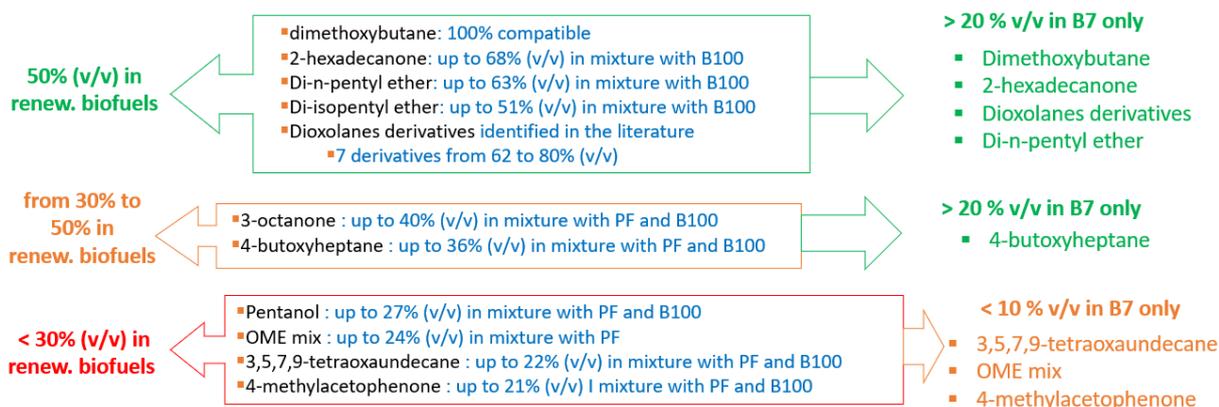
Finally, as expected, the use of extended specifications contribute to increase quite significantly the incorporation rates of most of the components.

### 5.2.1.3. Conclusions on fuel renewable content optimization

Following the identification of relevant components based on pure compounds properties, this section considered 17 species as relevant for an evaluation of blending properties. Both FAME and paraffinic fuels were considered as a base fuel even if certain identified components may be different in terms of physical and

chemical properties compared to the well known HVO and FAME commercial products.

The focus was thus made on oxygenated products including ethers, alcohols and ketones. Figure 45 summarizes the main findings of this study. First, it provides an overview of the maximum blending rate for the different base fuels considered. On the left, components at the top can be blended to renewable biofuels (HVO or B100) to at least 50 vol.%. The corresponding products are dimethoxybutane, 2-hexadecanone, DNPE, DIPE and dioxolane derivatives. Then, in orange are the products that can be blended from 30 to 50 vol.% to biofuels. Finally in red, the ones below 30 vol.%. On the right, the same approach is followed but with B7 as a base fuel. The species listed in green in this column correspond to the ones that can be blended to B7 at a rate above 20 vol.%. The ones in orange refer to products that can be incorporated at less than 10 vol.%. This summary further confirms the potential of ethers, dioxolane derivatives and potentially heavy ketones from a comparison with key specifications standpoint.



**Figure 45** Summary of the identified products and their associated maximum incorporation rates. The left section highlights the maximum incorporation rates in a mixture of PF/B100 and the right section in B7 only. Both cases assume EN590 as constraint.

### 5.2.2. Summary

This section aimed at evaluating the renewable fuel properties from different perspectives.

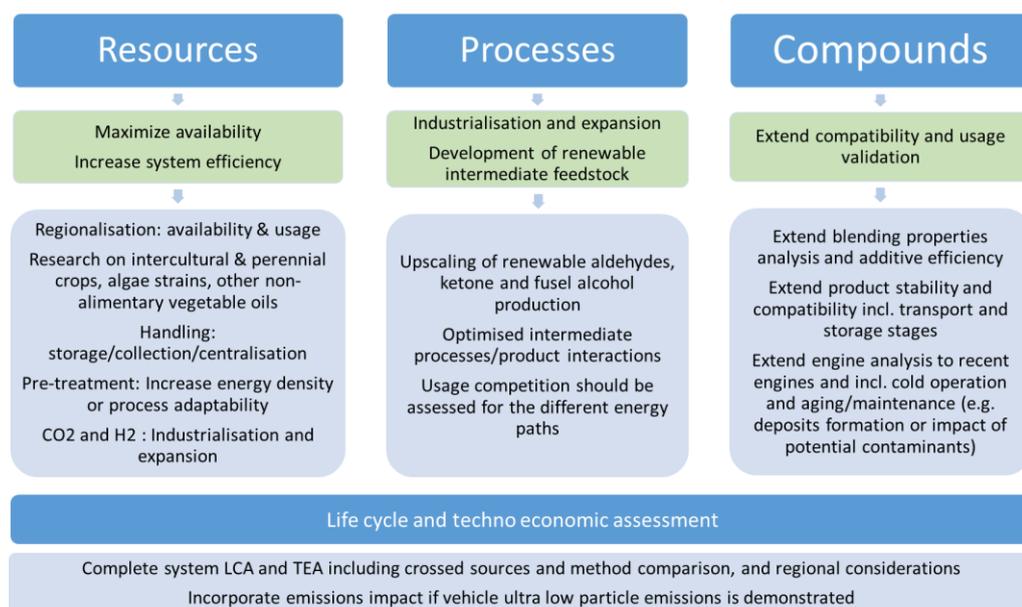
First of all, renewable components tested on different engine configuration were considered to discuss their performances and limitations. A large number of molecules from various chemical classes were identified leading to different conclusions depending on the component. The renewable product impact on emissions for unmodified engines was assessed. A positive impact on particulate matter could be identified for most of the products especially since the study mostly refers to oxygenates and paraffins. This positive observation is however contrasted with nitrogen oxides emissions increases for several products. These observations shed light on the fact that to take advantage of novel formulation, engine optimization may be of interest and this is not necessarily considered for every component in the literature. In addition, hardware compatibility often remains a question mark due to very limited data on important fuel properties such as material compatibility, oxidation stability or cold flow properties. Limited data were identified on this aspect but would certainly be contributing to eliminate fuel

candidates if a major vehicle upgrade, or alterations to supply logistics and thus investments, were required.

Secondly, renewable fuel candidates were evaluated based on their blending properties considering cetane number, flash point, viscosity and density. The objective was to determine to which extent these products could enable to either maximize the renewable content of a hypothetical fuel combining: B7, B100, PF and the renewable fuel candidate, or simply facilitate the incorporation of the product into current commercial B7 fuel. A dedicated internal code was used in order to explore the different blends and the multiple combinations of hypotheses (e.g. specifications, target for optimization, etc). This enabled to demonstrate that almost every renewable component mixed with B100 and PF could potentially match EN590 constraints for the four cited properties. Another interesting feature of the approach was related to the possibility to identify synergies between the renewable products and one of the current renewable market fuels. That supported for example the use of FAME products to counterbalance certain low density products. More generally, the opposite properties of B100 and PF led to optimize the blend accordingly. The high potential of certain products was highlighted for a significant incorporation into B7 (>20 vol.%) considering again EN590 boundaries.

### 5.3. RESEARCH AND OPTIMISATION NEEDS

Based on the literature research, suitability and maximal blending rate criteria defined within this study, three processes and their associated compounds have been identified. The compounds are Dioxolane derivatives, Dibutoxymethane and Di-n-pentyl ether (DNPE). Despite the advantageous properties, several research and development needs have been highlighted, given the limited literature data, and constraints present for this developing sector. These research needs are summarised in Figure 46 and discussed in the following paragraphs.



**Figure 26** Research and development needs regarding resources, processes and the three compounds identified

- **Resources**

In general, for the different resources, most research and optimisation needs intend to maximize resource availability and recovery impact. There is a need to assess recovery, process optimisation and upgrading routes with consideration of the different geographical areas. This includes continuous assessment of resource availability and sustainability, according to RED directives.

For further development and production increase, the following recommendations are provided:

- Improvement of dry matter storage solutions to avoid decomposition and quality losses.
- Optimization of waste material collection and centralisation to reduce GHG and economic impact, while maximising potentially available resource recovery.
- Enhancing in-situ pre-treatment sites in view of increasing the energy density before transportation and enabling the use of more diverse feedstocks.
  - Defining sustainable harvest rates of residues to avoid carbon soil loss, optimised by region/crop, and expanded beyond the European region.
  - Identifying optimal perennial crops and optimize their use (region/culture/harvest) to favour fuel production.
  - Concerning vegetable oils (waste or dedicated feedstock) resources are limited and further research on new efficient feedstock is necessary in order to expand and improve available resources, at limited cost.
  - Algae is a potential resource and much research is needed if bioengineering is to be considered as a possibility to enhance fuel production from algae strains, including butanol.
  - Gas resources H<sub>2</sub> and CO<sub>2</sub> are required in some renewable diesel fuel processes. Their production as renewable and low energy intensity remains challenging in order to scale-up:
    - Research and industrialisation of CO<sub>2</sub> capture, treatment (contaminants), transport (advanced: liquefied, dedicated tankers) and storage solutions (reservoir properties).
    - Research and development of renewable hydrogen production, including catalyst development for an efficient fast production, and corrosion avoidance.

- **Processes**

Three developing processes have been identified, and further research is necessary to ensure an advancement into demonstration and production phases.

For the dioxolane pathway, the following is listed:

- Optimisation of water and reactant separation techniques.
- Research on optimizing available solutions to reduce energy and hydrogen consumption, including processes interactions.

- For the dioxolane production through ketones, it is necessary to evaluate the integration of ketone and diols production into a single production pathway. The upscaling of ketone production is also required.
- For the dioxolane production through aldehydes, it is necessary to evaluate renewable production solutions as, for example, through renewable methanol processing.

For the di-n-pentyl ether (DNPE) pathway the following is listed:

- Development of renewable pentanol production pathways. Two pathways and their research needs are identified:
  - Research on microorganism fermentation to pentanol
  - Research on catalytic conversion solutions, to ensure large scale industrialised production. This includes for example the catalytic production of butane from biomass and its catalytic upgrading to 1-pentanol.
- Further research on production pathway through butanol, CO<sub>2</sub> and H<sub>2</sub> to ensure viability. The process would benefit from ongoing research on renewable H<sub>2</sub> production and CO<sub>2</sub> capture technologies.

For the dibutoxymethane pathway the following is listed:

- Optimisation of separation methods either through distillation or membrane.
- Development and upsizing of renewable butanol production, for which three pathways and their research needs have been identified:
- Development of conversion from ethanol, currently at laboratory scale.
- Research and development to ensure efficient butanol yield through fermentation.
- Research on catalytic technologies for syngas conversion into butanol.

- **Renewable compounds usage**

All three identified renewable compounds are new oxygenated species for which extended material compatibility and stability analysis should be carried out to ensure compatibility with all material and handling conditions, beyond the elastomer compatibility presented in this review. Moreover, complete elastomer compatibility tests would be required on dioxolane derivatives. Moreover, species and blend stability should be assessed for long term storage as in military and off-road conditions. The evaluation of compatibility with fossil fuel handling line and possible contaminants from and towards other fluids is also required.

Conventional correlations and existing models for the estimation of blending properties might not apply and need to be confirmed or developed for new compounds. Such correlations include, for example, blends' cetane number and flash point estimations. Additives' efficiency must also be assessed for new renewable blends as chemical composition interactions can occur.

Limited recent engine tests are available for selected compounds. Experimental data is required on current Heavy-Duty engines, either under drop-in (no calibration modified), and dedicated (calibration modified) operating

conditions. Engine-out and exhaust emissions analysis is recommended. Moreover, the assessment of cold behaviour operation and impact on maintenance, injector and chamber deposit formation, and optimization of additive package is required.

- **Life cycle and techno economic analysis**

Limited data is available on the life cycle and techno economical assessment of the production pathways proposed, especially considering a complete system from resource production and recovery, pre-treatment, and full process review. This analysis should consider crossed sources and method comparison to ensure sustainability and critical considerations. For example,

- Dioxolane production should include the production of input compounds as aldehydes, ketones and diols through renewable pathways should be considered.
- Di-n-pentyl ether analysis should include the renewable production of aldehydes, formaldehyde and pentanol pathways, as well of renewable H<sub>2</sub> and CO<sub>2</sub> production considerations.
- Dibutoxymethane production should incorporate butanol production, and include recycling, and optimising energy usage.

All these processes should analyse the impact of raw crop or feedstock production, recuperation stages, and pre-treatment, including regional analysis to optimise potential and minimize energy consumption and emissions factors. Usage emissions factors should also be considered, including impact on particle and NO<sub>x</sub> emissions.

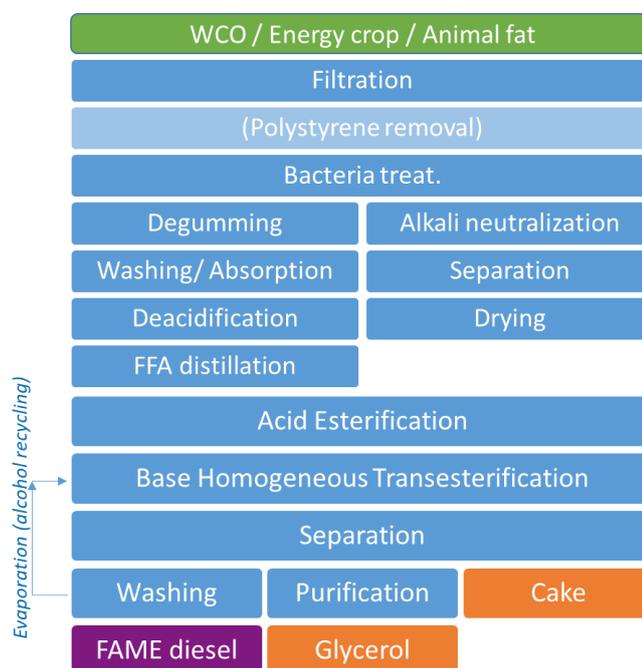
## 6. LIMITATIONS AND OPPORTUNITIES FOR PARAFFINS & FATTY ACIDS ESTERS DIESEL FUEL PRODUCTION PATHWAYS

### 6.1. FUEL PRODUCTION PATHWAYS

#### 6.1.1. Transesterification

Transesterification is the industrialised process available to produce FAME renewable fuel. It has the advantage of allowing the conversion of vegetable oil into esters under low temperature and pressure, relatively short reaction time, and to ensure a high conversion rate [185, 186]. The process was originally developed for the upgrading of vegetable oil. However, resources can be expanded to all triglycerides, as are animal fat, used cooking oil (UCO) and dedicated energy crops for vegetable oil production. The industrialised method of transesterification is through homogeneous catalyst [187]. Recent investment and research has aimed at: 1) the expansion of the process onto second generation resources requiring intensified pre-treatment [186], and 2) the technical development of new methods to improve the process selectivity and conditions.

The overall process layout is illustrated Figure 47. It includes a pre-treatment, followed by an esterification for most cases, a transesterification, separation of products, washing of biodiesel and purification of glycerol.



**Figure 47** Schematic representation of the transesterification process.

The main interest of this process resides in the development of small or regional scale applications that take advantage of the relatively simple process. Moreover, it can be applied over a variety of resources, provided convenient pre-treatment is applied. Its product properties are dependent on the resource, where UCO and animal fat and some dedicated crops do not have advantageous cold properties. Recent development observed in the literature is intended to small scale UCO processing, at producer site, to avoid disposal when collection for other processing

routes are not available. New technologies as heterogeneous, supercritical, or enzymatic transesterification are not expected to be industrialised by 2030.

The key steps of the transesterification pathway are described below.

#### 6.1.1.1. *Pre-treatment*

The removal of impurities is necessary to guarantee a stable process, especially when transforming products as UCO and animal fat. UCO's composition will be affected by polymerisation, hydrolysis, and oxidation in variable degree. Therefore, some properties that are expected to impact feedstock quality are free fatty acids (FFA) content, density, kinematic viscosity and acidity. The principal impurities in UCO, animal fats and energy crop oils are water, partial glycerides, phosphatides, oxidation products, pigments, and trace elements such as copper, iron, sulphur, and halogens [188]. Animal fat is also affected by the presence of pathogens [189]. The content of FFA must also be limited.

Several stages of pre-treatment can be mandatory.

- Filtration of impurities is carried out through filters of different sizes [189].
- Polystyrene removal might be mandatory in the case of animal fat, where polystyrene is used in the labelling and packaging of the resource [190].

Additional to these stages, refining can be either physical or chemical.

The physical refining stages are degumming, washing of phosphorus, soaps and other impurities, and removal of FFA through deacidification [189, 190]. For resources having FFA content above 1 %, as the case of animal fat or UCO, an acid catalyst esterification stage is necessary before the transesterification [191-193]. For example, the esterification through sulfuric acid can be employed to simultaneously reduce pathogens [194]. Separation of produced water and remaining alcohol is necessary before transesterification and can be carried out through a two-stage drying process. FFA distillation might also be necessary, especially if FFA content exceeds 3 % concentration. Distillation helps remove low and high boiling point impurities as well as odorous substances. It is important for distillation to take place at low temperatures to avoid alteration of triglycerides, for this, short-path or molecular technologies can be applied [195]. Extracted FFA can be used as animal feed or be esterified separately. Other processes proposed for the reduction of FFA and pre-treatment of 2<sup>nd</sup> generation resources are steam stripping, noncatalytic technology, biological conversion, glycerolysis, supercritical esterification, and simultaneous in-situ conversion.

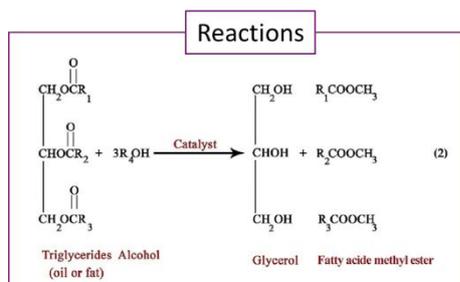
In chemical refining, washing is carried out under caustic soda addition, eliminating FFA, phosphorus and impurities. A separation stage is then required for their removal, followed by water wash.

The pre-treatment is a multistage process that incurs in energy demand, loss of nutrients, need for significant amount of water and chemicals, and imposes the proper disposal of polluted effluents. Research and optimisation aim at reducing these counter backs and maximizing recycling of water and chemicals.

#### 6.1.1.2. *Transesterification stage*

Transesterification is a reaction between triglycerides and alcohol that produces methyl ester and glycerol in a single stage process, at low temperatures (50 to 70 °C) and under the presence of a catalyst. Efficiency is dependent on ratio of reactant, catalyst dosage, reaction time and reaction conditions, namely temperature [185, 196]. The stoichiometric ratio of the reaction is 3:1 mol. However, the reaction rate and yield are improved under an excess alcohol reaction (near 5:1 mol to 11:1 mol),

but limited by the increasing difficulty of glycerine separation, necessary to avoid shift of the reaction equilibrium inducing a reduced yield. The excess alcohol ratio imposes a recycling stage. The conversion yield can achieve 95 to 98 % in most cases [186, 191].



**Figure 48** Transesterification reaction [185].

The reacting alcohol is most commonly methanol because of its higher reactivity and lower costs, despite the higher volatility. The transesterification under methanol results in fatty-acid methyl ester (FAME) fuel. Ethanol can also be proposed and is highlighted for its reduced toxicity. Reaction under ethanol produces fatty-acid ethyl esters (FAEE) that have advantageous properties due to their lower cloud and pour point. Reactors can be either batch or continuous reactors, the latter being more economical and efficient, and better adapted to large fuel production [185, 196]. Homogeneous catalysts are commonly used in industrialised projects. Alkaline catalysts are adopted for their faster reaction, lower catalyst concentration requirements, higher conversion rates and industrial viability to date. Most frequent catalysts are metal hydroxides (sodium NaOH and potassium KOH hydroxides), or alkoxides, potassium or sodium carbonates [186, 192, 196]. Acid catalyst have also been proposed. However, they are characterised by slower reaction rates, require higher temperatures, have higher alcohol to oil ratio, present risk of corrosion, and water formation can inhibit reactions. Consequently, all these properties render them less interesting for industrialised applications. Other transesterification technologies have been identified aiming at simplifying pre-treatment or separations stages, additional to increasing reaction time and yield. However, no industrialised project is reported in the literature to this date. These are listed in Table 15. According to the technology maturity observed in the literature, and communicated investments, their industrialisation is not to be expected by 2030.

There is only a limited number of reports of new FAME fuel plants available online, and the few exceptions concern the pre-treatment development to adapt transesterification to a variety of resources as UCO and animal fat, and the development of small scale facilities for in situ processing of waste, as is the case of large people gathering as hotels, universities, and military use [236]. Other facilities have been implemented to recycle waste cooling oil at a regional scale [237].

Other proposals include the processing of residues through simultaneous saccharification and fermentation, or anaerobic digestion to integrate the by-production of bioethanol, biohydrogen, biogas and digestate [238].

	Heterogeneous	Enzyme	Supercritical
Description	Metal or bioresource catalyst	Enzymatic catalysed hydrolysis and esterification reaction [186].	Simultaneous transesterification of triglycerides and esterification of FFA under solvent's supercritical conditions.
Advantages	Reusability No soap formation, Easy separation - Glycerine purity, Non-toxicity, Resources having high FFA, Improved efficiency, High yield > 90% wt. [196]	Higher conversion rate Reusability of enzyme Flexible to resource and water content, More economical. [186, 196] Easy glycerol recovery Washing of FAME not required	Reduced pre-treatment Resource flexibility Several solvents: alcohol, methyl acetate, dimethyl carbonate, MTBE Faster reaction times Catalyst-free operation, Higher purity of final product.
Inconvenient	Long reaction time High temperature Undesirable by-products Low maturity	Longer reaction time, High enzyme cost, Less mature process (no large-scale demonstration) [196]	Higher P/T required No pilot/industrialisation
Research topics	catalyst development, microwave irradiation and microreactor	Cost of enzyme production [197]	

**Table 15** Researched processes for advanced transesterification solution.

The product of transesterification is FAME fuel. The fuel is a composition of two building blocks: the fatty acid (triglyceride resource) and the alcohol. The fuel's properties depend hence on the resource's composition. According to the literature [53, 198], most common feedstocks present a composition of 16 to 18 carbons atoms, and in the case of UCO, animal fat and camelina, the main compounds are methyl laureate, methyl myristate, methyl palmitate, methyl oleate, methyl linoleate and methyl stearate. These are known for having insufficient cold properties, and CP above 0°C.

#### 6.1.1.3. Co-processing Possibilities

No co-processing possibility has been reported in the literature for transesterification.

#### 6.1.2. Fermentation

Two distinct processes are available to produce diesel-like fuel through fermentation: alcohol to diesel (ATD) process and direct fermentation into fatty acids roots.

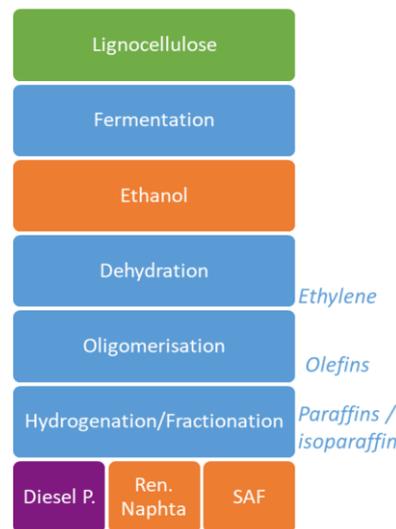
##### 6.1.2.1. Alcohol to diesel

The process is an adaption of the alcohol to jet pathway, for which the industrialised stages are readily available, and allow the ATJ and ATD slate, without impacting the production capacity.

The first stages concern the production of ethanol through fermentation from lignocellulose. Resources can be either agricultural and forestry residues, woody and grassy energy crops, or industrial residues (biomass residues). Ethanol is cleaned and subsequently dehydrated into ethylene [199, 200]. To ensure high purity, the product undergoes a primary separation and a purification. The stage is

followed by oligomerisation into olefins, and hydrogenation and fractionation for the production of paraffins and isoparaffins [201, 202]. The products are renewable diesel (EN590 / ASTM D975), jet, and naphtha in minor proportion.

The technology can be carried out over first- or second-generation ethanol, allowing additional flexibility towards resources and transition to the development of biomass recycling logistics.



**Figure 49** Researched processes for advanced transesterification solution.

#### 6.1.2.2. Direct fermentation

Several pathways exist for the direct fermentation of lignocellulose into diesel-like compounds. The most advanced is the fermentation into triglycerides. In the literature, a pilot plant project for the production of 1000 L batch production of FAME fuel, EN14214, has been observed [203]. The process has been developed over the fermentation of sugarcane juice, but could be extended to lignocellulose. Indeed, pre-treatment through acid hydrolysis of lignocellulose leads to the production of sugars that could be thereafter fermented into triglycerides [204]. The process comprises the fermentation of sugarcane, the decantation of oil, hydrolysis, oil extraction, separation of micelles, esterification, and transesterification (see Figure 50). Oil is subsequently recovered by distillation, and purified. The fermentation process takes place in 24 to 48h fed batches. Methanol recycling can be implemented.



**Figure 50** Researched processes for fermentation pathway from lignocellulose.

Work on direct fermentation routes focuses on pre-treatment, enzyme engineering, and selectivity. Pre-treatment research and development aims at enhancing the digestibility, while avoiding fermentation inhibitors [204]. The mechanical pre-treatment is the preferred method as it destroys crystallinity, minimizes particle size, and does not introduce inhibitors. However, its energy demand is relatively high. Alternatively, thermal and chemical pre-treatments have been proposed. Thermal pre-treatment is carried-out at 150°C, and a strict temperature control is necessary to avoid inhibitors formation beyond 160°C. Acid and alkali chemical pre-treatment are frequently used, where acid hydrolysis is the most practical solution. Alkali bases have the advantage of avoiding biomass degradation, but the risks of incurring in salt formation is a major drawback as it affects hydroxylates composition. Other less industrially mature technologies are the oxidative, steam explosion, liquid hot water, CO<sub>2</sub> supercritical, ozonolysis, green solvents, biological, or microwave pre-treatments.

Several enzyme engineering techniques are proposed in the literature [205-208]. Amongst recent research and developments, it is worth citing the improvements on biosynthetic generation of terpenoids, farnesane and bisabolene, which can be isomerised into complex hydrocarbon mixtures through heterogeneous acid catalysts [209, 210]. Moreover, oleochemical production from *Y.lipolytica* and *S.cerevisia* has seen improvement in their selectivity, and continuous research has advanced the development in r-BOX and *Rhodospiridium toruloides* pathways. The products of these pathways are variable, ranging from FAME, FAEE, fatty alcohols and alkanes, within ranges of 7 to 20 carbons. Upgrading will need to be adapted depending on the resulting product. However, barriers remain, as are the low yield, the selectivity towards desired chain lengths, tolerance to oleochemical products, wider understanding of regulation modes of producing hosts, and feedstock costs. Consequently, direct fermentation into triglycerides, ester or alkanes remains an industrialisation challenge.

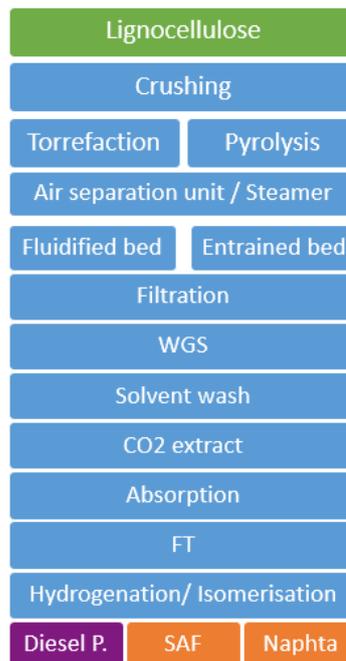
### 6.1.2.3. Co-processing Possibilities

Co-processing is possible for fermentation technology in petroleum refineries. The co-processing shares the hydrogenation and fractionation process between the two pathways, where oligomerization products from fermentation is inserted as inputs for hydrogenation. [211] A maximum co-processing ratio of 10% is reported for fermentation in petroleum refineries. [211]

### 6.1.3. Gasification - FT

Gasification followed by Fisher-Tropsch (FT) production of waxes, and upgrading to alkanes, is a proven technology that has been applied to coal since mid-twenties century. Extension to process application to lignocellulosic renewable resources has gained recent attention and pilot to demonstration plants have served to confirm the technology readiness.

Several resources of lignocellulose composition can be used as feedstock, as are agricultural and forestry residues, woody and grassy energy crops, and industrial residues (biomass). The process counts of four main steps: pre-treatment, gasification, gas cleaning, and FT and upgrading (see Figure 51).



**Figure 51** Researched processes for gasification with FT energy path.

#### 6.1.3.1. Pre-treatment

The mains goals of pre-treatment techniques are to increase the volumetric energy density, to homogenise the biomass composition, and to facilitate the continuous flow of the biomass into gasifier. For these, two approaches are proposed: the transformation into dry biomass or to slurry biomass [212].

Dry biomass preparation is carried out through the crushing and torrefaction of the lignocellulose into 50 to 100  $\mu\text{m}$  particles to facilitate mechanical flow. Small size particles are necessary for efficient gasification process. The torrefaction takes place between 200 and 300  $^{\circ}\text{C}$ . The temperature increase is slow and residence

time varies between 20 min to 1 h. As the temperature increases, the biomass undergoes water evaporation, hemicellulose decomposition, followed by cellulose and lignin transformation. The gas production in this stage comprises 10 to 30 % wt. During pre-treatment hydroxyl and methoxyl groups are decomposed. This and water evaporation result in H and O reduction, carbon content increase, reduction of volatiles, and calorific value increase from 18-19 MJ/kg to about 20-24 MJ/kg [195]. One advantage of the dry method resides in the hydrophore property of the resulting matter, and its stable composition through storage [212]. Research and development of dry biomass pre-treatment aims at improving the efficient and homogeneous heat transfer, the treatment of inert gas, optimising or processing gas (CO, CO<sub>2</sub>) and particle discharges, and improving the flexibility of operation between start-up and steady-state phases [195].

Slurry biomass preparation is a second solution to biomass pre-treatment through pyrolysis [212, 213]. When a fast pyrolysis is employed, a crushing stage will also be required to reduce biomass to 2-5 mm pellets. If the water content in the biomass exceeds 10 %, a previous drying stage is required. The pyrolysis of biomass results in gas, liquid, and solid fractions. The liquid fraction corresponds to 60-75 % wt., and it contains solid particles that are source of erosion and corrosion. The gas counts for 10-20 % wt., and char for 15-25 % wt. [212-214]. The interest in slurry pre-treatment is that it facilitates flow into high pressure gasifiers. Nevertheless, dry mass has also been adopted for this technology in the BioTFuel demonstration plant [215].

#### 6.1.3.2. Gasification

Gasification is a known technology typically applied to coal gasification. Current research and development works aim at adapting the bed conditions to optimise syngas composition for a FT process, improving yield, ensuring a continuous flow, and the integration onto FT stage [215].

Gasification reactions are exotherm and endotherm, as are listed in Figure 52. Further analysis on dominating reactions are proposed according to gasifier technology [216]. Reaction components are CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, at concentrations dependent on biomass composition, reactor type and reactor parameters, mainly temperature. The products of gasification vary according to biomass feedstock, gasifier design, gasifier agent, and conditions. Research on gasification reactions have observed that char gasification is the rate-limiting reaction in the production of gaseous fuels [217]. Moreover, other than syngas, gasification of biomass will produce particulate matter, ammonia, sulphur compounds, hydrochloric acid, and alkali metal species as impurities. Char and impurities are dependent on biomass feedstock. Mineral compounds are found in lignocellulose and are source of ashes which will find themselves on the produced gas [218]. Ashes' composition and concentration vary significantly depending on biomass resource and gasification reaction temperature. Most wood species have ash contents below two percent, and are suitable feedstock for fixed bed gasifiers [212]. Tar and particulate concentrations above the acceptable range are problematic for FT synthesis processes, amongst other, and require a cleaning stage [212, 213, 217]. Attempts have been made at modelling biomass to gasifier design and parameters, as biomass properties impact the syngas composition, having later an influence on the FT stage [219].

Tar control is a difficulty usually encountered by gasifiers [220]. Tar is a mixture of single to 5-ring aromatic compounds, and other oxygen containing hydrocarbons and complex polycyclic aromatic hydrocarbons. Tar treatment can take place inside the gasifier (primary tar treatment) through catalytic cracking of the tar, and can attain

a conversion of 99 %. Catalysts as dolomite and nickel-base are employed at high temperature (1075-1175 K) [217]. Hot gas cleaning after gasifier (secondary tar treatment) is another method employed.

Combustion reactions	
$C + 1/2O_2 \leftrightarrow CO$	$\Delta H = - 111 \text{ kJ} \cdot \text{mol}^{-1}$
$CO + 1/2O_2 \leftrightarrow CO_2$	$\Delta H = - 283 \text{ kJ} \cdot \text{mol}^{-1}$
$H_2 + 1/2O_2 \leftrightarrow H_2O$	$\Delta H = - 242 \text{ kJ} \cdot \text{mol}^{-1}$
Boudouard reactions	Methanisation reactions
$C + CO_2 \leftrightarrow 2CO$	$\Delta H = + 172 \text{ kJ} \cdot \text{mol}^{-1}$
Carbon reforming reactions	Vapour reforming reactions
$C + H_2O \leftrightarrow CO + H_2$	$\Delta H = + 131 \text{ kJ} \cdot \text{mol}^{-1}$
	$C + 2 H_2 \leftrightarrow CH_4$
	$\Delta H = - 75 \text{ kJ} \cdot \text{mol}^{-1}$
	$CO + H_2O \leftrightarrow H_2 + CO_2$
	$\Delta H = - 42 \text{ kJ} \cdot \text{mol}^{-1}$

**Figure 52** Gasification reactions [212].

Several gasifier technologies are available, having an impact over syngas properties, ash management and tar-char content. These are listed in Table 16. For biomass liquid fuel production, fluidified and entrained flow reactors are listed as optimal solution for their higher H<sub>2</sub> syngas concentration. Of these, the later facilitates tar and char management before FT process [212, 214], and thus has been chosen for pilot and demonstrator plants [215]. Gasifier technology impacts syngas composition and yield, mainly through the operating temperature and tar control. Fluidized and bed reactors, operating near 700-900 °C, characterise by lower H<sub>2</sub>, CO and water yield, and higher methane, CO<sub>2</sub> and tar yield. Entrained reactors, operate at higher temperature, produce higher CO and H<sub>2</sub> concentration, and reduce short chain hydrocarbons as methane [212]. At these high temperatures ash melts and can be extracted from gasifier bed. However, they can lead to risks of slag formation that generate equipment clogging/coating [222].

Gasifier type	Drawback	Advantage	Other properties
Fixed bed – downdraft and updraft (700- 900°C)	Poor control of temperature, mass, and heat transfer Inefficient char removal [221] High tar production [217]	Simple, robust Biomass flexibility [221]	Increase of methane yields (150 kWe–1 MWe)[217]
Moving bed – downdraft and updraft (700- 900°C)	Solid impurities in gas [212]	Simple, industrialised solution for coal gasification [212]	
Fluidized bed reactor (700- 900°C)[221] ↗ 10 MWth [217]	Biomass moisture requirements Ash management [220, 221]	Efficient temperature control, mass, and heat transfer Easy to scale up [221]	Promotes production of H <sub>2</sub> /CO [212, 219], ↗CO <sub>2</sub> production [212] ↗increase HHV [219] LCV gas for electricity [1]
Entrained flow reactor 1200 – 1600 °C [214] - 1700 °C	Complex Expensive [221] Material to sustain high temperature [219]	Compact No tars, char Ash management [221] ↗ conversion effi. (~100%)[219]	High temperature 1200- 1500°C [219] Reduced methane content [212]

**Table 16** Gasifier technologies and their main properties.

Most industrialised solutions use mixture of oxygen and steam agents, as these improve gas composition. For example, it has been indicated that gasification in a fluidified bed reactor, under high temperature tar cracking and O<sub>2</sub> agent increases FT yield [261]. Some publications have pointed at the optimisation of the gasification agent over the biomass composition [222].

O <sub>2</sub> agent	Steam	CO <sub>2</sub>
↗ Efficiency and HHV ↘ Nitrogen dilution. ↘ Tar formation Expensive Ideal biomass CH <sub>1.2</sub> O <sub>0.495</sub> [222] Requires a cryogenic separator stage (energy and cost impact) [212]	↗ H <sub>2</sub> /CO concentration. Less expensive than O <sub>2</sub> agent Water and vaporization unit are needed, external heat unit. ↗ Tar content Ideal biomass CH <sub>1.7</sub> O <sub>0.85</sub> Lower CO <sub>2</sub> emissions [222]	Lower hydrogen production than steam-assisted gasification. Cold gas efficiency is higher for low carbon and H/C of feedstock. Exhibits negative CO <sub>2</sub> emissions External heat source required. Char content is relatively high. Ideal biomass CH <sub>1.3</sub> O <sub>0.566</sub> [222] No know industrial application.

**Table 17** Characteristics of gasifier agents

#### 6.1.3.3. Syngas cleaning and conditioning

Cleaning and conditioning of biosyngas is critical for correct functioning and high yield of FT stage, as impurities would result in contamination and deactivation of the FT catalyst. More specifically, a ratio of H<sub>2</sub>/CO of 2 is necessary to ensure maximal conversion. Several publications refer to the syngas cleaning process [212, 223, 224]. Gas cleaning must be designed to allow high control flexibility as impurities are dependent on the biomass and the gasification temperature control [212]. Gas quality control can be employed using analysers capable of detecting impurities, as for example sulfur at ppb concentrations.

The cleaning and conditioning process comprises four stages:

1) Filtration for particles elimination

2) Water-gas-shift (WGS) carbon conversion to adapt H<sub>2</sub>/CO ratio from biosyngas value near 0.5 to 0.7, to optimised FT ratio of 2 to 3 [225]. WGS allows increasing FT yield by near 40 % [224].

3) Solvent wash for acid gas reduction and extract inert gas CO<sub>2</sub>. The latter lowers the CO conversion in the FT process leading to energy losses. The challenges of this stage are the recycling of CO<sub>2</sub> towards the gasification, its economic impact, and the sulphur reduction. Two options are possible:

- Chemical processes: low cost but high energy stage that requires ethanalamines [212].
- Physical processes: Three industrialised processes are Rectisol (methanol), Purisol and Selexol. They allow the separation of acid and CO<sub>2</sub> but require integrating multi-stag units. Sulfinol is a hybrid processes aiming at maximising benefits [212]

4) Solid absorbent beds for final purification to reduce sulfur and nitro components, metals, halogens and avoid FT poisoning [212].

#### 6.1.3.4. FT and post-processing

The Fischer-Tropsch process is a collection of polymerisation reactions, as described in Table 18. Catalysts as cobalt and iron are known to increase reaction rates, but other materials are also researched. For example, cobalt catalysts are better adapted to diesel fuel, while ruthenium is most efficient (yield) catalyst but is more expensive. The FT reaction is exothermic and it has been estimated that around 20 % of the energy is released as heat [224]. Reactors are multi tubular reactors having pressurized water jacket, or column reactors having and internal heat exchanger. Reactors operation conditions are within 20-40 bar, and 200-250 °C. FT catalyst metal losses are low, and do not account for a significant weight of the full operational cost [212].

Product fraction	Carbon range	Share of product fraction (%)
Tail gas	C1-C2	7
LPG	C3-C4	5
Naphtha	C5-C10	20
Distillate	C11-C22	22
Wax	>C22	44
Aqueous product	C1-C5	2

$$n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$$

$$n\text{CO} + (2n)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$$

$$n\text{CO} + (2n)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2}\text{O} + (n-1)\text{H}_2\text{O}$$

**Table 18** FT reactions [212] (left) and typical FT product composition.

Reaction temperature, reactor pressure, and space velocity have a significant influence on FT catalyst activity and product selectivity. Research on FT catalysts aims at improving efficiency and material selection, and integrate FT and isomerisation reactions into one stage. Furthermore, some research works focus on efficient (mass conversion) and robust FT catalytic system for converting H<sub>2</sub> deficient and CO<sub>2</sub> containing syngas, at high C<sub>5+</sub> selectivity in order to avoid the integration of a WGS stage and to reduce cost [225].

Products of FT process are a mixture of methane, ethane, LPG (liquefied petroleum gas), naphtha, distillates, light wax and heavy wax, which concentrations depend on the ASF alpha parameter [224]. The distillate fraction (near 22 % product) could be blended to diesel avoiding additional processing stages and reduce cost, but at limited blend ratio. Otherwise, treatment of the syncrude<sup>4</sup> is carried out through hydrogenation and hydrocracking and isomerisation stages. The first produces normal paraffins and long chain compounds, the later allow adapting chain length and cold properties to maximize blend ratio and ensure that diesel and jet quality properties are attained [226].

Several pilot to industrialised plants have proved the feasibility of each stage and the integrability of lignocellulosic upgrading [227], as for example:

- British Airways/Shell/Velocys; municipal solid waste; 60 million litres jet, diesel, naphtha; 2021 [228].
- BioTfuel (Avril, Axens, le CEA, IFP Energies nouvelles, Thyssenkrupp Industrial Solutions, Total), biomass residues, France, operational; 2021 [229].

<sup>4</sup> Refers to overall syntheses crude obtained from FT. It includes naphtha, distillate and wax.

- Comsym (VTT, AF-CONSULT OY, INERATEC, GKN, DLR EV, UniCRE AS, AMEC SRL); bark; pilot; 2021 [226].
- Red Rock biofuels; 460t/d municipal solid waste; 1100 bpd FTP; demonstrator; operational; 2017 [228].
- Syndiesel; forest and agricultural residue; 530 bbd liquid fuel; demonstrator plant; 2015 [228].
- VTT, INERATEC, Infraseriv Höchst, ALTANA, Provadis Hochschule, Politecnico di Torino; FT liquids, forest residues and CO<sub>2</sub>; operational; pilot plant; 2021.

#### 6.1.3.5. **Product**

Upgraded FT syncrude produce paraffinic Diesel fuel, having properties complying with EN590 except for a lower density [212, 226, 230]. Due to its lower density, FT diesel requires mixing with conventional fossil fuel in order to comply with specifications. The fuel characterises by the absence of aromatics, which would result in lower particle emissions, and high CN. Cold flow properties are improved and adapted through isomerisation stage. The coproduct kerosene obtained from hydrocracking and hydro/isomerisation responds to specification ASTM D7566 [226]. Gasoline can also be obtained at reduced yield and characterises by a high paraffinic content. Other coproducts of the overall process are CO<sub>2</sub>, methane, tars, ammonia, and water (for recycling or treatment).

The total process accounts for several stages of transformation, thus carbon content losses are present, and the overall mass efficiency is estimated to be between 15 and 25 % [212], thus represents a main optimisation challenge. The overall energy efficiency is estimated near 50 % due to the advantage of exothermal processes. The process can be coupled with vapour or electricity generation. It is estimated that the combination with combined heat and power unit (CHP) using off-gas and steam to boiler results in efficiency of near 80 % [226]. The low mass efficiency induces a strong impact of resource cost over product price, an additional challenge to the complex gasification and FT processes. However, synergies with current refinery installations in the post-processing of FT waxes facilitates co-production and reduced investment.

Gasification-FT is an industrialised solution for which recent developments have helped in the optimisation of the different stages, their integrability, and adaption to lignocellulose resources. Research and development could further improve mass conversion of the overall process. The literature proposes to optimise gasifier H<sub>2</sub>/CO ratio to reduce separated shift reactor, simplify acid gas removal, reduce CO<sub>2</sub> to be removed by means of recycling, reduce the recycle ratio of FT process, improve the tolerance of inert gas (CO<sub>2</sub>+N<sub>2</sub>+CH<sub>4</sub>) in FT stage whilst maintaining high efficiency [231]. Moreover, heat integration solutions can improve energy efficiency, and the combination with electrolyzers for green H<sub>2</sub> production for the FT stage and oxygen for the gasification stage can improve overall CO<sub>2</sub> emissions and mass conversion. It is estimated that such combination would attain a 90 % biomass conversion and 65 % energy efficiency [226].

#### 6.1.3.6. **Co-processing Possibilities**

Co-processing is possible for Gasification - FT technology in petroleum refineries, due to the various co-processing options for FT products. The end products of FT include tail gas, LPG, naphtha, distillate, wax, and aqueous product. They could be separated and therefore have different co-processing possibilities in petroleum refineries. A more favourable pathway is to co-process the mixtures of wax, naphtha, distillate, and residues through vacuum distillation and hydro cracking to produce gasoline, diesel, or jet fuels. [226] The same mixtures could also be co-

processed through hydroprocessing to produce gasoline, diesel, or base oils. Mixtures of wax, naphtha, and residues could be co-processed through hydroprocessing and hydrocracking to form gasoline, diesel, jet fuels, or base oils. The distillate alone could be co-processed through hydrotreatment to produce HVO for renewable diesel or jet fuels. [226]

#### 6.1.4. Hydrotreatment

- HVO is flexible in its feedstock requirements allowing the use of waste and residue materials. [372] Feedstock possible are triglycerides, sourced from UCO or animal fat. The overall process is schematised in

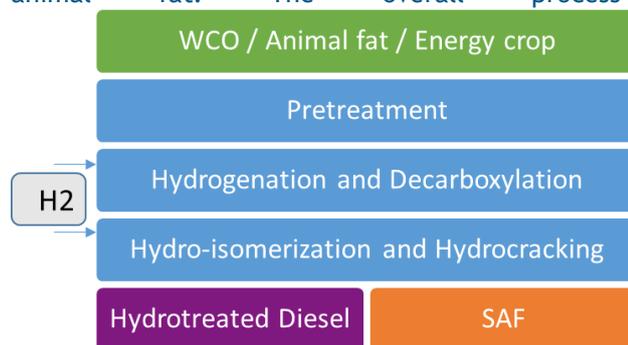
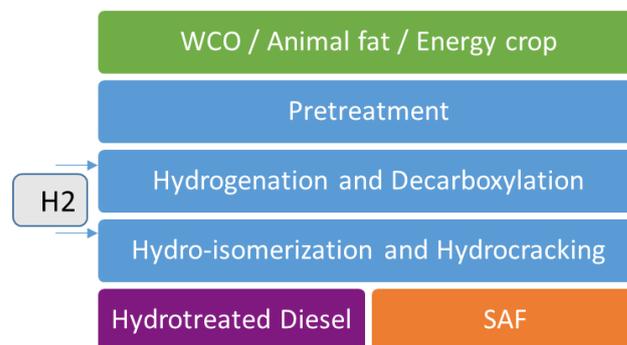


Figure 53.



**Figure 53** Hydrotreatment process overview.

##### 6.1.4.1. Pre-treatment

Pre-treatment ensures obtaining a feedstock absent of impurities and compatible with hydrotreatment process that will not have negative effects of its operation, independently of the feedstock origin and properties. Contaminants can be chlorides, insoluble impurities, phospholipids, proteins, metals, moisture, FFA and sulfur compounds. Their concentration can change significantly from one batch of resources to another especially for WCO and animal fat. This imposes pre-treatment than can be more stringent compare to neat vegetable oil resources. The process is schematised in Figure 54. Typical stages of pre-treatment are chloride mitigation, degumming, and absorption. However, the process must be adapted to resource and several solutions are listed in the literature [188, 232]. Polyethylene removal by crystallization and filtration might be necessary when treating animal fat as labelling and packaging could contaminate process and product [232]. Unlike pre-treatment for transesterification, hydrotreatment feedstock does not require elimination of bacteria as the process takes place at high temperature avoiding such contaminants.

Phosphatides and phospholipids are present in fats and oils, and are source of gum formation at high temperature processing, thus must be removed. The stage requires heating, acid and lye washing, reactor, centrifugation for gum removal, and water extraction. The absorption stage removes residual phosphatides and metal content. In this stage, oil is heated, bleached, filtered in several stages, and collected after a cyclone. Bleaching removes chlorophyll and gossypol that can impact heat sensibility and oxidation stability, as well as remove residual soap. In the absorption stage bleaching earth and acid (citric or phosphoric) will be consumed. All stages require water that must be treated and recycled, and impurities should be removed for disposal [232].



**Figure 54** Pre-treatment stages for animal fat, UCO, and energy crops.

#### 6.1.4.2. Hydrotreatment

Hydrotreatment is a process of oxygen removal. Oxygen is removed in the form of  $H_2O$ ,  $CO$  and  $CO_2$ , through decarbonylation, decarboxylation and hydrodeoxygenation reactions [233], as presented in Figure 55. The reactions result in a decrease of the total carbon yield. The process is mainly referred to as hydrotreated vegetable Oil (HVO), and later as Hydroprocessed Esters and Fatty Acids (HEFA) when referring to a variety of feedstock, including animal fat and UCO.

The process is decoupled into two steps, where the first takes place at lower temperature in order to address coking. The first steps are the stabilization stages of hydrogenation and decarboxylation [234, 235]. In this stage carbonyl and carboxyl functional groups are transformed into alcohols between 373 and 573 K, followed by oxygen removal and olefin saturation. Materials as Ru, Ni, or sulphide CoMo can be used for catalysts, and transition metal phosphides and carbides are also cited. The second step is the hydro-isomerization and hydrocracking [234, 235]. The process leads to a fuel composition adapted for cold properties, and takes place between 623 and 673 K. In this stage noble metals (Pt, Ru and Pd) are employed and supported on carbon and metal oxides. Throughout the process, temperature increase strongly impacts the sequenced reaction completion and product composition [236].

Numerous publications are available on catalyst technology [235]. Research works on catalyst development indicate a high conversion up to 99 %, that can be deteriorated due to coke deposit, and requiring regeneration [237]. Development of transition metal phosphides (TMPs) catalysts for the hydrodeoxygenation has been encouraged as they are a cost-effective solution, present higher resistance to

water, and do not require sulfur feed [238]. Other developments include catalyst production to maximise conversion of specific to renewable resources as waste cooking oils [239].

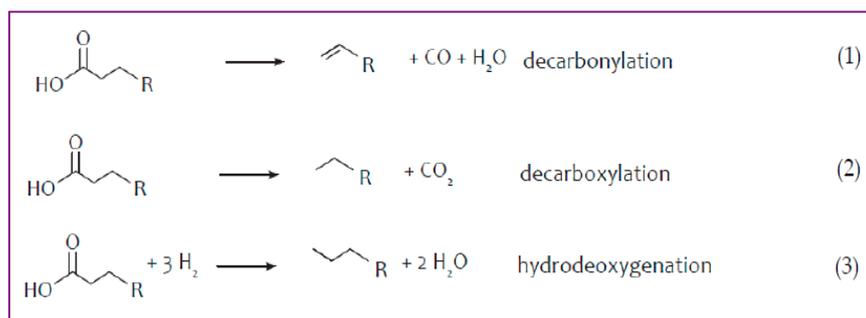
Undesired reactions as polymerization and coke formation are to be avoided, as they can damage catalytic conversion and can count for 2 to 30 wt.% of the feed. The main challenge of hydrotreatment process is the avoidance of coke formation. For this, it is desired to minimize polymerization and condensation reactions that occur at high temperature. Some solutions are the reduction of the HDO activation energy, the increase of HDO reaction rates, and avoid fast temperatures increase within the range of 473-523K, above the HDO reaction rate, as polymerization would quickly take place [235].

Optimisation of the process includes pressure increase to improve hydrogen solubilization and maximize deoxygenation, and acid conversion. Some of the parameters affecting optimisation are [235]:

- Residence time. Longer residence time increases oxygen content, thus formation of heavy species and coke. The literature notes that for continuous reactors, various organic species may experience different residence times in the reactor due to different molecule size, and such parameters influence optimal design.
- Temperature. High temperatures are required to significantly crack large oligomeric molecules. However, this also induces high hydrogen consumption. The reduction of that catalyst activation temperature, through catalysts as sulphide NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>, is cited by several publications.
- Pressure. High pressure is needed to achieve hydrogen solubilization levels for deep deoxygenation, and better conversion of acids.
- Hydrogen. Hydrogen flow rate influences the coke formation and its precursors, including heavy components. Heating of the hydrogen has been observed to decrease coke formation.

Moreover, the integration of organic solvents (e.g. guaiacol) is known to decrease coke formation.

Other research needs observed in the literature are catalyst materials, catalyst suitable for hydrogenating carbonyls into alcohols, dehydrating alcohols to olefins, and saturating olefins into alkanes. Further research is proposed on catalyst surface properties affecting reaction mechanism, and technologies to reduce conventional H<sub>2</sub> consumption. The economic feasibility of biomass pre-treatment is poorly documented [240].



**Figure 55** Hydrotreatment reactions [233].

#### 6.1.4.3. Product

Hydrotreatment produces alkane type diesel EN15940, jet and naphtha, with no aromatic content. Process allows flexibility of product properties between Diesel and Jet fuel [241], through a trade-off in fuel rich in paraffin, good auto-ignition properties or with good cold flow properties. The product allows for high blending into conventional base fuels (EN590) and stability [234].

#### 6.1.4.4. Industrialisation

Plant development are numerous, either in stand-alone facilities or co-processing. Several installations for the commercial production of HVO/HEFA are listed in the literature [242]. The stand-alone production facilities amount to 6-7 million t/year, and a 12 million t/year potential reported in 2020. Amongst them the following are mentioned [242, 243], citing when possible their annual production:

- Neste, Porvoo, Singapore, Rotterdam. HEFA Diesel and Jet. 2 million tons.
- Diamond Green, US. HEFA Diesel. 600 million liters.
- UPM Finland. HEFA Diesel. 100 ktons.
- Renewable Energy Group, US. HEFA Diesel. 1700 million gallons.
- Emerald Biofuels, US. HEFA Diesel. 330 million gallons.
- ENI S.P.A (ENI) has converted their Venice refinery for a production 400,000 tonnes.
- A second ENI refinery, Gela in Sicily, for a production of 0.5 million tonnes.
- Total refinery at La Mede, France.
- Repsol, ES. 250,000 tons of biodiesel, biojet, bionaphtha, and biopropane. Start of production 2023.
- Shell's Pernis refinery in Rotterdam for a production of 820 kt of fuel per year by 2024.
- UPM in Finland with an objective of 500 kt/year by 2024.
- Total in Grandpuits (France) with an objective of 400 kt/year by 2024.

Triglycerides hydrotreatment is a process counting with continuous development into industrialisation, and that can be applied to multiple oil resources, as UCO, animal fat, and energy crops. Prospective improvements are also listed as the integration of renewable hydrogen process stages, carbon-capture and processing [221]. For example, Aemetis proposes the combination of triglycerides hydrotreatment to cellulosic H<sub>2</sub> production for SAF and sustainable diesel fuel.

#### 6.1.4.5. Other application

Mercurius Biorefining proposes the hydrotreatment of products of lignocellulose through the REACH™ (Renewable Acid-hydrolysis Condensation Hydrotreating technology) [244] Lignocellulose, as agricultural and forestry residues, woody and grassy energy crops, and industrial residues (biomass), is converted through catalytic hydrolysis to produce bio-crude, as in pulp/paper industry. According to the communications, the process accommodates to high humidity resources, and does not require enzyme or microbes, and takes place under low temperature and pressure. Bio-crude is then hydrotreated by means of solid-bed-catalytic produce diesel and jet fuels. The diesel is indicated to have high cetane, no aromatic, and to be sulfur free. A pilot plant in Australia is under development. Other high-value products are furandicarboxylic acid, biochar, levulinic acid, formic acid, biochar. Only one communication refers to this process, and if industrialisation attempts are observed, it has not been retained for further techno-economical and life cycle analysis.

#### 6.1.4.6. Co-processing Possibilities

Pre-processed triglycerides can be integrated at FCC unit and studies have demonstrated the compatibility. A 75 % mass conversion is been reported. However, feedstock composition has an impact on cracking product's distribution. Most significant impacts of integrating triglycerides in FCC stage are the reduction of liquid fraction, increased gas production, increase of monoaromatics (> 95%wt.), increased coke formation [245].

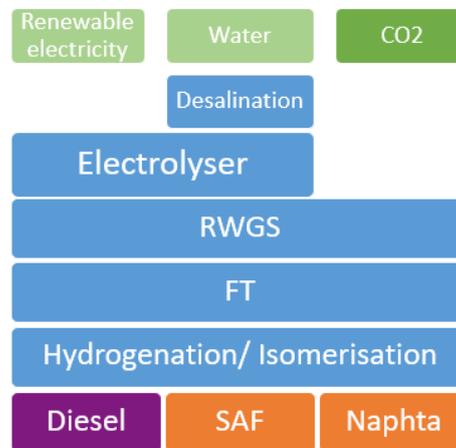
Triglycerides can also be hydrotreated in a desulphurisation unit resulting in a high diesel selectivity. Main impacts are the higher H<sub>2</sub> consumption as compared to triglycerides hydrotreatment. The feedstock compositions will impact the competitions between HDO and HDS reactions, reducing the efficiency and increasing H<sub>2</sub> consumption. Product's cold flow properties might be a limiting factor to maximal triglycerides integration. If high triglyceride content in feedstock, it is recommended to treat in dedicated hydrotreatment unit. Revamping of gas recycling is recommended to deal with deoxygenation products (CO<sub>2</sub>, CO and H<sub>2</sub>O) [245].

The co-processing takes advantage of the recent development of novel catalysts. [246-250] However, the efficiency and product quality still needs to be improved to be competitive to hydrotreatment or fluid catalytic cracking on pure gas oils. [246-250]

#### 6.1.5. E-Fuels

e-Fuels (or electrofuel) are manufactured using captured carbon dioxide or carbon monoxide, together with hydrogen obtained from sustainable electricity sources such as wind, solar and nuclear power. E-fuels can be either oxygenated, paraffinic or similar to conventional fuel blends with the use of alcohol to fuel process. The e-fuel production is discussed in section 3.2.2.14. For the production of paraffinic fuels, carbon and hydrogen conversion into paraffinic fuel is achieved through FT process [251].

Numerous projects have been announced aiming at the development of overall process or process' stages, or at their industrialisation. In 2020, a total of 220 PtX research and demonstration projects in Europe have either been realised, completed, or are currently being planned. 56 projects are mainly funded by the Horizon 2020 Program [252].



**Figure 56** e-Fuel pathway to liquid fuel production through FT process.

Different CO<sub>2</sub> resources are considered in the literature, having no impact on the process thereafter:

- Direct capture from air.
- CO<sub>2</sub> from industries, as for example cement and limestone production, and steel industry.
- Carbon from biomass, obtained through purification of biogas to biomethane, alcoholic fermentation processes, electricity generation from biogas / sewage gas in CHP plants and the combustion of solid biofuels (e.g. provision of district heating or industrial process heat).

#### 6.1.5.1. Electrolyser

The first stage is the water electrolysis by means of renewable electricity. Several technologies are proposed, of which alkaline electrolysis cells and proton exchange membrane are technologically mature. Other solutions are under development or research [252]. Amongst the research needs, the literature lists the co-electrolysis with CO<sub>2</sub>, under pressurized stack operation [253], aiming at the avoidance of the reverse water gas shift (RWGS) stage and the reduction of costs [254].

Research on co-electrolysis of Solid Oxide Electrolysis Cell (SOEC) to reduce start-up time, and improve ramping flexibility is proposed, allowing for the reduction of battery size and investment cost. Process heat integration and optimization of the operating conditions promoting internal methanation have also been proposed [253]. Research on plasma chemical conversion aims at increasing the power density and consequent productivity, and easing conditions for splitting CO<sub>2</sub> through vibrational excitation of the molecules [255]. Plasma technology increases productivity by a factor of 10 by volume as compared to SOEC electro-chemical conversion. However, the technology requires the optimisation of the reduced electric field, and the reduction of the CO<sub>2</sub> gas temperature to increased energy efficiency.

One of the main challenges of electrofuel production is the coupling of intermittent renewable electricity with continuous fuel production, requiring electricity and/or hydrogen storage facilities [256].

	AEC (Alkaline Electrolysis Cell)	PEM (Proton Exchange Membrane)	AEM (Anion Exchange Membrane)	SOEC (Solid Oxide Electrolysis Cell)	PCEC (Proton Ceramic Electrolysis Cell)
<b>State of development</b>	Mature	Mature	Under developing	Under developing	Research status
<b>Electrolyte</b>	Alkaline solution	Proton exchange ionomer	Anion exchange ionomer	Solid electrolyte	Ceramic solid electrolyte
<b>Cell separator</b>	Diaphragm	Electrolyte membrane	Electrolyte membrane	Electrolyte membrane	Ceramic membrane
<b>Temperature [°C]</b>	65 to 100 [26]	70 to 90 [26]	50 to 70 [26]	700 to 1000 [22]	300 to 600 [24]
<b>Advantages</b>	Available for large plant sizes, low costs, long lifetime	High efficiency, high dynamics	Low costs, high dynamics	High efficiency, possible integration of waste heat	Dry hydrogen produced, low costs
<b>Disadvantages</b>	Low current density, low dynamics, corrosive environment	Expensive, low durability	Not mature technology, expensive, low durability	Expensive, low durability, corrosive environment, low dynamics	Not mature technology, low durability

**Table 19** Electrolyser technologies [252].

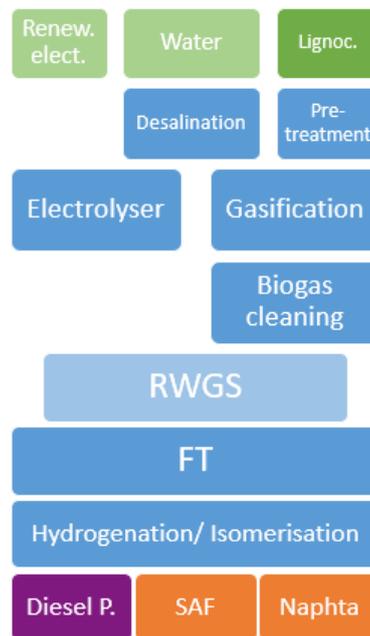
#### 6.1.5.2. Reverse Water Gas Shift (RWGS)

RWGS is a necessary step to produce carbon chain liquid fuels through CO<sub>2</sub> upgrading. The reaction of CO<sub>2</sub> with H<sub>2</sub> to produce CO and H<sub>2</sub>O must take place at high temperature to ensure CO selectivity. The process requires further research and development, and maturity for 2030 is not certain according to the literature. Repsol announced that they would set up an e-fuel pilot plant involving RWGS by 2024, and publications are at laboratory research and initial upscaling stage [257]. Amongst the research needs, it is observed that the process requires development of high temperature enduring catalysts as research aims at the avoidance of severe sintering of catalysts [258]. Avoiding thermodynamic limitations help achieve high conversion and suppress CO/CO<sub>2</sub> methanation [259]. Research needs also extend to catalyst solutions to avoid high cost of noble metal catalysts to facilitate commercialisation [260], and improving process stability under real working condition.

#### 6.1.5.3. Liquid Fuel production

The production of liquid fuel from CO and H<sub>2</sub> follows the FT process, and subsequent upgrading through hydrogenation and isomerisation, as presented in section 6.3.1.4. The product is of a paraffinic Diesel. An example of such implementation has been proposed but is not readily industrialised [261]. Plants are expected from 2026 [262].

Other solutions are the co-production through gasification and hydrolysis, where carbon is obtained by biomass gasification, and green H<sub>2</sub> is provided by means of an electrolyser (see Figure 57). Alternatively, integrating a RWGS allows full CO<sub>2</sub> upgrading and ultra-low GHG emissions, hence avoiding CO<sub>2</sub> emissions in the gasification-FT process [263, 264].



**Figure 57** Schema of eFuel pathway to liquid fuel production through Gasification to CO<sub>2</sub> and FT process.

#### 6.1.5.4. Co-processing Possibilities

The co-processing possibilities for E-fuels are the same as the FT process. Please refer to Section 6.1.3.6 for more details.

#### 6.1.6. Summary & conclusions

Table 20 provides a summary of the different energy pathways identified in this study. These combinations of resources and processes mostly lead to paraffinic components. Transesterification is the only pathway identified leading to FAME.

A few pathways are already at industrial scale. This is, for example, the case for alcohol to diesel (fermentation), transesterification and gasification combined with Fischer Tropsch. These processes can deal with different feedstocks but may require a certain adaptation for the pre-treatment for example. Fermentation to oil and lignocellulose hydrotreatment are two processes that are not mature yet and a lack of data is observed in the literature to further discuss their benefits or drawbacks. Finally, e-fuel can be associated to two pathways, either the use of biomass to generate CO which will be used during a Fischer Tropsch upgrading or direct CO<sub>2</sub> capture followed by a reverse water gas shift reaction. These approaches are still to be industrialised. Optimisations are also required regarding either carbon capture, renewable hydrogen production and sufficient renewable energy. These pathways have the advantage to potentially produce different fuels.

Based on this summary, the fermentation to oil pathway will be discarded for the next steps of this study.

**Table 20** Summary of the eight different energy pathways identified in this study to produce paraffines or esters as renewable diesel fuels

Resource	Process		Comments / Research needs
Lignocellulose	Fermentation ATD	Paraffinic distillate	Industrialised technology Flexibility to other products → diesel or kerosene optimisation impacts?
Lignocellulose	Fermentation to oil	Paraffinic Diesel	Limited industrialised projects Blending constrains
Lignocellulose	Gasification - FT	Paraffinic distillate	Industrialised technology - Optimisation prospects Flexibility to other products but integrability and adaptation to lignocellulose required
Lignocellulose	Hydrotreatment Lignoc.	Paraffinic distillate	Limited industrialised projects
WCO / Animal fat / Energy crop oil	Hydrotreatment of triglycerides	Paraffinic distillate (HVO / HEFA)	Industrialised technology Application to a wider range of resources Integration of renewable H <sub>2</sub> ?
WCO / Animal fat / Energy crop oil	Transesterification	FAME	Industrialised technology – adapted to small scale /close to resource Blending constrains
Lignocellulose	eFuel – Lignoc.	Paraffinic distillate	eH <sub>2</sub> and RWGS technology to industrialise Optimisation prospects (electrolysers, CO <sub>2</sub> capture, CO/CO <sub>2</sub> from biomass) High flexibility to other fuels
CO <sub>2</sub>	eFuel – CO <sub>2</sub>	Paraffinic distillate	

Co-processing possibilities are evaluated for the seven selected renewable diesel production pathways, as summarized in Table 21. The three pathways containing FT processes share the same co-processing options. The most common co-processing pathway uses the FT products (such as wax) as inputs to vacuum distillation and hydrocracking to produce various products, such as gasoline, diesel, jet fuels, or base oils. The maximum co-processing ratio of 7% is reported in the literature. [211] Co-processing up to 10% is possible for the fermentation pathway after oligomerization, whose products are inserted into hydrogenation or FCC units in petroleum refineries. For the hydrotreatment pathway, pre-processed triglycerides can be co-processed with atmospheric or vacuum gas oils in hydrotreatment or FCC units using novel catalysts. Concerning the hydrotreatment of lignocellulose and transesterification pathways, no co-processing option has been identified in the literature.

**Table 21** Co-processing possibilities for the selected renewable diesel production pathways

Pathways	CP Possibility	Max CP <sup>c</sup>	CP Input Location	Input Product	Comment	Re f.
Gasification + FT	Yes	7%	VD+HC	FT wax	Gasification -> FT -> wax -> VD+HC. Other locations possible but less favorable. Max CP fixed to maintain the initial feedstock capacity below 2000 metric tons per day (viable commercial scale feedstock capacity)	[21 1]
eFuel – CO <sub>2</sub>	Yes	7% <sup>a</sup>	VD+HC	FT wax	E-fuel -> FT -> wax -> VD+HC	[22 6]
eFuel – Lignoc.	Yes	7% <sup>a</sup>	VD+HC	FT wax	E-fuel -> FT -> wax -> VD+HC	[22 6]
Fermentation ATD	Yes	10%	Hydrogenation/ FCC	Oligomerization product	ATD and ATJ follow the same process, so we can refer to the available options for ATJ. Max CP also fixed according to viable commercial feedstock capacity.	[21 1]
Hydrotreatment oil	Yes	25% <sup>b</sup>	Direct	Raw oil from Energy crops,	Co-processing of RSO/AGO, HTL/VGO. Requires novel catalysts. Efficiency and product quality (e.g., cold flow	[24 6–

				waste cooking oil, animal fat	properties) of the co-processing still need to be improved to be competitive. Max CP is related to conventional catalysts efficiency loss due to sulfur leaching. The study tends to demonstrate that novel catalysts may enable to go further but did not go above 25%.	25 0]
Hydrotreatment Lignoc.	Not identified					
Transesterification	Not identified					

<sup>a</sup> Estimated based on GFT results.

<sup>b</sup> lab-scale results

## 6.2. ECONOMIC AND LCA ASSESSMENT FOR ESTERS & PARAFFINIC COMPONENTS

The objective of this section is to identify relevant life cycle and techno economic assessment (LCA and TEA) data for selected renewable diesel-like fuel pathways. Seven pathways were identified (see Table 22). The methodology was to combine several types of sources: open access reports, selected references of the database established in previous tasks and complementary scientific literature search targeted on the 7 pathways selected with IFPEN expertise.

For each reference the methodology consisted into identifying:

- The resource (lignocellulose / energy crops / animal fat / Waste cooking oil / CO<sub>2</sub>)
- The LCA methodology (functional unit, system boundaries, allocation)
- The LCA results: impact values and sources (process steps)
- The TEA results: CAPEX (capital expenditure) / OPEX (operational expenditure) / BEP (Breakeven Price) and sources of cost (process steps)

The following sections will review the available data in the literature for these fuel production pathways.

**Table 22** The seven selected renewable diesel production pathways

Ressource	Process
Lignocellulose	Fermentation ATD
Lignocellulose	Gasification - FT
Lignocellulose	E-fuel - Lignoc.
Lignocellulose	Hydrotreatment Lignoc.
WCO / Animal fat / Energy crop oil	Hydrotreatment oil
WCO / Animal fat / Energy crop oil	Transesterification
CO <sub>2</sub>	E-fuel - CO <sub>2</sub>

<sup>a</sup> Estimated based on GFT results.

<sup>b</sup> lab-scale results

VD : Vacuum distillation

HC : Hydrocracking

FCC: Fluid catalytic cracking

VGO : Vacuum gas oil

HTL: Hydrothermal liquefaction product

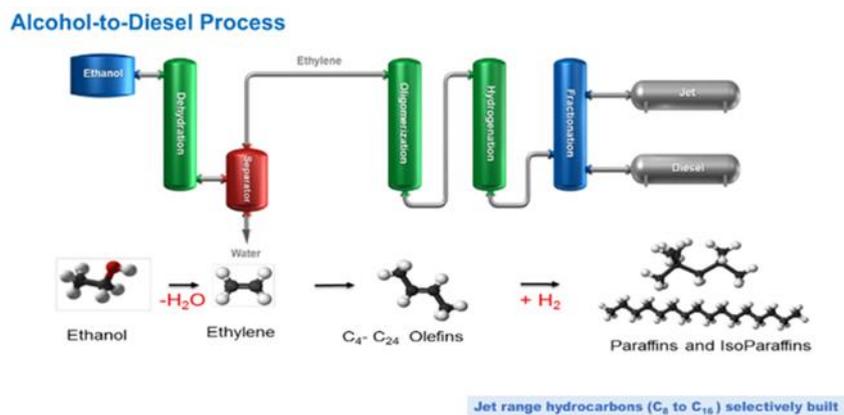
RSO: Rapeseel oil

AGO: Atmospheric gas oil

## 6.2.1. Alcohol-to-diesel (ATD)

### 6.2.1.1. Production process

The different stages of this process can be found in Figure 58. Fermentable sugars are obtained with hydrolysis. Then, iso-butanol and ethanol are produced thanks to the fermentation of sugars followed by dehydration, oligomerization, hydrogenation and fractionation. An advantage of this pathway is the resource flexibility. Bioethanol (or iso-butanol) is obtained at industrial scale from the fermentation of sugars, and it is the origin of such sugars that determines whether it is advanced bioethanol or not. The latter can be cereals (wheat, barley, corn and sorghum) and sugarcane but will then imply the use of edible feedstocks. In the advanced production, the sugar sources are cellulose and hemicellulose. These are found in feedstocks such as wheat straw, corn stover, wood, agricultural residues and municipal solid waste.



**Figure 58** Alcohol-to-diesel process (source: Alcohol-to-Diesel, LanzaTech, winterized diesel)

The ATD pathway relies on the same approach as Alcohol-to-jet (ATJ). There are very few or no references that deal directly with ATD. The identified references deal only with the ATJ process in which diesel is a co-product (or by-product) of Jet fuel. These results contribute to evaluate the distillation production which could potentially be used both for aviation or heavy duty applications. During the ATJ route, two types of by-products are generated. Firstly, lignin from the lignocellulosic biomass pretreatment. Secondly, the unsaturated diesel fraction produced during ethylene oligomerization. By-product refers to a component or a blend in an industrial or a biological process in addition to the main product. A by-product can be useful and marketable (as the case of diesel in ATJ process) or it can be considered as a waste. In this context, there are some issues to allocate impacts for LCA when there are several by-products. The environmental burden allocation is generally partitioned between products and by-products streams based on guidelines from ISO 14044:2006 guidelines and mass-, energy-, and economic-based methods.

### 6.2.1.2. LCA Review

Vela-García et al. (2021) [265] evaluate the efficiency of an integrated biorefinery model for producing biofuel as a Jet A1 blending component through the Alcohol-to-Jet (ATJ) pathway, using the lignocellulosic biomass of oilseed crops. This ATJ process involved cellulosic ethanol production through steam explosion hydrolysis, simultaneous saccharification and co-fermentation. The resulting life cycle GHG emissions was 75 gCO<sub>2</sub>-eq/MJ ATJ jet fuel. The emissions related to cultivation (11

gCO<sub>2</sub>eq/MJ ATJ jet fuel) were not considered. The environmental burden allocation was partitioned between products and by-products streams based on guidelines from ISO 14044:2006 guidelines and mass (flow)-, energy (LHV)-, and market (€)-based methods. The study shows that GHG emissions generated in the lignocellulose-to-ethanol biochemical conversion constitute 88% of the overall process, mainly attributed to the ethanol purification stage. The GHG emission value is high, but reductions can be estimated applying the RED II methodology for by-product displacement credit (remaining lignin / green diesel produced at the oligomerization stage). Indeed, the RED II grants GHG emissions credits when petroleum-derived CO<sub>2</sub> is replaced, i.e., one kg of green diesel produced at the oligomerization stage displaced 1 kg of petroleum-derived diesel equivalent.

A second reference from Klein et al. (2018) [266] aimed to calculate the impact of the ATJ process from a mix of first and second generation biomass (sugarcane: stalks and straw). The study gives an impact value of 24.8 g CO<sub>2</sub>.eq/MJ for the GHG emissions. The impact is concentrated in the biomass production phase of both sugarcane and vegetable oils, mainly due to fertilizers and diesel use. Since multiple products are obtained in each plant, it is necessary to split part of the environmental impacts to each one of them. In this study, an allocation procedure based on economic relationships was chosen. Ng, Farooq et Yang (2021) [267] presents different global warming impact values for different feedstocks (see Figure 59). There is substantial variation within the ATJ pathway, depending on feedstock, with crop-derived ATJ fuels having higher direct emissions than lignocellulosic feedstock-derived fuels. It can also be seen that utilising lignocellulosic biomass feedstock such as forest and agricultural residues and wood chips may result in lower GHG emissions. It is generally difficult to compare environmental impact such as GHG emissions as inconsistent assumptions are often being made across different case studies.

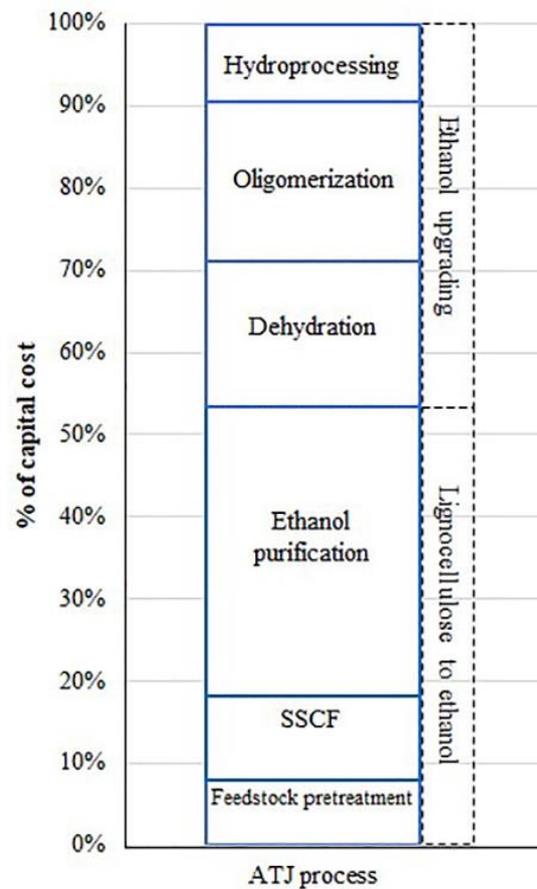
Feedstock	Production Capacity	Yield		Capital cost (CAPEX)	Operating cost (OPEX)	MFSP	Direct GHG emissions	ILUC emissions	Year of publication
	ML y <sup>-1</sup>	L t <sup>-1</sup> dry feed	GJ t <sup>-1</sup> dry feed	M\$ (\$ L <sup>-1</sup> )	M\$ y <sup>-1</sup> (\$ L <sup>-1</sup> )	\$ L <sup>-1</sup>	kg CO <sub>2e</sub> GJ <sup>-1</sup>	kg CO <sub>2e</sub> GJ <sup>-1</sup>	
<b>Alcohol-to-jet (ATJ)</b>									
Note: (a) ethanol-to-jet; (b) butanol-to-jet; (c) methanol-to-jet									
Forest residues <sup>(a)</sup>	294	419.9	5.98	56.1 (0.19)	51.4 (0.17)	2.08	91.0	–	2011
Wood chips <sup>(a)</sup>	98.6	136	–	479	85.2 (0.86)	0.75	1.6	–	2017
Wood chips <sup>(a)</sup>	90.2	125	–	500	82.4 (0.91)	1.11	10.0	–	2017
Corn grain <sup>(a)</sup>	230	432	–	(1.07)	(0.79)	1.86	65.0	14.0	2019
Sugarcane <sup>(a)</sup>	230	580	–	0.79	(1.07)	1.86	48.1	17.0	2019
Agricultural residues <sup>(a)</sup>	230	321	–	2.20	0.51	2.71	14.9	–	2019
Energy crops <sup>(a)</sup>	230	321	–	2.20	0.57	2.77	–	–	2019
Corn stover <sup>(b)</sup>	168	200	1.51	198 (1.21)	91.6 (0.55)	3.08	32.0	–	2013
Wood chips <sup>(b)</sup>	88.6	122	–	736	99.5 (1.12)	1.08	3.2	–	2017
Wood chips <sup>(b)</sup>	144	199	–	431	110.8 (0.77)	0.81	7.4	–	2017
Woody residues <sup>(c)</sup>	455	651	6.86	210 (0.46)	17.4 (0.04)	1.22	40.0	–	2011

**Figure 59** Techno-economic performance and emissions of various ATJ production routes [267]

Doliente et al. (2020) [268] obtain a value of 21 g CO<sub>2</sub>.eq/MJ for the production of ATJ from corn stover, which corresponds to a reduction in CO<sub>2</sub> emissions of 75% compared to the fossil reference (87 gCO<sub>2</sub>.eq/MJ).

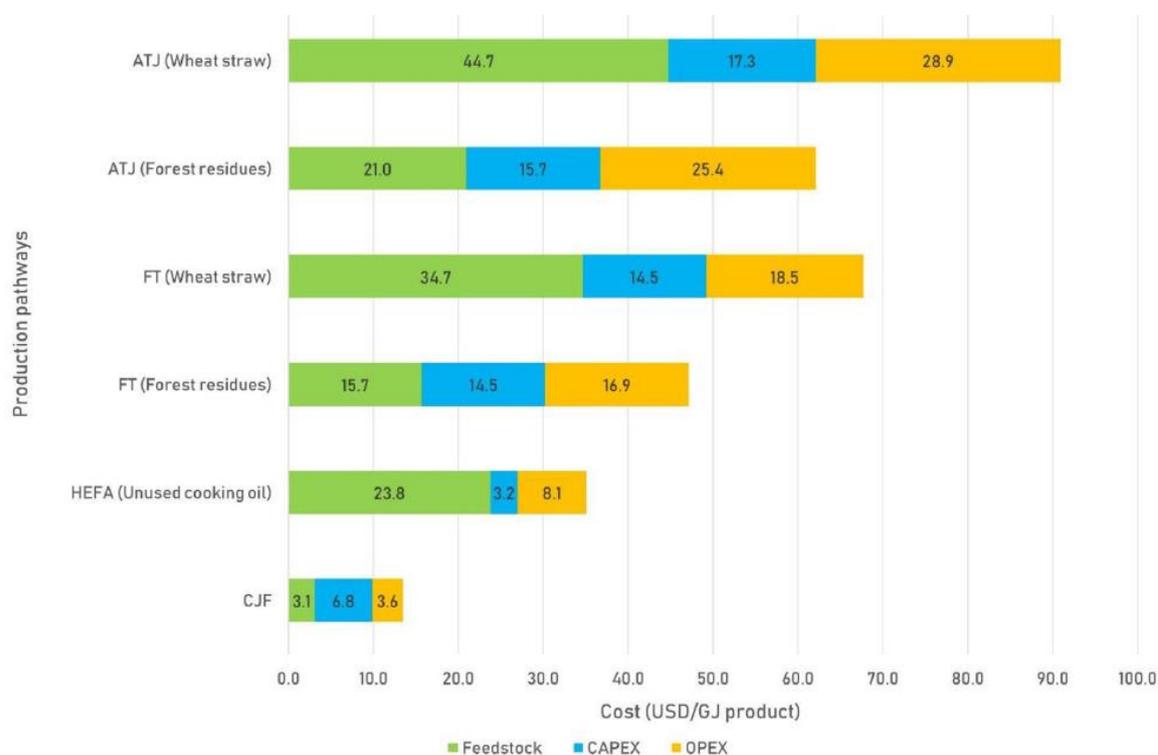
### 6.2.1.3. TEA Review

Regarding the TEA aspects, Vela-García et al. (2021) [265] show that the main installed equipment costs for the ATJ process are related to ethanol purification stage (30%) and oligomerization stage (20%). The lignocellulose to ethanol step is identified as more capital expenditure (CAPEX) intensive for the ATJ process, accounting for over 50% (see Figure 60). Among the operating costs, the feedstock is the most predominant one.



**Figure 60** Capital expenditure for the different stages of the Alcohol to fuel process [265]

Doliente et al. (2020) [268] shows the distribution between CAPEX, OPEX and feedstock for the production of ATJ from two types of lignocellulosic resources: wheat straw and forest residues (Figure 61). There is a difference in the feedstock cost with a lower price for forest residues compared to wheat straw. This contributes to highlight the resource impact on the production cost.



**Figure 61** CAPEX, OPEX and feedstock for the production of ATJ [268]

Klein et al. (2018) [266] report that ATJ involves the use of ethanol distillery, a plant which has a significantly higher capital investment in view of the equipment employed in sugarcane lignocellulose materials processing into advanced ethanol. Consequently, it highlights the fact that employing ATJ technology in sugarcane biorefineries did not present satisfactory economic results.

#### Results summary ATJ

The different global warming impacts and breakeven price values for the different resources can be found in Table 23.

**Table 23.** Global warming impact and breakeven price values for ATJ energy path

Ressource	Impact GWP (g CO <sub>2</sub> -eq/MJ)	BEP (\$/L)	Reference
Wood chips	10	1.11	Ng, Farooq et Yang (2021) [267]
Corn stover	21		Doliente et al. (2020) [268]
Lignocellulosic biomass from oleaginous crop	75	1.56	Vela-García (2021) [265]
Agricultural residues	14.9	2.71	Greet (2018)
Sugarcane (stalks and straw)	24.8	1.17	Klein et al. (2018) [266]
Energy crops	20.3	2.77	Greet (2018) [269]
Sugarcane	48.1	1.86	Greet (2018) [269]
Sugarcane (stalks and straw)	20.7	0.87	Klein et al. (2018) [266]
Corn grain	65	1,86	Greet (2018) [269]

## 6.2.2. Gasification and FT

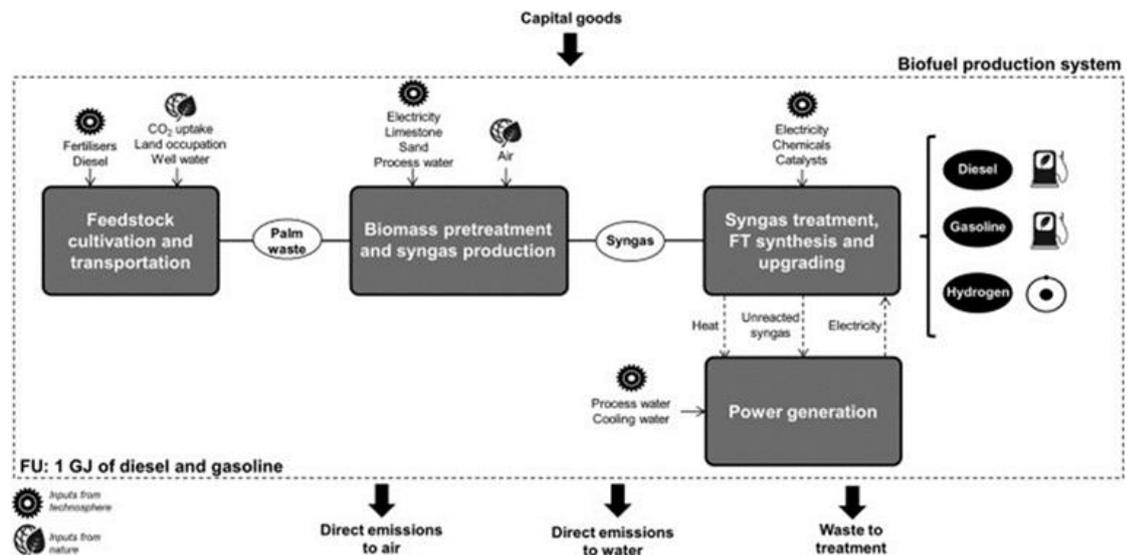
### 6.2.2.1. Production process

The second pathway considered in this study is the gasification followed by the FT process. This pathway has four main stages:

- Pre-treatment
- Gasification (Converts solid lignocellulose into gaseous components through the reaction with a gasification agent)
- Gas cleaning (Raw biomass gasification product gas includes impurities above the acceptable range are problematic for FT synthesis processes, amongst other)
- FT / Upgrading step

### 6.2.2.2. LCA review

Ben Hnich et al. (2021)[270] carried out a life cycle sustainability assessment of synthetic fuels from date palm waste. In this study, the ReCiPe 2016 midpoint method with hierarchist perspective was used as the impact assessment method. As for other methods, this approach relies on life cycle inventories. The flows inventories are translated into CO<sub>2</sub> or CO<sub>2</sub> equivalent impacts. This enables to characterise the potential life-cycle environmental impacts of 1 GJ of synthetic diesel and gasoline (Figure 62). Feedstock cultivation involves two main products: dates and palm waste. According to the production rates and the economic values of the products, an economic allocation was used. During the synthetic biofuel production, there are three products (diesel, gasoline and hydrogen). An energy allocation is used. Hence, 95% of the burdens were allocated to diesel and gasoline (as a whole) and 5% to hydrogen. The potential environmental impacts were concluded to be mainly associated to direct emissions (closely linked to syngas production and cleaning) and the system's demand for electricity and oxygen in this study. The impact values can be found in Table 24. Among these values, the global warming potential is 7.65 g CO<sub>2</sub>-eq/MJ.



**Figure 62** Gasification + FT process from palm waste [270]

**Table 24.** Impact values (per MJ of fuel) for Gasification + FT process from palm waste [270]

Indicator	Value	Units
Global warming	7.65	kg CO <sub>2</sub> eq
Fine particulate matter formation	0.25	kg PM <sub>2.5</sub> eq
Terrestrial acidification	0.70	kg SO <sub>2</sub> eq
Freshwater eutrophication	$1.21 \cdot 10^{-2}$	kg P eq
Fossil resource scarcity	28.58	kg oil eq

Ben Hnich et al. (2021)[271] present other results for this pathway. For this study, the feedstock is a residual lignocellulosic fraction of conventional sugarcane (CS) (bagasse and straw), together with eucalyptus and energy-cane as emerging lignocellulosic biomass options. Energy-cane (EC) is a variety of cane with higher fiber content and higher potential yields than CS. Therefore, the use of EC can be considered in substitution to CS since the focus of the process is the conversion of lignocellulosic materials to advanced liquid fuels. Eucalyptus is also an interesting biomass to complement both CS and EC, facilitating the plant operation during off-season. Since energy allocation is employed, GHG emissions from the production stages, i.e., discounting distribution and use emissions, are equal for all products in the same scenario. The value for global warming potential is 10 g CO<sub>2</sub>-eq/MJ. Klein et al. (2018) finds a similar value of 9.4 g CO<sub>2</sub>-eq/MJ fuel for the same type of feedstock but using an economic allocation.

### 6.2.2.3. TEA review

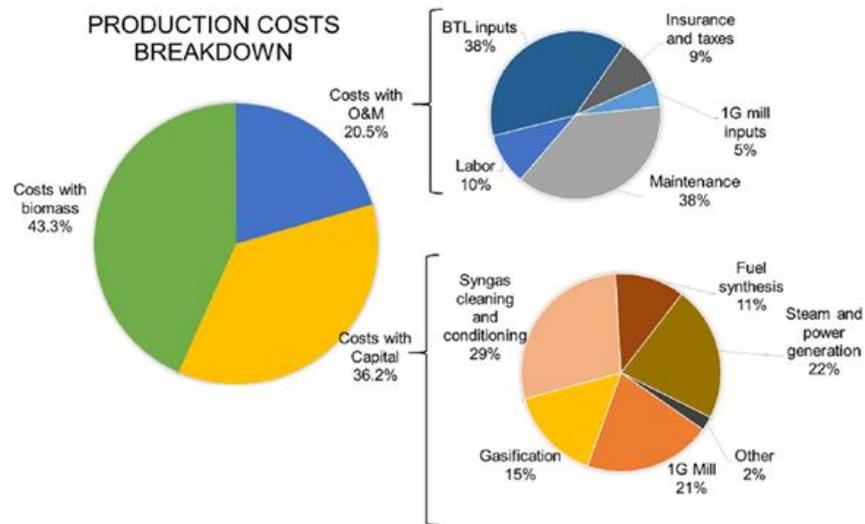
Ben Hnich et al. (2021) [270] report in their study that electricity and oxygen consumption and the investment in the plant's power section arose as critical economic aspects when it comes to synthetic fuels from date palm waste. The CAPEX, OPEX and BEP for the production of synthetic fuel from a residual lignocellulosic fraction of conventional sugarcane (CS) (bagasse and straw) are listed Table 25. Values for eucalyptus and energy-cane (1G2G-EC) as emerging

lignocellulosic biomass options are also reported (Bressanin et al. 2020) [271]. The BEP that enable the venture are between 30-32% higher than fossil fuel selling prices in the scenario 1G2G-EC. For 1G2G-CS, BEP are between 10-12% higher than the fossil ones, contributing to its better economic performance. OPEX decreases in scenario 1G2G-EC because EC production costs are lower than CS. Major capital costs contribution is attributed to 2G thermochemical processes since gasification plants are related to a higher building cost. The EC scenario requires more CAPEX due to the higher amount of lignocellulosic materials processed and the capacity increase in the steam and power generation areas. The latter is proved to be more impactful on capital costs than the increase of syngas cleaning and fuel synthesis from scenario 1G2G-CS.

**Table 25** CAPEX, OPEX and BEP values for the production of synthetic fuel from lignocellulosic biomass [271]. Assuming a density of 832.5 kg/m<sup>3</sup> and a lower heating value of 42600 kJ/kg, the correspond MSP for diesel product would be between 743 and 874 \$/toe according to this study.

Parameter	1G-CC	1G2G-CC	1G2G-EC
CAPEX (million US\$)	408.77	1096.58	1177.57
Fixed capital investment 1G (million US\$)	371.60	132.45	134.28
Fixed capital investment 2G (million US\$)	-	864.45	936.24
Working capital (million US\$)	37.16	99.69	107.05
OPEX (million US\$ per year)	118.03	231.26	207.28
Feedstock	98.18	136.59	115.76
Other inputs	3.33	51.66	45.67
Employee costs	2.77	6.13	6.24
Maintenance	11.15	29.51	32.12
Insurance and others	2.60	6.98	7.49
Revenue (million US\$ per year)	221.90	387.65	323.95
Electricity	45.46	17.33	72.30
Hydrous ethanol	171.41	171.41	111.68
Gasoline	-	74.27	53.55
Jet fuel	-	69.61	50.19
Diesel	-	40.01	25.81
Carbon credits	5.03	15.02	10.40
Minimum selling price			
Electricity (US\$/MWh)	51.62	67.61	79.46
Hydrous ethanol (US\$/L)	0.41	0.53	0.63
Gasoline (US\$/L)	-	0.57	0.67
Jet fuel (US\$/L)	-	0.67	0.79
Diesel (US\$/L)	-	0.63	0.74

Real Guimarães et al. (2021) [272] provides the distribution of production costs in the case of a BtL (Biomass-to-Liquid) plant processing sugarcane bagasse and straw integrated into a first-generation sugarcane ethanol distillery (Figure 63). The costs related to biomass production/transport and capital investment are the largest components of the production costs. Among the capital cost, the syngas cleaning and conditioning is the most expensive step.



**Figure 63** Production costs in the case of a BtL (Biomass-to-Liquid) plant [272]

#### Results summary ATJ

The different global warming impacts and breakeven price values for the different resources can be found in Table 26.

**Table 26** Global warming impact and breakeven price (BEP) values for Gasification - FT

Ressource	Impact GWP (g CO <sub>2</sub> -eq/MJ)	BEP (\$/L)	Reference
Date palm waste	7.65	0.56	Ben Hnich et al. (2021) [270]
sugarcane (bagasse and straw) + eucalyptus	10	0.63	Bressanin et al. (2020) [271]
sugarcane (energy-cane) + eucalyptus	10	0.74	Bressanin et al. (2020) [271]
sugarcane (bagasse and straw) + eucalyptus	9.4		Klein et al. (2018) [266]
Waste wood	9.7		JRC report [9]
Farmed	14		[4]
Black liquor	5.3		[4]

### 6.2.3. E-fuel

#### 6.2.3.1. Production process

E-fuels are synthetic fuels resulting from the combination of ‘green or e-hydrogen’ produced by electrolysis of water with renewable electricity and CO<sub>2</sub> captured either from a concentrated source (e.g. flue gases from an industrial site) or from air (via direct air capture, DAC). The catalytic conversion of CO<sub>2</sub> to CO via a reverse water gas shift (RWGS) reaction followed by well-established synthesis gas conversion technologies provides a potential approach to convert CO<sub>2</sub> to valuable chemicals and fuels. The direct pathway (also called PtL: Power-to-Liquid) of the production of E-fuel can be found Figure 64. There is also an indirect pathway (also

called PBtL: Power-Biomass-to-Liquid) where the carbon is obtained from lignocellulosic biomass gasification.

### 6.2.3.2. LCA Review

A recent paper (Isaacs et al. 2021 [273]) compares the environmental performance of these diesel production pathways in the United States. Regarding the Power and biomass-to-liquid pathway, corn stover, switchgrass, and willow were chosen as feedstocks to be representative of major lignocellulosic biomass types (PBtL). The diagram of the both pathways is provided Figure 64.

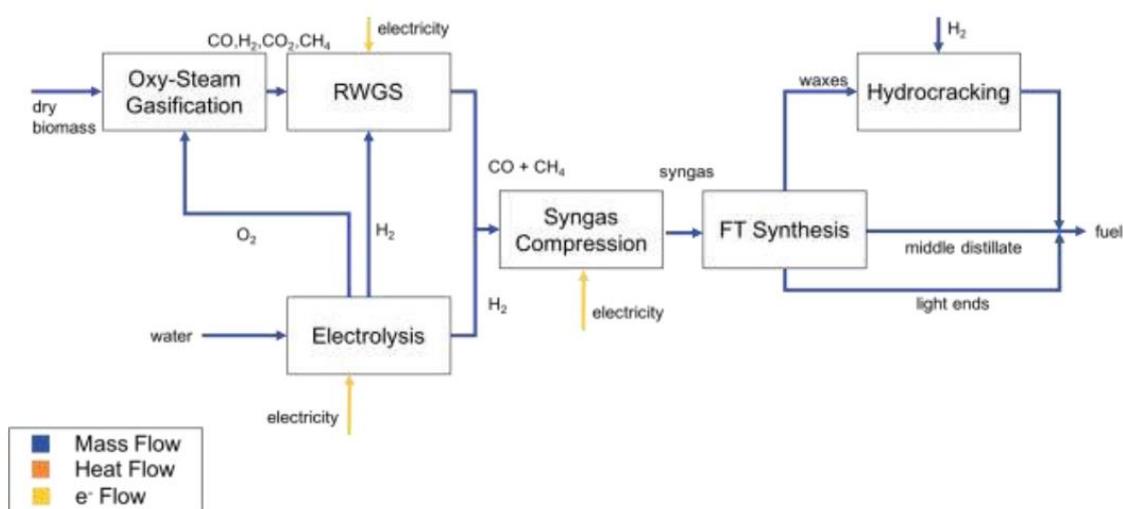


Figure S2. Power and Biomass-to-Liquid (PBtL) production pathway. Where FT Synthesis is the FT Synthesis unit, RWGS is the Reverse Water Gas Shift unit, and Gasification is assumed to use an Oxy-Steam gasification process unit.

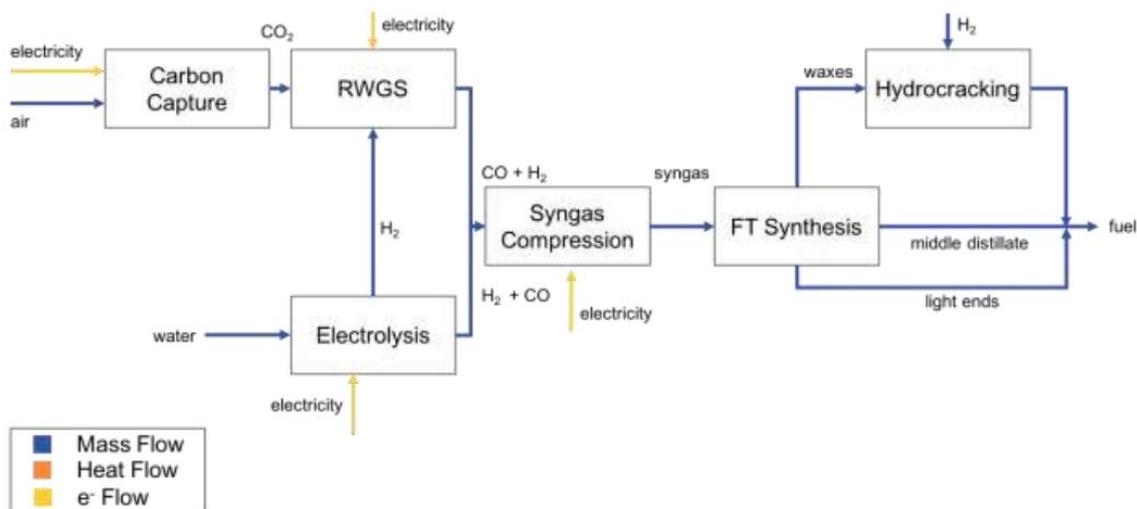
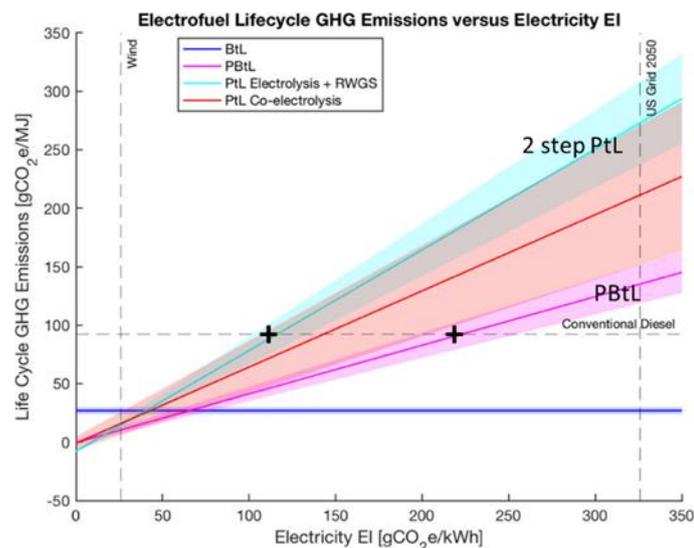


Figure S3. Two-Step Power-to-Liquid (PtL) production pathway using RWGS and electrolysis. Where FT Synthesis is the FT Synthesis unit, RWGS is the Reverse Water Gas Shift unit and the carbon capture is done with a Direct-Air Capture system.

Figure 64 Diagrams of the processes PtL and PBtL[273]



**Figure 65** LCA results as a function of the input power [273]

The study shows that life cycle GHG emissions of electrofuel pathways are a linear function of input power, with pathways that use more electricity being more sensitive to this value (see Figure 65). PtL pathways using low energy have the greatest potential for emission reductions relative to petroleum-derived fuels. For the PTL, the slope is higher than for the PBtL because this process uses more electricity. An energy allocation method is used to allocate the total plant life cycle emissions among each product.

**Table 27.** LCA and BEP results for PBtL and PtL pathways [273]. MSP refers here to the Breakeven price.

pathway	average US grid electricity in 2016		dedicated wind electricity	
	LCA results (gCO <sub>2</sub> e/MJ)	MSP (\$/L)	LCA results (gCO <sub>2</sub> e/MJ)	MSP (\$/L)
diesel	92	0.80	92	0.80
BtL	27	0.77	26	0.82
PBtL	187	1.89	4	1.64
PtL electrolysis + RWGS	380	3.39	2	2.89
PtL CoElec	292	3.40	6	3.06

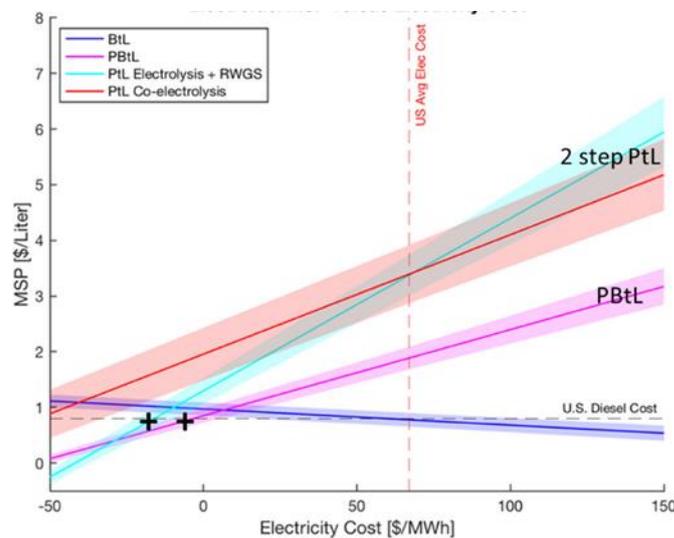
A value of 4 gCO<sub>2</sub>-eq/MJ is obtained when PBtL is produced from dedicated wind electricity while a value of 187 g CO<sub>2</sub>-eq/MJ is obtained when PBtL is produced from average US grid electricity (2016) (Table 27). The average US grid electricity in 2016 is assumed to have an electricity environmental impact of 450 gCO<sub>2</sub>-eq/kWh and dedicated wind power is assumed to emit 11 gCO<sub>2</sub>-eq/kWh. GHG emissions and BEP of electrofuel pathways are highly sensitive to the impact and cost (respectively) of hydrogen and so electricity generation.

Another study (Choe, Lee et Lim 2022 [274]) confirms previous conclusions by showing that GHG emissions mainly depend on the production of hydrogen by electrolysis.

To conclude, in the case of e-fuel from lignocellulose, the CO<sub>2</sub> cost for e-fuel production is almost equivalent to the one for hydrogen production. The CO<sub>2</sub> cost of hydrogen depends on how it is produced. Moreover, the CO<sub>2</sub> cost is impacted by the electricity environmental impact if it is produced by electrolysis.

### 6.2.3.3. TEA Review

Isaacs et al. (2021) [273] show that the BEP of electrofuel pathways is highly sensitive to the cost of electricity generation. The BEP of the fuel has a linear relationship with the cost of input power. It is also depending on the electrofuel pathway. For the PtL, the slope is higher than for the PBtL because this process uses more electricity. Indeed, the capture of CO<sub>2</sub> with PtL is related to a high energy demand (Figure 66).



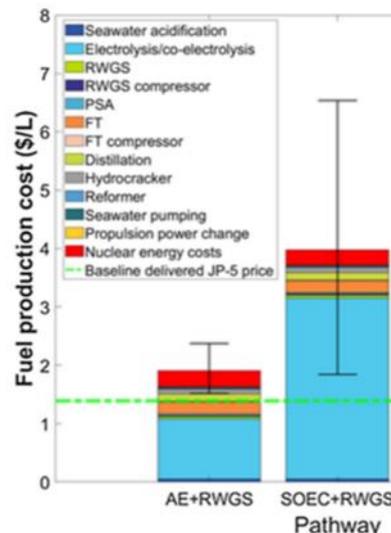
**Figure 66** BEP of electrofuel and PBtL pathways as a function of electricity cost [273]<sup>5</sup>.MSP refers here to the Breakeven price.

The cost range of PBtL fuel is 1.64-1.89 \$/L when using electricity from dedicated wind power or from the average US while the cost range of PtL fuel is 2.89-3.39 \$/L.

Choe, Lee et Lim (2022) [274] report that hydrogen production cost was the main parameter accounting for more than 60% of diesel production cost for every case. In addition, FT reactor in capital cost and raw material cost (i.e. CO<sub>2</sub> cost) in operating cost were the next key economic parameters for each case.

Comidy, Staples et Barrett (2019) [275] compare two technologies for electrolysis: Alkaline and SOEC for the production of Jet fuel. This study shows that electrolysis cost was accounting for more than 60% of fuel production (in the case of Alkaline for electrolysis). The lowest cost is obtained with Alkaline technology rather than SOEC technology (see Figure 67). There is no real difference in terms of GHG emissions between both technologies.

<sup>5</sup> Note that in this study, BTL's BEP decreases with electricity cost because higher electricity prices generate more income in BtL facilities from the sale of co-produced electricity, thereby reducing the BEP of fuel



**Figure 67** Fuel costs for Alkaline and SOEC technologies [275]

#### 6.2.4. Hydrotreatment

##### 6.2.4.1. Production process

Triglycerides hydrotreatment is a process with continuous development into industrialisation - Integrated or stand alone. This process can be applied to multiple resources (Waste cooking oil/Animal fat/Energy crops). Triglycerides hydrotreatment can also be applied to other resources. The process itself is well known and has been described section 6.1.4.

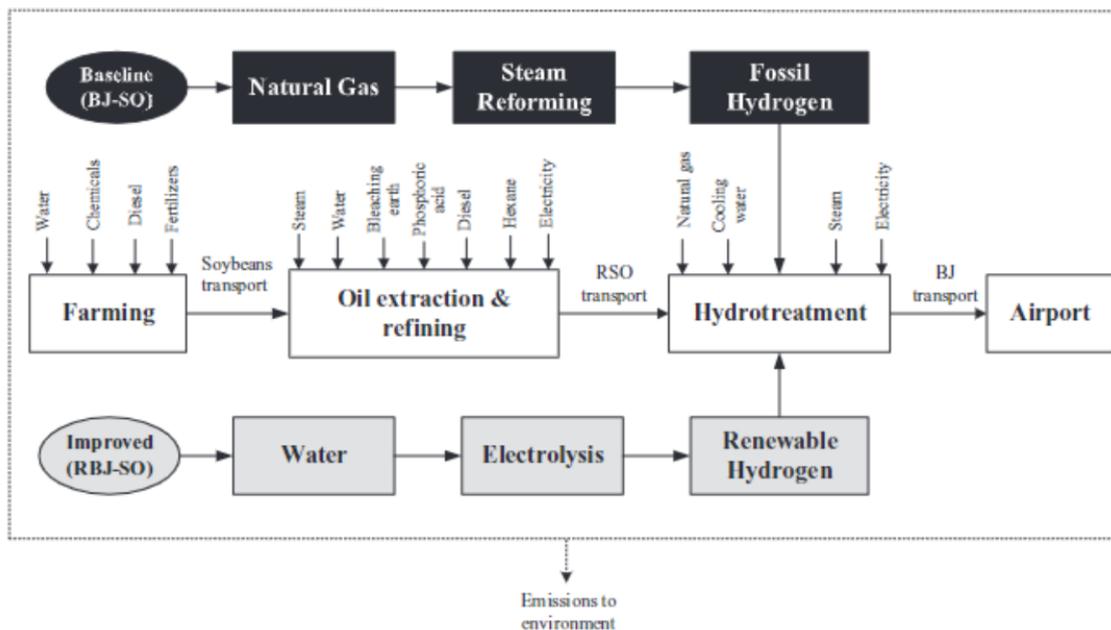
In addition, it should be highlighted that hydrotreatment is also considered for transforming lignocellulose into oil by acid hydrolysis. However such an approach was not identified as mature and no LCA or TEA data could be found in the scientific literature.

The LCA / TEA review focuses on the hydrotreatment pathway from WCO, animal fat and energy crop.

##### 6.2.4.2. LCA Review

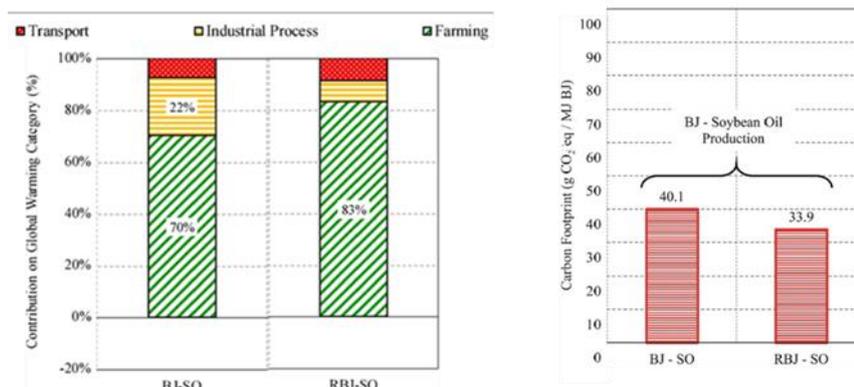
Vela-García et al. (2021) [276] evaluate HEFA (Hydroprocessed Esters and Fatty Acids) pathway with tricerides of kernel oil & fatty acid distillates as feedstock. The study gives an estimated net GHG emissions value of 8 gCO<sub>2</sub>.eq/MJ for the HEFA and demonstrates an improvement relative to palm oil and jatropha oil. Based on the EU directive on promoting energy use from renewable sources, the environmental burdens of the feedstocks are zero because they are waste (triglycerides of kernel oil & fatty acid distillates). The GHG footprint of the HEFA process is significantly influenced by the hydrogen source and its consumption during the decarboxylation and hydroprocessing stages. Lower net GHG emissions can be achieved by replacing the steam methane reforming of natural gas with its biomass-derived counterpart (off-gas) to produce hydrogen.

Vásquez et al. (2019) [277] evaluate two scenarios for the hydrogen production to discuss its impact on biokerosene production (see Figure 68): one reference case with the use of fossil hydrogen and one enhanced case with explored renewable alternatives for hydrogen production, such as water electrolysis.



**Figure 68** Baseline and improved conversion scenarios for hydrotreatment pathway from soybean “SO” for biojet production scenarios. “BJ” or “RBJ” refer to the baseline pathway and the improved one respectively [277]

The functional unit was set as 1.0 MJ of energy produced. Co-products were handled by energy allocation. The stages with the highest share of GHG emissions in baseline scenarios are farming and industrial process. In case of diesel production from waste cooking oil or animal fat, the GHG footprint of the HEFA process is mainly impacted by the hydrogen source. Indeed, the CO<sub>2</sub> cost for farming is not considered (Farming accounts for an emission of 28.2 g CO<sub>2</sub>-eq /MJ). A reduction of the GHG emissions associated with biokerosene conversion was accomplished by substituting hydrogen from fossil sources (natural gas) for renewable alternatives (water electrolysis) in the improved scenario (see Figure 69).



**Figure 69** Comparative global warming results for all production scenarios [277]. BJ-SO refers to the baseline scenario for biojet production from soybean and RBJ-SO to the improved scenario.

Soam et Hillman (2019) [278] evaluate the Life cycle GHG emissions (gCO<sub>2</sub>-eq./MJ) of HVO from different by-products/residues (see Table 28). The residual feedstocks such as PFAD (Palm Fatty Acid Distillate), tallow and tall oil have lower life cycle emissions since the system boundaries start from the collection of feedstocks and exclude all the environmental burdens from the cultivation phase. In general, feedstock is considered residual with JRC values. In case of diesel production from waste cooking oil / animal fat hydrotreatment, the GHG footprint of the HEFA process is significantly impacted by the hydrogen source and its consumption during the decarboxylation and hydroprocessing stages. There is no CO<sub>2</sub> cost for cultivation in this case.

**Table 28.** Life cycle GHG emissions (gCO<sub>2</sub>-eq./MJ) of HVO from different by-products/residues [278]

Feedstock	Pre-processing	Feedstock transport	HVO production	Distribution and use	Total
PFAD <sup>a</sup>	1	3	10	1	15
Tallow <sup>c</sup>	5	1	9	1	16
Tall oil <sup>d</sup>	0	1	5	1	7

a

Economic allocation (Johnson, 2017).

c

Mass allocation (Nikander, 2008).

The different global warming impact values for the different resources can be found in Table 29.

**Table 29.** Global warming impact values for hydrotreatment pathway

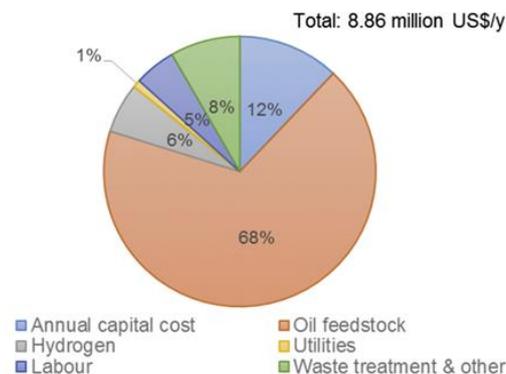
	Impact GWP (g CO <sub>2</sub> -eq/MJ)	Reference
WCO/ Animal fat /Energy crop	kernel oil & fatty acid distillates	Vela-Garcia et al. 2021 [276]
	PFAD (Palm Fatty Acid Distillate)	Soam et Hillman 2019 [278]
	Tallow	Soam et Hillman 2019 [278]
	Tail oil	Soam et Hillman 2019 [278]
	WCO	JEC report
vegetable oils	Palm oil (JRC)	JEC report
	Palm oil	
	Rapeseed oil	
	Soybean oil	Vásquez et al. 2019 [277]

#### 6.2.4.3. TEA Review

Vela-García et al. (2021) [276] found that the decarboxylation stage (45%) and hydrolysis stage (40%) are the primary installed equipment costs for the HEFA process. This study reports that the BEP (1.01 €/kg) is relatively lower because the process requires a limited amount of catalyst.

Martinez-Hernandez et al. (2019) [279] try to demonstrate that a 10 million L/y HVO plant can be profitable if minimum HVO price is 1 US\$/L. This papers explains that HVO could be competitive with current fossil diesel prices. This study shows

also that vegetable oil feedstock (palm oil) is one of the major cost component of producing renewable diesel (Figure 70).



**Figure 70** Major cost components of producing renewable diesel with hydrotreatment process [276]

## 6.2.5. Transesterification

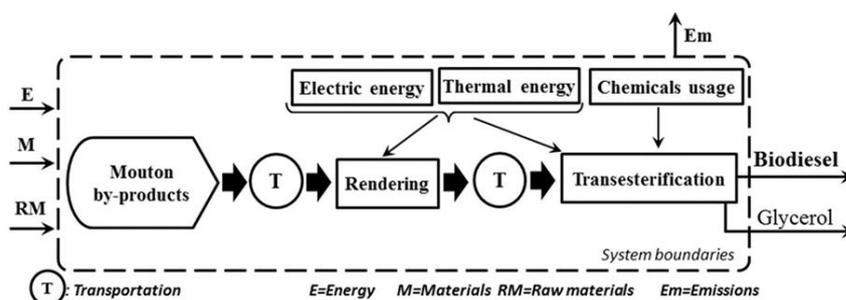
### 6.2.5.1. Production process

As compared to other methods, transesterification is a well-known, direct and simple conversion process with low temperature and pressure, short reaction time, and high conversion yield. Most recent works focus on flexibility of transesterification to wider resources in order to reduce cost and to expand from vegetable oil to waste cooking oil and animal fat. This imposes pre-treatment stages to ensure oil quality at the entry of transesterification stage.

### 6.2.5.2. LCA Review

LCA and LCC (life cycle cost) were conducted for typical biodiesel production from WCO in China (Zhao et al. 2021) [280] (see Figure 71). Transesterification is the largest contributor (54%-80%) to most of the environmental indicators. For this study, the Cradle-to-gate climate change impact of the WCO-based biodiesel is estimated to be 1383 kg CO<sub>2</sub>-eq per ton (or 37.38 g CO<sub>2</sub>-eq/MJ), of which 68% is derived from the transesterification stage. The transesterification of WCO requires high energy use and material input for the reaction and refining processes, resulting in substantial GHG emissions. The cradle-to-gate climate change impact of WCO-based biodiesel is 160% higher than that of fossil diesel (527 kg CO<sub>2</sub>-eq per ton). However, when considering the fuel combustion, the situation is reversed since the combustion of WCO-based biodiesel is considered to be carbon neutral from an LCA perspective (biocredit).

An exergo-environmental life cycle assessment of biodiesel production from mutton tallow (animal fat) transesterification was carried out (Faleh et al. 2018 [281]).



**Figure 71** Biodiesel production from mutton tallow transesterification [281]

This study shows that chemical products are a major contributor to the environmental burdens of the biodiesel system. More particularly, the methanol use is the greatest contributor to the environmental impact of chemical use. The thermal energy requirement comes in second position in terms of environmental influence. This involves the thermal energy for rendering and transesterification. For the global warming potential indicator, the value obtained is 17.81 gCO<sub>2</sub>-eq/MJ of the biodiesel produced (see Table 30). Thermal energy used accounts for approximately 63%. This is mostly due to the large amount of heat from fuel combustion consumed during distillation, followed by chemical uses (20%) and electricity consumption (10%). The mass allocation method was used to distribute the environmental burdens between the products biodiesel and glycerol.

**Table 30.** GWP results for transesterification from mutton talow [281]

	Total	Rendering	Transesterification	Transport
GWP (g CO <sub>2</sub> eq / MJ)	17.81	8.24	8.42	1.15

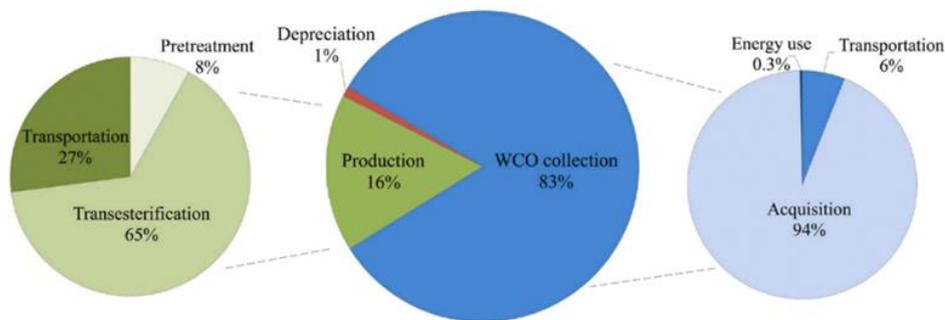
The different global warming impact values for the different resources can be found in Table 31.

**Table 31** Global warming impact values for transesterification pathway

			Impact GWP (g CO <sub>2</sub> -eq/MJ)	Reference
WCO/ Animal fat /Energy crop	WCO (China)	WCO (China)	37.38	Zhao et al. 2021 [280]
		mutton tallow	17.81	Faleh et al. 2018 [281]
		tallow oil (JRC)	13.8	JRC report
		WCO (JRC)	8.3	JRC report
vegetable oils	Rapeesed oil (JRC)	50	JRC report	
	Soybean oil (JRC)	55.9	JRC report	
	Palm oil (JRC)	51	JRC report	

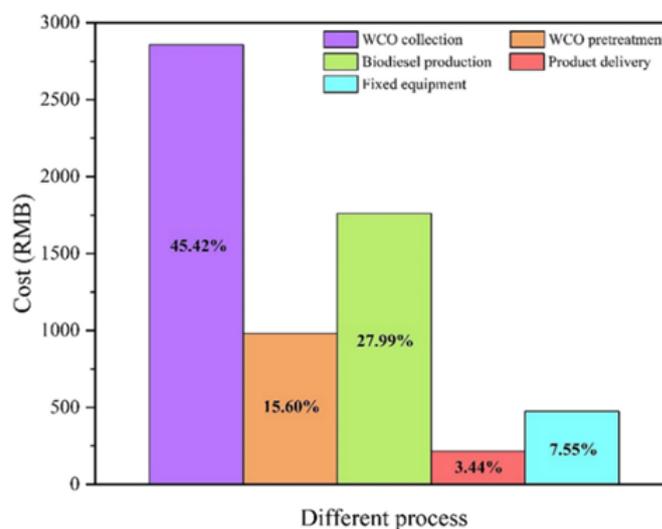
#### 6.2.5.3. TEA Review

Zhao et al. (2021) [280] explain that the significant cost of WCO collection is mainly driven by the high purchasing price and that the biodiesel production cost is dominated by the transesterification stage (Figure 72). Compared to WCO-based biodiesel, the total cost of fossil diesel is lower.



**Figure 72** Costs for diesel production for transesterification from WCO [280]

Liu et al. (2021) [282] present economic evaluation and production process simulation of biodiesel production from waste cooking oil. Compared to the cost of diesel, WCO biodiesel is about 65 % higher. In addition to feedstock oil, the costs of WCO biodiesel are influenced by the biodiesel production process, which is almost 28% of the overall prices (Figure 73). In this process, the catalyst has the greatest impact. The preparation process and cost of different catalysts are very different. At present, NaOH and CaO are the most commonly used catalysts in biodiesel production.



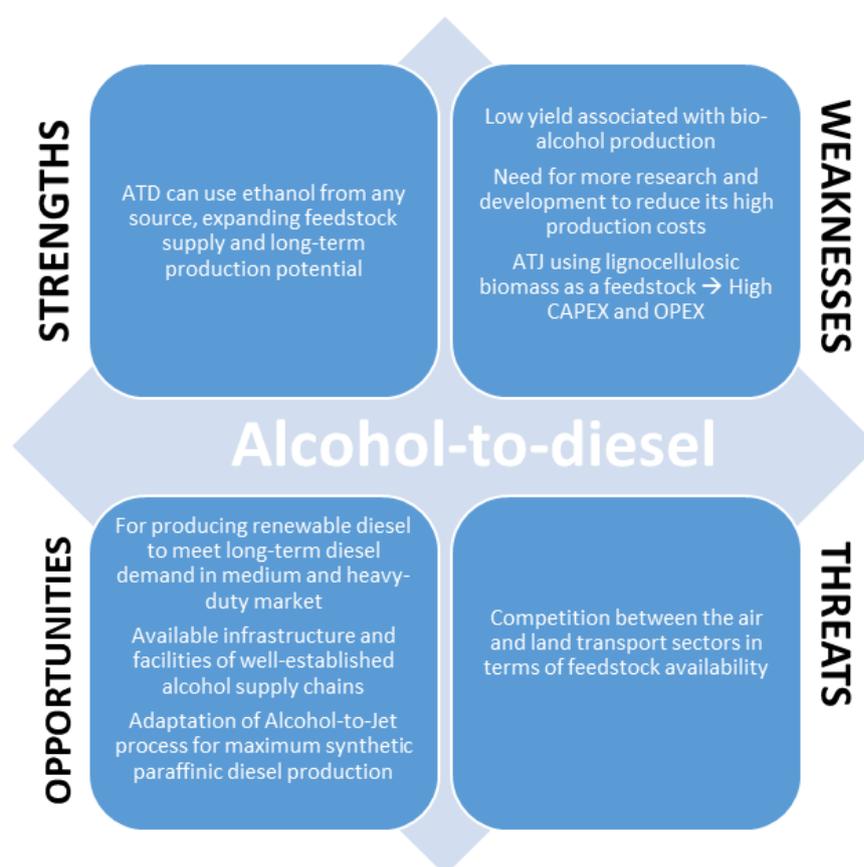
**Figure 73** Economic evaluation of biodiesel production from waste cooking oil / RMB: Chinese currency [282]

Lee et al. (2020) [283] confirms that methanol and WCO costs are highly sensitive to determine a biodiesel unit production cost. According to this study, profitability analysis shows that the suggested process can economically be applicable even though a biodiesel selling price was down to 1.55 \$/kg.

### 6.2.6. Summary

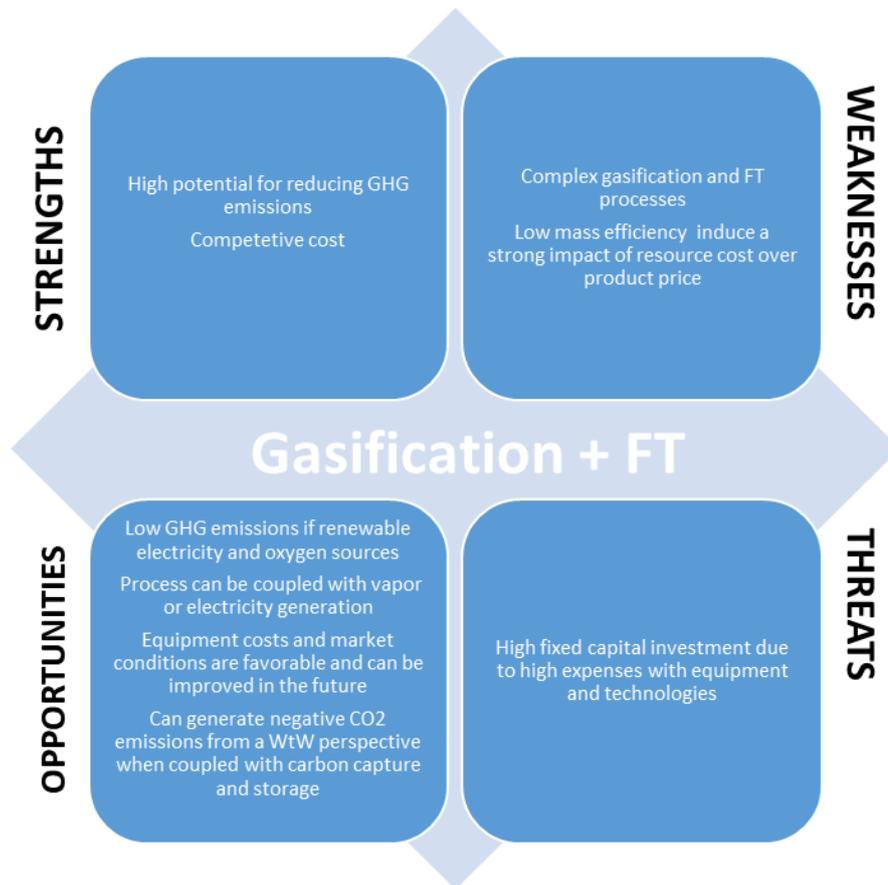
To summarize the main findings of this section, a SWOT (Strength, Weaknesses, Opportunities, Threats) analysis is proposed for each fuel production path.

Figure 74 shows the SWOT for alcohol-to-diesel pathway. This pathway can rely on available infrastructures and facilities with well-established alcohol supply chains. However, one must pay attention to the competition with other transport sectors including aviation. Indeed, the literature review highlights that most of the scientific communication focus on sustainable jet fuel production instead of diesel fuel.



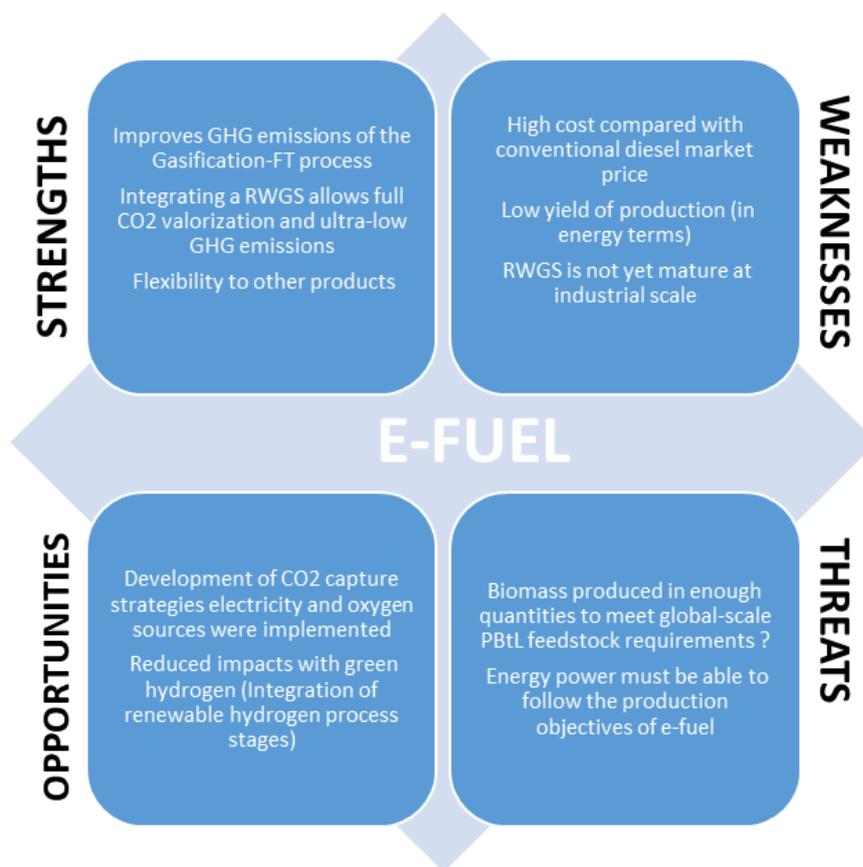
**Figure 74** SWOT for Alcohol-to-Diesel production path

Figure 75 shows the SWOT for gasification/Fischer-Tropsch pathway. This pathway is related to a high fixed capital investment but has a high potential for reducing GHG emissions. However, equipment costs and market conditions are favorable and could be improved in the future.



**Figure 75** SWOT for Gasification + FT production path

Figure 76 shows the SWOT for E-fuel pathway. This pathway can improve GHG emissions of the Gasification-FT process including a RWGS step. However, this is related to a high cost compared with conventional diesel fuel market price. For this pathway the impact and the cost depend directly on the hydrogen production. The production of renewable hydrogen availability and the carbon capture are key parameters for this energy pathway.



**Figure 76** SWOT for E-fuel production path

Figure 77 shows the SWOT for hydrotreatment pathway. GHG emissions of this process is partially driven by the hydrogen source. Also the feedstock availability could be an issue for this pathway. Finally, there was no scientific reference identified to discuss the characteristics of hydrotreatment process from lignocellulosic biomass.

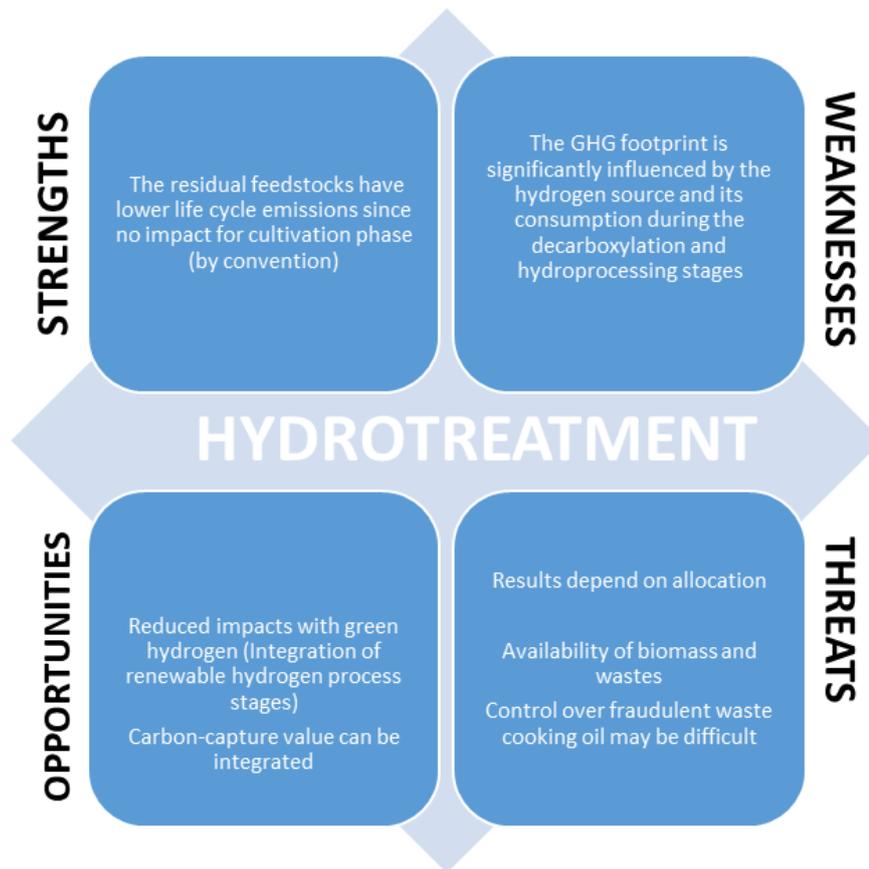


Figure 77 SWOT for Hydrotreatment production path

Figure 78 shows the SWOT for transesterification pathway. This process is already well established with the use of vegetable oils. The objective was to analyze the environmental and economic performance of this process using waste cooking oil, animal fat or energy crops. These feedstocks have lower emissions since the cultivation impacts are considered as zero. However with this kind of resource, a convenient pre-treatment is needed. Finally, the cost of WCO biodiesel is higher compared to fossil diesel but this is also the case for all renewable options.

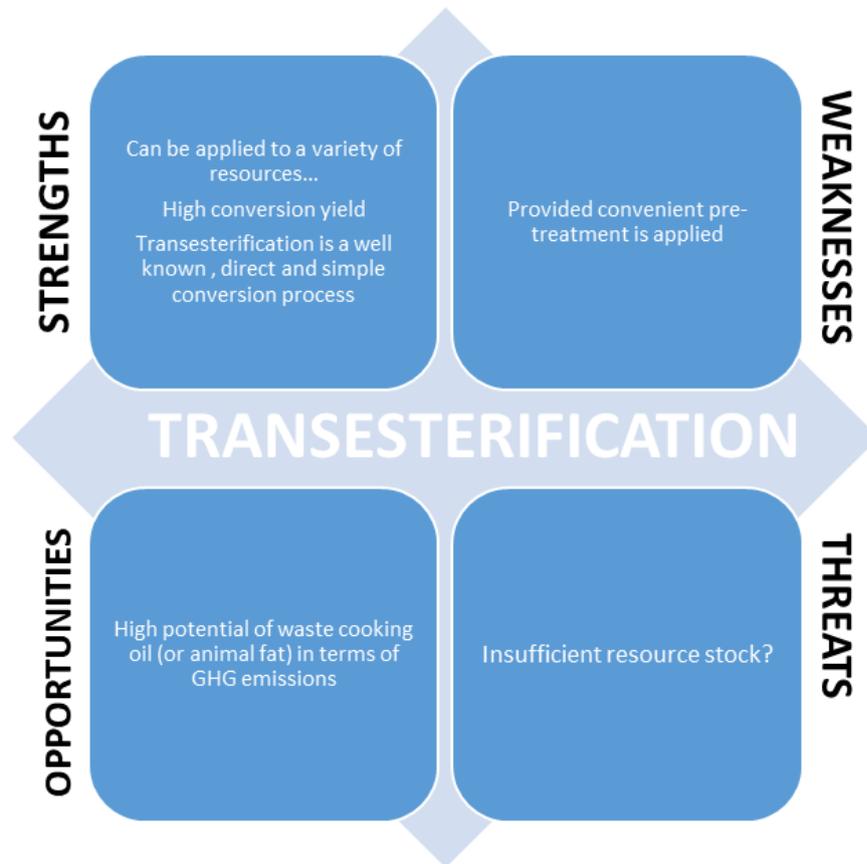


Figure 78 SWOT for Transesterification production path

### 6.3. RENEWABLE PARAFFINS AND ESTERS PRODUCTION CAPACITY

The aim of this section is to provide an evaluation of the renewable diesel potential production capacity from sustainable biomass availability in the European Union and the UK by 2030 for each previously identified energy pathway.

The presented work covers only diesel mass yields from the literature review presented in the previous sections. Real production capacity through existing or announced infrastructures is not considered. To simplify the analysis, there is no consideration whether the process is optimized for diesel production or not. Indeed, this study refers to distillate mass yields once the process can be optimized to produce either diesel or kerosene. This is consistent with the fact that distillate could certainly be suitable for diesel applications. Note that for hydrotreatment of lignocellulose and e-fuel from CO<sub>2</sub> capture, there is no data found in the literature for the diesel mass yield.

Regarding the resource availability, the data from Imperial College London (ICL) study [284] has been used as a reference. Only feedstocks from agricultural, forest and waste origin included in Annex IX of RED II [3] (Part A and B) are considered as they are the main ones reported by ICL. The latter does not include any food and feed crops.

Only the two extreme scenarios analysed by ICL have been considered here: i) Low biomass mobilisation and ii) enhanced availability through Research and Innovation (R&I) measures as well as improved mobilisation due to improvements in cropping and forest management practices.

This work first reports the current diesel or distillate mass yield for each energy pathway and then estimates the potential amount of renewable diesel that could be available for transport. These yields are assumed to be the same by 2030.

#### 6.3.1. Diesel or distillate mass yields from literature review

##### 6.3.1.1. Fermentation - Alcohol To Diesel

Klein et al. [266] investigate the techno-economic and environmental assessment of renewable jet fuel production in integrated Brazilian sugarcane biorefineries. In their study, they report a distillate mass yield for fermentation process. 4 Mt/y of sugarcane have been used to produce 360 ML/y of ethanol then used to produce around 200 ML/y of distillate. The yield (distillate-ethanol) of 53% is quite consistent with the theoretical transformation of ethanol to ethylene; considering a molar mass ratio of 28 to 46, i.e. 60%. The addition of different stages afterwards leads to a small yield loss. A typical yield of advanced ethanol is around 20% [285] which leads to 1400 kt/y of dry biomass, so the overall mass yield of the chain is about 10%.

Considering renewable carbon recovery in the biofuel and the carbon balance, distillate mass yield can vary from 9% to 12%. In this context, a mass yield of 11% has been considered as a reference for the estimation of renewable diesel production capacity.

##### 6.3.1.2. Triglycerides hydrotreatment

Hydrotreatment can be associated to different feedstocks:

- Hydrotreatment of vegetable oils

Vegetable oils have not been considered in the review of Imperial College London nor in this study. This resource is thus not considered here.

- Hydrotreatment of Waste Cooking Oils (WCO)

Bezergianni et al. [286] evaluate mainly the effect of temperature on diesel mass yield. In their study, depending on the reactor operating conditions, diesel mass yield varies from 64% to 90%.

A mass yield of 90% has been considered in order to match the maximum diesel production case.

- Hydrotreatment of animal fats

Dimitriadis et al. [287] evaluate the impact of reactor operating conditions on the diesel mass yield of animal fats hydrotreatment. They report a diesel mass yield varying from 92% to 97%.

For the estimation of renewable diesel production capacity, a mass yield of 95% has been considered.

#### 6.3.1.3. Transesterification

Transesterification can be associated to different feedstocks:

- Transesterification of vegetable oils

Vegetable oils have not been considered in the review of Imperial College London nor in this study. This resource is thus not considered here.

- Transesterification of WCO

The literature review shows that the diesel mass yield for transesterification of WCO varies from 83% to 97% [280, 282, 288]. For the estimation of renewable diesel potential production, a mass yield of 90% has been considered.

- Transesterification of animal fats

Biodiesel mass yield estimation for fermentation of animal fats process is based on Arpia et al. study [288]. In this paper, the reported diesel mass yield is 93%. This value has been selected in the current study.

#### 6.3.1.4. Gasification + Fischer-Tropsch

Distillate mass yield estimation for gasification + FT is based on three case studies from COMSYN & FLEXCHX webinar [226] which highlights energy efficiency of several processes. Energy data have been converted into mass values with a few hypotheses. They include a biomass LHV of 19 MJ/kg, a FT-wax LHV of 44 MJ/kg and a full FT wax conversion into distillate.

The literature review shows that the diesel mass yield for gasification + FT varies from 14% to 26%. For the estimation of renewable diesel capacity, a mass yield of 20% has been considered.

### 6.3.1.5. E-fuel

Distillate mass yield estimation for e-fuel from lignocellulose is based on two case studies from COMSYN & FLEXCHX webinar [226] which highlights energy efficiency of several processes. Similar hypotheses as for the previous energy pathway were used: a biomass LHV of 19 MJ/kg, a FT-wax LHV of 44 MJ/kg and a full FT wax conversion into distillate. This also includes the fact that a 15 MW of electricity represents 0.25 t/h of H<sub>2</sub>.

The literature review shows that the diesel mass yield for e-fuel from lignocellulose varies from 47% to 52%. For the estimation of renewable diesel capacity, a mass yield of 50% has been considered. This value may be overestimated as no carbon loss is assumed during CO<sub>2</sub> recycling. However, this mostly indicates that this energy pathway may contribute to double the reported mass yield of gasification + FT.

### 6.3.1.6. Summary of biomass conversion yields to biofuels from literature review

Table 32 below summarizes the biomass conversion yields to sustainable fuels reported in the literature and the selected one for each energy pathway.

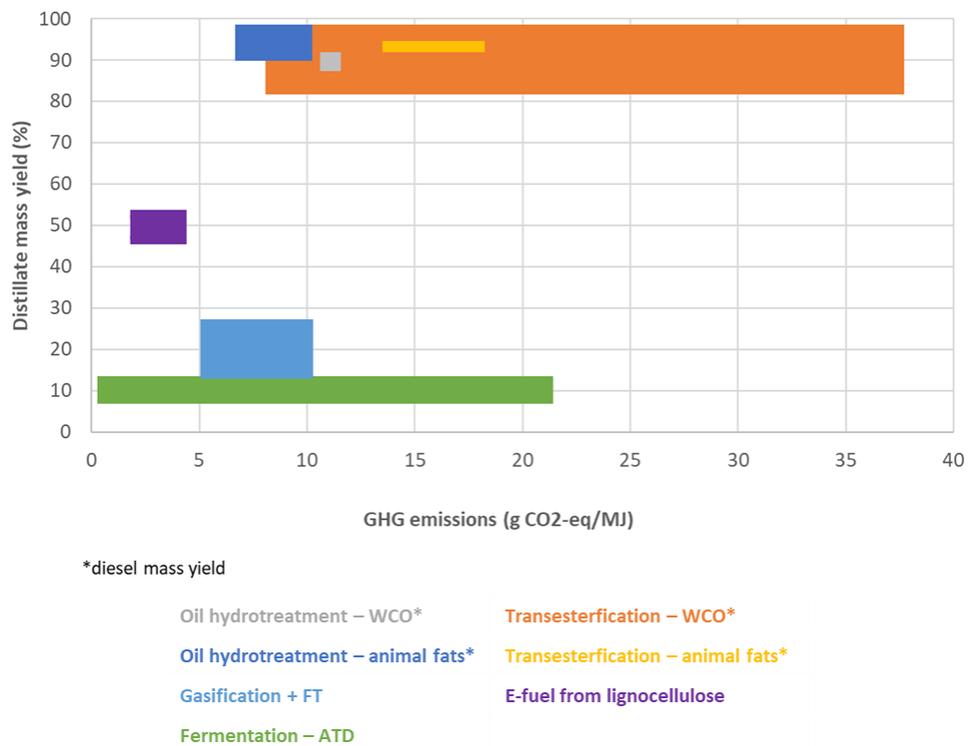
**Table 32** Summary of biomass conversion yields to biofuels from literature review for each energy pathway

Pathway	Feedstock	Fuel	Conversion yield to fuels (mass %)	
			Literature review	Selected
Fermentation - ATD	Sugarcane	Distillate	9 → 12	11
Triglycerides hydrotreatment	WCO	Diesel	90	90
	Lard and beef tallow animal fats	Diesel	92 → 97	95
Transesterification	WCO	Diesel	83 → 97	90
	Animal fats	Diesel	93	93
Gasification + FT <sup>6</sup>	Biomass	Distillate	14 → 26	20
E-fuel from lignocellulose <sup>7</sup>	Biomass + electricity	Distillate	47 → 52	50

Figure 79 illustrates the greenhouses gas (GHG) emissions and the identified mass yield for each energy path. The concatenated data is not exhaustive but it provides a range of variability that is observed in the recent scientific literature. This range can be discussed as it relies on different environmental assessments that may lead to different data for the same energy path. Consequently, the reported range should be considered as an indication of the potential variability for each energy path but not as a fixed range.

<sup>6</sup> Assuming full conversion of FT-wax into distillate

<sup>7</sup> Assuming full conversion of FT-wax into distillate



**Figure 79** Greenhouse gases emissions for different renewable fuels and their related mass yield. The different areas correspond to the resource sensitivity in terms of GHG emissions and diesel mass yield as identified in the literature. Attention should be paid to the identified variability for each path as the reported data may not be exhaustive. In addition, the reported range reflects the concatenation of several data that are based on different environmental evaluations which are also related to a certain variability depending on the hypotheses used. The latter may be different and are not necessarily reported.

Resource sensitivity in terms of GHG emissions can be very different for some energy path, particularly for fermentation - ATD and transesterification of WCO. Table 33 shows the identified resources and their Global Warming Potential (GWP) impact.

**Table 33** Resource GWP impact for fermentation - ATD and transesterification of WCO from literature<sup>8</sup>

Energy path	Resource	GWP impact (g CO <sub>2</sub> -eq/MJ)
Fermentation - ATD	Wood chips <sup>9</sup>	1.6
	Wood chips <sup>10</sup>	10
	Corn stover	21
	Agricultural residues	14.9
Transesterification	WCO (China)	37.4
	WCO (JRC)	8.3

### 6.3.2. Estimation of renewable diesel potential

#### 6.3.2.1. Projected biomass feedstock

The presented work uses potential resource availability data from Imperial College London study as a reference. It covers only domestic (EU27 & UK) feedstocks of agricultural, forest and waste origin included in Annex IX of RED II (Part A and B). Food and feed crops, and other sustainable feedstocks accepted by RED but not included in Annex IX, are not included in this study (see Table 34). The current work does not consider the 48 Mt of biomass that can be imported to Europe and does not consider the 130 Mt of this biomass which could be used by other bioenergy applications (such as power generation).

<sup>8</sup> See LCA and TEA sections: 6.2.1 and 6.2.5 for Fermentation and hydrotreatment respectively.

<sup>9</sup> Syngas fermentation to ethanol followed by fuel production via alcohol condensation (Guerbet reaction), dehydration, oligomerization, and hydrogenation

<sup>10</sup> Syngas fermentation to ethanol followed by fuel production via carbon coupling/deoxygenation (to isobutene), oligomerization, and hydrogenation

**Table 34** Biomass feedstocks from Annex IX (Part A and B) considered in the Imperial College London study<sup>1</sup>

Annex IX Part A	Agricultural feedstocks	Forest feedstocks	Biowastes	Algae
(a) Algae if cultivated on land in ponds or photobioreactors				Overview based on recent studies
(b) Biomass fraction of mixed municipal waste, but not separated household waste subject to recycling targets under point (a) of Article 11(2) of Directive 2008/98/EC			Paper cardboard, Wood waste, Animal & mixed food waste, Vegetal waste, Municipal solid waste (MSW),	
(c) Biowaste as defined in point (4) of Article 3 of Directive 2008/98/EC from private households subject to separate collection as defined in point (11) of Article 3 of that Directive;			Paper cardboard, Wood waste, Animal & mixed food waste, Vegetal waste, Municipal solid waste (MSW)	
(d) Biomass fraction of industrial waste not fit for use in the food or feed chain, including material from retail and wholesale and the agro-food and fish and aquaculture industry, and excluding feedstocks listed in part B of this Annex	Secondary agricultural residues from agro-industries			
(e) Straw	Cereal straw, maize stover			
(f) Animal manure and sewage sludge	Solid and liquid manure from poultry, pigs, cattle		Sewage sludge	
(o) Biomass fraction of wastes and residues from forestry and forest-based industries, namely, bark, branches, pre- commercial thinnings, leaves, needles, treetops, saw dust, cutter shavings, black liquor, brown liquor, fibre sludge, lignin and tall oil;		Primary forest residues Secondary forest residues		
(p) Other non-food cellulosic material	Oilseed crop residues Agricultural prunings			
(q) Other lignocellulosic material except saw logs and veneer logs		Fuelwood, Post-consumer wood		
<b>Annex IX Part B</b>				
(a) Used cooking oil			Used Cooking oil	
(b) Animal fats classified as categories 1 and 2 in accordance with Regulation (EC) No 1069/2009			Animal fats categories 1 and 2 are included in Animal & mixed food waste	

<sup>1</sup> Feedstocks from (g) to (o) [ (g) Palm oil mill effluent and empty palm fruit bunches; (h) Tall oil pitch; (i) Crude glycerine; (j) Bagasse; (k) Grape marcs and wine lees; (l) Nut shells; (m) Husks; (n) Cobs cleaned of kernels of corn] from Annex IX part A have not been included because there were no consistent statistical datasets available at the time of this study

Table 35 below presents the estimated potential sustainable biomass potential from agriculture, forestry and biowastes that can be available for bioenergy for 2030.

**Table 35** ICL study projected potential biomass quantity for bioenergy by 2030. The range refers to the low and high biomass availability scenarios.

Feedstock	Estimated biomass potential for bioenergy for 2030 (million tonnes)
Cereal straw	
Maize stover	137 → 165
Oil crop residues	
Lignocellulosic crops	36 → 108
Agricultural (woody) & forestry residues	5 → 7
Secondary residues from agro-industries	133 → 191
Secondary forest residues - post consumer wood	
UCO	3.1
Animal fats	2.2

#### 6.3.2.2. Potential renewable fuel production based on estimates of available biomass

This section provides an outlook of maximum theoretical production potential<sup>1</sup> of renewable diesel by 2030 based on estimated available biomass for bioenergy applications estimated in the Imperial College London study. Table 36 gives the biomass conversion yields used for the estimated diesel production capacity.

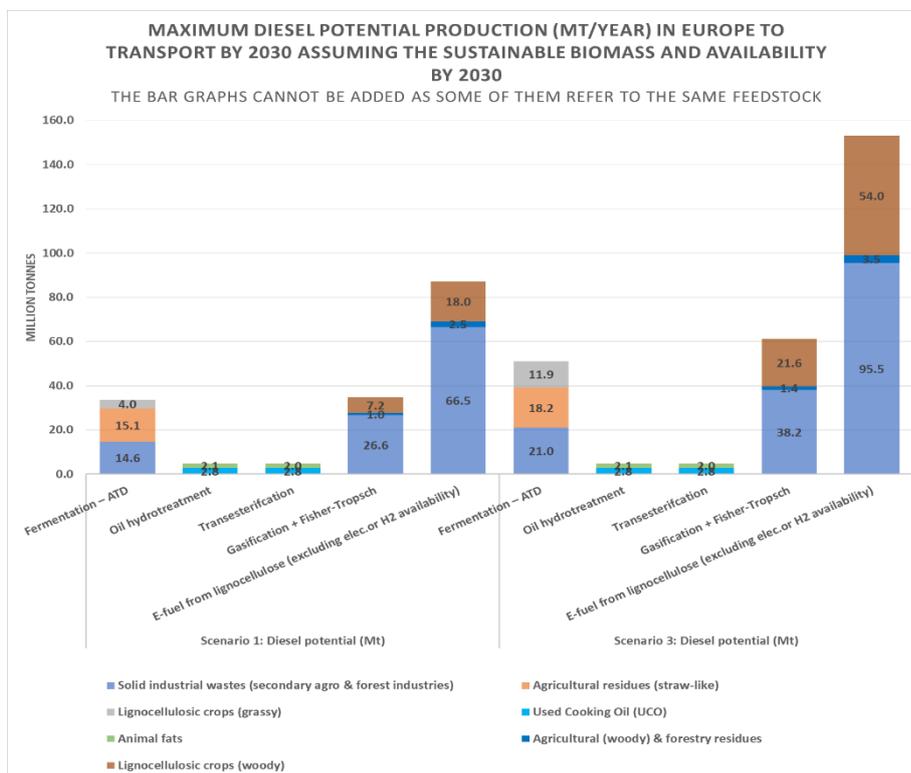
Table 36 also compares the ICL study and literature review on advanced diesel production in 2030 taking into account the total potential sustainable biomass for bioenergy. Two approaches can be considered. On the one hand, only the mature technologies are considered: ATD, triglycerides hydrotreatment, transesterification and gasification + FT. On the other hand, an evaluation is proposed assuming sufficient available renewable electricity and hydrogen to develop the e-fuel energy path. In their study, ICL did not consider e-fuel pathway to be available in 2030.

<sup>1</sup> The maximum theoretical production potential relies on infrastructures that are not available today. It is unlikely that these infrastructures can be deployed to convert the identified feedstock into low carbon fuels by 2030.

**Table 36** Maximum theoretical production potential renewable diesel production in 2030 (taking into account the total sustainable biomass for bioenergy from section 6.3.2.1). The range refers to the low and high biomass availability scenarios.

Pathway	Fuel	Feedstocks	2030 Estimated renewable diesel quantity (million tons)		2030 Estimated renewable diesel quantity (Mtoe)	
			ICL study	Literature review	ICL study	Literature review
Fermentation - ATD	Paraffinic fuel	Solid industrial waste (secondary agro & forest industries)	-	14.6 → 21.0	-	15.4 → 22.1
		Agricultural residues (straw-like)	-	15.1 → 18.2	-	15.8 → 19.1
		Lignocellulosic crops (grassy)	-	4.0 → 11.9	-	4.2 → 12.5
Oil hydrotreatment	HVO	UCO	2.6	2.8	2.6	2.9
		Animal fats	1.9	2.1	1.9	2.2
Transestrification	FAME	UCO	-	2.8	-	2.4
		Animal fats	-	2.0	-	1.8
Gasification + FT	Paraffinic fuel	Solid industrial waste (secondary agro & forest industries)	27.9 → 40.1	26.6 → 38.2	27.9 → 40.1	27.9 → 40.1
		Agricultural (woody) & forestry residues	1.0 → 1.5	1.0 → 1.4	1.0 → 1.5	1.1 → 1.5
		Lignocellulosic crops (woody)	7.6 → 22.7	7.2 → 21.6	7.6 → 22.7	7.6 → 22.7
E-fuel from lignocellulose	Paraffinic fuel	Solid industrial waste (secondary agro & forest industries)	-	66.5 → 95.5	-	69.8 → 100.3
		Agricultural (woody) & forestry residues	-	2.5 → 3.5	-	2.6 → 3.7
		Lignocellulosic crops (woody)	-	18 → 54	-	18.9 → 56.7

Figure 80 provides an overview of the estimated renewable diesel production capacity for transport in 2030 using the identified sustainable biomass from ICL study and excluding the issue of electricity or hydrogen availability by 2030. It should be highlighted that each column is independent. They cannot be added due to the fact that they certain pathways use the same feedstock.



**Figure 80** Estimated maximum theoretical production potential renewable diesel production in 2030 for transport (in million tonnes) for each energy pathway by type of biomass, assuming all the sustainable biomass considering European feedstocks listed in Annex IX A and B of RED II/2018. The bar graphs cannot be added as some of them refer to the same feedstock.

Figure 80 highlights that e-fuel from lignocellulose pathway allows to maximize solid industrial wastes and lignocellulosic crops conversion into distillates but biomass is not the only constraint, the related renewable electricity production must be considered and this will certainly contribute to limit the use of this pathway by 2030.

Regarding resources competition, solid industrial wastes can be used for fermentation - ATD, gasification + FT and e-fuel from lignocellulose process. Lignocellulose crops (woody) can be used for gasification + FT and e-fuel from lignocellulose. Regarding UCO and animal fats, they can be used in the same proportion to produce HVO (from triglycerides hydrotreatment) or FAME (from transesterification). Agricultural residues (straw-like) and grassy lignocellulosic crops are only assigned to fermentation.

### 6.3.3. Resources competition by considering “Fit for 55” package requirements

The “Fit for 55” includes a list of legislative initiatives across various sectors such as energy, land use, transport and taxation policies for achieving the EU target of a net domestic reduction of at least 55% in greenhouse gas emissions by 2030 compared to 1990.

In order to reach the EU objectives, a set of proposals have been made. These proposals would play a significant role in this, since their main objective is to increase both demand and supply of renewable fuels in the transport market.

In this context, the following section highlights the potential competition with the other transport sectors such as aviation and marine by considering the “Fit for 55” package requirements by 2030.

### 6.3.3.1. RED II Transport

Regarding transport sector, the amendment to the Renewable Energy Directive (RED II) suggests to express the renewable transport target as a GHG intensity reduction target instead of the currently applicable methodology (in energy terms). The proposal suggests to increase the sub-target for advanced biofuels (at least 2.2% energy in 2030) and suggests a new 2.6% energy sub-target for the use of RFNBOs in transport. The proposed new sub-targets are listed in the *Table 37* below.

**Table 37** Proposed new sub-targets by RED II revision for transport

	2021 proposed RED II revision
Advanced biofuels (Annex IX part A)	2.2% energy minimum (out of all energy supplied to transport)
Renewable fuels of non biological origin (RFNBOs)	2.6% energy minimum (out of all energy supplied to transport)
Waste oils (Annex IX part B)	1.7% energy maximum (out of all energy supplied to transport)

Required minimum renewable diesel incorporation have been estimated (see *Table 38*) with the following assumptions :

- The energy demand in Europe for transport by 2030 is estimated at 355 Mtoe/y<sup>2</sup> (including road transport, rail, maritime, aviation and off-road). The current demand is estimated at 375 Mtoe/y.
- If 100% of energy demand is related to paraffinic fuel (LHV<sub>paraffinic fuel</sub> = 43 961 kJ/kg): 1t of paraffinic fuel → 1.05 toe
- If 100% of energy demand to FAME (LHV<sub>FAME</sub> = 36 000 kJ/kg): 1t of FAME → 0.86 toe

<sup>2</sup> Data shared by Concawe

**Table 38** Required minimum renewable diesel incorporation with the targets mentioned in Table 37 and a total energy demand of 355 Mtoe/y (under the assumption that all the requirements would be routed to the diesel fuel pool).

2021 proposed RED II revision		
Advanced biofuels (Annex IX part A)	2.2	% out of all energy supplied to transport (RDE II)
	7.8	Mtoe
	7.4	Mt of paraffinic fuel
Renewable fuels of non biological origin (RFNBOs)	2.6	% out of all energy supplied to transport (RED II)
	9.2	Mtoe
	8.8	Mt of paraffinic fuel <sup>3</sup>
Waste oils (Annex IX part B)	1.7	% out of all energy supplied to transport (RED II)
	6.0	Mtoe
	5.7 / 7.0	Mt of paraffinic fuel / Mt of FAME

#### 6.3.3.2. ReFuelEU Aviation

Regarding sustainable aviation fuels (advanced biofuels and electrofuels), they have the potential to significantly reduce aircraft CO<sub>2</sub> emissions. However, this potential is largely untapped as such fuels currently represent only about 0.05% of total fuel consumption of the sector.

The ReFuelEU Aviation proposal aims to reduce the aviation sector's environmental footprint. The proposed sub-targets by 2030 are listed in the *Table 39* below.

**Table 39** SAF ramp-up trajectory by 2030 (volume based approach)

Total shares in the fuel mix (%)	2030
SAF ramp up out of which:	5
- Biofuels (including Part A and Part B biofuels)	4.3
- Specific sub-mandate on RFNBOs	0.7

Required minimum SAF incorporation has been estimated. *Table 40* assumes that the total demand of kerosene in Europe today is quite constant by 2030 and represents 54 Mt/y [289].

<sup>3</sup> Assuming that RFNBOs would only be e-fuels (extreme scenario). In reality, a significant share of green H<sub>2</sub> will be used for other purposes (e.g. hydrotreatment of fossil fuels or of biomass), and accounted as RFNBOs.

**Table 40** Required minimum SAF incorporation with the ReFuelEu targets and a total energy demand of 54 Mt/y.

Total shares in the fuel mix	2030	
SAF ramp up out of which:	5	% of total demand by 2030
	2.7	Mt of SAF
Biofuels (including Part A and Part B biofuels)	4.3	% of total demand by 2030
	2.32	Mt of biofuels
Specific sub-mandate on RNFBOs	0.7	% of total demand by 2030
	0.38	Mt of RNFBOs

#### 6.3.3.3. FuelEU Maritime

Regarding maritime sector, to support the uptake of sustainable maritime fuels, the Commission requests to limit the GHG intensity of the energy used onboard of ships. The limit shall be calculated by reducing the reference value of [X grams of CO<sub>2</sub> equivalent per MJ] by 6% from 2030. The yearly average greenhouse gas intensity of the energy used on-board by a ship during a reporting period shall not exceed this limit.

*Table 41* shows the minimum of renewable fuel incorporation that would have to be used, under the assumption that all the GHG intensity reduction is achieved by using renewable fuels (NB: a quite extreme case, as it is not the mainstream plan expressed by the ship owners, that rather anticipate the use of LNG (fossil-based, bio-LNG and e-LNG) and e-methanol). Both the best and worst sustainable fuels in terms of GHG impacts are reported in this table.

The following assumptions are used for this evaluation:

- The total demand of marine fuel in Europe today is quite constant by 2030 and represents 56 Mt/y [289]
- Marine fuel GHG emissions: 92 g CO<sub>2</sub>-eq/MJ<sup>4</sup> (ref. diesel), which corresponds to a targeted cap at 86 g CO<sub>2</sub>-eq/MJ by 2030 (6% reduction)

It should be reminded that using renewable diesel may not be the only option for the maritime sector by 2030 to achieve the target.

<sup>4</sup> Prussi, M. et al., JEC Well-to-Tank report v5, Luxembourg, 2020

**Table 41** Minimum of renewable fuel incorporation if only renewable diesel were to be considered by maritime sector by 2030. Best and worst sustainable fuels in terms of GHG impacts are reported in this table.

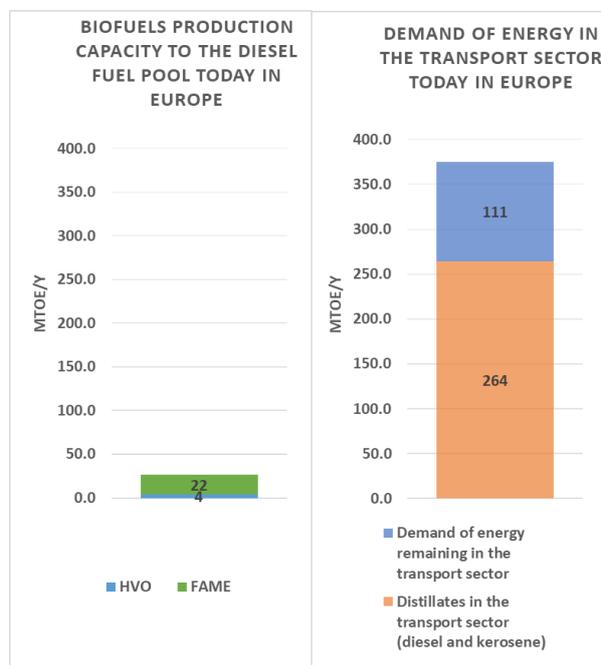
	Best HVO	Worst HVO	Best FAME	Worst FAME
GHG emissions (g CO <sub>2</sub> -eq/MJ)	7	11	8	37.4
Minimum of incorporation (%)	7.1	7.4	8	11
Minimum of incorporation (MT/y)	4	4.1	4	5.5

#### 6.3.4. Summary and conclusions

##### 6.3.4.1. Current production capacity and energy demand

*Figure 81* shows the current production capacity of sustainable diesel fuels (FAME and HVO) today in Europe and the total European distillates demand in transport.

Renewable diesel production today mainly relies on food and feed crops as feedstock (competition with food), which is capped by RED II at 7% of the demand of energy in transport and the European production capacity reaches this limit. In this context, the section aims at providing insights into the availability of sustainable advanced liquid fuel pathways by 2030 to increase the share of renewable fuels in the transport sector. The focus is made on FAME and paraffins, the two main products that are discussed in this chapter.

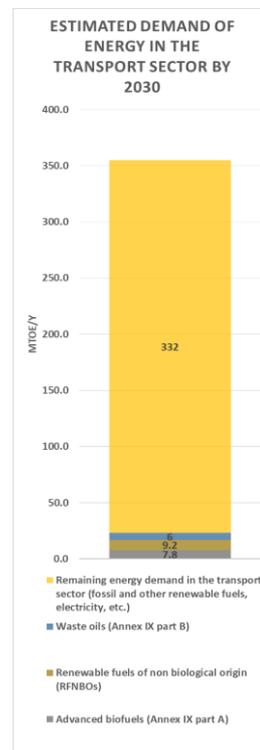


**Figure 81** Sustainable diesel fuels production capacity potential (left, also reported in Mt Figure 11) and current energy demand for transport (right) in Europe. (Concawe estimation for the energy demand for transport)

#### 6.3.4.2. Energy demand and renewable diesel production by 2030

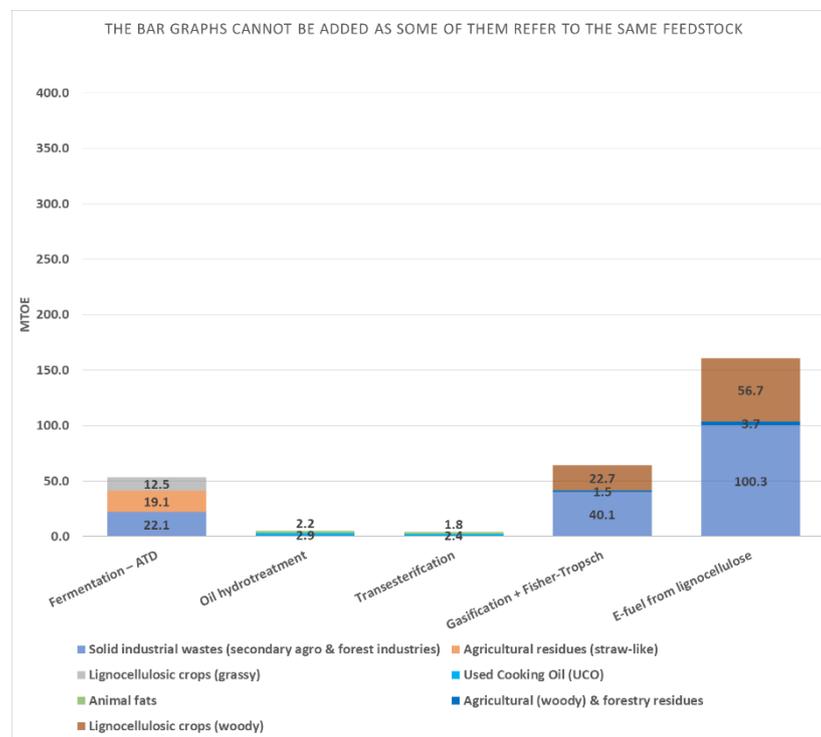
*Figure 82* illustrates the required minimum incorporation of non-food and feed crops-based renewable fuels. Regarding RNFBOs, they should represent at least 9.2 Mtoe (355 Mtoe of energy demand expected by 2030 and 2.6% of RFNBOs targeted) and could potentially be supplied through e-fuel from lignocellulose<sup>5</sup>. However this would only be related to the share of renewable H<sub>2</sub> that is required for e-fuel production. The rest is still counted as biofuels. Waste oils (Annex IX part B) which represent no more than 6 Mtoe could be supplied through triglycerides hydrotreatment (5.1 Mtoe) or transesterification (4.2 Mtoe) but the cap may not be reached by 2030 (unless there are further imports of waste feedstocks).

<sup>5</sup> Reminder: in an extreme scenario. In reality, a significant share of green H<sub>2</sub> will be used for other purposes (e.g. hydrotreatment of fossil fuels or of biomass), and accounted as RFNBOs.



**Figure 82** Estimated energy demand for transport considering RED II amendment requirements by 2030. The graph highlights the required minimum incorporation of advanced fuels, RFNBOs, and waste oils over the energy demand in the transport sector by 2030 (Concawe estimation for the energy demand in the transport sector).

Figure 83 shows the estimated renewable fuel production for different process technology selected in this study. Bar graphs list the resources that can be used by each process. Bar graphs cannot be added to each other but one should read the estimated renewable fuel production for each energy path. Consequently, it highlights that e-fuel from lignocellulose pathway allows to maximize solid industrial wastes and lignocellulosic crops conversion into distillates. The figure also enables to identify potential competitions for several feedstocks. As an example, animal fats and used cooking oil can either be used with transesterification or hydrotreatment. Agricultural residues are however only associated to fermentation pathway.



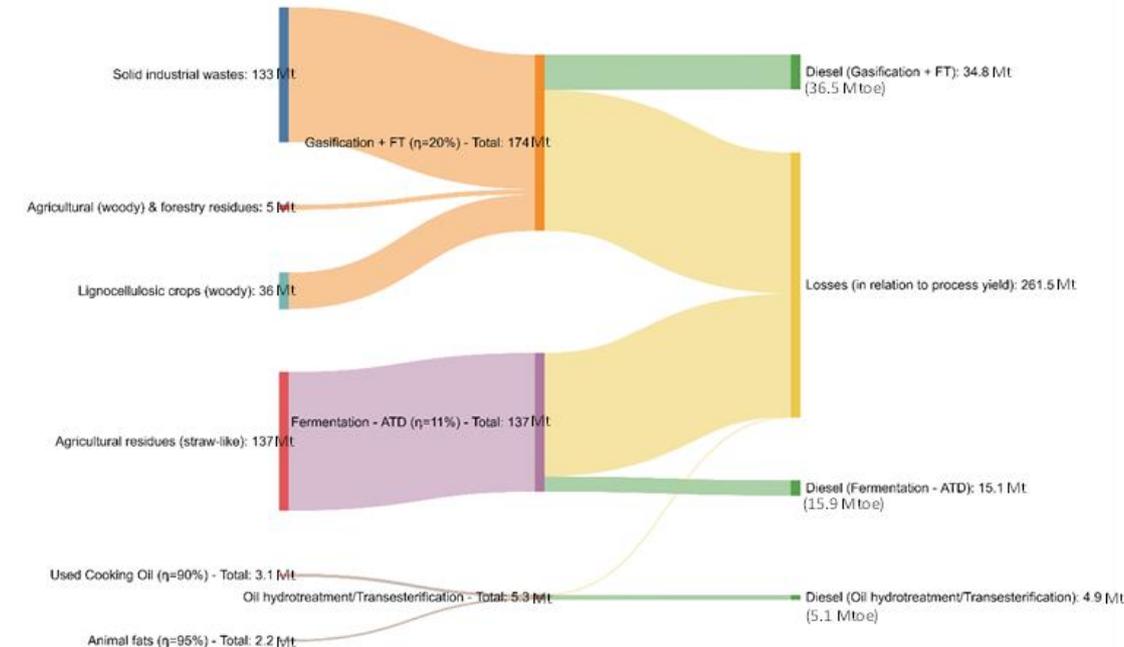
**Figure 83** Estimated maximum theoretical production potential of renewable diesel production in 2030 for transport (in million tonnes of oil equivalent). This is reported for each energy pathway and the related eligible biomass. The bar graphs cannot be added as some of them refer to the same feedstock.

#### 6.3.4.3. Resource contribution in energy demand for distillates by 2030

The reduction potential of conventional energy demand in the transport sector (i.e. mostly fossil-based) is evaluated by considering two approaches:

- A “base case”, using the most mature technologies (i.e. technologies already at industrial scale today: ATD, triglycerides hydrotreatment; and technologies expected to become at industrial scale by 2030: gasification + FT) with low and high mobilisation of bioresources.
- An “optimistic case”, where e-fuel technology is added, which implies sufficient renewable electricity and hydrogen availability by 2030. In addition, only the hydrogen share used to produce renewable fuels contributes to RFNBOs. The remaining counts as biofuel.

The renewable diesel potential production by 2030 is illustrated in



Distillates production potential in Mt (high resources mobilization and high TRL processes)

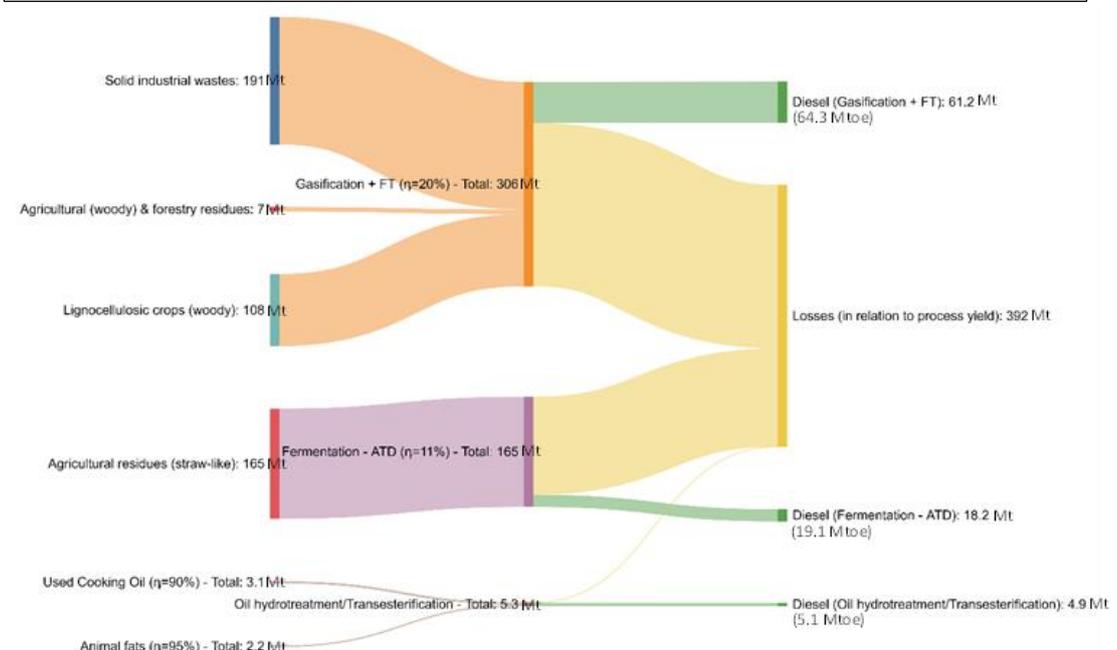
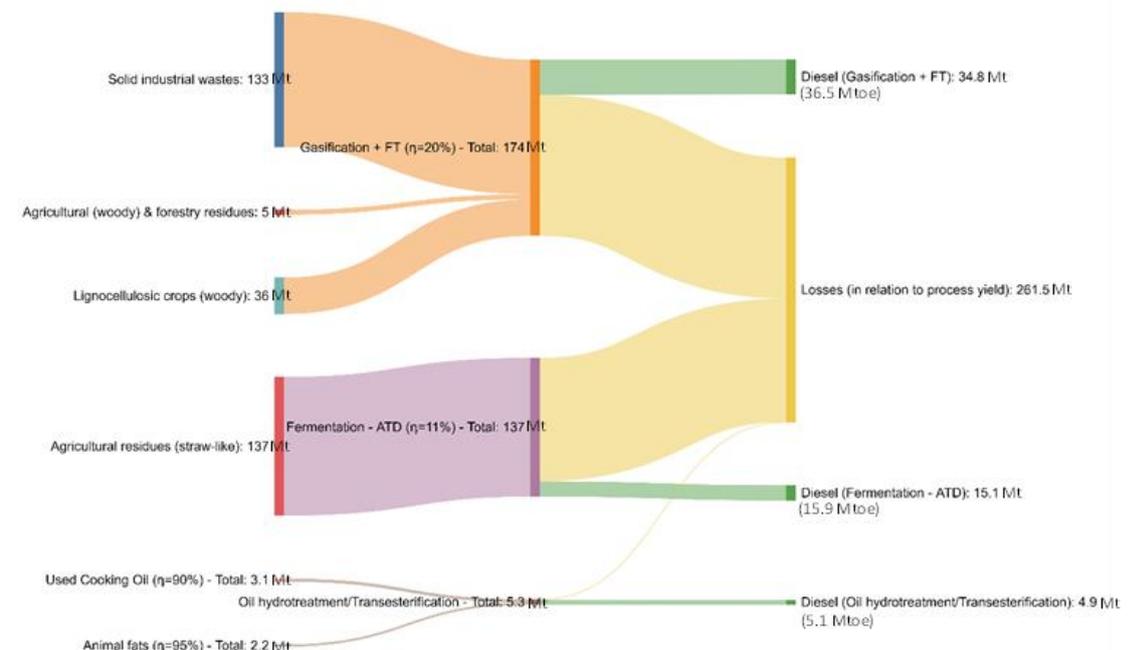


Figure and Figure 84. It ranges between:

- 57 and 88 Mtoe/y in the “base case” (considering most mature technologies), which represents between 24% and 37% of the demand of energy for distillates in the transport sector in 2030 (241 Mtoe for light

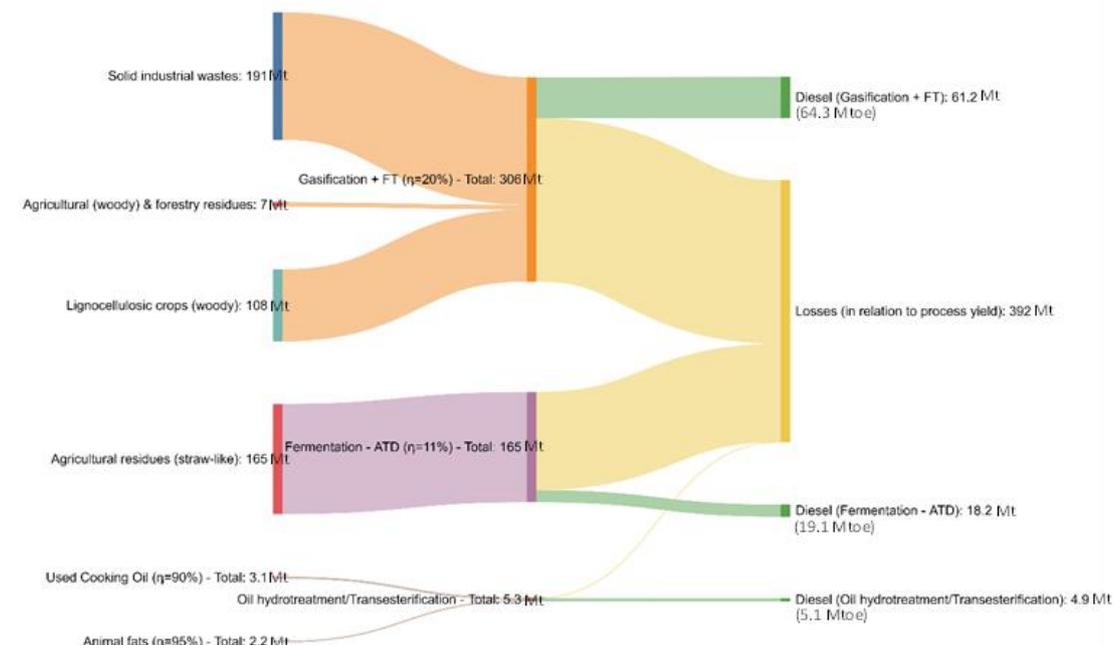
products ranging from kerosene to diesel<sup>6</sup> out of 355 Mtoe in total). These values must be seen as a maximum potential<sup>7</sup>, pending the development and upscaling of the technologies, the mobilisation of biomass to biorefineries, the necessary investments and development of a profitable business, etc. This maximum theoretical production potential is however highly unlikely to be reached in 2030, as it would require massive investments to be realized in technologies which today do not exist at industrial scale, without waiting for demonstration of a First-Of-A-Kind.



Distillates production potential in Mt (high resources mobilization and high TRL processes)

<sup>6</sup> The energy demand for middle distillates in the transport sector in 2030 is expected to be 241 Mtoe, including demand of diesel fuel for heavy-duty vehicles, for passenger cars and demand of Jet fuel for aviation. This report focuses on diesel-like fuels for heavy-duty vehicles only, but considering that similar feedstock are used to produce all distillates for the transport sector, the maximum theoretical production is compared to the overall demand for distillates in the transport sector.

<sup>7</sup> According to the report “Sustainable biomass availability in the EU, to 2050” from Imperial College London, between 208 and 344 Mt/y of sustainable biomass is locally available in Europe, which is the scenario considered in this study (resp. low and high mobilization scenarios). On top of that, 48 Mt of biomass can be imported to Europe and 130 Mt of this biomass could be used by other bioenergy applications (such as power generation). These two items are not studied in this work.

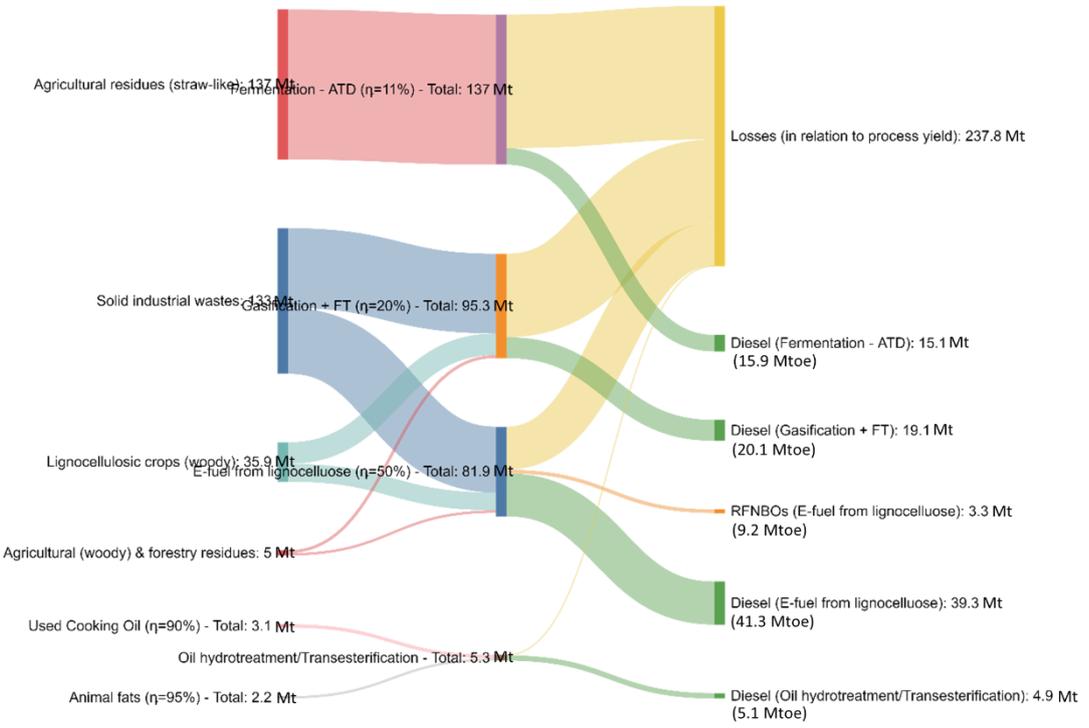


**Figure 84** Sankey diagrams illustrating the potential of distillates for transport considering low (top) and high (bottom) resources mobilization and high TRL processes only;

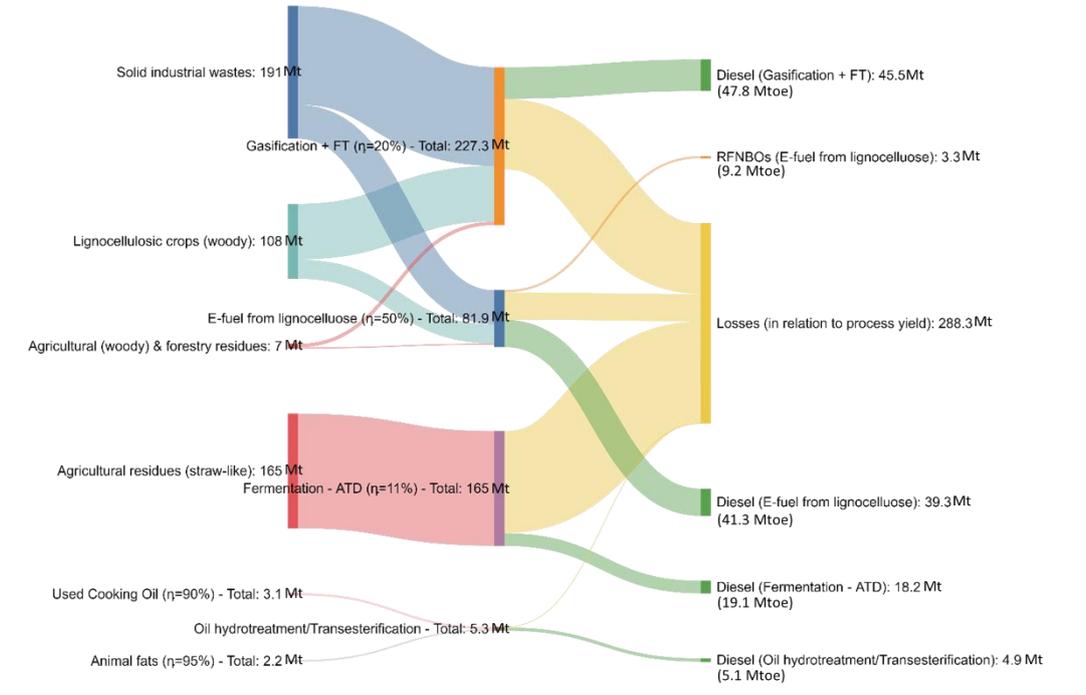
- 92 and 123 Mtoe/y in the “optimistic case”, assuming e-fuel from lignocellulose is also used to meet the RED II (revised) target in terms of RFNBOs production. This additional pathway will produce both RFNBOs and biofuels. The share counting as RFNBOs has to reach 9.2 Mtoe according to the RED II target. A total of 3.3 Mt/y of hydrogen and about 78.7 Mt/y of biomass would be required. This assumes:
  - an overall 50% process yield for e-fuel+lignocellulose pathway.
  - That the RFNBOs share is defined according to the mass ratio of renewable hydrogen required over the biomass as an input for the overall process (i.e. 3.3 Mt of H<sub>2</sub>/y for 78.7 Mt of biomass/y. This corresponds to 7.7% m/m of hydrogen as an input. These components are converted into 43 Mt/y of FT products 3.3 Mt of H<sub>2</sub>/y corresponds to the RFNBOs target: 9.2 Mtoe).

Figure 84 illustrates both the low and high mobilization scenarios. Both hypotheses rely on the use of every energy pathway identified. Again, this second approach assumes that Hydrogen would be available by 2030 (the evaluation of the likelihood of this assumption is out of the scope of this study). The infrastructures would also need to be developed and ready for such large scale production. Consequently, the biomass availability, which is the main aspect considered here, should not overshadow the lower maturity and important investments required for the e-fuel pathway development.

Distillates production requirement in Mt (low resources mobilization and RFNBOs target)



Distillates production requirement in Mt (high resources mobilization and RFNBOs target)



**Figure 84** Sankey diagrams illustrating the distillates requirement for transport considering low (top) and high (bottom) resources mobilization and assuming e-fuel from lignocellulose is used to meet the RED II (revised) target

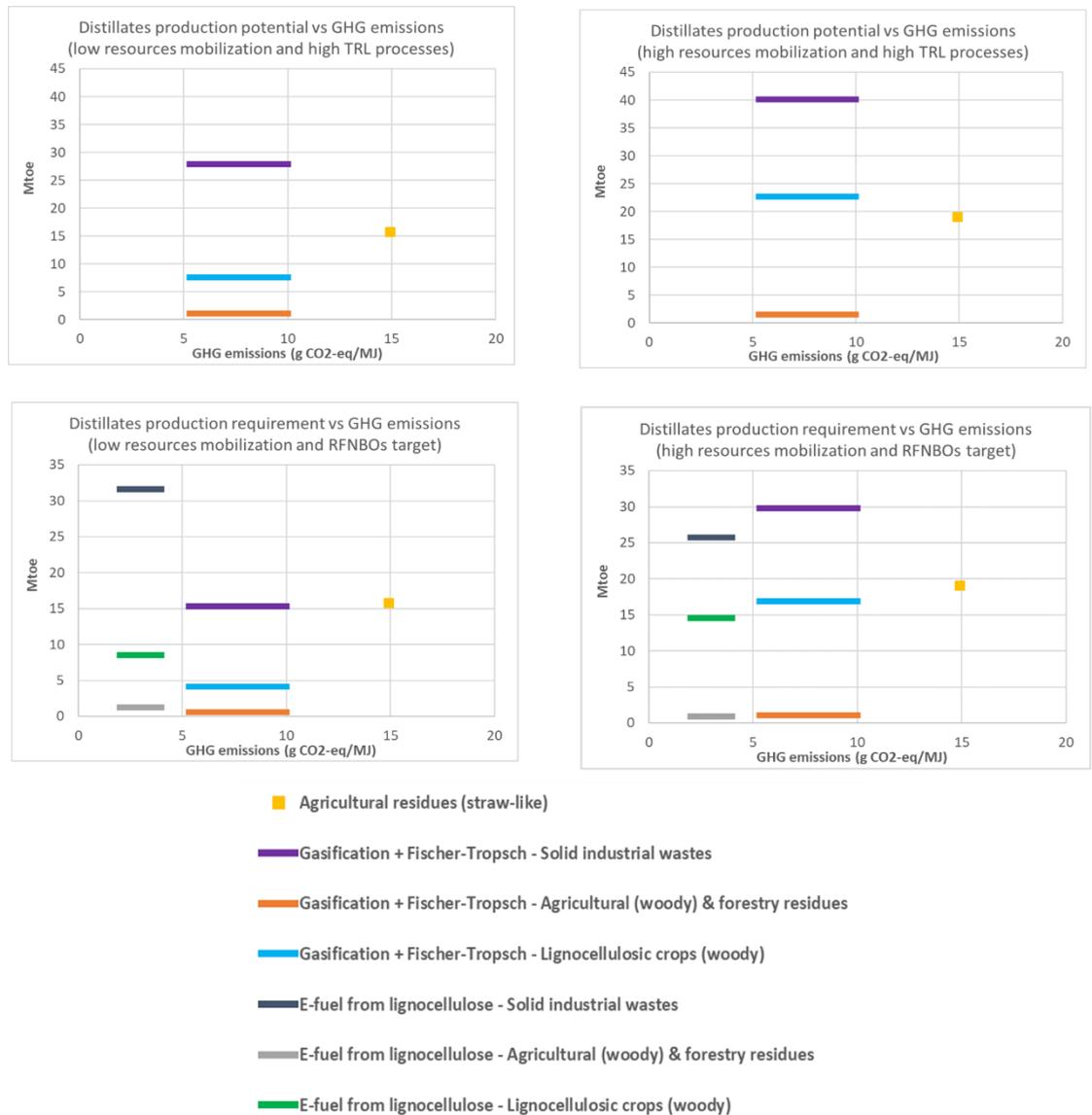
Finally, it should be mentioned that other products could contribute to increase the renewable share for the transport sector such as biogas, bioLPG, etc, but these options are out of scope for this study.

#### 6.3.4.4. **Potential production and RED II (revised) requirement vs GHG emissions by 2030**

*Figure 85* shows the GHG emissions for the most relevant energy pathways by 2030 in terms of production capacity. This figure also illustrates that, while biomass is deemed available in sufficient volume according to ICL study for e-fuel with lignocellulose pathway, the availability at scale of renewable electricity and infrastructures for renewable hydrogen production in 2030 has not been demonstrated. The figure at the bottom assumes that the RED II (revised) target will be reached or almost reached for RFNBOs and this corresponds to about 9.2 Mtoe.

This figure also highlights the resources impact on both the GHG and production capacity performances.

Triglycerides hydrotreatment and transesterification have not been added due to their limited production capacity.



**Figure 85** Renewable distillates production potential and required by RED II (revised) by 2030 and GHG emissions for each energy pathway excluding triglycerides hydrotreatment and transesterification. At the top the projected renewable fuel production quantity is reported assuming low and high resources mobilization using most mature technologies. At the bottom, a realistic e-fuel contribution is reported assuming that the already challenging Fit for 55 targets are reached or almost reached in terms of RFNBOs production. The bar size refers to the resource sensitivity in terms of GHG emissions.

## 6.4. BLENDING OPTIMISATION

The objective of this section is to evaluate the blending opportunities of the renewable products from the selected pathways in conventional B7 fuel within the EN590 standard or potential extended standard in the future, based on estimating the physiochemical properties of their mixtures. This section follows similar conceptualization and methodology as Section 5.2, but based on binary mixtures of new renewable diesel products with consideration of extended properties and standards, and effect of additives.

### 6.4.1. Materials & methods

#### 6.4.1.1. Properties

In Section 5.2, we considered 4 properties for the fuels: liquid density at 15°C, kinematic viscosity at 40°C, cetane number, and flash point. In this section, due to the known limitations of paraffinic components and FAME, we also considered cold flow properties and selected the cold filter plugging point (CFPP) as a representation for simplicity. Other cold flow properties such as pour point and cloud point are subject to future investigation.

**Table 42** List of properties considered for blend optimization.

Property	Unit
Liquid density at 15 °C	kg/m <sup>3</sup>
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s
Cetane number	-
Flash point	°C
Cold filter plugging point	°C

#### 6.4.1.2. Standards

In this section, we considered the EN590 standard and the same extended standard used in Section 5.2. This extended standard relaxes the constraint on both density and viscosity by considering EN14214 and EN15940 in addition to the EN590 standard. Concerning CFPP, the EN590 standard defines different classes to take into account the climatic difference in different countries. For simplicity, we define two cases: (i) Class F (CFPP < -20 °C) for common European countries, and (ii) Class D (CFPP < -10 °C) for warm European countries like Spain. Therefore, it gives in total 4 different cases to evaluate, as listed in *Table 43*.

**Table 43** Details of the standards and cases considered as constraints for blend optimization.

<i>Common EU countries: CFPP = Class F (&lt; -20 °C)</i>				
<u>Property</u>	<u>(EU)EN590</u>		<u>(EU)EN590-extended</u>	
	<u>Min</u>	<u>Max</u>	<u>Min</u>	<u>Max</u>
Density [kg/m <sup>3</sup> ]	820	845	765	900
Cetane Number	51	---	51	---
Flash Point [°C]	55	---	55	---
Kinematic Viscosity [mm <sup>2</sup> /s]	2	4.5	2	5
CFPP [°C]	---	-20	---	-20
<i>Warmer EU countries: CFPP = Class D (&lt; -10 °C)</i>				
<u>Property</u>	<u>(ES)EN590</u>		<u>(ES)EN590-extended</u>	
	<u>Min</u>	<u>Max</u>	<u>Min</u>	<u>Max</u>
Density [kg/m <sup>3</sup> ]	820	845	765	900
Cetane Number	51	---	51	---
Flash Point [°C]	55	---	55	---
Kinematic Viscosity [mm <sup>2</sup> /s]	2	4.5	2	5
CFPP [°C]	---	-10	---	-10

#### 6.4.1.3. Mixing rules for CFPP

The mixing rules for density, viscosity, cetane number, and flash point are kept the same as in Section 5.2. In this section, we identified and evaluated 3 different CFPP mixing rules in the literature, namely MODEC-modified [290], Semwal & Varshney 1995 [291], and Vrablik et al. 2019 [292]. As will be discussed below, we select Semwal & Varshney to produce normal estimations and MODEC-modified to generate conservative predictions.

##### Mixing rule 1: MODEC-modified

MODEC-modified is a mixing rule for CFPP developed in this work by modifying the modified empirical correlation (MODEC) model by Dunn [290]. The MODEC model is a simplified empirical model based on solid-liquid equilibrium (SLE) to predict CFPP using compositional information. It is selected because of its simplicity and sufficient accuracy. However, it is not a mixing rule which could predict the property of a mixture based only on the same property of its components. Therefore, modification was made in the present work to convert the MODEC model into a mixing rule (i.e., MODEC-modified). The conversion is realized through replacing the real structural parameter (mass fraction of C16 FAME,  $y_{C16}$ ) with a pseudo parameter (pseudo mass fraction of C16 FAME,  $y'_{C16}$ ) which does not have physical meanings. The pseudo parameter for each component ( $y'_{C16,i}$ ) in the mixture could be determined from their CFPP values (CFPP<sub>i</sub>) by reversing the equation proposed by Dunn [290].

$$y'_{C16,i} = \exp \left[ \frac{1}{A_1(CFPP_i + 273.15)} - \frac{A_0}{A_1} \right]$$

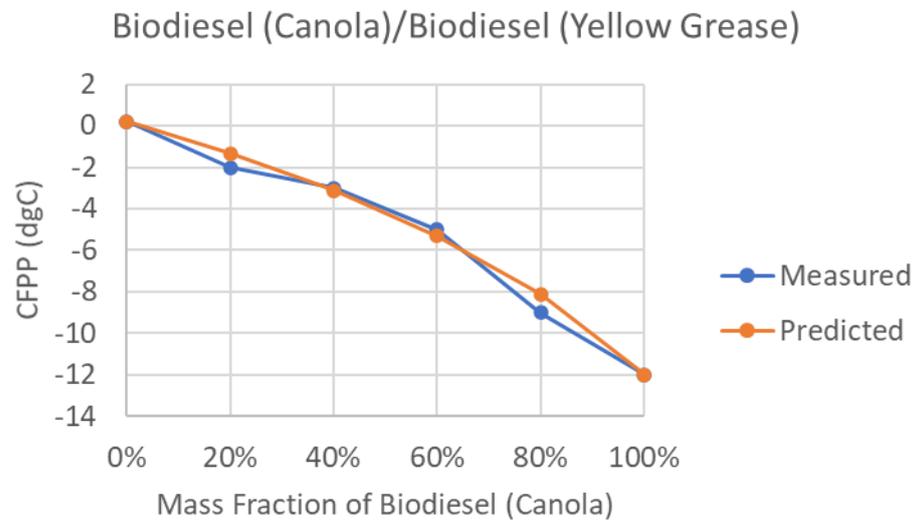
Where  $y'_{C16,i}$  is the pseudo mass fraction of C16 FAME for the  $i$ th component in the mixture,  $CFPP_i$  is its cold filter plugging point in °C.  $A_0$  and  $A_1$  are constants.  $A_0 = 0.00342$  and  $A_1 = -1.31E-4$ , according to Dunn [290]. In MODEC-modified mixing rule, we assume that the pseudo parameter  $y'_{C16}$  follows a linear mixing rule. Therefore, it could be used as a mixing index and we could derive the same parameter for the entire mixture ( $y'_{C16,mix}$ ).

$$y'_{C16,mix} = \sum_{i=1}^n Y_i \cdot y'_{C16,i}$$

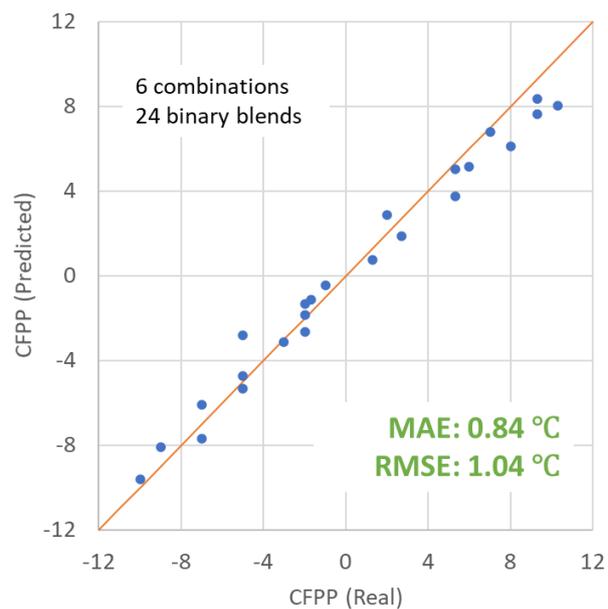
Then we could estimate the CFPP of the mixture from  $y'_{C16,mix}$  using the forward form of the same equation.

$$CFPP_{mix} = [A_1 \cdot \ln(y'_{C16,mix}) + A_0]^{-1} - 273.15$$

It is worth noting that the MODEC-modified mixing rule is only valid for FAME/FAME mixtures, as its origin MODEC model is only valid for FAME products. A comparison of CFPP for FAME/FAME mixtures between measurements and predictions by the MODEC-modified mixing rule is shown in *Figure 86*. The predictions by MODEC-modified agree well with experiments with less than 1°C of discrepancy. A validation on 6 combinations with 24 binary FAME/FAME blends, as shown in *Figure 87*, indicates a mean absolute error (MAE) of 0.84°C and a root-mean-square error (RMSE) of 1.04°C.



**Figure 86** CFPP of canola biodiesel/yellow grease mixture at various mass fraction. Experimental data from Dunn [290]. Predictions are performed using the mixing rule MODEC-modified.

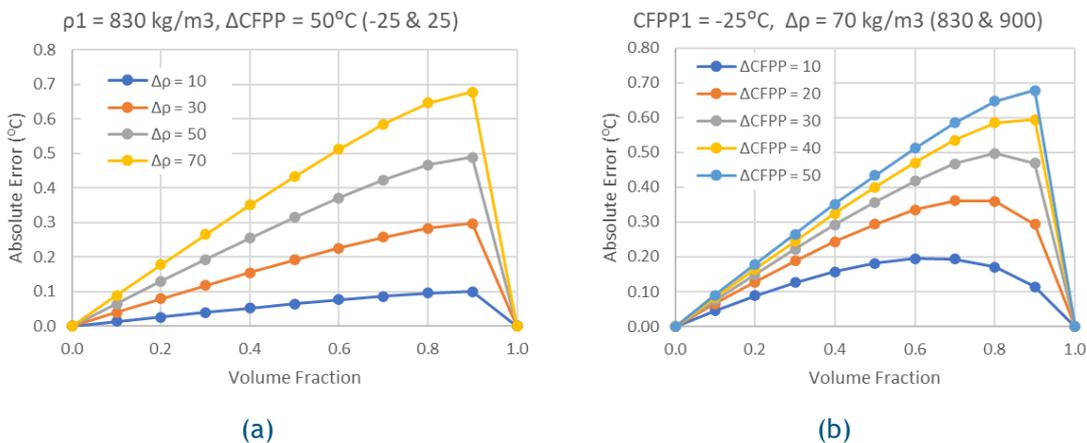


**Figure 87** Parity plot for the comparison of measured and predicted CFPP (unit in °C) for 24 binary FAME/FAME blends. Experimental data from Dunn [290]. Predictions are performed using the mixing rule MODEC-modified. MAE = mean absolute error. RMSE = root mean squared error.

Considering that volume fraction is more often used than mass fraction and also the the convenience of computation to avoid extra modification of the optimization code (introduced in Section 5.2), we need to replace the mass fraction  $Y_i$  in the above equations with volume fraction  $V_i$ .

$$y'_{C16,mix} = \sum_{i=1}^n V_i \cdot y'_{C16,i}$$

It relies on an extra approximation that the error is not significant if the density of the components are close, and inevitably it will introduce extra uncertainty. As shown in *Figure 88*, the effects of density difference were tested (maximum  $\Delta\rho = 70 \text{ kg/m}^3$ ) and CFPP difference (maximum  $\Delta\text{CFPP} = 50^\circ\text{C}$ ) on the uncertainty induced by replacing  $Y_i$  with  $V_i$ . It is found that the maximum error is about  $0.7^\circ\text{C}$  and occurs at about 90%/10% blending ratio with the maximum density and CFPP separation between the two components. Therefore, by combining the two, the overall uncertainty for the MODEC-modified mixing rule is about  $2^\circ\text{C}$  for binary FAME/FAME blends.



**Figure 88** Absolute error in predicted CFPP induced by replacing mass fraction with volume fraction in the MODEC-modified mixing rule, and its evolution with (a) density difference and (b) CFPP difference between the two components of a binary mixture.

#### Mixing rule 2: Semwal & Varshney 1995

In 1995, Semwal & Varshney [291] developed a CFPP mixing rule for diesel/diesel blends.

$$\text{CFPP}_{mix} [^{\circ}\text{R}]^{13.45} = \sum_i^n V_i^{1.03} \text{CFPP}_i [^{\circ}\text{R}]^{13.45}$$

Where  $\text{CFPP}_{mix}$  and  $\text{CFPP}_i$  are the CFPP for the mixture and its  $i^{\text{th}}$  component. The CFPP in this equation has the unit degree Rankine ( $^{\circ}\text{R}$ ) which could be converted from degree Celsius using the following equation.

$$T [^{\circ}\text{R}] = (T [^{\circ}\text{C}] + 273.18) \times 1.8$$

#### Mixing rule 3: Vrablik et al. 2019

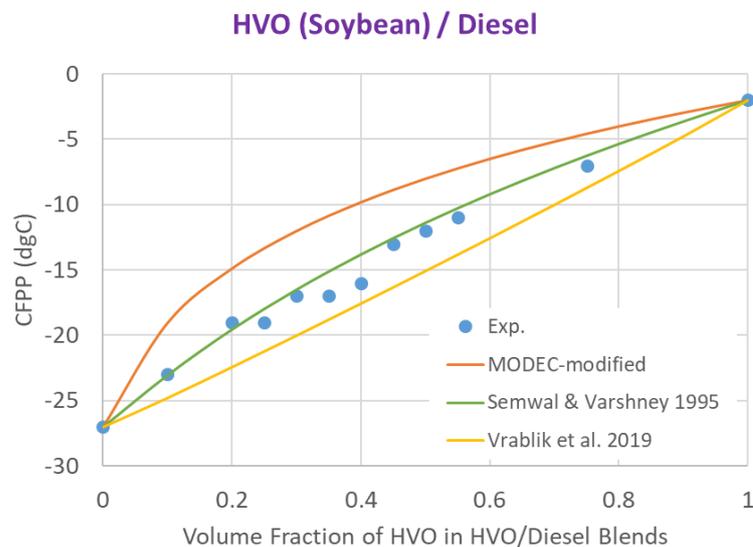
Recently, Vrablik et al. [292] proposed a new mixing correlation for diesel/diesel blends, which has the same and near to unity power exponent for both  $V_i$  and  $\text{CFPP}_i$ .

$$CFPP_{mix}[K]^{1.003169} = \sum_i^n (V_i CFPP_i[K])^{1.003169}$$

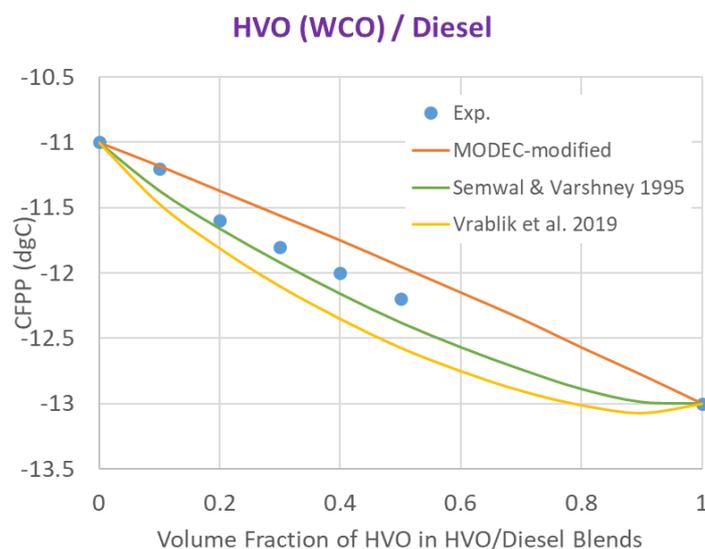
Where the CFPP are in the unit of degree Kelvin (K).

#### Comparison of the mixing rules

In this work, the interest is in the blends between renewable diesel product and conventional B7 diesel, but CFPP data for such mixtures are limited in the literature. Therefore, in this section the predictive performance of the 3 mixing rules based on HVO/diesel blends are compared as a compromise. More comprehensive validation is subject to future investigations. *Figure 89* and *Figure 90* shows such comparisons based on (i) HVO from soybean/diesel (large gap in CFPP) and (ii) HVO from WCO/diesel (small gap in CFPP) blends, respectively.



**Figure 89** Comparison of the predictions by the 3 mixing rules on the CFPP for a binary blend (HVO from soybean/diesel) with large CFPP difference between its two components ( $\Delta\text{CFPP} \approx 25 \text{ }^\circ\text{C}$ ). Experimental data from Lapuerta et al. [293]



**Figure 90** Comparison of the predictions by the 3 mixing rules on the CFPP for a binary blend (HVO from water cooking oils/diesel) with small CFPP difference between its two components ( $\Delta\text{CFPP} = 2 \text{ }^\circ\text{C}$ ). Experimental data from Sonthalia et al. [294]

It can be seen from both figures that Semwal & Varshney 1995 gives predictions closest to the measurements. MODEC-modified overestimates while Vrablik et al. 2019 underestimates. Semwal & Varshney 1995 and MODEC-modified yields greater curvature at large CFPP separation and lower curvature at small CFPP separation. However, Vrablik et al. 2019 yields the opposite trend which disagrees with what has been seen in the experimental data. In addition, the underestimated CFPP by this mixing rule gives over-optimistic predictions which is not desirable. Therefore, in the following sections for blend optimization, the mixing rule Semwal & Varshney

1995 was selected to yield normal predictions on CFPP, and the MODEC-modified mixing rule was selected to produce conservative predictions.

#### 6.4.1.4. Fuel properties

The renewable diesel products from the 7 selected pathways may have distinct properties. To facilitate the fuel definition, we generalized the products into 3 categories: (i) FT products, (ii) HDT products, and (iii) Transesterification products, as listed in *Table 44*.

**Table 44** Product categories used in the present work.

Production Pathways	Product Category
Gasification - FT	FT Products
eFuel - lignoc.	
eFuel - CO <sub>2</sub>	
Hydrotreatment Lignoc.	HDT Products
Hydrotreatment oil	
Fermentation ATD	
Transesterification	Transesterification

Nomenclature:

FT = Fischer-Tropsch, HDT = hydrotreatment, lignoc. = lignocellulose, ATD = alcohol-to-diesel

The three categories are further broken down into sub-categories by the feedstock used, in which best and worst cases are evaluated based on the 5 selected properties collected from literature data. A list of sub-categories and their properties are summarized in *Table 45*. Details of the properties are also provided in Appendix 9. The following blend optimizations will be based on these fuels and their properties.

**Table 45** Sub-categories of renewable diesel products and their properties. Green: comply with the (EU)EN590 standard (Category F). Orange: comply with the (EU)EN590-extended standard (Category F). Yellow: outside both standards.

Name	Density [kg/m <sup>3</sup> ]	Cetane Number	Kinematic Viscosity [mm <sup>2</sup> /s]	Flash Point [dgC]	Cold Filter Plugging Point [dgC]
<b>Hydrotreatment Products</b>					
HDT EC (Worst)	780	80	3.6	140	21
HDT EC (Best)	780	80	3.6	140	-44
HDT WCO (Worst)	780	71	3	42	19
HDT WCO (Best)	780	71	3	61	-11
White Diesel (WCO)	753	77	3.5	116	20
<b>Fischer-Tropsch Products</b>					
FT (Worst)	770	70	3	59	0
FT (Best)	790	70	3	59	-22
<b>Transesterification Products</b>					
TRANS EC (Worst)	876	51	5.6	130	11
TRANS EC (Best)	888	62	2.7	193	-9
TRANS WCO (Worst)	860	51(49) <sup>a</sup>	5.3	135	2
TRANS WCO (Best)	897	57	4	196	2
TRANS AF (Worst)	830	51(50) <sup>a</sup>	6.9	50	14
TRANS AF (Best)	883	60	3.5	175	-20

Nomenclature:

HDT = hydrotreatment, FT = Fischer-Tropsch, TRANS = transesterification, EC = energy crop, WCO = waste cooking oil, AF = animal fat, "white" diesel refers commonly to hydrotreatment and limited isomerisation of waste cooking oil.

<sup>a</sup> Assumed that the small gaps in CN from the standard could be compensated by additives.

#### 6.4.1.5. Base Fuel

The base fuel used in this section is B7 which has the same properties as the one used in Section 5.2. The CFPP of B7 is set to -25 °C for computation.

#### 6.4.1.6. Effect of additives

##### Additive effects on CFPP by cold flow improvers

Cold flow properties of fuels, such as CFPP, could be altered through cold flow improvers. They are usually molecules with low molecular weight, branched, and non-aromatic. [295, 296] They can change the crystallization behavior of n-alkanes [297-299], such as shape, size, growth rate, agglomeration, etc. The cold flow properties are improved, as they can inhibit the formation of large crystals at low temperature [295, 300-302] and promote the formation of small needle-shaped crystals (10-100 nm) [303].

When used for diesel and diesel/diesel blends, the reduction in CFPP ( $\Delta$ CFPP) could be in the range of 0-8 °C, but most commonly about 1-4 °C. [298] It is reported that  $\Delta$ CFPP mainly depends on the original CFPP values and n-alkane content [298]. When used in biodiesel/diesel blends,  $\Delta$ CFPP could range from -2 (negative effect) to 14 °C, but mostly commonly about 2-6 °C [295].  $\Delta$ CFPP could also depend on feedstock, diesel types, and biodiesel fractions [295]. Based on the above information, we defined two cases to facilitate the evaluation: (i) common case ( $\Delta$ CFPP = 5 °C), and (ii) best case ( $\Delta$ CFPP = 10 °C).

##### Additives for other properties

The effects of cetane number improvers were also taken into account and the common changes in cetane number (CN) were set to 5 for the simplicity of the computation. Additives for the other properties are not considered, because either the property could easily comply with the standards or additives are not available for the considered property.

##### Effects of additives used for Computation

3 cases are considered when evaluating the additive effects: (i) without additives, (ii) with additives (common case), and (iii) with additives (best case). They are summarized in Table 46.

**Table 46** The 3 cases considered for evaluating additive effects during blend optimization.

	Without additives	With additives (common case)	With additives (best case)
CFPP [°C]	0	-5	-10
CN	0	+5	+5
$\rho$ [kg/m <sup>3</sup> ]	0	0	0
KV [mm <sup>2</sup> /s]	0	0	0
FP [°C]	0	0	0

CFPP: cold filter plugging point. CN: cetane number.  $\rho$ : liquid density at 15 °C. KV: kinematic viscosity at 40 °C. FP: flash point.

#### 6.4.1.7. Software

This section uses the same in-house code as Section 5.2.

## 6.4.2. Optimisation results

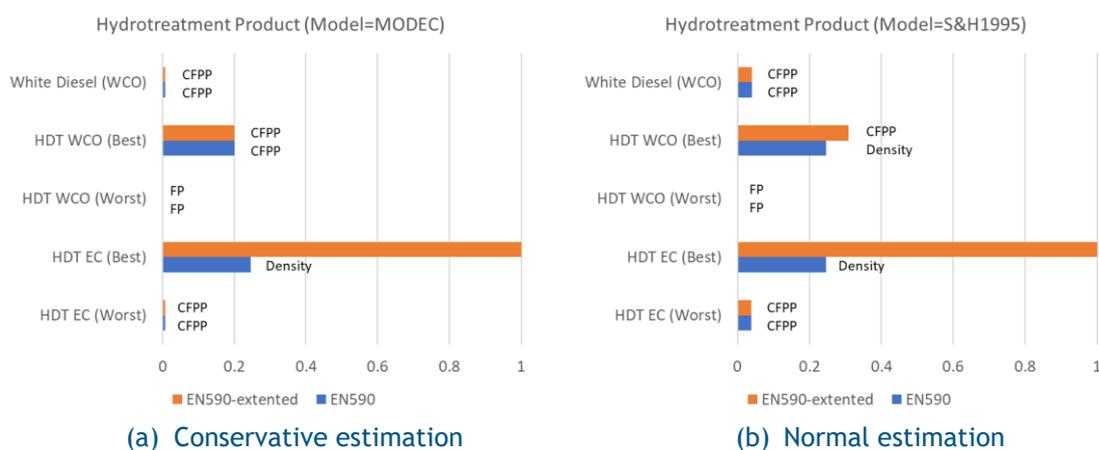
In this section, optimization based on the methods discussed above was performed to estimate the maximum volume fraction for each products to be blended with the B7 fuel. Unlike Section 5.2, only binary blends were considered, with one component to be the B7 fuel and the other one to be the renewable diesel product of interest. The results are presented in the following.

### 6.4.2.1. Maximum blending ratio without additives

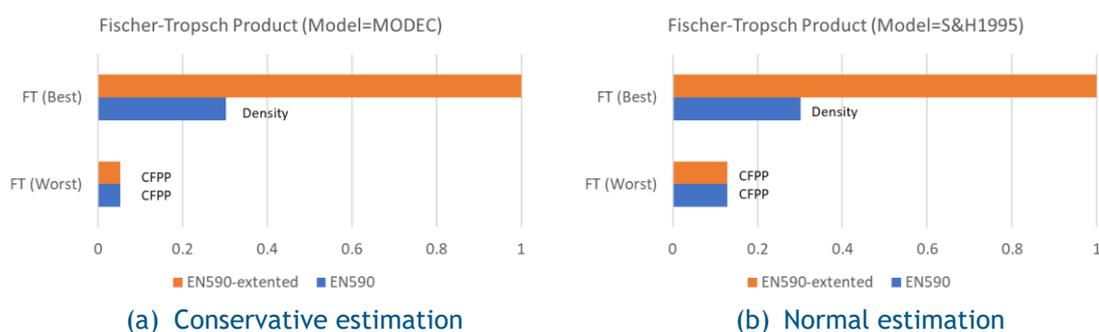
The case without additives was considered in a first instance, and the blending opportunity for each products were evaluated accordingly.

#### Scenario 1: Common European Countries

For common European countries, the selected standards are (EU)EN590 and (EU)EN590-extended which requires Class F for CFPP ( $< -20^{\circ}\text{C}$ ). Figure 91 to Figure 93 show the maximum blending ratios using both conservative and normal estimations for hydrotreatment, Fischer-Tropsch, and transesterification products, respectively.

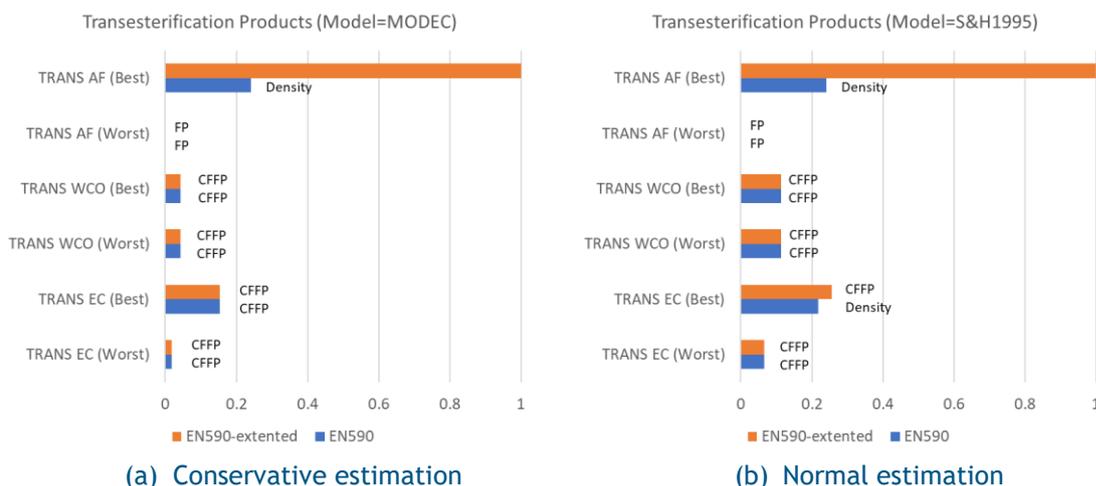


**Figure 91** Maximum blending ratio of hydrotreatment products in B7 while still complying with the EN590 and EN590-extended standards, with (a) conservative and (b) normal estimations, for common European countries (Scenario 1). The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is  $-25^{\circ}\text{C}$ . The CFPP value for the products (in the order from top to bottom) are 20,  $-11$ , 19,  $-44$ , and 21, respectively.



**Figure 92** Maximum blending ratio of Fischer-Tropsch products in B7 while still complying with the EN590 and EN590-extended standards, with (a) conservative and (b)

normal estimations, for common European countries (Scenario 1). The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -22 and 0, respectively.



**Figure 93** Maximum blending ratio of transesterification products in B7 while still complying with the EN590 and EN590-extended standards, with (a) conservative and (b) normal estimations, for common European countries (Scenario 1). The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -20, 14, 2, 2, -9, and 11, respectively.

As expected, the best cut of each product could allow more incorporation in B7 than the worst cut while still complying with the standards. The difference between best and worst cut are typically about 20-25%, regardless of conservative or normal model, for HDT and FT products. For TRANS products, it seems to depend on the feedstock. The difference is about 25%, 0%, and 15% for products from animal fats (AF), waste cooking oils (WCO), and energy crops (EC), respectively. This depends not only on the quality difference between best and worst cut, but also the limiting property.

The limiting property for most products is the CFPP, indicating that the cold flow properties of the renewable diesel products from the 7 selected production pathways are not optimal and improvement is needed for larger incorporation. Some products are limited by the flash point, which can lead to zero blending opportunity of the fuels. This is because the flash point of the base B7 fuel is on the edge of the specification.

The use of the extended standards could increase the maximum blending ratio only if the limiting property is density. For the best fuel in the 3 product categories, relaxation on density specification could lead to 100% incorporation, i.e., the best cut already comply with the extended standard. For situations where the blending is limited by CFPP, the extended standard does not bring any changes in maximum blending ratio, as it does not have relaxation on CFPP.

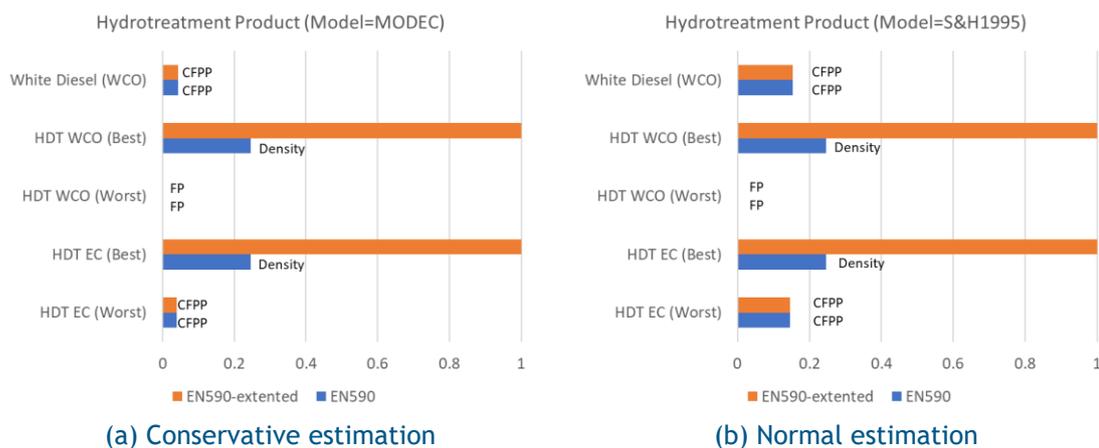
Conservative and normal estimations only show difference when blending is limited by CFPP using the conservative model, which is as expected as the two models only differ in the mixing rule of CFPP. The difference is typically 5-10% regardless of EN590 or extended standards. For the best cut of HDT WCO, blending is limited by

CFPP according to the conservative model while the limiting property is density according the normal model. The results with the extended standards show that the difference between the two model is about 10% with CFPP as the limiting property. It indicates that density comes in first as the limiting property with EN590, as it is quite strict in density.

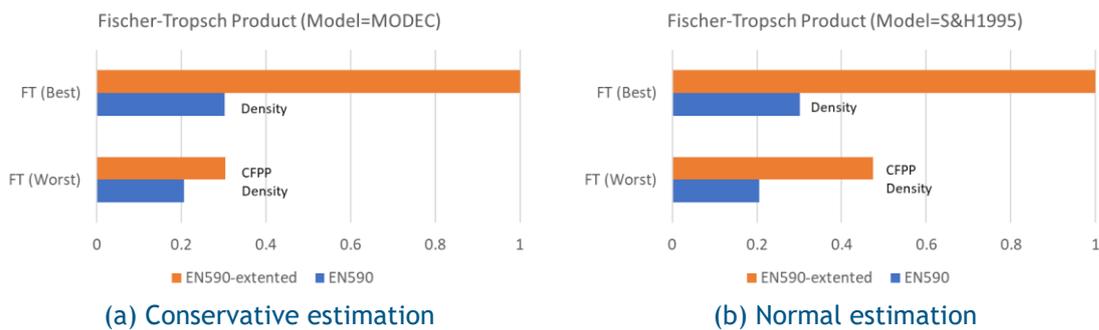
Last but not least, the maximum blending ratio for HDT products is typically 0-5% for the worst cut and about 25% for the best cut. For FT products, these numbers are about 15% and 30% for the worst and best cut. For TRANS products, the maximum blending ratio is about 0-10% and 10-25% for the worst and best cut depending on the feed stock. It indicates that FT products typically have higher blending possibilities than the other two categories.

### Scenario 2: Warm European Countries

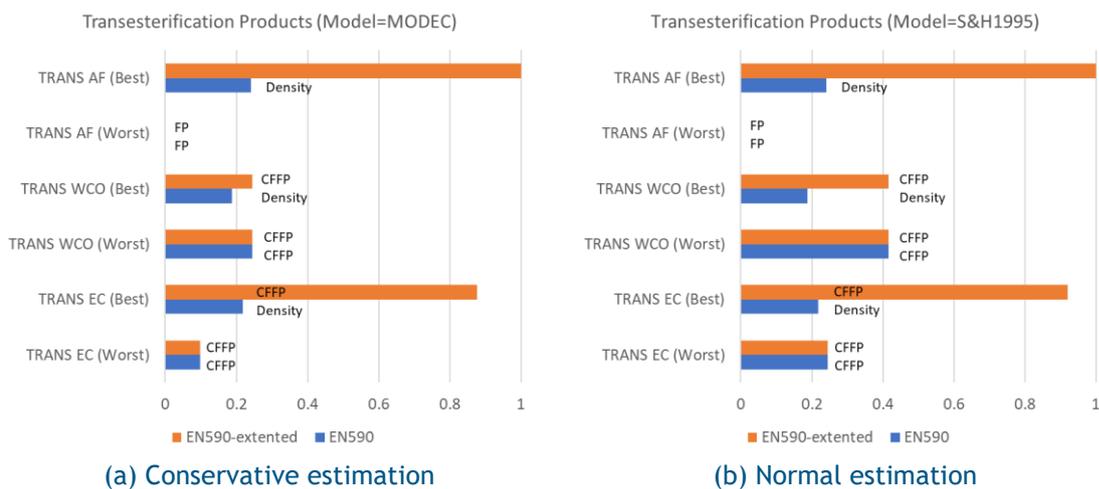
For warm European countries like Spain, the standards we selected are (ES)EN590 and (ES) EN590-extended which requires Class D for CFPP ( $< -10\text{ }^{\circ}\text{C}$ ). *Figure 94 to Figure 96* show the maximum blending ratios using both conservative and normal estimations for hydrotreatment, Fischer-Tropsch, and transesterification products, respectively.



**Figure 94** Maximum blending ratio of hydrotreatment products in B7 while still complying with the EN590 and EN590-extended standards, with (a) conservative and (b) normal estimations, for warm European countries like Spain (Scenario 2). The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is  $-25\text{ }^{\circ}\text{C}$ . The CFPP value for the products (in the order from top to bottom) are 20,  $-11$ , 19,  $-44$ , and 21, respectively.



**Figure 95** Maximum blending ratio of Fischer-Tropsch products in B7 while still complying with the EN590 and EN590-extended standards, with (a) conservative and (b) normal estimations, for warm European countries like Spain (Scenario 2). The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -22 and 0, respectively.



**Figure 96** Maximum blending ratio of transesterification products in B7 while still complying with the EN590 and EN590-extended standards, with (a) conservative and (b) normal estimations, for warm European countries like Spain (Scenario 2). The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -20, 14, 2, 2, -9, and 11, respectively.

The observations are mostly similar with those for Scenario 1, except that the relaxation of CFPP by 10 °C in warm European countries with respect to the common countries leads to significant increase in the maximum blending ratios. As the relaxation concerns only CFPP, the changes in maximum blending ratio concerns only the products whose blending is initially limited by CFPP. In other words, the relaxation does not have any effect on products limited by density or flash point. The improvement is about 10% with EN590 constraints for HDT and FT products. For TRANS products, the improvements depends on the feedstock, about 0%, 10-30%, and 0-20% for products from AF, WCO, and EC, respectively. It seems that the improvement may be more significant on TRANS products than the other two categories. For some products, such as HDT WCO (Best) and TRANS EC (Best), no improvement is estimated with EN590 as they are limited by density. But the improvement could be as significant as about 70% if the density is relaxed, i.e., with

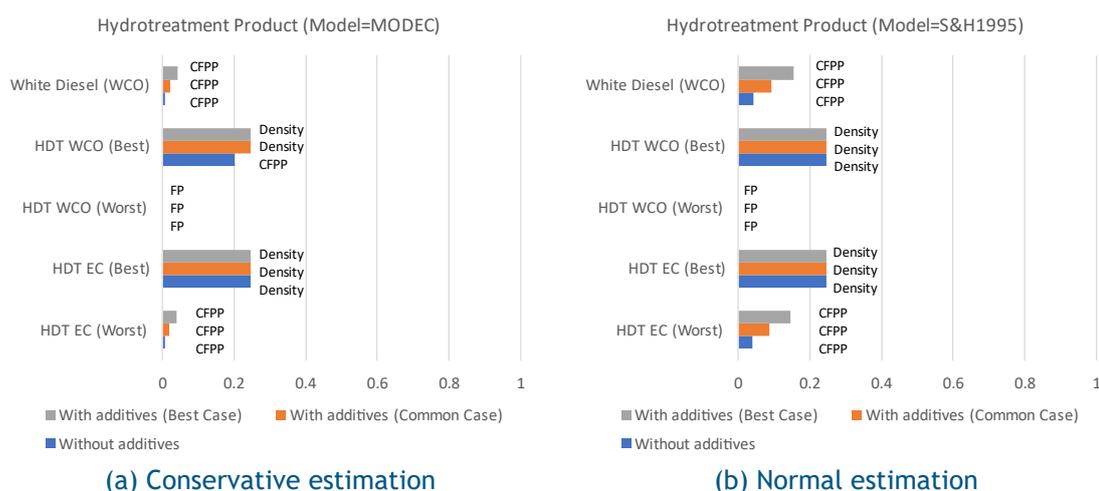
the extended standard. Therefore, it could be concluded that blending opportunity is greatly increased in warmer countries like Spain.

#### 6.4.2.2. Maximum blending ratio with additives

Additives are commonly used in fuels to improve their properties. Therefore, the maximum blending ratio is expected to increase if additives are considered. In this section, 3 cases were considered: (i) without additives, which is the same as the previous section and serves as the reference case, (ii) with additives (common case), which can improve CFPP by 5 °C, and (iii) with additives (best case), which can improve CFPP by 10 °C. Comparison between the 3 cases on the maximum blending ratio for common European countries is presented in the following. Results for warm European countries are provided in Appendix 10.

##### Scenario 1: EN590

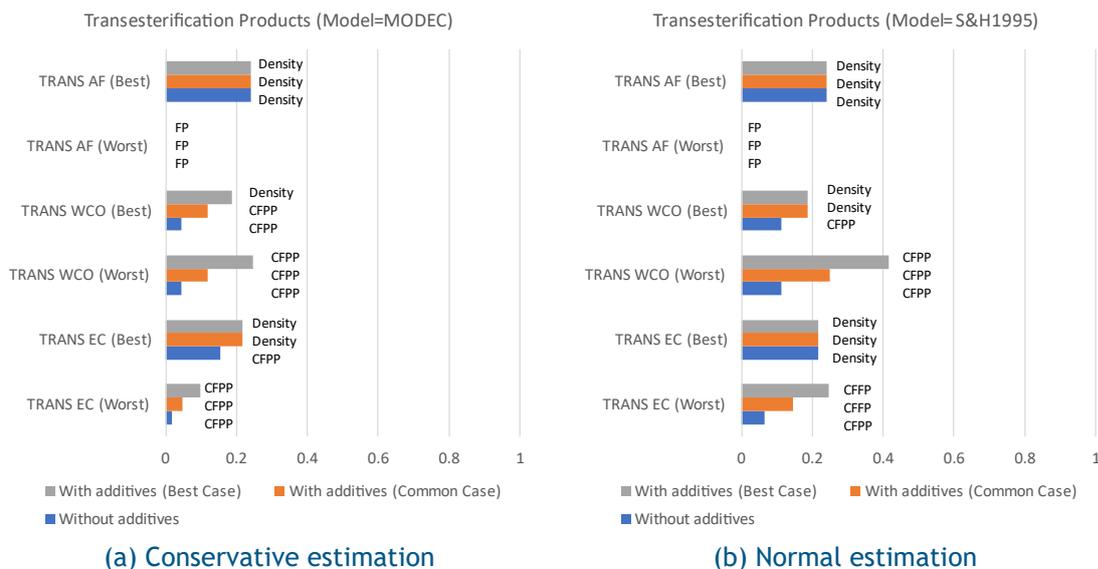
For Scenario 1, the EN590 standard is considered for common European countries. *Figure 97 to Figure 99* show the maximum blending ratios using both conservative and normal estimations for hydrotreatment, Fischer-Tropsch, and transesterification products, respectively.



**Figure 97** Maximum blending ratio of hydrotreatment products in B7 while still complying with the EN590 standard for common European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are 20, -11, 19, -44, and 21, respectively.



**Figure 98** Maximum blending ratio of Fischer-Tropsch products in B7 while still complying with the EN590 standard for common European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -22 and 0, respectively.

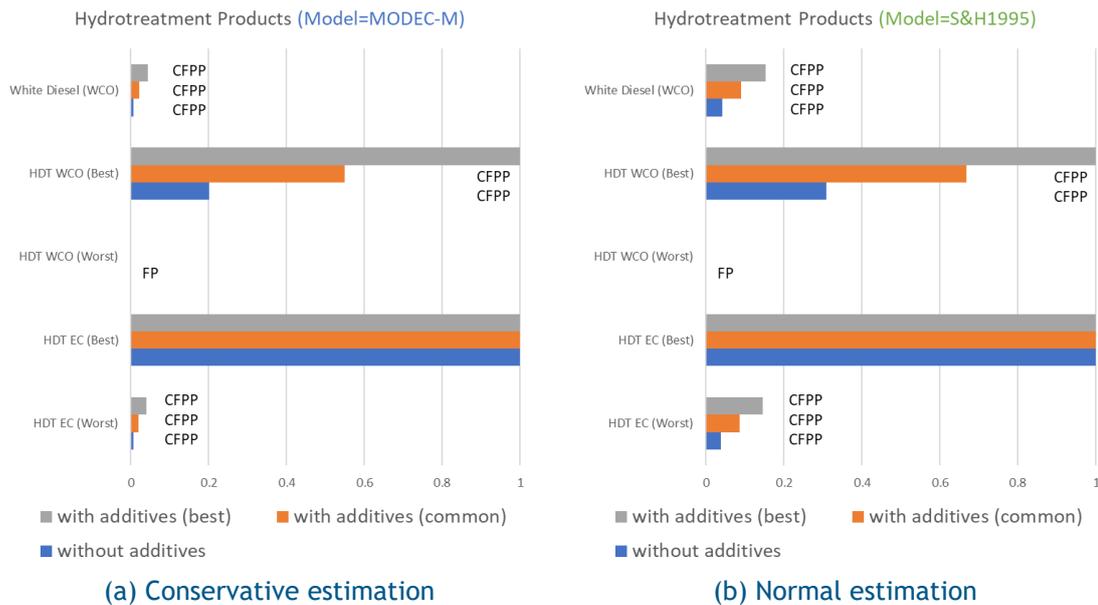


**Figure 99** Maximum blending ratio of transesterification products in B7 while still complying with the EN590 standard for common European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -20, 14, 2, 2, -9, and 11, respectively.

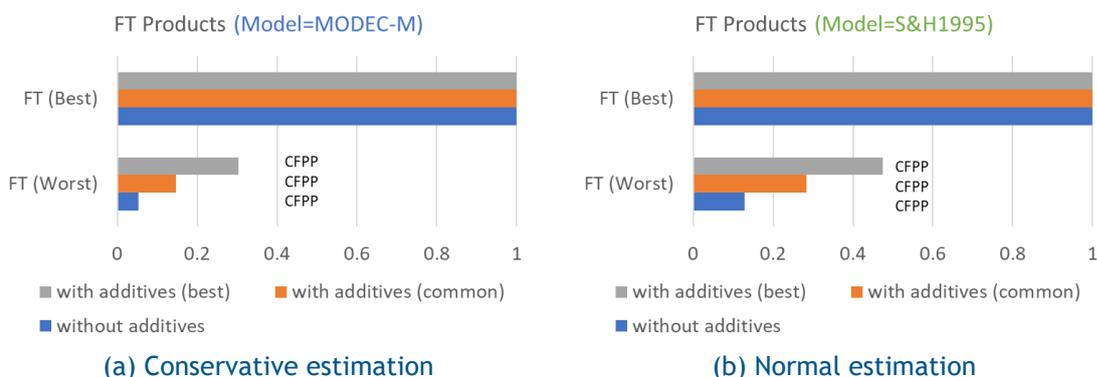
As cetane number is not limiting for all products and cases, the additives effects on maximum blending ratio is only effective through CFPP improvement. In addition, changes in maximum blending ratio by additives concern only the products whose blending is initially limited by CFPP. For HDT products, the common case (CFPP improved by 5 °C) leads to typically 2% increase in maximum blending ratio according the conservative model. More or less the same increase is observed from the common case to the base case (additional 5 °C of CFPP improvement). It indicates a potentially linear relationship between maximum blending ratio and CFPP improvement when the blending is always limited by CFPP. The increase is observed to be about 5% from the normal estimations. For FT products, with additives the limiting property changes quickly from CFPP to density. The common case is observed to increase the maximum blending ratio for the worst cut by 10% using the conservative model. It indicates that the maximum blending ratio of FT product is more sensitive to additive effects than HDT products. For TRANS products, the additive effect depends on feedstock. TRANS products from AF are not affected as they are limited either by density or flash point. The effect on products from WCO is about 7% while that from EC is about 3-6%. In addition, unlike HDT products, the relationship between maximum blending ratio and CFPP improvement is not linear, about 7% for the first 5 °C of CFPP improvement and 13% for the second, as observed from the worst cut of TRANS WCO product. In summary, using additives could lead to about 2-10% increase in maximum blending ratio with the conservative model, and about 5-13% with the normal model. The increase seems to be more effective on FT products than the others.

### Scenario 2: EN590-extended

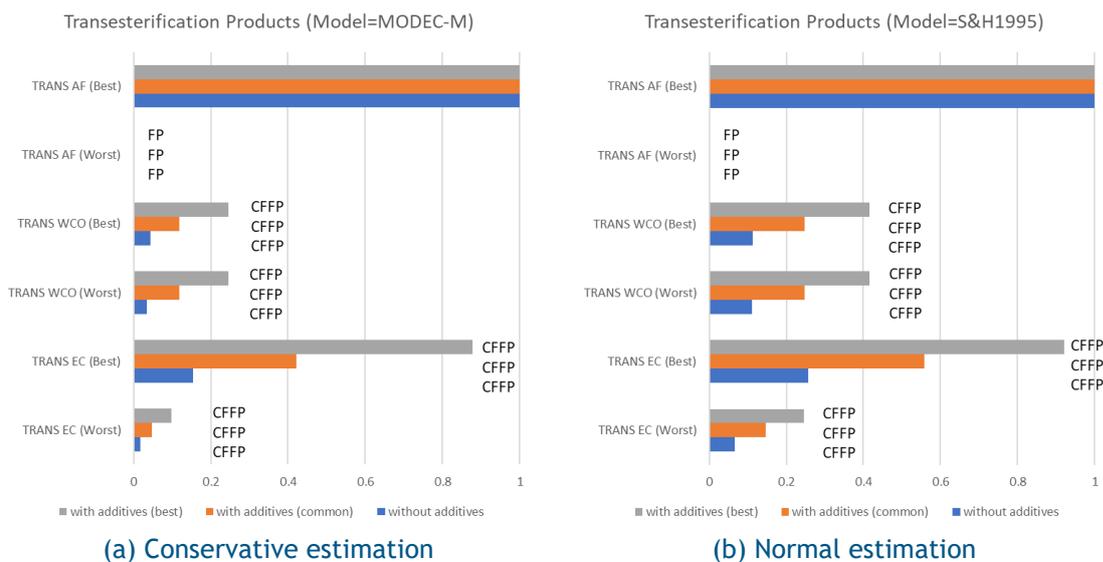
For Scenario 1, the EN590-extended standard is also considered for common European countries to evaluate the additive effect with relaxation on density. *Figure 100 to Figure 102* show the maximum blending ratios using both conservative and normal estimations for hydrotreatment, Fischer-Tropsch, and transesterification products, respectively.



**Figure 100** Maximum blending ratio of hydrotreatment products in B7 while still complying with the EN590-extended standard for common European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are 20, -11, 19, -44, and 21, respectively.



**Figure 101** Maximum blending ratio of Fischer-Tropsch products in B7 while still complying with the EN590-extended standard for common European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -22 and 0, respectively.



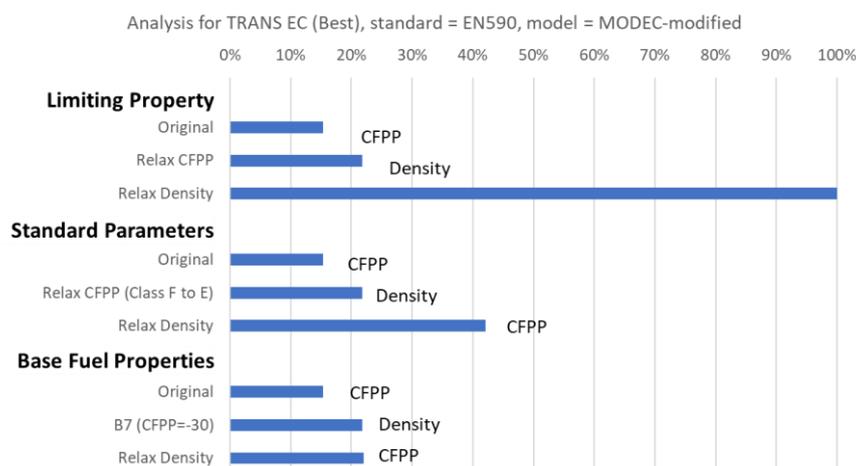
**Figure 102** Maximum blending ratio of transesterification products in B7 while still complying with the EN590-extended standard for common European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -20, 14, 2, 2, -9, and 11, respectively.

The EN590-extended standard relax the constraints on density. Therefore, maximum blending ratio for products limited by density are improved significantly, as observed in the above figures. It is found that the density relaxation also has effect on some CFPP-limiting products, not only increasing their maximum blending ratio at the reference case, but also increasing the improving effect of the additives. For the best cut of HDT product from WCO, 5 °C of CFPP improvement by the additives leads to 35% increase in maximum blending ratios even with the conservative model, while the same effect is estimated to be 2% without density relaxation (i.e., with the EN590 standard). For the best cut of TRANS EC product, the additives effect increases from 6% to about 30% by switch to E590-extended standard. Therefore, density relaxation with the extended standard could have

significant impact on the additive effects. For some CFPP-limiting products, no impact is observed with the density relaxation. This is most likely because their second limiting property is not density.

### 6.4.3. Sensitivity analysis

To better evaluate the effect of some parameters on maximum blending ratio, a simple sensitivity analysis was performed. *Figure 103* shows an example performed on the best cut of transesterification product from energy crops. The order of limiting properties is first assessed, by relaxing step by step the first limiting properties encountered. It is found the CFPP is the first limiting property while density is the second. After relaxation of CFPP and density, this product becomes fully compatible with the standard. The effect of relaxing standard parameters are also evaluated. As CFPP is relaxed by 5 °C, maximum blending ratio increases by 6%. Then density is relaxed to remove its interference, and a total increase by 27% is observed. The effect of changing the property of the base fuel is also tested. With removal of density interference, improve the CFPP of the B7 base fuel by 5 °C is observed to increase the maximum blending ratio by about 7%. Therefore, it indicates that the effect of relaxing the standard on improving maximum blending ratio is more significant than improving the base fuel.



**Figure 103** Sensitivity analysis on the effect of limiting property, standard parameters, and base fuel property on the maximum blending ratio.

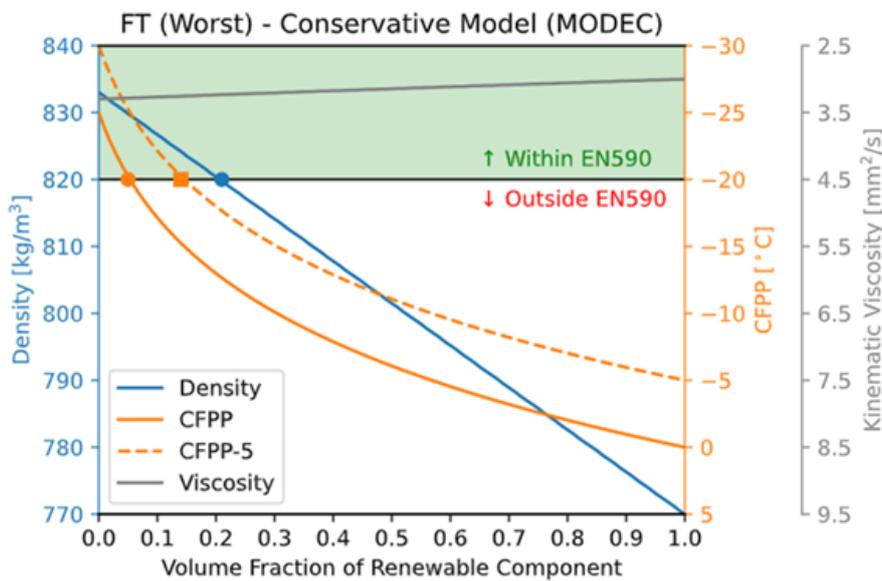
### 6.4.4. Insights to possible fuel specifications evolutions for an increased content of renewables in the diesel fuel pool

As shown in the previous section, extended specifications could lead to significant increase in the maximum blending ratio of renewable diesel products in conventional diesel fuels. However, choosing the right extent of modification could be difficult and delicate for policy makers. In this section, we aim to provide insights to the evolution of specification parameters, by estimating the limiting properties for the blends of B7 fuel with three representative renewable products.

The three selected products for demonstration are FT (Worst), TRANS EC (Worst), and TRANS EC (Best). They are selected because they are distinct in (i) density as some are lower than the lower bound of EN590 while others are higher than the upper bound, (i) CFPP (span from -9 to 11 °C), and (ii) viscosity as TRANS EC (Worst) is outside the EN590 boundaries. These characteristics could lead to different

limiting properties at different levels of incorporation. The mixing rules used in this section are unchanged compared to previous sections. For CFPP, the conservative model, MODEC-modified, is used.

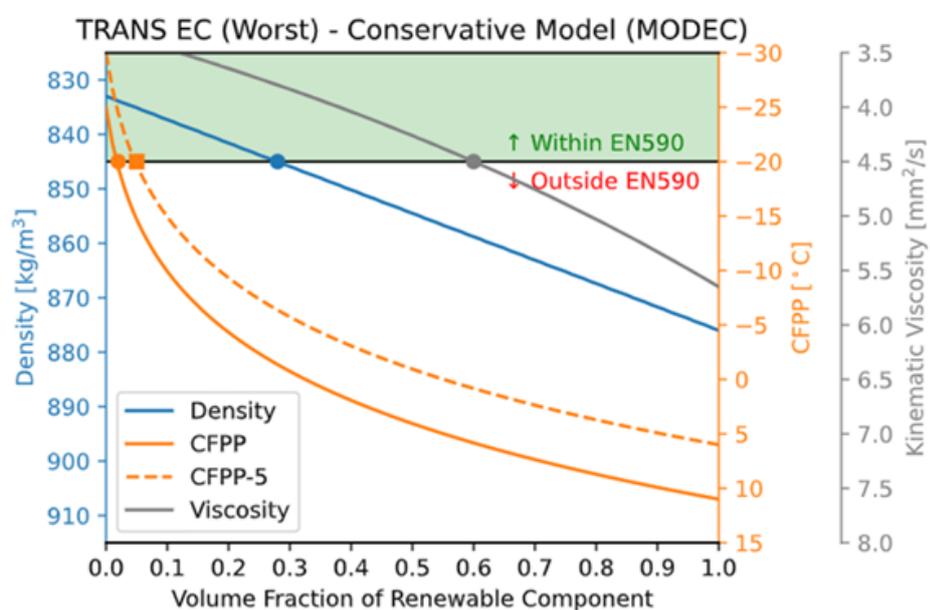
Figure 104 shows the evolution of density, CFPP, and viscosity with the incorporation ratio of FT (Worst) product in an average B7 fuel. The upper area of the black line refers to EN590 compatible blends. The intersection of the curves with the EN590 boundaries are identified with points, which indicate the maximum blending ratio limited by each property. The point with the lowest blending ratio corresponds to the max blending ratio possible while all properties comply with the specification. It can be seen that, for FT (Worst), the maximum blending ratio for all properties is about 5%, after which CFPP falls outside standards and limits further incorporation. If we consider the effect of cold flow improvers (assuming constant improvement of 5 °C), the max blending ratio can go to ~14%. At higher than 21% of incorporation, the density of the blend becomes lower than the boundary. At this point, the CFPP of the blend is -12.6 °C, already quite far from the boundary. In summary, the blend complies with EN590 when incorporation is lower than 5%. From 5% to 21%, incorporation is limited by CFPP. Higher than 21%, the incorporation is limited by both CFPP and density. The viscosity is not a limiting property for this case. In addition, if 50% of incorporation is targeted, it is necessary to extend the CFPP requirement by 14 °C (to -6 °C) and the lower bound of density requirement by 20 kg/m<sup>3</sup> (to -800 kg/m<sup>3</sup>).



**Figure 104** Estimated evolution of density, CFPP, and viscosity with the incorporation ratio of the FT (Worst) product in B7 fuel, compared with EN590 boundaries. The dashed curve “CFPP-5” provides estimates of blends with cold flow improvers, assuming the improvement of CFPP is 5 °C and constant regardless of blending ratio. The black horizontal line indicates the EN590 boundaries where the upper area (density > 820 kg/m<sup>3</sup>, CFPP < -20 °C, and viscosity < 4.5 mm<sup>2</sup>/s) corresponds to properties complying with EN590. The points indicate the max blending ratio limited by each property individually.

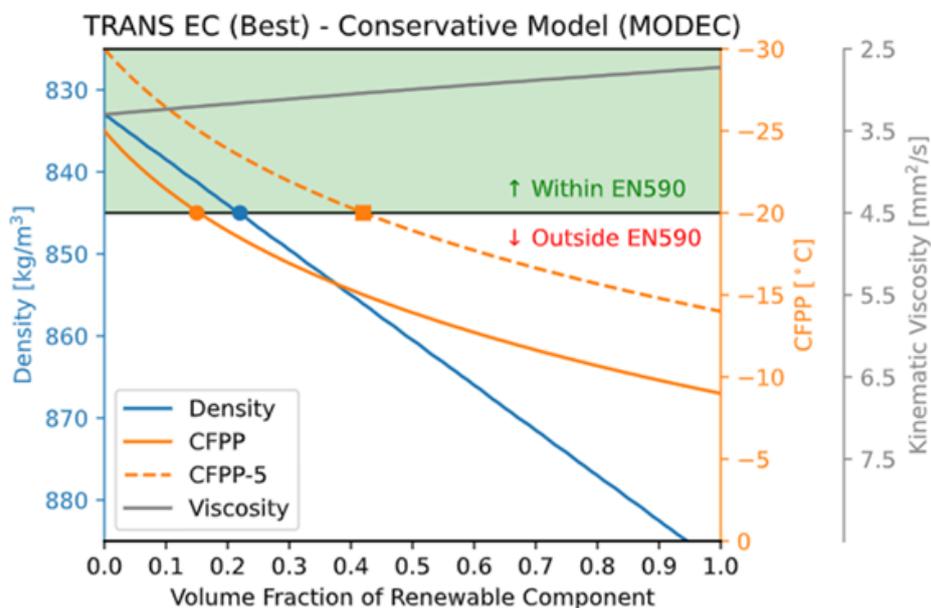
Figure 105 shows the same plot for TRANS EC (Worst) product, for which the viscosity could become a limited property at some point. The max blending ratio complying with EN590 for this product is very small and limited by CFPP, about 2%

without additives and 5% considering cold flow improvers. Density only becomes a limiting factor at blending ratio higher than 28%, at which the CFPP of the blend is about  $-1\text{ }^{\circ}\text{C}$ . At incorporation higher than 60%, viscosity becomes higher than the upper boundary, where the CFPP and density of the blend are about  $6\text{ }^{\circ}\text{C}$  and  $860\text{ kg/m}^3$ . If 50% of incorporation of this product is targeted, it would be necessary to modify the upper bound of density requirement to by  $10\text{ kg/m}^3$  (to  $855\text{ kg/m}^3$ ) and the CFPP requirement by  $24\text{ }^{\circ}\text{C}$  (to  $4\text{ }^{\circ}\text{C}$ ). In summary, for the incorporation of TRANS EC (Worst) in B7, the max blending ratio is 2%; from 2 to 28%, the incorporation is limited by CFPP; from 28 to 60%, it is limited by both CFPP and density; higher than 60%, the incorporation is limited by CFPP, density, and viscosity.



**Figure 105** Estimated evolution of density, CFPP, and viscosity with the incorporation ratio of the TRANS EC (Worst) product in B7 fuel, compared with EN590 boundaries. The dashed curve “CFPP-5” provides estimates of blends with cold flow improvers, assuming the improvement of CFPP is  $5\text{ }^{\circ}\text{C}$  and constant regardless of blending ratio. The black horizontal line indicates the EN590 boundaries where the upper area (density  $< 845\text{ kg/m}^3$ , CFPP  $< -20\text{ }^{\circ}\text{C}$ , and viscosity  $< 4.5\text{ mm}^2/\text{s}$ ) corresponds to properties complying with EN590. The points indicate the max blending ratio limited by each property individually.

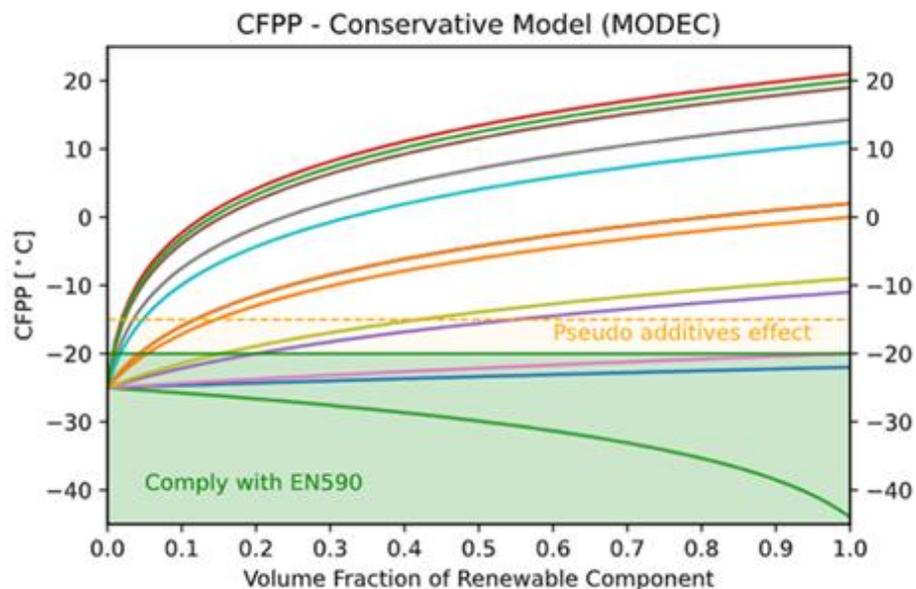
Figure 106 shows the same plot for TRANS EC (Best) product, for which the viscosity is not a limiting property, similar to FT (Worst). The max blending ratio complying with EN590 for this product is higher than the other two, about 15% without additives, limited by CFPP. If considering cold flow improvers, the max blending ratio cannot increase to the 42% limit for CFPP, because it will first meet the limitation by density. Therefore, the maximum blending ratio with additives is about 22%, limited by density. At this point, the CFPP with additives is about  $-18.5\text{ }^{\circ}\text{C}$ . At the 42% limit for CFPP with improvers, the density is about  $856\text{ kg/m}^3$ . If 50% incorporation is targeted, it is necessary to modify the standard by  $6\text{ }^{\circ}\text{C}$  (to  $-14\text{ }^{\circ}\text{C}$ ) for CFPP and  $15\text{ kg/m}^3$  (to  $860\text{ kg/m}^3$ ) for density.



**Figure 106** Estimated evolution of density, CFPP, and viscosity with the incorporation ratio of the TRANS EC (Best) product in B7 fuel, compared with EN590 boundaries. The dashed curve “CFPP-5” provides estimates of blends with cold flow improvers, assuming the improvement of CFPP is 5 °C and constant regardless of blending ratio. The black horizontal line indicates the EN590 boundaries where the upper area (density < 845 kg/m<sup>3</sup>, CFPP < -20 °C, and viscosity < 4.5 mm<sup>2</sup>/s) corresponds to properties complying with EN590. The points indicate the max blending ratio limited by each property individually.

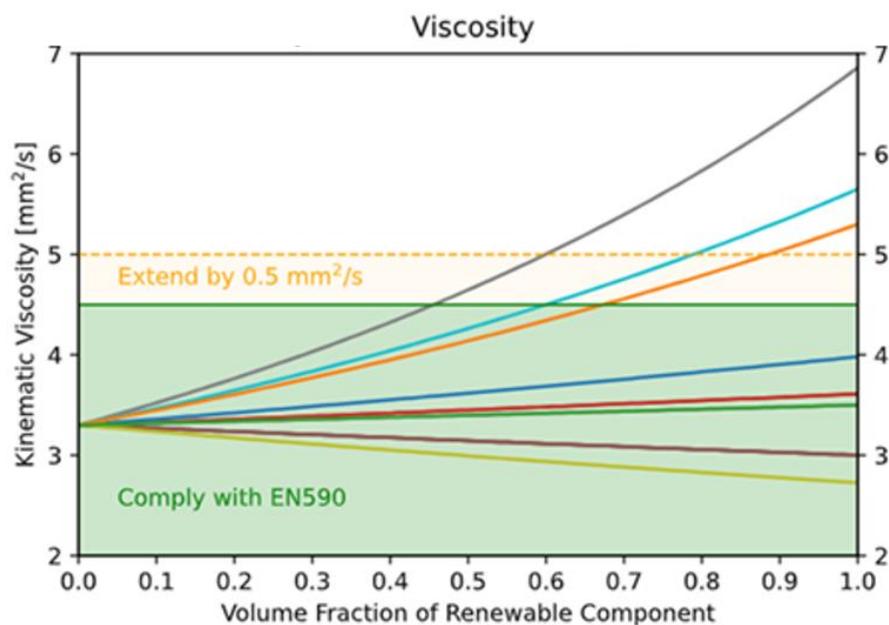
In the above examples, it is observed that various properties could limit the incorporation of biocomponents and their relative order varies for different products. Therefore, it could also be helpful to look at each property separately.

Figure 107 shows the evolution of CFPP with blending ratio for all the products summarized in the present work. It can be seen that for biocomponents with poor cold flow properties, CFPP increases rapidly at low blending ratio, limiting the incorporation ratio to only low concentration. This behavior also makes CFPP the most limiting property, comparing to density (linear mixing rule) and viscosity (slower increase at low incorporation). If one assumes an average CFPP increase with cold flow improvers of about 5 °C (equivalent to 5 °C increase in EN590 limit as mentioned in the figure caption), it can be seen that considerable impacts on max blending ratio are only seen for products with negative CFPP. For products whose CFPP is high, the effect of cold flow improvers on max blending ratio is negligible. In addition, CFPP is an important property ensuring the cold flow behavior and safe operation. Therefore, adjusting the standards for CFPP may be difficult. Instead, focusing on improving the cold flow properties of renewable diesel products through various means (e.g. isomerization of paraffinic compounds) is potentially an important lever for maximizing the use of sustainable products.



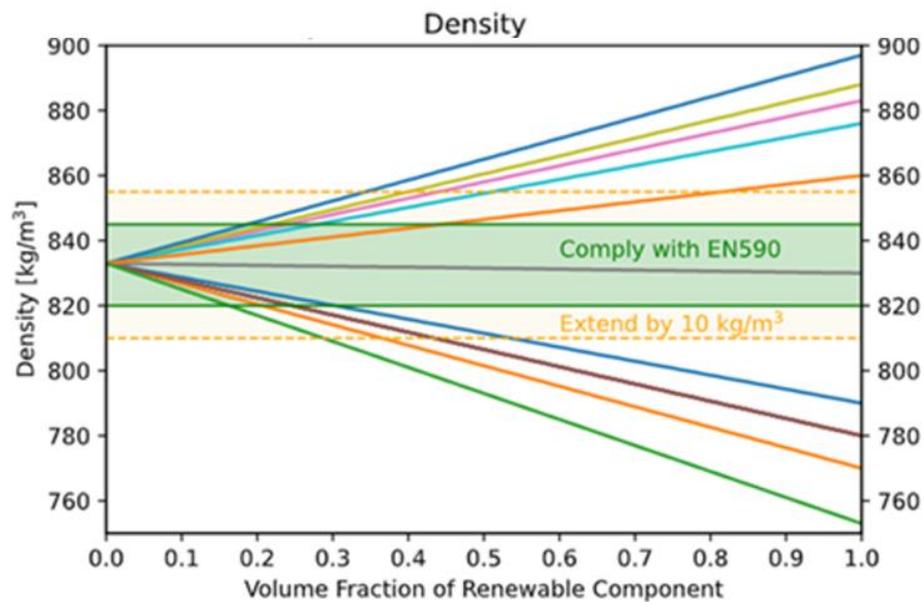
**Figure 107** Estimated evolution of CFPP with the incorporation ratio for all the renewable diesel products used in the present work, with indications of EN590 boundary (Class F, -20 °C). Legends are not provided in the figure but they could be identified by checking the property of pure products (i.e., the values at 100% incorporation ratio). The orange line and area demonstrates the effect of additives, which is arbitrarily chosen as 5 °C reduction in CFPP of the blend and whose effect on max blending ratio is equivalent to 5 °C increase in EN590 limit.

Figure 108 shows the evolution of kinematic viscosity with blending ratio. It shows that viscosity can become the limiting property only for certain fuel pathways. In addition, only a minor revision of the specification in the upper bound of viscosity, e.g., + 0.5 mm<sup>2</sup>/s (arbitrarily chosen for demonstration only), could allow very high incorporation rates for most of the products.



**Figure 108** Estimated evolution of kinematic viscosity with the incorporation ratio for all the renewable diesel products used in the present work, with indications of EN590 boundaries (min 2.0 and max 4.5 mm<sup>2</sup>/s). Legends are not provided in the figure but they could be identified by checking the property of pure products (i.e., the values at 100% incorporation ratio). The orange line and area demonstrates the effect of extending the EN590 boundary, which is arbitrarily chosen as 0.5 mm<sup>2</sup>/s increase of the upper bound.

Besides CFPP, the most important limiting property is density. As shown in *Figure 109*, the range of EN590 is narrow for renewable diesel products. Only one product is fully compatible. The other either cross the upper or the lower boundary. Therefore, in order to increase the incorporation ratio of renewable compounds, adjustment to both the upper and lower boundaries of EN590 would be necessary due to the large variety of renewable diesel products. As can be seen from *Figure 109*, their maximum blending ratios complying with EN590 ranges from 15% to about 45%. As density follows a linear mixing rule, the effect of relaxing EN590 boundaries could be well predicted. Extending the limits by  $\pm 10$  kg/m<sup>3</sup> (arbitrarily chosen for demonstration only) could lead to increase in the maximum blending ratio by about 15-25% (best case by 35%). Adjustment to EN590 boundaries for density is necessary to significantly improve the incorporation of renewable diesel products in B7 fuels.



**Figure 109** Estimated evolution of density with the incorporation ratio for all the renewable diesel products used in the present work, with indications of EN590 boundaries (min 820 and max 845 kg/m<sup>3</sup>). Legends are not provided in the figure but they could be identified by checking the property of pure products (i.e., the values at 100% incorporation ratio). The orange lines and areas demonstrate the effect of extending the EN590 boundary, which is arbitrarily chosen as 10 kg/m<sup>3</sup> extension of both upper and lower bound.

In summary, the current work evaluates to which extent the main renewable fuel pathways could potentially be incorporated in an average B7 fuel. It also provides an overview of the potential incorporation rates once the EN590 boundaries are extended. This contributes to better assess the sensitivity to the key identified properties. In this context, CFPP is the first limiting property for most renewable diesel products, while density is the second limiting property. Viscosity is usually not a limiting parameter. Updating EN590 limits would require a dedicated work, including an experimental verification of the blending laws used in this work, and considering both logistic and vehicle operational constraints, which is beyond the scope of this study.

#### 6.4.5. Summary and conclusions

In this section, blend optimization was performed to estimate the maximum blending opportunity for each fuel from the selected production pathways. In total 4 standards were used to take into account the cold flow properties, extended density and viscosity, and climatic difference in European countries. Information on the properties of the fuels are collected from the literature and summarized according to 3 product categories. 2 mixing rules for CFPP were identified to provide normal and conservative estimations.

Based on the optimization results, it is demonstrated that density and cold flow property (CFPP in this case) are the main limiting properties preventing higher incorporation ratio of renewable products. The main advantage of the extended standard is to be less density-dependent. For the best-quality product in each categories, the limiting property is usually only density, which can be relaxed using the extended standard. The difference between the conservative and normal estimations is typically 5-10% in max blending ratio, for products whose blending is

limited by CFPP. In other cases, CFPP is the main constraints which limits greatly the incorporation rate. Therefore, it is necessary to improve the cold flow properties of these renewable diesel products.

The cold flow properties could be improved with additives. It is found that the additives affect only the products whose blending ratio is limited by CFPP. When density is not limiting, the use of cold flow improvers could increase the max blending ratio by about 5-20% depending on the product types. The increase is relatively lower for products with higher CFPP values. For the best-quality products, density is either the first constraint or it becomes quickly the limiting property once cold flow improvers are used.

## 6.5. RESEARCH AND OPTIMISATION NEEDS

The literature review performed in this study enabled to identify seven processes that can produce either FAME or paraffinic fuels: fermentation (alcohol to diesel), gasification with FT, paraffinic e-fuel from CO<sub>2</sub> capture or paraffinic e-fuel from lignocellulose, lignocellulose hydrotreatment, triglycerides hydrotreatment and transesterification. No data could be found regarding lignocellulose hydrotreatment.

Previous sections discussed LCA, TEA as well as blending limitations or opportunities for the different pathways. This section reports the main research and optimisation needs that were identified during the literature review analysis.

First, it should be emphasized that several research needs identified for “novel components” (see section 5.3) are also present for FAME and paraffinic components. Indeed, Figure 46 suggests a research and optimisation need to better **assess resource availability and sustainability**.

The resource availability for FAME and paraffinic products is discussed in this report. Based on the literature review, a maximum potential of about 37% of the energy demand for distillates in the transport sector could be addressed with renewable fuels (EU resources and demand). To unlock this potential, the technology needs to be upscaled to industrial level, the impact on biodiversity must be evaluated, the corresponding supply chain (feedstock mobilisation) must be available by then, the regulations/incentives must be targeted properly and a (profitable) business case must be elaborated.

Regarding the sustainability of the different energy pathways, their environmental impacts mostly refer to GHG emissions. However, other impacts such as land use, biodiversity loss, water requirement, etc, are quite frequently not assessed.

Overall LCA results differ in the literature for a given energy pathway. For example, the results will depend on the allocation chosen in the study. Standard methodological choices could be proposed to enable energy pathways comparison.

Second, for most of the processes, further improvement of the GHG emissions could be reached if carbon capture and/or green hydrogen were to be implemented. Both the environmental and economical aspects of these developments would be of interest. The literature also highlights a few co-processing options enabling the reduction of GHG emissions from conventional refineries. If the studies indicate a potential to these solutions, further specific refinery case study would be required concerning detailed technical, LCA and TEA analysis. Finally, the fermentation pathway toward distillate mostly refers to kerosene production and not necessarily

to diesel fuel. Assessing the benefits or limitations in terms for example of LCA/TEA is required.

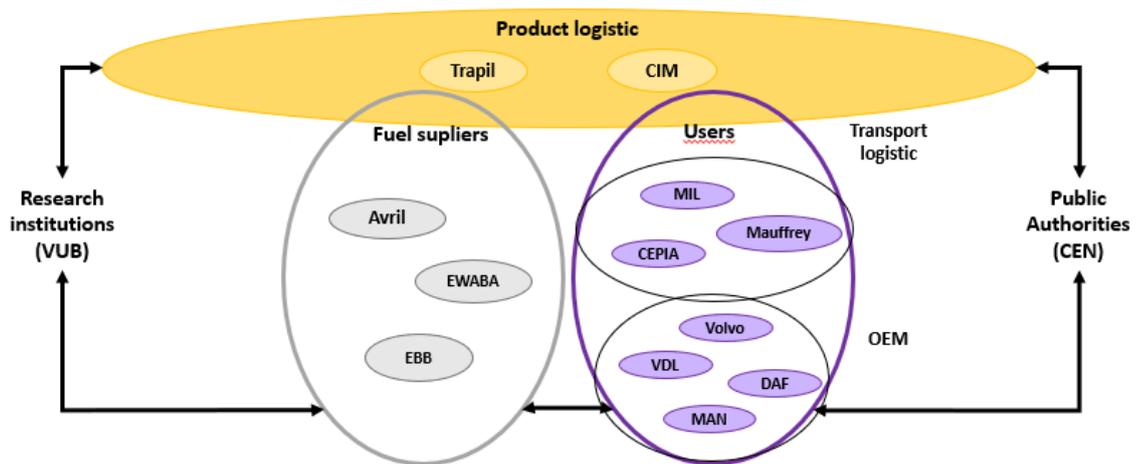
Third, FAME and paraffins chemical properties depend on the selected energy pathway. Several research and optimisation needs were thus highlighted. Density and cold flow property (CFPP in this case) are the main limiting properties preventing higher incorporation ratio of renewable products. Consequently, process optimisation to approach EN590 boundaries for both properties would be required to increase the incorporation rates. In addition, this study uses different models to evaluate the blending properties of FAME or paraffinic components with conventional fuel. Models validation range is rather limited. Paraffins and FAME blends or the use of additivations are not necessarily considered in the literature for such mixtures. This could be further investigated to better assess the limitation of sustainable blends.

## 7. INTERVIEWS SESSIONS

### 7.1. INTRODUCTION

On behalf of CONCAWE, interviews were carried out to discuss about the challenges/opportunities related to the development of low carbon fuels available by 2030.

The Survey was launched in June 2021 and was open for about 8 weeks. Invitation for interview session was sent to target stakeholders with expertise in related areas of interest to the study. The list of participants and their related area of expertise is illustrated Figure 110.



**Figure 110** Stakeholders mapping illustrating the list of participants and their related area of expertise

This summary of the interview sessions is intended to provide an overall view of the responses received. Overall, 15 stakeholders responded to the survey. Their distribution across the different area of expertise is also illustrated Table 47.

**Table 47** Analysis of responses by type of stakeholder

Stakeholder category	No. of responses	%
Biofuel associations & prod.	3	20%
OEM/Users	7	47%
Product logistic	2	13%
Public authorities	2	13%
Research/Engineering institutions	1	7%
<b>Total Respondents</b>	<b>15</b>	<b>100%</b>

The survey questionnaire comprised 20 questions related to the main findings of this literature review. Respondents had the option to respond only to the questions within their own area of expertise. This was to account for the breadth of the topics covered - it was recognised that respondents will not necessarily have expertise/knowledge across all areas.

Overall, respondents provided an answer to most of the questions in the survey as well as provided insightful comments to explain the reasoning behind their views.

The following sections describe the results of this consultation and are broken down into two parts:

- Open questions related to fuel production pathways, fuel/engine adequacy or challenges/limitations for novel renewable fuel development;
- Multiple choice questions in order to evaluate the potential competitions between low carbon liquid fuels and other routes.

It should be emphasised that the views presented can only be associated to respondents to this specific consultation. It does not necessarily reflect the view of each organization. In addition, the provided answers remain anonymous.

## 7.2. INTERVIEW SUMMARY

### 7.2.1. Part 1: Open questions regarding fuel production pathways, fuel/engine adequacy, challenges, and limitations

This first section deals with the open-questions and provides a summary of the different answers. It should be noted that since these are open questions, the summary provided for each question below may sometimes include comments that were actually shared in another question.

*“Question 1. Many parameters are considered once we deal with advanced resources. Do you see any impact or challenge related to the resources that should be addressed through novel directives?”*

The availability of resources is a major concern for most of the interviewees followed by environmental considerations (sustainability, biodiversity, emissions, etc). For example, it is mentioned that the use of waste animal fat can be encouraged but with limited availability. Moreover, additional constraints could emerge due to the competition of demand amongst different industrial applications. The integration of renewable resources might require more and more the coexistence with fossil products. This requires a certain flexibility to accommodate to a variable resource availability. Under these conditions, renewable fuels would represent a partial decarbonation solution. In any case, the guaranty of sustainability of products is essential.

*“Question 2. FAME, HVO and ethanol are the most developed energy pathways today even if they mostly refer to conventional biofuels (resources being in competition with food). Other than FAME or paraffinic fuels, do you expect other kinds of renewable fuels to be used, even marginally, by 2030?”*

About a third of the interviewees does not expect other kinds of renewable fuels to be used, even marginally, by 2030 considering that most of the trucks will be still ICE-based. Others mentioned different options including in that order biogas, e-fuel, alcohols, H<sub>2</sub> combustion and fuel cell and finally NH<sub>3</sub>.

*“Question 3. Regarding the energy pathways identified in this study (dioxolane derivatives, dibutoxymethane and DNPE), do you have any comment on either the resources/processes or fuel characteristics?”*

Most of the responses were not addressing specific concerns or advantages related to these three fuel production pathways even if each of them were actually briefly

described during the interview. Instead, more general comments were shared in order to highlight the potential limitations related to the introduction of novel fuels. The summary is provided below.

The introduction of new compounds could be of concern at different levels from fuel logistics (storage, transport and distribution) to vehicle operation. Evaluation of products properties is thus of first order as it should demonstrate that they can be operated safely. Indeed, the experience on biodiesel has highlighted the importance of validating the compatibility of new compounds (cold operation, stability, and tendency to generate deposits during fuel logistic and/or engine operation). Therefore, most of the answers actually underline the need for a wide validation by different stakeholders once the introduction of new compounds is foreseen.

The second aspect that is highlighted refers to the profitability and the sustainability of the novel option. Both parameters are essential as they refer to the product price, the demand and its evolution with time, and finally the environmental impact which can impact political and industrial trendover time.

Finally, fuel/engine co-optimisation is highlighted through references to the need for a fuel that enables a certain flexibility or adaptability with current fleet. In this context, the introduction of new compounds would require validating blending rules and product quality (novel contaminants/emissions increase?), as interviewees have expressed knowledge of reduced correlation with certain compounds, as is for example the case for cetane estimation, and the efficiency of certain lubricity additives. It should also be confirmed that energy density remains reasonable.

*“Question 4. Current biofuel production mostly relies on large biorefineries with discussions regarding co-processing. Do you expect smaller production sites to become significant and what would be the key challenges to develop them?”*

Some participants have commented that smaller production plants are interesting solutions for upstream pretreatment of resources. They could also contribute significantly to the development of local economic activity and favor energy security. Beyond economic concerns, one of the main application constraints of multiple small plants for the processing of final product is ensuring quality control. This should be established to facilitate supply chain integrity.

The constraints around resource availability are mentioned but at the same time if fuels are considered as drop-in and do not require specific storage facility this should not be an issue.

Interviewees expect that co-processing will be a natural transformation of current refineries, combined with the introduction of e-fuels or oxygenated compounds as relevant alternative fuels. It is possible that these renewable fuels will be aimed at the aviation and maritime sectors, which could therefore lead to competition with long-haul trucks, depending on the fuel properties.

Finally, a major challenge is related to the required time scale to develop and/or expand the production to significant and economically feasible renewable products.

*“Question 5. What would be the specifications for which an evolution would be acceptable or required to accelerate low carbon fuel incorporation?”*

Answers to this question were not only addressing specific properties but also providing comments regarding the possibility to develop a new specification for a given fuel. The main items discussed are provided below.

The stability and material compatibility are properties that should be respected, considering the EN590, or tightened compared to current specifications, for any novel fuel. Indeed, most of the participants said that any new compound formulation should not constrain the use of conventional fuels, hence ensure a certain flexibility.

Concerns have been expressed over storage and usage behaviour of these fuels, such as cold properties, corrosion performance, and abrasive potential.

According to most interviewees, the density is a property that could have a lower limit. The fuel composition could also evolve to allow more oxygenated products and could be updated to be less restrictive to the presence of synthetic fuels. Finally, distillation and lubricity limits could be modified to allow for more flexibility, but discussions are less mature.

Overall, the modification of current specifications remains challenging but some participants mentioned that it should be evaluated if it enables the introduction of sustainable compounds. Nevertheless, new product specifications lead to complexity and have a cost impact on the logistics, both for the OEMs as well as trucks owners. Such solutions would require high investment and this could slow their integration. However, if a fossil fuel ban is to be introduced, a new specification for low carbon fuels (e.g. e-fuels) could be a solution to counterbalance difficulties encountered by other none exhaust emitting technologies (electrification, H<sub>2</sub>).

*“Question 6. What modifications would be acceptable to facilitate the incorporation of a novel biofuel? (engine hardware, technical constraints within your activity, etc)”*

The first item cited by several participants is that modifications could be accepted only when the market size is big enough. Under such circumstances, they mentioned that modifications related to fuel properties (energy density, flash point, lubricity, viscosity) could be acceptable.

It is recommended by several participants that engine modifications should not be dictated by fuel producers, but driven by other constraints and driven by OEMs, as are emissions and engine efficiency improvement. Currently, the focus on electrification and hydrogen usage for the road transport sectors leads to limited incentives (economical and logistical) for thermal engine improvements or updates.

*“Question 7. If OMEx were assessed to be a low-carbon fuel / carbon-neutral fuel, would you develop an adapted or dedicated solution (combustion system, storage system, ...)?”*

The stakeholders were quite sensitive to economic returns. They would develop dedicated solution for OMEx only when the fuel production and supply chain is mature enough and the business is profitable. Many questions remain unanswered, including sourcing, storage, logistics and emissions.

According to the interviewees, liquid fuels will possibly remain the main option for heavy duty applications in the near to mid future, despite political communications

encouraging an early change. Reasons for this are the complexity, investment and logistics required for a full conversion of the energy sources.

*“Question 8. To which extent (i.e. vehicles share / mileage) do you expect to rely on low carbon fuels in your roadmap by 2030 / 2040 / 2050?”*

Some stakeholders provided their options relying on different renewable fuels (e-fuel, biodiesel, etc.) while some of them gave their expected time-scale when low carbon fuels will gain considerable market share. About half of the interviewees expect to rely on low carbon fuels in their roadmap until 2040. Six participants did not answer as they considered the question out of scope regarding their activity.

*“Question 9. Sustainable fuels may have a lower energy content. What would be an acceptable decrease in your opinion and how would you define it? (e.g. distance? Maximum weight?)”*

The stakeholders provided their definition or criteria to evaluate the energy content of fuels (distance, maximum onboard weight). Most of them could accept some decrease in energy content but a few stated that their activity does not enable any change. The reduction of mileage is indeed a concern for most of the users and several of them indicated that a 10 to 15 % energy density reduction compared to conventional diesel could be acceptable. A decrease up to 50% is also mentioned. The main parameters related to these comments are the fuel tank volume or the vehicle range which ideally is above 800 km. The latter also refers to some operational constraints (e.g. refueling time and frequency which should be shortest and no more than once a day respectively).

The maximum weight is also mentioned as a key parameter for trucks. A few participants highlighted the possibility to allow for a load increase in trucks to promote low carbon fuels.

*“Question 10. & Question 11. What would be the most important levers to facilitate the incorporation of renewable fuels? What would be the most difficult challenges to address to accelerate the incorporation of advanced fuels?”*

Stakeholders have emphasised difficulties with implementing advanced renewable fuels at different levels. Those closer to the production pathways underline the difficulty of investment. The ones closer to applications underline cost and compliance with specifications and legislation. Overall, prospective compound availability would be a concern. Modifications would require a cooperation amongst different stakeholders to ensure a response within a relevant timeframe.

*“Question 12. LCA is considered as a key parameter for future renewable fuels developments, what aspects should be of first order in your opinion for such analyses?”*

Most stakeholders mentioned that they do not have expertise in LCA. Although their comments are listed below as they reflect their main concern.

First, taking into account the impact of renewable fuel production and being able to have a fair comparison between electric vehicles and liquid renewable fuels is mentioned. This comment was most of the time related to resources availability which can be a concern for these applications.

The global environmental impact is the second most cited parameter through GHG emissions but not exclusively. Participants also mentioned other impacts such as other pollutants, the impact on biodiversity or human health.

Finally, following the idea of a fair comparison between different options, it has been mentioned that LCA should be a standard method for evaluating all energy types or technologies.

*“Question 13. Is there a tipping point for which the use of renewable fuel will make sense for you?”*

The key tipping point highlighted by most of the participant is related to the profitability of the business and the policies.

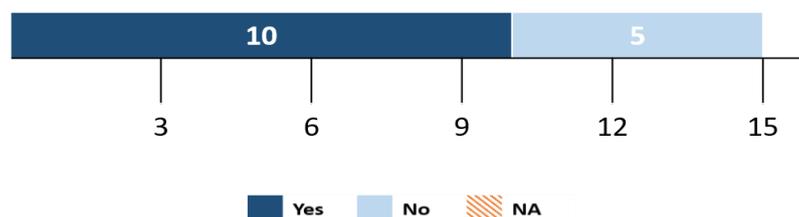
Indeed, government incentives to facilitate investment as tax reduction are essential to promote new fuel components. The willingness of OEM’s to provide support, validation or adaptability of their technology highly dependent on the product’s business size and refuelling cost.

## 7.2.2. Part 2: Multiple Choice Questions - Liquid fuels versus other routes

This second section deals with the closed-questions and provides a summary of the different answers.

*« Question 1. Do you expect novel fuel specifications to be developed or the current one to be modified by 2030 to facilitate the incorporation of sustainable fuels? »*

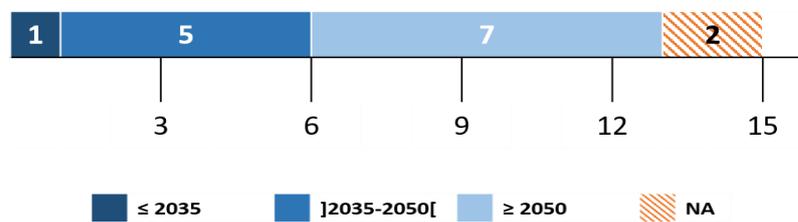
Most respondents expect that the current specifications will be changed by 2030 to facilitate the incorporation of sustainable fuels. It is even expected by one stakeholder that new specifications for e-fuels and non-biogenic fuels could be in place by 2030. On the other hand, 5 respondents did not think that new specifications will be developed or modified by 2030, as the timeframe is long, and today we can meet current standards with well established products FAME and HVO. (see Figure 111)



**Figure 111** Stakeholders answers regarding the expectation of novel fuel specifications or modification of the current one by 2030

*« Question 2. Liquid sustainable fuels development may be driven by long distance transport, how long do you expect them to compete with alternative options such as biogas, H<sub>2</sub>, NH<sub>3</sub>, whatever the powertrain is? »*

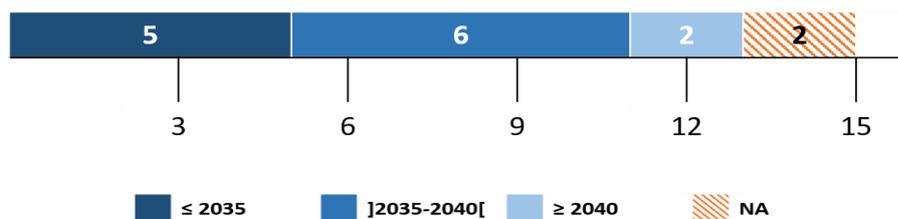
Most respondents expect that alternative options will not compete with sustainable liquid fuels before 2050. On the other hand, some respondents expect that in the mid-term (2035-2050) there will be competition between sustainable liquid fuels and alternative options. (see Figure 112)



**Figure 112** Stakeholders answers regarding the competition between liquid sustainable fuels and alternative options

« Question 3. When do you expect e-fuel processes to be ready at industrial scale? »

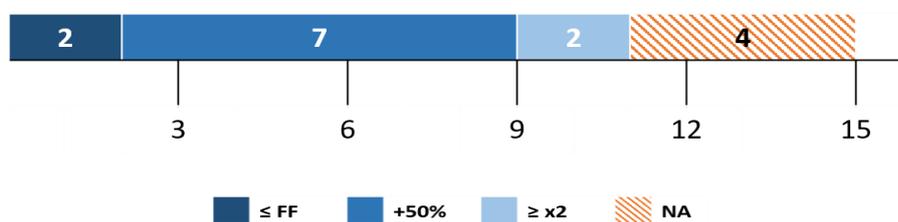
Regarding this question, respondent's opinions are divided. On the one hand, some respondents expect e-fuel processes to be ready at industrial scale between 2035 and 2040. On the other hand, some respondents believe that e-fuels will develop faster than expected at least at the margin, while others expect that e-fuels will not be available on an industrial scale before 2040. (see Figure 113)



**Figure 113** Stakeholders answers regarding the availability of e-fuel processes at industrial scale

« Question 4. What is a reasonable market price for pure advanced fuels? »

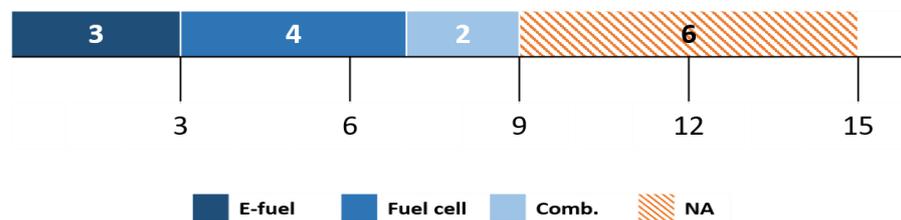
Most respondents agree that a realistic selling price for pure advanced fuels is +50% or even twice the price of fossil fuels and this will depend on the incentives. One respondent even expects that the market price for pure advanced fuels will be more than 5 times the price of fossil fuels. (see Figure 114)



**Figure 114** Stakeholders answers regarding the reasonable market price for pure advanced fuels

« Question 5. What will be the main hydrogen use from 2030 to 2040? »

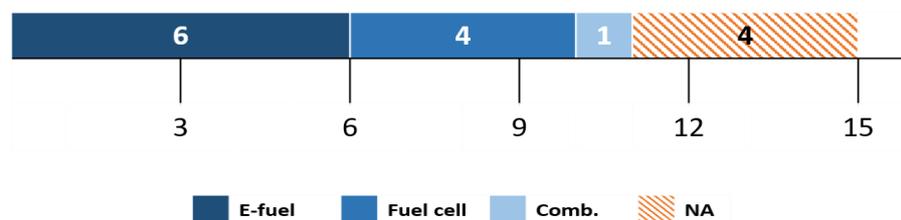
Regarding the main use of hydrogen from 2030 to 2040, respondents' opinions are divided between the three choices: e-fuel, fuel cell and combustion applications (see Figure 115).



**Figure 115** Stakeholders answers regarding the main hydrogen use from 2030 to 2040

« Question 6. What will be the main hydrogen use after 2040? »

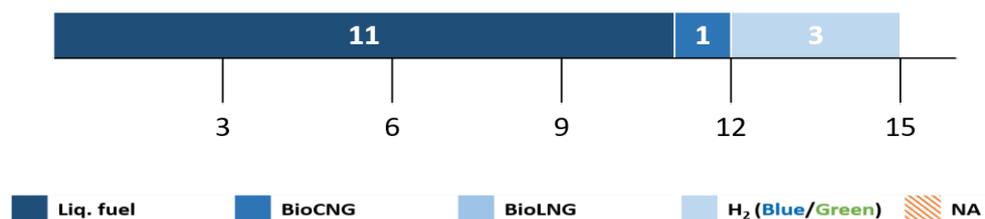
In contrast to the previous question where no consensus could be reached, most respondents expect that the main hydrogen use after 2040 will be e-fuel and then fuel cell. One participant commented that it could be e-fuel if we consider green H<sub>e</sub> and fuel cell if we consider blue H<sub>2</sub> (Figure 116).



**Figure 116** Stakeholders answers regarding the main hydrogen use after 2040

« Question 7. Which of low-carbon fuels have your preference in your strategy? »

Except 4 respondents, all agree that liquid fuels are preferred at least until 2030 (see Figure 117).



**Figure 117** Stakeholders answers regarding the low-carbon fuels preferred in their strategy

A deeper analysis of the results presented in this part 2 responses is available in Appendix 8. This additional step aims at demonstrating the potential correlations between the answers made and the different type of stakeholders.

The main results of this analysis are:

- OEM and users tend to consider that fuel specifications will evolve by 2030. They also consider that liquid sustainable product will compete with other options at least to 2035 and 43% to 2050. E-fuel production is expected to be available at industrial scale for most of the participants from 2035 to 2040. The acceptable price of the sustainable fuel will certainly be 50% higher than conventional diesel fuel. Interestingly, about half of the participants did not answer regarding the main hydrogen use from 2030 to 2040. The majority then

said that e-fuel will be the main H<sub>2</sub> use after 2040. Finally, more than half of the participants prefer liquid fuels as low carbon fuels in their strategy.

- Biofuel associations and fuel producers have mostly different opinions regarding the questions raised.
- Entities related to product logistic consider that fuel specifications will evolve by 2030.
- For public authorities, the two participants agree on the fact e-fuel will certainly be the long term use of H<sub>2</sub>. This led to the same agreement regarding the significant share of liquid renewable fuel for mobility.

### 7.3. CONCLUSIONS AND SUMMARY

15 organizations responded to the interview questions. These entities were selected from relevant stakeholders for heavy duty application including:

- Biofuel associations and producers
- OEM / users
- Product logistic
- Public authorities
- Research/engineering institutions

Two parts were addressed during the interview in order to first discuss about the main findings of this study and second to evaluate the potential competition with other fuel production pathways.

Open questions led to identify the main advantages or limitations related to the resources, the development of new processes and renewable fuels. The following paragraph summarizes the main opinions shared.

First of all resources availability and related environmental impacts were considered essential for any novel fuel production pathway.

Coexistence between fossil fuels and advanced options has to be considered carefully as it will be more and more important in a near future. Co-processing and development of smaller bio-refineries may be attractive in this context as they enable to move forward decarbonation but also contribute to promote energy security and economic activity locally. However these developments should not be associated to lower fuel quality. Considering the impact of coexistence is also essential as the development of novel resources or production plants will take time and require high investments.

However, amongst the many fuels cited in the literature, most stakeholders consider that FAME and paraffinic fuels will certainly remain the most important renewable fuel options until 2030. In any case, if a novel fuel is developed, the drop-in behaviour should be targeted. Stakeholders highlight that it should be evaluated from fuel logistic considerations to vehicle use including impact on emissions. In this evaluation step, it should be accepted by all stakeholders to be successful as the fuel properties may lead to a loss of overall performance or involve some changes for the activity.

The profitability over a certain period of time for the identified fuel will be a 1<sup>st</sup> order parameter and could be a tipping point for driving the transport sector to another fuel. Political decisions as incentives may contribute to reach that

objective and may be essential as the products will certainly be much more expensive than fossil bases.

Finally, the interviews also highlight the overall agreement of all participants regarding the important role of liquid sustainable fuels for the next 10 to 15 years.

Multiple choice questions enabled IFPEN to evaluate more precisely the role of liquid sustainable fuel compared to other routes. It led to the main following conclusions:

- Liquid low carbon fuels remains the preferred option for most of the stakeholders at least until 2030 and may compete with other options until 2050 for half of the participants. The development of a new specification by 2030 could be performed if that leads to increase the renewable content of the fuel.
- E-fuel process is likely to be ready at industrial scale before 2035 for a third of the participants. Hydrogen use is expected to be dedicated to e-fuel after 2040 for most of the participants even if fuel cells are also a significant application reported.

These interviews confirm that the stakeholders consider liquid sustainable fuels as essential for decarbonizing the transport sector not only for the short term but also for the next decades. This is however associated to many challenges that would have to be considered carefully by all stakeholders and will certainly require political decisions to promote their development.

## 8. GENERAL CONCLUSION

Evaluation of sustainable liquid fuels pathways by 2030 for heavy duty trucks was proposed in this study. Two approaches were followed. First, a systematic literature review for novel components was combined with 15 stakeholders interviews to identify the main opportunities or challenges of these liquid low carbon fuels. Second, the main advantages and drawbacks of energy pathways that can produce paraffinic and FAME (Fatty Acid Methyl Esters) fuels were evaluated. The latter refers to products that are available on the market today but facing challenges that are discussed here.

The selection of relevant energy pathways started with resources, processes and renewable liquid compounds identification and rating from the literature.

Amongst the nine resources types that were identified, three of them are considered as positive in terms of use by 2030: agricultural and forestry residues, industrial biomass residues, and woody and grassy energy crops. Their use in transport is fostered by regulatory aspects (in particular the Renewable Energy Directive, RED), and they are considered to be sustainable. Other resources either suffer from uncertainties regarding their availability or their cost by 2030; current conventional feedstocks (food and feed crops and waste cooking oil mainly) are capped by regulation even if they may still contribute significantly to the renewable fuel pool by 2030.

Regarding the processes, key steps were associated to a Technology Readiness Level (TRL) evaluated by 2030. This shed light on processes already existing at industrial scale including transesterification, fermentation, hydrotreatment, and process expected to become at industrial scale by 2030 such as gasification with Fischer-Tropsch (FT), pyrolysis or thermochemical processes. Intermediate TRL are expected for the upgrading of hydrothermal conversion products and fast pyrolysis. The same category is proposed for e-fuel/solar fuel due to limited demonstrations to date, notably concerning the RWGS stage.

Renewable compounds were assessed through an extensive literature review to identify the chemical components and their physical-chemical properties. More than one hundred species from different chemical classes were listed and ranked according to their estimated compatibility with current diesel fuel specifications, primarily EN590 (main grade Diesel) but also EN14214 (FAME fuel) and EN15940 (paraffinic diesel). This led to the assessment of carefully selected properties, considered as key for fuel use, such as density, flash point, viscosity, cetane number and phase change properties. About 30 neat components were characterised as compatible with a large incorporation rate into conventional diesel fuels based on their properties.

The literature review then addressed the evaluation of renewable fuels performance through engine tests and blending behavior. Engine test results were identified for many potentially renewable components, and one of the key findings was that most of the products contribute to decreased particulate matter emissions but can also lead to an increase in nitrogen oxides when certain oxygenated products are used. These observations shed light on the fact that in order to take advantage of novel fuel formulations, engine or calibration optimisation may be required and this is not necessarily considered for every component in the literature. In addition, hardware compatibility remains a question mark due to limited data on important fuel properties such as material compatibility, oxidation stability or cold flow properties. Limited data were identified on these aspects but

more information would certainly help eliminate fuel candidates if data showed that a major vehicle upgrade, and thus investment, was required, also leading to non-compatibility with the legacy fleet.

The previous steps enabled to identify relevant energy pathways that either refer to commercially available products such as paraffins or FAME, or novel components. Relevant pathways were selected based on the mapping of resources suitability, the process TRL and the product properties.

Two main routes were then considered: (1) the analysis of novel components or (2) components already available on the market.

First, the benefits and drawbacks of novel components were discussed. This led to highlight dioxolane derivatives and two ethers (di-n-pentylether and dibutoxymethane).

LCA (Life-Cycle assessment) and TEA (Techno-Economic Assessment) for selected pathways were first discussed for these products. Some opportunities were identified for these pathways regarding the development of new catalysts, the review also highlighted the lack of data and important limitations regarding the availability of key reactants. Despite these limitations, more recent data found for several pathways would suggest that ongoing research activities could lead to a renewed interest in these compounds.

Renewable novel fuel candidates were then evaluated based on their blending properties considering cetane number, flash point, viscosity and density. The objective was to determine to which extent these products could enable fuel suppliers to either maximize the renewable content of a hypothetical fuel combining: B7 (main grade diesel fuel), B100 (100% FAME), Paraffinic diesel (PF) and the renewable fuel candidate, or simply facilitate the incorporation of the product into current commercial B7 fuels. This step demonstrated that almost every component mixed with B100 and PF could potentially lead to a final blend that is compliant with EN590 limits for the four cited properties. Another comment is that certain physical chemical characteristics in B100 and HVO, such as the density, balance each other out contributing to increase the overall renewable content. In addition, the study highlighted the high potential of certain products for a high incorporation rate into B7 (>20 vol.%) considering again EN590 boundaries.

It was concluded that while such oxygenated compounds are promising and related to recent research and development studies, important downsides remain, especially regarding their maturity. However, encouraging developments were identified and these could contribute to accelerate the development of such pathways in the future.

Second, this work focused on paraffins and esters to assess and discuss the advantages or drawbacks of the related production pathways. The latter included hydrotreatment, gasification combined with Fischer Tropsch, esterification, fermentation and paraffinic e-fuel with lignocellulose.

A lack of environmental and economic assessment was identified in the case of hydrotreatment from lignocellulose or alcohol to diesel fermentation pathways. Otherwise the study concludes that fuels arising from these energy pathways could lead to significant CO<sub>2</sub> emissions reductions thanks to the resources and processes characteristics but also a high blending potential with respect to the EN590 specification. The main identified constraints are the density or the cold flow properties for further increasing the incorporation of such renewable components.

In addition, modelling cold flow properties is identified as a limitation to better assess the incorporation limit of paraffins or FAME components in hydrocarbons mixtures.

Another identified aspect for sustainable fuel development is the resources availability as the mobilisation of European biomass combined with these energy pathways lead to a production potential of renewable paraffins and esters ranging between 57 and 88 Mtoe by 2030 (low and high mobilization scenario, using the most mature technologies, i.e. the ones already at industrial scale today and the ones expected to be at industrial scale by 2030). It represents between 24% and 37% of the expected energy demand for distillates in the transport sector. These values must be seen as a maximum theoretical potential, pending the development and upscaling of the technologies, the mobilisation of biomass to biorefineries, the necessary investments and development of a profitable business, etc. This maximum theoretical production potential is however highly unlikely to be reached in 2030, as it would require massive investments to be realized in technologies which today do not exist at industrial scale, without waiting for demonstration of a First-Of-A-Kind. Competition may be present between heavy duty transport and aviation or maritime sectors to access the renewable feedstocks due to ambitious decarbonation targets by 2050 for all these sectors which might use similar energy pathways. Finally, these findings were shared with 15 stakeholders involved either in fuel production, fuel logistics, engine manufacturing, fleet operation or representing public authorities. Their feedback mostly highlighted the significant role that renewable liquid fuels will have to play to contribute to the decarbonization of the commercial transport sector in the short term and for the next decades. Related challenges were highlighted to maximize the chance of success of any novel fuel or simply to develop the current ones. In this context, most of the stakeholders considered that fuel evolution is required but would involve coordination from different stakeholders (as fuel producers, distributors, and OEMs) and political decisions to promote relevant candidates.

This work emphasizes the need to develop liquid sustainable fuels as a mean to decarbonise the HD transport sector in the short to medium timeframe and identifies the bottlenecks that need to be unlocked to avoid slowing down the process. It also helps highlight the importance of the existing renewable fuel production pathways which have already gone through the most important steps along their introduction in the market. The latter could contribute to decarbonize an increasing share of the transport sector within the next decade if biomass mobilization is optimized while meeting the sustainability criteria, and infrastructures are available and scaled up to produce the corresponding fuels.

## 9. GLOSSARY

ABE	Acetone-Butanol-Ethanol
AF	Animal Fat
ANCRE	Alliance for Coordination of Research on Energy
ATD	Alcohol-to-diesel
ATJ	Alcohol-to-jet
BEP	Breakeven price
BHT	Butylated hydroxytoluene
CAPEX	Capital expense
CFPP	Cold filterability plugging point
CHP	Combined heat and power unit
CN	Cetane number
CP	Cloud point
DAC	Direct air capture
DBM	Dibutoxymethane
DEE	di-ethyl-ether
DEGEE	Diethylene glycol ethyl ether
DIPE	Di-iso-pentyl ether
DNPE	di-n-pentyl ether
DOC	Diesel oxidation catalyst
DTBG	tert-Butyl glycerol ether
EC	Energy crops
EGR	Exhaust gas recirculation
EPDM	Ethylene propylene diene rubber
FAE	Fatty Alkyl Ether
FAFE	Fatty Acids Fusel Ester
FAME	Fatty acid methyl ester
FFKM	Perfluorinated rubber
FKM	Fluorocarbon-based fluoroelastomer
FP	Flash point
FT	Fischer-Tropsch
GHG	Greenhouse gas
GTL	Gas to Liquid
GWP	Global warming potential
HAA	Alkylation-Hydrodeoxygenation
HDO	Hydrodeoxygenation

HDT	Hydrotreatment
HMF	Hydroxymethylfurfural
HVO / HEFA	Hydrotreated vegetable oil / Hydroprocessed Esters and Fatty Acid
HTL	Hydrothermal liquefaction
ICAO	International Civil Aviation Organization
ICCT	International Council on Clean Transportation
IEA	International energy agency
ICE	Internal Combustion Engine
LCA	Life cycle analysis
LHV	Lower heating value
MTHF	Methyltetrahydrofuran
NBR	Nitrile butadiene rubber
NO <sub>x</sub>	Nitrogen oxides (NO, NO <sub>2</sub> )
OEM	Original Equipment Manufacturer
OME / OME <sub>x</sub> , POME	Oxymethylene ether / Polyoxymethylene ether
OPEX	Operating expense
PF	Paraffinic fuel
PG	propylene glycol
PtL	Power-to-liquid
PbTL	Power-biomass-to-liquid
RED	Renewable energy directive
RDE	Real Driving Emissions
RFNBOs	Renewable Fuels of Non-Biological Origins
RWGS	Reverse Water Gas Shift
SCR	Selective catalytic reduction
SVO	Straight vegetable oils
SWOT	Strength, Weaknesses, Opportunities, Threats
TBA	Tert-Butyl alcohol
TBGE	Tert butyl glycerol ether
TBHQ	Tert-butylhydroquinone
TEA	Techno economic analysis
THF	Tetrahydrofuran
TPGME	Tri Propylene Glycol Methyl Ether
TRANS	Transesterification
TTBG	tri-tert-Butyl glycerol ether
TRL	Technology Readiness level
UCO / WCO	Used cooking oil / Waste cooking oil

WLTC

Worldwide harmonized Light vehicles Test Cycles

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## 11. APPENDIX

## 1. EUROPEAN FUEL SPECIFICATIONS FOR DIESEL ENGINE

Property	Unit	EN 14214		EN 590		EN 16734		EN 16709				EN 15940				EC n° 582/2011	
		B100		B0 → B7		B10		B20		B30		Paraf. fuels Class A (HVO, XTL)		Paraf. fuels Class B (COD)		ED95	
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Cetane number	-	51,0	-	51,0	-	51,0	-	51,0	-	51,0	-	70,0	-	51,0	-	-	-
Density at 15 °C	kg/m <sup>3</sup>	860	900	820	845	820	845	820	860	825	865	765	800	780	810	793	815
Flash point	°C	101	-	55,0	-	55,0	-	55,0	-	55,0	-	55,0	-	55,0	-	10	-
Viscosity at 40 °C	mm <sup>2</sup> /s	3,50	5,00	2,00	4,50	2,00	4,50	2,00	4,62	2,00	4,65	2,00	4,50	2,00	4,50	-	-
Distillation: 95 % v/v recovered at:	°C	-	-	-	360	-	360	-	360	-	360	-	360	-	360	-	-
Polycyclic aromatic hydrocarbons	% m/m	-	-	-	8,0	-	8,0	-	8,0	-	8,0	-	-	-	-	-	-
Sulfur content	mg/kg	-	10,0	-	10,0	-	10,0	-	10,0	-	10,0	-	5,0	-	5,0	-	10,0
Oxydation stability	h	8,0*	-	20,0	-	20,0	-	20,0	-	20,0	-	20,0	-	20,0	-	-	-
Lubricity, wear scar diameter at 60 °C	µm	-	-	-	460	-	460	-	-	-	-	-	460	-	460	-	-
FAME content (EN 14 214) Total alcohol		96,5 % m/m	-	-	7,0 % v/v	-	10,0 % v/v	14,0 % v/v	20,0 % v/v	24,0 % v/v	30,0 % v/v	-	7,0 % v/v	-	7,0 % v/v	92,4 % m/m	-

\* At 110 °C

Note: For climate-dependent requirements (CFPP and cloud point) options are given to allow for seasonal grades to be set nationally. Each country shall in a National Annex detail requirement for a summer and a winter grade and may include (an) intermediate and/or regional grade(s) which shall be justified by national meteorological data.

## 2. DATABASE OF COMPOUNDS PROPERTIES

	Suitable	[765;900]	≥ 51	[2;5]	≥ 55	≤ 0	≤ 250	4						
	Challenging	other	[30;51[	< 2	[45;55[	]0;40]	]250;350]	3						
	Very challenging	< 730 or > 1000	[15;30[	> 5	[30;45[	> 40	]350;375]	2						
	Not suitable	-	< 15	-	< 30	-	> 375	1						
Classification	Products	Density		CN		Viscosity at 40 °C		Flash point		Melting point		Boiling point		Health & Envir. Tox
		[kg/m <sup>3</sup> ]		[-]		[mm <sup>2</sup> /s]		[°C]		[°C]		[°C]		[1;4]
		Nom. value	Ref. value	Nom. value	Ref. value	Nom. value	Ref. value	Nom. value	Ref. value	Nom. value	Ref. value	Nom. value	Ref. value	
	Alkanes/alkenes C5 to C19 (cyclic, branched and linear)													
	<i>Specific (1 process gives 1 molec)</i>													
1	Farnesane (2,6,10-Trimethyl dodecane)	773	773 [304]	58.0	59 [71] 58 [49]	3.0	2.82 [71] 3.1 [305]	103.0	103 [71]103 [39]	-73.0	-73 [71]	250.0	248 [306] 252 [39]	4
	<i>Standard (cyclic or paraffins)</i>													
	<i>Paraffins</i>													
2	n-undecane	742	744 [304] 740 [307]	76.0	71 [71]81 [307]	1.7	2.17 [71] 1.18 [308]	67.0	65 [71] 69 [307]	-26.0	-26 [71]	195.9	[308]	4
3	6-Methylundecane	750	750 [306]	67.0	67 [209]	3.0	[2;5] [b]	59.4	59.4 [306]	-66.6	-66.6 [306]	207.0	[306]	4
4	6-Butylundecane	800	[a]	55.0	>51 [b]	3.0	[2;5] [b]	55.0	> 55 [b]	0.0	<0 [b]	246.9	[76]	4
5	n-decane	730	730 [[308]	67.0	67 [39]	1.0	0.95 [308]	57.0	57 [39]	-29.5	-29.5 [308]	174.0	[308]	4
6	n-dodecane	750	750 [9]	73.0	73 [39]	1.4	1.4 [308]	71.0	71 [39]	-9.0	-9[308]	216.0	[308]	4
7	3-ethyldecane	800	[a]	48.0	48 [39]	3.5	[a]	55.0	>55 [b]	-63.5	-63.5 [306]	207.0	205 [306]209 [39]	4

8	n-tridecane	756	756 [308]	88.0	88 [39]	1.5	<2 [307]	79.0	79 [39]	-5.2	-5.2 [308]	234.8	235.5 [308] 234 [39]	4
9	5-butylnonane	800	[a]	53.0	53 [39]	3.5	[a]	65.0	65 [39]	-40.7	-40.7 [306]	218.0	[306]	4
10	n-tetradecane	764	764 [308]	93.0	93 [39]	2.1	2.1 [308]	100.0	100 [39]	6.0	6 [308]	252.8	253.6 [308] 252 [39]	4
11	n-pentadecane	769	769 [308]	98.0	98 [39]	2.5	2.5 [308]]	132.0	132[39]	10.1	10.1[308]	266.4	270.7 [308] 267 [39]	4
12	2-methyltetradecane	800	[a]	55.0	[a]	3.5	[a]	55.0	>55 [b]	-20.2	-20.2 [306]	261.0	260 [306] 262 [39]	4
13	n-hexadecane	770	770 [308]	100.0	100 [39]	3.0	2.97 [308]	135.0	135 [39]	18.0	18 [308]	284.0	286.9 [308] 281[39]	4
14	n-heptadecane	777	777 [308]	105.0	105 [39]	3.4	3.4 [308]	149.0	149 [39]	22.0	22 [308]	302.0	[308]	4
15	3,3,5-trimethyldecane	734	734 [306]	60.0	60 [309]	1.0	<2 [306]	81.0	81 [310]	-81.4	-81.4 [306]	210.0	[306]	4
16	7-butyltridecane	800	[a]	70.0	70 [39]	3.5	[a]	55.0	>55 [b]	0.0	<0 [a]	273.0	[39]	4
17	n-octadecane	777	777 [308]	110.0	110 [39]	4.0	3.9 [308]	166.0	166 [39]	32.0	32 [308]	317.0	[39]	4
18	n-eicosane	790	790 [308]	110.0	110 [39]	4.3	4.3 [308]	187.0	187 [39]	36.6	36.6 [308]	343.0	[39]	4
	<i>Market fuels</i>													
	HVO, XTL	783	765 - 800 [311]	70.0	70 [[311]	3.3	2 - 4.5 [311]	55.0	55 [311]	30.0	<30 [b]			4
	COD	795	780 - 810 [311]	51.0	51 [311]	3.3	2 - 4.5 [311]	55.0	55 [311]	30.0	<30 [b]			4
	<i>Cyclic</i>													
19	Decalin	896	896 [308]	42.0	42[39]	1.5	<2 [b]	57.0	57 [39]	-58.8	-58.8 [306]	190.0	[39]	3
20	Bicyclohexyl	864	864 [308]	53.0	53 [39]	3.0	2.96 [312]	92.0	92 [39]	-43.0	-43 [306]	227.0	[39]	4
21	Ethylcyclohexane	788	788 [308]	36.0	36 [39]	0.8	0.82 [308]	18.0	18 [39]	-111.2	-111.16 [308]	132.0	[39]	3
22	n-Butylcyclohexane	818	818 [308]	49.0	48 [39] 50 [71]	2.2	2.19[71]	45.5	41[39]50 [71]	-75.0	-75 [71]	180.0	[39]	4

	<i>Olefines</i>													
23	Pinene	858	858 [308]	16.0	16[309]	1.4	1.4 [308]	32.2	32.2 [309] 32 [308]	-63.9	-63.9 [308]	156.5	156 [308] 155 [52]	4
24	Limonene	841	841 [308]	22.0	22 [309]	0.9	0.92 [308]	45.4	42.8 [309] 48 [308]	-74.2	-74.2 [308]	176.8	177.5 [308] 176 [309]	3
25	Sabinene	844	844 [308]	7.0	7 [309]	1.5	<2 [a]	36.7	36.7 [309]	52.2	52.2 [308]	163.0	52]	4
	<b>Esters (fatty esters, fusel)</b>													
107	Fatty acid fusel esters (FAFE)	-	-	51	51 [55]	3.5	3.5 [55]	-	-	-	-	-	-	-
108	Fatty acid ethyl esters (FAEE)	882	882 [313]	52.8	52.8 [313]	4.3	4.3 [313]	55	55 [a]	20	20 [198]	300	-	4
	<b>Conventional esters (FAME)</b>													
26	Methyl laurate	870	870 [308]	62.0	62 [314]	2.4	2.4 [308]	121.0	121 [308]	5.0	5 [308]	266.9	[308]	4
27	Methyl myristate	855	855 [308]	69.5	69.5 [314]	3.5	3.5 [308]	142.0	142 [308]	19.0	19 [308]	296.8	[308]	4
28	Methyl palmitate	852	852 [308]	77.9	81.2 [314] 74.5 [55]	4.5	4.5 [308]	163.0	163 [308]	30.0	30 [308] 30 [55]	324.6	[308]	4
29	Methyl oleate	870	870 [308]	62.4	62.4 [314]	4.5	4.5 [308]	181.0	181 [308]	20.0	20 [308]	343.9	[308]	4
30	Methyl stearate	849	849 [308]	87.8	88.6 [314] 86.9 [55]	5.9	5.9 [308]	183.0	182 [308]	39.0	39.1 [55] 39 [308]	350.6	[308]	4
31	Methyl erucate	870	870 [308]	76.0	76 [314]	7.2	7.2 [308]	210.0	210 [308]	-1.2	-1.2 [308]	395.8	[308]	4
32	Methyl ricinoleate	924	924 [308]	37.4	37.4 [315]	15.6	15.6 [308]	207.0	207 [308]	-5.0	-5 [308]	375.7	[308]	4
33	Methyl linoleate	889	889 [308]	42.1	42.1 [314]	3.5	3.5 [308]	179.0	179 [308]	-39.0	-39 [308]	346.0	[308]	4
	<b>Markets fuels or potential market fuels</b>													
	B7	833	820 - 845 [316]	51.0	51 [316]	3.3	2 - 4.5 [316]	55.0	55 [316]	0.0	<0 [b]			4
	B10	833	820 - 845 [317]	51.0	51 0 [317]	3.3	2 - 4.5 [317]	55.0	55 0 [317]	0.0	<0 [b]			4

	B20	840	820 - 860 [318]	51.0	51 [318]	3.3	2 - 4.62 [318]	55.0	55 [318]	0.0	<0 [b]			4
	B30	845	825 - 865 [318]	51.0	51 [318]	3.3	2 - 4.65 [318]	55.0	55 [318]	0.0	<0 [b]			4
	B100	880	860 - 900 [319]	51.0	51 [319]	4.3	3.5 - 5 [319]	101.0	101 [319]	0.0	<0 [b]			4
	R33	833	820 - 845 [316]	51.0	51 [316]	3.3	2 - 4.5 [316]	55.0	55 [316]	0.0	<0 [b]			4
	<i>Other</i>													
34	Methyl myristoleate	879	879 [308]	51.0	>51 [b]	3.7	3.73 [198]	90.0	>55 [b]	0.0	<0[b]	306.6	[76]	3
35	Methyl decanoate	873	873 [304]	51.8	51.63 [314] 52 [71]	2.0	1.71 [314] 2.33 [71] 1.87 [198]	111.0	111 [71]	-15.6	-13.1 [314] -18 [71]	231.9	[308]	4
36	Methyl octanoate	877	877 [308]	39.8	39.75 [314]	1.2	1.2 [198]	94.2	94.2 [308]	-17.9	-17.9 [308]	193.0	[308]	4
37	Methyl palmitoleate	875	875 [308]	53.8	53.8 [314]	3.6	3.6 [308]	166.0	166 [308]	8.0	8 [308]	321.1	[308]	3
38	Hexyl hexanoate	862	862 [304]	40.0	40 [71]	2.4	2.38 [71]	99.0	99 [71]	-55.0	-55 [71]	246.0	[306]	4
	<i>Ethers</i>													
	<i>Linear ethers</i>													
39	ETBE	736	736 [308]	8.0	8 [320]	0.5	0.45 [321]	-20.0	-20 [308]	-94.0	-94 [308]	72.5	[308]	3
40	MTBE	740	740 [308]	10.0	[a]	0.4	0.39 [308]	-29.0	-29 [[308]	-108.5	-108.5 [308]	55.1	[308]	4
41	DME	670	670 [308]	57.5	55 - 60 [322]	0.2	0.18 [323]	-80.0	-80 [308]	-141.0	-141.3 [308]	84.6	[308]	3
42	DEE	713	713 [308]	125.0	125 [320]	0.3	0.272 [308]	-45.0	-45 [308]	-116.3	-116.3 [308]	34.4	[308]	3
43	DNBE	770	770 [324]	105.0	105 [324]	0.6	0.64 [324]	29.0	29 [324]	-98.0	-97.7 [308]	141.0	[308]	4
44	Di-n-pentyl ether (DNPE)	785	785 [308]	111.0	111 [71]	2.1	2.12 [71]	57.0	57 [71]	-69.0	-69 [71]	186.8	[308]	4
45	Di-isopentyl ether (DIPE)	778	778 [308]	100.0	[a]	2.5	[2;5] [b]	46.0	46 [325]	-79.9	<-79.9 [325]	173.0	[306]	4

	<i>Furanic platform components (furan derivatives, aromatics, etc)</i>													
46	MTHF	860	860 [326]	22.0	22 [326]	0.5	<2 [306]	-11	-11 [326]	-136.0	-136 [326]	79.0	[326]	4
47	2,5-Bis(hydroxymethyl)furan (BHMF) Fatty Acid Diesters	910	> 891 [39]	55.0	> 55 [39]	6.0	<16 [306]	188.0	> 188 [39]	51.8	51.8 [306]	252.0	[306]	4
48	2-methylfuran	910	910 [326]	8.9	8.9 [[326]	0.5	<2 [306]	-13.9	-17 [326] -10.7 [306]	-89.0	-89 [326]	64.0	[326]	1
49	5,5-((Tetrahydrofuran-2-yl)methylene)bis(2-methyltetrahydrofuran)	910	[a]	60.4	60.4 [314]	7.5	7.45 [314]	55.0	>55 [b]	-40.0	<-40 [314]	300.0	]250 ; 350] [a]	3
50	Tris(5-methyltetrahydrofuran-2-yl)methane	910	[a]	59.8	59.8 [314]	7.3	7.33 [314]	55.0	>55 [b]	-40.0	<-40 [314]	300.0	]250 ; 350] [a]	3
51	2,5-Bis(ethoxymethyl)tetrahydrofuran	910	[a]	87.8	87.8 [314]	6.0	>5 [a]	55.0	>55 [b]	-40.0	<-40 [a]	300.0	]250 ; 350] [a]	3
52	2,5-DMF	903	903 [326]	10.9	10.9 [326]	0.5	0.45[308]	7.0	7 [326]	-62.0	-62 [326]	94.0	[326]	1
53	anisole	995	995 [326]	6.0	6 [326]	0.8	0.79 [310]	52.0	52 [326]	-23.0	-23 [326]	154.0	[326]	4
54	4-methyl anisole	969	969 [326]	7.0	7 [326]	1.5	<2 [a]	59.0	59 [326]	-32.0	-32 [326]	177.0	[326]	3
55	p-cresol	1034	1034 [[326]	10.0	[a]	6.8	6.8 [308]	85.0	85 [[326]	31.0	31 [326]	202.0	[326]	1
56	guaiacol	1100	1100 [326]	19.0	19 [326]	2.9	2.9 [308]	82.0	82 [326]	28.0	28 [326]	205.0	[326]	3
57	1,2-dimethoxybenzene	1084	1084 [326]	17.0	17 [326]	1.5	<2 [306]	72.0	72 [326]	15.0	15 [326]	206.0	[326]	3
58	2,4-xyleneol	1011	1011 [326]	10.0	[a]	8.1	8.1 [306]	94.0	94 [326]	21.0	21 [326]	211.0	[326]	1
59	4-propylanisole	941	941 [326]	7.0	7 [326]	1.5	<2 [306]	90.0	90 [326]	-5.0	-5 [326]	215.0	[326]	4
60	2-phenylethanol	1020	1020 [326]	8.0	8 [326]]	6.0	6 [308]	102.0	102 [326]	-19.0	-19 [326]	218.0	[326]	3
61	4-methylguaiacol	1092	1092 [326]	21.0	20 [[326]	10.8	10.8 [308]	99.0	99 [326]	5.0	5 [326]	221.0	[326]	3
62	4-propylphenol	983	983 [326]	9.0	9 [326]	3.0	[2;5] [306]	106.0	106 [326]	22.0	22 [326]	232.0	[326]	1
63	4-ethylguaiacol	1063	1063 [326]	20.0	20 [326]	3.0	[2;5] [306]	108.0	108 [326]	15.0	15 [326]	235.0	[326]	3

64	4-propylguaiacol	1038	1038 [326]	18.0	18 [326]	3.0	[2;5] [306]	113.0	113 [326]	16.0	16 [326]	250.0	[326]	3
65	2,6-dimethoxyphenol	1134	1134 [326]	26.0	26 [326]	3.0	[2;5] [306]	140.0	140 [326]	55.0	55 [326]	263.0	[326]	3
66	4-methyl-2,6-dimethoxy phenol	1105	1105[326]	25.0	25 [326]	3.0	[2;5] [306]	113.0	113 [326]	40.0	40 [326]	268.0	[326]	3
67	4-propyl-2,6-dimethoxy phenol	1074	1074 [326]	25.0	[a]	3.0	[2;5] [306]	135.0	135 [326]	45.0	>40 [b]	299.0	[326]	3
	<i>OMEx</i>													
68	4-butoxyheptane	791	791 [41]	80.0	80 [41]	0.8	0.79 [41]	64.4	64 [41]	-80.0	<-80 [41]	198.0	[41]	4
69	OME mix	1047	[95]	60.7	[95]	1.4	[41]	59.0	[95]	0.0	[95]	250.0	[95]	4
71	3,5,7,9-Tetraoxaundecane	960	960 [306]	67.0	67 [71]	0.5	<2 [a]	68.0	68 [71]	-24.0	-24 [71]	185.0	[71]	4
72	Dibutoxymethane (DBM)	835	835 [304]	70.0	70 [71]	2.0	2.01 [71]	62.0	62 [71]	-58.0	-58 [71]	179.0	[306]	4
73	OME1 (dimethoxymethane)	861	850 [327] 863 [85] 864.5 [328] 867 [90] 861 [304]	39.2	30 [327] 37.6 [85] 50 [14.18]	0.3	0.33 [304]	-31.0	-32 [307] -30.5 [304]	-104.9	-104.8 [304] -105 [307]	42.1	[306]	4
74	OME2	969	978 [307] 960 [41]	63.0	63 [95]	0.6	0.64 [95]	45.0	[30;55] [b]	-69.9	-70 [307] -69.7 [95]	105.0	[307]	4
75	OME3	1017	1031 [307] 1020 [95] 1000 [306]	90.7	124 [307] 78 [95] 70 [71]	1.0	1.03 [95] 0.87 [329]	54.0	54 [307]	-43.0	-42.5 [95]	156.0	[307]	4
76	OME4	1058	1074 [18] 1070 [95] 1030 [306]	119.0	148 [307] 90 [95] 90 [71]	1.5	1.64 [95] 1.33 [329]	88.0	88 [307]	-9.9	-10[307] -9.8 [95] -10 [71]	202.0	202 [307] 201 [71]	4
77	OME5	1103	1106 [307] 1100 [95]	140.0	180 [307] 100 [95]	2.0	2.04 [95] 1.96 [329]	115.0	115 [307]	18.2	18 [307] 18.3 [95]	242.0	[307]	4
78	OME6	1130	1130 [95]	104.0	104 [95]	2.5	[2;5] [b]	55.0	>55 [b]	41.5	48 [95] 35 [329]	272.0	[329]	4
	<i>Dioxolanes derivatives</i>													
79	4,5-dimethyl-2-(pentan-3-yl)-1,3-dioxolane	860	[a]	55.0	>51 [b]	1.5	<2 [b]	55.0	>55 [a]	0.0	<0 [b]	200.0	<250 [a]	3

80	2-(heptan-3-yl)-4,5-dimethyl-1,3-dioxolane	875	[306]	55.0	>51 [b]	2.5	<5 [306]	78.7	78.7 [306]	-50.8	-50.8 [306]	224.0	[306]	3
81	4,5-dimethyl-2-pentyl-1,3-dioxolane	860	[a]	55.0	>51 [b]	1.5	<2 [306]	63.0	>55 [306]	-58.9	<-50 [38]	184.0	[306]	3
82	2-heptyl-4,5-dimethyl-1,3-dioxolane	860	[a]	55.0	>51 [b]	2.5	<5 [306]	94.2	> 55 [306]	-16.8	<-10 [306]	233.0	[306]	3
83	2,4,5-trimethyl-2-undecyl-1,3-dioxolane	868	868 [39]	84.0	84 [39]	4.4	4.44 [39]	55.0	>55 [b]	-18.0	-18 [39]	300.0	]250;350] [a]	3
84	2,4-dimethyl-2-undecyl-1,3-dioxolane	872	872 [39]	91.0	91 [39]	5.2	5.15 [39]	55.0	>55 [b]	-14.0	-14 [39]	300.0	]250;350] [a]	3
85	2-methyl-2-undecyl-1,3-dioxolane	883	883 [39]	81.0	81 [39]	5.0	4.98 [39]	120.0	> 55 [306]	-15.4	0 [39] -30.8[306]	295.0	[306]	3
	<i>Glycerol derivatives</i>													
86	Di-tert-butyl glycerol ethers (DTBGs)	886	886 [306]	45.0	<50 [b]	3.5	<6.46 [306]	94.2	94.16 [306]	-18.1	-18.1 [306]	246.0	[306]	4
87	tri-tert-butyl glycerol ether (TTBG)	830	830 [306]	45.0	<50 [b]	5.5	<12.4 [306]	99.2	99.2 [306]	-37.4	-37.4 [306]	270.0	[306]	4
88	Tripropyleneglycol methylether (TPGME)	963	963 [305]	53.1	53.1 [305]	8.4	8.43 [308]	117.1	121.2 [308] 113 [305]	-41.9	-41.9 [308]	262.0	[71]	4
89	Diethylene glycol monoethyl ether (DGME)	980	980 [308]	55.0	55 [71]	2.7	2.7 [308]	96.0	96 [71]	-80.0	-80 [71]	202.0	[71]	4
	<i>Other ethers</i>													
90	1,8-cineole	922	922 [308]	16.0	16 [309]	1.5	<2 [306]	50.9	50.9 [309]	1.3	1.33 [306]	176.0	[306]	3
	<i>Alcohols</i>													
	<i>Market fuels</i>													
	ED95	804	793 - 815 [330]	10.0	[a]	1.1	<2 [b]	10.0	10 [330]	-114.0	<-100 [b]			3
	<i>C5-</i>													
91	Ethanol	789	785 [331] 789 [332]	8.8	5 - 8 [331] 11 [332]	1.1	1.13 [332]	13.1	13.2 [308] 13 [331]	-114.0	-114 [308]	78.3	[308]	3
92	Iso-butanol	802	802 [331]	15.0	<15 [331]	2.7	2.66 [308]	28.7	29.3 [308] 28 [331]	-107.9	-107.9 [308]	-107.9	[308]	3

93	n-butanol	810	810 [331]	20.5	17 - 25 [331] 20 [332]	2.4	2.69 [332] 2.19 [310]	36.4	37.7 [308] 35 [331]	-89.2	-89.2 [308]	118.8	[308]	3
94	Pentanol	814	814 [332]	20.0	20 [332]	2.9	2.84 [308] 2.89 [332] 2.90 [310]	49.0	49.2 [308]	-77.4	-77.4 [308]	137.8	[308]	4
95	Methanol	792	787 [331] 791 [332]	3.8	3.8 [331]	0.6	0.55 [308] 0.58 [332]	11.6	11.2 [308] 12 [331]	-97.5	-97.5 [308]	64.7	[308]	4
	<b>C5+</b>													
96	Octanol	824	824 [308] 832 [331]	32.0	39[333] 23 [331] 34 [334]	5.5	5.42 [308] 5.56 [310] 5.5 [334]	80.6	86.7 [308] 75 [331] 80 [334]	-15.4	-15.4 [308]	194.5	194 [308] 195 [334]	4
97	2-ethylhexanol	833	833 [308]	24.1	25 [309]23.2 [334]	4.8	4.36 [308] 5.2 [334]	75.1	77.2 [309] 73 [308] 75 [334]	-69.9	-69.9 [308]	184.3	184.5 [308]184 [334]	3
98	1-decanol	830	830 [308]	49.3	50.3 [306] 48.2 [334]	8.3	8 [308] 8.5 [334]	93.0	104 [308] 82 [334]	7.0	7 [308]	225.7	229.9 [308] 221.5 [334]	3
99	1-nonanol	827	827 [308]	46.0	46 [333]	6.8	6.8 [308]	96.0	96 [308]	-4.9	-4.9 [308]	212.1	[308]	3
100	2-nonanol	827	827 [308]	40.0	40 [71]	4.3	2.77 [71] 5.9 [308]	89.0	96 [71] 82 [308]	-35.5	-36 [71] -34.9 [308]	198.6	[308]	3
	<b>Ketones</b>													
101	4-methylacetophenone	997	1005[326] 988 [306]	55.0	>51 [335]	0.5	<2 [b]	84.6	82 [326]87.1 [306]	-60.2	-64 [326] 3.83 [306]	226.0	[308]	4
102	2-hexadecanone	829	829 [308]	55.0	>51 [335]	1.5	<2 [b]	90.2	90.2 [306]	48.0	48 [306]	306.0	[306]	4
103	3-octanone	822	822 [308]	55.0	>51 [335]	0.9	0.87 [308]	50.0	50 [308]	-17.5	-17.5 [308]	167.5	[308]	3
104	2-hexanone	812	812 [326]	55.0	>51 [335]	0.6	0.59 [308]	23.1	23.2 [308] 23 [326]	-56.4	-55.7 [308] -57 [326]	127.6	[308]	3
105	2,2,5,5-tetramethyl-3-hexanone	805	805 [306]	19.0	19 [309]	0.5	<2 [306]	39.6	39.6 [309]	-17.2	-15.9 [336] -18.4 [306]	164.5	168 [306] 161 [309]	3
	<b>Polyketides</b>													

106	Poly-beta-keto-acyl-CoA derivatives	830	<1000 [335]	55.0	>[335]	1.5	<2 [b]	55.0	>55 [335]	45.0	>40 [b]	365.0	[b]	4
	<i>Others</i>													
70	Straight Vegetable Oil	930	900 - 960 [76]	36.0	29 - 43 [76]	35.0	30 - 40 [76]	220.0	> 220 [76]	40.0	< 40	376.0	> 375 [337]	4

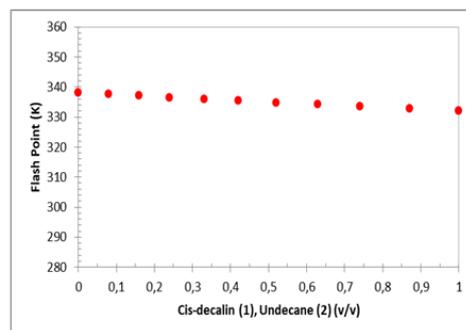
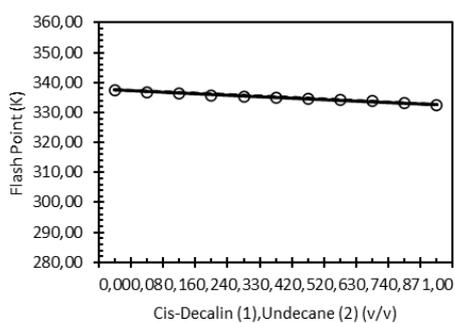
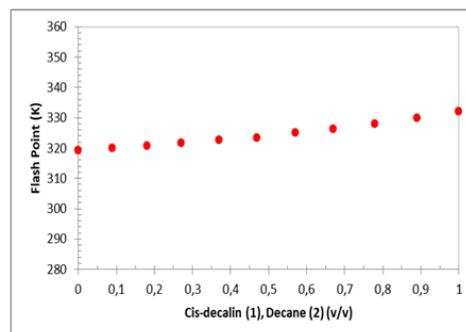
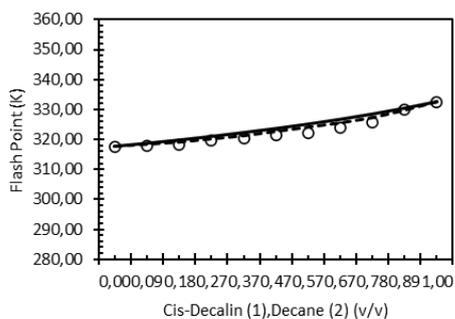
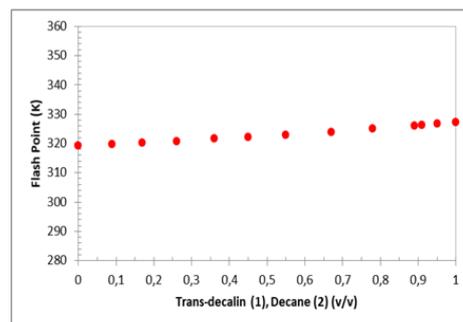
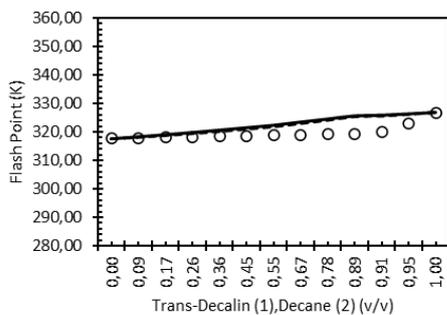
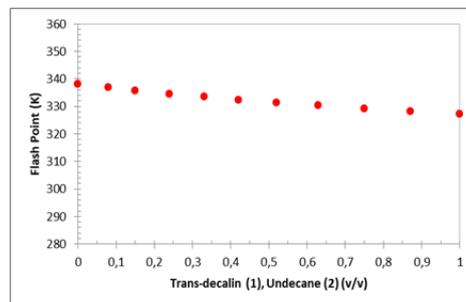
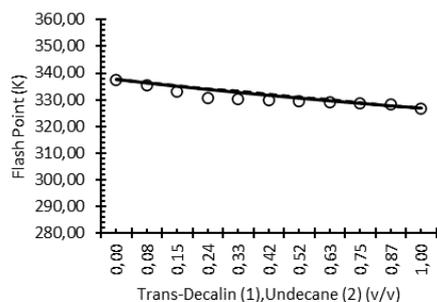
Note:

[a] Similar to product of the same family

[b] Consider lower or higher value

### 3. FLASH POINT

Example of validation data with the **mixing index (MI)** method considering a small FP difference between the products:



Source [S.M. Santos, et al. Fuel 263 (2020) 1163752] - [338]

Example of validation data with the **mixing index (MI) method** considering a significant FP difference between the products:

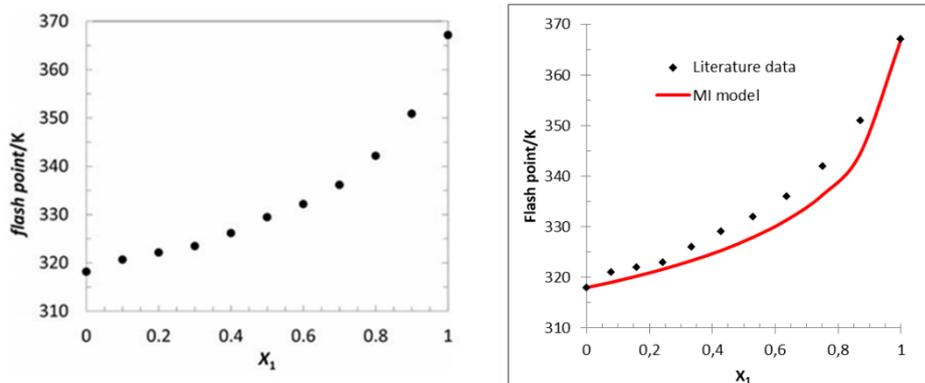


Figure 5. Flash point of 2,2,4,4,6,8,8-heptamethylnonane ( $X_1$ ) + 2,2,4,6,6-pentamethylheptane mixtures. Flash point is nonlinear with  $X_1$ .

Source [Luning Prak, C. et al., J. Chem. Eng. Data 2015, 60, 1157–1165] - [339]

#### 4. VISCOSITY

Example of validation data with the **mixing index (MI)** method

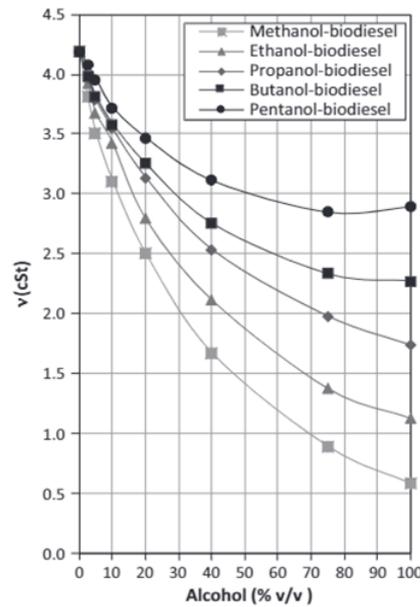
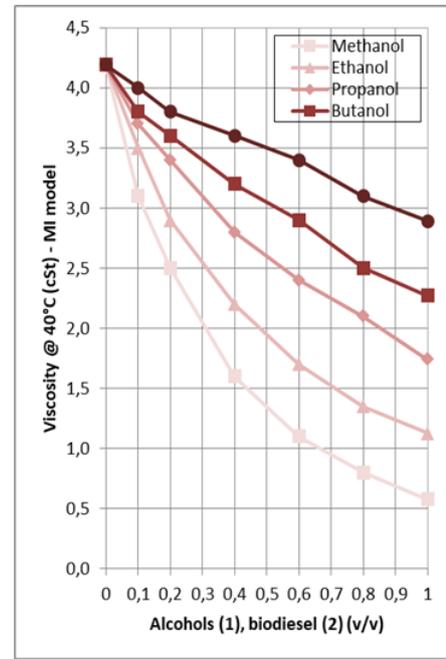
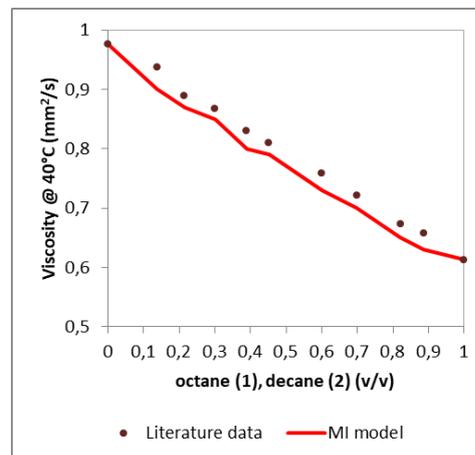


Fig. 3. Viscosity of alcohol-biodiesel blends.



Source [M. Lapuerta et al., Fuel 199 (2017) 332-338] - [138]



Source [Estrada-Baltazar, J. Chem. Eng. Data, 1998, 43, 441-446] - [340]

## 5. INCORPORATION RATE SUMMARY

Appendix 5 summarizes the maximum incorporation rate for every components mentioned in Table 12 considering the three base fuels (B7, B100 and HVO). Components were evaluated considering both EN590, EN14214 and EN15940 specifications for the optimization constraints. Property that limits the renewable component incorporation is highlighted for B7 case study. In addition, to provide a full overview of the available literature for these components, when any suitable information regarding miscibility, material compatibility, oxidation stability, emissions and incorporation limits into a base diesel fuel could be identified and be also reported. An example of results presentation is provided below.

Compound name	Ref. Fuel	Incorporation level (%vol)												
		5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	...	100%	
	B7, B100, HVO	Green	Green	Green	Green	Green								

*Blending base fuel*  
 B7: diesel (EN590)  
 B100: Biodiesel (FAME) (EN14214)  
 HVO: diesel paraffinic (EN15940)

*Blending rate (% vol).*

*Incorporation rate level colour code*

	Compatible with EN590
	Compatible with EN14214 or EN15940*
	Outside of the specification boundaries (OB)

Products	Properties																Misc. in HC	Mat. C.	Oxy. Stability*	Comments	
	Ref. Fuel	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	60%	70%	80%	90%	100%					
<b>1 challenging property</b>																					
Alkanes/alkenes C5 to C19 (cyclic, branched and linear)																					
<i>Standard (cyclic or paraffins)</i>																					

Paraffins				
6-Methylundecane	B7	density		
	B100			
	HVO			
n-tetradecane	B7	density		
	B100			
	HVO			
n-pentadecane	B7	density		
	B100			
	HVO			
2-methyltetradecane	B7	density		
	B100			
	HVO			
n-hexadecane	B7	density		
	B100			
	HVO			
n-heptadecane	B7	density		
	B100			

	HVO				
7-butyltridecane	B7	density			
	B100				
	HVO				
n-octadecane	B7	density			
	B100				
	HVO				
n-eicosane	B7	density			
	B100				
	HVO				
<b>Esters (fatty esters, fusel)</b>					
<i>Conventional esters (FAME)</i>					
Methyl linoleate	B7	cetane			
	B100				
	HVO				
<b>Ethers</b>					
<i>Dioxolanes derivatives</i>					
	B7	density			Viscosity is out-of bound

4,5-dimethyl-2-(pentan-3-yl)-1,3-dioxolane	HVO			
	B100			
4,5-dimethyl-2-pentyl-1,3-dioxolane	B7	 density		Viscosity is out-of bound
	HVO			
	B100			
2,4-dimethyl-2-undecyl-1,3-dioxolane	B7	 density		Viscosity is out-of bound
	HVO			
	B100			
Dioxolanes derivatives	B7	 density		
	extended			
<b>Ketones</b>				
2-hexadecanone	B7	 viscosity assumed 1,5 cst		
	HVO			
	B100	 viscosity assumed 1,5 cst		
<b>2 or 3 challenging properties</b>				
<b>Alkanes/alkenes C5 to C19 (cyclic, branched and linear)</b>				
<i>Standard (cyclic or paraffins)</i>				

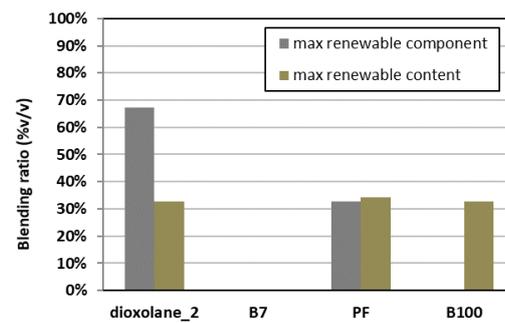
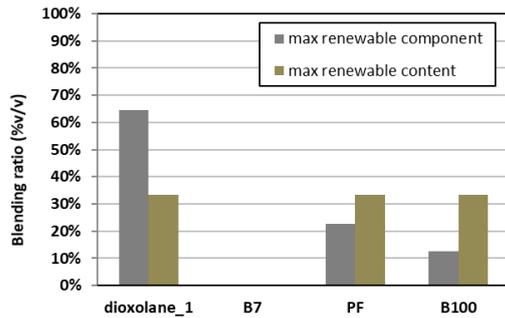
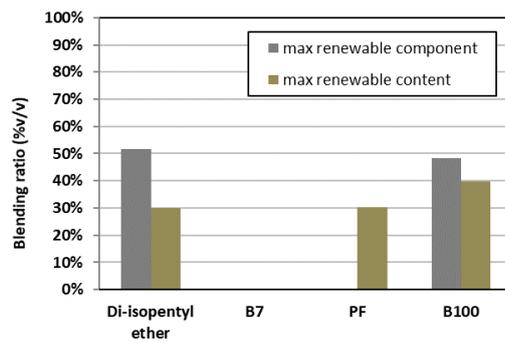
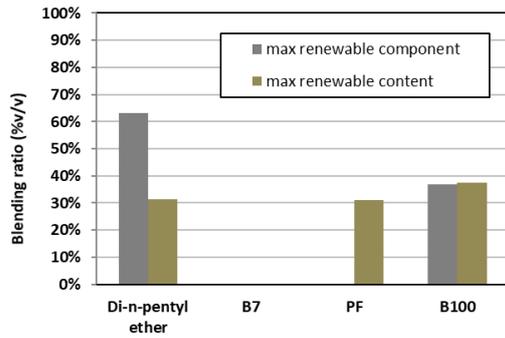
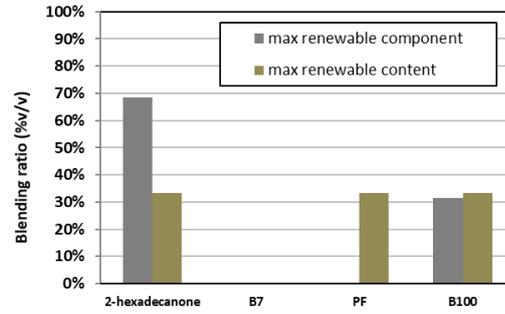
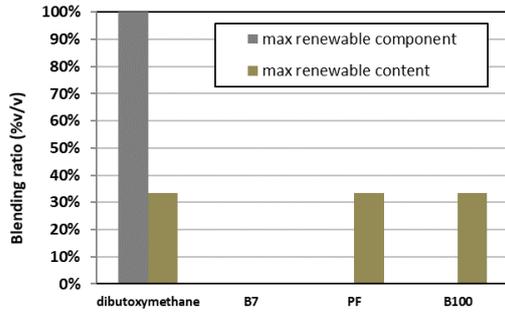
<b>Paraffins</b>					
n-undecane	B7	density			
n-decane	B7	density			
n-dodecane	B7	density			
3-ethyldecane	B7	cetane			
n-tridecane	B7	density			
3,3,5-trimethyldecane	B7	density			
<b>Cyclic</b>					
Decalin	B7	cetane			
n-butylcyclohexane	B7	FP			
<b>Olefines</b>					
Limonene	B7	cetane			
<b>Ethers</b>					
<b>Linear ethers</b>					
Iso pentyl Ether	B7	density			Density, flash point and lubricity are low
	B100				
	HVO				
<b>OMEx</b>					

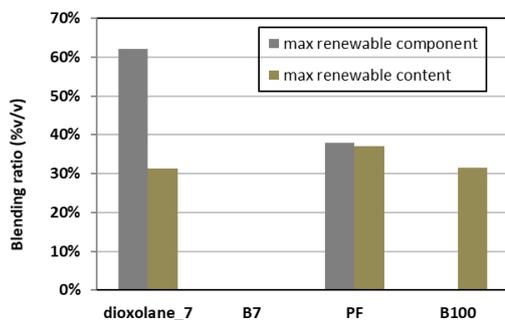
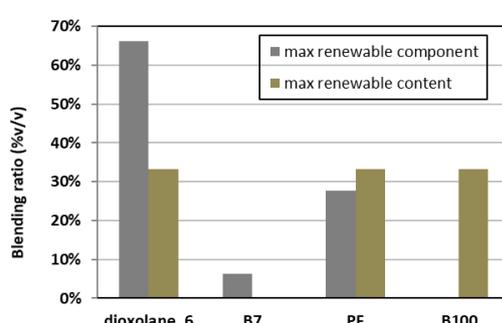
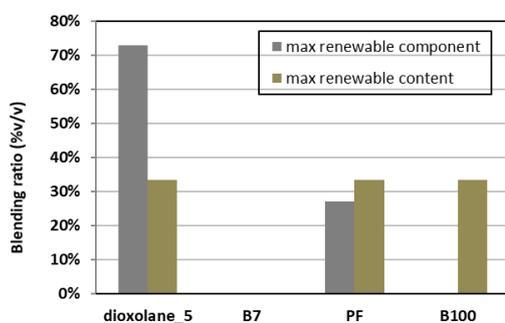
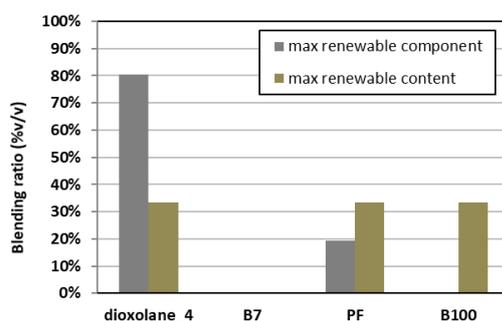
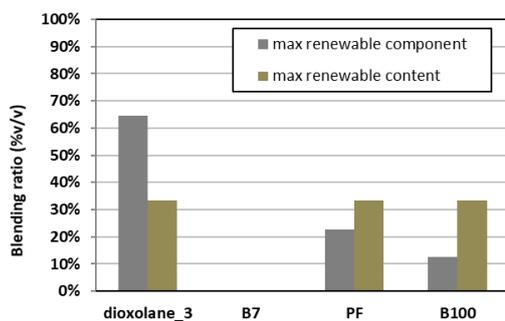
4-butoxyheptane	B7	viscosity			
	B100				
	HVO				
OME mix	B7	density			Density is high and viscosity is low. Modified nozzle is recommended above 20-30 %vol blends.
	B100				
	HVO				
3,5,7,9-Tetraoxaundecane	B7	density			
	B100				
	HVO	viscosity assumed 0,5 cst			
<b>Alcohols</b>					
<b>C5-</b>					
Pentanol	B7	cetane			Density, CN and flash point are low. In blends CN is outoff bounds
	B100				
	HVO	cetane			
<b>Ketones</b>					

4-methylacetophenone	B7	density	[Red bar]		[Green bar]	[Yellow bar]	High density, low viscosity
	B100		[Red bar]				
	HVO		[Yellow bar]	[Green bar]	[Red bar]		
3-octanone	B7	viscosity	[Green bar]	[Red bar]	[Green bar]	[Yellow bar]	Low viscosity
	B100		[Red bar]				
	HVO		[Yellow bar]	[Red bar]			

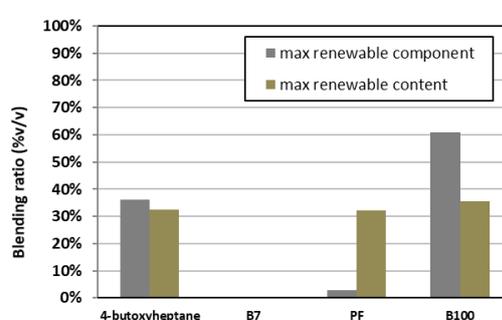
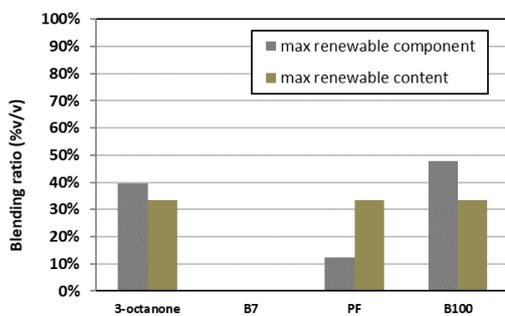
## 6. RENEWABLE COMPONENT AND RENEWABLE CONTENT OPTIMIZATION - EN590 CONSTRAINT

- Incorporation rate > 50% (v/v)

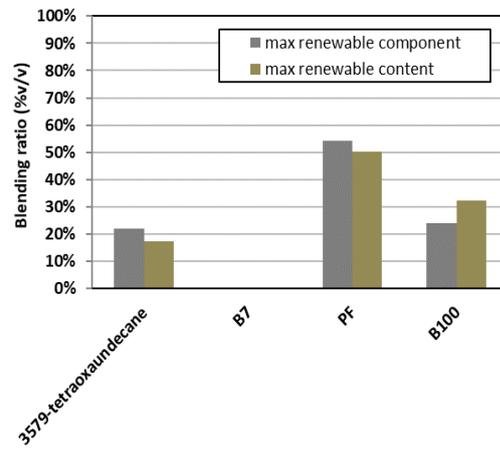
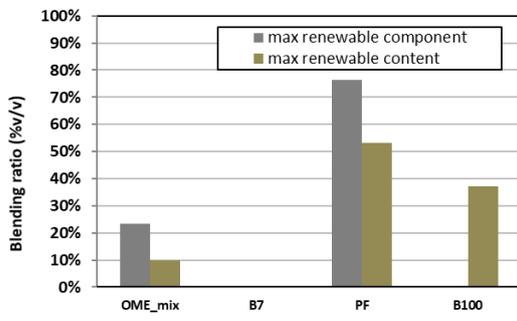
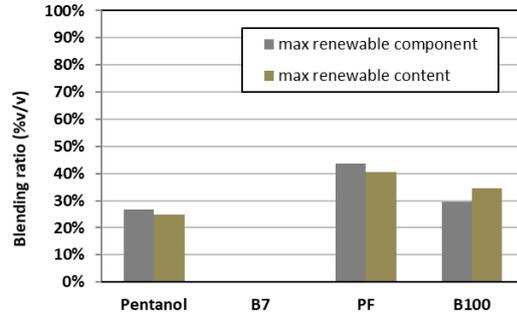
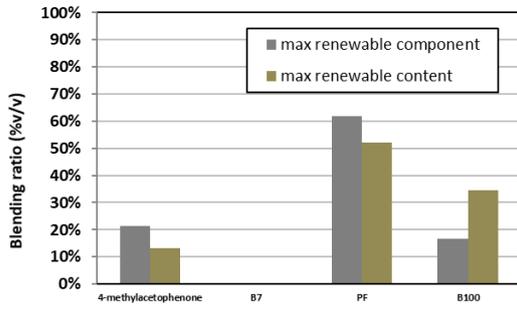




• Incorporation rate from 30% to 50% (v/v)



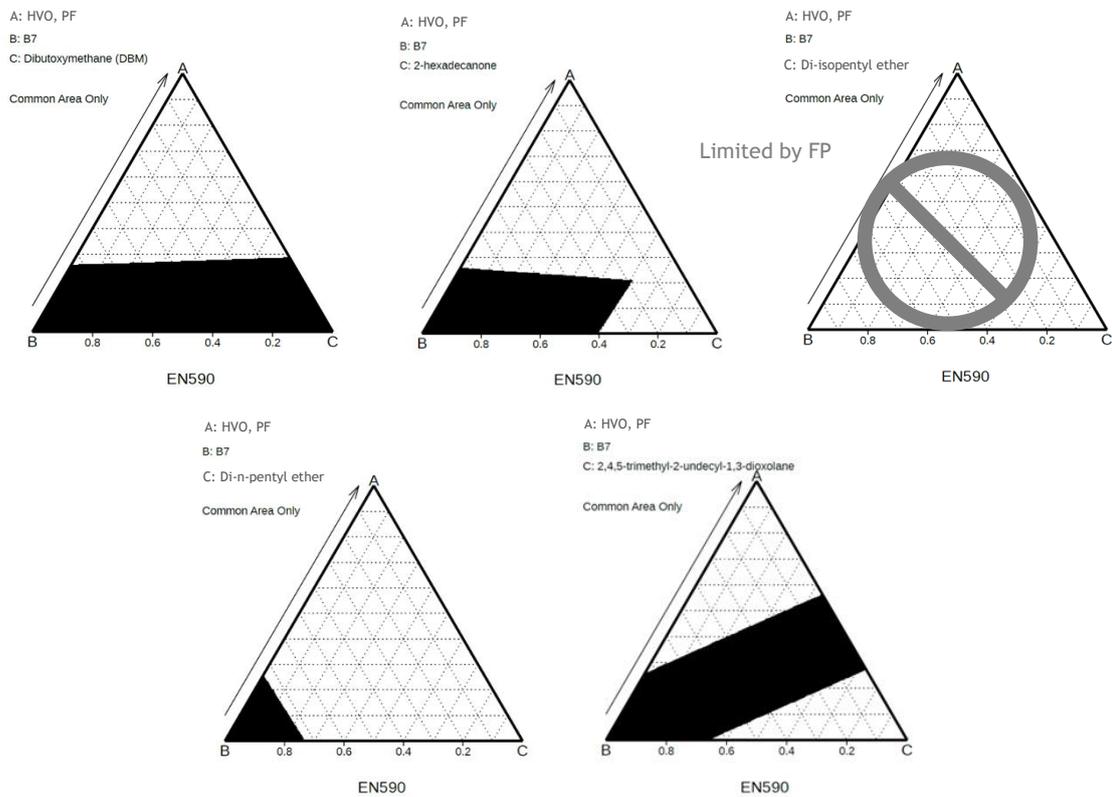
• Incorporation rate < 30% (v/v)



## 7. TERNARY PLOTS

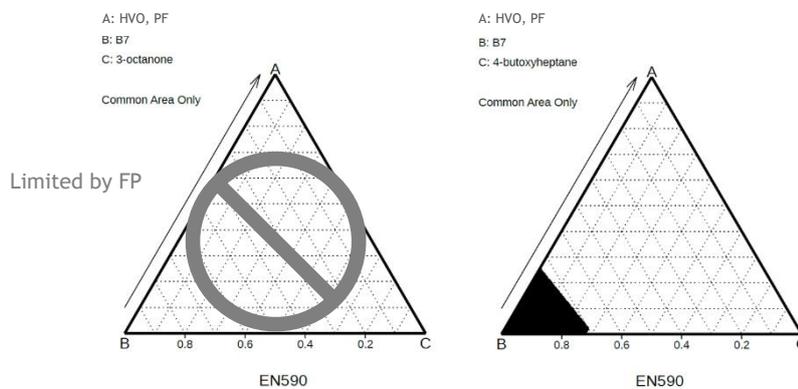
➤ PF+B7+renewable component → EN590 specifications

- Incorporation rate > 50% (v/v)

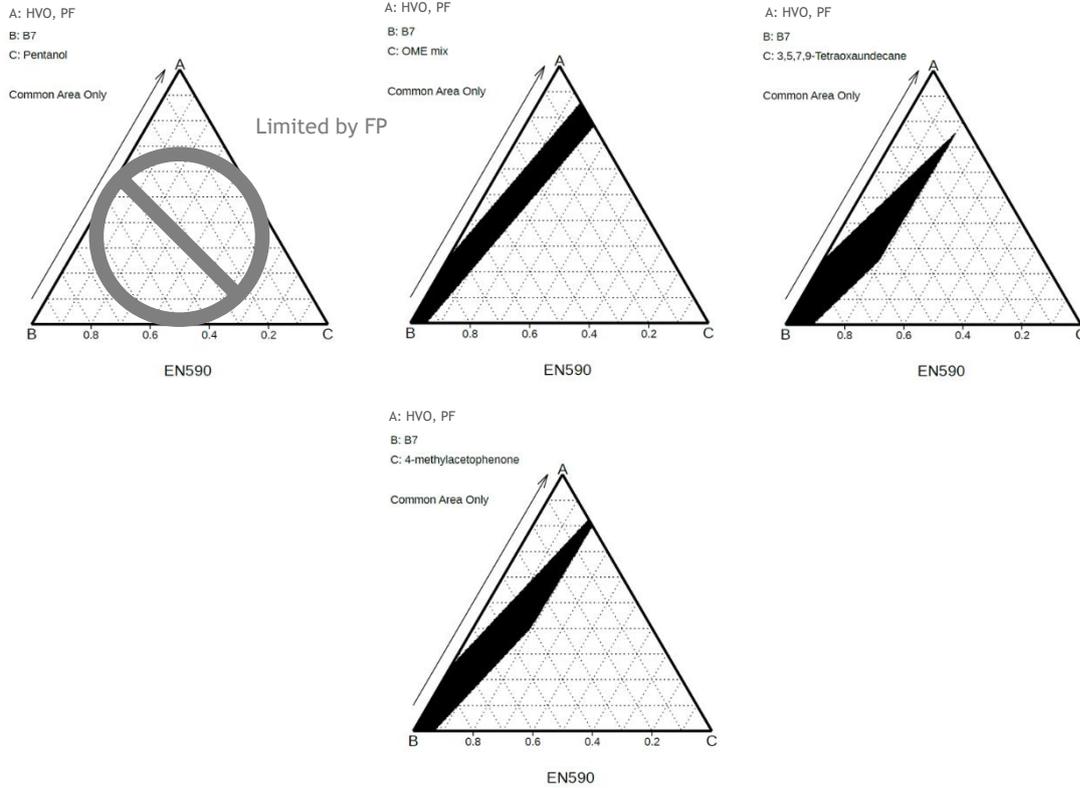


Note: Dioxolanes tend to have a similar range to the one illustrated here.

- Incorporation rate from 30% to 50% (v/v)



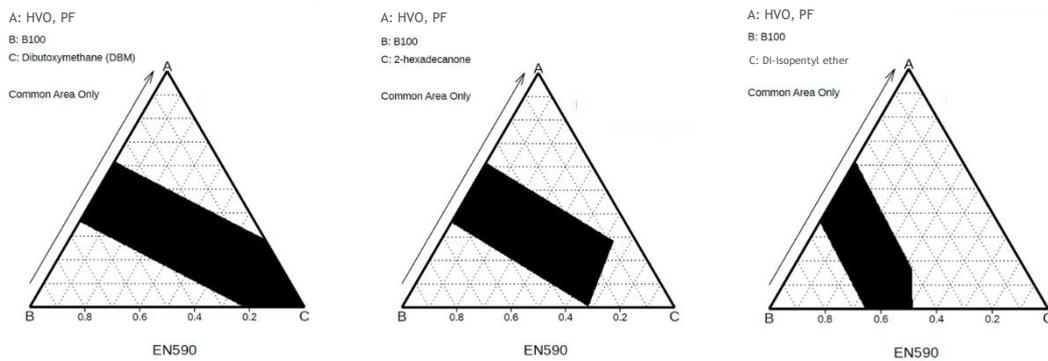
○ Incorporation rate < 30% (v/v)

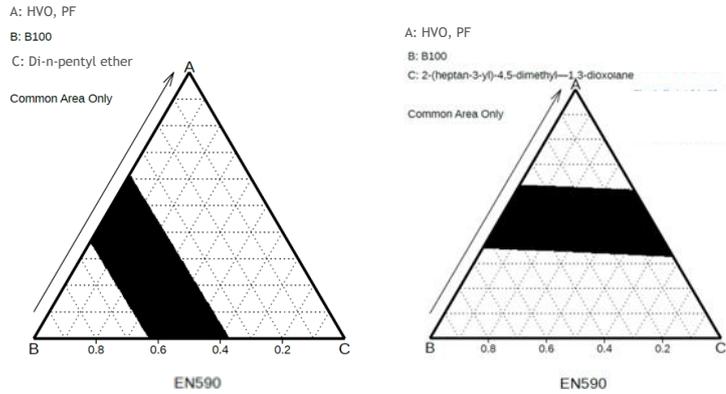


Note: Synergetic effect with PF is highlighted for the components listed here.

➤ PF+B100+renewable component → EN590 specifications

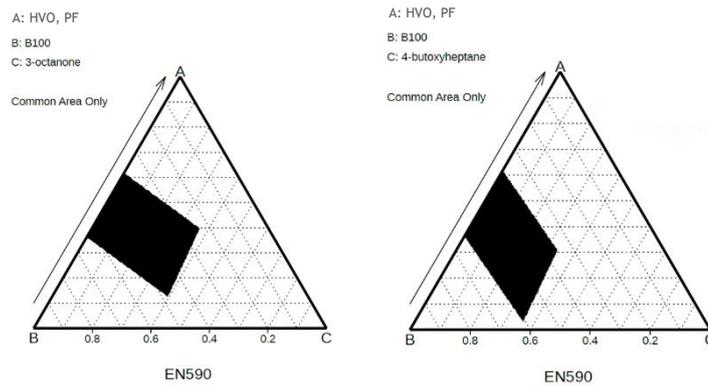
○ Incorporation rate > 50% (v/v)





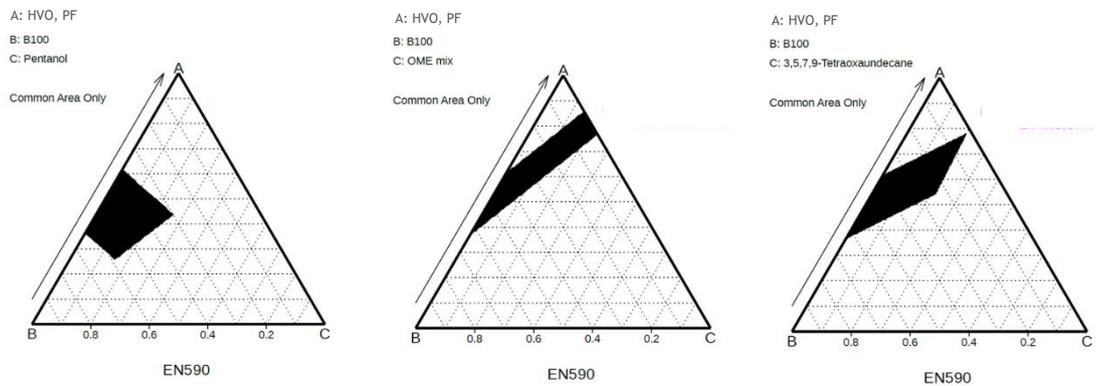
Note: A blend of PF and B100 is required to match the EN590 specifications. Dioxolanes tend to have a similar range to the one illustrated here.

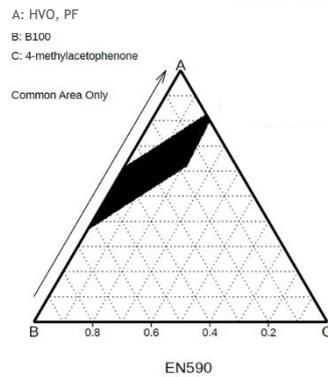
○ Incorporation rate from 30% to 50% (v/v)



Note: Again, a blend of PF and B100 is required to match the EN590 specifications.

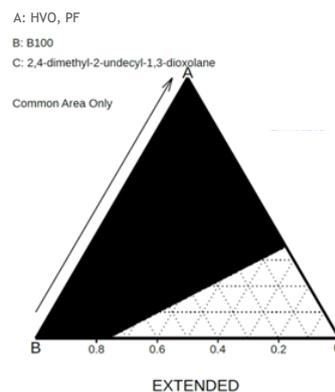
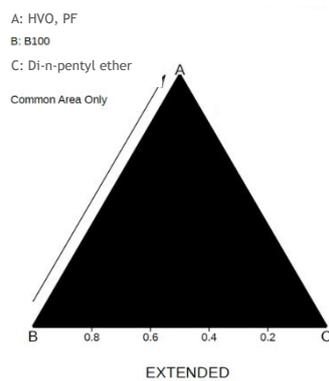
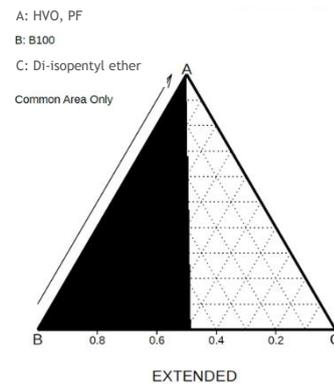
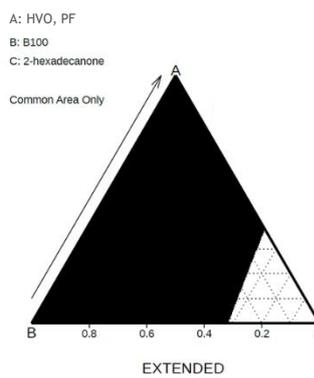
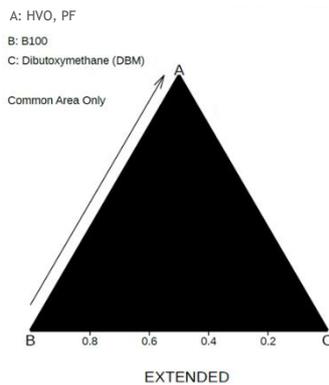
○ Incorporation rate < 30% (v/v)





Note: Synergetic effect with PF is highlighted again for OME, 3,5,7,9-tetraoxaundecane and 4-methylacetophenone.

- PF+B100+renewable component → Extended specifications
  - Incorporation rate > 50% (v/v)

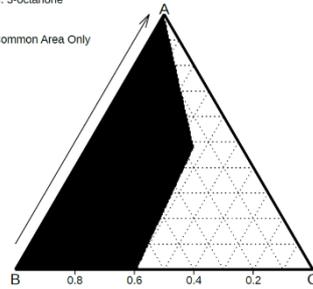


Note: As expected, a large range of mixtures are now within the extended specification boundaries. Worst case for the dioxolane derivatives. Others can be fully compatible.

○ Incorporation rate from 30% to 50% (v/v)

A: HVO, XTL  
B: B100  
C: 3-octanone

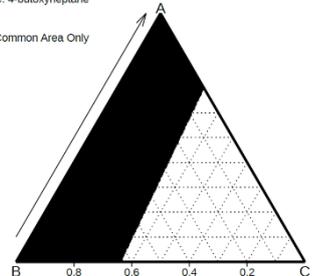
Common Area Only



EXTENDED

A: HVO, XTL  
B: B100  
C: 4-butoxyheptane

Common Area Only

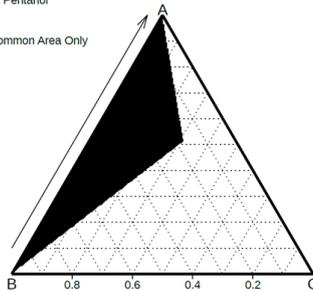


EXTENDED

○ Incorporation rate < 30% (v/v)

A: HVO, XTL  
B: B100  
C: Pentanol

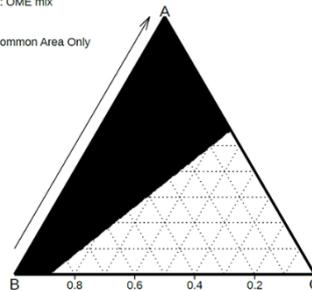
Common Area Only



EXTENDED

A: HVO, XTL  
B: B100  
C: OME mix

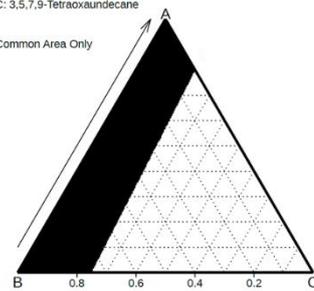
Common Area Only



EXTENDED

A: HVO, XTL  
B: B100  
C: 3,5,7,9-Tetraoxaundecane

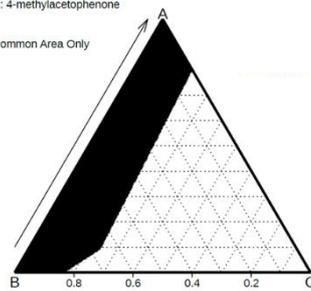
Common Area Only



EXTENDED

A: HVO, XTL  
B: B100  
C: 4-methylacetophenone

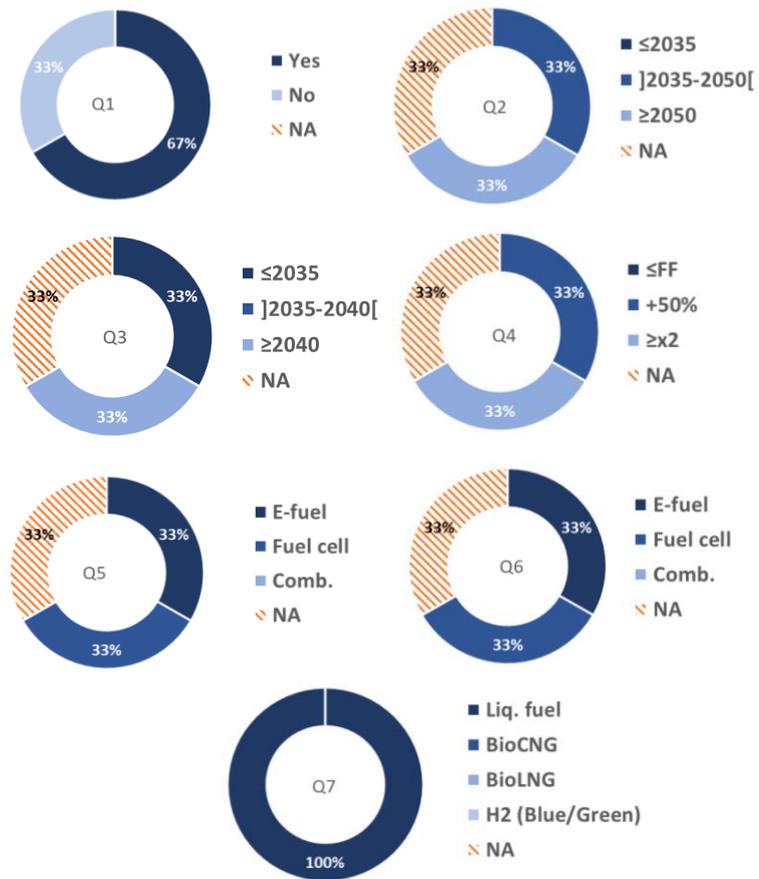
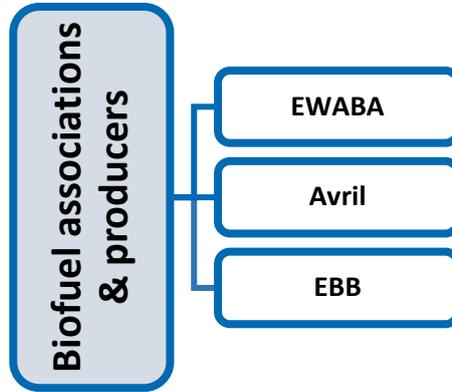
Common Area Only



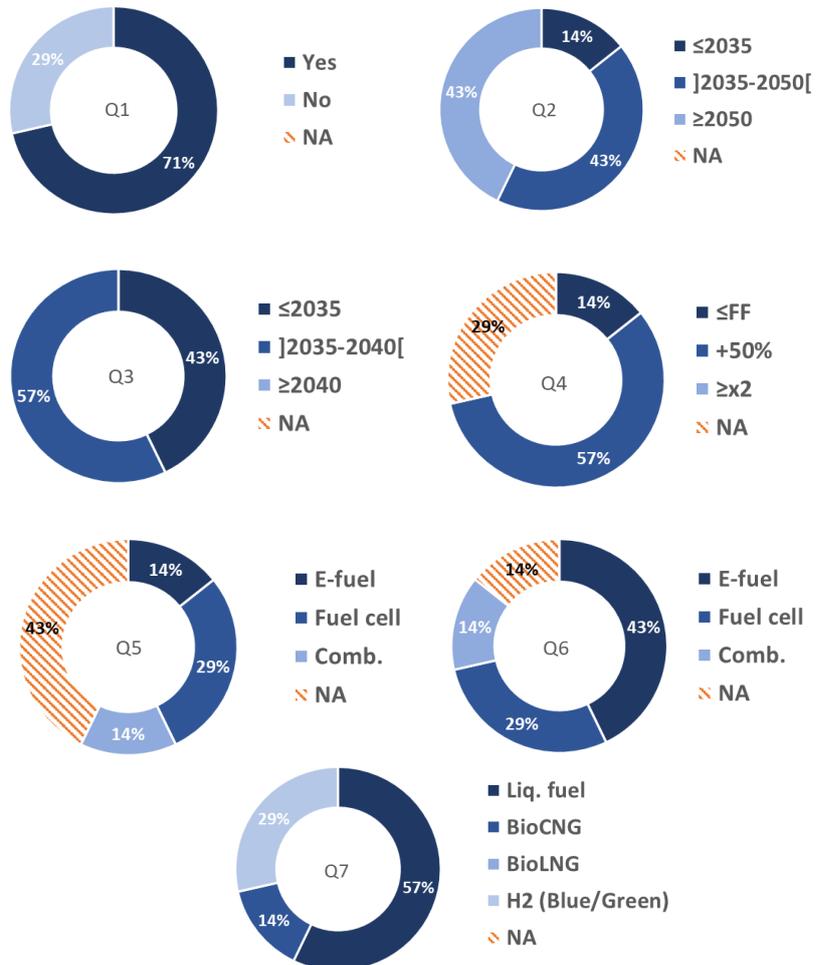
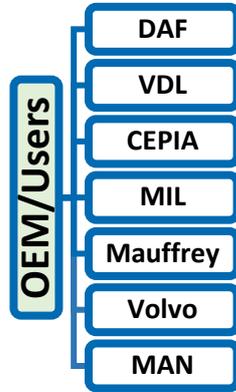
EXTENDED

8. PART 2 RESPONSES ANALYSIS BY STAKEHOLDER CATEGORY

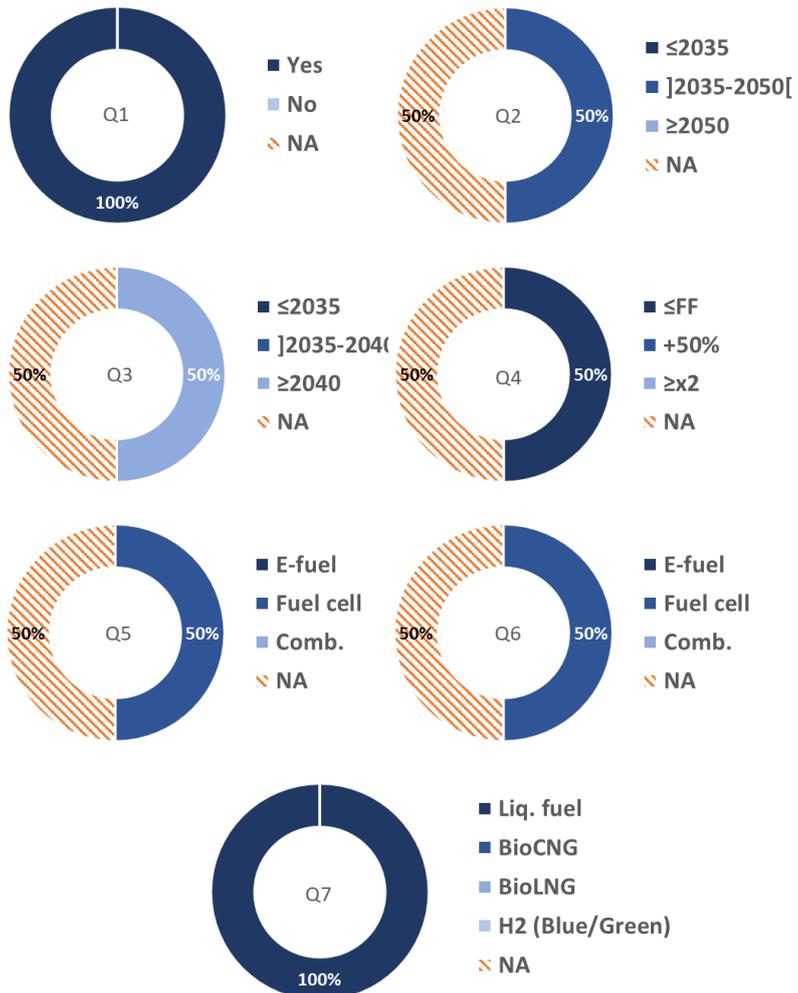
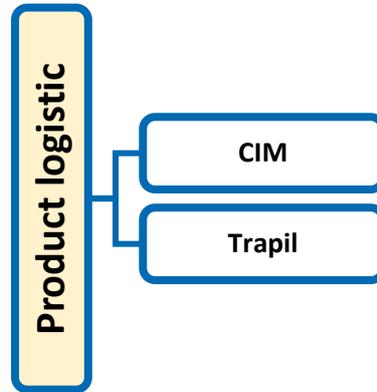
➤ Biofuel associations and producers



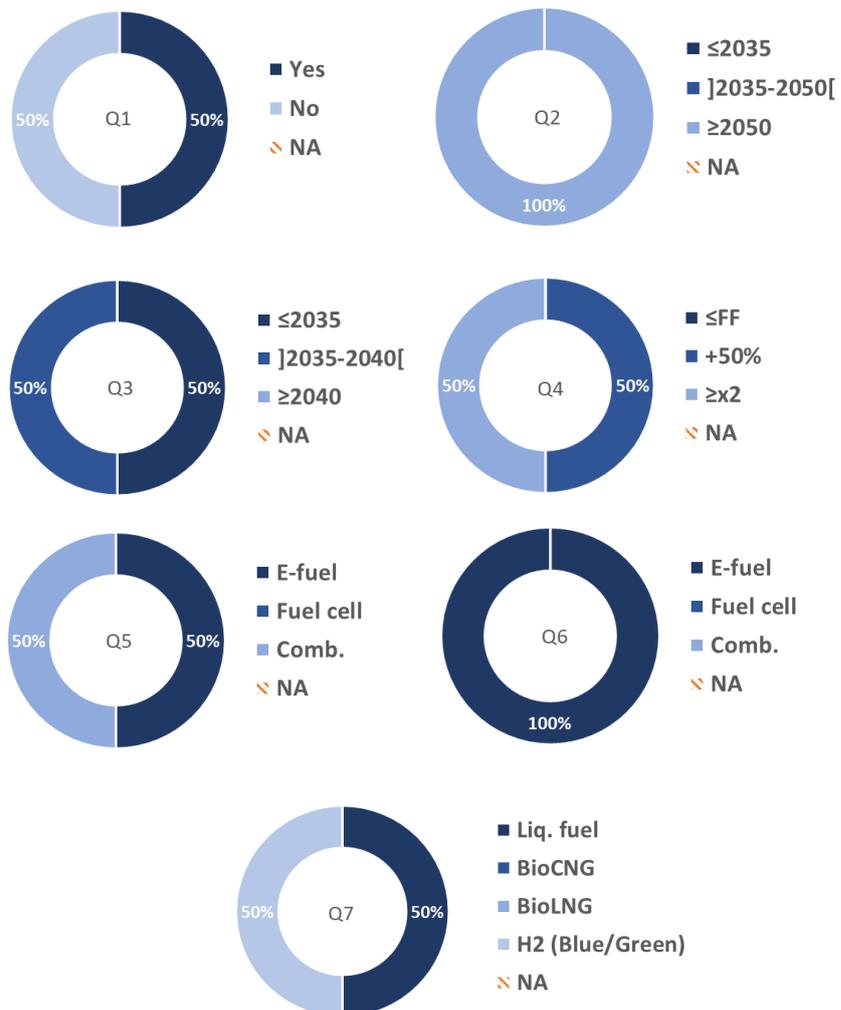
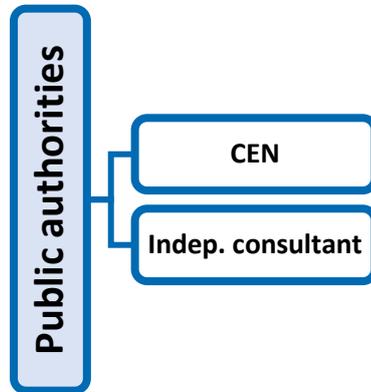
➤ OEM/Users



➤ Product logistic



➤ Public authorities



## 9. Details of the properties of the renewable diesel products from the 7 selected production pathways summarized in 3 product categories.

### ➤ Hydrotreatment products

Name	Density [kg/m <sup>3</sup> ]	Cetane Number	Kinematic Viscosity [mm <sup>2</sup> /s]	Flash Point [dgC]	Cold Filter Plugging Point [dgC]	Source
<b>Hydrotreatment Products</b>						
HVO (Camelina + other waste)	780	80	3.21	140	-44	[1,2,6-7,9-11]
HDT (Jatropha) (Worst)	780	93	4.17	145		[3,6-8,10-11]
HDT (Jatropha) (Best)	780	97	3.9	145		[3,6-8,10-11]
HDT (Camelina)	784.4	89.2	3.61	280	-20	[4-7,9-11]
HDT EC (Worst)	780	80	3.6	140	-20	
HDT EC (Best)	780	80	3.6	140	-44	
HVO (Worst)	770	71	4	60	-2	[1,2,10,11]
HVO (Best)	790	71	2	61	-2	[1,2,10,11]
HDT (WCO) (Worst)	778	74	4.231	42	19	[12,13]
HDT (WCO) (Best)	793	75.2	2.111	42	-11	[12,13]
HDT WCO (Worst)	780	71	3	42	19	
HDT WCO (Best)	780	71	3	61	-11	
White Diesel (WCO)	753	77	3.5	116	20	[14]

### ➤ Fischer-Tropsch products

Name	Density [kg/m <sup>3</sup> ]	Cetane Number	Kinematic Viscosity [mm <sup>2</sup> /s]	Flash Point [dgC]	Cold Filter Plugging Point [dgC]	Source
<b>Fischer-Tropsch Products</b>						
FT diesel (Worst)	774	74	4.5	71	0	[15,16]
FT diesel (Best)	782	80	2	71	-22	[15,16]
GTL (Worst)	770	70	4.5	59		[7]
GTL (Best)	790	71	2	59		[7]
FT without isom (Worst)	774.6	86.7	2.3	93		[17]
FT (Worst)	780	74		100	0	[14,18,19]
FT (Best)	780	75		120	-22	[14,18,19]
FT (Worst)	770	70	3	59	0	
FT (Best)	790	70	3	59	-22	

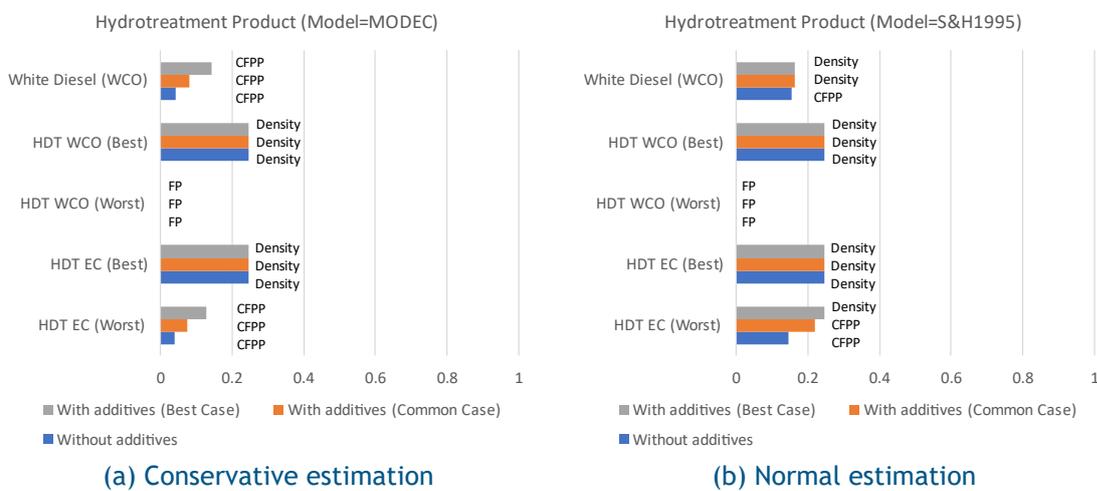
### ➤ Transesterification products

Name	Density [kg/m <sup>3</sup> ]	Cetane Number	Kinematic Viscosity [mm <sup>2</sup> /s]	Flash Point [dgC]	Cold Filter Plugging Point [dgC]	Source
<b>Transesterification Products</b>						
Biodiesel (Babassu)			3.239			[20-23]
Biodiesel (Camelina)		52.8	4.15			[20-23]
Biodiesel (Canola)	882	52.9	3.9	146		[20-23]
Biodiesel (Coconut)			2.726			[20-23]
Biodiesel (Cottonseed)			4.221			[20-23]
Biodiesel (Jatropha)	888	57.8	5.227			[20-23]
Biodiesel (Linseed)			3.752			[20-23]
Biodiesel (Neem)			5.213			[20-23]
Biodiesel (Palm)	876.4	58	3.7	130		[20-23]
Biodiesel (Peanut)	886.4	54	5.251	193		[20-23]
Biodiesel (Pongamia)		55.27	4.23	142		[20-23]
Biodiesel (Rapeseed)		61.8	5.65	179		[20-23]
Biodiesel (Rice Bran)			4.958			[20-23]
Biodiesel (Soybean)	885.2	51.3	4.057	173		[20-23]
Biodiesel (Sunflower)			4.439			[20-23]
TRANS EC (Worst)	876	51	5.6	130	11	
TRANS EC (Best)	888	62	2.7	193	-9	
Biodiesel (Waste Cooking Oil) #1	880	56.8	3.98			[20-23]
Biodiesel (Waste Cooking Oil) #2	860	49	7.8	135		[20-22,24]
Biodiesel (Waste Cooking Oil) #3	879		5.19	171		[20-22,25]
Biodiesel (Waste Cooking Oil) #4	897	54	5.3	196		[20-22,26]
Biodiesel (Yellow Grease)			4.552		2	[20-23]
TRANS WCO (Worst)	860	51(49)*	5.3	135	2	
TRANS WCO (Best)	897	57	4	196	2	
Biodiesel (Beef Tallow) #1		60.35	5.3	156.7	14.3	[20-23]
Biodiesel (Beef Tallow) #2			4.82	160	14	[20-22,27]
Biodiesel (Beef Tallow) #3	870		5.35	171	10	[20-22,27]
Biodiesel (Poultry Fat) #1			4.496		2	[20-23]
Biodiesel (Poultry Fat) #2			4.5	160	2	[20-22,27]
Biodiesel (Poultry Fat) #3	877		6.86	172	3	[20-22,27]
Biodiesel (Chicken Fat) #1	830	50	3.5	50		[20-22,27]
Biodiesel (Chicken Fat) #2	870	58.4	5.4	174		[20-22,27]
Biodiesel (Chicken Fat) #3	883		4.94	171.8		[20-22,27]
Biodiesel (Pork Lard) #1	873		5.08	147	5	[20-22,27]
Biodiesel (Pork Lard) #2	870	56.9	4.74	175	-20	[20-22,27]
Biodiesel (Mutton Tallow)	856	59				[20-22,27]
TRANS AF (Worst)	830	51(50)*	6.9	50	14	
TRANS AF (Best)	883	60	3.5	175	-20	

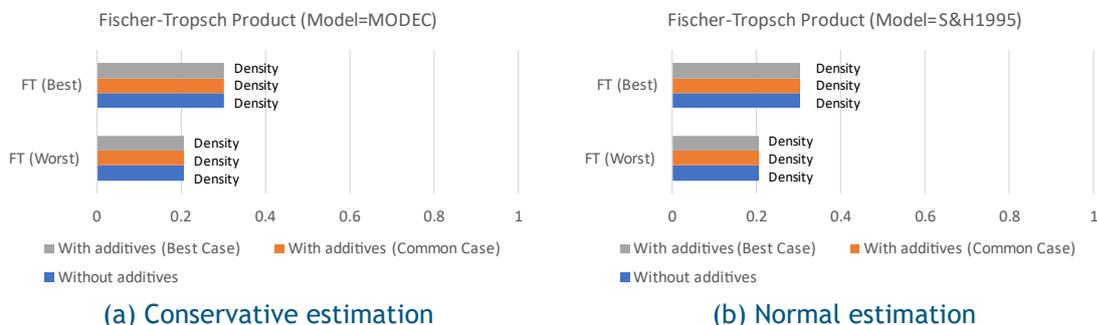
**10. Optimization results: Max blending ratio with additives for warm European countries.**

Scenario 1: EN590

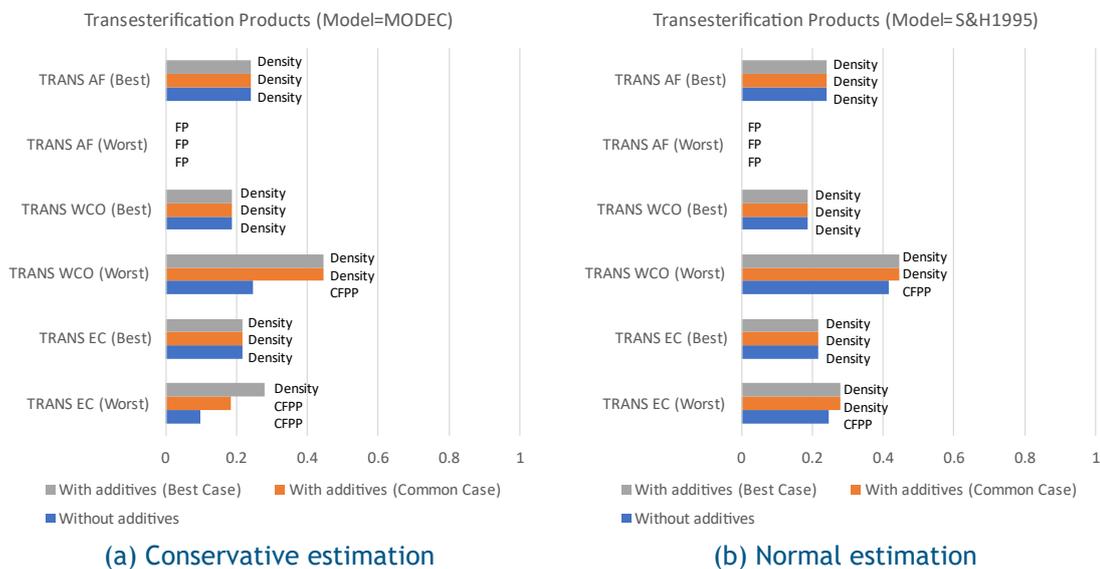
- Maximum blending ratio of hydrotreatment products in B7 while still complying with the EN590-extended standard for warm European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are 20, -11, 19, -44, and 21, respectively.



- Maximum blending ratio of Fischer-Tropsch products in B7 while still complying with the EN590-extended standard for warm European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -22 and 0, respectively.

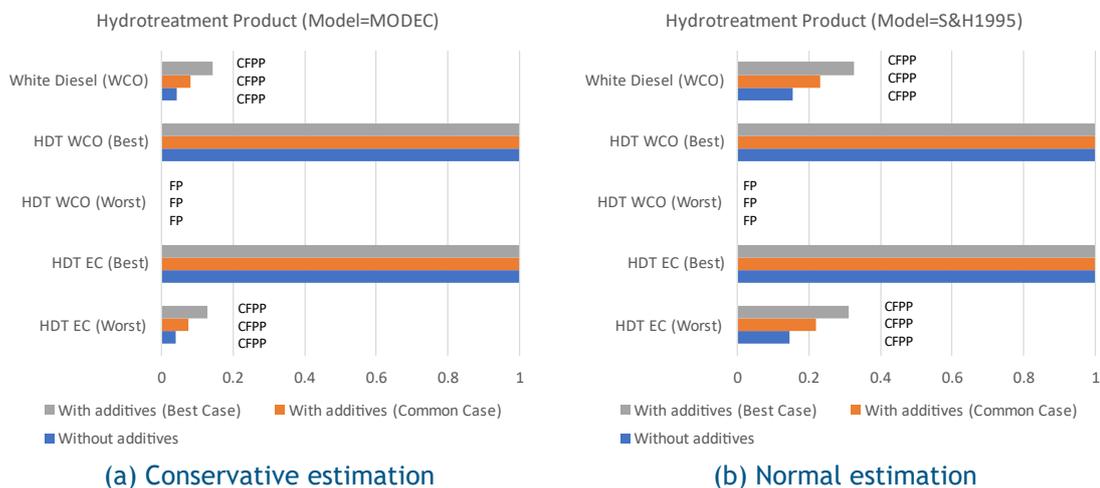


- Maximum blending ratio of transesterification products in B7 while still complying with the EN590-extended standard for warm European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -20, 14, 2, 2, -9, and 11, respectively.

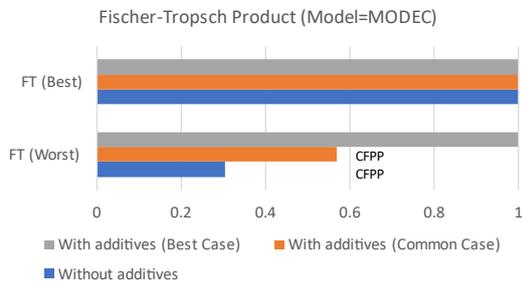


Scenario 2: EN590-extended

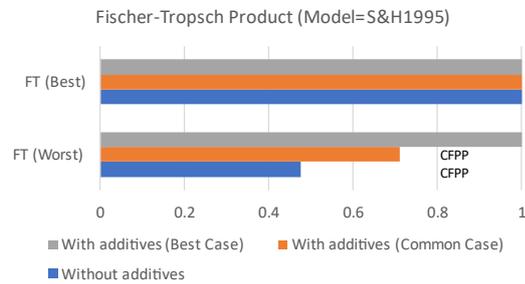
➤ Maximum blending ratio of hydrotreatment products in B7 while still complying with the EN590-extended standard for warm European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are 20, -11, 19, -44, and 21, respectively.



➤ Maximum blending ratio of Fischer-Tropsch products in B7 while still complying with the EN590-extended standard for warm European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -22 and 0, respectively.

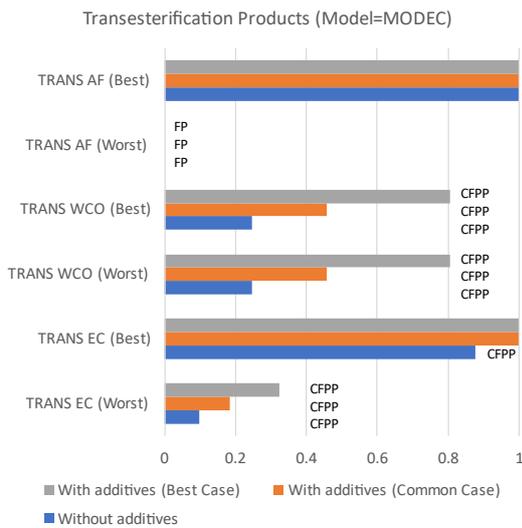


(a) Conservative estimation

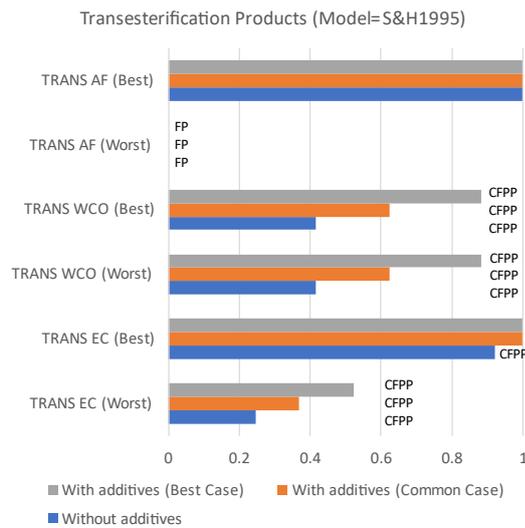


(b) Normal estimation

- Maximum blending ratio of transesterification products in B7 while still complying with the EN590-extended standard for warm European countries, with (a) conservative and (b) normal estimations. The text near the horizontal bar indicates the limiting property preventing higher blending ratio. The CFPP of B7 is -25 °C. The CFPP value for the products (in the order from top to bottom) are -20, 14, 2, 2, -9, and 11, respectively.



(a) Conservative estimation



(b) Normal estimation



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