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Impact of Synthetic Antioxidant Additives on Oxidation Stability of Diesel/Biodiesel Blends

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Introduction

The need to replace diesel with an alternative fuel that has similar properties lead the automotive industry to use diesel/biodiesel blends. The main physicochemical properties of biodiesel are comparable to those of conventional middle distillate fuels, thus it can be used as an alternative solution for diesel [1]. However, it is susceptible to oxidation causing corrosion to metal and elastomer parts. Hence, to improve the oxidation stability of the fuel, antioxidants can be used [2].

The purpose of this research was to study the oxidation stability of diesel/biodiesel blends with antioxidant additives using the method **Rancimat** (EN 15751) and the method **PetroOXY** (ASTM D7525-prEN 16091) [3-4]. More specifically, the diesel fuels that were used were a desulfurized straight run (SR) sample and a hydro cracking (HC) sample, which were provided by Hellenic Petroleum S.A., whereas the biodiesel was provided by ELIN Biofuels S.A. The ratios chosen for the study were B7 and B10. According to European Standard EN 590, B7 is the current required biodiesel ratio for the blends, whereas B10 is considered the most likely future specification [5]. All three of the antioxidants were produced in the Laboratory of Fuel Technology and Lubricants of the National Technical University of Athens in Greece. Two of them were of phenolic type, whereas the other one was of aminic. For each of the antioxidants the oxidation stability of the originated blends was measured at six concentrations (50, 100, 200, 400, 600, 1000 ppm).

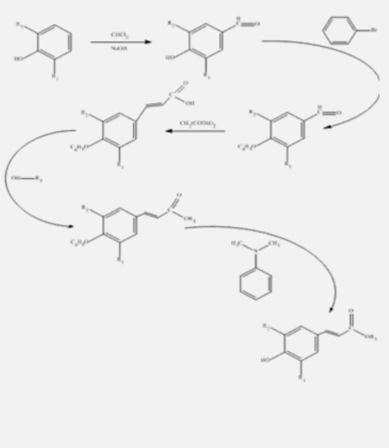

Figure 1: Synthesis of the phenolic antioxidants I, III

- ***Antioxidant I:*** R_1 = OH, R_2 = H, R_3 = C_4H_9
- ***Antioxidant III***: R_1 = OH, R_2 = H, R_3 = $C_{14}H_{29}$.

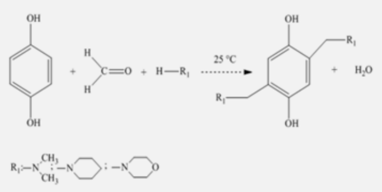

Figure 2: Synthesis of the aminic antioxidant II

- ***Antioxidant II:*** 4-tert-butyl-2,5-bis (dioctylamino)-1-benzenol

Table 1: Properties of the biodiesel sample

Chemical Physical Tests	Units	Method	Results
Density @15 oC	kg/m³	EN ISO 3675	884.22
Viscosity @40 oC	mm²/s	EN ISO 3104	4.29
C.F.P.P.	°C	EN-116	-10
Water in product	ppm-w	ISO-12937	84
Oxidation Stability	hr	ISO-14112	1,6
	min	prEN 16091	10,26
Flash point	°C	ASTM D-93	124
Acid value	mg KOH/g	EN-14104	0.29
Methyl esters	% w/w	EN-14103	98.3
Linolenic acid methyl esters	% w/w	EN-14103	0.28
Monoglycerides	% w/w	EN-14105	0.649
Diglycerides	% w/w	EN-14105	0.257
Triglygerides	% w/w	EN-14105	0.193
Free glycerol	% w/w	EN-14105	0.0057
Total glycerol	% w/w	EN-14105	0.229
Methanol content	% w/w	EN-14110	0.06

Table 2: Properties of the diesel samples

Property	Units	ULSD (H/C)	ULSD (S/R)	Method
Kinematic viscosity @ 40°C	mm²/s	4.15	3.72	EN 3104
Density @ 15°C	kg/m³	827.2	836.4	EN 3675
Total sulphur	mg/kg	<1	9	EN 20846
Total water	mg/kg	12	100	EN 12937
Flash point	°C	86	-	EN ISO 2719
C.F.P.P.	°C	-14	-	EN 116
Distillation	°C			EN 3405
IBP		207	197	
10%		246	238	
20%		258	253	
50%		296	282	
65%		316	296	
85%		342	321	
90%		349	333	
95%		357	353	
FBP		364	367	
Recovery (%)		-	97.8	
Recovery 250°C	%v/v	-	-	
Recovery 350°C	%v/v	-	-	
Cetane Index	-	65	57	EN 4264
Copper strip corrosion		1A	1A	EN ISO 2160
Polycyclic Aromatics Hydrocarbons	mg/kg	0.5	3.4	EN 12916
Lubricity, WS 1.4	μm	504	496	CEC F-06-A-96
Oxidation Stability	min	80,2	115	ASTM D7525

Results

At first, we measured the induction periods of neat biodiesel samples with the produced antioxidants. The results are presented extensively in the following figures.

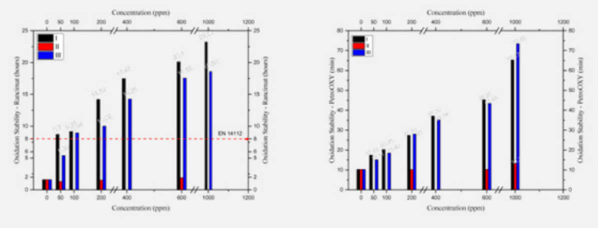

Figure 3: Oxidation Stability of biodiesel samples according to Rancimat and PetroOXY method

The induction periods of the blends are presented extensively for both methods in the following figures.

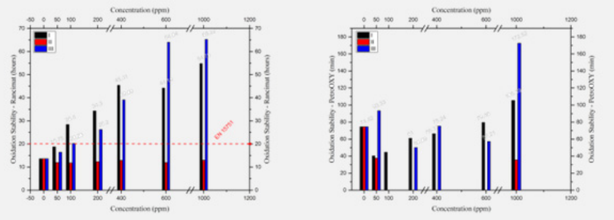

Figure 4: Oxidation Stability of HC diesel/biodiesel B7 according to Rancimat and PetroOXY method

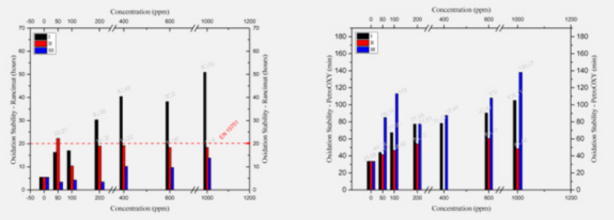

Figure 5: Oxidation Stability of SR diesel/biodiesel B7 according to Rancimat and PetroOXY method

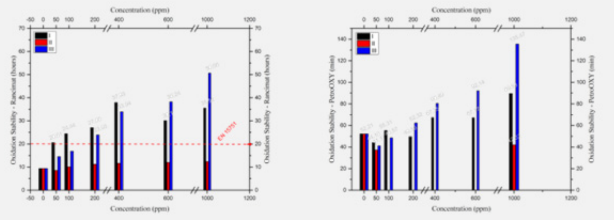

Figure 6: Oxidation Stability of HC diesel/biodiesel B10 according to Rancimat and PetroOXY method

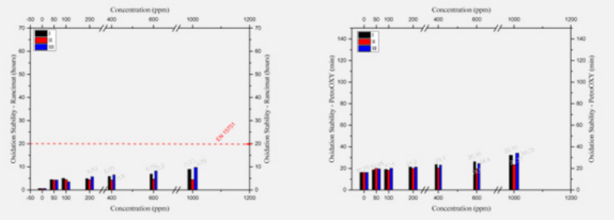

Figure 7: Oxidation Stability of SR diesel/biodiesel B10 according to Rancimat and PetroOXY method

Conclusions

As far as the biodiesel was concerned, it was observed that the aminic antioxidant (II) did not improve its oxidation stability. On the other hand, the two phenolic antioxidants (I and III) satisfied the specifications at the low concentrations of 50ppm and 100ppm respectively.

Moreover, during this study it was observed that both phenolic antioxidants improved the oxidation stability of all blends. However, the aminic antioxidant satisfied the specifications only for the blend of SR diesel/biodiesel B7. The B10 samples showed lower induction periods due to the increased ratio of biodiesel in the final sample, but overall similar behavior between the respective blends.

Table 3: Minimum required concentration for the satisfaction of the specifications

Sample	Concentration (ppm)		
	I	II	III
HC diesel/biodiesel B7	100	-	100
HC diesel/biodiesel B10	50	-	200
SR diesel/biodiesel B7	200	50	-
SR diesel/biodiesel B10	-	-	-
Biodiesel	50	-	100

Finally, even so the SR diesel presented better oxidation stability than the HC diesel; the respective blends did not show similar behavior. More specifically, the sample of SR diesel/biodiesel B7 could not satisfy the specifications with the use of phenolic antioxidant III, whereas the HC diesel/biodiesel B7 needed only 100ppm of the specific additive. Also, the SR diesel/biodiesel B7 blend needed 200 ppm of the antioxidant additive I, whereas the HC diesel/biodiesel B7 blend only 100ppm of the same additive.

Another interesting observation was that the only sample that satisfied the specifications for the aminic antioxidant was the SR diesel/biodiesel B7 at only 50ppm.

Acknowledgements

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References

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