ANALYTICAL CHARACTERISATION OF MINERAL OILS

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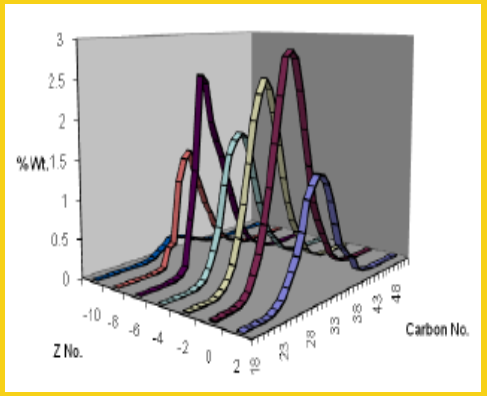


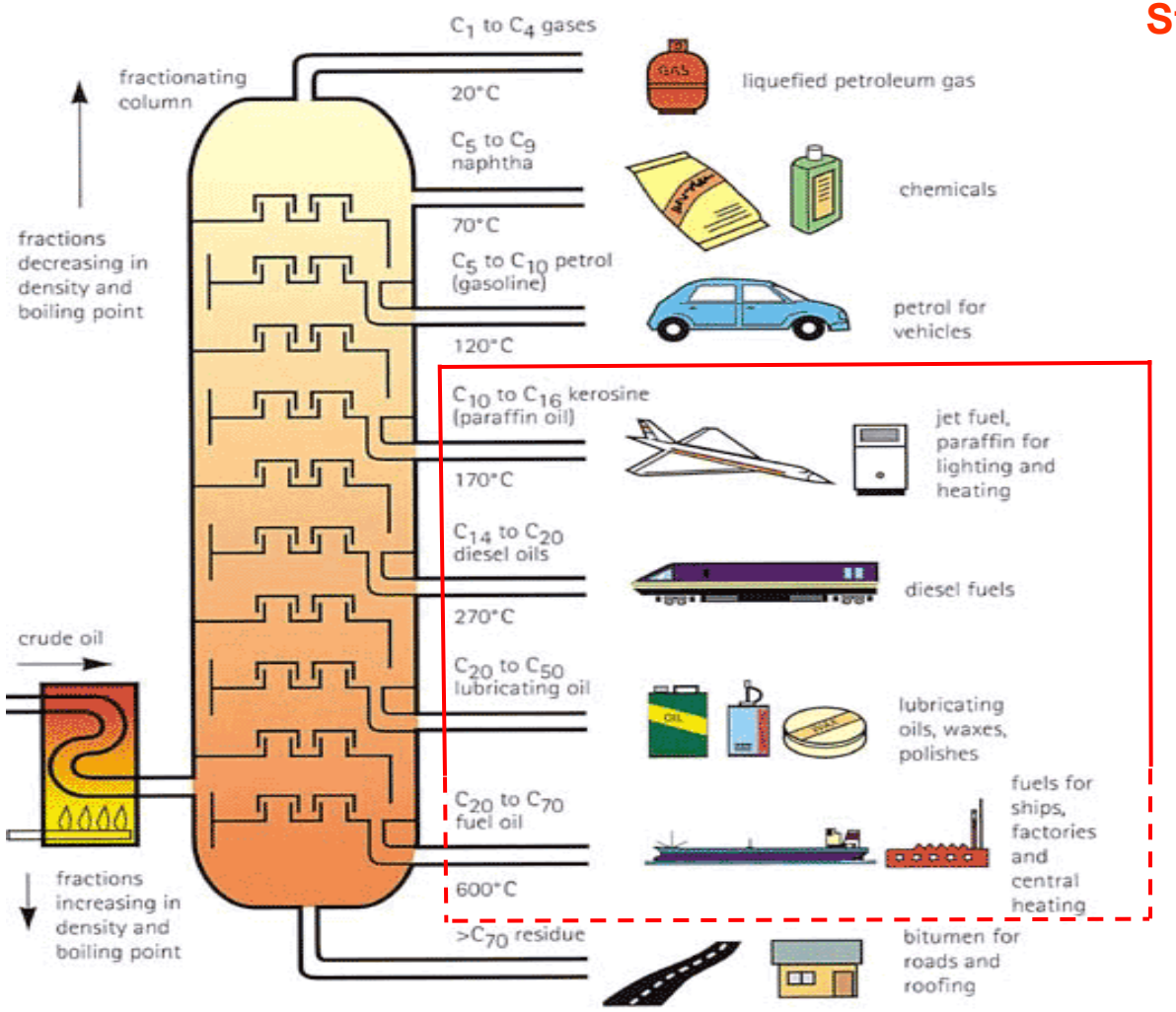
MOCRINIS Workshop
Bologna (10 - 11 September 2013)

EFSA SCIENTIFIC OPINION ON MOH IN FOOD (2012)

- MOH are hydrocarbons containing 10 to ~50 carbon atoms
- MOH in food typically range from C12 to C40
- Crude oil is the predominant source of MOH, but equivalent products are generated from other sources, including vegetable oils
- Numerous potential sources (from harvest through storage and processing to consumer) exist for the occurrence of MOH in food
- *"Technical grades of MOH"* typically contain 15-35% MOAH
- *"Of the many commercially available products, little is known about their composition, as specifications are generally expressed in terms of physico-chemical properties related to the applications of the products"*

MOH	*mineral oil hydrocarbons*
MOSH	*mineral oil saturated hydrocarbons*
MOAH	*mineral oil aromatic hydrocarbons*

REFINERY PRODUCTS



Possible Structures

10^1

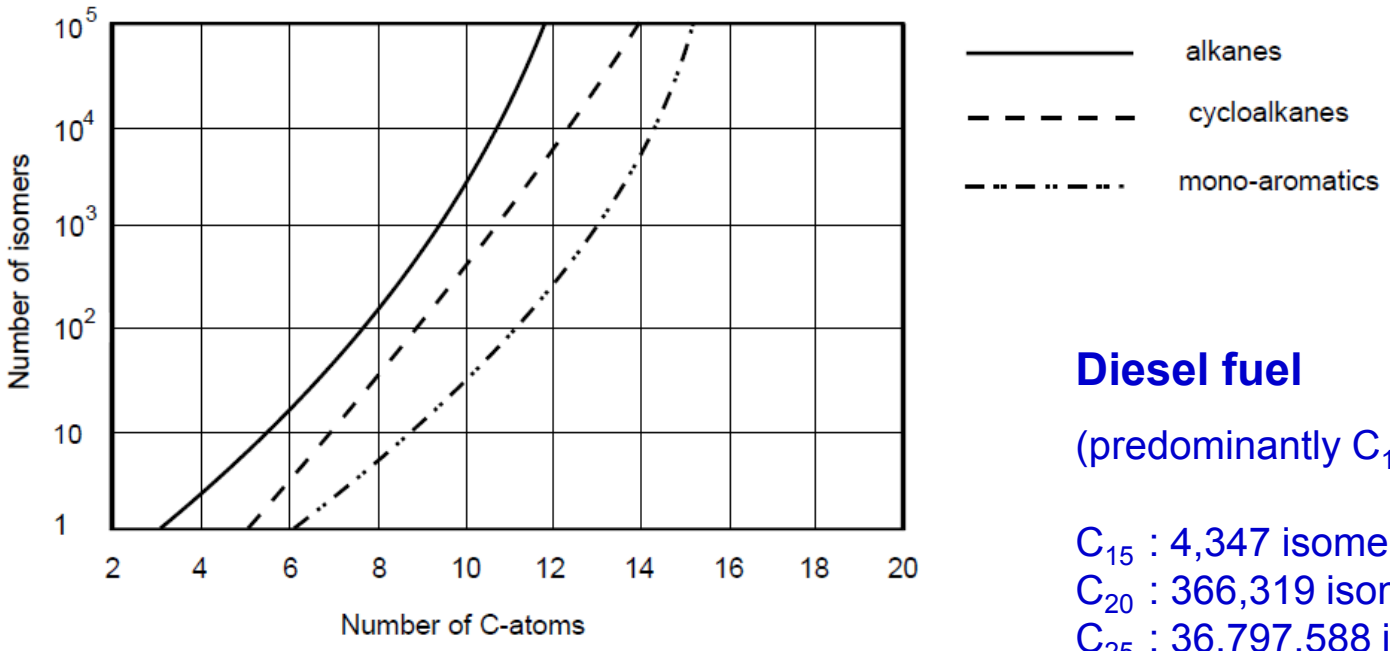
10^2

10^4

10^6

Increasing Molecular Complexity

COMPLEXITY OF PETROLEUM SUBSTANCES



Diesel fuel

(predominantly C_{11} – C_{25} components)

C_{15} : 4,347 isomers
C_{20} : 366,319 isomers
C_{25} : 36,797,588 isomers

theoretical number of alkane isomers
(cycloalkanes and aromatics not included)

PRODUCT COMPOSITION AND PERFORMANCE

"Of the many commercially available products, little is known about their composition, as specifications are generally expressed in terms of physico-chemical properties related to the applications of the products"

Kerosine (Aviation turbine fuel)

(predominantly C_9 – C_{16} components)

Final boiling point	:	300°C	(max)
Freezing point	:	- 47°C	(max)
Total aromatics	:	25%	(max)
Di-aromatics	:	3%	(max)
Total sulphur	:	0.3%	(max)

Although petroleum products are manufactured primarily to meet performance specifications, the chemical composition of fuels and base oils has been well characterised

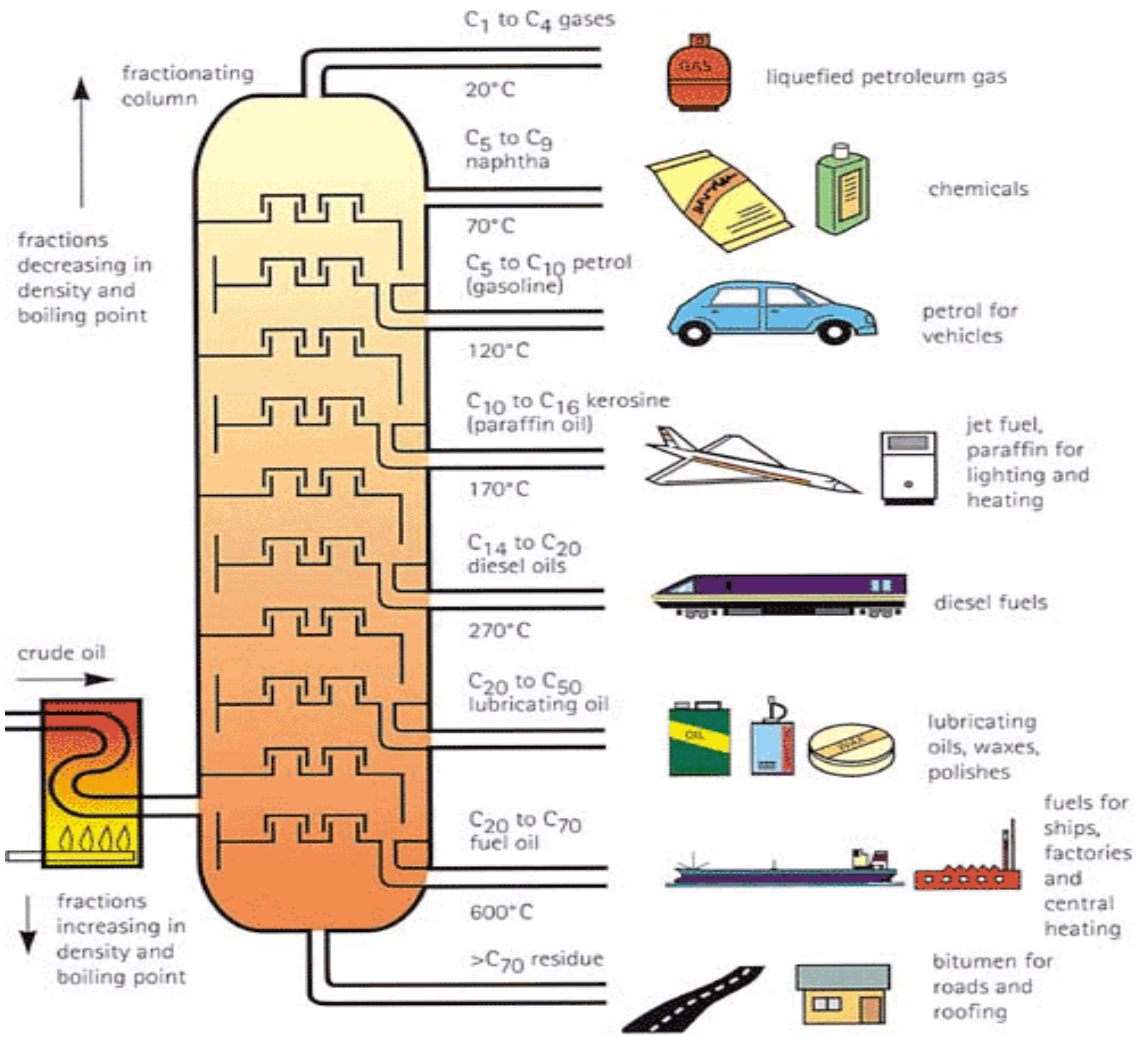
CHEMICAL COMPOSITION OF SOME AVIATION TURBINE FUELS

Sample	n-P	iso-P	m-N	di-N	m-A	Nm-A	di-A
Denmark (321)	9.0%	20.6%	31.8%	13.5%	15.4%	8.5%	1.2%
Kuwait (610)	15.8%	36.1%	26.3%	7.7%	10.6%	3.0%	0.5%
Germany (367)	6.7%	13.0%	33.8%	24.8%	15.3%	5.8%	0.6%

n-P : n-paraffins
iso-P : iso-paraffins
m-N : mono-naphthenes
di-N : di-naphthenes

m-A : mono-aromatics
Nm-A : naphthenic mono-aromatics
di-A : di-aromatics

REFINERY PRODUCTS



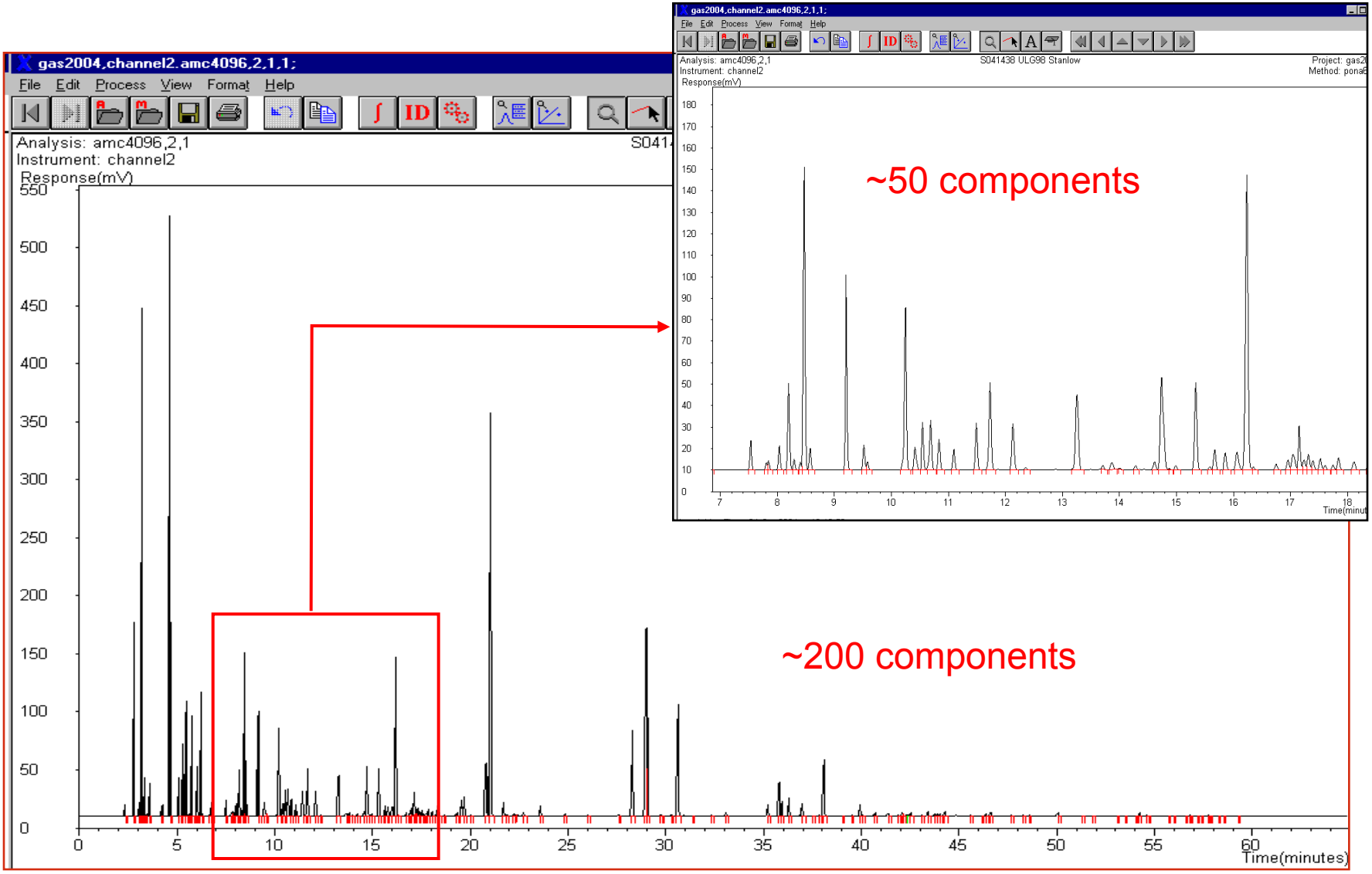
gasoline

kerosine

diesel fuel

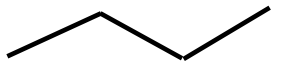
lubricating oil

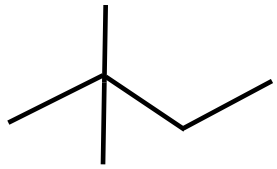
GC ANALYSIS OF GASOLINE

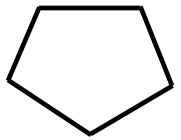


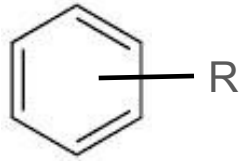
GC ANALYSIS OF GASOLINE

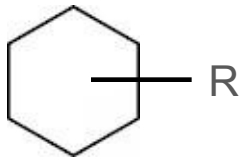
Retention Time	Area	Average RF	Component Name	Amount %m/m
2.445	4672	1.00000	Propane	0.1
2.585	159668	1.00000	IsoButane	2.0
2.665	554	1.00000	Unknown	0.0
2.705	285749	1.00000	n-Butane	3.5
2.767	3653	1.00000	Unknown	0.0
3.150	1327974	1.00000	IsoPentane	16.3
3.335	1178	1.00000	Unknown	0.0
3.383	168139	1.00000	n-Pentane	2.1
3.462	934	1.00000	Unknown	0.0
3.553	533	1.00000	Unknown	0.0
3.612	2517	1.00000	Unknown	0.0
3.833	131247	1.00000	2,2-DimethylButane	1.6
4.313	174365	1.00000	CycloPentane	2.1
4.340	137395	1.00000	2,3-DimethylButane	1.7
4.430	620493	1.00000	2-MethylPentane	7.6
4.730	346812	1.00000	3-MethylPentane	4.3
4.827	579	1.00000	Unknown	0.0
5.140	16902	1.00000	n-Hexane	0.2
5.330	923	1.00000	Unknown	0.0
5.427	704	1.00000	Unknown	0.0
5.732	963	1.00000	Unknown	0.0
5.877	5145	1.00000	2,2-DimethylPentane	0.1
5.972	278336	1.00000	MethylcycloPentane	3.4
6.088	19171	1.00000	2,4-DimethylPentane	0.2
6.280	1529	1.00000	2,2,3-TrimethylButane	0.0
6.838	45829	0.90000	Benzene	0.5
7.085	7283	1.00000	3,3-DimethylPentane	0.1
7.257	148668	1.00000	Cyclohexane	1.8
7.622	649	1.00000	Unknown	0.0
7.710	91729	1.00000	2-MethylHexane	1.1
7.780	44444	1.00000	2,3-DimethylPentane	0.5



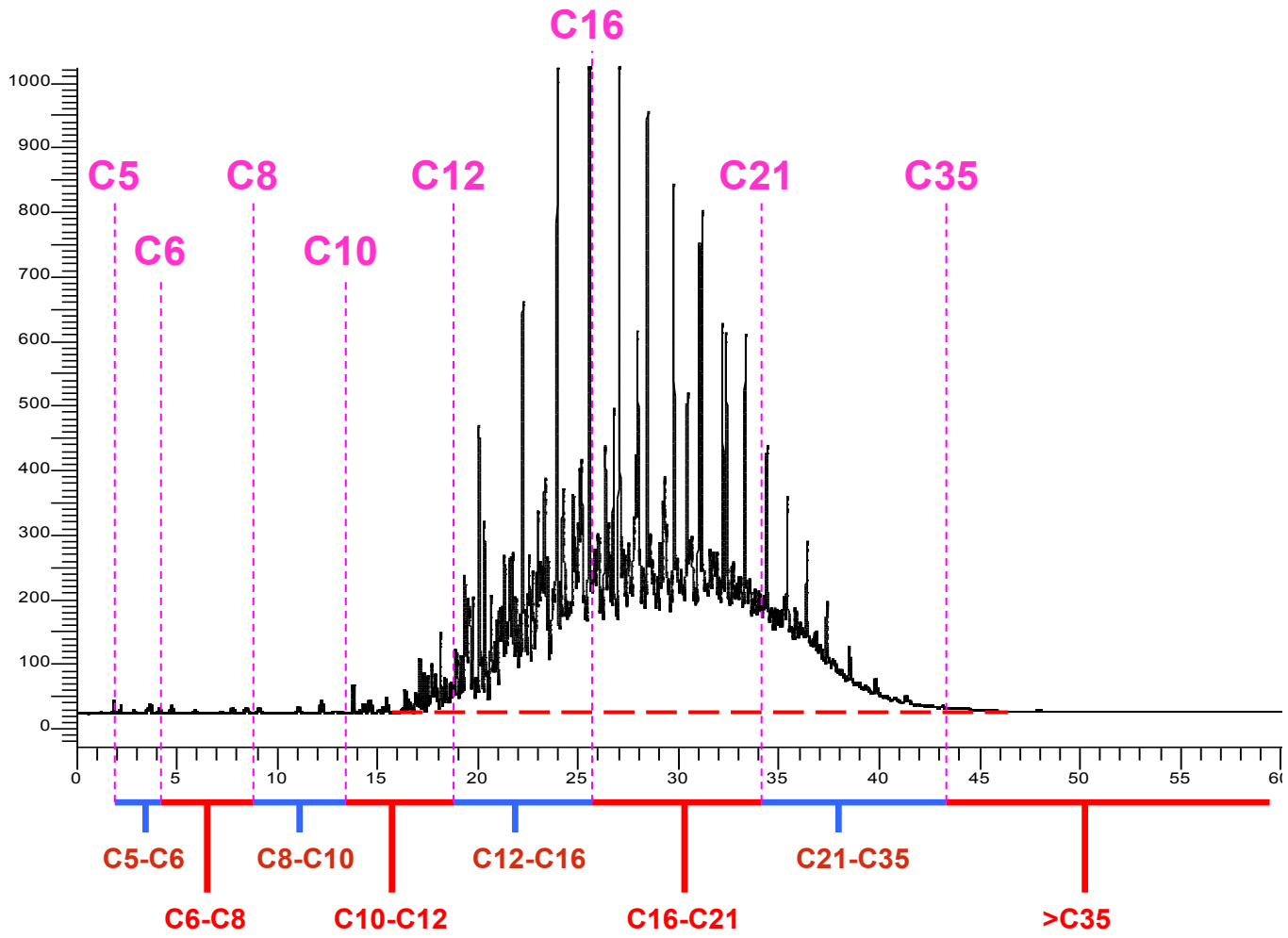




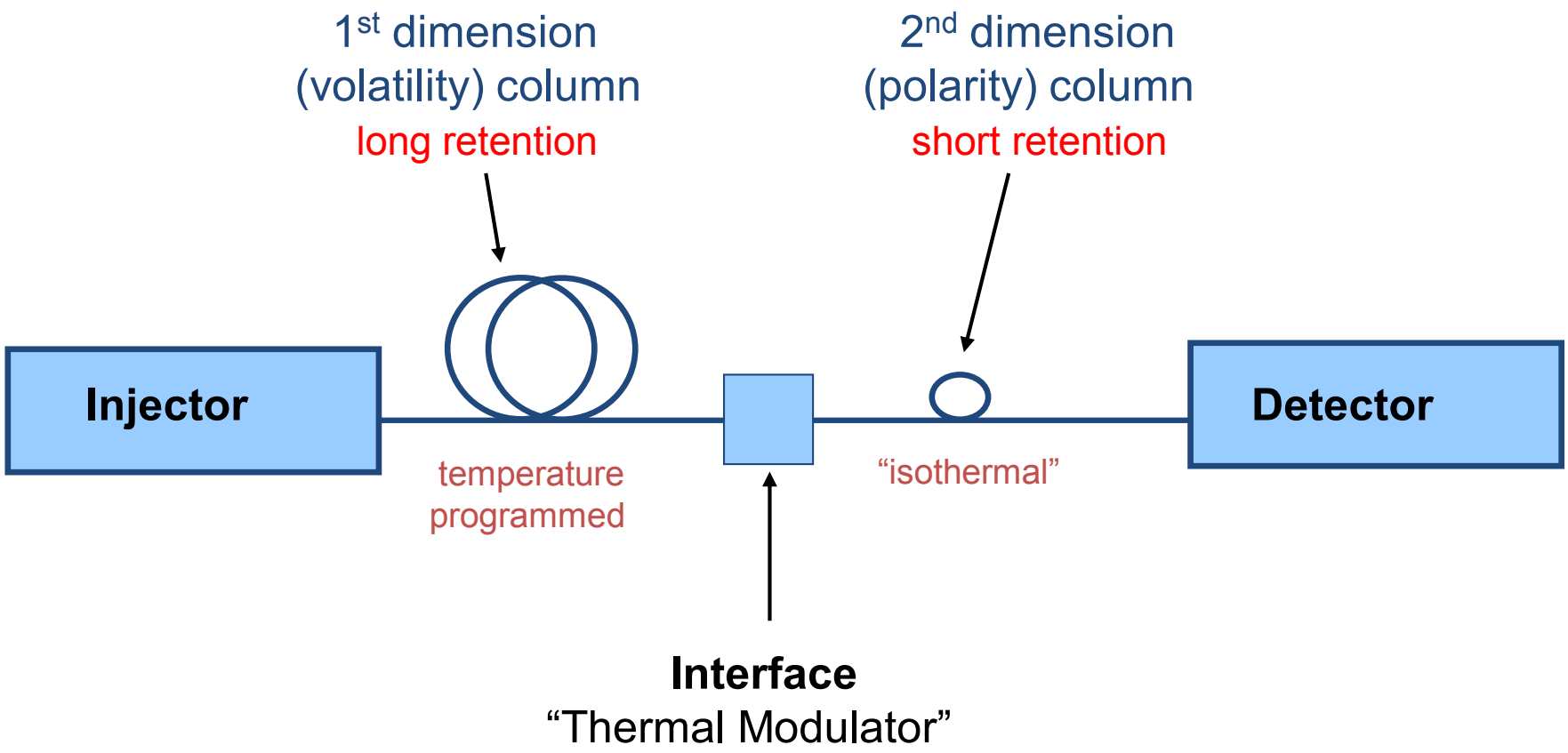




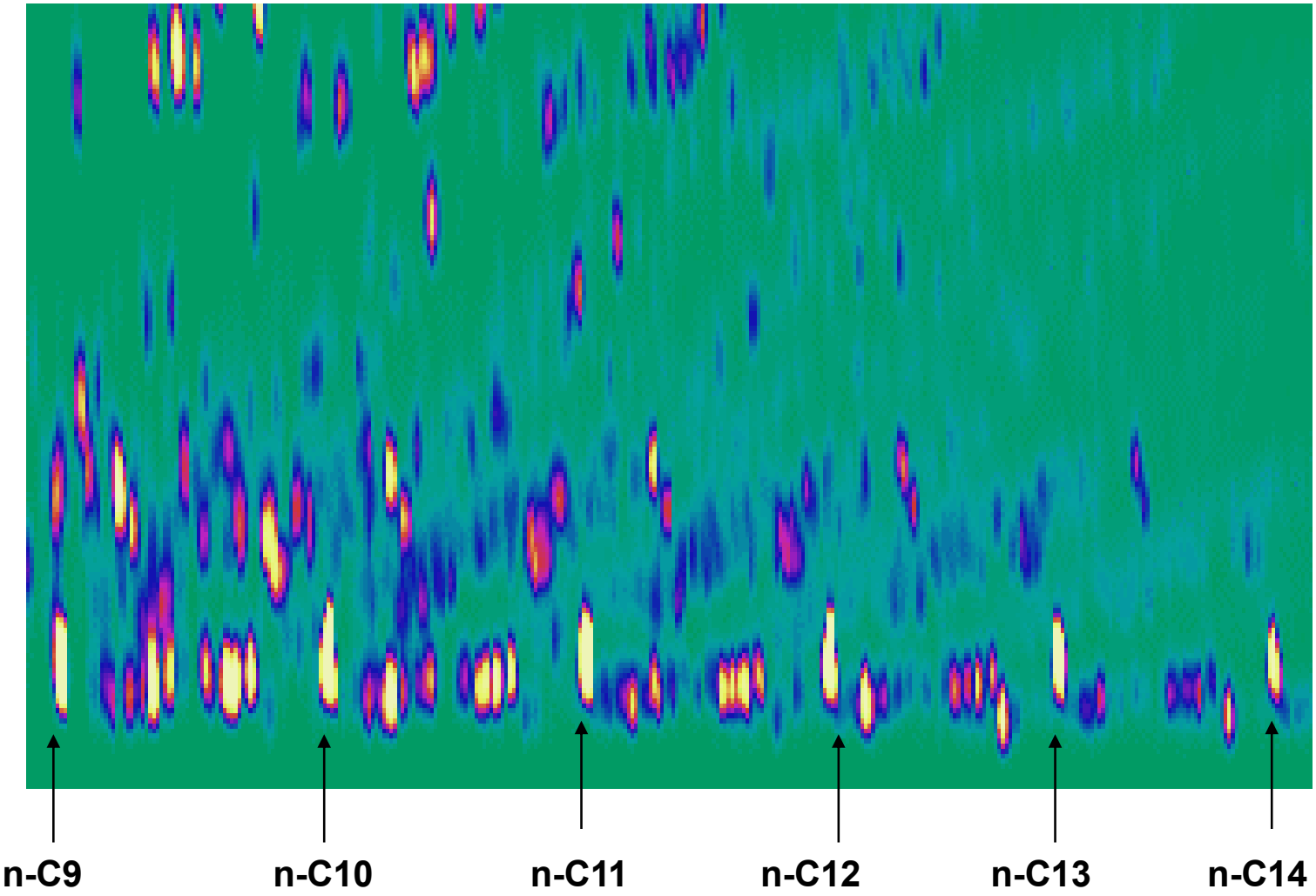
GC ANALYSIS OF DIESEL FUEL



SCHEMATIC DIAGRAM OF GCxGC INSTRUMENT



EXPANDED GCxGC 2D PLOT OF DIESEL FUEL



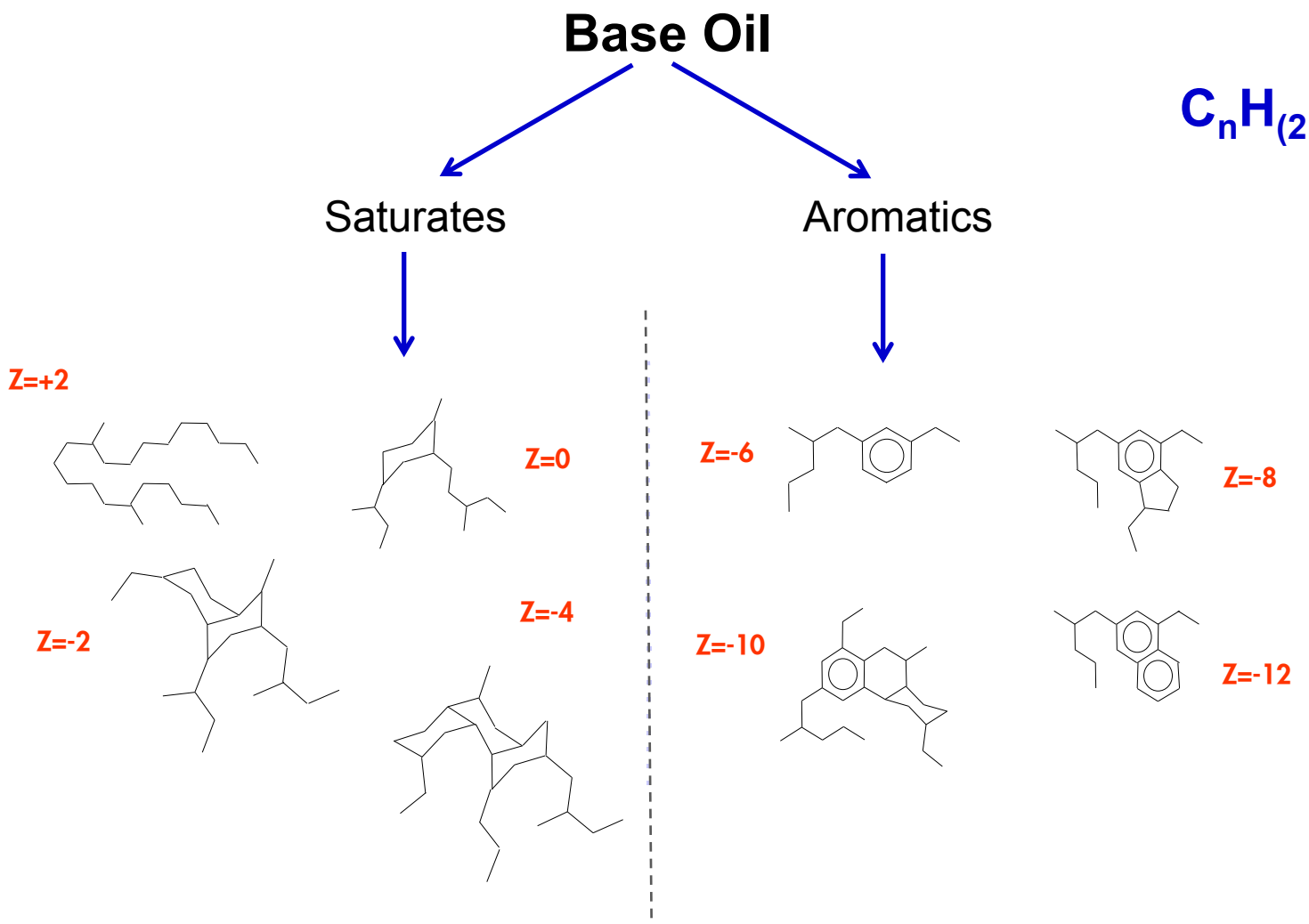
GCxGC RESULTS FOR CONVENTIONAL DIESEL FUEL

C No.	nP	isoP	N	DiN	MoAr	NmoAr	DiAr	NdiAr	TriAr	Total
<5	0.00	0.00								0.00
5	0.00	0.00	0.00							0.00
6	0.01	0.00	0.01	0.00	0.01					0.03
7	0.04	0.03	0.06	0.00	0.06					0.19
8	0.04	0.08	0.16	0.01	0.19					0.49
9	0.11	0.21	0.32	0.07	0.42	0.00				1.12
10	0.19	0.40	0.52	0.33	0.51	0.31	0.01			2.26
11	0.36	0.60	0.72	0.67	0.74	0.87	0.10			4.06
12	0.61	0.91	0.98	0.74	0.97	1.13	0.31			5.66
13	0.92	1.50	1.29	0.94	1.19	1.41	0.57	0.03		7.84
14	1.38	2.10	1.77	1.12	1.14	1.29	0.64	0.17	0.01	9.61
15	1.81	2.45	2.36	0.72	1.29	1.14	0.59	0.33	0.05	10.73
16	1.88	3.05	2.68	0.51	1.15	1.12	0.26	0.25	0.08	10.98
17	1.71	2.62	2.70	0.36	1.09	0.57	0.26	0.17	0.07	9.55
18	1.51	2.81	2.59	0.29	0.93	0.65	0.21	0.18	0.02	9.18
19	1.25	2.74	2.41	0.32	0.81	0.53	0.12	0.06	0.00	8.25
20	1.02	2.36	2.07	0.16	0.65	0.36	0.07	0.03	0.00	6.72
21	0.75	1.44	1.53	0.05	0.42	0.24	0.03	0.01	0.00	4.47
22	0.53	1.11	1.13	0.03	0.29	0.12	0.02	0.00	0.00	3.24
23	0.36	0.81	0.79	0.05	0.17	0.09	0.01	0.00	0.00	2.28
24	0.26	0.59	0.56	0.02	0.07	0.04	0.00	0.00	0.00	1.55
25	0.15	0.38	0.30	0.02	0.03	0.03	0.00	0.00	0.00	0.91
26	0.09	0.24	0.15	0.02	0.00	0.02	0.00	0.00	0.00	0.52
27	0.04	0.11	0.07	0.01	0.00	0.00	0.00	0.00	0.00	0.22
28	0.01	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.09
29	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
30	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
>30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.06	26.62	25.18	6.45	12.12	9.91	3.21	1.22	0.23	100.00

GCxGC RESULTS FOR RENEWABLE DIESEL FUEL (Vegetable Oil)

C No.	nP	isoP	N	DiN	MoAr	NmoAr	DiAr	NdiAr	Total
<5	0.00	0.00							0.00
5	0.00	0.00	0.00						0.00
6	0.13	0.00	0.01	0.00	0.00				0.14
7	0.16	0.27	0.07	0.00	0.00				0.50
8	0.30	0.71	0.15	0.01	0.00				1.17
9	0.48	1.51	0.26	0.02	0.00	0.00			2.27
10	0.60	2.42	0.29	0.02	0.00	0.00	0.00		3.32
11	0.50	2.88	0.25	0.01	0.00	0.00	0.00		3.64
12	0.42	2.85	0.20	0.00	0.00	0.00	0.00	0.00	3.47
13	0.35	2.58	0.15	0.00	0.00	0.00	0.00	0.00	3.08
14	0.92	3.77	0.12	0.00	0.00	0.00	0.00	0.00	4.80
15	0.68	2.73	0.04	0.00	0.00	0.00	0.00	0.00	3.45
16	4.04	16.75	0.04	0.00	0.00	0.00	0.00	0.00	20.83
17	1.11	5.73	0.13	0.00	0.00	0.00	0.00	0.00	6.97
18	6.09	38.97	0.15	0.00	0.00	0.00	0.00	0.00	45.21
19	0.04	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.35
20	0.05	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.57
21	0.01	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.15
22	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.06
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.87	82.21	1.86	0.06	0.00	0.00	0.00	0.00	100.00

LUBRICANT BASE OIL COMPONENTS



FIELD IONISATION MASS SPECTROMETRY (FIMS)

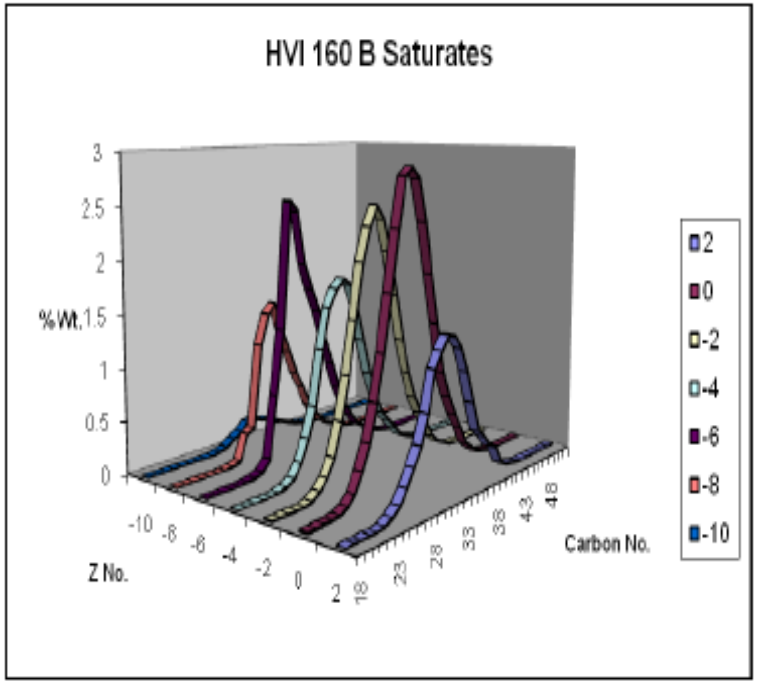
Hydrocarbon functionalities associated with specific Z-numbers

$$C_nH_{2n+z}$$

Z	Hydrocarbon type		Z	Hydrocarbon type
+2	Paraffins		-10	Tricyclobenzenes
0	Cycloparaffins		-12	Naphthalenes
-2	Dicycloparaffins		-14	Tricyclonaphthalenes, Biphenyls
-4	Tricycloparaffins		-16	Tetracyclonaphthalenes
-6	Tetracycloparaffins, Monoaromatics		-18	Triaromatics
-8	Indanes, Tetralins, Dicyclobenzenes			

FIMS (SATURATE FRACTION OF BASE OIL)

Carbon number	Z-number							Total
	2	0	-2	-4	-6	-8	-10	
18	0.00	0.02	0.01	-	-	-	-	0.03
19	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.03
20	0.00	0.03	0.01	0.00	0.00	0.00	0.00	0.04
21	0.01	0.03	0.01	0.00	0.00	0.00	0.00	0.04
22	0.00	0.04	0.01	0.00	0.00	0.00	0.00	0.06
23	0.02	0.08	0.03	0.01	0.01	0.00	0.00	0.15
24	0.06	0.16	0.09	0.03	0.02	0.00	0.00	0.36
25	0.13	0.33	0.18	0.08	0.05	0.01	0.00	0.78
26	0.25	0.55	0.34	0.20	0.15	0.04	0.00	1.53
27	0.40	0.88	0.64	0.40	0.73	0.28	0.02	3.35
28	0.56	1.29	1.03	0.68	1.33	0.32	0.04	5.26
29	0.82	1.80	1.51	1.19	2.53	1.11	0.10	9.06
30	1.18	2.35	2.02	1.56	2.43	1.40	0.15	11.09
31	1.32	2.80	2.33	1.72	1.92	1.49	0.23	11.81
32	1.44	2.87	2.52	1.80	1.67	1.22	0.24	11.76
33	1.42	2.77	2.39	1.75	1.44	0.99	0.21	10.99
34	1.30	2.38	2.08	1.53	1.15	0.75	0.20	9.38
35	1.07	1.90	1.66	1.18	0.90	0.59	0.15	7.44
36	0.77	1.43	1.22	0.84	0.63	0.39	0.13	5.41
37	0.48	0.96	0.89	0.60	0.43	0.27	0.09	3.74
38	0.41	0.71	0.63	0.41	0.31	0.18	0.06	2.71
39	0.30	0.52	0.46	0.31	0.20	0.12	0.04	1.96
40	0.26	0.37	0.32	0.21	0.15	0.09	0.03	1.41
41	0.09	0.19	0.18	0.11	0.09	0.05	0.02	0.74
42	0.04	0.12	0.10	0.07	0.05	0.03	0.01	0.42
43	0.03	0.06	0.06	0.04	0.03	0.01	0.00	0.23
44	0.01	0.04	0.02	0.02	0.01	0.01	0.00	0.12
45	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.06
46	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.02
47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
51	-	-	-	-	-	0.00	0.00	0



SUMMARY

- Chemical complexity of petroleum substances increases dramatically with carbon number
- The chemical composition of petroleum products can vary, but their composition has been well characterised
- Aromatic hydrocarbon (MOAH?) content of petroleum products can differ vastly (much broader than 15-35%)
- How do we differentiate hydrocarbons originating from mineral sources with those originating from vegetable sources?

FUNDAMENTAL QUESTIONS ABOUT MOH, MOSH AND MOAH

- What are MOH, MOSH and MOAH ?

  We need standard definitions for these terms

- What are *"technical grades of MOH"* ?

  Are these the same as petroleum products ?

- Can MOH only originate from crude oil ?

  If so, how do we differentiate between identical hydrocarbons originating from mineral and vegetable oils ?

- Are formally validated methods for measuring MOH, MOSH and MOAH available ?

  If so, what is the accuracy, precision and limit of determination of these methods ?

Q & A