Faculty of Science
Discovering for tomorrow

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Identification and composition of compounds and petroleum fractions of oils recovered from waste tyres

By: PC Tsipa

REDISA
RECYCLING AND ECONOMIC DEVELOPMENT INITIATIVE OF SOUTH AFRICA

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Supervisor: Dr PS Hlangothi
Co-supervisors: Prof B Zeelie, Dr N Mama & Dr M Phiri

Introduction

- Primary resources are exploited as there is an increase in demand to improve technology

- A tyre is one of the most engineered part of a car with natural rubber and crude oil being the primary resources

- The complex nature of a tyre makes it hard for tyres to be disposed which causes:
- Increase in landfills, abandoned tyres and some tyre are burnt for heat

Saudi Arabia – Kuwait city

South Africa - #Feesmustfall

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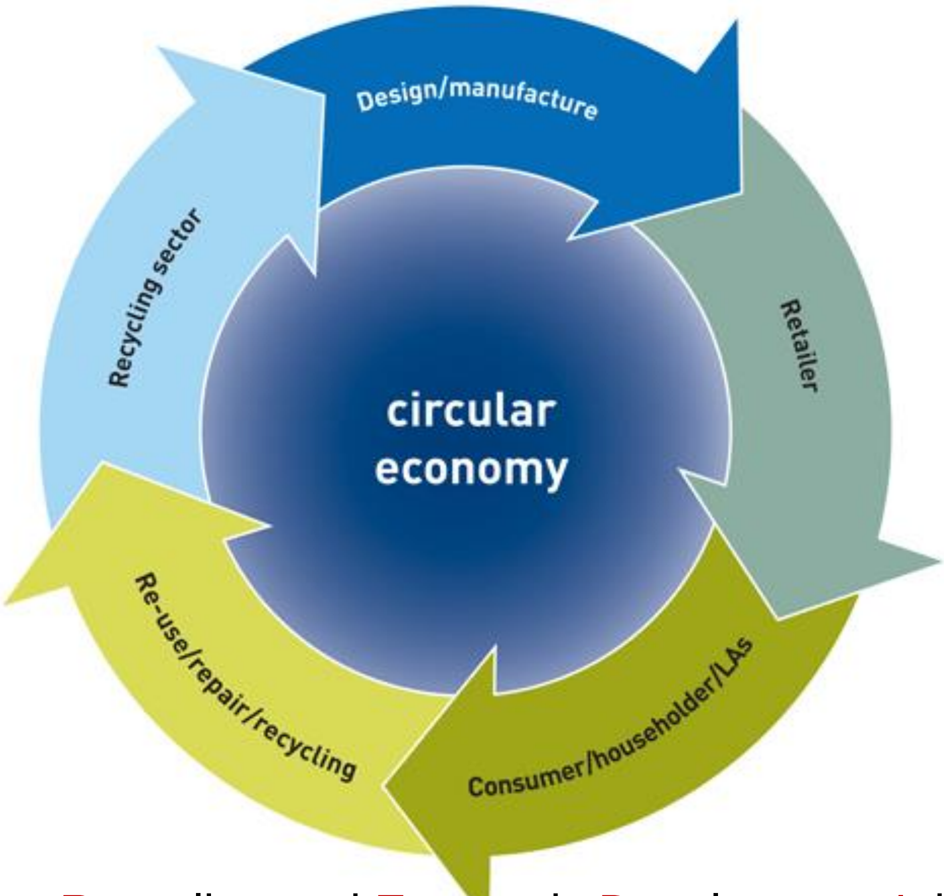
Introduction…

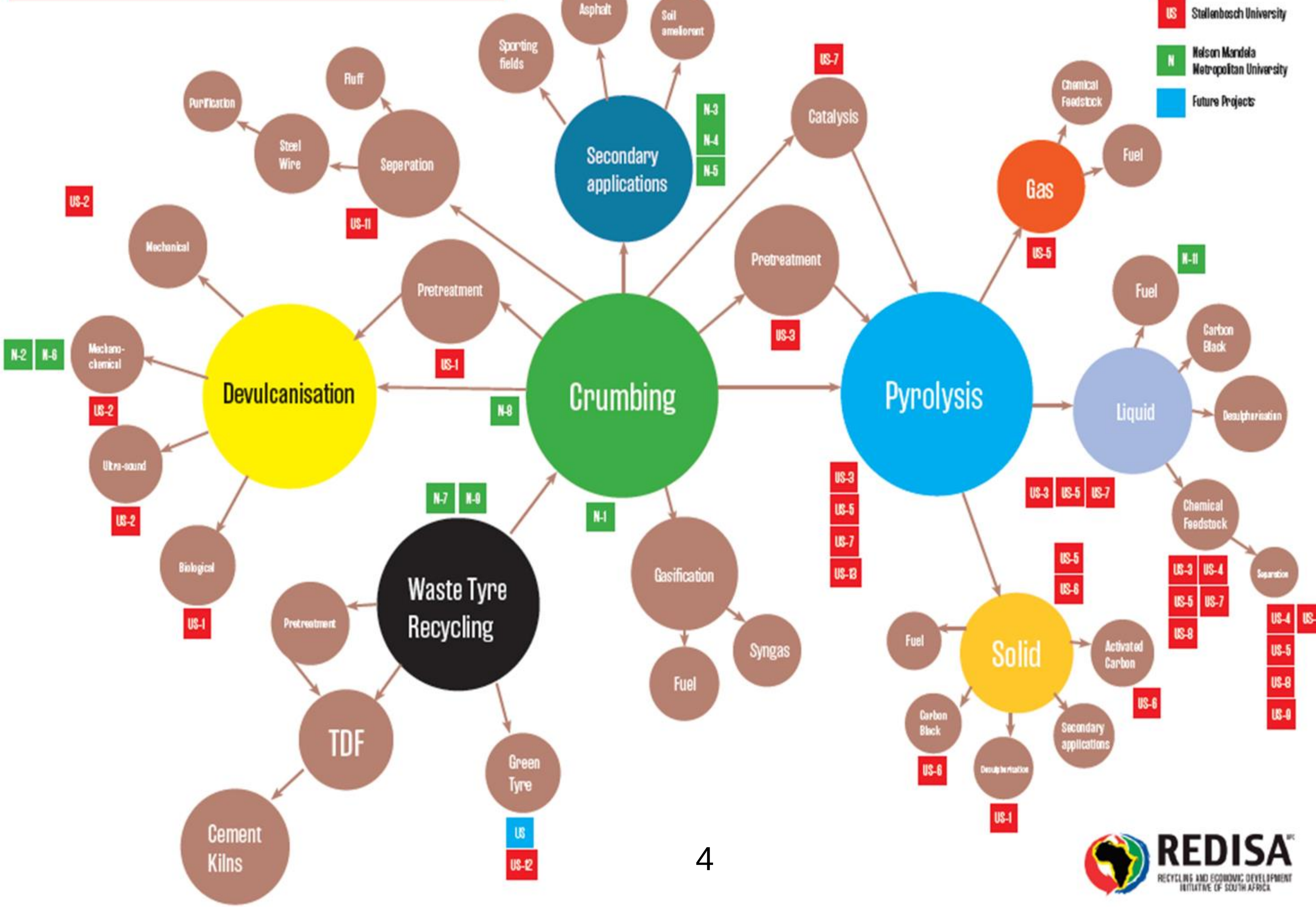
Linear economy = Take → Utilize → **Dispose**



- REDISA is trying to adopt the concept of circular economy
- The Circular Economy Package consists of an EU Action Plan for the Circular Economy that establishes a concrete programme of action, with measures covering the whole cycle: from production and consumption to waste management and the market for secondary raw materials.

Recycling and Economic Development Initiative of South Africa

Mind Map of REDISA R&D Waste Tyre Recycling



Literature review

- One of the ways to recycle tyres is the use of pyrolysis
- Pyrolysis is the process whereby a material is heated in the absence of oxygen
- The first type of pyrolysis was performed in South America – fertility of the soil
- Tyre pyrolysis produces three products:

50%

Gas – 8%

30%

12%

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Literature review…

- **Studies have shown that tyre pyrolysis process is a non-conventional method**
  - Heterogeneity of the products therefore make it difficult to utilize further
  - High sulphur content
- Pyrolysis oil is very unstable:-

- Is not consistent process - meaning it produces difference products every time.
- Consumes energy

Aims and Objectives

Aim

Develop an alternative chemical degradation method for pyrolysis and attempt to produce fuel from the tyre derived oil.

Objectives

- Like pyrolysis three products are produced: gas, solid and liquid
- Chemical reaction at room temperature
- Separate the oils based on their molecular weight by using different solvent systems – able to utilize further
- Low sulphur content
- Oil must be stable
- Study the quality of oils
- Attempt to produce fuel

Overview

Goal of the project!!!

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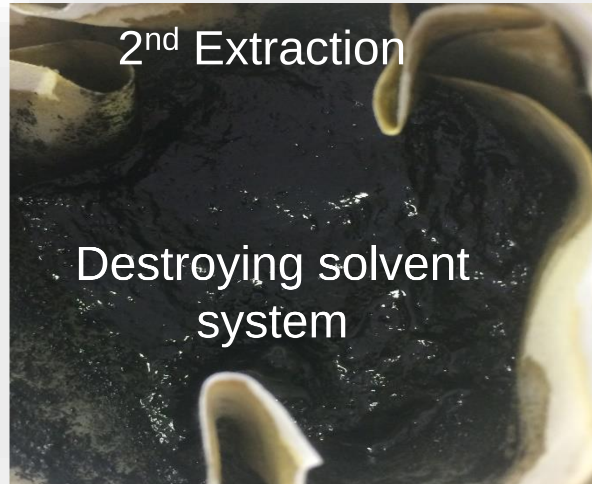
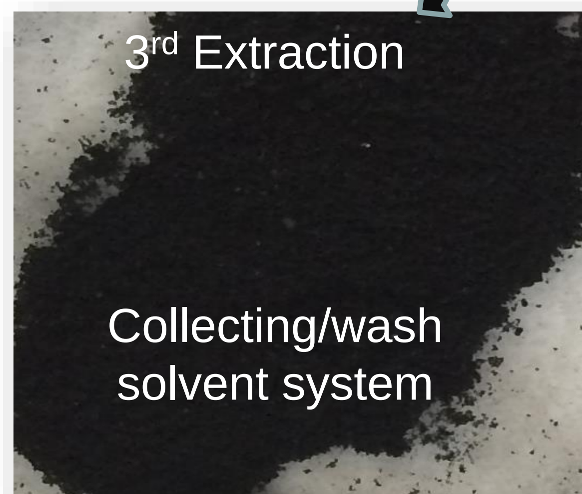
Overview Extraction Process

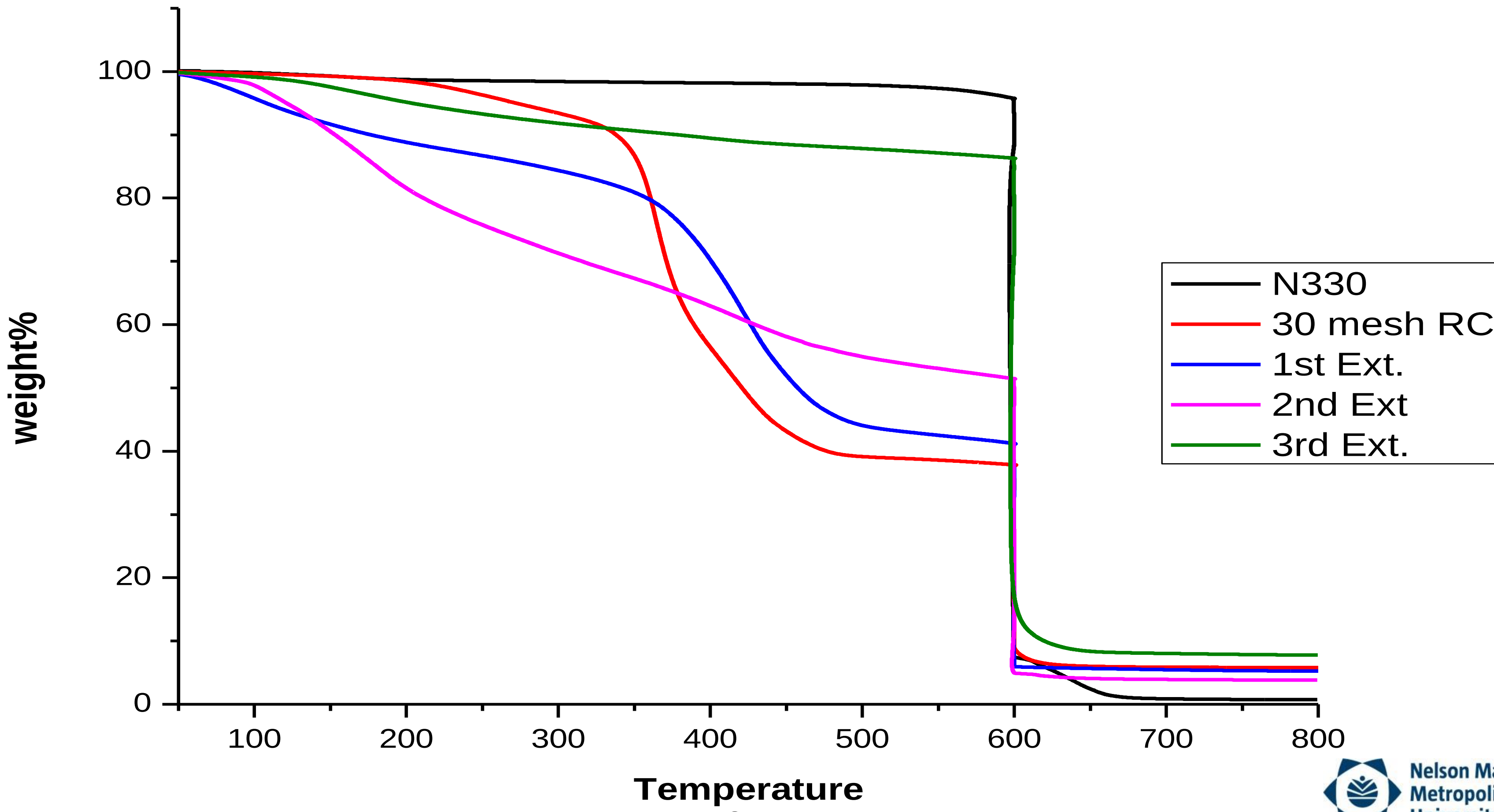


IM: 2g FM:0.49g
Residual - 24.5%



Overview: Solid product (Char)

TGA analysis comparing Carbon black, rubber crumb with extraction residual



Overview: Gas product

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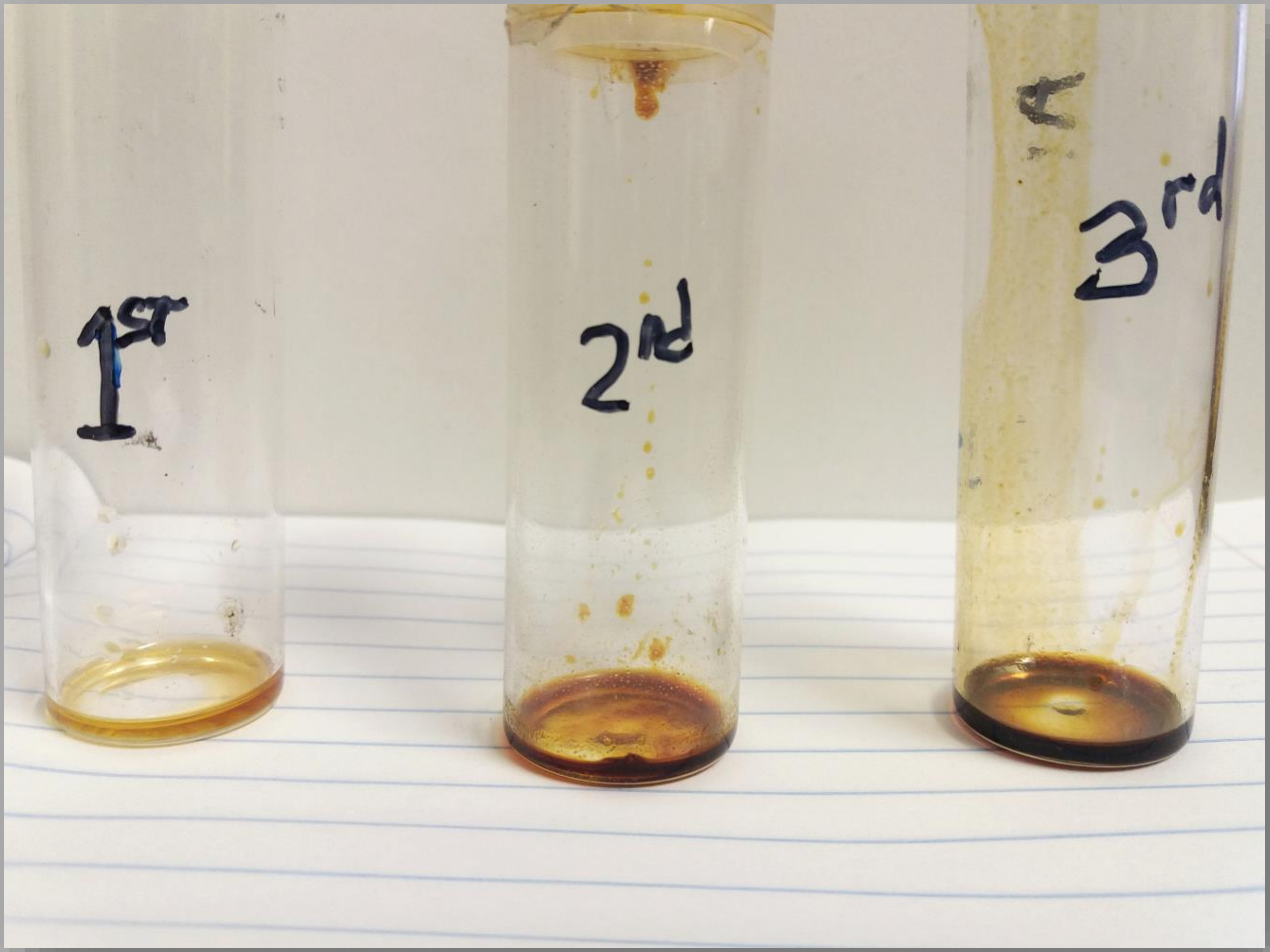
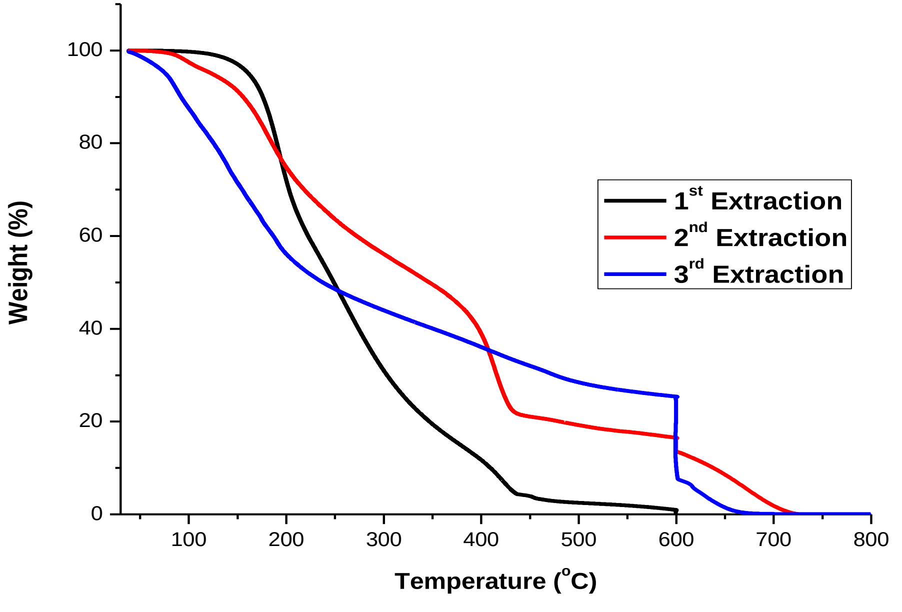
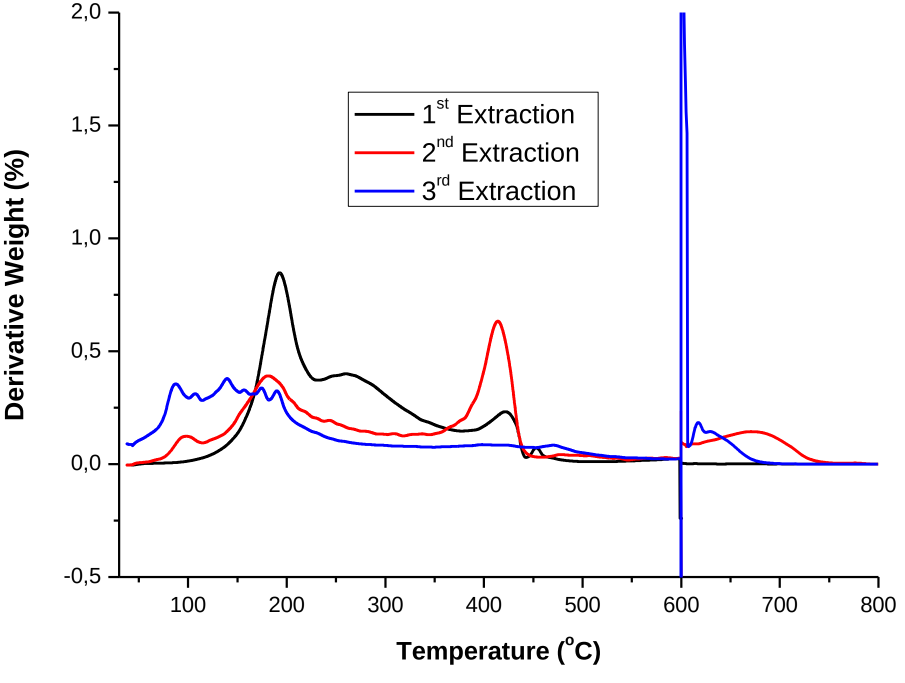
Overview: Liquid products



Overview: Liquid products

TGA & DTG analysis comparing extracted oils from rubber crumb





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Part 1: GC-MS – composition of the oil

This technique was performed to Identify and Quantify the compounds present in the extracted oil

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Tyre derived oil composition GC-MS

HP 5890 series II Hewlett packet GC-MS system (Agilent, Midland, Canada) coupled to Mass spectrometric detector (Agilent, Palo Alto, CA)

Oven:

The inlet head pressure of 348 kPa was used under constant flow mode (flow rate of 1.20 mL/min, linear velocity of 27.9 cm/s)

Injection program:

1ul volume of the clean extract was then injected at into the split/splitless injector operated at 300 ˚C using split 1:20

Column:

An apolar capillary column with dimensions: 60 m × 0.18 mm i.d. × 0.10 µm d_f Rxi-5 Sil-MS (Restek, Pann Eagle Park,CA,USA)

MS:

The transfer line to the MS was kept at 280 ˚C and the MS was operated in full scan mode from **35 to 500 *m/z*** at a scan rate of 3.15 scans/sec with standard electron ionisation energy of 70 eV. The electron multiplier (EM) voltage was 1 188 V.

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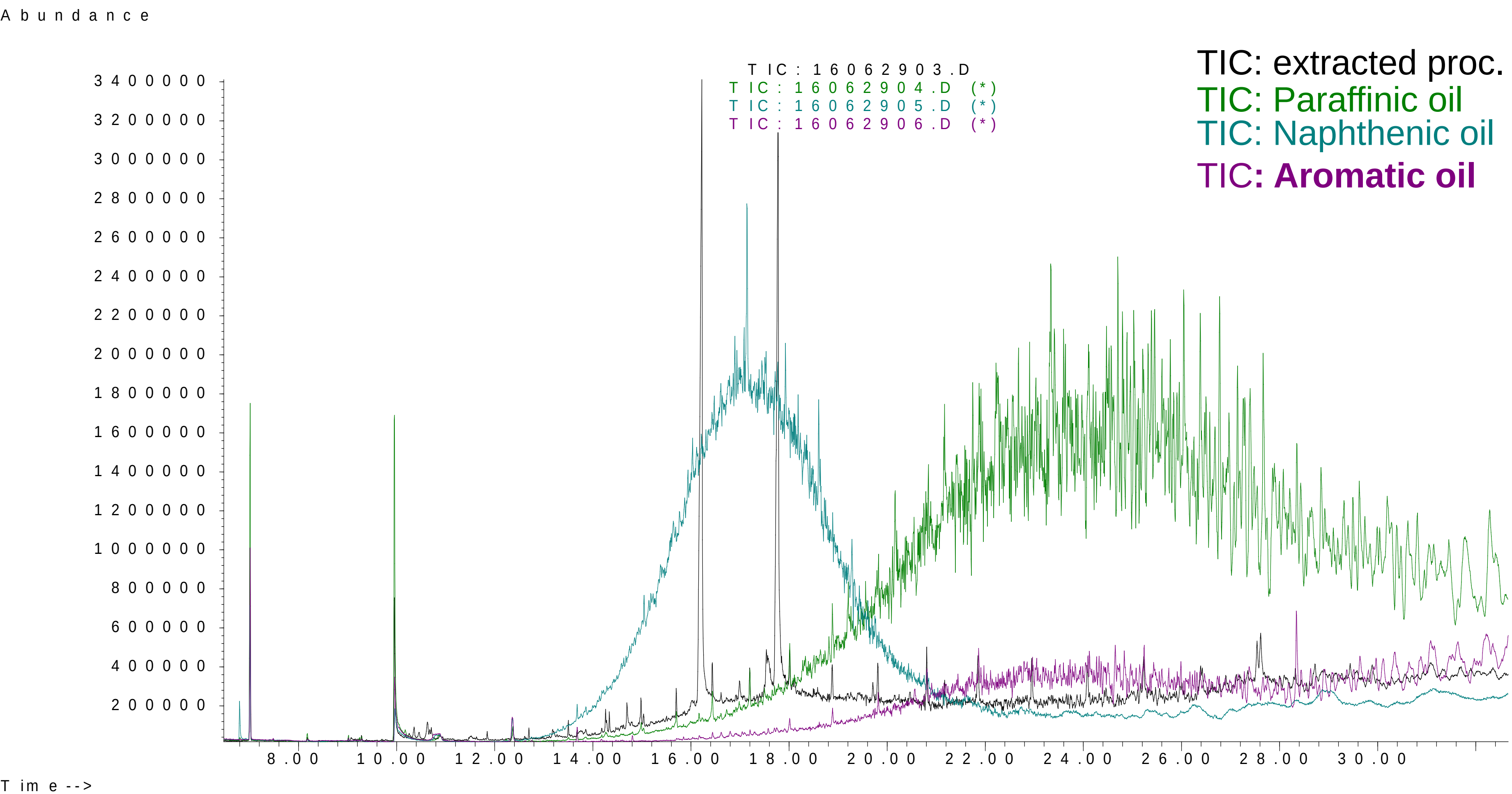
Composition of the oils: GC-MS



TIC: extracted proc. oil
TIC: Paraffinic oil
TIC: Naphthenic oil
TIC**: Aromatic oil**

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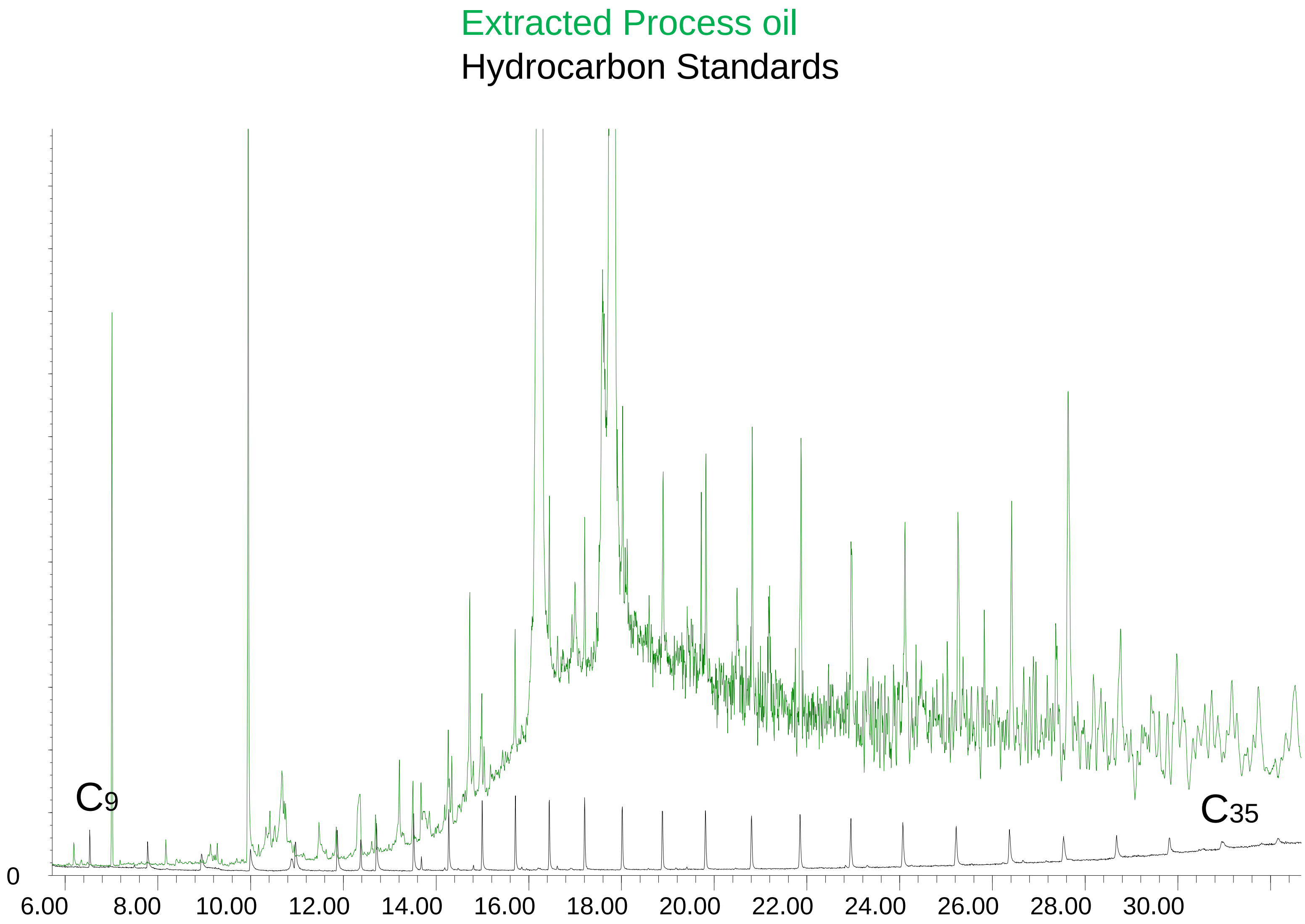
GC-MS analysis: External std. method for identification of hydrocarbons



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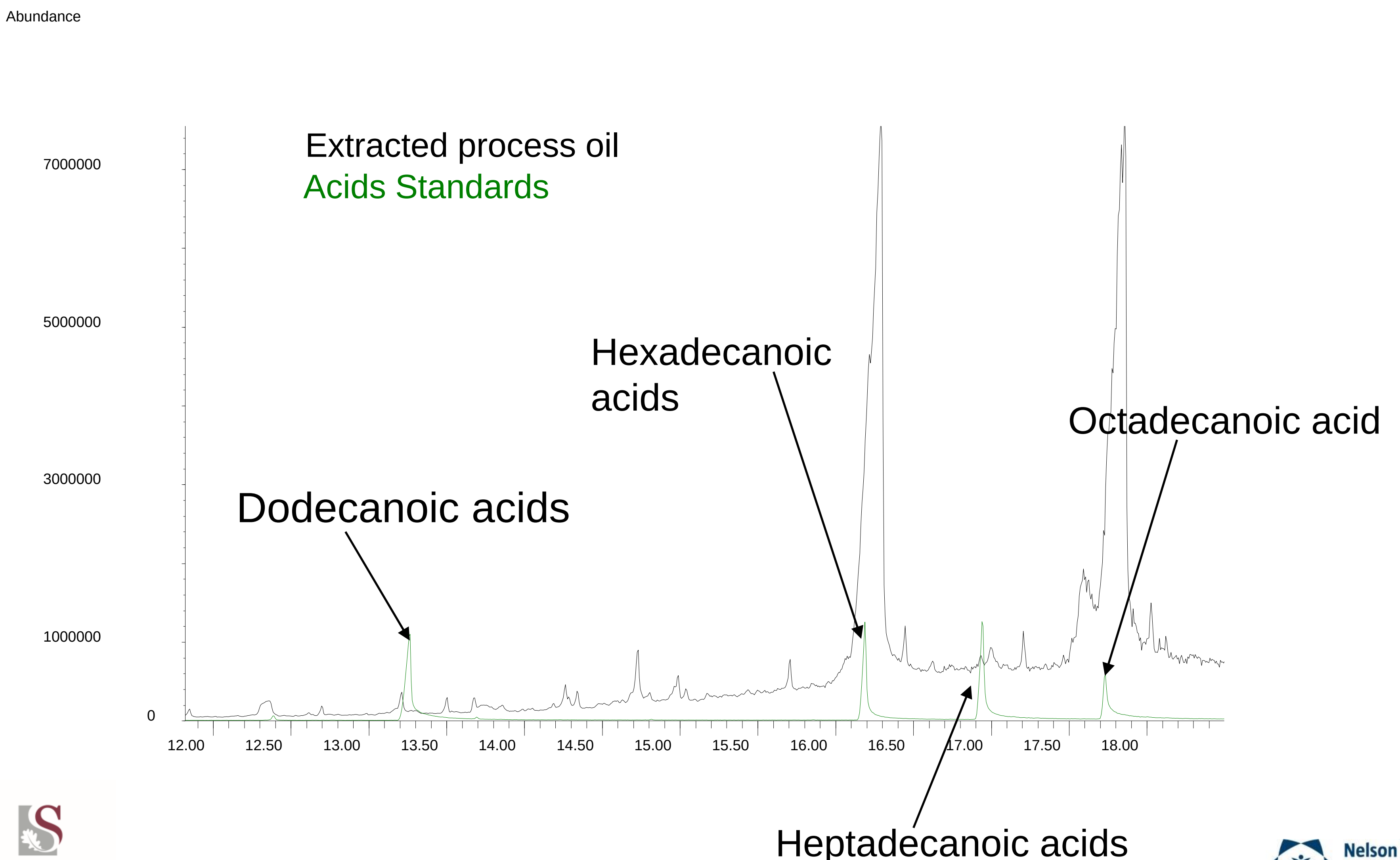
GC-MS analysis: External std. method and quantification of the acid in the extracted oil

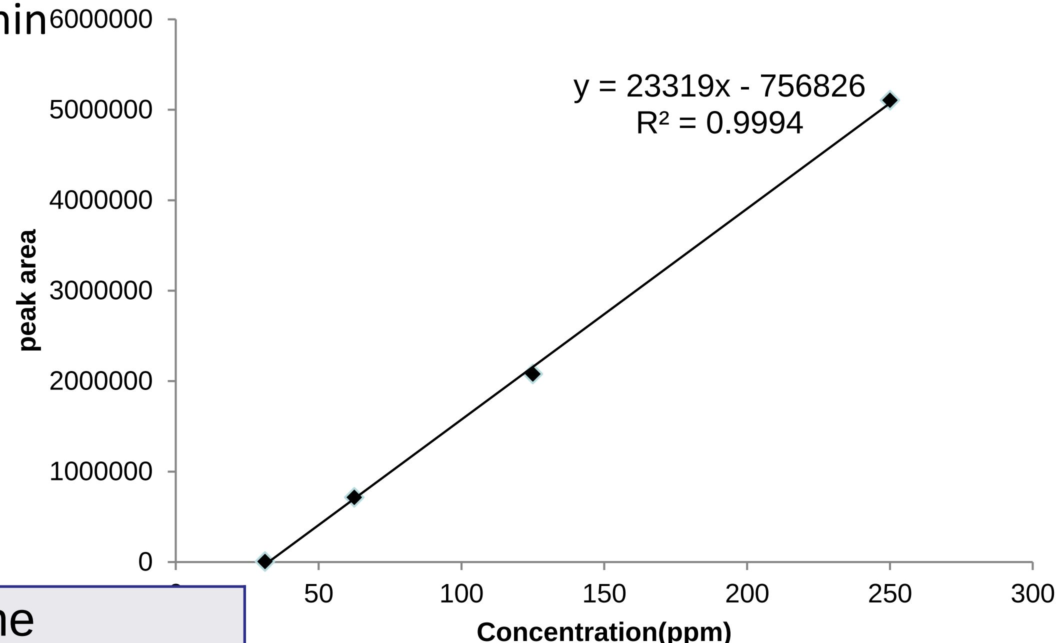


Calibration curves for quantification

Quantification of the Market value Acids identified from the oil

Compound: Dodecanoic acid RT:13.25 min

concentration(ppm)	concentration(ppm)
250	5104884
125	2078647
62.5	714209
31.25	5547
36.86946267	102933



Acid name	percentage in the sample(%)
dodecanoic acid	0.37
hexadecanoic acid	5.1
heptadecanoic acid	0.49
octadecanoic acid	9.98

Compounds identified

MS internal library: 90% accept

RI = 100 [n+($trx-trn$ /$trN-trx$)]

External Standards

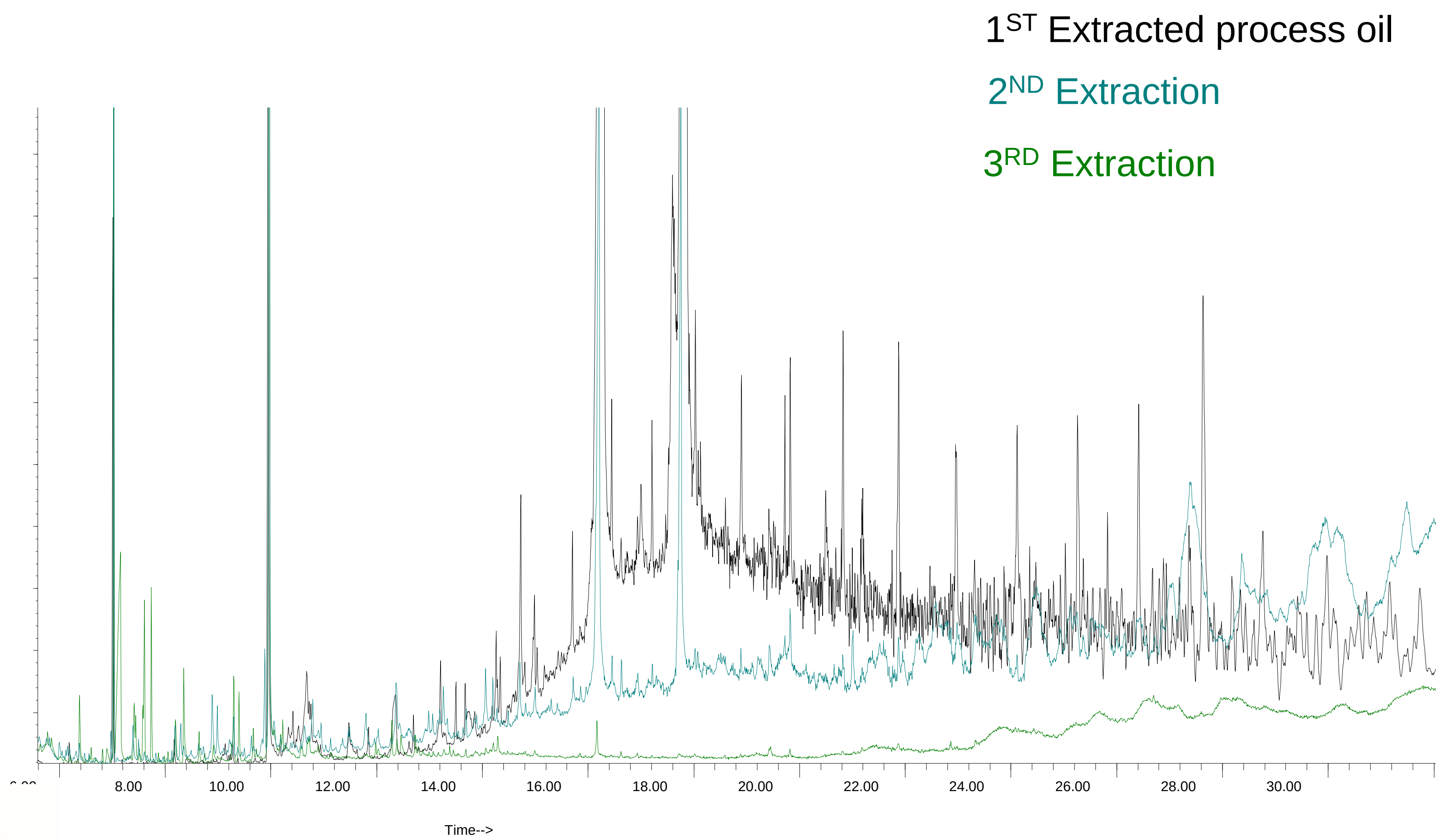
Peak No	Compound	RT	Ions/Mz	n	N	trn	trN	RI(CALC)	RI(litr)	difference
1	p[illegible]	[illegible]	[illegible]					<c9		
2	cyclohexylthiol	7.19	82 116	9	10	6.533	7.781	952.6442	MS	
3	li[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.781	8.945	1033.419	1031	2.419244
4	2-ethylhexanoic acid	9.14	78,88	11	12	8.945	10	1118.483	1122	-3.51659
5	1[illegible]	[illegible]	[illegible]4	11	12	8.945	10	1125.118	1123	2.118483
6	beta-ocimene	9.24	121 136	11	12	8.945	10	1127.962	MS	
7	α-campholene aldehyde	9.28	9 108	11	12	8.945	10	1131.754	1130	1.753555
8	Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-	10.17	107 135	12	13	10	10.97	1217.526	1209	8.525773
9	2,4-di(trimethylsiloxy)-6,7-(methylenedioxy)-2H-1,4-benzoxazin-3-one	10.52	73,102,341	12	13	10	10.97	1253.608	MS	
10	Hexanoic acid, 2-ethyl-, methyl ester	10.76	87,102	13	14	10.97	11.871	1276.693	MS	
11	Tetradecane	11.85	57,71	13	14	10.97	11.871	1397.669	STD	
12	3-methyltridecane	12.63	71,85	14	15	11.871	13.518	1446.084	MS	

Compounds identified

Peak No	Compound	RT	Ions/Mz	n	N	trn	trN	RI(CALC)	RI(litr)
1	p-xylene`	6.19	91 106					<c9	
2	cyclohexylthiol	7.19	82 116	9	10	6.533	7.781	952.6442	MS
3	limonene	8.17	93 136	10	11	7.781	8.945	1033.419	1031
4	2-ethylhexanoic acid	9.14	78,88	11	12	8.945	10	1118.483	1122
5	1,2,3,5-tetramethylbenzene	9.21	119 134	11	12	8.945	10	1125.118	1123
6	beta-ocimene	9.24	121 136	11	12	8.945	10	1127.962	MS
7	α-campholene aldehyde	9.28	9 108	11	12	8.945	10	1131.754	1130
8	Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-	10.17	107 135	12	13	10	10.97	1217.526	1209
9	2,4-di(trimethylsiloxy)-6,7-(methylenedioxy)-2H-1,4-benzoxazin-3-one	10.52	73,102,341	12	13	10	10.97	1253.608	MS
10	Hexanoic acid, 2-ethyl-, methyl ester	10.76	87,102	13	14	10.97	11.871	1276.693	MS
11	Tetradecane	11.85	57,71	13	14	10.97	11.871	1397.669	STD
12	3-methyltridecane	12.63	71,85	14	15	11.871	13.518	1446.084	MS
13	pentadecane	12.69	57,71	14	15	11.871	13.518	1449.97	STD
14	Dodecanoic acid	13.2	57,73	14	15	11.871	13.518	1480.692	STDS
15	Hexadecane	[illegible]	57,71	[illegible]	15	11.871	13.518	1499.514	STDs
16	Heptadecane	[illegible]	[illegible]	[illegible]	[illegible]	13.518	14.275	1799.339	STDs
17	Pentadecane, 2,6,10,14-tetramethyl-	[illegible]	[illegible]	[illegible]	18	13.518	14.275	1801.982	MS
18	tetradecanoic acid	14.72	60,73	18	19	14.275	15.996	1825.857	MS
19	octadecane	14.99	57,71	18	19	14.275	15.996	1841.546	STDs
20	Hexadecane, 2,6,10,14-tetramethyl-	15.04	57,71	19	20	14.996	15.996	1904.4	MS
21	anthracene	15.18	178	19	20	14.996	15.996	1918.4	MS
22	nonadecane	15.7	57,71	19	20	14.996	15.996	1970.4	STD
23	Hexanoic acid	16.2	60,73	20	21	15.713	16.44	2066.988	MS
24	eicosane	16.44	57,71	20	21	15.713	16.44	2100	STD
25	3,6-dimethyl phenanthrene	16.83	189 206	21	22	16.444	17.207	2150.59	MS
25	heptadecanoic acid	16.93	57 113	21	22	16.44	17.207	2163.885	STD
26	10,18-Bisnorabieta-8,11,13-triene	16.99	143 227	21	22	16.44	17.207	2171.708	MS
27	3,3,5,5-TETRAMETHYL-1,7-S-HYDRINDACENEDIONE (indacene)	17.02	143 227	21	22	16.444	17.207	2175.491	MS
28	2,7-Dimethylphenanthrene	17.04	191 206	21	22	16.444	17.207	2178.113	MS
29	heneicosane	17.21	57,71	21	22	16.444	17.207	2200.393	STD
30	pyrene	17.35	125 202	22	23	17.207	18.885	2208.522	MS
31	diphenyl sulphoxide	17.35	137 202	22	23	17.207	18.885	2208.522	MS
32	oleic acid	17.59	55,69	22	23	17.207	18.885	2222.825	MS
33	octadecanoic acid	17.84	73 284	22	23	17.207	18.885	2237.723	STD
34	heptadecane	18.03	57,71	22	23	17.207	18.885	2248.749	STD
35	docasane	18.03	57,71	22	23	17.207	18.885	2249.046	STD
36	tricosene	18.08	69,97	22	23	17.207	18.885	2252.026	STD
37	heptadecane	18.9	57,71	22	23	17.207	18.885	2300.894	STD
38	eicosanoic acid	19.5	55,73	24	25	18.885	19.813	2466.272	MS
39	Hexanedioic acid, bis(2-ethylhexyl) ester	19.7	57 129	24	25	18.885	19.813	2487.823	MS
40	tetracosane	19.82	57,71	24	25	18.885	19.813	2500.754	STD
41	1-phenanthrene ,carboxylic acid	20.5	239 285	24	25	18.885	19.813	2574.03	MS
42	eicosane	20.82	57,71	25	25	19.813	20.807	2601.308	STD
43	isooctyl phthalate	21.19	149 197	26	26	20.807	21.854	2636.581	MS
44	tetracosane	21.87	57,71	26	27	20.807	21.854	2701.528	STD
45	hexacosane	21.88	57,71	26	27	20.807	21.854	2702.483	STD
46	heptacosane	22.97	57,71	27	28	21.854	22.949	2801.918	STD
47	C29	24.12	57,71	28	29	22.949	24.071	2904.367	STD
48	C30	25.26	57,83	29	30	24.071	25.221	3003.391	STD
49	C31	26.42	57,71	30	31	25.221	26.37	3104.352	STD
50	C32	27.64	57,71	31	32	26.37	27.537	3208.826	STD
51	C33	28.77	57,71	32	33	27.537	28.681	3307.78	STD
52	C34	29.78	57,97	33	34	28.681	29.821	3396.404	STD
53	C35	30.17	57,97	34	35	29.821	30.948	3430.967	STD

53 compounds identified

GC analysis comparing tyre derived oil



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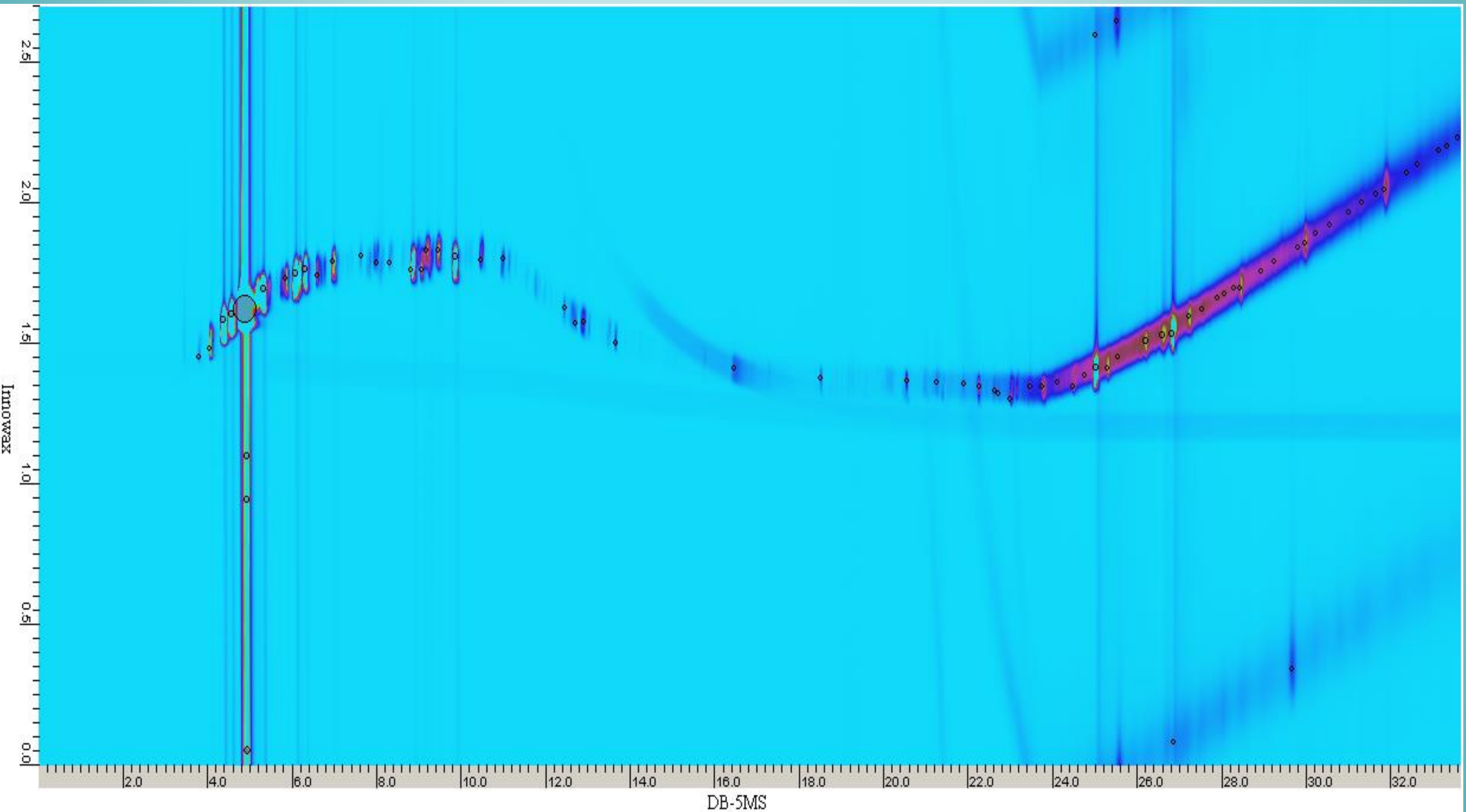
GC analysis comparing tyre derived oil

Peak No	Compound	RT	Ions/Mz	RI(Cal)	RI(lit)	A	E	F
1	p-xylene`	6.19	91 106			d	nd	nd
2	cyclohexylthiol	7.19	82 116	952.6442		d	nd	nd
3		7.16				nd	nd	d
		7.61				nd	nd	d
		7.74				nd	nd	d
3	limonene	8.17	93 136	1033.419	1031	d	d	d
4	2-ethylhexanoic acid	9.14	78,88	1118.483		d	nd	nd
5	1,2,3,5-trimethylbenzene	9.21	119 134	1125.118		d	d	nd
6	beta-ocimene	9.24	121 136	1127.962		d	d	nd
7	alpha-campholene adehyde	9.28	91 108	1131.754		d	d	d
8	Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-	10.17	107 135	1217.526		d	d	d
9	2,4-di(trimethylsiloxy)-6,7-(methylenedioxy)-2H-1,4-benzoxazin-3-one	10.52	73 102 341	1253.608		d	nd	nd
10	Hexanoic acid, 2-ethyl-, methyl ester	10.76	87 102	1276.693		d	nd	nd
11	Tetradecane	11.85	57,71	1397.669		d	d	nd
12	3-methyltridecane	12.63	71,85	1446.084		d	d	nd
13	pentadecane	12.694	57,71	1449.97		d	nd	nd
14	Dodecanoic acid	13.2	57,73	1480.692		d	d	d
15	Hexadecane	13.51	57,71	1499.514		d	nd	nd
				1799.33				

GC-GC: polar and non-polar column 2D



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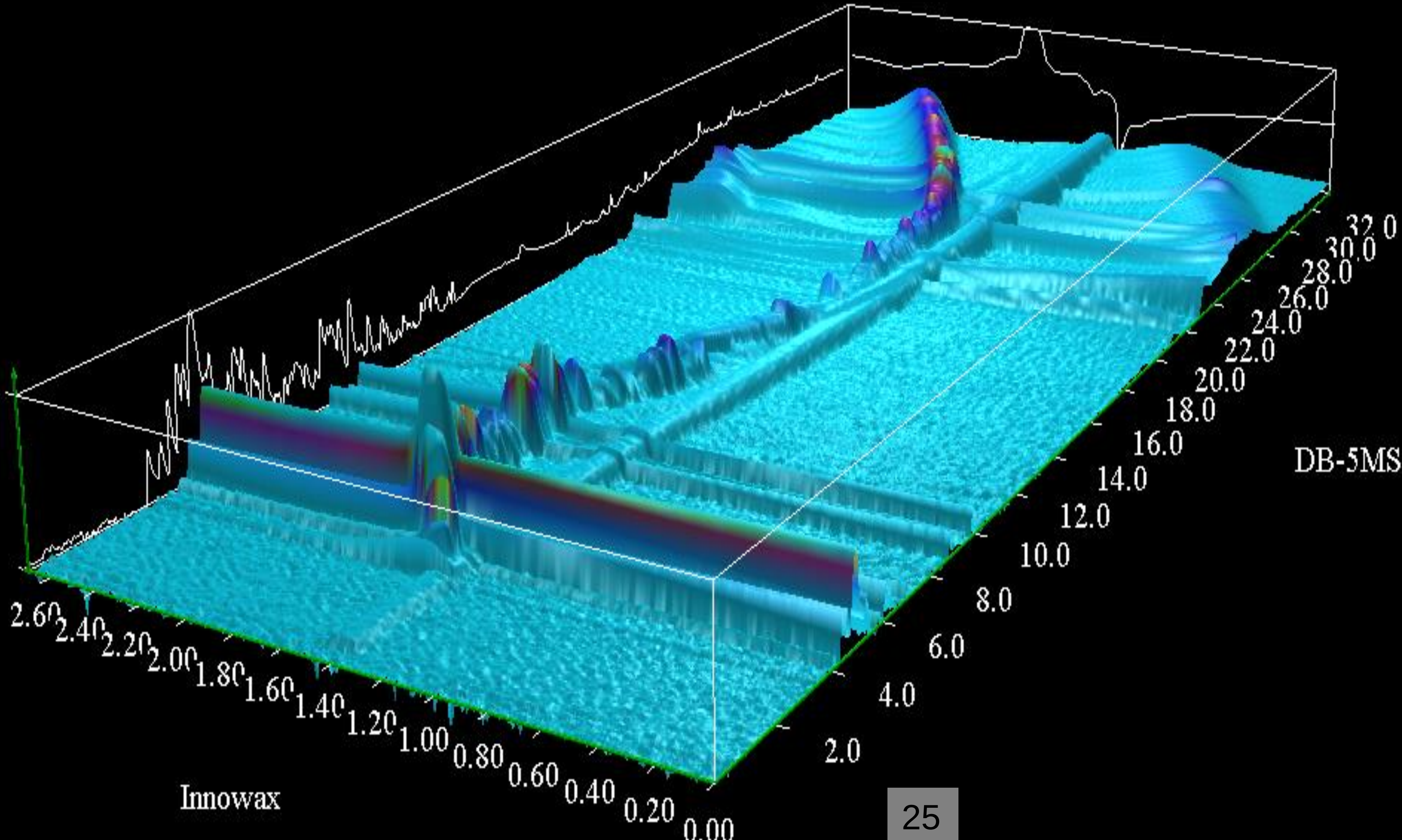
GC-GC: 3D representation…



Part 2: SIMDIST D86 - Oil and Petroleum fraction

This technique was performed to get the estimation of oil and petroleum fractions in the extracted oils

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SIMDIST D86 conditions

Agilent Technologies 7890 A GC
D 2887-06 (D86 Correlation BP Distribution)
IBP (ºC) = 322.5 WT4,270 WT5 and 179.6 WT6 10%
FBP (ºC) = 489.3 WT4, 490 WT5 and 491.5 WT6 90**%**
Flame Ionization Detector
200ºC; H_2 40 ml/min; Air 295 ml/min
Oven:
100ºC; Time: 0.5-1.2 min; Rate: 15ºC/min
Injector Program:
100-350ºC; Time: 0-2.5 min Rate: 35ºC/min
Column:
Injector volume: 0.1 µl; flow: 19 ml/min;
Gas flow (He): 26 ml/min;
Dimension: 10 m X 0.53 mm

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Oil fractions

PETROLEUM FRACTIONS	%	%	%
(Ref. Fischer, C.H: Composition of WASTE TYRE OILS)	1st EXT.	2nd EXT.	3rd EXT.
(0-170ºC) LIGHT OIL	n/a	n/a	n/a
(170-230ºC) MIDDLE OIL			6.90
(230-270ºC) HEAVY OIL			3.70
(270-350ºC) ANTHRACENE OIL	9.20	8.20	10.60
>350ºC RESIDUE CARBON	90.80	91.80	78.80
TOTAL	100.00	100.00	100.00

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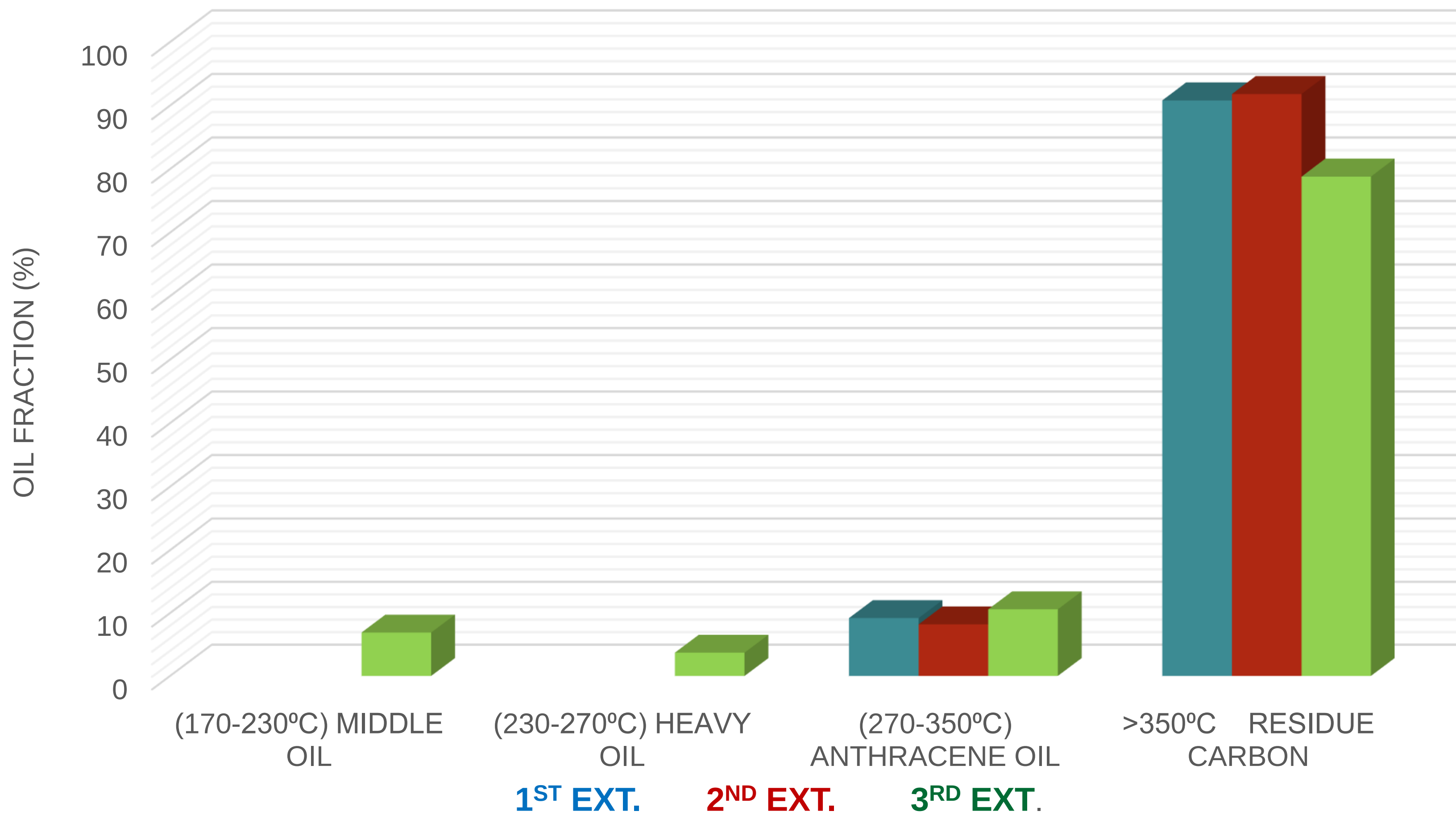
Oil fractions contd…



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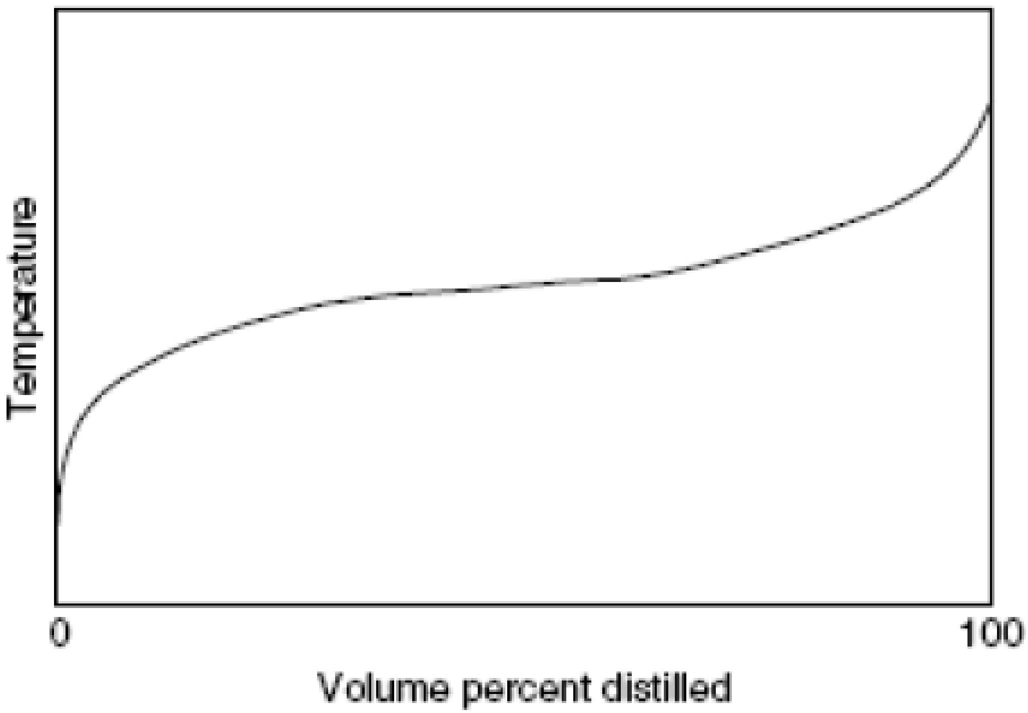
Pseudo-component curve

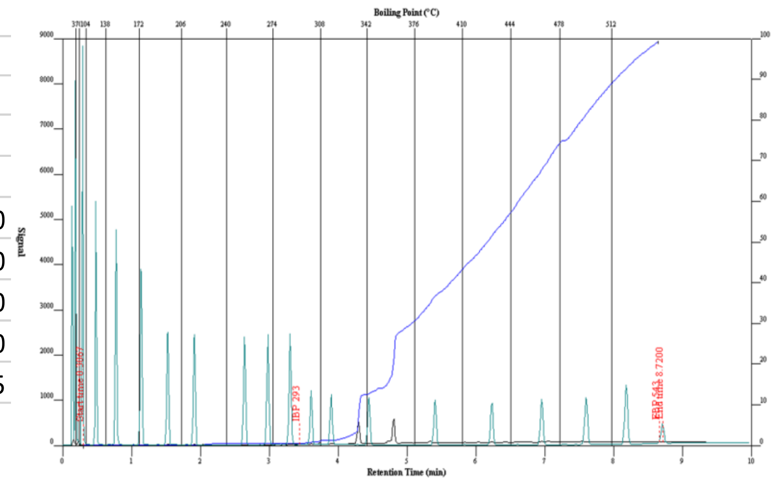


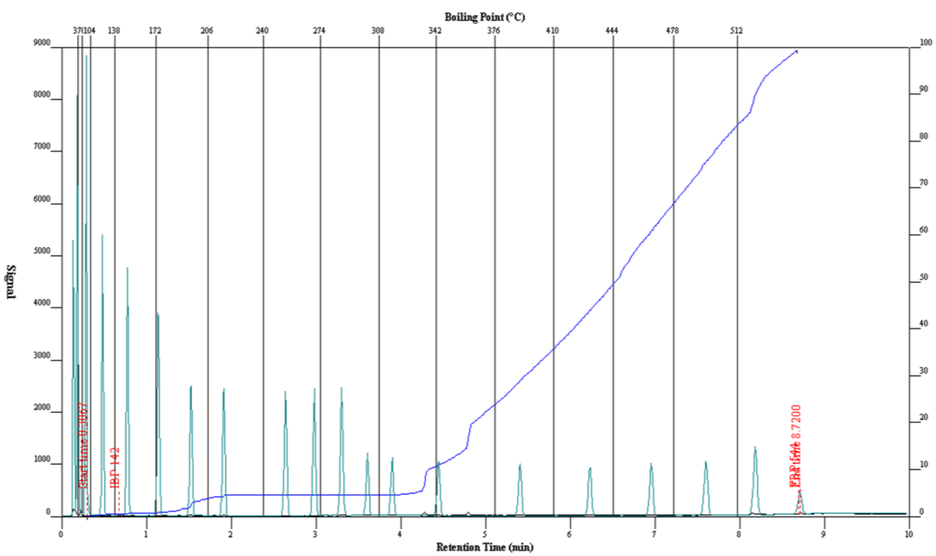
Properties of pseudo-component curve

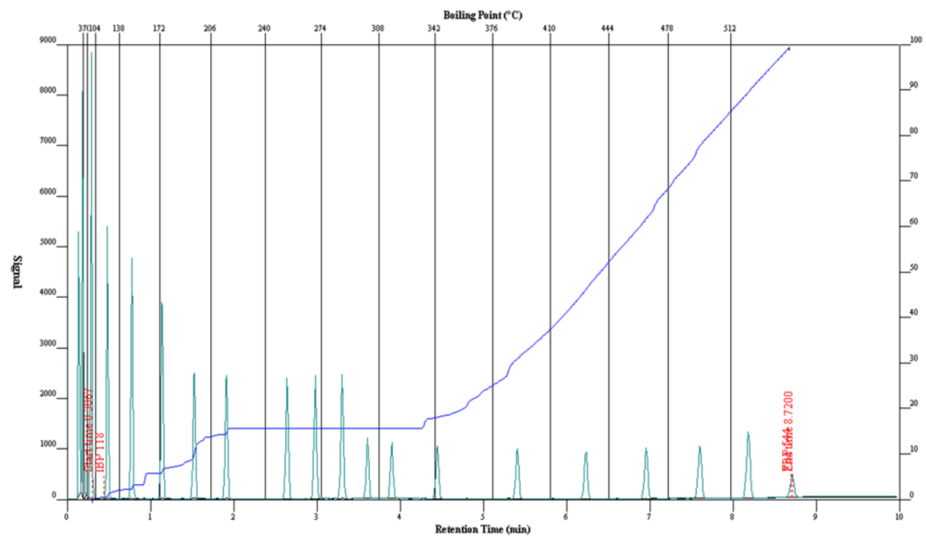
- Molecular weight
- Critical constant
- Acentric factor
- Heat of formation
- Ideal gas enthalpy
- Latent heat
- Vapour pressure
- Transport properties

Petroleum fractions contd…

PETROLEUM FRACTIONS	**%**	**%**	**%**
(Ref: RAND, 2003. Signifcance of tests for petroleum products)	**1st EXT**	**2nd EXT**	**3rd EXT**
C2-C4 GAS			
C5-79ºC LIGHT NAPHTHA			
121-191ºC HEAVEY NAPHTHA			2,20
191-277ºC KEROSENE		0,80	8,90
277-343ºC DISTILLATE FUEL OIL	5,40	5,0	8,40
343-455ºC LIGHT VACUUM GAS OIL	67,60	58,20	48,0
455-566ºC HEAVY VACUUM GAS OIL	27,0	36,0	32,5







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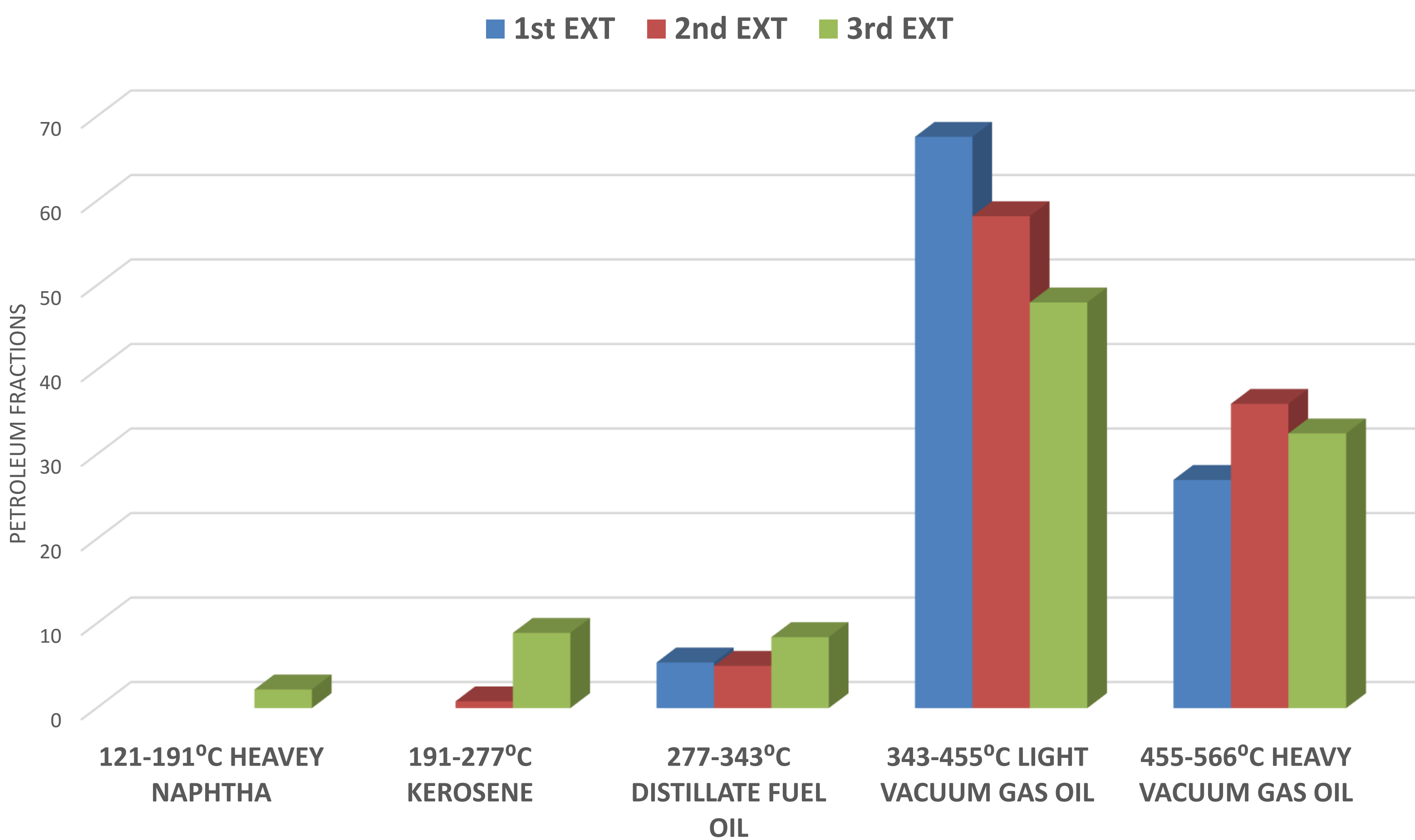
Petroleum fractions contd…



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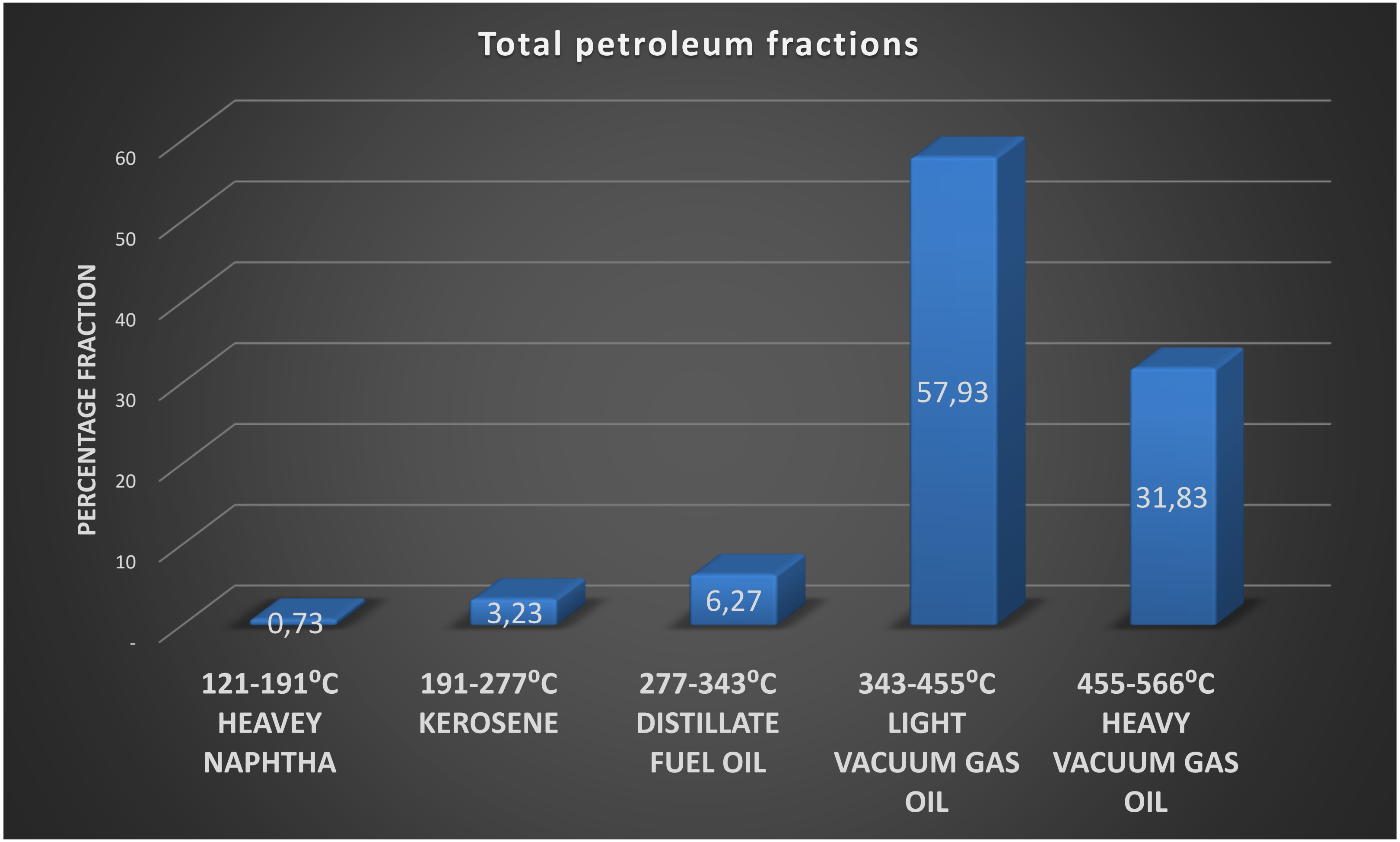
Petroleum fractions contd…



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Possible uses

Petroleum fractions	Boiling point (°C)	Average specific gravity	Number of C atoms	Test method	Uses
L.P.G	Up to 30	0.6	1 to 4	ASTM D86	Camping stoves
Light Naphtha	30 to 100	0.69	5 to 8	ASTM D86	Fuel for cars
Heavy Naphtha	100 to 150	0.758	8 to 10	ASTM D86	Reforming petrochemical feed
Kerosene	150 to 250	0.808	10 to 14	ASTM D86	Fuel for aeroplane
Light vacuum gas oil	250 to 350	0.84	15 to 20	ASTM D216	Fuel for lorries, trains and cars
Heavy vacuum gas oil	350 to 450	0.885	21 to 28	ASTM D158	Lubricant heating
Residual	Over 450	0.945	Over 28	ASTM D1160	Road surfacing

Conclusions…

- Based on the results obtained: GC-MS and SIMDIST we can conclude that the extracted oil is a heavy oil.

- From the previous work done it has been recorded that palmitic, oleic and steric acids are the stating material for biodiesel.
  - Extracted oil may be suitable for Biodiesel

- Light vacuum gas oil forms the largest part of the petroleum fractions in all the extracted oils.

- **Future work**

  - Use a sensitive instrument to get the quantitative sulfur content in the oil like Atomic Absorption spectroscopy (AA).

  - Build a reactor to upscale – currently designing one.

  - Crack the oil to produce diesel and petrol - possibility

  - Analysis the quality of the petroleum fuel from extracted oil compared to that of commercial fuels.

Acknowledgements

- REDISA
- Supervisor and co-supervisors
- Center for Rubber Science and Technology
- Physical and Polymer science staff NMMU
- SUN, Innoventon and NMMU

THANK YOU!

InnoVenton
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for tomorrow