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EVALUATION OF NIGERIAN BITUMEN YIELD AND COMPOSITIONS BY HYDROUS AND ANHYDROUS PYROLYSIS - A CASE STUDY OF ONDO STATE BITUMEN

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ABSTRACT

Petroleum is the world's most important source of energy. There is an ever increasing demand for energy and this has resulted to depletion and decline in production due to the fact that petroleum is extracted much faster than its rate of formation, hence the need to source for unconventional sources of crude oil. This research aims to establish the superiority of crude oil produced from bitumen by hydrous pyrolysis technique over crude oil produced from bitumen by anhydrous pyrolysis technique. The bitumen sample collected from Agbabu in Odigbo local government area of Ondo State was subjected to pyrolysis by two processes – hydrous pyrolysis and anhydrous pyrolysis. Initial protocol tests were carried out on the bitumen sample including TGA, FT-IR, SEM-EDX and GC-MS to determine the thermal behavior, functional groups, elemental composition and nature of the Saturates, Aromatics, Resins and Asphaltenes (SARA) composition of the bitumen. Anhydrous Pyrolysis was carried out with temperature ranging from 200°C to 400°C and time from 30minutes to 60minutes. Hydrous Pyrolysis was also carried out with temperature ranging from 300°C to 500°C and time from 30minutes to 60minutes. The synthetic crude obtained from both processes were subjected to further test to determine the viscosity, density, specific gravity, calculation of the API gravity and GC-MS analysis. The bitumen was found to have high viscosity of 28cSt and low API gravity of 8.6 which corresponds to standard for heavy oil. The bitumen SARA components determined are 35% saturates, 37% aromatics, 26% resins and 2% asphaltenes. At the end of the study, it was established that the yield of synthetic crude oil from hydrous pyrolysis has a greater API gravity of 29.20, *lower sulfur content 0.08%, lower viscosity 3.04cSt and a higher concentration of saturates 65% than the synthetic crude obtained from anhydrous pyrolysis which respectively has 23.99, 0.16%, 3.28cSt and 50%. From this research, exploitation of Nigerian bitumen becomes more economically viable such as seen in other countries around the world like Canada.*

Keywords: *hydrous pyrolysis, bitumen, synthetic crude oil, GC-MS, SARA content.*

Introduction

Petroleum has become the world's most important source of energy as it is used in supplying energy to power industries, generate electricity to heat homes and provide fuel for vehicles and airplanes to carry goods and people all over the world, also refined products of petroleum find application in the manufacture of chemical products, such as plastics, fertilizers, detergents and paints (Shedrach et al, 2018). However, there is an increasing scarcity of conventional oil reserves due to depletion and decline in production as argued in the studies of Dr. Marion King Huppert (Ogundele et al, 2011) based on the fact that petroleum is extracted much faster than its rate of formation, hence the need to source for unconventional sources of crude oil. (Lewan et al, 2018). These unconventional sources of petroleum are oil-shale, heavy oils, tar sands and bitumen. Bitumen in Nigeria is found across Lagos state, Ogun, Ondo and Edo states. Ondo State has one of the largest deposits of bitumen in the whole world and these have not been exploited for petroleum production (Arogundade & Ogunsuyi, 2021).

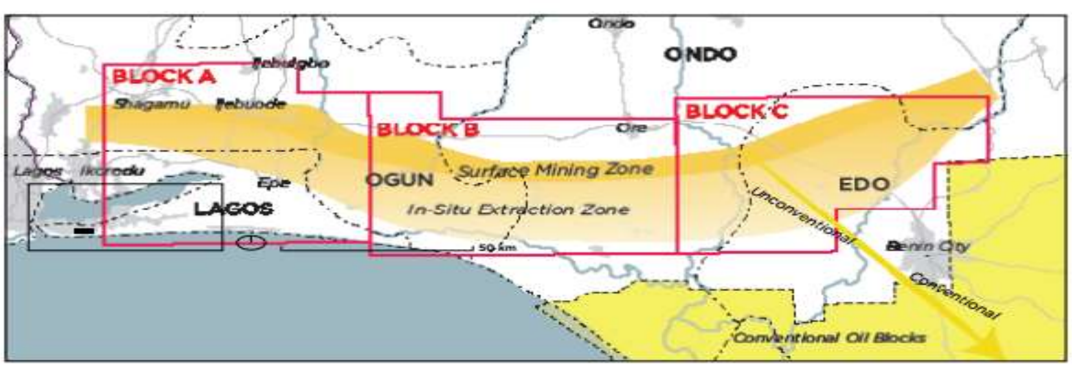

Figure 1: Bitumen in Nigeria across four states namely Lagos, Ogun, Ondo and Edo state (Shedrach et al, 2018).

Bitumen can be subjected to pyrolysis (hydrous or anhydrous) to produce petroleum. Whereas Anhydrous pyrolysis is thermal decomposition in an oxygen free and water-free environment, in Hydrous pyrolysis the heated material is in contact with water and the general name for all hydrothermal pyrolysis processes with water either in the liquid phase, vapour phase or steam is Aquathermolysis. (Lewan et al, 2018).

This research aims to establish the superiority of crude oil produced from bitumen by hydrous pyrolysis techniques over crude oil produced from bitumen by anhydrous pyrolysis techniques.

Methodology

The bitumen sample was collected from Agbabu which is situated in Odigbo local government area of Ondo State. Laboratory tests were carried out on the bitumen to determine its density, specific gravity, API gravity, viscosity and flash point. The Saybolt Furol Viscometer was used to determine the viscosity of the bitumen. The experimental setup includes Saybolt Furol viscometer, two thermometers, stopwatch and water bath. The flash point of the bitumen was determined with the 'open cup' test apparatus. Density of the Bitumen is determined using Anton-Paar digital density meter and the specific gravity is determined with the help of a 10ml beaker. The following analyses were carried out on the bitumen sample: Thermo-Gravimetric Analysis TGA, Fourier Transform Infrared Spectroscopy FT-IR, Scan Electron Microscopy SEM-EDX and Gas Chromatography Mass Spectrometry GC-MS respectively to determine the thermal behavior, functional groups, elemental composition and nature of the Saturates, Aromatics, Resins and Asphaltenes (SARA) composition of the bitumen. Hydrous and anhydrous pyrolysis experiment was carried out using the SA2-series 1200-degree lab-scale Nitrogen atmosphere horizontal tubular furnace pyrolysis manufactured by Chinese company Samlab and supplied by Vacutec, a South African equipment supplying company. The sulphur content was determined by the use of Energy Dispersive X-ray Fluorescence (EDXRF). The crude oil sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic radiation is measured and the accumulated count is compared with counts from previously prepared calibration standards. This corresponds to ASTM D4294 standards for testing.

Results

Table 1: results of viscosity, density, specific gravity, API gravity and flash point for bitumen

Parameter determined	Units	Sample: Bitumen
Viscosity @40 °C	St	2800
Density	g/cm^3	0.97
Specific Gravity	**-**	1.01
API Gravity	°API	8.60
Flash point	°C	255

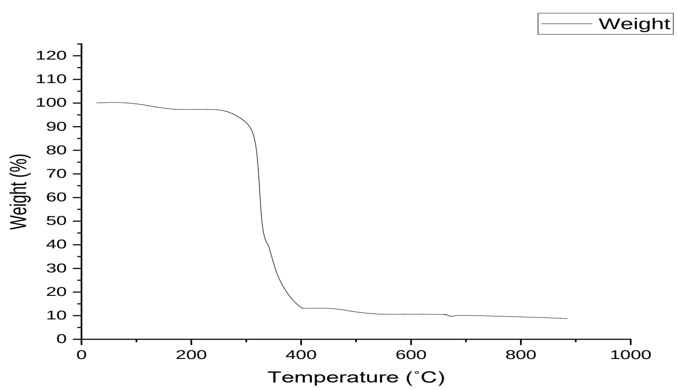

Figure 2: TGA for bitumen

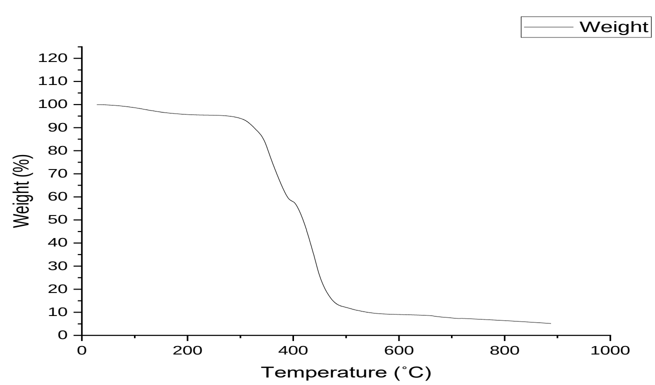

Figure 3: TGA for bitumen plus water

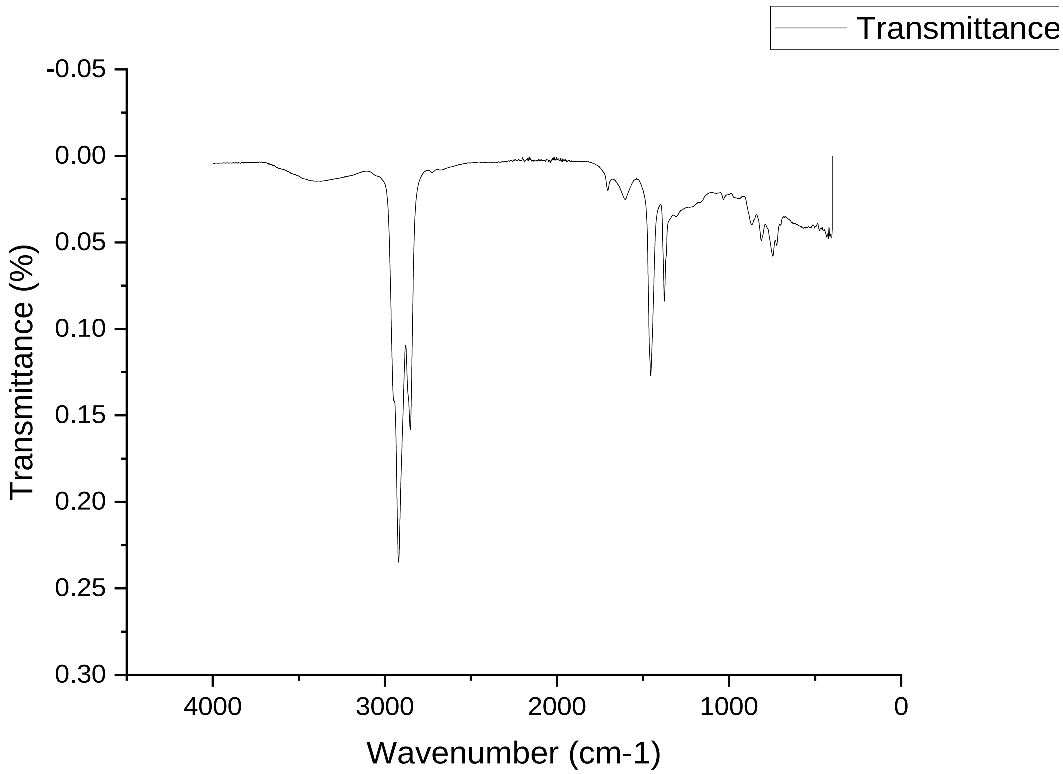

Figure 4: FT-IR for the bitumen showing peaks for the various functional groups

Table 2: Functional groups identified in the bitumen sample

Peak (cm^{-1})	Bond and Functional group	Source compound
2925	C-H Symetric stretch in CH_3	Alkane – Saturates
2860	C-H Stretch in CH_2	Alkane – Saturates
1730	C=O Stretch in carboxylic group	Carboxylic acid – Resinate
1650	C=C Stretch from Aromatic compound	Aromatics
1480	C-CH_3 Methylenic asymmetric	Alkane – Saturate
1395	C-[R] Asymmetric	Aromatic amines
1050	SO_2 Sulphoxides	Organic sulphate
890	C=H bond from alkene	Alkene – saturates
830	Two adjacent H on ring	Aromatics – para
770	Four adjacent hydrogen on ring	Aromatics – meta
750	Aromatic bending H-C modes	Aromatics – ortho

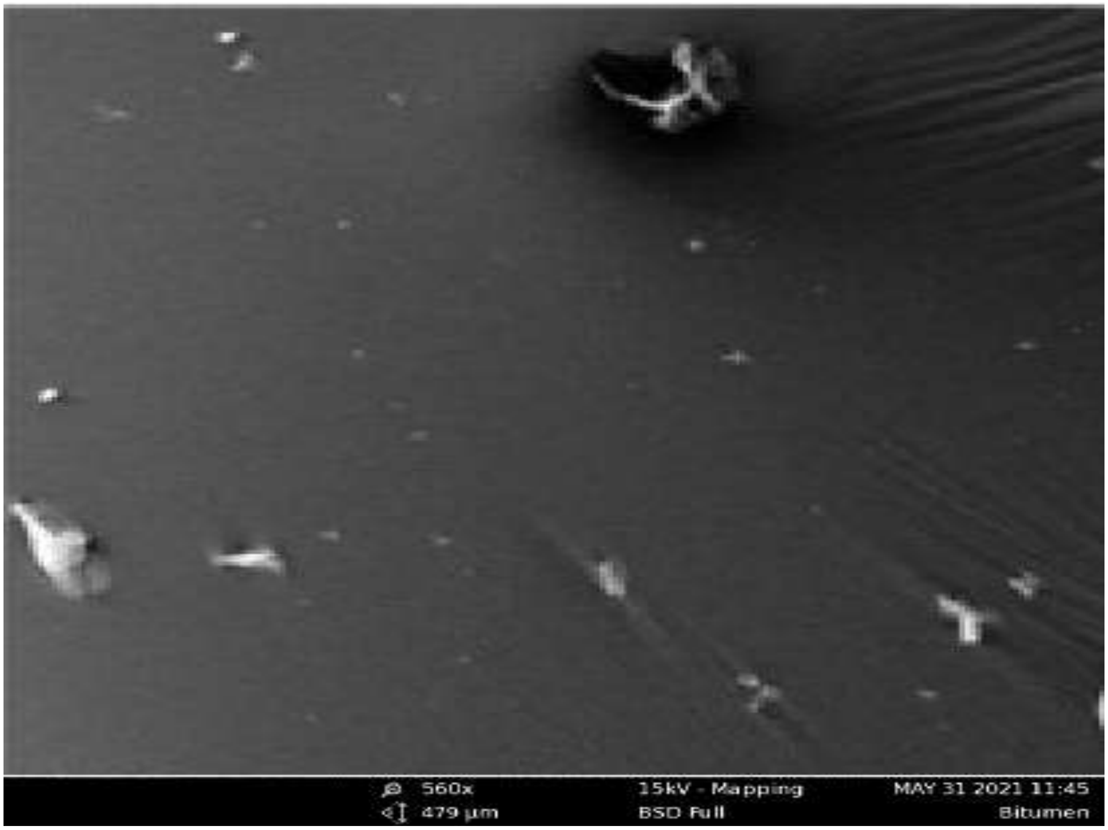

Figure 5: SEM of the bitumen sample

Table 3: Elemental composition of the bitumen sample from EDX

S/NO.	Element Symbol	Element Name	Weight Concentration (%)
1	C	Carbon	82.34
2	H	Hydrogen	8.31
3	N	Nitrogen	3.43
4	O	Oxygen	2.76
5	S	Sulphur	2.16
6	V	Vanadium	120ppm
7	Ni	Nickel	80ppm
8	Fe	Iron	50ppm
9	Al	Aluminium	5ppm
10	Ca	Calcium	30ppm
11	Cu	Copper	5ppm
12	Na	Sodium	40ppm

13	Mg	Magnesium	20ppm
14	Mn	Manganese	22ppm
15	Si	Silicon	15ppm

Table 4: GC-MS result for the bitumen

S/NO	Retention Time	Area Pct (%)	Compound Identified	Chemical Formula	SARA Group/ Molecular weight
1	3.29	0.510	2,6-dimethyloctane	$C_{10}H_{22}$	Saturate 142.28
2	4.061	0.163	Dodecane	$C_{12}H_{26}$	Saturate 170.33
3	7.574	0.372	2,4-bis(1,1-dimethylethyl)phenol	$C_{14}H_{22}O$	Aromatic 206.32
4	10.329	0.468	2,6,10,14-tetramethylpentadecane	$C_{19}H_{30}$	Saturate 268.51
5	10.926	0.202	Benzo[a]pyrene	$C_{20}H_{12}$	Aromatic 252.31
6	15.274	0.458	2-propylcyclohexane	C_9H_{18}	Saturate 126.24
7	15.928	0.404	Tridecane	$C_{13}H_{28}$	Saturate 184.36
8	20.362	2.138	1-methyl-3-ethyladamantane	$C_{13}H_{22}$	Saturate 178.31
9	20.441	2.082	1,5,4,6-tetramethyladamantane	$C_{14}H_{24}$	Saturate 192.34
10	25.61	0.190	nonane, 2-methyl	$C_{10}H_{22}$	Saturate 142.28
11	25.76	0.001	Pyrene	$C_{16}H_{10}$	Aromatic 202.25
12	27.83	0.673	3-methyloctane	C_9H_{20}	Saturate 128.25
13	27.962	0.492	2-methyl-2-butene	C_5H_{10}	Saturate 70.13
14	28.979	0.170	O-cresol	C_7H_{12}	Saturate 96.17
15	29.035	0.168	Heptadecane	$C_{17}H_{36}$	Saturate 240.50
16	29.038	0.566	1,2-benzenedicarboxylic acid	$C_8H_6O_4$	Aromatic 166.14
17	29.1592	0.632	2,6,10,14-tetramethylhexadecane	$C_{20}H_{42}$	Saturate 282.54
18	30.25	0.512	Benzo[b]flouranthene	$C_{20}H_{12}$	Aromatic 252.31

19	30.43	0.802	Cyclohexadecane	$C_{16}H_{32}$	Saturate 224.42
20	30.6948	0.503	1,2-dimethyl-5-nitroadamantane	$C_{12}H_{19}NO_2$	Resinate 209.28

Table 5: GC-MS result for synthetic crude oil E-I from anhydrous pyrolysis experiment

S/NO	Retention Time	Area Pct (%)	Compound Identified	Chemical Formula	SARA Group/ Molecular weight
1	3.79	0.510	1,2-diethylcyclooctane	$C_{12}H_{24}$	Saturate 168.32
2	4.125	0.163	2,2–dimethyloctane	$C_{10}H_{22}$	Saturate 142.28
3	4.386	0.372	1,2-benzenedicarboxylic acid	$C_8H_6O_4$	Aromatic 166.14
4	5.257	0.468	n-decane	$C_{10}H_{22}$	Saturate 142.28
5	5.869	0.202	1-ethylcyclopentene	C_7H_{12}	Saturate 96.17
6	10.234	0.458	1,3,5-trimethyladamantane	$C_{13}H_{22}$	Saturate 178.31
7	10.728	0.404	Benzo[a]anthracene	$C_{18}H_{12}$	Aromatic 228.29
8	12.365	2.138	2,4-dimethylhexane	C_8H_{18}	Saturate 114.23
9	15.248	2.082	2,4,4-trimethyl-2-pentene	C_8H_{16}	Saturate 112.21
10	15.61	0.190	Methylcyclohexane	C_7H_{14}	Saturate 98.19
11	17.176	0.001	1,3,5-trimethylbenzene	C_9H_{12}	Aromatic 120.19
12	20.832	0.673	2,3–dimethyl–1,3-butadiene	C_6H_{10}	Saturate 82.14
13	20.916	0.492	Naphthalene	$C_{10}H_8$	Aromatic 128.17
14	27.828	0.170	Hexadecanoic acid methyl esther	$C_{17}H_{34}O_2$	Resinate 270.45
15	25.535	0.168	1,3-dimethyladamantane	$C_{12}H_{20}$	Saturate 164.29
16	25.238	0.566	Tridecane	$C_{13}H_{28}$	Saturate 184.36
17	27.592	0.632	4-ethyl-1,2-dimethylbenzene	$C_{10}H_{14}$	Aromatic 134.22
18	30.625	0.512	Benzo[a]pyrene	$C_{20}H_{12}$	Aromatic 252.31
19	30.443	0.802	1,7-dimethyl-4-cyclodecane	$C_{15}H_{30}$	Saturate 210.40

20	30.698	0.503	3-methyl-1-adamantaneatic acid pyridine	$C_{13}H_{20}O_2$	Resinate 208.30

Table 6: GC-MS result for synthetic crude oil E-II from hydrous pyrolysis experiment

S/NO	Retention Time	Area Pct (%)	Compound Identified	Chemical Formular	SARA Group/ Molecular weight
1	3.29	0.510	Methylcyclohexane	$CH_3C_6H_{11}$	Saturate 98.19
2	4.061	0.163	m-Ethylmethylbenzene	$C_6H_3(CH_3)_3$	Aromatic 120.19
3	4.274	0.372	n-Decane	$C_{10}H_{22}$	Saturate 142.28
4	4.529	0.468	1,2,3 Trimethylbenzene	$C_6H_3(CH_3)_3$	Aromatic 120.19
5	4.859	0.202	Benzene	C_6H_6	Aromatic 78.11
6	4.974	0.458	1,4- Diethylbenzene	$C_6H_4(C_2H_5)_2$	Aromatic 134.22
7	5.328	0.404	2,4-dimethylhexane	$C_5H_9(CH_3)_3$	Saturate 114.23
8	5.362	2.138	p-Xylene	$C_6H_4(CH_3)_2$	Aromatic 106.16
9	5.441	2.082	o-Xylene	$C_6H_4(CH_3)_2$	Aromatic 106.16
10	5.61	0.190	2,4,4-Trimethyl-2-pentene	$C_4H_4(CH_3)_4$	Saturate 112.21
11	5.76	0.001	(S)-3,4-Dimethylpentanol	$C_7H_{16}O$	Resinate 116.2
12	5.83	0.673	Ethylcyclopentane	$C_5H_9C_2H_5$	Saturate 98.19
13	5.962	0.492	Benzene, 1,2,3,4-tetramethyl, o-Cymene	$C_{10}H_{14}$	Aromatic 134.22
14	5.979	0.170	Benzonitrile	$C_6H_5(CN)$	Resinate 103.12
15	6.035	0.168	D-Limonene	$C_{10}H_{16}$	Resinate 136.23
16	6.038	0.566	2-Propanone, methyl-2-propenylhydrazone	$C_7H_{14}N_2$	Resinate 126.20
17	6.1592	0.632	2-methyl-nonane	$C_{10}H_{22}$	Saturate 142.28
18	6.4	0.512	Sodium cyclopentadienide	C_5H_5Na	Saturate 88.08
19	6.43	0.802	1-Ethylcyclopentene	C_7H_{12}	Saturate 96.17
20	6.6948	0.503	1-methylethyl-cycloundecane	$C_{14}H_{28}$	Saturate 196.37
21	6.7574	0.361	2-Heptenal-(Z)	$C_7H_{12}O$	Resinate 112.17

22	7.55	1.080	2-Methyl-1-heptene	C_8H_{16}	Saturate 112.21
23	7.62	1.244	Isoprene	C_5H_8	Saturate 68.12
24	8.18	1.513	2-Methyl-2-butene	C_5H_{10}	Saturate 70.13
25	10.41	1.212	2,3,4,5,6-Pentamethylpyridine	$C_{10}H_{15}N$	Aromatic 149.23
26	10.45	0.985	1H-Indene, 2,3dihydro-1,1,5trimethyl-	$C_{12}H_{16}$	Aromatic 160.26
27	12.207	0.411	Naphthalene, 2,7dimethyl	$C_{12}H_{12}$	Aromatic 156.22
28	12.53	0.988	3-Methyl-octane	C_9H_{20}	Saturate 128.25
29	12.67	0.304	2,2-Dimethyloctane	$C_{10}H_{22}$	Saturate 142.28
30	12.9	1.015	2,3-Dimethyl-1,3-butadiene	C_6H_{10}	Saturate 82.14

Table 7: Results for the synthetic crude oil obtained by anhydrous pyrolysis (E-I) and hydrous pyrolysis (E-II)

Properties	**Unit**	**Synthetic Crude E-I**	**Synthetic Crude E-II**
Density	25 ^oC	0.89	0.87
Specific gravity	25 ^oC	0.91	0.88
API gravity	^{o}API	23.99	29.2
Viscosity @ 40^{o}C	St	328	304
Sulphur Content	%	0.16	0.08
Pour Point	^{o}C	21	18
Flash Point	25 ^oC	98	78

Discussion

The results obtained for determination of viscosity, density, specific gravity, API gravity and flash point for the bitumen as reported in Table 1, show that the viscosity of 2800St is high and its signifies the bitumen is of category of heavy oils. The API gravity of 8.6 confirms that the bitumen is of category of heavy oils and these values are in close range with viscosity 3200St, density 1.03g/cm^3, specific gravity 1.02, and API gravity 7.2 reported in previous studies (Shedrach et al, 2018) and (Arogundade & Ogunsuyi, 2021). The TGA for the bitumen and bitumen plus water, Figure 2 and Figure 3, show that there is significant material decomposition from around 280^{o}C up to 400^{o}C and 370^{o}C up to 500^{o}C respectively. The most dominant functional group as shown in

Figure 4 and reported in Table 2 is the CH_3, CH_2 methyl group of alkanes. The SEM for the bitumen, Figure 5, shows a uniform morphology with the metallic impurities coming up as bright or shiny spots. The elemental composition of the bitumen shows Carbon with the highest percentage of 82.34% and trace metals constitute 1% with Vanadium being the most notable present and these values correspond with the range for Carbon 80%-85% reported in earlier studies (Ogunsuyi et al, 2011). From Table 4, GC-MS for bitumen, it is deduced that the SARA composition for the bitumen is 35% Saturates, 37% Aromatics, 26% Resin and the n-heptane non-dissolvable Asphaltenes is 2%, these agree with reported findings in previous studies (Shedrach et al, 2018).

The GC-MS result, Table 6, for synthetic crude oil E-II from Hydrous Pyrolysis shows a higher percentage of saturates 65% and aromatics 25% and a lower percentage of resins 9.5% than the GC-MS result, Table 5, for the synthetic crude oil E-I from Anhydrous Pyrolysis with saturates 50%, aromatics 30% and resins 19.5%. The determined non-dissolvable asphaltenes for both crude oils is 0.5%. Furthermore, as reported in Table 7, the synthetic crude oil E-II has a higher API gravity of 29.2, a lower density 0.87g/cm^3, lower viscosity 304St and lower sulfur content of 0.08wt% than the synthetic crude oil E-I. Hence, the yield from hydrous pyrolysis is more physically, chemically and isotopically similar to crude oils obtained from natural maturation conditions and hydrous pyrolysis have also shown to increase gas generation and reduce maturation time. It is recommended that further research should be carried out on bitumen from other parts of Nigeria and these should be exploited for petroleum production as done in other parts of the world such as Athabasca, Canada.

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