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Effect of Temperature on the Compositional Changes on Crude Oil and Its Products

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ABSTRACT: The alteration in crude oil and its products are based on its extraction, production and storage activities. Their changes in composition can occur due to changes in temperature, pressure, salinity and wettability during its various processes. The crude oil, reduced oil, diesel and kerosene were analysed using GC-FID to determine the effect of temperature and their compositional content of the samples. The results obtained showed that changes in temperature affect the composition of the individual sample and the total composition of the different samples component. The highest amount of the individual component was observed in the liquid phase. The total individual composition of the samples was in the increasing order of diesel, reduced crude oil, kerosene and crude oil. Increased in the temperature, increasing their individual composition of the samples.

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Crude oil exploration, production, exportation etc in Nigeria started since 1956 at olobiri in Bayelsa State. Nigeria is the largest oil and gas producer in Africa. Crude oil found in the region is of two types; the light one of about 36 in gravity and heavy one between 20 – 25 gravities. The two types are paraffinic and low in sulphur. Though it has improved the nation's economy over the years, its activities have detrimental and significant impacts on the environment and human beings (Eluozo, 2018; Chang and Paul, 2019). Crude oils are naturally hydrocarbon together with non-hydrocarbon such as sulphur, nitrogen, oxygen, metals like vanadium, nickel, iron and dissolved inorganic compounds (hydrogen sulphide, nitrogen and carbon dioxide) present at high temperature and pressure conditions (Utin *et al.*, 2016, Ossai *et. al.*, 2020). The various types of hydrocarbons are alkanes, alkenes, alkynes and aromatics are determined depending on the bond in the compound. They are found in various states like gaseous, liquid and solid etc. In the reservoirs, they are found either in liquid or gaseous form. At standard conditions of pressure and temperature the light hydrocarbons from C_1-C_4 are gaseous, C_5-C_{17} are liquid while beyond C_{17} are in solid form. The impurities in crude oil are non-hydrocarbons organic and inorganic compounds (Utin *et al.*, 2016; Idris and Okoro, 2013; Aljamali and Salih, 2021). Crude oil composition differs depending on the location and age of the oil field. Their variation in their colour, odour and physiochemical properties is due to the different compounds found in the oil (Akmaz *et al.*, 2011; Mansoori, 2008; Al-Dahhan and Mahmood, 2019). The crude oil obtained from the well at different times of extractions is different in its chemical composition and physic-chemical behaviour and the same trends are observed in almost in each oil type. Their exact molecular composition of the oil varies greatly depending on the mixture from their source, but are relatively small compared to the difference in the proportion of chemical elements in the mixtures

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(Utin, 2017; Yasin *et al.,* 2013; Aljamali and Salih, 2021). Crude oil from any source can be tested to determine its quality and is classified based on three main categories, the geographic location where it was drilled, its sulphur content and its American Petroleum Institute (API) gravity (a measure of density). The sulphur is considered impurity in the crude oil. Crude oil with more than 0.5% sufur is described as sour with a rotten taste, while crude with less than 0.5% sufur is described as sweet. The Nigeria crude oil is known as the sweet crude oil because of its contents (Utin, 2017; Robbison, 2017). The classification of crudes in their decreasing volatility into gases, light, middle and heavy distillate /oil is based on the viscosity or density and residuum. This property depends on their boiling points. Crude oil can be refined into various fractions during distillation process like atmospheric, fractional, vacuum distillation etc. The distillation process and behavior provide information about composition, properties, and behavior during storage and use. These can affect the safety regulations as well as the handling and the performance of fuels and other hydrocarbon-based solvents. In terms of alkanes, their boiling points increases with increasing molecular weight. Increase in their molecular weight results in increasing the London forces due to the presence of more atoms increasing their surface area or molecule. Increasing molecular weight of the cycloalkanes is similar to that of the alkane except that their boiling points are higher than those of the alkanes containing the same number of carbon atoms (Ouellette and Rawn, 2018; Al-Dahhan and Mahmood, 2019). Kerosene and diesel are among the products obtained during distillation process. Kerosene is a moderate weight hydrocarbon mixture that ranges from ten (10) to sixteen (16) carbon atoms per molecule**.** Kerosene also known as paraffin or paraffin oil is flammable liquid commonly used as fuel or solvent for grease, insecticides and with wide applications in industry and household needs. It is a mixture of combustible hydrocarbon compounds. They are straight chain and branched chain alkane along with cycloalkanes. They are pale yellow or colourless depending on their fraction cut. Kerosene is less volatile than gasoline and is separated from crude oil after the napthas have boiled off and are obtained at around 180 to 260 °C temperatures. Diesel is a heavyweight hydrocarbon mixture that ranges from eight (8) to twenty-one (21) carbon atoms per molecule. They are saturated and aromatic hydrocarbon obtained at the boiling range between 260 °C to 350 °C. The diesel oils are liquid primarily used as transportation fuel, engine etc. There are less volatile (heavier) than gasoline and kerosene and are obtained around the boiling range of 300^{o}C (Robert and Rawn 2015; Utin, 2017; Al-Nahrain, 2019, Al-Nahrain, 2016). During crude oil exploration, extraction, production etc individual microorganisms metabolize only a limited range but biodegradation of crude oil requires mixture of different bacterial groups or consortia functioning to degrade a wider range of hydrocarbons and dominant weathering process can cause considerable changes in the chemical composition and physical properties of the spilled oil (Okorondu *et al.,* 2017; Chukwunonso *et al.,* 2020; Chen *et al.*, 2021; Chang and Paul, 2019). Hence the objective of this paper is to determine the effect temperature on the crude oil, reduced oil, diesel and kerosene and their individual compositions.

MATERIALS AND METHODS

The following materials and equipment were used in this research work; crude oil (Bonny light), industrial kerosene and diesel. The equipment includes: a distillation system. The bonny light crude from Bomu used was sourced from NNPC Research and Development Centre, Port Harcourt, Rivers State, Nigeria. Reduced crude oil (residue) was obtained by removing the distillate from the crude oil at 260^{0}C using atmospheric distillation in the laboratory. The diesel and kerosene were obtained from Petrol retail outlets within Port Harcourt. The raw crude oil, reduced oil, diesel and kerosene were extracted using methylene chloride. This was further concentrated and the different components were detected using a GC-FID (GC Model: Agilent 6890) with capillary column (30m x 250um x250um film thickness) in a temperature-controlled oven at a minimum temperature of 50^{0}C and maximum temperature of 350^{0}C.

RESULTS AND DISCUSSION

The results obtained as shown on table 1recorded more of the high amount of the lower molecular weight compound compared to the high molecular weight compound. This is also proof of the fact that reduced oil, industrial diesel and kerosene are not the heavy end products of the crude oil fraction. This report was in lined as reported by Utin, 2017. Also as reported by Wedad, 2020 that in the distillation process of crude oil, the different fractions obtained represent different components present in the oil sample. From the result it showed that the individual compounds of the various samples (reduced crude, kerosene and diesel) were high compared to that of the raw crude oil which confirmed that temperature changes in the oil sample alter both the individual as shown on table 1 and figure 1 above and total composition of the oil content as shown on table 2 and figure 2 above. This was in lined as reported by Okorondu *et al.,* 2017; Utin *et al.,* 2017; Chen *et al.,* 2021; Chang and Paul, 2019 that crude oil processes can alter its chemical composition of the oil.

They were gradual increase in the composition of the carbon number as it increases down the carbon number but gradually decreases in the lower molecular weight carbon. The increase as the carbon number increases was in lines as reported by Ouellette and Rawn, 2018; Al-Dhhan and Mahmood, 2019. The loss/absence of some lower molecular weight (C_1 - C_7) shown in all the samples confirmed they were not in gaseous phase as reported that C_1- C_4 are in gaseous state and loss of C_5 – C_7 may be due to weathering, biodegradation and bioremediation processes. This trend was equally reported by Okorondu *et al.,* 2017; Utin, 2017. The results showed predominance of C_{17} in all the samples with the highest amount found in diesel. The highest amount of C_{17} shown in all the samples shows the highest peak of the liquid phase; ie its high state characteristic of its liquid hydrocarbon compound. The high amount of the lower molecular weight compounds presents in the various sample confirmed that they are of lower boiling fractions of the crude oil and of the liquid phase.

Table 1: GC-FID Result of different samples (Crude oil, reduced oil, diesel and kerosine)

Compound	C/OIL (ppm)	R/OIL (ppm)	Diesel (ppm)	Kerosene (ppm)
C8	19.5873	0	30.8522	80.7452
C9	24.0064	0.67261	118.509	69.7974
C10	72.4934	67.9196	246.822	162.682
C11	79.7849	248.832	297.216	17.1402
C12	98.395	168.593	125.591	341.588
C13	90.9629	388.829	630.517	317.089
C14	77.051	314.961	655.495	758.38
C15	122.168	282.33	624.725	292.302
C16	101.736	289.545	356.325	228.886
C17	746.695	3732.71	5672.82	906.502
Pristane	531.428	1556.76	1898.12	33.0654
C18	75.1362	32.9102	302.58	72.4407
Phytane	70.4329	151.237	498.036	25.2947
C19	62.1477	171.847	405.4	34.1976
C20	66.8583	184.211	262.082	0
C21	46.8266	166.625	142.719	0
C22	39.1165	109.025	104.476	0.19065
C23	12.9257	62.8679	74.4892	0.8076
C24	7.37816	41.3592	57.802	1.39922
C25	8.74869	59.4753	2.48526	2.32299
C26	17.7887	19.9015	3.05888	3.00713
C27	12.9456	33.7969	3.33162	3.43068
C28	7.42028	5.45109	3.11721	3.11928
C29	10.9575	6.85409	2.23772	2.2423
C30	0.57994	0.67677	0.61601	0.600292
C31	0	0	0	3.52286
C32	0	0	0	0
C33	0	0	0	0
C34	0	0	0	0
C35	0	0	0	0
C36	0	0	0	0
C37	0	0	0	0
C38	0	0	0	0
C39	2.96368	2.89645	0	2.97851
C40	2.8252	2.82717	0	0
TOTAL	**2409.36**	**8103.114**	**12519.2**	**3363.732**

The little amount of the high molecular weight compound showed that the various samples were in liquid phase compared to the solid phase as reported that compounds C_{18} and above are in solid phase. This may be due to production, weathering, biodegradation and bioremediation processes of the sample from their various sources

Table 2: total composition of the individual compound in each of the sample (Crude oil, reduced oil, diesel and kerosine)

Sample	Crude Oil	Residue Oil (R/OIL)	Diesel	Kerosene
Total Hydrocarbon Value in parts per million (ppm)	2403.571	8097.39	12519.42	3357.23

They were high amount of the individual compounds especially in diesel in the samples from C_9- C_{22} with a similar trend in reduced oil. There were also significant variations in the individual components observed between the diesel and the reduced oil. The similar trend showed in these samples were an evidence of closed boiling range of the samples. The trend observed in the kerosene showed a significant amount of low molecular weight compounds in the C_{10} – C_{17} range. The trend shown in diesel and reduced oil is in line as reported that diesel is more of C_8-C_{21} while kerosene is more between C_8-C_{16} (Utin, 2017). There was increase in the original sample from C_{25}-C_{29} compared to diesel and kerosene but reverse in the residue except for C_{28} and inconsistence in the higher carbon compounds. The significant decrease in all the samples from C_{23} shows less of solid substance in the compound as has been shown that C_1-C_4 is liquid, C_5-C_{17} liquid and C_{18} and above solid state. The total individual component was shown in the increasing order of crude oil, kerosene, reduced oil and diesel due to increase in temperature. The extreme high amount pristane compared to the phytane in all the sample except in kerosene confirmed that the pristane was obtained immediately after the liquid phase while the phytane biomarkers are of the solid phase. The results of all the samples shows that the higher the temperature, the higher their individual composition of the oil. The highest amount of the total number of components in the diesel samples compared to that of the crude oil confirmed that increase in temperature increases the amount of the various components present and their molecular weight

Conclusion: The research confirmed that changes in temperature alter their individual composition and total composition of the oil and its products. Also, that as the temperature increases, the individual composition of the oil sample also increases. Their variation in composition was dependent on their boiling range characteristics, the crude oil, source of samples, degradation, extraction and production processes

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