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Effect of Temperature on Gas and Liquid Products Distribution in Thermal Cracking of Nigerian Bitumen

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Abstract

The increasing population growth resulting in the tremendous increase in consumption of fuels, energy, and petrochemical products and coupled with the depletion in conventional crude oil reserves and production make it imperative for Nigeria to explore her bitumen reserves so as to meet her energy and petrochemicals needs. Samples of Agbabu bitumen were subjected to thermal cracking in a tubular steel reactor operated at 10 bar pressure to investigate the effect of temperature on the cracking reaction. The gas produced was analyzed in a Gas Chromatograph while the liquid products were subjected to Gas Chromatography-Mass Spectrometry (GC-MS) analysis. Heptane was the dominant gas produced in bitumen cracking at all temperatures and the reaction products show a distribution of lighter hydrocarbons most of which are in the gasoline range. The product distribution of bitumen conversion depends strongly on the cracking temperature and the oil produced contains the valuable liquid fractions. The products of thermal cracking of bitumen can be classified into the following groups; alkanes, alkenes, amines, aromatics, alkanoic acids, alkanols, esters, ethers, ketones, sulphur compounds, and nitrogen compounds. The activation energies of the products formed were determined. The LNG produced all have unusually low values activation energy (hence easily converted) pointing to the high quality of Agbabu crude

The conversion process was affected by the reaction time and suggests that the transformation of bitumen into smaller fractions follows a definite reaction scheme in which the heavy oil transformed to lower fractions and was subsequently converted to smaller liquid fractions and gases.

Keywords: Agbabu bitumen, Petrochemicals, Cracking, Activation energy

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1- Introduction

The worldwide production of conventional crude oil is expected to reach its crest in the second decade and subsequently enter a phase of everlasting decline [1].

To meet the increasing need for light oil, interest has switched to unusual sources of which natural bitumen and heavy crude oil are the most readily accessible to meet-up with both the short- and long-term demand [2].

Bituminous sands are made up of mineral matters, heavy oil, water, and are rich in minerals. The heavy oil in bituminous sands is regarded as bitumen while the sandy and clayey mineral contents are referred to as mineral matter [3].

Bitumen is viscous with high density (1.0 g/cm^3) or low API gravities (< 22^o API). It has chemical properties comparable to conventional crude oils [4,5].

The Nigerian Bitumen reserve has been conventionally projected to be more than 50 million tons. Based on average bitumen content of 15% by weight the Nigerian rich bitumen deposits constitute a possible reserve of over 40 billion barrels of bitumen [6], which is about 40 % of Canada's deposit known to be one of the world's richest deposits of bitumen [7].

At low temperature and pressure (673 K, 620 kPa) bitumen is broken down to gasoline high in aromatic hydrocarbon, coke, and gases [8, 9]. It has been reported that the decomposition of the Utah bitumen to gases and oils occurred within 400 and 420 ^{o}C, and a further increases in the reaction temperature had little or no effect on product yield. [10]. Hayashitani, [11, 12] studied the decomposition of Athabasca bitumen using the thermal process at different reaction times at 360, 397, and 422 ^{o}C. The products' yield i.e coke, asphaltenes, heavy oils, gases, light oils, and middle oils as a function of time and temperature were employed in the determination of kinetic data for predicting the amount of combustion fuel obtainable in an *in-situ* operation and their composition.

Another study of the thermal decomposition of asphaltenes [13] showed that there was no induction stage for the formation of coke and that the molecular weight of asphaltenes did not change throughout the process.

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Speight investigated the mechanism of the thermal decomposition of asphaltenes sourced from Athabasca bitumen and deasphaltenated oil using the distillation method (destructive) [14]. An evaluation of the data obtained indicated that significant changes took place during cracking. In other studies [15, 16, 17], the thermal reactions of Athabasca bitumen and deasphated Athabasca bitumen were investigated at high temperatures using a micro-autoclave. The analysis of reaction products showed that about 46 wt% of pentane soluble (maltenes) was formed and that the composition of the maltenes is; 3.5 wt % polar compounds, 5 wt% mono and diaromatics, 17 wt % saturates, and 20.5 polyaromatics. They also found that partial deasphalting of bitumen leads to the production of products with better quality such as reduced metals content, viscosity, and micro carbon residue.

In another work, Yasar and co, [18] studied the pyrolysis of maltenes, isolated asphaltenes, and resids from Arabian light, Arabian heavy, Hondo, and Maya oils. At 673 and 698 K, isolated asphaltenes reacted selectively to form maltenes. At higher temperatures (723K), asphaltenes reacted predominantly to form coke. Detailed product analyses from the thermal cracking of Athabasca bitumen Vacuum Bottom and SARA fractions revealed that saturates and mono- and diaromatics were relatively unreactive, whereas polyaromatics and resins were converted to smaller molecules including saturates. The product obtained included aromatic fractions and a small amount of coke. The results of the study by Dawson *et al*. showed that side chain and dehydrogenation /hydrogenation reactions are major routes in the thermal cracking of heavy oils and bitumen [19].

Liu *et al*.,[20] in correlation studies of the pyrolysis of feedstock obtained by supercritical extraction from some Chinese light crude oils and oils from Saudi Arabia and Oman compared the behavior of oil to their properties. Eshraghian and Husein in another study investigated Athabasca vacuum residue and bitumen in a closed autoclave reactor system at 400-420 °C and produce gas yield below 10 wt% [21], a similar result was obtained by Yunanto *et al*, 2019[22].

The evolution of mass losses and production of gases from oils during Low –temperature oxidation (LTO) was also reported and the products analyzed by FTIR and SARA [23-25]

According to Atkins [26], the large reservoir of bitumen and heavy crude oil deposits in Angola, Nigeria, Egypt, and other African countries are yet to be exploited because of the limited or no studies on the upgrading technology. For example, the Southwest Nigerian Bitumen reserve has been predictably estimated to be over 50 million tons. On average bitumen content of 15%, wt the regional rich tar sand deposits constitute a latent reserve of over 40 billion barrels of bitumen [6] approximately 40 % of Canada's deposits regarded as the richest deposits of tar sands globally [7]. Thus, this work aims to carry out thermal cracking of Nigerian bitumen, analyze the gaseous and liquid products to obtain relevant kinetic data and information on product distribution.

2- Experimentals

2.1. Description of Reactor

A tubular batch steel reactor designed and constructed in-house was used for the cracking of bitumen. All pressure fittings were made of stainless steel 316 grade and purchased from Swagelok UK. The reactor is 1cm diameter and 15cm length connected to a ¼ in the tube. The control line of the reactor was fitted with a pressure relief valve for safe operation, gas inlet and outlet manual valves, and a pressure gauge to monitor the system pressure. A type K thermocouple (RS components) was inserted from the top of the pressure line to measure the temperature in the centre of the reactor tube. The furnace can operate at a maximum operating temperature of 550 °C, which was measured with an external type K thermocouple placed at its centre, connected to a temperature controller. The furnace and reactor were located inside a fume cupboard for safety during operation. A Schematic diagram of the apparatus including the reactor used for the cracking of the bitumen is presented in Fig. **1**.

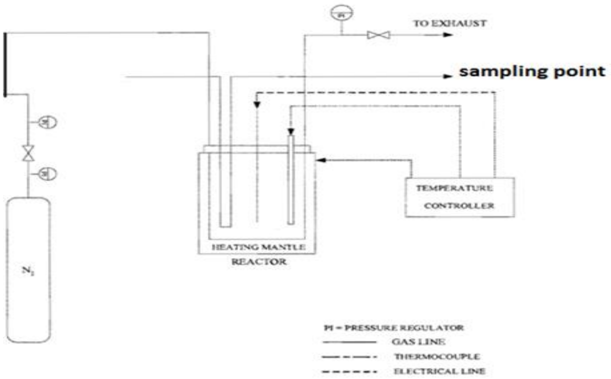

Fig. 1. Diagram of reactor used for cracking of bitumen

2.2. Thermal Cracking of Agbabu Bitumen

The cracking process was carried out in the laboratory using the constructed steel reactor (Figure 1). 10 g sample of bitumen was introduced into the reactor for each run.

The reactor tube was then connected to the ¼ in. pressure line through a straight union and a pressure nitrogen (N_2) cylinder was connected to the control line. The reactor was purged with nitrogen gas to remove air before the system was pressurized and checked for leakages. If any leakage was observed, the system was depressurized and the leaks fixed. Subsequently, the reactor was pressurized to 10 bar with nitrogen gas. The cracking of bitumen was carried out at 400, 450, and 500 ^{o}C. The cracking reaction was initiated after the operating conditions have been attained. The products of cracking which included gases and light oil were collected. The gases were then flashed off, and either vented or sent to the Refinery Gas Analyzer (RGA) for concentration and compositional analysis.

2.3. Refinery Gas Analyser (RGA)

The compositional analysis of the gases was done using Perkin Elber Auto system XL chromatographer fitted with flame ionization detector(FID). The gas chromatograph(GC) was equipped with Porapak Q as support, having mesh range 80/100, length of 6 Ft O.D1/8” I.D 0.085”. The hydrocarbon components in the gaseous stream were determined by the FID channel column capable of separating hydrocarbons based on the calibrated table. The operating conditions of the FID channel were: hydrogen (45 mL.min^{-1}), air (400 mL.min^{-1}), reference (45 mL.min^{-1}), and makeup flow N_2 (25 mL.min^{-1}); The oven temperature program was 40 °C for 2 min, and then a temperature program of 7.5 ^{o}C/min to 100 ^{o}C for 5min, 12.5 ^{o}C/min to 180 ^{o}C for 10 min and 15.0 °C/min up to 225 °C (20 minutes).

2.4. GC-MS Analysis of the Oil Produced From Bitumen Cracking

Quantitative and qualitative data were obtained by GC-MS analysis of the raw bitumen and oil produced from all cracking processes. Each sample was dissolved in 10 % tetrahydrofuran (THF) and then injected into an Agilent Tech 7820 A Gas Chromatograph hyphenated with an Agilent 5977E Mass Selective Detector (MSD) operating in electron impact mode. Products were analyzed in selected ion monitoring (SIM) mode. An HP-5 30 m x 0.25 mm x 0.25 µm capillary column was used for the GC with helium as carrier gas at a constant flow rate of 1.0 ml/min. The oven temperature program was 40 °C for 5 min, and then a temperature program of 40 ^{o}C/min to 140 ^{o}C for 3min, and 8 °C/min up to 280 °C where it was held to 20 minutes. The samples were run using full scan, single ion monitoring (SIM), and recorded using the HP chemstation data system [27] .The identification of the components was based on the comparison of retention times of the components and spectral with those data in the library.

3- Results and Discussion

3.1. Gaseous Products of Thermal Cracking of Bitumen

The cracking of bitumen was carried out in the temperature range 400 to 500 ^{o}C at 10 bar reactor pressure and five hours' time-on-stream. The changes in gas composition as a function of time at different temperatures are presented in Figures 2-4. The analysis of gas composition by refinery gas analysis showed that heptane, octane, decane, and dodecane are the major products obtained from the thermal cracking of bitumen at 400 ^{o}C, 450 ^{o}C, and 500 ^{o}C. Other components include; methane, ethane, propane, butane, isobutane, pentane, methyl pentane, hexane, and nonane. The production of gases increased as the reaction temperature attained 400 ^{o}C with heptane and octane dominating.

At an experimental run-time of 120 minutes, product generation drastically fell especially the higher components (heptane and octane) in the gas mixture. The amount of the different gases generated was not stable until about 240 min into the process and remained at a plateau.

At 450 ^{o}C, due to the increase in temperature, the production of intermediate compounds was observed. Heptane, dodecane, decane, hexane, pentane, and butane were produced more within the first one hour of reaction.

The amount of the different gases generated was not stable until about 180 to 240 minutes into the experiment and maintained the gas generation till the end of the experiment as was observed during the thermal cracking at 400 ^{o}C. The generation of all the gaseous products reached their climax after 60 minutes of cracking time producing more hydrocarbons with higher concentration at 500 ^{o}C. The amount of the different gases generated was not stable until about 180 to 240 minutes into the experiment and maintained the gas generation till the end of the experiment as was observed during the cracking at 400 ^{o}C.

The profiles in Figures 2-4 give the details of the gases obtained as a function of reaction time. Results showed that an increase in the reaction temperature enhanced the formation of gases. The formation of gas occurred at a higher rate within the first hours of reaction time and then declined. This phenomenon could be associated with the breaking down of the paraffinic chains present in asphaltenes and other large molecules present in the bitumen in the early stage of the reaction, and with the cracking of smaller ones in the latter stages of the reaction. The obtained result was similar to the one reported by Martinz-Grimaldo and co-workers [28].

Thermal cracking generally takes place via a free radical mechanism which involves a series of reaction steps, including chain initiation, hydrogen abstraction reaction, radical decomposition reaction, radical addition reaction, and termination reaction [29, 30, 31].

From the results shown in Figures 2-4, the gas formation was found to increase with an increase in the processing temperature. These observations are similar to what was reported for the coking of Arabian mix vacuum residue [32].The reaction products of bitumen cracking show the distribution of lighter hydrocarbons most of which are in the gasoline range. It was observed that C_5 to C_{12} components were present in the chromatogram with a peak of C_7 for thermal cracking at 400^{o}C and 500 ^{o}C while a peak of C_{12}, closely followed by C_7 was obtained at 450 ^{o}C. The C_1-C_4 are used as fuel(burned), ethane can be pyrolyzed to produce ethylene, propane or a mixture of propane and butane can be utilized as liquefied petroleum gas (LPG), the C_6-C_{15} fractions are used as jet fuel and kerosene, while C_5-C_8 which are hydrocarbons primarily suitable for gasoline and C_4 may be added to achieve additional volatility [30].

As the reaction temperature increases, thermal cracking becomes significant prompting the breakingdown of heavy molecules into smaller ones.

This was confirmed by the results of the investigation reported in the open literature, during hydrotreating/cracking of heavy oil in fixed and fluidized bed reactors under similar reaction conditions [33-35].

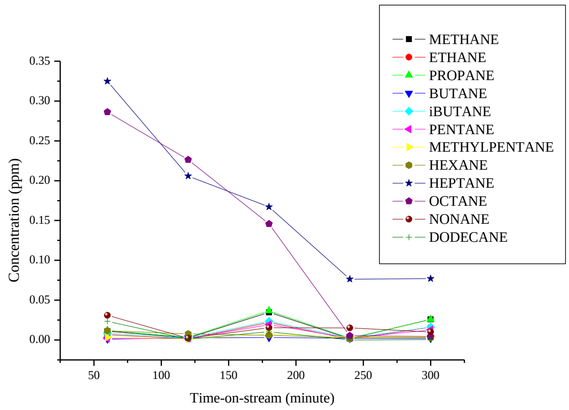

Fig. 2. Product distribution of thermal cracking at 400 ^{o}C

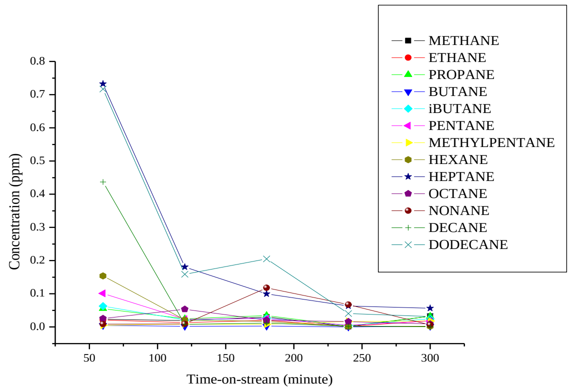

Fig. 3. The product distribution of thermal cracking at 450 ^{o}C

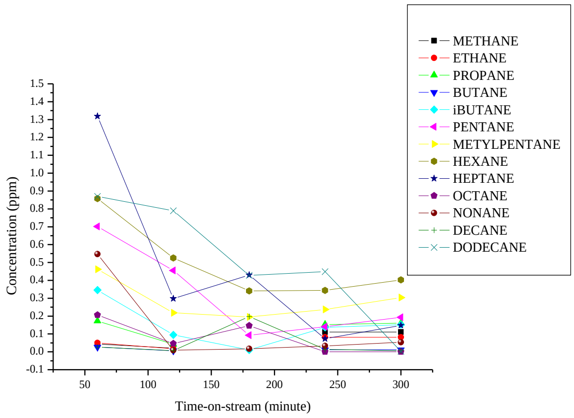

Fig. 4. The product distribution of thermal cracking at 500 ^{o}C

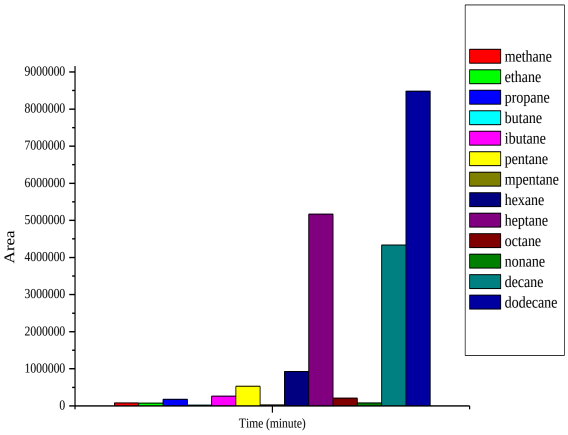

Fig. 5. Barchart for product distribution of thermal cracking of bitumen at 450 ^{o}C after minutes

3.2. Liquid Products

GC-MS spectra of the liquid products (oil) obtained during thermal cracking of Nigerian bitumen at temperatures of 400,450 and 500 ^{o}C are presented in Fig. **6** to Fig. **8** and Table **1** contains a summary of the classes of compounds identified at the various temperatures.

As the results show, the product distribution of bitumen conversion strongly depends on the cracking temperature. Numerous products were formed during the thermal cracking of the bitumen and they can be classified into the following groups; alkanes, alkenes, amines, aromatics, alkanoic acids, alkanols, esters, ethers, ketones, sulphur compounds, and nitrogen compounds. At all the cracking temperatures, alkanes, aromatics, and amines are the major products obtained from the cracking of bitumen.

According to Beaton and Bertolacini [36], as the temperature was increased to 450^{o}C, the production of other chemicals such as alkenes, alkanoic acids, alkanols, and esters were enhanced at different rates. But at 500 ^{o}C, the conversion to alkanes was enhanced by the high heating temperature. At low temperatures, the molecules are not provided with sufficient energy to break down the bonds and consequently few radicals are produced resulting in reactions proceeding slowly. This then resulted in the production of lower amounts of products at low temperatures compared to high-temperature operations. Free radicals are generated from the feed in the initiation step and these radicals can undergo further reactions and produce new and/or more stable radicals (propagation step). In the fragmentation step, however, a free radical forms an unsaturated molecule and a new radical.

The alkene double bond is weak and its production is not well-favored due to its weak bonds. As such, the driving force for the fragmentation reactions was associated with the presence of a highly weak radical, which led to alkene [37].

The results presented in Fig. **9** showed that the production of aromatics was high at lower temperatures.

This is because at relatively low temperatures, the aromatic rings are very hard to break down owing to their high bond dissociation energy. At the lower temperatures, the major conversions happened in the aliphatic bonds [37].

However, at 500 °C, the amount of aromatics was reduced from 37.71% to 32.83% as expected. Thermal cracking of bitumen, even at low temperatures, resulted in desulphurization. According to Fig. **10**, the naphthalene present in the products obtained during the thermal cracking of bitumen increased with increase in temperature.

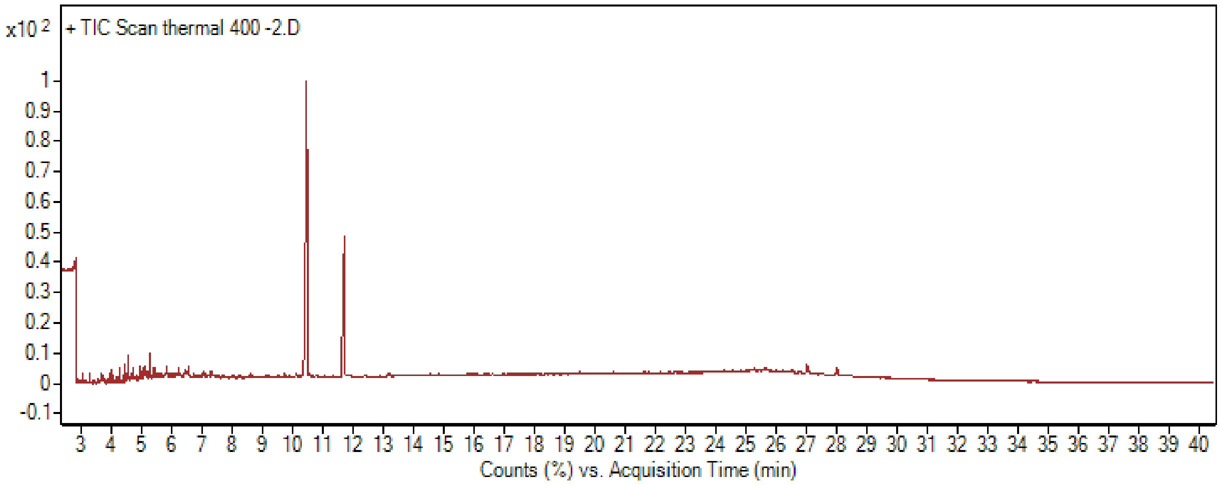

Fig. 6. GC-MS spectrum of products of thermal cracking of bitumen at 400 °C

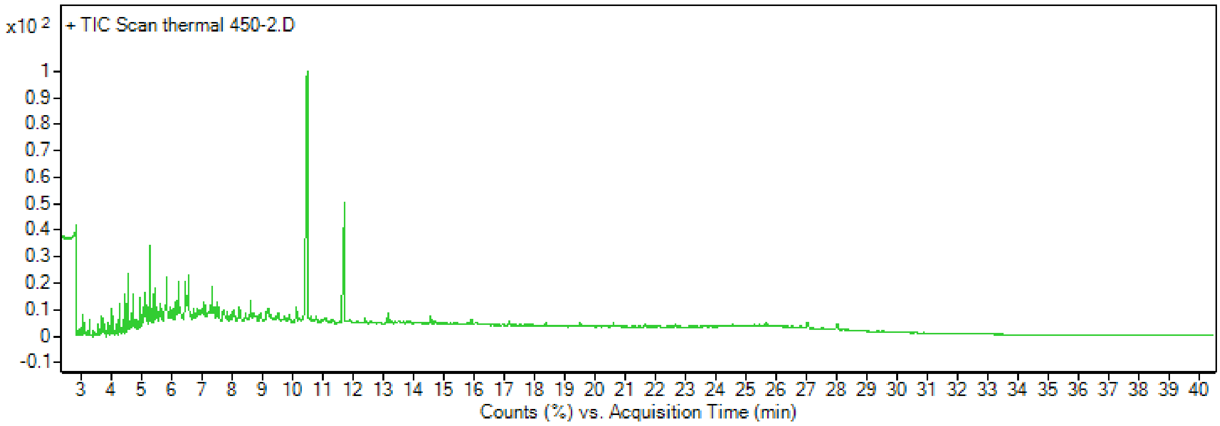

Fig. 7. GC-MS spectrum of products of thermal cracking of bitumen at 450 °C

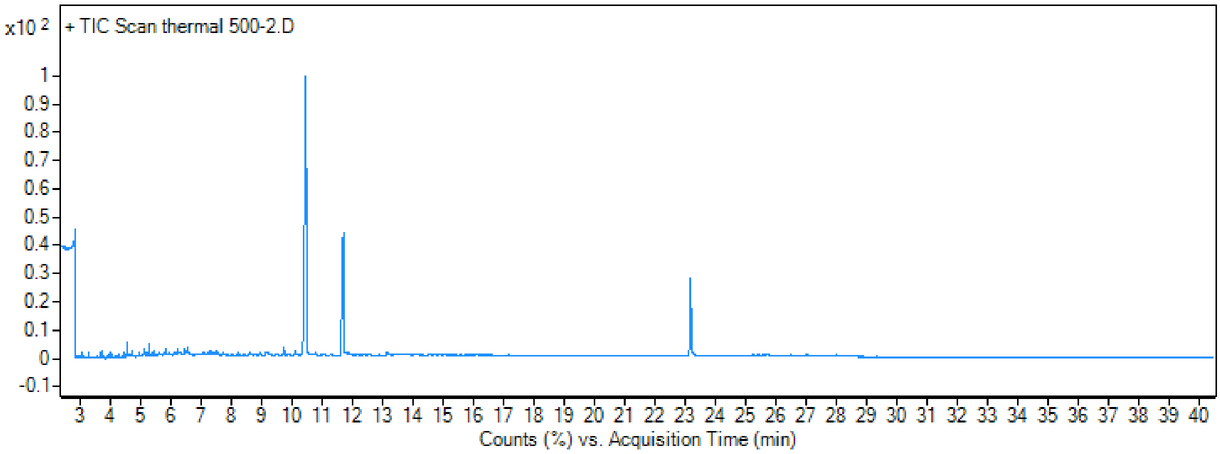

Fig. 8. GC-MS spectrum of products of thermal cracking of bitumen at 500 °C

Table 1. Summary of the class of compounds identified by GC-MS

Class of Compound	Amount Produced (%)		
	400 °C	450 °C	500 °C
Alkanes	22.1	16.71	39.34
Alkenes	-	2.88	-
Amines	27.12	27.63	20.05
Aromatics	37.71	37.58	32.83
Alkanoic acid	0.26	5.97	4.61
Alkanols	1.6	1.18	1.4
Esters	5.63	1.66	1.07
Ethers	0.23	-	-
Ketones	-	-	0.7
Sulphur compounds	5.27	5.48	-
Nitrogen compound	-	0.3	-
Others	0.01	0.61	0.00

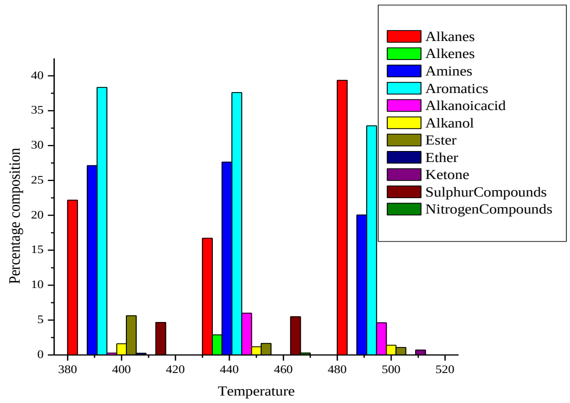

Fig. 9. Composition of liquid products during thermal cracking of bitumen at temperatures of 400, 450, and 500 °C

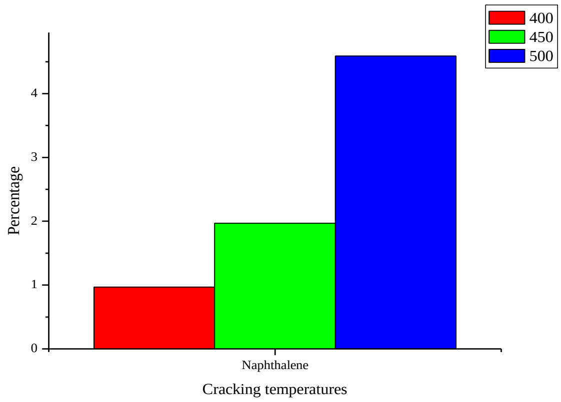

Fig. 10. Naphthalenes in products of thermal cracking at 400, 450, and 500 °C

Gaseous Products Distribution: Effect of temperature. Methane yield as a function of temperature during thermal cracking of bitumen is presented in Figure 11. At the lower temperature of 400 °C, moderate levels of bitumen cracking were observed with methane having a concentration of 0.01089 ppm after 60 minutes of cracking. Bitumen cracking improved with increasing temperature as methane had a concentration of 0.02292 ppm and 0.04328 ppm at 450 and 500 °C respectively after 60 minutes-time-on stream. This shows that the cracking of molecules became important as the reaction temperature was increased, leading to the breaking down of heavy molecules into smaller ones. This is agreed with literature reports [33-35]. The same trend was maintained for all the other gaseous hydrocarbon products generated during the thermal cracking of bitumen.

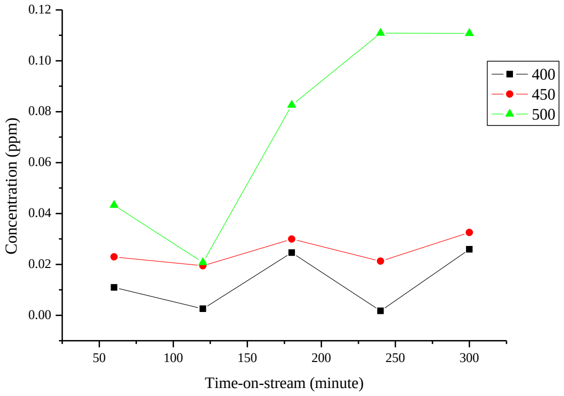

Fig. 11. Methane produced at 400°C, 450° C, and 500°C during thermal cracking of bitumen

3.3. Kinetic Analysis of Bitumen Thermal Cracking Data

Many complex reactions occur during the bitumen decomposition process, and it is almost impossible to estimate the intrinsic kinetics of all reactions [38]. However, reactions of primary interest are those that crack macromolecular bitumen into volatile compounds that can be measured using the Gas Chromatograph with the injection port temperature of 400^0 C.

The cracking reactions of bitumen and its fractions have been reported by previous researchers to be first order with respect to hydrocarbons [39] and zero with respect to hydrogen [40]. The first step in this kinetic assessment considers the translation of the bitumen into lighter products as an irreversible first-ordered reaction, represented by:

Bitumen fraction → lighter products

The first-order rate constant, *k*, for the decrease in the bitumen concentration from its initial value, x_0, to its value x_t at time t was obtained from the equation [41]:

$$k = 1/t \ln[x_o/(x_o - x_t)] \qquad (1)$$

The integrated form of the first-order rate equation was then used to analyze the data to determine first order rate constants for all the hydrocarbons produced during bitumen cracking. The linear first-order plots are presented in Figures 12-14 for bitumen cracking at 400 °C, 450°C, and 500 °C. The Arrhenius equation was used to determine the activation energy for the products. The results are presented in Table **2**

Table 2. Rate constant sand Activation Energy for different hydrocarbon molecules

	$k_{1,}$ s^{-1}	k_2, s^{-1}	k_3s^{-1}	$E_a(kJmol^{-1})$
Methane	0.00223	0.003358	0.00593	16.0963
Ethane	0.002235	0.004538	0.004258	11.1493
Propane	0.001855	0.005324	0.001891	1.6096
Butane	0.002004	0.005892	0.001612	2.1367
Ibutane	0.002021	0.005701	0.002113	1.9921
Pentane	0.007284	0.008173	0.006256	2.2831
Methylpentane	0.002134	0.004811	0.001978	0.2049
Hexane	0.006627	0.01834	0.00322	10.2431
Heptane	0.006448	0.01029	0.009625	6.9640
Octane	0.02013	0.005495	0.04093	9.7120
Nonane	0.0004638	0.002157	0.00546	41.2050
Decane	0.02054	0.0229	0.003454	28.2850
Dodecane		0.01268	0.0199	16.8778

The linear form of the plots in figures 12-14 suggests that a first-order mechanism described the transformation of the Nigerian bitumen thermally. A systematic change in rate constant was noticed as the reaction temperature was increased as expected. There was a slight decrease in the rate constants of lower hydrocarbons as the temperature was increased to 500°C because the cracking severity of bitumen increased leading to the production of more products which may increase the presence of light hydrocarbons.

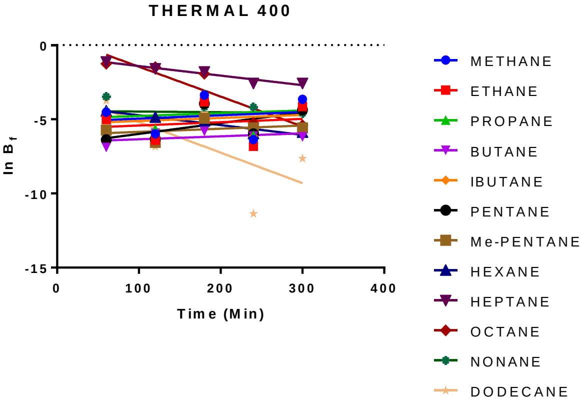

Fig. 12. Nigerian bitumen: thermal cracking at 400°C

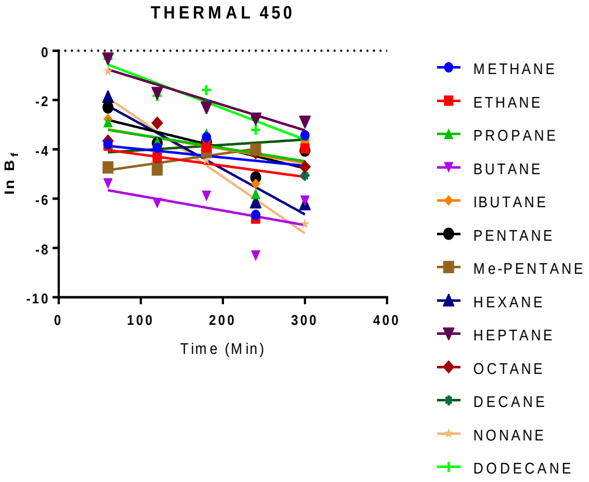

Fig. 13. Nigerian bitumen: thermal cracking at 450°C

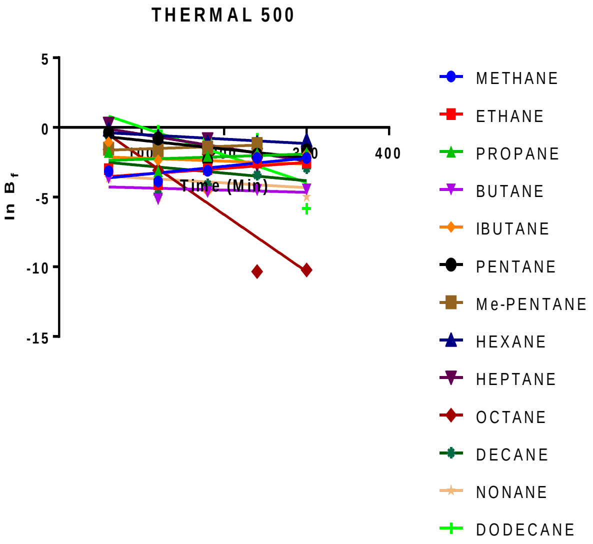

Fig. 14. Nigerian bitumen: thermal cracking at 500°C

According to the literature [42], the activation energy of the thermal cracking reactions lies between 174 and 268 $kJmol^{-1}$. The energies required to activate the decomposition of some light hydrocarbons majorly are between 24.3 (neo-C_5H_{12}) and 56.9 kJ mol^{-1} (CH_4). The value 102.5 kJ mol^{-1} was the highest discovered for CH_3CHO. Barbour *et al*.[37] reported that a first-order rate constant, *k*, was observed during the pyrolysis of bitumen with sand, and corresponding activation energy of138 kJ mol^{-1} was observed. However, AlSoufi et al. [43] during the cracking of atmospheric residue obtained a relatively low value of activation energy (99 kJ/mol). From the obtained results, values of activation energies in this study are also in the range from 102 to 206 $kJmol^{-1}$[44]. Most studies made use of solvent extractions in separating the different phases in the pyrolyzed-product. [42], however, the methods of separating products do not affect activation energies reported which are due to differences in the chemistry of pyrolysis, or the analytical procedures employed [45].

Vyazovkin has described the interpretation of activation energy as a concession in a way as to analyze the reasons for variation in activation energies in terms of mechanistic steps. [46]. As predicted by Nassar et. al.[47], we can obtain a variation in activation energy with conversion processes. Strauszet and co-worker reported unusually low values of the activation energies measured for products formation during the pyrolysis of Athabasca oil sand with values of 56.9kJ mol^{-1}, 34.7kJ mol^{-1}, 57.7kJ mol^{-1}, 48.5kJ mol^{-1}, 28.4kJ mol^{-1}and 48.kJ mol^{-1}for methane, ethane, propane, butane, ibutane and pentane respectively [48]. They ascribed the low activation energy to a catalytic effect of the mineral matter present in the crude.

However, in this work, according to table 2, the activation energies for the production of different products were relatively lower than what was reported for Athabasca bitumen. Methyl pentane had the lowest activation energy of 0.204kJmol^{-1}, followed by propane, ibutane, butane, and pentane. The C_1-C_4 are used as fuel(burned), ethane can be pyrolized to produce ethylene, propane or a mixture of propane and butane can be utilized as liquefied petroleum gas (LPG), C_6-C_{15} is used as jet fuel and kerosene, while C_5-C_8 which are hydrocarbons primarily suitable for gasoline and C_4 may be added to achieve additional volatility.

4- Conclusion

From this study, the following conclusions can be drawn:

1- The transformation of Agbabu bitumen into smaller fractions follows a definite reaction scheme in which higher molecular weight hydrocarbon's converts to smaller ones and these fractions are subsequently converted to liquid fractions and gases.
2- The gaseous hydrocarbons were produced from the higher fractions
3- Temperature and reaction time has a higher effect on the scheme
4- Products are lighter hydrocarbon's mostly in the gasoline range C_5 to C_{12} fractions were obtained with a peak at C_7 for thermal cracking at 400 and 500^oC while a peak of C_{12} closely followed by C_7 was obtained at 450^oC.
5- The liquid phase contains the most valuable products; hence, it is the most important product from the process. The results showed that the temperature of the reactor affects the percentage fraction of each component with reaction time. Numerous products were formed during the thermal cracking of the bitumen. These products can be classified into the following groups; alkanes, alkenes, amines, aromatics, alkanoic acids, alkanols, esters, ethers, ketones, sulphur compounds and nitrogen compounds.
6- The decomposition of Agbabu bitumen perfectly fit into first-order kinetics model and low energy of activation is required for the conversion of bitumen into valuable products

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