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Pyrolysis and Evaluation of Oil shale Product Yield and Composition from Tchikatanga-Makola (Congo) Oil Shale

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Abstract – In this work the pyrolysis and evaluation of the product yield from Tchikatanga-Makola (Congo-Brazzaville). The TGA and DTG were performed at different heating rates of (5, 10, 15, 30, 50 °C/min); the final temperature reached was 760°C. Fischer Assay analysis of oil shale is 8.12 wt%. The optimal pyrolysis temperature was between 480°C to 540°C, which in an average was 520°C. The results of this work revealed that increasing the pyrolysis temperature to 540°C increases the oil yield. Although the ratio of gas/oil was lower, it was found that at heating rates of 2 and 5°C/min the gas yield increased, and at heating rate of 30°C/min, the oil yield was higher representing the optimal heating rate of pyrolysis. The gas analysis indicated that the gas pyrolysis contain H_2, CO, CO_2, N_2, H_2S and some C_1-C_4 hydrocarbon. As the temperature increased to 520°C, the oil yield decreased while the gaseous emission still increased. The amount of gaseous hydrocarbon increases due to the secondary reactions such as cracking and aromatization of oil derived from oil shale during retorting, however, the content of CO did not change much. But CO_2 decreases due to the decarboxylation of organic matter. The oil analysis shows that the shale oil is essentially composed of 60% aliphatic, 23% non-hydrocarbons, 11% aromatics and 6% asphatenes. The elementary analysis of the oil from pyrolysis is mainly composed of C, H, S, N, O and H/C ratio. Hydrogen and carbon contents in oil shales are higher and increase by increasing the heating rate. This possibly explains the presence of aromatic hydrocarbon products existing in shale oil.

Keywords – Congo-Brazzaville oil shale, heating rate, oil yield, pyrolysis.

1. INTRODUCTION

With increasing demand for energy and a limited supply of fossil fuels, the development of diverse alternative sources to fossil fuels is necessary to meet future energy needs. In this quest, a viable option is oil shale deposits which are now deemed as abundant sources to meet the global energy needs [1]. The oil shale deposits occur in many countries around the world [2], [3], recent researches have proved the abundance of enormous reserves of oil shale in Congo-basin of the Republic of Congo [3],[4]. The Congo oil shale deposit is in Makola Dionga located in south Congo, 70km from Pointe-Noire city and its oil shale reserves are estimated to be equivalent to 2.5 billion tons and 500 million barrels of oil [5]. Retorting is one of the most attractive conversion approaches; it has been widespread in the conversion of oil shale [6]. Retorting the oil shale will convert oil shale into the different phases (shale oil, gas and semicoke). The application of thermal decomposition of oil shale is not a recent approach. To explore the optimal retorting conditions several investigators have studied these processes of pyrolysis and combustion parameters which can influence the oil yield and its characterization of different oil shale such as: time [7], mineral content [8], reaction temperature [9], particle size [10] and heating rate [11], [12]. Those parameters have been investigated on different oil shale. Wang *et al.* [13] studied the effect of heating rate on North-Korean oil shale by thermogravimetry; it reported that the increase of heating rate had a significantly positive effect on oil shale conversion. Al-Harahsheh *et al.* [14] examined the effect of demineralization and the heating rate on the pyrolysis of Jordanian oil shale. This suggests that the amount of coke formed decreased with the increase of heating rate. Wang *et al.* [15] have reported on the effect of retorting temperature on product yield and characteristics of non-condensable gases and shale oil of Huadian oil shale (China). Increasing the temperature from 430°C to 520°C improved both oil and gas yields, but reduced the oil/gas yield ratio. Raising the temperature increased nitrogen content in the derived shale oil and decreased the atomic H/C ratio and oxygen content, but had no significant effect on the sulfur content. Ahmad *et al.* [10] showed the influence of particle grain size on product yield on Pakistan oil shale. It was found that increasing the particle size up to the largest size of 10 mm used, resulted in an increase in oil yield. The total gaseous yield was decreased, reflecting a decrease in concentration of H_2, CO, CO_2 and the majority of the hydrocarbon gases. In addition, Wang *et al.* [16] investigated the effect of heating rate on products yield and characteristics of non-condensable gases and shale oil on Dachengzi oil shale and found that the shale oil yield first increased and then slightly diminished as the heating rate increased. The non-condensable gases yield increased by increasing the heating rate and the sulfur mass content was not significantly affected by increasing the heating rate.

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Earnest [17] studied the thermogravimetry of selected American and Australian oil shales in inert dynamic atmospheres, his work showed that the pyrolysis temperatures at maximum pyrolysis rates were related to the type of organic mineral components of the shale specimens.

The non-isothermal analysis has specific advantages and results in close proximity to practical procedure. The influence of heating rate on the mass loss during decomposition of oil shale using thermo gravimetric analysis (TGA) and differential thermogravimetry (DTG) have been studied by many researchers [18]-[21]. The TGA is used to determine the thermal characteristic and the mass loss of oil shale as function of the pyrolysis temperature. In optimizing the comprehensive utilization process of Tchikatanga-Makola oil shale, a series of investigations were performed by the authors. Employing a lab-scale retorting system, which involves pyrolysis characteristics, TG method at different heating rates, retorting characteristics of electric retorts etc. the results were then discussed. This work focused on the the pyrolysis characteristic, the influence of different heating rates, temperature on pyrolysis product yield, and composition (gas and oil), to determine the optimal pyrolysis condition and exploring the changes of chemical components of shale oil.

At last, the product yield, properties of shale oil and non-condensable gases on retorting temperature were comprehensively analyzed, giving a set of fundamental data in developing the comprehensive utilization system of oil shale. Therefore, research on retorting behavior of Tchikatanga-Makola oil shale should be performed comprehensively before exploration and developmental projects can proceed. This study was conducted in order to gain an understanding of the effectiveness of organic matter extraction from Congo oil shales. Congo oil shale samples, from different sites Tchikanga of congo deposits, have been studied and pyrolysis in a fixed bed reactor (which closely simulates the conditions that would be found in commercial scale retorts) at a different heating rate and final temperature in order to measure directly the rate of oil evolution from retorting such shales. Consequently, the yields of gaseous products, process water and retorted shale were determined. The derived products, as a result of pyrolysis, were analysed in order to determine their composition and yield, to provide important information for the design and optimization of the comprehensive utilization of Tchikatanga-Makola (Congo) oil shale.

2. EXPERIMENTAL SECTION

2.1. Materials

The oil shale samples used in this work were taken from Tchikatanga-Makola Basin located in Makola Dionga, 70 km from Pointe-Noire in Republic of Congo. Table 2 shows the data of proximate analysis, ultimate analysis and Fischer assay analysis of oil shale sample. The proximate analysis was carried out according to the international standards (ASTM D 5142). The ultimate analysis was made possible by the element analyzer (ASTM D 5373) and the Fisher assay was carried out according to the standards of (ASTM D3904-80). In the process 100 g of oil shale sample was heated to 500°C and maintained for 40 minutes at 12°C/min. The product yield was determined by the weight of the recovered water, oil, gas and the shale residue.

2.2. Experimental Apparatus

In this research, experimental TGA pyrolysis was performed in nitrogen atmosphere using a Netzsch STA 449C thermal analyzer system from Germany. In the experiment, 10 mg of oil shale samples were crushed, and sieved to a grain size of 0–0.09 mm according to the ASTM D2013-07 (USA) standards and heated from ambient temperature to 900°C, measured at five different averages of heating rates (5, 10, 15, 20 and 50°C/min) and the constant gas stream of nitrogen was used to purge with a flow rate of 60 ml/min.

The pyrolysis process was performed on an OTF-1200X retort, the scheme and detailed instructions of the experimental retorting system of oil shale have been given in [22] which are shown in Figure 1, in the experiment, 186.20 grams of the oil shale sample was used. The sample was placed inside a Tube furnace retort; the required final pyrolysis temperature and the heating rate were controlled according to the control panel. With the temperature increased, the pyrolysis product (shale oil and gas) was released then condensed in the liquid collector. The evolved gases were collected in plastic bag for analyzing the component concentrations as a function of temperature. The initial weight and the solid residues for each experiment were accurately recorded.

Methylbenzene was added to the mixture of the collected liquid products (water and shale oil) because of the presence of the aqueous phase. The weight of shale oil was calculated by calculating the mass changes before and after distillation. The yields of oil and solid residue are defined as follow:

$$x = \frac{Wi}{W} 100\% \qquad (1)$$

Where, x is the yield of products, Wi mass of the desired product and W is the initial mass of oil shale, the gas yield was determined by difference. Each experimental condition was repeated at least three times for each sample to ensure the reproducibility and accuracy of the obtained data. The average yields of experimental data were adopted in this part all the experiment conditions are shown in Table 1.

Table 1.The experimental conditions.

Experimental conditions	
Final pyrolysis temperature, °C	900
Heating rate, °C/min	5, 10, 15, 30, 50
Flow rate of carrier gas, ml/min	60
Mass of the sample, g	186.20
Gas carrier	N_2
Sample grain size ,mm	0-1.5

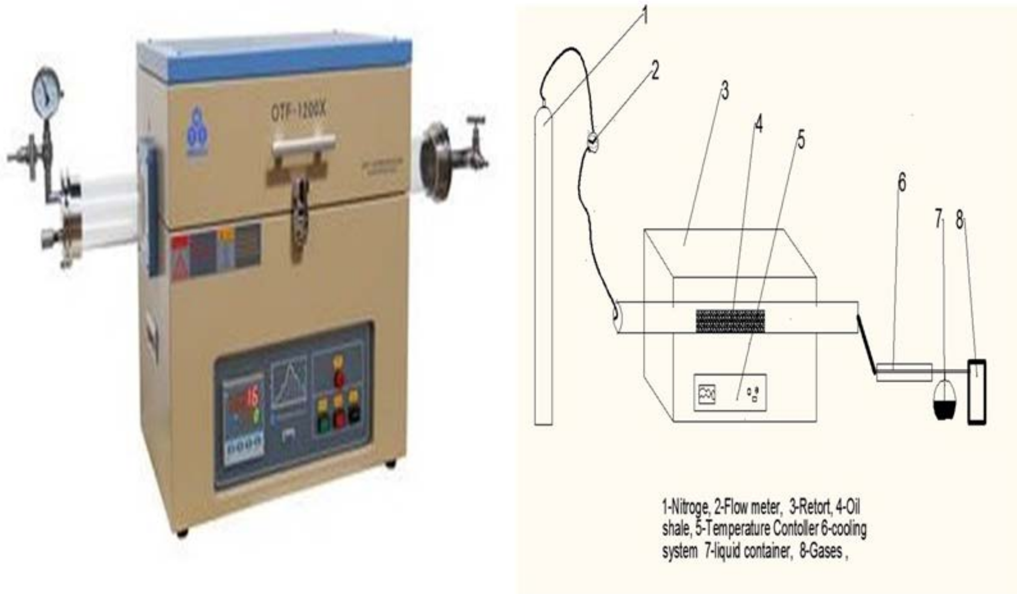

Fig. 1. Schematic diagram of the fixed bed reactor.

Table 2. Results of the basis analyses of Tchikatanga-Makola oil shale sample.

Fischer assay analysis , wt %		Proximate analysis,	wt%,ad	Ultimate analysis, wt%, ad	
Oil	8.12	Ash	68.03	C	16.23
		Volatile matter	22.16	H	2.68
Gas	5.03	Moisture	2.61		
		Fixed carbon	7.20	O	11.16
water	3.64			N	0.75
semicoke	82.21	Gross Calorific value (MJ.Kg^{-1})	5.43–6.14	S	1.15

2.3 Analysis

The gases collected during the experiment were analyzed by off-line packed column gas chromatography (GC). GC analysis was performed according to HP6890 gas chromatograph; molecular sieve size SA60-80 column was used for CO, CH_4 and H_2 gas. CO_2 was analyzed using a silica column both using argon as a thermal conductivity detector and the gas carrier. Then Nitrogen was used as purge gas during the pyrolysis and was also analyzed by the volumetric flow rate. The column quantity of nitrogen in the pyrolysis gas was determined by the difference (comparison) between the nitrogen flow rates. All the results of these analyses are shown in Table 5 and 7. The shale oil separation was carried out by Chinese Petroleum Industrial Standard SY/T 5119-2008 and the result is shown in Table 8.

The elemental analysis of oil shale was carried out by C.I. Analytics - 9600L Laboratory analyzer for CHNO. In the experiment, a Jena EA3100 NS analyzer was used to analyze the sulfur content. It is relevant to state that the oil from the pyrolysis is a complex mixture of water and its complexity cannot be directly measured by the chromatography analysis.

2.4 TG Analysis

The study also investigated the TGA and DTG by using Netzsch STA 449 C thermal analyzer system from Germany at different heating rates. The TGA apparatus provides for the continuous measurement of sample weight as a function of temperature, furthermore, provision is made for an electronic balance. The differentiation of the weight signals, the rate of weight loss (DTG), and the results are shown in Figures 2 and 3.

3. RESULTS AND DISCUSSION

The Fisher assay results of the oil content in the Tchikatanga-Makola oil shale is: 8.12 *wt*%, shown in Table 2, below. Tchikatanga-Makola oil shale has low oil content compared to other oil shales around the world For example Huadian oil shale in China shale oil is 19.20% [23], the Brazilian oil shale have 13.40% of oil yield [24] and Tarfaya (Morocco) oil shale is 17% [25].

3.1 TGA and DTG

The curves of conversion and the DTG of Tchikatanga-Makola oil shales have function of temperature at different heating rates which is illustrated in Figures 2, 3 and 4 (TGA and DTG). From Figure 3, it can be deduce that the decomposition and the yield of pyrolysis products directly depend on the heating rate.

It was observed from Figure 2 that, the percentage of the total mass loss is caused by evaporation and the decomposition of organic matter that is mainly the compound of oil shale. This conversion is strongly influenced by the pyrolysis temperature and the heating rate. This curve can be divided into three steps to explain this fact below:

(1) Temperature below 180°C represents the preheating phase and the mass loss decreases from 100% to 94% corresponding to the evaporation and devolatilization of water (moisture). The decrease is due to the high water content in Tchikatanga-Makola oil shale (Table 2).

(2) The second phase occurred between the temperatures of 282°C and 630°C, corresponding to the decomposition (conversion) of organic matter and emission of volatile hydrocarbons. From Figure 2, it is evident that the second stage is the main phase of pyrolysis due to the top conversion of kerogen to bitumen then to oil, gas and solid residue. During this stage the oil shale sample undergoes a lot of physical changes. The conversion of organic matter starts when the temperature increases from 350°C to 600°C and the curve of oil shale mass loss declines from 14% to21% of the initial mass of oil shale.

(3) The last stage occurred at a temperature up to 660°C, and leads to the decarbonation decomposition of carbonate [26] that is one of the main mineral components of oil shale. The pyrolysis of Tchikatanga-Makola oil shale at different heating rates within experimental error leads to approximately 28% of the original sample mass of oil shale which is shown in Figure 2.

The details are shown in Table 3, the results of TGA and DTG derived from this work are similar to those reported by different investigations conducted on different oil shale for example Yue [27] investigated Yoajie oil shale and concluded that with increasing heating rate, the decomposition rate of organics was accelerated and reaction time shortened. So the cracking and coking reactions of shale oil became less intensive and oil yield increased the corresponding change of oil yield of only 0.6% and 1.1% in the heating rate range from 2 to 20 °C/min. TiiT *et al*. [28] studied the thermo oxidative decomposition of four oil shale samples from Estonia, Jordan, Israel and Morocco at different heating rates (1, 3, 5, 10, 30, and 50°C/min) and the total mass loss of all oil shale samples remained almost constant irrespective of the heating rate employed, whereas it decreased with the increase of heating rate for kerogen (74.5 to 71.4%).

Bai *et al*. [29] have studied the effect of heating rate on rate of weight loss of Fushun oil shale during pyrolysis using TGA and Tmax1 increased from 448°C to 4489°C from 5°C/min to 50°C/min. According to their reports, the decomposition of kerosene in oil shale follows the above 3 steps.

The DTG curve (Figure 3) shows that the heating rate of 15 and 20°C/min have a high magnitude point between the temperatures of 480°C and 520°C at different rates.

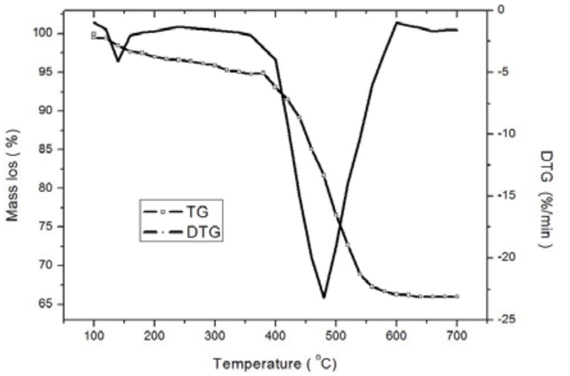

Fig. 2.TG and DTG curve of Tchikatanga-Makola oil shale.

Table 3. Characteristic parameters of the pyrolysis profiles of oil shale at different heating rates.

Heating rate,	Second stage			Third stage		
°C /min	T^a_2 ,°C	T^b_{max},°C	D^c_2, %/min	T^a_3, °C,	T^b_{max},°C	D^c_3, %/min
5	282–574	446	31.09	582-704	637	3.30
10	295–578	455	32.96	578-714	652	3.65
15	305–612	470	33.71	612-725	689	3.85
30	315–627	486	32.79	627-738	712	4.00
50	325–633	502	33.08	643-761	729	4.24

[a] T_2 and T_3 are the temperatures for the second and last DTG peaks, respectively.
[b] T_{max}(C) is the temperature for maximum reaction rate.
[c] D_2 and D_3 are the reaction rates of the second and last peak, respectively.

3.2 Effect of Heating Rate on the Pyrolysis of Tchikatanga-Makola Oil Shale

The heating rate influenced the decomposition and the yield of pyrolysis products (oil, water and gas) as shown in Figures 3 and 4. It has been shown from TGA and DTG of the Tchikatanga-Makola oil shale that different heating temperatures strongly affect the heating rates (15°C/min and 20°C/min) under the same final pyrolysis temperature.

The effects of the heating rate on pyrolysis of oil shale and the findings reported by several other investigations on different oil shale samples are similar to: Tiwari *et al*. [30] on green river oil shale, Wei *et al*. [13] on north-Korean oil shale and Aboulkas *et al*.[31] On Moroccan (Tarfaya) oil shale.

The heating rates at 30°C/min and 50°C/min have reduced conversion time caused by the different temperatures between the outside and inside, which according to Rajeshwar [32], indicates low thermal conductibility on oil shale. And therefore the result is a low volatile matter at heating rates of 30°C/min and 50°C/min, and less secondary reaction due to the short time period of the pyrolysis process.

All curves have the same shape at different heating rates up to 560°C and there is no more conversion above this temperature which means the end of the pyrolysis (Figure 4).

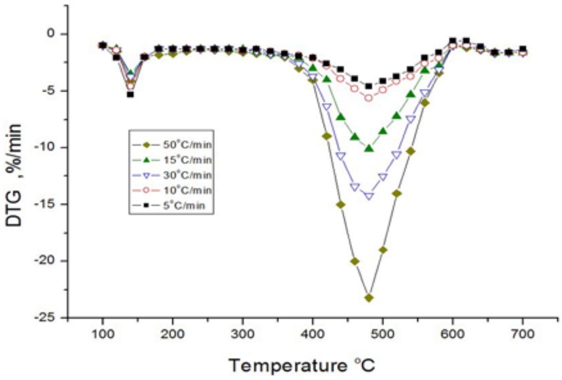

Fig. 3. DTG curve of Tchikatanga-Makola oil shale at different heating rates.

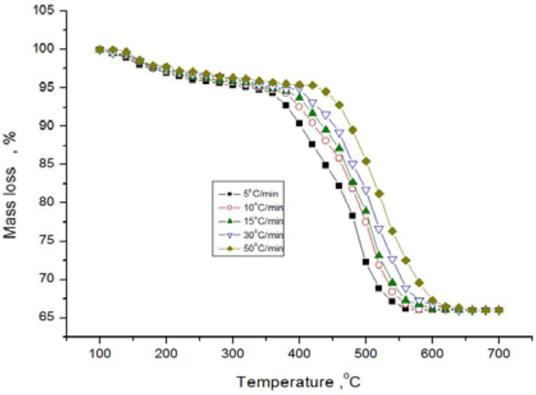

Fig. 4. TG curve of Tchikatanga-Makola oil shale at different heating rates.

Table 4. Effect of heating rate on the yield of pyrolysis products of oil shale.

Product, wt%	Heating rate, °C/min				
	5	10	15	30	50
Shale oil	21.22	23.14	24.25	25.14	24.09
Gases	9.36	6.72	6.45	5.80	7.36
Water	2.12	2.36	2.56	3.10	2.30
Shale char	67.30	67.85	66.80	67.30	66.76
End pyrolysis temperature, °C	632	640	650	645	640

Table 5. Yield and gas composition from Pyrolysis of Tchikatanga-Makola oil shale.

Gas ,wt%	Heating rate,°C/min				
	2	5	10	15	20
			Hydrocarbon gases		
Methane	1.37	1.45	1.36	1.26	1.68
Ethane	0.42	0.37	0.16	0.43	0.46
Propane	0.24	0.31	0.01	0.27	0.24
butane	0.23	0.23	0.11	0.21	0.25
Ethene	0.25	0.29	0.15	0.24	0.32
Propene	0.59	0.63	0.15	0.19	0.24
			Non-hydrocarbon gases		
Nitrogen	61.18	59.73	58.42	55.36	53.26
Hydrogen	13.75	12.43	10.45	9.43	9.12
Carbon monoxide	9.68	9.35	8.86	8.02	7.43
Carbon dioxide	18.25	17.77	17.23	16.32	15.45
Hydrogen sulfide	0.12	0.12	0.13	0.15	0.16
Ethene/ethane	0.0.79	0.73	0.67	0.61	0.59
Alkenes/alkanes	0.62	0.60	0.60	0.61	0.59
Butene/butane	3.01	2.19	2.10	2.02	1.77

3.3 Yield and Product Composition from Pyrolysis of Tchikatanga-Makola

The oil and gas yield from pyrolysis of Tchikatanga-Makola oil shale in relation to the heating rates are indicated in Table 3. Increasing the temperature increased the oil yield at the maximum temperature of 525°C with corresponding decrease of gas yield. The maximum oil yield was obtained at the temperature between 480°C and 540°C for all heating rates. It can be seen from Table 4 that the yield of shale oil increased with the increase in the heating rates (5, 10, 15, 30, 50°C/min). Then, the shale oil yield decreased and gas yield increased for the high heating rates. Increasing the temperature up to 520°C caused the yield of oil to decrease.

3.4 Gas Composition

Chromatography was used for the gas analysis from the pyrolysis of oil shale, Table, 5 shows that the gaseous products are mainly; nitrogen, carbon monoxide, hydrogen, carbon dioxide, methane, ethane, propane, butane, ethane, propane, butane and hydrogen sulfide. From Table 5, the variations in the gas yields at different heating rates can be seen.

At the pyrolysis temperature between 350°C and 550°C the gas yield increased on different heating rates due to many chemical reactions such as the decomposition of organic matter and some mineral matter. It is noted that the content of H_2 increased between 450°C to 729°C resulting from the condensation and aromatization of organic matter during the period of pyrolysis.

The content of CH compounds increased when the pyrolysis temperature reached 540°C and then decreased when the temperature was up to 550°C due to the decomposition of organic compound, and the cracking of macromolecules of oil on the surface of the oil shale samples. From 350°C and 520°C the content of CO_2 in gaseous products increased and it decreased when the temperature was above 660°C because the CO_2 was mainly generated from the decarboxylation of organic matter and fixed carbon according to the results in Table 2.The decarbonation of carbonate minerals (calcite ($CaCO_3$) and dolomite ($MgCO_3$) occur when the pyrolysis temperature is up to 650°C.

The content of CO did not change much; the CO was sourced mainly from decarbonation of carbonate and the oxidization of fixed carbon. The percentage of CO and CO_2 in retorting the gas decreased when the pyrolysis temperature was increased up to 630°C, it indicated the end of the decarboxylation of organic matter and the end of the second stage of pyrolysis.

The yield of hydrocarbon gas increased between 350°C to 550°C because of many secondary reactions such as the oxidation of shale oil on the surface and/or the inside particles of the samples that lead to the production of hydrocarbon gases such as ethane and methane. Above 550°C, some reactions occur during the cracking of macromolecules leading to the production of hydrocarbons such as (butane and butene) indicating the end of the pyrolysis. This proved that the organic matter content in the oil shale sample was strongly decomposed.

When it is up to 600°C the total gaseous yield decreased, reflecting a decrease in concentration of CO_2, CO, and the majority of the hydrocarbon gases.

The temperature range between 420°C and 550°C represents the main pyrolysis temperature conversion because many series of complex physical and chemical reactions take place at this interval. As the organic matter is being heated, the heavy organic macro molecules begin to crack into smaller molecules (organic gas, gaseous hydrocarbons and oil) and also the rupture of C-O, C-S and C-C bond occur during that time. The main products of the pyrolysis are: CO, CO_2, H_2, CH_4 and light hydrocarbons (C_1-C_4).

The ratio of Alkanes/alkenes in the gases during the pyrolysis of Tchikatanga-Makola oil shale indicates the pyrolysis conditions and to determine the reaction mechanisms. The ratio of ethene/ethane and propene/propane indicate the increase in cracking and reaction with the increase in heating rates which decreased the oil yield. The work shows that increasing the ratio of propane/propene and ethene/ethane resulted in secondary reaction such as aromatization and cracking reaction of shale oil on the surface of the shale sample.

3.5. Shale Oil Composition

3.5.1 Elemental analysis

Table 6 shows the elemental analysis and atomic ratio: H/C, of shale oil from pyrolysis of Tchikatanga-Makola oil shales under nitrogen atmosphere. The shale oil is mainly composed of oxygen, sulfur, Hydrogen, carbon, nitrogen and H/C ratio.

Table 6. Elemental analysis of shale oil from the pyrolysis of Tchikatanga-Makola oil shale, wt%.

%C	%H	%S	%N	%O (by difference)	H/C
85.27	11.73	0.38	0.16	4.98	1.80

The content of each vary at different temperatures, the Oxygen content decreases as the pyrolysis temperature increases from 420°C and 580°C, this can be explained by the amount of oxygen transformed to condensable gas as suggested by some researchers [29], [33],[34].

Nitrogen content increased as the pyrolysis temperature increased to 520°C, then, decreased as the oil yield decreased and increased as the heating rate increased, because of the presence of nitrogen in the aromatic molecules due to their resistance to high temperature [35].

3.5.2 Shale oil composition from the pyrolysis of Tchikatanga-Makola

The results of the analysis of oil separation process are presented in Table 8, both the yield and the composition of the shale oil depend on the heating rates. Table 7 shows the different fractions from shale oil as a function of the heating rates. It can be seen that the content of aliphatic and non-hydrocarbons increased with increasing heating rate, on the other hand, the content of aromatic fraction and non-hydrocarbon decreased slightly with increased heating rates. It is found that the content of aliphatic of the liquid shale oil increases by increasing the heating rates. The shale oil composition varies from different oil shale mineral composition and temperature.

Increasing the temperature has less effect on the sulfur content of shale oil, the sulfur content decreases slightly by increasing the heating rate. The carbon content of oil shale is high and increases by increasing the heating rate, the temperature could be caused by the presence of aromatic hydrocarbon products existing in the shale oil.

Also, by increasing the heating rate, the H/C ratio decreased in the shale oil due to the presence of the aromatic content in the oil.

The increased heating rate slightly decreased the sulfur and hydrogen contents of the shale oil and increased the percentage weight of carbon. The ratio of H/C decreased slightly at the heating rates of 15°C/min, 30°C/min and 50°C/min respectively.

The shale oil composition varies from different oil shale mineral composition and temperature pyrolysis. The shale oil composition from pyrolysis of Tchikatanga-Makola oil shale is closely similar with shale oil samples from Dachengzi (China) reported by Niu *et al*. [33], Comparing the Tchikatanga-Makola shale oil proportion with other investigations, the results revealed that the Gonghe shale oil had the largest proportion of hydrocarbons and Gonglangtou shale oil had the largest aromatic proportion [36]. Soone [37] observed the presence of hydrocarbon contents and oxygen compounds (paraffin and olefin compounds, aromatic hydrocarbon and oxygen compounds) in Estonian shale oil composition.

The shale oil produced at 580°C by Tchikatanga-Makola shale oil had similar (elemental Composition) atomic H/C ratio (1.942-1667%) ,nitrogen (0.1 to 2%) and sulfure (0.05 to 6.0%) as well as higher light oil content compared to crude oil produced [38], [39] and could be classified as sweet and high-nitrogen oil in terms of the classification method of crude oil and contained the lowest amount of saturates and the highest amount of aromatics, asphaltenes and non-hydrocarbons.

Table 7. Elementary analysis of shale oil composition from the pyrolysis of Tchikatanga-Makola by different heating rates.

Shale oil element	Heating rate,°C/min				
	5	10	15	30	50
Carbon	76.16	78.46	77.59	78.20	79.31
Hydrogen	11.80	11.67	11.46	11.80	11.94
Nitrogen	0.98	0.98	00.99	0.96	0.91
Oxygen	5.58	4.16	5.55	4.68	3.48
Sulfur	0.37	0.37	0.36	0.36	0.34
Atomic (H/C) ratio	1.943	1.913	1.772	1.721	1.667

Table 8. Table shale oil composition from the pyrolysis of Tchikatanga-Makola by different heating rates.

	Heating rate,°C/min				
Compounds , wt%	5	10	15	30	50
Aliphatics	58	59	60	64	66
Non-hydrocarbons	24	24	23	21	19
Aromatics	14	12	11	09	07
Asphaltenes	4	5	6	6	8

4. CONCLUSIONS

It was successfully accomplished the pyrolysis processes of Tchikatanga-Makola (Congo) oil shale.

The thermo gravimetric studies showed that thermal decomposition of oil shale involved three stages, the second stage at the temperatures ranging from 282 to 633°C, is the main stage of mass loss.

Increasing the temperature during the pyrolysis, firstly, increases the yield of water at 140°C to 260°C, then remains stable and unchanged while the oil yield increases. The oil yield has maximum yield at 520°C indicating the reasonable temperature of the pyrolysis of Tchikatanga-Makola shale oil. The gas yield first increased then remained stable but the composition was significantly affected by increasing the pyrolysis temperature. The decrease in oil yield was at 520°C which was due to the secondary reactions such as cracking and aromatization of the shale oil in the retort on the surface of the shale sample that also affected the product composition.

Increasing the maximum pyrolysis temperature showed a general increase in H_2, CO, CO_2 and hydrocarbon gases. This increase has been reported to be as a result of thermal cracking of the oil vapors.

Gas analysis from pyrolysis shows that: hydrocarbon gases such as (methane, ethane, propane, butane, ethene and propene) and non-hydrocarbon gases (nitrogen, hydrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide) in the order of nitrogen, hydrocarbon compound and hydrogen increased until the temperature got to 520°C, then, at 550°C, CO_2 and CO content decreased shale oil from the pyrolysis of Tchikatanga-Makolaoil shale is composed of aliphatics, asphaltenes, aromatics and non-hydrocarbons, but the aliphaphatic is the main compound of the shale oil.

According to the TGA, the optimum rate of the pyrolysis of the shale oil at the rate of 30°C/min was recommended for shale oil retorting with a fine high yield of shale oil.

The high presence of fraction of ethene/ethane, alkenes/alkanes and butene/butane gases on the heating rate at 5 and 10°C/min meant that the low heating rate has long pyrolysis time and leads to the increase in the secondary reaction such aromatization and cracking from oil to gas.

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