



PIC-02: PYROLYSIS CHARACTERIZATION AND KINETICS OF YAGBATABITUMEN USING A TGA

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Abstract

Pyrolysis kinetics of thermal decomposition of bitumen was investigated by thermogravimetric analysis (TGA). TGA experiments were conducted at multiple heating rates of 5, 10, 20°Cmin⁻¹ up to 800°C to obtain the pyrolysis characteristics of bitumen. Weight loss curve from TGA shows that three different stages occurred during bitumen pyrolysis. Weight loss profile and the final amount of coke formed changes with the heating rate. Differential method has been used for determining the kinetic parameters and the best fit for the order of reaction was found based on the R² values. Kinetics results confirm the presence of three different stages in bitumen pyrolysis with kinetic parameters. The average activation energy for the first, second and third stages was 27, 78 and 84 kJ mol⁻¹, respectively.

Keywords: Nigeria, bitumen, thermogravimetric analysis, thermal cracking, pyrolysis, kinetics.

1.0 INTRODUCTION

The Nigeria bitumen belts are large deposits of bitumen, located in southwestern state of Ondo, Lagos, Ogun, and Edo State. The bitumen deposit in Nigeria is in huge quantity and recorded as the largest deposit in Africa and second largest deposit in the world. The bitumen is hosted within the eastern Dohomey basin, of which has been of much geological interest as a result of the occurrences of bitumen, limestone, glass sands and phosphates (Nton, 2001). This bitumen remains untapped because of inadequate knowledge of the oil exploration and exploitation. With the rise of price of crude oil the need for the development of alternative and or additional sources of energy has become urgent. Bitumen has become an unconventional energy resource due to a huge source of solid fossil hydrocarbon compound in the form of bitumen on the surface of the earth. Consequently the need for a viable energy sources have become imperative.

Bitumen (tar or asphalt) is a natural polymer and the lowest grade of crude oil. Bitumens have much higher viscosities and heteroatom compositions than conventional light crude oils.

For many years, it has been used for paving applications, construction and maintenance of roads. Due to increasing demands and performance, bitumen is now often blended with polymer.

Bitumen-polymer blends have a better resistance to cracking in low temperatures, as well as lower flow and deformation in higher temperatures, than that of bitumen alone (Masson *et al.*, 2003). After oil sand is mined, the bitumen has to be recovered from the oil sand in order to upgrade and transport to refiners. At present, several methods may be applied to recover bitumen from oil sand, such as water-based extraction, solvent extraction and pyrolysis (Park *et al.*, 2009). Among these methods, pyrolysis is widely used by many researchers for the characterization of the heavy oils using in situ combustion (Kok *et al.*, 1998, Meng *et al.*, 2006).

Pyrolysis is a process of thermal decomposition of coal, biomass and oil shale in the absence of oxygen to obtain an array of char, oil and gaseous products. Several thermal analysis techniques have been used to obtain the experimental data. The most common and

suitable for fundamental kinetic characterization are thermogravimetry (TG). Due to the simplicity of the instrument and calculation methods, the authors have used these techniques to successfully estimate the kinetics of many processes such as pyrolysis of coal (coal), crude oil (Murugan et al., 2009) and bitumen. Many researchers have used the thermogravimetric analyser to study the thermal decomposition of Alberta oil sand (Park et al., 2009), Indonesian bitumen and Canadian bitumen (Alshareef et al., 2010).

The thermal stability of bitumen is a significant property to be considered in selection of the best processing conditions, depending on the quality of the products, and to fit their performances to the proper final applications. Many applications of bitumen involve a high temperature that requires a fundamental knowledge about thermal kinetics. Hence, the pyrolysis kinetics of bitumen was studied in this work using thermogravimetric analysis (TGA) under an inert atmosphere at different heating rates. In addition, the effects of different reservoir sand on bitumen pyrolysis were also studied.

2.0 EXPERIMENTAL

The bitumen used in this work was recovered from Yagbata Ondo State sand reservoir. The experimental setup consisting of Perkin Elmer STA 6000 Thermogravimetric analyser. This instrument has a capability of simultaneously measuring TG and differential thermal analysis (DTA). This unit includes built-in mass flow controller that monitors and controls the purge flow rates. About 20mg of the sample was used for all the experiments. Initially the sample was kept at room temperature for 5 min and then heated up to 800 °C with multiple heating rates from 5 to 20°C. The experiments were conducted under the nitrog flow rate of 45mLmin⁻¹ throughout the furnace. The weight change with respect to the temperature was measured by TGASTA 6000 and saved to the PC through pyris module interface.

2.1 Kinetics Theory

Non-isothermal kinetics of thermogravimetric analyses was usually performed by a differential method and integral method. In this work, differential method was used based on the empirical expression of Arrhenius. The different stages during the bitumen pyrolysis were determined based on the number of levels of the TG curve and on the number of peaks of the DTG curve. The rate of thermal devolatilisation of a solid can be expressed as follows (Benbouzid and Hafsi, 2008):

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (1)$$

The variable " α " is the degree of conversion of the stage i .

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

where m_0 , m_f and m_t are the weights before the reaction, after the reaction and at time t , respectively. E_{ai} is the apparent activation energy (J mol⁻¹). A_i is the pre-exponential factor (min⁻¹); R is universal gas constant (J mol⁻¹ K⁻¹). T is the heating temperature (K). At a given heating rate β , we have:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

The plot of $\ln[(d\alpha/dT)/(1-\alpha)^n]$ versus $1/T$ at different n_i is a straight line from which the activation energy and the preexponential factor can be determined. The optimum value of n_i gives the highest value of R^2 .

3.0 RESULTS AND DISCUSSION

3.1. Pyrolysis characteristics of oil sand bitumen

Figure shows the TG/DTG of bitumen at 5 °C/min. Fig. 2 (a) and (b) represent TG results showing weight loss and the rate of weight loss as a function of temperature, respectively, for raw bitumen, which were obtained by the release of volatiles during the non-isothermal pyrolysis at different heating rates of 5, 10, and 20 °C/min. It is observed that the TG and DTG curves shifted to higher temperatures as the heating rate

increased. This phenomenon, called as thermal lag, was caused by limited heat transfer to the sample, resulting in the temperature difference between the sample and the thermocouple (Anca-Couce *et al.*, 2014, Park *et al.*, 2006). In Fig. 2(a), it can be seen that bitumen lost approximately 93 % of original weight and yielded 7 wt% coke after the pyrolysis reaction was terminated. It is noticeable that the curves of weight loss rate for bitumen show one narrow peak and two shoulder peaks as shown in Fig. 2(b). This probably indicates that multiple reactions were involved in the pyrolysis of bitumen, and it was assumed that the nonisothermal pyrolysis of bitumen consists of three reaction stages (light volatilization, main volatilization and continuous volatilization). In general, TGA can be used to investigate chemical reactions or physical transitions occurring with weight changes, and then the shape of TGA curve is considered characteristic and identification of chemical reactions. Prior to the first stage, a small weight loss appeared in TG/DTG curve near 100 °C, probably caused by evaporation of water (Bai *et al.*, 2015). The first shoulder peak from ambient temperature to about 320 °C (at the heating rate of 1°C/min) in the DTG curve corresponds to light volatilization reactions which entail the desorption of light hydrocarbon volatiles with a weight loss of 29 %. From the boiling point distribution in Fig. 1, it can be observed that bitumen at boiling point lower than 400 °C contains about 28 % distillates. This indicates that a part of oil sand bitumen vaporized during the heating process of non-isothermal pyrolysis before main cracking reaction occurred. Therefore, it can be considered that volatile gases were generated by vaporization of light compounds in the first stage. Volatilization can be caused by the formation of light gases from primary pyrolysis, cross-linking reactions, and coke formation reactions (Caprariis *et al.*, 2012). The second shoulder peak which arrower temperature of the range 370 °C to 470 °C in the DTG curve corresponds to evolution of volatiles is probably due to thermal cracking with a weight loss of 34 %. The continuous evolution of volatiles at high

temperature (470 °C -600 °C) is probably due to thermal cracking of organic matter.

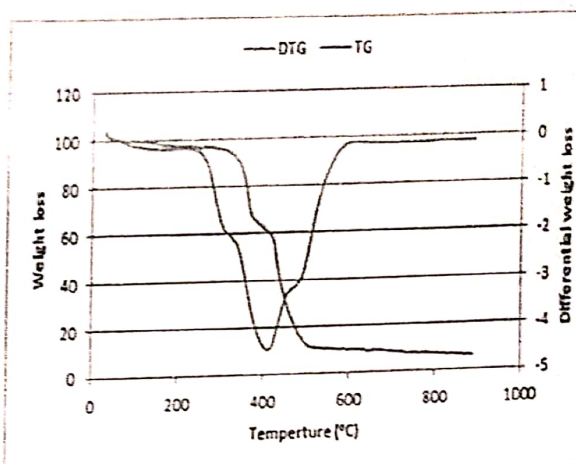


Figure 1. TGA analysis of Yagbata bitumen

3.2 Effect of heating rates

The TG and DTG curves for bitumen at different heating rates (5, 10 and 20 °C min⁻¹) indicate the presence of three stages (Figures 2a and b). As the heating rate increased from 5 to 20 °C min⁻¹, the curves are displaced to higher temperatures. At the final temperature of 800 °C, the amount of residue produced after pyrolysis increased as heating rate increased such as 6 %, 11.7 % and 14.6 % for 5, 10 and 20 °C min⁻¹, respectively. The difference in the amount of residue produced indicates the influence of heating rate in bitumen pyrolysis. At lower heating rates, the heating of the bitumen occurred more slowly, leading to a more effective heat transfer to the inner portions and throughout the sample (Mani *et al.*, 2010). As a result of the improved heat transfer, more efficient cracking took place, causing more weight loss in the form of volatiles. Therefore, as the heating rate increased, the residue at the end of the pyrolysis reactions also increased. Based on these results, it is noted that at lower heating rate (5 °C min⁻¹) of bitumen pyrolysis, thermal cracking occurred efficiently resulting in a lesser amount of residue compared to other heating rates. The DTG curves for different heating rates of bitumen pyrolysis also exhibit the difference in curves, more specifically at the peak points such as 435, 445 and 465 °C for 5, 10 and 20 °C

min⁻¹, respectively. The details of three stage bitumen pyrolysis characteristics are given in Table 1. The occurrence of three stages in this study is different from two different stages in the pyrolysis curve has been determined by Benbouzid and Hafsi (2008) for the pyrolysis of pure and oxidized bitumens.

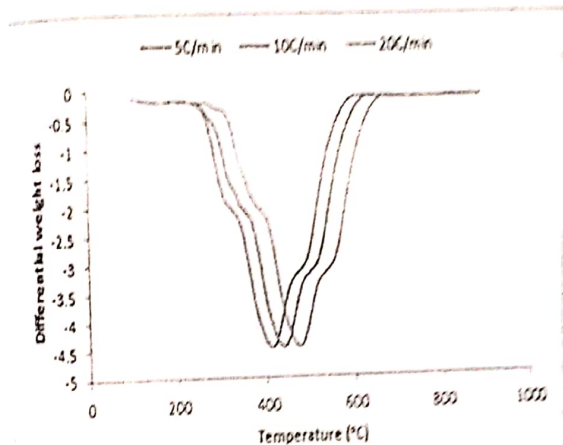


Figure 2a. DTG analysis of Yagbata bitumen at different heating rates.

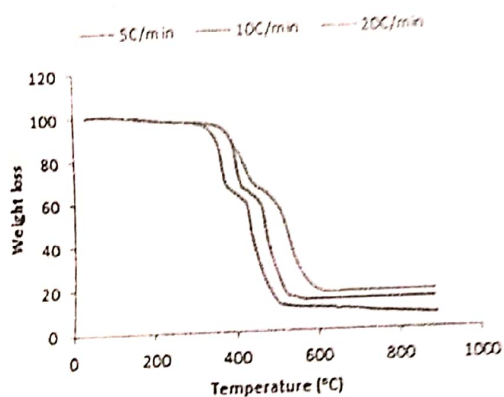


Figure 2b. TG analysis of Yagbata bitumen at different heating rates.

Table 1. Analysis of the thermogravimetric results of the bitumen

Pyrolysis characteristics	β ($^{\circ}\text{C}/\text{min}^{-1}$)		
	5	10	20
Number of stages	3		
Temperature interval ($^{\circ}\text{C}$)			
Stage 1	150-340	150-352	150-363
Stage 2	340-456	352-471	363-489
Stage 3	456-529	471-601	489-609
Maximum temperature ($^{\circ}\text{C}$)	451	459	468
Final temperature ($^{\circ}\text{C}$)	932	938	946

3.3 Kinetic Analyses

Kinetic analyses were performed individually for the three heating rates using TG data. The order of the reaction that provides minimum residuals between experimental and predicted data was chosen as the optimum value of n . The corresponding activation energy and frequency factor were determined based on the optimum order of reaction. The results of kinetic study for the first stage are different from the second and third stages (Table 2). The activation energy increased (i.e. 27, 31 and 33 kJ mol⁻¹ for 5, 10 and 20 $^{\circ}\text{C}/\text{min}^{-1}$, respectively) as the heating rate increased in the first stage of pyrolysis, indicating the minimum activation energy at 5 $^{\circ}\text{C}/\text{min}^{-1}$. The reason for lowest activation energy at low heating rate could be explained by several factors including total weight loss being lowest at this heating rate, or longer residence times at a given temperature, which will influence the conversion positively.

In the first stage of bitumen pyrolysis, increase in activation energy with respect to heating rate also reveals that for the initial weight loss, more heat is required, which is in contrast to the second stage of pyrolysis. During the second stage, the activation energy decreased (i.e. 78.3, 42.4 and 30.6 kJ mol⁻¹ for 5, 10 and 20 $^{\circ}\text{C}/\text{min}^{-1}$, respectively) with increase in the heating rate that indicates the requirement of less energy

at the end of the pyrolysis process. Due to high heating rate, the molecules heated up quickly that makes the diffusion fast, and therefore leading to lower energy demand for the final conversion.

During the first stage of bitumen pyrolysis average of 25 % of the weight loss occurred with low activation energy and high reaction order; while in the second stage, average of 75 % of the weight loss was observed with higher activation energy and lower reaction order compared to the first stage. The significant difference observed between the two stages indicates that the volatiles present in bitumen might be of two different categories with varying degrees of volatilization.

Table 2. Kinetic parameters of the bitumen pyrolysis at different heating rates

Pyrolysis characteristics	β ($^{\circ}\text{Cmin}^{-1}$)		
	5	10	20
Number of stages	3	3	3
Stage 1			
N			
Ea (kJ mol ⁻¹)	27	31	33
A (min ⁻¹)	7.5	24	105
R ²	0.976	0.976	0.967
CI (%)			
Stage 2			
N			
Ea (kJ mol ⁻¹)	78.3	42.4	30.6
A (min ⁻¹)	1.2×10^5	673	37
R ²	0.982	0.977	0.969
CI (%)			
Stage 2			
N			
Ea (kJ mol ⁻¹)	84.1	51.8	34.3
A (min ⁻¹)	1.3×10^5	703	41
R ²	0.9977	0.987	0.976
CI (%)			

4.0 CONCLUSIONS

A two-stage first-order model is inferred to define the pyrolysis of asphalt. In this, the activation energy, E, is different for each stage,

but is independent of the type of bitumen and the rate of heating. The frequency factor depends on the heating rate and is independent of the bitumen. The final yield of volatiles depends on the type of bitumen. The pyrolysis of bitumen exhibits three stages during devolatilisation process. The kinetic results were varied considerably between the stages and also for the different heating rates. Average activation energy for the first stage was lower than the second stage. About 25 % of the weight loss occurred in the first stage and the remaining 75% weight loss occurred during the second and third stages of bitumen pyrolysis.

REFERENCE

Murugan, P., N. Mahinpey, T. Mani and N. Freitag, "Pyrolysis and Combustion Kinetics of Fosterton Oil Using Thermogravimetric Analysis," Fuel 88, 1708–1713 (2009a).

Masson, J.-F., P. Collins, G. Robertson, J. R. Woods and J. Margeson, "Thermodynamics, Phase Diagrams, and Stability of Bitumen-Polymer Blends," Energy Fuels 17, 714–724 (2003).

Nton ME (2001) Sedimentological and geochemical studies of rock units in the eastern Dahomey basin, south western Nigeria, unpublished Ph.D thesis, University of Ibadan, pp 315

Park, Y. C., J.-Y. Paek, D.-H. Bae and D. Shun, "Study of Pyrolysis Kinetics of Alberta Oil Sand by Thermogravimetric Analysis," Korean J. Chem. Eng. 26(6), 1608–1612 (2009).

Meng, X., C. Xu and J. Gao, "Secondary Cracking of c4 Hydrocarbons From Heavy Oil Catalytic Pyrolysis," Can. J. Chem. Eng. 84(3), 322–327 (2006).

Kok, M. V., O. Karacan and R. Pamir, "Kinetic Analysis of Oxidation Behaviour of Crude Oil SARA Constituents," Energy Fuels 12, 580–588 (1998).

Benbouzid, M. and S. Hafsi, "Thermal and Kinetic Analyses of Pure and Oxidised Bitumens," Fuel 87, 1585–1590 (2008).

Anca-Couce, A., Berger, A., Zobel, N. (2014) How to determine consistent biomasspyrolysis kinetics in a parallel reaction scheme, Fuel 123 ,230–240.

Park, H.Y. Kim, T.H. (2006) Non-isothermal pyrolysis of vacuum residue (VR) in a thermogravimetric analyzer, Energy Convers. Manag. 47, 2118–2127.

Bai, F., Guo, W., Lü X., Liu, Y., Guo M., Li Q., Sun Y., (2015) Kinetic study on the pyrolysisbehavior of Huadian oil shale via non-isothermal thermogravimetric data ,Fuel 146, 111–118.

Cai J., Wu W., Liu R. (2014) An overview of distributed activation energy model andits application in the pyrolysis of lignocellulosic biomass, Renew. Sustain.Energy Rev. 36,236–246.

Caprariis B. de, De Filippis P., Herce C., N. Verdone (2012) Double-Gaussian distributed activation energy model for coal devolatilization, Energy Fuels 26, 6153–6159.

List of Acronym

R^2	Regression squared
TGA	Thermo gravimetric analysis
TG	Thermogravimetry
α	Degree of conversion
m_0	weights <i>before</i> the reaction,
m_f	weights after reaction at time t ,
E_a	apparent activation energy (J
mol^{-1}).	
A	pre-exponential factor (min^{-1});
R	is universal gas constant (J mol^{-1}
K^{-1}).	
T	heating temperature (K).
B	heating rate ($\text{K}/^\circ\text{C}$)
DTA	differential thermal analysis