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## Improvement on the Production Energy of Shale oil Using Waste Plastics

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# Improvement on the Production Energy of Shale oil Using Waste Plastics

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**Abstract.** An alternative fuels is obtained by co-pyrolysis of waste plastics and oil shale as well as contribute to the search of technologies that reduce the negative environmental impact of waste. Shale oil and waste plastic are unconventional sources of energy. The two materials are significant to Nigeria's economic sustainability but yet to be exploited efficiently. The aim of this work is to reduce the energy needed to obtain shale oil via kinetic parameters by the thermal decomposition of Lokpanta oil shale mixed with plastics. The kinetics of the thermal decomposition of Lokpanta oil shale/ polyethylene blend was determined using data provided by thermo-gravimetric analysis done at 28°C to 887.44°C with heating rate of 10°C/min and a nitrogen flow rate of 60ml/min. The decomposition of the co-pyrolysis of the mixture of Lokpanta oil shale and the polyethylene was recognized in three stages, of which the first stage was between 28 and 316.41°C which corresponded to the loss of water from the sample. The second stage was between 316.41°C and 481.47°C, which depicted an overlap of the organic matter (kerogen) and the degradation of polyethylene. The final stage was between 481.47°C and 887.44°C, and it exposed the decomposition of the mineral matter of the oil shale. The Kinetic parameter was determined using non-isothermal methods of degradation. Hence the presence of the plastic acted as catalyst in the decomposition of the organic matter of the shale which consequently lowered the activation energy required to obtain shale oil with relevant application as aliphatic fractions of petroleum.

## 1. Introduction

Waste plastic have become a significant urban waste, with plastics ranging from used containers to packaging bags. The composition of this materials are primarily polyolefins (low and high density polypropylene, polyethylene and high density poly ethylene), accounting for a major part of the total plastic waste by surveillance. Wherein Nigeria as only succeeded in recycling small amount of plastic waste and much of it are not biodegradable. The much uses have prompted the age of an expanded measure of plastic waste. In this way, some specialized techniques must be executed to lessen plastic waste and the negative effect on nature. The two means of disposals (landfilling and incineration) do not permit the recuperation of the organic/fuel substance of the waste plastics, which ought to be a part of the organic life-cycle. These are not the right approach, since landfills has the peril of soil leach and soil impregnation of its degradation fragment while burning produces contaminations that are poisonous releasing gases such as sulphur and nitrous oxides, tidies, and dioxins that have negative effect on the earth. The quest for non-conventional fuels, along with the need of new innovation to eliminate the negative effect of waste plastics, has prompted co-pyrolysis of plastic waste with oil shale. The plastics comprise of hydrocarbons with significant calorific value. These materials contain more hydrogen than the hydrogen present in coal and oil shale alone. Oil shale, then again, is viewed as the substitute for unrefined petroleum as a characteristic wellspring of vitality. Be that as it may, the production of oil from oil shale is generally costly. Accordingly, the research for processing oil shale to obtain fuel cuts is significant in Nigeria.

Oil shale blended with waste plastic undergo pyrolysis to give fuels or chemical substances can be accomplished by a thermochemical means. Pyrolysis has gotten uncommon consideration since it produces char, liquid and gas. With these purposes, the kinetics of decomposition of plastics are used for the design of reactors.



By and large the co-pyrolysis of oil shale and waste plastic is regarded as another methods for fractional replacement of petroleum products to create the vital vitality to meet the expanding demand for energy. It is also an innovation to diminish the negative condition waste plastics impose. Be that as it may, information on pyrolysis energy is critical for the construction and simulation of reactors so as to build up the ideal procedural conditions for their operations [1].

Many research has been carried out on the pyrolysis of oil shale and plastic mixture and the possible yield that can be realized from this mixture using different methodologies. For example [2] provided the kinetic of the thermal degrading of polypropylene, oil shale from Israel and their mix was subjected to thermogravimetric analysis in studying a pyrolysis phenomenon with the particle size of 23 to 24mg and a mathematical model was used to describe the kinetics. The main conclusion drawn from the experiment was that the accelerated change in feedstock of polypropylene and oil shale is due to the addition of polyethylene. A first order reaction was obtained for the decomposition of the materials using iso-conversion method.

A research was done to investigate the thermal degradation of polymer and oil shale using thermo-gravimetric analysis, the sample size was 20mg under non isothermal degradation under argon atmosphere from 298K to 1173K. The heating rate of 10 and 60 Kelvin/min. The main conclusion from this research was that the high density poly ethylene accelerated the decomposition of the organic matter in the oil shale [3]. In recent time, [4], has attempted to mix polyetyelene and no further work was reported thereafter about any Nigerian plastic used for co-pyrolysis. Therefore in this research, waste plastics containing high density polyethylene (HDPE) was mixed with shale oil under nitrogen at the inert atmosphere. Thermogravimetric analysis was done to obtain the stages of degradation starting with weight loss. The difference in weight loss between the pure oil shale and that mixed with HDPE was calculated as algebraic sums of the mixture included 1.17% under 550 °C. The maximum temperature of the mixture degradation is approximated and compared to the pure oil shale. The influence of waste plastic on the pyrolysis of the oil shale thus ascertain the potential oil produced from the oil shale, and a synergistic effect is reported to some extent for the pyrolysis of oil shale and HDPE. Co-pyrolysis improves the quality of shale oil.

## 2. Experimental Methodology

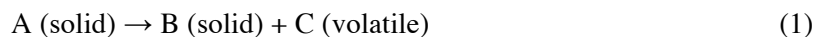
### 2.1. Procedure for TGA of raw oil shale sample

The differential thermo-gravimetric (DTG) analysis and the thermo-gravimetric analysis (TGA) were carried out concurrently using a TG/STA 4000 analyser. The calibration of the equipment for temperature reading was done before the analyser was used. The mass of the sample which was positioned in the platinum sample holder for heating is 20mg, the temperature of the Lokpanta oil shale sample was raised from 28 to 887.44°C in a flowing atmosphere of nitrogen. In conducting the experiment the linear heating rate and gas rate was 10 °C /min. The content of the analyser consists of an empty crucible onto which the samples was placed in the wire basket which was with the hang-down wire and that sample was heated under non isothermal condition from 28 to 887.44°C. At specific temperatures and at a successive time the pan was held in place by a precision balance which aided in the measurement of the weight of the sample. In controlling the sample atmosphere, an inert gas was used (nitrogen), throughout the experimental process the gas was passed over the oil shale and waste plastics and exist through the exhaust stream. The raw Lokpanta oil shale was analysed using PerkinElmer TG/STA 4000 thermogravimetric analyser located in Step-B at the federal university of technology Minna. The weight loss data was plotted against temperature which was recorded for each step increase in temperature for the analysis for the Lokpanta oil shale. The data obtained for the TGA and DTA were used to determine the decomposition of the organic matter as well as the kinetics parameters of the Lokpanta oil shale.

### 2.2. Determination of activation energy and frequency factor using TGA.

Kinetics modelling included the non-isothermal kinetic study of the weight loss of carbonaceous material under pyrolysis. The oil shale and plastic mix is a complex compound because of the

presence of numerous complex components which decomposes through parallel and consecutive reactions. Kinetic analysis for the isothermal and the non-isothermal analysis included processes which are represented by the reaction scheme in equation (1).



### 3. Discussion of results

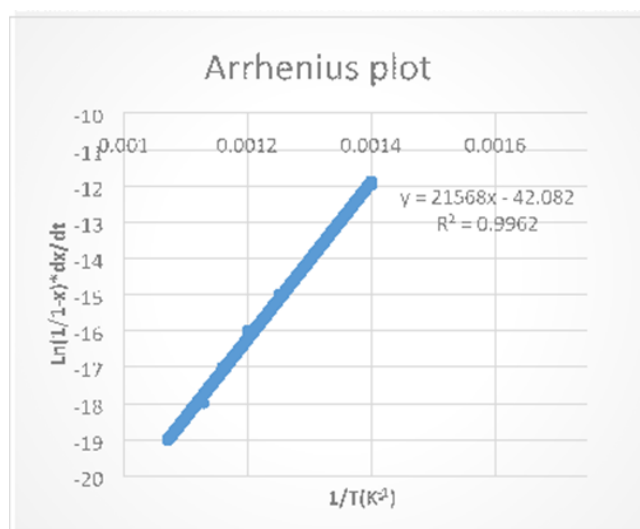
The discussion centres on the thermogravimetric analysis and kinetic modelling which was gotten from the TGA data. The kinetic parameter was calculated using Arrhenius method and the Coats-Redfern method.

#### 3.1. Thermogravimetric analysis of Lokpanta oil shale

The DTG of the Lokpanta sample has two major peaks, of which the first peak occurs within the ranges of 26.80°C and 181.75°C, indicating the loss of moisture from the Lokpanta oil shale. The second peak was within the ranges of 181.75°C to 565.05°C, and this conforms to the thermal decomposition of the organic matter. This is the decomposition of kerogen portion of the oil-shale. The absolute decomposable kerogen of the Lokpanta oil shale sample is gotten by subtracting the value of the weight loss due to moisture loss from the absolute weight loss.

Characteristic temperature consist of the peak temperature (Tmax) and the sample burn out temperature. The peak-temperature is the temperature that corresponds to the highest rate of weight decomposition. Thus burn-out temperature is the temperature at which the thermal decomposition of the sample is completed. Tmax is 421.75°C and the burn out temperature is 565.09°C.

In comparison to literature data by [5], it was reported that Tmax is within the ranges of 430 to 500°C at 10°C /min for oil shale. [6] also reported the value of Tmax to be 664°C at 10°C /min Moroccan oil shale which has similar characteristics with Lopanta oil shale.



**Figure 1:** The kinetic parameter of Lokpanta oil shale

#### 3.2. Analysis of the kinetic study of Lokpanta oil shale

The conversion rate ( $dx/dt$ ) for the TGA under constant temperature ( $\beta dT/dt$ ) is expressed by a kinetic scheme. From the TGA/DTG data obtained, using the Arrhenius equation and the term ( $\ln \beta$  vs  $1/T$ ). The activation energy was calculated from the line of best fit using regression analysis. 75.5kJ/mol was derived as an activation energy using the value of the slope.

Comparing the value to literature data, it was observed there was a difference in the values of activation energy of the oil shale because of the organic matter and location of the oil shale sample. [7]

realized an activation number of 167kJ/mol for non-isothermal thermo-gravimetric analysis [8] obtained an activation energy of 73.2 to 75.5kJ/mol for oil shale. [9] calculated the value of activation energy to be 25kJ/mol for low temperature and 43kJ/mol for the main decomposition for non-isothermal thermo-gravimetric analysis of Turkish oil shale. [10], stated that the activation energy for oil shale is 87kJ/mol.

The kinetic study of processes involving co-pyrolysis require careful calculations. This is because the degradation of any indigenous organic matter is the heterogeneous mixture of various organic compounds which are complex-mix. This kinetic study follow a complex multi stage process. [11], have explained the thermal decomposition of oil shale which occurs in two consecutive reactions with bitumen as an intermediate. These reactions are expressed in equation (2) and (3).

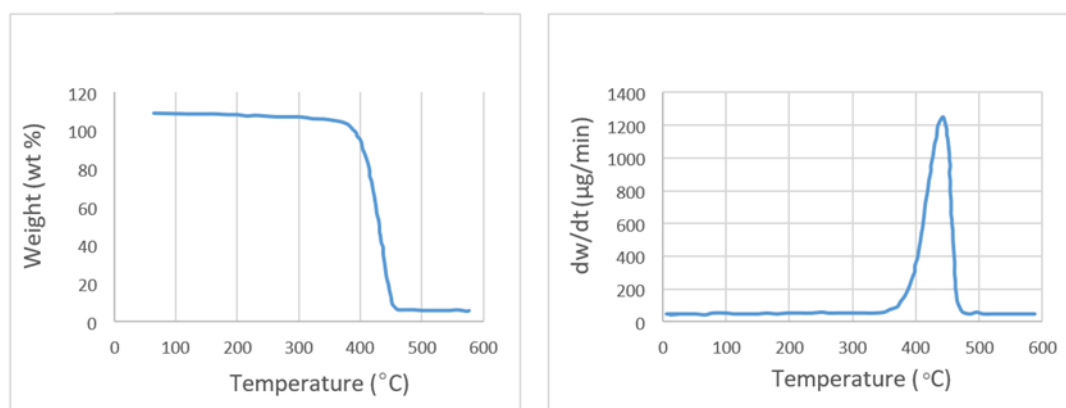


These two equations are reactions with first order index. This present work adopt the Coats and Redfern model which was built on Arrhenius theory. This way, data were generated. It was used to determine the kinetic parameter of the decomposition processes with the TGA/DTG. The overall reaction of Lokpanta sample was assumed to follow equation (4).

$$dx/dt = k(1 - x)^n \quad (4)$$

Here, “x” is the extent of conversion of Lokpanta sample. “k” is the specific rate constant. “n” is the order of reaction. The temperature dependence of parameter “k” was expressed by the Arrhenius equation. The fraction of material decomposed is the parameter “x”. This is the weight ratio. By using the weight ratio and the temperature values, the activation energy ‘E’ and the Arrhenius constant ‘A’ were evaluated. Next, the regression analysis had a least square which was used to draw the line of best. This yielded a linear. Thus the thermal decomposition of the sample took place at a temperature of 28.478 °C to 887.44 °C. From this data, the activation energy of the decomposition of the Lokpanta oil shale is 75.5kJ/mol.

This activation energy was compared to the values reported for oil shale, which was very different from those values. Hence it is convenient to state that the kinetic parameter are unique to each sample based on the geographical source of the oil shale and probably its associated mineral, for example [12] obtained 167 kJ/mol for the activation energy under the non-isothermal TG-analysis of Spanish kerogen sample. [13] acquired a mean activation number of 87kJ/mol for the Moroccan oil shale using an iso-conversional method. an approximate value of 25kJ/mol was gotten for Turkish oil shale [14] which was examined at a temperature lower than the decomposition temperature. It is up to 43kJ/mol for the main stage of decomposition. Although, a direct implication is obvious that the differences found in the results determined in this research and the literary value are due to the influence of the process parameters such as the heating rate and particle size, the location of the oil shale samples and the kerogen type. Hence, it might be uneasy to get the same values from experiments even for the same sample. In essence, for the same experimental technique which entails the proper sample collection, the sample preparation, the experimental procedure and the kinetic modelling should be adopted in order to ensure a direct comparison.



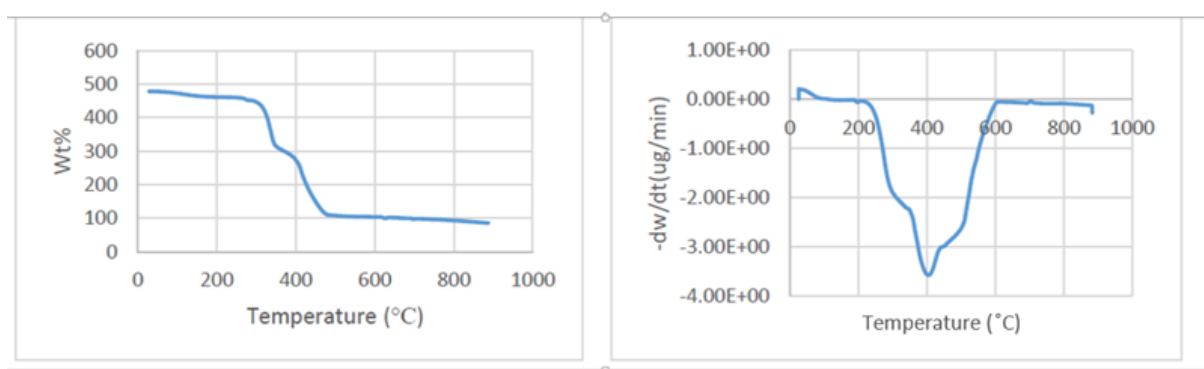
**Figure 2:** thermo-gravimetric analysis of HDPE (left) differential thermal analysis of HDPE (right)

The graphical representation of TGA/DTA curve is presented in figure 2, this plot is for the high density polyethylene. This data was obtained for heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . The weight losses from the curves shows that the decomposition of the plastic occurs almost in one step which is depicted by the presence of a peak in the differential-TG curve. The degradation of high density polyethylene occurs at the peak temperature, otherwise known as the  $T_{\text{max}}$  which is at  $442.27\text{ }^{\circ}\text{C}$ . The burn out temperature is at  $586.93\text{ }^{\circ}\text{C}$ . This is compared with literature data where the value of  $T_{\text{max}}$  was observed to be different due to the disparity of location. Burn out temperature was reported by Aboulkas et al. (2008) to be  $751\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$ . Also Kumar and Singh, (2014) reported  $T_{\text{max}}$  to be  $465\text{ }^{\circ}\text{C}$  under an experimental rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ .

### 3.3. Kinetics of HDPE

Due to the presence of one peak in the DTG curve, there would be only one dominant kinetic process of HDPE, the activation energy was gotten, by applying the Arrhenius equation on TGA data.  $207.4\text{ kJ/mol}$  was obtained as the activation energy of waste plastic. [15] reported on the pyrolysis of waste plastic mixtures gathered from municipal solid waste, their apparent activation energy for HDPE results to be  $1724\text{ kJ/mol}$ . [16] observed an activation energy of HDPE to be  $123\text{ kJ/mol}$ . Another value of the same parameter was calculated by [10], they reported the activation energy of high density polyethylene degradation to be  $437.23\text{ kJ/mol}$ .

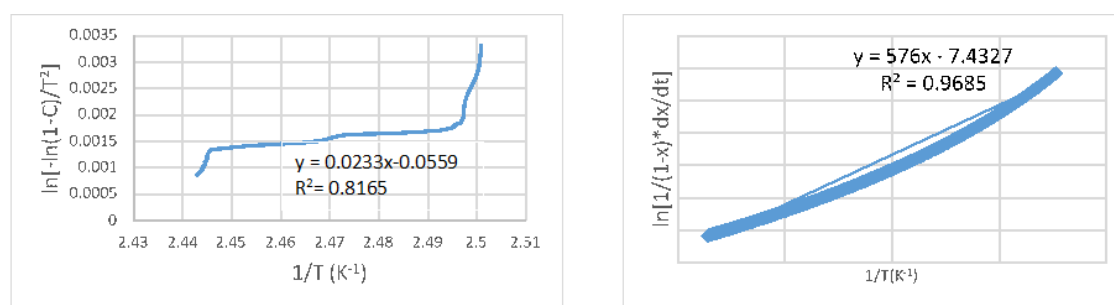
### 3.4. Kinetics of the decomposition of oil shale mixed with HDPE



**Figure 3:** Thermo-gravimetric analysis of Lokpanta oil shale and HDPE mixture (left) differential thermal analysis of Lokpanta oil shale and HDPE mixture (right)

Figure 3 presents the TGA and DTG plots of the Lokpanta oil shale mixed with HDPE, there is an overlapping in the area of degradation of both constituents. The TGA and DTG plots shows that the reaction happened in three stages. Stage one was attained in the temperature range of 28-316.41°C, which corresponded to the removal of water from the Lokpanta sample. Stage two occurred between 316.41 and 481.47°C which is the temperature at which an overlapping of the kerogen found in the oil shale interfered with the degradation of the HDPE. Stage three occurred between 481.47 and 887.44°C. This is the degradation of mineral matter present in the oil shale (calcite, quartz, kaoline and any mineral are commonly associated with oil shale).

This unsmooth bend before the point of trough indicates that an interaction was observed between organic matter of the oil shale and high density polyethylene occurring at 316.41 to 483.47°C. Meanwhile the degradation of mineral matter in the oil shale is not affected. However, the reaction temperature of the mixture shifted to a higher value of the reaction temperature. The maximum temperature ( $T_{max}$ ) is 407.49°C and the burn out temperature is 887.44°C. The presence of HDPE in the mixture yielded an increase of weight loss as it interacts with the organic matter. The yield from this research agrees with that of several literature aligned before commencement of this project, the similar work of [11] and the experiment done earlier [12], wherein they inferred that plastic could affect the reaction of organic materials under pyrolysis.



**Figure 4:** The Coats and Redfern method (left) while the right presents the Arrhenius kinetic regression

Figure 4 presents the Coats and Redfern method as well as the Arrhenius kinetic model of the mixture of Lokpanta oil shale mixed with HDPE.

The Arrhenius model was employed alongside the Coats and Redfern model. This method was applied in determining the activation energy of the mixture of Lokpanta sample and HDPE. From the TGA/DTG data obtained, using the Arrhenius equation, the energy of activation was calculated from the line of best fit using regression analysis. The activation energy activation gotten from the slope is 4.79kJ/mol and a pre exponential factor of 5.91E-03 was obtained. High density polyethylene (HDPE) From the Coats and Redfern method was the plotting of expression “ $\ln [-\ln (1-x)/T^2]$ ” versus “ $1/T$ ”. This evaluation was done, energy of activation which was gotten from the slope of the graph was estimated to be 1.94E-04kJ/mol with a pre exponential factor of 9.94.

The observed activation energy for the organic matter of Lokpanta sample and plastic during the decomposition of the mixture was 4.79kJ/mol and 1.94E-04kJ/mol at the overlap stage. This value is lower than that of the oil shale alone ( 75.5kJ/mol). From the review, it was noted that the activation energy of the HDPE in the mixture is lower than the activation energy of HDPE alone. The activation energy of the organic matter in the blend was observed to be of a higher value than that of the oil shale alone. [13] supported this finding in their review. The obtained activation energy for the Lokpanta oil shale mixed with HDPE is 4.79kJ/mol and 1.94E-04kJ/mol for decomposition under Arrhenius and the Coats and Redfern method respectively having a corresponding pre exponential factor of 5.91E-03 and

9.94. Thus the activation energy of the mixture turn out to be lower than that of the oil shale without any addition of HDPE (75.5kJ/mol.). This is in concordance with the literature data of [15-16]

#### 4. Conclusions

The thermogravimetric study shows that there are three basic stages of weight loss that occurred during the decomposition of Lokpanta oil shale/HDPE blend. The first stage is of high significant to that onset of oil shale degradation. It is attributed to the removal of moisture from the material. The second step is attributed to the overlap of the organic matter in the Lokpanta sample and waste plastic degradation. The third step corresponds to the degradation of mineral constituent in the oil shale.

The energy requirement for the mixture of Lokpanta oil shale and high density polyethylene was estimated using two methods for degradation, this enhance better estimation for energy. The obtained activation energy for the Lokpanta oil shale mixed with HDPE is reduced compared to that of oil shale void of HDPE. In essence the HDPE enhanced the co-pyrolysis of the oil shale, decreasing the activation energy by the direct proportionality of the maximum temperature which is 407.49°C so that the reaction rate of the organic matter in the oil shale can be increased, while the mineral matter in the oil shale acted as probable inhibitor in the co-pyrolysis of the oil shale blend. The direct implication of this reduction is that the energy required to carry out the process necessary to produce fuel from oil shale is reduced by the addition of HDPE

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