Kinetic and thermodynamic study on the pyrolysis of low density polyethylene in the production of polyethylene wax

Abstract

Polyethylene wax was obtained from pyrolysis experiments on Low Density Polyethylene (LDPE) wastes using a muffle furnace in inert condition. 60 – 80% of the initial mass of wax were obtained as heating was added at a rate of 10°C/min. Operating conditions for the reaction were 400 – 450°C over time of 30 – 50min and effects of these parameters were discussed. Using Friedman's iso-conversional model, the kinetic parameters - activation energy, pre-exponential factor and frequency factor were 58.71kJ/mol, 13.726E+12/s and 914378.61 respectively. Also, spontaneity of LDPE pyrolysis occurs at high temperatures and these were validated from the calculated thermodynamic parameters.

Keywords: Low Density Polyethylene, Pyrolysis, Wax, Thermodynamics studies.

1. INTRODUCTION

Plastics is integral part of our world due to the numerous purposes they serve and the benefits derived from them (Hahladakis et al., 2018). According to the survey conducted in 2016, 300 million tonnes of plastics were produced worldwide, 57 million tonnes in the European Union and 513,000 tonnes in Nigeria (Babayemi et al., 2019; Kassargy et al., 2017). However, these figures are expected to rise in the next decade due to the increasing demand for plastics occasioned by industrialization and population growth. Babayemi et al., (2017) estimated the world wide generation of plastic waste to be 250 million tonnes annually.

Considering the non-biodegradable nature of plastics, this statistics portend huge environmental concerns; thus has prompted many remedial actions from several quarters (Jambeck et al., 2015; Velghe et al., 2011). The European waste management framework – 2008/98/EC – identified recycling, recovery and disposal as the most commonly applied stages of solid waste management. Recycling could be either mechanical or thermochemical. Mechanical recycling entails incineration of wastes in the presence of oxygen or disposal in landfills. This is not generally suitable because engineered landfills remain limited in many nations in addition to the high probability of underground water contamination from waste disposal at dumpsites. Equally, incineration of plastics generates poisonous pollutants which are accompanied by attendant high energy consumption and economic costs (Kassargy et al., 2017). Thermochemical processing (e.g. hydrogenation, pyrolysis) offers a better alternative as effluents are handled efficiently in comparison with mechanical recycling. Pyrolysis is a process of treating waste in an inert atmosphere for conversion into a useful material. Primarily, it is utilized as a process for the reduction of solid wastes within the society and also energy recovery from the solid wastes. Furthermore, production of petrochemical feedstock; reduction of greenhouse gases; economic viability etc. are derived from pyrolysis (Al-Salem et al., 2017). The pyrolysis of low density polyethylene (LDPE), like other plastics, yields 3 products – pyrolysis oil (a liquid product containing diesel-range hydrocarbons), char and syngas (Adeniyi et al., 2018). Product yield and composition are influenced by the type of waste and process operating parameters as such, low temperatures favour the yield of oil while high temperatures enhance gaseous products (Anuar Sharuddin et al., 2016; Sogancioglu et al., 2017).

This paper focuses on the pyrolytic conversion of waste LDPE plastic to wax for the production of hair cream. This method is efficient because the molecular chain of polyethylene is $–CH_2–$ and whereas the liquid product obtained have a high freezing point, the octane number of the researched gasoline is close to 88 which is quite low (Jixing et al., 2003). Experiments were conducted at the temperatures ranges of 400 – 450^{O}C that lasted up to 50mins.

2.0 MATERIALS AND METHODS

2.1 Materials

The LDPE waste samples were collected from a local transfer station situated at the Nnamdi Azikiwe University, Awka, Anambra State, Nigeria. Other analytical reagents (xylene, lanolin, paraffin oil, industrial camphor, menthol crystals, petroleum jelly) used in the study were obtained from the chemical market in Onitsha, Anambra State, Nigeria.

2.2 Methods

Samples were washed with sodium stearate solution, de-inked with xylene solvent and rinsed in sodium sulfonate solution to remove impurities and colour. Subsequently, under ambient conditions, they were dried and equally reduced to 1cm sizes to create higher surface area for uniform distribution of heat. The reactor was pre-purged for 5mins with nitrogen gas, thereafter, 200g of the size-reduced samples were charged it. Heat was added to the system at a steady rate of 8^{0}C/min with reaction temperature ranges of 410 – 450^{0}C for the time duration of 60mins. It was observed that temperature of 420^{0}C and retention time of 35mins are the optimum operating conditions for maximum wax yield. Kinetic and thermodynamic parameters for the operation were obtained for the operation.

2.3 Pyrolytic reactor

The reactor was a bench-scale muffle furnace fitted with ports and measuring 10cm in length and 5cm in width. Aligned K-type thermocouples (with $\pm 0.5^0$C accuracy), manufactured by ATP Instrumentation Ltd. UK, were utilized to obtain temperature readings. These were joined with a USB module no. ATK-610B and a PC to record temperature during pyrolysis while maintaining a pressure of 1atm. The system was retrofitted with a condenser unit for easy withdrawal of products at the end of each operation. During pyrolysis, the reactor with its contents were continuously purged with nitrogen gas at the flowrate of 0.2L/min to ensure oxygen free medium at the end of the reaction. A slightly viscous grey coloured wax was obtained at the end of pyrolysis. The visibility of the colour on the wax could be attributed to incomplete removal of evolved product gases from the reactor. The wax colour can be changed with the addition of dyes without effects to its intrinsic properties (Jixing et al., 2003).

2.4 Kinetic model and thermodynamic parameter calculation

The rate of conversion in the thermal degradation of plastic is assumed to be proportional to its concentration and expressed as a first order reaction kinetic model:

$$\frac{dx}{dt} = k(T)f(x) \tag{1}$$

The degree of conversion, x, is defined as:

$$x = \frac{m_0 - m}{m - m_f} \tag{2}$$

where m_o, m and m_f are masses at the beginning, time t and end of pyrolysis respectively; $k(T)$ is the rate constant; $f(x)$is a kinetic-model dependent function. The rate constant $k(T)$ is modelled successfully using Arrhenius equation as:

$$k(T) = A.\exp\left(-\frac{E}{RT}\right) \tag{3}$$

Where;

A = pre-exponential factor (s^{-1})

E = activation energy (kJ/mol)

R = universal gas constant (8.314 J $K^{-1}mol^{-1}$)

T = temperature (K)

Addition of heat at a given rate, represented as $\beta = \frac{dT}{dt}$, and combining Eqs. (1) and (3) gives a re-arranged first order kinetic model as:

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(x) \tag{4}$$

The kinetic parameters were determined with Friedman's isoconversional model. This is a differential form of the Eq. (4) which is expressed to the natural logarithm as (Aboulkas et al., 2010):

$$\ln\left(\beta \frac{dx}{dT}\right) = \ln[Af(x)] - \frac{E}{RT} \tag{5}$$

The pre-exponential factor (A) and thermodynamic parameters $(\Delta H^o, \Delta G^o, \Delta S^o)$ of the samples were calculated using the following (Xu & Chen, 2013):

$$A = \beta . E_a . \exp\left(\frac{E_a}{R.T_m}\right) / \left(R.T_m{}^2\right) \tag{6}$$

$$\Delta H^o = E_a - RT \tag{7}$$

$$\Delta G^o = E_a + R.T_m . \ln\left(\frac{K_B.T_m}{h.A}\right) \tag{8}$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T_m} \tag{9}$$

where T_m is the peak pyrolysis temperature, K_B and h represent Boltzmann and Plank constant respectively.

3.0 RESULTS AND DISCUSSION

3.1 Effect of pyrolysis temperature and time on the yield of LDPE wax

The graphical illustrations of the effects of pyrolysis temperature and heating time on the yield of wax are shown in Figs. 1 and 2 respectively. No wax was formed at temperatures below 400^{0}C as the boiling point of LPDE has not been attained. With continuous application of heat over time, plastic denaturing occurred, hence, the breakdown of the molecular chained monomer of the material.

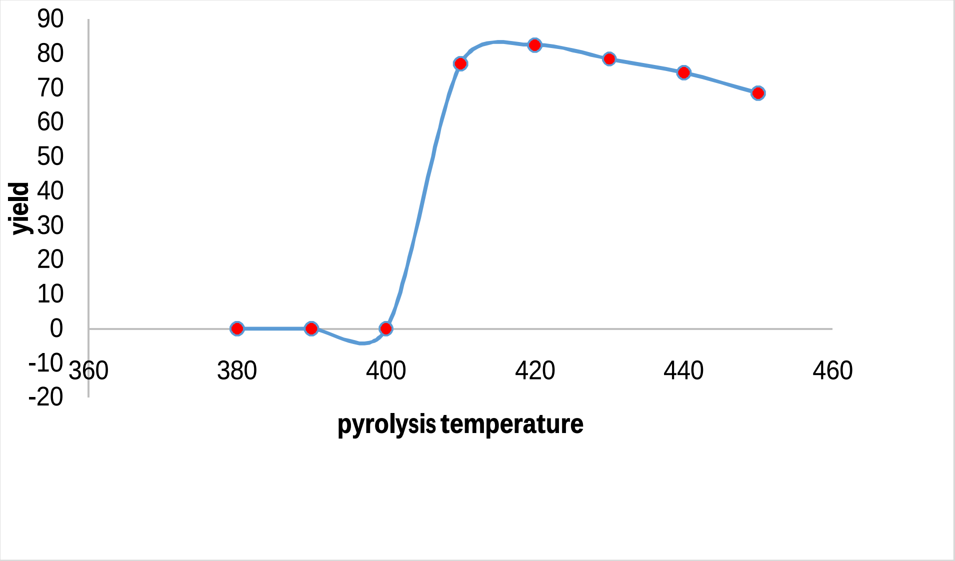

Figure 1: Graph of yield against temperature

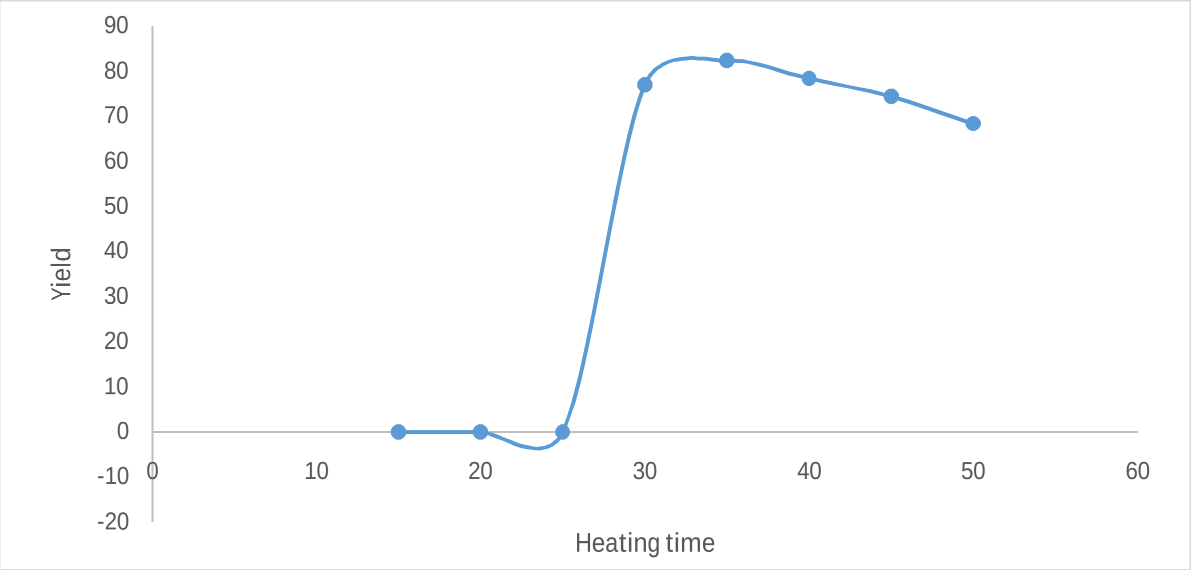

Figure 2: Graph of paraffin wax yield against heating time

Wax deposition commenced at 400^0C and progressed rapidly with maximum yield obtained at 420^0C after 35mins of pyrolysis operation. Flowing through a condenser retrofitted within the experimental setup enabled collection of wax after the reaction. Continued pyrolysis of plastics results in the evolution of gaseous products and decrease in wax yield (Arabiourrutia et al., 2012; Na et al., 2006).

3.2 Kinetic study

Friedman's model (Eq. 4) best described the kinetics of the process as illustrated graphically plot in Fig. 3. From this Arrhenius plot, the activation energy of LDPE pyrolysis of 91.44kJ/mol and pre-exponential factor of 13.726E+12/min were obtained by linear regression. More importantly, the pre-exponential factor explains the reaction chemistry of materials being pyrolysed, hence, a good parameter for optimization purposes.

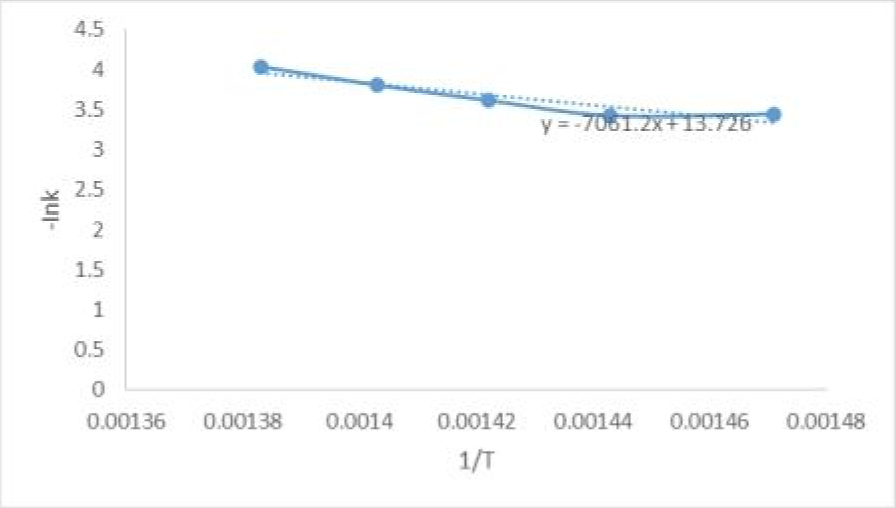

Figure 3: Graph of -ln K against 1/T

These parameters (activation energy and pre-exponential factor) represent the dynamic kinetic rate constants of the process and are dependent on factors such as sample weight, shape and type; heating rate and airflow rate within the reactor. For reactor design purposes, they remain essential.

Iso-conversional kinetic models are most reliable in the description of thermochemical reactions. They afford an evaluation of the effective activation energy (E_a) without assuming any particular form of the reaction model wherein E_a variations can be effectively measured with thermos-analytical techniques (Steps & Sbirrazzuoli, 2019).

3.3 Thermodynamic study

The thermodynamic parameters describing the reaction are calculated at peak pyrolysis temperature, T_m, and presented in Table 1 below.

Table 1: Thermodynamic parameters

Wax yield (g)	Time (min)	Temp (K)	ln k	$-E/RT$	ΔG° (J/mol)	ΔH^{o} (J/mol)	ΔS^{o} (J/mol)
3.85	30	683	- 3.445	10.338	-19235.78	58706.817	114.118
4.12	35	693	- 3.427	10.189	-20376.96	58706.817	114.118
3.92	40	703	- 3.619	10.044	-21518.14	58706.817	114.118
3.72	45	713	- 3.808	9.904	-22659.32	58706.817	114.118

3.42	50	723	- 4.040	9.767	-23800.50	58706.817	114.118

The available amount of energy for the reaction is reflected in the Gibbs free energy (ΔG^o) values obtained. In addition, these point to the spontaneity of LDPE pyrolysis as enthalpy and free entropy values remained constant throughout the reaction. Thus, it can be stated that LDPE pyrolysis is a spontaneous reaction at elevated temperatures.

The possibility of pyrolysis to occur is reflected in the difference between the activation energy and enthalpy values wherein lower and higher differences indicate presence of pyrolytic oil and syngas in addition to wax formation respectively (Sajjad et al., 2017). The higher difference indicates evolution of syngas that are absorbed in the withdrawn polyethylene wax while lower difference indicates higher formation of pyrolytic oil in the reactor. On another note, the extent of reaction for surface dependent mechanisms can be deduced from the degree of the activation energy values (Sajjad et al., 2017). This parameter is indicative of the amount of energy required to the break-up the heavily cross-linked constitutive elements of plastics.

4.0 CONCLUSION

a. Polyethylene wax obtained from the pyrolysis of LDPE wastes were investigated using a bench-scale pyrolytic reactor.
b. Yield curves were obtained at constant heating rate of 10^{O}C/min under non-isothermal and time-variant conditions. The yield represents about 60 – 80% weight of the raw LDPE plastics representing a high conversion for the reaction.
c. Kinetic parameters (E_a = 58.70682kJ/mol; pre-exponential factor = 13.726E+12/min and frequency factor of 914378.61) were obtained using Friedman’s isoconversional model.

Also, spontaneity of LDPE pyrolysis occurs at high temperatures as seen from the calculated thermodynamic parameters.

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