Asian Journal of Advanced Research and Reports

Volume 17, Issue 8, Page 20-25, 2023; Article no.AJARR.98879
ISSN: 2582-3248

Kinetic and Thermodynamic Study on the Pyrolysis of Low Density Polyethylene in the Production of Polyethylene Wax

Chinenye Faith Okey-Onyesolu [a*], Chukwunonso Chukwuzuloke Okoye [a*], Marcel Ikenna Ejimofor [a*] and Ikenna Chukwudi Nwokedi [a]

[a] Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJARR/2023/v17i8501

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/98879

Original Research Article

Received: 05/03/2023
Accepted: 09/05/2023
Published: 19/05/2023

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^{o}C/min. Operating conditions for the reaction were 400 – 450^{o}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.

**Corresponding author: Email: cf.okey-onyesolu@unizik.edu.ng, cc.okoye@unizik.edu.ng, mi.ejimofor@unizik.edu.ng;*

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 [1]. 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 [2,3]. 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. [4] 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 [5,6]. 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 [3]. 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 [7]. 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 [8]. 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 [9,10].

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 [11]. Experiments were conducted at the temperatures ranges of 400 – 450^{O}C that lasted up to 50mins.

2. 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 ±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 [11].

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 [12]:

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

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 [13]:

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

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

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

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

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

3. 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 400^0C 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.

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 [14,15].

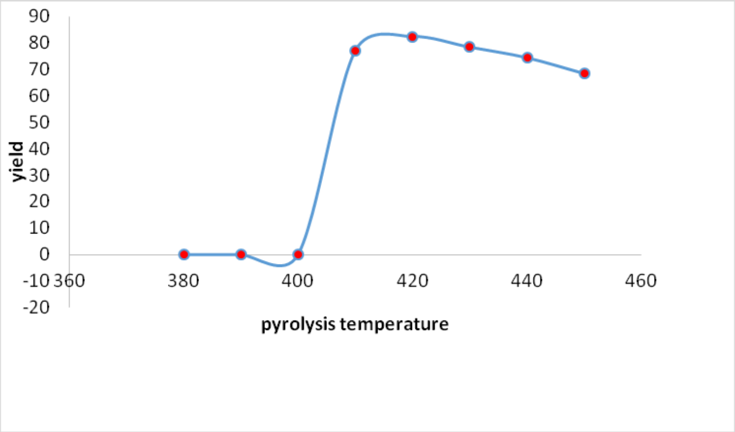

Fig. 1. Graph of yield against temperature

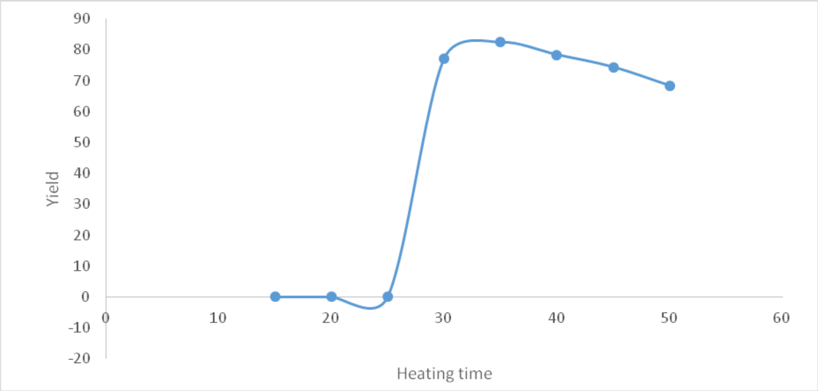

Fig. 2. Graph of paraffin wax yield against heating time

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.

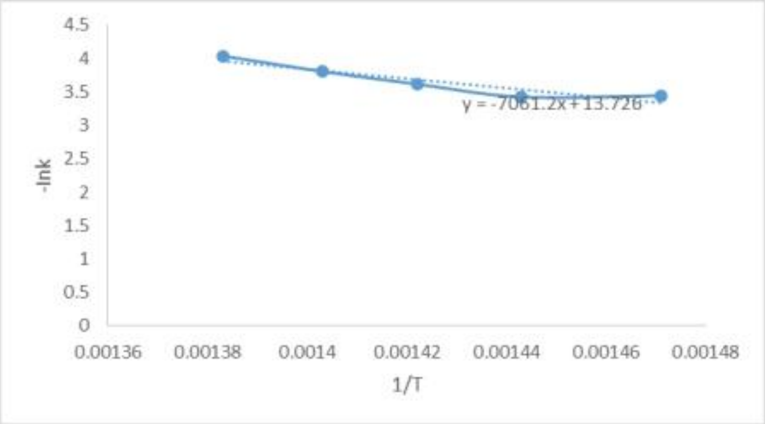

Fig. 3. Graph of -ln K against 1/T

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

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 [16].

3.3 Thermodynamic Study

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

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 [17]. 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 [17]. This parameter is indicative of the amount of energy required to the break-up the heavily cross-linked constitutive elements of plastics.

4. 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Hahladakis JN, Velis CA, Weber R, Iacovidou E, Purnell P. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. Journal of Hazardous Materials. 2018;344:179–199. Available:https://doi.org/10.1016/j.jhazmat.2017.10.014
2. Babayemi JO, Nnorom IC, Osibanjo O, Weber R. Ensuring sustainability in plastics use in Africa: consumption, waste generation, and projections. Environmental Sciences Europe. 2019;31(1). Available:https://doi.org/10.1186/s12302-019-0254-5
3. Kassargy C, Awad S, Burnens G, Kahine K, Tazerout M. Experimental study of catalytic pyrolysis of polyethylene and polypropylene over USY zeolite and

separation to gasoline and diesel-like fuels. Journal of Analytical and Applied Pyrolysis, 127(January). 2017;31–37. Available:https://doi.org/10.1016/j.jaap.2017.09.005

4. Babayemi JO, Ogundiran MB, Osibanjo O. Current levels and management of solid wastes in Nigeria. Environmental Quality Management. 2017;26(3):29-53.
5. Jambeck JR, Ji Q, Zhang YG, Liu D, Grossnickle DM, Luo ZX. Plastic waste inputs from land into the ocean. Science. 2015;347(6223):764–768. Available:https://doi.org/10.1126/science.1260879
6. Velghe I, Carleer R, Yperman J, Schreurs S. Study of the pyrolysis of municipal solid waste for the production of valuable products. Journal of Analytical and Applied Pyrolysis. 2011;92(2):366–375. Available:https://doi.org/10.1016/j.jaap.2011.07.011
7. Al-Salem SM, Antelava A, Constantinou A, Manos G, Dutta A. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). Journal of Environmental Management. 2017;197(1408):177–198. Available:https://doi.org/10.1016/j.jenvman.2017.03.084
8. Adeniyi AG, Eletta, O AA, Ighalo JO. Computer aided modelling of low density polyethylene pyrolysis to produce synthetic fuels. Nigerian Journal of Technology. 2018;37(4):945. Available:https://doi.org/10.4314/njt.v37i4.12
9. Anuar Sharuddin SD, Abnisa F, Wan Daud WMA, Aroua MK. A review on pyrolysis of plastic wastes. Energy Conversion and Management. 2016;115:308–326. Available:https://doi.org/10.1016/j.enconman.2016.02.037
10. Sogancioglu M, Ahmetli G, Yel E. A Comparative Study on Waste Plastics Pyrolysis Liquid Products Quantity and Energy Recovery Potential. Energy Procedia. 2017;118:221–226. Available:https://doi.org/10.1016/j.egypro.2017.07.020
11. Jixing Li S, Wang X, Li X. (Study on the conversion technology of waste polyethylene plastic to polyethylene wax. Energy Sources. 2003;25(1):77–82. Available:https://doi.org/10.1080/00908310290142136
12. Aboulkas A, El Harfi K, El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Conversion and Management. 2010;51(7):1363–1369. Available:https://doi.org/10.1016/j.enconman.2009.12.017
13. Xu Y, Chen B. Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis. Bioresource Technology. 2013;146:485–493. Available:https://doi.org/10.1016/j.biortech.2013.07.086
14. Arabiourrutia M, Elordi G, Lopez G, Borsella E, Bilbao J, Olazar M.(). Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor. Journal of Analytical and Applied Pyrolysis. 2012;94: 230–237. Available:https://doi.org/10.1016/j.jaap.2011.12.012
15. Na JG, Jeong BH, Chung SH, Kim SS. Pyrolysis of low-density polyethylene using synthetic catalysts produced from fly ash. Journal of Material Cycles and Waste Management. 2006;8(2):126–132. Available:https://doi.org/10.1007/s10163-006-0156-7
16. Steps R, Sbirrazzuoli N. Advanced Isoconversional Kinetic Analysis for the Elucidation of Complex Reaction Mechanisms; 2019.
17. Sajjad M, Aamer M, Taha S, Taqvi H. Pyrolysis, kinetics analysis, thermodynamics parameters and reaction mechanism of Typha latifolia to evaluate its bioenergy potential Bioresource Technology Pyrolysis, kinetics analysis, thermodynamics parameters and reaction mechanism of Typha latifo. Bioresource Technology. 2017;245:491–501. Available:https://doi.org/10.1016/j.biortech.2017.08.162

© 2023 Okey-Onyesolu et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/98879