
AIDIC
EFCE
ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Waste Plastics: Thermal degradation kinetics and lab scale pyrolysis

Pallab Das[1] and Pankaj Tiwari [1]*

[1]*Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India*

**Corresponding author: Tel.: +91 361 2582263; Fax: +91 361 2582291*

E-mail address: pankaj.tiwari@iitg.ernet.in

Highlights

- Detail thermal degradation kinetics of common packaging plastics
- Pyrolysis of plastics at low temperature with long holding time.
- Liquid (Oil) obtained resembles the fuel properties of middle distillates of petroleum.

1. Introduction

Waste plastic is one of the major contributors to the municipal solid waste. Pyrolysis of waste plastic can transform solid waste (plastic) into a wide range of valuable chemicals and hydrocarbon compounds. Designing and implementation of the pyrolysis process for complex materials like plastics depends primarily on kinetic analysis. The precision of the pyrolysis kinetics heavily depends upon the reliable evaluation of the kinetic triplets; activation energy (E_α), pre-exponential factor (A_α) and reaction model ($f(\alpha)$). The aim of the current study is to compare the quantitative aspects of the thermal decomposition process for low and high density polyethylene (LDPE and HDPE) and polypropylene (PP), majorly used as packaging materials. Reaction model ($f(\alpha)$) was calculated as R2 (contracting cylinder) and R3 (contracting sphere) models for LDPE/HDPE and PP, respectively. A semi-batch lab scale reactor with a low temperature (slow pyrolysis) scheme was utilized to convert the plastic waste into useful products.

2. Methods

Thermogravimetric analysis (TGA) was performed for all three materials, low and high density polyethylene (LDPE and HDPE) and polypropylene (PP) under inert condition of N_2 (constant flow rate of 40 ml/min) at seven heating rates (5, 10, 15, 20, 30, 40, 50 °C/min) in the temperature range of 30 – 700 °C (Figure 1 (a). The kinetic analysis was performed based on Arrhenius rate law. Mathematical manipulation of the rate equation and by appropriate fitting of the degradation data led to the determination of kinetic triplets (E, A and $f(\alpha)$) from TGA data (Figure 1(b)). Vyazovkin[1] advance isoconversional (AIC) method was found to be most suitable to analyze the distributed kinetic parameters (E_α). Criados masterplot technique was used to predict the reaction model ($f(\alpha)$). Lab scale pyrolysis experiments were performed for individual sample and their mixture (RMIX) having a ratio of 1:1:1.3 for LDPE, HDPE and PP respectively. Experiments were conducted in a semi-batch reactor of volume 1 ltr (Figure 2 (a)) heated by a tubular furnace (PID controlled. Low temperature slow pyrolysis (long isothermal holding time) scheme was used to convert solid to high quality liquid products. N_2 gas (200 ml/min) was supplied to maintain the inert condition of the reactor. The isothermal condition (300 – 400 °C) of the reactor was maintained for 8 h. Pyrolysis products particularly plastic derived oil (PDO) was analyzed, qualitative and quantitative, with the help of analytical techniques like ^{1}H NMR, FTIR and GC-Simdist analyses utilizing standard hydrocarbon mixture for compositional analysis.

3. Results and discussion

Figure 1 (a) showed the TGA profiles of LDPE degradation at seven different heating rates and Figure 1(b) demonstrated both activation energy distribution with associate uncertainties and $A\,f(\alpha)$ as a function of conversion (α) for all three materials obtained from AIC method. Similar degradation profiles were also obtained for HDPE and PP. The distribution of activation energy calculated from AIC method ranges 170-232 kJ mol^{-1} for LDPE, 143-231 kJ mol^{-1} for HDPE, 133-173 kJ mol^{-1} for PP [2]. The value of activation energy is low at the beginning of the degradation process since degradation starts at weak links of the polymer chain and increases as the reaction progresses. The findings confirmed the complex degradation mechanism of plastic pyrolysis.

The boiling point (carbon number) distribution curve with cumulative yield for the PDO obtained from mix feed (RMIX) is shown in Figure 2(b). It can be observed that around 90% yield of the liquid (distilled under 350 °C) obtained for the first two pyrolysis temperatures (350 °C and 375 °C) belongs to the middle distillates (C_{12} – C_{20}) like kerosene and diesel while the yield of same fraction decreases to 70% for the oil obtained at 400 °C. The PDO samples obtained from the pyrolysis at various conditions have the similar attribute to the existing refinery end products like gasoline and diesel (middle distillates). Interestingly the fuel properties (calorific value, viscosity, flash point and pour point etc.) of the PDOs also differs significantly with pyrolysis temperature[3].

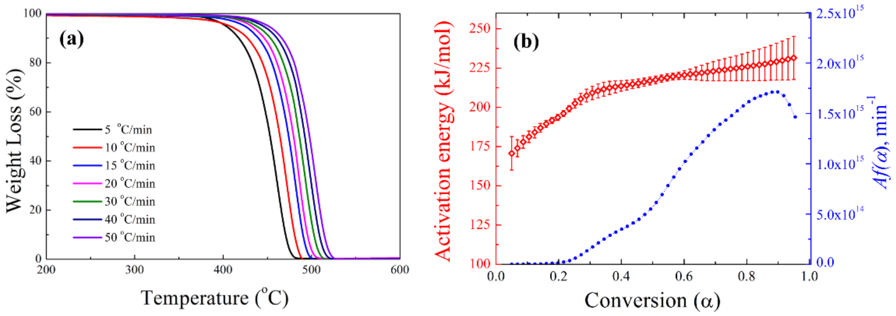

Figure 1. (a) TGA profile of LDPE at seven different heating rate, (b) Distribution of activation energy (E_α) (with uncertainty) and *Af(α)* values for LDPE

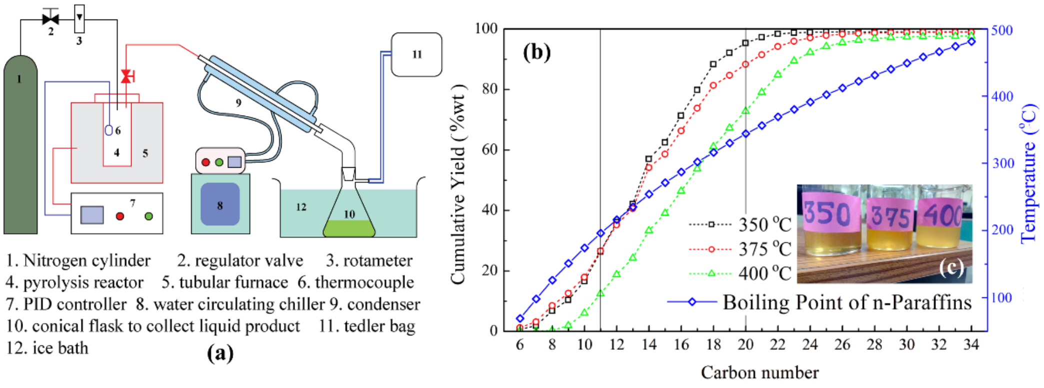

Figure 2. (a) Schematic representation of pyrolysis setup (b) Cumulative yield (% wt) of hydrocarbons with respect to carbon number and the boiling range of n-paraffins and for PDO obtained from the pyrolysis of plastic mixture (LDPE, HDPE and PP) collected from waste at three temperatures. (c) Camera image of three PDOs

4. Conclusions

The overall activation energy values of all three plastics differ due to their molecular structures. Thermal stability of polyolefins strongly affected by branching. The PDO samples obtained had shown variation in their compositions and fuel properties based on the pyrolysis temperature. PDO samples obtained at low temperature pyrolysis are lighter with low viscosity, high octane number and high calorific value. Low temperature and long duration supports the polymer scission reaction (end chain and random) and leads to the production of lighter hydrocarbons. The data obtained in this study are useful in the context of utilization of pyrolysis process to produce targeted value added products like gasoline or diesel from plastic waste.

References

[1] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescud, N. Sbirrazzuolie, Thermochim. Acta, 520 (2011) 1-19.
[2] P. Das, P. Tiwari, Thermochim. Acta, 654 (2017) 191-202.
[3] P. Das, P. Tiwari, Resour. Conserv. Recy, 128 (2018) 69-77.

Keywords

Plastics waste, thermal degradation kinetics, isoconversional methods, kinetic model selection, low temperature pyrolysis,