

Mathematical Modelling of Plastic Waste Pyrolysis Kinetics

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Abstract: In this work, mathematical models were developed and validated in order to monitor the optimal design and operation of the pyrolysis reactors. Mathematical models for plastic waste pyrolysis kinetics were developed. The simulated models are reliable as it predicted the experimental results and thermo-gravimetric properties of HDPE (its types/kinds), LDPE and PP types of plastic wastes. Pyrolysis temperature of plastic waste pyrolysis increases as the density and hardness of plastic waste types increases i.e. from HDPE to PS. At the same temperature HDPE laminate shows a higher rate of pyrolysis than that of HDPE pellets and HDPE powder. The results of the simulation (temperature profile for a reactor of 0.44m length using LDPE) depicts that during the first stage of the pyrolysis of the plastic waste type, the temperature increases rapidly from 100K to 700K. At temperatures 700K to 1000K fast or flash pyrolysis was observed between 0.07m to 0.37m reactor length. It can be concluded that pyrolysis temperature of plastic waste increases as the density and hardness of plastic waste types increases which implies that the conversion rate increases with the extent of branching (HDPE<LDPE<PP<PS), as HDPE chains are not branched at all, LDPE chains have some branches while PP and PS chains are very high.

Key words: *Pyrolysis, HDPE, LDPE, PP, Temperature profile*

1 INTRODUCTION

In recent years, the plastic materials have become an important part of solid urban waste, with plastics from containers and packaging representing around 60% of this type of waste. The composition of this residue is mainly polyolefins (high and low density polyethylene, polypropylene and polystyrene, accounting for around 70% of the total plastic waste [1]. Since the global energy crises of the 1970s, there has been a trend towards use of alternative energy sources to replace fossil fuel worldwide [2]. The fuel potential of many plastic wastes is a valuable resource for the generation of energy and considerable interest has been devoted to it recently to exploit its potential. However, it has been observed out that the energy content that could be practically recovered from the wastes would be a small percentage of the total energy required in any nation [3]. Over the years, different waste management, treatment and disposal methods have been adopted apart from the traditional options of landfill and incineration. Emphasis is now shifting to technologies that will be acceptable to the end users. One of such technologies is pyrolysis. Pyrolytic technology among other methods is a way of harnessing the energy in these wastes, providing a good method of disposing the wastes without affecting the ecological system. The products of pyrolysis of MSW are carbonaceous

char, oils, and combustible gases. The products of pyrolysis have different chemical and fuel properties. The heating value of char generally was between 25.52MJ/kg and 30.16MJ/kg [4]. The heating value of tar oil was said to be about 24.7MJ/kg; while the heating value of pyrogas was given as 1.51MJ/kg [5]. Pyrolytic process have been studied previously in other countries using several different types of equipment such as fluidized beds [6-8], rotary kilns [9, 10], and rotating reactors [11]. Some studies have been conducted using MSW or other sources of wastes [12-14]. The recent works on pyrolysis in Nigeria available for review are the pyrolysis of shredded plastic waste [15], corncobs [16], and wood [17, 18]. The product yield during the thermochemical conversion of MSW depends on temperature, pressure, time, reaction conditions and added reactants or catalysts [8, 19]. Although numerous projects have been promoted, pyrolysis commercialization is progressing at a low pace not only in Nigeria but also globally. Major efforts on researching are needed in order to maximize the advantages and minimize the disadvantages of this technology. The upsurge of interest in simulation and optimization of suitable reactors for thermochemical processes requires appropriate models that contemplate different operational conditions and varied feed stocks and helping to achieve a better understanding of the reactions in the corresponding processes. In this sense,

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a better knowledge of the kinetics concerning to the thermal decomposition of the plastic materials is required. Though not extensive, research has been conducted on the modeling of pyrolysis including: modeling based on thermokinetic analysis [20], modeling biomass pyrolysis kinetics [21], modeling pyrolysis using first order kinetics [22], competing reaction models in pyrolysis [23], modeling transport phenomena kinetics of pyrolysis [24], kinetic modeling study of pyrolysis [25], mathematical model of solid fuels pyrolysis [26] and modified model of pyrolysis for charring materials in fire [27]. Despite the numerous researches in kinetics modeling of pyrolysis, there is no report of an outstanding model that describes the pyrolysis reactor which can be used to predict the effect of variables on yield looking at thermogravimetric parameters. Moreover a model that can accurately predict temperature distribution in the pyrolysis reactor has not been realized.

In this work, thermal decomposition of plastics (high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP)) occurring in a counter current plug flow reactor considering primary and secondary pyrolysis was modelled. The main objective of the study presents simulated behavior of the aforementioned system. It focuses basically on predicting the temperature variation along the pyrolysis reactor so as to determine its effect on the yield of the pyrolysis reaction. In the model, the effect of heat generated by the reacting particles in the heat balance which has not been considered before was incorporated.

2 MATERIALS AND METHODS

2.1 The Apparatus

A simplified mode of the pyrolysis reactor under consideration is shown if Figure 1. Considering this model a simplified deterministic kinetic model is developed to describe the production of oil, gas and waste product (tar) from the pyrolysis of plastic waste in order to forecast the yield and production rate of the products generated. Also, a novel approach to mathematical modeling of the fundamental processes taking place in a pyrolysis reactor is presented. The model represents the complex physical and chemical processes occurring with the polymer (plastic) waste and incorporates a methodology for handling parameter uncertainties with model's input data in a manner that is consistent with the limited data generally available from field records and experimental results from various reliable sources. In this approach, stoichiometric relationships are used to maintain mass balance of constituent elements within the model. Also, with respect to the pyrolysis reactor's
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flow process, provision is made to capture the gas production such as momentum rate.

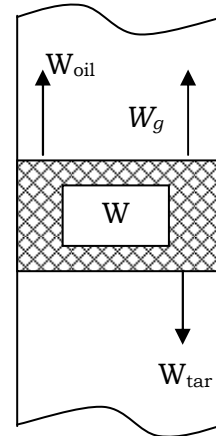


Figure 1: Simplified model of a pyrolysis reactor

2.2 The Model

To develop governing models for the prediction of some thermogravimetric properties of the pyrolysis reaction some thermodynamic related balances were considered. In all the models, a one dimensional solid plastic was assumed, plastic under study lying just before the pyrolysis front and an evaporating front as shown in Figure 2.

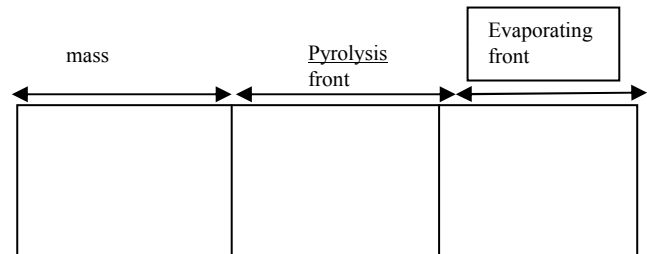


Figure 2: Pyrolysis front and evaporating front

Also, the heat conduction model across the cross section of the reactor to be able to establish the temperature profile was considered. The major terms in the heat balance of a pyrolysis reactor here considered are; Sensible and latent melting heat and Heat of reaction. The total heat change (heat accumulated) of the system can be given as the sum of; heat generated, heat conducted and heat convection over the entire volume of the reactor. The total heat change is therefore given as [28]:

$$dQ = \rho C_p \frac{\partial T}{\partial t} \quad (1)$$

The heat generated is the heat of reaction – the summation of the heat of heterogeneous reactions [29] i.e.

$$H_r = \sum (\Delta h_i W_i) \quad (2)$$

$W_i = \text{reaction rate}$

The heat conduction through the bulk of mass is given by the **Fourier equation** – the thermal gradient across the mass along the longitudinal direction (z)

$$H_c = k \left[\frac{b-1}{z} \frac{\partial T}{\partial z} + \frac{\partial^2 T}{\partial z^2} \right] \quad (3)$$

Where, b is a geometric factor defined for different geometries; for Slab = 1; Cylinder = 2; and Sphere = 3. The heat convection by the surrounding gas is given by [28]:

$$H_{cv} = \alpha A (T - T_g) \quad (4)$$

$T = \text{plastic temperature}$

$T_g = \text{outlet gas temperature}$

$\alpha =$

convective heat transfer coefficient-a property of the gas

$A = \text{surface area}$

Putting these expressions together to form the heat balance:

$$\rho C_p \frac{\partial T}{\partial t} = \sum (\Delta h_i W_i) - k \left[\frac{b-1}{z} \frac{\partial T}{\partial z} + \frac{\partial^2 T}{\partial z^2} \right] - \alpha A (T - T_g)$$

The reaction rate W_i can be defined for simplicity by neglecting secondary pyrolysis.

To define the reaction rate, W_i we consider a balance of chemical species in the system.

$$\frac{\partial W}{\partial t} = -K_1 C_A^n \text{ Such that;}$$

$$\rho C_p \frac{\partial T}{\partial t} = \sum \Delta h_i (-K_1 C_A^n)_i - k \left[\frac{b-1}{z} \frac{\partial T}{\partial z} + \frac{\partial^2 T}{\partial z^2} \right] - \alpha A (T - T_g)$$

$$\rho C_p \frac{\partial T}{\partial t} = \Delta H K_1 C_A^n - k \left[\frac{b-1}{z} \frac{\partial T}{\partial z} + \frac{\partial^2 T}{\partial z^2} \right] - \alpha A (T - T_g)$$

$$\frac{\partial T}{\partial t} = \frac{\Delta H}{\rho C_p} K_1 C_A^n - \frac{k}{\rho C_p} \left[\frac{b-1}{z} \frac{\partial T}{\partial z} + \frac{\partial^2 T}{\partial z^2} \right] - \frac{\alpha A}{\rho C_p} (T - T_g) \quad (5)$$

3 SIMULATION / VALIDATION OF RESULTS

Using the finite difference scheme, equation (5) was discretized with forward time and centered space finite difference and simulated with MATLAB 2007a software to generate temperature distribution in three cases. Case 1: considering that the heat equation involved only the heat conducted; Case 2: considering that the heat equation involved both conduction and convection; Case 3: Adding the effect of heat
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generated by the reaction. The simulated results were then validated with HDPE, LDPE and PP materials experimental pyrolysis data available in literatures.

Table 1: Constants used in the simulation

Properties	HDPE	LDPE	PP
C_p (J/KgK)	3640	3180	2790
ρ (g/cm ³)	0.96	0.92	0.91
k (W/mK)	0.49	0.34	0.14
H (J/Kg)	0.801	0.572	0.670

Case 1: Considering that the heat equation involved only the heat conducted.

The result of the simulation as shown in Figure 3 (temperature profile for a reactor of 0.44m length using LDPE in case 1) depicts that during the first stage of the pyrolysis of the named plastic waste types, the temperature increases rapidly from 100K to 700K. This is the first stage of the pyrolysis. Immediately after this stage, between temperatures 700K to 1000K fast or flash pyrolysis occurs. This takes place between 0.07m to 0.37m reactor length. Experimentally obtained temperature profiles along the reactor at seven temperatures of the quasi-isothermal zone between 0.10m and 0.35m in Norinaga et al. [29] are in close range with the model results. This validates the reliability of the model. The pyrolysis products/yield (pyrogas, tar oil and char) begin to form as the temperature remain constant. Shortly after the pyrolysis yields are formed, combustion reduces, consequently the temperature falls back to the starting temperature. The initial temperature rise takes virtually the same time with the drop in the final temperature. These situations (or result) are repeated in different time intervals. This is not the same with high density polyethylene where the reactor length at which the pyrolysis temperature occurs remains constant as the pyrolysis yield are formed remains the same during the pyrolysis (Figure 4) but its initial pyrolysis temperature increases higher to around 1100 K maximum temperature higher than that of LDPE due to its lower density (hardness) when compared with the HDPE type. This is consistent with the results of Norinaga et al. [29] who recorded a maximum pyrolysis temperature of 1200 K. Results of polypropylene (Figure 5) shows that the maximum pyrolysis yield occurs around 600K forming pyrolysis yield within the same range of reactor length. This temperature is very small compared with that of LDPE (around 1000K) and HDPE (around 1100K). This is simply a slow pyrolysis.

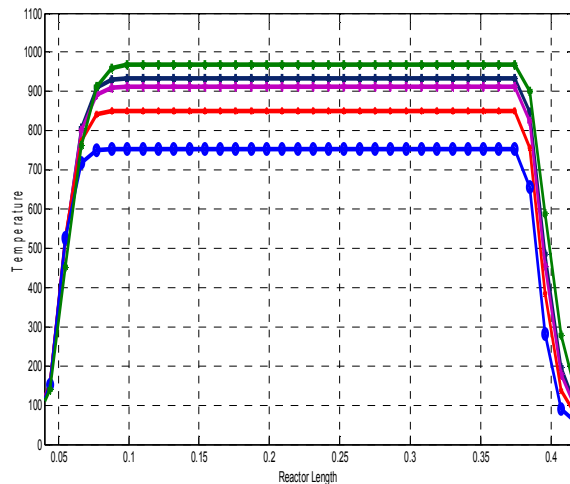


Figure 3: Temperature profile for a reactor of 0.44m length using LDPE in case 1.

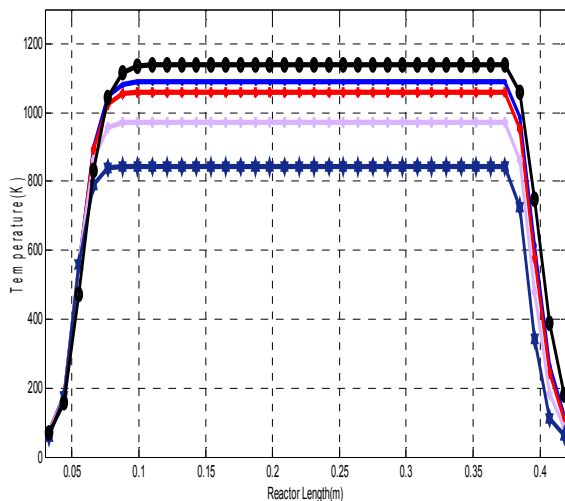


Figure 4: Temperature profile for a reactor of 0.44m length using HDPE in case 1.

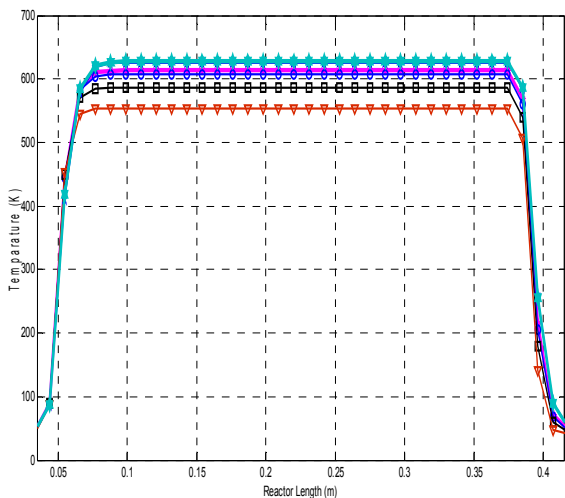


Figure 5: Temperature profile for a reactor of 0.44m length using polypropylene in case 1

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Case 2: Considering the effect of convection.

Figure 6 is the modeled temperature profile for the pyrolysis of LDPE. The results indicates that considering the effect of convection led to an increase in the temperature of pyrolysis greater than the previous case which considered temperature profile due to conduction only while pyrolysing the same plastic waste. The maximum pyrolysis temperature in this case is about 1350K. Modeled results for HDPE and PP showed the same trend in their temperature profile. These results were consistent with experimental results obtained by other researchers.

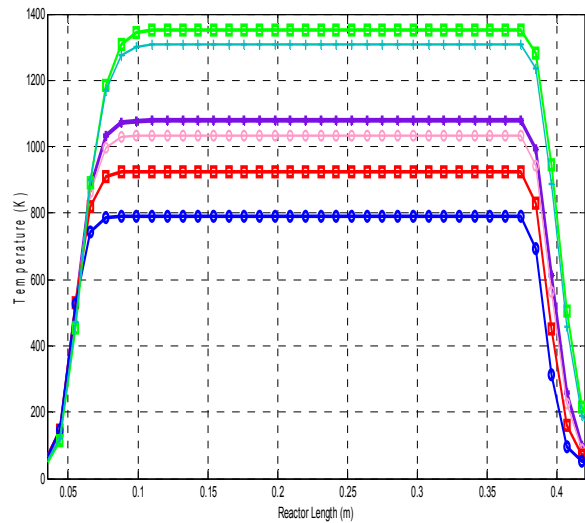


Figure 6: Temperature profile for a reactor of 0.44m length using LDPE in case 2.

Case 3: Adding the effect of heat generated by the reaction.

Adding the effect of heat generated by the reaction, the pyrolysis temperature is greater than the two afore-mentioned cases (Figures 7 – 9). The profiles here approximate the experimental results of Norinaga et al. [29] better than the cases discussed earlier. Investigation of the predicted surface temperatures at the onset of pyrolysis by Rein [30] shows values from 280 to 500 °C consistent with our results. The comparison with the measurements from Dakka et al. [31] for PMMA also shows very good agreement.

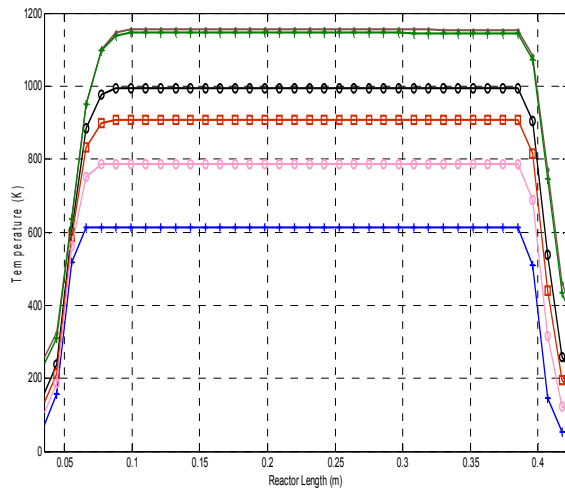


Figure 7: Temperature profile for a reactor of 0.44m length using LDPE in case 3

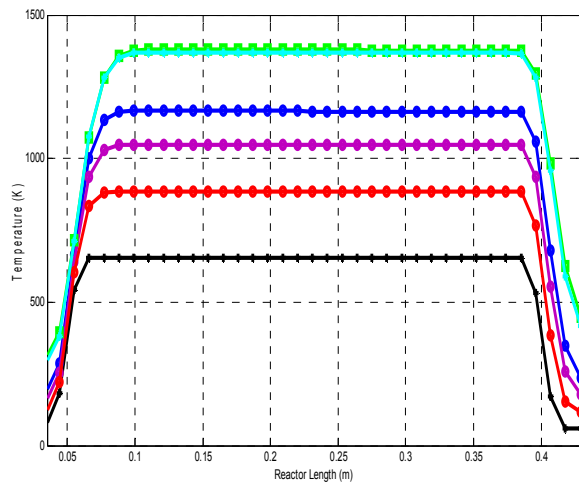


Figure 8: Temperature profile for a reactor of 0.44m length using HDPE in case 3.

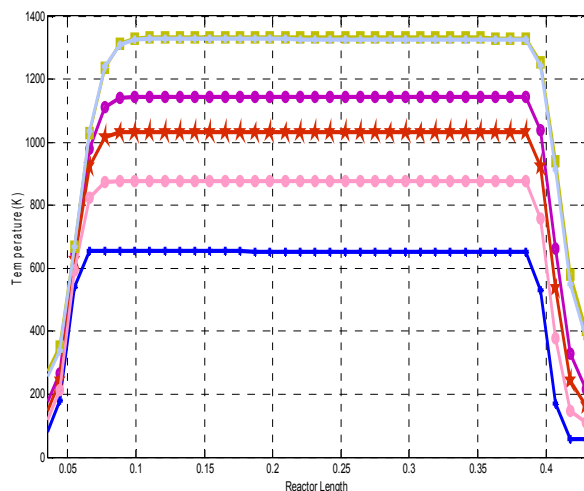


Figure 9: Temperature profile for a reactor of 0.44m length using Polypropylene in case 3

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4 CONCLUSION

Mathematical models for plastic waste pyrolysis kinetics were developed. The simulated models are reliable as it could be used to predict the outcome of anticipated thermogravimetric properties of plastic waste pyrolysis. The following conclusions are drawn:

1. Pyrolysis temperature of plastic waste pyrolysis increases as the density and hardness of plastic waste types increases. HDPE>LDPE>PP>PS which implies that the conversion rate increases with the extent of branching, as HDPE chains are not branched at all and LDPE chains have some branches (about 50 methyl groups/1000 carbon atoms), while PP and PS chains are highly branched (500 methyl or benzyl group/1000 carbon atoms) and also explain the stability of the free radicals produced during the pyrolysis process.

2. At the same temperature HDPE laminate shows a higher rate of pyrolysis than that of HDPE pellets and HDPE powder. The proposed mathematical model provided encouraging agreement with observed results of different types of plastic waste during pyrolysis.

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