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COMPUTER AIDED MODELLING OF LOW DENSITY POLYETHYLENE PYROLYSIS TO PRODUCE SYNTHETIC FUELS.

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ABSTRACT
The pyrolysis of waste low-density polyethylene (LDPE) is an excellent method of converting waste materials into useful products. Aspen HYSYS 2006 was used to develop a computational steady-state model to simulate the pyrolysis of LDPE. The Peng-Robinson fluid package was used for the simulation. A continuous stirred tank reactor with an Arrhenius kinetic expression was used to predict reaction extent and product yield. At a pyrolysis temperature of 450^{0}C and atmospheric pressure, 92.88% liquid yield was obtained. From the given feedstock, the char obtained was composed of only elemental carbon. The synthesis gas was composed mainly Hydrogen and C_1-C_4 hydrocarbons with traces of n-C_5 and n-C_6. The Pyrolysis oil was composed of higher hydrocarbon fractions (C_8-C_{24}). The conversion-temperature relationships from the simulation are in good agreement with experimental results. This proved that pyrolysis of waste LDPE can give an excellent yield of liquid product and is a viable recycling technique.

Keywords*: Pyrolysis, Simulation, LDPE, Synthetic fuels, Aspen HYSYS*

1. INTRODUCTION
The increase in production and application plastics has led to plastic waste making up a significant portion of municipal solid waste. After food waste and paper waste, plastic waste is the major constituent of municipal and industrial waste in cities [13]. Out of about 100 million tons plastics produced every year all over the world, 25 million tons is dumped [25]. Disposal is mainly by landfill and incineration as only about 10% of these plastic waste globally is recycled [10].

The disposal of these plastic wastes is now a major environmental problem in the world. Low density polyethylene (LDPE) is one of the constituents of plastic waste. Low density polyethylene is used for its relative strength, flexibility and transparency [13]. LDPE appears in plastic waste streams in the form of flexible bags and wraps for groceries, squeezable bottles, water sachets, shrink wraps and stretch films. Coupled with the desired properties, LDPE has a density of 0.910 - 0.925 g/cm^3 and about 25-50% crystallinity [14].

Recycling of plastic already occurs on a wide scale and with different techniques. Mechanical recycling requires homogenous and contaminant free feedstock. Also, products formed are of a lesser quality than the original plastics. Hence, mechanical recycling of mixed plastic waste appears to have only a limited future. The most attractive method, in line with the principles of environmental sustainability is chemical recycling also known as feedstock or tertiary recycling [1]. In this method, waste polymers can be either converted to original monomers or other valuable chemicals by the use of chemical reactions such as hydrolysis, methanolysis and ammonolysis etc.

Techniques of chemical recycling of waste includes pyrolysis, gasification, hydro-cracking catalytic cracking, coking and vis-breaking. A popular process for the recycle of plastics in general and waste LDPE in particular is pyrolysis. The pyrolysis process involves the thermal breakdown of waste in the absence oxygen/air [9]. The long chain polymers are broken into shorter chain hydrocarbons. Usually, three products are formed. A liquid product (mainly consisting of diesel-range hydrocarbons) known as pyrolysis oil, a gaseous product (mainly consisting combustible non-condensable gases) known as synthesis gas and a solid product (consisting of elemental carbon) known as char.

Generally, pyrolysis reactions for a single feedstock which usually end up in a large number of intermediates and end products. Developing an exact

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reaction mechanism for pyrolysis is difficult. Hence, pyrolysis reactions are modelled on the basis of visible kinetics [22]. The Kinetics and reaction sequence of numerous plastics under different conditions and equipment has been estimated by different researchers over the years [2, 4, 8, 11, 12, 16, 23, 26]. These parameters are important in modelling the system in Aspen HYSYS.

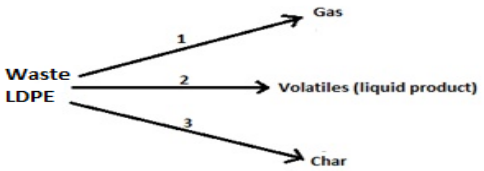
Simulation and modelling of different plastics has been attempted over the years [5-7, 19, 21]. In developing a simulation for LDPE pyrolysis, the idea is to have a modelled reference system. A model (reference system) is an ideal system whose response is agreed to be optimum. It responds to changes or fluctuations like an actual system and can be used the predicts the real world behaviour of the system [17]. Considering that LDPE pyrolysis is already in practice, efficiencies of current pyrolysis systems are still in question. This is an attempt to develop a model for LDPE simulation with the aim of preferring a functional and predictive simulation usable in the optimisation of current experimental processes to improve the efficiency recycling.

In this work, the simulation was carried out with Aspen HYSYS 2006. Aspen HYSYS was chosen for this work because it is a chemical process simulator able to perform most of the core calculations in chemical engineering mass and energy balance, vapour liquid equilibrium, mass transfer, heat transfer and chemical kinetics. The results obtained from this model were validated with those obtained from previous experimental works on LDPE pyrolysis [27], [18],[11], [20], [13]. The aim of this study is to develop a steady state model for the pyrolysis of waste lubricating oil. The model serves as a reference system for predicting product yield, product composition and process behaviour/response to operating factors. In this work, special attention is paid to the response of reaction conversion to pyrolysis temperature. This model can also serve as a framework for future process optimisation and economic analysis.

2. MATERIALS AND METHODS

2.1 Sequence and Kinetics LDPE pyrolysis Reaction

The reaction sequence to be used for this simulation is a simple one and is as illustrated in equation 1. Feedstock is directly and simultaneously converted into products as shown in equation 1.



(1)

This model noticeably does not possess any secondary reactions since it is considered that fast pyrolysis of plastics does not take place in enough time to involve secondary interactions between products. The equation of reaction used for this simulation was a modification of the one used by Alla and Ali [6] as shown in equation 2. The reaction was assumed to occur only in the vapour phase.

$$LDPE = H_2 + C_1 + C_2 + \cdots + C_{25} + 20C \quad (2)$$

The kinetics of plastic pyrolysis reactions has been previously implemented successfully with Arrhenius equation [7]. For this simulation, the kinetic parameters obtained by Kayacan and Doğan [15] for waste LDPE at a heating rate of 5 K/min was utilised. The reported values are A = 3.367 E17 s^{-1} and E = 279.74 KJ/mol. The Arrhenius rate equation is then given by the expression of equation 3

$$K = A\,Exp\left(-\frac{E}{RT}\right) \quad (3)$$

Where K (s^{-1}) is the rate constant, A (s^{-1}) is the pre-exponential factor, E (KJ/mol) is the activation energy, T (K) is temperature and R is the universal gas constant 8.314 KJ/molK.

2.2 Fluid Package and Components

The Peng-Robinson (PR) property package was used in the simulation. Aspen HYSYS Databank does not contain any polymers. Hence, the polymer is added to the simulation as a hypothetical component. The chemical species used to model the feed is ethylene. This information informs the software of the elemental composition of the feedstock. However, to completely predict all other physical and chemical properties of the feedstock, Aspen HYSYS requires the stipulation of three properties; density, molecular weight and normal boiling point. These properties were inputted into the hypothetical component manager and they served as the basis with which the software estimated all other necessary information about the polymer. The properties of LDPE like: Density (923 kg/m^3 [3]), Molecular weight (92200 g/mol [3]), Normal boiling point (543 K, assumed) and Normal melting point (383 K [15]) were used in the simulation works. Other reaction products (H_2, carbon, C_1-C_{24}) were added as components in the simulation while the product

distribution of the components in the pyrolysis oil and non-condensable gas were computed by the software.

2.3 Simulation Environment

The simulation technique used is a simple one. LDPE is fed into the reactor at ambient temperature and pressure. The pyrolysis reactor operates at a temperature of 450^{0}C and reaction results are based on the earlier stated kinetic parameters and equation of reactions. The reactor chosen was a continuous stirred tank reactor. The information about the entering feedstock are outlined in Table 1

The bottom product from the reactor was collected as char while the vapour was sent to a condenser. The condensate obtained at ambient temperature is known as pyrolysis oil while the non-condensable gases become the third product. The process flow diagram of the steady-state simulation is given in Figure 1. The design was developed by the researchers conducting this study.

Table 1: Feedstock Conditions

Parameter	Value
Feed rate	10 kg/hr
Feed Temperature	25 ^{o}C
Feed density	923 kg/m^3
Pyrolysis pressure	1 atm
Pyrolysis temperature	450 ^{o}C

Table 2: Pyrolysis Products Distribution

Pyrolysis Product	Weight Percentage (%)
Pyrolysis oil	92.88
Char	4.9
Synthesis Gas	2.22

Several key assumptions were made in the development of this model. The process is considered to occur at steady-state, hence time was not a considered factor. This work was more focused on temperature effects. It is also assumed that reaction occurs in the vapour phase alone. This supposition is valid as this is a consequent assumption taken from the reaction sequence chosen. The char formed was also assumed to be completely composed of elemental carbon. Practically, there are usually traces of heavy metals in the char but this will not be considered.

3. RESULTS AND DISCUSSION

At the end of pyrolysis, the results of the simulation obtained at feed rate of 10 kg/hr and pyrolysis temperature of 450 ^{o}C are presented in Table 2. The results presented were obtained after the simulation was run on the software at steady state. An excel worksheet was included in the process flow sheet to calculate the product yield percentages from the flow rates of the different products (mass basis).

The simulation results show a very good yield of oil from the pyrolysis process. In the model developed by Alla and Ali [6] for the pyrolysis of mixed plastic waste consisting of LDPE and other polymers, a liquid yield of 95.2% was obtained. This is in good agreement with the result of this work. Experimental works has been shown to produce noticeably less oil. Oil yields of 84.25% at 430^{0}C [27], 73% at 450^{0}C [18], 81.65% at 800^{0}C [11], 89.45% at 425^{0}C [20] and 90% at 400^{0}C [13] has been reported for LDPE pyrolysis.

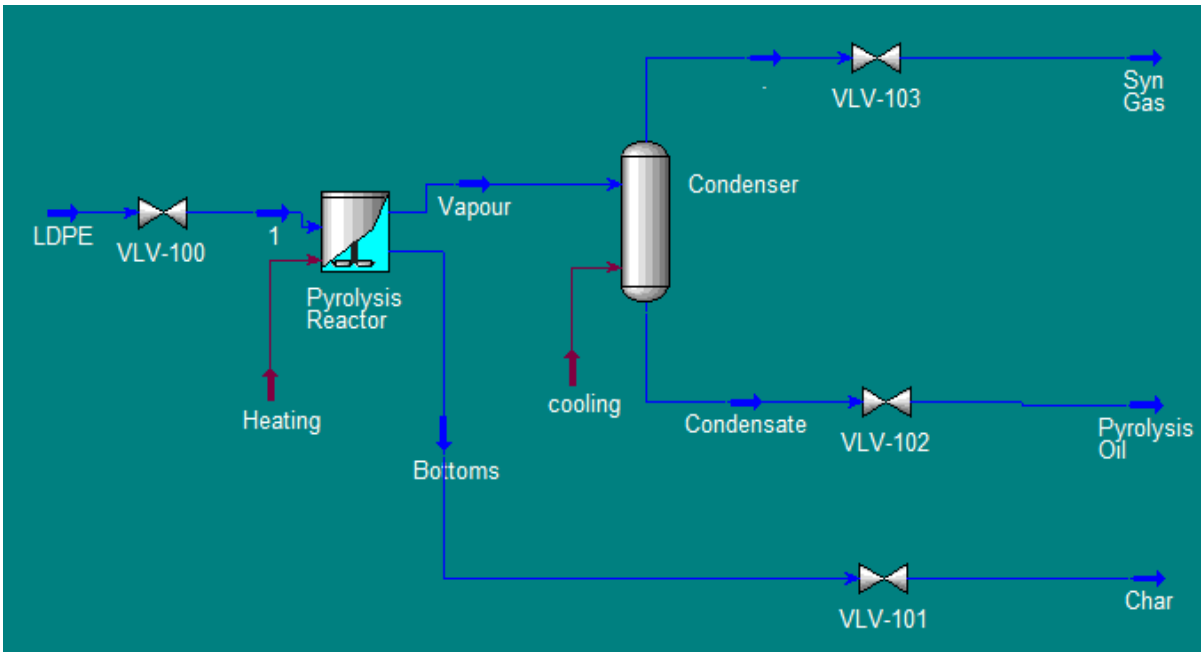


Figure 1: The process flow diagram of the steady-state simulation

Disparity in results is due to massive differences in heating rate, final pyrolysis temperature, reactor design and other extraneous factors. Simulation Liquid yields are significantly higher than experimental results as these can be considered as ideal systems.

Table 3: Pyrolysis Products Composition

Pyrolysis Product	Composition
Pyrolysis oil	C_8-C_{24}.
Char	Elemental Carbon only
Synthesis Gas	H_2, C1-C_4, traces of n-C_5 and n-C_6

The software also predicted the compositions of the reaction products as presented in Table 3. The Char obtained was composed of only elemental carbon. The synthesis gas was composed majorly of Hydrogen and C_1-C_4 hydrocarbons with traces of n-C_5 and n-C_6. The Pyrolysis oil was composed of all the higher hydrocarbon fractions present in the simulation (C_8-C_{24}). The product composition in Table 3 is consistent with experimental results [18, 20]. Low, Connor [18] reported from their experimental studies an oil composition of C_9-C_{25}. The properties of the pyrolysis oil were also computed by Aspen HYSYS. Simulated Liquid density of 766 kg/m^3 is similar to 750 kg/m^3 [13] and 750-800 kg/m^3 [18] from experimentally obtained oil. Also, oil kinematic viscosity of 3.103 cSt was computed in the simulation.

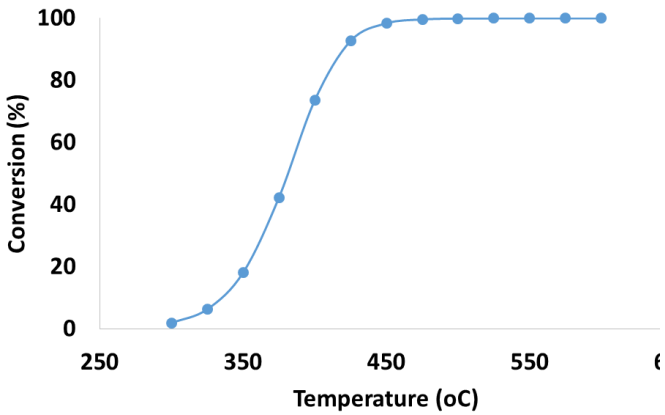


Figure 2: Effect of Temperature on Conversion

Figure 2 was obtained by varying reaction temperature in the simulation and monitoring actual reaction conversion from the reactor block. It can be summarised that product formation commences at about 300^{0}C and conversion is maximum at temperatures exceeding 450^{0}C. This curve is exactly the same as that obtained by Sharma and Ghoshal [24] and Bockhorn, Hornung [8]. It can be surmised form the plot that for the pyrolysis of waste low density polyethylene, the optimum reaction temperature (with reaction conversion in mind) is 450^{0}C.

4. CONCLUSION

Aspen HYSYS 2006 was used to simulate the pyrolysis of waste low-density polyethylene (LDPE) and the pyrolysis reaction was modeled by a continuous stirred tank reactor. The model serves as a reference system for predicting product yield, product composition and process behaviour/response to operating factors. At a feed rate of 10kg/hr, a pyrolysis temperature of 450^{0}C and at atmospheric pressure, 92.88% liquid yield was obtained. This has enforced the knowledge that LDPE pyrolysis can give a very good yield of liquid product and is a viable recycling technique. However, optimal reaction parameters (e.g. heating rate) and efficient reactor design (to ensure constant inert environment) must be implemented to get such fantastic results. The product composition, properties of the oil and conversion-temperature relationship from the simulation are in good agreement with experimental results. For the pyrolysis of waste low density polyethylene, the optimum reaction temperature as predicted by the simulation is 450^{0}C.

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