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# KINETICS STUDY OF POLYETHYLENE DEGRADATION IN BATCH REACTOR

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## Abstract

A kinetic study on the thermal and catalytic degradation of waste plastics was carried out under atmospheric pressure. Thermal gravimetric analysis (TGA) technique was used to identify the pyrolysis temperature used in this work. The cracking of waste polyethylene was carried out in vertical batch reactor at atmospheric pressure followed by catalytic conversion in horizontal fixed bed reactor, both the reactors being made of glass. Waste plastics pellets were fed in the vertical reactor and the reactor was heated to the desired temperature according to a predetermined ramp. The horizontal reactor was packed with catalyst and was maintained at a fixed temperature for vapour phase conversion of pyrolytic vapours. These vapours were subsequently condensed to obtain liquid products and C1-C5 gases. Weight loss curves have been generated using material balance and an empirical correlation for loss of weight plastics in the pyrolysis reactor has been proposed. In the present case the use of catalyst yields more of gaseous products and less of the liquid products as compared to the non-catalytic process. For kinetic study the end products were lumped into three fractions of monoaromatics, polyaromatics and non-aromatics hydrocarbons. Here one step and two step lumped kinetic models have been proposed for both non-catalytic and catalytic conversion of waste plastics. The one step and two step models contain three and six kinetic constants respectively and these have been determined from the experimental data.

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**Keywords:** Polyethylene, thermal cracking, catalytic cracking, kinetics, lumped model

## 1. Introduction

The consumption of plastics world over as well as in India is increasing at a rapid rate. This increased consumption has simultaneously resulted in generation of enormous amount of wastes, which being non biodegradable are environmental hazards. The usual methods of recycling and reuse like mechanical recycling, incineration and land filling have inherent disadvantages like turning enormous amount of land to waste, evolution of poisonous gases etc. Therefore their disposal in an environment friendly way has become a technological and social subject that has attracted a lot of attention from researchers, business people, environmental activists and the public in general. There are enough evidences in literature to suggest that chemical recycling of waste plastics has the potential to overcome the environmental problem concerned with the disposal of plastic wastes while simultaneously producing value added products. [1-5].

Waste polyethylene has been degraded into liquid and gaseous hydrocarbons with and without the use of catalyst by following a single stage two step process in involving melting, homogenization and vaporization of waste plastics in the first step and secondary conversion gaseous vapors in the second step followed by condensation to obtain liquid products. The kinetic parameters have been obtained for both catalytic and non-catalytic degradation.

## 2. Materials and Methods

### 2.1 Material:

The plastics (polyethylene) used in this study, is a high density polyethylene plant waste in pellet form having milky white colour. This plant waste is a low molecular weight by product accounting for about 1-5 % of the plant production.

The catalyst used in this study is a tailor made zeolite catalyst in extrudate form.

### 2.2 Procedure:

300 grams of waste plastic feed was pyrolyzed in an inert atmosphere. The pyrolysis unit was heated upto a fixed temperature (450 & 500 °C) according to a pre determined temperature ramp. The vapors from pyrolysis unit were subsequently passed through a fixed bed of catalyst and maintained at a constant temperature. The vapors were condensed in condensers maintained at a temperature of 4 °C and collected in the receiver.

The weight of the liquid hydrocarbons collected in the receiver and the residue from pyrolysis unit collected at the end of the experiment as well as the volume of uncondensed gases were recorded. The liquid hydrocarbon was characterized for aromatic content by super critical chromatography following ASTM D 5186 method and the composition of gas

was determined by GC analysis. The mass balance was confirmed after each experiment by equating the weight of feed taken to the sum of the weight of the liquid hydrocarbon, the residue in pyrolysis reactor and volume of uncondensed gases which was converted to corresponding weight based on their GC analysis.

### 3. Results and Discussion

#### 3.1 Effect of temperature on rate of degradation

It has been observed that the rate of degradation of plastics in the pyrolyzer depends upon the temperature and the mass remaining at any time in the pyrolyzer has been correlated

$$W(t) = W_0 * e^{-t^2 * 2 * 10^{-9} * (T-373) * 1.96}$$

Where,

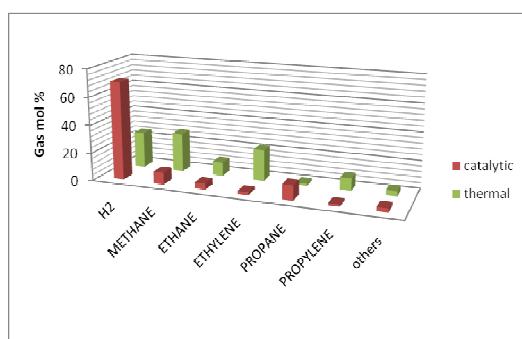
t : time in minutes

$W_0$  : Initial wt of feed

T : Temperature in °C

#### 3.2 Effect of temperature on nature of degraded products

The composition of uncondensed gases obtained with and without catalyst at different temperatures has been investigated. The net gas evolved drastically increases on increasing temperature and on addition of catalyst at the cost of liquid yield. The composition of gas as well liquid also changes with the addition of catalyst. The average molecular weight of uncondensable gases for the thermal case is 20.8 whereas molecular weight for the catalytic case is 11.6 mainly due to the presence of hydrogen. The aromatic content of liquid increases with the addition of catalyst.



Comparison of gas composition for the thermal and catalytic cases

#### 3.3 Kinetic model of waste plastics cracking

One step and two step lumped kinetic models were proposed including both thermal and catalytic cracking of waste plastics and rate constants for both models were studied under assumption that no mass transfer resistance inside and outside of catalyst. The rate constants were studied at 450 and 500 °C.

#### One step lumped model

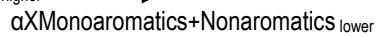
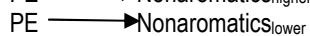
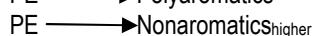
A one step kinetic model has been proposed based on cumulative weight of monoaromatics, polycyclic aromatic hydrocarbons and nonaromatics with time assuming the rate of formation of these lumps as a nth order reaction with respect to time the weight of plastics remaining in the reactor.i.e.



The order of reaction and rate constant were determined using derivative method.

#### Two step lumped model

An attempt at a two step model has also been made. The basic assumptions are as follows



The order of reaction and rate constants were determined using derivative method.

### 4. Conclusions

A correlation has been proposed for the rate of degradation with the temperature of the pyrolyzer. In the present case addition of catalyst increases the proportion of hydrogen in the uncondensed gases. The proposed one step model with three reaction rates constants is able to explain the thermal decomposition well and indicates an order transition takes place after a certain time for the formation of non-aromatic hydrocarbons. The two step mechanism models proposed with six reaction rate constants has the advantage as being more theoretically sound and modeling the real situation.

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