Catalytic Conversion of High Density Polyethylene (HDPE) Polymer as a means of recovering valuable energy content from the plastic wastes

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Abstract. A catalytic degradation of High Density Polyethylene (HDPE) polymer was carried out in a fixed-bed reactor at $400^{O}C$ using two sulfate modified Zirconium catalysts with aim of obtaining valuable and recyclable liquid products. The onset of degradation has moved from $420^{O}C$ for HDPE alone to less than $300^{O}C$ in the presence of the catalysts. The catalyst suppressed the bond energy, as low activation energy of 132.61 and 159.96 $KJmol^{-1}$ for CAT1 ($7\%SO_3$) and CAT2 ($3.5\% SO_3$) respectively, was observed. Further results from catalytic degradation shows how the catalysts improved the polymer degradation by achieving high conversion of about 99.8% with CAT1($7\%SO_3$) promoting high percentage of gaseous products(68%) of mainly aromatics and CAT2($3.5\%SO_3$) promoting high liquid products(about 53%) of mainly olefinic compounds. Generally, the carbon number distribution of the liquid products is within the gasoline range with composition of mainly aromatic and olefinic compounds with traces of naphthenic and aliphatic compounds which indicates the applicability of the products both as fuel and industrial raw material. Therefore, the method can be use as an alternative recycling method for converting plastic waste to more valuable energy sources.

Keywords: HDPE polymer, plastic wastes, chemical recycling, fixed-bed reactor.

1. INTRODUCTION

Plastics light weight, durability and energy efficiency makes them an indispensable part of our everyday activities [1, 2]. Thus, the world's annual plastic consumption increased dramatically from around 2million tonnes in the 1950s to about 245 million tonnes in 2006 with a 10% increase yearly [2]. This why plastic wastes are increasing considerably and thereby contributes extensively to the problem of waste management. Various methods such as land filling, mechanical, biological and other chemical recycling approaches are already in place, but still appeared inadequate [3] or not in conformity with current environmental regulations [2]. Therefore, there is the need for better approach to handle the menace without necessarily creating more problems. In view of this, catalytic conversion which is a chemical recycling method that involves the conversion of polymers to recover useful liquid products may be the appropriate method [4].

Many studies on catalytic conversion of different types of plastic polymers to different products including chemicals and fuels, using different type of catalysts have been published [5-7]. The most widely used are Zeolite base catalysts such as ZSM-5 [7, 8,], silica, alumina [9], basic catalysts, such as $BaCO_3$ [10], Bimetallic catalyst Al-Zn composite [11], and FCC catalyst [12]. Even though, most of these catalysts worked in terms of plastic waste conversion, but still they are associated with either high cost of production or the operating condition may not be industrially feasible as high temperature and more residence time with low percentage conversion might be the case.

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This work is aim at catalytically converting high density polyethylene (HDPE) plastic into products that could be used as fuel and feed-stock for chemical industries using a sulfate modified zirconium catalyst in a fixed-bed reactor with emphases on high conversion and product selectivity at low temperature.

2. MATERIALS AND METHOD

2.1 Plastic polymer and Catalysts

The model high density polyethylene (HDPE) polymer sample with density of 0.952gmL^{-1} and degradation index 42g/10min was obtained from Sigma-Aldrich, UK while the catalysts CAT1(7%SO$_3$) & CAT2(3.5%SO$_3$) were obtained from MEL chemicals. The plastic and catalysts particle size was 125-150 and 75-100 micron, respectively. Prior to use all the catalysts were calcined at 550°C for three hours and cool down in desiccator.

2.2 Experimental procedure and analysis
2.2.1 Thermogravimetric analysis (TGA)

TG analysis was conducted on the plastic sample with and without catalyst in a Pyris 1 Thermal Gravimetric analyzer (TGA1) a product of Perkin-Elmer using a heating rate 10oC/min at 35-900OC in a nitrogen gas atmosphere with flow rate of 20 ml/min. HDPE plastic and its mixture with catalysts were weighed between 20-30 mg and placed in quartz crucibles.

2.2.2 Kinetic studies using TGA data

Kinetic study of the thermal and catalytic decomposition of plastic was determined from Thermogravimetric analysis (TGA) data. Apparent kinetic parameters analysed include activation energy and pre-exponential factors. These kinetic parameters were determined based on the fact that, thermal decomposition of polymers are generally assumed to be as in eq.1.

$$A(Solid) \rightarrow B(Volatiles) + C(Solid) \tag{1}$$
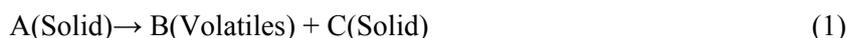
And the rate of polymer degradation is generally assumed to be proportional to the concentration of reactants which is defined as[13]:

$$r = -\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

And the extend of conversion; (α) is given as $\alpha = \frac{mo-mi}{mo-mf}$ \hfill (3)

By using Arrhenius equation: $k = Ae - (\frac{Ea}{RT}) \Rightarrow \frac{d\alpha}{dt} = kf(\alpha) = Ae - (\frac{Ea}{RT}) * f(\alpha)$ \hfill (4)

And for a constant heating rate, $\beta = \frac{d\alpha}{dT}, \Rightarrow \frac{d\alpha}{dt} = \frac{A}{\beta}e^{-(\frac{Ea}{RT})} * f(\alpha)$ \hfill (5)

After differentiating equation (5) separating variables, rearranging, integrating and taken the logarithm of the equation, equation (6) emerge: $ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = ln\left[\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right] - \frac{Ea}{RT}$ \hfill (6)

Because it is generally assumed that $\frac{RT}{E} << 1$ and $1 - \frac{2RT}{E} \approx 1$. Equation (6) now becomes:
Therefore, plot of:

$$ln\left[-\frac{ln(1-\alpha)}{T^2}\right] \; versus \; \frac{1}{T} \qquad (\text{for } n = 1)$$

By selecting appropriate reaction order, the plot will give straight line with -E/R as slope which can be use to obtain the activation energy and the pre-exponential factor A from the intercept. In this work a first order has been selected, as it has already been established that polymer degradation obeys first order kinetics [15].

2.2.3 Catalytic Degradation

The catalytic degradation was carried out in a horizontal stainless steel fixed-bed tube (Figure 1), in which the polymer and the catalyst at appropriate ratio were mixed thoroughly and transferred in to a crucible boot which was placed in the tube and heated to 400°C at heating rate approximately 20°Cmin^{-1} using nitrogen of flow rate 30cl min^{-1} to purge the products formed. Prior to heating, a nitrogen gas was passed through the reactor for 20 min to make the environment inert. The condensable liquid was collected through special cooling tarps. The gaseous products that pass were collected using gas bags. The percentage

yield of liquid product was calculated as the mass of a liquid collected divided by the initial mass of the polymer while that of coke (residue) yield was calculated by dividing the mass of unconverted polymer (minus the catalyst weight) by the original polymer weight.

2.2.4 Product analysis

The liquid products were analysed with Variant CP-3800 Gas Chromatogram interfaced to a 1200 Quadrupole mass spectrometer. About 1µl of the oil dissolved in dichloromethane (DCM) was injected Eluted components were monitored in both full scan mode and selected ion monitoring. Each peak was identified based on the MS software library.

Table 1. Characteristics of the HDPE polymer used

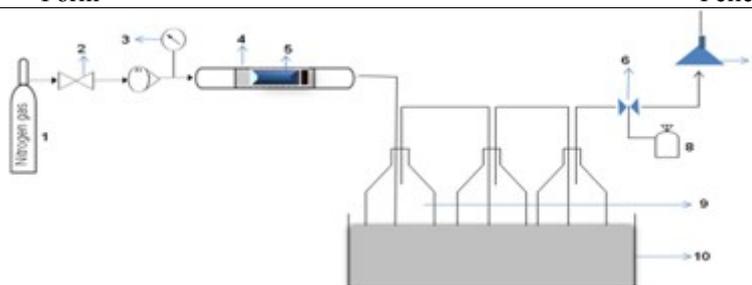| CHARACTERISTICS	
Proximate analysis	Wt (%)
Volatile matter	96.83
Ash	3.17
Elemental Analysis	(Wt.% dry ash free)
C	85.66
H	14.07
N	0.00
S	0.00
Physical properties	
Density	0.952gmL-1
Degradation index	42g/10min
Colour	White
Form	Pellet

Figure1. Schematic diagram of fixed-bed rector used for catalytic degradation of HDPE plastic polymer; 1. Nitrogen gas supply, 2. Mass flow control, 3. Gas flow meter, 4. Reactor, 5. HDPE + catalyst, 6. Two-way control valve 7. Exhaust gas trap, 8. Gas bag, 9. Liquid trap, 10. Cooling trap made up of ice bath.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric analyses (TGA)

Figure 1 is TGA curves illustrating the HDPE polymer degradation in the presence two catalysts (CAT1 (7%SO_3) and CAT1 (3.5% SO_3)) and HDPE alone. Comparing the curves from this figure, it can be deduce that with CAT1 and CAT2 the degradation commenced at considerably lower temperature even below 200oC and also about 92% conversion was achieved at 460°C while in the absence of any catalyst the HDPE degradation commenced only at about 420°C with only 3% at 460°C. This indicates that, CAT1 (7%SO_3) and CAT1 (3.5% SO_3) are very active catalysts and therefore suitable for polymer degradation.

3.2 Kinetic studies

Table 2 gives the summery of kinetic parameters calculated where the apparent activation energy of the HDPE polymer was found to be 342KJmol-1which is within the range value reported elsewhere [13, 14], but addition of the catalysts shows a dramatic reduction of the activation with lowest of 132.61 and 159.996 kJmol^{-1} when CAT1 (7%SO_3) and CAT2 (3.5%SO_3) were used, respectively. This indicates that, apart from being selective, the catalyst also enhances the reaction rate by almost twofold as confirmed by catalytic degradation using fixed-bed reactor.
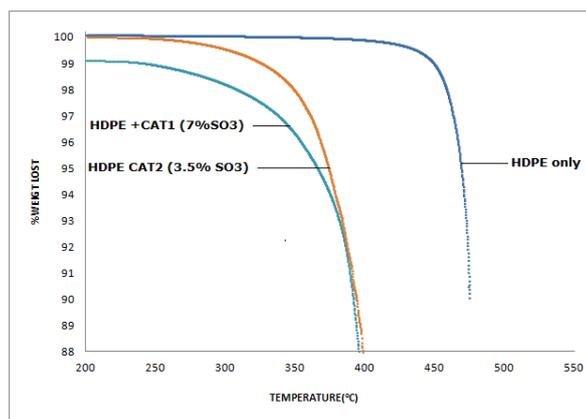
Figure 2. TGA curves comparing catalysed and unanalysed HDPE polymer degradation.

Table 2. Apparent kinetic parameter derived from TGA data

Sample	Activation Energy, Ea(KJmol-1)	Frequency Factor, A (S^{-1})	Correlation coefficient(R^2)
HDPE	342.95	5.22×10^{19}	0.9955
HDPE+ CAT1 (7%SO_3)	132.61	1.46×10^6	0.9924
HDPE+CAT2 (3.5%SO_3)	159.96	2.22×10^8	0.9959

3.3 Conversion, Yield and selectivity

The results catalytic polymer degradat on which include overall conversion, products yield (liquid and gases), and selectivity to oil are summarised in Table 3. From the Table, it is evident that CAT1 (7%SO_3) and CAT2 (3.5% SO_3) give prominent conversion of about 99.9% and in terms of product yield; a high liquid yield was observed when CAT2 (3.5% SO_3) was used while CAT1 (7%SO_3) gives high gas yields. This indicates that CAT1 (7% SO3) has high activity which promote gaseous product even at lower temperature of 400°C which could be related to its high acidity that probably led to end-chain scission which gives rise to light hydrocarbon [15,16]. However, CAT2 (3.5% SO_3) gives a better selectivity to liquid which probably due to low sulphide content leading to moderate acidity. This result is far from conclusion as optimisation of various reaction parameters has not been conducted. However one can unequivocally say that, these catalysts are promising catalysts going by the highest conversion of about 99% achieved at just 400°C in only 30 min.

Table 3. Comparison of the product yield of HDPE catalytic degradation at 400OC for the two catalysts.

Parameters	CAT1 (7%SO_3)	CAT 2 (3.5%SO_3)
% Conversion	99.98	99.96
% Oil Yield	34.31	53.00
% Gas yield	65.68	46.98
% Residue	0.01	0.02

3.4 Liquid Product analyses

Figure 2 compares chromatograms of the oils obtained from catalytic degradation of HDPE plastic polymer using the two catalysts. From the Figure, different peaks which are representing different compounds in the range of C7-C12 were detected. This indicates that the composition of the oil obtained using both catalysts differs but still within the gasoline range and the oil composed of broad mixture of hydrocarbon compounds consisting of mainly paraffinic, olefins naphthenic and aromatic which in line with GC/MS analysis reported from previous works published using other catalysts [10]. Interestingly C7, C12, C13 and C14 compounds were all detected in oil from CAT2 (3.5% SO_3) but none was found in the oil from CAT1 (7% SO_3). However, the composition of the liquid products from CAT1 (7% SO_3) contains mainly aromatics (70%) while oil from CAT2 (3.5% SO_3) largely contains the olefins (75%). This indicates that CAT1 is possibly promoting mainly aromatic products via aromatisation through dehydrocyclisation of the hydrocarbon fragments formed while CAT2 (3.5% SO_3) accelerates the formation of olefins and naphthenes but inhibits aromatisation which could have been resulted through isomerisation of the carbocation fragment

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via hydrogen atom shift that may give rise to unsaturated hydrocarbons[17]. The composition of the gaseous products composed broad mixture of gases ranging from C1-C7 with C6 and C7 very negligible and very little or no amount of methane both catalysts. This indicates that, catalyst compositional difference does not affect the gas composition.

In overall, this indicates that, the liquid products obtained from the two catalysts could be used as a transport fuel after some modifications such as hydrogenation are carried out. The liquid product from CAT1 (7%SO₃) which contains high amount of aromatic and some naphthenic compounds will a good motor fuel as aromatic and naphthenic improve the quality of gasoline by increasing the Octane number. While for oil obtained using CAT2 (3.5%SO₃) which has high olefinic and some aliphatic and naphthenic compounds, it could be use as a feedstock for petrochemical industries. This is because; olefinic compounds are industrially more attractive than even the pure saturated compounds [18], as they are intermediaries of many valuable and expensive chemicals. Therefore, both catalysts promote liquid that are of industrial benefit.
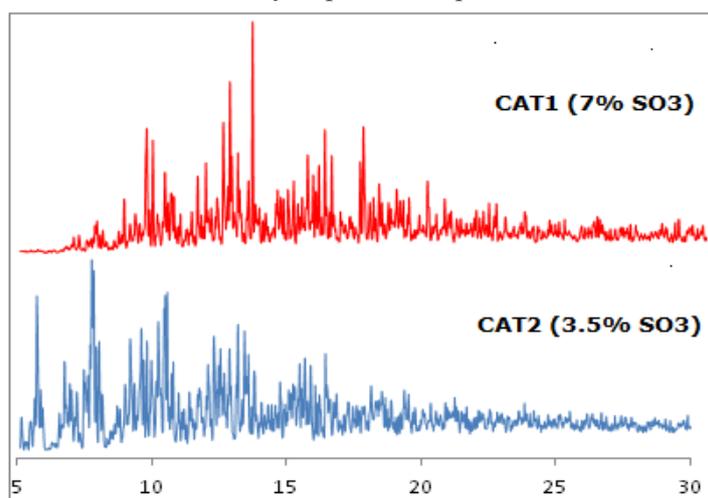

Figure 3. GC/MS chromatograms of the oil product from catalytic degradation of HDPE plastic polymer

Table 4. Composition of the oil obtained from catalytic degradation of HDPE plastic polymer

Composition	CAT1(7%SO₃)	CAT2(3.5%SO₃)
Aromatics	55%	0
Olefinic	30%	65%
Naphthenic & Aliphatic	15%	35

4. CONCLUSIONS

The catalytic degradation of HDPE polymer was found to be a useful method of managing plastic waste and obtain valuable products. The results obtained indicate that the catalysts used improved the polymer degradation greatly by achieving high conversion at temperature of400°C. The % yield and products composition varied grearly depending on the amount of sulfate in the catalyst. High % conversion (about 99.8%) was achieved for both CAT1 (7%SO₃) and CAT1 (3.5% SO₃). Thus, CAT1 (7% SO₃) appears to be favouring high percentage of gaseous products (68%) and liquid products (32%) of mainly aromatics while CAT2 (3.5% SO₃) is promoting the high liquid products (about 53%) of mainly olefinic compounds and some gaseous products (about 47%). The two catalysts seemed to be following different mechanisms.

Consequently, the high % conversion indicates that, the catalysts can be used efficiently even at industrial scale, also having all the liquid products with carbon number distribution within the gasoline range which consist of mainly aromatic and olefinic compounds indicates the applicability of the products both as fuel and industrial raw material. Despite the work is still at preliminary stage it can conveniently deduced that this method would offer a great deal of plastic polymer recycling to many valuable and renewable energy option. Thus, can be use as an alternative recycling method for converting plastic waste to valuable energy sources

5. Acknowledgement

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