ABSTRACT

Catalyst synthesized from coal fly ash (CCFA) was added to High density polyethylene (HDPE) polymer and degraded (catalytic thermolysis) in a semi batch reactor at 420°C with the purpose to convert waste HDPE plastic to valuable liquid fuels. Its performance on the degradation was compared with Silica-Alumina catalyst (CSA). The TGA results exposed that the degradation was initiated from 420°C for HDPE to less than 310°C in the presence of the catalysts. The catalyst improved the polymer degradation by achieving high conversion of more than 95%. These catalysts appeared to promote different product compositions based on GC/MS results. The selectivity of CCFA was higher towards gaseous products (62%) and the liquid of mainly aromatics was found to be about 34%, whereas CSA promoted high liquid products (54%) and the gaseous product was found to be about 41% of mainly olefinic compounds. A kinetic analysis by TGA was also carried out using a dynamic model. It offered reliable kinetic parameters for the catalytic degradation of HDPE over catalyst. Thus, catalytic conversion using cost effective CCFA catalyst may be used as an alternative method for recycling plastic wastes to valuable fuel range hydrocarbons.

KEYWORDS: HDPE, CCFA, CSA, TGA, GC/MS, Kinetic Analysis

INTRODUCTION

The outstanding assets of plastics such as lightweight, stability, sustainability and processing make them an essential part of our daily need[1] [2]. Thus, the world's annual plastic consumption increased dramatically from around 2 million tons in the 1950s to about 245 million tons in 2006 with a 10% increase yearly[2]. Accordingly, plastic wastes are increasing rapidly and contribute widely to the problem of waste management. Several methods, such as land filling, mechanical, biological and other chemical recycling approaches are already in place, but still appear unusual or do not conform to current environmental regulations act[2]. Therefore, there is the need for healthier method to handle the threat without necessarily creating more problems.

In view of this, catalytic thermolysis that is a chemical recycling method that involves the conversion of polymers to recover useful products may be the appropriate method [3]. Many research on catalytic conversion of different types of plastics and polymers to different products, including chemicals and fuels using different type of catalysts have been published [4]-[5]. Different catalysts were reported for catalytic conversion of plastic wastes. These contain ZSM-5 [5], Silica-Alumina [6], basic catalysts, such as BaCO₃ [7], Bimetallic catalyst, Al-Zn composite [8], FCC catalyst [9], and meso-porous catalysts, such as Al-MCM-41.

Conesa et al. (1994) studied the production of gases from polyethylene five nominal temperatures (ranging from 500°C to 900°C) using a fluidized sand bed reactor. From the study of HDPE pyrolysis in a fluidized sand bed reactor, they have found that the yield of total gas obtained increased in the range 500-800°C from 5.7 to 94.5%, at higher temperatures. [10] Jan et al. (2010) studied the degradation of waste high density polyethylene into a liquid fraction thermally and catalytically using MgCO₃ at 450°C in a batch reactor. Different conditions like temperature, time and catalyst ratio were optimized for the maximum conversion of HDPE into a liquid fraction. [11] Garforthet al. (1998) studied the catalytic
pyrolysis of high density polyethylene in a laboratory fluidizedbed reactor operating in the 290°C-430°C range under atmospheric pressure. The catalysts used were HZSM-5, Silicalite, HMOR, HUSY and SAHA and the yield of volatile hydrocarbons (based on the feed) was typically SAHA<HMOR<HUSY<HZSM-5.\[12\]

Manos et al. (2000) studied the catalytic degradation of HDPE to hydrocarbons over different zeolites. The product range was typically between C\(_3\) and C\(_{15}\) hydrocarbons.\[13\]

Zeolites based catalysts are extremely reported for this process. They work efficiently in terms of high conversion of plastic wastes at lower temperature and decrease the activation energy. In addition, they are very costly and require long processing time. Thus, the cost of production involving these catalysts may be excessive. OJHA K, et al., concluded that coal fly ash can be used to synthesize zeolite by alkali fusion followed by hydrothermal treatment. Mullite and quartz present in the fly ash are the sources of aluminum and silicon, respectively, for zeolite formation\[14\].

This work targets on catalytic thermolysis of HDPE polymer into liquid hydrocarbons over cost effective catalyst synthesized from coal fly ash and commercial Silica-Alumina catalyst. A kinetic analysis was also carried out using a dynamic model. It offered reliable kinetic parameters for the catalytic thermolysis of HDPE over catalysts.

**MATERIALS & METHODS**

**Materials**

High-density polyethylene (HDPE) sample with density of 0.95 gm/L and degradation index 40g/10min was obtained from Reliance petrochemicals, India. The two catalysts used were synthesized coal fly ash (CCFA) and Silica-Alumina (CSA). CCFA was prepared in laboratory by coal fly ash collected from B.T.P.S., Bokaro, Jharkhand, India. Silica-Alumina (Si/Al = 4.5) CSA catalyst was obtained from LobaChemie, India. The physical and chemical properties of the polymer are given in Table I. Thermo-gravimetric analysis (TGA) was conducted on the polymer samples with and without the catalyst.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate Composition</td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>97.25</td>
</tr>
<tr>
<td>Ash</td>
<td>2.75</td>
</tr>
<tr>
<td>Elemental Composition</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>85.6</td>
</tr>
<tr>
<td>H</td>
<td>14.2</td>
</tr>
<tr>
<td>Physical Properties</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.95gmL(^{-1})</td>
</tr>
<tr>
<td>Degradation index</td>
<td>40g/10min</td>
</tr>
<tr>
<td>Colour</td>
<td>White</td>
</tr>
<tr>
<td>Form</td>
<td>Pellet</td>
</tr>
<tr>
<td>Polymer sized used</td>
<td>75-100 micron</td>
</tr>
</tbody>
</table>

**Preparation of Catalysts**

Silica-Alumina (Si/Al= 4.5) CSA catalyst was calcined at 500°C for three hours and then kept at room temperature in a desiccator. Coal fly ash sample was first screened through a BSS Tyler sieve of 80-mesh size to eliminate the larger particles. The unburnt carbons (6-8%) along with other volatile constituents present in fly ash were removed by calcination at high temperature. Fly ash samples were then treated with hydrochloric acid to increase their activity in zeolite formation. The acid treatment helped to de-aluminate the fly ash and removed iron to a certain extent, thereby increasing the activity, thermal stability and acidity of the zeolite, all aiming for better catalytic applications. Mixture of
sodium hydroxide and fly ash (calcined and HCl treated) in a pre-determined ratio, was milled and fused in a stainless steel tray at high temperature for 16 hours.

Figure 1: Flow Diagram of the Synthesis Process of CCFA

The resultant fused mixture was then cooled to room temperature, pulverized and added to water. The slurry thus obtained was agitated mechanically in a glass beaker for several hours. It was then kept at around 90°C for 12 hours without any disturbance. The flow diagram of the synthesis process is shown in Figure 1. The resultant precipitate was then repeatedly washed with distilled water to remove excess sodium hydroxide, filtered and dried.

Experimental Procedure & Analysis
Thermo Gravimetric Analysis (TGA)

The kinetics of HDPE degradation at non-isothermal conditions has been investigated using TGA at various heating rates between 10 and 50°C/min in inert a nitrogen gas atmosphere with a flow rate of 20 ml/min. The HDPE polymer and its mixture with catalysts were weighed 25 mg and placed in quartz crucibles.

Kinetic Analysis Using TGA Data

Kinetic study of the thermal and catalytic degradation of HDPE polymer was determined from Thermo-gravimetric analysis (TGA) data. The activation energy and pre-exponential factors were determined based on the thermal decomposition of polymers from equation (1).

\[ A \text{ (Solid)} \rightarrow B \text{ (Volatiles)} + C \text{ (Solid)} \]  

(1)

The rate of polymer degradation is considered proportional to the concentration of reactants defined in Equation 2 \[ ^{[15]} \]. Where \( \alpha \) is the extent of polymer conversion with \( m_i; m_a \) and \( m_f \) are the initial, actual and final weight of the HDPE polymer, respectively, \( t \) is the time taken, \( \beta \) is the heating rate, \( T \) is the temperature and \( R \) is the gas constant whose value is 8.314 kJ mol\(^{-1}\)K\(^{-1}\).

\[ r = -\frac{d\alpha}{dt} = k f(\alpha) \]  

(2)

The extend of conversion \( (\alpha) \) is assumed as

\[ \alpha = \frac{m_i - m_f}{m_i - m_f} \text{where, } f(\alpha) = (1 - \alpha)^n \]  

(3)

By Arrhenius equation, \( k = Ae^{-\frac{E_a}{RT}} \). Equation 2 turn out to be,

\[ \frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} \times (1-\alpha)^n \]  

(4)
Still, as \( \int_0^\infty e^{-\frac{b}{x^2}} \, dx \) has no exact integral, \( e^{-\frac{b}{x^2}} \) can be expressed as an asymptotic series and integrated by overlooking high-order terms. Thus, Equation (7) is developed as,

\[
\frac{1-\left[1-\frac{k}{k-1}\right]^n}{T^2} = \frac{\AR^2}{\beta E} \left[1 - 2\AR \right] e^{-\frac{\beta E}{\AR T}}
\]

(7)

By taking the natural logarithm of both sides of Equation (7), Equation (8) is developed as,

\[
\ln \left[ \frac{1-\left[1-\frac{k}{k-1}\right]^n}{T^2} \right] = \ln \left[ \frac{\AR^2}{\beta E} \left[1 - 2\AR \right] \right] - \frac{\beta E}{\AR T}
\]

(8)

However, usually it is expected as,

\[
\frac{RT}{E} \ll 1 \text{ and } 1 - \frac{2RT}{E} \approx 1
\]

Thus, Equations (9) and (10) for \( n=1 \) and \( n=2 \) respectively, are developed as,

\[
\ln \left[ \frac{1-\left[1-\frac{k}{k-1}\right]}{T^2} \right] = \ln \left[ \frac{\AR^2}{\beta E} \right] - \frac{\beta E}{\AR T} \left( n = 1 \right)
\]

(9)

&

\[
\ln \left[ \frac{1-\left[1-\frac{k}{k-1}\right]}{T^2} \right] = \ln \left[ \frac{\AR^2}{\beta E} \right] - \frac{\beta E}{\AR T} \left( n = 1 \right)
\]

(10)

In this work, a first order \( (n=1) \) has been selected, as polymer degradation obeys first order kinetics \(^{15}\). Thus, a plot of \( \ln \left[ \frac{1-\left[1-\frac{k}{k-1}\right]}{T^2} \right] \) vs. \( \frac{1}{T} \) was used to calculate the apparent kinetic parameters. The plot gave a straight line with \( -\frac{\beta E}{\AR} \) as slope. Activation energy was calculated with the help of slope and the pre-exponential factor \( (A) \) from the intercept on the y-axis.

**Catalytic Thermolysis of HDPE**

The catalytic thermolysis of HDPE was carried out in a semi-batch reactor. The thermolysis setup used in this experiment is shown in Figure 2. It consists of a semi-batch reactor (steel made) of volume 2 liters, vacuum-packed with two outlet tubes towards vacuum pump and condenser. Vacuum pump with a gage is attached to the reactor so as carryout the reaction in vacuum.

The condenser is attached to collect condensed liquid hydrocarbons and gases separately. The reactor is heated externally by an electric furnace, with the temperature being measured by a Cr-Al: K type thermocouple fixed inside the reactor, and temperature is controlled by an external controller. HDPE and Catalyst in a ratio of 1:4 were loaded in each catalytic thermolysis reaction. The experiments were carryout several times to get appropriate results. The condensable liquid products were collected through the condenser and weighed. The uncondensed gases were separated out in a bladder from condenser.

After thermolysis, the solid residue left inside the reactor was weighed. Then the weight of gaseous/volatile product was calculated from the material balance. 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. Samples for testing are shown in Figure 3.
Liquid Products Analysis

The liquid products were analyzed with Gas Chromatogram interfaced mass spectrometer. About 1µl of the oil dissolved in dichloromethane (DCM) was injected. The eluted components were monitored in both full scan mode and selected ion monitoring.

Gaseous Products Analysis

The gaseous products were analyzed using a Gas Chromatographer fitted with FID and TCD detectors. The hydrocarbon gases were analyzed by FID. Helium was used as the carrier gas.

RESULTS AND DISCUSSIONS
Thermo-Gravimetric Analyses (TGA)

Figure 4. Shows the TGA curves showing the HDPE polymer degradation in the presence of the two catalysts CCFA, CSA, and HDPE. On studying the curves it can be assumed that with CCFA and CSA, the degradation commenced at considerably lower temperature even below 200°C compared to 420°C for HDPE alone. Also more than 95% conversion was achieved at 410°C for both catalysts contrasting to only 3% conversion for HDPE alone. This indicates that CCFA and CSA are very active catalysts and therefore suitable for polymer degradation.

![Figure 4: TGA Curves Comparing HDPE Polymer Degradation with and without any Catalysts](image)

Kinetic Studies

The summary of the kinetic parameters considered where the apparent activation energy of the HDPE polymer was found to be 320 KJ/mol is shown in table 2. This value is within the range of values reported elsewhere [16][17]. The addition of the catalysts shows a dramatic reduction in the activation energies down to 138.42 and 162.56 KJ/mol when
CCFA and CSA are used, respectively. This indicates that, these catalysts enhanced the reaction rate by double. They also played a significant role in product selectivity, as confirmed from the products of catalytic degradation using a semi-batch reactor.

**Table 2: Apparent Kinetic Parameters Derived from TGA Data**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy, E_a (kJmol⁻¹)</th>
<th>Frequency Factor, A (S⁻¹)</th>
<th>Correlation Coefficient (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>320</td>
<td>(5.22)10¹⁹</td>
<td>0.9955</td>
</tr>
<tr>
<td>HDPE + CCFA</td>
<td>138.42</td>
<td>(1.46)10⁶</td>
<td>0.9924</td>
</tr>
<tr>
<td>HDPE + CSA</td>
<td>162.56</td>
<td>(2.22)10⁸</td>
<td>0.9959</td>
</tr>
</tbody>
</table>

**Conversion & Product Analysis**

The results of the catalytic thermolysis which contain overall conversion, products yield (liquid & gases), are briefed in Table 3. From Table 3, it is marked that CCFA and CSA give noticeable conversion of more than 95% at 420°C in terms of products yield. However, a high liquid yields can be observed when CSA is used whereas CCFA gave high gas yields. This indicates that CCFA has high activity that promote gaseous product than CSA and might be related to its high acidity, which probably led to end chain scission that gave rise to light hydrocarbon.[18] However, CSA gave an indication of better selectivity to liquid.

**Table 3: Comparison of the Products Yield of HDPE Catalytic Thermolysis at 420°C**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CCFA</th>
<th>CSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Conversion</td>
<td>95.84</td>
<td>95.56</td>
</tr>
<tr>
<td>% Oil Yield</td>
<td>34.08</td>
<td>53.94</td>
</tr>
<tr>
<td>% Gas yield</td>
<td>61.76</td>
<td>40.62</td>
</tr>
<tr>
<td>% Residue</td>
<td>4.16</td>
<td>4.44</td>
</tr>
</tbody>
</table>

Although optimization of several reaction parameters have not been escorted, these catalysts are however, capable to give the maximum conversion of more than 95% attained at just 420°C in 45 minutes only. GC/MS analysis of the oils obtained from catalytic degradation of HDPE plastic polymer using the two catalysts are shown in figure 5. From the figure, different peaks that are representing different compounds in the range of C₇-C₁₄ were marked. This indicates that the oil composition obtained using both catalysts persist within the gasoline range and vary each other, the mixture of hydrocarbon compounds consisting of mainly paraffinic, olefins, naphthenic and aromatic which could have been resulted through isomerization of the carbonium ions fragment through hydrogen atom shift, that may offer unsaturated hydrocarbons.[20]
Remarkably C7, C12, C13 and C14 compounds were all detected in oil from CSA but were fewer found in the oil from CCFA. Still, it can be seen from Table IV that the composition of the liquid products from CCFA contains mainly aromatics (46%) whereas CSA contains largely olefinic hydrocarbon (63%).

This indicates that CCFA is possibly promoting mainly aromatic products through aromatization reaction. Whereas CSA accelerates, the formation of largely olefinic group of compounds and obstructs aromatization.

Table 4: Oil Product Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>CCFA</th>
<th>CSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>46%</td>
<td>1%</td>
</tr>
<tr>
<td>Olefinic</td>
<td>28%</td>
<td>63%</td>
</tr>
<tr>
<td>Naphthenic &amp; Aliphatic</td>
<td>26%</td>
<td>36%</td>
</tr>
</tbody>
</table>

Entirely this specifies that, the liquid products obtained from the two catalysts could be used as a transport fuel after some minor alterations. The liquid product from CCFA that contains high amount of aromatic and some naphthenic compounds could be a good engine fuel since aromatic and naphthenic compounds improve the quality of gasoline by increasing the Octane number. While for oil obtained using CSA which has high olefinic and certain paraffinic and naphthenic compounds, could be in addition used as a feedstock for petrochemical industries. Olefinic compounds are industrially more attractive than even the pure saturated compounds [19], as they are mediators of many valuable and expensive chemicals. Accordingly, both catalysts promote catalytic thermolysis of HDPE, and the catalyst synthesized from coal fly ash (CCFA) is appreciable.

Gaseous Products Analysis

GC chromatogram of the gaseous products showing peaks representing the components of the gas from each catalysts shown in figure 6. From the figure, it can be seen clearly that the gases from CCFA & CSA contains broad mixture of gases ranging from C1-C7. However, C3 (propane and propene), C4 (n-butane, iso-butane, bute-1-ene, bute-2-ene and isobutene), and C5 (n-pentane, pent-1-ene and isopentane) are more noticeable. Though, both C1 (Methane) and C2 appear very negligible, the gaseous products from both the catalysts are still of commercial value and could be used as a source of energy for heating the reactors thereby reducing the cost of the process.

Figure 6: GC Chromatograms of the Gaseous Products

CONCLUSIONS

The catalytic thermolysis of HDPE polymer over CCFA is found appreciable. The kinetic results from TGA revealed that both CCFA & CSA catalysts improved the reaction rate probably by suppressing the bond energy and subsequently reducing the activation energies from 320 KJ/mol to 138.42 and 162.56 KJ/mol for CCFA and CSA,
respectively. The catalysts also improved the polymer degradation greatly by achieving high conversion at a temperature of 420°C. The conversion, achieved for CCFA and CSA were 95.84 and 95.56 %, respectively. The products composition varies significantly depending on acidity and the pore size of the catalyst. CCFA favors high yield of gaseous products (62%), and the liquid products (34%) is found mostly aromatic compounds. CSA promotes high liquid products (54%) of composition that is mainly olefinic compounds, and gaseous products (about 41%). The two catalysts seemed to be following different mechanisms. Therefore, the high conversion obtained by the catalysts indicates that, the catalysts can be used efficiently as fuel and industrial raw material both. The synthesized coal fly-ash catalyst is very much cost effective in comparison to commercial zeolite used in catalytic thermolysis. Therefore, it can be deduced that the synthesized catalyst CCFA would offer a great deal of plastic polymer recycling and can be used as an alternative recycling method for converting plastic waste to valuable energy sources.

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REFERENCES


