Influence of Process Conditions on Syngas Production from the Thermal Processing of Waste High Density Polyethylene

Juniza Md Saad, Mohamad Anas Nahil and Paul T. Williams*

Energy Research Institute
University of Leeds, Leeds, LS2 9JT, UK
(Tel: #44 1133432504; Email: p.t.williams@leeds.ac.uk)

Abstract: A range of process conditions, including the type of reactor, the reacting atmosphere and the presence of catalyst, and their influence on the production of syngas i.e. hydrogen and carbon monoxide, from the thermal processing of waste high density polyethylene (HDPE) has been investigated. Pyrolysis in the presence of nitrogen and in the presence of carbon dioxide, two-stage pyrolysis-steam reforming and carbon dioxide/catalysis process conditions were investigated in relation to gas composition and particularly hydrogen and carbon monoxide yield. The influence of addition of a Ni-Mg-Al catalyst in the second reactor was also investigated. It was found that a two-stage pyrolysis at 500 °C, followed by second stage reaction at 800 °C resulted in a significant increase in hydrogen production. With the addition of carbon dioxide, the two stage process also increased carbon monoxide yield in addition to hydrogen. Addition of steam into the second stage reactor with the carbon dioxide produced a further increase in hydrogen production. Also, the presence of a Ni-Mg-Al catalyst in the second reactor increased the amount of hydrogen and carbon monoxide produced.

Keywords: High-density polyethylene; Waste; Carbon dioxide reforming; Gasification; Catalyst; Hydrogen
1. Introduction

There is current interest in the production of syngas from waste materials and in particular from waste plastics [1-5]. Pyrolysis and gasification of waste plastics is a promising route to produce high yields of a hydrogen-rich syngas. Pyrolysis of plastics produces low yields of hydrogen [6,7]. However, two-stage processing of waste plastics which combines thermal degradation of the plastic in a first stage pyrolysis step followed by gasification/reforming in a second stage, usually in the presence of catalysts generates high yields of hydrogen [8-10]. The gasification process produces reactions of the volatile products that are released from the pyrolysis process and recombines them to produce synthesis gas. The addition of steam via steam reforming of the waste plastic is recognized to be effective for hydrogen production through promotion of the water gas shift reaction [11]. Compared with steam reforming, studies on carbon dioxide reforming, also known as dry reforming, are limited especially on waste plastic.

The use of carbon dioxide for hydrocarbon reformation is of current interest because carbon dioxide is known to be a cost effective, recyclable and a toxic-free carbon source. In addition, the concerns around the increasing levels of carbon dioxide in the atmosphere particularly arising from anthropogenic activities has resulted in research into carbon capture schemes which are likely to generate large quantities of carbon dioxide which has the potential for use, rather than sequestration [12].

Widespread studies have been made specifically on methane dry reforming with carbon dioxide to synthesis gas [13-16]. One of the reasons for such interest is
because methane reforming with carbon dioxide produces synthesis gas with a ratio close to unity i.e., $H_2/CO = 1$ which has been suggested to be beneficial for the production of Fischer – Tropsch liquid hydrocarbon and oxygenate \cite{17-19}. Tsang et al. \cite{16} reported that the dry reforming of methane is more endothermic than steam reforming because it is thermodynamically favoured above 913K. Bulushev \cite{20} also suggested that the dry reforming process has to be performed at high temperature and low pressure to achieve maximum conversion because of the highly endothermic nature of the reaction.

In this paper, the influence of process parameters on the yield of syngas, i.e. hydrogen and carbon monoxide from waste high density polyethylene has been investigated. The yield of syngas from pyrolysis in nitrogen and carbon dioxide are compared, followed by comparison with two-stage pyrolysis-gasification/reforming. Further investigations on syngas production from carbon dioxide reforming of high-density polyethylene using the two-stage reactor with the addition of steam and Ni-Mg-Al catalysts were also carried out. A Ni-Mg-Al catalyst was used in this research since this catalyst has been shown to be effective, with good catalytic and stability results during our previous work on the steam reforming of waste plastics to produce a hydrogen-rich syngas \cite{8,21,22}.

2. Materials and Methods

2.1 Materials.

High-density polyethylene (HDPE) was obtained as 2 mm waste polymer pellets provided by Regain Polymers Limited, UK.
The Ni-Mg-Al catalyst with molar ratio of 1:1:1 was prepared by the rising-pH technique according to the method reported by Garcia et al. [1]. Ni(NO$_3$)$_2$·6H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were dissolved in 200 ml deionised water with moderate stirring at 40 °C. Ammonium solution was then added to the aqueous solution until the pH value of 8.3 was reached. The solution was filtered, dried overnight at 105 °C and calcined at 750 °C with a heating rate of 10 °C min$^{-1}$ for 3 hours. The catalyst was ground using a mortar and pestle and finally sieved to produce a particle size of 50-200 μm.

2.2 Experimental reactors.

Two types of reactor were used as shown in Figure 1 and Figure 2. Figure 1 shows a one-stage fixed bed reactor used for the pyrolysis of the waste HDPE under two different types of reaction atmosphere, nitrogen (N$_2$) or carbon dioxide (CO$_2$). The reactor was 250 mm in length by 30 mm internal diameter and was externally heated by an electrical tube furnace (1.2 kW). 2 g of waste HDPE was placed in the sample crucible boat. The pyrolysis temperature was increased from ambient to 500 °C at a heating rate of 10 °C min$^{-1}$ and maintained at 500 °C for 30 minutes. Nitrogen or carbon dioxide was used as the carrier gas with a flow rate of 200 ml min$^{-1}$. The oils were condensed in a three stage dry ice condenser system and the gases were collected in a Tedlar™ gas sample bag.

For two-stage pyrolysis-gasification/reforming experiments a two-stage fixed bed reactor was used as shown in Figure 2. The reactor was constructed of stainless steel and electrically heated by two separate furnaces. The experimental procedure involved heating the second stage gasification/reforming reactor which contained 1 g
of the Ni-Mg-Al catalyst to the desired temperature of 800 °C. 2 g of waste HDPE was placed in the 1st stage reactor and heated from ambient temperature to 500 °C at a heating rate of 10 °C min⁻¹. The volatile pyrolysis products passed directly to the 2nd stage reactor maintained at 800 °C, where further gasification/reforming reactions took place. Sand was used as the substitute when the experiment was carried out without the Ni-Mg-Al catalyst. N₂ or a mixture of N₂ and CO₂ were injected as the feed gases into the top of the 1st stage reactor. The flow rate of the nitrogen was fixed to 200 ml min⁻¹. Where steam was used, this was added to the second stage and used a syringe pump to deliver the water.

2.3. Gas analysis

The gases collected in the sample bag were analysed by gas chromatography (GC). Hydrocarbons (C₁-C₄) were analysed using a Varian 3380 GC with a flame ionisation detector, with a 80-100 mesh Hysep column in a nitrogen carrier gas flow. Hydrogen, oxygen, carbon monoxide and nitrogen (H₂, O₂, CO and N₂) were analysed using a different Varian 3380 GC with a 60-80 mesh molecular sieve column while carbon dioxide (CO₂) was analysed with a 80-100 mesh Hysep column, both in argon carrier gas.

In this work, the carbon dioxide conversion was calculated according to the formula reported by several researchers; Albarazi et al., Asencios et al. and Oyama et al. [23-25].

\[
\text{CO}_2 \text{ conversion} = \left( \frac{\text{molsCO}_2 \text{ input} - \text{molsCO}_2 \text{ output}}{\text{molsCO}_2 \text{ input}} \right)
\]

2.4 Characterization of reacted catalyst.
The properties of the carbonaceous coke deposited on the reacted catalysts were determined by temperature-programmed oxidation (TPO) experiments. TPO experiments were carried out using a thermogravimetric analyser (TGA-50 Shimadzu). About 8 mg of reacted catalyst was heated in an atmosphere of air with a heating rate of 15 °C min\(^{-1}\) from ambient temperature to a final temperature of 800 °C.

The reacted or coked Ni-Mg-Al catalysts from the pyrolysis-gasification of waste HDPE with and without carbon dioxide were also analysed using high resolution scanning electron microscopy (SEM, LEO 1530). The characteristics of carbon deposited on the reacted catalysts was examined and characterized.

3. Results and discussion

3.1 Influence of N\(_2\) and CO\(_2\) atmosphere.

The pyrolysis of waste (HDPE) was undertaken in the one-stage fixed bed reactor (Figure 1) in the presence of nitrogen or carbon dioxide atmosphere. Pyrolysis of 2g of waste HDPE was undertaken from ambient temperature to 500 °C final temperature. Table 1 shows the experimental results. The data show that only a small amount of hydrogen was produced during pyrolysis of the waste HDPE and the highest yield was for the nitrogen atmosphere compared to carbon dioxide. In addition, the methane concentration was correspondingly decreased in nitrogen compared to the carbon dioxide pyrolysis atmosphere. No carbon monoxide was detected with the nitrogen or carbon dioxide pyrolysis atmospheres. In comparison,
both atmospheres showed similar gas concentrations. Therefore, it can be suggested that the carbon dioxide does not significantly affect the pyrolysis products.

However, when the two-stage reactor system was used with pyrolysis of the waste HDPE in the 1st stage followed by reaction of the derived product volatiles in the presence of quartz sand in the 2nd stage at 800 °C there was a marked increase in hydrogen yield (Table 2). Regardless of the type of atmosphere, the hydrogen yield was significantly increased with the two-stage fixed bed reaction process compared to one-stage reactor. It is apparent from the results that the large improvement in hydrogen production was due to secondary reactions of hydrocarbons in the second furnace, as shown by the reduction of CmHn gas concentrations in the two-stage reactor system. The reaction at 800 °C in the 2nd stage enhanced the carbon dioxide reaction with hydrocarbons, hence raising the volume concentration of hydrogen.

In the presence of the nitrogen atmosphere, the hydrogen production in the two-stage fixed bed reactor increased from 0.23 to 20.10 mmol H₂ g⁻¹ plastic. While in the carbon dioxide atmosphere, the hydrogen yield increased from 0.1 to 33.58 mmol H₂ g⁻¹ plastic. There was also a marked increase in the production of carbon monoxide in the presence of the carbon dioxide atmosphere. This suggests that in the carbon dioxide atmosphere dry reforming reactions (Reaction 1) occurred between the methane and other hydrocarbons with carbon dioxide in the second stage as compared to the result obtained for the experiment with a nitrogen atmosphere. This was also suggested from the marked decrease in the concentration of methane and other hydrocarbon gases in the experiment using carbon dioxide atmosphere. Treacy et al. [12] reported that the highly endothermic characteristic of CO₂/dry reforming requires high temperature for the reaction to occur since both carbon dioxide and methane are stable compounds with low potential energies. Therefore, clear changes in the
hydrogen and carbon monoxide concentrations from the experiment with the carbon
dioxide atmosphere can be seen when the 800 °C second stage was introduced.

\[ C_{x}H_{y} + xCO_2 = 2xCO + y/2 H_2 \]  \hspace{1cm} (1)

3.2 Influence of steam and CO\textsubscript{2} on the non-catalytic pyrolysis-gasification of HDPE.

Table 3 shows the influence of varying the process conditions for the two-
stage reactor with 1\textsuperscript{st} stage pyrolysis at 500 °C, followed by reaction in the 2\textsuperscript{nd} stage at
800 °C in the presence of quartz sand. In this series of experiments, the carbon
dioxide was mixed with nitrogen at the inlet to the 1\textsuperscript{st} stage. In additional experiments,
steam was introduced into the 2\textsuperscript{nd} stage reactor. The carbon dioxide and steam were
introduced at different ratios, CO\textsubscript{2}:H\textsubscript{2}O = 1:0, CO\textsubscript{2}:H\textsubscript{2}O = 3:1 and CO\textsubscript{2}:H\textsubscript{2}O = 1:3 to
the system. The total amount of carbon dioxide and steam addition was 8 g and the
nitrogen flow rate was 200 ml min\textsuperscript{-1} for the all experiments.

The first experiment was with the addition of only carbon dioxide to nitrogen
(8g of CO\textsubscript{2}) introduced into the 1\textsuperscript{st} stage of the reactor system. The products from the
process were mainly gases, however a small amount of water was found in the
condenser system. Oyama et al. [25] suggested that the production of water was due
to the reverse water gas shift reaction (RWGS). From Table 3, the addition of carbon
dioxide into the system resulted in an increase in hydrogen production from 20.1
mmol H\textsubscript{2} g\textsuperscript{-1}\textsubscript{plastic} to 34.2 mmol H\textsubscript{2} g\textsuperscript{-1}\textsubscript{plastic} representing a 70 % increase in the
hydrogen production in mmol per gram. The carbon dioxide conversion was the
highest among others with 41 % conversion. The presence of carbon monoxide shows
that the CO\textsubscript{2} reforming or dry reforming process occurred. During the CO\textsubscript{2}/dry
reforming process, the hydrocarbons produced from the pyrolysis of the waste HDPE
reacted with the carbon dioxide producing more hydrogen as well as carbon monoxide. It is suggested that thermal cracking of heavy hydrocarbons during the gasification reactor was influenced by the addition of carbon dioxide. This was further supported by the large reduction in methane concentration, from 45.03 vol.% to 3.45 vol.% and reduction of other hydrocarbons, from 9.08 vol.% to 0.22 vol.% in the experiment with the addition of carbon dioxide.

The carbon deposition data in the table represents the formation of carbon on the sand in the 2nd stage reactor. The data indicates that with the addition of carbon dioxide, the carbon deposition was reduced from 0.2 gram per gram of sample (Table 2) to 0.14 gram per gram of sample (Table 4). Huang et al. [26] found that carbon dioxide has the ability to reduce carbon by the gasification reaction as shown in reaction 2a and 2b. This also contributed towards the amount of carbon monoxide produced from the process. In addition, the water gas shift reaction (Reaction 3) might also occur, thereby consuming carbon monoxide and producing carbon dioxide.

\[
C + CO_2 = 2CO \quad (2a)
\]
\[
C + H_2O = CO + H_2 \quad (2b)
\]
\[
CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (3)
\]

Table 3 also shows the results from the pyrolysis-gasification of waste HDPE with the addition of steam at a N\textsubscript{2}/CO\textsubscript{2}: H\textsubscript{2}O ratio of 3:1 and 1:3. The results show that the addition of steam into the system markedly increases the amount of hydrogen production. The highest amount of hydrogen produced was 66.47 mmol H\textsubscript{2} g\textsuperscript{-1} plastic which was achieved at a N\textsubscript{2}/CO\textsubscript{2}:H\textsubscript{2}O ratio of 1:3. From the table, it appears that more hydrogen yield resulted when more steam was injected into the system. The addition
of steam introduced the steam reforming reaction (Reaction 4), which contributes towards hydrogen production.

\[ \text{CxHy} + x\text{H}_2\text{O} = x\text{CO} + \frac{y}{2} + x \text{H}_2 \quad (4) \]

The addition of steam also produced high amounts of methane and other hydrocarbons and increased with a higher level of steam addition. Despite the consumption of methane in the reforming reaction, the increase in methane concentration might be caused by the lower hydrocarbon-cracking efficiency. The addition of steam might affect the reaction conditions inside the reactor and steam may consume some energy in the reactor, hence limiting the cracking of methane and other hydrocarbons. These results are consistent with those obtained in previous work [8], in which the hydrocarbon concentration of non-catalytic steam reforming of HDPE was higher compared to without steam addition. However, with the addition of catalyst in that study, the hydrocarbon-cracking efficiency was greatly improved resulting in higher hydrogen concentration but lower concentrations of methane and other hydrocarbons.

Figure 3 shows the relationship between hydrogen and carbon monoxide production in mmol g-1plastic with the carbon deposition in g g-1plastic. It appears that more carbon monoxide was produced when less steam was injected to the system. The carbon monoxide yields from the experiment with the addition of steam and carbon dioxide were produced from two different reactions; the steam reforming reaction and dry reforming reaction. Compared to the steam reforming reaction, the dry reforming reaction produces twice the number of moles of carbon monoxide in each reaction. Therefore when the concentration of steam was low in the system, the carbon monoxide production was higher. Furthermore, due to the high temperature,
the reverse water gas shift reaction might also occur, consuming more carbon dioxide and resulting in high carbon monoxide concentration. This is also suggested from the CO$_2$ conversion results, which showed 27.92 % CO$_2$ conversion when less steam was injected into the system as compared to 7.4 % CO$_2$ conversion at higher steam injection rate.

In terms of the carbon deposition, the lowest carbon deposition was achieved at a CO$_2$/N$_2$:H$_2$O ratio of 1:3. Edwards and Maitra [27] reported that methane dry reforming produced more carbon compared to steam reforming due to the lower H/C ratio in both the feed and product gases. However, with the addition of suitable catalyst, the carbon formation in methane dry reforming (without steam) can be reduced and might achieve a carbon-free process.

3.2 Influence of catalyst.

The Ni-Mg-Al catalyst was introduced into the 2$^{nd}$ stage reactor to investigate the effect on hydrogen production and carbon dioxide conversion from the pyrolysis-gasification of waste HDPE. The reactor was kept under 200 ml min$^{-1}$ N$_2$ flow with or without 8 g of carbon dioxide addition. 2 g of waste HDPE was placed in the 1$^{st}$ stage pyrolysis reactor and 1 g of Ni-Mg-Al catalyst maintained at 800 °C was introduced in the 2$^{nd}$ stage reactor. The results are shown in Table 4.

In the absence of carbon dioxide, the hydrogen yield significantly increased from 20.01 (Table 2) to 40.54 mmol H$_2$ g$^{-1}$ plastic with the addition of the Ni-Mg-Al catalyst (Table 4). The introduction of carbon dioxide to the system further increased the hydrogen yield from 34.2 mmol H$_2$ g$^{-1}$ plastic (Table 3) to 44.14 mmol H$_2$ g$^{-1}$ plastic (Table 4) with the Ni-Mg-Al catalyst which was the highest amount of hydrogen
achieved in the pyrolysis – gasification process in the presence of carbon dioxide and Ni-Mg-Al catalyst. The addition of Ni-Mg-Al catalyst also improved the carbon dioxide conversion from 40.81% (Table 3) to 53.07% (Table 4) as well as the amount of carbon monoxide produced from 43.07 vol% (Table 3) to 49.75 vol% (Table 4).

From the amount of methane and other hydrocarbons production which were reduced by more than 80%, it can be deduced that the addition of catalyst enhanced the CO₂/dry reforming reaction (Reaction 1), hence increasing the hydrogen production. The increase in hydrogen yield in the presence of catalyst in the CO₂ reforming of polyethylene was similarly reported by Yamada et al. [28], where hydrogen yield was increased from 1.7% in the absence of catalyst to 35.4% using a Pd/Al₂O₃ catalyst. The catalyst used was pre-treated with H₂ for 3 hours. They also reported that the decomposition of polyethylene into hydrogen and carbon monoxide was completely reformed at the catalyst temperature of 850 °C.

The reacted Ni-Mg-Al catalysts were analysed using temperature-programmed oxidation (TPO) and scanning electron microscopy (SEM). The DTG thermograms were plotted from the TPO results of the reacted catalyst derived from pyrolysis-gasification of waste HDPE without and with the carbon dioxide addition and are shown in Figure 4. The maximum mass loss for both samples was at around 600 °C in the DTG-TPO thermograms. The mass losses for TGA-TPO of the reacted Ni-Mg-Al catalyst derived from pyrolysis-gasification without carbon dioxide addition and with carbon dioxide addition were calculated as, 38.56 % and 4.49 % respectively. It is suggested that the mass loss was due to the combustion of carbon, demonstrating the amount of carbon deposition on the Ni-Mg-Al catalyst. The results suggest that, the reacted Ni-Mg-Al catalyst from catalytic dry pyrolysis-gasification had less deposited carbon than the catalytic pyrolysis-gasification without the carbon dioxide.
addition. From Figure 4, there is a mass increase in the DTG-TPO thermograms at around 400 °C which was attributed to the oxidation of the Ni particles during the TPO experiment.

From the SEM analysis shown in Figure 5, filamentous carbons were observed for the reacted Ni-Mg-Al catalyst derived from pyrolysis-gasification without carbon dioxide addition compared to the pyrolysis-gasification with carbon dioxide addition. The finding was in agreement with the amount of deposited carbon data shown in Table 4, which showed high deposited carbon (0.435 g g⁻¹ of sample) was found in the experiment without carbon dioxide addition. The lower deposited carbon in pyrolysis-gasification of waste HDPE with carbon dioxide addition was likely to be due to the reaction between filamentous carbons and carbon dioxide that significantly increased the amount of carbon monoxide production to 49.75 vol% in pyrolysis-gasification with carbon dioxide addition (Reaction 2a).

4. Conclusions

In this paper, the influences of thermal treatment type, carbon dioxide reforming, effects of steam injection and catalyst on the production of syngas, i.e. hydrogen and carbon monoxide from waste plastic (high density polyethylene) have been investigated. Based on the obtained results, it may be concluded:

(1) Thermal treatment of waste HDPE using a two-stage fixed bed reactor significantly improved the hydrogen production compared to the one-stage fixed bed reactor due to the gasification process in the second stage of the reactor.
(2) The addition of carbon dioxide as carrier gas not only increases the hydrogen and carbon monoxide production but also reduces carbon deposition.

(3) The addition of steam results in a marked increase of hydrogen produced from the water gas shift reaction.

(4) The addition of a nickel based catalyst, Ni-Mg-Al, also enhances the hydrogen production in pyrolysis–gasification of waste HDPE with carbon dioxide addition.

(5) Carbon deposits on the catalysts were of the filamentous type and were minimised in the presence of carbon dioxide addition due to reaction of the carbon to produce carbon monoxide.

Acknowledgements.

The authors are grateful for the financial support of the Majlis Amanah Rakyat (MARA) Malaysia (PhD scholarship for Juniza Md Saad) and the University of Leeds. The authors also thank Mr. Ed Woodhouse for his technical support and the analytical support from Dr. Chunfei Wu.
References

Table 1

Gas yields from the pyrolysis of waste HDPE

<table>
<thead>
<tr>
<th></th>
<th>Pyrolysis N₂</th>
<th>Pyrolysis CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass balance (%)</td>
<td>97.25</td>
<td>99.40</td>
</tr>
<tr>
<td>Hydrogen (mmol g⁻¹)</td>
<td>0.23</td>
<td>0.1</td>
</tr>
<tr>
<td>Gas concentration (vol%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂</td>
<td>6.59</td>
<td>4.37</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.19</td>
<td>17.68</td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>82.22</td>
<td>77.95</td>
</tr>
</tbody>
</table>
Table 2

Gas yields from the two-stage pyrolysis-gasification of waste HDPE

<table>
<thead>
<tr>
<th></th>
<th>Two-stage Pyrolysis-Gasification</th>
<th>Two-stage Pyrolysis-Gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>Mass balance (%)</td>
<td>99.87</td>
<td>111.45</td>
</tr>
<tr>
<td>Hydrogen (mmol g⁻¹)</td>
<td>20.1</td>
<td>33.58</td>
</tr>
<tr>
<td>Carbon deposition (g g⁻¹)</td>
<td>0.20</td>
<td>0.44</td>
</tr>
<tr>
<td>Gas concentration (vol%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.0</td>
<td>62.89</td>
</tr>
<tr>
<td>H₂</td>
<td>45.89</td>
<td>23.82</td>
</tr>
<tr>
<td>CH₄</td>
<td>45.03</td>
<td>11.94</td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>9.08</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Table 3

Influence of the reaction atmosphere on the pyrolysis-gasification of waste HDPE using the two-stage fixed bed reactor with sand in the second stage at 800 °C

<table>
<thead>
<tr>
<th></th>
<th>N₂/CO₂</th>
<th>N₂/CO₂:H₂O = 3:1</th>
<th>N₂/CO₂:H₂O = 1:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass balance (%)</td>
<td>95.64</td>
<td>99.64</td>
<td>92.17</td>
</tr>
<tr>
<td>Hydrogen (mmol g⁻¹)</td>
<td>34.2</td>
<td>58.39</td>
<td>66.47</td>
</tr>
<tr>
<td>Carbon deposition (g g⁻¹)</td>
<td>0.14</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>CO₂ conversion (%)</td>
<td>40.81</td>
<td>27.92</td>
<td>7.433</td>
</tr>
<tr>
<td>Gas concentration (vol%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>43.07</td>
<td>35.72</td>
<td>26.02</td>
</tr>
<tr>
<td>H₂</td>
<td>20.71</td>
<td>31.09</td>
<td>49.09</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.45</td>
<td>6.68</td>
<td>7.62</td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>0.22</td>
<td>0.26</td>
<td>1.65</td>
</tr>
</tbody>
</table>
Table 4

Influence of the reaction atmosphere on the pyrolysis – gasification of waste HDPE using the two-stage fixed bed reactor with Ni-Mg-Al catalyst in the second stage at 800 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N&lt;sub&gt;2&lt;/sub&gt; (NiMgAl)</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt; (NiMgAl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass balance (%)</td>
<td>93.34</td>
<td>94.99</td>
</tr>
<tr>
<td>Hydrogen (mmol g&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>40.54</td>
<td>44.14</td>
</tr>
<tr>
<td>Carbon deposition (g g&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.435</td>
<td>0.15</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; conversion (%)</td>
<td>-</td>
<td>53.07</td>
</tr>
</tbody>
</table>

Gas concentration (vol%)

<table>
<thead>
<tr>
<th>Gas</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;/CO&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>9.35</td>
<td>49.75</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>81.56</td>
<td>24.75</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>8.46</td>
<td>1.37</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.63</td>
<td>0.036</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1. Schematic diagram of one-stage fixed bed reactor.

Fig. 2. Schematic diagram of two-stage fixed bed reactor.

Fig. 3. Hydrogen, carbon monoxide and carbon deposition production relationship from pyrolysis – gasification of waste plastic with the addition of carbon dioxide and steam.

Fig. 4. DTG-TPO results for the reacted Ni-Mg-Al catalyst after pyrolysis-gasification of waste HDPE with and without the addition of carbon dioxide.

Fig. 5. SEM results for reacted Ni-Mg-Al catalyst after pyrolysis-gasification of waste HDPE, (a)-(b) without carbon dioxide and (c)-(d) with carbon dioxide addition.
Figure 1
Figure 2
Figure 3
Figure 4