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Manipulating the $\text{H}_2/\text{CO}$ Ratio from Dry Reforming of Simulated Mixed Waste Plastics by the Addition of Steam

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ABSTRACT

Two-stage pyrolysis-catalytic reforming of plastics was investigated with the aim of producing usable quality synthesis gases (syngas) comprised of $\text{H}_2$ and CO. The process consisted of pyrolysis of the plastics in the first stage and catalytic reforming with CO and steam as the reforming agents in the second stage. The plastics used were a mixture of waste plastics prepared to represent those found in municipal solid waste and the catalysts studied were Ni-Co/Al$_2$O$_3$ and Ni-Mg/Al$_2$O$_3$ prepared by the rising pH technique. A range of different CO$_2$/steam ratios were considered; 4:0, 4:0.5, 4:1, 4:1.5 and 4:2 for the Ni-Co/Al$_2$O$_3$ catalyst and 4:0, 4:0.5, 4:1, 4:2 and 4:3 for the Ni-Mg/Al$_2$O$_3$ catalyst. The results obtained demonstrated that the catalysts and the CO$_2$/steam ratio influence the syngas quality, as represented by the $\text{H}_2$/CO molar ratio value. With the Ni-Co/Al$_2$O$_3$ catalyst, the $\text{H}_2$/CO molar ratio was increased from 0.74 (no steam) to 0.94 (CO$_2$/steam ratio; 4:1) however the $\text{H}_2$/CO molar ratio decreased with further steam addition. Results using the Ni-Mg/Al$_2$O$_3$ catalyst showed a different trend, wherein the $\text{H}_2$/CO molar ratio increased with the increase of steam addition into the system. From the evaluation of the gas composition, the steam addition with the Ni-Mg/Al$_2$O$_3$ catalyst promoted hydrogen production while the Ni-Co/Al$_2$O$_3$ catalyst promoted carbon monoxide production. The addition of steam to the dry reforming of waste plastics has the potential to manipulate the $\text{H}_2$/CO molar ratio hence, the quality of syngas produced can be matched to the desired end-use industrial application.

Keywords: Waste; Plastics; Reforming; Carbon dioxide; Steam; Catalyst
1. Introduction

There is current interest in the production of alternative feedstock sources for the production of synthesis gas (syngas) composed of mainly hydrogen and carbon monoxide. Much of the research has focused on steam reforming or co-gasification processes with air and steam [1-5]. However, there are fewer reports that have investigated the dry reforming (CO₂ reforming) process [6]. The dry reforming process for producing syngas requires a hydrocarbon source, and waste plastics represents a novel potential hydrocarbon feedstock since they are rich in CH-CH molecular chains. Therefore, the dry reforming of waste plastics alleviates a problematic waste treatment issue and also utilises carbon dioxide which is a greenhouse gas and subject to intense research in regard to CO₂ capture and storage/utilisation processes.

The uses of syngas include producing methanol, ammonia and synthetic fuel through Fischer-Tropsch synthesis. The selection of the particular H₂/CO molar ratio is considered critical to match with the end-use product processing requirements [7-10]. Several studies on dry reforming of methane suggested that the addition of steam and/or oxygen were advantageous in controlling the H₂/CO molar ratio [11-14]. The H₂/CO ratio of methane dry reforming is unity, while the H₂/CO ratio of steam reforming is about four, hence the mixture of both produced a desired H₂/CO ratio for the Fischer-Tropsch process [15]. Furthermore, the addition of steam and/or oxygen may also act as a coke gasifier in the reforming process. Edreis et al. reported in their study on CO₂ co-gasification of petroleum coke and sugar cane bagasse that the char gasification occurred at the temperature more than 700 °C [16]. Moreover, the use of suitable catalysts further enhances the reforming process and can improve the coke resistance ability [17-20]. Whilst there is research into the combination of dry reforming and steam
reforming of methane, there are few studies investigating the combination of dry and steam reforming for the processing of waste plastics.

Previously we have reported that a Ni-Co/Al₂O₃ catalyst had high catalytic activity towards the dry reforming of waste high density polyethylene for syngas production [21]. In addition, no detectable carbon was formed on the catalyst during dry reforming. In this study, the use of both carbon dioxide and steam in the reforming process have been investigated with the aim of controlling the H₂/CO molar ratio as well as syngas yield. The catalyst used was the Ni-Co/Al₂O₃ catalyst as used before, but the results were also compared with a different catalyst, Ni-Mg/Al₂O₃. This work is also a continuation of our previous work on the influence of steam on non-catalytic-CO₂ reforming of HDPE [22].

2. Materials and methods

2.1 Materials.

A blended mixture of different plastics was prepared based on the typical composition of the plastics found in municipal solid waste [23]. The mixture consisted of, low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), polyethylene terephthalate (PET) and polypropylene (PP) and the composition was, 42 wt.% of LDPE, 20 wt.% of HDPE, 16wt.% of PS, 12 wt.% of PET and 10wt.% of PP. In this report, the plastics mixture was designated as simulated mixed waste plastics (SWP).

Two types of catalysts were used in the investigation; Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃. Ni-Co/Al₂O₃ was shown to be effective for the dry reforming of plastics on
our previous study [21] while Ni-Mg/Al₂O₃ was selected based on its high catalytic activity for the steam reforming process [24-26]. Both catalysts were prepared by the rising-pH technique [27] by first mixing nickel (II) nitrate hexahydrate and aluminium nitrate nonahydrate with deionised water. Either cobalt (II) nitrate hexahydrate or magnesium nitrate hydrate was also mixed into the solution. After two hours of moderate stirring at 40 °C, 1 M ammonium precipitant was added into the aqueous solution until a pH of 8.3 was reached. The precipitates were then filtered, dried and calcined at 750 °C and sieved to a particle size of 50 – 212 µm. The characterization of fresh Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ were discussed in detail in our previous paper [21], but briefly, the catalysts consisted of Ni-Co-Al with a molar ratio of 1:1:1 and Ni-Mg-Al, also with a molar ratio of 1:1:1 with BET surface areas of 48 m² g⁻¹ and 66 m² g⁻¹ respectively.

2.2 Experimental system.

The catalytic-steam/dry reforming of mixed waste plastics over Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ catalysts was carried out in a two-stage fixed bed reactor and the details of the reactor and experimental procedure is covered in our previous studies [21, 22]. The two-stages consisted of pyrolysis of the plastics at 500 °C to produce the hydrocarbons which were then reformed with CO₂/steam at 800 °C in the second catalyst stage reactor. The size of the reactor was 60 cm in length with 2.5 cm inner diameter and constructed of Inconel. 2 g of plastic sample and 1 g of catalyst were used. The CO₂/steam ratios of 4:0, 4:0.5, 4:1, 4:1.5 and 4:2 were used for the Ni-Co/Al₂O₃ catalyst and for the Ni-Mg/Al₂O₃ catalyst, the CO₂/steam ratios used were 4:0, 4:0.5, 4:1, 4:2 and 4:3. The Ni-Mg/Al₂O₃ catalyst showed very small differences with the
steam/CO$_2$ ratio of 4:1.5 (results not shown here), hence the ratio was increased up to 4:3. The CO$_2$ and/or steam was fed directly into the second catalytic stage of the reactor system. Nitrogen was used as a carrier gas for the entire process with a flow rate of 200 ml min$^{-1}$. The product gases were passed through a three-stage condenser system where any condensed oil/wax/unreacted water was trapped. However, during the investigation, no condensed oil/wax products in the condensation system were detected. This was due to the high temperature of the second stage reactor, 800 °C, where the catalyst was placed. The quantity of water that was consumed during reactions was calculated by difference via the quantity of water injected (syringe pump) and quantity of unreacted water (condensers). The non-condensed gases were collected in a Tedlar™ sample bag and analysed by gas chromatography as detailed previously [21, 22]. CO$_2$ conversion was measured by difference; the total amount of CO$_2$ introduced into the system and unreacted/produced CO$_2$ (left in the sample gas bag). It should be noted that CO$_2$ might also be produced during the gasification/reforming process. In addition, the weight of liquid, char and carbon deposition were determined by the difference before and after experimentation of the condensers, sample holder and reactor tube respectively.

After experimentation, the catalyst was removed and any carbonaceous coke deposited on the catalyst surface was analysed by scanning electron microscopy (SEM), X-Ray Diffraction (XRD) and temperature programmed oxidation (TPO). The morphology of the carbon deposits on the catalyst were determined by a Hitachi SU8230 high resolution SEM. The XRD analysis was conducted using a Bruker D-8 diffractometer and the pattern identification was obtained by HighScore Plus Software. For the TPO experiments, 10 mg of reacted catalyst was heated from ambient temperature to 800 °C under air atmosphere with a thermogravimetric analyser (TGA-
The deposited carbon was calculated based on weight difference of the reactor before and after the experiment. In addition, from SEM and TPO data, the same trend in deposited carbon on the catalyst surface was observed.

3. Results and discussion

3.1 Product yields.

Table 1 and Table 2 show the product yields from the catalytic-dry/steam reforming of the simulated mixture of LDPE, HDPE, PS, PET and PP in relation to the CO\textsubscript{2}/steam reforming gas ratio with the Ni-Co/Al\textsubscript{2}O\textsubscript{3} and Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalysts respectively. The product yield calculations can be expressed by the following formulae:

\[
\text{Products yield in relation to plastics, carbon dioxide and reacted water, (wt.%) =} \frac{W_{\text{Product}}}{W_{\text{swp}} + W_{\text{CO2input}} + W_{\text{steaminput}}} \times 100
\]

\[
\text{Products yield in relation to plastics only, (wt.%) carbon dioxide and reacted water, (wt.%) =} \frac{W_{\text{Product}}}{W_{\text{swp}}} \times 100
\]

The total gas yield in relation to all of the reactants (plastic, carbon dioxide and reacted water) reached the maximum point of 94.58 wt.% at the CO\textsubscript{2}/steam ratio of 4:1.5. However, calculation of the total gas yield in relation to only the mass of plastic used in the experiments showed an increase from ~268 wt.% to 356 wt.% as the CO\textsubscript{2}/steam ratio was increased. The reforming gases CO\textsubscript{2} and steam clearly contributing to the total gas product yield in addition to the hydrocarbons from the
plastic pyrolysis-catalysis. The residue of the simulated mixed waste plastics after the
experiment in the sample holder remained unchanged at 3.0 wt.%_{plastic only}. Increasing
the CO\textsubscript{2}/steam ratio produced a large impact on the amount of carbon deposited on the
catalyst, showing a decrease from 23.50 wt.%_{plastic only} with the experiment without
steam addition, to 0.50 wt.%_{plastic only} at the CO\textsubscript{2}/steam ratio of 4:2.

Similar trends of syngas yield corresponding to the mass of simulated mixed
waste plastic were also shown from the experiments with the Ni-Mg/Al\textsubscript{2}O\textsubscript{3} as presented
in Table 2. However, the carbon formation on the catalyst during the experiments first
decreased with the increase of CO\textsubscript{2}/steam ratio and then increased at the higher
CO\textsubscript{2}/steam ratios.

3.2 Gas composition.

The gases contained in the gas sample bag were analysed by gas chromatography
and the results for carbon monoxide (CO), hydrogen (H\textsubscript{2}), methane (CH\textsubscript{4}) and C\textsubscript{2}-C\textsubscript{4}
hydrocarbons from the catalytic-dry/steam reforming of simulated mixed waste plastics
over the Ni-Co/Al\textsubscript{2}O\textsubscript{3} and Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalysts are shown in Figure 1. Our previous
study [22] demonstrated that the addition of a gasification/reforming stage enhanced the
formation of H\textsubscript{2} from the pyrolysis-dry reforming of waste high density polyethylene
under a CO\textsubscript{2} atmosphere while the concentration of methane and C\textsubscript{2}-C\textsubscript{4} hydrocarbons
was markedly reduced from 96 vol.% to only 13 vol.%, suggesting the dominance of
the reforming reaction. In addition, based on our previous work [28] which reported gas
yields for individual plastics in the absence of CO\textsubscript{2}, calculation of the CO yield from
SWP could be made based on the CO yield from the individual plastics (LDPE, HDPE,
PP, PET and PS) used in the SWP mixture. The results showed that in this work there
was a large increase in CO yield when CO$_2$ was introduced to the system. In the presence of the Ni-Co/Al$_2$O$_3$ catalyst, the CO yield increased from 0.14 g g$^{-1}$SWP to 1.56 g g$^{-1}$SWP for the CO$_2$/steam ratio of 4:0 and with the Ni-Mg/Al$_2$O$_3$ catalyst the CO yield increased from 0.14 g g$^{-1}$SWP to 1.81 g g$^{-1}$SWP at a CO$_2$/steam ratio of 4:0.

In general, the main gases from the catalytic-dry/steam reforming process for both catalysts were carbon monoxide and methane and lower yields of hydrogen and C$_2$-C$_4$ hydrocarbons as shown in Figure 1, suggesting the reaction between pyrolytic gases and CO$_2$ and/or steam occurred in the second stage reactor. These two reactions representing the dry reforming reaction (Equation 1) and the steam reforming reaction (Equation 2).

\[ C_xH_y + xCO_2 \rightarrow 2xCO + y/2H_2 \quad \text{Equation 1} \]

\[ C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \quad \text{Equation 2} \]

The results obtained for the experiments with the Ni-Co/Al$_2$O$_3$ catalyst shown in Figure 1, shows a close relationship between the reactant gases produced from pyrolysis; methane and C$_2$-C$_4$ hydrocarbons, and the output gases; carbon monoxide and hydrogen. The decrease in the concentration of CH$_4$ and C$_2$-C$_4$ hydrocarbons corresponding to the reduction in the CO$_2$/steam input ratio from 4:0 to 4:1.5, resulting in an increase in the product CO and H$_2$. The relative increase in gas yield was more marked for CO compared to H$_2$, resulting in a change in the H$_2$/CO molar ratio. From the discussion previously, the carbon deposits on the catalyst were decreased with the increase in the CO$_2$/steam ratio. It is suggested that reaction occurred between carbon
dioxide/steam and char/fixed carbon as in the following reactions (Equation 3 and Equation 4).

\[ C + CO_2 \rightarrow 2CO \]  
Equation 3

\[ C + H_2O \rightarrow CO + H_2 \]  
Equation 4

Figure 1 also shows the influence of the CO$_2$/steam ratio for the reforming of the plastic mixture using the Ni-Mg/Al$_2$O$_3$ catalyst. In comparison with the cobalt containing Ni-Co/Al$_2$O$_3$ catalyst, the yield of CO was higher, but at higher inputs of steam, the yield of CO fell, with an improved yield of H$_2$. It is suggested that Ni-Mg/Al$_2$O$_3$ also promoted the water gas shift reaction (Equation 5) when more steam was added to the process, hence showing reduction of carbon monoxide yield and increase of hydrogen yield.

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  
Equation 5

3.3 Syngas production and H$_2$/CO molar ratio.

Figure 2 shows the relationship between CO$_2$ conversion, reacted water, syngas yield and H$_2$/CO molar ratio from the catalytic-dry/steam reforming process of simulated mixed waste plastics over the Ni-Co/Al$_2$O$_3$ catalyst. Syngas yield reached its maximum point at the CO$_2$/steam ratio of 4:1.5 at 159.77 mmol g$^{-1}_{SWP}$. The maximum peak of CO$_2$ conversion$_{inlet-outlet}$, at 56.55 % was also found at the CO$_2$/steam ratio of
4:1.5. The quantity of reacted water increased with the raising of the CO$_2$/steam ratio to a maximum, which was 0.56 g g$^{-1}_{\text{swp}}$ at the CO$_2$/steam ratio of 4:2.

However, the H$_2$/CO molar ratio shows a maximum at the CO$_2$/steam ratio of 4:1, producing a H$_2$/CO molar ratio of 0.94, but decreased as the amount of steam input was increased. This might be due to the large increase in CO production compared to the H$_2$ yield. This also suggests that the Ni-Co/Al$_2$O$_3$ catalyst enhanced the dry reforming reaction (Equation 1) as well as the Boudouard reaction (Equation 3) compared to the steam reforming reaction (Equation 2) hence, there was a high CO yield compared to H$_2$ yield. Butterman et al. [29] in their study on steam gasification of biomass with the addition of CO$_2$, also showed that an increase of CO$_2$ input into the system, enhanced the production of CO with reduced H$_2$ yield [29].

Figure 3 shows the results from the catalytic-dry/steam reforming of simulated mixed waste plastics over the Ni-Mg/Al$_2$O$_3$ catalyst. A maximum peak of syngas yield at 147 mmol g$^{-1}_{\text{swp}}$ was obtained at the CO$_2$/steam ratio of 4:1. The CO$_2$ conversion$_{\text{inlet-outlet}}$ and reacted water showing an opposite trend towards each other while the H$_2$/CO molar ratio showing a similar trend with the reacted water, which increased with the increased CO$_2$/steam molar ratio. The drop in CO$_2$ reaction and the rise in steam consumption with the increased of CO$_2$/steam ratio, suggesting that the Ni-Mg/Al$_2$O$_3$ might preferentially promote the steam reforming reaction rather than the dry reforming reaction. This further confirmed that the water gas shift reaction (Equation 5) occurred in the second stage reactor among the low molecular weight hydrocarbons (methane), condensable hydrocarbons (C$_2$-C$_4$) and steam yielding CO$_2$ hence, lessening CO$_2$ conversion$_{\text{inlet-outlet}}$ but promoting water consumption (reacted water) starting at the CO$_2$/steam ratio of 4:0.5.
3.4 Catalyst coke formation.

The reacted Ni-Co/Al$_2$O$_3$ and Ni-Mg/Al$_2$O$_3$ catalysts from the dry/steam reforming experiments with the simulated mixed waste plastics in relation to CO$_2$/steam feed ratio were characterized by temperature programmed oxidation (TPO). The results of TGA-TPO and DTG-TPO of both reacted catalysts are shown in Figure 4 and Figure 5 respectively. As shown in Table 1, the quantity of coke deposited on the Ni-Co/Al$_2$O$_3$ catalyst showed a significant decrease of 98 % with an increase in the CO$_2$/steam ratio. This result is in agreement with the TPO experiment, where the catalysts used with higher steam inputs showed little mass loss since there were few deposits of carbon on the catalyst surface available for oxidation (combustion). Therefore it is suggested with the increase of CO$_2$/steam ratio, more carbon was reacted with either carbon dioxide or steam via Reaction 3 and Reaction 4. It should also be noted that with the reacted Ni-Co/Al$_2$O$_3$ catalyst, there was a large increase of mass at around a temperature of 500 °C. Due to the low concentration of coke deposited on the reacted catalysts, it is suggested that the mass gain was due to oxidation of nickel and cobalt metal in the catalyst.

Compared to the reacted Ni-Co/Al$_2$O$_3$ catalyst, high oxidation temperature peaks (higher than 600 °C) were also observed for reacted Ni-Mg/Al$_2$O$_3$ catalyst as shown in Figure 5. Scanning electron microscopy observation of the used catalysts confirmed that only low levels of carbon deposition occurred on the Ni-Co/Al$_2$O$_3$ catalyst compared to the Ni-Mg/Al$_2$O$_3$ reacted catalyst.

The XRD spectra of the fresh catalysts and the used Ni-Co/Al$_2$O$_3$ and Ni-Mg/Al$_2$O$_3$ catalysts in relation to the different CO$_2$/steam ratios are shown in Figure 6 and Figure 7 respectively. Fewer diffraction peaks were observed from the used Ni-Co/Al$_2$O$_3$ catalyst compared to the fresh catalyst. Also the XRD spectra of the used Ni-
Co/Al₂O₃ catalysts show a similar profile with the increase of CO₂/steam ratio, however the peak intensity was reduced compared to the fresh catalyst. The NiO crystallite size determined for the fresh Ni-Co/Al₂O₃ catalyst at a 2-Theta value of 43.3° was 93.6 Å.

For the used Ni-Co/Al₂O₃ catalysts, Ni and Co metal peaks were detected at 2-Theta values of 44.2° and 51.5° [30], which indicates that the NiO was reduced to its metallic form in-situ by the reducing agents present in the pyrolysis gases and/or produced in the reformer reactor e.g H₂ [31, 32]. The size of the Ni and Co metal peaks (overlapped) was increased for the used catalyst at a 2-Theta of 44.2°, from 471.2 Å at the CO₂/steam ratio of 4:0 to 551.5 Å at the CO₂/steam ratio of 4:1 but was reduced to 493.5 Å at the CO₂/steam ratio of 4:2.

However, for the Ni-Mg/Al₂O₃ catalyst, more XRD peaks were observed from the reacted catalyst compared to the fresh Ni-Mg/Al₂O₃ catalyst. MgO peaks were observed for both the fresh and used catalysts. Basagiannis and Verykios [33] suggested that the spillover of O and/or –OH anions from the carrier surface to metal surface is improved with the existence of MgO in the catalyst. A Ni metal peak was observed at a 2-Theta value of about 44.4° and 51.8°. The Ni crystallite size from the XRD peak at a 2-Theta of 44.4° was increased with the increase of CO₂/steam ratio (4:0 at 241.6 Å, 4:1 at 276.9 Å and 4:2 at 280.6 Å) and sharper peaks were also observed. The NiO crystallite size for fresh Ni-Mg/Al₂O₃ at a 2-Theta of 43.2° was only 102.9 Å.

The results have shown that by changing the CO₂/steam input ratio, the syngas H₂/CO ratio can be manipulated between 0.74 and 0.94 for the Ni-Co/Al₂O₃ catalyst and between 0.6 and 1.4 for the Ni-Mg/Al₂O₃ catalyst. The optimum ratio of H₂/CO required for onward process utilisation depends on the application. Majewski and Wood [34] have reported that a H₂/CO ratio between 1.7 — 2.15 can be used for Fischer Tropsch processing for the production of liquid hydrocarbon fuels, depending on the
type of catalyst used and the process conditions. A H\textsubscript{2}/CO ratio between 1.5 — 2 can also be used for the production of methanol or for dimethyl-ether synthesis. Therefore, the syngas H\textsubscript{2}/CO ratio derived from waste plastics reported here would require supplemental hydrogen addition to raise the H\textsubscript{2}/CO ratio for use in such applications. Alternatively, the different catalysts used here have been shown to alter the H\textsubscript{2}/CO ratio by using different metal promoters. There is therefore scope for further research on different types of catalyst to also manipulate the product syngas H\textsubscript{2}/CO ratio.

4. Conclusions

Incorporating steam into the dry reforming process was investigated in order to manipulate the H\textsubscript{2}/CO molar ratio for end-use industrial applications. The results showed that by changing the CO\textsubscript{2}/steam feed ratio, as well as suitable catalyst selection, the syngas production and H\textsubscript{2}/CO molar ratio could be varied. For the catalytic-dry/steam reforming of simulated mixed waste plastics over Ni-Co/Al\textsubscript{2}O\textsubscript{3} catalyst, it is suggested that the optimum CO\textsubscript{2}/steam ratio was observed at 4:1. At this ratio, the highest H\textsubscript{2}/CO molar ratio was observed at 0.94 and an acceptable syngas yield was also obtained at 133.87 mmol\textsubscript{syngas} g\textsuperscript{-1 swp}. For the reforming process over the Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalyst, the optimum syngas production of 146.77 mmol\textsubscript{syngas} g\textsuperscript{-1 swp} was observed at the CO\textsubscript{2}/steam ratio of 4:1.

It is also suggested that the Ni-Co/Al\textsubscript{2}O\textsubscript{3} catalyst enhanced the dry reforming reaction and Bourdouard reaction (Equation 1 and 3) hence, high CO and high syngas yield was obtained. In the case of the Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalyst, the process was preferentially promoted towards the steam reforming and water gas shift reactions (Equation 2 and 5) hence, higher H\textsubscript{2} yield and higher H\textsubscript{2}/CO molar ratios were obtained.
In addition, increasing the CO$_2$/steam ratio with the Ni-Mg/Al$_2$O$_3$ catalyst showed an undesirable carbon build-up on the catalyst during the experiments.

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References


Table 1: Product yield distribution from catalytic-dry/steam reforming of simulated mixed waste plastics over Ni-Co/Al₂O₃ catalyst at the gasification temperature of 800 °C

<table>
<thead>
<tr>
<th>CO₂/steam ratio</th>
<th>(4:0)</th>
<th>(4:0.5)</th>
<th>(4:1)</th>
<th>(4:1.5)</th>
<th>(4:2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product yield in relation to plastic + carbon dioxide + reacted water (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>89.32</td>
<td>88.66</td>
<td>89.76</td>
<td>94.58</td>
<td>89.76</td>
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<tr>
<td>Residue</td>
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<td>0.96</td>
<td>0.86</td>
<td>0.82</td>
<td>0.76</td>
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<tr>
<td>Carbon deposition</td>
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<td>6.85</td>
<td>0.29</td>
<td>0.14</td>
<td>0.13</td>
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<tr>
<td>Mass balance</td>
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<td>96.47</td>
<td>90.91</td>
<td>95.54</td>
<td>90.65</td>
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<tr>
<td>Product yield in relation to plastics only (wt.%)</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Gas</td>
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<td>314.16</td>
<td>347.58</td>
<td>356.35</td>
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<tr>
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<td>3.00</td>
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<tr>
<td>Carbon deposition</td>
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<td>Mass balance</td>
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<td>318.16</td>
<td>351.08</td>
<td>359.85</td>
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Table 2: Product yield distribution from catalytic-dry/steam reforming of simulated mixed waste plastics over Ni-Mg/Al$_2$O$_3$ catalyst at the gasification temperature of 800 °C

<table>
<thead>
<tr>
<th>CO$_2$/steam ratio</th>
<th>(4:0)</th>
<th>(4:0.5)</th>
<th>(4:1)</th>
<th>(4:2)</th>
<th>(4:3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product yield in relation to plastic + carbon dioxide + reacted water (wt. %)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Gas</td>
<td>87.46</td>
<td>90.43</td>
<td>95.12</td>
<td>96.31</td>
<td>100.16</td>
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<td>Residue</td>
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<td>0.97</td>
<td>0.86</td>
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<tr>
<td>Carbon deposition</td>
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<td>6.46</td>
<td>1.28</td>
<td>1.85</td>
<td>4.14</td>
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<tr>
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<td>96.79</td>
<td>97.86</td>
<td>97.26</td>
<td>99.02</td>
<td>105.16</td>
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<tr>
<td><strong>Product yield in relation to plastics only (wt.%)</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Gas</td>
<td>262.37</td>
<td>279.89</td>
<td>333.39</td>
<td>337.57</td>
<td>351.06</td>
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<td>Residue</td>
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<tr>
<td>Carbon deposition</td>
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<td>20.00</td>
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<td>6.50</td>
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<td>302.89</td>
<td>340.89</td>
<td>347.07</td>
<td>368.56</td>
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Figure Captions

Figure 1. Gas composition for the catalytic-dry/steam reforming of simulated mixed waste plastics (SWP) with different CO\textsubscript{2}/steam ratios over Ni-Co/Al\textsubscript{2}O\textsubscript{3} and Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalysts.

Figure 2. Syngas yield, H\textsubscript{2}/CO molar ratio, reacted water and CO\textsubscript{2} conversion derived from the dry/steam reforming process over Ni-Co/Al\textsubscript{2}O\textsubscript{3} catalyst.

Figure 3. Syngas yield, H\textsubscript{2}/CO molar ratio, reacted water and CO\textsubscript{2} conversion derived from the dry/steam reforming process over Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalyst.

Figure 4. TGA-TPO and DTG-TPO analysis of catalysts after pyrolysis-dry/steam reforming of simulated mixed waste plastics over the Ni-Co/Al\textsubscript{2}O\textsubscript{3} catalyst.

Figure 5. TGA-TPO and DTG-TPO analysis of catalysts after pyrolysis-dry/steam reforming of simulated mixed waste plastics over the Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalyst.

Figure 6. XRD spectra patterns of catalysts after pyrolysis-dry/steam reforming of simulated mixed waste plastics over the Ni-Co/Al\textsubscript{2}O\textsubscript{3} catalyst.

Figure 7. XRD spectra patterns of catalysts after pyrolysis-dry/steam reforming of simulated mixed waste plastics over the Ni-Mg/Al\textsubscript{2}O\textsubscript{3} catalyst.
Figure 1

[Graph showing CO and CH₄ production for Ni-Co/Al₂O₃ and Ni-Mg/Al₂O₃ catalysts across different CO₂/steam ratios. The graph includes bars and lines representing the production of CO, CH₄, H₂, and C₂H₆ hydrocarbons in g/g Await.]
Figure 2
Figure 3
Figure 4

Ni-Co/Al₂O₃

Weight loss (wt. %)

Temperature (°C)

Derivative weight (°C⁻¹)

Temperature (°C)

- No H₂O
- 0.5 H₂O
- 1.0 H₂O
- 1.5 H₂O
- 2.0 H₂O
Fig. 5

Ni-Mg/Al₂O₃
Fig. 6

Diagram showing X-ray diffraction patterns for Ni-Co/Al₂O₃ in different states:
- Fresh
- Coked CO₂/steam = 4:0
- Coked CO₂/steam = 4:1
- Coked CO₂/steam = 4:2

Legend:
- NiO
- γ-Al₂O₃
- NiAl₂O₄
- Co₃O₄
- Ni
- Co
Fig. 7

Ni-Mg/Al₂O₃

Counts

2-Theta

Fresh

Coked

CO₂/steam = 4:0

Coked

CO₂/steam = 4:1

Coked

CO₂/steam = 4:2

NiO

γ-Al₂O₃

NiAl₂O₄

NiMgO

MgO

Ni

NiMgO