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Pyrolysis-Catalytic Dry (CO_2) Reforming of Waste Plastics for Syngas Production: Influence of Process Parameters

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Abstract:

Catalytic dry (CO_2) reforming of waste plastics was carried out in a two stage, pyrolysis-catalytic reforming fixed bed reactor to optimise the production of syngas (H_2 + CO). The effects of changing the process parameters of, catalyst preparation conditions, catalyst temperature, CO_2 input rate and catalyst:plastic ratio were investigated. The plastics used was a mixture of plastics simulating that found in municipal solid waste and the catalyst used was Ni-Co-Al_2O_3. The results showed that changing each of the process conditions investigated, all significantly influenced syngas production. An increase of 17 % of syngas production was achieved from the experiment with the catalyst prepared by rising-pH technique compared to preparation via the impregnation method. The optimum syngas production of 148.6 $\text{mmol}_{\text{syngas}}\ \text{g}^{-1}_{\text{swp}}$ was attained at the catalytic dry reforming temperature of 800 °C and catalyst:plastic ratio of 0.5. The increase of CO_2 input rate promoted a higher yield of syngas.

Keywords: Waste; Plastics; Reforming; Carbon dioxide; Catalyst

1. Introduction

According to Plastics Europe, the European trade association for the plastics industry in Europe, 25.2 million tonnes of waste plastic are generated annually, of which ~26% is recycled [1]. The vast majority of the recycling of the waste plastics is through mechanical processes, however, there is growing interest in thermal recycling [2, 3]. Since plastics are mainly composed of hydrocarbons, thermal recycling of waste plastics to produce a synthesis gas (syngas) composed of a mixture of hydrogen and carbon monoxide represents a low cost feedstock for syngas production. There have been many reports on the production of hydrogen and synthesis gases from waste plastics by pyrolysis and gasification processes [4-6]. The addition of steam, catalyst and partial oxidation enhancing the production of gases through a catalytic steam reforming type process [7, 8]. Recently, another approach to the production of syngas has been the utilisation of carbon dioxide instead of steam, this for the production of syngas where the feedstock was methane [9-12]. The process of reformation of methane by carbon dioxide is also known as dry reforming of methane (DRM). Since plastics are rich in hydrocarbons, it is interesting to pyrolyse the plastics to produce a suite of hydrocarbons which can then be directly catalytically reformed using carbon dioxide. This process would represent a novel option for the management of waste plastics, but also provide a route for the utilisation of carbon dioxide. High volumes of carbon dioxide are predicted to be produced from future carbon capture processes because of the concern over climate change. Dry methane reforming is an endothermic process, therefore high temperatures are required. Due to the high temperature, other side reactions apart from the dry reforming reaction can occur, especially those that could increase the carbon coke formation on the catalyst such as methane cracking and the

Boudouard reaction. A study on dry reforming of methane over a Ni/γ-Al_2O_3 catalyst in a fixed bed continuous flow quartz reactor and direct current corona discharge found an increase selectivity for CO and decreased carbon formation on the catalyst surface [13]. Dry methane reforming is not only affected by temperature, but also the CH_4/CO_2 ratio, mass to flow ratio, catalyst selection and reaction mixture [14-16].

This paper presents work on the dry reforming of a mixture of waste plastics (polyethylene, polystyrene, polyethylene terephthalate and polypropylene) with a Ni-Co-Al_2O_3 catalyst in a two-stage, pyrolysis-catalytic CO_2 reforming fixed bed reactor. The influences of catalyst preparation method, catalytic dry reforming temperature, CO_2 input rate and catalyst to plastic ratio on the product yields and syngas production were investigated.

2. Materials and Methods

2.1 Materials.

A mixture of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), polyethylene terephthalate (PET) and polypropylene (PP) was used in the experiments. The mixture proportions was based on the municipal solid waste plastics composition reported by Delgado et al. (2007) [17]; 42 wt.% of LDPE, 20 wt.% of HDPE, 16wt.% of PS, 12 wt.% of PET and 10wt.% of PP. The plastics used to make up the mixture of plastics consisted of HDPE, PP and PS provided by Regain Polymers Limited, Castleford, UK as waste plastics and LDPE and PET were obtained from Sigma-Aldrich UK and Good Fellow UK, respectively. All the plastic samples were received as pellets, size 2-3mm. The plastics mixture was designated as simulated waste plastic (SWP) in this research.

The Ni-Co-Al_2O_3 catalyst used in the experiments was chosen, based on its high activity in terms of syngas production as reported in our previous study [18]. Two types of catalyst preparations methods are investigated; rising-pH and impregnation. The rising-pH technique, or co-precipitation method was prepared as an adaption of a reported process [8]. The method involved dissolution of $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_26H_2O$ and $Al(NO_3)_39H_2O$ in deionised water at 40 °C, addition of 1 M ammonium solution to pH 8.3 until the precipitate formed. The impregnation method for Ni-Co-Al_2O_3 catalyst preparation involved dissolution of $Ni(NO_3)_2.6H_2O$ in deionised water at 80 °C, addition of $Co(NO_3)_2.6H_2O$ and after 30 minutes addition of γ-Al_2O_3 to form a slurry. Both precipitates were filtered, dried, then calcined at a temperature of 750 °C for 3 hours. All the catalysts were crushed and screened to particle size, 50-212 μm.

2.2 Characterization of catalysts.

The used/reacted Ni-Co-Al_2O_3 catalysts from the catalytic dry reforming of the plastics were characterized using a thermogravimetric analyser (Shimadzu TGA-50) for the combustion (oxidation) of the carbon deposited on the catalyst in relation to temperature i.e., temperature programmed oxidation (TPO). About 10 mg of the used catalysts were heated from room temperature to 800 °C with a heating rate of 15 °C min^{-1} in the TGA using air as the purge gas. In addition, a Hitachi SU8230 scanning electron microscope (SEM) examined the surface morphology and carbon deposition on the reacted Ni-Co-Al_2O_3 catalyst.

2.3 Experimental system.

The influence of process parameters on the catalytic dry reforming of the plastics was carried out in a two stage fixed bed reactor as shown in Figure 1. The reaction system consisted of two separate stainless steel reactors externally heated by electrical furnaces and the carrier gas was nitrogen. The first reactor pyrolysed the plastics (2 g) and the product gases were passed directly to the second reactor where the catalyst was located and where CO_2 was added to produce catalytic dry reforming of the pyrolysis gases. The pyrolysis reactor was heated to a temperature of 500 °C at 10 °C min^{-1} heating rate and the catalytic reforming reactor was held at a constant temperature of at 800 °C. Where the effect of catalyst temperature was investigated, temperatures in the catalytic reforming reactor were 600, 700, 800 or 900 °C. CO_2 input rate was 6.0 g h^{-1} of, except where the influence of input rate was investigated where CO_2 input was varied from 0.0 (N_2 only) to 9.0 g h^{-1} of CO_2 input. The mass of plastic used was kept constant at 2 g and the mass of catalyst was 1.0 g, except for the experiments investigating plastic:catalyst ratio where 0.25, 0.5, 1.0 and 1.5 g of catalyst was used.

The reformed product gases were then passed to a three stage condenser system cooled by dry ice. Effluent gases were trapped into a Tedlar^{TM} gas sample bag to be analysed offline using gas chromatography (GC). The GC's used were a Varian 3380 instrument with two different columns, a 60-80 mesh molecular sieve to determine H_2, CO, O_2 and N_2, and a HayeSep 80-100 mesh for CO_2. Both columns used Ar as carrier gas and with a thermal conductivity detector (TCD). C_1-C_4 hydrocarbons determination was by another Varian 3380 GC, HayeSep 80-100 mesh column, flame ionisation detector and N_2 carrier gas. The CO_2 used in the reactions was calculated by considering the mass of CO_2 gases injected to the system and the mass after the experiment determined by GC analysis of the CO_2.

The CO_2 conversion was used to monitor how much carbon dioxide was consumed during the experiment. The measurement was calculated by the difference of the weight of CO_2 gases injected to the reactor system and the weight after the experiment had finished (measured by the GC analysis). The carbon dioxide conversion (as g of CO_2 in relation to the g of simulated waste plastics used in the experiment) was calculated according to the formula shown below;

$XCO_2\ (g_{\ CO_2}\ g^{-1}{}_{plasti}) = [massCO_2]_{input} - [massCO_2]_{output} / \ [mass\ plastic]_{input}$

3. Results and discussion

3.1 Effect of catalyst preparation methods.

Two types of catalyst preparation methods were investigated, the rising-pH technique and the impregnation technique, were used to prepare a 1:1:1 molar ratio of Ni:Co:Al for the Ni-Co-Al_2O_3 catalyst. The catalytic dry reforming of the simulated mixture of waste plastics was carried out with 2 g of plastic, 1 g of Ni-Co-Al_2O_3 catalyst, 800 °C reforming temperature and 6.0 g h^{-1} of CO_2 input rate to compare the two catalyst preparation methods. The results are shown in Table 1, and show that the method of catalyst preparation had only a small influence on the product yield, gas composition, syngas yield or H_2:CO molar ratio. However, there were some small, but important, differences between the catalysts for example, the syngas yield (H_2 + CO) was higher with the catalyst prepared by the rising-pH technique at 148.6 $mmol_{syngas}\ g^{-1}{}_{swp}$ compared with 127.4 $mmol_{syngas}\ g^{-1}{}_{swp}$ for the catalyst prepared by impregnation.

In addition, the CO_2 conversion was higher with the Ni-Co-Al_2O_3 catalyst prepared by the rising-pH techniques compared to the impregnation method (Table 1)

Figure 2 and Figure 3 showed the characterization of the used Ni-Co-Al_2O_3 catalysts from catalytic dry reforming of SWP performed by TGA-TPO and SEM analysis respectively. The TGA thermographs for the catalyst prepared by the rising-pH technique, showed three peaks; around 450 °C, 570 °C and 725 °C. The mass increase starting from 300 °C and reach a peak at about 500 °C, suggests nickel oxidation. The mass loss peaks observed, at ~570 – 600 °C and ~725 °C has been attributed to oxidation of amorphous type carbon at the lower temperature and oxidation of filamentous, graphitic type carbon at the higher temperature. In addition, the catalyst prepared by the rising-pH method showed a larger increment of the weight gain peak compared to the catalyst prepared by the impregnation method. Tompkins and Augis [19] reported that the oxidation of metallic Co to CoO and Co_3O_4 occurred at a temperature of 425 °C. This suggests that overlapping weight gain as determined by the TGA-TPO analysis occurred between both nickel and cobalt particles for the reacted Ni-Co-Al_2O_3 catalyst prepared by the rising-pH method from the dry reforming of simulated waste plastics (SWP), hence a higher weight gain peak. This difference in weight gain properties also suggests that both nickel and cobalt particles of the catalyst prepared by rising-pH technique were not deactivated by carbon formation during the dry reforming process. This finding is also in agreement with the SEM morphologies from the surface of both Ni-Co-Al_2O_3 catalysts.

As shown in Figure 3, the scanning electron micropraphs show a smaller particle size for the rising-pH technique compared to the impregnation method of catalyst preparation. Since the catalyst prepared by the rising-pH technique produced a higher syngas (H_2 + CO) yield in terms of mmol per gram of plastic, the influence of process conditions on syngas yield was further investigated using the Ni-Co-Al_2O_3 catalyst prepared by the rising-pH technique.

3.2 Influence of catalyst reforming temperature.

The investigation of the effect of catalytic reforming temperature on syngas (H_2 and CO) production was carried out at 600 °C, 700 °C, 800 °C and 900 °C. The mass of plastic used was 2 g, with 1 g of Ni-Co-Al_2O_3 catalyst in the reforming reactor and the CO_2 was fixed at 6.0 g h^{-1} input rate. The results are shown in Table 2. The total gas yield increased from 96.90 wt.% at 600 °C to around 97 wt.% at both 700 °C and 800 °C. The gas yields were then reduced to 93.11 wt.% at the catalytic dry reforming temperature of 900 °C. The highest carbon deposited on the Ni-Co-Al_2O_3 catalyst surface was found at the catalytic dry reforming temperature of 900 °C at 5.50 wt.%.

The composition of product gases from the catalytic dry reforming of the mixed plastic in relation to temperature are shown in Figure 4. The data shows that with increased temperature, hydrocarbon gases were significantly reduced, from 0.08 g g^{-1}_{swp} to 0.01 g g^{-1}_{swp} for CH_4 and from 0.02 g g^{-1}_{swp} to 0.0 g g^{-1}_{swp} for C_2-C_4 hydrocarbons. In contrast, H_2 and CO yields increased as the catalyst temperature was raised from 600 to 800 °C, but thereafter declined. The production of high yields of H_2 and CO from the two-stage catalytic dry reforming of high density polyethylene with and without CO_2 has been reported to show a marked reduction in C_1─C_4 hydrocarbon gases [20], illustrating the dry reforming reaction of the hydrocarbon gases derived from pyrolysis of the plastic (Equation 1). In addition, it has been reported that the dry reforming reaction is favourable at high temperature [21-23].

$$CxHy + xCO_2 \rightarrow 2xCO + y/2\ H_2 \qquad \text{Equation 1}$$

H_2 yields steadily increased from 0.08 g g^{-1}_{swp} at 600 °C to 0.10 g g^{-1}_{swp} at 900 °C while CO yields increased from 2.10 g g^{-1}_{swp} at 600 °C to 2.79 g g^{-1}_{swp} at 800 °C and decreased slightly to 2.12 g g^{-1}_{swp} at 900 °C. The CO_2 conversion was closely related to syngas production, with high CO_2 conversion resulting in high syngas yields. The maximum syngas production and maximum CO_2 conversion occurred at a catalyst reforming temperature of 800 °C at 148.6 $mmol_{syngas}$ g^{-1}_{swp} and 2.07 g g^{-1}_{swp} CO_2 conversion.

The reduction in CO yield at high temperature (900 °C) may be due to reduced catalytic activity at high temperature due to sintering of the catalyst. Table 2 shows that catalyst activity had declined since the CO_2 conversion was reduced from 2.07 g g^{-1}_{swp} at 800 °C to 1.58 g g^{-1}_{swp} at 900 °C. In addition, scanning electron microscopy of the used catalyst at 900 °C also, showed an increase of the catalyst particle size, suggesting sintering had occurred.

The reduction in syngas yield at higher temperatures has also been reported by Rieks et al. [24] for methane dry reforming. But they suggested that a slight drop in the syngas yield was due to the reverse water gas shift reaction (Equation 2) at temperatures above 800 °C. However, Wang et al. [25] determined the upper temperature at which the reverse water gas shift no longer occurs, which corresponded to 820 °C [25]. This is in agreement with the results obtained in this study in which CO showed a decrease and H_2 an increase at higher temperatures above 800 °C.

$$CO_2+H_2 \rightarrow CO+H_2O \qquad \text{Equation 2}$$

At 900 °C catalyst reforming temperature, the deposited carbon on the catalyst increased to 5.5 wt.%. The formation of carbon on the catalyst surface leads towards the reduction of active sites on the catalyst surface, resulting on low activity on the performance of dry reforming reactions and thereby reduced CO_2 conversion and consequently reduced CO yield (Table 2 and Figure 4). In addition, Benguerba et al. [26] have reported that at higher temperature, the rate at which carbon gasification reactions (Equation 3) occurred were not high enough to remove the deposited carbon, hence leading to higher coke formation and reduced catalyst activity. Therefore, a greater rate of the methane decomposition reaction (Equation 4) compared to the carbon gasification reaction (Equation 3) may also be the reason behind the carbon build-up on the catalyst surface at 900 °C. The decomposition of methane also promotes H_2 production, hence H_2 continues to increase at 900 °C. Thermodynamic calculations [14] have shown that the conversion rate of CH_4 and CO_2 are greater than those expected from the dry reforming reaction alone, demonstrating the occurrence of secondary reactions.

$$C + CO_2 \rightarrow CO \qquad \text{Equation 3}$$

$$CH_4 \rightarrow C + 2H_2 \qquad \text{Equation 4}$$

3.3 Influence of CO_2 inlet flow rate

The CO_2 inlet flow rate of 3.0, 4.5, 6.0, 7.5 and 9.0 g h^{-1} were investigated with 2 g of the simulated mixture of waste plastics, 1 g of the Ni-Co-Al_2O_3 catalyst and a catalytic dry reforming temperature of 800 °C. In addition, an experiment with only nitrogen was also performed as a baseline experiment. The results are shown in Table

3. The data shows that with the increase of CO_2 flow rate, the total gas yield increased, from 52.41 wt.% with no addition of CO_2 to 92.70 wt.% at a CO_2 flow rate of 3.0 g h^{-1} and thereafter steadily increased to reach 99.40 wt.% at a CO_2 flow rate of 9.0 g h^{-1}. In the absence of CO_2 (N_2 carrier gas), there was a high mass of carbon deposited on the catalyst at 36.50 wt.%, however, introducing CO_2 to the catalytic dry reforming process reduced the catalyst carbon deposition to 7.3 wt.% at a CO_2 flow rate of 3.0 g h^{-1} reducing to 1.4 wt.% at a CO_2 flow rate of 9.0 g h^{-1}

As shown in Table 3 the increase of CO_2 flow rate also influenced syngas (H_2+CO) yields. The syngas yield increased from 60.68 $mmol_{syngas}$ $g^{-1}{}_{swp}$ in the absence of CO_2 to 121.37 $mmol_{syngas}$ $g^{-1}{}_{swp}$ at a CO_2 flow rate of 3.0 g h^{-1}; increasing continually at higher CO_2 inlet flow rates to reach more 155.03 $mmol_{syngas}$ $g^{-1}{}_{swp}$ at a CO_2 flow rate of 9.0 g h^{-1}.

Figure 5 shows the composition of the gases produced from the catalytic dry reforming of the plastics mixture. The results show that the major increase in total gas yield (Table 3) when CO_2 was introduced to the process compared to the absence of CO_2 was due to the formation of CO, with a marked increase in CO yield and thereby producing a high syngas yield. However, the yield of H_2 was low in the absence of the CO_2 and was not affected by the introduction of CO_2 even at higher inlet CO_2 flow rates. This was reflected in the H_2:CO molar ratios which was high in the absence of CO_2 at 4.32, reducing to 0.81 with the introduction of CO_2 and showing decrease with increasing CO_2 flow rate.

A low yield of hydrocarbons (C_2-C_4) was produced throughout the experiments. However, Figure 5 also shows a dependent trend between CH_4 and H_2 yields. High concentration of H_2 gas yield correlated with low concentrations of CH_4. The highest H_2 yield was obtained at the CO_2 flow rate of 3.0 g h^{-1} and was slightly reduced at 4.5

g h^{-1} of CO_2 flow rate. In this study, even after increasing the CO_2/plastic ratio up to 6.0 (CO_2 flow rate of 9.0 g h^{-1}), the syngas production was still increasing, since the major contribution was from CO, where CO yield kept increasing with the increase of CO_2 flow rate.

3.4 Influence of catalyst to plastic ratio

The catalyst to plastic ratios of 0.25, 0.5, 1.0 and 1.5 were studied to evaluate their influence in relation to syngas production from the dry reforming of SWP. As a baseline experiment, substitution of sand was used instead of the Ni-Co-Al_2O_3 catalyst in the reforming reactor. The catalytic reforming temperature and CO_2 flow rate were kept at 800 °C and 6.0 g h^{-1} respectively for the experiments. The weight of the simulated mixture of waste plastics was also fixed at 2 g. Table 4 shows the product yields from dry reforming of the plastics in relative to the catalyst to plastic ratio investigation. The results suggest that high carbon deposition occurred on the sand surface in the absence of catalyst, resulting in low gas production, at only 87.9 wt.%. The addition of the catalyst reduced carbon deposition from 5.5 wt.% to 1.8 wt.% at the catalyst:plastic ratio of 0.25 which steadily decreased to 1.7 wt.% at the catalyst:plastic ratio of 0.5. No obvious carbon deposition on the used catalyst surface could be found at the catalyst:plastic ratios of 1.0 and 1.5. It has been suggested that when more catalyst is used, more pyrolysis gases could react with the catalyst, resulting in lower carbon deposition on the catalyst and higher gas production [27, 28]. The highest gas yield was obtained at the catalyst:plastic ratio of 1.0, at 98.2 wt.%.

Table 4 also shows that the syngas yield from the different catalyst:plastic ratios for the catalytic dry reforming of the plastic mixture showing that there was a significant increase in syngas yields with the addition of catalyst, from 91.3 (sand) to 141.3 mmol g^{-1}_{swp} (catalyst addition). The syngas yield gradually increased to 148.6 mmol g^{-1}_{swp} with 1g of Ni-Co-Al_2O_3 catalyst was used, followed by a slight decrease as the catalyst:plastic ratio was increased. The gas composition derived from catalytic dry reforming of the mixed plastics are shown in Figure 6. The results show that there was a decrease in CH_4 and C_2-C_4 concentrations when the catalyst was introduced into the system. As a result, CO and H_2 were markedly increased, confirming that the addition of catalyst further enhanced the reforming reaction between CO_2 and hydrocarbons (Equation 1). The addition of further catalyst lowered CO concentrations, which might be due to CO methanation reaction (Equation 4).

4. Conclusions

This study has demonstrated that varying the experimental parameters has a significant influence on syngas production from the dry reforming of the simulated mixture of waste plastics. The catalyst preparation method also influences the properties of the catalyst and consequently the activity of the catalyst towards syngas production. The catalyst prepared using the rising-pH technique produced higher syngas yield that the catalyst prepared using the impregnation method. The optimum syngas production was obtained at the catalyst reforming temperature of 800 °C and with the catalyst:plastic ratio of 0.5, with a yield of 148.6 mmol g^{-1}_{swp}. The increase of CO_2 flow rate, further enhanced syngas production from 60.7 mmol g^{-1}_{swp} at no CO_2 addition to 155.0 mmol g^{-1}_{swp} at 9.0 g h^{-1} CO_2 flow rate.

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Table 1
Product yields and gas composition from the catalytic dry reforming of a simulated mixture of waste plastics (SWP) with different types of Ni-Co-Al_2O_3 catalyst preparation methods.

Catalyst preparation method	Rising – pH	Impregnation
Product yield in relation to SWP+CO_2 (wt.%)		
Gas	97.0	94.1
Liquid	0.6	1.0
Char	0.6	0.6
Catalyst carbon deposition	1.7	1.5
Mass balance	99.9	97.2
Product yield in relation to SWP only (wt.%)		
Gas	485.4	470.6
Liquid	3.0	5.0
Char	3.0	3.0
Catalyst carbon deposition	8.5	7.5
Gas composition (g g^{-1}_{swp})		
H_2	2.79	2.41
CO	0.10	0.08
CH_4	0.04	0.08
C_2-C_4	0.0	0.0
Syngas yield (mmol$_{syngas}$ g^{-1}_{swp})		
H_2+CO	148.6	127.4
H_2:CO molar ratio	0.49	0.48
CO_2 conversion (inlet-outlet) (g g^{-1}_{swp})	2.07	1.87

Table 2
Product yields and gas composition from the catalytic dry reforming of a simulated mixture of waste plastics (SWP) in relation to catalyst temperature.

Temperature (°C)	600	700	800	900
Product yield in relation to SWP+CO_2 (wt.%)				
Gas	96.9	97.1	97.1	93.1
Liquid	1.0	1.1	0.6	0.6
Char	0.5	0.5	0.6	0.8
Catalyst carbon deposition	2.6	1.7	1.7	5.5
Mass balance	101.0	100.4	100.0	100.0
Product yield in relation to SWP only (wt.%)				
Gas	484.5	485.3	485.4	465.6
Liquid	5.0	5.5	3.0	3.0
Char	2.5	2.5	3.0	4.0
Catalyst carbon deposition	13.0	8.5	8.5	27.5
Syngas yield (mmol$_{syngas}$ g^{-1}$_{swp}$)				
H_2+CO	116.2	144.0	148.6	125.8
H_2:CO molar ratio	0.55	0.48	0.49	0.66
CO_2 conversion (inlet-outlet) (g g^{-1}$_{swp}$)	1.43	2.02	2.07	1.58

Table 3
Product yields and gas composition from the catalytic dry reforming of a simulated mixture of waste plastics (SWP) at different inlet CO_2 flow rates.

CO_2 flow rate (g h^{-1})	0.0	3.0	4.5	6.0	7.5	9.0
Product yield in relation to SWP+CO_2 (wt.%)						
Gas	52.4	92.7	96.6	97.1	98.0	99.4
Liquid	2.0	1.7	1.3	0.6	0.5	0.4
Char	3.5	1.2	0.9	0.6	0.5	0.4
Catalyst carbon deposition	36.5	7.3	2.3	1.7	1.5	1.4
Mass balance	94.4	100.9	100.9	100.0	100.4	101.5
Product yield in relation to SWP only (wt.%)						
Gas	52.4	278.1	386.3	485.4	587.7	695.8
Liquid	2.0	5.0	5.0	3.0	3.0	2.5
Char	3.5	3.5	3.5	3.0	3.0	3.0
Catalyst carbon deposition	36.5	22.0	9.0	8.5	9.0	9.5
Syngas yield ($mmol_{syngas}$ g^{-1}_{swp})						
H_2+CO	60.7	121.4	136.8	148.6	149.0	155.0
H_2:CO molar ratio	4.32	0.81	0.52	0.49	0.46	0.45
CO_2 conversion (inlet-outlet) (g g^{-1}_{swp})	N/A	1.22	1.78	2.07	2.10	2.16

Table 4
Product yields and gas composition from the catalytic dry reforming of a simulated mixture of waste plastics (SWP) at different catalyst:plastic ratios.

Catalyst to plastic ratio (g g^{-1})	0.0	0.25	0.5	1.0	1.5
Product yield in relation to SWP+CO_2 (wt.%)					
Gas	87.6	94.7	97.1	98.2	98.0
Liquid	1.4	1.0	0.6	2.4	3.9
Char	1.0	0.7	0.6	0.3	0.5
Catalyst carbon deposition	5.5	1.8	1.7	0.0	0.0
Mass balance	95.5	98.2	100.0	100.9	102.4
Product yield in relation to SWP only (wt.%)					
Gas	438.0	473.7	485.4	490.9	490.1
Liquid	7.0	5.0	3.0	12.0	19.5
Char	1.0	0.7	0.6	0.3	0.5
Catalyst carbon deposition	5.5	1.8	1.7	0.0	0.0
Syngas yield ($mmol_{syngas}$ g^{-1}_{swp})					
H_2+CO	91.3	141.3	148.6	143.9	139.9
H_2:CO molar ratio	0.52	0.48	0.49	0.49	0.51
CO_2 conversion (inlet-outlet) (g g^{-1}_{swp})	1.53	2.06	2.07	1.92	1.79

Figure Captions

Fig. 1. Schematic diagram of the two-stage fixed bed reactor.

Fig. 2. TGA and TGA-DTG thermographs of the reacted catalysts from the dry reforming of the simulated mixture of waste plastics (SWP) with catalyst prepared by the rising-pH technique and the impregnation method.

Fig. 3. SEM micrographs of the reacted catalysts from the simulated mixture of waste plastics (SWP) with catalyst prepared by the rising-pH technique and the impregnation method.

Fig. 4. Gas compositions produced from the catalytic dry reforming of reforming of the simulated mixture of waste plastics (SWP) at different catalytic dry reforming temperatures.

Fig. 5. Gas compositions produced from the catalytic dry reforming of the simulated mixture of waste plastics (SWP) at different CO_2 flow rates.

Fig. 6. Gas compositions produced from the catalytic dry reforming of the simulated mixture of waste plastics (SWP) at different catalyst:plastic ratios.

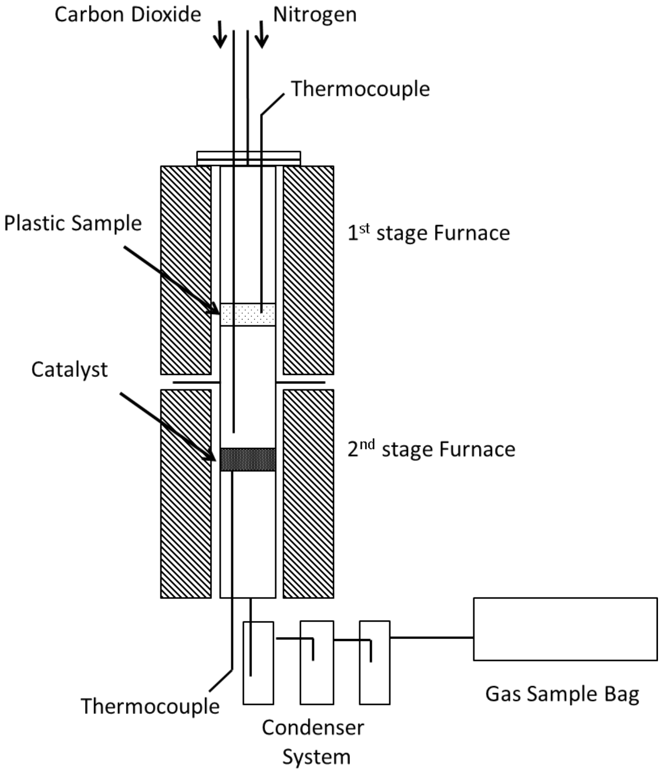
Carbon Dioxide
Nitrogen
Thermocouple
Plastic Sample
1st stage Furnace
Catalyst
2nd stage Furnace
Thermocouple
Condenser System
Gas Sample Bag

Figure 1

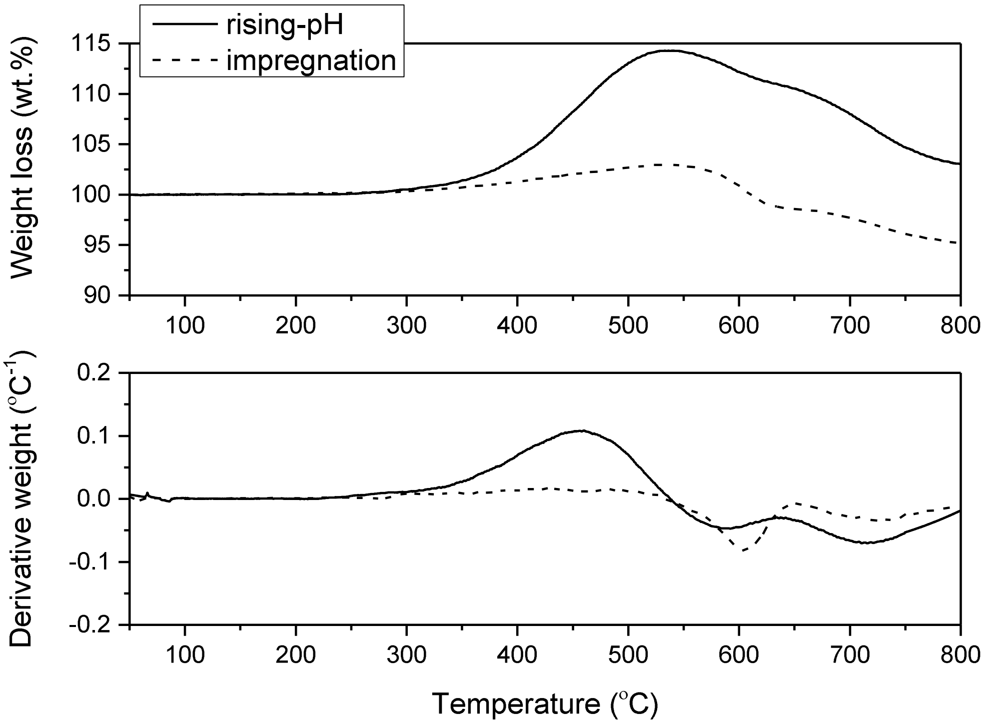
rising-pH
impregnation
Weight loss (wt.%)
115
110
105
100
95
90
100
200
300
400
500
600
700
800
Derivative weight (°C-1)
0.2
0.1
0.0
-0.1
-0.2
100
200
300
400
500
600
700
800
Temperature (°C)

Figure 2

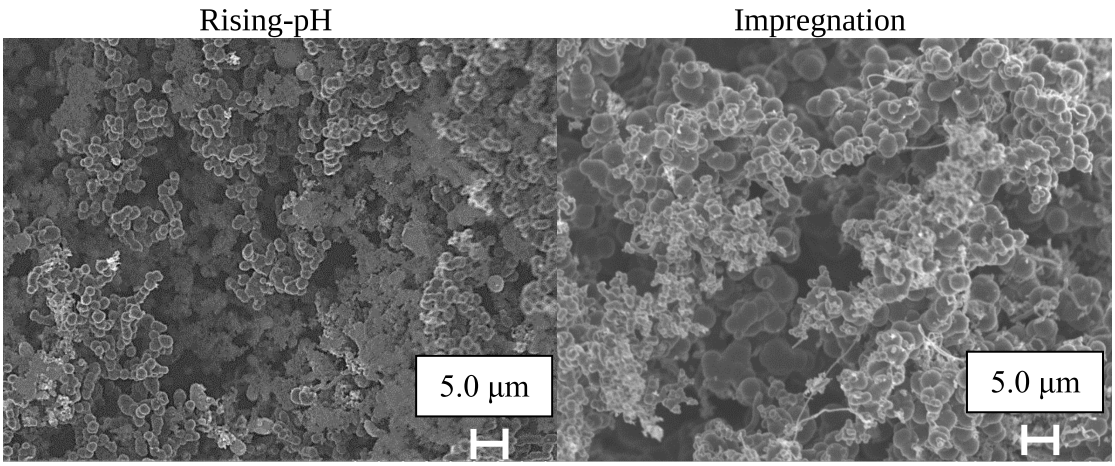

Figure 3

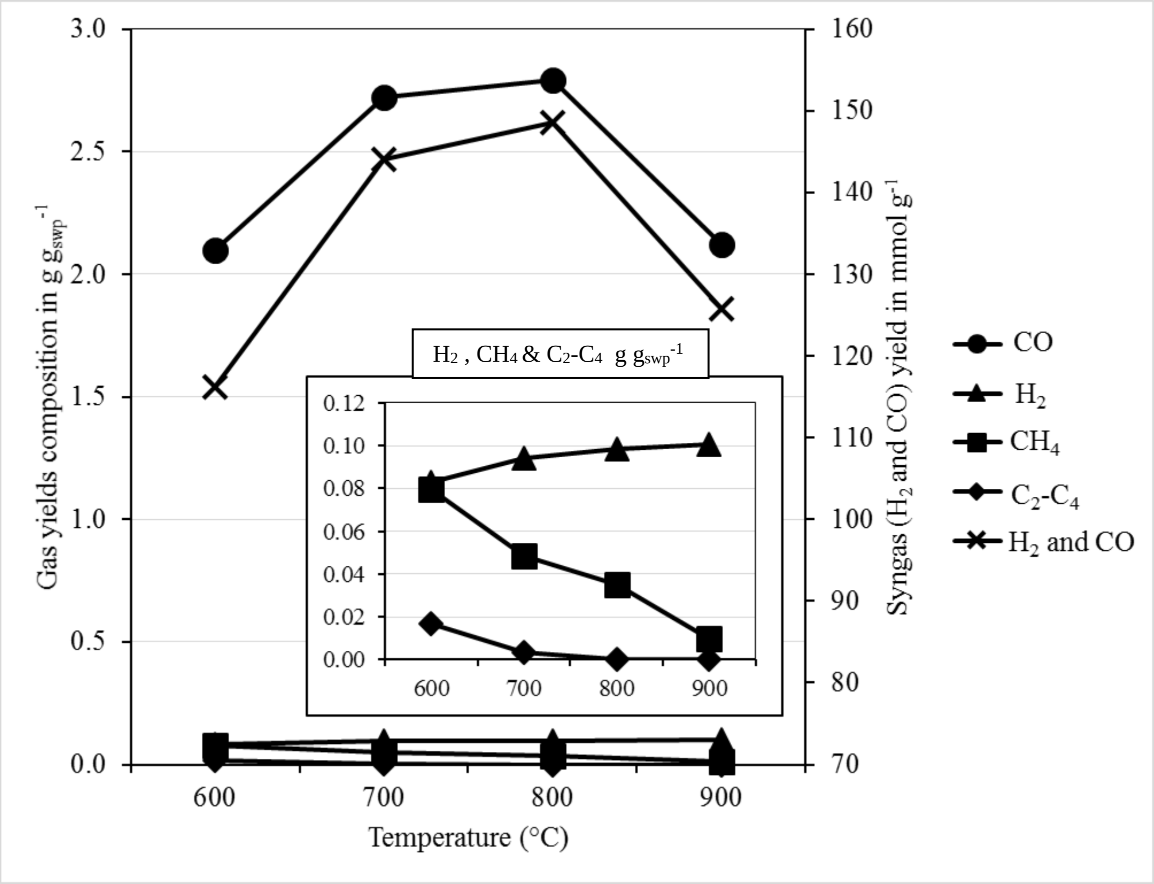
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Gas yields composition in g g_{swp}^{-1}
160
150
140
130
120
110
100
90
80
70
Syngas (H_2 and CO) yield in mmol g^{-1}
600
700
800
900
Temperature (°C)
H_2 , CH_4 & C_2-C_4 g g_{swp}^{-1}
0.12
0.10
0.08
0.06
0.04
0.02
0.00
600
700
800
900
CO
H_2
CH_4
C_2-C_4
H_2 and CO

Figure 4

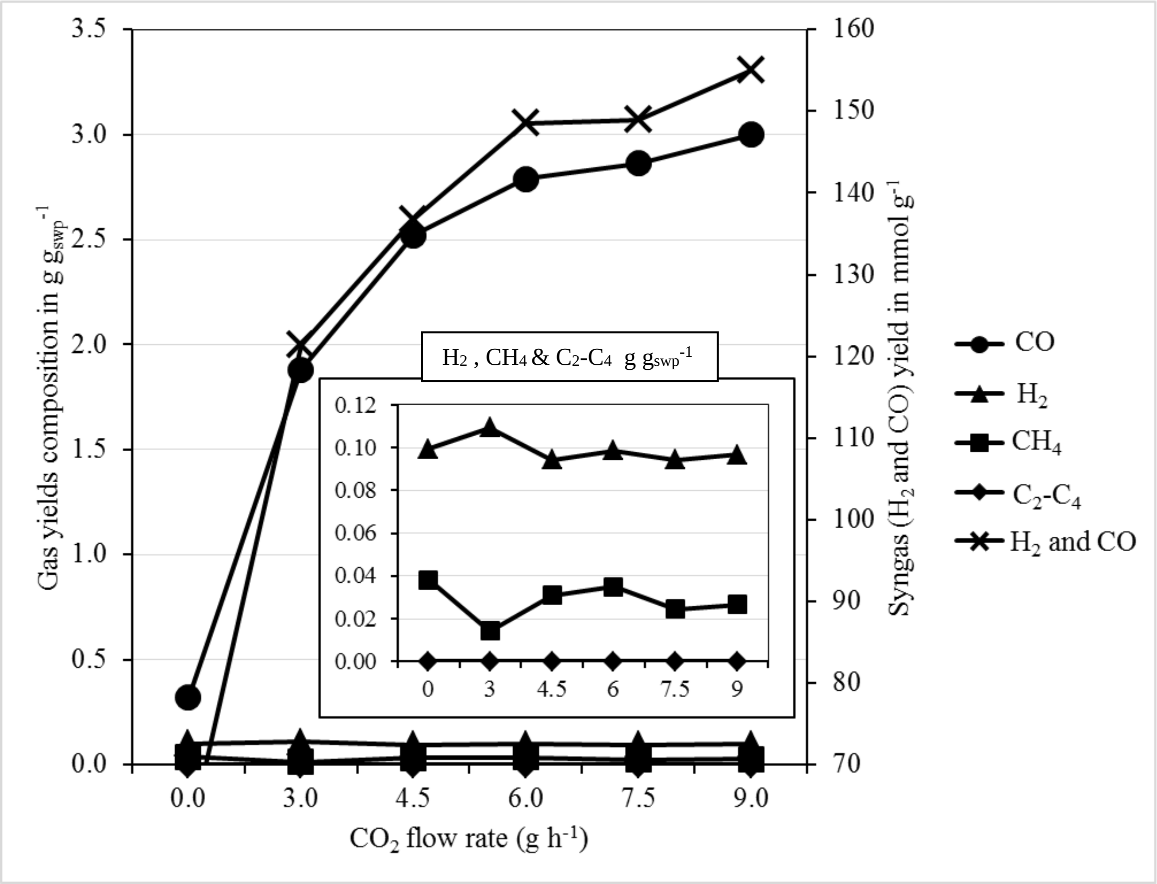
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Gas yields composition in g g_{swp}^{-1}
160
150
140
130
120
110
100
90
80
70
Syngas (H_2 and CO) yield in mmol g^{-1}
0.0
3.0
4.5
6.0
7.5
9.0
CO_2 flow rate (g h^{-1})
H_2 , CH_4 & C_2-C_4 g g_{swp}^{-1}
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
3
4.5
6
7.5
9
CO
H_2
CH_4
C_2-C_4
H_2 and CO

Figure 5

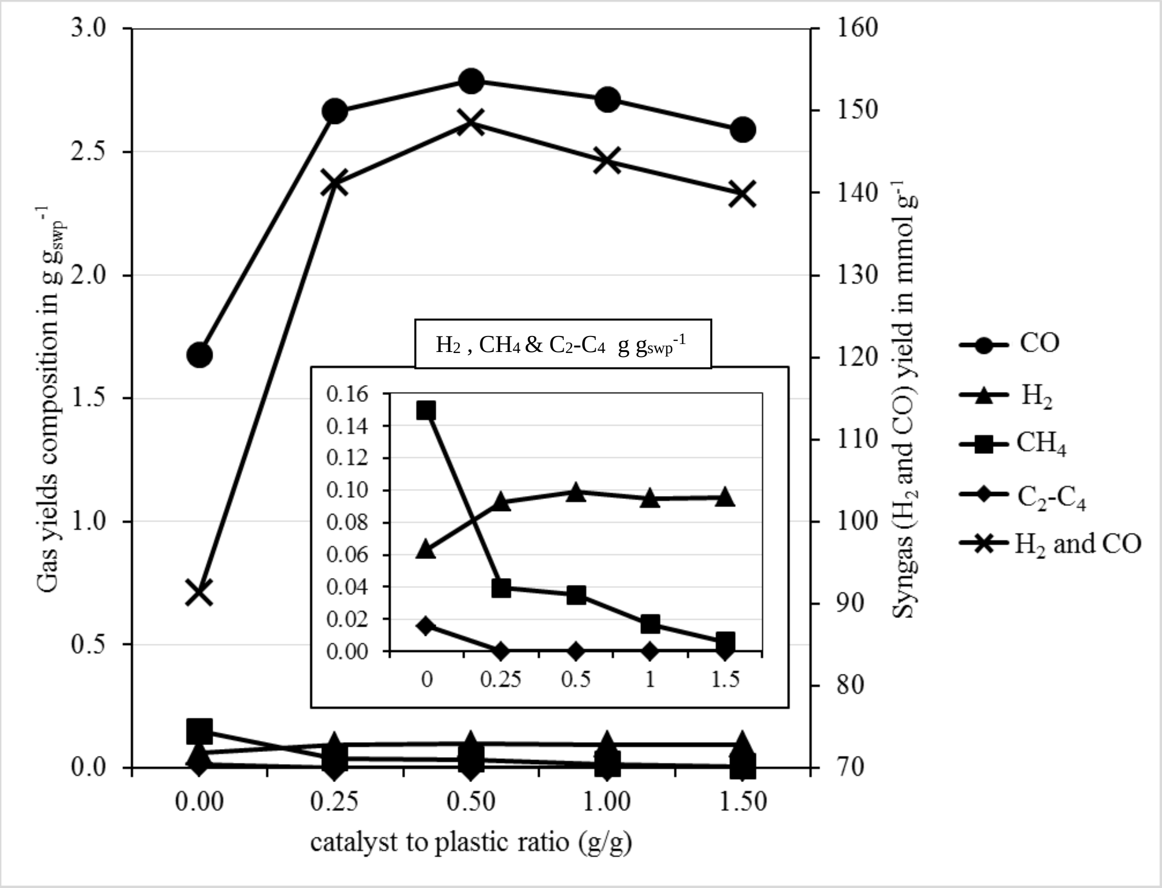
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Gas yields composition in g g_{swp}^{-1}
160
150
140
130
120
110
100
90
80
70
Syngas (H_2 and CO) yield in mmol g^{-1}
0.00
0.25
0.50
1.00
1.50
catalyst to plastic ratio (g/g)
H_2 , CH_4 & C_2-C_4 g g_{swp}^{-1}
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
0.25
0.5
1
1.5
CO
H_2
CH_4
C_2-C_4
H_2 and CO

Figure 6