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Hydrogen from waste plastics by way of pyrolysis-gasification

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Abstract: A screw kiln continuous reaction system was used to investigate the production of hydrogen from a representative waste plastic (polypropylene). The reactor system consisted of two-stages with pyrolysis of the plastic in the first stage screw kiln followed by catalytic gasification of the product pyrolysis gases in the second stage. Two catalysts (a laboratory prepared Ni-Mg-Al catalyst and a commercial Ni catalyst) were used and the process conditions of gasification temperature and water injection rate were investigated. The results showed that the introduction of catalyst into the gasification stage dramatically increased the hydrogen production. The gas and hydrogen production and amount of reacted water per hour were increased with the increase of the gasification temperature from 600 to 900 °C for both the Ni-Mg-Al and the commercial Ni catalysts. The rate of water injection was also shown to be critical for hydrogen production. The maximum hydrogen produced was 52% of the maximum theoretical hydrogen available in the polypropylene, representing 22.38 g of hydrogen per 100 g polypropylene, obtained with the Ni-Mg-Al catalyst, at 800 °C gasification temperature and with 28.46 g h⁻¹ water injection rate.

Keywords: Polypropylene; Nickel; Catalyst; Screw kiln

1. Introduction

There is increasing interest in the potential of hydrogen as a future fuel source due to its clean combustion compared to the emission of green house gases with fossil fuels and its predicted use in advanced technologies such as fuel cell etc., (Dunn, 2002, Johnston et al., 2005). At present, the majority of hydrogen is generated from fossil fuels and there have been investigations into more sustainable sources for hydrogen such as biomass (Wang et al., 1998, Garcia et al., 2002).

Waste plastics represent a significant potential source of hydrogen for fuelling the future. Total annual waste plastics production in Europe (EU-27) reached 25.1 million tonnes in 2011 (Europe, 2012). Approximately 6.3 million tonnes (~25%) of this waste was recycled typically via mechanical recycling to produce products such as dustbin sacks, sewer pipes, industrial plastic pallets, traffic cones, shoes, carpets and garden furniture. About 8.5 million tonnes (~34%) of waste plastics are used for energy recovery, mainly through mass burn incineration of municipal solid waste, but also through increasing use in cement kilns. The remaining 10.3 million tonnes (~41%) of plastic waste is landfilled.

There has been some research into the recovery of hydrogen from waste plastics, generally in fixed bed reactor systems at the research laboratory level (Czernik and French, 2006, Wu and Williams, 2009c, Wu and Williams, 2009a, Wu and Williams, 2010b). However, for the development of an industrial scale process, a continuous reactor system would be required to ensure commerciality. Among various reactors for the thermal processing of waste plastics, the continuous screw kiln has been proposed to be a preferred reaction system for industrial commercialization (Aguado et al., 2002, Day et al., 1999, Serrano et al., 2003). Furthermore, it has been suggested that the screw kiln reaction system might reduce the over-cracking of plastics,

and generate a comparatively narrow range of products that could be reformed in a second stage to produce hydrogen gas (Czernik and French, 2006). Such a reforming process is optimized by the presence of a catalyst in the second stage which increases the conversion to hydrogen. Nibased catalysts are used in the commercial production of hydrogen from a range of feedstocks including biomass and fossil fuels because of their relatively low cost compared to other noble metal-based catalysts.

In this paper, polypropylene was used as a representative waste plastic to investigate the production of hydrogen using a two-stage continuous reactor system. Polypropylene is one of the major plastics produced in Europe and approximately 9 million tones of polypropylene are used each year in the European Union (EU-27) (Europe, 2012). The polypropylene was pyrolysed in a first stage screw kiln reactor and the pyrolysis gases were passed directly to a second stage fixed bed catalyst reactor where gasification of the derived pyrolysis gases took place in the presence of steam to produce hydrogen. A laboratory prepared Ni-Mg-Al catalyst and a commercial Ni catalyst were compared. Experimental parameters of gasification temperature and water injection rate were also investigated to determine their influence on hydrogen production.

2. Experimental

2.1. Materials. Polypropylene was obtained as 2 mm virgin polymer pellets provided by BP Chemicals UK. A commercial catalyst of composition, 65wt.% Ni/SiO₂/Al₂O₃ obtained from Alfa Aesar, UK and a laboratory-prepared Ni-Mg-Al catalyst were used in this work. The Ni-Mg-Al catalysts were prepared using the rising pH technique according to the method reported by Garcia et al (Garcia et al., 2002). The precipitant NH₄(OH) was added to 200 ml of an aqueous solution containing Ni(NO₃)•6H₂O, Al(NO₃)₃•9H₂O and Mg(NO₃)₂•6H₂O. The

precipitation was carried out at 40 °C with moderate stirring until a final pH of 8.3 was obtained. The precipitates were filtered and washed with water at 40 °C, followed by drying at 105 °C overnight, and then were calcined at 750 °C for 3h. The initial Ni-Mg-Al molar ratio was 1:1:1. The Ni-Mg-Al (1:1:1) catalysts were crushed and sieved to granules with a size range between 0.065 and 0.212 mm.

2.2 Characterization of catalysts. Temperature-programmed oxidation (TPO) of the reacted Ni-Mg-Al catalysts was carried out using a Stanton-Redcroft thermogravimetric analyser (TGA) in the presence of air. TPO determines the burn-off temperature of any carbon deposited on the surface of the catalysts as the temperature of the TGA is raised in the presnce of an oxidising air atmosphere. Differential thermo-gravimetry (DTG) results obtained from the TPO experiments were also determined. The catalyst after reaction was heated in an atmosphere of air at a heating rate of 15 °C min⁻¹ to a final temperature of 800 °C, with a dwell time of 10 minutes at 800 °C.

The surface characteristics of the reacted catalysts was determined using scanning electron microscopy (SEM). A high resolution scanning electron microscope (SEM, LEO 1530) coupled to an energy dispersive X-ray spectroscopy (EDXS) was used to characterise and examine the characteristics of the carbon deposited on the coked catalysts.

2.3. Reaction system. A schematic diagram of the screw kiln reactor is shown in Figure 1. The screw kiln reaction system mainly includes a material feeding system, screw kiln pyrolysis system and a fixed-bed gasification system. The system was pourged with nitrogen throughout the experiments. The plastic material was continuously fed into the pyrolysis screw kiln reactor (62 mm diameter and 540 mm length), where a screw rotated by an electric motor slowly transported the plastic through the reactor and where pyrolysis took place. The screw kiln was

heated by a small pre-heat furnace and a large main furnace. The derived pyrolysis gases passed through a fixed-bed vertical gasification reactor (25 mm diameter and 260 mm length) which contained the catalysts and was heated and controlled separately. Steam was introduced into the gasification reaction system for the catalytic steam gasification of the product pyrolysis gases. The connection of the pyrolysis reactor to the gasification reactor was also heated to avoid gas condensation before entering into the gasification bed. The plastic feeding rate was kept at 11 g h^{-1} and the residence time in the screw kiln was about 60 seconds and the gas residence time in the second stage gasification reactor was about 38 seconds. The generated gases after pyrolysisgasification were passed through a condensation system to collect liquids and the noncondensable gases were collected with a TedlarTM gas sample bag, and analysed for the gas concentrations off-line using packed column gas chromatography. For each experiment, the reactor system was stabilized for about 30 minutes continuous operation before each gas sample was collected with TedlarTM gas sample bags for 5 min at 5 consecutive reaction times. Therefore, five gas concentrations are presented for each experiment. However, the amount of reacted and gas and hydrogen yields are presented as the average values of the whole experiment. More than 90 wt.% of conversion of the plastic to gas products was obtained at the pyrolysis temperature of 500 °C, gasification temperature of 800 °C and water injection rate of 28.46 g h^{-1} in the presence of Ni-Mg-Al catalyst.

The gaseous products collected in the TedlarTM sample bags were analysed by packed column gas chromatography to determine the concentration of hydrocarbons and permanent gases. C₁ to C₄ hydrocarbons were analysed using a Varian 3380 gas chromatograph with a flame ionisation detector, with a 80-100 mesh Hysesp column and nitrogen carrier gas. Permanent gases (H₂, CO, O₂, N₂ and CO₂) were analysed by a second Varian 3380 GC with two packed columns each with a thermal conductivity detector. Hydrogen, oxygen and carbon monoxide, methane and nitrogen were analysed on a 60-80 mesh molecular sieve column with argon carrier gas, whilst carbon dioxide was analysed on a Hysep 80-100 mesh column with argon carrier gas.

3. Results and discussion

3.1. Influence of steam and catalyst on the gas hydrogen production

Experiments were carried out to investigate the influence of steam and the presence of catalyst on gas and hydrogen production from the pyrolysis-gasification of polypropylene. The pyrolysis temperature and gasification temperature were controlled at 500 °C and 800 °C, respectively.

The maximum theoretical amount of H_2 produced from polypropylene steam gasification is estimated to be 42.9 g per 100 g polypropylene (Wu and Williams, 2009a). As shown in Equation (1), 100 g of polypropylene will generate a maximum 42.9 g of hydrogen, if all the carbons in the plastic are converted into CO₂. In this work, the term, potential hydrogen production, was calculated from the amount of hydrogen divided by the maximum hydrogen production (42.9 g H₂/100 g polypropylene).

$$C_nH_{2n} + 2nH_2O \to nCO_2 + 3nH_2$$
 (1)

The gas production and hydrogen production are presented in Table 1 and show that with the introduction of steam in the gasification process, gas production increased from 0.75 to 9.08 g h⁻¹ and the H₂ production increased from 0.03 to 0.99 g h⁻¹. The gas production rate was determined as the total weight of gases, including, CO, CO₂, H₂, CH₄, C₂-C₄ hydrocarbon gases per hour of operation. Gas samples were collected at 5 minute intervals and analysed by gas chromatography. The presence of catalyst significantly increases the gas and hydrogen production. For example,

the potential H_2 production was increased from 1.08 to 9.01 g hydrogen per 100 g polypropylene in the absence of a catalyst to 9.01 g hydrogen per 100 g polypropylene in the presence of the Ni-Mg-Al catalyst; representing 21.01% of the theoretical maximum hydrogen production. The commercial nickel catalyst did not perform, as well as the laboratory prepared catalysts, producing only 15.34% of the theoretical maximum hydrogen production. Czernik and French (2006) also investigated the two-stage pyrolysis and gasification of polypropylene for the production of hydrogen. They used a first stage fluidized bed reactor to pyrolyse the polypropylene at a temperature of 650 °C. The derived pyrolysis gases were passed to a second fluidized bed reactor operated at a temperature of 850 °C where gasification of the pyrolysis gases took place in the presence of steam and a commercial nickel-based catalyst. They reported that the product gas consisted of over 70 vol.% of hydrogen. They also reported that 34 g of hydrogen per 100 g of polypropyelene were produced, representing more than 80% of the maximum hydrogen production (42.9 g H₂/100 g polypropylene). Serrano et al., (2003) also reported that gas production was increased with the presence of Al-MCM-41 catalyst for the thermal conversion of polyethylene/lubricating oil using as continuous screw kiln reactor.

The Ni-Mg-Al catalyst prepared in the laboratory seems to have a higher catalytic activity in relation with the hydrogen and gas production, compared with the commercial Ni catalyst. However, the detailed composition of the commercial Ni catalyst was not known due to commercial confidentiality, therefore a direct comparison between these two catalysts is not legitimate.

3.2. Influence of gasification temperature

3.2.1 Influence of gasification temperature on gas and hydrogen production.

The gasification temperature has been investigated extensively during the pyrolysis/gasification process due to its importance, but mainly for the gasification of biomass (Boateng et al., 1992, Herguido et al., 1992). In this section, the gasification temperatures of 600, 700, 800 and 900 °C were studied with the continuous screw kiln reactor system in relation to the pyrolysis-gasification of plastic. The water injection rate was controlled at 14.23 g h⁻¹. Pyrolysis temperature was kept at 500 °C.

The gas production and hydrogen production at different gasification temperatures with the Ni-Mg-Al catalyst and the commercial Ni catalyst are presented in Table 2 and Table 3, respectively. From Table 2 and Table 3, the reacted water was increased with the increase of gasification temperature for both the Ni-Mg-Al catalyst and the commercial catalyst. Only 3.69 g h⁻¹ water consumption rate was obtained at the gasification temperature of 600 °C for the Ni-Mg-Al catalyst; the reacted water was increased to 12.59 g h⁻¹ when the gasification temperature was increased to 900 °C (Table 2). In this work, the amount of reacted water was calculated from oxygen content present in CO and CO_2 in the gas stream; with the assumption that all the oxygen in the reacted water is converted to CO and CO₂. It is proposed that water gas reaction was promoted at higher gasification temperature. The enhancement of reacted water with the increase of gasification temperature resulted in a higher production of hydrogen. For example, the potential H₂ production increased from 4.83 to 17.87 g hydrogen per 100 g polypropylene as the gasification temperature was increased, representing an increase of percentage increase of the potential hydrogen production from 11.27 to 41.65% with the Ni-Mg-Al catalyst (Table 2). The commercial nickel catalyst also showed an increase in hydrogen yield (Table 3), when the gasification temperature was increased from 600 to 900 °C. In our previous work using a twostage fixed bed reactor system and a polypropylene feedstock we also reported that the

percentage of the potential H_2 production was increased from 13.4% to 52.0 % with a Ni/CeO₂/Al₂O₃ catalyst when the gasification temperature was increased from 600 to 900 °C (Wu and Williams, 2008). In addition, we also reported a 57.1 % of the potential hydrogen production using a Ni-Mg-Al catalyst at a gasification temperature of 800 °C using the same two-stage fixed bed reaction system (Wu and Williams, 2008).

3.2.2. Influence of gasification temperature on gas concentration.

The gas (H₂, CH₄ and C₂-C₄) concentration from the pyrolysis-gasification of polypropylene using the screw kiln reaction system, in the absence of catalyst (in the presence of sand), and at different gasification temperatures is presented in Figure 2. The gas concentration is presented on a nitrogen free basis.

From Figure 2, it seems that the H₂ concentration was increased and the C₂-C₄ concentration was decreased with the increasing gasification temperature from 600 to 900 °C. However, the CH₄ concentration was increased from 600 to 700 °C, and then decreased with the further gasification temperature increase to 900 °C. The higher CH₄ concentration is suggested to be derived from the decomposition of C₂-C₄ gases when the gasification temperature increased from 600 to 700 °C. With the further increase of gasification temperature, the methane steam reforming reaction is suggested to be promoted and thereby reduced the concentration of CH₄.

Gas concentrations at different gasification temperatures using the screw kiln reaction system with the Ni-Mg-Al catalyst and the commercial Ni catalyst are shown in Figure 3 and Figure 4, respectively. H₂ concentration was increased for the experiment in the presence of the catalyst. For example, H₂ concentration was increased to higher than 65 Vol.% for the catalytic pyrolysis/gasification at the gasification temperature of 600 °C (Figure 3 and 4), while only around 10 Vol.% of H_2 was obtained for the non-catalytic pyrolysis/gasification of polypropylene (Figure 2). The increase of H_2 concentration with the presence of catalyst is consistent with the higher hydrogen production for the catalytic pyrolysis/gasification of polypropylene, compared with the non-catalytic gasification (Table 1).

When the gasification temperature was increased from 600 to 900 °C for the catalytic gasification, H_2 and CO_2 concentrations seemed to be slightly reduced, and the CO concentration was increased with the increase of gasification temperature for both the Ni-Mg-Al and the commercial Ni catalyst (Figure 3 and Figure 4). It might be due to the prohibition of the water gas shift reaction at higher gasification temperature, as the water gas shift reaction is exothermic. However, the reaction rate for the water gas shift reaction might be enhanced at higher gasification temperature, since more hydrogen was produced and more water was consumed at higher gasification temperature.

As was the case for the change of CH_4 concentration with increasing gasification temperature without the catalyst (in the presence of sand), the CH_4 concentration was also increased at the gasification temperature of 700 °C compared with 600 °C, then decreased with the further increase of gasification temperature in the presence of the Ni-Mg-Al catalyst. However, the CH_4 concentration appeared to be reduced with the increase of gasification temperature in the presence of the commercial Ni catalyst (Figure 4). The C₂-C₄ gas concentrations were very low when the catalyst was used during the gasification stage.

3.3. Influence of water injection rate

3.3.1. Influence of water injection rate on gas and hydrogen production

Water injection rate (steam content in the gasification stage) was also investigated for the screw kiln continuous reaction system for hydrogen and gas production from polypropylene. The commercial Ni catalyst and a laboratory prepared Ni-Mg-Al catalyst were used in this section. The pyrolysis temperature and gasification temperature were controlled at 500 and 800 °C, respectively. The investigated water injection rates were 9.49, 14.23, 18.98 and 28.46 g h⁻¹. The gas and hydrogen production in the presence of the Ni-Mg-Al and the commercial Ni catalyst are presented in Table 4 and Table 5, respectively. As shown in Table 4 and Table 5, the amount of reacted water was increased with increasing water injection rate for both catalysts. For example, the amount of reaction water per hour increased from 5.14 to 17.34 g for the Ni-Mg-Al catalyst, and increased from 3.52 to 11.38 g for the commercial Ni catalyst, when the water injection rate was increased from 9.49 to 28.46 g h⁻¹. It is suggested that the water gas shift reaction was promoted when more water was injected into the process resulting in increased hydrogen. From Table 4 and Table 5, the hydrogen and gas production were both increased with the increase of water injection rate for both the laboratory prepared Ni-Mg-Al and the commercial Ni catalysts. For example, the percentage of the potential hydrogen production was increased from 21.01% to 52.17% when the water injection rate was increased from 9.49 to 28.46 g h^{-1} for the pyrolysis/gasification of polypropylene in the presence of the laboratory Ni-Mg-Al catalyst (Table 4); this data represents 22.38 g of hydrogen per 100 g of polypropylene at the highest water injection rate. The percentage potential hydrogen production was also increased from 15.43% to 41.30 % for the commercial Ni catalyst. In this work, the saturation point of steam content in the process in terms of hydrogen and gas production was not observed during the gasification process. It has been reported (Wu and Williams, 2009b) that the amount of reacted water and gas production were firstly increased and then was reduced with increasing water injection rate from 1.90 to 14.20 g h^{-1} , when a Ni/ZSM-5 catalyst was used for pyrolysisgasification of polypropylene in a fixed-bed reaction system. The existence of a steam saturation point during the gasification process has been reported by Franco et al. (Franco et al., 2003) but the steam saturation point was not observed in catalytic steam gasification of pine sawdust (Martinez et al., 2004, García et al., 1999).

3.3.2. Influence of water injection rate on gas concentration

The gas concentration (H_2 , CO, CO₂ and CH₄) obtained from different water injection rates was investigated and the results for the Ni-Mg-Al catalyst and the commercial Ni catalyst are presented in Figure 5 and Figure 6, respectively.

From Figure 5, it is indicated that there is no clear changes in H_2 concentration (around 63 Vol.%) with the increase of water injection rate, when the Ni-Mg-Al catalyst was used. However, the H_2 concentration seemed to be slightly increased with the increase of water injection rate with the presence of the commercial Ni catalyst (Figure 6).

The concentration of CO reduced and the CO_2 increased which is attributed to the increasing of the water gas shift reaction for both the laboratory prepared Ni-Mg-Al and the commercial Ni catalyst (Figure 5 and Figure 6). This might be due to the promotion of the water gas shift reaction, when the steam content in the gasification stage was increased. The promotion of the water gas shift reaction contributed to the high hydrogen yield with the increase of water injection rate (Table 4 and 5). The concentration of CH₄ was reduced from around 1.6 Vol.% to less than 0.4 Vol.% when the water injection rate was increased from 9.49 to 28.46 g h⁻¹ in the presence of the Ni-Mg-Al catalyst (Figure 5). CH₄ concentration was also reduced with the increase of water injection rate for the commercial Ni catalyst, as shown in Figure 6.

3.4. Investigation of deactivation of the Ni-Mg-Al catalyst

The deactivation of the Ni-Mg-Al catalyst over a period of time was investigated. An 8 hour duration test was carried out for the Ni-Mg-Al catalyst for the pyrolysis-gasification of polypropylene, with the pyrolysis temperature of 500 °C, gasification temperature of 800 °C, screw kiln rotation rate of 13.0 rpm and water injection rate of 14.23 g h⁻¹. The CO, CO₂ and H₂ concentrations are shown in Figure 7 and shows that the gases display quite stable concentrations throughout the 8 hours test. H₂ concentration is around 63 Vol.%, and CO concentration is constant around 23 Vol.% during the process of pyrolysis/gasification of polypropylene. Therefore, it is suggested that the Ni-Mg-Al catalyst prepared in the laboratory showed good stability according to the gas production over the 8 hours of the experiment.

The reacted Ni-Mg-Al catalyst was examined using the temperature-programmed oxidation (TPO) method to obtain information of coke deposition. The TGA and DTG results are shown in Figure 8. From Figure 8, the mass increasing peak (around 350 °C) in the TPO experiment is suggested to be the oxidation of Ni particles which had been reduced from NiO to Ni in the Ni-Mg-Al catalyst in the gasification process. However, compared with the DTG results of the reacted Ni-Mg-Al catalyst derived from the pyrolysis-gasification of polypropylene with a fixed bed two-stage fixed bed reaction system (Wu and Williams, 2008, Wu and Williams, 2009b), the oxidation peak of Ni in this paper seems to be much higher than the one obtained from the fixed bed reactor. This might be attributed to the larger amount of sample which was used with the screw kiln reactor resulting in a greater extent of NiO reduction to Ni in the catalyst were reduced to Ni phases.

The use of TPO is also used to determine the different types of carbon which can occur on the surface of the catalysts. Carbon, or 'coke' deposition influences the catalytic activity of the catalysts by preventing the interaction of the active catalytic sites on the catalysts surface with the reactants (Wu and Williams, 2010a). Three different types of carbon have been identified on catalysts, pyrolytic, encapsulating and whisker type carbons (Sehested, 2006). Pyrolytic carbon is amorphous and is suggested to be formed by carbonisation of hydrocarbons in the hot zone of the reactor upstream of the catalytic reactions. Encapsulating or layered carbons are formed on the catalyst and are thought to be formed by interaction of the metal and hydrocarbons to form metal carbides and reactive carbon. These initially formed transition carbons are followed by growth of whisker or filamentous carbons. The layered carbons are more reactive than the filamentous carbons and are mostly responsible for the deactivation of catalysts. Figure 8 shows that two small carbon oxidation peaks were observed after the temperature of 500 $^{\circ}$ C, which may be attributed to the oxidation of the more reactive layered carbon at the lower temperature (~600 °C) followed by oxidation of the less reactive filamentous carbons at higher temperature (~800 °C). From Figure 8, the carbon oxidation peaks were quite low, indicating low carbon formation on the catalyst, however, filamentous carbons seem to be dominant due to the higher oxidation intensity compared with the layered carbons. It should also be noted that during the carbon formation process there will also occur gasification of carbon. Therefore, the total amount of deposited carbons would depend on the balance of the carbon formation rate and the carbon gasification rate

4. Conclusions

In this paper, a screw kiln continuous reaction system was investigated for hydrogen production from the pyrolysis-gasification of waste plastics as represented by polypropylene. The process conditions of gasification temperature and water injection rate were investigated with two catalysts (a laboratory prepared Ni-Mg-Al catalyst and a commercial Ni catalyst). In addition, the deactivation of the laboratory prepared Ni-Mg-Al catalyst was tested over a period of 8 hours duration time.

The results showed that the amount of reacted water, gas production and H_2 production were increased with both the increase of gasification temperature from 600 to 900 °C, as well as the water injection rate from 9.49 to 28.46 g h⁻¹.

The 8 hours investigation of catalyst deactivation with the Ni-Mg-Al catalyst shows a promising stability of the laboratory prepared catalyst according to the mainatined hydrogen production over the time period. The DTG-TPO result of the reacted catalyst shows that more Ni phases in the nickel catalyst might be generated with longer reaction time. Analysis of the coke formation on the used catalyst showed them to be mainly of the filamentous type of carbon.

The use of a two-stage pyrolysis-gasification reactor enables progression to a continuous operation. In addition, the separation of the pyrolysis stage from the gasification stage ensures that any solid ash or pyrolysis char is retained in the pyrolysis reactor. The evolved pyrolysis gases can then be easily gasified/reformed in the second stage with the use of catalysts to produce a high yield hydrogen-rich syngas.

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REFERENCES

- AGUADO, J., SERRANO, D. P., ESCOLA, J. M. & GARAGORRI, E. (2002). Catalytic conversion of low-density polyethylene using a continuous screw kiln reactor. Catalysis Today, 75(1–4), 257-262.
- BOATENG, A. A., WALAWENDER, W. P., FAN, L. T. & CHEE, C. S. (1992). Fluidized-bed steam gasification of rice hull. Bioresource Technology, 40(3), 235-239.
- CZERNIK, S. & FRENCH, R. J. (2006). Production of Hydrogen from Plastics by Pyrolysis and Catalytic Steam Reform. Energy & Fuels, 20(2), 754-758.
- DAY, M., SHEN, Z. & COONEY, J. D. (1999). Pyrolysis of auto shredder residue: experiments with a laboratory screw kiln reactor. Journal of Analytical and Applied Pyrolysis, 51(1–2), 181-200.
- DUNN, S. (2002). Hydrogen futures: toward a sustainable energy system. International Journal of Hydrogen Energy, 27(3), 235-264.
- EUROPE, P. 2012. Plastics the factors: 2012; An analysis of European plastics production, demand and waste data for 2011. Brussels.
- FRANCO, C., PINTO, F., GULYURTLU, I. & CABRITA, I. (2003). The study of reactions influencing the biomass steam gasification process ☆. Fuel, 82(7), 835-842.
- GARC A, L., SALVADOR, M. L., ARAUZO, J. & BILBAO, R. (1999). Catalytic Steam Gasification of Pine Sawdust. Effect of Catalyst Weight/Biomass Flow Rate and Steam/Biomass Ratios on Gas Production and Composition. Energy & Fuels, 13(4), 851-859.
- GARCIA, L., BENEDICTO, A., ROMEO, E., SALVADOR, M. L., ARAUZO, J. & BILBAO, R. (2002). Hydrogen Production by Steam Gasification of Biomass Using Ni–Al Coprecipitated Catalysts Promoted with Magnesium. Energy & Fuels, 16(5), 1222-1230.
- HERGUIDO, J., CORELLA, J. & GONZALEZ-SAIZ, J. (1992). Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale. Effect of the type of feedstock. Industrial & Engineering Chemistry Research, 31(5), 1274-1282.
- JOHNSTON, B., MAYO, M. C. & KHARE, A. (2005). Hydrogen: the energy source for the 21st century. Technovation, 25(6), 569-585.
- MARTINEZ, R., ROMERO, E., GARCIA, L. & BILBAO, R. (2004). The effect of lanthanum on Ni–Al catalyst for catalytic steam gasification of pine sawdust. Fuel Processing Technology, 85(2–3), 201-214.
- SEHESTED, J. (2006). Four challenges for nickel steam-reforming catalysts. Catalysis Today, 111(1–2), 103-110.
- SERRANO, D. P., AGUADO, J., ESCOLA, J. M. & GARAGORRI, E. (2003). Performance of a continuous screw kiln reactor for the thermal and catalytic conversion of polyethylene– lubricating oil base mixtures. Applied Catalysis B: Environmental, 44(2), 95-105.
- WANG, D., CZERNIK, S. & CHORNET, E. (1998). Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oils. Energy & Fuels, 12(1), 19-24.
- WU, C. & WILLIAMS, P. T. (2008). Effects of Gasification Temperature and Catalyst Ratio on Hydrogen Production from Catalytic Steam Pyrolysis-Gasification of Polypropylene. Energy & Fuels, 22(6), 4125-4132.
- WU, C. & WILLIAMS, P. T. (2009a). Hydrogen production by steam gasification of polypropylene with various nickel catalysts. Applied Catalysis B: Environmental, 87(3– 4), 152-161.

- WU, C. & WILLIAMS, P. T. (2009b). Hydrogen Production from the Pyrolysis–Gasification of Polypropylene: Influence of Steam Flow Rate, Carrier Gas Flow Rate and Gasification Temperature. Energy & Fuels, 23(10), 5055-5061.
- WU, C. & WILLIAMS, P. T. (2009c). Investigation of Ni-Al, Ni-Mg-Al and Ni-Cu-Al catalyst for hydrogen production from pyrolysis–gasification of polypropylene. Applied Catalysis B: Environmental, 90(1–2), 147-156.
- WU, C. & WILLIAMS, P. T. (2010a). Investigation of coke formation on Ni-Mg-Al catalyst for hydrogen production from the catalytic steam pyrolysis-gasification of polypropylene. Applied Catalysis B: Environmental, 96(1–2), 198-207.
- WU, C. & WILLIAMS, P. T. (2010b). Pyrolysis–gasification of post-consumer municipal solid plastic waste for hydrogen production. International Journal of Hydrogen Energy, 35(3), 949-957.

	Gasification catalyst				
			Commercial	Ni-Mg-Al	
	-	-	Ni catalyst	INI-INIG-AI	
Water injection rate $(g h^{-1})$	0	9.49	9.49	9.49	
Reacted water (g h^{-1})	0.00	0.58	3.52	5.14	
Gas production (g h^{-1})	0.75	2.35	6.54	9.08	
H_2 production (g h ⁻¹)	0.03	0.12	0.72	0.99	
Potential H ₂ production (g/100g polypropylene)	0.26	1.08	6.58	9.01	
Percentage of potential H ₂ production (%)	0.61	2.53	15.34	21.01	

Table 1. Gas and hydrogen production with and without steam or catalyst

	Gasification temperature (°C)			
	600	700	800	900
Reacted water (g h ⁻¹)	3.69	8.78	9.73	12.59
Gas production (g h^{-1})	5.49	14.35	13.79	21.59
H_2 production (g h ⁻¹)	0.53	1.56	1.68	1.97
Potential H ₂ production (g/100g Polypropylene)	4.83	14.16	15.26	17.87
Percentage of potential H ₂ production (%)	11.27	33.01	35.58	41.65

Table 2. Gas and hydrogen production at different gasification temperatures with the Ni-Mg-Al catalyst

	Gasification temperature (°C)			
-	600	700	800	900
Reacted water (g h ⁻¹)	1.90	4.67	5.00	9.2
Gas production (g h ⁻¹)	3.94	8.70	8.86	15.3
H_2 production (g h ⁻¹)	0.54	0.99	0.99	1.5
Potential H ₂ production (g/100g Polypropylene)	4.88	9.01	9.00	13.64
Percentage potential H ₂ production (%)	11.38	21.02	20.97	31.79

Table 3. Gas and hydrogen production at different gasification temperatures with the commercial Ni catalyst

	$\frac{\text{catalyst}}{\text{Water injection rate (g h}^{-1})}$			
	9.49	14.23	18.98	28.46
Reacted water (g h^{-1})	5.14	9.73	11.33	17.34
Gas production (g h ⁻¹)	9.08	13.79	18.10	28.54
H_2 production (g h ⁻¹)	0.99	1.68	1.77	2.46
Potential H ₂ production (g/100g Polypropylene)	9.01	15.26	16.12	22.38
Percentage of potential H ₂ production (w%)	21.01	35.58	37.57	52.17

Table 4.Gas and hydrogen production for different water injection rates with the Ni-Mg-Al catalyst

	Water injection rate $(g h^{-1})$			
	9.49	14.23	18.98	28.46
Reacted water (g h ⁻¹)	3.52	5.00	7.30	11.38
Gas production (g h ⁻¹)	6.54	8.86	12.61	18.47
H_2 production (g h ⁻¹)	0.72	0.99	1.45	1.95
Potential H ₂ production (g/100g Polypropylene)	6.58	9.00	13.14	17.72
Percentage of potential H ₂ production (%)	15.34	20.97	30.63	41.30

Table 5. Gas and hydrogen production for different water injection rate with the commercial Ni catalyst

Figure Captions

Figure 1. Schematic diagram of the screw kiln reactor system

Figure 2. Gas concentrations at different gasification temperature with steam without catalyst \blacksquare 600 °C, \circ 700 °C, \blacktriangle 800 °C, \bullet 900 °C

Figure 3. Gas concentrations from different gasification temperature with Ni-Mg-Al catalyst \bullet 600 °C, \circ 700 °C, \bullet 800 °C, \bullet 900 °C

Figure 4. Gas concentrations at different gasification temperatures with commercial Ni catalyst \blacksquare 600 °C, \circ 700 °C, \blacktriangle 800 °C, \bullet 900 °C

Figure 5. Gas concentrations from different water injection rate with Ni-Mg-Al catalyst; \blacksquare 9.49 g h⁻¹, \circ 14.23 g h⁻¹, \blacktriangle 18.98 g h⁻¹, \bullet 28.46 g h⁻¹

Figure 6. Gas concentrations at different water injection rates with commercial Ni catalyst; 9.49 g h⁻¹, \circ 14.23 g h⁻¹, \blacktriangle 18.98 g h⁻¹, \bullet 28.46 g h⁻¹

Figure 7. Gas concentrations from extended time experiments of the Ni-Mg-Al catalyst

Figure 8. TGA and DTG results of reacted Ni-Mg-Al catalyst under temperature programmed oxidation.

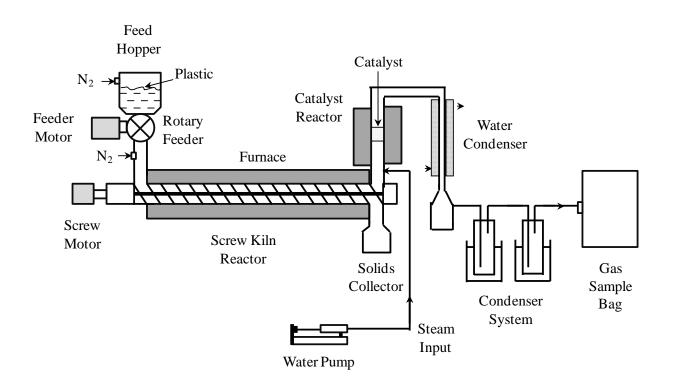


Figure 1. Schematic diagram of the screw kiln reactor system

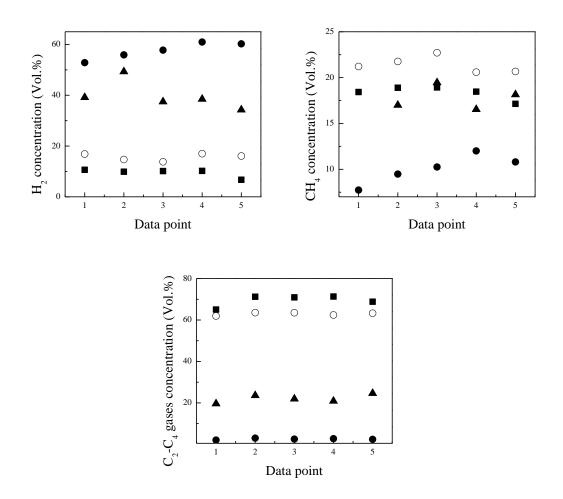


Figure 2. Gas concentrations at different gasification temperatures with steam and without catalyst; ■ 600 °C, \circ 700 °C, \blacktriangle 800 °C, \bullet 900 °C

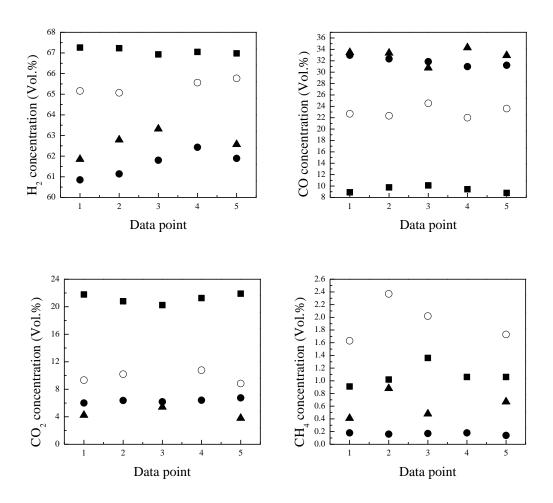


Figure 3. Gas concentrations in relation to different gasification temperatures with the Ni-Mg-Al catalyst; ■ 600 °C, ○ 700 °C, ▲ 800 °C, ● 900 °C

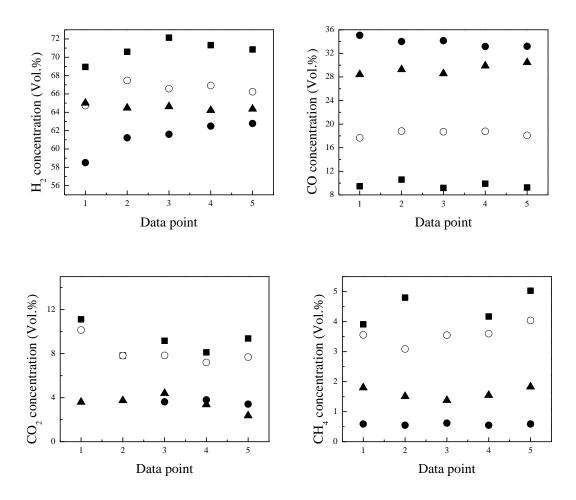


Figure 4. Gas concentrations at different gasification temperatures with the commercial Ni catalyst; ■ 600 °C, ○ 700 °C, ▲ 800 °C, ● 900 °C

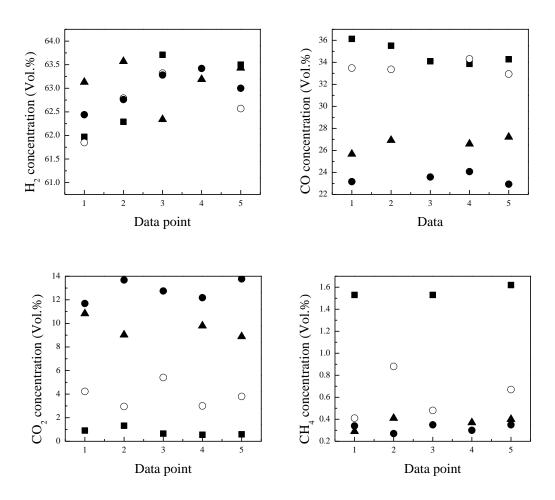


Figure 5. Gas concentrations from different water injection rates with the Ni-Mg-Al catalyst; \blacksquare 9.49 g h⁻¹, \circ 14.23 g h⁻¹, \blacktriangle 18.98 g h⁻¹, \bullet 28.46 g h⁻¹

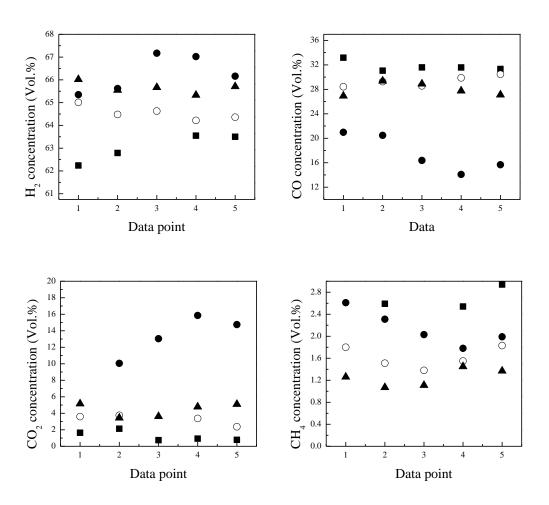


Figure 6. Gas concentrations at different water injection rates with the commercial Ni catalyst; \blacksquare 9.49 g h⁻¹, \circ 14.23 g h⁻¹, \blacktriangle 18.98 g h⁻¹, \bullet 28.46 g h⁻¹

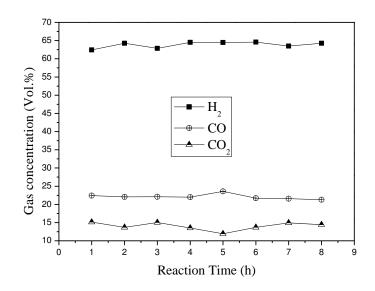


Figure 7. Gas concentrations from extended time experiments of the Ni-Mg-Al catalyst

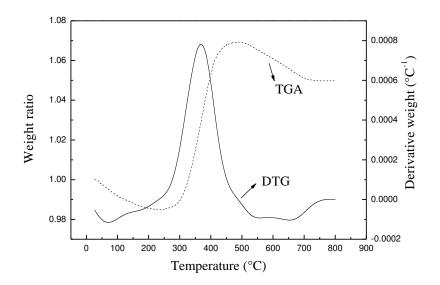


Figure 8. TGA and DTG results of reacted Ni-Mg-Al catalyst under temperature programmed oxidation.