



UNIVERSITY OF LEEDS

This is a repository copy of *Pyrolysis-Catalytic-Dry Reforming of Waste Plastics and Mixed Waste Plastics for Syngas Production*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/100772/>

Version: Accepted Version

Article:

Saad, JM and Williams, PT (2016) Pyrolysis-Catalytic-Dry Reforming of Waste Plastics and Mixed Waste Plastics for Syngas Production. *Energy and Fuels*, 30 (4). pp. 3198-3204. ISSN 0887-0624

<https://doi.org/10.1021/acs.energyfuels.5b02508>

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Pyrolysis-Catalytic-Dry Reforming of Waste Plastics and Mixed Waste Plastics for Syngas Production

Juniza Md Saad and Paul T. Williams*

School of Chemical & Process Engineering
University of Leeds, Leeds, LS2 9JT, UK
(Tel: #44 1133432504; Email: p.t.williams@leeds.ac.uk)

Abstract: The CO₂ dry reforming of various types of waste plastics (LDPE, HDPE, PS, PET and PP) and a simulated mixture of the different waste plastic was investigated over a Ni-Co-Al catalyst using a two-stage reactor. The first stage pyrolysed the plastics and the second stage involved catalytic dry reforming of the product pyrolysis gases with CO₂. The introduction of CO₂ without catalyst markedly increased the dry reforming reaction and significantly improved the production of H₂/CO synthesis gas (syngas). The introduction of the Ni-Co-Al catalyst further significantly improved the production of syngas. LDPE produced the highest yield of syngas at 154.7 mmol_{syngas} g⁻¹_{plastic} from the pyrolysis-catalytic dry reforming process. The order of syngas production for the different plastics was, LDPE<HDPE<PP<PS<PET. The syngas yield from the processing of the simulated waste plastic mixture was 148.67 mmol_{syngas} g⁻¹_{plastic} which reflected the high content of the linear polyalkene plastics (LDPE, HDPE, PP) in the simulated waste plastic mixture.

Keywords: Polypropylene; Polystyrene; Polyethylene; Waste plastic; Dry reforming

1. INTRODUCTION

Global plastics usage continues to increase due to high industrial and consumer demand¹. In 2012, 65.41 million tonnes of polyethylene (PE), 52.75 million tonnes of polypropylene (PP), 37.98 million tonnes of polyvinyl chloride (PVC), 19.8 million tonnes of polyethylene terephthalate (PET) and 10.55 million tonnes of polystyrene (PS) were produced worldwide². Inevitably, more plastics consumption results in more production of waste plastics. Waste plastics can be recovered from the waste stream and processed for example, through mechanical recycling to produce new plastic products, used for energy recovery via incineration, pyrolysed to produce oils, gasified to syngas or landfilled^{3,4}.

Synthesis gas mainly consisting of hydrogen and carbon monoxide is viewed as one of major alternative energy source. Waste plastics are among the potential sources for synthesis gas production due to their high hydrocarbon content⁵⁻⁷. Many researchers have reported on the thermal and catalytic cracking of waste plastics for H₂ as well as synthesis gas production⁸⁻¹¹.

Dry reforming or the use of carbon dioxide for hydrocarbon reformation, is an interesting process to produce syngas since CO₂ is known to be cost effective, recyclable and a toxic-free carbon source. In addition, with the increasing concern in regard to global warming linked to the emission of greenhouse gases there are projected to be an expansion of CO₂ captures processes. Rather than CO₂ storage underground, the utilisation of CO₂ for the production of syngas would be of economic and environmental benefit.

In this work, pyrolysis-catalytic-dry reforming of different types of waste plastics (LDPE, HDPE, PS, PET, PP) as well as a simulated mixture of the waste

plastics representative of municipal solid waste plastic has been investigated. A two-stage, pyrolysis-catalytic reforming reactor system has been used where the evolved gases from pyrolysis of the plastics are passed to the 2nd reactor where catalytic dry reforming takes place. The comparison between the thermal cracking and the CO₂ dry reforming process has been studied. The effect of Ni-Co-Al catalyst in relation to the CO₂ reformation of waste plastics pyrolysed gases has also been investigated. The Ni-Co-Al catalyst has been shown to be efficient for enhancing the syngas yields and reducing the coke formation on the catalyst surface from dry reforming of plastics as reported in our previous studies ¹². The characteristics of the coke deposited on the catalyst are also reported.

2. MATERIALS AND METHODS

2.1 Materials. High density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) were provided by Regain Polymers Limited, Castleford, UK. Low density polyethylene (LDPE) and polyethylene terephthalate (PET) were obtained from Sigma-Aldrich and Goodfellow respectively. All plastic samples were obtained as 2-3 mm sized polymer pellets. The simulated waste plastic (SWP) was a mixture of the different plastics made-up to represent the composition of plastics representative of that reported in municipal solid waste ¹³. The mixture consisted of 42 wt.% LDPE, 20 wt.% HDPE, 16 wt.% PS, 12 wt.% PET and 10 wt.% PP. Table 1 shows the elemental analysis of LDPE, HDPE, PS, PET and PP, determined using a CE Instruments Wigan, UK, FLASH EA2000 CHNS-O analyser.

The Ni-Co-Al catalyst was prepared by using a rising-pH technique ¹⁴. 200 ml deionised water were used to dissolve nickel nitrate hexahydrate, cobalt nitrate

hexahydrate and aluminium nitrate nonahydrate. The aqueous solution was then stirred at a temperature of 40 °C with moderate stirring. Ammonium solution was added to the aqueous solution until the pH value of 8.3 was reached. The solution was filtered and dried at 105 °C. Calcination of the catalyst involved heating the catalyst at a heating rate of 10 °C min⁻¹ to 750 °C with a 3 h hold at 750 °C. The catalyst was crushed and sieved to a particle size of 65–212 µm.

2.2 Characterization of Catalysts. The reacted catalysts were analysed by temperature-programmed oxidation (TPO) using a TGA-50 Shimadzu instrument to characterise the carbonaceous coke deposited on the catalyst. The reacted catalyst with the coke deposit was heated in air from ambient temperature to a final temperature of 800 °C with 15 °C min⁻¹ heating rate. Scanning electron microscopy (SEM) was used to characterise and examine the reacted catalysts (Hitachi SU8230 SEM high performance cold field emission, CFE).

2.3 Experimental Reactor System. The reactor system consisted of two stages (Figure 1). Pyrolysis of the plastics occurred in the first stage and CO₂ dry reforming of the product pyrolysis gases with the catalyst occurred in the second stage reactor¹². The 2nd stage reactor containing 1 g of the Ni-Co-Al catalyst was firstly heated to 800 °C, then the 1st stage reactor containing the plastic (2g) was then heated at a heating rate of 10 °C min⁻¹ to a final temperature of 500 °C. TGA analysis for each polymer was conducted prior to the experiments to determine the 1st stage pyrolysis temperature. The results (not shown here) showed that the thermal degradation of the polymers occurred between 350° C to 450 °C. For the 2nd stage reactor temperature, experiments (not reported here) showed that 800 °C gasification temperature produced the highest syngas production. N₂ was used as a purge gas. When CO₂ was used in the experiments, a total mass of 8 g of carbon dioxide was injected at the inlet to the 2nd stage reactor throughout

the experiment at a continuous CO₂ flow rate of 6.0 g h⁻¹. In regard to the possible back mixing of the injected CO₂ with the plastic in the first reactor, this was not deemed to be significant. The plastic sample was held in a stainless steel crucible and the evolved pyrolysis gases were swept into the second reactor by a continuous purge of nitrogen. CO₂ was injected into the second catalytic reactor after pyrolysis, thereby the CO₂ and hydrocarbons from pyrolysis of the plastics interact on the catalyst or sand.

The condensable product gases from the two-stage dry reforming experiments were condensed in a triple condenser system. Non-condensed gases were passed to a 80 L TedlarTM gas sample bag and analysed later using different packed column gas chromatographs (GC). C₁-C₄ hydrocarbons were determined with a Varian 3380 GC, equipped with a 80-100 mesh HayeSep column, N₂ carrier gas and FID. H₂, CO, O₂ and N₂ were determined with another Varian 3380 GC equipped with a 60-80 mesh molecular sieve column, Ar carrier gas and a TCD. CO₂ was determined with second Varian 3380 GC but using a 80-100 mesh HayeSep column, Ar carrier gas and TCD.

Several repeat experiments were carried out to ensure the reliability of the data. All the products of pyrolysis, including pyrolysis residue, liquid products, mass of gases and carbon deposition were determined to obtain the mass balance. In most of the experiment, the liquid yield consists of condensed oil and wax. In dry reforming, water could be produced due to the reverse water gas shift reaction (Reaction 1) at higher temperature¹⁵. However, only a little water was obtained for each dry reforming experiment.



The CO₂ conversion (%) was calculated according to the following equation:

$$XCO_2 = \frac{[molsCO_2]in - [molsCO_2]out}{[molsCO_2]in} \times 100$$

where $[molsCO_2]in$ is the molar flow rate of carbon dioxide introduced into the system and $[molsCO_2]out$ is the molar flow rate of the total carbon dioxide obtained after the experiment. It should be noted that some CO_2 might be produced during the experiment since the samples were collected as waste polymer pellets, however the amounts were very low and were neglected.

3. RESULTS AND DISCUSSION

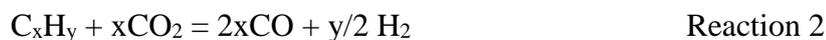
3.1 Non-catalytic CO_2 Dry Reforming of Waste Plastics. Baseline experiments were initially carried out with the HDPE, LDPE, PP, PS and PET in the absence of carbon dioxide and in the absence of the catalyst, where quartz sand was substituted for the catalyst bed in the 2nd stage reactor. The results for the product yield and syngas yield are shown in Table 2. The results indicate that the highest percentage of gases was found in relation to the thermal processing of PET with 69.5 wt.% followed by HDPE (51.7 wt.%), LDPE (49.3 wt.%), PP (33.8 wt.%) and PS (17.2 wt.%). PET was also highest in the yield of solid residue with 19.50 wt.% while no solid residue was detected for HDPE and LDPE. PET has a chemical structure and associated thermal behaviour, which is different, compared to the polyalkene plastics, thus increasing the final amount of solid residue. Alvarez et.al ¹⁶ also reported a high solid residue in their experiments with the pyrolysis-gasification of a mixture of biomass/plastic which was attributed to the PET content of the plastics.

Table 2 also shows the carbonaceous coke deposited on the catalyst from non-catalytic, non-CO₂ reforming of waste plastics. The highest carbonaceous coke deposited on the catalyst was found with the thermal processing of PS with 59.0 wt.% followed by PP (58.5 wt.%), LDPE (46.5 wt.%), HDPE (41.0 wt.%) and PET (6.0 wt.%). PS was also highest in liquid yield with 16 wt.% compared to other plastics, which may be due to PS which required higher reaction energy¹⁷. Kumagai et.al.¹⁸ in their study on the thermal decomposition of individual and mixed plastics in an electrically heated vertical tube reactor, also found that PS was mainly decomposed into liquid at 600 °C. They also concluded that the main component of the decomposition was styrene, principally responsible for the nC₉ fraction.

The gases produced for the non-catalytic none CO₂ reforming experiments showed only small amounts of CO₂ were produced. The CO₂ produced for the experiment with PET produced about 0.13g of CO₂, or 6.5 wt.% of CO₂. Therefore, the product CO₂ from the plastics was neglected in the CO₂ conversion calculations.

The two-stage dry-reforming of HDPE, LDPE, PP, PS, PET was carried out, again in the absence of catalyst (instead, substituting quartz sand) at a CO₂ flow rate of 6.0 g h⁻¹. The product yield and syngas yield are shown in Table 3. In these dry reforming experiments, all the plastics showed a large increase in gas yield with more than 90 wt.% gas yield for each of the waste plastics. There was a corresponding marked reduction in liquid yield for all the plastics. The sand therefore shows a significant activity in relation to the interaction of the pyrolysis gases and CO₂. Sand can contain trace levels of metal contaminants which may act as a catalyst for reaction. It is suggested that the presence of CO₂ contributes to the thermal cracking of large molecular weight hydrocarbons in the second stage reactor by introducing the dry

reforming reaction (Reaction 2), hence increasing the amount of gases yield compared to the experiment with no carbon dioxide.



In contrast, the amount of carbon deposited on the quartz sand in the second stage reactor was reduced by more than 85% with the introduction of CO₂ for the dry reforming experiments for all plastics (Table 3) compared to the experiment with no CO₂ addition (Table 2). The reduction of carbon deposition might be caused by the Boudouard reaction (Reaction 3) of CO₂ and carbon to produce carbon monoxide in the dry reforming experiment. Figure 2 shows that a marked increase in CO yield was obtained for the dry reforming of the plastics over the quartz sand. A study of CO₂-gasification in a macro-TGA by Meng et al.¹⁹ found a large impact of mass loss on CO₂-gasification of biomass due to their high fixed carbon, they also found a slight impact on mass loss from CO₂-gasification of PET, PVC, PP and PS at temperatures above 750 °C. Chen et al.²⁰ also concluded that there was a high conversion efficiency of CO₂ and carbon in the gasification of combustible solid waste including PE and PS at a high temperature range (> 700 °C) was found in a CO₂ atmosphere compared to that in a N₂ atmosphere.



The gas composition and syngas production from the two-stage dry reforming of HDPE, LDPE, PP, PS and PET with CO₂ in the presence of quartz sand (no catalyst) are shown in Figure 2 which shows the gas yields of CO, H₂, CH₄ and C₂-C₄. PET

showed the highest concentration of CO compared to other plastics in the experiment with no carbon dioxide. The gas concentration of HDPE, LDPE and PP showed comparable behaviour with quite high concentration of CH₄. The H₂ concentrations were also similar for these three plastics. By comparison, there was a large increase in CO yields for all plastics for the dry reforming experiments compared to the absence of CO₂. There were only small differences in the H₂ yields for all plastics in both conditions. It also appears that the introduction of carbon dioxide has only a small influence on the CH₄ and C₂-C₄ yields except for HDPE, which showed a reduction from 0.40 to 0.10 g_{gas} g⁻¹_{plastic}.

Figure 3 shows the yield of syngas (H₂ + CO) and CO conversion for the thermal processing of the waste plastics under the different process conditions. The highest syngas yield was produced by LDPE at 117.3 mmol_{syngas}g⁻¹_{LDPE} for the CO₂ dry reforming experiment compared with 41.8 mmol_{syngas}g⁻¹_{LDPE} for the experiment with no carbon dioxide (Figure 3). LDPE also showed a large reduction of carbon deposition on the quartz sand with an ~90% reduction when CO₂ was introduced as the reforming gas (Comparison of Table 2 and Table 3). CO contributed more than 70% to the total of syngas production in the dry reforming experiment. For the CO₂ dry reforming experiments, the highest CO₂ conversion was with HDPE at 40.8%, followed by LDPE (37.9%), PS (32.1%), PP (31.9%) and PET (2.9%) (Figure 3).

3.2 Ni-Co-Al Catalytic CO₂ Dry Reforming of Waste Plastics. The pyrolysis-CO₂ dry reforming of the different waste plastics, (HDPE, LDPE, PP, PS and PET) was carried out with the Ni-Co-Al catalyst. The product yields, gas compositions and syngas production/CO₂ conversion for the catalytic-dry reforming of HDPE, LDPE, PP, PS and PET are shown in Table 4, Figure 2 and Figure 3.

Table 4 shows that when the Ni-Co-Al catalyst was added to the 2nd stage, there appeared to be little change in the product yields, however, the composition of the gases was significantly changed (Figure 2). Also, the carbon deposited on the catalyst was reduced by more than 50% with the Ni-Co-Al catalyst addition for the dry reforming of the various waste plastics. For example, the carbon deposits on the catalyst were reduced from 3.4 to 0.9 wt.% for LDPE, 8.5 to 4.3 wt.% for PS, 4.9 to 1.0 wt.% for PP and almost no carbon was deposited on the catalyst for HDPE and PET. It is suggested that the Boudourd reaction (Reaction 3) is more active with the addition of catalyst, thus reducing the amount of carbon deposited on the catalyst.

Figure 2 shows the gas composition for CO₂ dry reforming of the waste plastics with the addition of Ni-Co-Al catalyst. A marked increase in CO yield for all of the plastics is shown in the presence of the CO₂ and catalyst. This is in agreement with the dry reforming (Reaction 2) and Bourdourd reaction (Reaction3) in which both reactions produced CO, twice the number of moles of CO for each reaction. This data was also supported by the major reduction of hydrocarbons concentration (CH₄ and C₂-C₄) for the catalytic dry reforming of all of the waste plastics, which are required in the dry reforming reaction. There was only a small increase of H₂ with the addition of catalyst for the dry reforming of the plastics.

Table 4 shows the yield of syngas (H₂ + CO) and the H₂:CO molar ratio for the catalytic dry reforming of the waste plastics. The addition of the Ni-Co-Al catalyst in the dry reforming experiments further increased the syngas yield for all plastics compared to the non-catalytic dry reforming of the plastics (Tables 3). The highest increase was found for HDPE with a 44% rise, from 105 to 149.4 mmol_{syngas} g⁻¹ plastic, followed by PP with a 41% increase, LDPE with 37%, PS with 35% and PET with a 24% rise in syngas yield (comparison of Table 3 and Table 4). The carbon dioxide

conversion was also increased for all plastics in the presence of the Ni-Co-Al catalyst. The addition of catalyst enhanced the dry reforming reaction in the gasification reactor as well as reducing the formation of carbon on the catalyst surface compared to the non-catalytic experiment. Goula et al. ²¹ also reported that the presence of catalyst in dry reforming process enhanced syngas production.

3.3 Catalytic CO₂ Dry Reforming of Mixed Waste Plastics. Catalytic (Ni-Co-Al catalyst) dry reforming of a simulated mixture of the waste plastics was carried out, blending the different waste plastics to produce a representative mixture as that found in municipal solid waste ¹³. In addition, a baseline experiment using quartz sand and CO₂ was carried out. The results are shown in Table 5. The experiment in the absence of CO₂ and catalyst/quartz sand was not carried out, since comparison here was to show the influence of the dry reforming Ni-Co-Al catalyst on syngas production.

As shown in Table 5, the addition of the Ni-Co-Al catalyst decreased the amount of product liquid from 1.4 to 0.6 wt.% and catalyst carbon deposits from 5.5 to 1.7 wt.%. However, the gas yield increased from 87.6 to 97.1 wt.%. Figure 2 shows the composition of gases produced from the dry reforming of the simulated waste plastic mixture. CO contributed the highest gas yield with the quartz sand and also the Ni-Co-Al catalyst. The introduction of Ni-Co-Al catalyst reduced the CH₄ yield from 0.15 to 0.04 g_{gas} g⁻¹_{swp}, and no C₂-C₄ was detected, hence increasing the CO from 1.7 to 2.8 g_{gas} g⁻¹_{swp} and H₂ yield from 0.06 to 0.1 g_{gas} g⁻¹_{swp}. This suggests that the addition of the catalyst enhanced the dry reforming reaction (Reaction 2), therefore more CO and H₂ was produced.

Figure 3 shows that the CO₂ conversion increased from 38.2% to 56.5% when the Ni-Co-Al catalyst was added into the CO₂ dry reforming reaction compared to quartz sand. This is also in agreement with the increase in the total syngas production

from 91.3 to 148.6 $\text{mmol}_{\text{syngas}} \text{g}^{-1}_{\text{swp}}$. By comparison, the gas compositions from the CO_2 dry reforming of the simulated mixture of the waste plastic were similar to the gas compositions from the dry reforming of LDPE and HDPE, suggesting the high fraction of these two plastics (42 wt.% LDPE, 20 wt.% HDPE) in the simulated mixture of waste plastics dominated the product yields and gas compositions.

3.4 Characterization of the Coked Catalyst. The carbonaceous coke deposits on the catalyst for the dry reforming experiments with the Ni-Co-Al catalyst were examined by SEM and TPO. Figure 4 shows the SEM micrographs of the reacted Ni-Co-Al catalyst from dry reforming of the different waste plastics and the simulated mixture of plastics. SEM observation shows that most of the carbons were amorphous in nature. Only the carbon deposited on the catalyst from dry reforming of LDPE showed any signs of the presence of filamentous carbon. The micrographs of the catalyst used for dry reforming of the different waste plastics suggest that the surface of each catalyst used developed a different surface structure depending on the type of plastic used. There was an indication that larger particles were observed for the used catalyst with PP and PS processing and LDPE produced a more amorphous structure compared with the used catalyst from SWP processing which showed smaller, more uniform particle. This may be associated with the formation of carbon on the surface or particle sintering during the catalytic dry reforming reactions²². The carbon formation on PS may also be due to layered carbons (reactive carbon) formation on the catalyst surface from the reformation of heavier hydrocarbon compounds from pyrolysis of PS²³.

Temperature programmed oxidation (TPO) was also carried out on the catalyst after reaction to determine the type of carbon deposited on the catalyst surface. The TGA-TPO and DTG-TPO thermograms of the coke formed on the Ni-Co-Al catalyst

from the dry reforming of LDPE, HDPE, PS, PET, PP and the simulated waste plastic mixture (SWP) are shown in Figure 5. TGA-TPO observation shows an initial weight gain for all of the used catalyst, which is attributed to the oxidation of the nickel in the Ni-Co-Al catalyst. The DTG-TPO thermograms shows that all the catalyst have an increase in peak weight at around a temperature of 400 °C – 500 °C, attributed to the oxidation of the nickel. LDPE showed a weight loss peak around 550 °C due to the combustion of carbon on the catalyst surface during the TPO experiment, this has been confirmed by SEM analysis where filamentous type carbons were observed on the catalyst surface. Some of the samples, e.g. PS and the SWP showed another weight loss peak at high temperature around 720 °C. Dong et al.²⁴ suggested that oxidation of carbon at these high temperature above 500 °C might be due to the formation of a large amount of inert carbon (such as amorphous or crystalline graphitic carbon) on the catalyst surface. Sengupta et al.²⁵ discussed in their TPH analysis of 15Ni/Al₂O₃, NiCo/Al₂O₃ and 15NiCo/Al₂O₃ that a high temperature peak of H₂-consumption around 820 K has been observed on these three catalysts. They concluded that these high temperature peaks were assigned to those carbon species that were inactive and may cause catalyst deactivation.

4. CONCLUSIONS

In this paper, the pyrolysis-catalytic CO₂ dry reforming of various types of waste plastics (LDPE, HDPE, PS, PET, PP) as well as a simulated mixture of waste plastics (SWP) have been investigated. The results show that the introduction of CO₂ dry reforming of the products of plastics pyrolysis in the absence of a catalyst dramatically increased the total gas production to over 90 wt.% for all of the plastics. The CO₂ was

involved in the reforming of the product hydrocarbons formed from the pyrolysis of the plastics. The introduction of a Ni-Co-Al catalyst significantly improved the production of syngas comprising the H₂ and CO content of the product gases. The highest yield of syngas was 154.7 mmol_{syngas} g⁻¹_{plastic} produced from the pyrolysis-catalytic dry reforming of LDPE. PET produced significantly lower concentrations of syngas. The syngas yield from the processing of the simulated waste plastic mixture was 148.67 mmol_{syngas} g⁻¹_{plastic} which reflected the high content of LDPE and HDPE in the simulated waste plastic mixture.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from the Majlis Amanah Rakyat (MARA) Malaysia (PhD scholarship for Juniza Md Saad) and the University of Leeds. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 643322 (FLEXI-PYROCAT).

References

1. Thompson, R. C.; Swan, S. H.; Moore, C. J.; vom Saal, F. S., Our plastic age. *Philosophical Transactions of the Royal Society of London B: Biological Sciences* **2009**, 364, (1526), 1973-1976.
2. Sagel, E., Polyethylene global overview. **2012**.
3. Wang, C.-q.; Wang, H.; Fu, J.-g.; Liu, Y.-n., Flotation separation of waste plastics for recycling—A review. *Waste Management* **2015**, 41, 28-38.
4. Al-Salem, S. M.; Lettieri, P.; Baeyens, J., Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste Management* **2009**, 29, (10), 2625-2643.
5. Wong, S. L.; Ngadi, N.; Abdullah, T. A. T.; Inuwa, I. M., Current state and future prospects of plastic waste as source of fuel: A review. *Renewable and Sustainable Energy Reviews* **2015**, 50, 1167-1180.
6. Buekens, A. G.; Huang, H., Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Resources, Conservation and Recycling* **1998**, 23, (3), 163-181.
7. Miskolczi, N.; Bartha, L.; Angyal, A., High Energy Containing Fractions from Plastic Wastes by Their Chemical Recycling. *Macromolecular Symposia* **2006**, 245-246, (1), 599-606.
8. Namioka, T.; Saito, A.; Inoue, Y.; Park, Y.; Min, T.-j.; Roh, S.-a.; Yoshikawa, K., Hydrogen-rich gas production from waste plastics by pyrolysis and low-temperature steam reforming over a ruthenium catalyst. *Applied Energy* **2011**, 88, (6), 2019-2026.
9. Mastellone, M. L.; Zaccariello, L., Metals flow analysis applied to the hydrogen production by catalytic gasification of plastics. *International Journal of Hydrogen Energy* **2013**, 38, (9), 3621-3629.
10. Ishii, A.; Amagai, K.; Furuhata, T.; Arai, M., Thermal gasification behavior of plastics with flame retardant. *Fuel* **2007**, 86, (15), 2475-2484.
11. Okajima, I.; Sako, T., Chapter 13 - Energy Conversion of Biomass and Recycling of Waste Plastics Using Supercritical Fluid, Subcritical Fluid and High-Pressure Superheated Steam. In *Supercritical Fluid Technology for Energy and Environmental Applications*, Fan, V. A., Ed. Elsevier: Boston, 2014; pp 249-267.
12. Md Saad, J.; Nahil, M. A.; Wu, C.; Williams, P. T., Influence of nickel-based catalysts on syngas production from carbon dioxide reforming of waste high density polyethylene. *Fuel Processing Technology* **2015**, 138, 156-163.
13. Oliver Wolf; Clara Delgado; Leire Barrueta; Salas, O. *Assessment of the Environmental Advantages and Drawbacks of Existing and Emerging Polymers Recovery Processes*; 2007.
14. Garcia, L.; Benedicto, A.; Romeo, E.; Salvador, M. L.; Arauzo, J.; Bilbao, R., Hydrogen production by steam gasification of biomass using Ni-Al coprecipitated catalysts promoted with magnesium. *Energy Fuels* **2002**, 16, (5), 1222-1230.
15. Oyama, S. T.; Hacıoğlu, P.; Gu, Y.; Lee, D., Dry reforming of methane has no future for hydrogen production: Comparison with steam reforming at high pressure in standard and membrane reactors. *International Journal of Hydrogen Energy* **2012**, 37, (13), 10444-10450.
16. Alvarez, J.; Kumagai, S.; Wu, C.; Yoshioka, T.; Bilbao, J.; Olazar, M.; Williams, P. T., Hydrogen production from biomass and plastic mixtures by pyrolysis-

- gasification. *International Journal of Hydrogen Energy* **2014**, 39, (21), 10883-10891.
17. Ahmed, I. I.; Gupta, A. K., Hydrogen production from polystyrene pyrolysis and gasification: Characteristics and kinetics. *International Journal of Hydrogen Energy* **2009**, 34, (15), 6253-6264.
 18. Kumagai, S.; Hasegawa, I.; Grause, G.; Kameda, T.; Yoshioka, T., Thermal decomposition of individual and mixed plastics in the presence of CaO or Ca(OH)₂. *Journal of Analytical and Applied Pyrolysis* **2015**, 113, 584-590.
 19. Meng, A.; Chen, S.; Long, Y.; Zhou, H.; Zhang, Y.; Li, Q., Pyrolysis and gasification of typical components in wastes with macro-TGA. *Waste Management*.
 20. Chen, S.; Meng, A.; Long, Y.; Zhou, H.; Li, Q.; Zhang, Y., TGA pyrolysis and gasification of combustible municipal solid waste. *J. Energy Inst.* **2015**, 88, (3), 332-343.
 21. Goula, M. A.; Charisiou, N. D.; Papageridis, K. N.; Delimitis, A.; Pachatouridou, E.; Iliopoulou, E. F., Nickel on alumina catalysts for the production of hydrogen rich mixtures via the biogas dry reforming reaction: Influence of the synthesis method. *International Journal of Hydrogen Energy* **2015**, 40, (30), 9183-9200.
 22. Sehested, J., Sintering of nickel steam-reforming catalysts. *Journal of Catalysis* **2003**, 217, (2), 417-426.
 23. Wu, C.; Williams, P. T., Pyrolysis-gasification of plastics, mixed plastics and real-world plastic waste with and without Ni-Mg-Al catalyst. *Fuel* **2010**, 89, (10), 3022-3032.
 24. Dong, L.; Du, Y.; Li, J.; Wang, H.; Yang, Y.; Li, S.; Tan, Z., The effect of CH₄ decomposition temperature on the property of deposited carbon over Ni/SiO₂ catalyst. *International Journal of Hydrogen Energy* **2015**, 40, (31), 9670-9676.
 25. Sengupta, S.; Ray, K.; Deo, G., Effects of modifying Ni/Al₂O₃ catalyst with cobalt on the reforming of CH₄ with CO₂ and cracking of CH₄ reactions. *International Journal of Hydrogen Energy* **2014**, 39, (22), 11462-11472.

Table 1. Elemental Analysis of the Waste Plastics

	N (wt.%)	C (wt.%)	H (wt.%)	O (wt.%)
HDPE	0.94	80.58	18.48	nd
LDPE	0.94	81.01	18.06	nd
PP	0.95	80.58	10.42	8.89
PS	0.86	86.19	12.43	0.52
PET	0.57	61.0	11.30	27.13

nd = not detected

Table 2. Two-stage Pyrolysis of Different Plastics with No Catalyst and No Carbon Dioxide (quartz sand in the 2nd stage at a temperature of 800 °C).

Plastic type	HDPE	LDPE	PP	PS	PET
Product yield (wt. %)					
Gas	51.7	49.3	33.8	17.2	69.5
Liquid	7.0	1.5	0.5	16.0	2.0
Residue	-	-	7.0	5.0	19.5
Carbon deposition	41.0	46.5	58.5	59.0	6.0
Mass balance	99.7	97.3	99.8	97.2	97.0
Syngas yield (mmol _{syngas} g ⁻¹ _{plastic})					
H ₂ + CO production	31.9	41.8	35.8	25.3	31.2
H ₂ :CO molar ratio	13.0	10.5	12.6	11.0	0.6

Table 3. Pyrolysis-catalysis of Different Plastics in the Presence of Carbon Dioxide and No Catalyst (quartz sand in the 2nd stage at a temperature of 800 °C)

Plastic type	HDPE	LDPE	PP	PS	PET
Product yield (wt. %)					
Gas	90.6	99.2	95.6	92.1	97.1
Liquid	2.0	0.6	0.6	1.3	2.9
Residue	0.2	0.1	1.4	0.9	4.1
Carbon deposition	2.8	3.4	4.9	8.5	0.8
Mass balance	95.6	103.3	102.5	102.8	104.9
Syngas yield (mmol _{syngas} g ⁻¹ _{plastic})					
H ₂ + CO production	105.4	117.3	94.6	91.1	39.0
H ₂ :CO molar ratio	0.5	0.5	0.5	0.4	0.2

Table 4. Pyrolysis-dry Reforming of Different Plastics in the Presence of Ni-Co-Al Catalyst and Carbon Dioxide (catalyst temperature 800 °C and CO₂ flow rate of 6.0 g h⁻¹)

Plastic type	HDPE	LDPE	PP	PS	PET
Product yield (wt. %)					
Gas	94.8	98.3	90.6	97.1	94.3
Liquid	2.4	0.3	2.5	2.4	1.0
Residue	-	-	1.7	1.0	4.0
Carbon deposition	-	0.9	1.0	4.3	-
Mass balance	97.2	99.5	95.8	104.8	99.3
Syngas yield (mmol _{syngas} g ⁻¹ _{plastic})					
H ₂ + CO production	149.4	154.7	136.0	126.3	63.0
H ₂ :CO molar ratio	0.5	0.6	0.5	0.3	0.2

Table 5. Pyrolysis-CO₂ Dry Reforming of a Simulated Mixture of Different Plastics in the Presence of Sand or Ni-Co-Al Catalyst (2nd stage reactor temperature, 800 °C and CO₂ flow rate of 6.0 g h⁻¹)

Catalyst	simulated mixture of plastics	
	sand	Ni-Co-Al
Product yield (wt. %)		
Gas	87.6	97.1
Liquid	1.4	0.6
Residue	1.0	0.6
Carbon deposition	5.5	1.7
Mass balance	95.5	99.9
Syngas yield (mmol _{syngas} g ⁻¹ _{swp})		
H ₂ + CO production	91.3	148.6
H ₂ :CO molar ratio	0.5	0.5

Figure Captions

Figure 1. Schematic diagram of the two-stage reactor system.

Figure 2. Gas compositions for the pyrolysis-dry reforming of the different plastics and the simulated mixture of plastics under various process conditions.

Figure 3. Syngas (hydrogen and carbon monoxide) production and carbon dioxide conversion from pyrolysis-dry reforming of various types of plastics.

Figure 4. SEM tomographic images for the reacted Ni-Co-Al catalyst surface.

Figure 5. TPO results for the reacted Ni–Co–Al catalyst after catalytic-dry reforming of waste plastics; (a) TGA-TPO, (b) DTG-TPO.

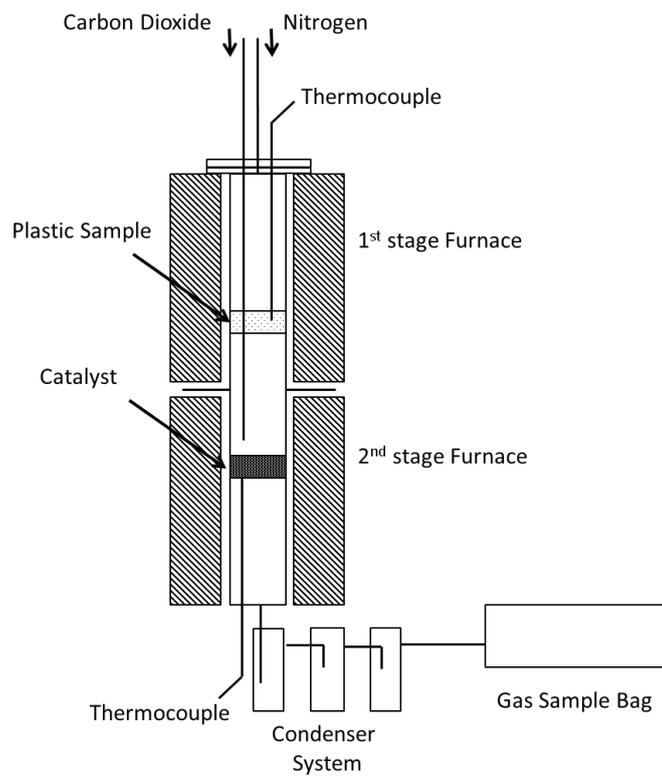


Figure 1. Schematic diagram of the two-stage reactor system

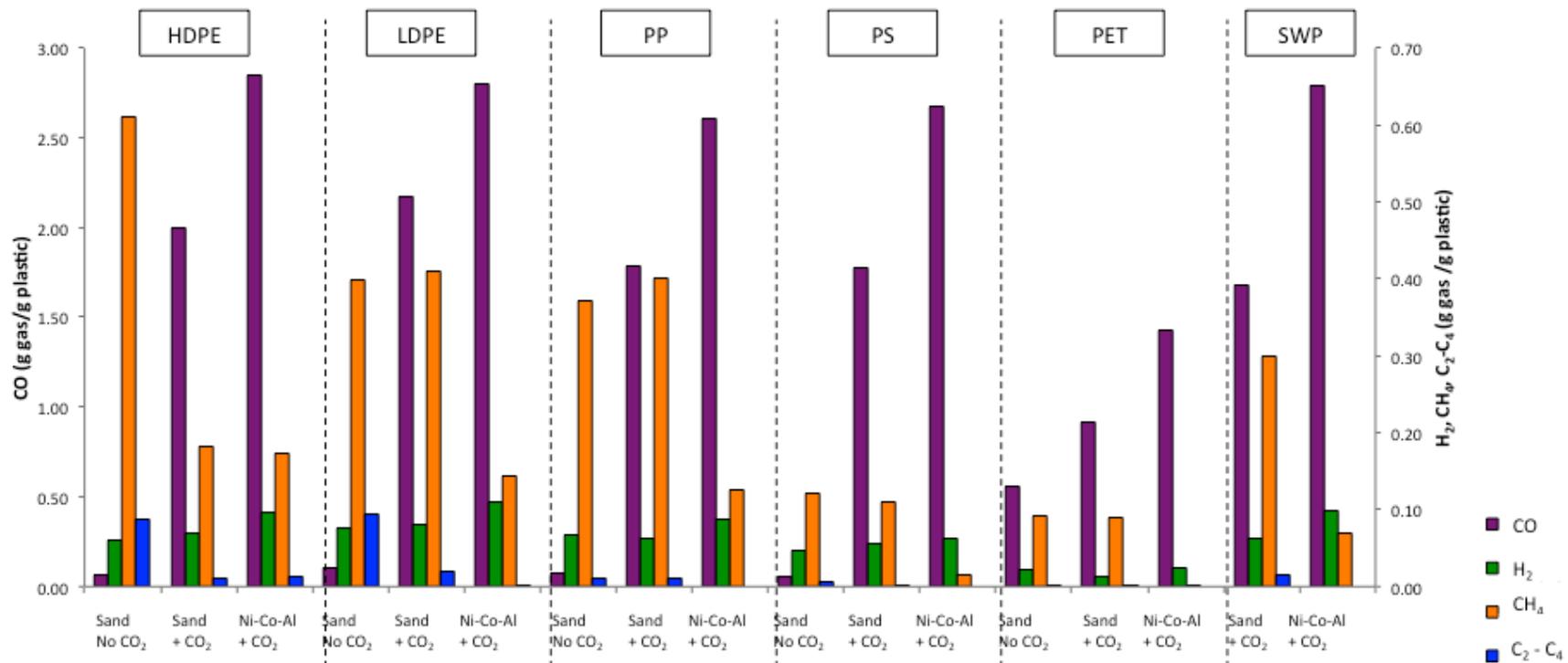


Figure 2. Gas compositions for the pyrolysis-dry reforming of the different plastics and the simulated mixture of plastics under various process conditions

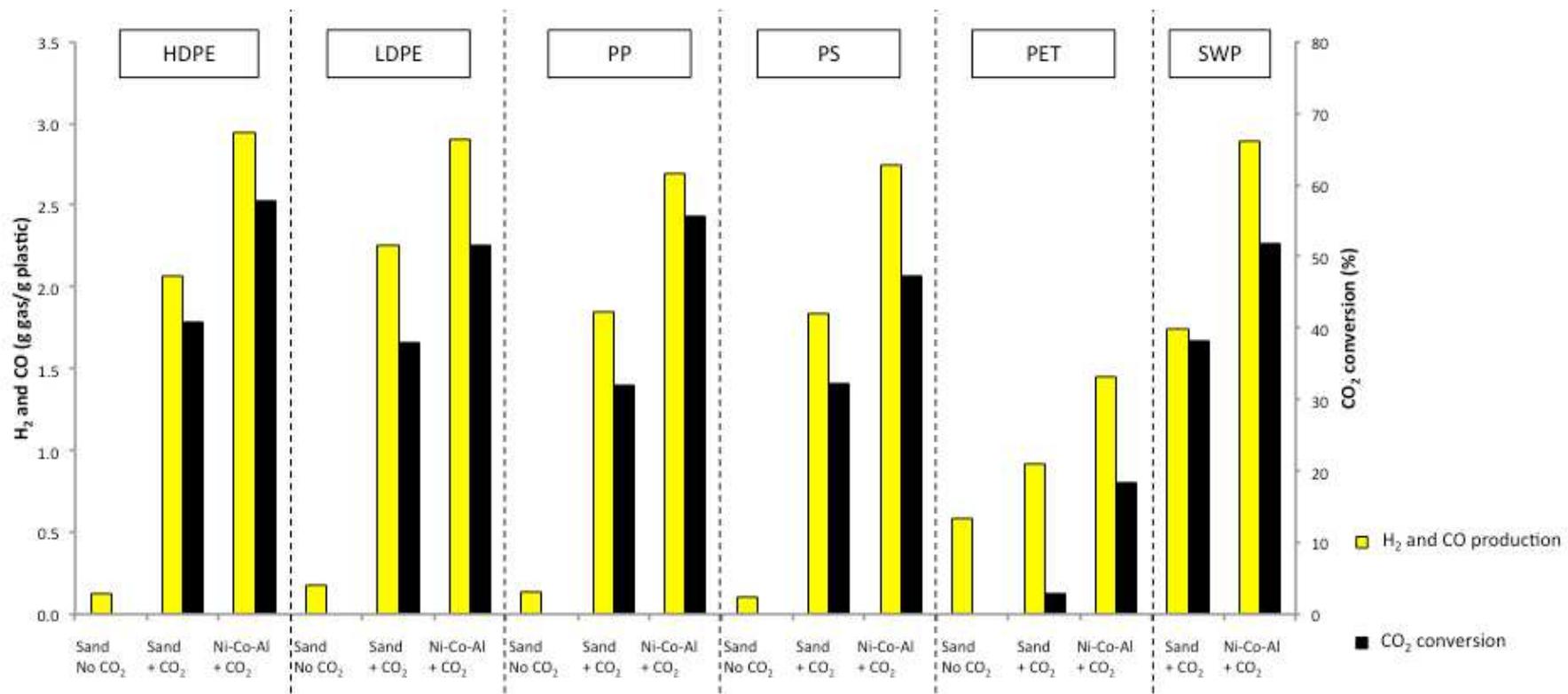
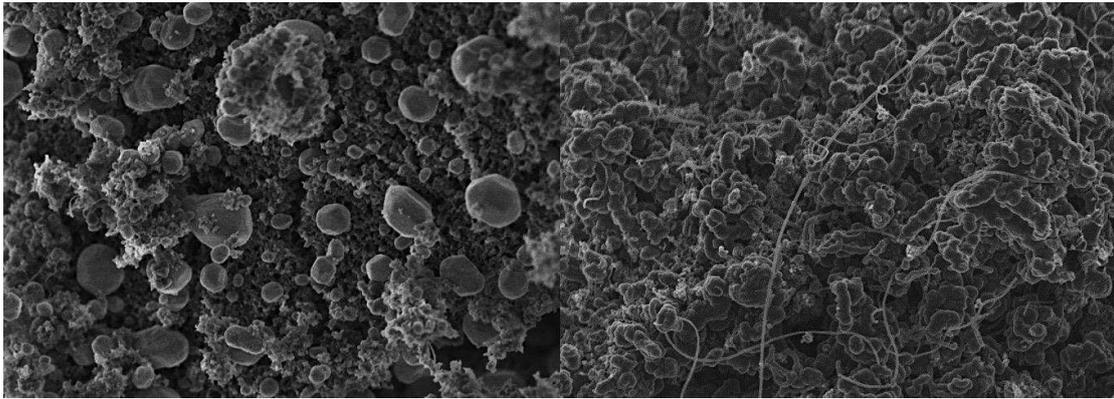


Figure 3. Syngas (hydrogen and carbon monoxide) production and carbon dioxide conversion from pyrolysis-dry reforming of various types of plastics

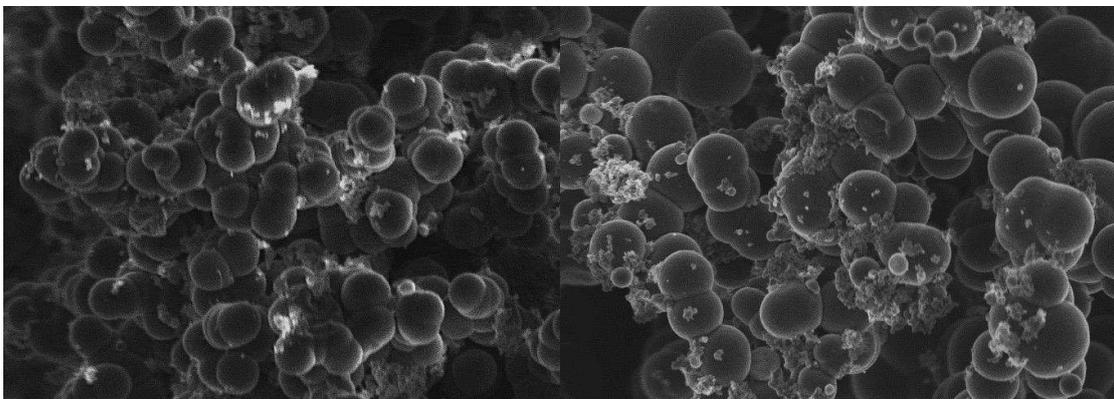
HDPE

LDPE



PP

PS



PET

SWP

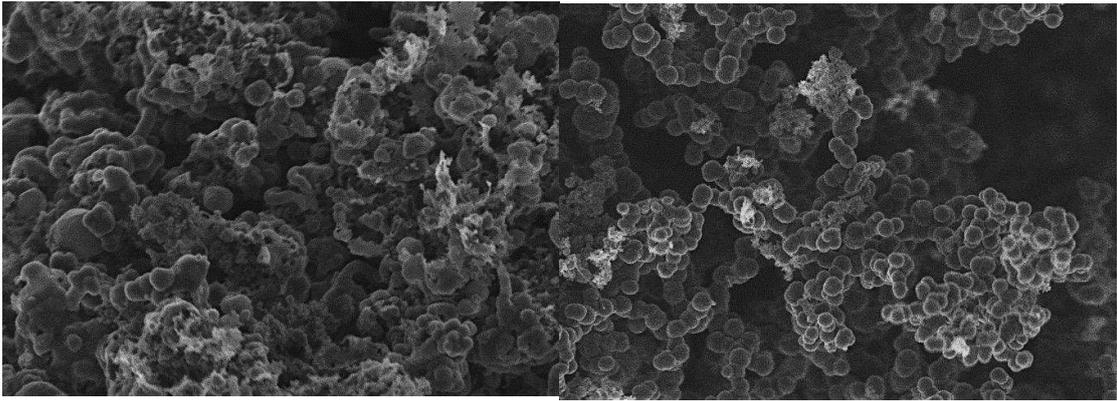
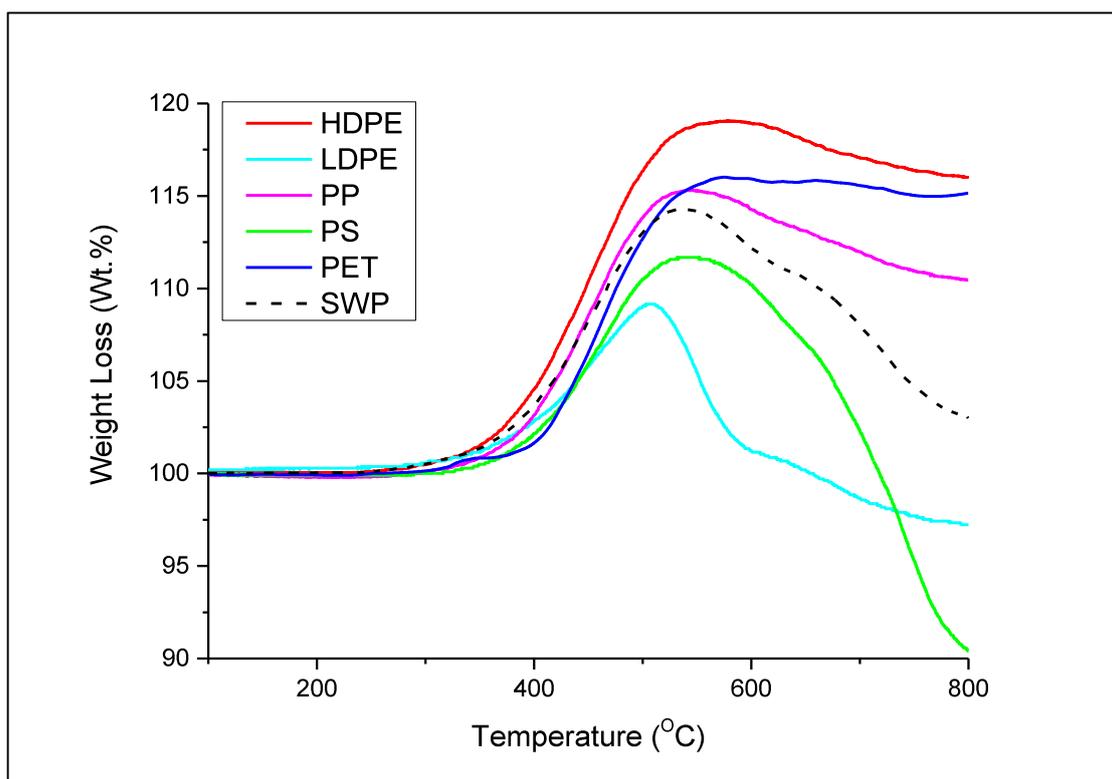
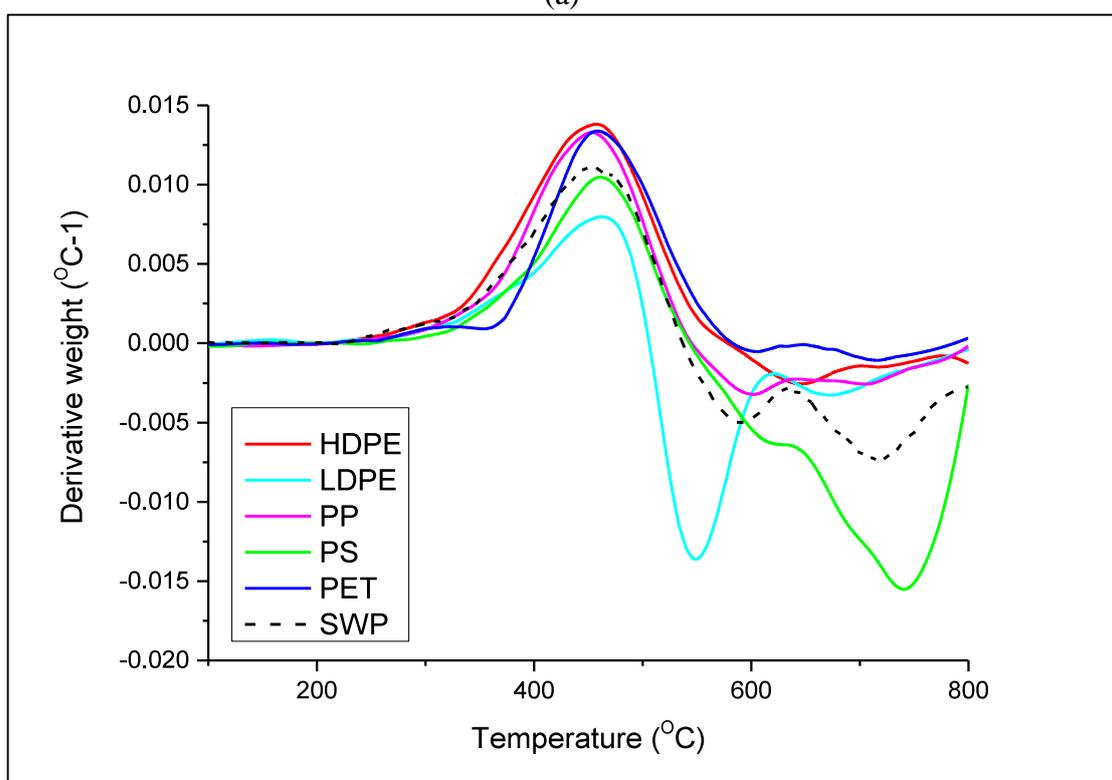


Figure 4. SEM tomographic images for the reacted Ni-Co-Al catalyst surface



(a)



(b)

Figure 5. TPO results for the reacted Ni–Co–Al catalyst after catalytic-dry reforming of waste plastics; (a) TGA-TPO, (b) DTG-TPO