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Wu, C, Nahil, MA, Miskolczi, N et al. (2 more authors) (2014) Processing real-world waste plastics by pyrolysis-reforming for hydrogen and high-value carbon nanotubes. Environmental Science and Technology, 48 (1). pp. 819-826. ISSN 0013-936X

https://doi.org/10.1021/es402488b

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Processing real-world waste plastics by pyrolysis-reforming for hydrogen and high-value carbon nanotubes

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ABSTRACT: Producing both hydrogen and high-value carbon nanotubes (CNTs) derived from waste plastics is reported here using a pyrolysis-reforming technology comprising a two-stage reaction system, in the presence of steam and a Ni-Mn-Al catalyst. The waste plastics consisted of plastics from a motor oil container (MOC), waste commercial high density polyethylene (HDPE) and regranulated HDPE waste containing polyvinyl chloride (PVC). The results show that hydrogen can be produced from the pyrolysis-reforming process, but also carbon nanotubes are formed on the catalyst. However, the content of 0.3 wt.% polyvinyl chloride in the waste HDPE (HDPE/PVC) has been shown to poison the catalyst and significantly reduce the quantity and purity of CNTs. The presence of sulphur has shown less influence on the production of CNTs in terms of quantity and CNT morphologies. Around 94.4 mmol H_2 g^{-1} plastic was obtained for the pyrolysis-reforming of HDPE waste in the presence of the Ni-Mn-Al catalyst and steam at a reforming temperature of 800 °C. The addition of steam in the process results in an increase of hydrogen production and reduction of carbon yield; in addition, the defects of CNTs e.g. edge dislocations were found to be increased with the introduction of steam (from Raman analysis).

KEYWORDS: Plastics; Reforming; Waste, Hydrogen, Carbon nanotubes

INTRODUCTION

Large amounts of waste plastics are generated each year, for example, 25.1 million tonnes for the EU in 2010,[1] and 31 million tonnes in the US in 2010 [2] causing huge pressure to the environment. Despite significant efforts being made to recover waste plastics, recycling rates are quite low, for example only 8% of total plastics were recycled in the US. [2] In the EU more than 40 % of waste plastics ended up in landfill in 2010 in the EU, representing a waste of resource. [1]

Pyrolysis and gasification of waste plastics has been investigated for many years to obtain valuable products such as syngas, gasoline, pyrolysis oil etc. [3-6]; however, this option of feedstock recycling was reported to be only 0.3% of waste plastics in 2007.[7] Waste plastics are mixtures of different polymers, such as polyethylene, polypropylene, polystyrene, polyvinyl-chloride, polyamide, etc. In addition, to improve the properties of the plastics, significant amounts of additives e.g. Br, N, Cl, Sb, Zn, Ti, Ca, etc. are often added into the virgin polymer during the production process. These elements subsequently appear in pyrolysis products causing problems for their utilisation in further applications. [8-10]

Therefore, extensive studies are being carried out to improve the environmental and economic feasibility of feedstock recycling of waste plastics through pyrolysis/gasification. For example, novel catalysts were developed for plastics gasification for improving production of hydrogen/syngas. [11-13] Co-gasification with biomass has also been reported to assist the feeding of gasification of plastics into the gasifier. [14-16] In addition, plastics pyrolysis has also been used to produce carbon nanotubes (CNTs), a high-value product having extraordinary physical and chemical properties, by either mixing plastics with catalyst in a single reactor,[17,18] or passing the pyrolysis products of plastics into a second stage catalyst reactor.[19,20] Both product yield and the properties of CNTs are basically determined by the raw materials, for example, CNT production has been investigated from laser ablation, plasma assisted deposition, pyrolysis or chemical vapour deposition.[21,22] However, only limited information is available about the pyrolysis of real-world waste plastics for CNT production.

In addition, very limited work has focussed on the combination of producing both CNTs and hydrogen from plastics gasification.[20, 23] Liu et al.[20] reported the production of hydrogen-rich gas and CNTs in a moving-bed reactor with gases derived from catalytic pyrolysis of polypropylene in a screw kiln without steam addition. The pyrolysis vapours were condensed before entering the moving bed for CNTs production.

We have recently proposed that producing CNTs as a by-product during hydrogen production from the catalytic steam pyrolysis-gasification of polypropylene.[23] The novelty of this process is to control the deactivation of catalyst to form valuable CNTs, instead of designing high-stable catalyst. The co-production of CNTs and hydrogen will significantly increase the profit from the gasification of plastics and also provides an alternative for catalyst development in the gasification process. The process uses a two-stage fixed-bed reaction system where vapours from plastics pyrolysis produced in the first stage pyrolysis reactor are reformed in the presence of steam and catalyst in the second reactor. In this process, high yields of hydrogen can be produced by using efficient catalysts and sufficient steam, and problematic amorphous carbons deposited on the surface of reacted catalyst can be substituted by high-value CNTs.

In this work, real-world waste plastics were investigated to determine the influence of contaminants on the production of hydrogen and CNTs. Waste plastics with contaminates of motor oil and the presence of polyvinyl chloride (PVC) was investigated in terms of the yield and production rate of hydrogen and the characteristics of the derived CNTs in the presence of a Ni-Mn-Al catalyst.

MATERIALS AND METHODS

Materials. Commercial waste high density polyethylene (HDPE), regranulated HDPE waste containing polyvinyl chloride (PVC) and a waste plastic from a motor oil container were obtained from TVK Plc, Remat ltd and a Hungarian Regional Waste Collecting Company, respectively. The plastic motor oil container was contaminated by motor oil, and the composition was 68.3 wt.% HDPE, 13.3 wt.% LDPE, 9.5 wt.% polypropylene (PP), 1.1 wt.% polystyrene (PS) and 4.8 wt.% others. The three raw materials are denoted in this paper as HDPE, HDPE/PVC and MOC.

Catalyst Preparation. A Ni-Mn-Al catalyst was prepared by a co-precipitation method. The precipitant $NH_4(OH)$ was added to an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ until the final pH (around 8.0) was obtained, while the solution was kept at 40 °C with stirring during the precipitation process. The precursor was dried at 105 °C for around 12 h and further processed by calcination under air atmosphere at 750 °C (heating rate of 20 °C min^{-1}) for 3 h. The catalysts were then crushed and sieved to give granules of between 0.065 and 0.212 mm.

Reactor. The two stage, fixed pyrolysis-reforming reaction system used to process the waste plastics has been described before, including a schematic diagram.[24] The raw plastic sample was pyrolysed in the first reactor, the derived pyrolysis vapours were passed directly to a second heated reactor and reformed in the presence/absence of catalyst, where carbon nanotubes were produced on the surface of the catalyst. For each experiment, 1 g of waste plastics sample was placed in a sample boat in the first stage pyrolysis reactor, and 0.5 g of Ni-Mn-Al catalyst (if used) was placed in the second stage catalytic reactor. N_2 was used as a carrier gas with a flow rate of 80 ml min^{-1}. The experiment was started by heating the catalytic bed to the desired temperature of 800 °C with a heating rate of 40 °C min^{-1}. Once the catalysts bed temperature was attained, the pyrolysis reactor was started to be heated up to 500 °C with a heating rate of 40 °C min^{-1} and water was injected with a flow rate of 2.85 g h^{-1}. The products after exiting the catalytic bed were condensed in two condensers, using an air and dry ice cooled atmosphere, respectively. The non-condensed gases including H_2, CO, CO_2, CH_4, C_2-C_4 hydrocarbon gases and N_2 were collected with a 25 L Tedlar™ gas sample bag and analysed off-line using gas chromatography. The reaction time was around 40 min.

Materials Characterisation. The reacted catalysts were analysed by high resolution scanning electron microscopy (SEM) (LEO 1530), transmission electron microscopy (TEM) (FEI Tecnai TF20) and Raman spectroscopy (Renishaw Invia) at a wavelength of 514 nm at Raman shifts between 100 and 3200 cm^{-1}. Temperature program oxidation (TPO) has also been used to obtain information of coke type and formation on the reacted catalyst using a thermogravimetric analyser (TGA) (Shimadzu). During the TPO analysis, around 30 mg of the reacted catalyst was heated in an atmosphere of air (50 ml min^{-1} flow rate) at a heating rate of 15 °C min^{-1} up to a temperature of 800 °C and with a hold time of 10 minutes. X-ray diffraction (XRD) (Bruker D8) with Cu Ka radiation was also used to characterize the fresh and reacted Ni-Mn-Al catalysts. The oil content in the MOC sample was determined by using light naphtha to extract the oil. Sulfur and nitrogen contents were obtained using standard methods: ASTMD 6428 99 and ASTMD 6366 99, respectively. Chlorine determination was carried out using a Mitsubishi TOX-100 instrument.

Gas Analysis. The non-condensed gases collected in the gas sample bag were analysed by packed column gas chromatography (GC). Permanent gases (H_2, CO, O_2, N_2 and CO_2) were analysed with Varian 3380 GC/TCD. A 2 m long and 2 mm diameter column packed with 60-80 mesh molecular sieve was used to analyse hydrogen, nitrogen, carbon monoxide and oxygen; and a 2 m long and 2 mm diameter column with Hysep 60-80 mesh molecular sieve was used to analyse CO_2. Hydrocarbons (C_1-C_4) were analysed using a Varian 3380 GC with a flame ionisation detector, with an 80-100 mesh Hysep column and nitrogen carrier gas.

RESULTS AND DISCUSSION

Characterisation of Plastics and Fresh Catalyst. The properties of the raw samples are shown in Table 1. The plastic waste motor oil container (MOC) had 1.79 wt.% of ash, 8.1 wt.% of residual motor oil and 1.7 wt.% of moisture. Less moisture was present in the HDPE waste sample (0.3 wt.%) and the HDPE/PVC sample (0.8 wt.%), and also less ash content was contained in HDPE (0.09 wt.%) and HDPE/PVC (0.83 wt.%). Contaminants such as Cl (0.01 wt.%), S (0.046 wt.%), Ca (0.019 wt.%), Zn (0.057 wt.%) were present in the MOC sample. High Cl content (0.349 wt.%) and Ca content (0.062 wt.%) were found in the HDPE/PVC waste plastic.

The XRD analysis of the fresh Ni-Mn-Al catalyst (Fig. 1(a)) identified the presence of NiO, MnO_2, $MnAl_2O_4$ and $NiAl_2O_4$ crystals. The active NiO will be transferred into catalytic Ni sites for hydrogen production during gasification reactions; in addition, the spinels are also suggested to contribute to the gasification reactions for hydrogen production.[25]

Gas and Hydrogen Production. Mass balance and gas concentrations for the pyrolysis-reforming of the MOC, HDPE and HDPE/PVC are shown in Table 2, 3 and 4, respectively. The influence of addition of steam and catalyst into the process on the productions of hydrogen and gas and its concentrations will be discussed in this section.

As shown in Table 2, the introduction of the Ni-Mn-Al catalyst and steam has significantly increased the gas yield from 103 to 147.1 wt.%, and hydrogen production from 27.7 to 81.8 mmol g^{-1} plastic in the pyrolysis-reforming of the MOC sample. The gas yield was calculated as the amount of gas produced divided by the amount of plastic sample used in the experiment (over 100% gas yield was obtained due to the reacted steam). A similar trend has been observed for the HDPE and HDPE/PVC sample as shown in Tables 3 and 4, respectively. The improvement of gas and hydrogen production is well known due to the catalytic effect of the catalyst. [24, 26-28]

From Tables 2, 3 and 4, a higher gas yield was obtained for the HDPE (170.1 wt.%) and the HDPE/PVC (173.9 wt.%) samples compared with the MOC sample (147.1 wt.%). In addition, the lowest hydrogen production (81.8 mmol H_2 g^{-1} plastic) was produced using the MOC waste plastic. As presented in the experimental section, the MOC contains 9.5 wt.% polypropylene (PP), 1.1 wt.% polystyrene (PS) and 4.8 wt.% other plastics; these plastics are suggested to be responsible for the lower gas and hydrogen production for the MOC sample. As reported in the literature, polypropylene and polystyrene generate lower hydrogen production compared to HDPE during the pyrolysis/gasification process in the presence of a Ni-based catalyst.[29, 30] It has also been suggested that the derived gases from HDPE pyrolysis are mainly alkenes which are more easily reformed to hydrogen. Additionally, the high content of sulphur (455 ppm) in the MOC and 8.1 wt.% of residual motor oil is also suggested to lower the gas and hydrogen production from the pyrolysis-reforming experiments.

Lower hydrogen production was observed for the HDPE/PVC sample (43.2 mmol H_2 g^{-1} plastic) compared with the HDPE waste sample (56.6 mmol H_2 g^{-1} plastic) for the non-catalytic experiment. When the Ni-Mn-Al catalyst was added, the difference of hydrogen production (around 93 mmol H_2 g^{-1} plastic) was reduced between these two plastic samples.

The majority of gases produced were CO, H_2, CO_2 and CH_4 for the pyrolysis-reforming of waste plastics, except for the non-catalytic experiments where large amounts of C_2-C_4 hydrocarbon gases were produced (Table 2, 3 and 4). More than 60 Vol.% of H_2 was obtained in the presence of the Ni-Mn-Al catalyst for all the plastic samples. The lowest H_2

concentration (41.0 Vol.%) and the highest CH_4 concentration (23.6 Vol.%) and the highest C_2-C_4 concentration (14.6 Vol.%) were obtained using the MOC sample in the absence of the Ni-Mn-Al catalyst, compared with the HDPE and HDPE/PVC samples (Table 2, 3 and 4). These results are consistent with the lowest hydrogen production being obtained for the MOC sample during the catalytic pyrolysis-reforming process.

Carbon Nanotubes Production. SEM and TEM analysis. Filamentous carbons are clearly observed from the SEM analysis of the reacted catalyst for the pyrolysis-reforming of all of the waste plastics, as shown in Fig. 2. Further analysis by TEM (Fig. 3) confirms the presence of multi-walled carbon nanotubes (CNTs) with parallel graphene layers, with the average diameter around 30 nm (~10 nm of wall thickness). In addition, so-called bamboo-shaped CNTs [31] can be observed in Fig. 3 (b).

As shown in Fig. 2, a similar morphology of CNTs was observed from the SEM analysis of the carbon formed on the reacted catalyst for the MOC and HDPE samples. However, CNT's were less prevalent for the HDPE/PVC waste plastic sample. The presence of chlorine in the HDPE/PVC waste plastic mixture is suggested to poison the catalyst during the formation of CNTs. The negative performance of chlorine in relation to the presence of PVC has been reported for the formation of CNTs which were entangled more densely compared with CNTs produced from polyethylene. [32]

The introduction of steam in the reforming process seems to change the morphology of the CNTs, as more clear, smooth and uniform CNTs with length around 10 μm were found for all the MOC and HDPE plastics when steam was added to the process. Without steam addition, the length of CNTs was around 1 μm for MOC and HDPE samples. Steam has been used as a weak oxidizer to selectively remove amorphous carbon and promote the catalytic activity for production of CNTs by Hata et al., [33] the authors reported a massive growth of vertically aligned nanotubes using a water-stimulated catalytic chemical vapour deposition (CVD) process. However, from TEM analysis, the influence of steam injection on the MOC pyrolysis-reforming process in terms of morphology of CNTs is difficult to determine.

XRD analysis of reacted catalysts. The reacted Ni-Mn-Al catalysts derived from the catalytic steam gasification of MOC, HDPE and HDPE/PVC were analysed by XRD (Fig. 1 (b-d)). Comparing the fresh catalyst, Ni and MnO crystals were observed derived from reduction of NiO and MnO_2, respectively, during the gasification process where reduction agents such as H_2 and CO were present (MnO_2 diffraction disappeared after reaction).

It is interesting to note that all the reacted catalysts derived from the different waste plastics expressed similar diffraction patterns. In particular, the diffraction of graphitic carbon was confirmed from Fig. 1, proving the presence of filamentous carbons/CNTs after the reforming/gasification process.

TPO analysis. Temperature program oxidation (TPO) was used to obtain the quantities of carbon materials produced from pyrolysis-reforming of waste plastics. The analysis uses a thermogravimetruic analyser with air as the purge gas, which oxidises the different types of carbon in relation to increasing temperature. As shown in Fig. 4, the sample mass increased at a temperature of around 400 °C which is suggested to be due to the oxidation of Ni into NiO for the reacted catalyst. Up to 40 wt.% of the weight of the reacted catalyst was ascribed to the deposited carbons after reaction. Weight loss from the reacted catalyst started after 500 °C for the TPO experiments, except for the reacted catalyst derived from the HDPE sample with steam (weight loss started from 550 °C). Carbon oxidation which occurred at around 550 °C is assigned to amorphous type carbons and oxidation at around 650 °C is assigned to filamentous carbons. [24, 34]

In order to compare the quantity of carbon materials, it is assumed that the weight loss between 450 and 600 °C is due to the oxidation of amorphous carbons and weight loss after

600 °C is attributed to the oxidation of filamentous carbons (Fig. 4). The ratio of amorphous and filamentous carbon was obtained from TPO analysis. The total carbon yield was calculated from the weight increase of the reactor divided by the weight of plastic sample. It was assumed that the total carbon was largely deposited on the catalyst, as was also confirmed by visual observation of the reactor and catalyst. Therefore, the yields of amorphous and filamentous carbons calculated in relation to the weight of plastic sample used in each experiment are shown in Table 2, 3 and 4 for the MOC, HDPE and HDPE/PVC, waste plastic samples respectively.

As shown in Table 2, the total carbon yield was reduced from 46.0 to 22.0 wt.% when steam was introduced into the catalytic pyrolysis-reforming of the MOC sample, while only 7 wt.% of carbon yield was obtained for the non-catalytic non-steam experiment. The decrease of carbon formation was also observed for the HDPE and HDPE/PVC samples (Table 3 and 4, respectively), when the steam was added to the experiment in the presence of the Ni-Mn-Al catalyst.

The addition of steam is known to gasify carbons formed during reforming, [35, 36] resulting in an increase of hydrogen production and CO concentration, as observed from Table 2, 3 and 4. In addition, the selective removal of amorphous carbons using steam to increase CNTs production has been reported. [33] In this work, a higher reduction of amorphous carbons was also observed compared to the reduction of graphitic (filamentous) carbons, with the addition of steam to the process. For example, the yield of amorphous carbon was significantly reduced from 15.4 to 2.4 wt.% for the HDPE sample, and reduced from 20.9 to 4.7 wt.% for the HDPE/PVC sample with the addition of steam to the catalytic experiment; while a comparatively lower reduction of filamentous carbons was observed (e.g. from 25.1 to 11.3 wt.% for the HDPE/PVC sample).

Therefore, the addition of steam is suggested to improve the fraction of filamentous carbons formed from the catalytic pyrolysis-reforming of waste plastics. This is consistent with the SEM analysis of the reacted catalyst, where comparatively smooth and clear CNTs were observed for the catalytic experiment in the presence of steam. However, the increase of the fraction of filamentous carbons is sacrificed in terms of the total overall yield of filamentous carbons when steam was injected to the system. While hydrogen production increases with the introduction of steam into the gasification process, this balance of productions of hydrogen and CNTs should be considered in future applications.

It is interesting to note that similar levels of carbon formation (around 46 wt.% in total) was obtained for the three plastics sample for the experiments without steam and with the Ni-Mn-Al catalyst. The HDPE/PVC sample resulted in the lowest yield of filamentous carbons (25.1 wt.% without steam and 11.3 wt.% with steam) compared with the MOC (33.8 wt.% without steam and 16.8 wt.% with steam) and HDPE (32.6 wt.% without steam and 16.6 wt.% with steam) samples in the presence of the Ni-Mn-Al catalyst; this is suggested to be due to the poisoning of the catalyst by chlorine from the HDPE/PVC sample.

Raman analysis. Raman spectroscopy, is used to characterise different types of carbon materials and has been used in this work to determine the graphitization of the product CNTs. As shown in Fig. 5, three main bands have been observed. The band at ~1343 cm^{-1} is assigned as the D-band, indicating the disorder of carbons. The band at ~ 1569 cm^{-1} and ~ 2690 cm^{-1} is assigned as G and G’ bands, respectively; the G band indicates the graphitic nature of the sample (i.e., crystallinity of the sample, pristine arrangement of atoms) and the G’ band is derived from the two-phonon, second order scattering process. [37] The G’ band is used as an indication of the purity of CNTs, as coupling two-phonon process does not occur for disordered samples. [38] In this work, the ratio of intensity of the D to G band (I_D/I_G), and the ratio of intensity of the G’ to G band ($I_{G'}/I_G$) are used to evaluate the degree of defects (i.e. edge dislocations) [39] and crystallinity of the product CNTs. [40]

As shown in Fig. 5, a high I_D/I_G ratio (>1.28) for the carbons produced from the pyrolysis-reforming of the HDPE/PVC sample was obtained compared with the MOC (<0.90) and HDPE (<0.98) waste plastic samples. The increase of crystallinity and decrease of defects have been reported when the I_D/I_G ratio was reduced. [41] Therefore, it is indicated that the highest defects of CNTs were obtained for the gasification of the HDPE/PVC sample; the results are supported by the SEM analysis, where very poor morphology characteristics of the CNTs could be observed. The lowest purity of CNTs produced from the HDPE/PVC sample is also supported by its lower $I_{G'}/I_G$ ratio (<0.45) compared with the other plastic samples (>0.49) (Fig. 5). In addition, a much higher yield of amorphous carbons (20.9 wt.%) was obtained for the HDPE/PVC sample compared with the MOC (12.2 wt.%) and HDPE (15.4 wt.%) samples (Table 2, 3 and 4). Therefore, it is suggested that the higher I_D/I_G ratio of carbons derived from the HDPE/PVC sample is related to the higher content of amorphous carbons. Furthermore, the results suggest that the presence of chlorine is inhibiting the formation of ordered CNTs during the reforming/gasification process.

When comparing the MOC with the HDPE sample, it seems that a higher purity of CNTs was produced from the HDPE sample in the presence of steam, as lower I_D/I_G and higher $I_{G'}/I_G$ ratios were obtained for the HDPE sample (Fig. 5). However, the morphologies of the CNTs as shown in the SEM micrographs, and the yield of amorphous carbons are similar for the reacted Ni-Mn-Al catalyst derived from both MOC and HDPE samples.

The addition of steam has shown a significant influence on the Raman spectroscopy results produced for the product carbons. From Fig. 5, the I_D/I_G ratio was increased from 0.80 to 0.90 for the MOC, from 0.63 to 0.98 for the HDPE sample, and from 1.28 to 1.53, when the steam was added to the gasification process. Additionally, the $I_{G'}/I_G$ ratio was also reduced with the introduction of steam into the gasification process. From Table 2 and 3, the yield of amorphous carbons was significantly reduced with the addition of steam for the MOC and HDPE samples; suggesting that there is little relation between I_D/I_G ratio and yield of amorphous carbons. This might be due to the fraction of amorphous carbon which was too small to influence I_D/I_G ratio. Here, the I_D/I_G ratio was mainly influenced by the defects of CNTs. Therefore, it is suggested that the addition of steam has increased the defects of the CNTs produced from pyrolysis-reforming of waste plastics. The increase of defects (increase of intensity of D band) has also been reported after purification of CNTs. [31] However, the I_D/I_G ratio has also been reported to be influenced by the alignment of the CNTs; a poor alignment results in a high I_D/I_G ratio. [42] The higher I_D/I_G ratio for the CNTs with the addition of steam might be due to the nature of the CNTs which were more tangled (SEM analysis, Fig. 2), as compared with the CNTs obtained from the process without steam addition.

CONCLUSIONS

In this work, real-world waste plastics were processed through pyrolysis-reforming for the production of hydrogen and high-value CNTs. The main conclusions are summarized as:

(1) Hydrogen production was significantly increased with the addition of the Ni-Mn-Al catalyst. The lowest hydrogen production (81.8 (mmol H_2 g^{-1} plastic)) was produced using the waste plastic from used motor oil plastic containers (MOC) compared with HDPE and HDPE/PVC sample. The reduction in hydrogen was ascribed to contamination of the MOC from residual motor oil, polystyrene and other plastics in the waste plastic sample.

(2) The presence of chlorine reduced the hydrogen production for the HDPE/PVC sample (43.2 mmol H_2 g^{-1} plastic) compared with the HDPE sample (56.6 mmol H_2 g^{-1} plastic)

in the absence of catalyst. However, the addition of the Ni-Mn-Al catalyst levelled the difference of hydrogen production (around 93 mmol H_2 g^{-1} plastic) between these two plastic samples.

(3) The injection of steam in the catalytic steam pyrolysis-reforming process reduced the total carbon yield; the fraction of filamentous carbons over amorphous carbons was increased with the addition of steam, as obtained from the TPO analysis. More clear and smooth CNTs were observed from the SEM analysis, when steam was added to the process.

(4) Raman analysis shows that the CNTs with the poorest quality (i.e. ordering and purity) were obtained for the HDPE/PVC sample due to the presence of chlorine. The introduction of steam is suggested to increase the defects of CNTs, as the I_D/I_G ratio was increased and $I_{G'}/I_G$ ratio was reduced.

ACKNOWLEDGEMENTS

This work was supported by the International Exchange Scheme from the Royal Society (IE110273), and the Early Career Research Scheme from the University of Sydney.

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Table 1 Properties of waste plastics (wt.%)

	Motor oil container (MOC)	HDPE	HDPE/PVC
Ash content	1.79	0.09	0.83
Oil	8.1	-	-
Moisture	1.7	0.3	0.8
Contaminants			
N	0.026	-	-
Cl	0.010	-	0.349
S	0.046	-	-
Ca	0.019	-	0.062
Zn	0.057	-	-
Ti	-	-	0.046

Table 2 Production of gas, hydrogen and carbons from pyrolysis-reforming of motor oil containers (MOC)

Catalyst/steam	No catalyst with steam	Ni-Mn-Al no steam	Ni-Mn-Al with steam
Gas yield (wt.%)	103	53.2	147.1
Amorphous carbon (wt.%)	-	12.2	5.2
Filamentous carbon (wt.%)	-	33.8	16.8
Total carbon (wt.%)	7.0	46.0	22.0
Hydrogen yield (mmol g^{-1} plastic)	27.7	61.1	81.8
Gas concentrations (vol.%)			
CO	18.3	8.1	23.2
H_2	41.0	75.6	63.4
CO_2	2.5	0.6	5.2
CH_4	23.6	15.7	8.0
C_2-C_4	14.6	0.1	0.2

Table 3 Production of gas, hydrogen and carbons from pyrolysis-reforming of commercial waste HDPE

Catalyst/steam	No catalyst with steam	Ni-Mn-Al no steam	Ni-Mn-Al with steam
Gas yield (wt.%)	126.3	46.1	170.1
Amorphous carbon (wt.%)	-	15.4	2.4
Filamentous carbon (wt.%)	-	32.6	16.6
Total carbon (wt.%)	22.0	48.0	19.0
Hydrogen yield (mmol g^{-1} plastic)	56.6	56.3	94.4
Gas concentrations (vol.%)			
CO	22.6	6.9	24.1
H_2	55.2	76.6	63.4
CO_2	2.4	0.4	4.8
CH_4	15.2	15.9	7.4
C_2-C_4	4.6	0.2	0.3

Table 4 Production of gas, hydrogen and carbons from pyrolysis-reforming of commercial waste HDPE mixed with 1 wt.% PVC (HDPE/PVC)

Catalyst/steam	No catalyst with steam	Ni-Mn-Al no steam	Ni-Mn-Al with steam
Gas yield (wt.%)	116.6	42.8	173.9
Amorphous carbon (wt.%)	-	20.9	4.7
Filamentous carbon (wt.%)	-	25.1	11.3
Total carbon (wt.%)	19.0	46.0	16.0
Hydrogen yield (mmol g^{-1} Plastic)	43.2	42.8	91.8
Gas concentrations (vol.%)			
CO	20.3	6.3	24.1
H_2	49.4	72.3	62.4
CO_2	3.4	1.1	5.8
CH_4	21.3	18.3	7.6
C_2-C_4	5.6	2	0.1

Figure captions:

Figure 1 XRD analysis of (a) fresh Ni-Mn-Al catalyst; and reacted catalyst from MOC (b); HDPE/PVC (c) and HDPE (d) in the presence of steam injection.

Figure 2 SEM analysis of the reacted Ni-Mn-Al catalyst after pyrolysis/reforming of various waste plastics

Figure 3 TEM analysis of the reacted Ni-Mn-Al catalyst derived from pyrolysis-reforming of MOC; (a) (b) – without steam; (c) (d) – with steam injection

Figure 4 Temperature program oxidation (TPO) of the reacted catalyst derived from different waste plastics

Figure 5 Raman spectroscopy of the reacted catalyst

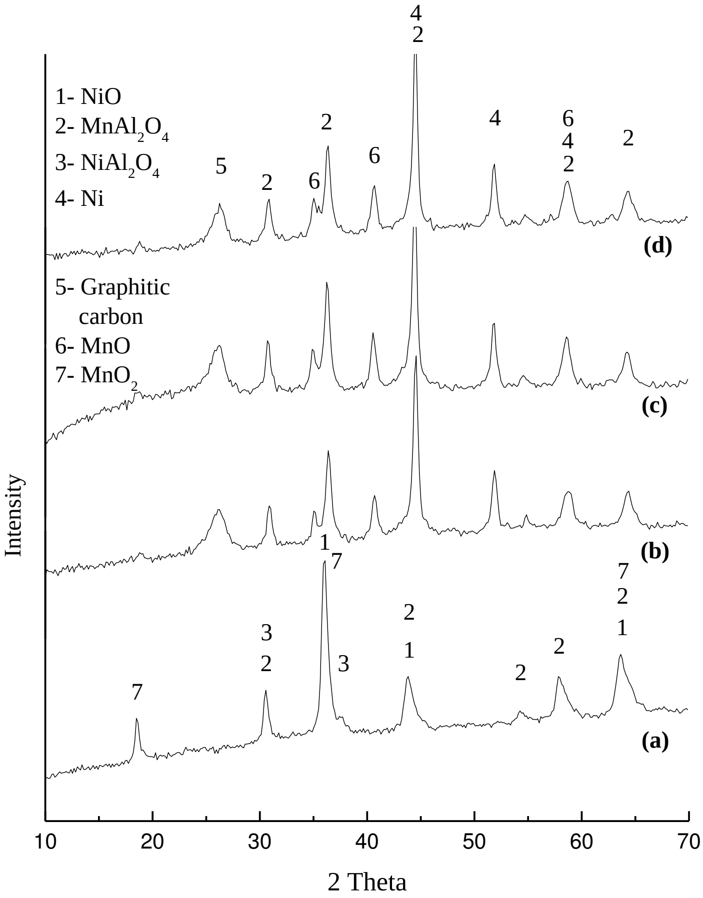
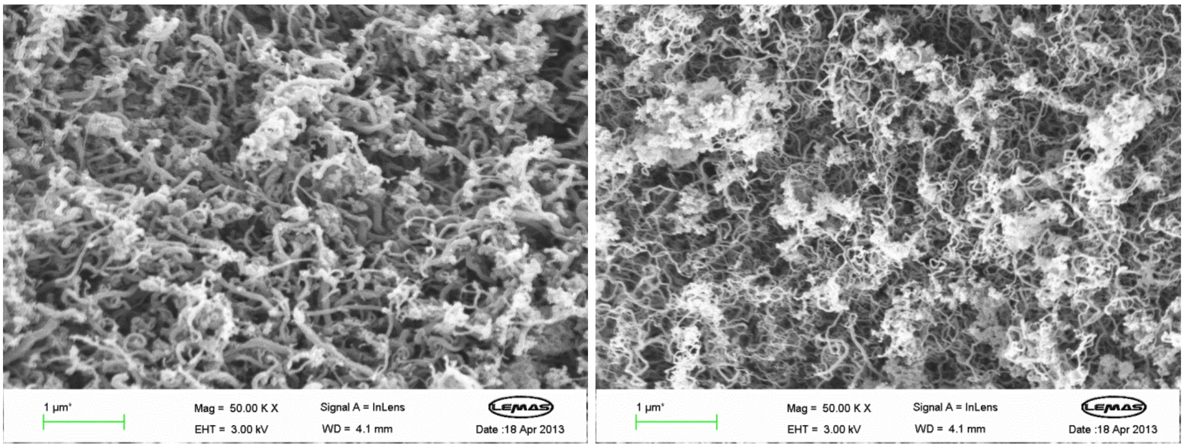
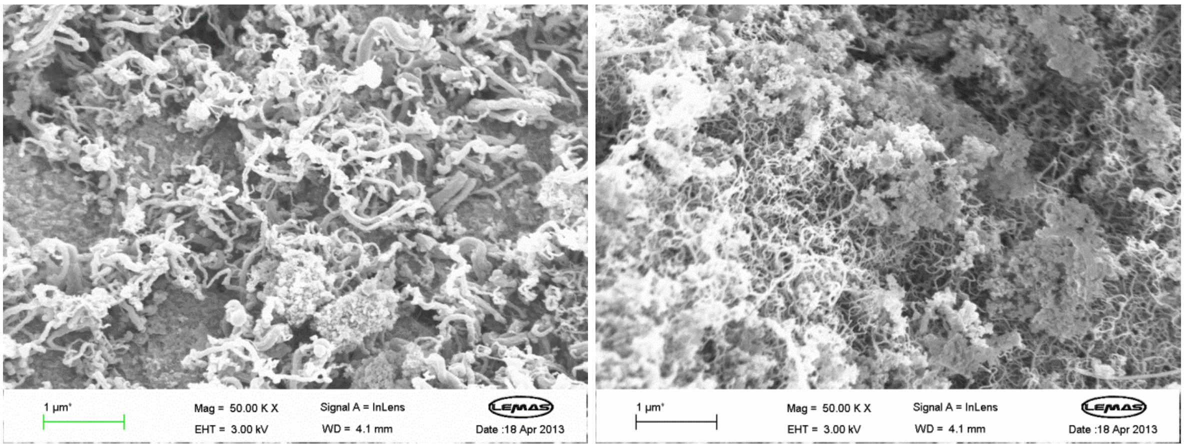


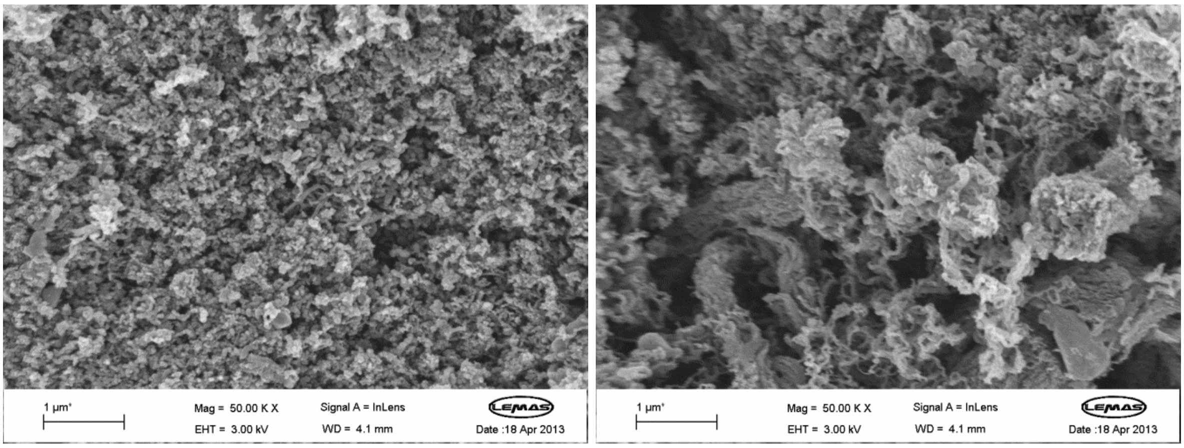
Figure 1 XRD analysis of (a) fresh Ni-Mn-Al catalyst; and reacted catalyst from MOC (b); HDPE/PVC (c) and HDPE (d) in the presence of steam injection.



MOC without steam MOC with steam

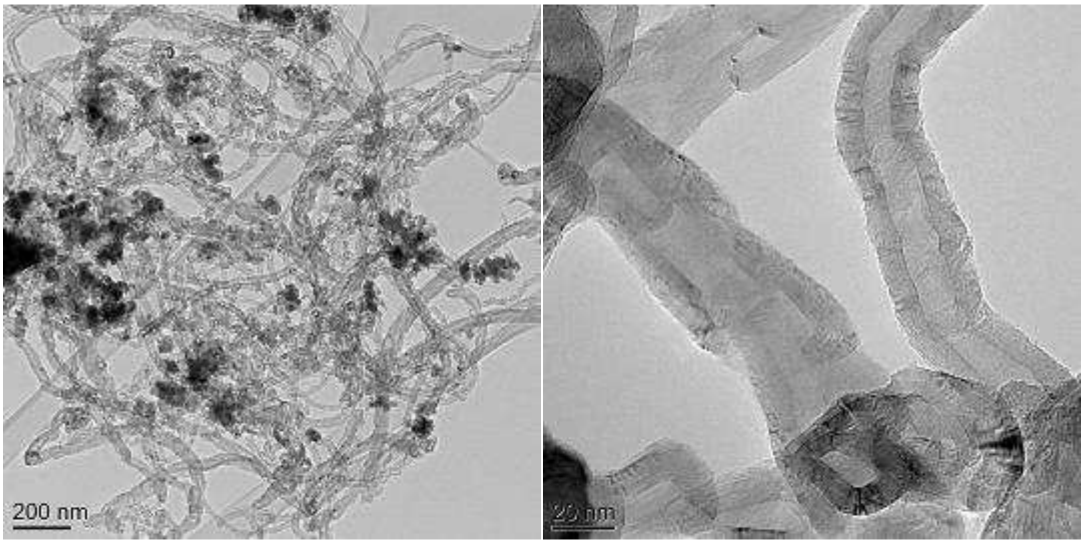


HDPE without steam HDPE with steam



HDPE/PVC without steam HDPE/PVC with steam

Figure 2 SEM analysis of the reacted Ni-Mn-Al catalyst after pyrolysis/reforming of various waste plastics



(a) (b)

Figure 3 TEM analysis of the reacted Ni-Mn-Al catalyst derived from pyrolysis-reforming of MOC without steam injection

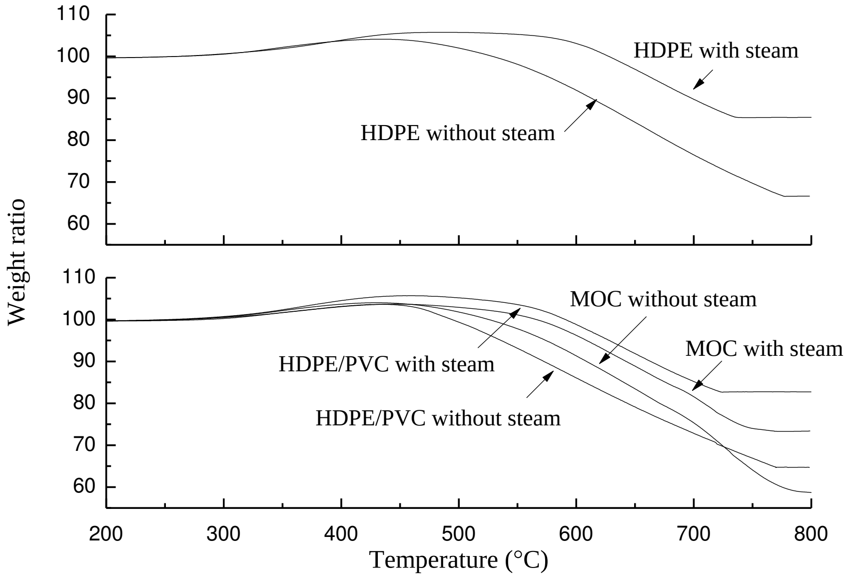


Figure 4 Temperature program oxidation (TPO) of the reacted catalyst derived from different waste plastics

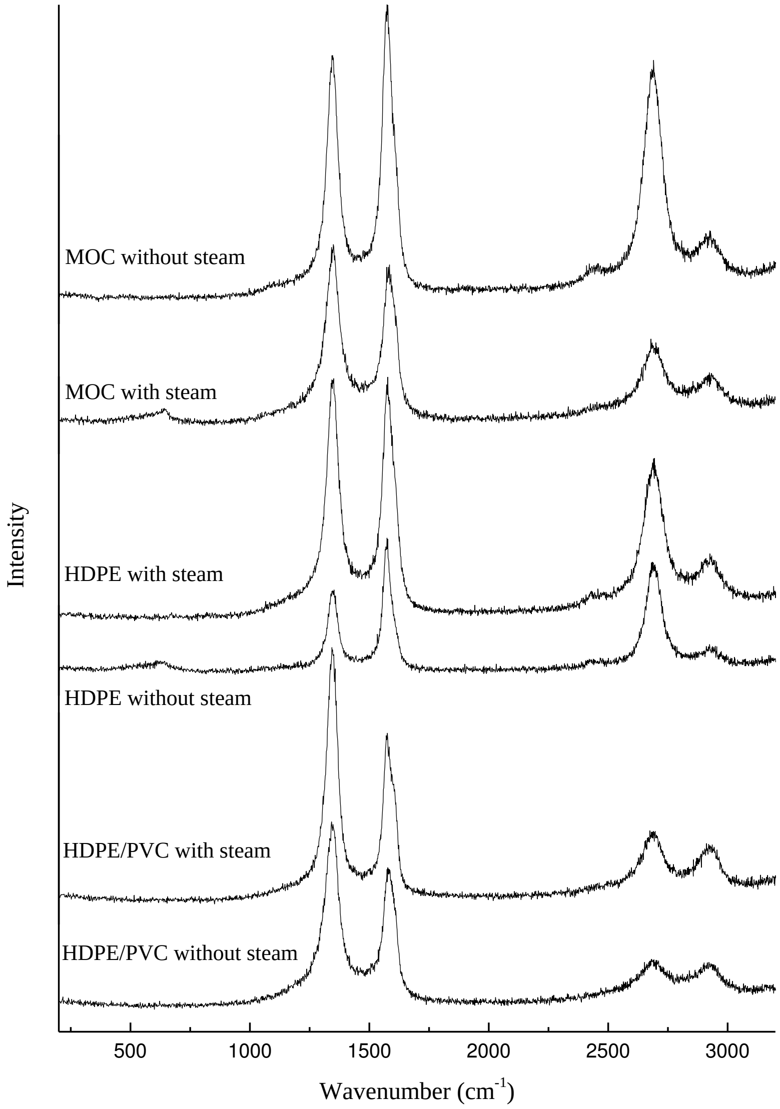


Figure 5 Raman spectroscopy of the reacted catalyst