Introduction

Waste tyre disposal represents a major worldwide problem. In 2014, 4.67 million tonnes of tyres were produced in Europe (ETRMA, 2015), eventually leading to a similar number of waste tyres arising annually to be managed. The current main treatment routes for waste tyres include fuel for cement kilns as a replacement for fossil fuels, recycling as rubber crumbs for sports fields or playgrounds, retreading of part-worn tyres, civil engineering applications and export (Williams, 2013). However, recently, there has been much interest in advanced thermal treatment technologies such as pyrolysis and gasification as a means of producing higher-value products from waste tyres. For example, the solid char product from pyrolysis of the tyres can be upgraded to produce high surface area activated carbons (Cunliffe and Williams, 1998; Nunes et al., 2011; Zabaniotou et al., 2004). In addition, the product oil and gas can be upgraded for the production of high-grade liquid fuels, hydrogen or aromatic chemicals (Leung and Wang, 2003; Williams, 2013; Williams and Brindle, 2003; Xiao et al., 2008; Zhang et al., 2015).

The production of hydrogen from waste tyres has been investigated by only a few research groups (Elbaba and Williams, 2012; Lerner et al., 2012). However, there is predicted to be high demand for hydrogen in the future to support the proposed hydrogen economy. Whilst hydrogen is currently mostly produced from fossil fuels, production of waste materials such as waste tyres would represent a novel route to recycle waste tyres. Alternative feedstocks for hydrogen production have included biomass, waste plastics and municipal solid waste (Wang et al., 2012; Wu and Williams, 2009a).

Catalysts are extensively used for increasing hydrogen yield from the steam reforming of hydrocarbon sources (Sutton et al., 2001; Wu and Williams, 2009a). Catalysts containing metals such as Ru, Pt and Rh have been shown to be effective for hydrogen production; however, nickel is a preferred metal due to its low cost (Sehested, 2006; Srinakruang et al., 2005). The type of support used to support the nickel will also influence the catalytic...
activity of the catalyst through the characteristics of surface area, porous structure and mechanical strength, and chemical interaction between the metal and catalyst. For example, Miyazawa et al. (2006) investigated the performance of nickel-based catalysts on various supports for the steam reforming of tar from biomass pyrolysis. The catalyst supports tested were Al2O3, ZrO2, TiO2, CeO2 and Ni/MgO. It was reported that the production of hydrogen was influenced by the support material, with Ni/Al2O3, Ni/ZrO2 and Ni/TiO2 catalysts producing the largest hydrogen yields. The interaction between the nickel and the support was shown to influence the metal dispersion and the size of the metal particles, which in turn affected catalyst activity. Wu and Williams (2009a) reported on the use of Ni/Al2O3, Ni/MgO, Ni/CeO2 and Ni/ZSM-5 catalysts with 10 wt.% nickel for the pyrolysis-catalytic steam reforming of waste plastics. The Ni/MgO catalyst produced the lowest yield of hydrogen and the Ni/ZSM-5 catalyst the highest yield, which could be linked with the surface area of the catalysts. In addition, Ni/Al2O3 and Ni/CeO2 catalysts also showed significant amounts of carbon deposition. Inaba et al. (2006) investigated Ni/SiO2, Ni/ZrO2, Ni/CeO2 and a series of zeolites for use as catalysts in hydrogen production from the gasification of cellulose. The highest hydrogen yield was with the Ni/SiO2 catalyst. Srinakruang et al. (2005) investigated the gasification of tar using nickel catalysts supported on SiO2–Al2O3 and Ni/ZSM-5 catalysts with 10 wt.% nickel for the pyrolysis-catalytic steam reforming of waste plastics. The Ni/MgO catalyst produced the lowest yield of hydrogen and the Ni/ZSM-5 catalyst the highest yield, which could be linked with the surface area of the catalysts. In addition, Ni/Al2O3 and Ni/CeO2 catalysts also showed significant amounts of carbon deposition. Inaba et al. (2006) investigated Ni/SiO2, Ni/ZrO2, Ni/CeO2 and a series of zeolites for use as catalysts in hydrogen production from the gasification of cellulose. The highest hydrogen yield was with the Ni/SiO2 catalyst. Srinakruang et al. (2005) investigated the gasification of tar using nickel catalysts supported on SiO2–Al2O3, Al2O3 and dolomite. The nickel catalysts on SiO2–Al2O3 and Al2O3 produced larger amounts of carbon deposition than the Ni/dolomite catalyst, which led to deactivation.

Experimental system

The reactor for the pyrolysis-reforming of waste tyres consisted of a two-stage fixed bed reactor. Figure 1 shows the schematic diagram of the experimental system. After being pyrolysed in the first pyrolysis stage, the gas products from the tyres are passed directly to the second stage where either catalysis or catalytic reforming takes place (Elbaba and Williams, 2013; Elbaba et al., 2010; Zhang et al., 2015).

The reactors for both stages were constructed of stainless steel with a diameter of 2.2 cm and a height of 16 cm. The two stages are heated separately by two external electrical heaters, which controlled the heating rate and the target temperature for the experiments. Both of the stages were purged with nitrogen gas continually. The real-time internal temperatures of the reactors were monitored by thermocouples near the catalyst and tyre sample (Elbaba and Williams, 2012).

The reforming and pyrolysis temperature was 800 and 600°C, respectively. In each of the experiments, 1.0 g tyre sample and 0.5 g catalyst were introduced. The heating rate of the pyrolysis stage was 10°C min⁻¹ to the final temperature of 600°C, and was held at that temperature for 20 minutes. No steam was introduced to the experiments with different SiO2/Al2O3 ratios catalysts.
Experiments with steam reforming were performed with different water injection rates where experiments were carried out with the catalyst which produced the highest hydrogen yield.

**Analytical methods**

X-ray diffraction was used to identify the composition of the freshly prepared catalysts. The gaseous products from the pyrolysis-reforming of the waste tyres were collected by a Tedlar™ gas sample bag, and further analysed by packed column gas chromatography (GC). Permanent gases which included H₂, CO, O₂, N₂ and CO₂ were analysed by a Varian 3380 GC/TCD with a 2 m long, 2 mm diameter and 60–80 mm mesh molecular sieve packed column. Hydrocarbons including C₁–C₄ were analysed by a Varian 3380 with a flame ionization detector with 80–100 mesh HayeSep column and nitrogen carrier gas. The gases are reported on a nitrogen-free basis.

Thermogravimetric analyser-temperature programmed oxidation (TGA-TPO) was used to analyse the reacted catalysts to investigate the types of carbon formed during the pyrolysis-catalytic/reforming of waste tyres. Raman spectroscopy was used to determine the degree of graphitization of the carbon productions. The results were obtained using a Renshaw Invia Raman spectrometer at a wavelength of 514 nm and Raman shifts between 100 and 3000 cm⁻¹. Scanning electron microscopy (SEM) and transmission microscopy (TEM) were used to observe the surface characteristics of the fresh and reacted catalysts to help determine the structure of the carbon deposition on the catalyst surface. The instruments used were a Hitachi SU8230 SEM and a FEI Tecnai TF20 TEM.

**Results and discussion**

**Product yields and gas composition**

*Influence of different Al₂O₃ to SiO₂ ratios for the pyrolysis-catalysis of waste tyres.* Table 1 shows the product yield from pyrolysis-catalysis of waste tyres with different 20 wt.% Ni/Al₂O₃/SiO₂ catalysts in relation to different Al₂O₃ to SiO₂ ratios. The solid residue left after pyrolysis, carbon on the catalyst and oil were measured by the weight difference before and after reaction. The gas yield was calculated by comparing the concentration of product gases and reference gas (nitrogen). The results produced a mass balance of between 94 and 95 wt.%, where errors could occur from condensation of heavy molecular weight hydrocarbons within the reactor, or variations in the flow rate of nitrogen carrier gas, etc.

From Table 1, the results show that as the Al₂O₃ to SiO₂ ratio was increased, the influence on hydrogen production was small, with the highest amount of 14.0 mmol g⁻¹ hydrogen produced at the Al₂O₃:SiO₂ ratio of 1:1. The calorific values of the produced gases did not change significantly by changing the Al₂O₃ to SiO₂ ratios, which were in the range of 18.7 to 20.7 MJ m⁻³. There was no significant difference in liquid yield between the different catalysts with different Al₂O₃ to SiO₂ ratios. It can be concluded that the catalyst with an Al₂O₃:SiO₂ ratio 1:1 showed the best performance in terms of the gas yield and hydrogen production. Table 1 shows that the increased content of Al₂O₃ in the 20 wt.% Ni/Al₂O₃/SiO₂ catalyst at the higher Al₂O₃ to SiO₂ ratio produced reduced amounts of catalyst carbon deposition, decreasing from ~18/19 to ~13 wt.%.

*Influence of different water injection rates.* The 20 wt.% nickel catalyst at a Al₂O₃ to SiO₂ ratio of 1:1 produced the highest yield of hydrogen in the pyrolysis-catalysis experiments. Therefore, further work was carried out to increase the production of hydrogen from the waste tyres by introducing steam (injected water) to the second stage to produce a pyrolysis-catalytic steam reforming process. Table 2 shows the product yields and gas compositions from waste tyre pyrolysis-catalytic steam reforming with the 20 wt.% Ni/Al₂O₃/SiO₂ (1:1) catalyst at different water injection rates. The gas yields with water injection rate at 2 and 5 ml h⁻¹ were similar at 58.0 and 57.8 wt.%, respectively, which were much higher than the experiments without water at only 27.3 wt.%. The hydrogen production from the process showed a similar trend, at 14.0, 33.8 and 34.5 mmol g⁻¹ for the water injection rates of 0, 2 and 5 ml h⁻¹, respectively.

These increases in total gas yield and hydrogen production are attributed to the reacted water, since at a water injection rate of 5 ml h⁻¹ the reacted water was 0.5 g, whereas at 2 ml h⁻¹ the reacted water was 0.48 g. Table 2 also shows the calorific values of the gas product. The results show that as the water injection rate was increased from 0 to 5 ml h⁻¹, there was
decrease in the calorific value of the product gases, from 19.47 to 10.72 MJ m⁻³, due mainly to the decrease of the methane and C₂–C₄ hydrocarbons due to the catalytic steam reforming process of these hydrocarbons.

Table 2 shows that the product oil and carbon deposition on the catalyst decreased as the amount of water injected into the second stage reforming process was increased. Wu and Williams (2009b) reported that increasing water flow rate contributes to a significant decrease of carbon deposition on the catalyst in relation to hydrogen production from the pyrolysis-catalytic reforming of polypropylene. The results show the oil yields were 13.0, 2.7 and 7.0 wt.% at water injection rates of 0, 2 and 5 ml h⁻¹, respectively. It should be noted that Table 2 shows data calculated in relation to the amount of injected water and reacted water, which shows that there was 36.00 wt.% of residue with no water added, with 2 and 5 ml h⁻¹ water injections, the pyrolysis residues decreased to 26.34 and 24.59 wt.%.

However, determination of the pyrolysis residue in relation to tyre sample weight produced pyrolysis residue data that were very similar 37±2 wt.% (as was also shown in Table 1). Table 2
also shows that the CO concentration increased up to 19.11 and 17.41 vol.% from 13.26 vol.% with the introduction of water injection at the rates of 2 and 5 ml h⁻¹. The CO₂ concentration increased from 0 vol.% to 12.80 and 14.58 vol.% at water injection rates of 2 and 5 ml h⁻¹. The increase of water injection rate produced a reduction in CH₄ and C₂-C₄ hydrocarbons through steam reforming reactions. The CH₄ concentration was 22.01 vol.% without water in the experiment, but decreased to 8.43 and 8.52 vol.% at water injection rates of 2 and 5 ml h⁻¹, and C₂–C₄ concentrations decreased from 4.47 vol.% at no water addition to 1.55 and 1.75 vol.% at water injection rates of 2 and 5 ml h⁻¹, respectively.

Turn et al. (1998) found similar results in their experiments for biomass, where an increase of steam to biomass ratio produced an increase in H₂ and CO₂ yields. Further increasing steam to the process to high levels can saturate the catalyst surface and reduce hydrogen production; also, higher water inputs require more energy for steam generation (Wu and Williams, 2009b).

**Characteristics of the produced carbon**

*Influences of different Al₂O₃ to SiO₂ ratios.* The reacted Ni/Al₂O₃/SiO₂ catalysts with different Al₂O₃ to SiO₂ ratios were further analysed by TGA-TPO. For this analysis the weight loss is mainly due to the oxidation of carbon production on the catalyst surface. Figure 2 shows the TGA-TPO and differential thermogravimetric (DTG)-TPO results of the carbon oxidation for the reacted catalysts in relation to Al₂O₃ to SiO₂ ratio. It can be observed that there are two peaks for all the four different catalysts in the DTG-TPO figure. All of these four DTG-TPO curves show similar trends. There were no peaks below 600°C for any of the catalysts; this could be attributed to the lack of formation of amorphous carbon on the catalyst surface, since such carbons are known to oxidize at lower temperature. Musumeci et al. (2007) have suggested that the amorphous carbons are easily oxidized from the surface of the nickel-based catalyst.

The oxidation peaks for all of the catalysts are present at similar temperatures, in which the first peak occurs at around 600°C and the second peak arises between 650°C and 675°C. The first peak could indicate the oxidation of filamentous carbon which has less graphitization and which is of smaller size. The second oxidation peak could indicate the oxidation of filamentous carbon of larger size and with a higher degree of graphitization. In addition, carbon nanotubes are reported to oxidize at a high temperature above 600°C (Wu and Williams, 2010); Musumeci et al. (2007) also suggested that the more graphitic filamentous carbon are more stable and oxidize at higher temperature with a sharp oxidation peak. Therefore, from the TPO results it can be suggested that the carbon produced in these experiments is mostly filamentous-type carbon with different degrees of graphitization. Examination of the corresponding SEM images, shown in Figure 3, also confirms that the carbon formed on the catalyst surface is mostly filamentous carbon. The corresponding TEM images, shown in Figure 4, also confirm that a large proportion of the filamentous carbon is multi-walled carbon nanotubes (MWCNTs). The first oxidation peaks in the DTG-TPO curves for the Ni catalysts with Al₂O₃ to SiO₂ support ratios of 3:2 and 1:1 are produced at lower temperatures than the other two Al₂O₃ to SiO₂ ratios. This can be assigned to the diameters of the MWCNTs produced with Al₂O₃ to SiO₂ ratios of 3:2 and 1:1 are produced at lower temperatures than the other two Al₂O₃ to SiO₂ ratios. This can be assigned to the diameters of the MWCNTs produced with Al₂O₃ to SiO₂ ratios of 3:2 and 1:1 catalysts, which are smaller than the MWCNTs produced with ratios at 3:5 and 2:1 catalyst from the waste tyre pyrolysis-catalysis process. The TEM images in Figure 4 confirm the difference in diameters of the MWCNTs. The inner diameters of the MWCNTs
produced with catalysts with Al₂O₃ to SiO₂ ratios at 3:5, 1:1, 3:2 and 2:1 are approximately 36 nm, 18 nm, 11 nm (and 20 nm) and 25 nm, respectively.

Fang et al. (2012) suggested that smaller NiO and CeO₂ particles of the catalysts contribute to higher reactivity of the smaller size of filamentous carbon. They reported that the oxidation peak of smaller-diameter filamentous carbons in TPO results is larger and shifted to lower temperature compared with the larger-sized filamentous carbon. The largest inner diameter of carbon nanotubes was produced with the highest SiO₂ content (Al₂O₃:SiO₂ is 3:5) 20 wt.% Ni/Al₂O₃/SiO₂ catalyst. Kukovecz et al. (2000) also found that increasing the amount of silica in the catalyst support slightly increased the thickness of the carbon nanotubes.

Raman spectroscopy analysis was used to determine the degree of graphitization of the carbon deposited on the different catalysts in the pyrolysis-catalysis of waste tyres. The D band, which occurs at the wavelength around 1350 cm⁻¹, indicates the presence of amorphous carbons or disordered carbons; the G band, which occurs at the wavelength around 1584 cm⁻¹, indicates a graphite carbon structure. The ratio of the intensity of the D band to the intensity of the G band (I_D/I_G) can help to evaluate the graphitization level of the produced carbons (Zhang et al., 2015). Table 3 shows that the I_D/I_G ratios of catalysts with Al₂O₃ to SiO₂ ratios 3:5, 1:1, 3:2, 2:1 are 0.89, 0.93, 0.91, and 0.93, respectively. The lowest I_D/I_G ratio shows the highest graphitization of the carbon produced on the catalyst at Al₂O₃ to SiO₂ ratio was 3:5, suggesting that the carbons produced have the highest crystallinity.

The amounts of the different types of carbon produced on the catalysts are shown in Figure 5. The results show that as the Al₂O₃:SiO₂ ratio was increased from 3:5 to 2:1, the filamentous carbon production increased marginally from 171.68 mg g⁻¹ waste tyre to 179.12 mg g⁻¹ at the ratio 1:1 and then decreased to 124.40 mg g⁻¹.

**Influences of different water injection rates.** Figure 6 shows the TPO and DTG-TPO results of the reacted catalysts from pyrolysis-catalytic steam reforming of waste tyres with the 20 wt.% Al₂O₃/SiO₂ catalyst with an Al₂O₃ to SiO₂ ratio of 1:1 at different water injection rates. The results show that the introduction of water leads to a significant decrease in the amount of carbon deposited on the catalyst. Filamentous carbons oxidized at high temperature were observed from the DTG-TPO results. SEM images in Figure 7 confirm filamentous carbon formation. Figure 8 shows the TEM analysis of the filamentous carbons formed with the 20 wt.% Al₂O₃/SiO₂ catalyst with an Al₂O₃ to SiO₂ ratio of 1:1 at different water injection rates. The results show that the introduction of water leads to a significant decrease in the amount of carbon deposited on the catalyst. Filamentous carbons oxidized at high temperature were observed from the DTG-TPO results. SEM images in Figure 7 confirm filamentous carbon formation. Figure 8 shows the TEM analysis of the filamentous carbons formed with the 20 wt.% Al₂O₃/SiO₂ catalyst with an Al₂O₃ to SiO₂ ratio of 1:1 at different water injection rates, showing that they are mostly solid carbon fibres. Figure 4 showed earlier that for the 1:1 ratio Al₂O₃/ SiO₂ nickel catalyst in the absence of water (steam) input, the deposited carbons were MWCNTs. The Raman analysis of the carbons deposited on the catalysts in relation to input of steam (Table 2) shows that for the I_D/I_G ratios for the deposited carbons for the experiments with 2 and 5 ml h⁻¹ water injection rates are...
which indicates the lower water injection rate contributes to higher graphitization of carbon formation.

Figure 3 shows that when water was introduced into the waste tyre pyrolysis-catalytic steam reforming process, less filamentous carbon was produced and less amorphous carbon was produced. As the water injection rate was increased from 0 to 5 ml h⁻¹, the amount of filamentous carbon production decreased from 179.12 to 46.33 mg g⁻¹ of waste tyre. Also, the amorphous carbon production decreased simultaneously. Therefore, the water introduction inhibited the carbon production in the waste tyre pyrolysis-catalytic reforming process and also inhibited filamentous carbon production.

The production of MWCNTs identified in this work for certain process conditions might have benefits to the process of hydrogen production instead of causing a problem to catalyst activity. There has been great interest in the application of carbon nanotubes in a wide variety of industrial sectors (Nessim, 2010; de Volder et al., 2013). Carbon nanotubes are currently produced from pure hydrocarbon feedstocks such as methane, benzene, acetylene, etc.; however, there is current interest in the use of waste materials such as plastics as alternative hydrocarbon feedstocks (Acomb et al., 2014; Arena et al., 2006; Chung and Jou, 2005; Liu et al., 2011; Zhang et al., 2008). Waste tyres are produced in large tonnages throughout the world and are usually

0.87 and 0.90, which indicates the lower water injection rate contributes to higher graphitization of carbon formation.

Table 3. Raman analysis of the catalyst coke from the pyrolysis-catalysis of waste tyres with a 20 wt.% Ni/Al₂O₃/SiO₂ catalyst with different Al₂O₃ to SiO₂ ratios and water injection rates.

| A₂O₃:SiO₂ ratio and water injection rate | D(ν) | G(ν) | ID/IG(ν) |
|----------------------------------------|------|------|----------|
| 3:5 without water                      | 4160 | 4680 | 0.89     |
| 1:1 without water                      | 2628 | 2819 | 0.93     |
| 3:2 without water                      | 3426 | 3775 | 0.91     |
| 2:1 without water                      | 7212 | 7729 | 0.93     |
| 1:1 with 2ml h⁻¹ water                 | 12831| 14774| 0.87     |
| 1:1 with 5ml h⁻¹ water                 | 6713 | 7467 | 0.90     |

Figure 4. TEM images of carbon deposited on different reacted 20 wt.% Ni/Al₂O₃/SiO₂ catalysts with different Al₂O₃ to SiO₂ ratios derived from pyrolysis-catalysis of waste tyres.
Figure 5. Proportion of amorphous and graphitic type carbons formed from the pyrolysis-catalysis of waste tyre with different Al$_2$O$_3$ to SiO$_2$ ratios (3:5, 1:1, 3:2 and 2:1) and different water injection rate (2 and 5 ml h$^{-1}$).

Figure 6. TPO and DTG-TPO results of used catalysts from pyrolysis-catalysis of waste tyres with 20 wt.% Al$_2$O$_3$/SiO$_2$ catalyst at Al$_2$O$_3$ to SiO$_2$ ratios of 1:1 and pyrolysis-catalytic steam reforming of tyres at different water injection rates (2 and 5 ml h$^{-1}$).

Figure 7. SEM images of carbon deposited on the catalysts from pyrolysis-catalysis of waste tyres with 20 wt.% Al$_2$O$_3$/SiO$_2$ catalyst with Al$_2$O$_3$ to SiO$_2$ ratio of 1:1 at different water injection rates (2 and 5 ml h$^{-1}$).
collected as a separate waste stream, thereby aiding feedstock acquisition. The production of carbon nanotubes in the form of MWCNTs represents a potential valuable by-product from the production of hydrogen from waste tyres.

Conclusions

In this paper, 20 wt.% Ni/Al₂O₃/SiO₂ catalysts with four different Al₂O₃ to SiO₂ mole ratios (3:5, 1:1, 3:2, 2:1) were studied for the pyrolysis-catalysis of waste tyres for hydrogen production and to determine the catalysts carbon deposition. The catalyst with an Al₂O₃ to SiO₂ mole ratio of 1:1 gave the highest gas yield (27.3 wt.%), highest hydrogen production (14.0 mmol/g tyre) and highest syngas production (17.3 mmol/g tyre) when no steam was introduced to the system. In addition, the Ni catalysts with Al₂O₃ to SiO₂ mole ratio 1:1 produced the highest deposition of carbon onto the catalyst at 164 mg g⁻¹ of waste tyre. The carbon deposits were of the filamentous type and consisted of a large proportion of MWCNTs which have the potential to be of commercial value.

The introduction of steam to the process to produce pyrolysis-catalytic steam reforming of the waste tyres at different water injection rates was also investigated to determine the influence on both hydrogen and catalyst carbon deposition. The results showed that water addition to the process promoted higher hydrogen production and markedly reduced carbon deposition. The maximum yield of hydrogen produced was 34.5 mmol g⁻¹ tyre at a water input rate of 5 ml h⁻¹. As the water injection rate was increased from 0 to 5 ml h⁻¹, the catalyst carbon deposition decreased from 19 to 4.6 wt.%.

Acknowledgements

The authors also gratefully acknowledge the support from Adrian Cunliffe, Hualun Zhu, Chunfei Wu and Jude Onwudili.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The authors disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 643322 (FLEXI-PYROCAT). In addition, support from the Faculty’s Energy and Materials Clusters and MCR Scheme from the University of Sydney is acknowledged.

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