View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by White Rose Research Online

UNIVERSITY OF LEEDS

This is a repository copy of *High-value resource recovery products from waste tyres*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/133273/

Version: Accepted Version

Article:

Zhang, Y orcid.org/0000-0003-0095-3015, Wu, C, Nahil, MA et al. (1 more author) (2016) High-value resource recovery products from waste tyres. Proceedings of the Institution of Civil Engineers - Waste and Resource Management, 169 (3). pp. 137-145. ISSN 1747-6526

https://doi.org/10.1680/jwarm.16.00001

© ICE Publishing, all rights reserved. This is an author produced version of a paper published in Proceedings of the ICE - Waste and Resource Management. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

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.

White Rose
university consortium
Universities of Leeds, Sheffield & York

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

High value resource recovery products from waste tyres

Yeshui Zhang [a], Chunfei Wu [b], Mohamad A. Nahil [a], Paul Williams [a*]

[a] School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

[b] Department of Chemical Engineering, University of Hull, Hull, HU6 7RX, UK

(*Corresponding author: Tel: #44 1133432504; Email: p.t.williams@leeds.ac.uk)

Abstract

A novel process has been developed which enables the production of high value carbon nanotubes (CNTs) and hydrogen-rich syngas from the two-stage pyrolysis-catalysis of waste tyres. The waste tyre samples originated from truck tyres and from car tyres. In addition, three of the main rubber elastomers used in tyre manufacture, polybutadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR), were also investigated. The waste car tyres produced a syngas yield of 30.2 wt.% which was composed largely of hydrogen (53.8 vol.%) with a calorific value of 18.8 MJ m^3. Increasing the tyre:catalyst ratio increased the yield of hydrogen. The component rubber elastomers produced much higher yields of syngas and hydrogen gas concentration. The carbon deposited on the catalyst during reaction was found to be mostly composed of graphitic carbon nanotubes. Changing the process conditions in terms of tyre:catalyst ratio could increase the yield of the carbon deposited on the catalyst to up to 14 wt.%.

Key words: Pyrolysis; Tyres; Carbon nanotubes; Hydrogen; Catalysis

1. Introduction

The treatment and disposal of waste tyres represents a major waste management issue with an estimated 1.5 billion end of life waste tyres generated annually worldwide (ETRMA, 2011). The waste tyre problem in Europe is major, with more than 3 million tonnes of waste tyres generated annually (ETRMA, 2013) and where there is an estimated stock pile of 5.7 million tonnes deposited throughout Europe (Williams, 2013). The treatment of waste tyres in Europe is mostly through their use as an alternative fuel for energy recovery in cement kilns (35 wt.%), material recovery via sports fields and playgrounds (33 wt.%) in civil engineering applications such as embankments and foundation material (7 wt.%), tyre retreading (8 wt.%) and export (10 wt.%) (Williams, 2013).

There is significant resource invested in tyre manufacture, including fossil fuel petroleum for synthetic rubber manufacture and for production of carbon black for filler material. For example, it has been estimated that a new passenger car tyre can contain the equivalent of ~30 litres of petroleum oil and heavy duty tyres contain an oil equivalent of ~93 litres (ETRMA, 2013). With heightened concern in relation to sustainability and resource recovery, there is growing interest in alternative technologies that can recover valuable products from tyres rather than tyre combustion and low grade uses (Sienkiewicz et al., 2012). Sienkiewicz et al. (2012) have comprehensively reviewed the progress of waste tyre management in Europe and highlighted the considerable potential of pyrolysis as an alternative treatment option for waste tyres.

Pyrolysis has been investigated as a process route to thermally degrade waste tyres. At a typical pyrolysis temperature of ~500 °C and an inert atmosphere, the tyre rubber is decomposed to produce a solid carbon, liquid oil and gaseous product (Sienkiewicz et al. 2012; Williams, 2013). The gaseous products are typically hydrogen and C_1-C_4 hydrocarbons with high calorific value and can be used as process fuel, the oil product can be used directly as a fuel with similar characteristics to a gas oil and the solid char product can be used as solid fuel or low grade carbon black. In more advanced systems, pyrolysis can be coupled with catalysts to upgrade the oils to premium grade fuels or chemicals or to produce hydrogen (Williams, 2013).

There is particular interest in the production of hydrogen since it is regarded as a clean energy carrier that only generates water on combustion and features as a major energy resource in potential future energy scenarios. Two-stage pyrolysis-catalysis reactors have been used to enhance hydrogen production from waste tyres with the catalyst used to improve the efficiency of hydrogen production. For example, Elbaba et al. (2011) and Elbaba and Williams (2013) investigated several nickel based catalysts to improve the production of hydrogen for the pyrolysis-catalytic steam reforming of waste tyres. Nickel catalysts are commonly used for hydrogen production. However, nickel-based catalysts become deactivated due to the deposition of carbonaceous coke on the catalyst surface, adversely influencing hydrogen production (Sutton, et al. 2001; Sehested, 2006; Yung et al., 2009). There are three main types of carbon deposited on the catalyst, pyrolytic carbon, encapsulating amorphous carbon and whisker type carbon (Sehested, et al., 2006; Rostrup-Nielsen, 1975). It is the amorphous carbons that primarily deactivate the catalyst be encapsulating the active metal sites of the catalyst. The whisker type carbons are solid and filamentous in nature but in some cases hollow carbon nanotubes have been identified (Wu, et al., 2013). Carbon nanotubes comprise a tubular material composed of a graphitic hexagonal carbon structure with diameters which range from 1 to 50 nm and lengths which range from several micron to several cm. Carbon nanotubes are of current interest due to their unique physical and chemical characteristics which have been demonstrated to have great potential in several materials industries, such as advanced electronics, carbon-composites and energy storage (Volder, et al., 2013). They are regarded as high value materials, with single-wall nanotubes generally of much higher value than multi-walled carbon nanotubes. Therefore, the problem of coke formation on the catalyst during hydrogen production, may in fact be a benefit if carbon nanotubes can be produced in addition to the co-production of the hydrogen. Additionally, using waste tyres as the feedstock for the process means that a problematic waste is turned into an attractive process solution by producing valuable carbon nanotubes and hydrogen as resource recovered products.

In this paper, we report on the pyrolysis-catalysis of waste tyres with the aim of determining the yield and composition of the product syngas, with an emphasis on hydrogen production and also the production of multi-walled carbon nanotubes. Waste truck tyres and car tyres were used as the feedstock and the catalyst used was a Ni-alumina catalyst. In addition, the production of hydrogen and carbon nanotubes from some of the main rubbers used in tyre manufacture were also investigated to better understand the process.

2. Materials and Methods

2.1 Materials. The waste tyre samples used in the experiments were waste truck tyre and waste car tyre with the metal and reinforcing fabric removed and the rubber then shredded to a particle size of ~ 6mm. A typical tyre may contain ~46 wt.% rubber, ~22 wt.% carbon black filler/strengthener, ~19 wt.% of metal reinforcement and a balance of textile, reinforcement, sulphur, zinc and other additives (Evans and Evans, 2006). In addition, three rubber elastomers commonly used in tyre manufacture were also investigated, being, polybutadiene rubber (BR), styrene–butadiene rubber (SBR) and natural rubber, which were shredded to the same particle size as the waste tyres. The elemental analysis of the different tyres and rubbers is shown in Table 1. The thermal decomposition characteristics of the tyres and rubbers were determined on a Shimadzu thermogravimetric analyser (TGA) where the tyre/rubber (15 mg) was heated from room temperature to 800 °C at 10 $^{\circ}$C min^{-1} and hold time of 10 min. under a N_2 atmosphere. The loss of the sample weight as a function of temperature is recorded continuously.

The Ni/Al_2O_3 catalyst was prepared by a wetness impregnation method. Nickel was impregnated onto an alumina support to produce 10 wt.% of metal with the alumina support. The catalyst preparation process involved; nickel nitrate was dissolved in ethanol; alumina was added into the mixture of nickel nitrate/ethanol to produce a slurry; the slurry was dried at 90 °C; calcination at 750 °C in air; crushing and sieving to produce a 0.05─ 0.18 mm particle size range.

2.2 Experimental system. The tyre pyrolysis-catalysis experiments were conducted in a two stage fixed-bed reactor consisting of two separate stainless steel reactors that were externally electrically heated (Figure 1). Pyrolysis of the tyres and rubbers (1 g) took place in the first stage reactor at pyrolysis heating conditions of ambient temperature to 600 °C at 40 °C min^{-1} heating rate and held at 600 °C for 20 min. The volatiles from tyre/rubber pyrolysis passed to the second stage reactor which contained the Ni-alumina catalyst (0.5 g) which was maintained at 800 °C. The tyre:catalyst ratio was therefore 1:0.5. In addition, other experiments were undertaken to determine the influence of increasing the amount of catalyst in the second stage reactor at tyre:catalyst ratios of 1:1 and 1:2. The two-stage reactor was continually purged with nitrogen to maintain pyrolytic conditions and to carry the product gases into the condensation system. The condensation of condensable liquids was by water and dry ice condensers. Gases passing through the condensers were collected in a 25L Tedlar^{TM} gas sample bag for later analysis. Experiments were repeated to ensure the accuracy of the results.

2.3. Analytical Methods. The gases collected in the Tedlar^{TM} gas sample bag were analysed using gas chromatography. The permanent gases (H_2, CO, O_2 and N_2), were determined on a Varian 3380 gas chromatograph (GC) with a 60-100 mesh molecular sieve 13X column, Ar carrier gas and a thermal conductivity detector. CO_2 was analysed on the same Varian GC but with a separate 80-100 mesh HayeSep column and thermal conductivity detector.

Hydrocarbons from C_2─C_4 were analysed using a second Varian 3380 GC with a HayeSep 80-100 mesh molecular sieve column, N_2 carrier gas and flame ionization detector.

The carbon deposition, including the amorphous, pyrolytic, filamentous and carbon nanotubes deposited on the Ni-alumina catalyst were characterised through temperature programmed oxidation (TPO) using a Shimadzu TGA. Around 4 mg of the catalyst after reaction was heated to 800 °C at a heating rate of 15 °C min^{-1} in air. In addition, the deposited carbon on the catalyst surface was examined using an Hitachi SU8230 scanning electron microscope (SEM) and a FEI Tecnai TF20 transmission electron microscope (TEM). A Renishaw Invia Raman spectroscopy with a wavelength of 514 nm at Raman shifts between 100 and 3200 cm^{-1} was used to obtain the Raman analysis results which were used to indicate the graphitic nature of the carbon.

3. Results and Discussion

3.1 Characterisation of the Feedstock Rubber Samples. The thermal degradation of the waste tyres and rubber samples were characterised using thermogravimetric analysis. Figure 2 shows the resultant thermograms and shows that the main decomposition for natural rubber occurs at a peak temperature of 385 °C, for styrene-butadiene rubber, the main decomposition peaks at 460 °C and for polybutadiene rubber at a temperature of 475 °C. The three rubbers also showed much smaller weight loss at higher temperature for the natural rubber and lower temperature for the styrene-butadiene and polybutadiene rubbers. Kandasamy and Gokalp (2015) reported slightly different maximum thermal degradation temperatures of 375 °C, 445 °C and 465 °C for natural rubber, styrene-butadiene and polybutadiene rubbers respectively, probably due to minor differences in the rubber compositions. Figure 2 also shows the TGA thermograms for the waste car and truck tyres which indicate two decomposition peak temperatures. The data suggests that the lower temperature weight loss peak at a temperature of 385 °C may be ascribed to the thermal decomposition of natural rubber and the higher weight loss temperature peaking at ~430 °C may be ascribed to the thermal decomposition of styrene-butadiene and polybutadiene rubber. However, the interpretation of weight loss is more complicated, since a typical automotive tyre can be composed of up to 30 different synthetic rubbers and 8 different kinds of natural rubber (Evans and Evans, 2006). Sulkowski et al. (2004), have also suggested that the two temperature weight loss regimes for waste tyres is due to the thermal decomposition of the different rubber components in tyres. In addition, Seidelt et al. (2006) have reported the presence of a third weight loss peak at lower temperature which they attributed to the volatilization of the additives used in tyre manufacture, including hydrocarbon oils, moisture, plasticizers and other additives

3.2. Product Yield from Pyrolysis-Catalysis of tyres and rubbers. Pyrolysis-catalysis of the waste car and truck tyres and the tyre rubber samples in the presence of the Ni/Al_2O_3 catalyst was carried out in the two-stage reactor system and the results for product yield and gas composition are shown in Table 2. The comparison of car tyre and truck tyre at a tyre:catalyst ratio of 1:0.5 showed small differences in product yield, for example, the gas yield from the pyrolysis-catalysis of car tyres was 30.2 wt% and 27.5 wt.% for truck tyres. Also, the residual char residue left in the pyrolysis reactor after reaction differed, producing 40 wt.% for the waste car tyre and 37 wt.% for the waste truck tyre. These differences were most probably due to the different rubbers and formulations used to produce the tyres. The residual char is produced from polymerisation reactions of the evolved high molecular weight hydrocarbon species during pyrolysis, but also the char is derived from the carbon black added to the tyre which, as discussed before, can be typically 22 wt.% of the tyre (Evans and Evans, 2006). Of more significance was the difference between the two tyre samples in terms of the carbon deposition, which represented carbon deposited mainly on the catalyst and also some on the walls of the catalytic reactor. For the truck tyre, this was 8 wt.%, but for the car tyre was 3 wt.%, again, probably representing different formulations of each tyre sample which influenced the pyrolysis-catalysis process. Table 2 also shows the influence of increasing the tyre:catalyst ratio on the product yield, with higher amounts of catalyst producing greater conversion of the tyre rubber to carbon deposits, rising from 8.0 wt.% at 1:0.5 tyre:catalyst ratio to 13.0 ─ 14.0 wt.% at higher ratios.

Analysis of the gas composition (Table 2) showed the gas product from the pyrolysis-catalysis of waste tyres was mainly carbon monoxide, hydrogen and methane. The hydrogen content of the product gas was high, producing 49.6 vol.% for the waste truck tyre and 53.8 vol.% for the waste car tyre. The hydrogen yield in terms of the mass of tyre rubber was similar for the two tyres at 11.0 ─ 12.0 mmol g^{-1} tyre. Increasing the amount of catalyst relative to the amount of tyre resulted in a large increase in hydrogen production from 11.0 mmol g^{-1} tyre at a tyre:catalyst ratio of 1:0.5 to 21.8 mmol g^{-1} tyre at a tyre:catalyst ratio of 1:2. The hydrogen concentration in the product gas correspondingly increased to 68.3 vol.%. Table 2 also shows the calculated calorific value (CV) of the product gases. The CV of the gases produced from the tyres was between 16.4 and 20.9 MJ m^{-3}, depending on process conditions, which is sufficient to provide the energy requirements for the pyrolysis-catalysis process. Considering also, that the total gas yield was between 27.5 and 30.2 wt.% of tyre, the gas could also be exported off-site for use as fuel gas.

Pyrolysis-catalysis of the three rubber samples is also presented in Table 2 where the product yields show a much higher conversion of the rubbers to gas and carbon deposits on the catalyst, with low residual char formation in the first stage reactor compared to the yields from the waste tyres. The highest gas yield was from natural rubber at 52.8 wt.% and was largely composed of hydrogen and methane, giving a rubber conversion to hydrogen of 25.0 mmol g^{-1} of natural rubber. The total gas yields from the two synthetic rubbers (polybutadiene rubber and styrene-butadiene rubber) was much lower at ~40 wt.% and lower hydrogen yield in terms of mass of rubber at ~16.5 mmol g^{-1} rubber compared to the tyres results. The carbon deposits formed on the catalysts from the pyrolysis-catalysis of the three rubber samples were very high compared to the tyre feedstock at 36 wt.%, 40 wt.% and 36.wt% for the polybutadiene rubber, styrene-butadiene rubber and natural rubber respectively.

Overall, the pyrolysis-catalysis of waste tyres has shown a high conversion of the tyre rubber to gas which is largely composed of hydrogen, methane and carbon monoxide, producing a product gas with a high calorific value of between 16.4 and 20.9 MJ m^{-3} depending on the tyre of tyre and the tyre:catalyst ratio. The three rubber samples investigated, polybutadiene rubber, styrene-butadiene rubber and natural rubber, all have a major contribution to the total gas yield produced and also hydrogen yield. The product gas can be used as process fuel and/or exported off-site. Alternatively, the hydrogen could be separated and used in high purity hydrogen applications such as fuel cells and hydrogen fuelled engines to fuel the predicted future hydrogen economy.

The three rubber samples produced a major contribution to the carbon deposits on the catalyst at between 36 and 40 wt.%. Consequently, the individual rubber formulation in the tyre strongly influences the amount of carbon deposition on the catalyst during the pyrolysis-catalysis process. Normally high formation of coke on the catalyst is deemed as a major problem to the catalytic process since the active metal sites of the catalyst become blocked and hence the catalyst becomes deactivated. However, as discussed above, the more problematic carbons which coke the catalyst surface are the amorphous encapsulating type. Therefore, detailed characterisation of the coke deposits formed on the catalyst during pyrolysis-catalysis of the waste tyres and rubber samples with the Ni/Al_2O_3 catalyst was carried out. Figure 3 shows the temperature programmed oxidation (TPO) results for the carbon deposits on the catalysts used with the waste car tyre, waste truck tyre, and the polybutadiene, styrene-butadiene and natural rubber. During the oxidation process, the weight loss of the catalyst/carbon is recorded as the different types of carbon (amorphous or graphitic) are oxidised as the temperature of the thermogravimetric analyser is raised. Figure 3 shows that the main weight loss of the reacted catalysts resulting from carbon oxidation occurred between temperatures of 450 °C and 600 °C and was assigned to the oxidation of amorphous carbon. The oxidation that occurred after a temperature of 600 °C was assigned to the oxidation of filamentous/whisker type carbon (Wu and Williams, 2010; Wu et al., 2013).

3.3 Carbon formation. Table 2 shows that carbon formation on the catalyst (coke deposits) for the catalyst used in the pyrolysis-catalysis of waste tyre samples was significant, being up to 14 wt.% depending on process conditions.

Figure 3 indicates that the used catalysts for waste car tyre and waste truck tyre display one peak representing the oxidation of the coke deposited on the catalyst, whereas the catalysts used with polybutadiene rubber, styrene-butadiene rubber and natural rubber have two temperature peaks representing carbon oxidation. The oxidation peak of the coke deposits on the catalyst for the car tyre pyrolysis-catalysis occurred at a lower temperature (585 °C) compared to the oxidation of the coke deposits on the catalyst from the waste truck tyre (615 °C) suggesting that the coke deposits were a mixture of amorphous and graphitic type carbons, but amorphous dominating for the car tyre and more graphitic filamentous carbons produced with the truck tyre reaction. The TPO thermograms for the rubber samples show that polybutadiene rubber and styrene-butadiene rubber show two temperature peaks, but the largest is at the lower temperature range, below 600 °C indicating a dominance of amorphous carbon, but also significant graphitic type carbons indicated by carbon oxidation at around 650 °C. In contrast, the natural rubber sample produced mainly graphitic carbons (oxidising at ~650 °C) and less amorphous carbon (oxidising at 580 °C). The proportions of amorphous and graphitic type carbons have been estimated from the TPO thermograms shown in Figure 3 and the results are shown in Figure 4. Figure 4 indicates that much higher yields of catalyst carbon are produced for the pyrolysis-catalysis of the three rubber samples. The amorphous carbons comprised between 164 and 196 mg carbon g^{-1} rubber and the graphitic carbons a higher proportion comprising between 196 and 204 mg carbon g^{-1} rubber. The waste tyre samples produced much lower deposition of carbon on the catalysts during reaction, with the truck tyre generating higher carbon deposition compared to the car tyre. Increasing the amount of catalyst resulted in higher carbon deposition per mass of tyre, for example the truck tyre produced 44 mg of graphitic carbon g^{-1} tyre at a tyre:catalyst ratio of 1:0.5, which increased to 78 mg of graphitic carbon g^{-1} tyre at a tyre:catalyst ratio of 1:2. Therefore, the graphitic carbon representing 54% of the carbon present on the catalyst at a tyre:catalyst ratio of 1:0.5, rising to 60% at a tyre:catalyst ratio of 1:2.

The deposits of carbon (coke) formed on the Ni/Al_2O_3 catalyst during pyrolysis-catalysis of the tyres/rubbers were examined using scanning electron microscopy and transmission electron microscopy (Figure 5). The coke deposited on the catalyst produced from the pyrolysis-catalysis of the three rubber samples all show the presence of filamentous or whisker type carbons (Sehested, 2006). These appear as entangled string-like filaments of approximately 10 nm diameter and several microns in length. Examination of the TEM micrographs reveals that the vast majority of these filamentous carbons are in fact hollow nano-sized filaments, i.e. carbon nanotubes. Figure 5 also shows that the carbon deposited on the catalyst used for the pyrolysis-catalysis of the truck tyres also shows this entangled nanotube structure. However, the car tyre showed a poorer development of the carbon nanotubes, as also shown in Figure 3 and 4 where a more amorphous type of catalyst carbon deposition was indicated. Most probably due to the particular rubber and additive formulation of the car tyre compared to the truck tyre. Carbon nanotubes have several different structures, including for example, straight, coiled, waved, branched, and entangled carbon nanotubes (Zhang and Li, 2009; Sears et al., 2010; Karthikeyan and Mahalingam, 2013). Entangled carbon nanotubes as shown in Figure

5 have been proposed for use in water and air purification applications (Sears et al., 2010; Karthikeyan and Mahalingam, 2013). In relation to the TPO results shown in Figure 3, Li.et al. (2004) have also suggested that the weight loss in relation to carbon oxidation at temperatures <600 °C may also be due to oxidation of single-walled carbon nanotubes as they are less thermally stable compared to multi-walled carbon nanotubes; stability arising from the strong interaction between graphite layers in multi-walled carbon nanotubes. The TEM micrographs of the carbon deposited onto the catalyst during reaction presented in Figure 5, show that there are carbon nanotubes with different diameters, where thinner walled carbon nanotubes may be thermally less stable than thicker walled nanotubes.

Raman spectroscopy is commonly used to determine the quality of carbon nanotubes and Raman spectroscopy analysis was used to further characterise the quality of carbon nanotubes, the results are shown in Figure 6. The two main spectral peaks for the carbon deposits occur at ~1580 cm^{-1} and 1350 cm^{-1}. The ~1580 cm^{-1} peak is designated the G peak and represents the resonance peak of graphitic carbon indicating a well crystallised carbon structure and the peak at ~1350 cm^{-1} designated as the D peak is the scattering peak of disordered carbon indicating defects in the graphitic crystalline structure or amorphous carbon (Yang et al., 2010; Karthikeyan and Mahalingam, 2013). The intensity (I) of each peak and the ratio of the two peak intensities I_D/I_G is used to determine the degree of crystallisation of the carbon structure, with a higher I_D/I_G ratio indicating higher quality in regard to carbon nanotubes. A G' peak is also obtained at Raman shifts around 2709 cm^{-1} and is a further indication of CNT purity. The intensity of the D band (I_D) normalized to the intensity of the G band (I_G) (I_D/I_G) and intensity ratio of G' to G ($I_{G'}/I_G$) was used to evaluate the quality of the carbon nanotubes. The I_D/I_G and $I_{G'}/I_G$ values for the carbons produced with natural rubber, polybutadiene rubber and styrene butadiene rubber showed no significant differences being 0.83 ± 0.01 for the I_D/I_G value and 0.54 ± 0.02 for the $I_{G'}/I_G$ values. The Raman spectra for the carbon derived from the waste tyres were similar to each other with a small increase in both I_D/I_G and $I_{G'}/I_G$ values at 0.89 ± 0.01 and 0.57 ± 0.02 respectively. The data confirm that the carbons deposited on the catalyst during the pyrolysis-catalysis of the waste tyres and rubber samples contained both amorphous and carbon nanotubes and also indicated by the TGA results (Figure 3) and TEM micrographs (Figure 5).

4. Conclusions

The pyrolysis-catalysis of waste car and truck tyres has been investigated using a Ni/Al_2O_3 catalyst to investigate the production of a hydrogen-rich syngas and also carbon nanotubes. In addition, the results were compared with the production of hydrogen and carbon nanotubes from the three main rubbers used in the manufacture of automotive tyres. The main conclusions were:

1) The yield of gas obtained from the pyrolysis-catalysis of the waste car tyre was 30.2 wt%. The gas was composed of 53.8 vol.% of hydrogen with the other main gases being carbon monoxide and methane, giving a product gas with a calorific value of 18.8 MJ m^{-3}. The conversion of the tyre rubber to hydrogen was 12.0 mmol H_2 g^{-1} tyre. The pyrolysis-catalysis of the waste truck tyre produced slightly lower yields of gas (27.5 wt.%), lower hydrogen gas concentration (49.6 vol.%) and lower conversion of the tyre rubber to hydrogen (11.0 mmol H_2 g^{-1} tyre).

2) Increasing the tyre:catalyst ratio for the waste truck tyres was found to improve the conversion of the tyre rubber to hydrogen to 21.8 mmol H_2 g^{-1} tyre at a tyre:catalyst ratio of 1:2 which produced a hydrogen concentration in the product gas of 68.3 vol.%.

3) For the three rubber samples, product gas yields and conversion of the rubber to hydrogen were much higher than was the case with the waste tyres; for example, natural

rubber produced the largest gas yield at 52.8 wt% of rubber feedstock and the highest conversion to hydrogen, yielding 25.0 mmol H_2 g^{-1} rubber.

4) The pyrolysis-catalysis process also produced significant deposition of carbon onto the catalyst. Examination of the carbon using transmission electron microscopy supported by temperature programmed oxidation and Raman spectroscopy showed that the carbons produced from the waste tyres and the rubber samples were carbon nanotubes of diameters between 5-10 nm and lengths of several microns. For the waste tyres, the maximum deposition of carbon was found at ~14 wt.% of tyre (tyre:catalyst ratio 1:1). However, for the rubber samples, polybutadiene, styrene-butadiene and natural rubber, the carbon deposition on the catalyst was 36.0, 40.0 and 36 wt.% respectively.

5) The process of pyrolysis-catalysis of waste tyres has the potential to provide a novel alternative waste treatment process to produce a hydrogen-rich syngas which can be used as process fuel or with the option to be upgraded to high purity hydrogen gas for the projected future hydrogen economy. In addition, the process produces carbon deposits on the catalyst which comprise mostly carbon nanotubes which have the potential to be further processed to produce a high value product to support the advanced materials industry.

REFERENCES

ELBABA, I.F. & P.T. WILLIAMS, (2013) High yield hydrogen from the pyrolysis–catalytic gasification of waste tyres with a nickel/dolomite catalyst. Fuel, 106, 528-536.

ELBABA, I.F., C. WU, & P.T. WILLIAMS, (2011) Hydrogen production from the pyrolysis–gasification of waste tyres with a nickel/cerium catalyst. International Journal of Hydrogen Energy, 36(11), 6628-6637.

EVANS A. & EVANS R., (2006) The composition of a tyre: Typical components, Waste & Resources Action Programme, Banbury Oxford, UK.

ETRMA, (2011); EUROPEAN TYRE & RUBBER MANUFACTURERES' ASSOCIATION, ELT Management, ETRMA, Saint-Josse-ten-Noode, Belgium

ETRMA (2013); EUROPEAN TYRE & RUBBER MANUFACTURERES' ASSOCIATION, Introduction to Tyre Recycling: 2013 (Twenty years of tyre recycling in the EU), ETRMA, Saint-Josse-ten-Noode, Belgium

KANDASAMY, J. & I. GÖKALP, (2015) Pyrolysis, Combustion, and Steam Gasification of Various Types of Scrap Tires for Energy Recovery. Energy & Fuels, 29(1), 346-354.

KARTHIKEYAN S., & MAHALINGAM, P. (2013) Carbon nanotubes from unconventional resources: Part A: Entangled multi-walled carbon nanotubes and Part B: Vertically aligned carbon nanotubes, Chapter 11 in Suzuki S. (Ed.), Synthesis and Applications of Carbon Nanotubes and their Composites, InTech Publishers, Rijeka, Croatia.

LI, Q., YAN, H., ZHANG J., & LIU, Z. (2004) Effect of hydrocarbons precursors on the formation of carbon nanotubes in chemical vapor deposition. Carbon, 42(4), 829-835.

ROSTRUP-NIELSEN, J.R., (1975) Steam Reforming Catalysts. Danish Technical Press, Copenhagen, Denmark.

SCHWARTZ, N.V. & BRAZIER D.W.T. (1978) he effect of heating rate on the thermal degradation of polybutadiene. Journal of Applied Polymer Science, 22, 113-124.

SEARS K., DUMEE L., SCHUTZ J., SHE M., HUYNH C., HAWKINS S., DUKE M., & GRAY S., (2010) Recent developments in carbon nanotube membranes for water purification and gas separation. Materials, 3, 127-149.

SEHESTED, J., (2006) Four challenges for nickel steam-reforming catalysts. Catalysis Today, 111(1–2), 103-110.

SEIDELT, S., M. MÜLLER-HAGEDORN, & H. BOCKHORN, (2006) Description of tire pyrolysis by thermal degradation behaviour of main components. Journal of Analytical and Applied Pyrolysis, 75(1), 11-18.

SIENKIEWICZ, M., KUCINSKA-LIPKA, J., JANIK H. & BALAS A. (2012) Progress in used tyres management in the European Union: A review. Waste Management, 32(10), 1742-1751.

SULKOWSKI, W.W.D., A., MOCZYNSKI, M., RADON, A., SUUKOWSKA, A. & BOREK, J., (2004) Thermogravimetric study of rubber waste-polyurethane composites. Journal of Thermal Analysis & Calorimetry, 78 (3), 905-921.

SUTTON, D., KELLEHER, B., & ROSS, J.R.H. (2001) Review of literature on catalysts for biomass gasification. Fuel Processing Technology, 73(3), 155-173.

VOLDER, M.F.L.D., TAWFICK S.H., BAUGHMAN R.H. & HART A.J. (2013) Carbon anotubes: Present and future commercial applications. Science, 339(6119), 535-539.

WILLIAMS, P.T., (2013) Pyrolysis of waste tyres: A review. Waste Management, 33(8), 1714-1728.

WU, C. & P.T. WILLIAMS, (2010) Pyrolysis–gasification of post-consumer municipal solid plastic waste for hydrogen production. International Journal of Hydrogen Energy, 35(3), 949-957.

WU, C., NAHIL M.A., MISKOLCZI N., HUANG J., & WILLIAMS P.T. (2013) Processing Real-World Waste Plastics by Pyrolysis-Reforming for Hydrogen and High-Value Carbon Nanotubes. Environmental Science & Technology, 48(1), 819-826.

YANG Z., ZHANG Q., LUO G., HUANG J.Q., ZHAO M.Q. & WEI F.(2010) Coupled process of plastics pyrolysis and chemical vapour deposition for controllable synthesis of vertically aligned carbon nanotube arrays. Applied Physics A: Materials Science & Processing, 100, 533-540.

YUNG, M.M., JABLONSKI, W.S., & MAGRINI-BAIR, K.A. (2009) Review of catalytic conditioning of biomass-derived syngas. Energy & Fuels, 23(4), 1874-1887.

ZHANG M. & LI J. (2009) Carbon nanotube in different shapes, Materials Today, 12(6), 12-18.

Table 1. Elemental analysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)

Components (wt.%)	**Truck tyre**	**Car tyre**	**BR**	**SBR**	**NR**
C	81.2	81.7	87.4	87.0	86.3
H	7.2	6.5	10.7	9.9	11.2
N	0.8	0.6	nd	nd	nd*
S	2.1	1.9	nd	nd	nd

* nd: not detected

Table 2. Product yield and gas concentrations from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)

Feedstock	**Truck tyre**	**Truck tyre**	**Truck tyre**	**Car tyre**	**BR**	**SBR**	**NR**
Tyre: Catalyst Ratio	**1:0.5**	**1:1**	**1:2**	**1:0.5**	**1:0.5**	**1:0.5**	**1:0.5**
Product yield							
Gas yield (wt.%)	27.5	29.7	29.5	30.2	41.3	39.3	52.8
Liquid yield (wt.%)	22.0	12.0	14.0	21.0	23.0	17.0	17.0
Char residue (wt.%)	37.0	38.0	38.0	40.0	2.0	1.0	0.0
Carbon deposits (wt.%)	8.0	14.0	13.0	3.0	36.0	40.0	36.0
Hydrogen production (mmol g^{-1} tyre/rubber)	11.0	16.7	21.8	12.0	16.3	16.8	25.0
Gas concentrations (vol.%)							
CO	19.4	16.0	18.9	27.1	4.8	4.6	8.9
H_2	49.6	60.0	68.3	53.8	46.8	47.1	51.8
CH_4	23.4	15.7	9.4	5.8	35.4	40.6	31.8
CO_2	0.0	0.0	0.0	0.0	0.2	0.2	0.5
C_2-C_4	5.9	6.4	3.4	10.7	7.6	6.2	5.3
Calorific Value (MJ m^{-3})	20.9	19.3	16.4	18.8	24.4	25.5	22.8

Figure captions

Figure 1. Schematic diagram of the two stage fixed-bed pyrolysis-catalytic reactor system

Figure 2. TGA and DTG analysis results of the feedstock truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR).

Figure 3. TGA-TPO and DTG-TPO results of the used catalysts from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)

Figure 4. Proportion of amorphous and graphitic type carbons formed from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)

Figure 5. SEM and TEM images of the carbon deposited on the catalyst from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR).

Figure 6. Raman analysis of the carbon deposited on the catalyst from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR).

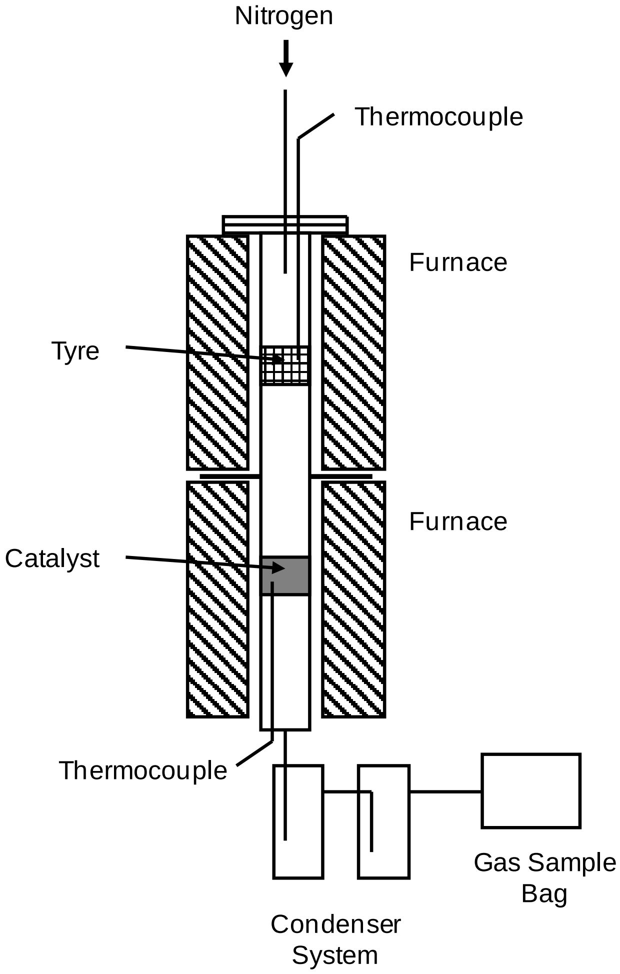

Figure 1. Schematic diagram of the two stage fixed-bed pyrolysis-catalytic reactor system

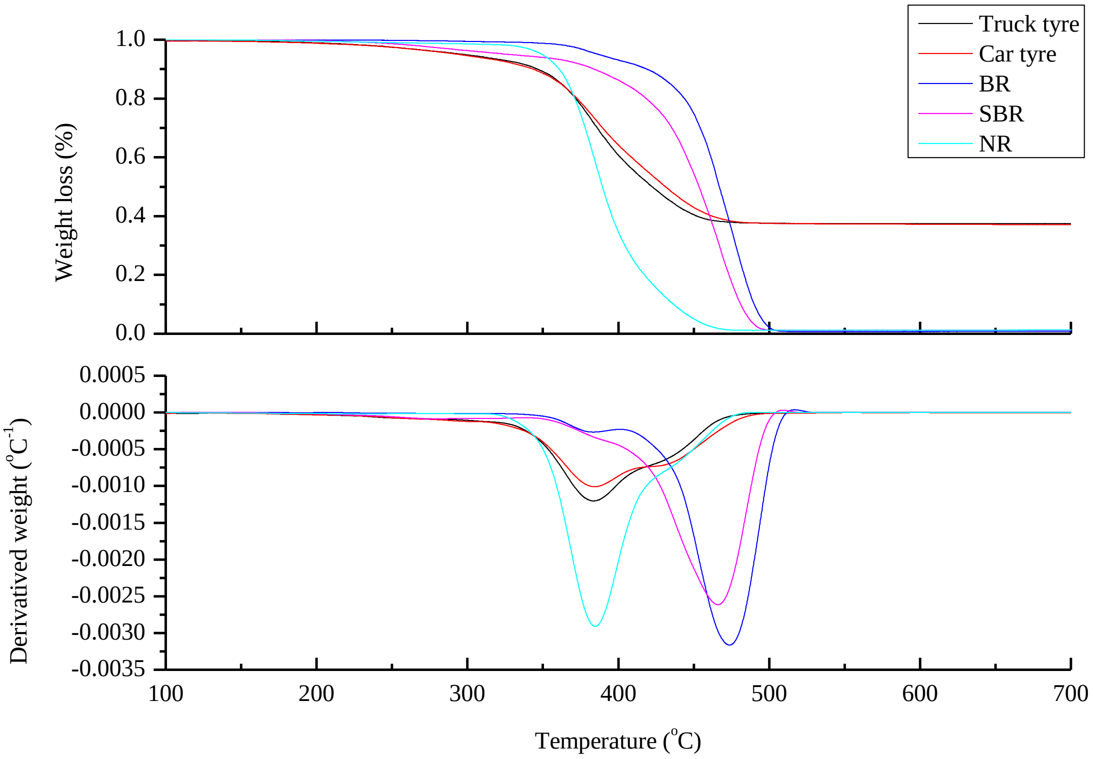

Figure 2. TGA and DTG analysis results of the feedstock truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR).

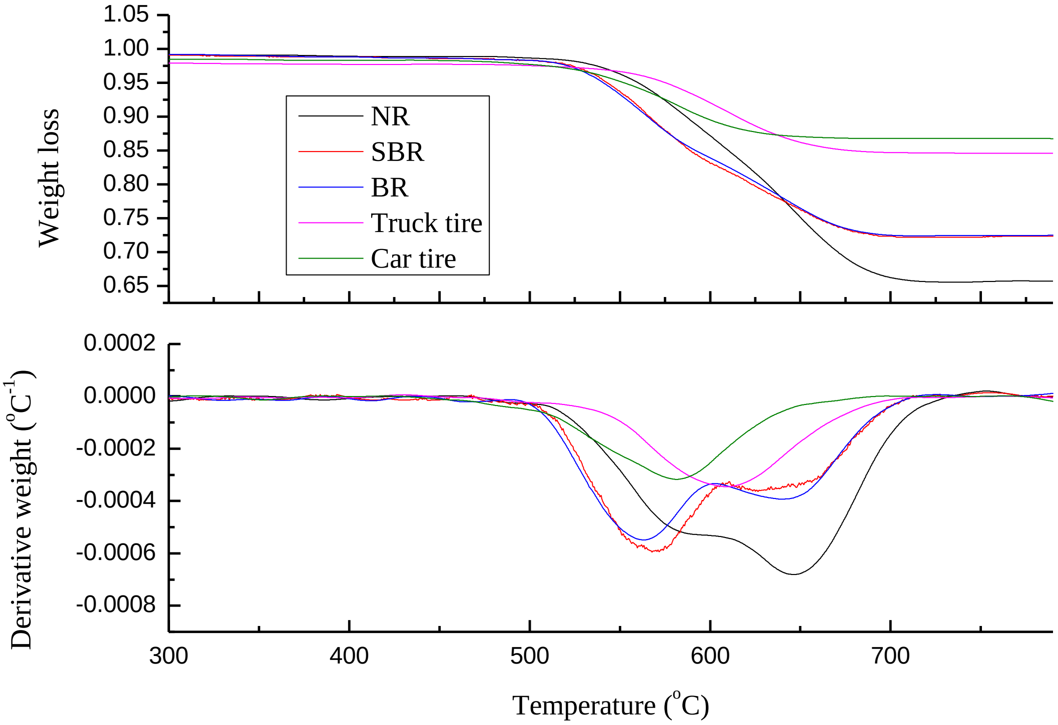

Figure 3. TGA-TPO and DTG-TPO results of the used catalysts from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)

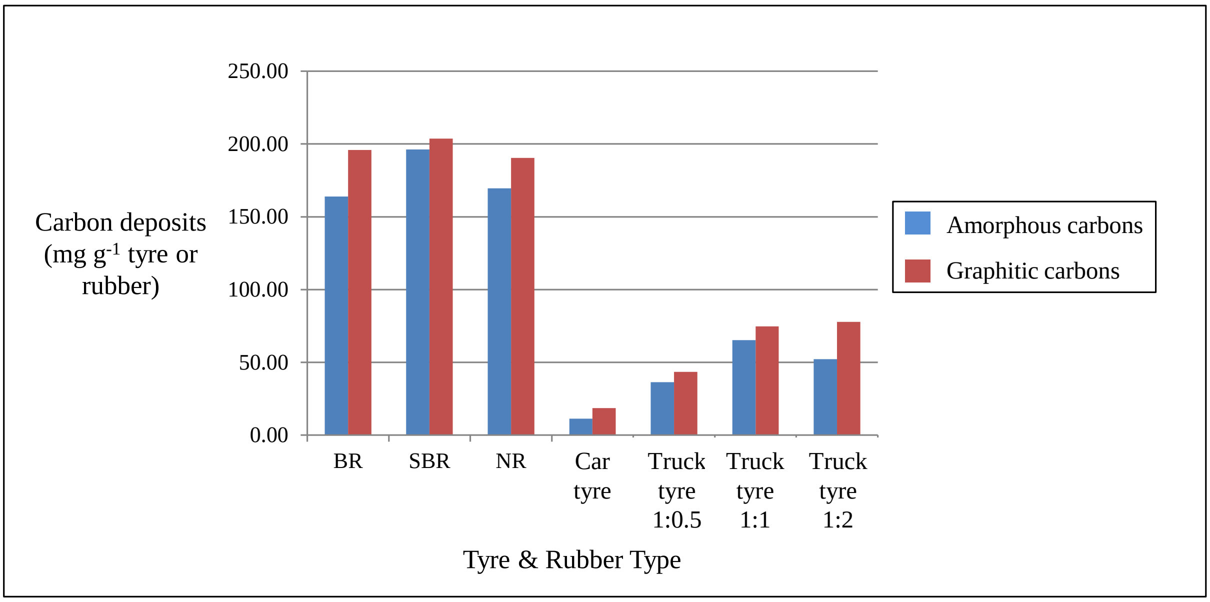

Figure 4. Proportion of amorphous and graphitic type carbons formed from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)

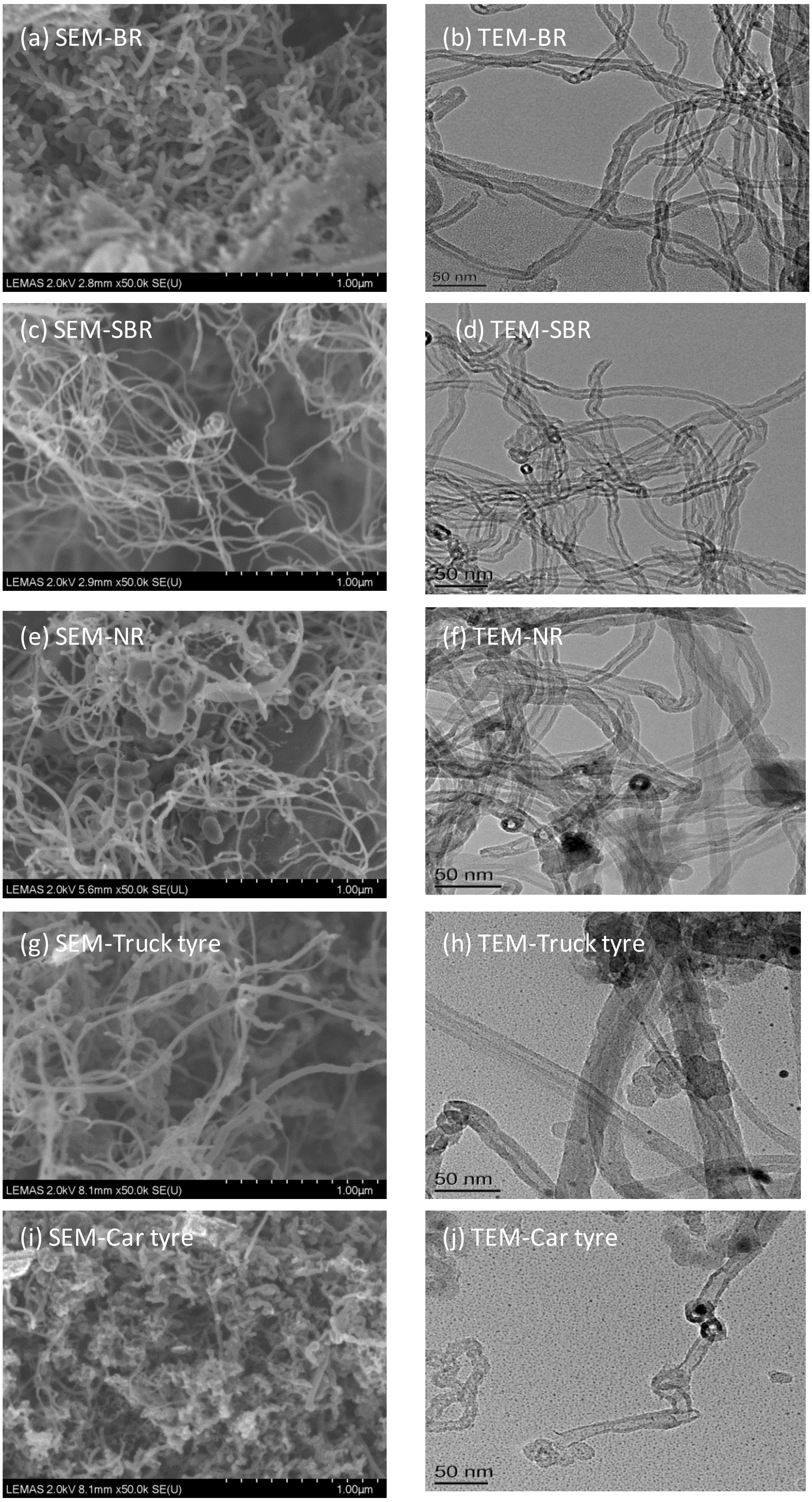

Figure 5. SEM and TEM images of the carbon deposited on the catalyst from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR).

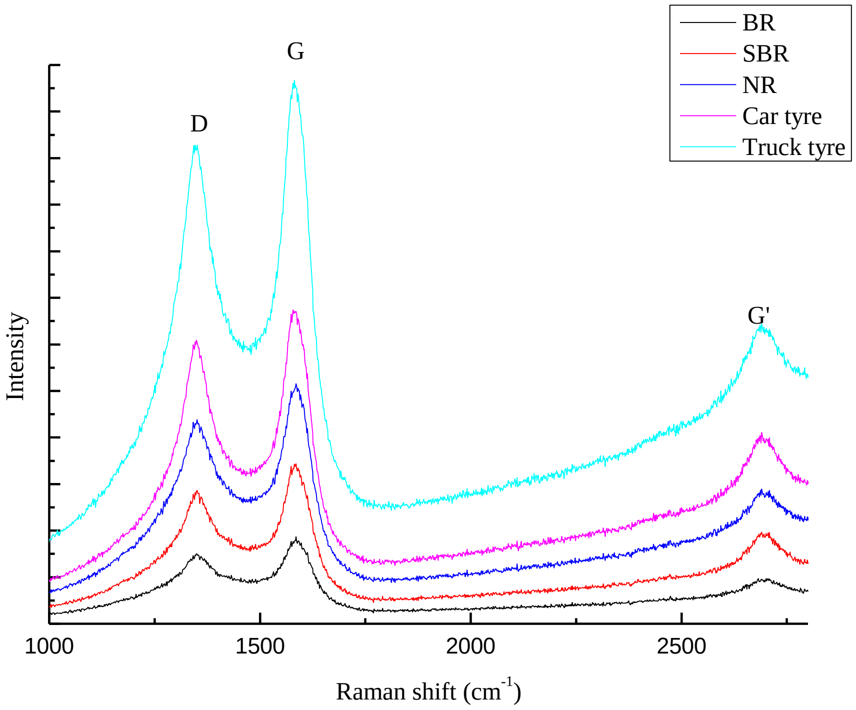

Figure 6. Raman analysis of the carbon deposited on the catalyst from the pyrolysis-catalysis of truck tyre, car tyre, poly-butadiene rubber (BR), styrene-butadiene rubber (SBR) and natural rubber (NR)