promoting access to White Rose research papers



# Universities of Leeds, Sheffield and York http://eprints.whiterose.ac.uk/

This is an author produced version of a paper published in **Journal of Analytical** and **Applied Pyrolysis** 

White Rose Research Online URL for this paper:

http://eprints.whiterose.ac.uk/id/eprint/77989

### Paper:

Acomb, JC, Nahil, MA and Williams, PT (2013) *Thermal processing of plastics from waste electrical and electronic equipment for hydrogen production.* Journal of Analytical and Applied Pyrolysis, 103. 320 - 327. ISSN 0165-2370

http://dx.doi.org/10.1016/j.jaap.2012.09.014

White Rose Research Online eprints@whiterose.ac.uk

## Thermal Processing of Plastics from Waste Electrical and Electronic Equipment for Hydrogen Production

Jonathan C. Acomb, Mohamad Anas Nahil and Paul T. Williams\*

Energy Research Institute, The University of Leeds, Leeds LS2 9JT, UK.

#### ABSTRACT

Plastic waste from waste electrical and electronic equipment (WEEE) produced from a real-world commercial WEEE recycling centre has been processed using pyrolysisgasification using a two-stage reaction system to produce hydrogen. In the first stage, the plastic fraction was pyrolysed at 600 °C and the evolved pyrolysis gases were passed directly to a second reactor at 800 °C and reacted with steam in the presence of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. In addition, high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) which were the main components of the WEEE plastic were reacted to compare with the WEEE plastic. The results showed that the introduction of steam and the catalyst increased the yield of hydrogen. Increasing the nickel content in the catalyst also resulted in higher hydrogen yield. The comparison of the results of WEEE with those of HIPS and ABS showed that WEEE plastic was mainly composed of ABS. The catalyst, after reaction, showed significant deposition of coke composed of filamentous and layered type carbon. Overall the novel processing of waste plastic from electrical and electronic equipment using a two stage pyrolysis-gasification reactor shows great promise for the production of hydrogen.

Keywords: WEEE; Plastic; Hydrogen; Pyrolysis; Gasification; Waste

<sup>\*</sup>Corresponding Author (Tel: 44 1133432504; Email: <u>p.t.williams@leeds.ac.uk</u>)

#### **1. Introduction**

Modern society faces major energy challenges as current fossil fuel sources cause environmental pollution and their finite supplies start to run low. Hydrogen energy offers a desirable alternative since it is emission free as its combustion generates only water. World consumption of hydrogen is growing rapidly and reached about 70 million tonnes in 2009, growing at around 7% per year [1]. Hydrogen can be produced from a number of different methods [2], but the majority is currently produced from fossil fuel sources [3] including natural gas, liquid hydrocarbons and coal. When hydrogen is produced via these routes there are associated carbon dioxide emissions which contribute to global climate change, making this means of production unfavourable. Another option for hydrogen production is the electrolysis of water. Low temperature electrolysis is a proven technology, however due to the high electrical energy demand the hydrogen produced is more expensive than that produced from fossil fuel sources, unless a cheap source of electricity is readily available. As a result there is much interest in the use of alternative feedstocks for the production of hydrogen [4-6]. The use of waste materials for hydrogen production has the benefit that it would simultaneously solve waste treatment problems and produce hydrogen as a clean energy source. One feedstock that offers a potential source of hydrogen is waste plastic and in particular, in relation to this work, plastic that arises in waste electrical and electronic equipment (WEEE).

As electronics become ever more integral to our society and electronics products have an increasingly short life time as they become outdated and replaced by newer models, WEEE has become one of the most important waste streams. The amount of WEEE generated in the 27 European Union (EU27) Member States was estimated to be 8.3-9.1 million tonnes per year in 2005, which corresponds to around 17 kg per capita [7]. WEEE is also a complex

waste stream, because electrical and electronic equipment (EEE) covers a wide variety of products, including hair dryers, refrigerators, equipment that contained cathode ray tubes as well as highly integrated systems such as computers and mobile phones. These products contain many materials that can already be recycled, such as glass and metals, but the plastic fraction, which can be based on more than 15 different types of engineering plastics [8], is currently more difficult to treat.

The EU has recently introduced the WEEE Directive which aims to promote the re-use, recycling and other forms of recovery of electrical and electronic waste and hence minimise the WEEE stream sent to landfill and incineration [9]. Pyrolysis-gasification of WEEE for hydrogen production is a promising technology for chemical recycling of the plastics involved and holds the potential to increase the production efficiency of hydrogen.

The use of catalysts is considered as a key factor to maximise the production of hydrogen [10-12]. Nickel-based catalysts have been reported as the most appropriate catalysts for tar reduction and hydrogen production due to their availability, catalytic activity and comparatively low cost [5, 13-15]. The percentage of nickel in the catalyst used plays an important role in determining the performance of the catalyst [16-18], with the amount of hydrogen produced and carbon deposited on the catalyst being affected. Whilst there are various preparation methods for the production of Ni-Al<sub>2</sub>O<sub>3</sub> the impregnation method is one that much shows promise for the production of catalysts [19].

In this paper, plastics derived from the commercial scale processing of waste electrical and electronic equipment and the pure plastic constituents of the waste plastic, acrylonitrile– butadiene–styrene (ABS) and high-impact polystyrene (HIPS), have been investigated for hydrogen production by using a two-stage pyrolysis-catalytic gasification reactor system. During the experiments, different Ni loadings were used in the nickel alumina catalysts produced by the impregnation method.

#### 2. Materials and methods

#### 2.1 Materials

The WEEE plastic waste was collected from a commercial WEEE recycling plant, in particular from waste computer monitors and television sets. The computer monitors and television sets are recycled by removing the plastic outer casing before separation of the glass screen from the electronic components. The glass and circuit boards are separated for recycling while the plastic fraction is ground into small flakes of approximately 10-20 mm in size and then sold for low level recycling applications, such as plastic fencing, pallets, garden furniture, and traffic cones. A representative 1 kg sample of the plastic was taken from a large 1 tonne mixed batch of the WEEE plastic. This was carefully sampled using a multiple grab procedure to ensure that it was a representative sample of the WEEE plastic waste. An elemental analysis of the plastics samples was carried out using an elemental analyser (Carlo Erba Flash EA 1112) to achieve the precise determination of nitrogen, carbon, hydrogen, sulphur and oxygen. A proximate analysis was completed using a Shimadzu TGA-50H thermogravimetric analyser, using roughly 15 mg of each sample. Moisture content was determined by the weight loss associated with heating the sample in nitrogen up to 100 °C. The composition of volatiles then corresponded to the weight loss associated with an increase in temperature up to 925 °C, with fixed carbons then determined from the weight loss when the atmosphere was switched to air. Any remaining mass then determined the ash content of the plastic samples. Details of the elemental compositions and results from proximate analysis of the three plastics samples are detailed in table 1 based on an as received basis.

In addition, the major components of the WEEE plastic, in terms of pure acrylonitrile– butadiene–styrene (ABS) and high-impact polystyrene (HIPS) were also investigated to determine the production of hydrogen and to relate the product yields and composition of the components of WEEE to the WEEE results.

Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with different Ni contents of 5 and 10 wt % were prepared by an impregnation method. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, deionised water and Al<sub>2</sub>O<sub>3</sub> were used as the raw materials. The desired amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was mixed in deionised water and heated at 80°C until dissolved, at which point the Al<sub>2</sub>O<sub>3</sub> was added. This mixture was then left to mix until a slurry was formed. This was then dried overnight in an oven at 105°C to remove the remaining water before calcination at 500 °C in an air atmosphere for 3 h. The catalysts were then crushed and sieved to give granules of between 0.065 and 0.212 mm.

#### 2.2 Experimental system

The experimental system consisted of a two-stage pyrolysis-gasification reactor as shown in Figure 1. The total length of the reactor is 320 mm and has an internal diameter of 22 mm. 1 g of the plastic sample was used in each experiment and first pyrolysed in the first reactor, where the temperature was 600 °C. The generated gaseous products were then passed through to the second reactor, where the temperature was maintained at 800 °C. 0.5 g of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was placed in the second reactor. When the experiment was carried out without catalyst, 0.5 g sand was used as the place of the catalyst. Nitrogen was used as the carrier gas with a flow rate of 80 ml min<sup>-1</sup>. The procedure was to heat the second gasification reactor to the desired temperature, then heat the first reactor to 600 °C with a heating rate of 40 °C min<sup>-1</sup>. Water was injected with a flow rate of 4.74 g h<sup>-1</sup> into the second reactor via a syringe pump, therefore passing steam through the catalyst bed (gasification) together with the pyrolysed gases derived from the thermal degradation of the plastic from the first stage reactor.

The volatile products after the gasification process were passed through two condensers, where any condensed products were collected. The non-condensed gases were collected in a 25 L Tedlar<sup>™</sup> gas sample bag. The reproducibility of the reaction system was tested and experiments were repeated to ensure the reliability of research results.

#### 2.3 Products analysis

The gases collected in the gas sample bag were analysed by packed column gas chromatography (GC). Hydrocarbons ( $C_1$ - $C_4$ ) were analysed using a Varian 3380 gas chromatograph with a flame ionisation detector, with an 80-100 mesh Hysep column and nitrogen carrier gas. Permanent gases (H<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub>) were analysed with a separate Varian 3380 GC/TCD, thermal conductivity detector, with two packed columns. A 2m long and 2mm diameter column packed with 60-80 mesh molecular sieve was used to analyse hydrogen, nitrogen, carbon monoxide and oxygen. Carbon dioxide was analysed on a 2 m long and 2 mm diameter column with Haysep 60-80 mesh molecular sieve. The carrier gas was argon.

The oil obtained during the pyrolysis-gasification of the plastic samples was selectively analysed by Gas Chromatography/Mass Spectrometry (GC/MS). The GC/MS system employed consisted of a Hewlett Packard 5280 gas chromatograph coupled to a HP 5271 ion trap detector. The gas chromatographic column was a 30 m length with 0.25 mm internal diameter Restek RTX-5MS column fitted with fused silica 5% diphenyl and 95% dimethyl polysiloxane of 25  $\mu$ m film thickness. Helium was used as a carrier gas.

High resolution scanning electron microscopy was undertaken to characterise the nature of the carbon that was deposited on the surface of the catalysts during the experimental procedure. The microscope used was a SEM, LEO 1530.

#### 3. Results and discussion

#### 3.1 Gas yield

Table 2 shows the gas yield (wt%) from the two-stage pyrolysis gasification of WEEE, HIPS and ABS. The results are presented in the case of no steam or catalyst, where sand was used in place of the catalysts, for the addition of steam, also with sand instead of catalysts and for the catalytic steam gasification of the plastics. Also presented are the gas yields in relation to the Ni content of the catalyst. As shown in table 2, when no catalyst or steam was used WEEE plastic produced 10.8 wt% gas, ABS produced 11.6 wt% gas, whereas HIPS only produced 5.9 wt% gas. Encinar and Gonzalez [20] undertook a thermogravimetric investigation of the pyrolysis of thermosetting plastics and thermoplastics. They found that the yield of gases from ABS (thermosett) was significantly lower at between 2.89 and 8.86 (depending on heating rate) compared to polyethylene and polypropylene wt% (thermoplastics) which gave between 18.17 - 38.76 wt% gas and 16.55 - 31.84 wt% gas respectively. Wu and Williams [21] have also shown for the same reaction system and pyrolysis-gasification temperatures, that the yield of gas in the absence of steam or a catalyst produced 59.6 wt% gas for polypropylene and 53.5 wt% gas for polyethylene compared to the 5.9 wt% and 11.6 wt% gas for HIPS and ABS in this work respectively. It has been shown [21] that for mixed polyalkene post-consumer plastic waste, gas yields of 45.5 wt% were produced compared to 10.8 wt% for the thermosetting based mixed WEEE plastic waste reported here. In addition, styrene based polymers such as ABS and polystyrene have been shown to produce less gas than polyalkene plastics such as polyethylene and polypropylene [21, 22].

The addition of steam to the non-catalytic pyrolysis-gasification of WEEE, HIPS and ABS showed only a small influence on gas yield (Table 2). However, with the introduction of the nickel catalysts there was a marked increase in yield of gas, particularly for the HIPS plastic sample which produced 32.0 wt% and 40.5 wt% gas yield for the 5wt% and 10wt% nickel catalysts. Whilst ABS also showed an increase in the gas yield when the catalyst was added, the increase observed was far more modest with values of 15.4 wt% and 16.2 wt% obtained for the 5 wt% and 10 wt% nickel catalysts. The results for the WEEE plastic gave gas yields of 21.5 wt% and 28.3 wt% for the 5 wt% and 10 wt% nickel catalysts respectively which are between the values obtained for both HIPS and ABS, suggesting that the WEEE contains both HIPS and ABS.

#### 3.2 Hydrogen production

Figure 2 shows the volume percent of hydrogen displayed along with that of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and C<sub>2</sub>-C<sub>4</sub> hydrocarbons for the pyrolysis-gasification of the WEEE plastic, HIPS and ABS and the influence of steam and the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. As shown in figure 2, all the samples give similar gas compositions when no catalyst or steam was used, with varying amounts of hydrogen, CH<sub>4</sub> and C<sub>2</sub>-C<sub>4</sub> hydrocarbons and smaller amounts of CO and CO<sub>2</sub>. HIPS shows the largest hydrogen composition at around 50 vol% compared with 36 vol% for WEEE and 32 vol% for ABS. In relation to ABS, the HIPS plastic itself has a larger hydrogen content, as shown in table 1, suggesting why more gaseous hydrogen is produced. ABS is constructed from an acrilonitrile-styrene polymer being grafted onto a polybutadiene backbone, whilst HIPS is similar but contains no acrilonitrile monomers [22]. As a result it has a comparatively larger amount of styrene monomers and hence a larger amount of hydrogen. HIPS also shows the smallest

methane yield, 26 vol%, whilst ABS displays the highest, 36 vol%. WEEE shows a methane yield in between the two pure plastics further suggesting that it is comprised of a mixture of the HIPS and ABS polymers. The similarity in the yield and composition of gas obtained from WEEE and ABS suggests that ABS makes up a larger proportion of the WEEE sample.

As shown in figure 2, when steam is introduced into the second stage gasification of the plastics the hydrogen composition of the gas is seen to increase, with a corresponding decrease in the amount of methane and  $C_2$ - $C_4$  hydrocarbons which suggests that they are consumed in a steam reforming reaction. The yield of hydrogen in the presence of steam, but no catalyst, was higher for HIPS compared to WEEE and ABS.

The addition of the 5% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst to the catalytic gasification of the plastics showed an increase in hydrogen production (Figure 2). This was the case for all three plastic samples tested, however as before, HIPS and ABS produced the largest amount of hydrogen at 63 vol%, with WEEE producing 52 vol% hydrogen gas by composition. Methane and C<sub>2</sub>-C<sub>4</sub> hydrocarbons decreased with corresponding increase in the formation of CO with the introduction of the catalyst, suggesting that the catalyst may promote hydrogen production by decomposition of hydrocarbons and the reaction of steam with carbon on the coked catalyst to produce CO.

Compared to the 5% Ni catalyst, the 10% catalyst can be seen to be an improvement on catalytic activity. Figure 2 shows a clear increase in the hydrogen yield from the pyrolysis-gasification of the WEEE plastic, as the hydrogen composition of the gas increased to 57 vol%. The increase in nickel content raises the catalytic activity in terms of decomposition of the hydrocarbon gases into hydrogen as decreases in the yield of methane and  $C_2$ - $C_4$  are seen. The amount of CO is also seen to increase significantly as the nickel content of the catalyst is raised.

Figure 3 shows the theoretical hydrogen conversion for each of the three plastic samples tested. This was calculated as the amount of hydrogen produced from the sample and reacted water as a percentage of the amount of hydrogen in the original plastic sample. When no catalyst or steam was used the hydrogen conversion was consistently low for each of the plastics, with conversions of below 10%. Whilst the addition of steam led to an increase in the hydrogen yield, it was not until the nickel catalyst was used that the hydrogen conversions began to rise significantly. The increase was seen for all the samples but was largest for the HIPS plastic which had a conversion of 55% compared with 30% and 18% for ABS and WEEE respectively. The high value for HIPS is attributed to the high hydrogen content in the gas coupled with a high yield of gas due to catalytic cracking. Raising the nickel content of the catalyst continued the increasing trend in the hydrogen conversion again with HIPS giving the largest conversion with values of 73%, compared with 33% and 28% for ABS and WEEE respectively. Despite having the lowest conversion WEEE actually generated a higher yield of hydrogen than ABS, with its low conversion value due to the plastic samples higher hydrogen content. Again ABS and WEEE gave similar results, suggesting the ABS proportion in the WEEE plastic sample was large.

#### 3.3 Characterisation of oils

Table 3 shows the GC/MS results for the oils obtained from the pyrolysis of the three plastics when no catalyst or steam was used. Fifteen of the most abundant compounds in the oils are shown for the WEEE, HIPS and ABS. Styrene was present in all of the oil samples, which is to be expected since all of the plastics are formed from styrene based polymers. Nitrogen containing compounds including benzyl nitrile, benzonitrile-3-methyl, and naphthalene, 1-isocyano were observed in the oils derived from ABS and WEEE but not in

HIPS. In contrast to HIPS, ABS contains acrilonitrile monomers which could breakdown to form the nitrogen containing compounds found in both ABS and WEEE oils. This suggests that these compounds in the WEEE oil are likely to have originated from ABS within the WEEE plastic. Similarly there are some compounds including indene and Phenanthrene, 3methyl which are present in HIPS and WEEE but not in ABS. This suggests that the WEEE plastic also contains HIPS, further cementing the idea that it is comprised of a mixture of the HIPS and ABS plastics.

The effect of steam and the catalyst on the composition of the oils are shown in table 4 and figure 4. Table 4 shows the same fifteen compounds that were displayed in table 3, with the relative abundance of each compound denoted by the number of stars. Smaller aromatic compounds such as ethylbenzene, styrene, phenol and indene increase when the catalyst is added, however, there is a subsequent reduction seen when the nickel content of the catalyst is increased. It is suggested that larger aromatic compounds are cracked into these smaller compounds with the introduction of the catalyst, leading to the initial increase shown. Once the nickel percentage was increased the smaller compounds are themselves broken down into gases via cracking due to the higher catalytic activity that results. Larger compounds such as phenanthrene and benz[a]anthracene on the other hand show a reduction in abundance when the 5% nickel catalyst is introduced and also a subsequent reduction when the nickel content is increased. This suggests that these larger compounds are cracked when the catalyst is used, and are broken down into smaller molecules.

The GC/MS composition of the product oils are shown in figure 4 and table 4, with reductions seen in the concentration of larger molecular weight compounds at higher retention times. Figure 4 a shows the profile for WEEE pyrolysis without steam and without a catalyst. The major peaks seen are at 12.15 and 24.47 minutes retention time which are styrene and naphthalene respectively, however there are also a substantial number of peaks seen at the

higher retention times. The peaks at the higher retention times are seen to reduce with the addition of steam (figure 4 b) and reduce further when the catalyst was used (figures 4 c and d), with some disappearing completely. This reinforces the theory that the nickel catalyst promotes the breakdown of oils via cracking, with the products being smaller aromatic compounds or even gaseous hydrocarbons.

#### 3.4 Characterisation of coke on Ni/Al<sub>2</sub>O<sub>3</sub> catalyst

SEM images of the reacted catalysts obtained from the pyrolysis-gasification of the plastics samples can be seen in figure 5. Figure 5(a) shows the SEM of the reacted catalysts for 5 wt% Ni, whilst 5(b) shows the 10 wt% Ni catalysts used for WEEE plastics, 5 wt% Ni (5c) and 10 wt% Ni (5d) catalysts used for HIPS and 5 wt% Ni catalysts, 5% Ni (5e) and 10% wt Ni (5f) used for ABS. The images of the catalysts in figures 5(a-f) show the nature of the carbon deposits on their surfaces. Figure 5(a) shows an image of the 5% nickel catalyst where filamentous carbons can clearly be seen on the catalyst surface, but were sparsely scattered in the sample, as the majority of the catalyst surface contained more amorphous carbon deposits. The SEM image of the reacted 10% nickel catalyst shown in figure 5(b) likewise shows a similar sparse scattering of filamentous carbons.

The reacted catalyst surface shown in figures 5(c) and (d) show the SEM images of catalyst particles from the pyrolysis-gasification of HIPS in relation to catalyst nickel contents of 5% and 10% respectively. A large amount of carbon deposition can be seen composed of filamentous carbons. The filamentous carbons seen on both catalysts from HIPS appear to be longer and more abundant than those when WEEE was the feedstock, however very little difference is seen between the two different catalyst types. This suggests that the feedstock

used has a strong effect on the carbon deposits in contrast to the nickel content which has less of an effect.

Figures 5(e) and (f) show the SEM images of the 5% and 10% nickel catalysts obtained from pyrolysis-gasification of ABS. Filamentous carbons are again observed however the nature of the carbons are distinctly different from those from the other feedstocks, as the filaments appear bound together, themselves forming larger cylindrical structures. The 5% and 10% nickel catalysts again produce similar results with the nature of the carbon deposits remaining largely unchanged.

When the nickel percent of the catalyst was increased there was no significant change in the nature of the carbon deposits, suggesting instead that the higher hydrogen yield observed was due to an increase in catalytic cracking. This is likely since cracking was suggested from the analysis of the oils, and the increase in the yield of gas.

#### 4. Conclusions

Nickel catalysts have proven successful in increasing the yield of hydrogen obtained from WEEE plastics. The addition of the catalyst produced higher hydrogen and carbon monoxide levels, and it is thought that these were produced by cracking of hydrocarbons and reaction of steam with the coke deposited on the catalyst surface. Increasing the nickel content of the catalyst also saw a corresponding increase in the yield of hydrogen, suggesting that this played an important role in catalytic activity. When comparing the three different plastics investigated, HIPS was seen to produce the largest amount of hydrogen, with ABS and the WEEE plastic giving smaller yields. Higher molecular weight polyaromatic hydrocarbons are thermally degraded via cracking when the nickel catalysts were used, forming smaller

molecular weight aromatic compounds and hydrocarbon gases. Based upon the GC/MS of the pyrolysis oils and GC results from the gases, it may be suggested that for this particular WEEE plastic, the sample is formed of both HIPS and ABS, with a higher proportion of ABS. The carbon deposits seen on the nickel catalysts were all of the filamentous type, however the nature and abundance of the filaments varied with the feedstock.

#### Acknowledgements

We would like to thank the UK Engineering & Physical Sciences Research Council for scholarship support for Jonathan Acomb. We would also like to thank the Syrian Ministry of Higher Education and Al Baath University, Homs, Syria and also to Prof. Saad Kherfan for support for Mohamad Anas Nahil.

### References

- 1. H. Li, G. Tan, W. Zhang, S. Suppiah, *Development of direct resistive heating method* for SO<sub>3</sub> decomposition in the S–I cycle for hydrogen production. Appl. Energ., 93 (2012) 59.
- 2. C. Coskun, M. Bayraktar, Z. Oktay, I. Dincer, *Investigation of biogas and hydrogen* production from waste water of milk-processing industry in Turkey. Int. J. Hydrogen Energ., In Press.
- 3. J.D. Holladay, J. Hu, D.L. King, Y. Wang, An overview of hydrogen production technologies. Catal. Today, 139(4) (2009) 244.
- 4. J. Wang, G. Cheng, Y. You, B. Xiao, S. Liu, P. He, D. Guo, X. Guo, G. Zhang, Hydrogen-rich gas production by steam gasification of municipal solid waste (MSW) using NiO supported on modified dolomite. Int. J. Hydrogen Energ., 37(8) (2012) 6503.
- 5. C. Wu, P.T. Williams, A novel Ni–Mg–Al–CaO catalyst with the dual functions of catalysis and CO<sub>2</sub> sorption for H<sub>2</sub> production from the pyrolysis–gasification of polypropylene. Fuel, 89(7) 1435.
- 6. I.F. Elbaba, C. Wu, P.T. Williams, *Catalytic Pyrolysis-Gasification of Waste Tire and Tire Elastomers for Hydrogen Production*. Energ. Fuel., 24(7) (2010) 3928.
- 7. *Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE)* (*Final report*). United Nations University, Tokyo, Japan, 2008.
- 8. G. Martinho, A. Pires, L. Saraiva, R. Ribeiro, *Composition of plastics from waste* electrical and electronic equipment (WEEE) by direct sampling. Waste Manag. 32(6) (2012) 1213.
- 9. EC, Directive 2002/96/EC Waste Electrical and Electronic Equipment, L27/34. *European Union, Brussels,* 2003.
- 10. L. Chen, Q. Zhu, Z. Hao, T. Zhang, Z. Xie, *Development of a Co–Ni bimetallic aerogel catalyst for hydrogen production via methane oxidative CO*<sub>2</sub> reforming in a magnetic assisted fluidized bed. Int. J. Hydrogen Energ., 35(16) (2010) 8494.
- 11. C. Wu, L. Wang, P.T. Williams, J. Shi, J. Huang, *Hydrogen production from biomass gasification with Ni/MCM-41 catalysts: Influence of Ni content.* Appl. Catal. B-Environ. 108 (2011) 6.
- 12. A. Tanksale, J.N. Beltramini, G.M. Lu, *A review of catalytic hydrogen production processes from biomass.* Renew. Sus. Energ. Revs., 14 (2010) 166.
- 13. S.J. Yoon, Y.-C. Choi, J.-G. Lee, *Hydrogen production from biomass tar by catalytic steam reforming*. Energ. Convers. Manag. 51(1) (2010) 42.
- 14. S.M. de Lima, A.M. da Silva, L.O.O. da Costa, J.M. Assaf, L.V. Mattos, R. Sarkari, A. Venugopal, F.B. Noronha, *Hydrogen production through oxidative steam reforming of ethanol over Ni-based catalysts derived from La1-xCexNiO<sub>3</sub> perovskite-type oxides. Appl. Catal. B-Environ. 121 (2012) 1.*
- 15. Q. Xie, S. Kong, Y. Liu, H. Zeng, *Syngas production by two-stage method of biomass catalytic pyrolysis and gasification.* Biores. Technol. 110 (2012) 603.

- 16. L.B. Avdeeva, O.V. Goncharova, D.I. Kochubey, V.I. Zaikovskii, L.M. Plyasova, B.N. Novgorodov, S.K. Shaikhutdinov, *Coprecipitated Ni-alumina and Ni-Cu-alumina catalysts of methane decomposition and carbon deposition. II. Evolution of the catalysts in reaction.* Appl. Catal. A-Gen. 141 (1996) 117.
- 17. S. Takenaka, S. Kobayashi, H. Ogihara, K. Otsuka, *Ni/SiO2 catalyst effective for methane decomposition into hydrogen and carbon nanofiber*. J. Catal. 217 (2003) 79.
- 18. C. Wu, P.T. Williams, *Investigation of Ni-Al, Ni-Mg-Al and Ni-Cu-Al catalyst for hydrogen production from pyrolysis–gasification of polypropylene*. Appl. Catal. B-Environ. 90 (2009) 147.
- 19. Y. Lu, S. Li, L. Guo, X. Zhang, Hydrogen production by biomass gasification in supercritical water over Ni/yAl<sub>2</sub>O<sub>3</sub> and Ni/CeO<sub>2</sub>-yAl<sub>2</sub>O<sub>3</sub> catalysts. Int. J. Hydrogen Energ., 35 (2010) 7161.
- 20. J. M. Enciar, J.F. Gonzalez, *Pyrolysis of synthetic polymers and plastic wastes*. *Kinetic study*. Fuel Proc. Technol. 89 (2008) 678.
- 21. C. Wu, P.T. Williams, *Pyrolysis–gasification of plastics, mixed plastics and realworld plastic waste with and without Ni–Mg–Al catalyst.* Fuel, 89(10) (2010) 3022.
- 22. Maul, J., Polystyrene and Styrene Copolymers, in Ulmann's Encyclopedia of Industrial Chemistry 2007, Wiley-VCH.

## Table 1

	Elemental analysis			Proximate analysis				
Plastic	C (wt %)	H (wt %)	N (wt %)	Moisture (wt %)	Volatiles (wt %)	Fixed carbons (wt %)	Ash (wt %)	
WEEE	83.3	8.5	4.1	0.06	96.74	1.18	2.02	
ABS	73.3	6.0	4.5	0.02	95.67	2.59	1.72	
HIPS	78.8	6.6	1.2	0.04	95.16	2.22	2.58	

## Elemental and proximate analysis of plastic samples

Plastic	WEEE	WEEE	WEEE	WEEE	HIPS	HIPS	HIPS	HIPS	ABS	ABS	ABS	ABS
Water flow rate (g/h)	0	4.74	4.74	4.74	0	4.74	4.74	4.74	0	4.74	4.74	4.74
Catalyst	Sand	Sand	5% Ni	10% Ni	Sand	Sand	5% Ni	10% Ni	Sand	Sand	5% Ni	10% Ni
Gas	10.8	12.7	21.5	28.3	5.9	6.0	32.0	40.5	11.6	11.3	15.4	16.2

**Table 2**Gas yield obtained from pyrolysis-gasification of WEEE plastics

Table	3
-------	---

Retention Time	Identified Species						
(min)	ABS	HIPS	WEEE				
9.74-9.99	Ethylbenzene	Ethylbenzene	Ethylbenzene				
11.94-12.15	Styrene	Styrene	Styrene				
17.01-17.05	Phenol	-	Phenol				
19.51	-	Indene	Indene				
20.35-20.49	Benzonitrile, 3- methyl-	-	Benzonitrile, 3- methyl-				
22.90-23.03	Benzyl nitrile	-	Benzyl nitrile				
24.34-24.47	Naphthalene	Naphthalene	Naphthalene				
30-30.08	Biphenyl	Biphenyl	Biphenyl				
32.88-32.94	Naphthalene, 1- isocyano-	-	Naphthalene, 1- isocyano-				
37.94-37.96	1,2-Diphenylethylene	1,2-Diphenylethylene	1,2-Diphenylethylene				
39.45-39.47	Phenanthrene	Phenanthrene	Phenanthrene				
41.01	1H-Indene, 1-	1H-Indene, 1-	1H-Indene, 1-				
41.01	(phenylmethylene)-	(phenylmethylene)-	(phenylmethylene)-				
42.25	-	Phenanthrene, 3- methyl-	Phenanthrene, 3- methyl-				
43.30	2-Phenylnaphthalene	2-Phenylnaphthalene	2-Phenylnaphthalene				
51.74	Benz[a]anthracene	Benz[a]anthracene	Benz[a]anthracene				

GC-MS identified species in WEEE, HIPS and ABS pyrolysis

	Concentration					
Identified Species	WEEE + Sand	WEEE + Sand + Steam	WEEE + 5 % Ni/Al <sub>2</sub> O <sub>3</sub> + Steam	$WEEE + 10 \%$ $Ni/Al_2O_3 +$ Steam		
Ethylbenzene	*	**	****	**		
Styrene	****	***	****	***		
Phenol	***	**	****	**		
Indene	****	**	***	*		
Benzonitrile, 3-methyl-	****	***	**	**		
Benzyl nitrile	****	**	***	**		
Naphthalene	****	**	***	*		
Biphenyl	****	**	**	*		
Naphthalene, 1-isocyano-	****	**	**	*		
1,2-Diphenylethylene	****	**	**	*		
Phenanthrene	****	**	**	*		
1H-Indene, 1- (phenylmethylene)-	****	**	**	*		
Phenanthrene, 3-methyl-	**	*	*	-		
2-Phenylnaphthalene	****	**	**	*		
Benz[a]anthracene	***	**	*	-		

 Table 4

 GC-MS results showing the effect of catalyst on WEEE oils

### **Figure Captions**

Figure 1. Schematic diagram of the pyrolysis-gasification reactor

Figure 2. Composition of gases from the pyrolysis-gasification of WEEE plastics, HIPS and ABS.

Figure 3. Theoretical hydrogen conversion based on amount of hydrogen produced from steam and plastic

Figure 4. GC-MS total ion chromatograms of oils obtained from WEEE pyrolysis-gasification using (a) no steam, no catalyst, (b) steam, no catalyst, (c) steam and 5% Ni (d) steam and 10% Ni

Figure 5. Scanning electron micrographs of reacted catalysts for 5 wt% Ni (3a (low resolution)), 5 wt% Ni (3b (high resolution)), 10 wt% Ni (3c) catalysts used for WEEE plastics, 5 wt% Ni (3d) and 10 wt% Ni (3e) catalysts used for HIPS and 5 wt% Ni catalysts (3f) used for ABS.

Figure 1 Schematic diagram of the pyrolysis-gasification reactor





Figure 2 Composition of gases from the pyrolysis-gasification of WEEE plastics, HIPS and ABS.

Figure 3

Theoretical hydrogen conversion based on amount of hydrogen produced from steam and plastic



### Figure 4

GC-MS total ion chromatograms of oils obtained from WEEE pyrolysis-gasification using (a) no steam, no catalyst, (b) steam, no catalyst, (c) steam and 5% Ni and (d) steam and 10% Ni



25

Figure 5.

Scanning electron micrographs of reacted catalysts for 5 wt% Ni (a), 10 wt% Ni (b) catalysts used for WEEE plastics, 5 wt% Ni (c) and 10 wt% Ni (d) catalysts used for HIPS and 5 wt% Ni (e) and 10wt % Ni (f) catalysts used for ABS.

