

This is a repository copy of Catalytic pyrolysis of waste plastic from electrical and electronic equipment.

White Rose Research Online URL for this paper: http://eprints.whiterose.ac.uk/87462/

Version: Accepted Version

#### Article:

Muhammad, C, Onwudili, JA and Williams, PT (2015) Catalytic pyrolysis of waste plastic from electrical and electronic equipment. Journal of Analytical and Applied Pyrolysis, 113. 332 - 339. ISSN 0165-2370

https://doi.org/10.1016/j.jaap.2015.02.016

© 2015, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International http://creativecommons.org/licenses/by-nc-nd/4.0/

#### Reuse

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

### **Takedown**

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



# Catalytic Pyrolysis of Waste Plastic from Electrical and Electronic Equipment

Chika Muhammad, Jude A. Onwudili, Paul T. Williams\*

Energy Research Institute, Faculty of Engineering,

University of Leeds, Leeds, LS2 9JT, UK

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

### **ABSTRACT**

Plastic waste collected from waste electrical and electronic equipment (WEEE) was pyrolysed in the presence of zeolite catalysts to produce a gasoline range aromatic oil. The plastic was from equipment containing cathode ray tubes (CRTs) and also plastic waste from refrigeration equipment. In addition, for comparison the main plastics contained in the WEEE, in the form of high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) were also pyrolysed in the presence of the zeolite catalysts. Two zeolite catalysts; Y zeolite and ZSM-5 were used. Catalytic pyrolysis took place in a two stage fixed bed, batch reactor with the plastic pyrolysed in the first stage and the evolved pyrolysis gases catalysed in the second stage reactor. The quantity of oil produced from uncatalysed pyrolysis of plastics from CRTs and refridgerators was more than 80 wt%. The gases consisted of hydrogen, methane and C<sub>2</sub>-C<sub>4</sub> hydrocarbons. When the zeolite catalysts were introduced there was a decrease of between 5-10 wt% in oil yield and a corresponding increase in gas yield. The composition of the oils derived from the uncatalysed pyrolysis of WEEE plastics were mainly aromatic with high concentrations of styrene, derived from the HIPS and ABS present in the plastic waste. Addition of the zeolite ZSM-5 and Y zeolite to the pyrolysis process resulted in significant concentrations of benzene, toluene and ethylbenzene in the product oil but reduced concentrations of styrene. The oils from both thermal and catalysed pyrolysis also contained significant concentrations of polycyclic aromatic hydrocarbons for example, naphthalene, phenanthrene and pyrene.

Keywords; Pyrolysis; Catalysts; Zeolite; Plastic; Waste; WEEE

### 1. Introduction

The countries of the European Union (EU-27) generate approximately 9 million tonnes of waste electrical and electronic equipment (WEEE) each year [1]. WEEE is one of the fastest growing waste streams in the EU with a forecast that waste arisings will reach a total annual tonnage of 12.3 million tonnes by 2020 [2]. WEEE is subject to legislative control in the EU through the Waste Electrical and Electronic Equipment Directive which seeks to promote the re-use, recycling and recovery of the waste [2]. WEEE includes a wide range of different waste types, for example; refrigerators; freezers; washing machines; dish washers; microwave ovens; vacuum cleaners; electric irons, toasters; electric shavers; computers; keyboards; calculators; mobile telephones; radios; televisions; video recorders; electric drills; saws; sewing machines; video game consoles, electric train sets; video game machines; medical equipment, laboratory diagnosis equipment. It has been estimated that approximately 32 wt% of WEEE consists of plastics [3]. The plastics consist of a wide range of polymers, mainly acrylonitrile butadiene styrene, polypropylene, polystyrene, polycarbonate, styrene acrylonitrile, polyamide, high impact polystyrene, polyethylene terephthalate, polyethylene, polyvinyl chloride etc. [3].

Pyrolysis has been suggested to be a promising processing path for the treatment of WEEE plastics, but generates an oil with a high content of bromine, derived from the brominated flame retardants added to the plastic [4-6]. Zeolite catalysts have been used to reduce the amount of bromine in the product pyrolysis oil [6,7]. Zeolite catalysts have also been used in the pyrolysis of other types of waste plastics, for example, municipal solid waste polyalkene plastics such as high density polyethylene and polypropylene to improve the quality of the product oils [8-14]. The use of zeolite catalysts allows a narrower range of hydrocarbons to be produced [13]. For example, Garcia et al [8] used a fixed bed reactor to

investigate the catalytic pyrolysis of high density polyethylene with a hybrid zeolite-MCM-41 mesoporous catalysts and reported a high product yield of light hydrocarbons, mainly C<sub>2</sub>-C<sub>5</sub> alkenes. Aguado et al., [10] used a two-stage pyrolysis-catalysis reaction system to process low density polyethylene with a zeolite HZSM-5 catalyst and reported a high conversion to alkene gases (73.5 wt% at 450 °C). The liquid products (16.4 wt%) contained a high proportion of aromatic and branched hydrocarbons in the gasoline range (C<sub>5</sub>-C<sub>12</sub>).

Whilst there have been several reports on the use of zeolite catalysts with linear plastics and there are few in regard to 'real-world' plastics and few into WEEE plastics where the aim of the research is to produce gasoline range hydrocarbon products or chemical feedstocks rather than for bromine removal. In this work, the catalytic pyrolysis of plastic waste collected from waste electrical and electronic equipment (WEEE) in a two-stage reactor system using Y zeolite and ZSM-5 zeolite has been investigated. In addition, virgin high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS), which are known to be the main plastics found in WEEE, were also pyrolysed in the presence of the zeolite catalysts for comparison with the 'real world' WEEE plastic waste.

### 2. Materials and methods

### 2.1 Materials

The waste feedstock consisted of plastics collected from a waste electrical and electronic equipment recycling plant which separately recovered the plastics. Plastics from waste refridgerators and freezers and plastic from waste cathode ray tubes (televisions and computer monitors) were collected. For the refridgerator and freezer equipment waste

(designated as 'Fridge'), the compressors were first removed followed by shredding before various WEEE fractions were separated. Foam insulation is removed by air blowing, ferrous metals are removed by electromagnets and non-ferrous metals and plastics are separated by cyclones. However, complete separation could not be achieved and a significant proportion of non-ferrous metal pieces remained in the sample. The second WEEE sample was collected from the recycling unit which handled the waste cathode ray tubes from old style waste television sets and computer monitors (designated as CRT). The plastic outer casings were removed before separation of the glass screen from the electronic components. The circuit board and glass are separated from the CRT equipment and the plastic fraction is ground into small flakes of approximately 10-20 mm in size. Representative 1 kg samples of the two types of the shredded WEEE plastics were taken using standard sampling procedures. In addition to the waste plastic, samples of virgin high-impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) were obtained from Atofina UK and Vamptech UK, respectively. Both of the plastic HPIS and ABS contained brominated flame retardants. The HIPS and ABS are major components of WEEE plastic and were used for comparison with the WEEE plastic. Elemental analysis of the plastics was determined using a CE Instrument Flash EA 1112 Elemental Analyzer to estimate carbon, hydrogen and nitrogen. The results of elemental analysis for the four plastics are given in table 1. The high bromine content of the HIPS and ABS plastic samples, reflects the high content of brominated flame retardant added to the plastic. The antimony is added as antimony trioxide as a synergist to aid the effectiveness of the flame retardant. The ash content of the plastics derived from the recycled WEEE was high, particularly from the plastic sample produced from waste fridges and freezers which consisted of mainly metals carried over from poor separation of the materials and plastics. Interestingly, the bromine content of the plastics from the waste televisions and computer monitors and fridge and freezers plastics samples was very low, below the

detection limit of the analysis procedure. This was most likely due to dilution of the brominated plastic waste with non-brominated fire retardant plastics.

The catalysts used were Y zeolite and ZSM-5 zeolite which were in pellet form of approximate size, 1mm by 5 mm obtained from Zeolyst International (USA) and BDH UK. The Y zeolite had a Si:Al ratio of 5.4, pore size of 7.8 Å and high acidity, the ZSM-5 zeolite catalyst had a Si:Al ratio of 40, pore size of 5.6 Å and lower acidity.

## 2.2. Two-stage pyrolysis-catalytic reactor

The waste plastic samples were pyrolysed in a fixed bed, two-stage batch reactor of 480 mm length with an internal diameter of 39 mm and was externally heated by two 1.5 Kw tube furnaces. Pyrolysis of the plastic was undertaken in the first stage as the sample was heated from ambient temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup>. Nitrogen was used as the carrier gas. The evolved volatiles from pyrolysis were passed directly to a second stage reactor containing the catalyst which was maintained at a catalyst temperature of 500 °C. The plastic was located in a stainless steel crucible and a sample size of 2 g of the plastic was used. The catalyst (2 g) was supported on quartz wool in the second stage reactor. For comparison, where no catalyst was used, quartz sand was substituted for the catalyst. The experimental procedure consisted of stabilisation of the second stage catalyst reactor at 500 °C, followed by the pyrolysis of the plastic from ambient temperature to 500 °C and held at that temperature for 30 minutes. The condenser system consisted of three solid dry ice cooled condensers. The condenser system was connected to a Tedlar<sup>TM</sup> gas sample bag.

# 2.3. Product analysis

The gas sample bag was taken for analysis immediately after each experiment and the gases analysed by packed column gas chromatography. Hydrocarbon gases from C<sub>1</sub> to C<sub>4</sub> were analysed using a Varian CP 3380 Gas Chromatograph (GC) with a flame ionization detector equipped with a 2m long x 2mm diameter column packed with 80-100 mesh size HayeSep packing. The injector was held at a temperature of 150 °C while the detector temperature was 200 °C. For permanent gases, H<sub>2</sub>, N<sub>2</sub>, CO and CO<sub>2</sub>, the analysis were performed on a separate Varian CP-3380 GC with thermal conductivity detector equipped with a 2 m x 2 mm i.d. column packed with a 60-80 mesh molecular sieve for analysis of H<sub>2</sub>, N<sub>2</sub> and CO. Carbon dioxide was analysed separately on a HayeSep 80–100 mesh column with argon carrier gas. The temperature of the detector and the filament were 120 °C and 160 °C respectively.

The oil was analysed using a Varian 430 Liquid GC with flame ionization detector (FID). The gas chromatograph was equipped with a split/splitless injection port. The analysis was carried out on a ZB-1 capillary column (30 m long  $\times$  0.53 mm i.d., 0.5  $\mu$ m solid phase thickness). Hydrogen was used as carrier gas with a constant flow of 1.0 mL min<sup>-1</sup>. The injection volume was 2.0  $\mu$ L; the column was temperature programmed from 40 °C to 310 °C at 5 °C min<sup>-1</sup> heating rate. The system was calibrated with aromatic and polycyclic aromatic hydrocarbon standards. The product oil samples were diluted in dichloromethane (analytical reagent grade) prior to injection into the gas chromatograph.

### 3. Results and Discussion

# 3.1 Product Yield and gas composition

Figure 2 shows the product yield from the pyrolysis and pyrolysis-catalysis of plastics from television and computer monitors (CRT) and plastics from refridgerators and freezers (Fridge) using the Y zeolite and ZSM-5 catalysts. The product mass balances were all close to 100 wt%, with the main product being the pyrolysis oil. Table 2 shows that the main gases were hydrogen, methane and ethane and lower concentrations of other hydrocarbons. Without the presence of a catalyst, the CRT plastics produced an oil yield of 84.0 wt% but with the zeolite catalyst produced a decrease in oil yield to 80 wt% for the Y zeolite and 77.5 wt% for the ZSM-5 catalyst. There was a consequent increase in gas yield, mainly the alkene gases, particularly ethene and propene. Similar results were found for the Fridge plastics. The char included the carbonaceous pyrolysis char and ash derived from the metal contamination. The ash content of the Fridge sample (Table 1) was high at 13.8 wt% which would transfer to the solid char product resulting in a higher 'char' result for the Fridge sample compared to the CRT sample which only had 1.3 wt% ash content.

Figure 3 and Table 3 shows the product yield and gas composition respectively for the pyrolysis and pyrolysis-catalysis of high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) with the Y zeolite and ZSM-5 catalysts. As with the WEEE plastics, the largest product for uncatalysed pyrolysis was the pyrolysis oil at 84 wt% for HIPS and 66.5 wt% for ABS. The influence of the addition of a zeolite catalyst to the process was to decrease the oil yield and increase the gas yield for the HIPS, but there was less of an effect on the overall product distribution for the ABS plastics. Table 3 shows there were some changes in gas composition in the presence of the catalysts, in relation to

increased concentrations of alkene gases, mainly ethene and propene. The char from HIPS and ABS would contain some of the residual antimony trioxide added as a synergist with the organo-bromine fire retardant compounds. The presence of the bromine fire retardant would also influence the yield of oil from pyrolysis and also increase the char from pyrolysis of the plastic. The elemental analysis of the HIPS and ABS (Table 1) shows that the bromine content, from the addition of brominated fale retardant, was significantly higher for the ABS sample (11.8 wt%) compared to the HIPS sample (7.6 wt%). The flame retardant mechanism of brominated flame retardants operates through the release of bromine free radicals at a lower temperature of thermal decomposition than the host plastic, preventing the formation of flammable gases. High energy OH and H radicals, formed during combustion, are removed by reaction with the released brominated species in the gas flame phase [15]. considerably slows or prevents the combustion process, thus reducing heat generation and consequently the production of further pyrolysis vapours which later condense to produce the pyrolysis oil. In addition, the presence of brominated flame retardants in waste plastics have been shown to increase the yield of char [16]. Therefore, the higher bromine content would produce more charring reactions resulting in a higher solid product yield and also lower oil yield for the ABS compared to the HIPS.

## 3.2 Oil Compostion

Figure 4 shows the single ring to four ring aromatic compounds present in the oils derived from the pyrolysis and the pyrolysis-catalysis of CRT and Fridge plastics with the Y zeolite and ZSM-5 catalysts. The oils are dominated by single ring aromatic compounds with lower concentrations of 2-4 ring polycyclic aromatic hydrocarbons (PAH). The addition of the catalysts results in only a slight increase in the single ring aromatic compounds in the product oils, however Figure 5 shows that the relative concentrations of the main aromatic

compounds present in the oil show significant differences due to the effects of the catalysts. The uncatalysed pyrolysis oil is dominated by styrene, also present in high concentration are the single ring toluene and ethylbenzene. At lower concentrations were two-ring naphthalene, alkylated naphthalenes and three ring PAH such as phenanthrene and four ring PAH such as pyrene. The addition of the Y zeolite to the CRT pyrolysis-catalysis process for both the CRT and the Fridge plastics results in a marked decrease in styrene concentration in the product oil and a consequent marked increase in benzene and toluene. The influence of the zeolite ZSM-5 catalyst on the pyrolysis-catalysis of the CRT and Fridge plastics was less than that of the Y zeolite catalyst, with less reduction of the styrene concentration and a lower increase in toluene.

Figure 6 shows the single-four ring aromatic compounds found in the oils derived from the pyrolysis and the catalytic pyrolysis of HIPS and ABS for the Y zeolite and ZSM-5 zeolite and Figure 7 shows the identified main aromatic components in the oils. Figure 8 shows gas chromatograms for the pyrolysis oil derived from HIPS in the absence of a catalyst and also the product oil from the pyrolysis catalysis of HIPS with the Y zeolite and the ZSM-5 zeolite. The results were on the whole similar to those found with the CRT and Fridge plastics, the uncatalysed pyrolysis oils containing high concentrations of single ring aromatic compounds (Figure 6) which were mainly styrene, directly derived from the styrene-based high impact polystyrene and acrylonitrile-butadiene-styrene and also toluene and ethylbenzene. Addition of the Y zeolite and ZSM-5 catalysts produced increased concentrations of mainly benzene and toluene, with ethylbenzene and styrene also present. Comparison of the results from the HIPS and ABS suggest, as expected, that the CRT and Fridge plastics were mainly composed of HIPS and ABS plastics. However, the real-world WEEE waste plastics derived from the computer and television plastic casings (CRT) and the refridgerators and freezers would also contain other plastics.

The Y zeolite has different characteristics compared to the ZSM-5 zeolite, with the Y zeolite having a pore size of 7.8 Å and a Si:Al ratio of 5.4 and the zeolite ZSM-5 a pore size of 5.6 Å and Si:Al ratio of 40. The lower silica/alumina ratio of the Y zeolite at 5.4 results in an increase in the relative surface concentration of aluminium compared to the ZSM-5 zeolite with a much higher Si:Al ratio of 40. The consequence of a high aluminium content for the Y-zeolite results in a higher surface acidity of the catalyst which in turn results in a higher catalytic activity [17,18]. The active catalytic sites producing increased conversion to aromatic products [19]. Zeolites are known as solid acid catalysts because they can have strongly acidic protons uniformly distributed throughout the internal volume of the catalyst channels. The manipulation of the silica/alumina ratio influences both the number and strength of the acid sites. The Y zeolite also had a larger pore size of 7.8 Å compared to the ZSM-5 zeolite catalyst at 5.6 Å, the pore size influencing the size of molecules that can enter the three dimensional zeolite structure and react with the active catalyst sites.

Other researchers have investigated the influence of zeolite catalysts on the pyrolysis of waste plastics and their influence on the composition of the product oil. Miskolczi et al [9] investigated the catalytic pyrolysis of a mixture of polyethylene and polystyrene waste plastics in a batch reactor. The liquid products were reported to consist of a wide range of hydrocarbons (C<sub>5</sub>-C<sub>28</sub>), with polyethylene producing linear non-branched hydrocarbons and polystyrene producing aromatic compounds including ethylbenzene, styrene, toluene and benzene. Lee [12] also investigated the catalytic pyrolysis of a mixture of polyethylene and polystyrene in a stirred batch reactor using spent FCC (zeolite based fluid catalytic cracking (FCC) catalyst). The presence of styrene and ethylbenzene in high concentrations was reported and their concentrations were dependent on reaction time, and the relative composition of polyethylene and polystyrene. Lopez et al [14] used a ZSM-5 zeolite catalyst (Si:Al ratio of 50) in the pyrolysis processing of mixed plastics (18 wt% polystyrene) and

showed that the uncatalysed oil contained aliphatic compounds derived from the linear plastics and also aromatic compounds which were mainly toluene, ethylbenzene and styrene. The influence of the ZSM-5 catalyst was reported to significantly reduce the styrene concentration and increase the concentration of toluene, ethylbenzene and xylenes. Ates et al [19] investigated the batch reactor catalytic pyrolysis of the plastic fraction produced from municipal solid waste using a range of different catalysts. They reported that the Si:Al ratio influenced the production of aromatic compounds in the product oil, with a zeolite ZSM-5 catalysts with a Si:Al ratio of 12.6 producing higher aromatic content product oils compared to a  $\beta$ -zeolite with a Si:Al ratio of 17.1. Lee [20] investigated the influence of different types of zeolite catalyst on the upgrading of pyrolysis oil/wax derived from the pyrolysis of the plastic fraction of municipal solid waste. Comparison of a ZSM-5 zeolite catalyst (Si:Al ratio of 30) and a Y zeolite (Si:Al ratio of 80) showed that the ZSM-5 catalyst with the lower Si:Al ratio produced an oil with 78.9 wt% aromatic compared to the Y zeolite at 31.95 wt% aromatics. The raw oil/wax produced from the pyrolysis of the municipal solid waste plastics had negligible aromatic content. It should also be noted that the zeolite catalysts had different surface areas (ZSM-5 at 400 m<sup>2</sup> g<sup>-1</sup> and Y zeolite at 780 m<sup>2</sup> g<sup>-1</sup>) and would have different pore structures in addition to the differences in Si:Al ratio. Therefore, the results of Lee et al [20] suggest that surface acidity has more influence on the aromatic forming catalytic reactions of the pyrolysis degradation products than the catalyst surface area and wider pore size as found in the Y zeolite.

The main polymeric structure found in the high impact polystyrene, acrylonitrile-butadiene-styrene and WEEE plastics would be based on the polystyrene structure. The mechanism for the degradation of polystyrene in the presence of zeolite catalysts has been discussed by several authors [21-24]. Serrano et al [24] suggest that the catalytic cracking of polystyrene may proceed through a complex combination of different reactions. Thermal

pyrolysis is represented by random scission of the polystyrene polymer to produce polymer radicals. However, acid catalysis involves degradation of the polystyrene at Bronsted active sites to produce carbenium ions which undergo further scission and hydrogen transfer [24]. Cross-linking reactions of the polymer degradation products may also occur and also cracking and hydrogenation of the thermally produced styrene may occur on the catalyst [25]. Antonakou et al [21] undertook catalytic pyrolysis of waste plastics containing HIPS (compact disc waste) in the presence of a zeolite ZSM-5 catalyst. They reported that styrene concentration was reduced from 75.75 wt% in the thermal pyrolysis oil to 64.82 wt% for the catalytic pyrolysis, with an increase in benzene. They suggested that the thermal degradation of polystyrene starts with random initiation to form polymer radicals, but in the presence of the catalysts degradation is extended in the form of cracking and hydrogenation reactions resulting in decreased styrene concentration. Lopez et al [22] also suggested that the styrene produced from thermal pyrolysis is further degraded to other hydrocarbons via secondary reactions in the presence of the catalyst. Puente et al [23] investigated the catalytic pyrolysis of polystyrene and polystyrene-polybutadiene using an FCC catalyst (fluid catalytic cracking catalyst from the petroleum refining industry). Miskolczi et al. [9] have described FCC catalyst as being mainly Y zeolite typified by a faujasite type crystal structure with open The open pores allowing larger molecules to enter the catalyst structure to increase reaction on the catalyst sites. The concentrations of styrene obtained by Puente et al [23] in the presence of fresh FCC catalyst showed a marked reduction, decreasing from 75.59 wt% to 14.90 wt% for the catalytic pyrolysis of polystyrene, with increased formation of toluene, benzene and ethylbenzene. They also suggest the key degradation mechanism in the presence of a zeolite catalyst is via polymer thermal cracking, surface oligomerisation of styrene molecules and further cracking, in parallel to hydrogen-transfer reactions.

Audisio et al. [26] investigated the thermal degradation of polystyrene in the presence of several catalysts, including a Y zeolite. They reported that the main degradation products from the non-catalytic pyrolysis of catalytic pyrolysis of polystyrene with the Y zeolite were benzene, ethylbenzene, toluene,  $\alpha$ -methylstyrene and indane. They proposed several reaction schemes to describe the thermal degradation of polystyrene to give the reaction products. For example, benzene was proposed to be formed via catalytic addition of hydrogen to the aromatic ring producing polymeric ions which further react through one route to produce benzene and a polymer ion as a result of  $\beta$ -scission.

In this work, the Y zeolite which has more catalytically active sites and the larger pore size results in higher conversion of the pyrolysis volatile material to other products compared to the ZSM-5 catalyst. In particular, the larger pore size of the Y zeolite allows the larger molecular size pyrolysis products derived from the polystyrene polymer, including larger polymer fragments and styrene to enter the pores of the catalyst to react at the catalyst sites to reduce styrene concentration. In addition, because of the lower Si:Al ratio of the Y zeolite equating to increased surface aluminium concentration and higher surface acidity of the catalyst which in turn results in a higher catalytic activity higher levels of styrene degradation were found compared to the ZSM-5 zeolite catalyst.

### 4. Conclusions

The research reported here shows that pyrolysis of plastics produced from commercial waste electrical and electronic equipment produces a mainly oil product containing mostly styrene. The influence of the addition of a zeolite catalyst to the process was mainly dependent on the Si:Al characteristics of the zeolite catalyst used. Zeolite catalyst with a lower Si:Al ratio (Y zeolite) produced a higher conversion of the styrene to other aromatic

products, particularly benzene and toluene. Comparison of the catalytic pyrolysis of high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) with the WEEE plastics results suggests that the WEEE plastics consisted of mostly, but not exclusively HIPS and ABS plastics.

# Acknowledgements

The financial support of a scholarship from the Petroleum Technology Development Fund of Nigeria is gratefully acknowledged by one of us (C.M.)

### REFERENCES

- [1] EC Review of Directive 2002/96/EC: Waste Electrical and Electronic Equipment (WEEE). Final Report (Contract No. 07010401/2006/442493/ETU/G4 ENV.G.4/ETU/2006/0032). Brussels, August, (2007).
- [2] EC Directive 2002/96/EC.: Waste Electrical and Electronic Equipment, L27/34, European Union, Brussels, (2003).
- [3] WRAP, Separation of mixed WEEE plastics (WRAP Project MDD018 and MDD023) Waste & Resource Action Programme (WRAP), Banbury, Oxfordshire UK, (2009).
- [4] W.J. Hall, P.T. Williams, Fast pyrolysis of halogenated plastics recovered from waste computers. Energ. Fuel. 20 (2006) 1536-1549.
- [5] W.J. Hall, P.T. Williams, Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment. J. Anal. Appl. Pyrolysis 79 (2007) 375-386.
- [6] W.J. Hall, P.T. Williams, Removal of organobromine compounds from the pyrolysis oils of flame retarded plastics using zeolite catalysts. J. Anal. Appl. Pyrolysis 81 (2008) 139-147.
- [7] N.M.M. Mitan, M. Brebu, T. Bhaskar, A. Muto, Y. Sakata, Individual and simultaneous degradation of brominated high impact polystyrene and brominated acrylonitrile-butadiene-styrene and removal of heteroelements (Br, N and O) from degradation oil by multiphase catalytic systems. J. Mater. Cycles Waste 9 (2007) 56-61.
- [8] R.A. Garcia, D.P. Serrano, D. Otero, Catalytic cracking of HDPE over hybrid zeolitic-mesoporous materials. J. Anal. Appl. Pyrolysis 74 (2005), 379-386.
- [9] N. Miskolczi, L. Bartha, G.Deak, Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks. Polym. Degrad. Stabil. 91 (2006) 517-526.
- [10] J. Aguado D.P., Serrano G., SanMiguel, M.C. Castro, S. Madrid, Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. J. Anal. Appl. Pyrolysis 79 (2007) 415-423.

- [11] A. Marcilla, M. del Remedio Hernandez, A.N. Garcia, Study of the polymer-catalyst contact effectivity and the heating rate influence on the HDPE pyrolysis. J. Anal. Appl. Pyrolysis 79 (2007) 424-432.
- [12] K.H. Lee, Composition of aromatic products in the catalytic degradation of the mixture of waste polystyrene and high-density polyethylene using spent FCC catalyst. Polym. Degrad. Stabil. 93 (2008) 1284-1289.
- [13] M. Olazar, G. Lopez, M. Amutio, G. Elordi, R. Aguado, J. Bilbao, Influence of FCC catalyst steaming on HDPE pyrolysis product distribution. J. Anal. Appl. Pyrolysis 85 (2009) 359-365.
- [14] A. Lopez, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, A. Aranzabal, Catalytic pyrolysis of plastic wastes with different types of catalysts: ZSM-5 zeolite and Red Mud, Appl. Catal. B-Environ. 104 (2011) 211-219.
- [15] F. Rahman, K.H. Langford, M.D. Scrimshaw, J.N. Lester. Polybrominated diphenyl ether (PBDE) flame retardants. Sci. Total Environ. 275 (2001) 1-17.
- [16] A.M. Cunliffe, P.T. Williams. Pyrolysis of flame retardant brominated polyester composites. Environ. Technol. 25 (2004) 1349-1356.
- [17] P.B. Venuto, T.E. Habib. Fluid catalytic cracking with zeolite catalysts. Marcel Dekker, New York (1979).
- [18] I.M. Campbell (1988) Catalysis at surfaces. Chapman & Hall, London.
- [19] F. Ates, N. Miskolczi, N. Borsodi, Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part 1: Product yields, gas and pyrolysis oil properties. Bioresource Technol. 133 (2013) 443-454.
- [20] K.H. Lee, Effects of the types of zeolites on catalytic upgrading of pyrolysis wax oil. J. Anal. Appl. Pyrolysis 94 (2012) 209-214.
- [21] E.V. Antonakou, K.G. Kalogiannis, S.D. Stephanidis, K.S. Triantafyllidis, A.A.Lappas, D.S. Achilias. Pyrolysis and catalytic pyrolysis as a recycling method of waste CDs originating from polycarbonate and HIPS. Waste. Manag. 34 (2014), 2487-2493.
- [22] A. Lopez A. Lopez, I. de Marco, B.M. Caballero, A. Adrados, M.F. Laresgoiti. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. Waste Manag. 31 (2011) 1852-1858.

- [23] G. Puente, J.M. Arandes, U.A. Sedran. Recycled plastics in FCC feedstocks: Specific contributions. Ind. Eng. Chem. Res. 36 (1997) 4530-4534.
- [24] D.P. Serrano, J. Aguado, J.M. Escola. Catalytic conversion of polystyrene over HMCM-41, HZSM-5 and amorphous Si<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>: Comparison with thermal cracking. Appl. Catal. B-Environ. 25 (2000) 181-189.
- [25] S.Y. Lee, J.H. Yoon, J.R. Kim, D.W. Park. Catalytic degradation of polystyrene over natural clinoptilolite zeolite. Polm. Degrad. Stab. 74 (2001) 297-305.
- [26] G. Audisio, F. Bertini, P.L. Beltrame, P. Carniti. Catalytic degradation of polymers: Part III Degradation of polystyrene. Polm. Degrad. Stabil. 29 (1990) 191-200.

Table 1
Elemental analysis of the plastics (wt%)

	High impact polystyrene (HIPS)	Acrylonitrile- butadiene- styrene (ABS)	Plastics from waste Cathode Ray Tubes (CRT)	Plastics from waste refridgerators (Fridge)
Carbon	80.5	72.3	81.6	71.4
Hydrogen	7.3	6.4	7.5	7.0
Nitrogen	0.2	4.1	5.5	1.8
Oxygen	0.8	2.8	3.9	4.7
Bromine	7.6	11.2	< 0.01	< 0.01
Chlorine	-	-	0.26	1.30
Antimony	3.6	3.2	-	-
Ash	-	-	1.3	13.8

**Table 2**Gas composition for the pyrolysis and pyrolysis-catalysis of CRT and Fridge plastic wastes with Zeolite Y and ZSM-5 catalysts.

	Television & PC monitor plastics (CRT)		Refrigerator plastics (Fridge)			
Gas composition	No	Y zeolite	ZSM-5	No	Y zeolite	ZSM-5
(Vol.%)	Catalyst		zeolite	Catalyst		zeolite
$H_2$	37.6	28.1	35.2	35.1	21.7	19.2
$CH_4$	26.7	16.2	11.6	16.1	19.7	10.9
$C_2H_4$	10.9	19.5	21.8	12.8	21.8	32.3
$C_2H_6$	9.2	7.5	5.5	11.8	8.7	5.6
$C_3H_6$	7.8	19.3	19.5	12.7	15.9	23.1
$C_3H_8$	2.0	6.2	0	2.7	6.4	0
$C_4H_8$	3.2	1.7	4.3	5.2	3.3	6.3
$C_4H_{10}$	2.6	1.4	2.1	3.7	2.4	2.6
$C_2$ - $C_4$	35.7	55.7	53.2	48.8	58.5	69.8
Alkanes	40.5	31.3	19.2	34.3	37.2	19.1
Alkenes	21.9	40.5	45.6	30.7	41.0	61.7

**Table 3**Gas composition for the pyrolysis and pyrolysis-catalysis of HIPS and ABS plastic wastes with Zeolite Y and ZSM-5 catalysts.

	High-impact polystyrene (HIPS)		Acrylonitrile-Butadiene-styrene (ABS)			
Gas Composition (Vol.%)	No Catalyst	Y zeolite	ZSM-5 zeolite	No Catalyst	Y zeolite	ZSM-5 zeolite
$H_2$	60.6	31.0	37.3	69.7	45.7	49.5
$CH_4$	16.6	20.8	8.8	12.9	18.4	11.8
$C_2H_4$	5.9	18.3	33.1	3.7	9.3	13.5
$C_2H_6$	6.9	7.0	3.6	5.6	6.5	5.1
$C_3H_6$	4.2	11.2	13.8	2.6	17.2	15.1
$C_3H_8$	2.7	7.6	0	2.0	0.0	0
$C_4H_8$	1.6	3.8	2.3	2.2	1.2	3.3
$C_4H_{10}$	1.4	0.5	1.0	1.4	1.6	1.7
$C_2$ - $C_4$	22.8	48.2	53.9	17.5	35.9	38.7
Alkanes	27.6	35.9	13.4	19.8	26.6	18.6
Alkenes	11.7	33.3	49.2	8.5	28.0	31.9

## **Figure Captions**

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

Figure 2. Product yield from the pyrolysis and pyrolysis-catalysis of CRT and Fridge plastics with Zeolite Y and ZSM-5 catalysts.

Figure 3. Product yield from the pyrolysis and pyrolysis-catalysis of HIPS and ABS plastics with Zeolite Y and ZSM-5 catalysts.

Figure 4. Aromatic compounds (AR) composition for oil from pyrolysis of CRT (television and computer monitor) and Fridge (refridgerator and freezer) plastics (1R = single ring; 2R = two ring; 3R = three ring; 4R = four ring aromatic compounds)

Figure 5. Relative proportions of the main aromatic compounds in the oil derived from the pyrolysis of CRT and Fridge plastics

Figure 6. Aromatic compounds (AR) composition for oil from pyrolysis of HIPS and ABS plastic (1R = single ring; 2R = two ring; 3R = three ring; 4R = four ring aromatic compounds)

Figure 7. Relative proportions of the main aromatic compounds in the oil derived from the pyrolysis of HIPS and ABS plastic

Figure 8. Gas chromatograms for (a) the product oil from the pyrolysis catalysis of HIPS with ZSM-5 zeolite catalyst (b) the product oil from the pyrolysis catalysis of HIPS with Y zeolite catalyst (c) the pyrolysis oil derived from pyrolysis of HIPS.

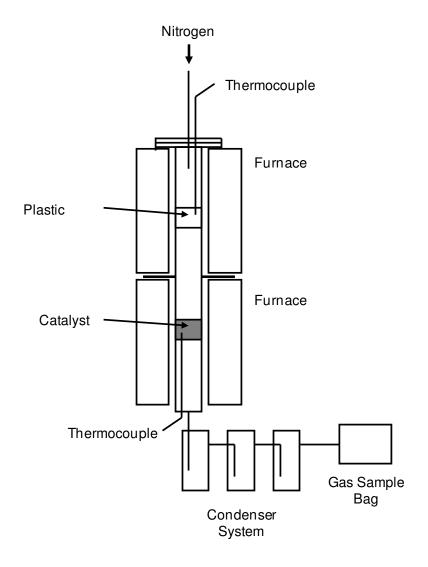


Figure 1. Schematic diagram of the two-stage pyrolysis-catalysis reactor system.

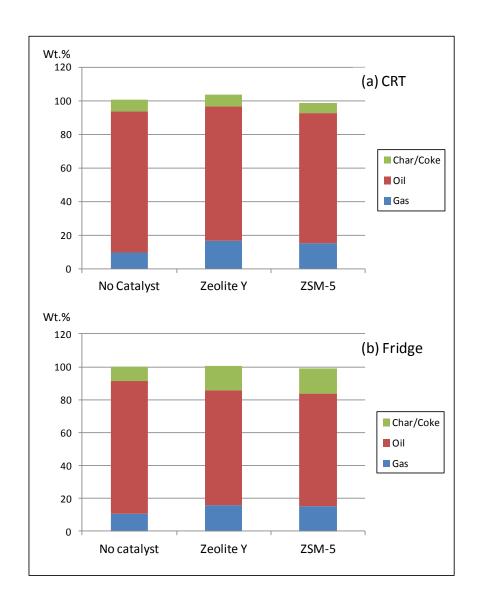


Figure 2. Product yield from the pyrolysis and pyrolysis-catalysis of CRT and Fridge plastics with Zeolite Y and ZSM-5 catalysts.

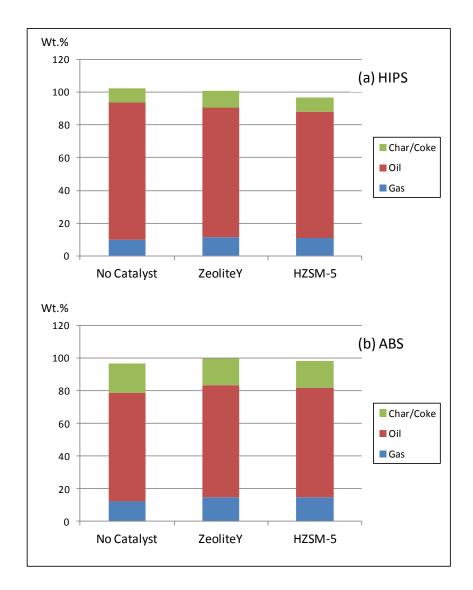


Figure 3. Product yield from the pyrolysis and pyrolysis-catalysis of HIPS and ABS plastics with Zeolite Y and ZSM-5 catalysts.

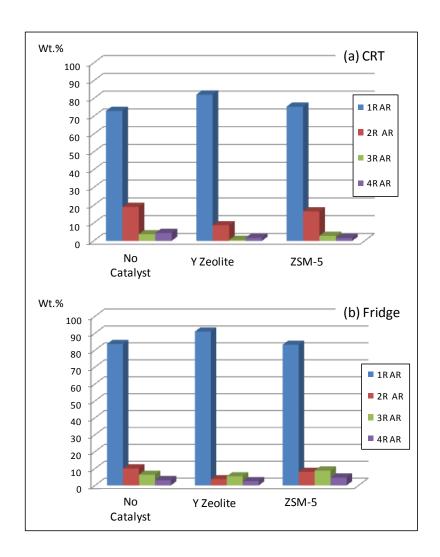


Figure 4. Aromatic compounds (AR) composition for oil from pyrolysis of CRT (television and computer monitor) and Fridge (refridgerator and freezer) plastics (1R = single ring; 2R = two ring; 3R = three ring; 4R = four ring aromatic compounds)

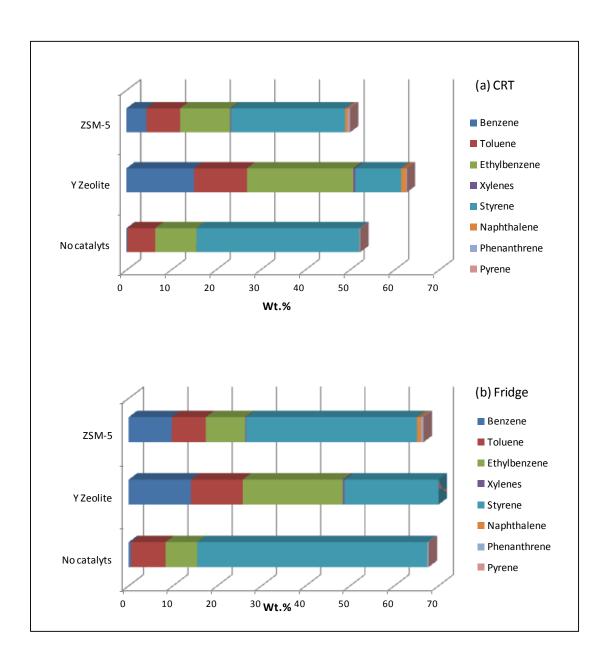


Figure 5. Relative proportions of the main aromatic compounds in the oil derived from the pyrolysis and catalytic pyrolysis of (a) CRT and (b) Fridge plastics

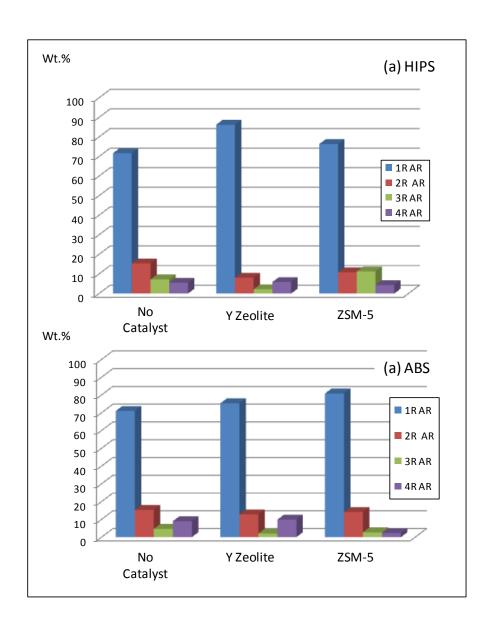
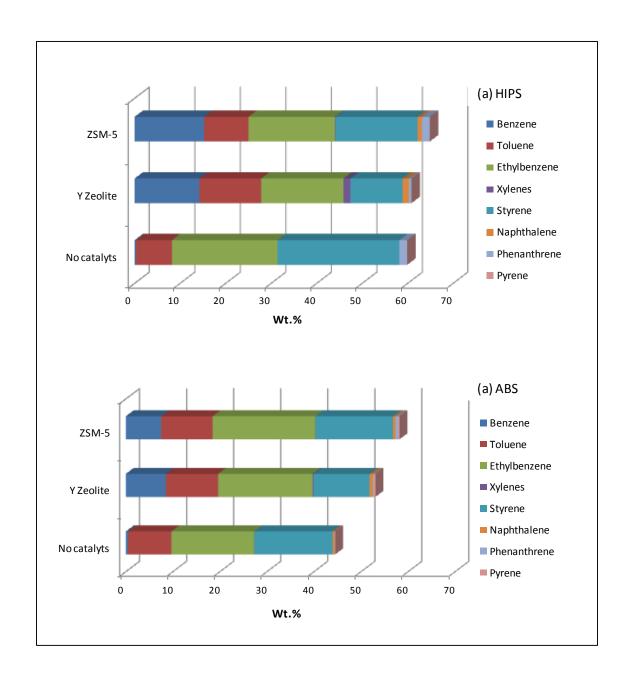


Figure 6. Aromatic compounds (AR) composition for oil from pyrolysis of HIPS And ABS plastic (1R = single ring; 2R = two ring; 3R = three ring; 4R = four ring aromatic compounds)



**Figure 7.** Relative proportions of the main aromatic compounds in the oil derived from the pyrolysis and catalytic pyrolysis of (a) HIPS and (b) ABS plastic

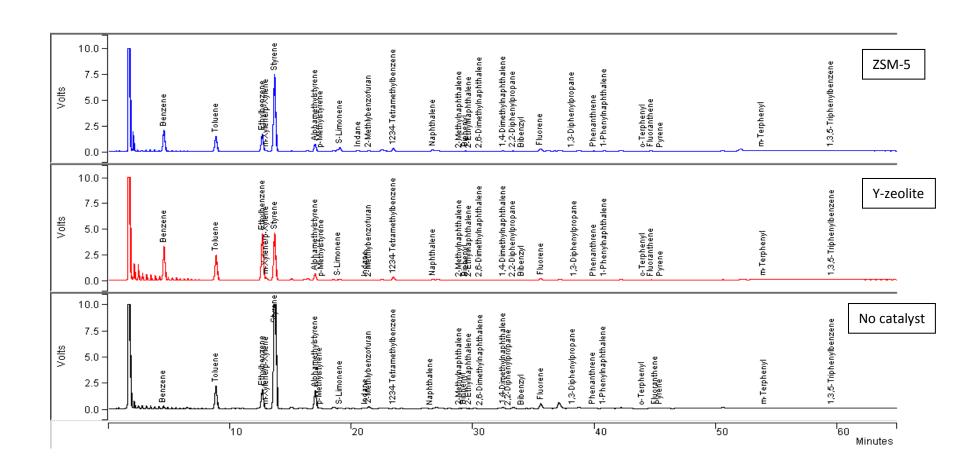


Figure 8. Gas chromatograms for (a) the product oil from the pyrolysis catalysis of HIPS with ZSM-5 zeolite catalyst (b) the product oil from the pyrolysis catalysis of HIPS with Y zeolite catalyst (c) the pyrolysis oil derived from pyrolysis of HIPS.