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IMPROVING CHAR AND OIL FOR COMMERCIAL APPLICATIONS FROM THE PYROLYSIS OF AUTOMOTIVE SHREDDER RESIDUE THROUGH THE USE OF DIFFERENT TYPES OF CATALYSTS

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ABSTRACT

Pyrolysis of automotive shredder residue (ASR) may be a solution for end-of-life vehicles (ELV) to meet legislative targets and to future proof against any reclassification as a hazardous waste. Prior to pyrolysis commercialization, firm markets for all byproducts produced are required. Identified commercial outlets for byproduct char include: (i) activated carbon; (ii) a soil conditioner and (iii) a partial replacement for cement in concrete. Commercialization of pyrolysis treatment for the UK alone would require outlets capable of taking around 100,000 tpa of char, compliant with quality protocols. The challenge for these applications is any retained persistent organic pollutants (POPS) within the matrix of char particles. A solution would be to break these compounds down during the pyrolysis process through the introduction of catalytic material. This paper explores the effectiveness of four catalysts in reducing the organic contamination within pyrolysis byproducts. A purpose-built lab-based pyrolysis unit (30 g of ASR) was used for initial investigations. ASR (pre-shredded to <10mm) was sourced from a UK ELV recycling company using a systematic sampling approach. A control without catalyst was pyrolysed at 500°C for 30 minutes. Each sample was mixed with the catalyst at a ratio of 1:10. The four catalysts used were: (i) 3Å molecular sieve zeolite; (ii) 4Å molecular sieve zeolite; (iii) MCM-41 mesostructured silica and (iv) AL-MCM-41 mesostructured aluminosilicate. Byproducts were collected and chemically analyzed using organic elemental (CHNS) analysis, FT-IR and GC-MS. Findings indicated that all catalysts offered some improvement in reducing the residual organic fractions in char. 4Å was the most effective, increasing the overall carbon percentage by 17.32%. GCMS and FTIR analysis of the oil indicated that catalysts were effective in deoxygenation without reducing the carbon percentage. In conclusion, catalysts may offer a commercial solution to support the uptake of char as a commercial product.

Keywords: ASR, pyrolysis products, catalysts, commercialisation, zeolites.

1 INTRODUCTION

Recycling end-of-life vehicles (ELVs) is a growing challenge for the automotive sector, where changes to car composition over the last 20 years to improve car efficiency and meet greenhouse gas emission legislation has increased the typically non-recyclable components (plastics and foams) and reduced the heavy metal composition. This poses a major challenge to the ELV waste recycling industry, which has to meet strict recycling targets set by the ELV Directive (2000/53/EC) [1]. The fraction of material which is currently non-recyclable and sent to landfill is automotive shredder residue (ASR). ASR is a heterogenous material composing of mainly plastics, foam, textiles and wood. Recent technology has been developed at a pilot-scale to recover energy from this material using pyrolysis [2]. Pyrolysis is the thermochemical conversion of biomass using heat in the absence of oxygen. Alongside meeting the ELV Directive by diverting the material from landfill, commercialisation of this process could increase circularity of the waste recycling process by utilising the energy created to power the industrial upstream and downstream waste processing.

Upon commercialisation of the pyrolysis process, numerous challenges may be faced upon upscale. Although pyrolysis methodology has been adapted to produce the maximum

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amount of clean energy in a pilot scale system [3], the amount of byproducts expected at this scale, particularly char, will be high (approximately. 400 tpa yr^{-1} of char production). Analysis of the byproducts suggest that they will be difficult to utilise in commercial applications due to the POPs content in the oils [4] and the high metal concentration within the char fractions [5]. Previous experiments in the laboratory and pilot-scale of ASR pyrolysis use the raw feedstock with no additives to the process to enhance products. Addition of a catalyst to remove contaminants to improve byproducts is something that has not yet been explored, yet has been utilised to improve byproducts in other pyrolysis systems using other feedstocks [6]–[8].

Common catalysts used within industrial pyrolysis processes are zeolites. Zeolites are aluminosilicate complex structured minerals containing a range of earth metals including Na, Ca, Mg and Fe and are formed through the crystallisation of ash and rocks during volcanic eruptions in response to groundwater and saline lakes [9]. Synthetic zeolites have been developed from mineral sources to have a better performance in pyrolysis processes, where the higher pH and increased porosity increases the syngas yield [10]. Common synthetic zeolites used in the petrochemical industry are molecular sieves, crystalline alumino-silicates with a three-dimensional interconnecting network of aluminium and silica tetrahedra [9]. The increased acidity of synthetic zeolites can increase the deoxygenation and isomerization of hydrocarbons, improving the use as a biofuel and within energy systems [11]–[13]. Molecular sieves, such as 3Å and 4Å, are synthesized to increase the adsorption of hydroxyl compounds and to dehydrate unsaturated hydrocarbons within pyrolysis vapours, which improves the quality of bio-oil and cleans the syngas [11], [14]. Another common synthetic mesoporous catalyst used in pyrolysis is MCM-41, an SiO_2 complex with cylindrical mesopores, which can be loaded with different metal bases. MCM-41 complexes are efficient at the dehalogenation of feedstocks, increasing decontamination of the byproducts [15], [16]. With ASR containing a large number of halogenated compounds within the plastic and foam fractions, utilisation of synthetic catalysts could be used to adsorb these contaminants.

A laboratory scale experiment has been designed to investigate the effects of synthetic catalyst addition on the effects on the yield and quality of char and oil byproducts. The aim of this experiment is to determine whether catalyst addition can upgrade the byproducts from ASR pyrolysis to meet demands of commercial markets.

2 MATERIALS AND METHODS

The ASR used for this laboratory-scale experiment was sourced from a commercial ELV recycling company located in the UK. Prior to conducting the lab-scale pyrolysis experiment, compositional analysis was conducted on 3 kg of a one tonne sample of ASR to determine accurate mass of each fraction to apply to each pyrolysis sample when scaled down. The composition of the ASR fractions was similar to that used by Khodier et al. [3].

Four catalysts were tested during this experiment: (1) 3Å molecular sieve: $(Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]xH_2O)$; (2) 4Å molecular sieve: $K_nNa_{12-n}[(AlO_2)_{12}(SiO_2)_{12}]xH_2O$; (3) MCM-41: SiO_2; (4) Al-MCM-41: $(SiO_2)_1(Al_2O_3)_{25}$. These catalysts were chosen because they are commonly used within the petrochemical industry yet to be used in ASR pyrolysis. Both 3Å and 4Å were predicted to improve the oil by adsorption of hydroxyl compounds and MCM-41 were predicted increase cracking of PAHs. The catalysts were applied in-situ at a ratio of 1:10, which is a common dosage used in other research studies [17]–[19]. In addition to the catalyst, a control sample of ASR without catalyst was also tested.

These experiments were conducted using a laboratory scale system set-up at the University of Central Lancashire (UCLan), UK (Fig. 1). ASR samples were prepared by separating the heterogenous mixture into fractions and these were individually weighed. The

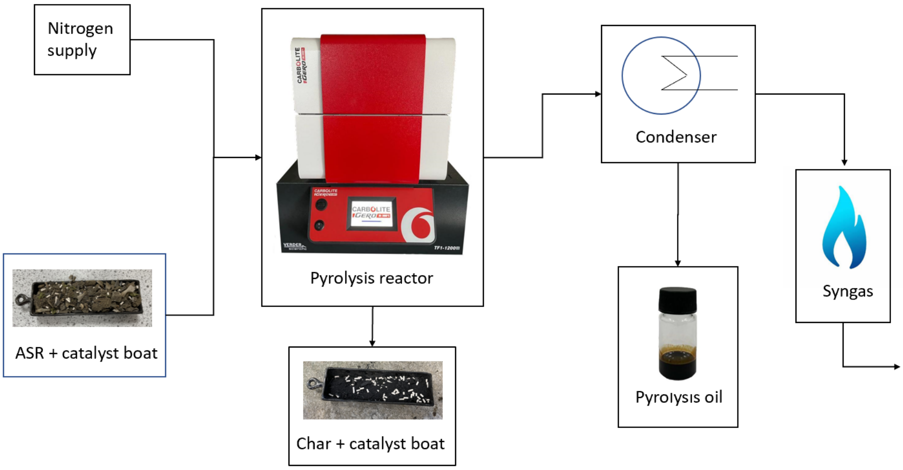

Figure 1: Laboratory scale pyrolysis process (10 g).

test sample was prepared by adding 1g of catalyst to the reconstituted sample. The catalyst and ASR were added to a quartz sample holder and weighed prior to pyrolysis.

The 10 g sample was added to the pyrolysis reactor at 500°C for 30 minutes under a nitrogen atmosphere. This was chosen as the optimum temperature for the catalysts was between 450–550°C. Oil deposits were collected from the condenser and measured. The percentage yield for the non-gaseous byproducts was determined. The collected char and oil were chemically characterised. Pyrolysis char was analysed for metal concentration and organic elemental analysis. Pyrolysis oil was analysed for POPs, organic elemental analysis and deoxygenation.

Metal concentration was analysed using ICP-OES. Firstly, char was prepared by acid digestion, where 0.1 g sample was added to 10 ml nitric acid and microwaved at 200°C for 25 minutes (0–200°C over 10 minutes, held for 15 minutes). Acid digests were diluted 100x in 18mQ e-pure water and analysed on the ICP-OES (ThermoScientific iCap 7000 series) for 11 analytes.

Organic elemental analysis was conducted using a CHNS-O organic elemental analyser (ThermoScientific Flash 2000 series). The pyrolysis byproduct was measured (2–3 mg for char, 5–6 mg for oil) using an analytical balance and pyrolysed at 900°C and passed through a GC column. A BBOT (2,5-Bis(5-tert-butyl-2-benzo-oxalzol-2-yl) thiophene, ($C_{26}H_{26}N_2O_2S$)) standard was used to calibrate the system.

POPs in pyrolysis oil were analysed using a ThermoScientific Trace 1300 GC-MS (Gas Chromatography–Mass Spectrometry). 1 µl of oil sample was injected into the GC, with an inlet temperature of 250°C and passed through a 5 MS column under a gradient temperature program ((1)50°C, isocratic for 3 minutes; (2) temperature gradient of 10°C min^{-1} until a maximum temperature of 320°C; (3) isocratic at 320°C for 5 minutes). The separated compounds were detected by the mass spectrometer and identified using the NIST library. The composition of the compounds within the sample were determined through measuring the percentage of the compound within the total sample.

In addition to GCMS analysis, oil was analysed using a ThermoScientific is5 Fourier Transform Infrared (FTIR). The spectrum was used to identify any changes in molecular structure within the compound and identified changes in the oil product from the control.

3 RESULTS

3.1 Effect on yields

The percentage yield of byproducts changed under catalyst addition, with differences identified between catalyst type (Fig. 2). Under all catalyst treatments, the oil percentage yield was lower, with the reduction ranging from 2.17–6.06%. Char yield increased under 3Å (26.19%), 4Å (39.53%) and MCM-41 (8.33%).

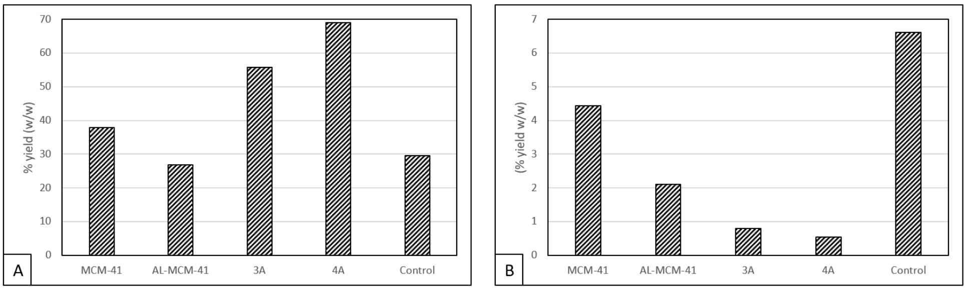

Figure 2: The percentage yield of pyrolysis byproducts. (A) Char; and (b) Oil under four catalyst treatments (MCM-41, Al-MCM-41, 3Å and 4Å) and a control.

3.2 Char results

In comparison with the control, char increased C% under three catalysts (MCM-41, Al-MCM-41 and 4Å). The highest increase was under the Al-MCM-41 catalyst (17.32%). The lowest C% was 3Å, which also had the highest moisture content (9.9%). All catalyst treatments reduced the sulphur contamination in the char (Table 1). Metal concentration reduced for all analytes except for the metal Mg. The catalyst Al-MCM-41 reduced the concentration of the maximum number of analytes (Table 1).

3.3 Oil results

In comparison with the control, the C% was not significantly different under the catalysts (Table 2). This trend was replicated in H%. Under all catalyst treatments, there was an increase in N%. No sulphur was detected in pyrolysis oil from ASR feedstock.

The number of PAHs present in pyrolysis oil reduced under catalyst addition. In the control sample, the top five compounds represented 79.9% of the total sample composition, of which all were PAHs. The PAH compounds found in the control were larger in structure with more aromatic rings than the catalyst samples. The top five compounds detected in the control sample were: (1) Benz[a]azulene (33.8%); (2) Benzonitrile (13.8%); (3) Fluoranthene (11.6%); (4) Pyrene (10.7%); (5) Biphenylene (10.0%). In comparison, there were small amounts of PAHs detected in pyrolysis oil with catalysts (i.e. biphenyl) but these were detected at smaller quantities within the overall composition (i.e. 3.84% Biphenyl detected under 3Å catalyst; Table 3). The molecular structure of PAHs detected in oils produced with a catalyst were lower in mass with less benzene rings than the control sample. Of the compounds present within all catalyst samples (Table 3), there are similar amounts of smaller

Table 1: Physio-chemical analysis of char produced from pyrolysis of ASR with catalysts (MCM-41; Al-MCM-41; 3Å; 4Å) and a control.

	MCM41	**ALMCM41**	**3Å**	**4Å**	**Control**
Moisture content (%)	0.56	0.18	9.90	0.16	1.92
Loss on ignition (%)	41.53	52.54	51.95	54.95	48.81
Mg (mg kg^{-1})	6065	5241	11,158	3581	3472
K (mg kg^{-1})	0	0	85	0	624
Ca (mg kg^{-1})	18,866	34,293	19,659	39,809	39,788
Ba (mg kg^{-1})	3273	3205	1456	1749	4965
Mn (mg kg^{-1})	115	243	75	156	768
Fe (mg kg^{-1})	13,793	21,331	11,311	15,365	49,188
Cr (mg kg^{-1})	64	20	652	48	272
Ni (mg kg^{-1})	0	0	0	454	53
Cu (mg kg^{-1})	6104	681	3407	1260	5368
Zn (mg kg^{-1})	3622	6644	2862	4736	7900
Pb (mg kg^{-1})	529	1006	457	899	1867
N (%)	0.90	0.64	0.60	0.73	1.10
C (%)	45.50	52.23	32.50	45.26	34.91
H (%)	4.04	6.31	2.98	6.10	3.68
S (%)	0.00	0.00	0.00	0.00	0.42

Table 2: Organic elemental analysis of pyrolysis oil following pyrolysis of ASR under catalyst addition (3Å; 4Å; Al-MCM-41; MCM-41) and a control treatment.

	3Å	**4Å**	**MCM-41**	**Al-MCM-41**	**Control**
N (%)	1.10	0.94	1.86	1.70	0.90
C (%)	83.27	81.35	77.82	80.71	80.92
H (%)	12.85	12.43	11.29	11.42	11.70
S (%)	0.00	0.00	0.00	0.00	0.00

Table 3: Common compounds detected within pyrolysis oil produced with addition of a catalyst and a control sample.

	Control	**MCM-41**	**Al-MCM-41**	**3Å**	**4Å**
Benzenebutanitrile (%)	0.0	3.6	5.6	5.0	6.1
11-Methyldodecanol (%)	0.0	4.5	6.2	3.0	9.7
Biphenyl (%)	2.7	2.1	0.0	3.9	1.6
Styrene (%)	0.0	4.5	1.8	0.3	0.0
Naphthalene isomers (%)	5.0	1.9	7.3	0.3	4.9
Total number of compounds detected	55	77	56	74	79

PAHs (Table 3) such as naphthalene isomers. A reduction in large chain PAHs without reducing the C% (Table 2) indicates a positive effect on the oil, without negatively impacting calorific value.

FTIR analysis indicated differences in absorbance between the control sample and oils produced with a catalyst (Fig. 3). It was indicated in the FTIR spectra that addition of a catalyst reduced the absorbance of O-H bonds (Fig. 3(A): 3253.84 cm^{-1}, circled) and increased the absorbance of C-H bonds within the alkane stretch (2868–2960 cm^{-1}). Molecular sieve catalysts (3Å and 4Å) presented a similar composition to the control, with peaks at 1718 cm^{-1} and 1100 cm^{-1}, where MCM catalysts (MCM-41 and Al-MCM-41) absorbed at different wavelengths within the fingerprint region.

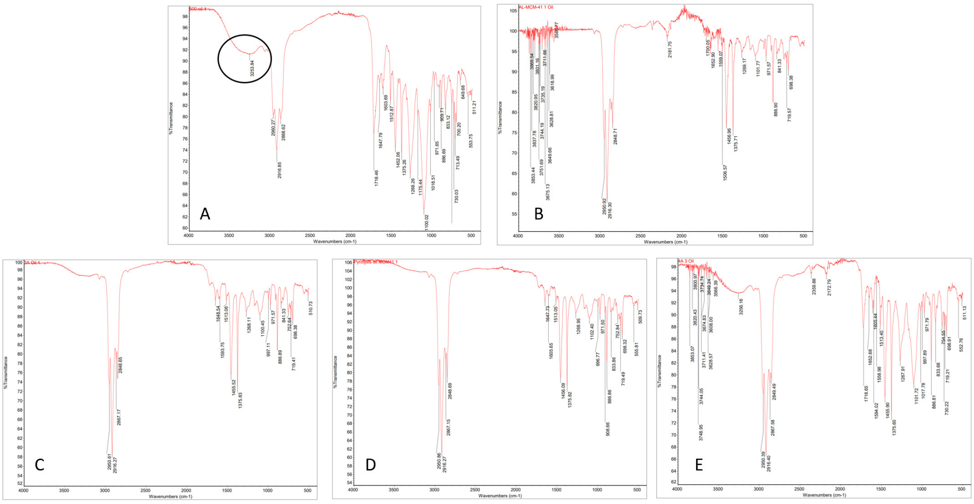

Figure 3: FTIR transmission spectra of pyrolysis oil produced from pyrolysis of ASR feedstock with catalyst addition. (A) Control; (B) Al-MCM-41; (C) 3Å; (D) MCM-41; and (E) 4Å.

4 DISCUSSION

4.1 Effects of catalyst on char production

Pyrolysis char with high carbon concentration can increase the utilisation within commercial markets, where a higher carbon concentration increases carbon sequestration in soil applications [20], [21] and improves catalytic reforming of tar in gasification [22]. Char can be used as a substitute for activated carbon in adsorption processes, where the porosity of char and a high carbon content are the main limitations for its use within these markets [23]. The carbon concentration was increased under three catalyst treatments; 4Å (10.35%), MCM-41 (10.59%) and Al-MCM-41 (17.32%), where the maximum C% recorded was under Al-MCM-41 (52.23%; Table 2). This is an acceptable C% for soil applications [24], however further upgrading would be required to replicate activated carbon and gain access to these markets [25]. It was indicated in Benedetti et al. [23] that the C% could be influenced by temperature, where chars produced at 650°C temperature were between 22.76–43.36% lower than the highest C% (91.39%; 850°C). Increasing the pyrolysis temperature could potentially improve the char consistency and char yield as seen in previous experiments [3], however would reduce the activation energy of the catalyst. Further experiments could explore secondary pyrolysis processing of improved char at increased pyrolysis temperatures to determine whether it improves the carbon properties further.

The metal concentration within char produced from ASR limited its usability within commercial markets, with the main contaminant being Pb [5]. Catalyst addition to char reduced the metal concentration of ten metal compounds, where the highest reduction in Pb concentration came from 3Å, where a 75.6% reduction was determined (Table 1). A general trend between the carbon concentration and metal concentration was detected, where a lower metal contamination correlated with an increase in carbon concentration. In addition to Pb, there are other analytes which may influence the char's utilisation in more specific markets. For example, a char with a high Fe limits its utilisation in concrete applications, where a high Fe can reduce the mechanical strength [26]. The lower Fe concentration and lower organic content determined in char under MCM-41 catalyst (Fe = 71.96% reduction; Table 1) indicated that this treatment would be most effective to trial as a concrete additive. Cu and Ni are also metals in already high concentration within contaminated land [27], where activated carbons are designed to remove these ions from soil [28], [29]. A reduction in both Cu and Ni was determined under Al-MCM-41 and 3Å catalyst upgrading (Table 1). These catalyst treatments would be better suited for activated carbon applications.

The results in this experiment suggested that Al-MCM-41 was the most effective catalyst in upgrading char, where 10 of 11 metal concentrations were reduced compared with the control sample, and the highest C(%) was recorded (53%). However, further upgrading would be required to meet commercial market requirements (EN ISO 21340) for activated carbon [30]. For soil applications, although a reduction in Pb was determined (46.1%) the resulting concentration was still too high (1006 mg kg^{-1}; Table 2) to meet environmental standards [31]. This was the only metallic element tested that limited utilisation within this market. If the commercial product of pyrolysis char was decided to be a soil improver, 3Å catalyst would be more effective, which had the highest reduction in Pb concentration (75.5%). Further analysis of the PAH concentration would confirm whether pyrolysis char could be utilised in soil applications. Previous research suggested a lower pyrolysis temperature can reduce the PAH concentration in char [32], therefore it might be lower than previous findings [4], where pyrolysis temperature was 850°C.

4.2 Effects of catalyst on oil composition

The oil produced from pyrolysis ASR feedstock at a pilot-scale system indicated that there were high levels of PAHs within the oils and high oxygen concentration [4]. In its current state, the pyrolysis oil produced using optimum methodology for gas production (pyrolysis at 850°C; [2]) would require upgrading or secondary processing before utilisation in commercial markets. This experiment used a lower pyrolysis temperature (500°C), as it was the maximum activation temperature for the catalysts selected. In turn, this pyrolysis temperature was predicted to benefit oil production, where oil yield and heating value is higher at lower temperatures [33], [34]. The control sample at 500°C produced a higher yield of oil (6.61% w/w) compared with catalyst treatments (0.55–4.44%; Fig. 1). A reduction of yield under catalyst addition has also been experienced in experiments trialling other feedstocks with catalysts, where the dehydrogenation effects reduced the water content within the oil [35], [36].

The PAH compounds detected in the control (Table 3) were no longer present in any of the catalyst samples. Lower concentrations of PAHs were detected within the catalyst samples, however these compounds consisted of two benzene rings (Table 3) compared with multiple in the control (66.1% of top five compounds detected). This indicates that the catalysts were effective in cracking the hydrocarbon chains [37]. Table 3 shows the common compounds determined in all of the catalyst samples, of which some were not present in the control. These could be some of the compounds being produced following cracking. Although a lower yield of oil in catalyst samples compared with the control (Fig. 2), it is apparent from the reduction in PAHs determined from the GCMS results that the oil is of better quality, where for all catalyst samples the quantity of PAHs were reduced and an increase in single aromatic hydrocarbon chains was determined [38]–[40]. A reduction in PAHs in oil from addition of catalysts could increase the saleability of pyrolysis oil to commercial and industrial markets, whilst reducing the environmental impact of the oil by reducing its hazardous properties.

To utilise oil as a fuel substitute within industrial or automotive applications, it is required that there is $< 0.005\%$ contamination of sulphur [41]. In addition to this, the heating value of the oil will determine how effective it is as a fuel, where long chain hydrocarbons with low aromaticity and low oxygen concentration have higher calorific contents [42]. Low oxygen concentration also increases the C=O bonds. No sulphur was detected in the oil (Table 2), therefore, it would meet the specifications required for usage as a fuel [41]. Further investigations of the calorific content of the oil produced under catalyst addition would provide more information on the oil value.

Of the four catalyst samples, this experiment indicated that 4Å was the most effective. Under this catalyst, 0% of the oil composed of PAHs and sulphur-compounds. The oil sample also contained 0% of halogenated compounds compared with the other catalysts, which will reduce the toxicity and corrosion effects of the oil. Chlorinated compounds are present in the feedstock in plastic wiring which contains PCBs and fluorinated and brominated compounds are present in fire retardants, which are often in the textiles fraction where retardants are applied [43], [44]. The catalysts used are designed to adsorb Cl and F gasses [45], however, to confirm this, further tests on the catalysts would be required.

5 CONCLUSION

The application of readily available catalysts within the pyrolysis of ASR reduced the PAHs within the oil and elemental content of the char. However, there are many challenges ahead in meeting commercial requirements. Catalyst performance at a larger scale may react differently to a lab-scale, so further work testing the effective catalysts at a pilot-scale will provide further information on upgrading pyrolysis byproducts from ASR. To enhance sustainability of ELV waste recycling, it is essential that the catalysts do not create any further hazardous waste and can be economically viable. Further testing of the catalyst effects on adsorption of contaminants and recycling within the pyrolysis system will determine whether this is an effective option for treating ASR.

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REFERENCES

[1] European Commission, Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of-life vehicles. Official Journal of the European Communities. https://eur-lex.europa.eu/resource.html?uri=cellar:02fa83cf-bf28-4afc-8f9f-eb201bd61813.0005.02/DOC_1&format=PDF. Accessed on: 25 Jun. 2023.

[2] Khodier, A., Williams, K.S. & Dallison, N., Pilot-scale thermal treatment of automotive shredder residue: Pyrolysis char is a resource or waste? *WIT Transactions on Ecology and the Environment*, vol. 224, WIT Press: Southampton and Boston, pp. 439–450, 2017.

[3] Khodier, A., Williams, K.S. & Dallison, N., Challenges around automotive shredder residue production and disposal. *Waste Management*, **73**, pp. 566–573, 2018.

[4] Williams, K.S. & Khodier, A., Meeting EU ELV targets: Pilot scale pyrolysis automotive shredder residue investigation of PAHs, PCBs, and environmental contaminants in the solid residue products. *Waste Management*, **105**, pp. 233–239, 2020.

[5] Bentley, P., Williams, K. & Khodier, A., How the physio-chemical properties of char from the pyrolysis of automotive shredder residue (ASR) influences its future uses. *Pure and Applied Chemistry,* pp. 1–15, 2023.

[6] Yu, F.-W., Ji, D.-X., Yong, N., Yao, L., Huang, C.-J. & Ji, J.-B., Study on the pyrolysis of cellulose for bio-oil with mesoporous molecular siev catalysts: Biorefinery of biomass for bioenergy. *Applied Biochemistry and Biotechnology*, **168**(1), pp. 174–182, 2012.

[7] Li, Z., Zhong, Z., Zhang, B., Wang, W., Seufitelli, G.V.S. & Resende, F.L.P., Catalytic fast co-pyrolysis of waste greenhouse plastic films and rice husk using hierarchial micro-mesoporous composite molecular sieve. *Waste Management*, **102**, pp. 561–568, 2020.

[8] Sun, T. et al., Effects of reaction temperature and molecular sieve catalyst on the distribution of pyrolysis products of biomass components. *Industrial Crops and Products*, **191**, 116012, 2023.

[9] Inglezakis, V.J. & Zorpas, A.A., *Handbook of Natural Zeolites*, Bentham Science: Oak Park, IL, 2012.

[10] Rehan, M. et al., Effect of zeolite catalysts on pyrolysis liquid oil. *International Biodeterioration and Biodegradation*, **119**, pp. 162–175, 2017.

[11] Kubička, D. & Kikhtyanin, O., Opportunities for zeolites in biomass upgrading: Lessons from the refining and petrochemical industry. *Catalysis Today*, **243**, pp. 10–22, 2015.

[12] Li, X., Chen, G., Liu, C., Ma, W., Yan, B. & Zhang, J., Hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts: A critical review. *Renewable and Sustainable Energy Reviews*, **71**, pp. 296–308, 2017.

[13] Han, T., Ding, S., Yang, W. & Jönsson, P., Catalytic pyrolysis of lignin using low cost materials with different acidities and textural properties as catalysts. *Chemical Engineering Journal*, **373**, pp. 846–856, 2019.

[14] Rjeily, M.A., Gennequin, C., Pron, H., Abi-Aad, E. & Randrianalisoa, J.H., Pyrolysis-catalytic upgrading of bio-oil and pyrolysis-catalytic steam reforming of biogas: A review. *Environmental Chemistry Letters*, **19**, pp. 2825–2872, 2021.

[15] Ma, C. et al., Pyrolysis-catalytic upgrading of brominated high impact polystyrene over Fe and Ni-loaded catalysts: Influence of HZSM-5 and MCM-41 catalysts. *Polymer Degradation and Sustainability*, **146**, pp. 1–12, 2017.

[16] de Souza, M.J.B., Silva, T.H.A., Ribeiro, T.R.S., da Silva, A.O.S. & Pedrosa, A.M.G., Thermal and catalytic pyrolysis of polyvinyl chloride using micro/mesoporous ZSM-35/MCM-41 catalysts. *Journal of Thermal Analysis and Calorimetry*, **140**(1), pp. 167–176, 2020.

[17] Zou, R. et al., Microwave assisted co-pyrolysis of lignin and waste oil catalyzed by hierarchical ZSM-5/MCM-41 catalyst to produce aromatic hydrocarbons. *Bioresource Technology*, **289**, 121609, 2019.

[18] Yang, Y., Zhang, J., Zhang, J., Liu, Q. & Qian, G., Influence of catalysts on bio-oil yield and quality: A review. *Environmental Science and Pollution Research*, **29**(21), pp. 30986–31002, 2022.

[19] Singh, T.S., Verma, T.N. & Sing, H.N., A lab scale waste to energy conversion study for pyrolysis of plastic with and without catalyst: Engine emissions testing study. *Fuel*, **277**, 118176, 2020.

[20] Crombie, K. & Mašek, O., Pyrolysis biochar systems, balance between bioenergy and carbon sequestration. *Global Change Biology*, **7**(2), pp. 349–361, 2015.

[21] Cisse, I., Hernandez-Charpak, Y.D., Diaz, C.A. & Trabold, T.A., Biochar derived from pyrolysis of common agricultural waste feedstocks and co-pyrolysis with low density polyethylene mulch film. *Waste and Biomass Valorization*, **13**, pp. 3913–3932, 2022.

[22] Šuhaj, P., Husár, J. & Haydary, J., Gasification of RDF and its components with tire pyrolysis char as tar-cracking catalyst. *Sustainability*, **12**(16), p. 6647, 2020.

[23] Benedetti, V., Patuzzi, F. & Baratieri, M., Characterization of char from biomass gasification and its similarities with activated carbon in adsorption applications. *Applied Energy*, **227**, pp. 92–99, 2018.

[24] Osman, A.I. et al., Biochar for agronomy, animal farming, animal digestion, composting, water treatment, soil remediation, construction, energy storage and carbon sequestration: A review. *Environmental Chemistry Letters*, **20**(4), pp. 2385–2486, 2022.

[25] Li, Y., Chang, F., Huang, B., Song, Y., Zhao, H. & Wang, K., Activated carbon preparation from pyrolysis char of sewage sludge and its adsorption performance for organic compounds in sewage. *Fuel*, **266**, 117053, 2020.

[26] Rickard, W.D.A., Williams, R., Temuujin, J. & van Riessen, A., Assessing the suitability of three Australian fly ashes as an aluminosilicate source for geopolymers in high temperature applications. *Materials Science and Engineering. A, Structural Materials: Properties Microstructure and Processing*, **528**(9), pp. 3390–3397, 2011.

[27] Gopalapillai, Y., Siciliano, S.D. & Hale, B.A., Is assuming additivity of single-metal toxicity thresholds a conservative approach to assessing risk of ecotoxicity from elevated soil concentrations of cobalt, copper, and nickel at contaminated land sites? *Integrated Environmental Assessment and Management*, **17**(4), pp. 753–766, 2021.

[28] Buraschevskaya, M. et al., The effect of granular activated carbon and biochar on the availability of Cu and Zn to hordeum sativum distichum in contaminated soil. *Plants*, **10**(5), p. 841, 202.

[29] Mukhopadhyay, R. et al., Nanomaterials for sustainable remediation of chemical contaminants in water and soil. *Critical Reviews in Environmental Science and Technology*, **52**(15), pp. 2611–2660, 2022.

[30] ISO (International Standards Organisation), ISO 21340: Test methods for fibrous activated carbon, 2017.

[31] Environmental Agency, Derivation and use of soil screening values to assess ecological risks, 2017. https://www.gov.uk/government/publications/soil-screening-values-for-assessing-ecological-risk. Accessed on: 22 Jun. 2023.

[32] Sajdak, M. et al., Perspectives of using sewage sludge char in CO_2 sequestration on degraded and brownfield sites. *Energies*, **16**(9), pp. 3945–3955, 2023.

[33] Kumar Singh, R. et al., Pyrolysis of three different categories of automotive waste tyre wastes: Product yield analysis and characterization. *Journal of Analytical and Applied Pyrolysis*, **135**, pp. 379–389, 2018.

[34] Wijayanti, W., Musyaroh, M. & Sasongko, M., Low-density polyethylene plastic waste to liquid fuel using pyrolysis method: An effect of temperatures on the oil yields physiochemical properties. *Journal of Sustainable Development of Energy, Water and Environment Systems*, **10**(3), pp. 1–18, 2022.

[35] Yu, F., Ji, D., Nie, Y., Luo, Y., Huang, C. & Ji, J., Study on the pyrolysis of cellulose with mesoporous molecular sieve catalysts. *Applied Biochemistry and Biotechnology*, **168**(1), pp. 174–182, 2012.

[36] Kumar, P., Kumar, P., Rao, P.V.C., Choudary, N.V. & Sriganesh, C., Saw dust pyrolysis: Effect of temperature and catalysts. *Fuel*, **199**, pp. 339–345, 2017.

[37] Fuentes, C., Colman Lerner, J., Vázquez, P. & Sambeth, J., Analysis of the emission of PAH in the thermal and catalytic pyrolysis of polystyrene. *Catalysis Today*, **372**, pp. 175–182, 2021.

[38] Vispute, T.P., Zhang, H., Sanna, A., Xiao, R. & Huber, G.W., Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. *Science*, **330**(6008) pp. 1222–1227, 2010.

[39] Zhang, J., Choi, Y.S. & Shanks, B.H., Catalytic deoxygenation during cellulose fast pyrolysis using acid-base bifunctional catalysts. *Catalysis Science and Technology*, **6**(20), pp. 7468–7476, 2016.

[40] Kabir, G. & Hameed, B.H., Recent progress on catalytic pyrolysis of lignocellulosic biomass to high grade bio-oil and bio-chemicals. *Renewable and Sustainable Energy Reviews*, **70**, pp. 945–967, 2017.

[41] HM Revenue and Customs, UK Government, Biofuels and other fuel substitutes (Excise Notice 179e) from 1 April 2022.

[42] Evangelopoulos, P., Sophonrat, N., Jilvero, H. & Yang, W., Investigation on the low temperature pyrolysis of automotive shredder residue (ASR) for energy recovery and metal recycling. *Waste Management*, **76**, pp. 507–515, 2018.

[43] Czarnecka-Komorowska, D., Kanciak, D., Barczewski, M., Barczewski, M. & Regulski, R., Recycling of plastics from cable waste from automotive industry in Poland as an approach to the circular economy. *Polymers (20473630)*, **13**(21), pp. 3845–3846, 2021.

[44] Bansal, O.P., Bhardwaj, M.K. & Gupta, V., Per- and polyfluoroalkyl substances (PFAs) in the environment: A review. *Journal of Advanced Scientific Research*, **13**(7), pp. 1–26, 2022.

[45] Kawai, T. & Tsutsumi, K., Adsorption behaviour of organic halides on zeolites. *Colloid and Polymer Science,* **287**(5), pp. 569–575, 2009.