Conversion of End-of-Life Vehicle Tyres as Chemical Feedstock for the Production of Diesel Range Liquid Fuel and Char*

E. A. Arthur[1], G. Mensah-Sackey[2], S. I., Baisi Ebo[1], D. Asubonteng[3], J. Dankwah[1, 4], E. Abotar[1], Y. Ankomah[1],

I. Adimado[1] and J. R. Dankwah[1]

[1]University of Mines and Technology (UMaT), Tarkwa, Ghana
[2]Egypt-Japan University of Science and Technology (EJUST), Alexandria, Egypt
[3]Universiti Teknologi PETRONAS, Perak, Malaysia
[4]Goldfields Ghana Limited (Damang Mine), Tarkwa, Ghana

Abstract

Globally, over 780 billion plastics are used and discarded annually, with no proven avenues for value recovery. End-of-life vehicle tyres from the mining industry which cannot be re-used are burnt (as a disposal method) at isolated areas by scrap dealers and steel wires retrieved for sale to the iron and steel making industry. The huge amounts of gaseous pollutants released into the atmosphere as a result promote greenhouse effect and global warming. The focus of this research was investigating the feasibility of creating a diesel-compatible liquid fuel and char from end-of-life vehicle tyres (EVTs) using a temperature range of 300 °C – 670 °C from a charred palm kernel shell-fired reactor-blower assembly as a sustainable method of disposing EVTs. Samples of EVTs were collected from Tarkwa Municipality in the Western Region of Ghana and were shredded and dried in the open. Approximately 2 kg of samples of the shredded EVTs were introduced into a stainless-steel reactor and subjected to pyrolysis for 55 minutes at a heating rate of 40 °C/min. The gas exiting the reactor was collected, cooled and liquefied in a plastic container, after which its mass was measured, and its properties were analyzed by FT-IR and GC-MS. The findings show that diesel-range liquid fuel (density 0.936 g/cm^3) can be generated with a yield of approximately 0.33 – 0.40 litres/kg from EVTs. Results from FT-IR and GC-MS analyses revealed that the liquid fuel is primarily composed of aromatic hydrocarbons, specifically alkyl benzenes, as well as aliphatic hydrocarbons and minor amounts of naphthenes. SEM-EDS analysis of the chars revealed partly carbonaceous material (67.18 ~ 86.67 wt.% C) that could burn to yield an ash rich in CaO, ZnO and TiO_2. It was concluded that the feasibility of end-of-life vehicle tyres pyrolysis offers a viable solution to end-of-life vehicle tyres disposal challenges faced by the mining industry and Ghana.

Keywords: End-of-life, Vehicle Tyres, Pyrolysis, Liquid Fuel, Char.

1 Introduction

The frequent use of polymeric articles and their averagely short in-service periods thereof increase plastic waste generation daily. According to Miandad *et al.* (2016) and Ratnasari *et al.* (2017), estimated global plastic production was about 300 million tons every year and the rise go on perpetually annually.

Frequently used polymeric articles like vehicle tyres play a significant role in the mining industry as they serve various transportation purposes. There is however a concern about the manner in which the vehicle tyres are disposed after use and the environmental challenges that arise due to the disposal. In the mining industry, worn-out or end-of-service vehicle tyres are scrapped off to "vulcanizers" or scrap dealers for re-use as second-hand vehicle tyres or for disposal. In terms of disposal, the scrap dealers burn the end-of-life vehicle tyres at isolated areas to retrieve steel wires from the tyres for sale to the iron and steel making industry. The huge amounts of gaseous pollutants released into the atmosphere by this action contribute to the greenhouse effect and global warming.

According to Rodriguez *et al.* (2001) and Islam and Nahian (2016), the open burning or incineration of tyres release toxic emissions such as polyaromatic hydrocarbons, benzene, styrene, butadiene, phenol-like substances, CO_2, CO, SO, and NO that pose significant risks to human health and the environment causing widespread harm and pollution. Plastic wastes must be managed to mitigate these risks posed to the environment and living things dwelling therein. Some other conventional and innovative ways of disposing and repurposing scrap vehicle tyres aside the aforementioned ones include landfilling, indiscriminate dumping, stockpiling, crumbling, remoulding/recycling and pyrolysis (Gandidi *et al.,* 2018; Swain, 2013; Galvagno and Cornacchia, 2002). Developing countries often resort to low-cost and straightforward scrap tyre disposal methods such as landfilling, dumping and open burning which unfortunately generate substantial health and environmental issues. These practices although easier and cheaper are detrimental to the environment and public health (Islam and Nahian,

2016; Rodriguez *et al.*, 2001). Some of the challenges of landfilling, indiscriminate dumping and stockpiling include the inability to compact the end-of-life tyres because they are bulky and 75% of the space a tyre occupies is void. Therefore, a large land space is required for these disposal methods while providing breeding grounds for insects and rodents that may cause various kinds of diseases (Alexandra, 2012; Islam and Nahian, 2016; Rodriguez *et al.*, 2001). Worse of it all, the composition of plastics includes hydrocarbons derived from petroleum, combined with additional chemicals like flame-retardants, stabilizers and oxidizers that make the bio-degradation of plastics challenging when landfilled (Ma *et al.*, 2017).

Recycling is one preferred waste disposal method due to its minimal impact on the environment. Producing fuels and chemicals from wastes with minutest effects on the environment brings hope of shutting the interval between global energy provision and request and also mitigates gases of greenhouse emission into the air (Matos *et al.*, 2013). Recycling methods however come with some setbacks such as mixing and segregation of wastes, high costs of labour in relation with segregation and processing, disposal of byproduct and its usage (Manickavelan *et al.*, 2022). Furthermore, transportation cost, labor cost and maintenance cost may elevate the overall expenditure associated with recycling projects (Gandidi *et al.*, 2018).

Researchers have thus developed keen interest in energy recovery systems due to these disadvantages. Comprehensive investigation in this area paved way to the conversion of plastic wastes into liquid fuel through a process known as pyrolysis (Manickavelan *et al.*, 2022). Pyrolysis technically involves all manners of heat disintegration (Abraham *et al.*, 2011). The pyrolysis method disintegrates long chain polymers into smaller but useful molecular weight compounds that can be harnessed as fuels or chemicals in a variety of ways. Pyrolysis is a conversion process, which means thermal decomposition at different high temperatures (300 – 900 °C) in an environment void of oxygen. This yields liquid products, char, volatiles and gases from waste rubbers or polymeric articles. The process of pyrolysis can be catalytic or solely thermal (Abraham *et al.*, 2011; O'Hara, 1981; Songip *et al.*, 1993; Uddin *et al.*, 1997; Manos *et al.*, 2000; Akpanudoh *et al.*, 2005; Gulab *et al.*, 2010; Jan *et al.*, 2010; Panda *et al.*, 2010; Cleetus *et al.*, 2013). Demirbas *et al.* (2016) produced a liquid product from waste tyres at elevated temperature (~600 °C) employing sodium carbonate as a catalyst. The rates of the conversion were increased using temperature and Na_2CO_3 catalyst. At 458 °C, a yield of 45.4% was achieved without Na_2CO_3 with 39.6% liquid produced. The highest yield of 54.8%

was obtained at 452 °C using 10% Na_2CO_3 resulting in a 49.2% of liquid production. In 1998, Uemichi *et al.* investigated the catalytic pyrolysis of polyethylene (PE) utilising HZSM-5 catalysts. The synthetic catalysts improved the overall pyrolysis process and enhanced the quality of liquid product obtained. The utilization of the synthetic catalysts, however, raised the cost of the pyrolysis process (Miandad *et al.*, 2019). A pyrolytic oil was produced non-catalytically by Quaicoe *et al.* (2020) from end-of-service vehicle tyres. The oil was described as a single-phase liquid with relatively lower density (850.6 kg/m^3) (at 15 °C), flashpoint (34.5 °C) and viscosity (0.904 cSt). Arthur *et al.* (2023) produced and investigated the products obtained from end-of-latex gloves pyrolysis (without the use of catalyst). The results indicated that samples of diesel range liquid fuel (density 0.858 g/cm^3) can be produced from end-of-latex gloves with a yield in the range of 0.40-0.78 litres/kg.

Accordingly in this investigation, researchers aimed at the non-catalytic conversion of end-of-life vehicle tyres into diesel range liquid fuel and char via pyrolysis.

2 Resources and Method

2.1 Materials
Feedstock (Fig. 1) used for the investigation was a sample of end-of-life vehicle tyres collected from within the Tarkwa Municipality.

Fig. 1 A sample of End-of-life Vehicle Tyres utilised for the Investigation

Samples of the shredded vehicle tyres which weighed about 2 kg were used for four sets of pyrolysis runs and the average outcome determined.

2.2 Methods

The experimental setup consisted of a heating assembly (charred palm kernel shell fired furnace), self-designed pyrolysis reactor (Fig. 2), condensers A and B kept at 42 °C and 30 °C respectively, and a collecting plastic container. Condenser A was a coiled copper tube and condenser B was water in the plastic container. Samples of end-of-life vehicle tyres were fed from the top of the reactor for pyrolysis.

Fig. 2 Experimental Reactor used for the Investigation

2.2.1 Thermal Degradation (Non-Catalytic Pyrolysis)

The experiment was done using only heat to help determine the maximum temperature of the spontaneous conversion process without the action of catalysts. Temperature readings were recorded using a BENETECH GM900 Infrared Thermometer (Fig. 3).

Fig. 3 BENETECH GM900 Infrared Thermometer used for Temperature Measurements in this Investigation

The steps involved in the non-catalytic pyrolysis of the vehicle tyres are shown in Fig. 4.

Samples of the shredded EVTs weighing approximately 2.0 kg were introduced into the stainless-steel reactor from the top and pyrolysed for 55 minutes at a spontaneous heating rate of 40 °C/min. The experiment ran in a temperature range of 300 °C to 670 °C.
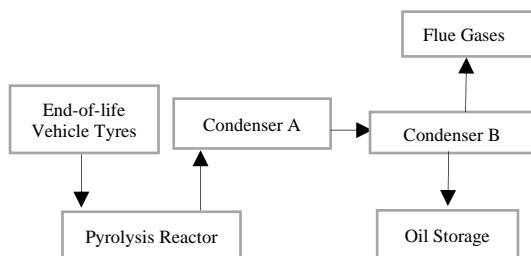

Fig. 4 Reaction Scheme for the Non-Catalytic Pyrolysis of End-of-Life Vehicle Tyres

After reaching a suitable temperature of 300 °C, the tyres in the reactor decomposed, causing volatile products to leave the reactor and move through air-cooled copper coils and high-pressure gas hose as primary condensers. The gas hose carrying volatile products was directed through 3.6 litres of water contained in an eight-litre HDPE gallon, serving as the secondary condenser, to help condense any gases that could not condense previously. This process could lead to a decrease in gas emissions. Any gases that could not condense escaped through a hole in the cork of the eight-litre gallon and got collected. The water in the container collected the liquid fuel that was obtained and was then extracted for analysis.

2.3 Yield of the Fuel Production Process

The yield of the process (l/kg) was calculated from the volume of liquid fuel per weight of vehicle tyres pyrolysed as shown in equation (1):

$$Yield = \frac{Volume\ of\ fuel\ (L)}{Weight\ of\ vehicle\ tyre\ pyrolysed\ (kg)} \quad (1)$$

2.4 Characterisation of Liquid Fuel and Char Residue Produced

The liquid fuel and char produced from the pyrolysis of the end-of-life vehicle tyres were characterised by FT-IR analysis with the aim of identifying various functional groups present to determine whether the liquid fuel produced mimics a diesel fuel. The liquid fuel was also characterised by GC-MS and the various polymers present were detected. The char was further analysed using SEM/EDS and XRD to detect the various elements and compounds present respectively.

3 Results and Discussion

3.1 Results of Thermal Degradation (Non-Catalytic Pyrolysis)

Gas emissions (evident by bubbling in condenser 'B') commenced at 35 seconds of heating. This gas upon testing with naked fire was flammable, indicating shorter range hydrocarbon gases $(C_1 – C_5)$ which could not be condensed at the temperatures of the condensers. The condensation process of the condensable gases beyond C5 mainly occurred in condenser 'A' throughout the pyrolysis process. The flow of liquid from condenser 'A' to 'B' began shortly after the bubbling of gases had begun. This continued until approximately 55 minutes where bubbling in condenser B ceased, and no liquid flowed from condenser A. The oil was later collected and stored in mini-HDPE gallons (Fig. 5) with a yield in the range of 0.33 – 0.40 l/kg (33 wt.% - 40 wt.%) which overlaps with 34.03 wt. % yield obtained by Osayi *et al.*, (2017) and close to 45.5 % yield of liquid fuel by Demirbas *et al.* (2016) for the non-catalytic pyrolysis of vehicle tyres. A black char residue (47.5 wt. %) which is rich in carbon (Fig. 6) remained in the reactor.

Fig. 5 Samples of Liquid Fuel obtained from the Pyrolysis of End-of-Life Vehicle Tyres

Fig. 6 Char obtained after Non-Catalytic Pyrolysis

3.2 Characterisation of Materials and Pyrolytic Products

3.2.1 FT-IR Analysis of Raw Vehicle Tyre

Fig. 7 is the FT-IR spectrum of raw vehicle tyres which shows that it is predominantly made of aromatics. The peaks from the graph shown in Fig. 7 correlate with the alkanes, aromatics, alcohols, carboxylic acids, esters and alkyl halides in the infrared absorption spectrum. In Fig. 7, a weak peak at 2919 cm^{-1} and 2849.67 cm^{-1} conform characteristically to C-H stretch in alkanes of diesel fuel. The next three peaks at wavenumbers 1583 cm^{-1}, 1001.56 cm^{-1}, 526.28 cm^{-1} conform to C-C stretch (in-ring) in aromatics, C-O stretch in alcohols, carboxylic acids and esters, C-Br stretch in alkyl halides respectively.
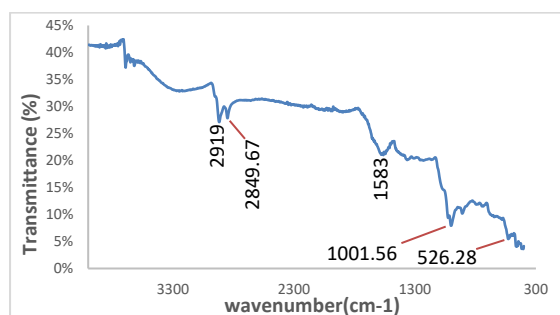

Fig. 7 FT-IR Spectrum of Raw Vehicle Tyre

Table 1 shows the frequencies with the related bonds and functional groups in the liquid fuel derived from the end-of-life vehicle tyres pyrolysis.

Table 1 Major Absorption Peaks and Assigned Configurations in the FT-IR Spectra of Raw Vehicle Tyre

Frequency (cm^{-1})	Bond	Functional group
2919	C-H stretch	alkanes
2849.67	C-H stretch	alkanes
1583	C-C stretch (in-ring)	aromatics
1001.56	C-O stretch	Alcohols, carboxylic acids, esters
526.28	C-Br stretch	Alkyl halides

3.2.2 FT-IR Analysis of Liquid Fuel Produced

Fourier Transform Infrared spectroscopy (FT-IR) was carried out to determine the various characteristic functional groups present in the oil. The FT-IR of the pyrolytic oil produced from the end-of-life vehicle tyres revealed strong peaks of alkanes, moderate and weak peaks of aromatics in the liquid fuel. Fig. 8 shows the various peaks and frequencies relating to functional groups in the liquid fuel.
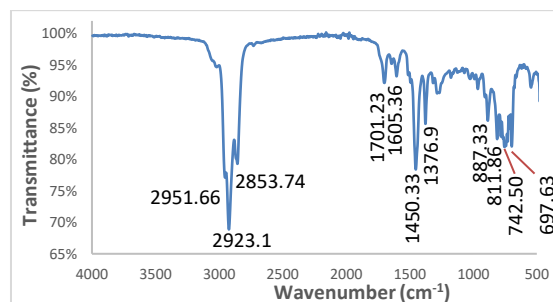

Fig. 8 FT-IR Spectrum of Liquid Fuel Produced from Vehicle Tyres

As observed in Fig. 8, weak peaks at 2951.66 cm^{-1} and 2853.74 cm^{-1} combine with a very prominent peak at wavenumber 2923.1 corresponding characteristically to Sp^3 C-H stretch in alkanes of diesel fuel. The next peak at wavenumber 1701.23 cm^{-1} is weak and conforms to C=O stretch in carboxylic acid. There is a weak peak at 1605.11 cm^{-1} which agrees with C-C stretch (in-ring) in aromatics. The prominent peak at 1450.33 cm^{-1} and moderate peak at 1376.9 cm^{-1} match to C-H bend and C-H rock in alkanes respectively. A weak peak at 887.33 cm^{-1}, 811.86 cm^{-1}, 742.50 cm^{-1} and 697.63 cm^{-1} conform to C-H "oop" in aromatics. The strong peaks of alkanes suggest the dominance of aliphatics in the pyrolytic fuel which is characteristic of diesel. Table 2 shows the frequencies with the related bonds and functional groups in the liquid fuel derived from the end-of-life vehicle tyres pyrolysis.

Table 2 Major Absorption Peaks and Assigned Configurations in the FT-IR Spectrum of the Liquid Fraction Derived from Vehicle Tyres

Frequency (cm^{-1})	Bonds	Functional Group

2951.66	Sp^3 C-H stretch	alkanes
2923.1	Sp^3 C-H stretch	alkanes
2853.74	Sp^3 C-H stretch	alkanes
1701.23	C=O stretch	carboxylic acid
1605.11	C-C stretch (in-ring)	aromatics
1450.33	C-H bend	Alkanes
1376.9	C-H rock	Alkanes
887.33	C-H "oop"	aromatics
811.86	C-Cl stretch	aromatics
742.50	C-H "oop"	aromatics
697.63	C-H "oop"	aromatics

3.2.3 Physicochemical Properties of Liquid Fuel Produced from End-of-life Vehicle Tyres

Table 4 shows comparison of the chemical and physical properties of the liquid fuel produced from vehicle tyre pyrolysis and those of SANS 342:2016 standard diesel.

Table 4 Physicochemical Properties of Liquid Fuels

Properties	Test Method	Unit	Vehicle Tyre Fuel	Standard Diesel* fuel
Density @ 20°C	ASTM D7042	g/cm³	0.936	0.800 min
Viscosity @ 40 °C	ASTM D7042	cSt	4.0	2.0-5.3
Flashpoint	ASTM D93	°C	27	55 min
Water Content	ASTM D6304	mg/kg	1.300	0.035 max
Total Contamination	IP440/SANS 52662	mg/kg	427.7	24 max
Sulphur	ASTM D4294	mg/kg	5900	500 max

*SANS 342:2016 standard diesel

At 20 °C, the density of the pyrolysis fuel from the vehicle tyre was 0.936 g/cm³ which is above the minimum standard density of conventional diesel fuel (0.800 g/cm³). High mass density of liquid fuel in general increases engine efficiency as it influences calibration of engine and its power, as the mass of fuel injected changes with fuel density (Radovanovic *et al.,* 2000; Islam and Beg, 2004; Demirbas, 2007). Therefore, fuel density primarily affects engine combustion and emission. Rise in the density of the liquid fuel directly causes increase in its viscosity, which consistently reduces particulates emission (e.g., PM 2.5) into the atmosphere (Radovanovic *et al.,* 2000; Islam and Beg, 2004; Islam and Nahian, 2016).

The viscosity value at 40 °C of the pyrolysis fuel (4 cSt) was within the permissible limits of conventional standard diesel (2.0 – 5.3 cSt). The

kinematic viscosity of the fuel if reduced could affect its application in two ways. The pyrolysis fuel may be easier to pump if it has a lower viscosity which would also make it easy to atomise and when utilised in fuel injectors, help attain finer droplets and vice versa. Moreover, lower viscosity could make it easy to flow via pipelines, injector nozzles and orifices (Islam and Beg, 2004; Radovanovic *et al.,* 2000). Howbeit, lower viscosity could lead to easy evaporation of the pyrolysis fuel which may cause challenges involving fuel injection during engine preheating (Demirbas, 2007).

The flashpoint of the liquid fuel produced was 27 °C and is lower than the 55 °C minimum requirement of conventional diesel fuel. The lower flashpoint could be that the composition of the pyrolytic oils is a blend of compounds with a broad distillation temperature range (Osayi *et al.*, 2018). The lower flashpoint indicates that the pyrolysis fuel produced from the end-of-life vehicle tyres are highly flammable, therefore to store and transport, an environment highly ventilated and free from fire is a major requirement. The lower flashpoints will however have a minimum consequence on the output of engine which is negligible but it is necessary for satisfying legislation necessities concerning transportation of fuel and storing it (Demirbas, 2009).

The water content of the vehicle tyre fuel (1.300 mg/kg) was far higher than that of conventional fuel (0.035 mg/kg). Due to the high water content, the pyrolysis fuel produced is obviously characterised by lower energy density and flame temperatures. Due to that, there will be inadequate combustion, elevated particulate emissions and ignition challenges, especially utilizing it in engines that use diesel fuel (Oasmaa *et al.*, 2001; Oasmaa *et al.*, 2005).

Total contamination in the vehicle tyre pyrolytic liquid fuel (427.7 mg/kg) was far above the permissible limit of 24 mg/kg of conventional diesel as shown in Table 2. Usage of the pyrolysis fuel with the higher solid content would have adverse effects on equipment, specifically injectors in engines and turbine blades. Moreover, the elevated total contamination could certainly lead to elevated particulate emission (Oasmaa *et al.*, 2001; Oasmaa *et al.*, 2005). Total contamination can be reduced by filtering the liquid fuel

The sulphur level being higher in the liquid fuel (5900 mg/kg) could be due to the high levels of sulphur in the chemistry of the vehicle tyre (1.0 wt. %) (Zakaria *et al*., 2011). Unfortunately, higher sulphur content of liquid fuel is not desired due to environmental challenges that arise from it. During combustion, oxidation of sulphur in the fuel could

produce sulphur dioxide (SO_2) which is commonly released into the environment (Islam and Nahian, 2016). Furthermore, some of the SO_2 released into the atmosphere may condense or oxidise to produce sulphuric acid haze particles or sulphate aerosol in the presence of water according to Islam and Nahian (2016). Further research is ongoing to rectify these anomalies.

3.2.4 GC-MS Analysis of Liquid Fuel Produced from End-of-life Vehicle Tyres

According to GC-MS, the pyrolytic oil from the vehicle tyres consisted of about sixty-eight (68) compounds. The 68 compounds detected had peak areas about or higher than 0.1% as illustrated in Fig. 9. Table 3 illustrates the list of compounds detected in the liquid fuel obtained from the experiment. The results revealed the oil to be a mixture of C_8-C_{40} with the highest between C_8 to C_{13}, identified to be aliphatic hydrocarbons, aromatic hydrocarbons (alkyl benzenes) and minor amounts of naphthenes. Limonene (an olefin) was the constituent with the most elevated peak area. After limonene, several aromatic compounds such as naphthalenes, benzenes, indenes, biphenyls and xylenes were the other commonly found constituents. The result suggests that both aliphatics and aromatics dominate the pyrolytic oil with the aromatics being relatively higher..
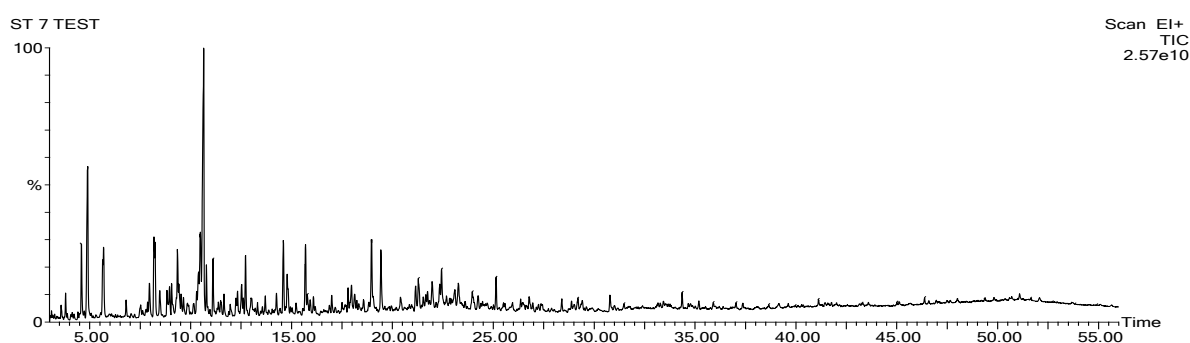

Fig. 9 GC-MS Spectrum of Liquid Fuel obtained from Pyrolysis of End-of-life Vehicle Tyres

Table 3 List of Compounds detected in the End-of-life Vehicle Tyres Pyrolytic Liquid Fuel

Retention Time (min)	Compound Name	Molecular Formula	Retention Time (min)	Compound Name	Molecular Formula
3.799	Cyclohexene, 4-ethenyl-	C_8H_{12}	17.801	1H-Indene, 2,3-dimethyl-	$C_{11}H_{14}$
4.579	ethylbenzene	C_8H_{10}	17.971	1H-Indene, 2,3-dimethyl-	$C_{11}H_{14}$
4.899	p-Xylene	C_8H_{10}	18.121	1H-Indene, 2,3-dimethyl-	$C_{11}H_{14}$
5.679	p-Xylene	C_8H_{10}	18.972	Naphthalene, 2-methyl-	$C_{11}H_{10}$
6.799	Benzene, (1-methylethyl)-	$C_{11}H_{16}$	19.422	Naphthalene, 2-methyl-	$C_{11}H_{10}$
7.519	1,3,6-Heptatriene,2,5,6-trimethyl-	$C_{10}H_{16}$	20.392	3-Penten-1-ol, 2,2,4-trimethyl-	$C_8H_{16}O$
7.949	D-Limonene	$C_{10}H_{16}$	21.512	1H-Indene, 1,1,3-trimethyl-	$C_{12}H_{14}$
8.179	Benzene, 1-ethyl-3-methyl-	C_9H_{12}	21.282	Biphenyl	$C_{12}H_{10}$
8.229	Cyclopropyl phenylmethanol	$C_{10}H_{12}O$	21.962	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$
8.470	Benzene, 1,2,4-trimethyl-	C_9H_{12}	22.342	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$
8.820	Benzene, 1-ethyl-3-methyl-	C_9H_{12}	22.432	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$
8.950	à-Methylstyrene	C_9H_{10}	23.092	Quinoline, 2,4-dimethyl-	$C_{11}H_{11}N$
9.050	Benzonitrile	C_7H_5N	23.262	Dimethyl phthalate	$C_{10}H_{10}O_4$
9.340	Benzene, 1,2,4-trimethyl-	C_9H_{12}	23.953	Acenaphthene	$C_{12}H_{10}$
9.410	Indane	C_9H_{10}	24.243	1,1'-Biphenyl, 4-methyl-	$C_{13}H_{12}$
9.840	2,6-Dimethyl-1,3,6-heptatriene	C_9H_{14}	25.133	Naphthalene, 1,6,7-trimethyl-	$C_{13}H_{14}$
10.300	Cyclohexene, 1-methyl-4-(1-methylethyl)-, (R)-	$C_{10}H_{18}$	25.953	Naphthalene, 1,6,7-trimethyl-	$C_{13}H_{14}$
10.390	Benzene, 1,2,3-trimethyl-	C_9H_{12}	26.773	1,1'-Biphenyl, 3-methyl-	$C_{13}H_{12}$
10.480	o-Cymene	$C_{10}H_{14}$	29.184	(2-Methyl-3-biphenyl) methanol	$C_{14}H_{14}O$
10.640	Limonene	$C_{10}H_{16}$	29.404	Naphthalene, 1,2,3,4-tetramethyl-	$C_{14}H_{16}$
10.780	Benzene, 2-propenyl-	C_9H_{10}	30.774	Phenanthrene	$C_{14}H_{10}$
11.100	Benzene, 1-propynyl-	C_9H_{10}	47.997	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$
11.650	Benzene, 2-ethyl-1,4-dimethyl-	$C_{10}H_{14}$	48.848	Rhodopin	$C_{40}H_{58}O$
12.240	Phenol, 2-methyl-	C_7H_8O	49.178	7,8-Epoxylanostan-11-ol, 3-acetoxy-	$C_{32}H_{54}O_4$
12.320	o-Cymene	$C_{10}H_{14}$	49.378	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$
12.530	o-Cymene	$C_{10}H_{14}$	49.818	17-Pentatriacontene	$C_{35}H_{70}$
12.720	Benzene, 1-methyl-4-(1-methylethyl)-	$C_{10}H_{14}$	50.358	17-Pentatriacontene	$C_{35}H_{70}$

12.990	2,2-Dimethyl-3-vinyl-bicyclo[2.2.1]heptane	$C_{11}H_{18}$	50.688	17-Pentatriacontene	$C_{35}H_{70}$
13.701	Benzene, 1,2,3,4-tetramethyl-	$C_{10}H_{14}$	51.078	17-Pentatriacontene	$C_{35}H_{70}$
14.251	Benzene, 1-methyl-2-(2-propenyl)-	$C_{10}H_{12}$	51.248	a-Homocholest-4a-en-3-one	$C_{27}H_{45}NO$
14.591	1H-Indene, 1-methyl-	$C_{10}H_{10}$	51.518	7,8-Epoxylanostan-11-ol, 3-acetoxy-	$C_{32}H_{54}O_4$
14.781	1H-Indene, 1-methyl-	$C_{10}H_{10}$	51.628	7,8-Epoxylanostan-11-ol, 3-acetoxy-	$C_{32}H_{54}O_4$
15.691	Naphthalene	$C_{10}H_8$	52.068	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$
15.781	Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	$C_{13}H_{18}$	52.808	Rhodopin	$C_{40}H_{58}O$
16.991	Benzothiazole	C_7H_5NS	53.659	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	$C_{26}H_{54}$

3.2.5 FT-IR Analysis of Char Produced from End-of-life Vehicle Tyres

FT-IR carried out on the char produced from the vehicle tyres pyrolysis revealed no definite peak and hence no definite functional group as demonstrated by the spectrum in Fig. 10. This could mean that the vehicle tyre char is extremely carbonaceous.
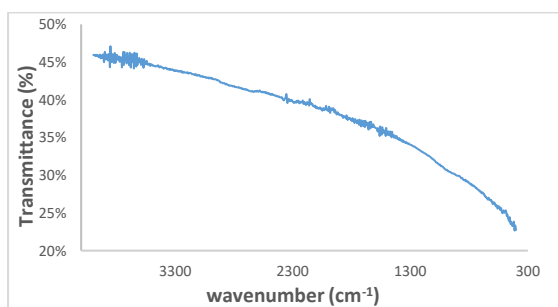

Fig. 10 FT-IR Spectrum of Char after Non-Catalytic Pyrolysis

3.2.5 SEM-EDS Analysis of Char

SEM-EDS analysis conducted on the vehicle tyre char showed that there is uneven intrinsic particle size distribution. There are regions of coarse particle sizes and smaller particle sizes. Particles shapes also differ across portions of the char as shown in Fig. 11.
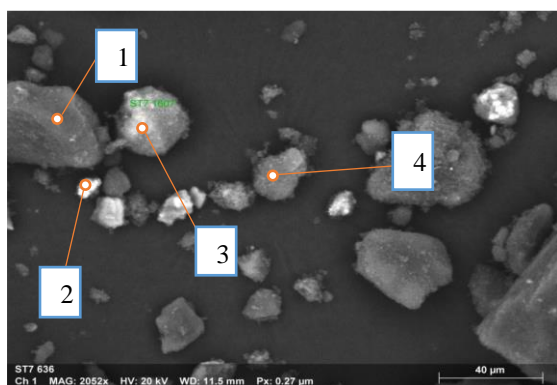

Fig. 11 SEM/EDX Photomicrograph of Char (2052X)

The SEM-EDS analysis at point 1 in Fig. 11 detected a strong peak of carbon and weak peaks of sulphur, zinc, sodium and oxygen in the spectrum illustrated in Fig. 12. From the point analysis, carbon is the predominant element at point 1 in the char with an abundance of 88.41 wt.%.

The SEM-EDS analysis at point 2 in Fig. 11 detected strong peaks of calcium and lead, a moderate peak of sulphur and oxygen and weak peaks of zinc, sodium, aluminium, chlorine and silicon in the spectrum illustrated in Fig. 13. From the analysis, oxygen is the predominant element at point 2 in the char (28.29 wt.%).
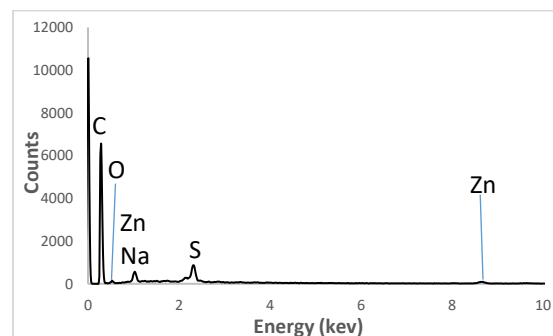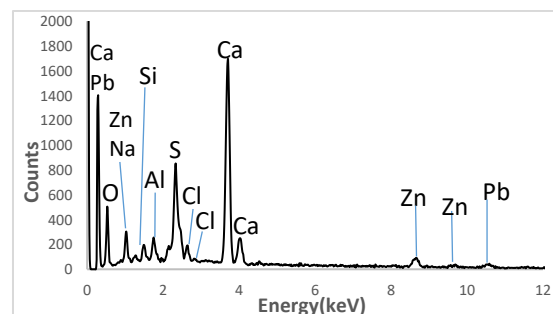

Fig. 12 SEM-EDS Spectrum at Point 1

Fig. 13 SEM-EDS Spectrum at Point 2

The SEM-EDS analysis at point 3 in Fig. 11 detected strong peaks of elements such as carbon, titanium and silicon and weak peaks of zinc, sodium, aluminium, oxygen and copper in the spectrum shown in Fig. 14. From the analysis, carbon with a very strong peak is the predominant element at point 3 having an abundance of 67.18 wt.%.
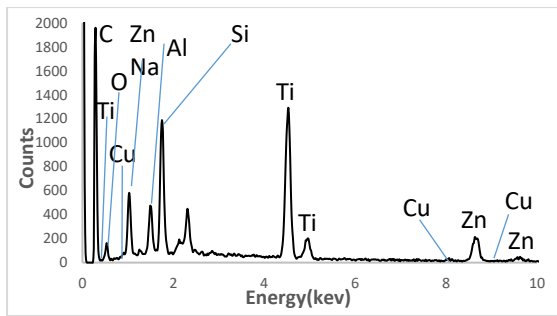
Fig. 14 SEM-EDS Spectrum at Point 3

The SEM-EDS analysis at point 4 in Fig. 11 detected a strong peak of carbon and weak peaks of zinc, sodium, silicon, sulphur, oxygen and aluminium in the spectrum illustrated in Fig. 15. From the point analysis, it was observed that carbon with a very strong peak is the predominant element at point 4 with an abundance of 88.67 wt.%.
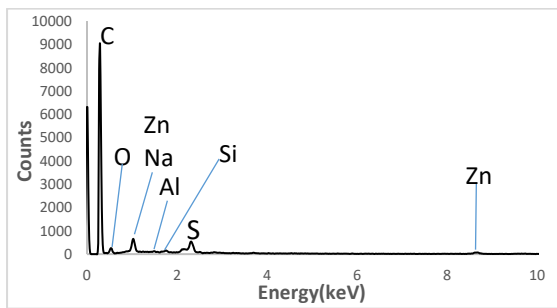

Fig. 15 SEM-EDS Spectrum at Point 4

All elements detected in the char by SEM-EDS point analyses with their percentage abundances are detailed in Table 5a which include carbon, zinc, aluminium, calcium, copper, titanium and silicon.

Table 5a Weight Percentages of Elements in the Vehicle Tyre Char

Points Analysed in Char	Elements Detected	Weight Percentages (wt.%)
1	Carbon	88.41
	Sulphur	4.53
	Oxygen	4.03
	Zinc	2.57
	Sodium	0.45
2	Calcium	22.89
	Lead	22.57
	Sulphur	4.76
	Oxygen	28.29
	Zinc	12.05
	Sodium	2.71
	Aluminium	3.17
	Chlorine	1.2
	Silicon	2.34
3	Carbon	67.18
	Titanium	0.39
	Silicon	3.34
	Zinc	18.6
	Sodium	2.97

	Aluminium	1.66
	Oxygen	5.02
	Copper	0.84
4	Carbon	88.67
	Zinc	2.40
	Sodium	0.53
	Silicon	0.19
	Sulphur	1.94
	Oxygen	6.08
	Aluminium	0.15

The average abundances of the elements in the char are indicated in Table 5b. There is an average carbon content of 61.07 wt.%, zinc 8.91 wt.%, calcium 5.72 wt.%, copper 0.21 wt.%, titanium 0.10 wt.% and silicon 1.46 wt.% in the char.

The high concentration of carbon highlights the usefulness of the char as a reducing agent in metallurgical processes such as in the reduction of iron ore into metallic iron. The presence of silicon favours the production of ferrosilicon for the iron and steel making industry. The char can be ashed and high value metals such as zinc, aluminium, copper and titanium extracted from it.

Table 5b Average Weight Percentages of Elements in the Vehicle Tyre Char

All Elements detected in Char	Average Weight Percentages (wt.%)
Carbon	61.07
Oxygen	10.86
Zinc	8.91
Calcium	5.72
Lead	5.64
Sulphur	2.81
Sodium	1.66
Silicon	1.46
Aluminium	1.24
Chlorine	0.30
Copper	0.21
Titanium	0.10

3.2.6 X-Ray Diffraction Analysis of Char

XRD patterns of vehicle tyre char shows crystalline peaks of $CaCO_3$ and ZnS in Fig. 16. Table 6 shows the levels of the detected compounds in the end-of-life vehicle tyre char. ZnS was predominant with a score of 59 whiles $CaCO_3$ scored 22. This implies that the sample contains a higher proportion of zinc sulphide whiles the concentration of calcium carbonate is relatively low. Thermal decomposition of $CaCO_3$ produces lime which is useful as a pH modifier while ZnS could be extracted and processed to metallic zinc.
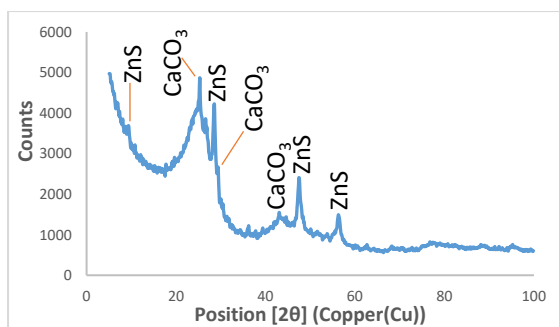
Fig. 16 XRD Spectrum of End-of-Life Vehicle Tyre Char

Table 6 Pattern List with Details of the Composition of the Sample Derived from the Peak Table for Vehicle Tyre Char

Compound Name	Chem. Formula	Score	Displ [°2θ]	Scale Fac.
Calcium Carbonate	$CaCO_3$	22	0.000	0.365
Zinc Sulphide	ZnS	59	0.000	0.887

4 Conclusions and Recommendations

4.1 Conclusions

It is feasible to recycle end-of-life vehicle tyres into useful fuel products and chars through pyrolysis in a self-designed stainless steel laboratory reactor.

The liquid fuels obtained from the study (diesel range) will need to be refined before use.

Analyses of the solid by-products (chars) revealed partly carbonaceous material (67.18 ~ 86.67 wt.% C) that could burn to yield an ash rich in ZnO, CaO and TiO_2.

The chars obtained can be used as reducing agents in the iron and steel making industry due to the high carbon content.

The feasibility of end-of-life vehicle tyres pyrolysis is a solution to end-of-life vehicle tyres disposal challenges faced by the mining industry and the country as a whole.

4.2 Recommendations

In light of the growing concern of the environmental impacts caused by end-of-life vehicle tyres in mining operations, the implementation of pyrolysis plants is strongly recommended. By properly recycling these used tyres, the mining industry can greatly reduce their carbon footprint and contribute to a sustainable future while also benefiting through the use and sale of sustainable products.

Scrap vendors instead of usually burning scrap tyres in isolated areas to separate the steel wires, can employ the method of pyrolysis to retrieve the steel wires for sale to the metal manufacturing sector. This process will do away with the emission of significant amounts of gaseous pollutants into the environment, caused by open-air burning of scrap vehicle tyres thereby decreasing greenhouse effect and reducing contribution to global warming.

References

Abraham, E., Cherian, B. M., Elbi, P. A., Pothen, L. A. and Thomas, S. (2011), "Recent Advances In The Recycling Of Rubber Waste", *Recent Developments in Polymer Recycling*, vol. 47, pp. 100.

Ahmad, N., Abnisa F., and Daud, W.M.A.W., (2016), "Potential Use Of Natural Rubber To Produce Liquid Fuels Using Hydrous Pyrolysis - A Review", *RSC Advances*, Vol. 6, pp. 68906 -21.

Akpanudoh, N. S., Gobin, K. and Manos, G. (2005), "Catalytic Degradation of Plastic Waste to Liquid Fuel over Commercial Cracking Catalysts: Effect of Polymer to Catalyst Ratio/Acidity Content", *Journal of Molecular Catalysis A*, Vol. 235, pp. 67–73.

Arthur, E. A., Mensah-Sackey, G., Baisi Ebo, S. N., Cobbinah, I. J., Dankwah, J., Abotar, E., Dankwah, J. R. (2023), "Conversion of End-of-Life Latex Gloves as Chemical Feedstock for the Production of Diesel Range Liquid Fuel", *Ghana Journal of Technology*, vol. 7, pp. 53 – 61.

Cleetus, C., Thomas, S. and Varghese, S. (2013), "Synthesis of Petroleum-Based Fuel from

Waste Plastics and Performance Analysis in a CI Engine", *Journal of Energy*, Vol. 608979, pp. 1-10.

Demirbas A. (2007), "The Influence of Temperature on the Yields of Compounds Existing in Bio-Oils Obtained from Biomass Samples Via Pyrolysis", *Fuel Processing Technology*, Vol. 88, pp. 591−597.

Demirbas A. (2009), "Progress and Recent Trends in Biodiesel Fuels", *Energy Conversion and Management*, Vol. 50, pp. 14 −34.

Demirbas, A., Al-Sasi, B. O. and Nizami, A. S. (2016), "Conversion of Waste Tires to Liquid Products via Sodium Carbonate Catalytic Pyrolysis", *Energy Sources*, *part A*: *Recovery, Utilization and Environmental Effects,* Vol. 38, pp. 2487 – 2493.

de Marco Rodriguez, I., Laresgoiti, M. F., Cabrero, M. A., Torres, A., Chomon, M. J. and Caballero, B. (2001), "Pyrolysis of Scrap Tyres", *Fuel Processing Technology*, Vol. 72, pp. 9 – 22.

Gandidi, I. M., Susila, M. D., Mustofa, A. and Pambudi, N. A. (2018), "Thermal-catalytic Cracking of Real MSW into Bio-crude Oil", *Journal of the Energy Institute*, Vol. 91, pp. 304 – 310.

Gulab, H., Jan, M. R., Shah, J. and Manos, G. (2010), "Plastic Catalytic Pyrolysis to Fuels as Tertiary Polymer Recycling Method: Effect of Process Conditions," *Journal of Environmental Science and Health*, vol. 45, no. 7, pp. 908 – 915.

Ishola, F. A., Ajayi, O. O., Oyawale, F. and Akinlabi, S. A. (2018), "Sustainable End-of-Life Tyre (EOLT) Management for Developing Countries - A Review", In: *Proceedings of the International Conference on Industrial Engineering and Operations Management*, Vol. 29, pp. 1054 – 1058.

Jan, M. R., Shah, J. and Gulab, H. (2010), "Catalytic Degradation of Waste High Density Polyethylene into Fuel Products using $BaCO_3$ as a Catalyst," *Fuel Processing Technology*, Vol. 91, pp. 1428-1437.

Manickavelan, K., Ahmed, S., Mithun, K., Sathish, P., Rajaesekaran, R. and Sellappan, N. (2022), "A Review on Transforming Plastic Wastes into Fuel", *Journal of the Nigerian Society of Physical Sciences*, pp. 64 – 74.

Manos, G., Garforth, A. and Dwyer, J. (2000), "Catalytic Degradation of High-Density Polyethylene on an Ultrastable-Y Zeolite. Nature of Initial Polymer Reactions, Pattern of Formation of Gas and Liquid Products, and Temperature Effects", *Industrial and Engineering Chemistry Research*, Vol. 39, pp. 1203-1208.

Miandad R., Barakat M. A., Aburiazaiza A. S., Rehan M. and Nizami A. S. (2016), "Catalytic Pyrolysis of Plastic Waste: a Review", *Process Safety Environment Protection*, Vol. 102, pp. 822–838.

Miandad, R., Rehan, M., Barakat, M. A., Aburiazaiza, A. S., Khan, H., Ismail, I. M., Dhavamani, J., Gardy, J., Hassanpour, A. and Nizami, A. S. (2019), "Catalytic Pyrolysis of Plastic Waste: Moving toward Pyrolysis Based Biorefineries", *Frontiers in Energy Research*, pp. 27.

O'Hara J. B. (1981), "Liquid Fuels from Coal", *Coal Handbook*, pp. 715–816.

Osayi J. I, Iyuke S., Daramola M. O., Osifo P., Van Der Walt I. J. and Ogbeide S. E. (2018), "Pyrolytic Conversion of Used Tyres To Liquid Fuel: Characterization And Effect Of Operating Conditions*", Journal Of Material Cycles and Waste Management*, Vol 20, pp. 1273-1285.

Panda, A. K., Singh, R. K. and Mishra, D. K. (2010), "Thermolysis of Waste Plastics to Liquid Fuel: a Suitable Method for Plastic Waste Management and Manufacture of Value Added Products," *Renewable and Sustainable Energy Reviews*, vol. 14, pp. 233–248.

Ratnasari Ratnasari D. K., Nahil M. A. and Williams P. T. (2017), "Catalytic Pyrolysis of Waste Plastics Using Staged Catalysis for Production of Gasoline Range Hydrocarbon Oils", *Journal of Analytical and Applied Pyrolysis*, Vol. 124, pp. 631– 637.

Rowhani, A. and Rainey, T. J. (2016), "Scrap Tyre Management Pathways and Their Use as a Fuel-A Review", *Energies*, Vol. 9, pp. 888.

Songip, A. R., Masuda, Kuwahara, T. H. and Hashimoto, K. (1993), "Test to Screen Catalysts for Reforming Heavy Oil from Waste Plastics," *Applied Catalysis B*, Vol. 2, pp. 153–164.

Stoler, J., Weeks, J.R., and Fink, G. (2012), "Sachet Drinking Water in Ghana's Accra-Tema Metropolitan Area: Past, Present, and Future", *J Water Sanit Hyg Dev.*, Vol. 2(4), pp. 223 – 240.

Uddin, M. A., Koizumi, K., Murata, K. and Sakata, Y. (1997), "Thermal and Catalytic Degradation of Structurally Different Types of Polyethylene into Fuel Oil," *Polymer Degradation and Stability*, Vol. 56, pp. 37–44.

Zakaria N., Ani F. N., Yunus, M. N. M. and Husain M. A. S. (2011), "Oxidative Pyrolysis of Examination Rubber Gloves in the Integral Pyrolysis Test Plant", *International Journal of Mechanical and Materials Engineering (IJMME)*, vol. 6, pp.1-9.

Authors

E. A. Arthur holds an MPhil in Minerals Engineering from the University of Mines and Technology (UMaT), Tarkwa, Ghana as well as a BSc degree in Materials Engineering from the Kwame Nkrumah University of Science and Technology (KNUST), Kumasi, Ghana. His expansive research interests encompass material/mineral processing, hydro and electrometallurgy, high-temperature metallurgical processes, alloying, corrosion and corrosion control, and the judicious deployment of waste polymers in metal extraction processes while also exploring and implementing methods to repurpose waste polymers into desirable chars and liquid fuel.

G. Mensah-Sackey obtained a BSc degree in Minerals Engineering from the University of Mines and Technology (UMaT). He is currently enrolled in MSc programme in Environmental Engineering at Egypt - Japan University of Science and Technology (EJUST). His research interest is in environmental remediation, water treatment, solid waste management and liquid fuel production.

S. I. Baisi Ebo holds a BSc in Minerals Engineering at the University of Mines and Technology, Ghana (2021). He is a member of the West Africa Institute of Mining, Metallurgy and Petroleum. His current research interest includes pyrolysis of waste plastics to produce valuable products, including liquid fuels and carbon black (char), water quality assessment and purification of water using natural coagulants.

D. Asubonteng is an MSc student at Universiti Teknologi PETRONAS, Perak, Malaysia. He holds a BSc in Minerals Engineering from the University of Mines and Technology, Ghana. He is a member of the West Africa Institute of Mining, Metallurgy and Petroleum. His current research interest includes sustainable waste plastics management, high temperature metallurgical processes, ironmaking and steelmaking technologies, pyrolysis of waste plastics to produce valuable products, including liquid fuels and carbon black (char).

J. Dankwah is a Metallurgist at Goldfields Ghana Limited, Damang Mines. She holds an MPhil Degree in Minerals Engineering from the University of Mines and Technology, Tarkwa and BSc degree in Chemical Engineering from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. She is part of the research group at the University of Mines and Technology currently involved in the recycling of post-consumer plastics in the reduction of metal oxides and the production of liquid fuels (diesel, kerosene and aviation fuel).

E. Abotar is a Lecturer and a PhD candidate at the Minerals Engineering Department of the University of Mines and Technology, (UMaT), Tarkwa. He obtained his MPhil and BSc Degrees in Minerals Engineering at the University of Mines and Technology. His current research areas include mineral processing, iron and steelmaking, high-temperature metallurgical processes and utilisation of waste polymers in metal extraction processes.

Y. Ankomah is a research assistant at the Minerals Engineering Laboratory, University of Mines and Technology UMaT. He is an MSc student in Minerals Engineering, University of Mines and Technology and holds a BSc degree in Natural Resources, Environmental Management Option from the University for Development Studies (UDS). His current research interest focuses on hydrometallurgy, pyrometallurgy, electrometallurgy and includes; Lithium extraction, The Kinetics of Alumina Extraction from Bauxite through the Bayer process, Phase Characterisation and Extraction of Critical mineral oxides from Bauxite Residue, Biofuel Extraction and Optimization of Gold Heap Leaching Kinetics.

I. K. O. Adimado had his MPhil and BSc. Degrees in Minerals Engineering from the University of Mines and Technology, Tarkwa, Ghana. He worked on production of metallic iron from Talata Mafara iron ore using palm kernel shells, polystyrene, and their blends as reductants. His current research interest includes pyrometallurgy, recycling of waste plastics and biomass and alumina extraction processes.

J. R. Dankwah is an Associate Professor of Metallurgical and Materials Engineering at the University of Mines and Technology, Tarkwa, Ghana. He obtained his PhD from the School of Materials Science and Engineering, UNSW-Australia, MSc (Process Metallurgy) from the Norwegian University of Science and Technology and BSc (Metallurgical Engineering) from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. He is a fellow of the West Africa Institute of Mining, Metallurgy and Petroleum. His research and consultancy works cover low temperature electrochemical production of metallic iron from alkaline baths, iron and steelmaking, high-temperature metallurgical processes, utilisation of waste polymers in metal extraction processes, and utilisation of waste polymers in liquid fuel production.