

Investigation on the Potential Production of Diesel from Waste Tires

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How to cite this paper: Mudono, S., Jim, N. and Chigova, J.T. (2022) Investigation on the Potential Production of Diesel from Waste Tires. *Journal of Power and Energy Engineering*, 10, 1-12.

<https://doi.org/10.4236/jpee.2022.1010001>

Received: May 26, 2022

Accepted: October 21, 2022

Published: October 24, 2022

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Abstract

An alternative fuel production was performed by catalytic-pyrolysis of waste tires under a nitrogen (N₂) environment and with a zeolite catalyst. Pyrolysis of scrap tires has been pointed out as an alternative to the incorrect disposal of tire wastes. Pyrolysis processes can produce tire-derived oils that may be used as fuel or added to conventional fuels, producing fuel blends with improved properties and reduced cost. The pyrolysis process can contribute to removing tire residues from inadequate sites and it can be a sustainable process to produce alternative fuels. The project investigated the conversion of the waste tires into diesel as one way of waste management and also as a viable process which in turn helps to meet the fuel demand. Uses of the diesel and the by-products from the process were also outlined. Experiments were conducted on the pyrolysis process in order to find the optimum conditions for producing the diesel through pyrolysis; the temperature and residence time were optimized in order to get maximum output from the process. The optimum temperature of the reaction was found to be 520°C and the optimum residence time was 92.5 minutes. Quality tests of the product were then conducted on the obtained product and most of the properties were found to meet the required standard specifications. The most critical properties which are density, final boiling point, flash point and kinematic viscosity, were found to be 0.8495 g/cm³, 370°C, 50.5°C and 3.681 cSt, respectively, and they were within the required specifications. Quality analysis showed that a quality product that is suitable for automobiles could be obtained from the process. The process also produces useful by-products such as char, which can aid in the purification process of the diesel after conversion to activated carbon. The process is environmentally friendly if the appropriate pollution prevention methods like gas absorption are thoroughly implemented. Waste tires are an alternative source of diesel and hence the feasibility of implementing the project on a large scale.

Keywords

Density, Pyrolysis, Residence Time, Diesel, Flash Point, Kinematic Viscosity

1. Introduction

The energy crisis and environmental pollution are some of the main problems mankind is facing today. These problems owe their origin to a growing population and rapid industrialization. Overall the global demand for fuels has been supplied mainly by non-renewable resources deriving from petroleum distillation [1]. The industrial process for obtaining these resources has a strong impact on the environment, promoting ecological damage and impairment to human health. Extensive effort has been devoted to the production of fuels from other sources and processes besides petroleum. The use of alternative energy sources has been an option for reducing the use of fossil fuels. To alleviate part of our energy crisis and environmental degradation, it is imperative to make use of appropriate technologies for the possible recovery of resources from non-conventional sources, like waste tires. Scrap tire is one of the very common and most important hazardous solid wastes all over the world. Converting the waste tires is an alternative way of managing the pollution problems caused by the waste tires in the environment as well as largely benefiting from them; the process will also mitigate the problem of fuel supply in the country by providing an additional source of fuel. Waste management is once a technical problem that has to be solved under thrifty yet environmentally acceptable and hygienic conditions and preferably performed by skilled labor. The disposal of waste vehicle tires is one of the most important problems that should be solved. It is estimated that worldwide, over one billion waste tires are generated annually [1]. The tire is one of the most common items in the contemporary world with more than 800 million new tires produced annually, in every region of the world, in a wide range of sizes and types, to serve an equally dazzling multiplicity of users on vehicles of every kind and description. However, as more and more tires are put into use, more and more are scrapped. Many countries are confronting the problems posed by scrap tires and are seeking to identify useful economic and regulatory techniques for managing these tires [1] [2] [3].

In Zimbabwe, approximately 2.4 million tires are disposed of each year. The town municipalities are facing challenges in solid waste management and the Environmental Management Agency (EMA) is stringent in its regulations as far as waste management is concerned. One of the noticeable problems associated with large piles is the fire hazard they pose which can be triggered by veld fires; the combustion of tires adds to the release of carbon dioxide, a greenhouse gas as well as other toxic organic compounds that cause various chronic diseases with cancer as a typical example [1] [2]. Diseases such as encephalitis, dengue fever and malaria have also been reported around waste tire stacks, particularly in

warmer climate areas since these piles are an ideal breeding ground for disease carrying mosquitos. Waste tires are almost everywhere in the modern world; they are without question the leading mode of transportation in the world and as a result, also a major form of pollution. Waste tires are mostly generated by automobiles, trucks, buses, aircraft landing gears, tractors and other farming equipment, industrial vehicles such as forklifts, and common conveyances such as baby carriages, shopping carts, wheel chairs, bicycles, and motorcycles. In Zimbabwe, millions of used tires are generated from these sources annually and hence there is a need for proper management to be carried out [3] [4].

The tire is a complex composite of many materials including natural and synthetic rubber; reinforcing fabrics, typically polyester, nylon, aramid, or steel; steel wire woven into reinforcing tread belts and beads; carbon black and silica reinforcing and filling agents; and various chemicals, oils and additives that aid in the curing process, help the tire resist oxidation, or serve some other useful purpose in the tire. Vulcanization makes a tire a temperature stable, thermoset material but makes it difficult to recycle into a new tire. The recycling of scrap tires using pyrolysis technology as a thermochemical conversion route may be useful for the production of valuable organic commodity chemicals, which can be fed into existing petrochemical infrastructure, and reducing waste streams at the same time. The most common reactors used are fixed-bed (batch), screw kiln, rotary kiln, vacuum and fluidized-bed. Pyrolysis of tires is the degradation of the tire rubber by using heat in the absence of oxygen. The tires rather than burning, break down and result into oil and gas, leaving a residual solid; the yield of oil from the process can be high up to the order of 60% [5]. In the catalytic-pyrolysis process, the organic volatile matter of tires is decomposed to low molecular weight products, liquids or gases. Catalytic-pyrolysis oils may be used as fuel after blending or as feedstock for the production of commodity chemicals after downstream processing. The inorganic components and the non-volatile carbon black remain as a solid residue that is relatively unaltered and therefore can be recycled in worthwhile applications.

Tire rubber can be pyrolyzed by several processes and these involve a number of reactor types, process conditions, and heat addition methods. During this process, in the case of tire catalytic-pyrolysis, sulphide bonds present in the rubber are broken and followed by the bursting of carbon chains and finally gaseous, liquid and solid products are formed, which then can be subjected to further processing. The main components are methane gas (and other simple hydrocarbons), hydrogen, hydrogen sulphide and carbon monoxide (which constitute about 10%). Oil represents around 44%, and part of solids is about 46% [5] [6]. The liquid phase consists of a mixture of aliphatic and aromatic hydrocarbons, such as benzene, toluene and others. The separation of these components from the liquid fraction can be achieved by distillation and refining. The solid fraction consists of char, remnants of steel, silica, ZnO, ZnS, and any residues of catalysts that were used [6] [7] [8]. The key influence on the product yield and gas and oil composition is the type of reactor used which in turn de-

termines the temperature and heating rate. Tire pyrolysis oil is a chemically very complex containing aliphatic, aromatic, hetero-atom and polar fractions. The fuel characteristics of the tire oil show that it is similar to diesel oil or light fuel oil and has been successfully combusted in test furnaces and engines [2] [5]. To obtain a higher quality diesel oil, refining is needed and this is achieved by distillation and the addition of additives.

The composition of the products formed, both qualitative and quantitative, is dependent on the pyrolysis process parameters such as temperature, the duration of the process, the conditions of pressure, inert gas and the catalyst presence [9] [10]. The temperature and residence time of pyrolysis are also important in determining the extent to which high molecular weight compounds are cracked; hence, higher pyrolysis temperatures and longer vapor residence times promote gas production at the expense of the liquid fraction. Hence, for the highest production of liquid fraction, the temperature should be carefully controlled. Also, the residence time of the vapors released from the tires should be minimized. The processes that are presently commercial do minimize the residence time for gases by removing and condensing them as they are evolved [11] [12] [13]. The objectives of the study were to find the optimum operating time and temperature which will give high yield, required viscosity and density of the diesel as an alternative fuel that can be blended and used in vehicles, firing boilers and furnaces.

2. Experimental Procedure

2.1. Materials

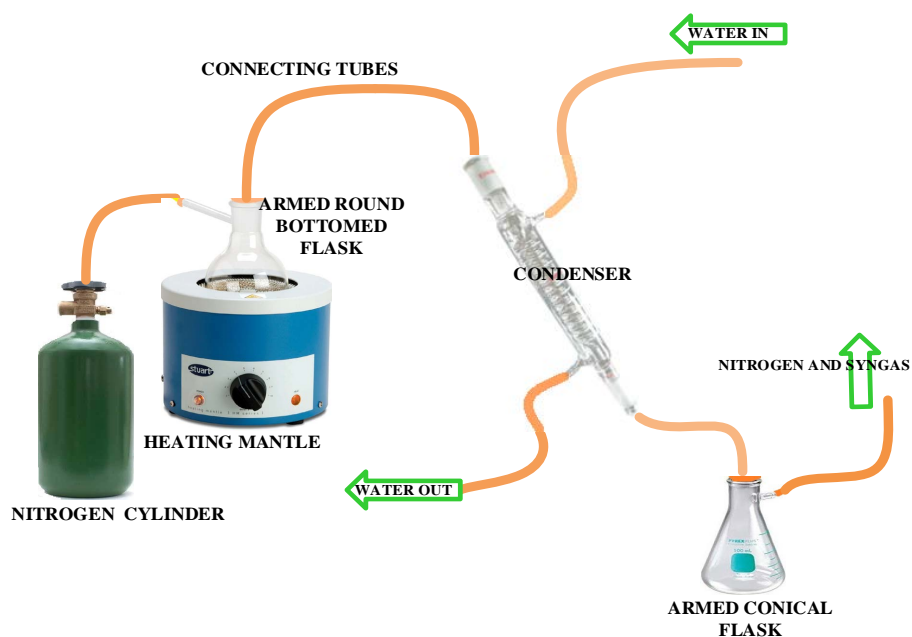
The waste tire material was obtained by shredding end-of-life tires used in drive vehicles, producing pieces with a size of 2.0 - 5.0 cm. The waste tires were cleaned to remove any unwanted material attached to the tires and then they were dried and then shredded to become ready for use. The shredded material contains approximately 1 wt% of steel. The raw material was pyrolyzed in a 15 kg stainless steel reactor under N₂ inert atmosphere. The pyrolysis process was carried out in the batch process. The product content was 43 wt% of carbon black, 45 wt% of liquid phase (oil) and 11 wt% of non-condensed gases. An automated heating mantle was used and set at the required operating temperatures.

2.2. Method

100 g of the shredded tires were weighed using an electronic balance. The clean shredded tires were introduced into the round bottomed flask and heated using a heating mantle at different times and temperatures (Table 1). Nitrogen gas was continuously passed through the pyrolysis equipment to maintain an inert atmosphere within the flask (Figure 1). The gas produced from the heating process was condensed in the condenser and collected in a separate flask as the pyrolysis oil. The residual gas (syngas) was collected in a separate gas collector.

Table 1. Conditions for carrying out the pyrolysis experiments.

Residence Time (mins)	Temperature (°C)
45, 60, 75, 90, 105	300, 350, 400, 450, 500, 550

**Figure 1.** A diagram showing the apparatus set up.

A solid residue (char) that remained in the heated flask was then removed and weighed. The density of the product was determined using a Digital Density Meter Method using ASTM D4052/D7777, the water content was determined by using an ASTM D6304, the diesel strength was determined by using gas chromatography, the acid number in diesel was determined by titration with potassium hydroxide (0.01M KOH), the flash point was determined by using ASTM D93, and the kinematic viscosity was analyzed by ASTM D445. Determination of the ASTM color was done using ASTM D1500, copper corrosion ability was determined by using ASTM D130, and X-ray radiation was used to determine the sulphur content of petroleum products.

2.3. Determination of the Sulphur

The ASTM D 7039 Standard Test Method for Sulfur in Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry is similar to the WDXRF technique, ASTM D 2622, in that it relies on exciting K α -shell electrons in sulfur and then measuring the resulting fluorescence as they return to the ground state. The method involves the use of X-ray radiation to determine the sulphur content of petroleum products. The sample was placed in the path of a beam of X-rays, which resulted in the excitation of the sulphur present. When the sulphur returns to the ground state, it emits its characteristic X-ray fluorescence. This was measured by the detector and converted into a percentage mass.

3. Results and Discussion

3.1. Properties of Tire Pyrolysis Oil

The organic liquid phase obtained from the waste tire pyrolysis was a dark brown oil (Figure 2), termed tire pyrolysis oil, presenting an intense and distasteful odor. The results obtained from the experiments were generally showing consistency with the information provided by the literature.

The diesel obtained was sent for quality analysis at the National Oil Infrastructure Company Analytical Laboratory, Harare, Zimbabwe. Quality tests were conducted using the ASTM standards. Table 2 shows a certificate of analysis showing the results obtained from the quality analysis. As can be seen from the results, after the quality analysis tests, all the parameters which were tested were found to be on spec, save for the ASTM color and the sulphur content. The color of the product was too dark as compared to the required standard. This was because of the nature of the raw material which was used in the pyrolysis process, the sulphur linkages in the tire were also responsible for the amount of sulphur that was reported to the product. The color can be reduced by placing the product in a tank laid with clay and left to settle for over 24 hours.

Table 2. Fractional distillation product quality tests analysis.

METHOD	TEST	UNIT	RESULT	SPECIFICATIONS	
Visual	Appearance		Dull	Clear and bright	
Visual	Colour		Dark brown	Yellow	
				Minimum	Maximum
ASTM D1500	Colour		10.0		2.0
ASTM D1298	Density @ 20 °C	kg/m ³	0.8495	0.8161	0.8656
ASTM D93	Flash point	°C	50.5	50	
ASTM D6304/D95	Water content	% volume	0.01		0.02
ASTM D4294/D1266	Sulphur content	% mass	0.1267		0.05
ASTM D445	Kinematic viscosity @ 40 °C	Cst	3.681	2.2	4.5
ASTM D974	Total acid number	mg/100ml	0.2		0.25
ASTM D130	Copper corrosion, 3 hrs @ 100 °C		1A		1
ASTM D4737	Cetane index, calculated		54.5	48.0	
ASTM D86	Distillation IBP	°C	47	Report	
	10% Recovered	°C	219	Report	
	50% Recovered	°C	275	Report	
	90% Recovered	°C	350		362
	Final boiling point	°C	370		400
	Recovery	% volume	97	97.0	
	Residue	% volume	1		2.0
	Loss		2		2.0



Figure 2. Pyrolysis products.

The sulphur content in the diesel product can be reduced in various ways; these include Chemical and physico-chemical methods. A chemical approach involves the use of hydrotreating and purification with sulphuric acid and physico-chemical methods involves absorption and adsorption purification. The method of using activated carbon adsorption is the one which is the most economical to use in this process since the char, which is one of the by-products of the pyrolysis process can be converted to activated carbon and used to adsorb the sulphur from the diesel. The adsorption process using activated carbon has been found to reduce the sulphur content by 75% so as to meet the required standards for diesel to be used in vehicles, firing boilers and furnaces [14].

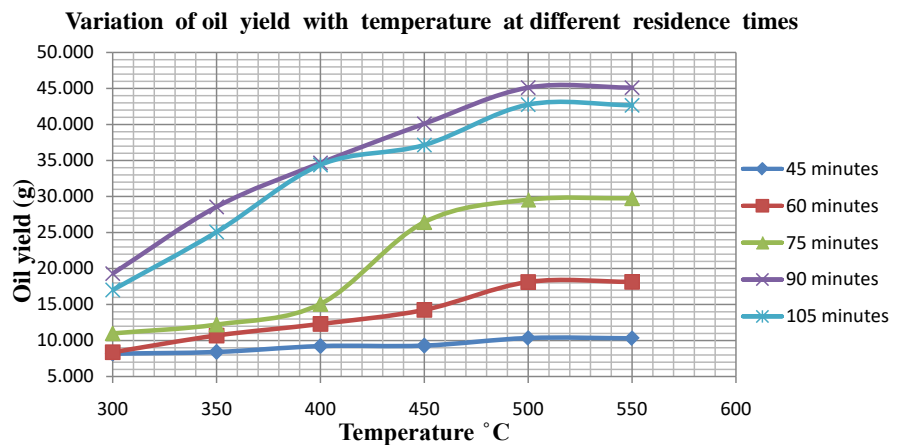
3.2. Optimum Reaction Temperature

The average percentage of pyrolytic oil was generally increasing as the temperature and residence time increased as shown in **Table 3** and **Figure 3**. However, the gas yield had some slightly higher values as compared to those indicated by literature; this was due to some leakages of gas from the apparatus that were used since the coke stoppers which were used, were affected by high temperatures. The experiments were conducted up to a temperature of 550°C due to the inadequacy of apparatus that would provide higher temperatures at NUST labs where the experiments were conducted. From **Table 3**, at 500°C and 105 minutes' residence time, the product yield was observed to be 42.756%, which is in great agreement with most of the research [14].

Figure 3 shows the graphs obtained after plotting the temperature against time at different residence times for the 100 g samples of shredded tires to obtain the optimum residence time and pyrolysis temperature. As what can be seen from **Figure 3**, generally the oil yield increases with an increase in temperature; this is because, as more energy is applied to the rubber molecules, more of the larger polymer chains will find sufficient energy to break the bonds within them and hence producing more of the shorter hydrocarbon molecules responsible for the formation of the oil until the optimum temperature is reached, this is the

Table 3. Data for oil yield against the residence time and reaction temperatures.

Residence time	45 minutes	60 minutes	75 minutes	90 minutes	105 minutes
Temperature (°C)	Oil yield (g)	Oil yield (g)	Oil yield (g)	Oil yield (g)	Oil yield (g)
300	8.178	8.386	10.991	19.298	17.025
350	8.420	10.698	12.220	28.566	25.079
400	9.234	12.309	15.082	34.654	34.391
450	9.299	14.257	26.432	40.102	37.149
500	10.345	18.129	29.559	45.119	42.756
550	10.312	18.148	29.754	45.113	42.666

**Figure 3.** Optimum pyrolysis reaction temperature.

temperature which corresponds to the maximum oil yield. From **Figure 3**, the optimum temperature was found to be 520°C; this is the optimum temperature that corresponds to the heating rate that was used in the experiment. The reduction in oil yield as the temperature continues to increase coupled with a corresponding increase in the gas yield is due to the vapor decomposing into permanent gases and secondary re-polymerization as well as carbonization reactions of oil hydrocarbons into char [12] [13] [14].

3.3. Optimum Residence Time

The optimum residence time was determined using the data from **Figure 3** at the optimum temperature conditions. **Figure 4** shows the plot of the oil yield against residence time at an optimum temperature of 520°C. From **Figure 4**, the initial oil yield at a temperature of 45°C was 10.5%; as the residence time increased, more bonds would find sufficient time to break, thus causing a continuous increase in the oil yield up to a residence time of 92.5 minutes, and this is the residence time at which the maximum oil yield occurred. After 92.5 minutes, the yield of the oil started decreasing; this was due to the decomposition of some oil vapor into secondary permanent gases hence producing more gaseous products. The optimum residence time is the one which yields the maximum amount

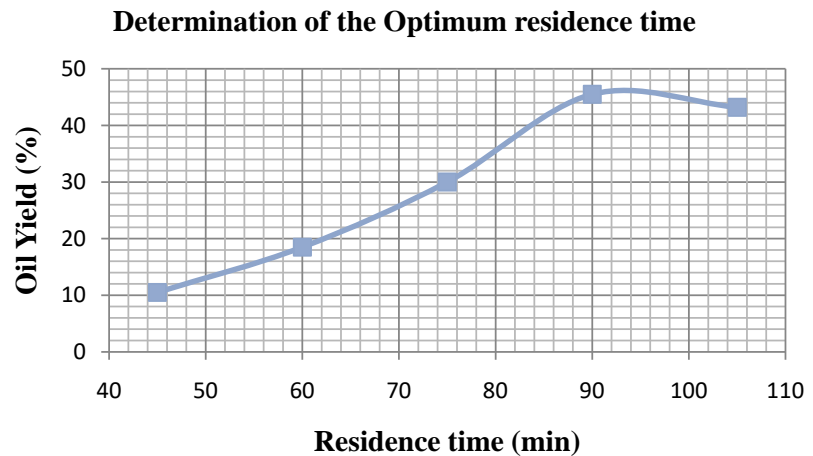


Figure 4. Determination of optimum residence time.

of the oil therefore 92.5 minutes was the time at an optimum pyrolysis reaction temperature of 520°C.

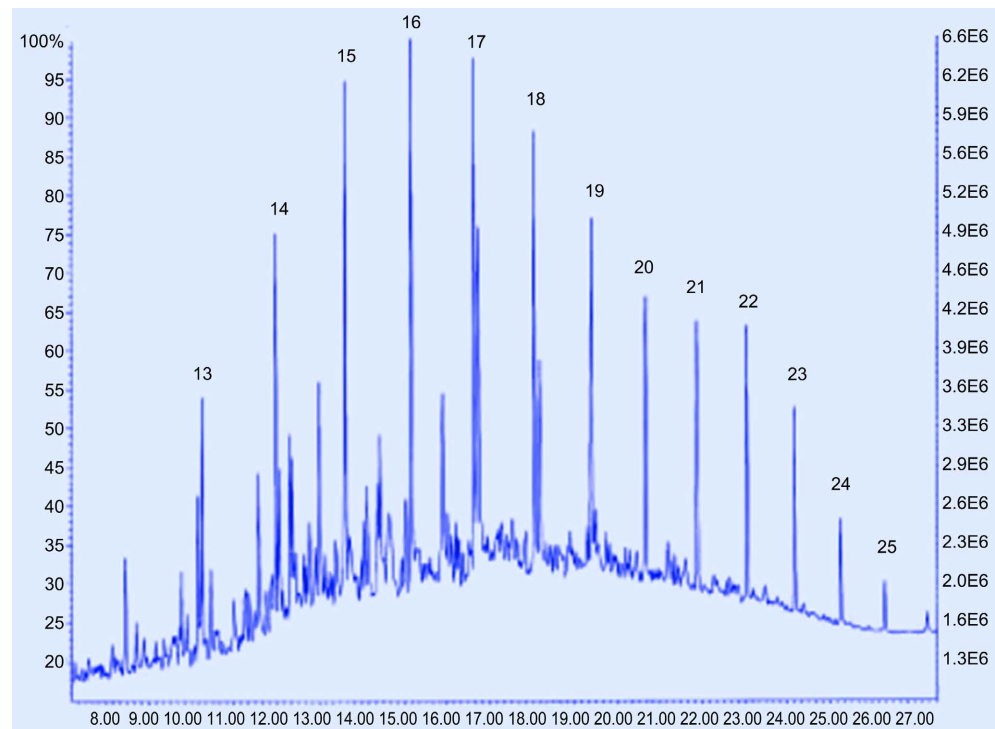
An optimum sample of the pyrolytic oil obtained from the pyrolysis process was collected and first filtered using a paper filter to remove most of the residue. This reduced the density as well as the darkness of the color. Fractional distillation was then conducted on the sample to extract the diesel fraction. The percentage diesel yield in the experiment after the fractional distillation of 50 ml (50 g) samples are shown in **Table 4** and the results show that the diesel yield from the distillation process was found to be 85.27%. The lighter fraction can also be collected at an industrial scale and the product is also used as a heating fuel, although the properties are not fit enough to be used in automobiles.

The sulphur content in the diesel product can be reduced in various ways these include Chemical and physico-chemical methods. A chemical approach involves the use of hydro-treating and purification with sulphuric acid and physico-chemical methods involve absorption and adsorption purification. The method of using activated carbon adsorption is the one which is the most economical to use in this process since the char, which is one of the by-products of the pyrolysis process can be converted to activated carbon and used to adsorb the sulphur from the diesel. The adsorption process using activated carbon has been found to reduce the sulphur content by 75% [13] [14].

The components of the diesel product were tested using a gas chromatography analyzer model 7820A GC system (G4350), Agilent Technologies. A photograph of the output from the gas chromatography is shown in **Figure 5**; the horizontal axis represents the number of carbon atoms in spices while the vertical axis represents the frequency of the number of carbon atoms. As what can be seen from the results, the product resembles diesel since it consists mainly of the C15 - C18 fraction. Generally, this is the distribution that is shown by a diesel product from a gas chromatography test. A high resolution gas chromatography test would be required in order to identify the exact species indicated by the peaks; this could not be shown by the machine that was used during the test.

Table 4. Diesel yield from fractional distillation.

50 g Sample	Diesel Yield (g)	% Yield	Lighter Fraction (g)	% Yield
1	42.10	84.20	7.90	15.820
2	43.00	86.00	7.00	14.00
3	42.80	85.60	7.20	14.40
Average	42.63	85.27	7.37	14.73

**Figure 5.** Diesel gas chromatography results.

4. Conclusion

The production of diesel from waste tires is a viable process and can be conducted at a larger scale in order to be used for firing equipment such as boilers, kilns and furnaces. In this project, the experiments conducted showed that an economic yield of the pyrolytic oil from the pyrolysis process is obtained with a recovery of 45% being obtained from the waste tires fed into the reactor and an 85% recovery obtained in the refining stage. The optimum temperature of the reaction was found to be 520°C and the optimum residence time was 92.5 minutes. Quality analysis showed that a quality product that is suitable for automobiles could be obtained from the process. The process also produces useful by-products such as char, which can aid in the purification process of the diesel after conversion to activated carbon. The process is environmentally friendly if the appropriate pollution prevention methods like gas absorption are thoroughly implemented. Waste tires are an alternative source of diesel and hence the feasibility of implementing the project at a large scale.

Acknowledgements

The research team thanks the National University of Science and Technology (Bulawayo, Zimbabwe) for providing the resources and funding for the success of the research. The research team also acknowledges and thanks NOIC (Msasa, Harare, Zimbabwe) for testing and analysis of the samples.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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