Waste Tire Pyrolysis Product: An Alternative to Petrochemical Feedstock

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Authors' contributions

This work was carried out in collaboration among all authors. Authors CEC and UAR designed the study. Author CEC wrote the protocol, managed the analyses of the study and wrote the first draft of the manuscript and author CAP performed the statistical analysis. Author CIV managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Aim: The amount of waste tire generated constantly in the modern society is on a rapid increase due to the world's urbanization, industrialization and population increase. This research was conducted to recover useful products from waste tyre and harness the possibility of using these products as a petrochemical feedstock alternative.

Study Design: Conventional pyrolysis was used to produce bio char, bio-oil and bio-gas

Place and Duration of Study: The research was carried out in the department of Pure and Industrial Chemistry and Mechanical Engineering Nnamdi Azikiwe University between January 2020 and march 2020

Methodology: Waste tyre was pyrolyzed using a conventional pyrolysis over three different temperature 400,550 and 750°C. The yield of the oil and char was determined by weight measurement, while that of gas was determined by mass balancing. The oil produced was characterized using GC/MS (gas chromatography/mass spectrometry)

Results: The percentage yield of char, oil and gas at 400°C, 550°C and 750°C respectively are 62, 24, 14; 48, 36.2, 15.8 and 42, 40, 18. The statistical analysis of yield gave a p-value of 0.785211 this showed that there is no significant change across the three samples statistically. The GC/MS

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analyses of the oil showed that the oil contains more than 35 compounds of which 6 accounted for more than 50% of the oil, these six include d-limonene with 12.83%, 1-2- benzene dicarboxylic acid with 10.48%, benzene, 1-ethyl-3methyl with 8.89%, benzene 1-methyl-3-(1-methylethyl) with 8.6%, benzene 1-ethenyl-4-methyl with 6.13% and hexadecenoic acid at 5.27%,while another six accounted for less than 5% of the oil, they includes (1-methylenebut-2-enyl)benzene with 0.89%, 1-methylbut-1,3-dienyl)benzene with 0.71%, naphthalene-2,7-dimethyl with 0.71%, quinoline with 0.96%, Spiro[4,5]dec-7-ene,1,8-dimethyl-4-(1-methylethenyl) with 0.74%, phenol 4-(1,1,3,3-tetramethylbutyl).

Conclusion: The composition of tire derived oil are very important petrochemicals derivatives which can be separated or can be used as feedstocks for petrochemical industries.

Keywords: Tire derived oil (TDO); conventional pyrolysis; bio oil; petrochemicals.

NOMENCLATURE

POPs: *Persistent organic pollutants*
PM10: *Particulate matter with 10 micrometres or less in diameter*
PAHs: *Polycyclic aromatic hydrocarbons*
NR: *Natural rubber*
SBR: *Styrene-butadiene rubber*
BR: *Butadiene rubber*
WHO: *World health organization*

1. INTRODUCTION

1.1 Background of Study

The disposal of solid (polymeric) wastes such as municipal wastes, industrial wastes, used plastics, poly-ethylene and tires is a menace and a serious problem globally due to their non-biodegradable nature [1]. In 2007, 303.2 million scrap tires were generated, two third were from passenger cars and the remainder came from trucks, heavy equipment, aircraft, off-road and scrapped vehicle [2], due to the rapid increase in population, industrialization, urbanization, motorization and change in the life style of people, this amount is constantly on the increase. Globally, approximately 64% of used tires went to landfill or were illegally dumped or stockpiled while only 13% were recycled [3]. Nowadays there are several technologies suitable and convenient to deal with waste tires, which include re-treading: this is the most environmentally friendly way of recycling used tires allowing an additional life. However, this option is not always possible (tire damaged or too old) and may be applied no more than three times. Other physical approaches are also available: direct reuse of old tires as road side barriers, chopped or grinded tires, as feedstock for engineering works, street furniture, and filler for new tires production [4]. Scrap tires threatens not only our environment, but the public health as well, When burnt in an open space, it causes problems in the modern society such as soil contamination, air contamination, water contamination, climatic change and discharge of heavy metals into the environment [5],this also increases the amount of PM10 above the acceptable standard [6]. One of the most important components of the PM10 is POPs such as PAHs and dioxins, which are widely acknowledged as carcinogens and mutagens that originated from incomplete combustion of tire. Because of its property as a carcinogen, WHO set PAHs (expressed as a concentration of benzo[a]pyrene), safety limit at 1nanogram per cubic meter (ng m^{-3}). POPs concentrations on PM10 are varied according to the combustion condition and fuel type, therefore, emission source type could lead to cancer in human. Among various emission source types of POPs, the open burning of scrap tires will be of particular concerns due to the rapid increasing vehicles on road which is as a result of the increase in population. Nigeria being among the top ten most populated countries in the world is faced with challenges of environmental pollution and degradation, increase in energy demand and waste generation. Nigeria's energy demand is focused on Non-Renewable sources mainly fossil fuel and solar energy, to tackle part of our energy crisis and environmental pollution and degradation, systematic approaches are now been considered to manage wastes which are generated by this population, it has become demanding and important to create approaches for energy recovery from these materials that cause environmental pollution and degradation. Tires are built to be tough and durable, the properties that ensure a safe ride, long service life as well as the ability to withstand biological degradation make scrap tire disposal a difficult task but also made it possible for it to be 100% recyclable, NR, SBR and BR are the most

common rubbers used for the production of tire. Sulphur is used as a vulcanizing agent, steel and carbon black are used as reinforcing agents and aromatic extender oil is used to soften and enhance the workability of rubber, all of these components are 100% recyclable [7]. Several studies have been carefully investigating the applications of pyrolysis as an alternative green technology to convert waste tires into energy sources [8,9] as well as an alternative to petrochemical feedstock. Solid waste especially waste tire has become a house hold commodity in Nigeria, it is commonly disposed in landfills as well as along the roads. The waste tire conversion into chemicals by means of pyrolysis yields high added-value products that can be used as reaction precursors and fuels[10].There are millions of these waste tires along the Nigeria roads, which are usually burnt openly. This causes several environmental and health problems such as release of incompletely burnt poly-aromatic hydrocarbons into atmosphere which has been described as carcinogenic as well as mutagenic. Researchers are still trying to find suitable management system and utilization of the products from this waste tire. It is based on this that the research is embarked upon to generate useful products from waste tire and analyse the possibility of using the oil produced as an alternative for petrochemical feedstock.

2. MATERIALS AND METHOD

2.1 Material

Waste tire was collected from a dump site situated in Awka in Awka south local government area, Anambra state, Nigeria.

2.2 Methods

2.2.1 Experimental set-up

The experimental setup of a conventional pyrolysis system is shown in Fig 1. The heating filament was modified to increase the heating rate and reduce residence time, a glass condenser was connected to the reactor to cool down the generated vapour produced during the process. The Temperature of the process was measured using a Cr-Al: K-type metallic thermocouple connected to a digital temperature reader that reads up to 1000^oC acquired from china and a PID temperature regulator. The thermocouple was inserted into the fixed bed reactor and the temperature of the system monitored.

2.2.2 Sample preparation

The waste tire was cut into small sizes using an iron saw and the iron reinforcement in the tire was removed. The sample was washed and allowed to dry.

2.2.3 Procedure

The sample to be pyrolyzed was weighed using an electronic weighing balance (labtech ECS electronic weighing balance BL-7501). The weighed 500g of the sample was transferred into the reactor and sealed with screws. The heating filament was switched on and allowed to heat the reactor to 400^oC for 150minutes, the vapour produced during heating was allowed to pass through the condenser that is been cooled by water at room temperature. The incondensable gases produced was burnt, the condensable gases condense and the liquid collected. The procedure was repeated two more times and the temperature attained were 550^oC for 195minutes and 750^oC for 240 minutes. At the end of each experiment, the bio-oil and bio-char produced was collected and weighed using same electronic weighing balance to determine yield, while the yield of the bio-gas was measured through mass balance using the formulae.

$$Total\ mass\ of\ waste\ tire \\ = mass\ of\ char \\ + \ mass\ of\ oil \\ + mass\ of\ gas$$

Using the mass of each product, the percentage yield was calculated using the formulae;

$$yield\ =\ actual\ yield\ /\ theoritcal\ yield\ x\ 100$$

2.2.4 Oil analysis

Composition of the tire derived oil as well as its structure was determined using gas chromatography coupled to mass spectrometer. The oil obtained were well mixed and homogenized prior to analysis. The analysis was carried out using Agilent 6890 GC coupled to a 5973 MS detector. An ion source temperature of 200^0C and electron energy of 70 ev was used. Helium (1mL/min) was used as the carrier gas. The oven temperature programme for analysing the bio oil utilized an initial oven temperature of 40^0C, maintained for 2 min, followed by steady climb to 350^0C at a rate of $5^0C/min$.
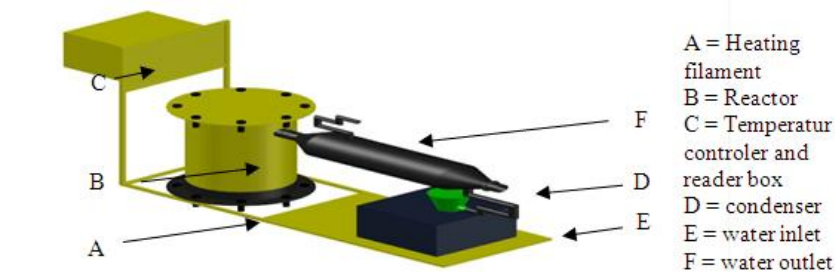
A = Heating filament
B = Reactor
C = Temperatur controler and reader box
D = condenser
E = water inlet
F = water outlet

Fig. 1. Experimental set up of a conventional pyrolizer

Chart 1. Typical composition of a car passenger tire

Material	Weight in percentage
Rubber (Natural and synthetic)	43
Filler (Carbon black, silicon)	27
Reinforcing material	16
Metals	11
Textiles	5
Chemical additives	14
Vulcanization aids	3
Other additives	3
Aromatic oils	8

Source: Shulman 2004

3. RESULTS AND DISCUSSION

3.1 Analysis of Variance for the Various Yields

The result in the Table 2 having a test statistic of .25 and a p value of .79, shows that there is no significant difference between treatments i.e. there is no significant difference in the weight of the char, gas and oil produced in the process. Despite the fact that by observation, it can be seen that the lower the temperature, the higher the weight of char, the lower the weight of oil and the lower the weight of gas; it can however also be observed that there is variance in the time of heat; i.e. sample1 that has the lowest temperature was also allotted the least time. So, a conclusion cannot be made about the effect of temperature on the experiment until each sample at different temperatures are allotted the same time.

Fig. 2 gives a clear pictorial view of the result of the experiment; sample 3 was heated to a temperature of 750°C with heat residence time of 240 minutes which means that sample 3 has the highest temperature and was also allotted the highest time in the experiment. The weight of oil and that of gas produced by sample 3 is the highest in the experiment; however, the weight of char produced by sample 3 is the smallest when compared to those of sample 1 and sample 2.

From the Fig. 2, inasmuch as lower temperature yields bigger weight of char, smaller weight of oil and smaller weight of gas, the ANOVA test shows that the differences in the weights of char and gas and oil across the three samples are statistically not significant.

3.2 Multiple Comparisons

From the result of the analysis as shown in Table 3, all the p values are above .05 which indicates that there is no significant difference across the samples.

3.3 Composition of Tire Derived Oil

The oil sample was analysed using GC and MS which is the most powerful instrumental tool for separating and analysing an organic compound based on their ability to vaporise without decomposition.

The gas chromatography was used to separate the mixture and the fraction separated where identified bases on retention time and peak area on a given column, flow rate, temperature and liquid phase. Based on these parameters'

Table 1. Percentage yield of waste tire at different temperature

Waste tire (S)	Temperature(^{o}C) attained	Percentage yield of char	Percentage yield of oil	Percentage yield of gas	Residence time (mins)
Sample 1 (S1)	400	62.0	24.0	14.0	150
Sample 2 (S2)	550	48.0	36.2	15.8	195
Sample 3 (S3)	750	42.0	40.0	18.0	240

Table 2. Analysis of variance for the various yields

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	19443.33	2	9721.667	0.246742	0.785211	3.885294
Within Groups	472802	12	39400.17			
Total	492245.3	14				

Table 3. Multiple comparison test for the samples

	(I) sample	(J) sample	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						lower bound	upper bound
LSD	sample 1	sample 2	-39.000	125.539	.761	-312.53	234.53
		sample 3	-88.000	125.539	.497	-361.53	185.53
	sample 2	sample 1	39.000	125.539	.761	-234.53	312.53
		sample 3	-49.000	125.539	.703	-322.53	224.53
	sample 3	sample 1	88.000	125.539	.497	-185.53	361.53
		sample 2	49.000	125.539	.703	-224.53	322.53

compounds with similar retention time and area where identified and recorded. The mass spectrometric analysis of the oil was done after the GC has separated the composition of the oil. It gives the structure of each compound present as well as its relative abundance as shown in table.

3.3.1 The gas chromatography of tire derived oil

The result of the analysis TDO is shown in Fig. 3. Table 4 shows compounds present in TDO, possible compounds with same retention time are grouped together, the area of each peak shows the relative abundance of each compound present, this table indicates. the presence of nitriles, aromatic and aliphatic acids, aromatics and poly aromatics compounds, bicyclo compounds, esters, sulphonated arom atic compounds, halogenated aromatic comp ounds and also substituted aromatic groups. The oil contain more than 35 compounds of which 6 account for more than 50% of the oil, those six include d-limonene with 12.83%, 1-2-benzene dicarboxylic acid with 10.48%, benzene-1-ethyl- 3methyl with 8.89%, benzene-1-methyl-3-(1-methylethyl) with 8.6%,
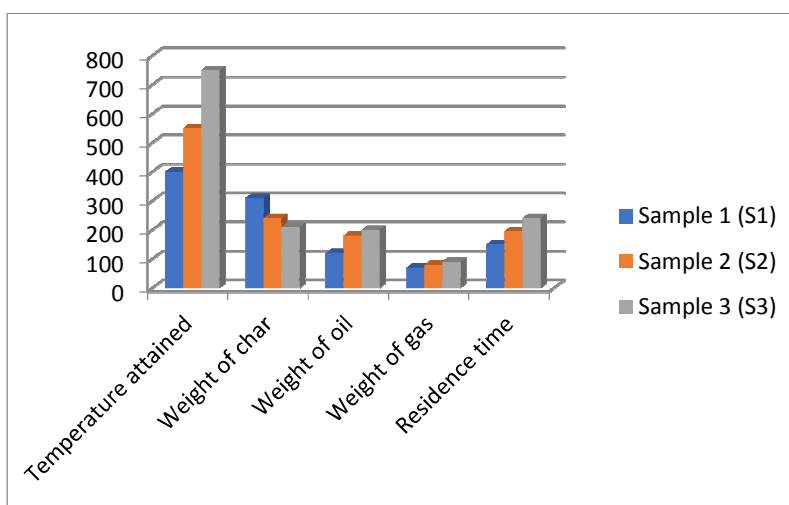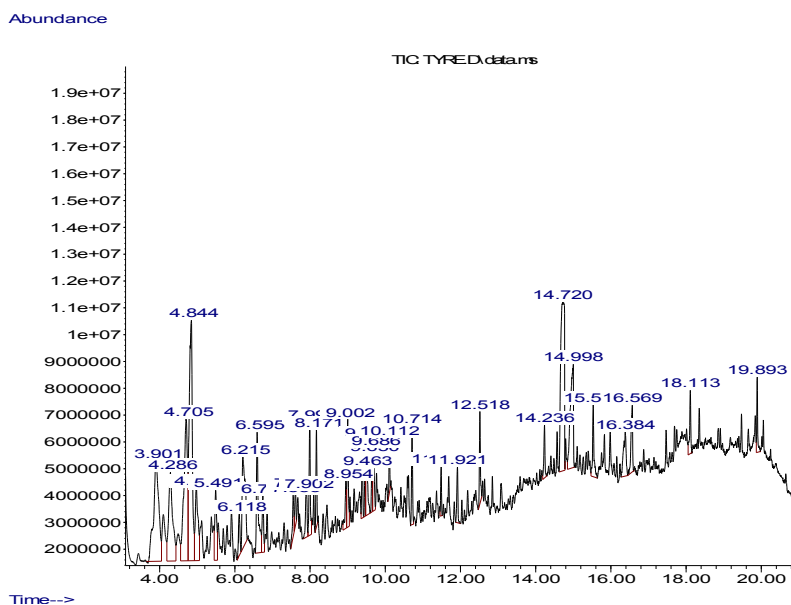

Fig. 2. Composition of waste tire

Fig. 3. GC Chart of TDO

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Table 4. Result of the gas chromatography of TDO

Peak number	Retention time	Area%	MS Peak type	Library identity/possible compound
1	3.901	8.89	BV	Benzene, 1-ethyl-3-methyl- Benzene, (1-methylethyl)- Benzene, 1,2,4-trimethyl
2	4.287	6.13	VV	Benzene, 1-ethenyl-4-methyl 1-(2-Methylphenyl) ethanol Benzene, 1-ethyl-3-methyl-
3	4.706	8.60	VV	Benzene, 1-methyl-3-(1-methylethyl) o-Cymene o-Cymene
4	4.844	12.83	VV	D-Limonene Limonene 1,5-Cyclooctadiene, 1,5-dimethyl
5	4.973	3.41	VV	Sulfurous acid, cyclohexylmethyl heptadecyl ester, cis-1-Ethyl-3-methyl-cyclohexane, Sulfurous acid, cyclohexylmethyl pentadecyl ester
6	5.492	2.22	VV	Benzene, 1-methyl-4-(1-methylethenyl)- Benzene, 1-methyl-2-(2-propenyl)- Benzene, 1-methyl-3-(1-methylethenyl)-
7	6.120	1.06	PV	3a,6-Methano-3aH-indene, 2,3,6,7-tetrahydro- Azulene, 1,2,3,3a-tetrahydro- Cyclohexene, 3-methylene-4-(1,2-propadienyl)-
8	6.215	4.65	VV	1H-Indene, 1-methyl- 2-Methylindene Benzene, (1-methyl-2-cyclopropen-1-yl)-
9	6.596	3.89	PV	Naphthalene Naphthalene 1H-Indene, 1-methylene-
10	6.744	1.36	VV	1H-Indene, 2,3-dihydro-1,2-dimethyl- Benzene, 2-ethenyl-1,3,5-trimethyl Benzene, (2-methyl-1-butenyl)-
11	7.554	0.89	PV	(1-Methylenebut-2-enyl) benzene (1-Methylbuta-1,3-dienyl) benzene Benzene-(2cyclopropylethenyl)-

Peak number	Retention time	Area%	MS Peak type	Library identity/possible compound
12	7.616	0.71	VV	(1-Methylbuta-1,3-dienyl) benzene
				1H-Indene, 1,1-dimethyl-
				1H-Indene, 1,3-dimethyl-
13	7.901	1.27	BV	2-Propenal, 3-(4methylphenyl)-
				4-Methyl-2H-benzopyrane
				Benzene, 2-ethenyl-1,3,5-trimethyl
14	7.992	2.30	VV	Naphthalene, 1-methyl-
				Naphthalene, 2-methyl-
				Naphthalene, 2-methyl-
15	8.173	1.54	PV	Naphthalene, 1-methyl-
				Naphthalene, 2-methyl-Methanonaphthalene, 1,4-dihydro-
16	8.954	1.12	VV	Biphenyl
				Biphenyl
				1,3-Cyclohexadien-5-ol, 1-phenyl-
17	9.001	2.23	VV	3-Cyclohexene-1-carboxylic acid-(dimethylamino)-1-phenyl-, ethyl ester, trans-
				7-Ethyl-4-tridecen-6-one
				2,4,4,6,6,8,8-Heptamethyl-2-nonene
18	9.392	1.131	VV	Propanedioic acid, ethyl-, diethyl ester
				1H-isoindole-1,3(2H)-dione, 2-(3,3-dimethyl-2-oxobutyl)-
				Pimelic acid, ethyl 2,4,4-trimethylpentyl ester
19	9.463	0.71	VV	Naphthalene, 2,7-dimethyl-
				Naphthalene, 2,6-dimethyl-
				Naphthalene, 2,6-dimethyl-
20	9.501	2.02	VV	Naphthalene, 2,6-dimethyl-Naphthalene, 1,3-dimethyl-
				Naphthalene, 1,3-dimethyl-
21	9.649	0.96	PV	Quinoline, 2,4-dimethyl-
				Dimethylquinoline
				1-Naphthalenamine, N-methyl-
22	9.687	1.52	VV	2,4,4-Trimethyl-3,4-dihydroquinoline
				4H-Pyrrolo[3,2,1-ij] quinoline, 1,2,5,6-tetrahydro-4-methyl-
				1H-Pyrazole, 3-methyl-5-phenyl-

Peak number	Retention time	Area%	MS Peak type	Library identity/possible compound
23	10.111	0.74	PV	Spiro [4.5] dec-7-ene, 1,8-dimethyl-4-(1-methylethenyl)-, [1S-(1.alpha.,4.beta.,5.alpha.)] 1H-Benzocycloheptene, ….. 2,4a,5,6,7,8,9,9a-octahydro-3,5,5-trimethyl-9- methylene-, (4aS-cis)- Longifolene-(V4)
24	10.716	1.67	PV	Naphthalene, 1,6,7-trimethyl- Naphthalene, 1,6,7-trimethyl- Naphthalene, 2,3,6-trimethyl-
25	11.487	0.71	VV	Phenol, 4-(1,1,3,3-tetramethylbutyl)- 4-tert-Butylphenyl acetate Pentanoic acid, 5-hydroxy-, p-t-butylphenyl ester
26	11.920	1.07	PB	Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)- 2-Methyl-6-tert-octylphenol 2-tert-Butyl-6-methylphenol, 2-methhylpropyl ether
27	12.516	1.54	PV	Bicyclo[3.2.0]heptan-2-one, 6-hydroxy-5-methyl-6-vinyl- (2-Hydroxy-3-methoxy-phenyl)- (3,5-trimethyl-4,5-dihydro-pyrazol-1-yl)-acetonitrile Cyclohexane, 1-ethyl-1-methyl-
28	14.235	1.00	VB	Hexadecanenitrile Hexadecanenitrile Hexadecanenitrile
29	14.720	10.48	VV	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester Dibutyl phthalate Dibutyl phthalate
30	14.997	5.27	VV	n-Hexadecanoic acid n-Hexadecanoic acid n-Hexadecanoic acid
31	15.530	1.68	VV	Bicyclo[3.2.0]heptan-2-one, 6-hydroxy-5-methyl-6-vinyl- 1,1,1-Trichloro-4-methyl-4,4-divinyl-di silethylene 2-Hexenoic acid, 2-hexenyl ester, (E, E)-
32	16.382	1.95	PV	1-Oxaspiro [2.5] octane, 5,5-dimethyl-4-(3-methyl-1,3-butadienyl)- 4-Chloro-2,6,8-trimethyl-quinolin-5-ylamine 5-(2,4-Dimethoxyphenyl)-1H-1,2,4-triazol-3-amine

Peak number	Retention time	Area%	MS Peak type	Library identity/possible compound
33	16.568	1.86	PV	Octadecanoic acid
				Octadecanoic acid
				Octadecanoic acid
34	18.116	1.26	VV	Cyclohexene, 1-(1,1-dimethylethoxy)-3-methyl-
				Sulfurous acid, cyclohexylmethyl hexadecyl ester
				Cyclopentane, 1,1'-ethylidenebis-
35	19.892	1.14	VV	Succinic acid, cyclohexylmethyl 3-fluorophenyl ester
				Cyclohexene, 1-(1,1-dimethylethoxy)-3-methyl-
				Sulfurous acid, cyclohexylmethyl octadecyl ester

benzene-1-ethenyl-4-methyl with 6.13% and hexadecenoic acid at 5.27%, these are very important petroch emicals compounds, This shows that the derived oils apart from been used as fuel can also be as an important source of chemicals because they contain high concentrations of valuable chemical.

4. CONCLUSION

From the study, the bio-oil and bio gas produced showed energy potential as a fuel source[11], thus can be utilized in place of heavy or residual oil and liquefied petroleum gas. The method used to recover these useful products from waste tire can be modified or improved upon to achieve higher oil yield as well as trap the bio gas produced. The relative abundance of these compound showed that some chemicals are present in higher quantity compared to others, which are very scares chemicals as such the oil produced can serve as raw material. The parameters analysed, which include the comp osition of the bio- oil showed the presence of imp ortant chemicals that can be used as feedstock for petrochemical companies as well as build special waste recovery refinery. We recommend that:

1. Relevant stakeholders must see the need to recover waste especially waste tire.
2. Research on the isolation of bio oil from waste should be done to separate chemical constituents.
3. Development of modular refineries is advised to recover bio-oil and bio-gas from waste to meet Nigeria's energy need.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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