Modification of waste tire pyrolytic oil as base fluid for synthetic lube oil blending and production: waste tire utilization approach

Emmanuel E. Okoro, Nehemiah O. Erivona, Samuel E. Sanni, Kale B. Orodu & Kevin C. Igwilo

ONLINE FIRST

Journal of Material Cycles and Waste Management
Official Journal of the Japan Society of Material Cycles and Waste Management (JSMCWM) and the Korea Society of Waste Management (KSWM)

ISSN 1438-4957

J Mater Cycles Waste Manag
DOI 10.1007/s10163-020-01018-1

Springer

Journal of Material Cycles and Waste Management
https://doi.org/10.1007/s10163-020-01018-1

ORIGINAL ARTICLE

Modification of waste tire pyrolytic oil as base fluid for synthetic lube oil blending and production: waste tire utilization approach

Emmanuel E. Okoro[1] · Nehemiah O. Erivona[1] · Samuel E. Sanni[2] · Kale B. Orodu[1] · Kevin C. Igwilo[3]

Received: 8 October 2019 / Accepted: 11 March 2020

Abstract

This study provides an environmentally friendly process for the production of waste tire pyrolytic oil from fast pyrolysis for use in lube oil production. The produced waste tire pyrolytic oil was further distilled to provide an almost pure base fluid for production of lube oil. The distilled pyrolytic oil was further transformed to lube oil via polyol synthesis. Characterization of the distilled pyrolytic oil from waste tire pyrolysis shows that the oil after distillation contained 2.04 g/100 g of Aliphatic hydrocarbons, 1.96 g/100 g of naphthalene, and 5.99 g/100 g of paraffin. The synthetic base fluid was blended with additive to obtain the desired lube oil. Based on the results obtained, the properties of the produced lubricant fall within the acceptable criteria for standard lube oils/commercial lubricants. Six different blends (A–F) were produced using varied percentages of the selected additives and the base fluid, however, sample C gave the best lube oil blend considering its average density (0.97 kg/L), average viscosity which compares favourably with ISO viscosity (68 mm^2/s) of class 68 oil at 40 °C with a flash point above 200 °C.

Keywords Waste tire · Pyrolytic oil · Lube oil · Fast pyrolysis · Base fluid · Waste tire utilization

Introduction

According to Machin et al. [1] the life cycle of a tire consists of five basic steps. The extraction of the raw materials, production of tire with the raw materials, use of the tire for vehicles/trucks, collection of the tire as waste after usage and processing or recycling of the waste tire. Improper disposal of waste tires can lead to accumulation of rainwater which can create favorable conditions for the spread of disease-carrying pests. Solid waste tires are considered as part of the waste disposal menace experienced in many countries in recent years [2, 3]. The adopted means of reducing these non-biodegradable material is recycling. Recycling tires to generate new products is another laudable means of waste tire utilization and disposal. This process completely employs shredded, intact and cut-up used tires in producing innovative products. Ding et al. [4] and Rofiqul et al. [5] identified and characterized liquid fuels obtained from used tires as well as their chemical and physical properties. Their high carbon content and high heating value paved way for their use as inputs/feedstocks for thermochemical processes [6–8]. The difficulty in disposing these polymeric wastes is due to their non-biodegradable nature and the adverse effects of carbon emissions on the environment during combustion. Hence, an ideal solution is the conversion of the waste tires into useful end products that have immediate demand in the society.

According to Osayi et al. [9], conversion/recycling of these polyisoprene-based materials into useful end products under controlled/optimized process conditions is an effective way of adequately disposing off waste tires. Acosta et al. [10] outlined different thermochemical treatments that can be used in valourizing waste tire. They went further to analyze the products obtained from pyrolysis as well as identified some process conditions and raw materials as

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10163-020-01018-1) contains supplementary material, which is available to authorized users.

✉ Emmanuel E. Okoro
emeka.okoro@covenantuniversity.edu.ng

1 Petroleum Engineering Department, Covenant University Ota, Ota, Nigeria

2 Chemical Engineering Department, Covenant University Ota, Ota, Nigeria

3 Petroleum Engineering Department, Federal University of Technology, Owerri, Nigeria

Published online: 27 March 2020

determining factors for the yields obtained when utilizing this process. The use of waste tires as fuel or feedstocks in low-emission thermal conversion processes is a very promising alternative in today's marketplace. Waste tires, despite being an environmental issue, also have economic benefits. Pundlik [11] in a review on the future of waste tire pyrolysis, gave the compositions of the waste tire pyrolytic oil/fuels and gases produced during pyrolysis. Waste tire pyrolysis has recently attracted more interests due to its advantages in solving tire recycling problems [12, 13]. The thermal energy for waste-tire decomposition, i.e. pyrolysis-enthalpy is the energy needed to raise the temperature of a tire feedstock from ambient condition to the reaction temperature so as to further aid pyrolysis [1, 10, 14]. Pyrolytic oil, a by-product of pyrolysis has been characterized and compared with natural rubber oil [9, 15]. The results showed some similarities and the possibility of utilizing these known non-biodegradable environmental wastes.

To turn used tires into valuable products, they must be reduced in size and then recycled; recycling reduces the negative environmental impacts of waste tires. The purpose of pyrolysis is to decompose the tire into its original components: gas, solid waste (char), low-grade carbon soot and oil/liquid. The pyro-process can possibly turns used tires into pyrolytic diesel oil, industrial furnace oil and high grade light speed diesel oil. US EPA recognizes fuel derived from tire as a viable alternative to those obtained from fossils, provided that adequate regulatory controls are in place. Crude oil is classified as naphthenic, paraffinic or aromatic, depending on the underlying structures of the complex molecule. Aromatic crude cannot not be used to produce base oils for lubricants because aromatic compounds have poor viscosity-temperature relationships (i.e. their viscosities decrease rapidly with temperature). There are also problems of thermal and oxidative stabilities. Paraffins have very good viscosity-temperature relationships besides their high thermal and oxidative stabilities. Thus, most of the base oils produced in modern refineries are paraffin-based and the focus is on these oils. The molecular weight range of paraffin oils is from C_{25} to C_{40}, however, most of the molecules in the oils have mixed structures.

Most lubricant-based fluids are obtained by refining crude oil and the base fluid from obtained from the refining process are used as starting materials for synthetic lubricants. Estimates of global demands for petroleum base oils exceed 41 million tonnes. Non-petroleum base-fluids are used where special properties are necessary, i.e. where petroleum base oils are in short supply or where substitution by natural products is practicable or desirable. Unlike mineral oils which are derived from crude oil, synthetic lubricants can be defined as chemically synthesized base oils. Synthetic lubricants account for approximately 2% of the growing global lubricant market. However, it is clear from literature that besides recycling, an additional means of safely discarding these tires which considers optimizing the process of producing pyrolytic oil (base oil) from waste tires in order to obtain high product (lube oil) yields. The pyrolytic oil obtained from the waste tires collected for this study was analyzed using GC–MS in order to ascertain its suitability as a base oil prior its conversion to lube oil. Thus, Nigerians and the whole world can take advantage of the approach adopted in this study for adequate disposal of used tires without destroying the environment. This will also stimulate a balance between "tire consumption and the environment" and, "social and economic development"; this supports the sustainable development drive.

Materials and methods

Raw materials

The waste tire used in this study was collected from a dumpsite in Ota, Nigeria. The tire was washed to remove stones and debris, and the sidewalls of the used tires that contained no wire were chopped into 10, 15 and 20 mm sizes due to the size of the pyrolytic reactor in the Covenant University Mechanical Engineering Department workshop. The maximum used tire chopped piece from literature is 10 mm [16]; thus, this study designed a reactor that will contain 10 mm size and above. The pyrolytic reactor allows for further degradation of the weighty polymeric compounds in the waste tires into lower molecular weight oils or compounds.

The reagents used for formulation of the lube oil are maleic anhydride, naphthalene, styrene acrylate, ethylene glycol and sodium methoxide purchased from BH Chemicals Ltd., Poole.

Methods

Pyrolysis of the waste tires

Pyrolysis of the waste tires can be divided into four functional units: waste tire pretreatment and preconditioning (drying and size reduction), pyrolysis of waste tire, product separation, and quenching to obtain the pyrolytic oil. Figure 1 shows the process scheme for the conversion of the waste tire to lube oil.

The waste tire pyrolysis was carried out in a fixed bed reactor (Figs. 2, 3); type S-304 stainless steel was selected for fabrication of the reactor and all pipes connected to the reactor. The reactor was placed in a muffle furnace (J.P. Selesta, S.A., 582543 S/N, 230 VAC, 00-C/2000367, 50/60 Hz, 3500 W, Spain) with a PID temperature controller which was used as heat source. The furnace was powered electrically and heated up to 1100 °C. The reactor design

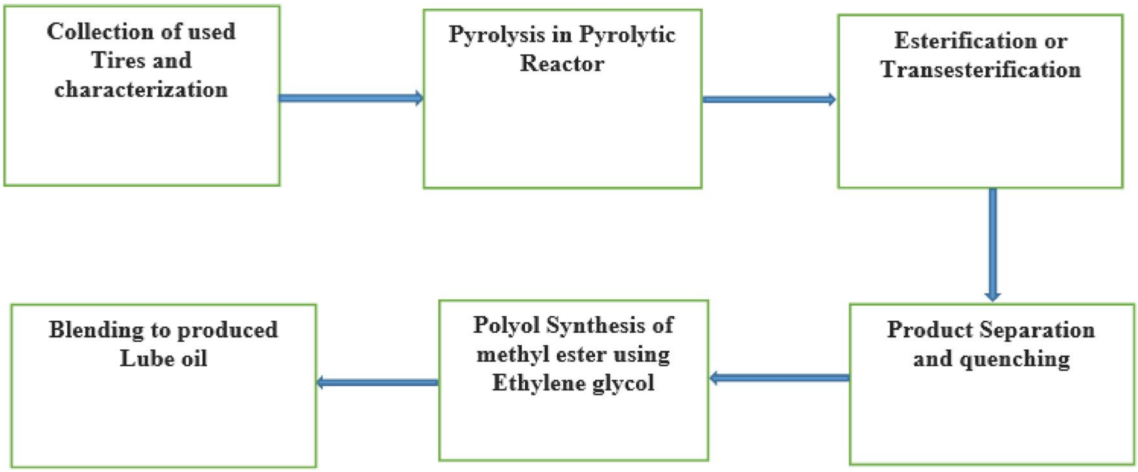


Fig. 1 Proposed process scheme for lube oil synthesis from waste tires

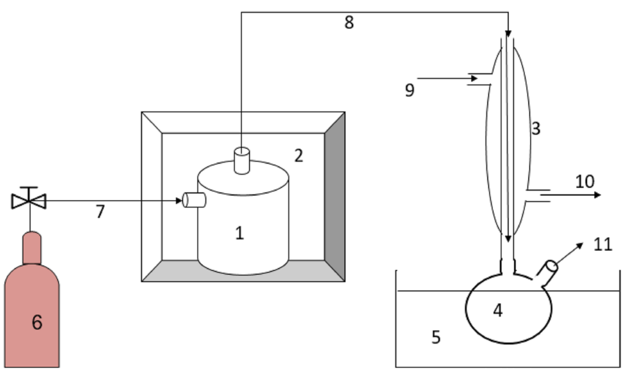


Fig. 2 Schematics of the waste tire pyrolysis set-up (1—Reactor, 2—Furnace, 3—Reflux condenser, 4—Bio-oil collector, 5—Ice trap, 6—Nitrogen bottle, 7—Inert/sweep gas inlet, 8—Vapor outlet, 9—Cooling water inlet, 10—Hot water outlet, 11—Non-condensable gas outlet)

parameters are 10 cm internal height, 14.5 cm external height, 13.3 cm diameter. Nitrogen gas was circulated at a maximum value of 0.055 m/s and 45 L/min maximum sweep gas flow rate. The introduced gaseous nitrogen, helped to provide an inert atmosphere and also acts as a carrier gas during pyrolysis. The reactor has two openings, one opening is located at the side of the reactor for transportation of the pyrolytic oil produced in the process, and the second is above the level of the waste tire in the reactor and serves to connect the reactor to the nitrogen gas cylinder via a stainless steel pipe. After transferring the sample to the reactor, the system was purged with gaseous nitrogen to remove air from the system before pyrolysis. Clearance was provided in the reactor by not filling it up totally in order to allow for easy passage of gaseous products. After turning on the heat source of the furnace, the temperature controller was programmed at a set value, say 610 °C as operating temperature with a heat transfer rate of 18 °C/min. The temperature of the reactor was kept constant for 20 min after the process reached the set temperature, after which it was cooled to 20 °C. This was to allow all possible liquid and vaporous products to leave the reactor and reach the collection unit. At

Fig. 3 Pyrolytic reactor for pyrolysis process

the end of the pyrolysis, the nitrogen gas flow was stopped and the reactor was shut down. After cooling the system, the collection unit was removed from the reactor, and the pyrolytic oil was collected in a glass bottle and measured.

The produced pyrolytic oil (Fig. 4) was characterized to determine the properties (i.e., pour and flash points, viscosity index, saponification value, density, kinematic viscosity) and its suitability for use as base oil for producing lube oil. The characterization was done in accordance with American Standard Test Method for Diesel (ASTM-D).

Bench scale distillation of the pyrolytic oil

Waste tire pyrolytic oil was distilled at specified temperature using a bench scale distillation set-up consisting of an electric heating mantle, glass round bottom flask and water cooled glass condenser (Fig. 5). The temperature of the crude oil was raised to 370 °C in the distillation unit for easy separation of the oil into light and heavy fuel fractions, while oxidizing the sulphur compounds as discussed in Tsietsi et al. [17]. The pyrolytic oil was further distilled to reduce sulphur, aromatic compounds and long chain normal Paraffins which can form wax. It is believed that sulphur is easily removed at the specified temperature because, lower boiling oil fractions primarily contain sulphur-based compounds that are in the form of sulphides, mercaptans, di-sulphides or lower member ring compounds which are relatively easier to de-sulphurise (Fig. 6 are compounds identified from the GC–MS analysis).

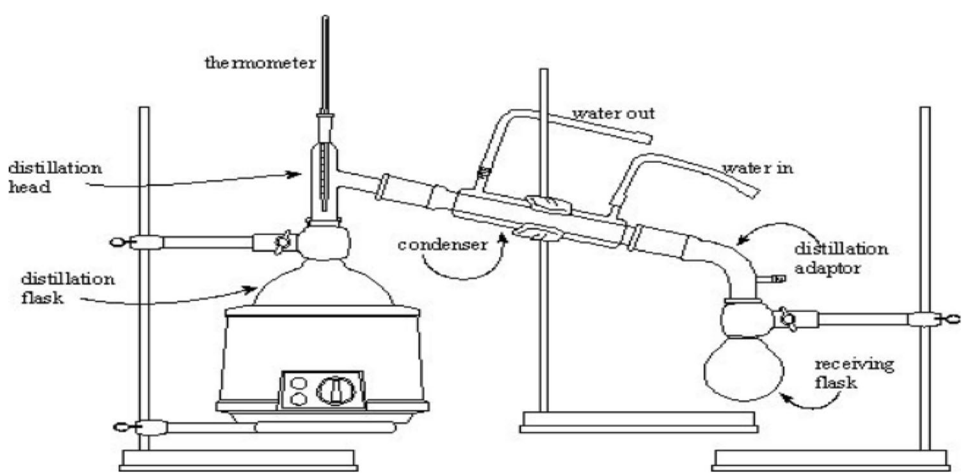
A lubricant-base oil must not contain components which corrode metal parts of an engine or a machine. The GC–MS analysis shows that the properties of the waste tire pyrolytic oil are quite similar to those of a commercial base oil for blending of lube oils during the upgrading process. According to some studies, the impurities in the pyrolytic oil can be filtered [18, 19].

Characterization of the distilled pyrolytic oil

On receipt of the sample (distilled waste tire pyrolytic oil) in the laboratory, it was kept at a temperature of about 4 °C until the commencement of the laboratory analysis. The extraction method for the analysis of hydrocarbon profiles in the sample was according to the ASTM D3328 and ASTM 3415 standards.

Fig. 4 Produced waste tire pyrolytic oil

Fig. 5 Bench scale distillation of waste tire pyrolytic oil schematic diagram



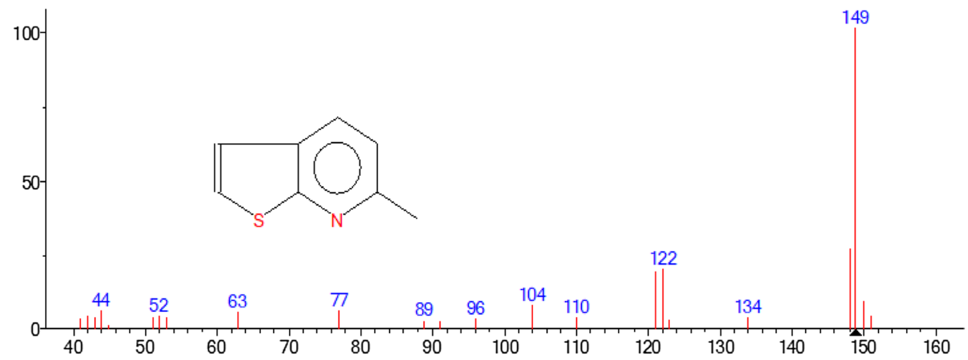


Fig. 6 GC–MS El mass spectrum and chemical structure of 6-Methylthieno [2,3-*b*] pyridine

Extraction

The oil sample was carefully emptied into a 27 mL capacity McCartney bottle of borosilicate material and a 10 mL mixture containing 3:1 redistilled hexane: dichloromethane was added. The bottle and its content were placed in the sonicator to extract the hydrocarbon for about 2 h. The organic layer was filtered into the 250 mL capacity borosilicate beaker.

The extract was carefully transferred into a 1 L separating funnel, and 20 mL of the redistilled dichloromethane was added. The separating funnel was shaken vigorously for about 2 min with periodic venting to release excess vapour pressure. The organic layer was allowed to separate for 10 min and was later collected in the 250 mL flask. The aqueous layer was re-extracted twice with 20 mL of the extractant. The combined extract was dried by passing it through the funnel containing anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas.

Paraffin/saturated/PAH separation

The concentrated oil was separated into the saturated paraffin and naphthalene compositions by packing the glass column with packing materials made of activated alumina (grade 1) of neutral activity. 10 mL of the treated alumina was packed into the column and cleaned properly with redistilled hexane. The extract was poured onto the alumina and was allowed to run with the aid of the redistilled hexane to remove the saturated paraffin into the pre-cleaned 20 mL capacity glass container. The naphthalene fraction was recovered by mixing it with the mixture containing hexane and dichloromethane in ratio 3:1; finally, this was followed by the removal of the most polar PAHs by introducing dichloromethane into the pre-cleaned borosilicate beaker.

Blending of lube oil using distilled pyrolytic oil as base oil

Lubricants are formulated by mixing base oils and additives to meet various performance requirements. These specifications relate to the physical and chemical properties of the new blended oil and help to ensure that the oil continues to work and protects the engine or machine in use.

Series of properties can be used to measure various properties and predict performance when choosing the right base oil for use in the formulation of lubes. Many of these functions are used as quality control measures in the manufacturing process in order to ensure consistent product quality. Many of these properties are altered or improved with additives, but knowledge of the properties of the base oil is essential for effective formulation of lubricants.

To improve and alter the properties of the lube oil processed from the waste tire pyrolytic oil, selected chemical additives that are compatible with the base oil from the treated and untreated waste tire pyrolytic oils were used. These chemical additives and their functions are;

1. Maleic anhydride, an anti-oxidant;
2. Naphtalene, a pour point depressant;
3. Styrene acrylate, a viscosity index improver.

The ratio/amount of chemical additives used for blending the lube oil was varied to determine the best combination for the formulated lube oil from the pyrolytic base oil (Table 1).

If the lubricant does not meet the specifications, the formulations were re-worked until the desired specifications were met.

Table 1 Additives and their Blends

Sample	Lube oil (mL)	Naphthalene (g)	Maleic anhydride (g)	Styrene acrylate (g)
A	85	5	5	5
B	70	10	10	10
C	55	15	15	15
D	60	10	10	20
E	40	20	20	20
F	70	5	5	20

Results and discussion

Proximate and ultimate analyses

Prior to pyrolysis, proximate and ultimate analyses of the tire were conducted for better understanding of its constituent properties following the ASTM D-7582 and ASTM D-5865 standards. Table 2 shows the results from these analyses and the results are similar to the results obtained in the review by Rowhani and Rainey [16], and study by Idris et al. [20]. The chemical constituents of the waste tire adopted in this study play a major part in estimating the pyrolytic oil yield and quality. The volatile matter recovered from the waste tire comprises 61.79 wt%, while the fixed carbon, moisture content, ash content and high heating values (HHV) are 26.93, 1.22, 12.2 and 38.03 wt% respectively. The ultimate analysis result shows high carbon content of 81.34 wt%

Properties of the base oil from the waste tire pyrolysis

Base oil serves as the starting material for a prospective lubricant before mixing with the additive. Lubricants can be classified in several ways. One of the most common classifications is by base oil constituent. The synthetics are made artificially using a process scheme and come in many formulations with unique properties for their intended purposes. The starting properties of any base oil greatly affects the type and quantity of additives to match the required enhancement. Another important aspect of additives is the regular addition of various additives to improve certain properties. The amount of base oil used for lubricants is mostly important, because it accounts for 70–90% of lubricant formulations. Mang and Dresel [21] highlighted that the high price of lubricants is increasingly characterized by their base oils than their additives. Thus, a cheap base oil will probably be accepted by manufacturers that will benefit from lower overall system costs. The base oil produced in this study is a dark-brown oily liquid with a strong acrid smoky smell probably due to its Sulphur content (1.58 wt%).

The characteristics of the pyrolytic oil from waste tire were determined using Gas Chromatography-Mass Spectrometry (GC–MS) and ASTM D standard techniques. The API gravity of the pyrolytic oil is 43.7 and can be classified as light oil. The kinematic viscosity of the oil which is the ratio of absolute viscosity and base fluid density, is 3.2 mm^2/s, this puts the waste tire pyrolytic oil in the ISO VG three category (International Standardization Viscosity Grade). This is an important property of the lubricant and affects the ability of the base oil to form a lubricating film and minimizes friction to reduce wear. The aniline point is 18 °C, and the cetane index is 39.65; thus, the waste tire pyrolytic oil according to cetane index rating is classified as a diesel. Higher cetane index generally indicates that the fuel will combust more quickly in the engine. This does not necessarily guarantee better efficiency, but it should indicate a quieter and smooth-running engine. It can also mean that there will be less harmful emissions from the exhaust pipe, thus helping the environment.

Table 2 Proximate, ultimate and high heating values of the waste tire

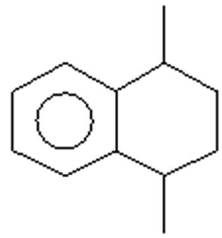
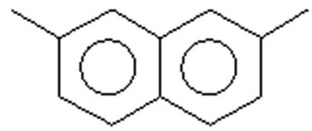
S/N	Content	Values
1	Volatile matter (wt%)	61.79
2	Fixed carbon (wt%)	25.80
3	Moisture content (wt%)	1.21
4	Ash (wt%)	11.20
5	HHV (MJ kg^{-1})	38.03
6	Carbon (wt%)	81.74
7	Hydrogen (wt%)	7.04
8	Nitrogen (wt%)	0.62
9	Sulphur (wt%)	1.18
10	Oxygen (wt%)	9.42

Bench scale distillation analysis

Table 3 shows the typical structures in base oil that were identified in the treated and analyzed waste tire pyrolytic oil. The paraffin structure has a very good viscosity-temperature relationship and stability. Since most of the base oils produced in modern refineries are paraffinic in nature, hence, the focus is on these oils. Naphthenic intermediate oils are produced in limited quantities, mainly for low temperature applications, due to their good fluidity at low temperatures. These two structures were identified in the GC–MS analysis of the treated waste tire pyrolytic oil proposed as base fluid for lube oils.

The pyrolytic base oil properties were compared with those of other standard base oils used in producing commercial lube oils (Table 4). The density of the waste tire pyrolytic oil was found to be higher than that of the commercial base oil; although, it was found to be within the acceptable range of standard base oils used for lube oil blending (860–890 kg/m^3). Literature shows that density is dependent on the oil's molecular weight, thus, the pyrolytic oil produced in this study has higher molecular weight than that of other standard base oils. The kinematic viscosity at 100 °C for the produced pyrolytic oil and 150SN (Solvent neutral) are within the same range, but are lower than that of 600SN (Solvent neutral) and 150BT (Bright stock). Solvent neutral (SN) and Bright stock (BS) are American Petroleum Institute (API) common Group 1 grade of lubricant base oils that are suitable as engine oils for diesel and heavy machine engines respectively. Rofiqul et al. [5] highlighted

Table 3 Typical structures of the base oil found in the pyrolytic oil

S/N	Structures	Description
1		Two naphtheno-aromatic rings bridged by normal paraffin chain
2		2-ring condensed aromatic linked to two small alkyl groups
3		Long chain paraffinic nature

the importance and advantages of low viscosity pyrolytic oils during transportation and handling. The low flash point of the pyrolytic oil can be as a result of it containing compounds with far boiling points.

Density, pour and flash points are among the physical properties relating to specialized lubricant applications. Though lube oil is measured in volume, it can be formulated based on weight; from analysis, the treated pyrolytic oil has the highest density (Table 4). The base oil yield is dependent on the quantity of desirable components in the boiling range of the lubricant. The pour point of the base oil sample and that of the treated pyrolytic oil are in close agreement with the standard base oil, but it they closer to the API grade 150SN which is suitable as engine oil used in the transportation industry. The flash point of the pyrolytic oil is lower than the standard base oils, and can be attributed to the complex mixtures of hydrocarbon compounds identified during the GC–MS analysis.

The GC–MS analysis identified the nature and type of compounds present in the pyrolytic oil. The pyrolytic oil derived compounds as indicated by the chromatogram peaks as shown in Fig. 7 were analyzed with the NIST search software. From the area percent of compounds identified by the GC–MS, compounds with a match peak ≥ 70% and an area percent ≥ 0.1 are as presented in Table 5. Most of the compounds identified in Fig. 7 are shown in Table 5, and the compounds identified in this study are in line with other published literature [16, 22]. The high PAHs and aromatic compounds can be linked to the type of rubber used in manufacturing the tire. One of such example is polystyrene butadiene which often acts as an additional benzene ring source. In this study, D-limonene and limonene were identified in the GC–MS analysis. Limonene has the capacity to increase the market value of the pyrolytic oil obtained from the waste tire [23, 24].

Characterization of the distilled pyrolytic oil from waste tire pyrolysis shows that the oil after distillation to remove Sulphur compounds contained 2.04 g/100 g of aliphatic hydrocarbons (saturated cyclic hydrocarbons), 1.96 g/100 g of naphthalene, and 5.99 g/100 g of paraffin. Figure 8 shows the chromatograph of the aliphatic, naphthenic and paraffinic constituents in the oil. The equipment condition and raw data are attached as supplementary document.

Table 4 Comparison of the waste tire pyrolytic oil and other standard base oil

Oil properties	ASTM test	150SN	600SN	150BS	This study
Density, kg/L	ASTM D-1298	0.868	0.876	0.879	0.891
Kinematic viscosity @ 100 °C, mm^2/s	ASTM D-4741	5.2	12.4	30.52	5.7
Flash point, °C	ASTM D-92	216	258	260	156
Pour point, °C	ASTM D-2097	− 15	− 9	− 6	− 13
Water by crackle		Neg	Neg	Neg	Neg
Appearance	Visual	Clear and bright	Clear and bright	Clear and bright	Dark-brown

SN solvent neutral, *BS* bright stock

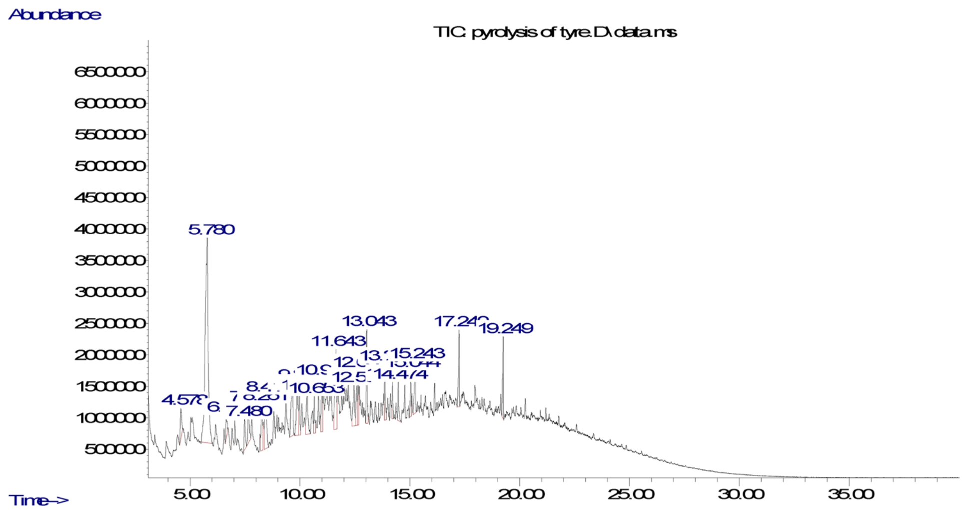


Fig. 7 GC–MS total compound chromatogram for the pyrolytic oil obtained from waste tire

Table 5 Carbon atom number from pyrolytic oil GC–MS analysis and their boiling points

Compounds	Number of carbon atoms	Boiling point (°C)
Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl	12	238.81
Benzene, 1-(1-methylethenyl)-2-(1-methylethyl)	12	228.59
Cyclohexane, 1-(cyclohexylmethyl)2-methyl-, cis	14	264
Benzene, 1,4-bis(1-methylethenyl)	14	227.85
(1-Methylpenta-1,3-dienyl)benzene	12	240
Naphthalene, 2,7-dimethyl	12	264.85
1,1′-Biphenyl, 2-methyl	13	266.85
1,1′-Biphenyl, 3-methyl	13	270
α-acorenol	15	322
7-epi-trans-sesquisabinene hydrate	15	374.52
cis-Thujopsene	15	298.4
Pentadecane	15	276.4
Nonadecane	19	329.75
Naphthalene, 2,3,6-trimethyl	13	262.85
Naphthalene, 1,6,7-trimethyl	13	285.05
1,1′-Biphenyl, 2-methyl	13	266.85
1,1′-biphenyl, 2,6-dimethyl	14	262.85
1,4-Methanonaphthalene,1,4-dihydro-9-(1-methylethylidene)	14	301
1,2-Benzenedicarboxylic acid, dipropyl ester	14	303.5
Heptadecane	17	301.85
Tetradecane	14	254.85
Chamazulene	14	306.85
Naphthalene, 1,2,3,4-tetramethyl	14	312.15
Hexadecanenitrile	16	333.05
Heptadecanenitrile	17	350
Octadecanenitrile	18	356.85
Nonadecanenitrile	19	463.05

Blending of lube oil using pyrolytic oil as base fluid

Base oil alone cannot satisfy the requirements of high performance lubricants without the addition of synthetic and natural chemical substances known as additives, which will help improve or boost different existing properties of lubricants and also suppress undesirable properties. The distilled waste tire pyrolytic oil was optimized by converting

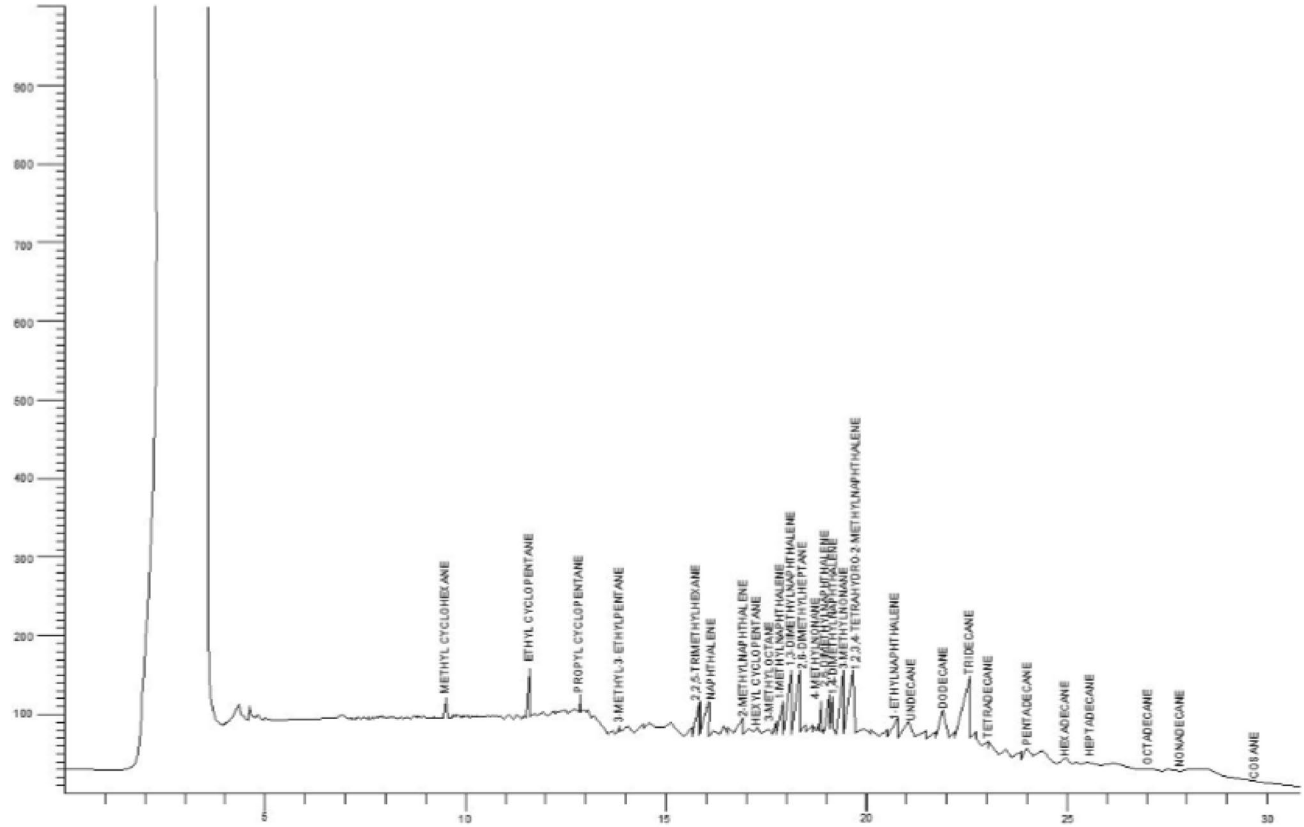


Fig. 8 Summary of the chromatogram analysis for aliphatic, naphthalene and paraffin

it to lube oil through a process called "Polyol Synthesis". This process involved the blending of ethylene glycol and sodium methoxide with the distilled waste tire pyrolytic oil. The optimized waste tire pyrolytic oil was blended with the selected additives, naphthalene, styrene acrylate, maleic anhydride in different compositions as shown in Table 1; this was done in other to identify the composition with the optimum lube oil formulation. These additives serve different purposes, i.e. naphthalene is a pour point depressant, styrene acrylate a viscosity index improver and maleic anhydride an anti-oxidant. These additives influence the physical and chemical properties of the base oil produced from the waste tire.

These additives were mixed in the distilled pyrolytic oil to enhance the properties of the base fluid and suppress most of its undesirable properties. Additives typically make up about 10–30% of the finished lubricating oil depending upon the target application of the lubricant. In this present study, the additives were varied up to 50% to see the interactions with the proposed base fluid. Many lubricant additives are available and they are selected for use based on their ability to perform their intended functions. Mineral lubricants are normally based on paraffinic and/or naphthenic oils, and additives are normally added to satisfy the specified performance requirements. The required additives were initially dissolved in small portions of the proposed base fluid using mechanical blending. Heating was controlled to avoid thermal decomposition of the additives. The additive concentrate was then decanted into a container with large volume of the base fluid and further blended, and the sample was analyzed.

The produced lube oil physical properties were analyzed using American Standard Test Method for Diesel (ASTM-D) (Table 6). The fundamental characteristic of every fluid is its viscosity, and it is dependent on the external parameters such as temperature and pressure. Figure 9 shows the Kinematic viscosity at 40 and 100 °C. Sample F has the highest kinematic viscosity (73.7) while sample A has the lowest kinematic viscosity. Sample F has a greater percentage (20%) of the viscosity index improver additive (styrene acrylate) compared to sample A (5%). Thus, the more the viscosity index improver in lube oil, the higher the kinematic viscosity. From the analysis conducted, it was deduced that 70% volume of the tire pyrolytic oil as based fluid with 30% volume of the identified additives gave the best blend of the formulated lube oil in this study.

Factors that have effects on the lubricant efficiency

The Pareto graph (Fig. 10) was used to determine which variables had the most statistically important effects on the

Table 6 Properties of the lube oil samples and their comparison with commercial lube oil

S/N	Parameters	Unit	A	B	C	D	E	F	Commercial lube oil
1	Density (15 °C)	kg/L	0.94	0.96	0.97	0.99	1.1	1.1	0.89
2	API gravity		0.99	1.01	1.02	1.04	1.16	1.16	1.00
3	Kinematic viscosity (40 °C)	mm^2/s	46.5	47.1	48.0	49.8	52.9	53.7	68.7
4	Kinematic viscosity (100 °C)	mm^2/s	24.3	25.0	25.9	27.4	29.6	31.9	40.9
5	Pour point	(°C)	−10	−11	−11	−12	−12	−13	−45
6	Cloud point	(°C)	2	2	1	0	0	0	–
7	Smoke point	(°C)	255	255	257	257	257	258	–
8	Flash point	(°C)	242	243	244	245	247	247	226
9	Acid value	mg/L	1.92	1.95	1.98	1.95	2.01	1.98	–
10	TBN	Mg KOH/g	1.92	1.95	1.98	1.95	2.01	1.98	10.4

Fig. 9 Kinematic viscosities of the blended lube oil samples

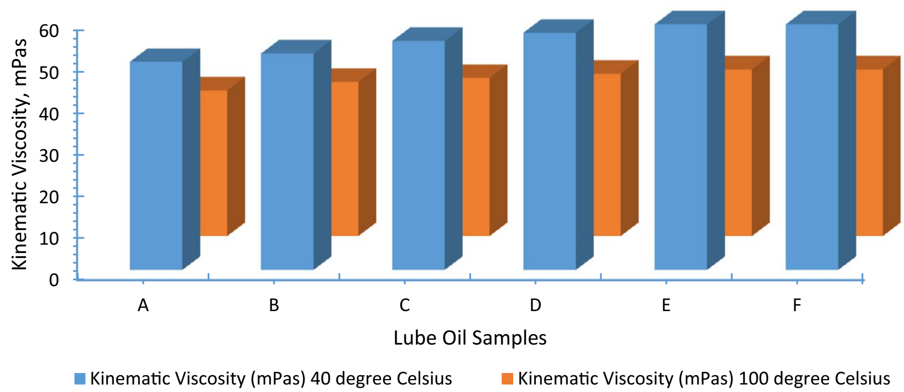
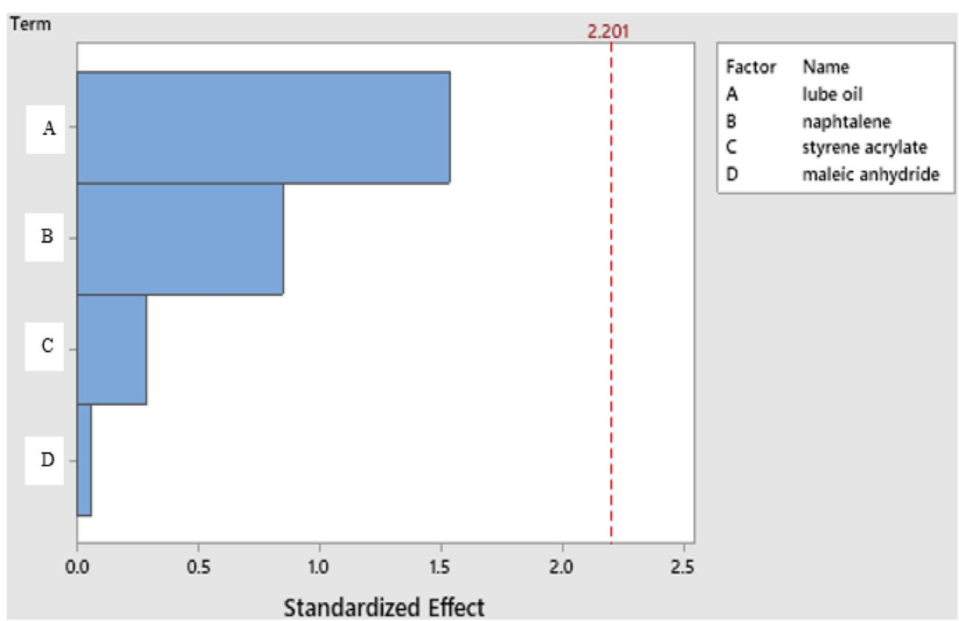


Fig. 10 Pareto plot of the standardized effects of the blended lube oil samples



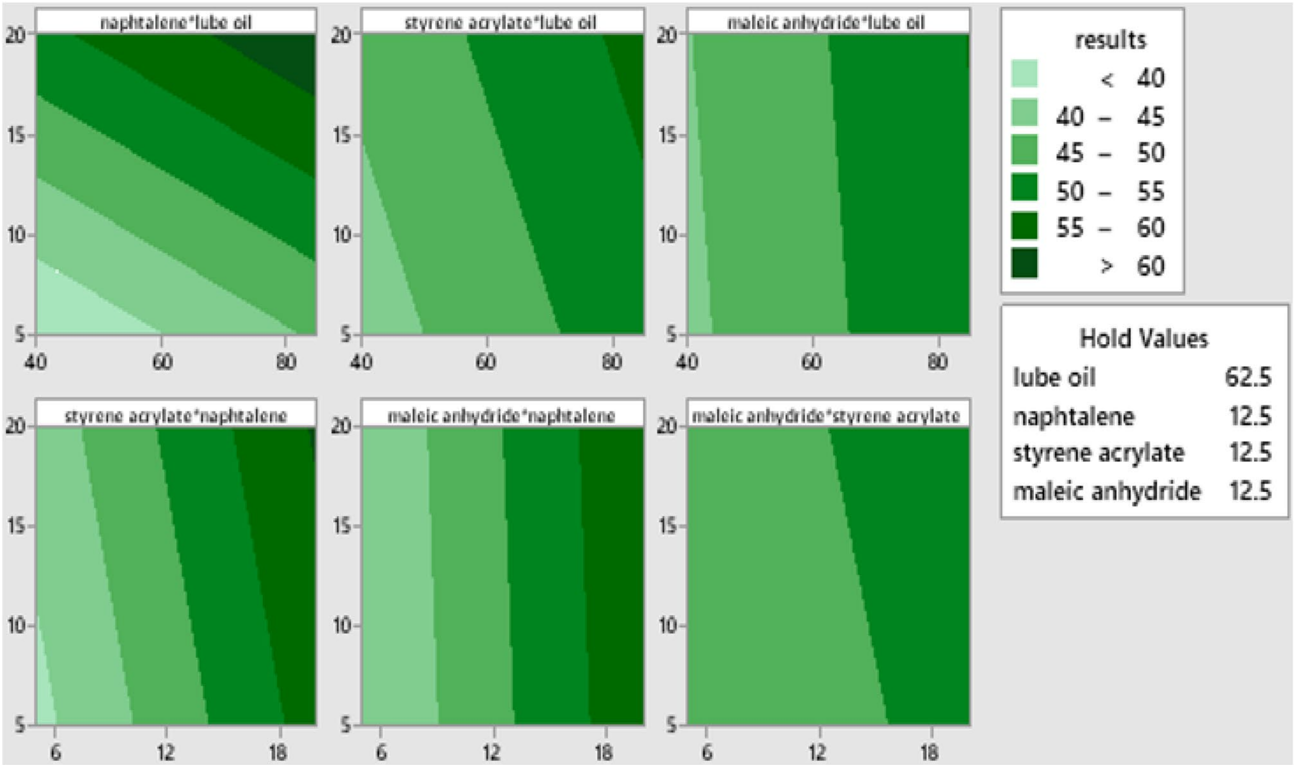


Fig. 11 Contour plots of results for the blended lube oil samples (color figure online)

efficiency of the blended lube oil. The reference blue bar row on the graph helped in identifying which impacts (single or mixed) are significant to the responses received. The farther a factor is, the greater the effect of the reaction from the red dotted line. From the Pareto chart in Fig. 10, it was observed that naphthalene had the greatest impact on the efficiency followed by lube oil, then styrene and the maleic anhydride.

A contour chart (Fig. 11) indicates the effect of lube oil, naphthalene, styrene acrylate and maleic anhydride on the quality of lubricants produced. The darkest green area disclosed the ratios that would form the lubricant of best quality while the light green color displayed the lowest impact mixture (mixture of low quality). Figure 11 shows the combined effect of styrene acrylate, naphthalene, maleic anhydride and lube oil at constant time; the darkest green area disclosed the combination (combined ratio) with the most significant effect. The light green color indicates the ranges where the combine effect of temperature and concentration combined will be irrelevant.

Comparison of blended lube oil samples with commercial lube oil

The blended lube oil samples were compared with a commercial lube oil with sufficient stringent requirements for oil specs used in vehicle engines. Table 6 shows that the density of the commercial lube oil (0.89 kg/L) is lower than all the blended lube oils in this study. Samples E and F of the blended lude oil show the highest density of 1.1 kg/L. The viscosity of the commercial lube oil (68.7 mm^2/s) is greater than viscosities of samples A, B, and C; but lower than that of samples D, E, and F. The viscosities of blended lube oil samples in this study and the commercial lube oil under consideration can be classified under ISO Viscosity class 68 (max 74.8, midpoint 68, min 61.2). All lube oil flash points were within the regulatory flash point value of lubricants > 200 °C. The total base number (TBN) value of the commercial lube oil (10.4) is relatively higher than all TBN values of the blended lube oil samples (A–F). High TBN values are a measure of the alkalinity or acid neutralizing ability of the lube. Alkaline pHs help reduce the tendencies for the formation of organic sulphur compounds such as mercaptans or sulphuric acids in the oil.

Sample C can be referred to as the optimal lube oil blend, because it has the average density (0.97 kg/L), average viscosity for ISO viscosity class 68 (68 mm^2/s) at 40 °C, and the flash point is within the standard lube oil value, i.e. > 200 °C for both the commercial oil and blended oils under consideration.

Conclusion

This study was designed to provide an environmentally friendly process involving production of lubricant from waste tire pyrolytic oil produced during pyrolysis. The optimized pyrolytic oil was used as base oil in blending selected additives to formulate a commercial lube oil. It can be concluded from this study that;

1. The waste tire pyrolytic oil can be used as base oil for lubricants after distillation so as to remove light hydrocarbon components and sulphur.
2. Distilled waste tire pyrolytic oil was used to formulate lube oil by blending it with selected additives (viscosity index improver, pour point depressant and anti-oxidant) to the improve properties of the oil through "Polyol Synthesis".
3. The blended lube oil samples met standard property criteria for commercial lube oils such as the purchased commercial lube oil used as control in this study.

Acknowledgements The authors appreciate Covenant University Centre for Research Innovation and Discovery Ota, Nigeria for their support in making the publication of this research possible.

Compliance with ethical standards

Conflict of interest There are no conflicts to declare as regards this manuscript.

Ethical statement Authors state that the research was conducted according to ethical standards.

References

1. Machin EB, Pedroso DT, Andrade de Carvalho J Jr. (2017) Energetic valorization of waste tires. Renew Sustain Energy Rev 68(2017):306–315
2. Song Z, Yaqing Y, Zhao X, Jing S, Wenlong W, Yanpeng M, Chunyuan M (2017) Microwave pyrolysis of tire powders: evolution of yields and composition of products. J Anal Appl Pyrolysis 123:152–159
3. Osayi JI, Iyuke S, Ogbeide SE (2014) Biocrude production through pyrolysis of used tyres. J Catal 2014:1–9
4. Ding K, Zhong Z, Zhang B, Song Z, Qian X (2015) Pyrolysis characteristics of waste tire in an analytical pyrolyzer coupled with gas chromatography/mass spectrometry. Energy Fuels 29:5
5. Rofiqul IM, Haniu H, Rafiqul A, Beg M (2008) Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: product yields, compositions and related properties. Fuel 87(13–14):3112–3122
6. Mahlangu L (2009) Waste tire management problems in South Africa and the possible opportunities that can be created through the recycling thereof. University of South Africa, Pretoria
7. Molewa BE (2013) National Environmental Management: Waste Act (59/2008): approval of an integrated industry waste tyre management plan of the recycling and economic development initiative of South Africa. South African National Department of Environmental Affairs, Pretoria
8. Pilusa TJ, Shukla M, Muzenda E (2013) Tyre derived fuel as an alternative fuel for CI engines. In: 2nd international conference on environment, agriculture and food science (ICEAFS'2013), Kuala Lumpur, Malaysia, 25–26 August 2013
9. Osayi JI, Iyuke S, Daramola MO, Osifo P, Van Der Walt IJ, Ogbeide SE (2018) Evaluation of pyrolytic oil from used tires and natural rubber (Hevea brasiliensis). Chem Eng Commun. https://doi.org/10.1080/00986445.2017.1422493
10. Acosta R, Tavera C, Gauthier-Maradei P, Nabarlatz D (2015) Production of oil and char by intermediate pyrolysis of scrap tyres: influence on yield and product characteristics. Int J Chem React Eng 13(2):189–200
11. Pundlik SW (2015) Pyrolysis of waste tyres and future. Chem Biol 1(1):1–9
12. Marchiori H (2007) Tire use feasibility study as fuel in power generation. Final Report. United States Environmental Protection Agency, Washington, DC
13. Teng HS, Chyang CS, Shang SH, Ho JA (1997) Characterization of waste tire incineration in a prototype vortexing fluidized-bed combustor. J Air Waste Manag Assoc 47(1):49–57
14. Lewandowskia WM, Januszewicz K, Kosakowski W (2019) Efficiency and proportions of waste tyre pyrolysis products depending on the reactor type—a review. J Anal Appl Pyrol. https://doi.org/10.1016/j.jaap.2019.03.018
15. Wiriyaumpaiwong S, Jamradloedluk J (2017) Distillation of pyrolytic oil obtained from fast pyrolysis of plastic waste. International Conference on alternative energy in developing countries and emerging economies, AEDCEE, 25–26 May, Bangkok, Thailand. Energy Procedia 138:111–115
16. Osayi JI, Iyuke S, Daramola MO, Osifo P, Van Der Walt IJ, Ogbeide SE (2017) Pyrolytic conversion of used tyres to liquid fuel: characterization and effect of operating conditions. J Mater Cycles Waste Manage. https://doi.org/10.1007/s10163-017-0690-5
17. Tsietsi P, Edison M, Mukul S (2014) Reduction of sulphur in crude tyre oil by gas–liquid phase oxidative adsorption. S Afr J Chem Eng 19(1):22–30
18. Ramirez JA, Brown RJ, Rainey TJ (2015) A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels. Energies 8:6765–6794
19. Rowhani A, Rainey TJ (2016) Scrap tyre management pathways and their use as a fuel—a review. Energies 9:888. https://doi.org/10.3390/en9110888
20. Idris R, Chong CT, Ani FN (2019) Microwave-induced pyrolysis of waste truck tyres with carbonaceous susceptor for the production of diesel-like fuel. J Energy Inst. https://doi.org/10.1016/j.joei.2018.11.009
21. Mang T, Dresel W (2007) Lubricants and lubrication, 2nd edn. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
22. Williams PT (2013) Pyrolysis of waste tyres: a review. Waste Manage 33(8):1714–1728
23. Undri A, Rosi L, Frediani M, Frediani P (2014) Upgraded fuel from microwave assisted pyrolysis of waste tyre. Fuel 115:600–608
24. Pradhan D, Singh RK (2011) Thermal pyrolysis of bicycle waste tyre using batch reactor. Int J Chem Eng Appl 2(5):332