

## Review Article

# Biocrude Production through Pyrolysis of Used Tyres

Julius I. Osayi,<sup>1</sup> Sunny Iyuke,<sup>1</sup> and Samuel E. Ogbeide<sup>2</sup>

<sup>1</sup> School of Chemical and Metallurgical Engineering, University of the Witwatersrand, 1 Jan Smut Avenue, Braamfontein, Private Bag 3, Johannesburg 2050, South Africa

<sup>2</sup> Department of Chemical Engineering, Faculty of Engineering, University of Benin, P.M.B. 1154, Benin City, Edo State, Nigeria

Correspondence should be addressed to Julius I. Osayi; ojgrants@yahoo.com

Received 27 January 2014; Revised 16 April 2014; Accepted 17 April 2014; Published 15 May 2014

Academic Editor: Murid Hussain

Copyright © 2014 Julius I. Osayi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A review of the pyrolysis process of used tyre as a method of producing an alternative energy source is presented in this paper. The study reports the characteristics of used tyre materials and methods of recycling, types and principles of pyrolysis, the pyrolysis products and their composition, effects of process parameters, and kinetic models applied to pyrolysis. From publications, the proximate analysis of tyre rubber shows that it is composed of about 28.6 wt.% fixed carbon, 62 wt.% volatile material, 8.5 wt.% ash, and 0.9 wt.% moisture. Elemental analysis reveals that tyre rubber has an estimated value of 82 wt.% of C, 8 wt.% of H, 0.4 wt.% of N, 1.3 wt.% of S, 2.4 wt.% of O, and 5.9 wt.% of ash. Thermogravimetry analysis confirms that the pyrolysis of used tyre at atmospheric pressure commences at 250°C and completes at 550°C. The three primary products obtained from used tyre pyrolysis are solid residue (around 36 wt.%), liquid fraction or biocrude (around 55 wt.%), and gas fraction (around 9 wt.%). Although there is variation in the value of kinetic parameters obtained by different authors from the kinetic modeling of used tyre, the process is generally accepted as a first order reaction based on Arrhenius theory.

## 1. Introduction

One of the main challenges of modern society is the rising rate of solid waste generated by man's activities which has poised a major environmental concern [1–3]. The disposal of used tyres and other polyisoprene based products is a large fraction of such problems as 1.3 billion tyres are estimated to reach their end of life cycle annually worldwide [4–9]. This is because of their excellent properties which have made them useful in all areas of human life [10]. However, these excellent properties also place them at a disadvantage [3, 11, 12] as they are not biologically degradable leading to problems with their disposal [2, 7, 11, 13–16]. Over the years landfill and open dumping (stock piling) were the common ways in handling the problem of used tyres. However, landfills take up valuable land space due to the bulky nature of tyres which cannot be compacted neither does it degrade easily [7, 11, 17–19]. Dumped used tyres in massive stockpiles do not only occupy a large land space but also serve as a potential health and environmental hazard due to the possibility of a fire outbreak with high emissions of toxic gases and as

a breeding ground for disease carrying vectors [7, 15, 16, 20, 21]. Despite other tyre recycling options such as reclaiming, grinding, incineration, retreading, and so forth being used, these processes have their setback and do not fully utilize used tyres as an excellent material for energy recovery [8, 22]. For this reason, pyrolysis has received renewed attention as the process conditions can be optimized to produce high valued products [4–6, 11, 23–27]. Pyrolysis mainly involve the decomposition of polyisoprene materials to low molecular weight component at high temperature (250°C–900°C) in an inert atmosphere [3, 7, 22, 28]. The process being an excellent energy recovery route can be performed under atmospheric or reduced pressure. It is an environmentally friendly technique to thermally decompose a wide variety of wastes, including used tyres [2, 4, 6, 11, 15, 16, 20, 27, 29–44]. The three basic products of pyrolysis are solid residue (char), liquid (biocrude), and gases [6]. Solid residue may be used in the manufacture of activated carbon, reinforcement in rubber industry, or as solid fuel. The pyrolytic liquid can serve as replacements for conventional liquid fuel due to its high gross calorific value of about 41–44 MJ/kg. It can also be

used as petroleum refinery feedstock or a source of chemicals for wide industrial applications. Gaseous fraction can be used as fuel or as a source of energy for the pyrolysis process [22, 28, 29, 45–49].

This paper presents a literature review of the pyrolysis process with a focus on the characteristics of used tyres materials and methods of recycling, types and principles of pyrolysis, properties of the pyrolysis products, effects of process parameters, and kinetic models applied to pyrolysis.

## 2. Used Tyres

Used tyres also referred to as waste tyres can be defined as tyres that have expired as a result of exceeding their production life span or are no longer safe for usage due to defects, such as degradation of its physical composition/structure from use and cannot be retreaded. It is one of the most challenging hazardous solid wastes facing modern society, particularly in developing countries [3, 10, 11]. It is estimated that the EU, Japan, and USA generate  $6 \times 10^6$  tons of waste tyres annually [6, 22, 23, 46, 64]. According to a report, 160,000 tons of waste tyres are generated in South Africa annually and up to 28 million used tyres are dumped unlawfully or burnt [70]. This figure is projected to increase by 9.3 million yearly [70]. The nonbiodegradable nature of this polymer material makes its disposal difficult. Disposal by massive stockpiling and landfilling is one of the common ways of handling waste tyre, but this requires a large space as the volume of tyres cannot be compacted. These also pose the danger of the possibility of fire outbreak with the emission of harmful gases [1, 7, 19, 21, 22, 64, 71–75].

*2.1. Methods of Recycling of Used Tyres.* The various methods in which used tyres are recycled are discussed below.

*2.1.1. Retreading Method.* Retread also referred to as “remold” involves buffing away of the remaining tread in a spent tyre and replacing it with a new tread rubber strip by vulcanization. It is carried out only on used tyres casing that have been inspected and repaired. Although it is economically advantageous, product quality confidence is a major challenge of the process.

*2.1.2. Mechanical or Cryogenic Method.* Both mechanical and cryogenic (grinding of waste tyres at temperatures of  $-80^\circ\text{C}$  to  $-100^\circ\text{C}$  using liquid nitrogen) recycling of used tyres involve the milling of tyres to produce ground rubber of different particle sizes. The fine grounded rubber can be used in varieties of application such as an additive in road asphaltting, sports and children playground surfacing, carpets, and other rubber products. However, the limited market for the product and a high cost of running the process are a disadvantage.

*2.1.3. Reclaiming Rubber Raw Materials Methods.* Different methods and processes for reclaiming rubber have been

developed. The most relevant of them are thermomechanical reclaiming [48], microwave reclaiming [49], mechanical shearing process [69], reclaiming by biotechnological process, ultrasonic reclaiming [76], reclaiming by renewable resource materials, reclaiming by use of different chemical agents [9], and pyrolysis of waste tyre [77]. These methods actually help in transforming used tyres from a three dimensionally interlinked thermoset polymer state to a two-dimensional polymer exhibiting the properties of a virgin rubber. The high cost of the process, quality of products, and lack of acceptance of reclaim rubber by industries as a raw material are a setback on the process.

Although used tyres can be used as a source of fuel in cement kilns by combustion method, it is not economically wise and environmentally friendly [1, 4, 7].

*2.2. Characteristics and Composition of Used Tyres.* Tyres are made up of different types of rubber elastomers (natural or synthetic rubber) with varying composition, carbon black, stabilizers, antioxidants, sulphur, hydrocarbon oils, zinc oxides, textile or steel cords [4, 6, 11, 69], and so forth. Proximate and ultimate analyses of used tyres reported by various authors are shown in Tables 1 and 2. The difference in values can be attributed to the manufacturers' formulation which is closely guarded and determines to a large extent the weight percent of the various components of tyres.

*2.3. Study of Thermal Degradation of Used Tyre.* Thermogravimetry analysis is used to study the general behavior of thermal degradation of used tyres [13]. Both the thermogravimetry (TG) and differential thermogravimetry (typical curve is shown in Figures 1 and 2) are standard techniques used in the study of mass change of tyre rubber sample as a function of temperature and time [73, 74, 78]. With the results data (shown in Table 3) obtained in this study and those of other authors in the literature, it can be understood that there is more than one degradation temperature zone during tyre rubber pyrolysis. This also gives an idea of the commencement and end point temperature for the different rubber components in the waste tyre [3, 10]. For example, NR (natural rubber), SBR (styrenebutadiene rubber), and BR (butadiene rubber) decompose at a temperature range of  $375^\circ\text{C}$  to  $500^\circ\text{C}$ .

## 3. Pyrolysis, Process Conditions, and Reactors

Pyrolysis mainly involves the thermal degradation of tyre rubber at high temperatures ( $250\text{--}900^\circ\text{C}$ ) in an oxygen absent environment. It can be performed under vacuum or atmospheric pressure [23, 29]. Amongst other methods such as combustion and gasification used to extract energy from biomass, pyrolysis has received more attention in the area of research because the process conditions can be optimized to produce high energy density liquids, char, and gas. Also, the condensable fraction (biocrude) can be stored and easily transported to where it can be most proficiently utilized. Tyre pyrolysis can be said to be made up of three stages, that is, the release of volatile and moisture at lower temperature

TABLE 1: Proximate analysis of used tyre rubber.

Author	Moisture (wt.%)	Ash (wt.%)	Volatile (wt.%)	Fixed carbon (wt.%)	HHV (MJ/kg)
This study	0.5	16.0	56.4	27.1	31.2
Donatelli et al. [31]	0.8	4.4	61.3	33.5	37.1
Kar [32]	1.72	19.13	59.69	19.45	27.37
Chang [33]	1.31	10.21	62.32	26.26	33.24
Trongkaew et al. [14]	1.22	8.73	62.4	27.6	35.7
González et al. [19]	0.7	8.0	61.9	29.5	36.2
Su and Zhao [34]	0.8	7.41	64.64	27.15	39.56
Juma et al. [9]	1.72	14.01	61.61	22.66	—
de Marco et al. [35]	58.8	27.7	1.72	—	—
Williams and Bottrill [36]	0.8	2.4	66.5	30.3	—

TABLE 2: Ultimate analysis of used tyre rubber.

Author	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Ashes (inorganic)
Donatelli et al. [31]	85.2	7.3	0.4	2.3	0.4	4.4
Kar [32]	67.08	6.12	0.17	2.05	24.58	—
Chang [33]	74.41	6.94	0.21	1.60	5.02	—
Trongkaew et al. [14]	80.10	7.48	0.42	1.54	10.50	—
González et al. [19]	86.7	8.10	0.40	1.40	1.30	2.1
Su and Zhao [34]	81.84	6.06	1.77	1.64	0.48	—
Juma et al. [9]	81.24	7.36	0.49	1.99	8.92	—
de Marco et al. [35]	74.20	5.80	0.3	1.50	4.70	13.5
Williams and Bottrill [36]	85.8	8.0	0.4	1.0	2.3	2.4

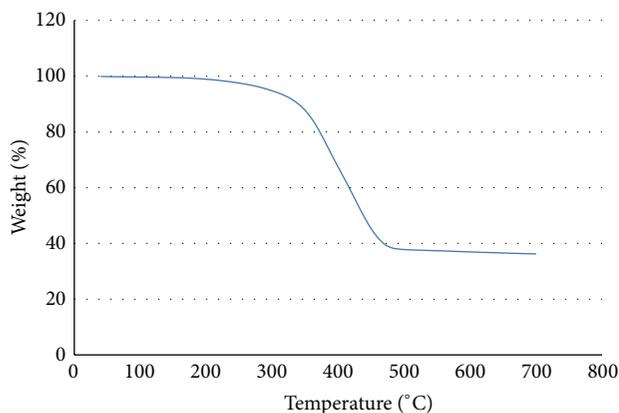


FIGURE 1: Typical TGA curve of used tyre sample.

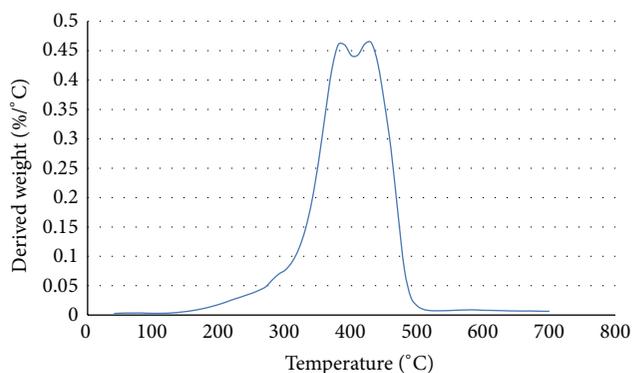


FIGURE 2: Typical DTG curve of used tyre sample.

succeeded by the thermal decomposition of natural rubber (NR) and the decomposition of polybutadiene (BR) and polybutadiene-styrene rubber at higher temperature, respectively [79, 80].

The process conditions that can influence the percentage weight of each fraction of pyrolysis include pressure, heating rate, temperature, feed particle sizes, catalysis, flow rate of inert carrier gas, configuration of reactor used [2], and so forth.

**3.1. Pyrolysis Reactors.** The reactor is a very important part of the pyrolysis process. Over the years, the innovation and technological advancement of pyrolysis has advanced considerably. Researchers have developed and studied different reactors and processes to the point where pyrolysis is now an acceptable technique to the deriving of gaseous, liquid, solid fuels, and chemicals. Table 4 presents the chronology of pyrolysis process from the 1970s to date. Reactors can greatly influence the pyrolysis performance, product quality, and yield [2, 46]. However, each reactors type has its benefits

TABLE 3: Commencement and end temperatures of pyrolysis of used tyre.

Author	Pyrolysis commencement temperature (°C)	Pyrolysis end temperature (°C)	Heating rate (°C/min)
This study	210	520	20
Juma et al. [9]	250	550	5
Conesa et al. [38]	250	500	5
Su and Zhao [34]	200	500	10
Senneca et al. [39]	200	450	5

and limitations. Table 5 shows different types of reactors and their heating methods.

**3.2. Types of Pyrolysis.** Pyrolysis process can be performed under different operating conditions which can be used in classifying it. They are differentiated by residence time of the pyrolysed material in the reactor, process temperature, feed particle size, heating rate [81–83], and so forth. These include the following.

**3.2.1. Slow Pyrolysis.** The solid residence time(s) in the reactor is 450–550, heating rate (°C) is 0.1–1, and feed particle size (mm) is 5–50 with temperature (°C) of 550–950. This process enhances char production and is unlikely to be unsuitable for high quality bio-oil production. Also, due to high residence time secondary reaction is favorable as cracking of primary product occurs which could adversely affect bio-oil yield and quality [84] (Table 6).

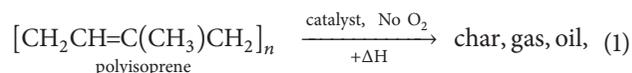
**3.2.2. Fast Pyrolysis.** Fast pyrolysis involves the rapid heating of the feed material to a high temperature in the absence of oxygen with a short residence time of the condensable vapor in the reactor. Its operating parameters are solid residence time between 0.5 and 10s, heating rate of 10–200°C, feed particle size less than 5 mm, and reaction temperature of 550–1200°C. The technology has received much popularity in producing liquid fuels and a range of specialty and commodity chemicals. Typically on weight basis, fast pyrolysis yields 60%–75% pyro oil with 15%–25% compared to other processes; it has reasonably low investment costs and high energy efficiencies particularly on a small scale [85].

**3.2.3. Flash Pyrolysis.** This process is characterized by residence time of less than 0.5 s, high heating rate of more than 200°C, particle size of less than 0.2 mm, and high reaction temperature of more than 1000°C. However, the major technological challenge of the process is poor thermal stability, solids in the oil, and production of pyrolytic water [86, 87].

**3.2.4. Catalytic Pyrolysis.** Catalytic pyrolysis is a pyrolysis process that includes the use of a catalyst. The catalyst helps

enhance the pyrolysis reaction kinetics by cracking down higher molecular weight hydrocarbon compounds to lighter hydrocarbon products. It has been reported that the use of catalyst in tyre pyrolysis systems can greatly influence the composition, quality, and yield of products [6, 88]. Examples of catalysts used in tyre pyrolysis include Na<sub>2</sub>CO<sub>3</sub>, NaOH, MgO, CaCO<sub>3</sub>, aluminium-based catalyst, perlite, CaC<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, zeolite-based catalyst, and so forth [6, 7, 89]. Operating conditions can determine different product distribution for different catalysts. Pyrolysis catalyst can be grouped based on their method of application. The first group is when the catalyst is added to the feedstock before being fed into the reactor. The second group is when catalyst is added after the feed is already heated up in the reactor allowing it to have immediate contact with vapors, solid, and char. The third group is when the catalyst is placed in another reactor located downstream from the pyrolysis reactor [46, 90].

**3.3. Chemical Reaction of the Catalytic Pyrolysis.** The chemical reaction of catalytic pyrolysis is an endothermic process. Three stages involved include dehydration, fragmentation, and product formation which occur at different temperatures during the process. It is carried out in an inert environment in order to avoid combustion. The mechanism of the reaction is shown below:



where  $\Delta\text{H}$  = heat.

**3.4. Pyrolysis Products and Their Composition.** The three primary products obtainable from tyre rubber pyrolysis are listed and discussed below.

(1) *Solid residue* or char (34–38 wt.% of feedstock) is made up of carbon black and other nonvolatile materials such as tyre rubber additives like zinc, sulphur, silica, clays, and so forth, initially present in the tyre. This char can be used as solid fuel, carbon black, or as precursor for activated carbon manufacturing [22]. From the literature, elemental analysis shows that the solid residue contains 71 wt.% of C, 13.3 wt.% of O, 5.4 wt.% of Fe, 2.8 wt.% of S, 2.3 wt.% of Zn, 1.3 wt.% of Ca, and 0.3 wt.% of Al.

(2) *Liquid product* (48–58 wt.% of feedstock) also known as pyrolysed tyre oil or biocrude is the most significant product of the process. It is gotten from the condensation of vapor of a pyrolysis reaction. Several publications on the study of the properties of the pyrolytic oil abound [18, 45]. It is reported that the calorific value of the oil is 42 MJ/kg, percentage content of sulphur ranges between 1.2 and 1.36, and the oil is a mixture of C<sub>6</sub>–C<sub>24</sub> organic compounds (53.4–74.8%) specified to be paraffins, olefins, and aromatic compounds with some nitrogenated (2.47–3.75%) and some oxygenated compounds (2.29–4.85%) [17, 18, 28]. Such pyrolytic oil can be used directly as low-sulphur-emission fuels or blend with petroleum products such as gasoline, feedstock for petroleum refinery, and as an important source for chemicals in chemical industries due to high concentration of benzene, toluene, xylene, and limonene

TABLE 4: Chronology of processes used for pyrolysis of used tyres.

Researcher(s)	Reactor used	Process type	Year
Gotshall [50]	n.r	Destructive distillation	1970
Alpert [51]	n.r	Hydroconversion	1972
Grannen and Robinson [52]	Microwave	Microwave pyrolysis	1974
Crane and Kay [53]	n.r	Pyrolization	1976
Herbold [54]	n.r	Subatmospheric pyrolysis	1978
Kaminsky and Sinn [55]	Fluidized bed	Pyrolysis	1980
Ito et al. [56]	Fluidized bed and incineration fluidized bed chamber	Pyrolysis and incineration	1982
Engman et al. [57]	Quartz tube	Pyrolysis	1984
Bouvier and Gelus [58]	Heated cylindrical glass flask	Tyre copyrolysis with oil	1986
Chou et al. [59]	Quartz tube	Flash pyrolysis	1988
Roy et al. [60]	Batch reactor	Vacuum pyrolysis	1990
Roy et al. [61]	Batch reactor	Vacuum pyrolysis	1992
Pakdel and Roy [62]	Continuous feed reactor	Vacuum pyrolysis	1994
Conesa et al. [63]	Fluidized bed reactor	Pyrolysis	1996
Leung and Wang [64]	Platinum pan	Pyrolysis and combustion	1998
Mastral et al. [30]	Swept fixed bed	Pyrolysis and hydropyrolysis	2000
Galvagno et al. [65]	Rotary kiln reactor	Pyrolysis	2002
Laresgoiti et al. [66]	Autoclave reactor	Pyrolysis	2004
Murillo et al. [67]	Fixed bed reactor	Pyrolysis	2006
Zhang et al. [12]	Fixed bed reactor	Vacuum pyrolysis	2008
Aylón et al. [68]	Moving bed	Pyrolysis	2010
Aydin and Ilkilic [15]	Fixed bed reactor	Pyrolysis	2012
Undri et al. [4]	Microwave oven	Microwave assisted pyrolysis	2014
This study	Plasma reactor	Catalytic copyrolysis	2014

n.r.: not reported.

TABLE 5: Reactors and their heating methods [23, 40–42].

Reactor type	Heating method
Fixed bed	Heated wall surface
Bubbling fluidized bed	Heated recycle gas
Circulating fluidized bed	Wall and sand heating
Rotating cone	Gasification of char to heat
Auger	Fire tube
Fluidized bed/quartz	Solar
Plasma	Radio frequency
Vacuum	Direct contact with hot surface
Ablative	Wall heating

TABLE 6: Physical and chemical properties of used tyre oil and diesel fuel [15].

Fuel/property	Diesel fuel	Used tyre oil
Density (kg/m <sup>3</sup> ) @ 20°C	845	945
Kinematic viscosity @ 40°C in mm <sup>2</sup> /sec	3.4	3.8
Flash point	60°C	50°C
Diesel index	55.2	41.9
Heat value (MJ/kg)	46	43.34
Sulphur amount (%)	0.1	0.906
Cetane number	53	44

[18]. Elemental analysis of the tyre pyrolysis oil shows that it contains 86.871 wt.% of C, 10.07 wt.% of H, 1.169 wt.% of N, 0.906 wt.% of S, and 1.169 wt.% of O.

(3) *Gas fraction* (9–14 wt.% of feedstock) from the pyrolysis process is mainly composed of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>S, and other light hydrocarbons with SO<sub>2</sub>, NO<sub>x</sub>, CO, and PAHs reported as the main pollutant gases. It has a high heating value of about 37 MJ/m<sup>3</sup>, an amount of energy enough for the pyrolysis process.

It is worthy to note that the composition of the various fractions is influenced by the pyrolysis conditions used and the composition of the tyre [2, 3, 7, 10, 17].

#### 4. Pyrolysis Kinetics

Kinetic models for used tyre pyrolysis have been presented by various authors [91–97]. Generally, the degradation of the tyre rubber is split into two or more steps, while thermogravimetry data and Arrhenius equation form the basis of the models. In the kinetic analysis of the data for the tyre decomposition, the Arrhenius theory based on first order reaction is mostly assumed by researchers:

$$k = A \exp\left(-\frac{E}{RT}\right), \quad (2)$$

TABLE 7: Kinetic parameters obtained by Leung and Wang [64].

Heating rate	Activation energy, $E$ (KJ/mol)		Preexponential factor, $A$ ( $\text{min}^{-1}$ )		Reaction order, $n$	
	Lower temperature	Higher temperature	Lower temperature	Higher temperature	Lower temperature	Higher temperature
10	164.5	136.1	$6.29 \times 10^{13}$	$2.31 \times 10^9$	1	1
30	180.9	133.6	$1.32 \times 10^{14}$	$2.09 \times 10^9$	1	1
45	203.4	107.0	$7.58 \times 10^{15}$	$3.34 \times 10^7$	1	1
60	218.7	99.1	$1.13 \times 10^{17}$	$1.02 \times 10^7$	1	1

TABLE 8: Kinetic parameters obtained by Williams and Besler [69].

Heating rate	Activation energy, $E$ (kJ/mol)		Preexponential factor, $A$ ( $\text{min}^{-1}$ )		Reaction order, $n$	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
5	142.7	120.8, 145.0	$2.1 \times 10^8$	$9.3 \times 10^7, 1.1 \times 10^8$	—	—
20	90.8	128.3, 137.7	$2.6 \times 10^4$	$3.3 \times 10^5, 2.1 \times 10^8$	—	—
40	70.4	66.1, 136.2	$1.3 \times 10^3$	$5.9 \times 10^2, 6.3 \times 10^7$	—	—
80	66.4	55.6	$1.1 \times 10^3$	$1.3 \times 10^2$	—	—

where  $k$  is the rate constant,  $A$  is the preexponential factor ( $\text{min}^{-1}$ ),  $E$  is the activation energy (J/mol), and  $R$  and  $T$  are the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and temperature of reaction (K), respectively. Equation (3) can be used to represent the rate of tyre decomposition:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n, \quad (3)$$

where  $\alpha$  is the fraction of reactant decomposed at time  $t$  and  $n$  is the order of reaction. Application of the above given equations for tyre pyrolysis under different conditions along with experimental conditions and obtained kinetic parameters published in the literature by some authors is given below.

*Leung and Wang [64].* Consider the following.

*Model:*

$$\frac{d\alpha_T}{dt} = \sum_{i=1}^3 \frac{d\alpha_i}{dt} = \sum_{i=1}^3 A_i \exp\left(-\frac{E_i}{RT}\right) (1 - \alpha), \quad (4)$$

where  $\alpha_T$  ( $\text{min}^{-1}$ ) is normalized mass loss rate,  $A$  is preexponential factor,  $E$  is activation energy,  $R$  is ideal gas constant,  $T$  is absolute temperature,  $t$  is time, and index ( $i = 1, 2, 3$ ) is reaction.

*Experimental Conditions.* Temperature: 20–600°C, particle size: 0.355–0.425 mm, heating rate: 10–60°C/min, and used mobile gas:  $\text{N}_2$ . The kinetic parameters obtained by Leung and Wang are given in Table 7.

*Williams and Besler [69].* Consider the following.

*Model:*

$$\frac{dw}{dt} = -k(W - W_f), \quad (5)$$

where  $W$  is the weight of sample at time  $t$ ,  $W_f$  is the weight of residue at the end of the reaction, and  $k$  represents the rate constant defined by Arrhenius equation.

*Experimental Conditions.* Temperature: 720°C, sample sizes: <1 mm, heating rate: 5°C/min, and used mobile gas:  $\text{N}_2$ .

Table 8 shows the kinetic parameters obtained.

## 5. Conclusion

Biocrude production from used tyres and natural rubber is a viable means of an alternative renewable energy source that can help caution the fast depletion of crude oil reserves, its fast rising cost due to high demand, along with its adverse negative environmental impact. This review reports the present stage of research in used tyre pyrolysis. From the literature, the proximate analyses of tyre rubber show that it is composed of about 28.6 wt.% fixed carbon, 62 wt.% volatile material, 8.5 wt.% ash, and 0.9 wt.% moisture. Elemental analyses reveal that tyre rubber has an estimated value of 82 wt.% of C, 8 wt.% of H, 0.4 wt.% of N, 1.3 wt.% of S, 2.4 wt.% of O, and 5.9 wt.% of ash. Both the proximate and ultimate analysis value of the used tyres is dependent on the tyre formulation by the tyre manufacturers. Thermogravimetry analysis confirms that the pyrolysis of used tyre at atmospheric pressure commences at about 250°C and completes at around a temperature of 550°C. Usually, during tyre pyrolysis, there exist different degradation temperatures. This was also confirmed by the thermogravimetric analysis performed in our laboratory. It was also observed that pyrolysis products yields and their characteristics are greatly affected by the composition of the feed, operating conditions, and the specific properties of the system used.

Thus, results vary from different researchers making it difficult to compare results. Nevertheless, the three primary products obtained from used tyres pyrolysis are solid residue or char (around 36 wt.%), liquid fraction or biocrude (around 55 wt.%), and gas fraction (around 9 wt.%) with average

higher heating values (HHV) of 28 MJ kg<sup>-1</sup>, 42 MJ kg<sup>-1</sup>, and 36 MJ N<sup>-1</sup> m<sup>-3</sup>, respectively.

Studies have also shown that the main components of the liquid fractions are aliphatic and aromatic hydrocarbons and hydroxyl compounds while the gases that make up the gas fractions are H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>S, and other light hydrocarbons with SO<sub>2</sub>, NO<sub>x</sub>, CO, and polycyclic aromatic hydrocarbons (PAHs) reported as the main pollutant gases. The char contains high fixed-carbon content and inorganic matter.

Although there is a wide difference in results of kinetic modeling of used tyres by different authors in the value of kinetic parameters obtained, generally it is accepted that the process is a first order reaction based on Arrhenius theory.

Therefore, there is the need to investigate the effect of copyrolysis of natural rubber (biomass obtained from rubber tree) and used tyre on the pyrolysis product yields in relation to the following.

- (i) Composition and quantity of gas yield.
- (ii) Enhancing the possibility of more valuable chemical products from the liquid fraction such as limonene which is closely related to polyisoprene (NR) present in used tyre.
- (iii) Analyzing the amount of sulphur content in the biocrude (liquid fraction).
- (iv) The quality of char produced in comparison with commercial carbon black will be the area of our research.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

Financial support from the National Research Foundation (NRF) under the South Africa NRF Focus Area and student bursaries made available by the University of the Witwatersrand are deeply appreciated.

## References

- [1] M. Bianchi, G. Bortolani, M. Cavazzoni et al., "Preliminary design and numerical analysis of a scrap tyre pyrolysis system," *Energy Procedia*, vol. 45, pp. 111–120, 2014.
- [2] J. D. Martinez, A. Veses, A. M. Mastral et al., "Co-pyrolysis of biomass with waste tyres: upgrading of liquid to bio-fuel," *Fuel Processing Technology*, vol. 119, pp. 263–271, 2014.
- [3] S. Frigo, M. Seggiani, M. Puccini, and S. Vitolo, "Liquid fuel production from waste tyre pyrolysis and its utilization in a diesel engine," *Fuel*, vol. 116, pp. 399–408, 2014.
- [4] A. Undri, L. Rosi, M. Frediani, and P. Frediani, "Upgraded fuel from microwave assisted pyrolysis of waste tyre," *Fuel*, vol. 115, pp. 600–608, 2014.
- [5] H. Hu, Y. Fang, H. Liu et al., "The fate of sulfur during rapid pyrolysis of scrap tyres," *Chemosphere*, vol. 97, pp. 102–107, 2014.
- [6] P. T. Williams, "Pyrolysis of waste tyres: a review," *Waste Management*, vol. 33, pp. 1714–1728, 2013.
- [7] A. Quek and R. Balasubramanian, "Liquefaction of waste tyres by pyrolysis for oil and chemicals—a review," *Journal of Analytical and Applied Pyrolysis*, vol. 101, pp. 1–16, 2013.
- [8] S. Karthikeyan, C. Sathiskumar, and S. R. Moorthy, "Effect of process parameters on tyre pyrolysis: a review," *Journal of Scientific and Industrial Research*, vol. 71, no. 5, pp. 309–315, 2012.
- [9] M. Juma, Z. Korenova, J. Markos, J. Annus, and L. Jelemensky, "Pyrolysis and combustion of Scrap tyre," *Petroleum & Coal*, vol. 48, no. 1, pp. 15–26, 2006.
- [10] J. Haydary, Z. Korenova, L. Jelemensky, and J. Markos, "Thermal decomposition of waste polymers," in *ThermoPhysics*, pp. 62–68, 2008.
- [11] M. R. Islam, M. S. H. K. Tushar, and H. Haniu, "Production of liquid fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes," *Journal of Analytical and Applied Pyrolysis*, vol. 82, no. 1, pp. 96–109, 2008.
- [12] X. Zhang, T. Wang, L. Ma, and J. Chang, "Vacuum pyrolysis of waste tires with basic additives," *Waste Management*, vol. 28, no. 11, pp. 2301–2310, 2008.
- [13] D. Pradhan and R. K. Singh, "Thermal pyrolysis of bicycle waste tyre using batch reactor," *International Journal of Chemical Engineering and Application*, vol. 2, no. 5, pp. 332–336, 2011.
- [14] P. Trongkaew, T. Utistham, P. Reubroycharoen, and N. Hinchiranan, "Photocatalytic desulfurization of waste tire pyrolysis oil," *Energies*, vol. 4, no. 11, pp. 1880–1896, 2011.
- [15] H. Aydin and C. Ilkilic, "Optimization of fuel production from waste vehicle tyres by pyrolysis and resembling to diesel fuel by various desulfurization methods," *Fuel*, vol. 102, pp. 605–612, 2012.
- [16] H. Schnecko, "Rubber recycling," *Macromolecular Symposia*, vol. 135, pp. 327–343, 1998.
- [17] R. Aguado, M. Olazar, D. Vélez, M. Arabiourrutia, and J. Bilbao, "Kinetics of scrap tyre pyrolysis under fast heating conditions," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 2, pp. 290–298, 2005.
- [18] A. M. Cunliffe and P. T. Williams, "Influence of process conditions on the rate of activation of chars derived from pyrolysis of used tires," *Energy and Fuels*, vol. 13, no. 1, pp. 166–175, 1999.
- [19] J. F. González, J. M. Encinar, J. L. Canito, and J. J. Rodríguez, "Pyrolysis of automobile tyre waste. Influence of operating variables and kinetics study," *Journal of Analytical and Applied Pyrolysis*, vol. 58–59, pp. 667–683, 2001.
- [20] M. Bajus and N. Olahova, "Thermal conversion of scrap tyres," *Petroleum & Coal*, vol. 53, pp. 98–105, 2011.
- [21] C. Roy, H. Darmstadt, B. Benallal, and C. Amen-Chen, "Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber," *Fuel Processing Technology*, vol. 50, no. 1, pp. 87–103, 1997.
- [22] S. Boxiong, W. Chunfei, L. Cai, G. Binbin, and W. Rui, "Pyrolysis of waste tyres: the influence of USY catalyst/tyre ratio on products," *Journal of Analytical and Applied Pyrolysis*, vol. 78, no. 2, pp. 243–249, 2007.
- [23] M. I. Jahirul, M. G. Rasul, A. A. Chowdhury, and N. Ashwath, "Biofuels production through biomass pyrolysis—a technical review," *Energies*, vol. 5, pp. 4952–5001, 2012.
- [24] G. Harrison and A. B. Ross, "Use of tyre pyrolysis oil for solvent augmentation in two-stage coal liquefaction," *Fuel*, vol. 75, no. 8, pp. 1009–1013, 1996.

- [25] A. Hershafit, "Solid waste: treatment technology," *Environmental Science and Technology*, vol. 6, no. 5, pp. 412–421, 1972.
- [26] S. R. Fix, "Microwave devulcanization of rubber," *Elastomerics*, vol. 112, no. 6, pp. 38–40, 1980.
- [27] A. A. Phadke, A. K. Bhattacharya, S. K. Chakraborty, and S. K. De, "Studies of vulcanization of reclaimed rubber," *Rubber Chemistry and Technology*, vol. 56, no. 4, pp. 726–736, 1983.
- [28] A. I. Isayev, S. P. Yushmanov, and J. Chen, "Ultrasonic devulcanization of rubber vulcanizates. I: process model," *Journal of Applied Polymer Science*, vol. 59, no. 5, pp. 803–813, 1996.
- [29] M. Beecham, *Global Market Review of Automotive Tyres—Forecasts to 2014*, Pub ID JA1867566, Aroq Limited, Bromsgrove, UK, 2008.
- [30] A. M. Mastral, R. Murillo, M. S. Callen, and T. Garcia, "Optimization of scrap automotive tyres recycling into valuable liquid fuels," *Resources, Conservation and Recycling*, vol. 29, no. 4, pp. 263–272, 2000.
- [31] A. Donatelli, P. Iovane, and A. Molino, "High energy syngas production by waste tyres steam gasification in a rotary kiln pilot plant. Experimental and numerical investigations," *Fuel*, vol. 89, no. 10, pp. 2721–2728, 2010.
- [32] Y. Kar, "Catalytic pyrolysis of car tire waste using expanded perlite," *Waste Management*, vol. 31, no. 8, pp. 1772–1782, 2011.
- [33] Y. M. Chang, "On pyrolysis of waste tire: degradation rate and product yields," *Resources, Conservation and Recycling*, vol. 17, no. 2, pp. 125–139, 1996.
- [34] Y. Su and B. Zhao, "Pyrolysis of waste tire and its model," in *Proceedings of the 4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE '10)*, June 2010.
- [35] I. R. de Marco, M. F. Laresgoiti, M. A. Cabrero, A. Torres, M. J. Chomón, and B. Caballero, "Pyrolysis of scrap tyres," *Fuel Processing Technology*, vol. 72, no. 1, pp. 9–22, 2001.
- [36] P. T. Williams and R. P. Bottrill, "Sulfur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil," *Fuel*, vol. 74, no. 5, pp. 736–742, 1995.
- [37] J. Yang, P. A. Tanguy, and C. Roy, "Heat transfer, mass transfer and kinetics study of the vacuum pyrolysis of a large used tire particle," *Chemical Engineering Science*, vol. 50, no. 12, pp. 1909–1922, 1995.
- [38] J. A. Conesa, R. Font, A. Fullana, and J. A. Caballero, "Kinetic model for the combustion of tyre wastes," *Fuel*, vol. 77, no. 13, pp. 1469–1475, 1998.
- [39] O. Senneca, P. Salatino, and R. Chirone, "Fast heating-rate thermogravimetric study of the pyrolysis of scrap tyres," *Fuel*, vol. 78, no. 13, pp. 1575–1581, 1999.
- [40] L. Tang and H. Huang, "Plasma pyrolysis of biomass for production of syngas and carbon adsorbent," *Energy and Fuels*, vol. 19, no. 3, pp. 1174–1178, 2005.
- [41] A. Domínguez, Y. Fernández, B. Fidalgo, J. J. Pis, and J. A. Menéndez, "Bio-syngas production with low concentrations of CO<sub>2</sub> and CH<sub>4</sub> from microwave-induced pyrolysis of wet and dried sewage sludge," *Chemosphere*, vol. 70, no. 3, pp. 397–403, 2008.
- [42] X. Zhao, Z. Song, H. Liu, Z. Li, L. Li, and C. Ma, "Microwave pyrolysis of corn stalk bale: a promising method for direct utilization of large-sized biomass and syngas production," *Journal of Analytical and Applied Pyrolysis*, vol. 89, no. 1, pp. 87–94, 2010.
- [43] A. Quek and R. Balasubramanian, "Mathematical modeling of rubber tire pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 95, pp. 1–13, 2012.
- [44] M. Balat, M. Balat, E. Kirtay, and H. Balat, "Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: pyrolysis systems," *Energy Conversion and Management*, vol. 50, no. 12, pp. 3147–3157, 2009.
- [45] T. Bridgwater, *Pyrolysis of Biomass*, IEA Bioenergy Task 34, Bioenergy Research Group, Aston University, Birmingham, UK, 2007.
- [46] A. V. Bridgwater, S. Czernik, and J. Piskorz, "An overview of fast pyrolysis," in *Progress in Thermochemical Biomass Conversion*, vol. 2, pp. 977–997, 2001.
- [47] A. Demirbaş and G. Arin, "An overview of biomass pyrolysis," *Energy Sources*, vol. 24, no. 5, pp. 471–482, 2002.
- [48] R. Aguado, M. Olazar, B. Gaisán, R. Prieto, and J. Bilbao, "Kinetic study of polyolefin pyrolysis in a conical spouted bed reactor," *Industrial and Engineering Chemistry Research*, vol. 41, no. 18, pp. 4559–4566, 2002.
- [49] T. Cornelissen, J. Yperman, G. Reggers, S. Schreurs, and R. Carleer, "Flash co-pyrolysis of biomass with polylactic acid. Part 1: influence on bio-oil yield and heating value," *Fuel*, vol. 87, no. 7, pp. 1031–1041, 2008.
- [50] W. W. Gotshall, "Reinforcing agent from scrap rubber char," US Patent 3644131 A, February 1972.
- [51] S. B. Alpert, "Hydroconversion of waste natural rubber and synthetic rubbers," US Patent 3704108, November 1972.
- [52] E. A. Grannen and L. Robinson, "Microwave pyrolysis of wastes," US Patent 3843457, October 1974.
- [53] G. Crane and E. L. Kay, "Pyrolyzation," US Patent 3966487, June 1976.
- [54] O. Herbold, "Method and apparatus for the pyrolysis of waste products," US Patent 4084521, April 1978.
- [55] W. Kaminsky and H. Sinn, "Pyrolysis of plastic waste and scrap tyres using a fluidized process," in *Thermal Conversion of Solid Wastes and Biomass*, J. L. Jones and S. B. Radding, Eds., vol. 130 of *American Chemical Society Symposium Series*, pp. 423–439, 1980.
- [56] K. Ito, Y. Hirayama, Y. Ishii, and N. Ando, "Pyrolyzing apparatus," US Patent 4324620, April 1982.
- [57] H. Engman, H. T. Mayfield, T. Mar, and W. Bertsch, "Classification of bacteria by pyrolysis-capillary column gas chromatography-mass spectrometry and pattern recognition," *Journal of Analytical and Applied Pyrolysis*, vol. 6, no. 2, pp. 137–156, 1984.
- [58] J. M. Bouvier and M. Gelus, "Pyrolysis of rubber wastes in heavy oils and use of the products," *Resources and Conservation*, vol. 12, no. 2, pp. 77–93, 1986.
- [59] M. I. M. Chou, M. A. Lake, and R. A. Griffin, "Flash pyrolysis of coal, coal maceral, and coal-derived pyrite with on-line characterization of volatile sulfur compounds," *Journal of Analytical and Applied Pyrolysis*, vol. 13, no. 3, pp. 199–207, 1988.
- [60] C. Roy, B. Labrecque, and B. de Caumia, "Recycling of scrap tires to oil and carbon black by vacuum pyrolysis," *Resources, Conservation and Recycling*, vol. 4, no. 3, pp. 203–213, 1990.
- [61] V. Roy, B. de Caumia, and C. Roy, "Development of a gas-cleaning system for a scrap-tire vacuum-pyrolysis plant," *Gas Separation and Purification*, vol. 6, no. 2, pp. 83–87, 1992.
- [62] H. Pakdel and C. Roy, "Simultaneous gas chromatographic—Fourier transform infrared spectroscopic—mass spectrometric analysis of synthetic fuel derived from used tire vacuum pyrolysis oil, naphtha fraction," *Journal of Chromatography A*, vol. 683, no. 1, pp. 203–214, 1994.

- [63] J. A. Conesa, R. Font, and A. Marcilla, "Gas from the pyrolysis of scrap tires in a fluidized bed reactor," *Energy and Fuels*, vol. 10, no. 1, pp. 134–140, 1996.
- [64] D. Y. C. Leung and C. L. Wang, "Kinetic study of scrap tyre pyrolysis and combustion," *Journal of Analytical and Applied Pyrolysis*, vol. 45, no. 2, pp. 153–169, 1998.
- [65] S. Galvagno, S. Casu, T. Casabianca, A. Calabrese, and G. Cornacchia, "Pyrolysis process for the treatment of scrap tyres: preliminary experimental results," *Waste Management*, vol. 22, no. 8, pp. 917–923, 2002.
- [66] M. F. Laresgoiti, B. M. Caballero, I. de Marco, A. Torres, M. A. Cabrero, and M. J. Chomón, "Characterization of the liquid products obtained in tyre pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 71, no. 2, pp. 917–934, 2004.
- [67] R. Murillo, E. Aylón, M. V. Navarro, M. S. Callén, A. Aranda, and A. M. Mastral, "The application of thermal processes to valorise waste tyre," *Fuel Processing Technology*, vol. 87, no. 2, pp. 143–147, 2006.
- [68] E. Aylón, A. Fernández-Colino, R. Murillo, M. V. Navarro, T. García, and A. M. Mastral, "Valorisation of waste tyre by pyrolysis in a moving bed reactor," *Waste Management*, vol. 30, no. 7, pp. 1220–1224, 2010.
- [69] P. T. Williams and S. Besler, "Pyrolysis-thermogravimetric analysis of tyres and tyre components," *Fuel*, vol. 74, no. 9, pp. 1277–1283, 1995.
- [70] J. Bi, X. Guo, M. Liu, and X. Wang, "High effective dehydration of bio-ethanol into ethylene over nanoscale HZSM-5 zeolite catalysts," *Catalysis Today*, vol. 149, no. 1–2, pp. 143–147, 2010.
- [71] J. A. Conesa and A. Marcilla, "Kinetic study of the thermogravimetric behavior of different rubbers," *Journal of Analytical and Applied Pyrolysis*, vol. 37, no. 1, pp. 95–110, 1996.
- [72] L. M. Mahlangu, *Waste tyre management problems in South Africa and the possible Opportunities that can be created through the recycling therefore [M.S. thesis]*, 2009.
- [73] J. H. Chen, K. S. Chen, and L. Y. Tong, "On the pyrolysis kinetics of scrap automotive tires," *Journal of Hazardous Materials*, vol. 84, no. 1, pp. 43–55, 2001.
- [74] M. Liompart, L. Sanchez-Prado, J. P. Lamas, C. Garcia-Jares, E. Roca, and T. Dagnac, "Hazardous organic chemicals in rubber recycled tyre playgrounds and pavers," *Chemosphere*, vol. 90, pp. 423–431, 2013.
- [75] J. P. Lin, C. Y. Chang, and C. H. Wu, "Pyrolysis kinetics of rubber mixtures," *Journal of Hazardous Materials*, vol. 58, no. 1–3, pp. 227–236, 1998.
- [76] H. Cui, J. Yang, and Z. Liu, "Pyrolysis of tires and tire components by TG/DTA analyzer," *Journal of Chemical Industry and Engineering*, vol. 50, no. 6, pp. 826–833, 1999.
- [77] J. G. Brammer and A. V. Bridgwater, "Drying technologies for an integrated gasification bio-energy plant," *Renewable & Sustainable Energy Reviews*, vol. 3, no. 4, pp. 243–289, 1999.
- [78] M. Olazar, G. Lopez, M. Arabiourrutia, G. Elordi, R. Aguado, and J. Bilbao, "Kinetic modelling of tyre pyrolysis in a conical spouted bed reactor," *Journal of Analytical and Applied Pyrolysis*, vol. 81, no. 1, pp. 127–132, 2008.
- [79] California Integrated waste management Board (CIWMB), "Effects of waste tires, waste tire facilities, and waste tire projects on the environment," CIWMB Report 432-96-029, 1996.
- [80] S. Ucar, S. Karagoz, A. R. Ozkan, and J. Yanik, "Evaluation of two different scrap tires as hydrocarbon source by pyrolysis," *Fuel*, vol. 84, no. 14–15, pp. 1884–1892, 2005.
- [81] E. L. K. Mui, W. H. Cheung, and G. McKay, "Tyre char preparation from waste tyre rubber for dye removal from effluents," *Journal of Hazardous Materials*, vol. 175, no. 1–3, pp. 151–158, 2010.
- [82] O. Doğan, M. B. Elik, and B. Özdalyan, "The effect of tire derived fuel/diesel fuel blends utilization on diesel engine performance and emissions," *Fuel*, vol. 95, pp. 340–346, 2012.
- [83] S. Murugan, M. C. Ramaswamy, and G. Nagarajan, "The use of tyre pyrolysis oil in diesel engines," *Waste Management*, vol. 28, no. 12, pp. 2743–2749, 2008.
- [84] S. Uçar, S. Karagöz, J. Yanik, M. Sağlam, and M. Yuksel, "Copyrolysis of scrap tires with waste lubricant oil," *Fuel Processing Technology*, vol. 87, no. 1, pp. 53–58, 2005.
- [85] A. M. Fernández, C. Barriocanal, and R. Alvarez, "Pyrolysis of a waste from the grinding of scrap tyres," *Journal of Hazardous Materials*, vol. 203–204, pp. 236–243, 2012.
- [86] K. Unapumnuk, T. C. Keener, M. Lu, and F. Liang, "Investigation into the removal of sulfur from tire derived fuel by pyrolysis," *Fuel*, vol. 87, no. 6, pp. 951–956, 2008.
- [87] S. Murugan, M. C. Ramaswamy, and G. Nagarajan, "Performance, emission and combustion studies of a DI diesel engine using distilled Tyre pyrolysis oil-diesel blends," *Fuel Processing Technology*, vol. 89, no. 2, pp. 152–159, 2008.
- [88] S. Murugan, M. C. Ramaswamy, and G. Nagarajan, "Assessment of pyrolysis oil as an energy source for diesel engines," *Fuel Processing Technology*, vol. 90, no. 1, pp. 67–74, 2009.
- [89] D. Bunthid, P. Prasassarakich, and N. Hinchiranan, "Oxidative desulfurization of tire pyrolysis naphtha in formic acid/H<sub>2</sub>O<sub>2</sub>/pyrolysis char system," *Fuel*, vol. 89, no. 9, pp. 2617–2622, 2010.
- [90] M. Miranda, F. Pinto, I. Gulyurtlu, I. Cabrita, C. A. Nogueira, and A. Matos, "Response surface methodology optimization applied to rubber tyre and plastic wastes thermal conversion," *Fuel*, vol. 89, no. 9, pp. 2217–2229, 2010.
- [91] O. Doğan, M. B. Elik, and B. Özdalyan, "The effect of tire derived fuel/diesel fuel blends utilization on diesel engine performance and emissions," *Fuel*, vol. 95, pp. 340–346, 2012.
- [92] A. Napoli, Y. Soudais, D. Lecomte, and S. Castillo, "Scrap tyre pyrolysis: are the effluents valuable products?" *Journal of Analytical and Applied Pyrolysis*, vol. 40–41, pp. 373–382, 1997.
- [93] C. İlkiliç and H. Aydin, "Fuel production from waste vehicle tires by catalytic pyrolysis and its application in a diesel engine," *Fuel Processing Technology*, vol. 92, no. 5, pp. 1129–1135, 2011.
- [94] S. Hariharan, S. Murugan, and G. Nagarajan, "Effect of diethyl ether on tyre pyrolysis oil fueled diesel engines," *Fuel*, vol. 104, pp. 109–115, 2013.
- [95] P. Behera and S. Murugan, "Combustion, performance and emission parameters of used transformer oil and its diesel blends in a DI diesel engine," *Fuel*, vol. 104, pp. 147–154, 2013.
- [96] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68–94, 2012.
- [97] Y. Yang, J. G. Brammer, M. Ouadi et al., "Characterisation of waste derived intermediate pyrolysis oils for use as diesel engine fuels," *Fuel*, vol. 103, pp. 247–257, 2013.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

