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## VALORIZATION OF SOLID TIRE WASTES AVAILABLE IN BANGLADESH BY THERMAL TREATMENT

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### ABSTRACT

*In this study available solid tire wastes in Bangladesh were characterized through proximate and ultimate analyses, gross calorific values and thermogravimetric analysis to investigate their suitability as feedstock for thermal recycling by pyrolysis technology. A new approach in heating system, fixed-bed fire-tube heating pyrolysis reactor has been designed and fabricated for the recovery of liquid hydrocarbons from solid tire wastes. The tire wastes were pyrolysed in the internally heated fixed-bed fire-tube heating reactor and maximum liquid yield of 46-55 wt% of solid tire waste was obtained at a temperature of 475 °C, feed size 4 cm<sup>3</sup>, with a residence time of 5 s under N<sub>2</sub> atmosphere. The liquid products were characterized by physical properties, elemental analysis, FT-IR, <sup>1</sup>H-NMR, GC-MS techniques and distillation. The results show that the liquid products are comparable to petroleum fuels whereas fractional distillations and desulphurization are essential to be used as alternative for diesel engine fuels.*

### INTRODUCTION

The standard of living and quality of life of a nation depend on its per capita energy consumption. Bangladesh's per capita energy consumption is very low, the lowest within the Indian subcontinent. The 2005 energy consumption value stands at 227 kgOE, compared to 512 kgOE for India, 490 kgOE for Pakistan, 478 kgOE for Sri Lanka and 450 kgOE for South Asia, and it was much below the world average of 1778 kgOE. Total primary energy consumption in 2004 was 30.70MTOE and the energy consumption mix was estimated as: indigenous biomass 60%, indigenous natural gas 27.45%, imported oil 11.89%, imported coal 0.44% and hydro 0.23%. More than 76.9% of the country's population lives in rural areas, meeting most of their energy needs from traditional biomass fuels. Around 32% have access to electricity, while in rural areas the availability of electricity is only 22%. Only 3-4% of the households have connection of natural gas for cooking purposes. Only about 2-3% households use kerosene for the same purpose and the rest (over 90%) of people depend on biomass for their energy needs. Thus it is crucial to find out alternative and sustainable resources to mitigate the energy crisis in Bangladesh.

Bangladesh a developing country, and is one of the most densely populated (914 persons/km<sup>2</sup>) countries in the world, with a total population of 135 million. About 77% of people in Bangladesh live in rural areas, and 50% of them do not own any land [1]. More than 2.5% of the adult (15-64 years old) male population (43 million total) earn their living by pedaling rickshaws (light three-wheeled hooded vehicles). A private car is unattainable for 99% of people in Bangladesh, and the vast majority of people therefore use rickshaws and bicycles to get around. The road conditions in the rural areas are often narrow and unpaved, and more than 2% of the adult male populations therefore use motorcycles for faster transit on these roads. Heavy automobiles (trucks and buses) are usually used for long-distance transportation of goods and passengers. It is estimated that 20.50 million

bicycle/rickshaw tires ( $30.75 \times 10^3$  metric tons), 1.72 million motorcycle tires (5160 metric tons), and 6,35,328 bus and truck tires (28907.50 metric tons) become scrap and are disposed of every year [1].

The disposal of non-biodegradable solid tire wastes from human activity is a growing environmental problem for the modern society, especially in developing countries. Unfortunately, most of these scrap tires are simply dumped under open sky and in landfills in developing countries. Open dumping may result in accidental fires with highly toxic emissions or may act as ideal breeding grounds for disease carrying mosquitoes and other vermin with the aid of rain water. Landfills full of tires are not acceptable to the environment because tires do not easily degrade naturally. In recent years, many attempts have been made to find new ways to recycle tires, *i.e.*, tire grinding and crumbling to recycle rubber powders and tire incineration to supply thermal energy in utility boilers to produce electricity, in cement kilns and brick fields. However, grinding is quite expensive because it is performed at cryogenic temperatures and requires energy-intensive mechanical equipment, while incineration may produce hazardous polycyclic aromatic hydrocarbons (PAHs) and soot during the combustion process.

Pyrolysis as an attractive method to recycle scrap tires has recently been the subject of renewed interest. Pyrolysis of tires can produce oils, chars, and gases, in addition to the steel cords, all of which have the potential to be recycled. Tire pyrolysis liquids (a mixture of paraffins, olefins and aromatic compounds) have been found to have a high gross calorific value (GCV) of around 41-44 MJ/kg, which would encourage their use as replacements for conventional liquid fuels [2-10]. In addition to their use as fuels, the liquids have been shown to be a potential source of light aromatics such as benzene, toluene and xylene (BTX), which command a higher market value than the raw oils [2-4, 8, 11, 12]. Similarly, the liquids have been shown to contain monoterpenes such as limonene [1-methyl-4-(1-methylethenyl)-cyclohexene], a high value light hydrocarbon. Limonene has rapidly growing and wide industrial applications including the formulation of industrial solvents, resins and adhesives, as a dispersing agent for pigments, as a fragrance in cleaning products, and as an environmentally acceptable solvent [7-9, 13]. Pyrolytic char may be used as a solid fuel or as a precursor for the manufacture of activated carbon [2, 8, 10, 14]. Roy et al. [9] found that another potentially important end-use of the pyrolytic carbon black (CBp) may be as an additive for road bitumen. Furthermore, active carbons were prepared from used tires and their characteristics were investigated by Roy et al. [9], Zabaniotou and Stavropoulos [15], and Zabaniotou et al. [16]. Some of the previous research groups [2, 4, 8, 11, 17] studied the composition of evolved pyrolysis gas fraction and reported that it contains high concentrations of methane, ethane, butadiene and other hydrocarbon gases with a GCV of approximately  $37 \text{ MJ/m}^3$ , a value sufficient to provide the energy required by the pyrolysis process.

Very different experimental procedures have been used to obtain liquid products from automotive tire wastes by pyrolysis technology including fixed-bed reactors [3, 4, 8, 11, 18-28], fluidized-bed pyrolysis units [6, 29], vacuum pyrolysis units [7, 9, 30-31], spouted-bed reactors [32], etc. but not fixed-bed reactors with fire-tube heating have been studied. Within the past several years, research and development works have been carried out for the fixed-bed fire-tube heating pyrolysis reactor system at Rajshahi University of Engineering & Technology (RUET) in collaboration with National University Corporation Kitami Institute of Technology by the research grants from Japan Society for the Promotion of Science. Pyrolysis of various organic solid wastes in the laboratory scale fixed-bed fire-tube heating pyrolysis reactor has been successfully completed [33-38].

## TIRE SAMPLES AND THEIR CHARACTERIZATIONS

The locally made “GAZI” brands of bicycle/rickshaw tires (B/RT), Indian made “MRF” brands of motorcycle tires (MT) and truck tires (TT), which are the most prevalent types in their category in Bangladesh, were used as experimental substrate throughout the experimental studies. The samples were collected locally from a dumped site of the Rajshahi City Corporation. The process of solid tire waste characterization has been reported elsewhere in details [39]. Proximate and ultimate analyses of the tire waste samples are presented in Table 1. Characterizations showed that the main rubber

Table 1 Proximate and ultimate analysis and gross calorific values of solid tire wastes

Tire samples	Proximate analysis (wt%)				Ultimate analysis (wt%)					GCV (MJ/kg)
	Volatile	Fixed carbon	Ash	Moisture	C	H	N	O + Ash	S	
Bicycle/rickshaw tire	55.20	22.30	21.00	1.50	74.50	6.50	0.95	16.42	1.63	28.75
Motorcycle tire	59.50	20.85	18.12	1.53	75.50	6.75	0.81	15.50	1.44	29.18
Truck tire	62.70	32.31	4.17	0.82	80.30	7.18	0.50	10.83	1.19	33.30

component in the representative bicycle/rickshaw and truck tire waste samples was natural rubber (NR), and that in the motorcycle tire waste sample was styrene butadiene rubber (SBR). The bicycle/rickshaw and motorcycle tire rubber formulation comparatively use larger amount of inorganic materials as additives consequently energy content of the solid tire wastes is lower than that of truck tire waste. The reaction begins with the dehydration and decomposition of processing oils, plasticizer and other organic additives, followed by decomposition of NR and SBR. The pyrolysis of truck tire waste was found to be easier than that of bicycle/rickshaw and motorcycle tire wastes while it was more difficult for motorcycle tire waste. Among the three samples the percentage of total weight loss was higher for truck tire waste and was lower for bicycle tire waste. The volatile content of all tire wastes completely decomposed within the temperature around 475°C.

## **FIXED BED FIRE TUBE HEATING PYROLYSIS EXPERIMENTAL PROCEDURE**

The geometric features of the fixed-bed fire-tube heating pyrolysis reactor system and detail experimental procedure are presented elsewhere [33-38, 40]. The experimental unit consists of a fixed-bed fire-tube heating reactor chamber, a gravity feed type reactor feeder, two ice-cooled condensers, a N<sub>2</sub> gas cylinder, N<sub>2</sub> gas pre-heater, an air compressor, char collection bag and thermocouples. At a distance of 30mm from the closed bottom of the reactor, a distributor plate was fitted to support the feedstock. Eight equally spaced stainless steel, 10mm diameter fire-tubes containing insulated electric coil of a total capacity 1.60 kW were fixed inside the reactor. The fire-tubes and pre-heated N<sub>2</sub> gas provided uniform heating across the cross-section of the reactor chamber.

In each pyrolysis run, by the action of gravity force a quantity of 750 (±2.0) gm tire sample was supplied from the feeder into the reactor chamber. Then the reactor was purged before experiments by the flow of N<sub>2</sub> gas at 4 L/min for 5 min to remove air inside. The pyrolysis experiments were performed by varying the temperature within the range of 375-575°C at every 50°C for a particular feed size and vapor residence time. The reaction time was 50 min for every pyrolysis run. Pyrolysis vapor product was passed through two sets of condenser tubes to quench into liquid and then collected into the glass bottles. The uncondensed gases were flared into the atmosphere. The char product was pushed out from the reactor chamber with the aid of compressed air supplied from the air compressor. Char was collected in the char collection bag. Gas weight was determined by subtracting the liquid and char weight from the total weight of feedstock. Once the temperature of maximum liquid yield (475°C) was selected, additional experiments were conducted at the optimum temperature by varying the feed size and the vapor residence time to find out the optimum process conditions. Before analyzing, the liquid product was centrifuged at 3000 rpm for 15 min to remove heavy condensate and impurities.

## **PYROLYSIS PRODUCT YIELDS**

The product distributions obtained from pyrolysis of prepared representative samples for temperature range of 375-575°C at every 50°C, feedstock size of 4cm<sup>3</sup> and vapor residence time of 5sec are presented in Table 2. The pyrolysis experiments were repeated three times for a particular product yields data. The pyrolysis yields presented in Table 2 are the mean value of the three equivalent experiments with standard deviation for the product yields data. Table 2 shows that when the temperature increases from 375 to 575°C, the yield of liquid increases first to a maximum value at 475°C, and then decreases to a minimum value at 575°C for the three types of feedstock. The gas yield increases over the whole temperature range, while char yield decreases up to 475°C and then remains almost constant. It is apparent that a fairly sharp optimum exists in temperature at which maximum yield of liquid was achieved probably due to strong cracking of the selected tire wastes at this temperature. Tire rubber is not totally decomposed (pyrolysis is not complete) at a temperature less than 475°C. The thermal decomposition of the tire rubber increases (*i.e.* solid yield decreases) up to a temperature of 475°C and hence increasing the liquid and gas yields. In the temperature range of 475-575°C, the solid yields are almost equivalent to those of the values obtained by TGA of tire rubber at around 475°C, which are presented elsewhere [39]. The decrease in liquid yields and increase in gas yields above the temperature of 475°C are probably due to the decomposition of some oil vapors into permanent gases [6], and secondary repolymerization and/or carbonization reactions of oil hydrocarbons into char [8]. The increase in gas yields at higher temperatures is also provided by the char loss reactions. Thus, at higher temperatures the gas yields gradually become dominating. However, 475°C seems to be the optimum temperature to obtain liquid product from

thermal recycling of bicycle/rickshaw, motorcycle and truck tire rubber by pyrolysis technology, since decomposition is complete and the liquid yields become maximized at this temperature.

Pyrolysis product yields and their distributions over the whole range of temperature depend not only on the feedstock composition and operating temperature used for the experiments, but also on the specific characteristics of the system used, such as size and type of reactor, efficiency of heat transfer from the hot reactor surface to and within the tire mass, feed particle size, vapor residence time, etc. Therefore, results from different authors are many times difficult to compare. Moreover, sometimes contradictory data can be found in the literature. Some of the research groups [4, 6, 26, 28] found very similar product distributions to those of the presented study *i.e.* solid yield decreases and gas and liquid yields increase up to an intermediate temperature and then solid yield remains almost constant while gas yield increases, and liquid yield decreases with further increase in temperature.

Table 2 Effect of reactor operating temperature on the product yields

Types of tire wastes	Types of products	Product yields at different reactor temperature (wt%)				
		375°C	425°C	475°C	525°C	575°C
Bicycle/rickshaw tire	Liquids	38±2.5	44±2	46±1	44±1.5	38±1.8
	Solid char	53±3	46±2.3	43.5±2.5	42.5±2	42±2.3
	Gases	9±1.5	10±1.5	10.5±1.5	13.5±1	20±1.5
Motorcycle tire	Liquids	42±2.3	47.5±2	49±1.3	47±1.5	42±1.4
	Solid char	50±2.8	44±2.3	41.5±1.5	40.5±1.7	40±2.6
	Gases	8±1.5	8.5±1.7	9.5±1.9	12.5±1	18±1.5
Truck tire	Liquids	47.5±3	53±2.2	55±1.5	52±2.1	47±3
	Solid char	45±2	39±2.6	36±1.8	35.5±1.6	35±1.5
	Gases	7.5±1	8±1.1	9±1.6	12.5±1.5	18±2

The liquid yields from bicycle/rickshaw and motorcycle tire wastes are lower and char yields are higher compared to those of the previous studies [4, 6, 8, 10, 22, 28, 31]. The liquid yields from the truck tire waste are somewhat higher and char yields are somewhat lower compared to those of the quoted previous studies. These variations in the product yields are due to mainly the compositional differences in tire feeds. The bicycle/rickshaw and motorcycle tire wastes, which were used as feedstock in the presented study, have lower volatile and higher ash content than those of car and truck tire wastes result in lower liquid yields. Although the bicycle/rickshaw and motorcycle tire feed used in the presented study contained higher amount of ash and lower amount of volatile, the liquid yields were equivalent or somewhat higher and char yields were equivalent or somewhat lower than those obtained by other researchers [3, 20, 25-26] because of mainly variations in the design of reactors and operating conditions used.

The effects of feed size and vapor residence time on the product yields under optimum reactor temperature have been described in the author's previous publications [34-38]. The results show that a feed size of 4cm<sup>3</sup> and a vapor residence time of 5 sec are optimum values to obtain pyrolytic liquids at 475°C.

## PHYSICAL AND CHEMICAL PROPERTIES OF PYROLYTIC LIQUIDS

### Fuel Properties of the Pyrolytic Liquids

The pyrolytic liquids obtained from pyrolysis of selected tire wastes, which are oily organic compounds, appear dark-brown-color with a strong acrid smell. No phase separation was found to take place in the storage bottles. Total pyrolysis liquids were characterized in terms of both fuel properties and chemical compositions. The fuel properties of the pyrolytic liquids in comparison to commercial fuel oil are shown in Table 3. The table shows that the density of pyrolytic liquids was found higher than that of the diesel fuel but lower than that of heavy fuel oil. The viscosity of liquid products from the tire wastes was slightly higher than that of the No.2 fuel oil but too much lower than that of heavy fuel oil. Low viscosity of the liquids of 4.75-4.90 cSt at 30°C is a favorable feature in the handling and transporting of the liquid. The flash point of the tire-derived liquids was ≤32°C. The flash point is low when compared with petroleum-refined fuels; for example, kerosene has a required minimum flash point of 23°C, diesel fuel of 55°C and light fuel oil 60°C. The low flash points of the tire-derived liquids are not surprising since the product liquids represent un-refined liquids with a mixture

of components having a wide distillation range. The pour point of the tire-derived liquids is not low compared to the fuel oils. The pH value of the pyrolytic liquids is 4~5, which is in weak acidic nature.

Therefore, the pyrolytic liquids require preliminary treatments such as filtration, centrifugation, desulphurization and hydrotreating to be used as transport fuels. The treated pyrolysis oil can be used directly as fuel oils or blended with diesel fuels, which will reduce the viscosity and, increase the pH value and flash point of the resulting blends. Based on the fuel properties, the tire-derived pyrolytic liquids may be considered a valuable component for use with automotive diesel fuels. Moreover, the total pyrolysis liquids may be directly used as fuels for industrial furnaces, power plants, and boilers.

Table 3 Characteristics of the pyrolytic liquids in comparison to petroleum product

Analyses	B/RT liquid	MT liquid	TT liquid	Fuel oil No.2	Fuel oil No.6
<b>Elemental (wt%)</b>					
C	84.80	85.86	85	87.20	88.00
H	9.01	9.15	9.33	12.50	10.60
C/H	9.41	9.38	9.11	6.98	8.30
N	0.70	0.65	0.50	0.02	0.40
S	1.36	1.25	0.90	0.30	1.00
Ash	0.31	0.22	0.10	0.03	0.06
O	3.82	2.87	4.17	-	-
H/C molar ratio	1.28	1.27	1.32	-	-
O/C molar ratio	0.03	0.025	0.037	-	-
Density (kg/m <sup>3</sup> @ 30°C)	970	957	965	870	980
Viscosity (cSt @ 30°C)	4.90	4.75	4.89	4.2	1850 (200@50°C)
Flash point (°C)	≤32	≤32	≤32	≤60	≤66
Pour point (°C)	-3	-6	-5	-18	15
pH value	4.80	4.40	4.25	-	-
GCV (MJ/kg)	40.80	42.00	42.50	45.00	42.65

Empirical formula for B/RT, MT, and TT liquids are CH<sub>1.28</sub>O<sub>0.03</sub>N<sub>0.007</sub>, CH<sub>1.27</sub>O<sub>0.025</sub>N<sub>0.006</sub>, and CH<sub>1.32</sub>O<sub>0.037</sub>N<sub>0.005</sub>, respectively.

### Chemical Composition of the Product Liquids

FT-IR analysis for pyrolytic liquids derived from B/RT, MT and TT wastes have been carried out and the results obtained from the transmittance spectrums are presented in Table 4. The data shows therefore that the present liquids contain mainly aliphatic and aromatic compounds. Similar FT-IR analysis results for automotive tire-derived pyrolytic liquids were also obtained by the former research groups [4, 22].

Table 4 The FT-IR functional groups and the indicated compounds of pyrolysis liquids

Frequency range (cm <sup>-1</sup> )			Functional groups	Class of compounds
B/RT liquid	MT liquid	TT liquid		
3100-3005	3100-3005	3100-3010	C=C stretching	Alkenes
3000-2800	3000-2800	3000-2800	C-H stretching	Alkanes
1685-1635	1675-1605	1680-1615	C=C stretching	Alkenes
1600-1530	1600-1545	1605-1550	Carbon-carbon stretching	Aromatic compounds
1520-1115	1520-1115	1520-1200	C-H bending	Alkanes
1030-835	1020-845	1035-845	C=C stretching	Alkenes
830-655	810-660	830-675	C-H out-of-plane bending	Aromatic compounds

The <sup>1</sup>H NMR has been performed for the pyrolytic liquids and the hydrogen distributions obtained from the <sup>1</sup>H NMR spectrums are given in Table 5, indicating that no aliphatic carbon is still bound to oxygen (peaks in 3.3-4.5 ppm chemical shift range). Clearly, the main structure of the liquids seems to be aliphatic bonded to aliphatic only (0.4-1.8 ppm chemical shift range), and as a result the carbon aromaticity of the liquids is comparatively low. The alkanes and long alkyl spectrums are probably largely derived from solid tire wastes.

Table 5 <sup>1</sup>H NMR results for the product liquids

Type of hydrogen	Chemical shift (ppm)	Mol% (% of total hydrogen)		
		B/RT	MT	TT
Aromatic	9.0-6.5	6.10	13.31	11.50

Phenolic (OH) or olefinic proton	6.5-4.5	7.90	9.74	2.50
Aliphatic adjacent to oxygen/hydroxyl group	4.5-3.3	--	--	--
Aliphatic adjacent to aromatic/alkene group	3.3-1.8	25.58	17.55	18.78
Other aliphatic (bonded to aliphatic only)	1.8-0.4	60.42	59.40	67.22

GC/MS analysis was carried out with the pyrolysis liquids obtained at 475°C temperature for feed size of 4cm<sup>3</sup>, and apparent vapor residence time of 5 sec to get an idea about the nature and type of compounds in such liquids. Details of this analysis and list of possible compound identified have been presented in the authors previous papers [34-38]. It was found that, tire pyrolysis liquids were very complex mixture from C<sub>5</sub>-C<sub>20</sub>, containing many aliphatic and aromatic compounds. The GC/MS results support well the results obtain from FT-IR (Table 4) and <sup>1</sup>H NMR (Table 5) analyses. The aliphatic compounds were mainly of alkane and alkene groups but the second was predominant in all of the three tire-derived liquids. The aromatic compounds were only single ring alkyl aromatics. In addition to the main hydrocarbons, small percentage of nitrogen, sulphur, oxygen and chlorine containing compounds were also identified. Other oxygen-containing compounds in the form of acid and alcohol were present in the tire derived liquids. The oxygenated compounds are probably derived from the thermal degradation of oxygenated components of the tire, such as stearic acid, extender oils, etc. The presence of nitrogenated, nitro-oxygenated and nitro-sulphurated compounds may be explained by thermal degradation of the accelerators used in tire compounding, which are frequently sulfur and/or nitrogen-based organic compounds, such as 2-mercaptobenzothiozoe, benzothiozoyl disulphide, etc. The presence of chlorine containing compounds in the present pyrolytic liquids may be explained by thermal decomposition of sulphur monochloride, which sometimes is used as vulcanizing agent with main vulcanizing agent, sulphur. The total concentrations of the important identified compounds for each of the derived liquids are summarized in Table 6. The most abundant compound in the pyrolytic liquids obtained from the selected tire wastes is limonene. Ucar et al. [18] also found similar results from their truck tire pyrolysis liquids obtained at 650°C, where the concentration of limonene was 28.78%. The tire wastes for this study are composed of mainly NR and small amount of SBR. It is known that limonene is the most important product form pyrolysis of polyisoprene [7, 25]. Besides, formation of limonene depends on operating conditions such as pyrolysis pressure, temperature, vapor residence time and sample size. Pakdal et al. [7] studied in detail for optimum operating conditions for the production of limonene from used tire by vacuum pyrolysis. They reported that low pyrolysis pressure and temperature, and short vapor residence time increase the limonene yields.

Table 6 Summary of identified compounds in the tire-derived liquids

Compounds identified	Total concentrations (% peak area)		
	B/RT liquid	MT liquid	TT liquid
Aliphatic	42.22	49.54	65.75
Aromatic	16.14	17.23	4.12
Nitrogenated	7.51 (C <sub>11</sub> H <sub>13</sub> NOS; C <sub>9</sub> H <sub>13</sub> NO <sub>2</sub> )	4.25 (C <sub>11</sub> H <sub>13</sub> NOS; C <sub>7</sub> H <sub>7</sub> N <sub>3</sub> )	0.69 (C <sub>11</sub> H <sub>13</sub> NOS; C <sub>2</sub> H <sub>5</sub> N)
Sulphurated	5.04 (C <sub>11</sub> H <sub>13</sub> NOS)	0.80 (C <sub>11</sub> H <sub>13</sub> NOS)	0.56 (C <sub>11</sub> H <sub>13</sub> NOS)
Oxygenated	9.82 (C <sub>10</sub> H <sub>16</sub> O; C <sub>19</sub> H <sub>30</sub> O <sub>2</sub> + ...)	2.16 (C <sub>11</sub> H <sub>13</sub> NOS; C <sub>6</sub> H <sub>5</sub> ClO; C <sub>8</sub> H <sub>15</sub> ClO + ...)	1.57 (C <sub>10</sub> H <sub>16</sub> O; C <sub>11</sub> H <sub>13</sub> NOS; C <sub>19</sub> H <sub>30</sub> O <sub>2</sub> + ...)
Chlorinated	1.82 (C <sub>12</sub> H <sub>25</sub> Cl; C <sub>14</sub> H <sub>29</sub> Cl)	1.58 (C <sub>6</sub> H <sub>5</sub> ClO; C <sub>8</sub> H <sub>15</sub> ClO; C <sub>12</sub> H <sub>25</sub> Cl)	2.45 (C <sub>12</sub> H <sub>25</sub> Cl; C <sub>16</sub> H <sub>33</sub> Cl)
Limonene	10.95	29.54	50.86

Rodriguez et al. [2] carried out the pyrolysis of automotive tires in a fixed-bed reactor at 500°C and reported that product oils consist of 62.4 wt% aromatic compounds, 31.6 wt% aliphatic compounds, 4.2 wt% nitrogen-containing compounds, and 1.8 wt% sulfur-containing compounds. Laresgoiti et al. [3] studied with an exhaustive effort to characterize total pyrolytic product oils from car tire wastes obtained at every 300, 400, 500, 600, and 700°C and reported that tire pyrolysis oil was mainly aromatic and aliphatic in composition but with nitrogen, sulfur, and oxygenated species present. They found that at every temperature the tire pyrolysis oils are predominately aromatic. They also found a range of compounds in tire pyrolysis oils, showing that the oil is composed mainly of alkylated benzenes, naphthalenes, and phenanthrenes, *n*-alkanes from C<sub>11</sub>-C<sub>24</sub>, and alkenes from C<sub>8</sub>-C<sub>15</sub>. Kyari et al. [19] carried out GC/MS of total pyrolysis liquids obtained from pyrolysis of a mixture of seven brands of used car tire feeds at 500°C. They reported that the oil contained mainly aromatic and

aliphatic compounds such as alkylated benzenes, alkylated naphthalenes, alkanes and alkenes. They found ethyl-, propyl-, butyl-, pentyl-, hexyl-, and heptylbenzene and ethenyl-, propenyl-, and butenylbenzenes in high concentrations. Naphthalene and methyl, dimethyl, and trimethyl naphthalenes were present in their oils in significant concentrations. The identified alkanes were pentadecane, heptadecane, octadecane, nonadecane, eicosane and some other high molecular weight alkanes. In addition to the main hydrocarbons, sulfur-containing compounds and nitrogen-containing compounds were also identified in their product oils. Moreover, some oxygenated compounds in the form of acids such as hexadecanoic, heptadecanoic and octadecanoic acids were identified.

Laresgoiti et al. [3] reported that the aromatic nature of the tire oils is due: (i) to the aromatic nature of the source polymeric materials, SBR and (ii) to cyclization of olefin structures through dehydrogenation reaction, which happens during pyrolysis process. Several of the former research groups [2, 3, 7, 8] demonstrated that the proportion of aromatics increases with pyrolysis temperature. It is known that the formation of aromatic at high temperature is due to the expense of aliphatic compounds but Laresgoiti et al. [3] suggests that when the reactor temperature is raised, non aromatic compounds link to aromatic structures yielding a higher proportion of aromatic compounds. The greater non-identified peaks in the chromatograms are due to the presence of heavier and more complex products, which are produced during pyrolysis and hence are more difficult to identify.

Fuel oil No. 1 is a light distillate which consists primarily of hydrocarbons in the C<sub>9</sub>-C<sub>16</sub> range; fuel oil No. 2 is a heavier, usually blended, distillate with hydrocarbons in the C<sub>11</sub>-C<sub>20</sub> range. Diesel fuels predominantly contain a mixture of C<sub>10</sub> through C<sub>19</sub> hydrocarbons, which include approximately 64% aliphatic hydrocarbons, 1-2% olefinic hydrocarbons, and 35% aromatic hydrocarbons. Thus, it may be concluded from the above discussions that total tire derived pyrolysis liquids are almost similar fuel oil and diesel fuel in physical properties and chemical compositions.

### Distillation Test of the Product Liquids

In order to investigate the potential uses of pyrolysis oils, TGA distillation test at atmospheric pressure was carried out, with a mixture of three types of pyrolysis oils obtained at 475°C. A summary of the results compared to those of the previous studies is presented in Table 7. It is observed that more than 30 wt% of such oils is easily distillable fraction with boiling points between 70°C, and 210°C, which is the boiling point range specified for commercial petrol. In order to establish the real potential use of such fraction mixed with petrol, standard tests typical of petrol, such as induction time, Amodeo gums, corrosive properties, octane MON and RON numbers, etc., should be carried out.

On the other hand, Table 7 shows that 75 wt% of the pyrolytic oils has a boiling point under 370°C, which is the upper limit specified for the 95% of distilled product in diesel oils. However, the whole <370°C tyre oil fraction should not be acceptable as diesel oil because of its significant proportion of low boiling products. A typical boiling range for diesel oil is from 150 to 370°C. The pyrolytic oil fraction corresponding to the 150-370°C is about 60 wt% of the total oils. From Table 7 it may be concluded that the 150-370°C tyre pyrolytic oil has a higher proportion of the lighter and heavier products, and a lower proportion of the middle boiling range products, than the commercial diesel oil. In order to establish the real potential use of such tyre oil fraction as diesel oil, a more thorough characterisation of it, which should include cetane index, corrosive properties, flash point, etc., is needed.

Table 7 Boiling point distribution results of the pyrolytic liquids

Fractional volume (%)	Present pyrolysis oils	Car tire derived pyrolysis oil [2]	Tire derived liquid from pilot plant [42]	Commercial diesel
0	60	78	55	158
10	105	114	110	190
20	132	168	130	220
30	163	198	165	240
40	195	249	200	260
50	245	296	250	280
60	278	333	280	290
70	325	359	350	310
80	352	374	--	320
90	385	386	--	340
100	572	388 (94% distilled)	--	370 (96.9% distilled)



## CONCLUSIONS

The research findings of the studies show that fixed-bed fire-tube heating pyrolysis is a good option for production of bio-crude oils from solid tire wastes. The optimum liquid yields conditions for the fixed-bed fire-tube heating reactor system are: operating temperature 475 °C, feed size 4 cm<sup>3</sup> and apparent vapor residence time 5 s. The fuel properties of the pyrolysis liquids such as density, viscosity, GCV, carbon and hydrogen contents are found almost comparable to those of the automotive diesel fuels but fractional distillations and desulphurization are essential to be used as alternative for engine fuels. The pyrolytic liquids abundantly contain olefins, especially limonene and light aromatics, which have higher market values as chemical feedstock than their use as fuels.

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