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Fire-tube Heating Pyrolysis of Car Tire Wastes: End Uses of Product Liquids as Fuels and Chemicals

M.R. Islam*[1], K.S. Il+, H. Haniu+ and M.R.A. Beg*

Abstract – *Car tire wastes were pyrolysed in a fixed-bed fire-tube heating reactor system under nitrogen to determine the effect of final temperature, feed size and sweeping gas flow rate on the product yields and liquid product compositions. The highest liquid product yield was obtained at* 475^oC *for feed size of* $4cm^3$ *and sweeping gas flow rate of 8L/min. Liquid products were characterized including fuel properties, elemental analyses, FT-IR,* ^1H*-NMR, GC-MS and distillation. The analytical results showed that the tire derived liquids are a complex mixture of* $C_5 – C_{17}$ *organic compounds, with a lot of valuable single ring alkyl-aromatics (23.12%), a high value light hydrocarbon, limonene (11.11%), long-chain (including small amount of ring) hydrocarbons (30.94%) and oxygenated compounds (2.89%). The fuel properties and distillation data represent that the total pyrolytic liquid can be used as liquid fuel.*

Keywords – Car tire wastes, end uses, fire-tube heating pyrolysis, product liquids.

1. INTRODUCTION

The accumulation of huge piles of tires is a threat to the environment making tire recycling a necessity. It is estimated that the annual tire waste generation amounts (in million tons per year) are 15 in the European Union, 2.5 in North America, 2.4 in UK, 1 in China, 0.5 in Japan, 0.17 in Korea, and 0.09 in Bangladesh [1], [2]. One common method of disposal is landfilling. Landfilling for disposal of used tires is associated with certain problems. First, it requires a considerable amount of space because the volume of tires cannot be reduced by compaction. Massive stockpiles of dumped scrap tires provide ideal breeding grounds for disease carrying mosquitoes and other vermin. In addition, landfilling is a potential danger because of the possibility of accidental fires that produce high emissions of hazardous gases. Various alternatives to landfilling are often used for tire recycling: including re-treading, reclaiming, incineration, and grinding all of which have significant drawbacks and/or limitations [2].

Used tires can be a source of energy and valuable chemical products, and their thermal decomposition makes the recovery of useful compounds possible. The pyrolysis of solid tire waste has received increasing attention because the process condition may be optimized to produce high energy density liquids, solid char and gases. The liquid products can be stored until required, or readily transported to where they can be most efficiently utilized. Tire pyrolysis liquids have been found to have a high calorific value of around 41-44 MJ/kg, which would encourage their use as replacements for conventional liquid fuels [3]. 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 oil [3], [4]. Similarly, the liquids have been shown to contain monoterpenes such as limonene [1-methyl-4-(1-methylethenyl)-cyclohexene], a high value light hydrocarbon used in industrial applications including 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 [3], [4]. Limonene is very common in cosmetic products and is also used as a flaming combustible liquid. Sometimes, the liquids also contain aromatic source comparatively light hydrocarbons octahydro-1,4,9,9-tetramethyl-1H-3a,7-methanoazulene, which can be used as fragrance ingredients.

The marketability of tire pyrolysis liquids is low due to several demeritorious factors such as extreme odor and a high aromatic content. In order to enhance the marketability, limonene-enriched tire liquids have been reacting with methanol to produce limonene ethers [5], [6]. Methyl limonene ether is a high value product and has a very pleasant fragrance. It can be used alone or as an odor-improving additive. Besides, aromatics and limonene separation from tire pyrolysis liquids have been extensively investigated by several authors using various techniques [3], [7]-[9].

In the present study, to provide a new approach in heating system for fixed-bed pyrolysis technology to the recovery of hydrocarbons from used tires; fixed-bed pyrolysis with a fire-tube heating reactor was investigated. This process of heating has proved very effective in the technology for fire-tube steam boilers. The thermal recycling of car tire wastes by pyrolysis technology has been carried out in the internally heated fire-tube heating reactor system under N2 atmosphere. The effects of operating temperature, feed size and vapor residence time on the yields and compositions of product liquids were investigated. A detailed characterization of the whole pyrolysis liquids obtained at optimum operating conditions has been carried out including physical properties, elemental analyses, GCV, Fourier Transform InfraRed (FT-IR), 1H NMR, GC–MS analysis and distillation.

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*Department of Mechanical Engineering, Rajshahi University of Engineering and Technology, Rajshahi-6204, Bangladesh.

+Department of Mechanical Engineering, Kitami Institute of Technology, Kitami City, Hokkaido 090-8507, Japan.

[1] Corresponding author;
Tel: + 88-0721-750743 ext 217; Fax: + 88-0721-750319.
E-mail: mrislam1985@yahoo.com.

2. COMPOSITION AND CHEMISTRY OF TIRE

While considering the disposal of used tires, it is essential to be aware of chemical composition of the different materials and substances used in the manufacturing of tires. Natural and/or synthetic rubber, mixed with several ingredients, originates the mixture that, upon vulcanization and coupling with the wire gauze, forms the tire.

Material Mixture for Manufacturing Tire Rubber

The mixture, which is generally used for manufacturing tire rubber, is composed of the following materials:

- Elastomer
- Reinforcing agents
- Plastificants
- Vulcanizing agents
- Accelerating agents
- Protective agents

Elastomer

Rubber also known as elastomer, is a high polymer having elastic properties in excess of 300%. Both of natural and synthetic rubbers are used for manufacturing tires.

Natural Rubber (Polyisoprene)

The source of polyisoprene (C_5H_8 or $C_{10}H_{16}$) is a group of plants comprising nearly 500 different species, which yield a white milky substance, known as latex (which is a dispersion of isoprene). The latex contains about 25-40% of rubber hydrocarbons dispersed in water in presence of stabilizer proteins and some fatty acids. The latex collecting pots like half a coconut shells are attached to the tapped rubber tree via a short sharp stick and the latex drips down into it overnight. The latex from multiple trees is then poured onto flat pans, and this is mixed with formic acids, which serves as a coagulant. After a few hours, the very wet sheets of rubber are wrung out by putting them through a press before they are sent onto factories where vulcanization and further processing is done.

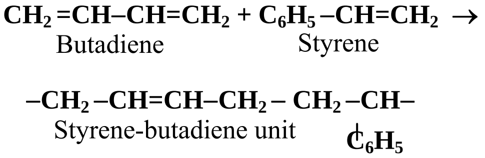
Synthetic Rubber

A synthetic rubber is any vulkanizable man made high polymer possessing same and similar physical properties as that of natural rubber. The most common sythetic rubbers which are used for manufacturing of tires are butadiene rubber, styrene-butadiene rubber and butyl rubber.

Butadiene rubber also known as polybutadiene rubber is manufactured from polymerization in which small monomer molecules are joint together in large numbers.

$$\underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \rightarrow \underset{\text{Polybutadiene}}{[-CH_2{-}CH{=}CH{-}CH_2{-}]_n}$$

Styrene-butadiene rubber is made by emulsion co-polymerization of styrene and butadiene usually in the ratio of 1:3, in presence of a free radical catalyst (such as benzoyl peroxide or sodium per sulphate) at about 5^{o}C for 12-15 hours. To control the temperature, a soap in water emulsion is added.



$$\underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + \underset{\text{Styrene}}{C_6H_5{-}CH{=}CH_2} \rightarrow$$

$$\underset{\text{Styrene-butadiene unit}}{-CH_2{-}CH{=}CH{-}CH_2{-}\ CH_2{-}\underset{\underset{C_6H_5}{|}}{CH}{-}}$$

Butyl rubber also known as polyisobutylene (C_4H_8) is manufactured from co-polymerization of about 98% of isobutylene, $(CH_3)_2C{=}CH_2$ with about 2% of isoprene or butadiene. The butyle rubber is neighter formed neither by emulsion polymerisation nor at ordinary and elevated temperatures. No usual catalyst is used in its preparation. Polyisobutylene is impermeable to air and used in many applications requiring an airtight rubber. Inner liner is made of butyl rubber lining attached to the inside of the tire, used instead of a tube.

Reinforcing Agents

Inorganic substances, such as zinc oxide, magnesium carbonate and carbon black are added to improve the tensile strength and rigidity of the rubber. Carbon black is the most important reinforcing agent. It also improves resistance to abrasion.

Plastificants

Plastificants are added to give the rubber greater tenacity and adhesion. The common plastificants used are naphthenic oils, aromatic oils, resins etc. (petroleum origin), pine tar, resins, pitch (pine tree derivatives), coaltar oils, pitch, resins (coaltar origin), vegetable oils, blown oils, fatty acids etc. (natural oils and fats).

Vulcanizing Agents

The most important vulcanizing agent is still sulphur. The other vulcanizing agents are sulphur monochloride, selenium, tellurium sulphides, polysulphite polymers etc.

Accelerators

Organic compounds having nitrogen or sulphur or both are used to increase the rate of vulcanization of rubber from several hours to few minutes. Examples of accelerators are 2-mercaptobenzothiozole, benzothiozolyl disulphide, zinc diethyldithio carbamate, tetramethyl thiuram disulphide etc.

Protective Agents

Rubber decomposes when exposed to air, heat, light, or oxygen. Protective agents protect the rubber from attack of air, heat, light and even ozone in the atmosphere. Commercial protective agents widely used in tires are N-phenyl 2-napthylamine and alkylated diphenylamine.

3. MATERIALS AND METHODS

Feed Materials

Car tire waste was collected locally from a dumpsite of Rajshahi City Corporation. The main components of tires such as rubber, fillers like carbon black, steel, sulfur, zinc oxide, processing oil, and vulcanization accelerators, are heterogeneously distributed over the cross-section. Therefore, in order to maintain uniformity of the components in the representative samples, the same tires were divided along the cross-section into different size pieces of 8cm×1cm×0.25cm = $2cm^3$; 8cm×1cm×0.50cm = $4cm^3$; 8cm×1cm×1cm = $8cm^3$; and 8cm×1cm×1.50cm = $12cm^3$. The scrap tire samples were contained no steel thread but the textile netting. The proximate and elemental analyses and higher heating value of the waste tire feedstock are presented in Table 1. Comparison with the typical values for bituminous coal the tabulated values show higher carbon content, lower nitrogen content, higher hydrogen content, much higher volatile content, higher HHV, lower moisture, fixed-carbon and similar ash content of car tire waste. For these favorable characteristics of the car tire, the production of liquids through pyrolysis is may be a potential method for utilization of waste tires.

Table 1. Proximate and ultimate analysis of solid tire waste

Proximate analysis [wt%]		Elemental analysis [wt%]	
Moisture content	1.60	Carbon (C)	75.80
Volatile	58.20	Hydrogen (H)	7.20
Fixed carbon	21.30	Nitrogen (N)	0.90
Ash content	18.90	sulphur (S)	1.21
HHV [MJ/kg]	30.50	Others	14.89

Experimental Section

The schematic diagram of the experimental set-up has been presented in Figure 2. The experimental unit consists of eight major components: (1) a fixed-bed fire-tube heating reactor chamber with a power system; (2) a gravity feed type reactor feeder; (3) two ice-cooled condensers, each of them having a liquid collecting glass bottle; (4) a N_2 gas cylinder with a pressure regulator and a gas flow meter; (5) a N_2 gas pre-heater with LPG burner; (6) an air compressor; (7) char collecting bag and (8) K-type (chromel–alumel) thermocouples, whose measurement accuracy is ±2.5°C with a temperature controller. At a distance of 30mm from the closed bottom of the reactor, a distributor plate was fitted to support the feedstock. The distributor plate was made of stainless-steel plate having 208 holes of 3mm diameter.

The N_2 gas inlet was 20mm bellow the distributor plate. 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_2 gas provided uniform heating across the cross-section of the reactor chamber. The reactor was thermally isolated with asbestos cylinder. The reactor height from the distributor to the gas exit was 270mm and its diameter was 100mm, which provided an apparent vapor residence time of 5sec. The sweeping gas flow rate or vapor residence time for the fire-tube heating reactor system was calculated by the following equation. Free space in the reactor for the flow of sweeping gas (N2):

$$V_{fsp} = \left[\frac{\pi d^2 l}{4} - \frac{n\pi d_1^2 l_1}{4}\right] \times \left(1 - \frac{V_m}{100}\right) + \frac{\pi d_2^2 l_2}{4}$$

$$= 661\text{cm}^3 = 0.661 \text{ L and}$$

the sweeping gas flow rates, Vf = (Vfs/t). The values of Vf were 8, 4 and 2 L/min for residence time, t = 5, 10 and 20sec respectively.

Where, for the present reactor system: internal diameter of the reactor, d = 10cm; effective length of the reactor, l = 27cm; length of each fire-tube, l_1 = 27cm; outer diameter of fire-tube, d_1 = 1cm; number of fire-tubes, n = 8; reactor volume occupied by feed materials, V_m = 70%; diameter of vapor outlet pipe, d_2 = 2.54cm; and length of vapor outlet pipe (from reactor to condenser), l_2 = 15cm.

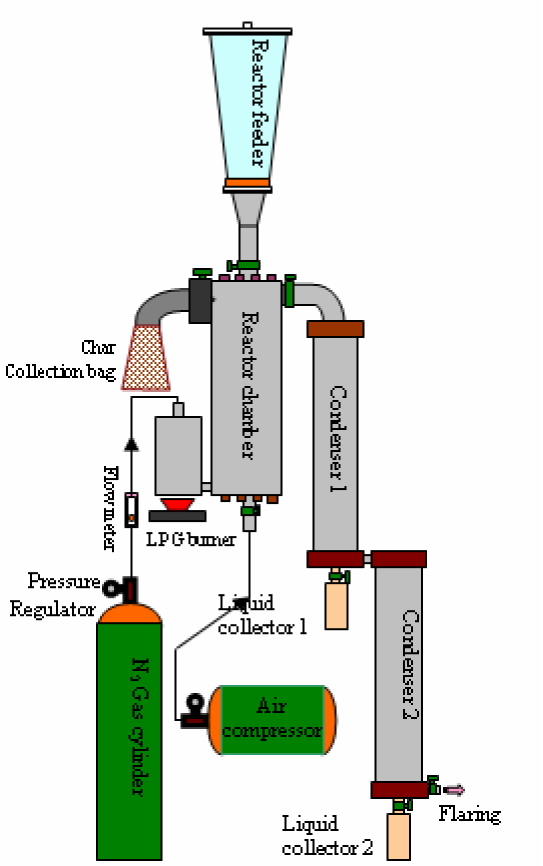


Fig. 2. Schematic diagram of the fixed-bed fire-tube heating pyrolysis system

In each pyrolysis run, by the action of gravity force a quantity of 750 (±2.0) gm of tire sample was supplied from the feeder into the reactor chamber by opening the feed control valve. Then the reactor was purged before experiments by the flow of N_2 gas of 4 L/min for 5 minutes to remove air inside. The reactor heater (power system) and LPG burner were switched on, and the temperature of the reactor was increased to a desired value of temperature of either 375, 425, 475, 525 or 575°C. The reaction time was 50 minutes for every pyrolysis runs after which usually no further visible vapor product came out. Nitrogen gas was supplied in order to maintain the inert atmosphere in the reactor and also to sweep away the pyrolyzed vapor product to the condensers. Pyrolysis vapor product was passed through two sets of condenser pipes to quench into liquid and then collected in the glass bottles. The uncondensed gases were flared to the atmosphere. The bottles were completely filled up with liquid so that no air could be trapped into the bottles. When pyrolysis of the feed material in the reactor was completed, the vapor exit port was closed and, the reactor heater and LPG burner were switched off. N_2 gas supply was also stopped. After cooling down the system, the char product was pushed out from the reactor chamber with the aid of compressed air supplied from the air compressor by opening char exit port. Char was collected in the char collection bag and weighed. The liquid was then weighed and gas weight was determined by subtracting the liquid and char weight from the total weight of feedstock. Afterwards, the system had been made ready for the next run just repositioning the valves. Before analyzing, the liquid product was centrifuged at 3000 rpm for 15 minutes to remove heavy condensate and impurities.

Pyrolytic Product Liquid Analysis

Pyrolytic liquids obtained under the maximum liquid yield conditions were well mixed and homogenized prior to analysis being made. Some physical properties of pyrolytic liquids: density, viscosity, flash point, pour point and GCV were determined by using the following standard methods: ASTM D189, ASTM D445, ASTM D92, ASTM D97 and ASTM D240 respectively. Elemental analysis (C, H, N and S) of liquids was determined with an elemental analyzer of model EA 1108, which followed the quantitative "dynamic flash combustion" method. The boiling point range distribution of hydrocarbons in the pyrolytic liquids was determined by using Thermo-gravimetric Analyzer (TGA) of model SHIMADZU TGA-50 according to ASTM D2887-89 standard test method. The sample (15-20 mg) was heated from ambient temperature to 600°C at a heating rate of 10°C/min in a high purity helium atmosphere at a flow rate of 100ml/min. The data obtained from TGA was used to evaluate the simulated distillation curves. The functional group compositions of the product liquids were analyzed by Fourier Transform InfraRed (FT-IR) spectroscopy. The FT-IR instrument of model PERKIN ELMER FTIR 2000 was used to produce the ir-spectra of the derived liquids. Identification of compounds in pyrolytic liquids was carried out by a gas chromatograph mass spectrometer of model GCMS-QP5000. The analysis was performed on a 60m×0.32mm capillary column coated with a 1μm film of DB-1. The oven temperature was programmed, 40°C hold for 10 min to 300°C at 5°C/min hold for 10 min. Compounds were identified by means of the NIST12 and NIST62 library of mass spectra and subsets HP G1033A. The ^{1}H NMR analyses of pyrolytic liquids were recorded at a frequency of 500 MHz with an instrument of model JEOL A-500 using $CDCl_3$ as solvent.

4. RESULTS AND DISCUSSIONS

Pyrolysis Product Yields

Three products are usually obtained from pyrolysis of tire rubber: liquids, solid char and gases. The product distributions from pyrolysis of car tire waste at different operating temperature and feedstock size are presented in Figures 3 to 4. From the Figure 3, 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 tire rubber at this temperature. The liquid yield increased form approximately 44% of the feed weight at temperature of 375°C to the maximum value of 51% at 475°C before it dropped to about 44% at temperature of 575°C. Tire rubber is not totally decomposed (pyrolysis is not complete) at a temperature less then 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. The solid char consists of carbon black, some solid hydrocarbons, and lower amounts of tire rubber additives such as zinc, sulfur, clays, and silica, or metal oxides [10]. Therefore, there is no obvious mechanism for char loss with increasing temperature, excepting only the higher temperature volatilizes some of the solid hydrocarbons content of the char. Competing with char loss reactions, certain amount of char or coke like carbonaceous material is formed in the pyrolysis of many polymeric materials, due to secondary repolimerization reactions among the polymer derived products. Since solid yields do not decrease in the temperature range of 475-575°C, it may be concluded that tire decomposition is completed and carbonaceous material has been formed. 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 [11], and secondary repolimerization and/or carbonization reactions of oil hydrocarbons into char. The increase in gas yields in higher temperatures is also provided by the char loss reactions. Thus, at higher temperatures the gas yields become gradually dominating. However, 475°C seems to be optimum temperature to obtain liquid product from thermal recycling of car tire rubber by pyrolysis technology, since decomposition is complete and the liquid yields become maximized at this temperature.

The thermochemical conversion of rubber from scrap tires by pyrolysis and hydropyrolysis has been studied by Mastral italics [12]. They observed that neither the total conversion nor liquid yield increased with increasing temperature above 500°C for the pyrolysis at a heating rate of 300°C/min. Similar results have been reported by other researchers. The pyrolysis of scrap tires was carried out in a fixed bed reactor at the temperatures from 300 to 700°C at the heating rate of 15°C/min [1], [9], [13]. It was reported that there is no influence of the temperature on the product distributions over 500°C. On the contrary, the decrease in liquid yields with increasing temperature and the corresponding increase in gas yield, have been observed by other workers. Day Italiged [14] have carried out the pyrolysis of auto shredder residue in a laboratory screw kiln reactor from 500 to 700°C. They found that the yield of oil fraction was high at the lower pyrolysis temperatures.

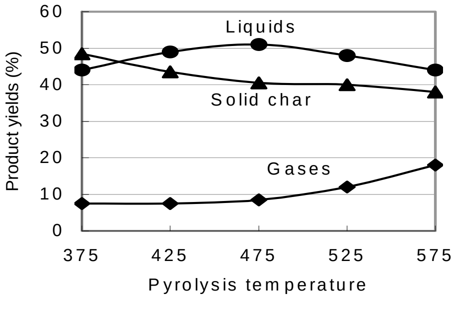


Fig. 3. Effect of temperature (in °C) on product yields

Figure 4 shows that the liquid yield was high for feed size of 4 cm^3 at the pyrolysis temperature of 475°C. It can be seen from the figure that liquid yield first slightly increases up to a maximum value for feed size of 4cm^3 and then decreases for larger feed size while the char yield increases and gas yield decreases through all the piece sizes from 2 to 12cm^3. The thermal conductivity of organic solid pieces is very poor (0.1 W/m^2-^{o}C along the grain, 0.05 W/m^2-^{o}C cross grain) [15]. During pyrolysis, a high heating rate (claimed up to 10000^{o}C/s) may be achieved at thin reaction layer but the lower thermal conductivity of organic solid piece prevents such heating rate through the whole piece. Smaller feed size provides more reaction surface causes high heating rate and too quick decomposition of the rubber feed occurs [16]. The product oil vapors comparatively get enough time for secondary reaction in the reactor and consequently increase in gas yields and, decrease in liquid and char yields. On the other hand, the heating rate in larger tire feed is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller pieces. Thus, the rubber core of the larger pieces becomes carbonized and/or cannot be decomposed completely resulting increase in char yields and decrease in liquid and gas yields. Similarly, Dai *et al.* [10] also found that the char yield of the 0.8 mm tire sample was higher, and the gas and oil yields were lower, than those of the 0.32 mm sample. In the present study, it may be concluded that the optimum feed size is 4cm^3 for which decomposition of tire pieces is complete and has less possibility of secondary cracking at the optimum reactor temperature and for a vapor residence time of 5 seconds.

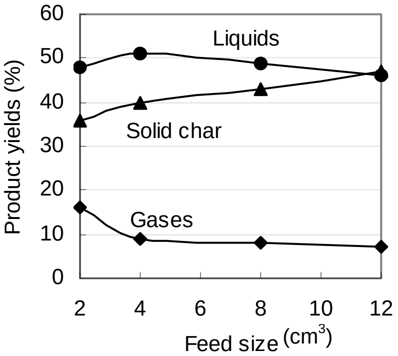


Fig. 4. Effect of feed size on product yields

The effect of vapor residence time on gas, char and liquid yields for pyrolysis temperature of 475^{o}C and feed size of 4 cm^3 shows that: as the vapor residence time increases from 5 to 20 seconds (*i.e.* N_2 gas flow decreased from 8 to 2 L/min), the liquid and char yields decrease while the gas yield increases slightly. The increase in gas yields with increasing vapor residence time in the present investigation is due to the decomposition of some oil vapor into secondary permanent gases. Primary vapors are first produced from pyrolysis of tire rubber at optimum reactor temperature and the primary oil vapors then degrade to secondary gases {for instance: oil vapors → heavy hydrocarbons + light hydrocarbons (CH_4 + C_2H_4 + C_3H_6 +…...) + CO + CO_2 + H_2} within the period of higher vapor residence time, which leads to less oils and more gaseous products. Besides, long contact time between the volatiles and the char leads to another parallel secondary pyrolysis reaction (for instance: $C + CO_2 \rightarrow 2CO$) and hence reduces in char yields. The results of the present work *i.e.* the decrease in liquid and char yields, and increase in the gas yields with increasing vapor residence time are in good agreement with those of the published paper [10].

Analysis of Product Liquids

a. Fuel Properties of the Liquids

The pyrolytic liquids obtained from pyrolysis of car tire wastes were characterized in terms of both fuel characteristics and chemical composition. Some properties of pyrolytic liquids in comparison to petroleum-refined fuels are shown in Table 2. Density of pyrolytic liquids was found higher than that of the commercial diesel fuel but lower than that of heavy fuel oil. The viscosity of liquid products from car tire wastes was slightly higher than that of commercial diesel fuels. Low viscosity of the liquids of 4.62 cSt at 30^{o}C is a favorable feature in the handling and transporting of the liquids. The flash point of the tire-derived liquids was <30^{o}C. The flash point is low when compared with petroleum-refined fuels; for example, kerosene has a required minimum flash point of 23^{o}C, diesel fuel of 55^{o}C and light fuel oil of 79^{o}C. The low flash points of the tire-derived liquids are not surprising since the product liquids represents un-refined liquids with a mixture of components having a wide distillation range. The calorific values for pyrolytic liquids were close to that of commercial diesel. Therefore, the pyrolytic liquids can be used as fuels for combustion systems in industry.

Table 2. Characteristics of the pyrolytic liquids in comparison to petroleum products

Analyses	Car tire liquids	Commercial diesel
Elemental [wt%]		
C	86.52	84.00-87.00
H	9.35	12.80-15.70
C/H	9.25	5.35-6.80
N	0.53	65-3000ppm
S	1.30	0.11-0.70
Ash	0../;2	0.0
O	2.1	0.01
H/C molar ratio	1.3	1.83
O/C molar ratio	0.018	-
Empirical formula	$CH_{1.30}O_{0.018}N_{0.005}$	-
Density [kg/m^3]	943	820-860
Viscosity [cSt]	4.62$^\#$	2.0-4.5$^®$
Flash point [^{o}C]	<30	>55
Pour point [^{o}C]	-4	-40 - -30
Moisture [wt%]	N/A	80ppm
pH value	4.30	-
HHV [MJ/kg]	41.6	44.00-46.00

$^\#$@ 30^{o}C; $^®$@ 40^{o}C

b. Chemical Composition of the Liquid Products

Condensable liquids are the major products of solid car tire wastes pyrolysis. Since the liquids consist of numerous and diverse components, it is difficult to quantify them. All most all of the researchers have been using elemental analysis, FT-IR, NMR and GC-MS modern analytical techniques to identify and to quantify possible compounds in the pyrolytic liquids derived from different types of organic solid wastes.

Elemental analysis, H/C and O/C molar ratios, empirical formula and calorific values for the liquids are listed in Table 2. The average chemical composition of the pyrolytic liquid has been analyzed as $CH_{1.30}O_{0.018}N_{0.005}$. Further, comparison of H/C ratios with conventional fuels indicates that the H/C ratio of the liquids close to that of light petroleum products. However, the sulphur content in pyrolysis liquid was found in this study lie between those of commercial diesel and heavy fuel oil. Also, calorific values indicate that the energy contents of the liquids were very close to that of petroleum fuels. These results are in good agreement with the previous reports [17], [18]. The long chain diesel like structure attributes to high C/H ratio as reflected by very high heating value, comparable to fuel oil and diesel, as well as indicates the high miscibility with diesel fuel as per like dissolves like principle.

The FT-IR is not the most appropriate analytical tool to determine saturated, aromatic and polar components. Nevertheless, it allows functional group analysis to reveal the chemical properties of the liquids. The FT-IR spectrum for pyrolytic liquids derived from car tire waste is shown in Figure 5 and the results from the transmittance spectrums is presented in Table 3. The data shows therefore that the present liquids contain mainly aliphatic and aromatic compounds.

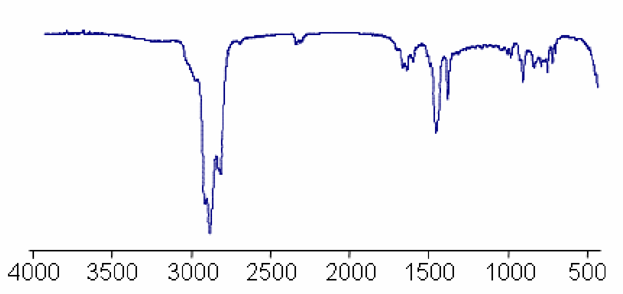


Fig. 5. FT-IR spectra for car tire derived liquids

The ^1H NMR spectrum of the car tire derived liquids is presented in Figure 6. The hydrogen distribution of ^1H NMR is given in Table 4, 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 (0.4–1.8 ppm chemical shift range), and the carbon aromaticity of the liquids is also very significant. The alkanes and long alkyl spectrum are probably largely derived from solid tire wastes.

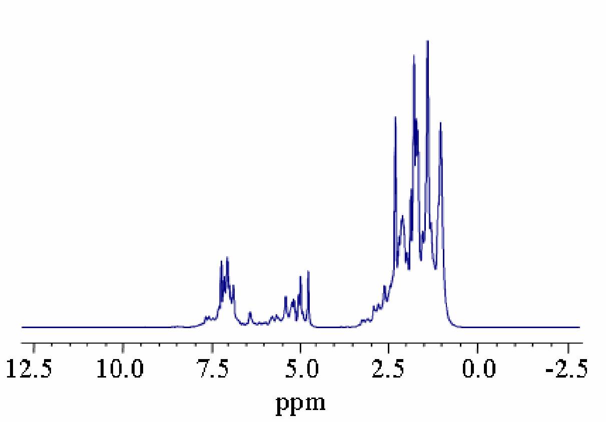


Fig. 6. ^1H NMR spectra for car tire derived liquids

Table 5 shows that tire pyrolysis liquids are a very complex mixture, containing many aliphatic and aromatic compounds. The GC-MS results support well the results obtain from FT-IR [Table 3] and ^1H NMR [Table 4] analyses. The aliphatic compounds are mainly of alkene group in the tire-derived liquids. The aromatic compounds are only single ring alkyl aromatics. In addition to the main hydrocarbons, small percentage of nitrogen and oxygen-containing compounds, 1,2,3,4-tetrahydro-5-nitro-naphthalene ($C_{10}H_{11}NO_2$); oxygen, and sulphur-containing compound, 1-phenyl-2-ethylprop-1-ene-(1-3)sultine ($C_{11}H_{12}O_2S$); chlorine-containing compound, 1,7-dichloroheptane ($C_7H_{14}Cl_2$) were also identified. Other oxygen-containing compounds in the form of acid such as 2,5-octadecadiynoic acid is also present in the present tire derived liquids.

Table 3. The FT-IR functional groups and the indicated compounds of pyrolysis liquids.

Frequency range (cm^{-1})	Functional groups	Class of compounds
3095-3005	C=C stretching	Alkenes
3000-2800	C-H stretching	Alkanes
1680-1620	C=C stretching	Alkenes
1600-1525	Carbon-carbon stretching	Aromatic compounds
1520-1220	C-H bending	Alkanes
1035-830	C=C stretching	Alkenes
825-650	C-H out-of-plane bending	Aromatic compounds

Table 4. ^1H NMR results for the product liquids

Type of hydrogen	Chemical shift [ppm]	Mol% [% of total hydrogen]
Aromatic	9.0-6.5	21.33
Phenolic (OH) or olefinic proton	6.5-4.5	12.54
Aliphatic adjacent to oxygen/hydroxyl group	4.5-3.3	--
Aliphatic adjacent to aromatic/alkene group	3.3-1.8	8.51
Other aliphatic (boded to aliphatic only)	1.8-0.4	57.62

The GC-MS results show that the liquid products comprise significant amount of limonene. At the reaction conditions, the polyisoprene part of the rubber thermally decomposes through *β*-scission mechanism to an isoprene intermediate radical. It is then transformed to isoprene (depropagation). The isoprene molecules in the gas phase dimerise to *dl*-limonene following a low energy reaction mechanism. Mastral *et al.* [12] has presented an explanation for formation of limonene taking into account the natural rubber (polyisoprene) used in tire manufacturing together with the thermal decomposition mechanism. At reaction conditions the polyisoprene is depolymerised forming dimeric species. As this activation giving the diradical species takes place in the absence of oxygen, a cyclization could be produced. This dimmer species, a short-life radical, could be stabilized through a two-step process driving to limonene by pyrolytic isomerization. Tamura *et al.* [19] have also shown that isoprene and D, L-limonene are formed in high concentration in natural rubber pyrolysis and they suggest that they are produced by depolymerisation from polymer radicals, by *β*-scission of the double bond. The polymer radicals are liable to form six-membered rings, especially under mild pyrolysis conditions and therefore the D,L-limonene is formed predominantly at lower temperature. The pyrolysis of polybutadiene rubber has been examined by [20] in a nitrogen atmosphere up to 550°C using TGA. They showed a two stage thermal decomposition of polybutadiene rubber, with maximum rates of weight loss at 370°C and 470°C, which was dependent on heating rate and sample size. Analysis of the products from the first stage of weight loss showed they were mainly butadiene and D, L-limonene formed as a result of depolymerisation. Madorsky et al. [21] have also examined the pyrolysis of polybutadiene rubber and similarly showed that butadiene vinylcyclohexene and D, L-limonene were formed in high concentrations. Cunliffe and Williams [3] reported that limonene is formed in high concentration at lower temperatures and degrades as the pyrolysis temperature is increased from 450 to 600°C.

Table 5. The Main compounds identified in car tire liquids by GC-MS.

Retention time (min)	Tentative assignment	Peak area (%)
7.75	2-Methyl-1,3-butadiene	2.91
8.18	2-Methyl-2-butene	2.96
9.95	2,3-Dimethyl-2-butene	0.18
11.66	4-Methyl-2-pentene	0.66
12.90	2,3-Dimethyl-1,3-butadiene	1.37
13.83	Benzene	5.97
14.95	Cyclooctene	0.20
16.09	3-Heptene	0.59
17.32	(Z)-3-Undecen-1-yne	0.35
17.87	(Z)-3-Dodecan-1-yne	0.19
19.25	2-Propenylidene-cyclobutene	3.03
19.39	Toluene	5.82
19.66	1,7-Dichloroheptane	0.95
20.96	(Z)-3-Decen-1-yne	0.16
21.65	1,1-Dimcyclopropyl-ethylene	0.24
22.33	4-Methyl-1,4-heptadiene	0.37
22.75	1,1-Dimcyclopropyl-ethylene	1.08
24.35	*p*-Xylene	7.29
24.47	*m*-Xylene	1.56
24.60	*o*-Xylene	3.60
25.35	1,7-Octadiyne	2.34
25.38	3,3-Dimethyl-4-pentenyl-benzene	3.68
26.80	(E)-4-Hexadecen-6-yne	0.42
27.37	6,6-Dimethyl-2-methylene-bicyclo 3.1.1 heptane	0.68
27.70	Decahydro-1,1,4,7-tetramethyl-1H-cyclopropeazulene	0.71
27.98	Octahydro-1,4,9,9-tetramethyl-1H-3a,7-methanoazulene	0.50
28.54	5,9-Tetradecadiyne	3.28
29.51	7,11-Dimethyl-3-methylene-1,6,10-dodecatriene	2.11
29.77	3,7,11-Trimethyl-1,3,6,10-dodecatetraene	1.93
30.03	2-Methyl-3,5-dodecadiene	1.99
31.74	Limonene	9.17
31.78	Limonene	1.94
31.95	(Z)-3-Heptadecen-5-yne	0.73
32.22	1-Propynyl-benzene	1.23
32.38	8-Methylene-dispiro 2.0.2.5 undecane	0.98
33.56	2,5-Octadecadiynoic acid	1.84
34.30	4,4-Dimethyl-1-(2,7-octadienyl)-cyclobutene	0.44
34.44	1,5-Dimethenyl-3-methyl-2-methylene-cyclohexane	0.25

34.93	Caryophyllene	0.32
35.15	3-Methylene-spiro bicyclo 6.1.0 nonane-9,1-cyclopentane	0.27
35.23	(E,E)-12-methyl-1,5,9,11-tridecatetraene	0.15
35.40	(Z)-3-Heptadecen-5-yne	0.23
35.70	(E,E)-12-methyl-1,5,9,11-tridecatetraene	0.31
36.12	1,2,3,4-Tetrahydro-5-nitro-naphthalene	0.67
36.35	1-Phenyl-2-ethylprop-1-ene-(1-3)sultine	0.34
Total identified		75.99

According to the results of ^{1}H NMR [Table 4], the aromatic content of the pyrolytic liquids was found comparatively very significant. This result is also supported by the GC-MS results. The aromatic content of the pyrolytic liquids may stem from two possible reasons: (i) the aromatic nature of the source polymeric materials, SBR and (ii) ciclation of of olefin structures through dehydrogenation reaction, which happen during pyrolysis process.

The present pyrolytic liquids also contain small amount of oxygenated, nitro-oxygenated and sulphurated compounds. 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 nitro-oxygenated and 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, benzothiozolyl disulphide, etc. The presence of chorine 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.

c. *Boiling Point Distribution of the Pyrolytic Liquids*

The boiling point distribution of hydrocarbons in pyrolytic liquids from pyrolysis of car tire waste at the temperature of 475°C is presented in Figure 7. For comparison purpose, the simulated distillation curves of commercial gasoline and diesel fuel are also presented in Figure 7. The data shows that the pyrolytic liquids have a wide boiling point range.

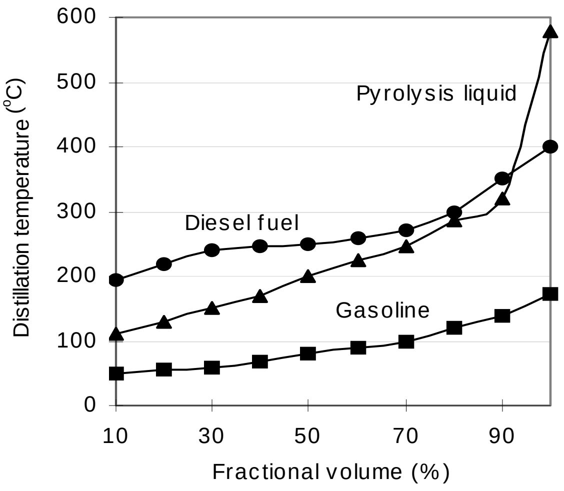


Fig. 7. Boiling point distribution of pyrolytic liquids compared to petroleum products

Pyrolytic liquids derived from car tire waste contains about 40% gasoline fraction (boiling point range <172°C). It should be noted that the boiling point of pyrolytic liquids is lower than that of diesel fuel up to 92% by volume. The rest 8% has higher boiling point than that of diesel, which indicates the presence of some heavy compounds of high boiling point. It can be concluded that the pyrolytic liquids from scrap tire wastes can be blended with the gasoline or diesel fuels after treatment such as desulphurization and fractional distillation.

d. *Stability Characteristics of the Pyrolytic Liquids [Viscosity Variation]*

The variations of viscosity of pyrolytic liquids over time of 12 months and over a temperature range of 30 to 100°C are presented in Table 6. It is very interesting to note that the pyrolytic liquids when stored at room temperature show almost no change in viscosity with time and hence proving that the liquids is very stable at room temperature. The data also shows that there is a significant reduction in viscosity with increasing temperature. Thus, the viscosity of the pyrolytic liquids may be maintained as of diesel fuel by flowing exhaust gases over the fuel tank during its usages in IC engines.

Table 6. Variation of viscosity over time and temperature.

Variation of viscosity over time		Variation of viscosity with temperature	
Time [Months]	Viscosity [cSt]	Temperature [^{o}C]	Viscosity [cSt]
3	4.63	30	4.62
6	4.62	50	3.81
9	4.61	75	2.58
12	4.64	100	1.62

e. *Miscibility Study of the Pyrolytic Liquids with Diesel*

The tire derived pyrolytic liquids have been found completely miscible in commercial diesel. The liquids have been mixed with diesel in different ratio and the physical properties like pH and viscosity of each mixture have been reported in Table 7. From the results it is seen that the liquids can be upgraded in terms of increase of pH and decrease of viscosity by mixing with diesel as required.

Table 7. Miscibility study of pyrolytic liquids with diesel

Liquids:Diesel	pH	Viscosity [cSt]
9:1	4.64	4.41
4:1	5.00	4.22
1:1	6.00	3.51

5. CONCLUSION

There are significant effects of the reactor temperature, feed size and apparent vapor residence time on the product distribution for pyrolysis of car tire waste. The fuel properties of the product liquids from pyrolysis of car tire waste found almost comparable to those of petroleum-derived fuels. The experimental investigations on the solid wastes and instrumental analyses results of the product liquids show that it is possible to obtain limonene and single ring alkyl-aromatics-rich liquids from used car tire if the pyrolysis conditions are chosen accordingly.

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NOMENCLATURE

ASTM	American Society of Testing Materials
NR	Natural rubber
SBR	Styrene-butadiene rubber
BR	Butadiene rubber
LPG	Liquefied petroleum gas
N_2 gas	Nitrogen gas
HHV	Higher heating value
L/min	Litter per minute
V_{fsp}	Free space in the reactor for the flow of sweeping gas (N_2),
V_f	The sweeping gas flow rate inside the reactor chamber
t	Apparent vapor residence time
d	Internal diameter of the reactor
l	Effective length of the reactor
l_1	Length of each fire-tube
d_1	Diameter of fire-tube
n	Number of fire-tubes
V_m	Reactor volume occupied by feed materials
d_2	Diameter of vapor outlet pipe
l_2	Length of vapor outlet pipe (from reactor to condenser)
t_R	Retention time
PET	Polyethylene terephthalate

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