

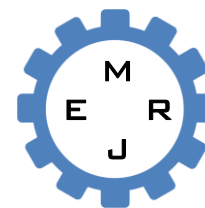


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UPGRADING OF WASTE TIRE PYROLYSIS OIL TO BE USED IN DIESEL ENGINE

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Abstract: The product yield distribution in pilot scale tire waste pyrolysis process is about 47 wt%, 43 wt% and 10 wt% of solid, liquid and gases, respectively at optimum reactor operating temperature of 450 °C. The liquid phase is a complex mixture of hydrocarbons that could not be used directly as engine fuel. Upgrading experiments of product liquids have been conducted by fractional distillation, oxidative desulfurization and de-colorization. In fractional distillation 33.08%, 25.33%, 10.67% and 2.17% oils by volume are obtained over the temperature ranges 171-270 °C, 121-170 °C, 71-120 °C and 40-70 °C, respectively. Then the desulfurization step removed around 60-65 wt% sulfur. Hydrogen peroxide and formic acid (2:1 ratio) were used at constant temperature and magnetic stirring rate in desulfurization process. The color of fractionated oil automatically changes by air oxidation. Because it contains unsaturated groups more than diesel fuel. The obtained fractionates were characterized by analyzing fuel properties, elemental analysis and FT-IR techniques and compared with conventional diesel fuel. The results show that a reasonable percentage of clear diesels like fuels can be obtained if the upgrading conditions are chosen accordingly.

Keywords: Scrap tire, Crude pyrolysis oil, Upgrading, Fractional distillation.

1. INTRODUCTION

The increasing industrialization and motorization of the world led to a steep rise in demand of petroleum products. Petroleum based fuels are stored in the earth. There are limited reserves of these stored fuels and they are irreplaceable. These finite resources of petroleum are highly concentrated in certain regions of the world have given rise to uncertainty in its supply and price and are impacting growing economies like Bangladesh.

By the year 2100, the world population is expected to be in excess of 12 billion and it is estimated that the demand for energy will be increased by five times from what it is now. Also it is estimated that petroleum reserve of the world will be nearly exhausted by (2040) recent future [1]. This makes it difficult for government to subsidize petroleum products in future. Around the world, there are initiatives to replace gasoline and diesel

fuel due to the impact of fossil fuel crisis and hike in oil price. Millions of dollars are being invested in the search for alternative fuels. On the other hand, the disposal of waste tires from automotive vehicles is becoming more and more complex. Many attempts have been made by different researchers to find out alternative fuels for IC (Internal Combustion) engines. Many alternative fuels like biodiesel, LPG (Liquefied Petroleum Gas), CNG (Compressed Natural Gas) and alcohols are being used nowadays by different vehicles. In this context pyrolysis of scrap tires can be used effectively to produce oil, thereby solving the problem of waste tire disposal [2].

The second author of the present paper developed and operating a fixed-bed fire-tube heating tire wastes pilot scale pyrolysis plant at RUET. In the present study, firstly upgrading experiments of product liquids obtained from the pilot plant have been conducted by fractional distillation, oxidative desulfurization and de-colorization. In the second phase of the

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investigations, obtained fractionates were characterized by analysing fuel properties, elemental analysis and FT-IR techniques and compared with conventional diesel fuel.

2. MATERIALS AND METHODS

Tire waste pyrolysis oil samples for the present research work were collected from the pilot plant installed in the Department of Mechanical Engineering, Rajshahi University of Engineering & Technology (RUET). The upgrading experiment was performed by two steps: (1) fractional distillation of pyro-crude oil and (2) desulfurization and de-colorization of fractionated oils.

2.1 Fractional Distillation of Pyro-Crude Oil

The complete arrangement for fractional distillation is presented in Fig. 1. Total height of packed column is 72 cm and 2.5 cm diameter. The column was packed by glass rachis ring diameter of 5 mm. In this investigation packed 60 cm of this column, which is equivalent to 6-7 HETS. A 2000 ml round bottom flux is used as pyro-crude oil reservoir.

For heat generation 3000 watt capacity micro wire is used, which was controlled by variation of variac voltage. A thermometer holder holds the thermometer in appropriate position. For proper condensing purpose a bulb condenser is used as living condenser.

The crude pyrolysis liquid volume was measured accurately and filled into the round bottom flux of fractional distillation apparatus. Heat resistance glass wool was sealed of the packed column. Cooling water was flown through the condenser. The electric heater was started and selected the required temperature by using the regulating switch. The operation time was recorded by means of stop watch. When one fraction was separated then adjust the next temperature by regulating switch of variac. The fractionated pyrolytic liquid and the rest heavy liquid were collected and measured volume by using measuring cylinder. All parts of the system were cleaned and the component was dried before reassembling for the next run.

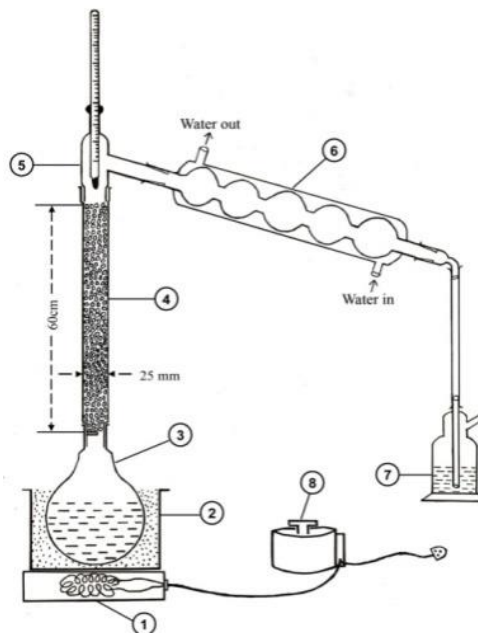
2.2 Desulfurization and De-colorization of Fractionated Oil

2.2.1 Desulfurization

For desulfurization 300 ml of fractionated oil, 30 ml of hydrogen peroxide and formic acid (2:1 ratio) were taken in one liter of reagent bottle. The mixture was stirred at 1000 rpm with constant temperature during 120 minute for each sample. For extraction of oxygenated compound in previous step 300 ml of N, N-dimethyl form amide (1:1 ratio) were taken for every case in one liter reagent bottle. The mixture was also stirred at 1000 rpm with room temperature during 120 minute for each sample. The mixture was taken in separation funnel and the solvent and oil layer are formed by adding small amount of water. Then the fractionated oil is collected in separate bottle for each and every operation [3-5].

2.2.2 De-colorization

For decolorization 200 ml of desulfurized oil, 20g of thermally activated bentonite powder were added for each one. The mixture was stirred at 1000 rpm with constant temperature during 60 minute for each sample. The mixture of oil is filtered by using what man filter paper [6].



1. Electric heater, 2. Sand bath, 3.Round bottom flux, 4.Packed column, 5.Thermometer adaptor, 6.Condenser, 7.Oil collector and 8.Variac

Fig. 1 Packed distillation column.

3. STANDARD METHODS FOLLOWED FOR PYROLYTIC 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: pH value, density, viscosity, flash point, pour point etc. and GCV were determined by using the American Society of Testing Materials (ASTM) standard test methods. Elemental analysis (CHNS) of liquids was determined with an elemental analyzer of model EA 1108, which followed the quantitative "dynamic flash combustion" method. The functional group compositions of the product liquids were analyzed by Fourier Transform Infra-Red (FT-IR) spectroscopy to identify the basic compositional groups. The FT-IR instrument of model SHIMADZU FT-IR 4500 and on-line pen plotter were used to produce the IR-spectra of derived oils. The standard ir-spectra of hydrocarbons were used to identify the functional groups of the components of the derived oils.

4. RESULTS AND DISCUSSIONS

4.1 Fractional Distillation Yields

During upgrading work, crude pyrolytic liquid were fractionated into five parts by using packed distillation as the

temperature ranges 40-70 °C, 71-120 °C, 121-170 °C and 171-270 °C. The products obtained from the fractional distillation process are presented in Table 1. Previous research group [7] also obtained more or less similar distillation results working with raw tire pyrolysis oil.

Table 1 Oil obtained at different temperature ranges by fractional distillation

Temp. range (°C)	40-70	71-120	121-170	171-270	Residue oil	Dist. loss
Oil obtained (vol. %)	2.17	10.67	25.33	33.24	25.17	3.42

4.2 Physical Properties Analysis

The fuel properties of the oil samples analyzed in the present work compared to conventional diesel fuel are

Table 2 Comparison for the properties of crude tire pyrolytic oils, fractionated oil with diesel fuel

Properties	Crude tire pyrolytic oil	Upgrading fractionated oil °C				Conventional diesel fuel
		40-70	71-120	121-170	171-270	
p ^H	4.36	6.01	5.36	5.32	5.32	5.40
Density (kg/m ³) @ 27 °C	919	766	814	842	911	831
Viscosity (cSt) @ 27 °C	3.80	0.28	0.50	1.78	4.17	4.87
Flash point (°C)	69	41	53	65	73	65
Fire point (°C)	95	70	77	130	172	228
Pour point (°C)	<-20	<-20	<-20	<-20	<-20	-30 to -40
Color (observed)	Brownish black	Brownish black	Green tea liquor	Pink orange	Brownish black	Green tea liquor
Volatility (wt%)	3.18	27.70	10.95	2.38	0.24	0.26
Ash content (wt%)	0.002	Nil	Nil	Nil	0.001	Nil
Water content (wt%)	0.12	0.11	0.16	0.08	0.003	0.003
Sedimentation (wt%)	Nil	Nil	Nil	Nil	Nil	Nil
Acid value (mg)	0.12	0.11	0.12	0.13	0.13	0.05
Sulfur content (wt%)	1.93	0.58	0.54	0.54	0.54	0.11
Iodine value	20.34	25.68	24.58	21.51	17.85	1.98
GCV(MJ/kg)	42.79	36.63	39.74	42.79	43.81	44.83

4.2.2 Density

The density of fractionated pyrolytic liquids was found slightly higher or lower than that of the commercial diesel fuel and also lower than that of light fuel oil (890 kg/m³). The density of the fractionates obtained at 40-70 °C, 71-120 °C, 121-170 °C, 171-270 °C are 776, 814, 842 and 911 kg/m³ at 27 °C and conventional diesel fuel is 831 kg/m³. Table 2 shows that the density of the upgraded pyrolysis oil is lower than that of raw pyrolysis oil.

4.2.3 Viscosity

The viscosity of pyro crude oil and all fractionated liquids was lower than that of the diesel and much lower than that of light fuel oil (79 cSt). Low viscosity of the fractionates obtained at 40-70 °C, 71-120 °C, 121-170 °C, 171-270 °C and conventional diesel is 0.28, 0.65, 1.87, 4.17, 4.87 cSt at 27 °C is favorable feature in the handling and transporting of the pyro-liquids. The viscosity of different fractions of upgraded

presented in Table 2.

4.2.1 p^H value

The pH value of the pyrolytic liquids is 4-6, which is in weak acidic nature. It is found that there is very little contamination of the liquids with metals (V, Mn, Mg, Ba, Ni, Ti, Cu, Cr, Cd, Co, Fe, Al, and Zn), and does not contaminate with glass and PET plastic and/or other plastics. The pH value of soft drinks like Cola and Pepsi of Coca Cola Company is 2.5 and they use PET plastic bottles for its storage and handling. Thus, storage and handling of the liquids are little problematic in industrial usage in this regard. Islam *et al.* [8] found P^H value of 4.80 for raw pyrolysis oil derived from tire wastes. Their P^H value shows higher acidic in nature compared to the present upgraded pyrolysis oil.

pyrolysis oil are lower than that obtained by previous research groups [9-10] and commercial diesel fuel. Viscosity affects injector, lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps or injector plungers resulting in leakage or increased wear. Fuels which do not meet viscosity requirements can lead to performance complaints. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke and emissions.

4.2.4 Flash point

The flash point of a liquid fuel is the temperature at which the oil begins to evolve vapors in sufficient quantity to form a flammable mixture with air. The temperature is an indirect measure of volatility and serves as an indication of the fire hazards associated with storage and application of the fuel. The flash point of the tire-derived crude liquid fractionates obtained

at 40-70 °C, 71-120 °C, 121-170 °C, 171-270 °C oils and conventional diesel fuel are 41 °C, 53 °C, 65 °C, 73 °C and 65 °C, respectively. The flash point is low when compared with petroleum-refined fuels; for example, kerosene has a required minimum flash point of 40 °C, diesel fuel of 65 °C and light fuel oil 79°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.

4.2.5 Fire point

The fire point of the fractionates obtained at 40-70 °C, 71-120 °C, 121-170 °C, and 171-270 °C oils are 70 °C, 77 °C, 130 °C and 172 °C and conventional diesel fuel is 228 °C, which is greater than fractionated oil.

4.2.6 Pour point

The pour point of the tire-derived liquids is comparatively low compared to the automotive diesel fuel but the laboratory experience of the authors of the present paper found that it is problematic while lower than -20 °C.

4.2.6 Color

The color of fractionated oil is automatically change by air oxidation. Because it has contain unsaturated group more than diesel fuel.

4.2.7 Volatility

A high vapor pressure (which often indicates a low flash point) can also cause cavitation and gas pockets in the fuel pipes. These can be avoided by using an elevated pressure in the fuel handling system. The volatility of the fractionates obtained at 40-70°C, 71-120°C, 121-170°C, 171-270°C oils and conventional diesel fuel are 27.70, 10.95, 2.38, 0.24 and 0.26 wt% at atmospheric temperature and pressure. It should be noted that some insurance companies demand the use of fuels with a flash point higher than 60°C.

4.2.8 Ash Content

High ash content may be detrimental in several ways. The ash content of 40-70 °C, 71-120 °C, 121-170 °C oils and conventional diesel fuels are nil and 171-270°C oils are 0.001 (wt%). Different ash constituents, like vanadium, nickel, sodium, aluminum and silicon can cause different kinds of problems.

4.2.9 Water Content

Water and sediment may cause shortened filter life or plugged fuel filters which can in turn lead to fuel starvation in the engine. In addition, water can have negative impact on fuel corrosion and on microbial growth which is found to be slight value for the tire oil. The water content of the fractionates obtained at 40-70 °C, 71-120 °C, 121-170 °C, 171-270 °C oils and conventional diesel fuel are 0.12, 0.11, 0.16, 0.08, 0.003 and 0.003 wt%, respectively. The copper strip corrosion test

indicates potential compatibility problems with fuel system components made of copper, brass or bronze. The limit requires that the fuel not darken these parts under the test conditions.

4.2.10 Sedimentation

Sedimentation is one of the big problems of fuel oil which disturb proper running of engine. No sedimentation is found in crude tire pyrolysis oil, upgraded oil and conventional diesel fuel.

4.2.11 Calorific Value

The calorific value of the tire oil is 42-44 MJ/kg. The calorific value is high and comparable with that of a diesel fuel oil, indicating the potential for the use of tire derived oils as fuel. Polycyclic Aromatic Hydrocarbons (PAHs) are a group of chemicals that occur naturally in coal, crude oil and gasoline. PAHs also are present in products made from fossil fuels. Some of the PAH have been shown to be carcinogenic and/or mutagenic. PAHs also can be released into the air during the incomplete burning of fossil fuels. The less efficient the burning process, the more PAHs is given off but studies have shown that combustion of tire oil with excess air results in negligible emissions of PAH. Since diesel engine always operate lean with combustion efficiency of 98% there may be less emission of PAH. It is shows the concentration of the main PAH in the tire pyrolysis oil compared to the diesel fuel and is found to be 24% by mass for tire oil almost double the value of diesel. The gross calorific value of catalytic pyrolysis oil [11] is of 41.31 MJ/kg and raw pyrolysis oil [12] is 41.7-42.66 MJ/kg whereas, the gross calorific values of upgraded fractions of pyrolysis oil are 36.63-43.81 MJ/kg.

4.2.12 Acid value

The acid value (AV) is the number that expresses, in milligrams the quantity of potassium hydroxide required to neutralize the free acids present in 1 g of the substance. The acid value may be overestimated if other acid components are present in the system, e.g. phenolic group. The acid value is often a good measure of the breakdown of the triacylglycerols into free fatty acids, which has an adverse effect on the quality of many lipids. Acid value is the measure of hydrolytic rancidity. In general, it gives an indication about edibility of the lipid. Edible oil contain >1% and pharmaceutical oil must not have any acidity. The lower acid value is better for internal combustion engine.

4.2.13 Iodine value

The iodine value (IV) gives a measure of the average degree of unsaturation of a lipid: the higher the iodine value, the greater the number of C = C double bonds. By definition the iodine value is expressed as the grams of iodine absorbed per 100g of lipid. Iodine value (IV) is directly proportional to the degree of unsaturation (no of double bonds) and inversely proportional to the melting point (MP) of lipid. An increase in

IV indicates high susceptibility of lipid to oxidative rancidity due to high degree of unsaturation. The IV value of the fractionates obtained at 40-70 °C, 71-120 °C, 121-170 °C, 171-270 °C oils and conventional diesel fuel are 20.34, 25.68, 24.58, 21.51, 17.85, 1.98, respectively. The lower iodine value is better for diesel engine because it has higher carbon content. Other side higher iodine value lighters the hydrocarbon chain.

4.3 Compositional Analysis

Table 3, shows the elemental analysis of crude tire pyrolysis oil and desulfurized oil fractions compare to conventional diesel fuel. From the analysis results in Table 3 it is found that 60-65 wt% sulphur is removed by the mild oxidative desulfurization extraction method. The sulphur amount of upgraded oil fraction is lower than that of commercial diesel fuels. The carbon and sulfur contents of upgraded fractions of pyrolysis oil are always higher and lower respectively than that of obtained by previous works [13]. The overall composition of the upgraded oil fraction is improved than that of tire derived pyro-crude oils. The ir-spectra of hydrocarbons in tire pyrolysis oil and conventional diesel fuel are presented in Figs. 2 and 3, respectively. The FT-IR is not the most appropriate tool to determine saturated, aromatic and polar components. Never the less, it allows functional group analysis to reveal the chemical properties of the liquids. The FT-IR analysis for crude tire pyrolysis liquids and commercial diesel fuels has been carried out and the results obtained from the transmittance spectrums are presented in Table 4 and 5, respectively. Tables 4 and 5 show that five functional groups are different in crude tire pyrolysis oil compared to conventional diesel fuel while three functional groups are different fuel compared to crude tire pyrolysis oil. The six functional groups are common for both crude tire pyrolysis oil and conventional diesel fuels. Overall observation is that the phenolic and aromatic compounds present in CTPO are higher than that of diesel fuels.

Table 3 Elemental analysis of tire pyrolysis oil and conventional diesel fuel

Oil Samples	C (wt %)	H (wt%)	N (wt%)	S (wt%)
Pyro-crude oil:				
Crude TPO	86.05	10.16	1.89	1.01
Desulfurized oil:				
(40-70) °C oil	87.01	10.00	1.00	0.43
(71-120) °C oil	87.80	10.86	1.49	0.48
(121-170) °C oil	87.96	10.88	1.75	0.47
(170-270) °C oil	88.00	10.82	2.02	0.46
Conventional fuels:				
Conventional diesel fuel	87.00	15.70	0.13	0.16

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

Frequency range(cm ⁻¹)	Functional group	Class of compounds
3640–3530	OH stretch	Phenols

3500–3200	O–H stretch	alcohols, phenols
3100–3000	=C–H stretch	Alkenes
3000–2850	C–H stretch	Alkanes
1680–1640	–C=C– stretch	Alkenes
1650–1580	N–H bend	1° amines
1470–1450	C–H bend	Alkanes
1410–1310	OH bend	tertiary alcohol
1000–650	=C–H bend	Alkenes
900–675	C–H “oop”	aromatics
850–550	C–Cl stretch	alkyl halides

Table 5 The FT-IR functional groups and the indicated compounds of conventional diesel fuel

Frequency range (cm ⁻¹)	Functional group	Class of compounds
3620–3540	OH stretch	Tertiary alcohol
3500–3200	O–H stretch, H–bonded	alcohols, phenols
3000–2850	C–H stretch	alkanes
2970–2950	Methyl C–H asym. stretch	Methyl
2935–2915	Methylene C–H asym. stretch	Methylene
1740–1720	C=O stretch	aldehydes
1650–1580	N–H bend	1° amines
1470–1450	C–H bend	alkanes
1410–1310	OH bend	tertiary alcohol
1300–1150	C–H wag (–CH ₂ X)	alkyl halides

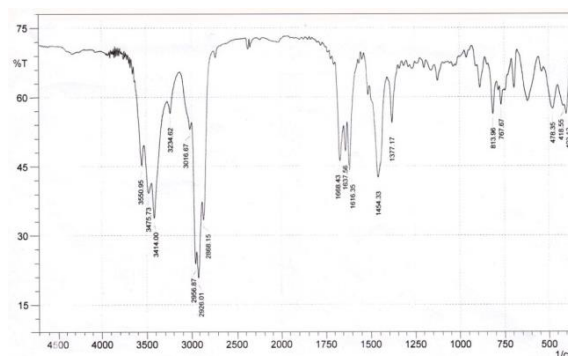


Fig. 2 FT-IR spectra for crude tyre pyrolysis oil.

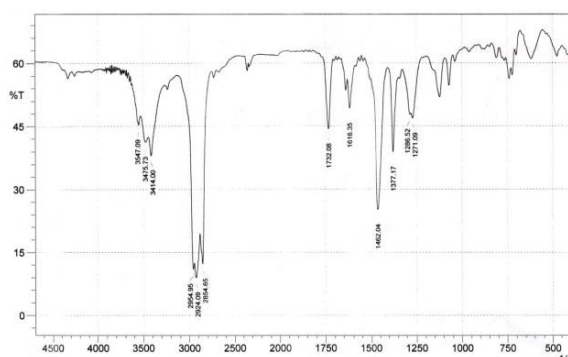


Fig. 3 FT-IR spectra for conventional diesel fuel.

5. CONCLUSIONS

In the fractional distillation method the packed distillation column showed satisfactory results. The upgraded fractionated

oil components have lower viscosity, lower sulfur content, good spray quality and proper combustion properties compared to conventional diesel fuel. The selected desulfurized method removed 60-65 wt% sulfur in upgraded oil fractions and the color also improved by activated bentonite clay treatment. Therefore, we may recommend the upgraded fractions specially obtained at the temperature ranges 71-120 °C and 121-170 °C as alternative to diesel fuels. The other functions can be used as furnace oils.

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