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Thermal recycling of solid tire wastes for alternative liquid fuel: the first commercial step in Bangladesh

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Abstract

The first small scale commercial tire waste pyrolysis plant has been installed by the Radiant Renewable Energy (RRE) Ltd. at Gazipur, Dhaka for reducing liquid fuel crisis in Bangladesh. The plant has two pyrolysis unit, each of them consists of a horizontal axis rotary type batch mode reactor with a recycling capacity of 4.5 tons/run. Solid tire wastes in half/whole size are feed into the reactor chamber, operating at 420°C with a light over-pressure of 0.03 bar. The reactor is heated externally by burning product pyrolysis liquids for first three hours and by burning product pyro-gas for rest five hours. The products distribution at optimum reactor operating condition were found oil: 45 wt%, char: 35 wt%, and gases: 10 wt%, in addition to the steel cords: 10 wt% of solid tire waste. The product liquids have been found to have a high gross calorific value (GCV) of around 44 MJ/kg, which would encourage their use as replacements for conventional liquid fuels. Pyrolytic char may be used as a solid fuel, activated carbon, priters ink etc. Pyrolysis gas contains high concentrations of methane, ethane, butadiene and other hydrocarbon gases with a GCV of approximately 37 MJ/m³, a value sufficient to provide the energy required by the tire pyrolysis process. However, the presented plant should be followed some recommended pionts for better operation and its further extension, and also for our sincere corner to safe environment. The plant can be run only under continuous monitoring and consultancy support of a tire pyrolysis specialist team because of new technology and waste material concern.

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Keywords: Solid tire wastes; first small scale commercial plant; alternative liuid fuels

Nomenclature

B/RT	bicycle / rickshaw tire
GC/MS	gas cromatography / mass spectrometry
GOB	government of Bangladesh
K ₁₃	reaction kinetics
MT	motorcycle tire
PCT	passenger car tire
PM	particulate matter
TG/DTG	thermalgravimetry/differential thermalgravimetry
TT	truck tire
VOC	volatile organic compounds
kgOE	kilogram of oil equivalent
MTOE	million ton of oil equivalent

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1. Introduction

The standard of living and quality of life of a nation depend on its per capita energy consumption. Bangladesh a developing country, and is one of the most densely populated (914 persons/km²) countries in the world, with a total population of 135 million. 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 30.70 MTOE 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 77% of the country's population lives in rural areas, meting 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.

It is estimated that about 90,000 metric tons tires become scrap and are disposed of every year in Bangladesh [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:

- Reconstruction of waste tires
- Shredding or grinding and crumbling to recycle rubber powders
- Incineration to supply thermal energy in utility boilers to produce electricity, in cement kilns and brick fields
- Utilisation in building applications
- Landfilling, heaping and abandonment and
- Other treatments

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, 11-13]. Similarly, the liquids have been shown to contain monoterpenes such as limonene [1-methyl-4-(1-methylethenyl)-cyclohexene], a high value light hydrocarbon. 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 MJ/m³, a value sufficient to provide the energy required by the pyrolysis process.

Very different experimental procedures have been using to obtain liquid products from 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. all over the world for the last two decades. Within the past ten years, research and development works have also been carried out for the fixed-bed fire-tube heating pyrolysis reactor system at Rajshahi University of Engineering & Technology (RUET). Pyrolysis of various organic solid wastes in the fixed-bed fire-tube heating pyrolysis reactor have been successfully completed and the results are published elsewhere [33-39].

The Radiant Renewable Energy (RRE) Ltd. has installed a small commercial scale pyrolysis plant at Kainzanul, Vawal Mirzapur, Gazipur, Dhaka to take part as a potential contributor for mitigating liquid fuel crisis in Bangladesh. The pyrolysis technology for production of alternative liquid fuel from solid tire waste is new in Bangladesh and it is the first commercial plant in the country. The RRE Ltd. has applied for consultancy support to the Department of Mechanical Engineering of RUET for better operation and extension of its plant, and also for pyro-products quality improvement and new usages of the products. It is, however, to be noted that many problems, both technical and operational, need to be solved before the said process could satisfy the reliability and economic conditions set forth by the world market.

2. The tire waste pyrolysis process

Pyrolysis, essentially an endothermic process, an environmentally attractive method for the treatment of tire wastes. The process uses medium temperatures ($400 \sim 500^{\circ}$ C) and an oxygen-free environment to decompose solid tire wastes chemically, thus producing minimum emissions of nitrogen oxide and sulphur oxide compared to the commonly practised conventional technology, incineration. Pyrolysis also allows valuable materials to be recovered.

Pyrolysis is a thermal degradation process in which the solid tire waste is heated indirectly in an oxygen-free atmosphere. The whole process is the sum of a series of parallel and subsequent reactions that take place in the pyrolysis reactor. The most common rubbers used for tires are natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). The rubbers consist mostly of blends of two or three rubbers, together with minor constituents including oil, plasticizer, and other additives. All of these constituents lose their weight at different rates and at different temperatures when pyrolysed. A review of the available international literature and the laboratory results show that the decomposition temperature is about 150-350°C for processing oils, plasticizer, and other organic additives, 330-400°C for NR, and 400-480°C for SBR and BR.

A flow diagram of tire pyrolysis process, including the proposed thermal decomposition model, is presented in Fig. 1. The three types of arrows in the flow diagram indicate three decomposition reactions. The higher weight or color deepness of the arrows indicates the decomposition of the corresponding tire material in the higher temperature regions.



Fig. 1. Flow diagram of tire pyrolysis process including the proposed thermal decomposition model

Thus, the global pyrolysis reaction that takes place into a reactor can be described in the following manner:

- Tire wastes \rightarrow volatile hydrocarbon + gases + solid residues
- Tire wastes, fed into the pyrolysis reactor undergoes a thermal cracking, by cleaving itself into volatile hydrocarbon, gases and solid residue.
- Volatile hydrocarbon can be cooled and condensed into a liquid fraction
- Gaseous fraction remains uncondensed during quenching
- Solid residues wait in the reactor chamber for their removal

Normally, the process provides:

- A gaseous fraction (10 15 wt%) essentially composed of CH₄, and higher hydrocarbons C_mH_n, H₂, CO₂, CO etc.
- A liquid fraction (40 45 wt%), composed of water, tar and oils (organic compounds);
- Solid residues containing steel cord (10 12 wt%) and char (30 35 wt%), containing fixed carbon and ashes (metals, oxides and inert matter).

Thermal decomposition (pyrolysis) behaviour for a typical solid tire waste at tow different heating rates are presented in Fig. 2. The TG and DTG curves show that the volatile fraction completely decomposed within the reactor temperature below 500°C and the decomposition rate is maximum around 400°C.

3. Brief description of the small commercial scale pyrolysis plant at RRE Ltd.

The Radiant Renewable Energy Ltd. has installed a small commercial scale pyrolysis plant on more or less one acre land at Kainzanul, Vawal Mirzapur, Gazipur, Dhaka. Its main office is located at House No.: 44, Road No.: 03, Sector: 13, Uttara

Model town, Dhaka - 1230 that is about 30 km far from the plant. The plant is situated in a populated village area and is surrounded by many living houses, a mosque, a road and a playground. However, the plant yard is devided into four sections:

- (i) Main plant section
- (ii) Plant site office houses
- (iii) Warehouse
- (iv) Tire wastes stock site



Fig. 2. TG and DTG plots for a typical tire waste at heating rates of 10 and 60°C/min

There are two pyrolysis unit each of capacity 4.50 tons solid tire wastes per run in the Radiant Renewable Energy Ltd. Each pyrolysis unit consists of the following main systems with some accessories and mountings:

- (i) A horizontal axis rotary type batch mode reactor
- (ii) Furnace
- (iii) Atmolysis tower
- (iv) Condensers
- (v) Fractionating column
- (vi) Gas condenser
- (vii) Cooling water tank
- (viii) Gas-oil seperator
- (ix) Oil-water separator
- (x) Gas-water separator

Aceesories:

- (i) Flue gas treatment and exhaust systems
- (ii) Liquid handling and storage systems
- (iii) Cooling water supply pumps
- (iv) Water cooling pond
- (v) Three generators for supplying electricity for lighting and water pumps

Mountings:

- (i) Thermometer
- (ii) Pressure gage
- (iii) Oil-gas vavle
- (iv) Steam vavle
- (v) Observation port
- (vi) Check vavle
- (vii) Emergency exhaust valve
- (viii) Gas outlet valve
- (ix) Back-fire relief valve
- (x) Gas valve

Each pyrolysis unit consists of a horizontal axis rotary (15 rph) type batch mode reactor (37.50 dm³ in volume and 2.0 m in diameter). Solid tire wastes in half/whole size are feed into the reactor chamber manually and then leackage is checked

The heating system consists of a furnace under the reactor drum. The provision for burning both liquid and gasious fuels are equipt in the furnace. The reactor drum is surrounded by a annular space that is covered by insulating cage. The produced hot gases pass through the annular space between reactor drum and insulating cage, and provide sufficient energy for pyrolysis reaction. The process temperature vs time plot is shown in Fig. 3.



Fig. 3. Reactor temperature distribution during heating and cooling

The vapour condensation system consists of five components: a jacketed atmolysis towers - that removes tars and heavy fraction, condenser and fractionating column – that cool and further seperate vapor from heaver fraction, gas condenser and cooling water tank – that condense vapor into pro-liquids. The product liquid and gas mixture are then pass through gas-oil seperator, oil-water separator and gas-water separator - that remove light fraction and cool the gaseous stream further to about 30°C. Steel and char (carbon black) are collected manually. When the reactor is cooled well below 70°C the reactor drum is open, and steel cord and char are removed manually. The char fraction is found inside the reactor in powdered form and separated from steel cord because of continuous rotation of the reactor drum.



Fig. 4. Material and energy flow diagram for the tire waste pyrolysis plant installed by RRE Ltd. in Gazipur

Flue gas exhaust system for each pyrolysis unit consists of a wet-scruber, a draught fan and a chimney. The flue gas are filtered in two demister filters (to be incorporated) to separate particulate matter, and pass through a wet-scrubbing system

designed to remove acid components by CaOH/NaOH column. After that the flue gas is explausted into the atmosphere. The material and energy flow diagram for the plant at RRE Ltd. is shown in Fig. 4.

3.1 Tire wastes found in the Radiant Renewable Energy Ltd. pyrolysis plant

There are many different manufacturers and countless different types and formulations available in the marketplace; the composition of the tires varies depending on the tire grade, age and manufacturers. The Radiant Renewable Energy Ltd. collects the used tires locally from the scraped material suppliers. The specialist team found used tires of 20 brands in the plant yard that are presented in Table 1. The table shows that tires used in Bangladesh are imported from mostly South Asian and some of European countries.

Sl.	Tire brands	Tire types	Country of	Sl.	Tire brands	Tire types	Country of
No.			origin	No.			origin
1.	Dunlop	Truck/bus and car	Japan	11.	Pioneer	Truck/bus and car	China
2.	Bridgestone	Truck/bus and car	Japan	12.	Kendoa Radial	Truck/bus and car	China
3.	Continental	Truck/bus and car	Great Britain	13.	GAJAH TUNGGAL	Truck/bus and car	Indonesia
4.	Goodyear	Truck/bus and car	South Africa	14.	MAXXIS	Truck/bus and car	Taiwan
5.	Courier	Truck/bus and car	Italy	15.	DEESTONE	Truck/bus and car	Thailand
6.	Michelin	Truck/bus and car	Italy	16.	Road star	Car	Bangladesh
7.	Eurotour	Truck/bus and car	Korea	17.	Gazi	Car	Bangladesh
8.	MRF	Truck/bus and car	India	18.	HT Super	Car	Bangladesh
9.	XPL	Truck/bus and car	India	19.	HT Army	Car	Bangladesh
10.	Birla	Truck/bus and car	India	20.	MUSAFIR	Autorickshaw	Bangladesh

Table 1. Tire brands found in Radiant Renewable Energy Ltd. pyrolysis plant yard

3.2 Physical and chemical charateristics of solid tire wastes

The elemental and proximate analysis results and gross calorific values of the solid tire wastes from a servey of a quite number of international literature of more than 10 research groups [2 - 5, 8 - 9, 18 - 19, 22 - 24, 35 - 38, 43 - 45] allover the world are presented in Table 2. From the information in the table, it can be seen that solid tire wastes contain very little moisture and a small amount of ash. The variation in the ash content is due to the variation in the inorganic material content of the tire rubber, including zinc, clay, and silica, as rubber additives. The relative magnitudes of these additives are greatly dependant on the rubber formulations and manufacturers. Higher presence of inorganic compounds in the solid tire wastes lowers their the GCV. One result of the high oxygen content is the relatively low lower heating value (LHV). The GCV for solid tire waste is 30 to 40 MJ/kg, compared to the GCV for hydrocarbon fuels of 40 to 44 MJ/kg. The GCV for tire waste is about twice that of woody biomass (19 to 20 MJ/kg). The volatile matter content of tire waste is comparatively high. A comparison with the typical values for bituminous coal shows similar carbon content, lower nitrogen and sulfur contents, higher hydrogen content, much higher volatile content, higher GCV, and lower moisture, ash and fixed-carbon content. These data indicate that tire waste is a potential source of energy and suitable for pyrolysis conversion.

Table 2. Elemental and proximate analysis, and GCVs of solid tire wastes

Analysis	Tire wastes generated allover the world	Bituminous Coals (India, Indonesia)	Bangladeshi coal ([#] Barapukuria)
Elemental analysis (wt %)			
Ċ	85.00 - 88.50	60.00 - 75.00	64.41
Н	6.50 - 8.00	3.75 - 6.00	3.96
Ν	0.30 - 0.50	1.00 - 1.22	1.32
О	1.00 - 3.50	7.30 - 12.00	7.29
S	0.80 - 1.90	0.50 - 3.00	0.52 - 0.60
Cl	Non-trace -1.00	N/A	N/A
Ashes	Trace – 5.00	13.00 - 38.00	12.40
Proximate analysis (wt%)			
Moisture	0.80 - 1.70	5.00 - 9.50	10.00
Volatile fraction	57.00 - 70.00	20.00 - 30.00	29.20
Fixed carbon	22.00 - 35.00	30.00 - 50.00	48.40
Ashes	3.50 - 7.00	13.00 - 38.00	12.40
GCVs (MJ/kg)	28.00 - 40.00	28.00 - 32.00	25.68

#High volatile bituminous coal; Coal analysis presented here as received basis

4. Charateristics of pyrolysis products derived from solid tire wastes

4.1. Physical and chemical characteristics of the pyrolytic oil fractions

The pyrolytic liquids obtained from pyrolysis of selected tire wastes, which are oily organic compounds, appear darkbrown-color with a strong acrid smell. No phase separation was found to take place in the storage bottles. The physical and chemical properties of used tire derived pyrolysis liquids are presented in Table 3.

Details of the GC/MS analysis and lists of possible compounds identified in the tire derived pyrolysis liquids have been presented in the authors previous papers [35-38]. It was found that, tire pyrolysis liquids were very complex mixture from C_5-C_{20} , containing many aliphatic (42-65% peak area) and aromatic (5-18% peak area) compounds. The aliphatic compounds were mainly of alkane and alkene groups but the second was predominant in all of the four different 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. The summery of identified compounds presented in the four different tire derived pyrolysis liquids are presented in Table 4.

Table 3. Charateristics of pyrolytic liquids in comparison to petroleum products

Analysis	Tire derived pyrolysis	Typical fuel oil (furnace oil)	Commercial automotive
	liquids		No. 2 diesel
Elemental analysis (wt %)			
С	84.80 - 86.50	84.00	84.00 - 87.00
Н	9.00 - 9.50	12.00	12.80 - 15.70
Ν	0.50 - 0.70	Trace	65 – 3000ppm
0	2.10 - 4.70	1.00	0.00
S	0.90 - 1.40	Up to 4.00	1100 – 7000ppm
Cl	90 – 270ppm		
Ashes	0.10 - 0.31	Trace	0.00
Density (kg/m^3)	940 - 970	880 - 950	820 - 860
Viscosity (cSt)	4.60 - 4.90		2.00 - 4.50
Flash point (°C)	≤32	66 - 93	>55
Pour point (°C)	-3 to -5	18 - 72	-40 to -30
Moisture	N/A	≤1.00	≈80ppm
pH value	4.25 - 4.80		
GCVs (MJ/kg)	40.80 - 42.90	43.00 - 45.00	44.00 - 46.00

TGA distillation test shows 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. 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. In order to establish the real potential use of such tire oil fraction as diesel oil, a more thorough characterisation of it, which should include cetane index, corrosive properties, flash point, etc., is needed. Fuel oil No. 1 is a light distillate which consists primarily of hydrocarbons in the C₉-C₁₆ range; fuel oil No. 2 is a heavier distillate with hydrocarbons in the C₁₁-C₂₀ range. Diesel fuels predominantly contain a mixture of C₁₀ through C₁₉ hydrocarbons. Therefore, after filtration, centrifugation and desulphurization the pyrolytic liquids can be used directly as fuel oils or blended with diesel fuels for industrial furnaces, power plants and boilers.

4.2. Solid char fractions

The solid char fractions obtained at optimum reactor conditions were of equal size and shape as original tire pieces, which were easily disintegrable into black powder and steel cords. Elemental analysis of the pyrolytic char showed the results (by weight): C = 77.30-83.34%; H = 0.70-1.10%; N = 0.25-0.40%; S = 2.35-3.35% and O + ash = 13.36-18.15% [39]. Almost similar chemical compositions were found by the previous studies [46] while metallic elements Zn, Si, Ti, Al, Fe, Na, Ca, Pb and Mg in the ash were also indentified. The GCV of char fraction is 23.28-27.80 MJ/kg, which is compareable with that of the good quality coal. Pyrolytic char has potential as semireiforcing commercial carbon blacks for footwear and conveyor belts, as a carbon absorbent after proper activation, as a solid or slurry fuel etc. [2].

4.3. Gas fractions

The compositional analysis of gas fractions showed that tire derived pyrolysis gases are consisted of high concentrations

of methane, ethane, propane, butene, butadiene and other hydrocarbons together with some CO, CO₂, H₂, SO₂, H₂S, NH₃ and N₂. The GCV of the pyrolysis gases is $37.85 - 40.72 \text{ MJ/m}^3$, which is very close to that of natural gas (about 39 MJ/m³ at NTP) and hence it would be sufficient to provide the heat energy required by the pyrolysis process. More or less similar gas compositions are also obtained by Rodriguez et al. [2] with better GCV of 75.50 MJ/m³ or 42.1 MJ/kg. The former research group [47] also found the GCV of tire derived pyrolytic gas 35-40 MJ/kg and reported that this value is sufficient to heat pyrolysis reactor.

Compounds	Total concentrations (% peak area)					
identified	B/RT liquid	MT liquid	PCT liquid	TT liquid		
Aliphatic	42.22	49.54	43.04	65.75		
Aromatic	16.14	17.23	29.15	4.12		
Nitrogenated	7.51 (C ₁₁ H ₁₃ NOS; C ₉ H ₁₃ NO ₂)	4.25 (C ₁₁ H ₁₃ NOS; C ₇ H ₇ N ₃)	0.67 (C ₁₀ H ₁₁ NO ₂)	0.69 ($C_{11}H_{13}NOS;$ $C_{2}H_{5}N$)		
Sulphurated	5.04 (C ₁₁ H ₁₃ NOS)	0.80 (C ₁₁ H ₁₃ NOS)	$\begin{array}{c} 0.34 \\ (C_{11}H_{12}O_2S) \end{array}$	0.56 (C ₁₁ H ₁₃ NOS)		
Oxygenated	9.82 ($C_{10}H_{16}O;$ $C_{11}H_{13}NOS; C_{19}H_{30}O_2$ +)	2.16 (C ₁₁ H ₁₃ NOS; C ₆ H ₅ ClO; C ₈ H ₁₅ ClO +)	$\begin{array}{c} 2.85 \\ (C_{19}H_{30}O_2; \ C_{10}H_{11}NO_2; \\ C_{11}H_{12}O_2S) \end{array}$	$\begin{array}{c} 1.57 \\ (C_{10}H_{16}O; \\ C_{11}H_{13}NOS; \\ C_{19}H_{30}O_2 +) \end{array}$		
Chlorinated	$\begin{array}{c} 1.82 \\ (C_{12}H_{25}Cl; C_{14}H_{29}Cl) \\ 10.05 \end{array}$	1.58 (C ₆ H ₅ ClO; C ₈ H ₁₅ ClO; C ₁₂ H ₂₅ Cl) 20.54	0.95 (C ₇ H ₁₄ Cl ₂)	$\begin{array}{c} 2.45 \\ (C_{12}H_{25}Cl; \\ C_{16}H_{33}Cl) \\ 50.86 \end{array}$		
Limonene	10.95	29.54	11.11	50.86		

Table 4. Summery of identified compounds in the four different tire-derived pyrolysis liquids

5. Conclusions and recommendations

The fuel properties of the tire derived pyrolysis liquids including density, viscosity, GCV, carbon and hydrogen contents are found almost comparable to those of the commercial diesel fuels but higher sulphur content and lower flash point are problematic. The liquid may be used as diesel fuel or heating oils after the upgrading such as desulphurization and dehydrogenation or blending them with petroleum refinery streams. The pyrolytic liquids abundantly contain olefins, especially limonene and light aromatics; whose have higher market values as chemical feedstock than their use as fuels. The pH value of the pyrolytic liquids is 4~5, 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. Thus, storage and handling of the liquids are little problematic in industrial usage in this regard.

Now Bangladesh is suffering from strong liquid petroleum crisis and the price of furnace oil is about 60 TK/ litre. Several number of furnace oil based new power plants have been ideal due to lack of oil supply. Besides, a lot of steam boilers used in garmens factories and other industries are using furnace oil. It is estimated that the production cost of pyrolysis oil is 30 TK/litre that is much lower than the present furnace oil price in Bangladesh. Thus, at this crucial moment of the country's liquid fuel, it is undoubtly a noble initiative of RRE Ldt. for production of alternative diesel from scrap tires. A total of 7 pyrolysis plants of capacity 720 tons/month may be established for annual tire waste generation (64000 metric tons) in the country. If it would be pyrolysed all of tire wastes in the country, the import bills will reduce for 29400 tons (205000 barrels) of oils, 6400 tons of steel and 22400 tons of coal every year. Moreover, a big amount of hazardous solid waste like used tires would be managed properly; the dependence on imported petroleum crude oils and unemployment problem of Bangladesh would be reduced as well.

Pyrolysis of used tire is a concern of waste material with a reasonable amount of sulfur and trace amount of other objectionable elements and hence its conversion into enegry sholud be considered very carefully. Tire waste pyrolysis plant at RRE Ltd. is small and hence the concentration of emission surrounding the plant compound is possibly lower than standard prescrition values. However, the following recommended pionts should be followed for better operation and further extension of the plant, and also for our sincere corner to safe environment:

- Solid tire wastes should be cleaned properly before loading into the reactor to maintain the quality of the product liquids as well as to reduce emissioms from the plant.
- (ii) The excess gasious product should not be released into the atmosphere. It may be stored in a container to burn in the furnace from the beginning of firing or may be supplied to the local people for coocking.
- (iii) Handling and transpotation of the product liquid and char should be in a closed conduit/system to reduce fugitive

VOC and PM emissions, respectively.

- (iv) To ensure environment friendly production of alternative diesel from tire wastes, demister filters and wetscrubber with CaOH/NaOH column should be incorporate properly, and their operation must be monitored carefully.
- (v) The standard design of the chimney must be followed to exhaust flue gas in a safe layer of atmosphere.
- (vi) Wastewater generated in the plant must be treated and disposed sincerely.
- (vii) Mountings should be inspected regularly and replace them by wright one while require for safer running of the plant.
- (viii) To make the technology sustainable, upgrading of liquid product and better utilization of char are very important.
- (ix) Some of the operators employed in the pyrolysis plant need to be skilled in the relavent field.
- (x) Sulfur and clorine content of solid tire wastes should be checked twice a year for controling SOx and dioxin emissions from the plant as well as sulfur and clorine containing compounds in the liquid and char products.
- (xi) The plant is installed/situated in a populated area and hence its further extension in the present location should not be considered.
- (xii) Finally, it may be concluded that the plant can be run only under continuous monitoring and consultancy support of a tire pyrolysis specialist team because of new technology and waste material concern.

References

- Bangladesh Bureau of Statistics, Government of Peoples Republic of Bangladesh. Statistical Year Book of Bangladesh 2008. 28th ed.; Dhaka, 2009.
- [2] Rodriguez IM, Laresgoiti MF, Cabrero MA, Torres A, Chomon MJ, Caballero B. Pyrolysis of scrap tires. Fuel Processing Technology 2001;72:9–22. [and references therein]
- [3] Laresgoiti MF, Caballero BM, De Marco I, Torres A, Cabrero MA and Chomon MJJ. Characterization of the liquid products obtained in tire pyrolysis. J. Anal. Appl. Pyrolysis 2004;71:917–934.
- [4] Gonzalez JF, Encinar JM, Canito JL, Rodriguez JJ. Pyrolysis of automotive tire waste. Influence of operating variables and kinetic study. J. Anal. Appl. Pyrolysis 2001;58–59:667–83 [and references therein].
- [5] Diez C, Martinez O, Calvo LF, Cara J, Moran A. Pyrolysis of tires. Influence of the final temperature of the process on emissions and the calorific value of the products recovered. Waste Management 2004;24:463-469.
- [6] Dai X, Yin X, Wu C, Zhang W, Chen Y. Pyrolysis of waste tires in a circulating fluidized-bed reactor. Energy 2001;26:385-399.
- [7] Pakdel H, Pantea DM, Roy C. Production of dl-limonene by vacuum pyrolysis of used tires. J. Anal. Appl. Pyrolysis 2001;57:91–107.
- [8] Cunliffe AM, Williams PT. Composition of oils derived from the batch pyrolysis of tires. J. Anal. Appl. Pyrolysis 1998;44:131–52. [and references therein]
- [9] Roy C, Chaala A, Darmstadt H. Vacuum pyrolysis of used tires End-used for oil and carbon black products. J. Anal. Appl. Pyrolysis 1999;51:201–221.
- [10] Barbooti MM, Mohamed TJ, Hussain AA, Abas FO. Optimization of pyrolysis conditions of scrap tires under inert gas atmosphere. J. Anal. Appl. Pyrolysis 2004;72:165–170.
- [11] Williams PT, Brindle AJ. Aromatic chemicals from the catalytic pyrolysis of scrap tires. J. Anal. Appl. Pyrolysis 2003;67:143–164.
- [12] Williams PT, Brindle AJ. Temperature selective condensation of tyre pyrolysis oils to maximise the recovery of single ring aromatic compounds. Fuel 2003;82:1023–1031.
- [13] Pakdel H, Roy C, Aubin H, Jean G, Coulombe S. Formation of limonene in used tire vacuum pyrolysis oils. Environ. Sci. Technology 1992;9:1646.
- [14] Cunliffe AM, Williams PT. Influence of process conditions on the rate of activation of chars derived from pyrolysis of used tires. Energy & Fuels 1999;13(1):166–175.
- [15] Zabaniotou AA, Stavropoulos G. Pyrolysis of used automotive tires and residual char utilization. J. Anal. Appl. Pyrolysis 2003;70:711–722.
- [16] Zabaniotou AA, Madau P, Oudenne PD, Jung GC, Delplancke MP, Fontana A. Active carbon production from used tire in two-stage procedure: industrial pyrolysis and bench scale activation with H₂O-CO₂ mixture. J. Anal. Appl. Pyrolysis 2004;72:289–297.
- [17] Murena F, Garufi E, Smith RB, Gioia F. Hydrogenative pyrolysis of waste tires. Journal of Hazardous Materials 1996;50:79-98.
- [18] Ucar S, Karagoz S, Ozkan AR, Yanik J. Evaluation of two different scrap tires as hydrocarbon source by pyrolysis. Fuel 2005;84:1884-1892.
- [19] Kyari M, Cunliffe A, Williams PT. Characterization of oil, gas and char in relation to the pyrolysis of different brands of scrap automotive tires. Energy & Fuel 2005;19:1165-1173.
- [20] Laresgoiti MF, De Marco I, Torres A, Caballero B, Cabrero MA and Chomon MJ. Chromatographic analysis of the gases obtained in tyre pyrolysis. J. Anal. Appl. Pyrolysis 2000;55:43–54.
- [21] Merchant AA, Petrich MA. Pyrolysis of scrap tires and conversion of chars to activated carbon. AIChe J. 1993;39:1370–1376.
- [22] Williams PT, Besler S, Taylor DT. The pyrolysis of scrap automotive tires: The influence of temperature and heating rate on product composition. Fuel 1990;69:1474-1482.
- [23] Napoli A, Soudais Y, Lecomte D, Castillo S. Scrap tyre pyrolysis: Are the effluents valuable products? J. Anal. Appl. Pyrolysis 1997;40-41:373-382.
- [24] Morillo R, Aylon E, Navarro MV, Callen MS, Aranda A, Mastral AM. The application of thermal processes to valorize waste tire. Fuel processing Technology 2006;87:143-147.
- [25] Mastral AM, Murillo R, Callen MS, Garcia T, Snape CE. Influence of process variables on oils from tire pyrolysis and hydropyrolysis in a swept fixed bed reactor. Energy & Fuels 2000;14(4):739-744.
- [26] Chang YM. On pyrolysis of waste tire: Degradation rate and product yields. Resour. Conserv. Recy. 1996;17:125-139.
- [27] Zailani RB. Fluidized-bed pyrolysis of organic solid waste, M.Sc. Engg. Thesis, Universiti Teknologi Malaysia, Malaysia, 1995.
- [28] Islam MN, Islam MN, Beg MRA. Fixed bed pyrolysis of scrap tyre for liquid fuel production. International Energy Journal 2004;5(1):11-18.
- [29] Kaminsky W, Mennerich C. Pyrolysis of synthetic tire rubber in a fluidised-bed reactor to yield 1,3-butadiene, styrene and carbon black. J.

Anal. Appl. Pyrolysis 2001;58-59:803-811.

- [30] Mirmiran S, Pakdel H, Roy C. Characterization of used tire vacuum pyrolysis oil: Nitrogenous compounds from the naphtha fraction. J. Anal. Appl. Pyrolysis 1992;22:205-215.
- [31] Roy C, Rastegar A, Kaliaguine S, Darmstadt H. Darmstadt, Physicochemical properties of carbon blacks from vacuum pyrolysis of used tires. Plast. Rubber Compos. Proc. Appl. 1995;23:21-30.
- [32] Aguado R, Olazar M, Arabiourrutia M, Alvarez S, Bilbao J. In: Proceedings of the VIII Congress de Ingenier and Ambiental PROMA'03, Bilbao, Spain, 2003.
- [33] Islam, M. R., Parveen, M., and Haniu, H. Properties of sugarcane waste-derived bio-oils obtained by fixed-bed fire-tube heating pyrolysis. Bioresource Technology, Vol. 101, No. 11; pp. 4162-4168; June 2010.
- [34] Islam, M.R., Parveen, M., HANIU, H and Sharker, M. R. Innovation in pyrolysis technology for management of scrap tire: a solution of Energy and Environment. International Journal of Environmental Science and Development, Vol. 1; No.: 1; pp. 89-96; April 2010.
- [35] Islam, M. R, Kim, S. I., Haniu H. and Beg, M. R. A. Fire-tube heating pyrolysis of car tire wastes: end uses of product liquids as fuels and chemicals. International Energy Journal, Vol. 9, No. 3; pp: 189-198; September 2008.
- [36] Islam, M. R., Haniu, H. and Beg, M. R. A. Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: product yields, compositions and related properties. FUEL, Vol. 87, No. 13-14; pp. 3112-3122; October 2008.
- [37] Islam, M. R., Tushar, M. S. H. K. and Haniu, H. Production of liquid fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes. Journal of Analytical and Applied Pyrolysys, Vol. 82, No. 1; pp. 96-109; May 2008.
- [38] Islam, M. R., Haniu, H. and Beg, M. R. A. Limonene-rich liquids from pyrolysis of heavy automotive tire wastes. Journal of Environment and Engineering, Vol. 2, No. 4; pp. 681-695; October 2007.
- [39] Islam, M. R., Joardder, M. U. H., Hasan, S. M., Takai, K. and Haniu, H. Feasibility study for thermal treatment of solid tire wastes in Bangladesh by using pyrolysis technology. Waste Management, Vol. 31; pp. 2142-2149; 2011.
- [40] Islam, M. R. Fixed-bed fire-tube heating pyrolysis of solid tire wastes available in Bangladesh for production of alternative liquid fuels and valuable chemicals. PhD Thesis, Department of Mechanical Engineering, National University Corporation Kitami Institute of Technology, Hokkaido, Japan; 2008 (and references therein).
- [41] Sharma, V. K., Mincarini, M., Fortuna, F., Cognini, F. and Cornacchia, G. Disposal of waste tires for energy recovery and safe environment review. Energy Conv. and Manag., Vol. 39, No. 5/6; pp. 511-528; 1998.
- [42] Islam, M. R., Haniu, H., Fardoushi, J. Pyrolysis kinetics behaviour of solid tire wastes available in Bangladesh. Waste Management, Vol. 29; pp. 668-677; 2009.
- [43] Galvagno, S., Casu, S., Casabianca, T., Calabrese, A., Cornacchia, G. Pyrolysis process for treatment of scrap tires: preliminary experimental results. Waste Management, Vol. 22, pp. 917-923; 2002.
- [44] Berrueco C, Esperanza E, Mastral FJ, Ceamanos J, Garcia-Bacaicoa P. Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: Analysis of the gases obtained. J. Anal. Appl. Pyrolysis 2005;74:245–253.
- [45] Qu, W., Zhou, Q., Wang, Y., Zhang, J., Lan, W., Wu, Y., Yang, J., Wang, D. Pyrolysis of tire waste on ZSM-5 zeolite with enhanced catalytic activities. Polymer Degradation and Stability, Vol. 91; pp 2389-95; 2006.
- [46] Helleur B, Popovic N, Ikura M, Liu D. Characterization and potential applications of pyrolytic char from ablative pyrolysis of used tires. 14th International Symposium on Analytical and Applied Pyrolysis, April 2–6, Sevilla-Spain, J. Anal. Appl. Pyrolysis, Vol. 58–59; pp. 813–824; 2001.
- [47] Roy, C. and Unsworth, J. Pilot-scale plant demostration of used tyres vacuum pyrolysis. In Pyrolysis and gasification; Ferrero, G. L., Maniatis, K., Buekens, A., Eds.; Elsevier Applied Science: London, U. K., 1989.