



Catalytic Pyrolysis of Tire Wastes for Liquid Fuel

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Severity of energy crisis is so acute in our society whereas environmental degradation is another challenging issue. Combining these two, environmental pollution can be eradicated permanently which is the burning issue for many countries of the world. Nowadays recycling of tire waste can be a dependable solution for minimizing energy crisis and environmental pollution as well as energy crisis. Similar to bio resources these wastes tire have the features of manufacturing energy by altered thermochemical conversion process. In the previous time waste tire pyrolysis was conducted without catalyst whereas the present pyrolysis with catalyst. The objectives were investigating the effect on oil extraction and the composition of derivative oil from tire waste in presence of catalyst. The effect of pyrolysis heating rate, temperature, operating time, catalyst/tire ratio (CT ratio) and sample size etc. on yield were also investigated. The pyrolysis process was carried out in temperature range of 300 to 600°C. The most favorable pyrolytic oil attained was 42.0% (wt) for without catalyst as well as 36.67% (wt) for catalytic pyrolysis at 450°C. Characterization of physical properties of the resulting pyrolytic oil showed that increase in pyrolysis temperature and CT ratio resulted in higher yield of gas at the expense of oil. When CT ratio is increased from 0.13 to 0.30, the gas yield is increased from 13.33 to 15.33% (wt) and oil yield decreased from 36.67 to 28.0% (wt) at temperature of 450°C. High CT ratio favored an increase in the concentration of light naphtha in the pyrolytic oil. A yield of 97% (wt) is obtained from of the pyrolytic oil at 450°C with CT ratio 0.3 by fractional distillation below 350°C. It could be concluded that after proper treatment these oil can be used as substitute of alternative fuel or chemical feedstock to naphtha..

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INTRODUCTION

Nowadays, population is growing rapidly. This huge population require more energy which results rapid industrial revolution and in some cases environmental degradation [1]. So, whole world is looking for the alternatives of fossil fuel. Different types of organizations are taking different initiatives to replace the fossil fuel to do so they are investing millions of dollars. On the other hand waste tires from different kinds of vehicles are also increasing and the disposal of those waste tires becomes a big challenge [2]. At every year about 20.5 million tires of rickshaw/bicycle become waste and they are considered as useless waste is near 37% (wt) of entire waste tire production in Bangladesh. It is projected that about 30,750 tons rickshaw/bicycle tires, 5160 tons tire from motorcycle, and 28,900 tons tire

from bus/truck are becoming scrap at every single year and disposed to environment [3]. Therefore, recycling of tires and disposed to environment create a major problem for our surroundings. Usually recycling market is not a big market. Thus, the total annual tire is not recycled fully at every year which results the disposal of tires in wood lines, fields, and other areas. Due to some drawback it is not fruitful the recycling process. So tires are burn in different brick fields which creates CO₂, CO, SO_x, NO_x, these gases are indirect threat to our existence. So considering all these aspects tire pyrolysis of the scrap tire transformation into energy is a relatively economic and environment friendly method. A large fraction of the scrap tires is simply dumped in sites where they represent hazards such as diseases and accidental fires. The most common ways of disposing of waste tire is land filling, but land filling process of used tires needs a huge area because the size of tires cannot be trampled [4].

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Various processes of recycling are being used for example incineration, reclaiming, grinding retreading etc. but these various process of recycling have some disadvantage [5]. If the tire waste decomposed by fire directly in various ignition plants or in brick fields then numerous detrimental gases for example CO₂, CO, SO_x, NO_x, etc. will generate which can causes serious environmental pollution. Thus, there is inevitability to discover the unconventional recycling sources for these tire wastes. Recycling of non-bio-degradable waste to a beneficial goods is a sustainable verge upon for the upcoming aspects. One recent method which has received substantial attention is pyrolysis. Pyrolysis is a relatively economically and environmentally attractive method of waste tire transformation into useful products and energy. It is a simple thermal decomposition process of different organic material at certain temperature and in absence of oxygen. After thermal decomposition of the pyrolytic oil will be found, solid char and gas which has great perspective for the other important applications. Such yielded oil that might be used as fuel directly or blended to the petroleum feed materials and also it might be an significant source for superior chemicals [6, 7]. After pyrolysis of the product gases are beneficial as fuel; solid char can be used as less smoke fuel, activated carbon or carbon black .

The pyrolytic liquids have been demonstrated because it have a great gross calorific value approximately 41–44 MJ/kg, that would persuade their important use as substitute for predictable Liquid fuels [8]. On the hand, high concentration of the aromatic hydrocarbons [8, 9] being limited the pyrolytic oil get from waste tire pyrolysis to be utilizes as fuel. In addition to their utilization as fuel, the liquid was revealed to be a probable rich source of aromatics such as benzene, toluene and xylene (BTX), which control a higher market value than the unprocessed oils. Similarly, the aqueous phase exposed to contain monoterpenes such as limonene [1-methyl-4-(1-methylethenyl)-cyclohexene], a high value light hydrocarbon. Limonene has quickly rising and wide industrial applications including the formulation of industrialized solvents, resins and adhesives, as a dispersing agent for pigments, as a perfume in cleaning products, and as an environmentally acceptable solvent [10].

Since the derived oils comprise concentrations of valuable chemicals like toluene, benzene, xylenes, etc., consequently these chemicals can be extracted from the derived oils and reused as chemical feedstock in the chemical industry. For instance, toluene is used in the manufacture of dyestuffs, pesticides, surfactants and solvents; benzene is used as dyestuffs, surfactants and pharmaceutical compound; O-xylene is used to yield dyes and pigments, plasticizers, p-xylene byproducts are used in the manufacture of polyester fibers and m-xylene byproducts are used in the fiber industries [11]. But, their

concentrations are not adequately high to allow their extraction from the oil and use as a chemical feedstock, consequently catalysts are presented to create supplementary single ring aromatic compounds. Williams and Brindle [12, 13] have accompanied some significant research in this field through using zeolite type catalysts with different pore sizes and Si/Al ratios to study the effects of catalytic temperature, pyrolysis temperature, and catalyst/tire ratio on the composition of derived oils and the yields of products. They acquired the oil through high concentration of certain aromatic compounds with single ring like benzene, xylenes and toluene after catalysis. The significance of such high rate chemicals proposes that identification of new procedures which lead to augmented concentrations of such chemicals would prominently improve the economic feasibility of the pyrolysis of tires.

Tire pyrolysis without catalyst was carried out earlier at KUET (Bangladesh) at different temperatures with various tire sizes and the results were published in literature [6]. The optimal 42% pyrolytic oil was attained at 450°C. Smaller particle size and higher temperature raises the heating rate that consequence reduced char yield. Around 37.98 MJ/kg was the high calorific value of the liquid. In the present work, an exertion has been complete to study the effect of catalyst on tire pyrolysis. In this study, pyrolysis of waste tire at different temperatures with zeolite Si/Al-catalysts was performed in nitrogen-purged fixed bed reactor. The effects of pyrolysis heating rate, temperature and catalyst/tire (CT) ratio on yield and segment of the derived oils were explored in this work. By FT-IR the property of the derived oil has been examined for the determination of aromatic content used as chemical feedstock.

MATERIAL AND METHODS

Feed Materials Preparation

The feed materials used for the present study are tire waste of various sizes. The waste tires were collected and gathered from the bus repairing garage at Khulna City, Bangladesh. Therefore, to continue the uniformity in the constitute in the illustrative samples, similar brand waste tires were cut down cross-section part into four diverse sizes, for example, 1.00×1.00×0.75 cm; 1.00×1.75×0.75 cm; 2.00×1.00×0.75 cm and 2.00×1.50×0.75 cm. These small diverse pieces were considered as the emissary of the entire sample. They contain textile fabrics but did not comprise steel cords. The samples were properly washed and cleaned to remove foreign materials, dirt and mud. The sample pieces were dried to remove moisture. After that it was loaded to the reactor.

Elemental and proximate analysis of solid tire waste: The elemental and proximate analysis of solid tire waste is very important to discover different properties of tires

solid. The volatile components and heating value are the key factors for tire pyrolysis. Upper volatile components specified upper liquid product in tire pyrolysis process. Elemental and proximate analyses of solid tire waste with high calorific value are shown in below Table 1.

Table 1. Elemental and proximate analysis of solid tire waste [11]

Proximate Analysis (wt %)		Elemental analysis (wt %)	
Moisture	0.82	Carbon (C)	80.2
Volatile	61.01	Hydrogen (H)	7.0
Fixed carbon	32.01	Nitrogen (N)	0.41
Ash	4.01	Oxygen (O)	6.99
H.C.V (MJ/kg)	36.5	Others	5.4

Experimental setup

A batch type and fixed-bed reactor for pyrolysis was constructed for the study as shown in the Figure 1. The main chamber of the reactor was made from 0.7 mm thickness MS sheet that have a length of 56 cm. This chamber's outer diameter was 16.7 cm. The main constituent of the experimental set-up were the electrical heater to maintain the inside temperature of the reactor fixed-bed reactor chamber, the cooling water system for condensation of vapour for pyrolytic liquid, the liquid collecting bottle, the gravity-fed reactor feeder, N₂ cylinder with a connection pipes; K-type thermocouples with temperature display. A distributor plate which made of stainless steel, supporting the feed materials was placed 30 mm distance from the end of the chamber of reactor. The distributor plate has 90 holes of 2.5 mm diameter. The N₂ gas inlet connection was below the distributor plate. Four 10 mm diameter tube-heater of 500W each was used as heating element. These heaters were controlled by separate switches. The reactor surface was thermally insulated with glass wool and asbestos rope.

Experimental procedure

There search were directed by changing the temperature range inside the range of 300-600°C for every 50°C intermission for various feed sizes. The thermocouple sensors were extruded inside the chamber of the reactor for record the inside temperatures. For every run a sample size of 1.5 kg of was fed into the reactor. The feed materials were loaded by gravity action by opening the top portion. Initially, the reactor chamber was purged through flowing N₂ gas for two minutes for remove all air from inside. The heater of the reactor was switched on for allow the temperature augmented up to 300°C. During the experiments the temperatures were recorded. When pyrolysis of tire started a visible reddish/bright brown vapor come out through the outlet pipe. N₂ gas supply was carried on for retain an inert atmospheric condition in the reactor. Pyrolysed vapor were passed over the

condenser pipes for condensate into pyrolytic oil and after that conserve in a bottles. The gases which were uncondensed that spreading in the atmosphere. After completion of the decomposition, from the reactor colorless gas came. When the colorless flaring came out, it was the indication of completion of thermal decomposition of sample tire. After completion of pyrolysis the vapor exit port and N₂ gas supply line was stopped. The reactor heater was also switched off. When cooling down the whole system, the solid product char was carried out from the chamber of the reactor and weighed. The condensed liquid portion was weighed first. The determination of uncondensed gas content was carried out by subtracting the sum of the char and liquid weight from the total weight of feedstock. After that, the whole system was ready for the next run.



Figure 1. Schematic view of Experimental Set-up

RESULTS AND DISCUSSION

Effect of temperature and catalyst on pyrolytic yield

kiln temperature range of 300 to 600°C. The experiments were conducted to examine the effect of pyrolysis catalyst and temperature on product yield and also to make a comparison between the two processes i.e., without catalyst and with catalyst. The effects of temperature on pyrolytic products acquired from pyrolysis of tire waste without catalyst are shown in Figs. 2 and 3. The same tests were carried out in presence of catalyst with feed size of only 0.75 cm³. The results are presented in Figs. 4 to 6.

As mentioned in literature [14], three types of products viz. liquid oil, solid and gas were obtained. It is pragmatic from Figs. 2 and 3 that with increasing temperature the liquid production rate increases until it reaches to a maximum and then decreases. Both the figures show similar nature. Among the four sizes of samples the best result was obtained with feed size of 0.75 cm³ which is shown in Fig. 2. The maximum yield of liquid 42.0% (wt) was found at 450°C without catalyst.

But the liquid yield has decreased to 32.67 % (wt) at a temperature of 600°C. It is also seen that yield of gas has increased above the entire temperature range to a maximum value of 21.33% at 600°C, while yield of char has reduced rapidly up to 450°C and formerly very slowly. This is possibly due to better cracking of the waste tire up to this type of temperature and rubber of tire is partially decomposed at temperature beyond 450°C. Further it is observed that the char yield decreases slowly beyond this temperature. It was apparent that at lower temperature the tire was incompletely pyrolysed to produce fewer oil and volatiles with full retention of materials in solid form as char.

In presence of catalyst, the thermal pyrolysis of tire also yields three different products oil, char and gas. After using catalyst, the liquid yield is termed to be catalytic liquid/oil. The effect of catalytic cracking on product yield is shown in Figs. 4 to 6. It is observed from Fig. 4, with CT ratio 0.13, as temperature rises from 300 to 600°C, the yield of catalytic oil rises first to a maximum value of 36.67% (wt) at 450°C and then reduces to a minimum of 32.67% (wt) at 600°C for various sizes of tire feedstock.

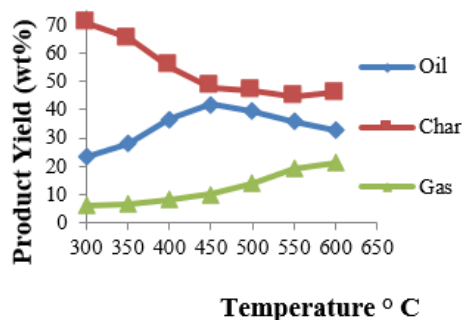


Figure 2. Effect of temperature on product yields for tire pyrolysis with feed size 0.75 cm³

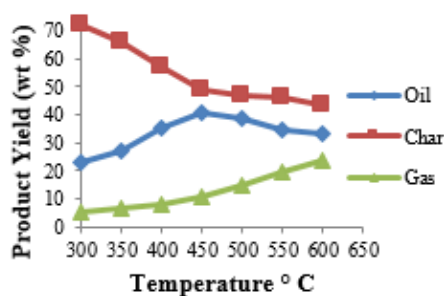


Figure 3. Effect of temperature on product yields for tire pyrolysis with feed size 1.31 cm³

Fig. 5 depicts that when catalyst is increased (CT ratio 0.20) in feedstock, as temperature rises from 300 to 600, the production of catalytic oil rises first to a maximum of 34% (wt) at 450°C and then declines to a minimum 28.67% (wt) at 600°C for the same sizes of tire feedstock

which are slightly lower than that obtained with CT ratio 0.13.

On the other hand from Fig. 6, when catalyst is increased (CT ratio 0.30) in feedstock, as the temperature rises from 300 to 600°C, the production of catalytic oil escalations first to maximum 33.33% (wt) at 450°C and then declines to a minimum 28.0% (wt) at 600°C for same size. When CT ratio is 0.30, the gas yield is augmented markedly at the expenditure of oil yield with rising temperature. Such as, the gas yield augmented from 15.33 to 24.67% (wt) while the temperature augmented from 450 to 600°C. It indicates that oil yield reduced with the increasing temperature. For instance, oil yield reduced from 33.33 to 28.0% (wt) when the temperature augmented from 450 to 500°C.

It is also envisaged that the oil yield is reduced while catalyst is used in the process of pyrolysis. The reason might be influence of zeolite catalyst and more cracking of materials converted to un-condensed products. Williams and Brindle [12, 13]. in their research found that the oil yield was reduced by the catalyst cracking of tire pyrolysis and Venuto and Habib [15] stated that catalytic cracking had contribution to yield of large amounts of gaseous products. Thus, the present result agreed to publish valuable information.

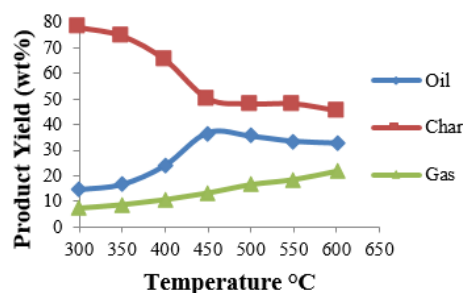


Figure 4. Effect of catalyst on product yields with CT ratio 0.13 and feed size 0.75 cm³

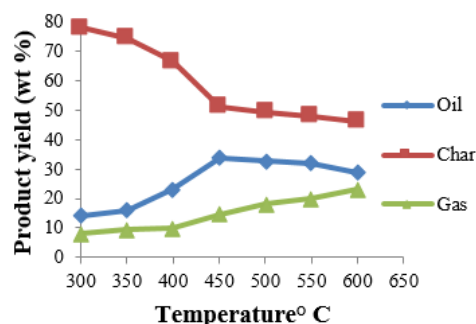


Figure 5. Effect of catalyst on product yields with CT ratio 0.20 and feed size 0.75 cm³

Effect of CT ratio on product yield

The consequence of various CT ratios on product yields of tire pyrolysis below optimum reactor temperature

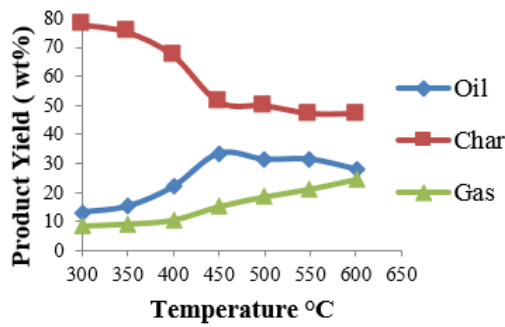


Figure 6. Effect of Catalyst on product yields with CT ratio 0.30 and feed size 0.75 cm³

(450°C) is presented in Fig. 7. The weight fractions of liquid oil, char and gas produced were plotted together with sample size in the Fig. 7 shows that, the liquid yield from tire pyrolysis first slightly increases up to a maximum value of 36.67% (wt) with CT ratio 0.13 for sample size of 0.75 cm³ and then liquid production slowly decreases for increasing CT ratio while the char yield increases first then slightly decreases and gas yield slightly increases with the same sample sizes.

Effect of operating time on product yield

The operating time effect on product yield is shown in Fig. 8 for without catalyst and in Fig. 9 for with catalyst. It is pragmatic from Fig. 8 that more operating time is needed to entire the renovation which consequences in partial depolymerisation of the taster that escort to manufacture of supplementary char and a smaller amount of oil.

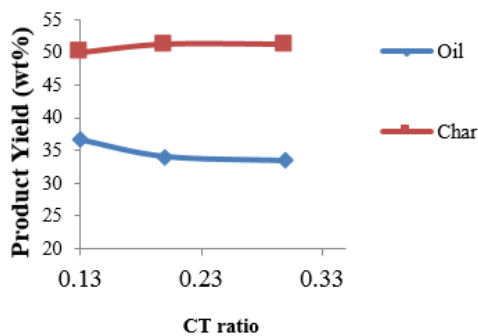


Figure 7. Effect of various CT ratios on product yields at 450°C of tire pyrolysis

As lesser operating time was essential for the whole conversions that conduct more oil and fewer char, there is no noticeable method for gas loss with operating time. It was also experiential that squat temperature and longer operating time put in to secondary pyrolysis of primary products, which guides a reduced amount of oil and supplementary char products [15].

In Fig. 9, it is perceived that the effect of catalyst and operating time with the yield follow the similar trend but

the gas production is slightly more than in absence of catalyst.

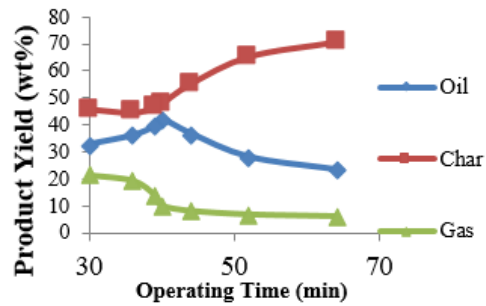


Figure 8. Effect of operating time on product yield with feed size 0.75 cm³

In Fig. 10, it is perceived that the effect of catalyst with the yield follows the similar trend but the oil production is little bit decreased due to increased CT ratio as well as the gas production is slightly more than that in absence of catalyst. However, the oil production is slightly more than that for without catalyst.

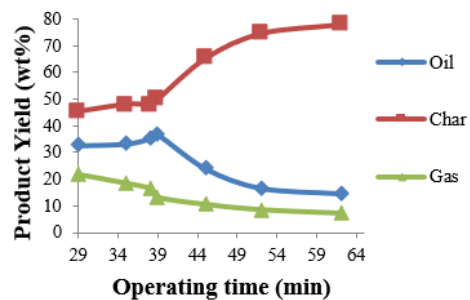


Figure 9. Effect of operating time on product yields with CT ratio 0.13 and feed size 0.75 cm³

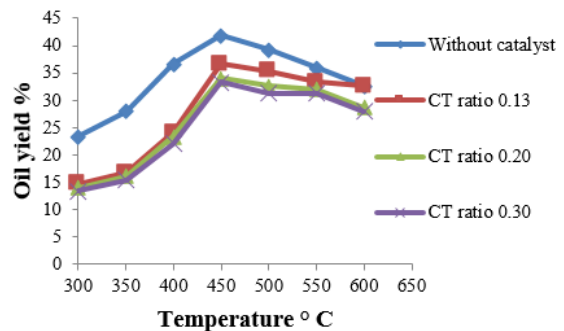


Figure 10. Variation of liquid yield at different temperature for various compositions

Comparison of pyrolytic oil, catalytic oil with petroleum products

The pyrolytic oil and catalytic oil resulting from waste tire were investigated and contrasted with that of diesel oil and furnace oil is shown in Table 2. From the table, it

is seen that the density of pyrolytic oil is 935.1 kg/m³ and for catalytic oil is 909.2 kg/m³ with CT ratio 0.13, 898.5 kg/m³ with CT ratio 0.20, 895.3 kg/m³ for CT ratio 0.30, commercial furnace oil from 890 to 960 kg/m³ which is more than that of the commercial diesel (820-860 kg/m³) and petrol at 700-800 kg/m³. The viscosity of pyrolytic oil was 6.59 cSt at 40°C and diesel from 3 to 5 cSt at 40°C. The viscosity of pyrolytic was slightly heavier than diesel; however, much low-grade than that of furnace oil at 45 cSt for 40°C. The viscosity of pyrolytic oil from the tire pyrolysis with CT ratio of 0.13 and 0.20 are 2.59 cSt at 40°C, 2.12 cSt at 40°C, respectively. The viscosity of obtained fuels are lower than that of the diesel (3 to 5 cSt at 40°C). When catalyst in the pyrolysis process is increased the viscosity of derived oil is decreased. The liquids low viscosity of 4.62-4.90 cSt at 30°C is a promising attribute for the management and transportation of the liquid. The flash point of the liquid derived from tire was 37°C. On the other hand, the flash points of the liquid derived from tire in the presence of catalyst were 35, 32 and 32°C, respectively. The flash point was low while compared with petroleum-refined fuels; such as, furnace oil has an obligatory least flash point of 70°C, diesel of 55°C. The liquids derived from tire pyrolysis has low flash point are not amazing since the product obtained is unrefined with a combination of components devising a wide distillation range. The pour point of the waste tire pyrolysis oil share relatively low compared to the motorized diesel fuel but the laboratory practice of the present study shows that it is not difficult even at 7°C. Gross calorific values (GCV) the pyrolytic oil for without catalyst is 37.97MJ/kg and

TABLE 2. Comparison the properties of raw pyrolytic oil, catalytic oil with conventional diesel and furnace oil

Physical Properties	Oil extracted with catalyst without	Oil extracted with CT ratio 0.13	Oil extracted with CT ratio 0.20	Oil extracted with CT ratio 0.30	Reference with	
					Diesel	Furnace oil
Density (kg/m ³), 30°C	935.1	909.2	898.5	895.3	820 to 860	890 to 960
Kinematic Viscosity in @40°CSt	6.59	2.5	2.12	2.01	3 to 5	45
Flash Point °C	37	35	32	32	≥ 55	70
Pour Point °C	-7	-12	-14	-16	-40 to -1	10 to 27
Gross Calorific Value (MJ/kg)	37.98	38.1	38.95	39.01	42 to 44	42 to 43

the tire pyrolysis with CT ratio 0.13, 0.20, and 0.30 are 38.10 MJ/kg, 38.95 MJ/kg and 39.01 MJ/kg respectively is lower than that of diesel and gasoline.

Compositional group fourier transform Infra-Red (FTIR) spectroscopy

The functional group configurations of the pyrolytic oil were investigated through Fourier Transform Infra-Red (FTIR) spectroscopy to identify the basic compositional group. The ordinary FTIR spectrum of hydrocarbons was used to recognize the functional group of the components of the pyrolytic oil and catalytic oil. The results of FTIR are presented in Table 3.

Analysis of Char Product after Pyrolysis of Tire

The obtained solid char fractions at most favorable reactor situations were of equivalent size and shape as unique all tire pieces, which were simply disintegrable into steel cords and black powder. The gross calorific value of char product was 22–25 MJ/kg, which is comparable with that all good quality coal. Similar data is found in literature [16].

TABLE 3. The FTIR Functional Groups and the Indicated Compound of Pyrolysis

Absorbance Range (cm ⁻¹)	Functional Group	Class of Compound	Without catalyst	CT ratio 0.13
3200-3650	O-H	Alcohol, phenol, Carboxylic acid	3300-3700	3300-3700
3300-3500	N-H	Amines		
2850-2960	C-H	Alkanes and Alkyl group	2800-3000	2800-2900
1660-2000	C=C	Aromatic	1600-1700	1600-1800
1450-1600	C-H	Alkanes	1450-1600	1400-1600
1325-1425			1300-1450	1300-1400
1175-1300	C-O	Primary, esters and ethers	1030-1370	1200-1300
1000-1150	C-H	Alkanes	966-1030	1000-1200
875-950	HC≡CH	Alkynes	812-966	
600-950		Aromatic compound	752-812	750-850

CONCLUSION

Under this study, the revival of value added products, i.e., pyrolysis oil from waste tire, were investigated. Catalytic pyrolysis and thermal pyrolysis of waste tire has been studied inside the series of experimental limit the subsequent decisions can be made from the analysis of the results. The maximum yield of pyrolytic oil from the waste tire was 42.0% (by weight) at temperature of 450°C with the tire size of 0.75 cm³ with a lot size of 1.5 kg. The maximum yield of pyrolytic oil from the waste tire in presence of catalyst (CT ratio 0.13) was 36.67% (wt) at a temperature of 450°C when the tire size is also 0.75 cm³ with same lot size. Physical properties of

pyrolytic oil derived from wastes tire are comparable with that of kerosene, naphtha and diesel fuel. Pyrolysis of waste tire in presence of catalyst using zeolite type of catalyst have been examined in relation to the stimulus of pyrolysis temperature going on yield of products. The results presented that the effect of the presence of catalyst was to decrease the yield of oil with a consequent rise in the gas yield. The pyrolytic oils obtained were examined with FTIR four groups: alkane, alkenes, alkynes and aromatic compound. It presented that the additional aromatic hydrocarbons were found in derived oil from the pyrolysis of the tire waste with catalyst. Subsequently upper concentrations of certain aromatic compound can be obtained from the derived oil; it could be used for instance a chemical feedstock relatively than a fuel. By considering all these outcomes, it can be concluded that the pyrolytic oil found from tire pyrolysis could be used as alternative fuel or chemical feedstock after some treatment.

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چکیده

در حالی که بحران انرژی در جهان به شدت جدی است، تامین انرژی بدون صدمه زدن به محیط زیست از اهمیت بالایی برخوردار است. ترکیب این دو مورد به راه حل مورد نیاز جوامع بشری یعنی تامین انرژی پاک منجر می شود. تایرهای مستهلک همانند منتبع قابل تجزیه منبع انرژی محسوب می شوند. در مطالعه ی حاضر هدف بررسی شدت حرارت دهی، دما، زمان عملیات، نسبت کاتالیست به تایر و مقدار نمونه بوده است. فرآیند پیرولیز در دمای ۳۰۰ تا ۶۰۰ درجه سانتی گراد انجام شد. بیشترین میزان روغن استخراج شده ۴۲٪ بدست آمد. افزایش دمای فرآیند منجر به افزایش میزان روغن بدست آمده شده است.