
The Effect of Catalyst Ratio on the Pyrolysis Yields for Waste Tyre

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Abstract: This paper focus on the thermal pyrolysis of used tyre with different catalysts at a temperature 550°C and at a heating rate of 15°C/min. The effect of process parameters on liquid yield, char formation and volatiles were also studied. In the present work, thermal pyrolysis of waste tyre samples with two selected catalysts, namely Jordan zeolite (zeolite Jo) and activated alumina was carried out in a fixed-bed reactor. The catalyst was mixed with feedstock in different percentages (10%, 15%, 25% and 35% w/w). The effects of catalysts and their ratio on the pyrolysis product oil were investigated and the results were compared with the results of experiments performed without catalyst under the same conditions (temperature 550°C at a heating rate of 150C/min). The maximum liquid yield obtained from pyrolysis of waste tyre via catalyst were found as 49.32% and 51.54% on using activated alumina and zeolite Jo as catalysts, respectively, while these values were 42.48%, without catalyst. The mass loss of tyre was examined using the thermo gravimetric analysis profiles (TGA) at heating rate of 15°C/min in air atmosphere from room temperature up to 600°C. The tyre pyrolysis liquid product has been characterized including fuel properties, proximate analysis, and ultimate analysis and FTIR. Fuel properties show that it can be used as liquid fuels.

Keywords: Catalysts, Waste Tyre, Zeolite, Pyrolysis, Bio-Oil

1. Introduction

Disposal of waste vehicle tyres is one of the most important problems that should be solved. It is assessed that around the world, more than one billion waste tires are produced every year [1]. The huge quantity of waste tires presently produced in the world will absolutely increment in the future as the associated automotive industries grow. The disposal of scrap tires becomes a serious environmental problem scrap tyres are not biologically degradable, and not destructible waste through time, This polymer solid waste is non-biodegradable as a result of their complex mixture of very different materials, which include several rubbers, carbon black, steel cord and other organic and inorganic components, this fact creates problems with their disposal [2]. The impact of scrap tyres on the environment can be minimized by recycling with material or energy recovery [3]. As the disposal of scrap tyres in landfills is prohibited in many countries including Jordan, it is important to find an

alternative route to take advantage of their high potential as energetic and raw material source. Subsequently, the tyre Pyrolysis, as a process to recover tyre energy, offers products that may likewise change regarding yield, chemical composition and characteristics. Even so, tyre Pyrolysis liquids have been found as a mixture of paraffin's, olefins and aromatic compounds, In addition, some physico-chemical properties of the tyre Pyrolysis liquids are fairly comparable to those found in commercial automotive diesel fuels [4, 5, 6]. Consequently, pyrolysis has received renewed attention as the process conditions can be optimized to produce high valued products. pyrolysis usually proceeds at low (<400°C), medium (400–600°C) or high temperature (>600°C). Despite the fact that pyrolysis is considered a major alternative to exploit the useful chemicals and resources from waste tyre, the process is still not in high usage and this is largely due to the high amount of energy required for the process, various attempts have been made by researchers to make tyre pyrolysis an economic viable process [5, 7]. The process being an excellent energy

recovery route can be performed under atmospheric or reduced pressure. It is an environmentally friendly technique to thermally decompose a wide variety of wastes, including used tyres [4, 6, 8,]. The three basic products of pyrolysis are solid residue (char), liquid (bio crude), and gases [6-8]. Solid residue may be used in the manufacture of activated carbon, or as solid fuel. Much interest is laid in the production of hydrocarbon liquids from waste tyres since the production of liquid product can be a substitute of fossil fuel [9-11]. It can also be used as petroleum refinery feedstock or a source of chemicals for wide industrial applications. Gaseous fraction can be used as fuel or as a source of energy for the pyrolysis process [12-15]. This paper focus on the thermal pyrolysis of used tyre with different catalysts at a temperature 550°C and at a heating rate of 15°C/min. The effect of process parameters on liquid yield, char formation and volatiles were also studied. The obtained liquid was characterized for different physical and chemical analysiscondition.

2. Materials and Methods

2.1. Materials

The material used for Pyrolysis was waste scrap tyre. First it was freed from metal cords and textiles, cleaned and cut into size 5mm. The activated alumina and zeolite Jo catalysts were selected for the catalytic Pyrolysis of waste tyre. Natural zeolite was selected as a catalyst for our application. There is an abundance of sediment beds in east Jordan. The samples were taken from the north-east region and, the purity was about 95%. For activation, it was calcined at 400°C for 3 hours [10, 16]. They were activated and kept in a desiccator for the experiments. The surface area, pore volume and average pore diameter of activated alumina were found as 304.7 m²/g, 0.407 ml/g and 53.42 Å, respectively, while these values for zeolite Jo. were found, as Surface area (m²·g⁻¹) 69.12, Particle diameter (mm) D_p>1.6, Pore diameter (Å) 33.12 and Density (kg·m⁻³) 2150 [17, 18]

2.2. Experimental Procedure

Pyrolysis of scrap tyres was performed in stainless steel batch reactor, volume of 310 cm³ and is externally heated by an electric furnace with the temperature being controlled by a

thermocouple inside the bed. The experiments were conducted to decide the effect of catalyst ratio on the pyrolysis yields for waste tire samples, during experiments 20 gram of waste tyres having average particle size of 0.45-0.65, was mixed with catalyst (10%, 15%, 25% and 35% w/w) and after that put into the reactor. The optimum experimental conditions determined in a previous study were a final pyrolysis temperature of 550°C, a heating rate of 15°C/min, a sweeping gas flow rate of 50 ml/min [10]. The vapor from the reactor was condensed in a water cooled condenser and the non-condensable gas vented to atmosphere. The liquid phase was collected from the outlet of the condenser in cold measuring cylinder and weighed. After pyrolysis, the solid char was removed and weighed, then the gas yield was calculated by the difference.

2.3. Analysis

The elemental analysis was done using Elementor CHNS analyzer. Thermo gravimetric analysis (TGA) of waste tyres was carried out using TGA/DTG-60 at a rate of 20°C/min in air atmosphere from room temperature up to 600°C. to know the decomposition temperature or to find out the range of maximum degradation temperature. Functional group composition analysis of pyrolytic oil was carried out using Fourier Transform Infrared spectroscopy (FT-IR) analyzer (Perkin Elmer RX) in range 400-4000 cm⁻¹with 8 cm⁻¹ resolution.

3. Results and Discussion

3.1. Element Analysis of Bio-Oils

The Element Analysis of obtained oil from scrape tire are given in Table 1. As can be seen from this table, derived oils contain less oxygen than the scrap waste tyre. The significant decrease in oxygen content of the derived oil is important contrasted with the original feedstock on the grounds that the high oxygen content is not attractive for the production of transport fuels. Further comparison of the H/C ratios with conventional fuels shows that the H/C ratios of the utilized tire oils got via catalyst are similar to those of petroleum diesel oil.

Table 1. Element analysis of waste tyre and pyrolytic oil.

	waste tire	Pyrolytic oil without catalyst	Pyrolytic oil via alumina catalyst	Pyrolytic oil Via zeolite Jo	petroleum diesel oil
Carbon (C)	81.48	84.48	85.18	86.22	87.2
Hydrogen (H)	7.24	10.10	11.21	11.96	13.02
Nitrogen (N)	0.41	1.11	1.21	0.97	0.4
Sulphur (S)	1.66	0.93	0.91	0.88	-
Oxygen (O)	4.03	2.27	1.23	1.11	-
H/C	1.06	1.42	1.34	1.38	1.40

3.2. Thermo Gravimetric Analysis

TGA analysis demonstrates the decomposition behaviors during heating or it is characterized as a thermal analysis

method technique which explores the mass change of sample as a component of temperature and time. From the figure 1, it predicts that two phase weight losses were watched. At initial stage first stage decomposition happen

from 250-380°C which might be because of the loss of oils, plasticizers and additives present in the tyre [19]. This is followed by second phase of decomposition treated as active pyrolytic zone from 380-550°C which includes the continuous cracking and rapid decomposition of the other tyre parts, for example, NR, SBR [10, 20]. Amid the second stage, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains might be broken and some little gaseous molecules are produced. Accordingly, the bigger molecule decomposes to smaller molecules in the form of gas phase. At that point after 550°C the molecule contains just fixed carbon and constant weight of ash content. Similarly many researchers reports were found that the thermal decomposition begins at ~250°C, there take after two major losses of weight during the main devolatilization, and Pyrolysis is basically complete by 550°C above which there is essentially no further weight reduction [11, 14, 16].

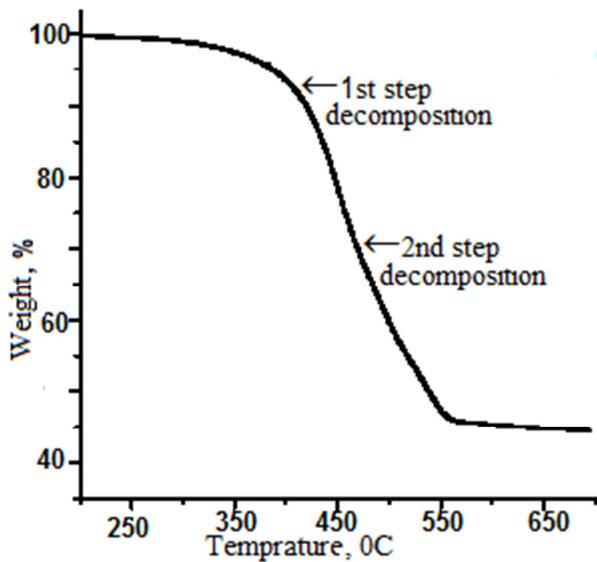


Figure 1. Thermo Gravimetric Analysis of waste tyre.

3.3. Effect of Catalyst Ratio on the Pyrolysis Yields

The utilized tyre samples were pyrolysed to decide the impact of catalyst ratio (10%, 15%, 25% and 35%) on the pyrolysis derived oil. The outcomes are given in Figure 2, 3. The pyrolysis derived oil increased as the catalyst ratio increased. The obtained oil from the scrap tyre, which was 42.48% without catalyst, achieved the maximum value of 49.32% on utilizing activated alumina catalyst at 15% by weight. The outcomes got with zeolite Jo, another catalyst, demonstrate that the highest obtained oil is 51.54% on utilizing this catalyst at 15% by weight. The gas product for these two catalysts smoothly expanded contrasted with the non-catalytic pyrolysis. The gas, got as 12.57% without catalyst, expanded to 14.23% with activated alumina (35% w/w) and expanded to 15.12% with zeolite Jo (35% w/w) as catalysts. Pyrolysis char qualities did not change essentially in samples by using different catalyst ratios. The two catalysts have critical impacts in the perspective of

expanding the bio-oil yield when it is contrasted with non-catalytic case

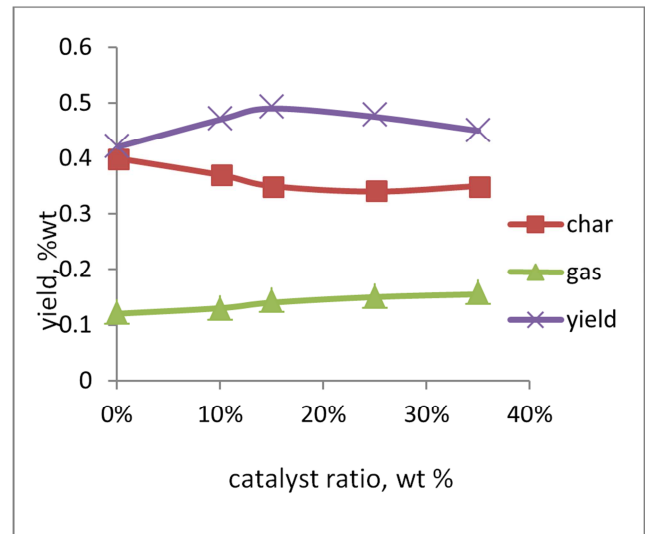


Figure 2. The change in the yields obtained from waste tier on alumina catalyst (pyrolysis temperature of 550°C, heating rate of 15°C/min, nitrogen flow rate of 150 ml/min).

3.4. Physical Properties of the Pyrolytic Oil

In table 2. fuel properties of derived oil got from pyrolysis of waste tyre, demonstrates that density of the tyre oil without catalyst was found more than that of petroleum diesel, while the density of pyrolytic oil with catalyst Pyrolysis less than that of tyre oil and similar to that of petroleum diesel. According to [10, 21], low viscosity shows the positive quality in the handling and transporting of the fuel oil. The obtained flash point was low when contrasted with petroleum diesel and pyrolytic oil derived with or without catalyst. But it was more than that of gasoline. The low flash points of the tyre-derived oil are not surprising since the product fuel represent unrefined liquids with a mixture of components having a wide distillation range [11, 15].

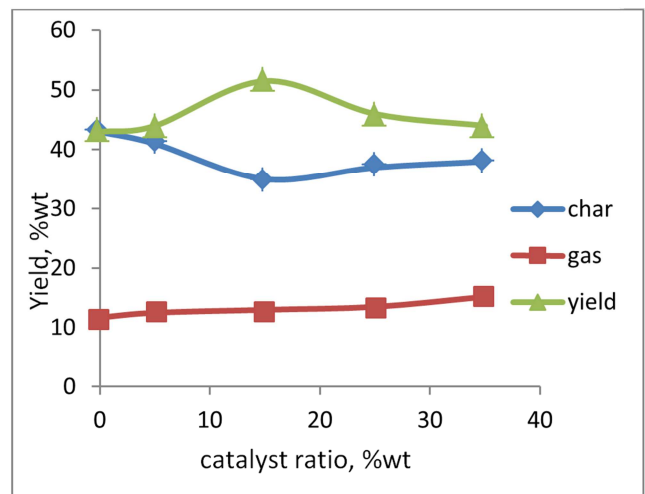


Figure 3. The change in the yields obtained from waste tier on Zeolite Jo (pyrolysis temperature of 550°C, heating rate of 15°C/min, nitrogen flow rate of 150 ml/min).

The sulphur content was slightly higher than that of petroleum diesel and it is very like to light fuel oil Which is typically around 1.3-1.5 wt% clarified by [15, 21]. The oil produced consisting of different fraction in the boiling range of 82-356°C which is to some degree like diesel. The important requirements for diesel fuel are its ignition quality, viscosity, and sulfur contents. In this manner, the pyrolytic oil require preliminary treatments such as filtration, desulphurization, and hydro treating to be utilized as fuels

The treated pyrolysis oil could be used directly as fuel oils or mixed with diesel fuels, which will reduce the viscosity and, increase the pH value and flash point of the resulting blends. Consequently, the atomization will be improved, ensuring a complete burnout of the fuel [18]. In light of its fuel properties, tire-derived pyrolytic oil might be considered as a valuable component for use with automotive diesel fuels. Moreover, the fuel oil may be directly used as fuels for industrial furnaces and power plants. [10, 22, 23].

Table 2. Physical properties of pyrolytic oil.

Fuel Properties	pyrolytic oil without catalyst	pyrolytic oil via Alumina catalyst	pyrolytic oil via zeolite Jo	Diesel fuel
Density at 20°C, Kg/m ³	911.7	862.8	858.6	860
K. Viscosity at 40°C in mm ² /s	4.6	3.9	3.6	3.4
Flash point, °C	50	55	56	60
Pour point, °C	-48	-45	-44	-40
Heat Value, MJ/Kg	43.47	45.5	48.3	48
Sulphur content, %	1.13	0.37	0.34	0.2
Conradson Carbon Residue, %	0.62	0.63	0.56	0.3
Distillation Range, °C	82-356	101-337	107-342	180 - 340
Diesel index	42.4	50.4	52.1	55.5
Cetane number	45	45	48	54

Table 3. FT-IR Analysis of tyrepyrolytic oil.

Functional groups	Wave length range		
	uncatalysed Pyrolysis oil	Alumina catal. Pyrolysis oil	Zeolite Jo catal. Pyrolysis oil
C-H	2955.67		
C-H Aldehyde	2724	2832	2898
C=O	1665	1666	1679
C=C Alkane+N-H bend	1634	1626	1628
C-H Phenyl ring Substitution	1602	1602	1601
C-H alkane	1460	1457	1460
C-H alkane	1367	1365	1365
C-N Amines	1290	1288	1282
C=O Alkene	1148	1152	1148
C-H Alkene	957	957	957
C-H Alkene + Phenyl Ring Substitution	808	805	806

3.5. FT-IR Analysis

The FT-IR analysis of the oil indicates that, the uncatalysed pyrolysis bio-oil shows the presence of oxygenated groups. For instance, peaks representing C=O extending vibrations between 1665 and 1150 cm. In any case, these oxygenated peaks are likewise present in the catalysed pyrolysis bio-oils recommending that the catalyst does not completely remove the oxygenated species, as as has just been appeared by the huge oxygen content in the bio-oils [10]. Table 3. also shows that, Representatives of nonoxygenated compounds were also present in the catalysed oils. Analysis of the oil shows that the functional group present mainly aromatics groups alkanes, alkenes, ketones and aldehydes, all of which have been recognized in the oil got from pyrolysis of tyres by other researchers [12,, 24, 25]. For example, the C–H extending vibrations in the vicinity of 2724 and 3000 cm and C–H deformation vibrations in the vicinity of 1367 and 1460 cm show the presence of the functional groups –CH₃, –CH₂ and –CH which are normal for alkane groups. The adsorption peaks between 808 and 957 cm and 1148 and 1602 cm are characteristics of single ring aromatic compounds and

polycyclic aromatic compounds.

4. Conclusion

The effect of catalyst on the product distribution demonstrates that observed that, uncatalysed

Pyrolysis, decomposition was incomplete, with increase char yields and decrease in liquid and gas yield. while, at catalysed Pyrolysis, secondary cracking reaction takes place, in result, an increase in gaseous and bio-oil products is observed, the maximum bio-oil obtained from Pyrolysis of waste tyre via catalyst were found as 51.54% on using catalyst, while this value was 42.48%, without catalyst. The oxygen contents were also reduced in pyrolytic oil by when use catalysts compared with bio oil obtained without catalyst.. FT-IR study on the pyrolytic oil shows that the oil obtained from catalysed Pyrolysis of waste tyre has same functional groups as compared with oil obtained from waste tyre without catalyst.

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