Bio Oil Production by Thermal and Catalytic Pyrolysis of Waste Tires

Dunya Ahmed Khalaf¹, Zaidun Naji Abudi²*, Saadi Muhammed Dhaher²

¹ Environmental Engineering Department, College of Engineering, Mustansiriayah University, Baghdad, Iraq
² Environmental Research, University of Technology, Baghdad, Iraq
* Corresponding author’s e-mail: zaidun.naji77@uomustansiriyah.edu.iq

ABSTRACT
In this study, pyrolysis of shredded waste tire was carried out thermally and catalytically in a fixed bed reactor. Thermal pyrolysis was performed at temperatures of 330 °C, 430 °C, 530 °C, and 630 °C under Ar. flow rate of 0.5 L/min as a carrier gas and retention time of 15 min catalytic pyrolysis was carried out at temperature of 530 °C. The effects of temperature and two types of catalysts (CaCO₃ and SiO₂/Al₂O₃) were studied on the yield of pyrolysis products. Fourier transform infrared spectroscopy (FTIR) and Gas chromatography mass spectrometry (GC-MS) analysis for the oil products that were obtained by thermal and catalytic pyrolysis at 530 °C for chemical characterization. Oil, solid, and gas products yield by thermal pyrolysis at 530 °C were 50 wt. %, 35.6 wt. %, and 14.4 wt. % respectively, when the CaCO₃ catalyst was used, the products distribution was 52 wt. %, 38.5 wt. %, and 9.5 wt. % respectively. While using SiO₂/Al₂O₃ the pyro oil, and char, and gas were decreased to 47 wt. %, 38 wt. %, and 15 wt. % respectively. The chemical composition of pyrolysis oil mainly included hydrocarbons compounds, predominantly Limonene which was represented by Cyclohexene, 1-methyl-4-(1-methylethenyl).

Keywords: Waste tire, pyrolysis, catalyst, limonene

INTRODUCTION
Human activities influence the environment through production of waste and discarding it in some way [Abdelbasir, 2021]. One of these production wastes includes vehicle tires [Ruiz et al., 2018]. They are inert materials, non-biodegradable, and very difficult to treat [Toteva and Stanulov, 2021]. The life period of tires in a landfill ranges between 80 and 100 years, [Martinez et al., 2013]. Therefore, waste tire landfilling increased the community concerns and becomes a less acceptable choice, reclaimed waste tires can be combusted to recover energy, and the materials can be recycled [Feraldi et al. 2013]. Solid waste management has been progressed through the sustainability and the circular economy concepts from the simple disposal to recycling and recovery [Iqbal et al., 2020]. All over the world, scientists are researching for new technologies for fuel production from waste [Suchocki et al., 2020]. The pyrolysis process is one of the best techniques for handling the waste tire in solid waste management practice [Shah et al., 2017]. Conversion of waste tires to fuel by pyrolysis process provides an alternative method for managing end-of-life tires [Quaicoe et al., 2020].

One of these products is tire pyrolysis oil (TPO) which is suitable for use as alternative combustion fuel in the diesel engine [Yaqoob et al., 2021], and as source of a valuable chemical derivatives, such as limonene which has beneficial properties in medicine [Januszewics et al., 2020]. In turn, the pyrolysis gas is suitable as hydrogen, and manufacturing fuel [Sathiskumar and Karthikeyan, 2019].

This technology shows minimization of the threat on public health, and decreased the levels of dangerous substances in released gases, has low costs of operating, and has no need for collecting waste separately [Rasheva et al., 2020]. Despite the high efficiency of this technology for bio oil production [Mikuliski et al., 2021] it is influenced by certain limitations, involving the high temperature required, sulfur content which is the main impurity.
found in the oil product [Efeovbokhan et al., 2020], high content of oxygen, high viscosity, high acidity, and low calorific value compared with petroleum [Zhou et al., 2017]; hence, catalytic pyrolysis is an alternative to enhance the products quality, and the process selectivity [Arabiourrutia et al, 2020].

Catalysts, such as acid and base types, were used in the pyrolysis process for this purpose, and for minimizing the content of sulfur compounds [Dick et al., 2020] also to increase the aromatic compounds content in oil product [Lewandowski et al., 2019]. The use of the catalytic pyrolysis for recycling waste rubber is beneficial from the economic and environmental standpoint [Muhammed et al., 2021]. The main aim of this project is the safe disposal of waste tires through converting them into an alternative fuel, by using thermal and catalytic pyrolysis processes in a fixed bed reactor made of stainless steel, investigating the effect of temperature and catalysts on the quality and quantity of the pyrolysis oil product.

MATERIAL AND METHOD

Materials

Waste tire composting a mixture of different tire types (truck, passenger, etc.) with particle size of 10-20 mm with separation of steel from rubber was used as a raw material, calcium carbonate (CaCO$_3$), and silica- alumina (SiO$_2$ / Al$_2$O$_3$) were used as catalysts in the pyrolysis process.

Experimental work

The pyrolysis system of waste tires was designed to consist of fixed bed reactor, electrical furnace, and condenser. A fixed bed reactor was made of stainless steel (height: 22 cm, diameter: 13.2 cm) having three openings at the top for (flow gas inert, thermocouple, and third for connecting the condenser by it) provided with a stirrer in the middle of the reactor to ensure continuous stirring and uniform distribution of heat, the reactor vertically placed inside an electrical furnace, the dimensions of which are: height: 36 cm, long: 55 cm, wide: 50 cm. It was covered with a loop of an electrical heater, insulated by metal box provided with heat insulating bricks inside it, and externally controlled temperature to achieve the desired temperatures with a maximum of 900 °C. The temperature control on the front of electric board sets the temperature the reactor, while the thermocouple was fixed inside the reactor with outside censer to set the temperature for the pyrolysis process. Figure 1 shows the schematic diagram of pyrolysis system.

First, a thermal pyrolysis of waste tire rubber was examined, about 100 g of sample was used in every run to be heated in the reactor, subjected to pyrolysis temperatures of 330 °C, 430 °C, 530 °C, and 630 °C, under inert gas (argon) with flow rate (GFR) of 0.5 L/ min, heating rate (HR) of 20 °C / min, and retention time (RT) of 15 min, the pyrolytic oil was obtained by condensation of the organic volatile released through

![Figure 1. Schematic diagram of waste tire pyrolysis system](image-url)
heating the raw material, when the temperature inside the reactor reached 300 °C the feedstock began vaporizing, and the organic vapors passing through the condenser were converted to a liquid phase, which is called pyro-oil. It was collected into a flask fixed at the end of the condenser. The solid residue that undecomposed was collected from the vessel at the end of each run. Each run ended after process completion (liquid product) stopped distilling from condenser, and after waiting the system to cool down.

The yields were calculated based on the equations (1), (2), and (3) shown below [Singh et al., 2019]:

\[
\text{Oil yield} (\%) = \frac{\text{mass of oil obtained}}{\text{total mass of feed input}} \times 100 \tag{1}
\]

\[
\text{Char yield} (\%) = \frac{\text{mass of solid obtained}}{\text{total mass of feed input}} \times 100 \tag{2}
\]

\[
\text{Gas yield} (\%) = 100 – \text{oil yield} (\%) – \text{char yield} (\%) \tag{3}
\]

Bio oil characterization

The chemical characterizations of the pyrolysis oil products were analyzed by gas chromatography (GC) (GC-MSS QP 2010 plus, SHIMADZU) using capillary column type HP-5 (32 m x 0.25 mm and 0.25 µm thicknesses) with flame ionization detector (FID) that operated at 300 °C. Fourier Transform Infrared (FTIR) technique (IRAffinity-1- SHIMADZU) was used to classify the functional groups of bio-oil, depending on the infrared frequency absorption ranges of 4000-500 cm⁻¹ wavenumber which is plotted versus intensity.

RESULTS AND DISCUSSION

Effect of temperature on the yield of pyrolysis products

The product yields from pyrolysis used tire with particle size in the range of 10-20 mm, with RT of 15 min were shown in Table 1, and Figure 2. It reveals that when the pyrolysis temperature was increased from 330 °C to 630 °C, the obtained yield of pyrolysis oil was increased from 33.5 wt. % to maximum value of 51.7 wt. % at 630 °C consequently, the obtained pyrolysis residue was decreased from 57.8 wt. % to 32 wt. %.

In turn, pyro-gas, which was counted as the difference between sample weight and the total weight of distilled oil and the residue weight, increased linearly from 8.7 wt. % at a temperature of 330 °C to 16.3 wt. % at 630 °C. The increases of oil yield, and the reduction of solid yield with the increase of temperature is in agreement with [Osayi et al., 2018]. In their investigation of waste tire thermal pyrolysis at temperatures ranging from 350 °C to 750 °C, they found that the optimum temperature for maximum oil yield was at 600 °C, HR of 15 °C by using feed particle size of 6 mm. In addition, [Yazdani et al., 2019] who used pyrolysis temperature ranging from 500 °C to 800 °C, and gained maximum oil yield of 44 wt. % at 550 °C. The increasing gas yield along with temperature is in agreement with [Alias & Rafee, 2020], in their study of waste tire pyrolysis at temperature from 300 °C to 500 °C.

From the previous results it was concluded that the optimum pyrolysis temperature that will be used in the catalytic pyrolysis is 530 °C.

Table 1. Yield of pyrolysis products at various temperatures

| Temperature °C | Oil wt. % | Solid wt. % | Gas wt. % |
|----------------|-----------|-------------|-----------|
| 330            | 33.5      | 57.8        | 8.7       |
| 430            | 40.9      | 47          | 12.1      |
| 530            | 50        | 35.6        | 14.4      |
| 630            | 51.7      | 32          | 16.3      |
because of the maximum possible of the production of pyro oil was achieved at temperature of 530 °C; increasing temperature higher than 530 °C shows no significant difference in mass.

**Effect of catalysts on the yield of pyrolysis products**

The product yields obtained from the two types of catalyst could be easily compared for equivalent amounts of (1) % mixing ratio of catalysts at pyrolysis temperature of 530 °C, GFR of 0.5 L/min, HR of 20 °C/ min, and constant retention time of 15 min. The results were shown in Table 2, and Figure 3. The results show that the higher yield of liquid, solid products, and lesser gas yield were gained by the CaCO₃ catalyst which were 52 wt. %, 38.5 wt. %, and 9.5 wt. % respectively. While using the SiO₂/Al₂O₃ catalyst, the oil product decreased to 47 wt. %; on the other hand, it caused increase in solid and gas products to 38, and 15%, respectively. The increased gas yield when using SiO₂/Al₂O₃ is in agreement with [Zhang et al., 2017].

A few studies used CaCO₃ and SiO₂/Al₂O₃ as catalysts in tire pyrolysis under closed operation condition of this study, [Shah et al., 2008] used CaCO₃ as a catalyst in pyrolysis of tires with particle size ranging of 5-10 mm by using a batch reactor at 350 °C, oil, char, and gas products were 32.2 wt. %, 32.5 wt. %, and 35.2 wt. % respectively. [Mabood et al., 2010] used 1 g of CaCO₃ at 350 °C obtaining oil, char, and gas products of 30.27 wt. %, 38.73 wt. %, and 31 wt. % respectively. [Ahoor et al., 2014] used 0.5 % of SiO₂/Al₂O₃ catalyst at pyrolysis temperature of 400 °C their oil, solid, and gas product yields were 14.8 wt. %, 80.2 wt. %, and 5 wt. % respectively. These contrasts in products yield may be due to the low temperatures which they used that caused incomplete conversion, and difference of catalyst ratios that they used.

**Pyrolysis oil characterization**

**Gas chromatography (GC-MS)**

The GC-MS of the investigated three samples displayed that they are significantly different in their chemical compositions. Table 3 shows the compounds determined and the area percentage for the identified peak. In the data it is interesting

### Table 2. Comparison between products yield from thermal and catalyst pyrolysis

| Operation condition | Yields wt. % | Thermal pyrolysis | Catalyst pyrolysis |
|---------------------|-------------|-------------------|-------------------|
|                     |             |                   | CaCO₃             | SiO₂/Al₂O₃         |
| 530 °C 0.5 L/min of Argon | Oil         | 50                | 52                | 47                |
| RT of 15 min        | Solid       | 35.6              | 38.5              | 38                |
| With 1% catalyst    | Gas         | 14.4              | 9.5               | 15                |
that tire pyrolysis oils are a complex mixture of organic compounds of C\textsubscript{8}–C\textsubscript{24} there are quite many compounds in pyrolysis tire oils that the peak areas are very low, especially in thermal cracking, as shown in Table 4. The pyrolysis oil obtained by thermal pyrolysis has the most apparent products, with peak areas higher than 1%, which are o-xylene, benzene, Cyclohexene, 1-methyl-4-(1-methylene)-, Pentene, and di (cyclohexyl methyl) ester. The greatest peak was to Cyclohexene, 1-methyl-4-(1-methylene) C\textsubscript{10}H\textsubscript{16}, it was 28.9%. Moreover, thermal pyrolysis gave a high value of oxygenated compounds which is around 33.62%, as shown in Table 3 that was represented by sulfur compounds as esters, such as C\textsubscript{14}H\textsubscript{28}O\textsubscript{3}S, C\textsubscript{18}H\textsubscript{36}O\textsubscript{3}S, C\textsubscript{8}H\textsubscript{18}O\textsubscript{2}S, C\textsubscript{11}H\textsubscript{22}O\textsubscript{3}S and etc. Sulfur is added to tires during the vulcanization process to improve the product stability, hardness, and heat resistance, making it more useful for industrial applications [Muenpol and Jitkarnka, 2016]. The nitrogenated and oxygenated compounds exist in tire pyrolysis oil such as the quinoline and [2-Piperidinone, N-[4-bromo-n-butyl]-] but in small amounts, as shown in Table 4. In turn, catalytic pyrolysis by using CaCO\textsubscript{3} and SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} as a catalyst decreased the amount of oxygenated compounds to 12.49%, 1.61%, respectively, as shown in Table 3 decarbonylation and deoxygenation reactions took place when using base catalysts [Kabir and Hameed, 2017].

Using CaCO\textsubscript{3} as catalyst, the yield of oil is enhanced and the selectivity of product is improved. Table 3 displays the increase in the productivity of cycloalkane to 51.9% represented by [Cyclohexene, 1-methyl-4-(1-methylene)-] and [Cyclopropane, 1-(5-hexenyl)-2-iodo]. Therefore, the increase in hydrocarbon percentage to 87.51% with other compounds such as alkenes, alkane and aromatic can be seen in Table 3.

The SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst promoted the selective liquid fraction. Table 3 shows sharp increase in cycloalkanes to 72.14% represented by [Cyclohexene, 1-methyl-4-(1-methylene)-], formulated by C\textsubscript{10}H\textsubscript{16} as apparent in (Table 6). The yield of hydrocarbon is drastically increased to 98.39% whereas Carboxylic acid, ketone, ester and alcohol disappear. The remarkable change in the yield of the organic fraction cycloalkanes may be associated with the surface area of the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of 137.41 m\textsuperscript{2}/g, which enhances the adsorption-desorption reaction and the highest purity of the material, because it was designed as a selective catalyst for the pyrolysis oil. In addition, the increase in aromatics to 15.24% may be attributed to the increase in decomposition of styrene-butadiene rubber. Table 3 displays that alkenes are decreased from 17.92% in thermal pyrolysis and 17.45% CaCO\textsubscript{3} pyrolysis to 8.79% in SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} pyrolysis. This result is interesting since the existence of alkenes in fuel is supposed to be limited because of their tendency towards polymerization and oxidation which produces harmful deposits to the engine [Mariusz et al. 2020].

| Compositions     | Thermal pyrolysis | Catalytic pyrolysis |
|------------------|-------------------|---------------------|
|                  | Peak Area%        | CaCO\textsubscript{3} | SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} |
| Alkanes          | 3.39              | 2.32                | 0.64 |
| Alkenes          | 17.92             | 17.45               | 8.78 |
| Cycloalkane      | 29.43             | 51.9                | 72.14 |
| Cycloalkene      | 6.01              | 4.11                | 2.96 |
| Aromatic         | 9.38              | 11.1                | 15.24 |
| Ester            | 18.34             | 2.45                | ---  |
| Carboxylic acid  | 0                 | 1.35                | ---  |
| Ketone           | 4.09              | 1.75                | ---  |
| Alcohol          | 8.04              | 1.43                | ---  |
| Others           | 3.4               | 6.14                | 0.24 |
| Total            | 100               | 100                 | 100  |
| Hydrocarbon      | 66.38             | 87.51               | 98.39 |
| Oxygenated       | 33.62             | 12.49               | 1.61 |
| Total            | 100               | 100                 | 100  |
| Peak | R. time | Compound name                                                | M. Formula   | Area % |
|------|---------|---------------------------------------------------------------|--------------|--------|
| 1    | 3.249   | Sorbic acid vinyl ester                                       | C_{12}H_{16}O | 0.37   |
| 2    | 3.414   | cis-1,2-Divinylcyclobutane                                    | C_{12}H_{12}  | 0.16   |
| 3    | 3.782   | Ethylbenzene                                                 | C_{12}H_{10}  | 0.34   |
| 4    | 3.83    | 2,4-Hexadiene, 2,3-dimethyl                                  | C_{14}H_{14}  | 0.4    |
| 5    | 3.923   | o-Xylene , Benzene                                            | C_{10}H_{10}  | 3.35   |
| 6    | 4.272   | 1-Hexen-4-ol                                                | C_{12}H_{20}O | 0.71   |
| 7    | 4.632   | Benzene                                                      | C_{12}H_{12}O | 0.1    |
| 8    | 4.806   | 5,10-Pentadecadienoic acid                                   | C_{12}H_{20}O | 0.14   |
| 9    | 5.072   | 1,5-Heptadiene                                               | C_{10}H_{16}  | 0.52   |
| 10   | 5.357   | 7-Propylidene-bicyclo                                        | C_{16}H_{16}  | 3.03   |
| 11   | 5.468   | 2,4-Nonadiyne                                                | C_{12}H_{12}  | 1.16   |
| 12   | 5.574   | 1,5-Heptadiene                                               | C_{10}H_{16}  | 0.54   |
| 13   | 5.642   | 1-Hexene                                                     | C_{10}H_{20}  | 0.9    |
| 14   | 5.772   | 2,6-Octadien-1-ol, 2,7-dimethyl                              | C_{12}H_{12}O | 1.44   |
| 15   | 5.854   | 1,6-Octadiene, 2,6-dimethyl                                  | C_{12}H_{16}  | 1.03   |
| 16   | 6.001   | 6,10-Dodecadien-1-yn-3-ol                                     | C_{12}H_{20}O | 2.52   |
| 17   | 6.1     | 5-Pentadecen-7-yn-7(9)-                                      | C_{15}H_{15}  | 0.39   |
| 18   | 6.25    | Cyclohexene, 1-ethyl-6-ethylidene                             | C_{10}H_{15}  | 0.76   |
| 19   | 6.533   | Cyclohexene                                                  | C_{10}H_{18}  | 1.96   |
| 20   | 6.661   | Cyclohexene, 1-methyl-4-(1-methylethenyl)-                    | C_{12}H_{18}  | 28.9   |
| 21   | 6.773   | 1-Methylene-2-vinylcyclopentane                               | C_{12}H_{14}  | 0.37   |
| 22   | 7.037   | 1-Pentene                                                    | C_{16}H_{16}  | 1.76   |
| 23   | 7.45    | 2,7-dimethyloct-7-en-5-yn-4-y1 ester                         | C_{16}H_{20}O | 0.33   |
| 24   | 7.578   | Cyclohexene                                                  | C_{10}H_{15}  | 1.49   |
| 25   | 7.674   | Benzene                                                      | C_{12}H_{12}  | 1.32   |
| 26   | 7.836   | 1-Pentene                                                    | C_{16}H_{16}  | 1.41   |
| 27   | 8.463   | Bicyclo[3.1.0]hex-2-ene, 4,4,6,6-tetramethyl-                 | C_{16}H_{18}  | 0.38   |
| 28   | 10.032  | Benzothiazole                                                | C_{12}H_{12}NS| 2.05   |
| 29   | 10.41   | 1H-Indene, 1,1-dimethy                                        | C_{12}H_{12}  | 0.42   |
| 30   | 10.553  | cyclohexylmethyl heptyl ester                                 | C_{14}H_{18}O, | 1.38   |
| 31   | 10.816  | 1-Heptene                                                    | C_{16}H_{16}  | 0.38   |
| 32   | 10.928  | Nonane                                                       | C_{16}H_{14}  | 0.45   |
| 33   | 11.058  | Heptane                                                      | C_{16}H_{16}  | 1.13   |
| 34   | 11.713  | di(cyclohexylmethyl) ester                                   | C_{16}H_{20}O | 3.31   |
| 35   | 12.195  | Benzene                                                      | C_{12}H_{12}  | 0.7    |
| 36   | 12.254  | 1-Hexene                                                     | C_{12}H_{12}  | 2.73   |
| 37   | 12.745  | 1H-3a,7-Methanoazulene                                        | C_{12}H_{16}  | 1.22   |
| 38   | 12.908  | 1-(2-Isopropylcyclopropyl)-2-methyl-1-propanol                | C_{12}H_{16}O | 1.15   |
| 39   | 13.083  | 3,5,9-Undecatrien-2-one                                      | C_{12}H_{16}O | 0.89   |
| 40   | 13.19   | Quinoline                                                    | C_{12}H_{16}N | 0.44   |
| 41   | 13.366  | 3-Cyclohexene-1-carboxaldehyde                               | C_{12}H_{16}O | 1.01   |
| 42   | 13.758  | Nonane                                                       | C_{12}H_{16}  | 0.99   |
| 43   | 13.907  | 3-Methyl-trans-3a,4,7a-tetrahydroindane                      | C_{16}H_{18}  | 0.55   |
| 44   | 14.063  | 3-Cyclohexene-1-carboxaldehyde                               | C_{12}H_{16}O | 0.79   |
| 45   | 14.418  | Naphthalene                                                  | C_{14}H_{14}  | 0.66   |
| 46   | 15.012  | cyclohexylmethyl undecyl ester                               | C_{14}H_{20}O | 1.31   |
| 47   | 15.228  | 1,2-Benzenediol,                                             | C_{18}H_{18}ClO, | 0.12 |
| 48   | 15.5    | 4-Heptanone                                                  | C_{10}H_{18}O | 0.57   |
Table 4. Cont. GC-MS analysis of tire pyrolysis oil of thermal pyrolysis

| Peak | R. time | Compound name | M. Formula | Area % |
|------|---------|---------------|------------|--------|
| 49   | 16.061  | cyclohexylmethyl heptyl ester | C_{19}H_{20}O_3S | 3.15   |
| 50   | 16.266  | Tridecane | C_{13}H_{28} | 0.6    |
| 51   | 16.527  | 1-Pentene | C_{10}H_{20} | 1.07   |
| 52   | 17.077  | Propane, 2-[(1,1-dimethylethyl)sulfonyl]-2-methyl-1-butene | C_{13}H_{20}O_3S | 0.22   |
| 53   | 17.994  | 1,5-Heptadiene, 2,6-dimethyl | C_{16}H_{20} | 0.44   |
| 54   | 18.102  | 1,5-Heptadiene, 2,8-dimethyl | C_{16}H_{20} | 0.36   |
| 55   | 18.592  | 2-Piperidinone, N-[4-bromo-n-butyl]- | C_{14}H_{15}BrNO | 0.33   |
| 56   | 18.813  | Cyclohexane | C_{16}H_{12}O | 1.6    |
| 57   | 19.24   | 1-Pentene | C_{10}H_{18} | 0.8    |
| 58   | 19.747  | cyclohexylmethyl isobutyl ester | C_{13}H_{20}O_3S | 2.68   |
| 59   | 20.158  | 1-Pentene | C_{10}H_{18} | 0.86   |
| 60   | 22.104  | cyclohexylmethyl heptyl ester | C_{17}H_{30}O_3S | 1.09   |
| 61   | 22.476  | 3-tridecy1 ester | C_{19}H_{32}O_3S | 0.69   |
| 62   | 22.941  | 3-Octyne-2,5-dione | C_{10}H_{14}O | 1.59   |
| 63   | 23.312  | Cyclopropanemethanol, alpha,-2-bis(1-methylethyl) | C_{12}H_{20}O | 1.06   |
| 64   | 24.193  | 2-ethylhexyl isobutyl ester | C_{13}H_{20}O_3S | 0.27   |
| 65   | 24.999  | cyclohexylmethyl heptadecyl ester | C_{25}H_{30}O_3S | 0.86   |
| 66   | 25.341  | di(cyclohexylmethyl) ester | C_{14}H_{22}O_3S | 0.27   |
| 67   | 25.755  | cyclohexylmethyl heptadecyl ester | C_{25}H_{30}O_3S | 2.17   |
| 68   | 26.091  | 2,4,4-Trimethyl-1-pentanol | C_{10}H_{18}O | 0.53   |
| 69   | 26.576  | Butanal, 4-[(tetrahydro-2H-pyran-2-yl)oxy]- | C_{12}H_{20}O | 0.51   |
| 70   | 28.813  | cyclohexylmethyl hexyl ester | C_{14}H_{22}O_3S | 0.46   |

Table 5. GC-MS analysis of tire pyrolysis oil of Catalytic pyrolysis by CaCO_{3}

| Peak | R. time | Compound name | M. Formula | Area % |
|------|---------|---------------|------------|--------|
| 1    | 3.046   | 5-Cyano-1-pentene | C_{5}H_{4}N | 0.34   |
| 2    | 3.26    | 1,4-Pentadiene, 2,3,3-trimethyl | C_{10}H_{12} | 1.24   |
| 3    | 3.425   | Cyclohexene, 4-ethenyl | C_{10}H_{12} | 0.96   |
| 4    | 3.80    | Ethylbenzene | C_{10}H_{12} | 1.44   |
| 5    | 3.933   | o-Xylene | C_{10}H_{12} | 4.2    |
| 6    | 4.282   | 1,3,5,7-Cyclooctatetraene | C_{10}H_{8} | 1.66   |
| 7    | 4.641   | Benzenemethanol, alpha,-methyl-Alpha,-(1-methyl-2-propenyl)- | C_{10}H_{10}O | 0.13   |
| 8    | 4.818   | 5,10-Pentadecadien-1-ol | C_{15}H_{10}O | 0.27   |
| 9    | 5.082   | 7-Propylidine-bicyclo[4.1.0]heptane | C_{10}H_{18} | 1.08   |
| 10   | 5.365   | 1,5-Cyclooctadiene, 1,5-dimethyl | C_{10}H_{18} | 3.9    |
| 11   | 5.48    | Benzene, 1-ethyl-2-methyl- | C_{10}H_{12} | 1.49   |
| 12   | 5.587   | (22,42,6,6E)-2,6,8-Undecatriene | C_{16}H_{18} | 0.51   |
| 13   | 5.722   | Ethane, 1-cyclopropyl-2-(3-pyridinyl) | C_{10}H_{18}NO | 0.72   |
| 14   | 5.785   | 1,4-Hexadiene, 5-methyl-3-(1-methylethylidene) | C_{12}H_{18} | 1.8    |
| 15   | 5.864   | 1,6-Octadiene, 2,6-dimethyl, (Z) | C_{12}H_{18} | 1.39   |
| 16   | 6.011   | 1,5-Heptadiene, 2,3,6-trimethyl | C_{13}H_{18} | 2.88   |
| 17   | 6.261   | 1,5-Hexadiene, 2,5-dimethyl-3-methylene | C_{14}H_{18} | 1.12   |
| 18   | 6.538   | (+)-3-Carene, 2-(acetylmethyl) | C_{14}H_{18}O | 3.99   |
| 19   | 6.664   | Cyclohexene, 1-methyl-4-(1-methylethenyl) | C_{10}H_{14} | 49.52  |
| 20   | 6.782   | 1-Methylen-2-vinylcyclopentane | C_{12}H_{12} | 0.56   |
| 21   | 7.046   | 5,10-Pentadecadiyne, 1-chloro | C_{15}H_{22}Cl | 0.63   |
| 22   | 7.463   | 1-Pentane, 1-(4-methylphenyl) | C_{12}H_{20}O | 0.31   |
| 23   | 7.592   | Cyclohexene, 4-methyl-3-(1-methylethylidene) | C_{10}H_{14} | 1.15   |
### Table 5. Cont. GC-MS analysis of tire pyrolysis oil of catalytic pyrolysis by CaCO₃

| No. | Wavenumber | Compound Description                                                                                                 | Formula | Intensity |
|-----|------------|---------------------------------------------------------------------------------------------------------------------|---------|-----------|
| 24  | 7.686      | Benzene, (2-methylcyclopropyl)                                                                                       | C₁₀H₁₂  | 1.04      |
| 25  | 7.846      | Ethanone, 1,2-diphenyl                                                                                                | C₁₀H₂O  | 0.52      |
| 26  | 7.998      | 3-Methylbenzoic acid, 2-formyl-4,6-dichlorophenyl ester                                                             | C₁₅H₁₂Cl₂O₂ | 0.19     |
| 27  | 8.181      | Ethanone, 1-(4-methylphenyl)                                                                                        | C₁₀H₁₂O  | 0.1       |
| 28  | 8.332      | E-2-Methyl-5-(furan-3-yl)-pent-1-en-3-one                                                                           | C₁₅H₁₂O₂ | 0.1       |
| 29  | 8.475      | Benzene, 1-trifluoromethyl-4-(2-methoxybenzylxyloxy)-3-nitro                                                         | C₁₅H₁₂F₃NO₄ | 0.12     |
| 30  | 8.706      | 1H-Indene, 1-methyl                                                                                                | C₁₅H₁₆  | 0.53      |
| 31  | 9.325      | 2-Methyl-4-phenyl-2-trimethylsilyloxybutane                                                                          | C₁₅H₁₂OSi | 0.35     |
| 32  | 9.468      | 1H-Indene, 1-ethyl-2,3-dihydro-1-methyl                                                                           | C₁₅H₁₆ | 0.37      |
| 33  | 10.04      | 1,2-Benzisothiazole                                                                                                | C₁₅H₁₆NS | 1.31      |
| 34  | 10.42      | Oxazirane, 2-(dimethylethyl)-3-methoxy                                                                              | C₁₅H₁₆NO₂ | 1.05     |
| 35  | 10.56      | Octanoic acid, 2-methoxy-, methyl ester                                                                            | C₁₅H₂O₃ | 0.5       |
| 36  | 10.94      | Oxalic acid, butyl propyl ester                                                                                     | C₁₀H₂O  | 0.7       |
| 37  | 11.11      | Butanoic acid, 3-[(1-phenylethyl-2-propynyl)oxy]                                                                    | C₁₅H₁₂O₂ | 0.6       |
| 38  | 11.72      | 3-Butene-1,2-diol, 1-(2-furanyl)                                                                                     | C₁₅H₁₂O₂ | 1.03      |
| 39  | 12.21      | Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)                                                                        | C₁₅H₁₆ | 0.72      |
| 40  | 12.26      | 1-Hexene, 5,5-dimethyl                                                                                              | C₁₅H₁₆ | 0.93      |
| 41  | 12.42      | 1-Chloroundecane                                                                                                | C₁₅H₁₂Cl | 0.62      |
| 42  | 12.76      | Cyclopropane, 1-(5-hexeny)-2-iodo                                                                                   | C₁₅H₁₀I | 0.74      |
| 43  | 12.92      | 3,4-Octadiene, 7,7-dimethyl                                                                                        | C₂₃H₂₀S | 0.97      |
| 44  | 13.38      | Santoltriene                                                                                                       | C₁₅H₁₂S | 1.37      |
| 45  | 13.77      | Tetradecane, 1-iodo                                                                                                | C₁₅H₁₀I | 0.62      |
| 46  | 14.07      | 3,9-Dodecadiene                                                                                                   | C₁₅H₁₂  | 0.69      |
| 47  | 16.07      | 3-Pentenoic acid, 2,2,4-trimethyl                                                                                | C₁₅H₂O₂ | 0.75      |
| 48  | 16.28      | Tetradecane, 1-iodo                                                                                                 | C₁₅H₁₂I | 0.57      |
| 49  | 18.79      | Cyclohexene, 3-methyl-6-(1-methylthylidene)                                                                          | C₁₅H₁₄S | 0.65      |
| 50  | 19.75      | Sulfurous acid, cyclohexymethyl isobutyl ester                                                                       | C₁₅H₂O₃S | 0.65     |
| 51  | 22.94      | Cyclohexane, 1-bromo-3-methyl                                                                                       | C₁₅H₁₂Br | 0.51      |
| 52  | 25.01      | Acetic acid, trifluoro-, 2,2-dimethylpropyl ester                                                                   | C₁₅H₁₂F₂O₂ | 0.41     |

### Functional group scanning

The comparison of the main functional groups between thermal and catalytic cracking is shown in Figure 4. The FTIR spectrum shows a sharp medium peak that is ascribed to C=O stretch at 1635 cm⁻¹ which asserts the existence of alkenes and that confirmed in GC-MS analysis as shown in Table 3. In addition, broad medium peak between the wavenumber range 3250-3400 cm⁻¹, indicated the presence of nitrogen compounds which are represented by functional group N-H stretching. Table 4, Table 5 and Table 6 for GC-MS analysis confirmed the existence of nitrogen compounds in small amounts. Figure 4 shows broad medium peaks in the wavenumber range 500–600 cm⁻¹ which refers to the halogen compounds represented by carbon-bromine bond, carbon-iodine bond and carbon-chlorine bond all of them are stretching vibration mode. In turn, the small peaks as shown in Figure 4 at the wavenumber range 1250–2000 cm⁻¹ prove the presence of aromatic rings in the fractions of tire pyrolysis oil and are consistent with [Mariusz et al. 2020].

The characteristic vibrational range in (Table 7) displays sulfurous compounds from 1300–1440 cm⁻¹ as sulfoxide and sulfone derivatives. The pyrolysis oil produced from thermal cracking shows characteristic vibrational mode at 1415 cm⁻¹ for the S=O stretching for sulfuric compounds such as C₁₅H₂O₃S, C₁₅H₂O₃S, C₁₅H₂O₃S and C₁₅H₂O₃S, as shown in Table 3. The sulfur compounds production mechanisms vary according to the reactor temperature, the reactor type, the heating rate, and the length of treatment and the catalysts used [Toteva, 2021]. The benzothiazol compound, which is used as an accelerator in the tire industry, is responsible for the amount of sulfuric compounds generated.
Table 6. GC-MS analysis of tire pyrolysis oil of catalytic pyrolysis by SiO$_2$/Al$_2$O$_3$

| Peak | R. time | Compound name                      | M. Formula       | Area % |
|------|---------|------------------------------------|------------------|--------|
| 1    | 3.257   | 1-Cyclopropane                     | C$_8$H$_{14}$    | 0.76   |
| 2    | 3.422   | Cyclohexene                        | C$_9$H$_{12}$    | 0.5    |
| 3    | 3.792   | Ethylbenzene                       | C$_9$H$_{10}$    | 0.95   |
| 4    | 3.933   | Benzene                            | C$_{10}$H$_{16}$ | 5.53   |
| 5    | 4.283   | Benzenepropanoyl bromide           | C$_{10}$H$_{16}$BrO | 0.79   |
| 6    | 4.812   | Cyclopropane (2-methylenebutyl)     | C$_{10}$H$_{16}$ | 0.14   |
| 7    | 5.082   | 7-Propylidene-bicyclo[4.1.0]heptane| C$_{11}$H$_{16}$ | 0.59   |
| 8    | 5.363   | 1,5-Dimethyl cyclooctadiene        | C$_{15}$H$_{24}$ | 2.24   |
| 9    | 5.477   | Benzene                            | C$_{10}$H$_{16}$ | 1.27   |
| 10   | 5.578   | Tetracyclo[6.2.1.0(2,4).0(4,7)]undecane | C$_{13}$H$_{26}$ | 0.38   |
| 11   | 5.725   | 1-Heptene-3-yne                    | C$_{10}$H$_{16}$ | 0.46   |
| 12   | 5.838   | 1,5-Heptadiene, 2,5-dimethyl-3-methylene- | C$_{10}$H$_{18}$ | 0.91   |
| 13   | 5.86    | 1,6-Octadiene, 2,6-dimethyl-(Z)-   | C$_{10}$H$_{18}$ | 0.7    |
| 14   | 6.008   | 1,6,10-Dodecatriene, 7,11-dimethyl-3-methylene- | C$_{16}$H$_{26}$ | 2.01   |
| 15   | 6.258   | Cyclohexene, 3-(3-methyl-1-butanyl)-(E) | C$_{10}$H$_{18}$ | 0.36   |
| 16   | 6.547   | Benzene, 1-methyl-2-(1-methylethyl)  | C$_{10}$H$_{18}$ | 4.98   |
| 17   | 6.657   | Cyclohexene, 1-methyl-4-(1-methylethynyl) | C$_{10}$H$_{18}$ | 70.97  |
| 18   | 6.774   | 1,3-Cyclopentadiene, 1-(3-butylnyl) | C$_{10}$H$_{16}$ | 0.22   |
| 19   | 7.033   | 1-Pentene, 2,4,4-trimethyl-         | C$_{10}$H$_{16}$ | 0.26   |
| 20   | 7.401   | Cyclohexene, 1-ethyl-6-ethyldiene   | C$_{12}$H$_{22}$ | 0.22   |
| 21   | 7.589   | 1,5-Heptadiene, 2,5-dimethyl-3-methylene- | C$_{10}$H$_{18}$ | 1.18   |
| 22   | 7.685   | Benzene, 1-methyl-4-(1-methylethynyl) | C$_{10}$H$_{18}$ | 1.06   |
| 23   | 7.839   | Propane, 2-methyl-2-nitro           | C$_{12}$H$_{22}$NO$_2$ | 0.26   |
| 24   | 8.704   | 1H-Indene, 2,3-dihydro-4-methyl     | C$_{14}$H$_{12}$ | 0.41   |
| 25   | 9.324   | Benzene, 1-methyl-2-(1-methyl-2-propenyl)- | C$_{10}$H$_{16}$ | 0.12   |
| 26   | 9.467   | Benzene, 1-methyl-4-(1-methyl-2-propenyl)- | C$_{10}$H$_{16}$ | 0.18   |
| 27   | 10.043  | Benzothiazole                       | C$_{8}$H$_{11}$N$_2$S | 0.45   |
| 28   | 10.508  | 1H-Indene, 1,1-dimethyl             | C$_{10}$H$_{12}$ | 0.34   |
| 29   | 10.945  | Benzene, 1-ethoxy-4-[2-(4-pentylcyclohexyl)ethyl]- | C$_{15}$H$_{26}$O | 0.29   |
| 30   | 11.116  | Naphthalene, 2-methyl               | C$_{14}$H$_{16}$ | 0.34   |
| 31   | 11.717  | Methylphosphonic acid, dinonyl ester | C$_{15}$H$_{32}$O$_3$P | 0.43   |
| 32   | 12.209  | Benzene                            | C$_{8}$H$_{12}$ | 0.23   |
| 33   | 12.917  | 4-Nonene, 2,3,3-trimethyl-           | C$_{10}$H$_{24}$ | 0.21   |
| 34   | 12.986  | Pentobarbital                       | C$_{12}$H$_{21}$N$_2$O$_3$ | 0.27   |

in tire pyrolysis oil [Susa and Haydary 2014]. In catalytic cracking, the S=O bond disappeared, as shown in Figure 4, which indicates that the catalyst absorbs the sulfur existing in pyrolysis oil and these findings are consistent with [Demirbas et al. 2016]. They asserted that depending on the catalysis mechanism by using different types of catalysts. due to its basic natural which has a significant role in occurring desulfurization reaction [Ilikkilic and Aydin, 2011] and catalytic cracking by using SiO$_2$/Al$_2$O$_3$, the amount of sulfuric compound was 0.45%, represented by benzothiazole compound as shown in Table 3.

CONCLUSIONS

The implementation of the pyrolysis technique generally for municipal solid waste and particularly for waste tire is a good solution for reducing the environmental pollution and controlling the waste tire accumulation, as well as providing a new source of fuel. This study concluded that when increasing temperature from 330 °C to 630 °C, the oil and gas yields were increased linearly, while the yield of pyro- solid was decreased. Catalysts have a significant influence on the products yield and chemical compositions of oil.
product. Generally, the two catalysts improved the quality of oil product by using 1 wt. % of the CaCO$_3$ catalyst, the oil and char yields were maximized to 52 wt. %, and 38.5 wt. % respectively. Using the same ratio of the SiO$_2$/Al$_2$O$_3$ catalyst, the oil and char yield were decreased to 47 wt. %, 38, respectively, while the pyrolysis gas when using SiO$_2$/Al$_2$O$_3$ was higher than that when using CaCO$_3$. The hydrocarbon compounds were increased from 66.38% in thermal TPO to 87.51% by using CaCO$_3$, and 98.39% with the SiO$_2$/Al$_2$O$_3$ catalyst. The oxygenated compounds were decreased from 33.62% in thermal TPO to 12.49% by using CaCO$_3$, and 1.61% with the SiO$_2$/Al$_2$O$_3$ catalyst. Limonene is the dominant compound in pyrolysis oil which was obtained by both thermal, and catalytic pyrolysis, amounting to 28.9% by thermal pyrolysis, 49.52%, and 70.97% with CaCO$_3$, and SiO$_2$/Al$_2$O$_3$ respectively.

**REFERENCES**

1. Abdelbasir, S.M. 2021. Recycling, Management, and Valorization of Industrial Solid Wastes. Waste Recycling Technologies for Nano materials Manufacturing, 25–63.

2. Ahoor, A.H. & Zandi-Atashbar, N. 2014. Fuel production based on catalytic pyrolysis of waste tires as an optimized model. Energy conversion and management, 87, 653–669.

3. Alias, R. & Rafee, A.M. 2020. Characterization of liquid oil from pyrolysis of waste tire. Malaysian Journal of Chemical Engineering and Technology (MJET), 3(1), 62–68.

4. Arabiourrutia, M., Lopez, G., Artetxe, M., Alvarez, J., Bilbao, J., Olazar, M. 2020. Waste tire valorization by catalytic pyrolysis – A review. Renewable and Sustainable Energy Reviews, 129.

5. Demirbas, A., Al-sasi, B.O., Nizami, A. 2016. Environmental Effects Conversion of waste tires to liquid products via sodium carbonate catalytic pyrolysis. Energy sources, part A: recovery, utilization, and environmental effects, 38(16), 2487–2493.
6. Dick, D.T. & Agboola, O. 2020. Pyrolysis of waste tyre for high-quality fuel products: A review. AIMS Energy, 8(5), 869–895.

7. Efekovbokhan, V.E., Akinneye, D., Ayeni A.O., et al. 2020. Experimental dataset investigating the effect of temperature in the presence or absence of catalysts on the pyrolysis of plantain and yam peels for bio-oil production. Data Brief 31, 105804.

8. Feraldi, R., Cashman, S., Huff, M., Raahauge, L. 2013. Comparative LCA of treatment options for US scrap tires: material recycling and tire derived fuel combustion. Int J Life Cycle Assess 18, 613–625.

9. Guven, N., Gunes, A.N., & Yucedag, C. 2016. Energy Yield from Waste Tires Using Pyrolysis Method.

10. Iqbal, A., Liu, X., & Chen, G.H. 2020. Municipal solid waste: Review of best practices in application of life cycle assessment and sustainable management techniques. Science of the Total Environment, 138622.

11. Januszewicz, K., Kazimierski, P., Kosakowski, W., & Lewandowski, W.M. 2020. Waste tires pyrolysis for obtaining limonene. Materials, 13(6), 1359.

12. Martinez, J.D, Puy, N., Murillo, R., Garcia, T., Navarro, M.V., Mastral, A.M. 2013. Waste tire pyrolysis: A review. Renewable and Sustainable Energy Reviews, 179–213.

13. Kabir, G. & Hameed B.H. 2017. Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals. Renew Sustain Energy Rev, 70, 945–967.

14. Lewandowski, W.M., Januszewicz, K., & Kosakowski, W. 2019. Efficiency and proportions of waste tyre pyrolysis products depending on the reactor type – A review. Journal of Analytical and Applied Pyrolysis, 140, 25-53.

15. Mabood, F., Jan, M.R., Jabeen, F. 2011. Catalytic pyrolysis of waste inner rubber tube into fuel oil using alumina and calcium carbonate base catalysts. Journal of the Chemical Society of Pakistan, 33(1), 38–42.

16. Mariusz, W., Janus, R. & Lewandowski, M., 2020. Pyrolysis Oil from Scrap Tires as a Source of Fuel Components : energy & fuel, 34(5), 5917–5928.

17. Mikulska, M., Ambrosewicz-Walacik, M., Hunicz, J., Nitkiewicz, S. 2021. Combustion engine applications of waste tyre pyrolytic oil. Progress in Energy and Combustion Science, 85, 100915.

18. Muenpol, S., Jitkarnka S. 2016. Effects of Fe supported on zeolites on structures of hydrocarbon compounds and petrochemicals in waste tire-derived pyrolysis oils. J Anal Appl Pyrolysis, 117, 147–156.

19. Muhammad, R., Ali, Y., Messaddeq, Y., Martines, M.A.U., Naveed Umar, M., Khan, S.W., Riaz, A. 2021. Conditions Optimization and Physiochemical Analysis of Oil Obtained by Catalytic Pyrolysis of Scrap Tube Rubber Using MgO as Catalyst. Catalysts, 11(3), 357.

20. Ngxanga, S., 2016. Development of GC-MS methods for the analysis of tyre pyrolysis oils. Stellenbosch University.

21. Osayi, J.J., Iyuke, S., Daramola, M.O., Osifo, P., Van Der Walt, I.J., Ogbeide, S.E. 2018. Pyrolytic conversion of used tyres to liquid fuel: characterization and effect of operating conditions. Journal of Material Cycles and Waste Management, 1273–1285.

22. Pooja S., Kachhadiya P., Khsiria P. 2017. Pyrolysis of waste tires to fuel oil. ICCI. 2017.

23. Quaicoe, I., Souleymane, A.A., Kyeremeh, S.K., Appiah-Twum, H., & Ndur, S.A. 2020. Vacuum Pyrolysis of Waste Vehicle Tyres into Oil Fuel Using A Locally, Fabricated Reactor. Ghana Mining Journal, 20(1), 59–65.

24. Rasheva, V., Komitov, G., Binev, I., & Valtchev, G. 2020. Structural and Technological Features of an Installation for Recovery of End-of-life Automobile Tires. In E3S Web of Conferences (Vol. 180, 01016). EDP Sciences.

25. Sathishkumar, C. & Karthikeyan, S. 2019. Recycling of waste tires and its energy storage application of by-products – a review. Sustainable Materials and Technologies, 22, e00125.

26. Singh, D.P., Kothari, R., & Tyagi, V.V. (Eds.). 2019. Emerging Energy Alternatives for Sustainable Environment. CRC Press.

27. Suchocki, T., Lampart, P., Kazimierski, P., Januszewicz, K., Gawron, B. 2021. Experimental investigation of performance and emission characteristics of a miniature gas turbine supplied by blends of kerosene and waste tyre pyrolysis oil. Energy, 215, 119125.

28. Susa, D. & Haydary, J., 2014. Sulphur distribution in the products of waste tire pyrolysis Sulfur distribution in the products of waste tire pyrolysis. Chemical papers, 67(12), 1521–1526.

29. Tavera-Ruiz, C., Gauthier-Maradei, P., Capron, M., Ferreira-Beltran, D., Palencia-Blanco, C., Morin, J.C., Dumeignil, F. 2019. An alternative to the cymenes production from scrap tire rubber using heteropolyacid catalysts. Waste and Biomass Valorization, 10(10), 3057–3069.

30. Toteva, V., & Stanulov, K. 2020. Waste tires pyrolysis oil as a source of energy: Methods for refining. Progress in Rubber, Plastics and Recycling Technology, 36(2), 143–158.

31. Yaqoob, H., Teoh, Y.H., Jamil, M.A., & Gulzar, M. 2021. Potential of tire pyrolysis oil as an alternate fuel for diesel engines: A review. Journal of the Energy Institute.

32. Yazdani, E., Hashemabadi, S.H., & Taghizadeh, A. 2019. Study of waste tire pyrolysis in a rotary kiln reactor in a wide range of pyrolysis temperature. Waste Management, 85, 195–201.

33. Zhang, Y., Tao, Y., Huang, J., & Williams, P. 2017. Influence of silica–alumina support ratio on H2 production and catalyst carbon deposition from the Ni-catalytic pyrolysis/reforming of waste tires. Waste Management & Research, 35(10), 1045–1054.

34. Zhou, Y., Wang, Y., Fan, L., Dai, L.; Duan, D., Liu, Y., Ruan, R., Zhao, Y., Yu, Z., Hu, Y. 2017. Fast microwave-assisted catalytic co-pyrolysis of straw stalk and soap stock for bio-oil production. J. Anal. Appl. Pyrolysis. 124, 35–41.