

Bio Oil Production by Thermal and Catalytic Pyrolysis of Waste Tires

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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 [Januzsewics 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 ($\text{SiO}_2 / \text{Al}_2\text{O}_3$) 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 censor 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

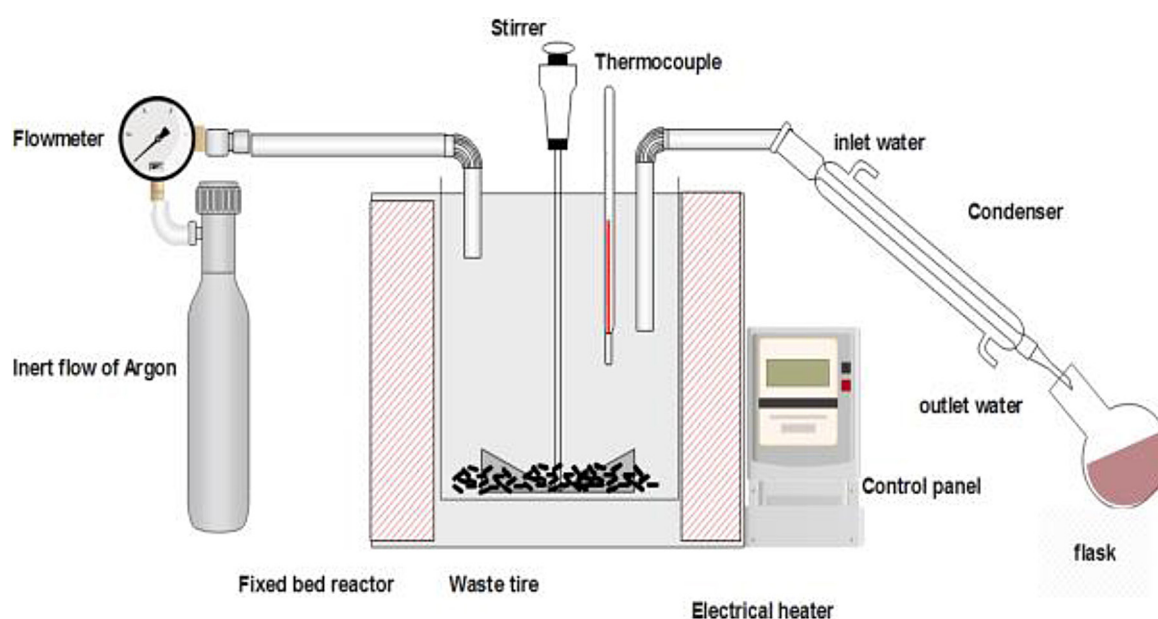


Figure 1. Schematic diagram of waste tire pyrolysis system

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]:

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

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

$$\text{Gas yield (\%)} = 100 - \text{oil yield (\%)} - \text{char yield (\%)} \quad (3)$$

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,

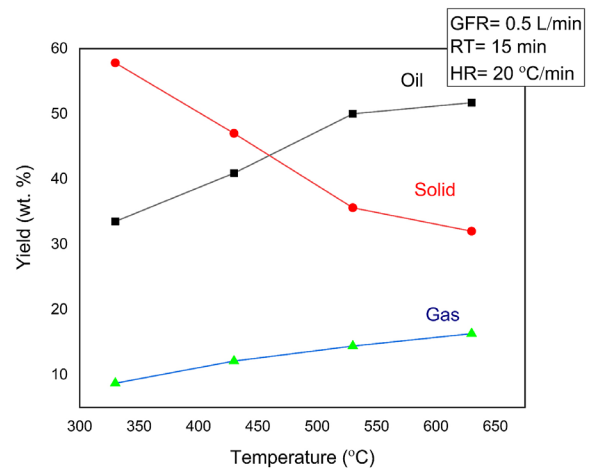


Figure 2. The effect of varying pyrolysis temperature on products yield

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	
			CaCO ₃	SiO ₂ /Al ₂ O ₃
530 °C 0.5 L/min of Argon RT of 15 min With 1% catalyst	Oil	50	52	47
	Solid	35.6	38.5	38
	Gas	14.4	9.5	15

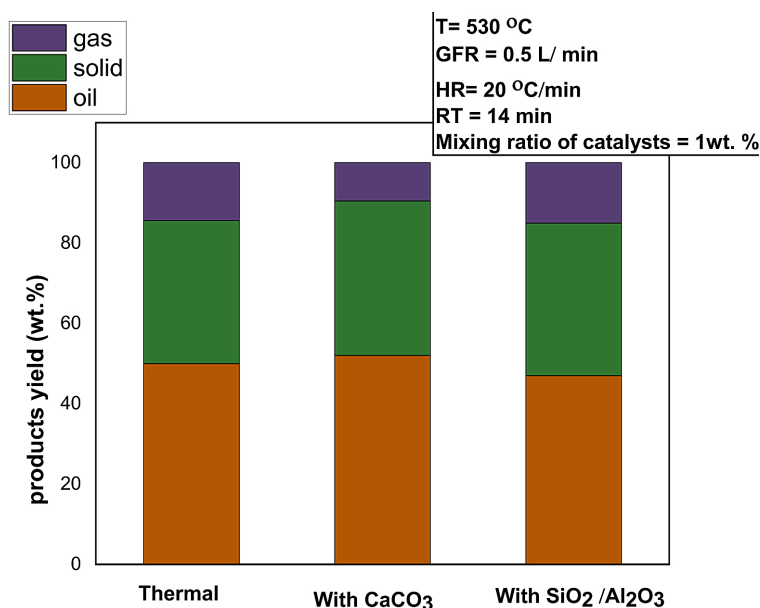


Figure 3. Product yields from thermal and catalyst pyrolysis

that tire pyrolysis oils are a complex mixture of organic compounds of C_8 – C_{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-methylethenyl)-, Pentene, and di (cyclohexyl methyl) ester. The greatest peak was to Cyclohexene, 1-methyl-4-(1-methylethenyl) $C_{10}H_{16}$, 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 $C_{14}H_{28}O_3S$, $C_{18}H_{36}O_3S$, $C_8H_{18}O_2S$, $C_{11}H_{22}O_3S$ 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 $CaCO_3$ and SiO_2/Al_2O_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 $CaCO_3$ 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-methylethenyl)-] 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_2/Al_2O_3 catalyst promoted the selective liquid fraction. Table 3 shows sharp increase in cycloalkanes to 72.14% represented by [Cyclohexene, 1-methyl-4-(1-methylethenyl)-], formulated by $C_{10}H_{16}$ 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_2/Al_2O_3 of 137.41 m^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% $CaCO_3$ pyrolysis to 8.79% in SiO_2/Al_2O_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].

Table 3. Chemical composition of TPO from thermal and catalytic pyrolysis

Compositions	Peak Area%		
	Thermal pyrolysis	Catalytic pyrolysis	
		$CaCO_3$	SiO_2/Al_2O_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

Table 4. GC-MS analysis of tire pyrolysis oil of thermal pyrolysis

Peak	R. time	Compound name	M. Formula	Area %
1	3.249	Sorbic acid vinyl ester	$C_8H_{10}O_2$	0.37
2	3.414	cis-1,2-Divinylcyclobutane	C_8H_{12}	0.16
3	3.782	Ethylbenzene	C_8H_{10}	0.34
4	3.83	2,4-Hexadiene, 2,3-dimethyl	C_8H_{14}	0.4
5	3.923	o-Xylene , Benzene	C_8H_{10}	3.35
6	4.272	1-Hexen-4-ol	$C_{13}H_{18}O$	0.71
7	4.632	Benzene	$C_{13}H_{18}O$	0.1
8	4.806	5,10-Pentadecadienoic acid	$C_{15}H_{26}O_2$	0.14
9	5.072	1,5-Heptadiene	$C_{10}H_{16}$	0.52
10	5.357	7-Propylidene-bicyclo	$C_{10}H_{16}$	3.03
11	5.468	2,4-Nonadiyne	C_9H_{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	$C_{10}H_{18}O$	1.44
15	5.854	1,6-Octadiene, 2,6-dimethyl	$C_{10}H_{18}$	1.03
16	6.001	6,10-Dodecadien-1-yn-3-ol	$C_{15}H_{24}O$	2.52
17	6.1	5-Pentadecen-7-yne,(Z)-	$C_{15}H_{26}$	0.39
18	6.25	Cyclohexene, 1-ethyl-6-ethylidene	$C_{10}H_{16}$	0.76
19	6.533	Cyclohexene	$C_{10}H_{18}$	1.96
20	6.661	Cyclohexene, 1-methyl-4-(1-methylethenyl)-	$C_{10}H_{16}$	28.9
21	6.773	1-Methylene-2-vinylcyclopentane	C_8H_{12}	0.37
22	7.037	1-Pentene	C_8H_{16}	1.76
23	7.45	2,7-dimethyloct-7-en-5-yn-4-yl ester	$C_{18}H_{22}O_2$	0.33
24	7.578	Cyclohexene	$C_{10}H_{16}$	1.49
25	7.674	Benzene	$C_{10}H_{12}$	1.32
26	7.836	1-Pentene	C_8H_{16}	1.41
27	8.463	Bicyclo[3.1.0]hex-2-ene, 4,4,6,6-tetramethyl-	$C_{10}H_{16}$	0.38
28	10.032	Benzothiazole	C_7H_5NS	2.05
29	10.41	1H-Indene, 1,1-dimethy	$C_{11}H_{12}$	0.42
30	10.553	cyclohexylmethyl heptyl ester	$C_{14}H_{28}O_3S$	1.38
31	10.816	1-Heptene	C_8H_{16}	0.38
32	10.928	Nonane	$C_9H_{19}I$	0.45
33	11.058	Heptane	$C_7H_{15}I$	1.13
34	11.713	di(cyclohexylmethyl) ester	$C_{14}H_{26}O_3S$	3.31
35	12.195	Benzene	$C_{12}H_{14}$	0.7
36	12.254	1-Hexene	C_8H_{16}	2.73
37	12.745	1H-3a,7-Methanoazulene	$C_{15}H_{26}$	1.22
38	12.908	1-(2-Isopropylcyclopropyl)-2-methyl-1-propanol	$C_{10}H_{20}O$	1.15
39	13.083	3,5,9-Undecatrien-2-one	$C_{13}H_{20}O$	0.89
40	13.19	Quinoline	$C_{11}H_{11}N$	0.44
41	13.366	3-Cyclohexene-1-carboxaldehyde	$C_{10}H_{16}O$	1.01
42	13.758	Nonane	$C_{13}H_{28}$	0.99
43	13.907	3-Methyl-trans-3a,4,7,7a-tetrahydroindane	$C_{10}H_{16}$	0.55
44	14.063	3-Cyclohexene-1-carboxaldehyde	$C_{10}H_{16}O$	0.79
45	14.418	Naphthalene	$C_{13}H_{14}$	0.66
46	15.012	cyclohexylmethyl undecyl ester	$C_{18}H_{36}O_3S$	1.31
47	15.228	1,2-Benzenediol,	$C_{19}H_{19}ClO_5$	0.12
48	15.5	4-Heptanone	$C_{15}H_{30}O$	0.57

Table 4. Cont. GC-MS analysis of tire pyrolysis oil of thermal pyrolysis

49	16.061	cyclohexylmethyl heptyl ester	$C_{14}H_{28}O_3S$	3.15
50	16.266	Tridecane	$C_{13}H_{28}$	0.6
51	16.527	1-Pentene	C_8H_{16}	1.07
52	17.077	Propane, 2-[(1,1-dimethylethyl)sulfonyl]-2-methyl-	$C_8H_{18}O_2S$	0.22
53	17.994	1,5-Heptadiene, 2,6-dimethyl	C_9H_{16}	0.44
54	18.102	1,5-Heptadiene, 2,6-dimethyl	C_9H_{16}	0.36
55	18.592	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	0.33
56	18.813	Cyclohexanone	$C_{12}H_{22}O$	1.6
57	19.24	1-Pentene	C_7H_{14}	0.8
58	19.747	cyclohexylmethyl isobutyl ester	$C_{11}H_{22}O_3S$	2.68
59	20.158	1-Pentene	C_8H_{16}	0.86
60	22.104	cyclohexylmethyl heptyl ester	$C_{14}H_{28}O_3S$	1.09
61	22.476	3-tridecyl ester	$C_{19}H_{32}O_2S$	0.69
62	22.941	3-Octyne-2,5-dione	$C_{11}H_{16}O_2$	1.59
63	23.312	Cyclopropanemethanol, .alpha.,2-bis(1-methylethyl	$C_{10}H_{20}O$	1.06
64	24.193	2-ethylhexyl isohexyl ester	$C_{14}H_{30}O_3S$	0.27
65	24.999	cyclohexylmethyl heptadecyl este	$C_{24}H_{48}O_3S$	0.86
66	25.341	di(cyclohexylmethyl) ester	$C_{14}H_{26}O_3S$	0.27
67	25.755	cyclohexylmethyl heptadecyl ester	$C_{24}H_{48}O_3S$	2.17
68	26.091	2,4,4-Trimethyl-1-pentanol	$C_8H_{18}O$	0.53
69	26.576	Butanal, 4-[(tetrahydro-2H-pyran-2-yl)oxy]-	$C_9H_{16}O_3$	0.51
70	28.813	cyclohexylmethyl hexyl ester	$C_{13}H_{26}O_3S$	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_6H_9N	0.34
2	3.26	1,4-Pentadiene, 2,3,3-trimethyl	C_8H_{14}	1.24
3	3.425	Cyclohexene, 4-ethenyl	C_8H_{12}	0.96
4	3.80	Ethylbenzene	C_8H_{10}	1.44
5	3.933	o-Xylene	C_8H_{10}	4.2
6	4.282	1,3,5,7-Cyclooctatetraene	C_8H_8	1.66
7	4.641	Benzenemethanol, .alpha.-methyl-.alpha.-(1-methyl-2-propenyl)-	$C_{12}H_{16}O$	0.13
8	4.818	5,10-Pentadecadien-1-ol	$C_{15}H_{28}O$	0.27
9	5.082	7-Propylidene-bicyclo[4.1.0]heptane	$C_{10}H_{16}$	1.08
10	5.365	1,5-Cyclooctadiene, 1,5-dimethyl	$C_{10}H_{16}$	3.9
11	5.48	Benzene, 1-ethyl-2-methyl-	C_9H_{12}	1.49
12	5.587	(2Z,4Z,6E)-2,4,6-Undecatriene	$C_{11}H_{18}$	0.51
13	5.722	Ethanone, 1-cyclopropyl-2-(3-pyridinyl)	$C_{10}H_{11}NO$	0.72
14	5.785	1,4-Hexadiene, 5-methyl-3-(1-methylethylidene)	$C_{10}H_{16}$	1.8
15	5.864	1,6-Octadiene, 2,6-dimethyl-, (Z)	$C_{10}H_{18}$	1.39
16	6.011	1,5-Heptadiene, 2,3,6-trimethyl	$C_{10}H_{18}$	2.88
17	6.261	1,5-Hexadiene, 2,5-dimethyl-3-methylene	C_9H_{14}	1.12
18	6.538	(+)-3-Carene, 2-(acetylmethyl)	$C_{13}H_{20}O$	3.99
19	6.664	Cyclohexene, 1-methyl-4-(1-methylethenyl)	$C_{10}H_{16}$	49.52
20	6.782	1-Methylene-2-vinylcyclopentane	C_8H_{12}	0.56
21	7.046	5,10-Pentadecadiyne, 1-chloro	$C_{15}H_{23}Cl$	0.63
22	7.463	1-Pentanone, 1-(4-methylphenyl)	$C_{12}H_{16}O$	0.31
23	7.592	Cyclohexene, 4-methyl-3-(1-methylethylidene)	$C_{10}H_{16}$	1.15

Table 5. Cont. GC-MS analysis of tire pyrolysis oil of catalytic pyrolysis by CaCO₃

24	7.686	Benzene, (2-methylcyclopropyl)	C ₁₀ H ₁₂	1.04
25	7.846	Ethanone, 1,2-diphenyl	C ₁₄ H ₁₂ O	0.52
26	7.998	3-Methylbenzoic acid, 2-formyl-4,6-dichlorophenyl ester	C ₁₅ H ₁₀ Cl ₂ O ₃	0.19
27	8.181	Ethanone, 1-(4-methylphenyl)	C ₉ H ₁₀ O	0.1
28	8.332	E-2-Methyl-5-(furan-3-yl)-pent-1-en-3-one	C ₁₀ H ₁₂ O ₂	0.1
29	8.475	Benzene, 1-trifluoromethyl-4-(2-methoxybenzyloxy)-3-nitro	C ₁₅ H ₁₂ F ₃ NO ₄	0.12
30	8.706	1H-Indene, 1-methyl	C ₁₀ H ₁₀	0.53
31	9.325	2-Methyl-4-phenyl-2-trimethylsilyloxybutane	C ₁₄ H ₂₄ OSi	0.35
32	9.468	1H-Indene, 1-ethyl-2,3-dihydro-1-methyl	C ₁₂ H ₁₆	0.37
33	10.04	1,2-Benzisothiazole	C ₇ H ₅ NS	1.31
34	10.42	Oxazirane, 2-(dimethylethyl)-3-methoxy	C ₈ H ₁₃ NO ₂	1.05
35	10.56	Octanoic acid, 2-methoxy-, methyl ester	C ₁₀ H ₂₀ O ₃	0.5
36	10.94	Oxalic acid, butyl propyl ester	C ₉ H ₁₆ O	0.7
37	11.11	Butanoic acid, 3-[(1-phenylethyl-2-propynyl)oxy]	C ₁₅ H ₁₈ O ₃	0.6
38	11.72	3-Butene-1,2-diol, 1-(2-furanyl)	C ₈ H ₁₀ O ₃	1.03
39	12.21	Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)	C ₁₂ H ₁₄	0.72
40	12.26	1-Hexene, 5,5-dimethyl	C ₈ H ₁₆	0.93
41	12.42	1-Chloroundecane	C ₁₁ H ₂₃ Cl	0.62
42	12.76	Cyclopropane, 1-(5-hexenyl)-2-iodo	C ₉ H ₁₅ I	0.74
43	12.92	3,4-Octadiene, 7,7-dimethyl	C ₁₀ H ₁₈	0.97
44	13.38	Santolina triene	C ₁₀ H ₁₆	1.37
45	13.77	Tetradecane, 1-iodo	C ₁₄ H ₂₉ I	0.62
46	14.07	3,9-Dodecadiene	C ₁₂ H ₂₂	0.69
47	16.07	3-Pentenoic acid, 2,2,4-trimethyl	C ₈ H ₁₄ O ₂	0.75
48	16.28	Tetradecane, 1-iodo	C ₁₄ H ₂₉ I	0.57
49	18.79	Cyclohexene, 3-methyl-6-(1-methylethylidene)	C ₁₀ H ₁₆	0.65
50	19.75	Sulfurous acid, cyclohexylmethyl isobutyl ester	C ₁₁ H ₂₂ O ₃ S	0.65
51	22.94	Cyclohexane, 1-bromo-3-methyl	C ₇ H ₁₃ Br	0.51
52	25.01	Acetic acid, trifluoro-, 2,2-dimethylpropyl ester	C ₇ H ₁₁ F ₃ O ₂	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=C 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 sulfuric 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 C₁₄H₂₈O₃S, C₁₈H₃₆O₃S, C₁₄H₃₀O₃S and C₂₄H₄₈O₃S, 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 SiO₂/Al₂O₃

Peak	R. time	Compound name	M. Formula	Area %
1	3.257	Cyclopropane	C ₃ H ₆	0.76
2	3.422	Cyclohexene	C ₆ H ₁₀	0.5
3	3.792	Ethylbenzene	C ₈ H ₁₀	0.95
4	3.933	Benzene	C ₆ H ₆	5.53
5	4.283	Benzenepropanoyl bromide	C ₉ H ₉ BrO	0.79
6	4.812	Cyclopropane, (2-methylenebutyl)	C ₈ H ₁₄	0.14
7	5.082	7-Propylidene-bicyclo[4.1.0]heptane	C ₁₀ H ₁₆	0.59
8	5.363	1,5-Dimethyl cyclooctadiene	C ₁₀ H ₁₆	2.24
9	5.477	Benzene	C ₆ H ₆	1.27
10	5.578	Tetracyclo[6.2.1.0(2,4).0(4,7)]undecane	C ₁₁ H ₁₆	0.38
11	5.725	1-Hepten-3-yne	C ₇ H ₁₀	0.46
12	5.783	1,5-Heptadiene, 2,5-dimethyl-3-methylene-	C ₁₀ H ₁₆	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 ₁₅ H ₂₄	2.01
15	6.258	Cyclohexene, 3-(3-methyl-1-butenyl)-, (E)-	C ₁₁ H ₁₈	0.36
16	6.547	Benzene, 1-methyl-2-(1-methylethyl)-	C ₁₀ H ₁₄	4.98
17	6.657	Cyclohexene, 1-methyl-4-(1-methylethenyl)-	C ₁₀ H ₁₆	70.97
18	6.774	1,3-Cyclopentadiene, 1-(3-butynyl)	C ₉ H ₁₀	0.22
19	7.039	1-Pentene, 2,4,4-trimethyl-	C ₈ H ₁₆	0.26
20	7.401	Cyclohexene, 1-ethyl-6-ethylidene	C ₁₀ H ₁₆	0.22
21	7.589	1,5-Heptadiene, 2,5-dimethyl-3-methylene-	C ₁₀ H ₁₆	1.18
22	7.685	Benzene, 1-methyl-4-(1-methylethenyl)-	C ₁₀ H ₁₂	1.06
23	7.839	Propane, 2-methyl-2-nitro-	C ₄ H ₉ NO ₂	0.26
24	8.704	1H-Indene, 2,3-dihydro-4-methyl	C ₁₀ H ₁₂	0.41
25	9.324	Benzene, 1-methyl-2-(1-methyl-2-propenyl)-	C ₁₁ H ₁₄	0.12
26	9.467	Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	C ₁₁ H ₁₄	0.18
27	10.043	Benzothiazole	C ₇ H ₅ NS	0.45
28	10.508	1H-Indene, 1,1-dimethyl-	C ₁₁ H ₁₂	0.34
29	10.945	Benzene, 1-ethoxy-4-[2-(4-pentylcyclohexyl)ethyl]-	C ₂₁ H ₃₄ O	0.29
30	11.116	Naphthalene, 2-methyl-	C ₁₁ H ₁₀	0.34
31	11.717	Methylphosphonic acid, dinonyl ester	C ₁₉ H ₄₁ O ₃ P	0.43
32	12.209	Benzene,	C ₁₂ H ₁₄	0.23
33	12.917	4-Nonene, 2,3,3-trimethyl-, (E)-	C ₁₂ H ₂₄	0.21
34	12.986	Pentobarbital	C ₁₁ H ₁₈ 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 nature which has a significant role in occurring desulfurization reaction [Ilikilic and Aydin, 2011] and catalytic cracking by using SiO₂/Al₂O₃, 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

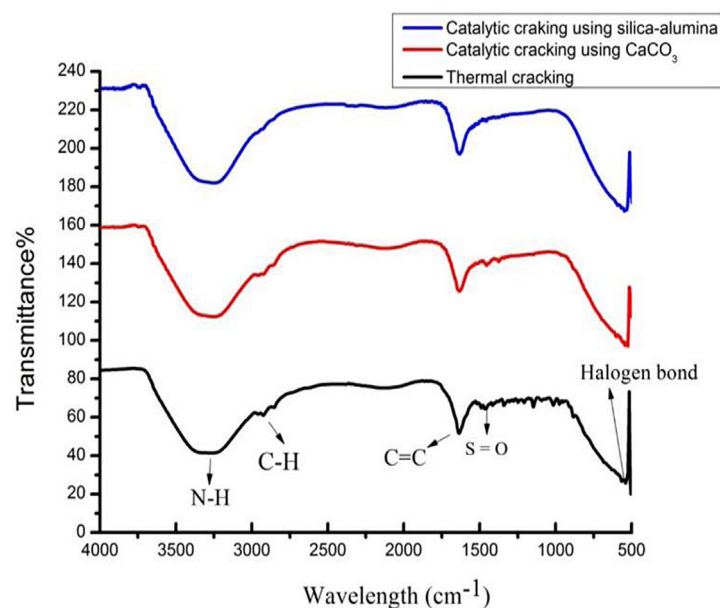


Figure 4. FTIR of TPO obtained by thermal and catalytic pyrolysis

Table 7. Summary of characteristic IR absorption for TPO

Absorption peak cm^{-1}	Vibrational mode range cm^{-1}	Functional Group	Compound class
3363, 3356, 3336	3250-3400	N-H stretch	Aliphatic primary amine
2924, 2850	2500-3000	C-H stretch	Alkane
1635	1638-1648	C=C stretch	Alkene
1415	1300-1440	S=O stretch	Sulfuric compounds
1334, 1377	1330-1420	O-H stretch	Alcohol
3336	3300-3400	N-H stretch	Aliphatic primary amine
1246, 1465	1250-2000	C-O stretch, C-H bend	Aromatic compounds
551, 594, 543, 540	500-600	C-Br stretch, C-I stretch	Halogen compounds

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst, the oil and char yield were decreased to 47 wt. %, 38, respectively, while the pyrolysis gas when using $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst. The oxygenated compounds were decreased from 33.62% in thermal TPO to 12.49% by using CaCO_3 , and 1.61% with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ respectively.

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