



GC-FID Estimation of BTEX Compounds in Liquid Oil Resulting from Catalytic Pyrolysis of Used Tires

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Abstract

Thermal decomposition of used tires was studied under atmospheric pressure and thermal heating program up to 350 °C for 110-120 min in a glass reactor. The effects of using MgO or SiO₂ as catalyst in the thermal pyrolysis of tires waste on the yield ratio, reaction time, initial degree of decomposition also the contents of BTEX compounds in resulting pyrolytic oil was estimated via GC-FID. The results showed that the MgO catalyst gave a gas output in proportion of 17.063%, a liquid in a proportion of 38.245% and a solid product in proportion of 44.733%, while the SiO₂ catalyst gave proportions of 14.308%, 40.161% and 45.448% for gas, liquid and solid products respectively. The results revealed that the thermal pyrolysis produced minor content of BTEX as compared with catalytic SiO₂ and MgO pyrolysis, also Toluene is the highest concentration among compounds in all types of thermal decomposition while Ethyl benzene is the lowest one. The reaction time and the initial temperature were decreases by use their cofactors MgO or SiO₂, also the sum of the total BTEX concentrations was increased at 17.4% and 30.8% with MgO and SiO₂ respectively.

Keywords: BTEX; Recycling; Pyrolysis; Catalytic pyrolysis; Waste tires.

1. Introduction

The global production of tires ranges from 1.5-3.3 billion annually [1] with roughly the same number of tires consumed after use [2]. Scrap tires are considered solid waste that appearance great challenges due to the difficulty of treatment them by traditional methods such as metal, glass and plastic wastes. The difficulty lies in the nature of the complex chemical components that make up the tires, such as [3] steel, carbon black, fillers, ash and rubber which are composed of Cross-linked polymers whose chemical bonds cannot be easily broken. Therefore, one of the methods that are widely used in solving this problem is the pyrolysis by which the chemical bonds of the components are broken by exposing them to a thermal program and converting them into gaseous, liquid and solid products in different proportions depending on the conditions and system of pyrolysis which we are focused in [4-10]. The liquid oil resulting from pyrolysis is the most economically valuable among other products, because it contains a very large number of important

organic chemical compounds that have economic benefit such as paraffins, olefins as well as homogeneous and heterogeneous aromatic compounds containing sulfur, nitrogen and oxygen. Among these important compounds are the monocyclic aromatic compounds such as benzene (B), toluene (T), ethyl benzene (E) and xylenes (X), Fig.1, which are used as sources of fuel and as raw materials in the petrochemical industry [11-15].

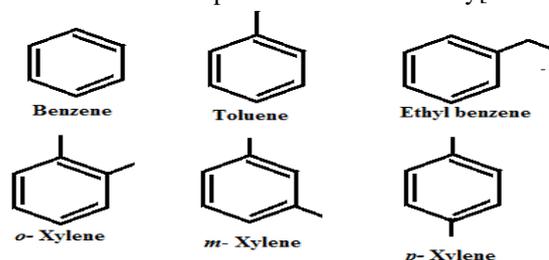


Figure 1: Structure formula of BTEX compounds

Gas chromatography is widely used in the separation and characterization of the aromatic BTEX compounds depending on their physical properties. Due to the difficulty of make direct analysis of the

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resulting liquid because of the contamination that destroy the injection port and the column with residues of high boiling points in addition to the possibility of forming active sites that can increase the noise and give inaccurate analysis results, the mode was modified using the solvent dilution method which it is easy used and can be performed routinely [16-19].

The aim of this research is to study the effect of using acidic SiO₂ or basic MgO catalyst on the concentration of BTEX compounds resulting from thermal and catalytic pyrolysis that produced from pyrolysis of scrap tire via GC-FID technique as well as the conditions of reaction which included reaction time and initial temperature.

2. Experimental

2.1. Materials

Waste tire samples obtained from local market after removing steel and fiber was granulated at size ranging 5-10 mm using mortar. Magnesium oxide and silica were obtained from BDH Company and had purity more than 99%. Benzene, toluene, ethyl benzene, xylenes, and n-heptane were supplied from BDH too also had purity more than 99%.

2.2. Methods

In general, the polymers have low thermal conductivity, so they need high temperature for thermal pyrolysis [20]. Pyrex glass reactor has been used for pyrolysis process under atmospheric pressure in batch system. The reactor can work as catalytic and thermal pyrolysis system. Limited amount of granulated scrap tire and catalyst MgO or SiO₂ were mixed and heated with external electrical heater for 110-120 min. at 350°C via thermocouple to keep on and record the temperature. During heating, the mixture was melted and produced gases that passed through trap and liquid fraction which was collected after condensation upon cooling with tap water, leaving the char in the bottom of the reactor at the end of the reaction. Solid and liquid phases yield were estimated by weighing each one and calculating the percentage while the gas phase yield was determined by difference between the starting material weight and sum weight of solid and liquid phases. The experiments were recurring three times of each parameter and obtain the average value [15].

2.3. Determination of BTEX compounds content in resultant pyrolytic oil

Five standard solutions of BTEX compounds were prepared and diluted with n-heptane to 25ml volume. A GC-FID was used for analysis and create standard curve for each component by plotting peak area against concentration for each one. BTEX were analyzed via GC, Shimadzu- 210 equipped with flame ionization detector, FID. The analysis conditions are: (i) Sampling method: A split/splitter. (ii) Injector temperature was 260 °C. (iii) Carrier gas: Nitrogen ≥99 purity was obtained from Nitrogen generator supplied from Henter Domenic Company with flow rate of 1.11 mL/min. (iv) Fuel gas: H₂ from Hydrogen generator and air compressor at flow rate of 30 mL/min. (v) GC column characteristic: A SE-30 (3m×2mm) column and its temperature was 80-250 °C for 50 min at heating rate of 5 °C/min. (vi) Detector temperature: 270 °C. Table-1 illustrated the concentration of standard BTEX compounds. The working concentration of BTEX compounds were chosen upon observed concentration of them in resulting pyrolytic oil. The analysis was carried out three times in order to achieve the average value.

Table 1: Molar concentrations of standard solutions of BTEX compounds

Standard Solution	Benzene (M)	Toluene (M)	Ethyl benzene (M)	o-Xylene (M)	m- & p-Xylene (M)
1	0.475	0.409	0.314	0.302	0.355
2	0.60	0.58	0.353	0.34	0.396
3	0.823	0.758	0.56	0.551	0.63
4	1.021	0.921	0.7	0.688	0.786
5	1.294	1.18	0.891	0.882	0.994

3. Results and Discussion

Waste Tires are a serious environmental problem due to the difficulty in decomposing the materials that make up these tires. Great efforts have been made to solve this problem and invest this waste to produce useful materials. Several steps have been done to yield the products of pyrolysis of scrap tyre such as shredding, powdering, drying, pyrolysis, and condensing, Figure-2.

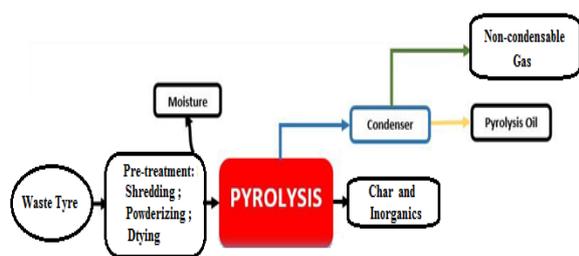


Figure 2: Waste tyre pyrolysis block flow diagram[21]

3.1. Reaction mechanism

Thermal pyrolysis of scrap tyre forms radicals with random cleavage [22] but the catalytic pyrolysis in the presence of alkali oxide, MgO is started by formation carbanions which is stabilize by positive metal ions [23]. Catalyst characteristic such as acidity is the important factor that has great influence on the pyrolysis reaction [24], and then the catalytic pyrolysis in the presence of acidic oxide, SiO₂ is started by formation carbocations by adding hydrogen ions to the alkyl hydrocarbons [25]. Further reactions of alkali or acidic catalytic pyrolysis is similar to that occur in thermal pyrolysis such as; addition, alkylation, isomerization, esterification, Diels-Alder reaction are occurring during reaction [26-28].

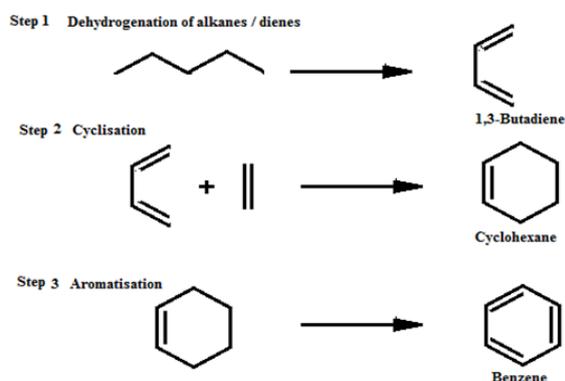


Figure 3: Diels-Alder reaction pathway for formation benzene ring [26, 27].

3.2. Effect of catalyst on scrap tire pyrolysis yield

The weight fractions of gas, liquid and solid phases produced from pyrolysis of scrap tyre were plotted together against concentration of MgO and SiO₂ in catalytic pyrolysis which was shown in Figures 4, while the yield of thermal pyrolysis is presented in Figure 5.

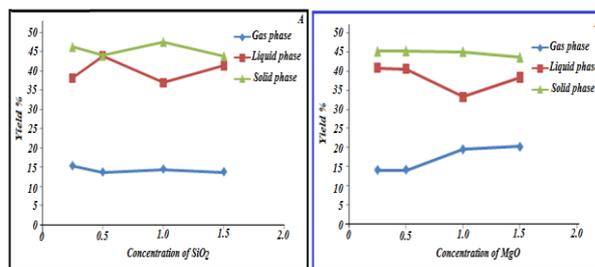
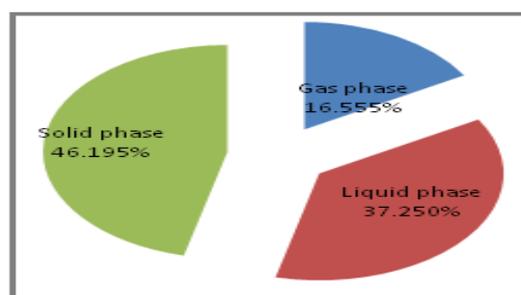
Figure 4: Product yield from MgO and SiO₂ catalytic pyrolysis

Figure 5: Product yield from thermal pyrolysis

The effect of using MgO, SiO₂ catalysts and no using on product yield of gas, liquid and solid phases are summarized in Table-2 which shows that the gases yield ranged 14 -17 %, liquid yield ranged 37-40% which agreed with the literature data that fixed the quantities about 35 – 50% and solid yield ranged 44 - 46% for thermal and catalytic pyrolysis of scrap tyre; this means that the using of catalyst or not have limiting effect on product yield at same reactor and fixed conditions of pyrolysis [29-32].

Table 2: Yield of pyrolysis products of scrap tyre

	% yield		
	Gas	Liquid	Solid
MgO	17.063	38.245	44.733
SiO ₂	14.308	40.161	45.448
No catalyst	16.555	37.250	46.195

The use of MgO in catalytic pyrolysis increased the gas phase yield compared with thermal pyrolysis; this result agreed with obtained by Zhao et al., [33] also the results shown that the liquid phase yield resulting using MgO catalyst was about 38.245% which was close to that obtained by Shah [34]. In the case of using SiO₂, it worked to reduce the gas and solid phases and increase the liquid phase comparing with thermal pyrolysis, Figure 5.

3.3. Study the initial temperature and reaction time of pyrolysis process

The effect of using MgO, SiO₂ and without catalyst on the initial temperature and reaction time of pyrolysis process were presented in Figure 6, Table 3. The use of SiO₂ or MgO offers some changes in initial temperature which was decreases from 88°C to 80°C with catalyst, also, the reaction time decreasing from 110 to 90 min. These results agreed with other results illustrate that the thermal pyrolysis require long time and higher initial temperature compared with catalytic pyrolysis[35].

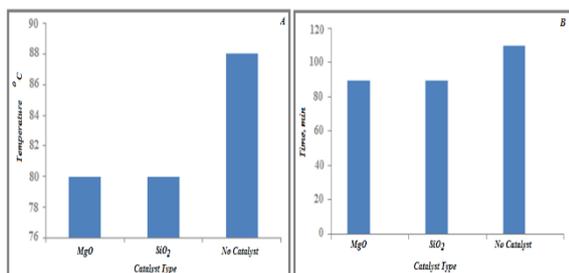


Figure 6: Effect of MgO and SiO₂ catalyst on the temperature, A and reaction time, B of scrap tyre pyrolysis

Table 3: Initial time and temperature of scrap tyre pyrolysis products by different catalyst

parameter	No catalyst	Catalyst type	
		MgO	SiO ₂
Reaction time, min	110	90	90
Initial temperature, °C	88	80	80

3.4. GC-FID Analysis of BTEX compounds

GC-FID technique was used to separate and analysis of BTEX compound under different conditions to find the best one. A good separation was achieved with optimal parameters that appeared in experimental part, Figure 8. The injecting of standard solution of BTEX compounds showed well linearity detector response of FID which appeared in Table 4 and Figure 7.

3.5. Concentration of BTEX compounds in the pyrolytic oil produced from scrap tyres

The results revealed that the thermal pyrolysis produced minor content of BTEX distributions in the liquid phase as compared with catalytic SiO₂ and MgO pyrolysis, Figure 9, Table 5. The oil produced

from SiO₂ compared to MgO had higher concentration of BTEX compounds due to its acidity of SiO₂[36] these results refer to fact that the mechanism of cleavage of polymers has been fixed as free radicle in the case of thermal pyrolysis ,while it is ionic mechanism in catalytic pyrolysis [37]. When catalyst either SiO₂ or MgO are applied in the reaction, two type of cleavage mechanism occurred thermal cracking include random and end scission of chain, elimination of some group and catalytic cracking include adsorption process between carbonium ion and the surface of catalyst, desorption process as well as beta scission. At final, different compounds are produced and may react with each other to generate hydrocarbons at different quantities [38].

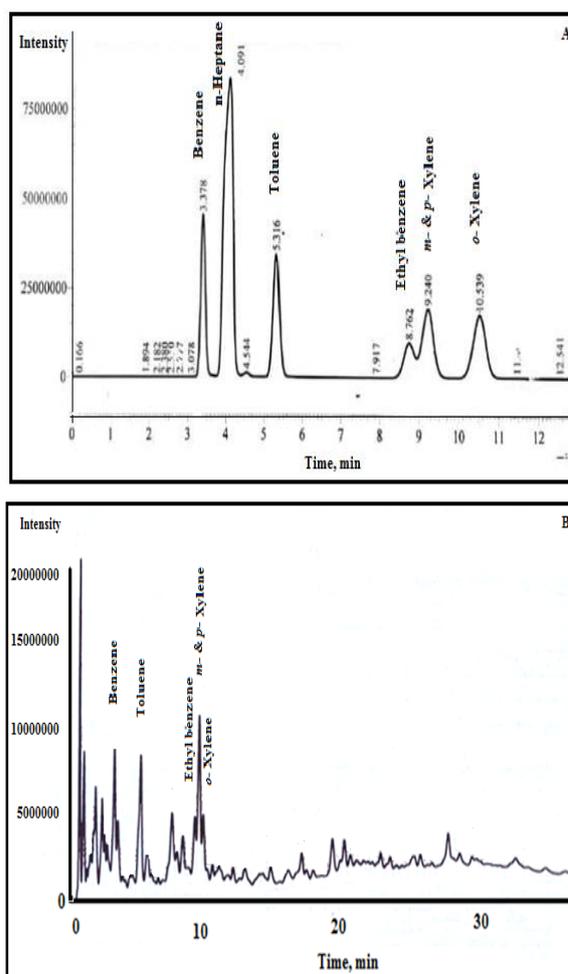


Figure 7: GC-FID chromatograms for standard BTEX solutions, A and for life sample, B

Table 4: Analytical data for BTEX compound using GC-FID

Variable	Benzene	Toluene	Ethyl benzene	<i>m</i> - and <i>p</i> -Xylene	<i>o</i> - Xylene
Retention time, min.	3.265	5.128	8.475	8.937	10.167
Regression equation	$Y=121.2 X + 0.303$	$Y= 142.1X + 5.842$	$Y= 158.7X - 3.992$	$Y= 338.1X - 8.346$	$Y= 168.3 X - 5.3119$
Conc. Range, M	0.465- 1.3	0.425- 1.18	0.339- 0.941	0.376- 1.045	0.3398 - 0.9440
Linearity , R ²	0.9890	0.9900	0.9680	0.9660	0.9675
Correlation Coefficient, r	0.9945	0.9949	0.9838	0.9828	0.9836
Slope, b	121.2	142.1	158.7	338.1	168.335
Intercept, a	0.303	5.842	- 3.992	- 8.346	- 5.3119
LOD, M	0.1175	0.1016	0.1477	0.168	0.15
LOQ, M	0.3917	0.3387	0.4924	0.561	0.50
S _{y/x}	4.74937	4.81291	7.81925	18.9952	8.4621
S _b	7.2904	7.388	16.486	36.06138	17.78275
S _a	6.4983	9.0102851	10.7025	33.56216	15.0507
Confidence limit of the slope	121.2± 23.1835	142.1 ±23.4938	158.7 ± 52.4257	338.174 ± 114.6751	168.335 ± 56.55
Confidence limit of the intercept	0.303 ± 20.6647	5.842 ± 28.6527	- 3.992 ± 34.034	- 8.3446 ± 106.7276	- 5.3119 ± 47.86

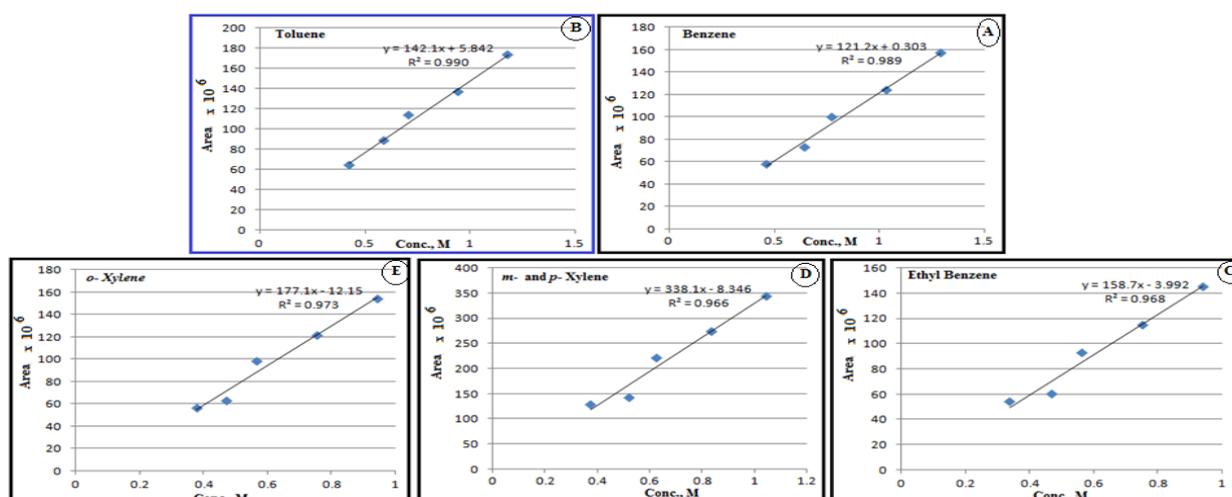


Figure 8: Calibration curves of GC-FID for BTEX analysis

Table 5: BTEX distribution in liquid phase of scrap tyre pyrolysis using different catalyst

		Benzene, 78.1118g/mol	Toluene, 92.14 g/mol	Ethyl Benzene, 106.17 g/mol	<i>m</i> - & <i>p</i> - Xylene 106.17 g/mol	<i>o</i> - Xylene 106.17 g/mol
No Catalyst	Area x10 ⁶	59.78	91.68	14.34	100.78	38.1
	Conc, M	0.491	0.604	0.065	0.273	0.195
	Conc., g/L	38.353	55.65	6.9	28.98	20.70
0.8 % MgO Catalyst	Area x10 ⁶	66.86	100.23	19.4	122.53	48.1
	Conc, M	0.545	0.664	0.097	0.338	0.254
	Conc., g/L	42.57	61.18	10.29	35.88	26.97
	Increases %	10.6	8.5	26.1	17.8	20.8
0.8 % SiO ₂ catalyst	Area x10 ⁶	75.58	111.37	21.33	131.62	52.36
	Conc, M	0.621	0.743	0.109	0.365	0.280
	Conc., g/L	48.51	68.46	11.57	38.75	29.73
	Increases %	21.0	17.7	32.8	23.4	27.0

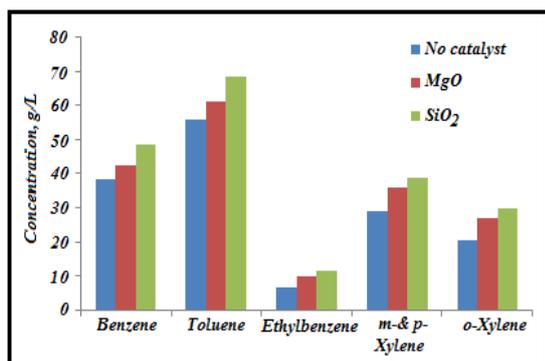


Figure 9: BTEX compounds distribution in resulting pyrolytic oil

Toluene is the compounds with the highest concentration among compounds in all types of thermal decomposition in the presence and absence of the catalyst followed by benzene, m- and p-xylenes, o-Xylene and finally ethyl benzene. Ethyl benzene is the lowest concentration among other BTEX compounds; this may be referring to the additional degradation of ethyl benzene to reach the more stable compounds like benzene, toluene and xylenes.

The sum of the total BTEX concentrations was increased at 17.4% and 30.8% with MgO and SiO₂ respectively, Figure 10, this results are consistent with that has been in scientific journals with an increase in BTEX compounds yield by using zeolite as catalyst in catalytic scrap tire pyrolysis [39], also Shah et al. showed that the percentage of aromatic compounds especially benzene and alkyl substituted single aromatic ring have 30% by using SiO₂ as catalyst[23]. The advantage of catalytic pyrolysis may be exerted on the content of BTEX compounds in the pyrolytic oil because of their morphology and chemical properties of catalyst.

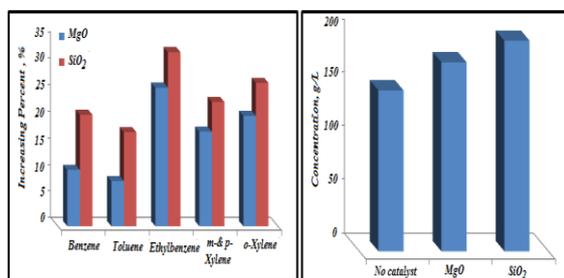


Figure 10: Increasing percent and total BTEX amounts distribution in resulting pyrolytic oil

4. Conclusion

Catalytic pyrolysis of scrap tyre pyrolysis in the presence of MgO or SiO₂ as a catalyst was investigated in relation to effects of catalyst on the yield, reaction time, initial temperature and the

content of BTEX compounds in pyrolytic oil and compared the results with that of thermal pyrolysis. These results agreed with that of catalytic pyrolysis can occur faster and at lower temperature as compared with thermal pyrolysis, also it was revealed that BTEX compounds content that resulted from thermal pyrolysis was lesser than of either MgO or SiO₂ catalytic pyrolysis at fixed condition.

Conflicts of interest

There are no conflicts to declare.

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