



Research Article

Catalytic Pyrolysis of Municipal Solid Waste: Effects of Pyrolysis Parameters

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Abstract

Burning municipal solid waste (MSW) increases CO₂, CH₄, and SO₂ emissions, leading to an increase in global warming, encouraging governments and researchers to search for alternatives. The pyrolysis process converts MSW to oil, gas, and char. This study investigated catalytic and noncatalytic pyrolysis of MSW to produce oil using MgO-based catalysts. The reaction temperature, catalyst loading, and catalyst support were evaluated. Magnesium oxide was supported on active carbon (AC) and Al₂O₃ to assess the role of support in MgO catalyst activity. The liquid yields varied from 30 to 54 wt% based on the experimental conditions. For the noncatalytic pyrolysis experiment, the highest liquid yield was 54 wt% at 500 °C. The results revealed that adding MgO, MgO/Al₂O₃, and MgO/AC declines the liquid yield and increases the gas yield. The catalysts exhibited significant deoxygenation activity, which enhances the quality of the pyrolysis oil and increases the heating value of the bio-oil. Of the catalysts that had high deoxygenation activity, MgO/AC had the highest relative yield. The loading of MgO/AC varied from 5 to 30 wt% of feed to the pyrolysis reactor. As the catalyst load increases, the liquid yield declines, while the gas and char yields increase.

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Keywords: Municipal Solid Waste; Pyrolysis; Bio-oil; Catalytic Pyrolysis; Waste Management

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1. Introduction

Today, municipal solid waste (MSW) production has been enhanced by the increase in population and the demand by citizens for luxury lifestyles [1,2]. More than 2 billion tons of MSW

are produced annually, and 218 kg of MSW are produced per person [3], which affects the environment because MSW occupies land, contaminates the soil and groundwater, and produces undesirable gases [4]. Additionally, MSW has been treated using several methods, such as landfilling, recycling, and burning. The common and oldest method to treat MSW is landfilling,

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which buries the waste in the ground [5]. However, landfilling has long-term effects on human health by contaminating underground water via the emission of gases and organics [6]. Furthermore, the incineration method has been investigated to produce energy from MSW through combustion [2,7]. This method could minimize the accumulation of MSW in the ground; however, it significantly influences the environment by increasing greenhouse gas emissions. The environmental effects of this method are significant obstacles in this process [7].

Treating MSW by burning or dumping in landfills creates environmental and health issues that encourage governments and researchers to search for alternatives and convert MSW into useful products. The MSW is a biomass source containing an average of 30–34 wt% food, 18–22 wt% paper, 16–20 wt% plastic, 8–12% glass, 8–12 wt% metals, and 4–8 wt% agriculture waste [8]. Moreover, 50% to 60% of MSW (paper, glass, plastic, and metals) could be recycled, and 30% to 50% of MSW could be converted to fuel and energy [9]. In the last two decades, thermochemical treatments of MSW to produce oil and chemical have been a tremendous and interesting challenge for researchers and technologists [10–12]. One of the thermochemical treatment methods is pyrolysis, which converts MSW into liquid fuel, gases, and char [2,10–12]. The gases that contain light hydrocarbon and CO can be used for energy and heat production. The char could be used as a fertilizer or carbon material or be burned to produce heat and energy for the pyrolysis reactor [13]. Furthermore, it is an environmentally friendly process due to fewer emissions than gasification [14,15].

Several factors, such as: the pyrolysis temperature and catalysts, have a significant impact on the product yields of MSW pyrolysis [16,17]. The primary product is pyrolysis oil [18,19]. Ersan Pütün [20] examined the impact of the temperature on the yield of biomass pyrolysis products. He found that, as the temperature increased from 400 to 550 °C, the bio-oil yield improved from 40 to 45 wt% and the char yield declined from 35 to 24 wt%. He stated that the optimum temperature for biomass pyrolysis was 550 °C, because the bio-oil yield declines and gas yield increases at higher temperatures [20]. His results were supported by the findings by Miandad *et al.* [21], who conducted a pyrolysis experiment for plastic waste using a batch reactor, and the reaction temperature varied from 400 to 500 °C [21]. The char yield declined as the reaction temperature increased.

They reported that the optimum temperature for pyrolyzing plastic waste is 450 °C [21].

Using pyrolysis oil as fuel for vehicles is a significant outlet [22,23]. Production from MSW content, water, and oxygenated organics leads to a decrease in the oil's heating value [23]. Furthermore, the high oxygen content in the bio-oil decreases its thermal stability. Thus, it can not be used directly as fuel for vehicles. Upgrading the pyrolysis oil using hydrotreatment or hydrodeoxygenation methods enhances oil stability and increases the heating value [24,25]. However, the hydrotreatment process requires high pressure, high temperature, and catalysts, making the process very expensive and complicated [13]. Catalytic pyrolysis of MSW could upgrade the quality of bio-oil.

In catalytic pyrolysis of MSW, several catalysts have been investigated and examined, such as zeolites, metal oxides, and metal hydroxide [2]. Different catalysts exhibit specific catalytic activity. For example, dolomite is inexpensive but has a limited lifetime at higher temperatures (>500 °C) [26]. Synthesized metal oxides are expensive materials and have a quick deactivation rate. Zeolites have highly active catalytic pyrolysis, but the oil yield is meager due to high coke formation. Bi-metallics are expensive catalysts and exhibit high catalytic activity, but the coking formation is very high [26]. Zeolite catalysts have been investigated for catalytic pyrolysis of MSW or biomass [27]. Y-zeolite, β -zeolite, and HZSM-5 catalysts have been examined for catalytic pyrolysis owing to their high surface area and acidity [12]. These catalysts produce oil with a high yield of aromatics and coke due to their higher acidity, increasing the coke formation rate [28]. Ates *et al.* [12] studied the impact of adding Y-zeolite, β -zeolite, and HZSM-5 catalysts to a batch reactor pyrolysis of MSW at 500 °C. The feedstock contained paper, plastic, organic waste, and textile, and 50 g of MSW was placed in the reactor. The reaction time was set up to be in the range of 72 to 85 min [12]. The results indicated that Y-zeolite produced a lower char yield (48 wt%) and a higher gas yield because Y-zeolite's high surface area enhanced the contact between the feedstock and catalysts and increased the cracking reaction rate [12]. Moreover, the pyrolysis oil yield and quality could be improved by the zeolite catalysts, as observed by Gandidi *et al.* [29]. They used zeolite catalysts to pyrolyze MSW, including biomass, rubber, paper, textile, and plastic. A fixed-bed vacuum reactor was applied to pyrolyze particles of MSW of 5

to 10 cm. The feedstock-to-catalyst ratio was 2, and the reaction time was 60 min [29]. Adding the catalysts to the reactor increased the liquid yield from 15 to 48 wt% and the gas yield from 21 to 50 wt% [29].

Metal oxide catalysts have been widely used for the pyrolysis of MSW [2,12,30,31]. Some, such as V_2O_5 and MnO_2 , are precious and cannot be synthesized easily on a large scale. However, some of them, such as Al_2O_3 and CaO , are inexpensive and could be synthesized on a large scale. Li *et al.* [31] studied the impact of reaction temperature and Al_2O_3 catalysts on the product yields of MSW catalytic pyrolysis [31]. The pyrolysis oil yield increased from 12 to 45 wt% as the reaction temperature increased from 350 to 500 °C. However, the pyrolysis oil yield declined to 26 wt% when the temperature increased to 540 °C because the cracking and coking reactions increased at a high temperature (500 °C) [31]. Adding Al_2O_3 increased the carbon and hydrogen content in the pyrolysis oil, improving the higher heating value (HHV) of the pyrolysis oil [31]. Furthermore, MgO catalysts have been used in the catalytic pyrolysis of MSW, because adding MgO to a pyrolysis reactor improves the deoxygenation rate and the oil quality, as reported by Fang *et al.* [32]. The MSW included food, wood, paper, and plastic [32]. The catalyst load was 5 wt% of the feedstock. The presence of MgO improved the yield of aromatic compounds and declined the yield of oxygen-containing compounds because the MgO catalyst enhanced deoxygenation [32]. Moreover, Ryu *et al.* [33] investigated the pyrolysis of lignin in the presence of MgO or active carbon (AC) and MgO/ Al_2O_3 . They found that MgO/ Al_2O_3 enhanced the bio-oil quality compared to noncatalytic pyrolysis because MgO/ Al_2O_3 increased the cracking rate [33]. Additionally, MgO/AC increased the aromatic compound yield compared to MgO/ Al_2O_3 because the high surface area of the support enhanced the deoxygenation rate [33].

From the literature results and findings, a stable, inexpensive, and active catalyst for the catalytic pyrolysis of MSW is still under investigation. Thus, this study evaluates the impact of pyrolysis parameters on the yield of MSW

Table 1. MSW contents.

Composition of MSW	Wt(%)
Food	42.4
Agriculture	9.5
Paper	15.9
Plastic	32.2

pyrolysis products. The reaction temperature, catalyst loading, and catalyst support were evaluated. In addition, MgO supported AC and Al_2O_3 to evaluate the support role of MgO catalyst activity.

2. Materials and Methods

2.1 Materials

The materials of Mg (NO_3)₂ · 6H₂O (Sigma-Aldrich, 99%), commercial γ - Al_2O_3 (Sasol North America, 99%), and Darco AC (Sigma-Aldrich, 100%) were used for preparing the catalysts (MgO, Al_2O_3 , AC, MgO/ Al_2O_3 , and MgO/AC). A mix of MSW was used as the feedstock for the pyrolysis reactor, and Table 1 presents the MSW content. Table 2 presents the ultimate analysis and HHV of MSW, which is determined by using the following formula [34]:

$$HHV_{dry} \left(\frac{MJ}{kg} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.015N - 0.0211A \quad (1)$$

where C, H, S, O, N, and A represent mass percentages on a dry basis of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash, respectively, for the contents in feedstock.

2.2 Catalyst Preparation

An aqueous solution prepared from 0.1 N HNO_3 and Mg(NO_3)₂ · 6H₂O (Sigma-Aldrich) was used to prepare MgO. The precipitate was stirred for 4 h at 70 °C. Then, it was filtered and dried at 115 °C for 18 h. Then, the MgO catalyst was calcined at 500 °C for 5 h. Commercial γ - Al_2O_3 (Sasol North America) was crushed and sieved to attain a γ - Al_2O_3 powder, which was dried at 115 °C for 18 h. Then, it was calcined at 500 °C for 4 h. Next, γ - Al_2O_3

Table 2. Ultimate and proximate analyses of MSW.

Ultimate Analysis	
Elements	(dry basis) MSW (wt%)
C	47.31
H	6.28
O	38.42
S	0.17
N	0.98
Proximate Analyses	
Volatile	77.94
Fixed carbon	15.22
Ash	6.84
HHV (MJ/kg)	19.8

was co-impregnated with an aqueous solution prepared from 0.1 N HNO₃ and Mg(NO₃)₂·6H₂O (Sigma-Aldrich) using the incipient wetness impregnation method to prepare MgO/Al₂O₃. Then, the catalysts were dried at 115 °C for 18 h and calcined at 450 °C for 5 h. The AC catalysts were prepared using Darco AC (Sigma-Aldrich), which was crushed, dried at 115 °C for 18 h, and calcined at 500 °C for 6 h. Finally, the MgO/AC catalyst was prepared using the same method of MgO/Al₂O₃.

2.3 Catalyst Characterization

The catalysts' texture properties, such as: Brunauer-Emmett-Teller (BET) surface area, pore-volume, and average pore size, were determined using N₂ adsorption-desorption isotherms calculated at 77 K using a Micromeritics ASAP 2020 analyzer [3]. The samples were dried at 115 °C under a vacuum for 6 h prior to the analysis. Crystalline phases in the catalysts were identified using X-ray diffraction (XRD). A Bruker D8 Focus (LynxEye detector) with Co-Kα1 radiation ($\lambda = 1.79 \text{ \AA}$) was used to collect the XRD catalyst patterns. The step size was 0.05, and the time step was 0.8 s [3].

2.4 Thermogravimetric Analysis

A Mettler Toledo TGA (SDTA851) was used to conduct the thermogravimetric analysis (TGA) of MSW to assess the optimum reaction temperature. The analysis was performed by heating 2 mg of MSW from 30 to 800 °C at the

heating rate of 10 °C per min under N₂ flow of 40 mL/min [21].

2.5 Pyrolysis of Municipal Solid Waste

Figure 1 presents the pyrolysis process schematic, where MSW with an average particle size of 2 mm was used as feedstock for the pyrolysis reactor. Moreover, 200 g of biomass was placed in a fixed-bed reactor operated in batch mode. The pyrolysis reactor was made up of 40 stainless steel with 4 cm i.d. and 24 cm in length. The pyrolysis reactor was heated from 30 °C to the set temperature at a heating rate of 10 °C/min. Four thermocouples were placed inside the reactor to monitor the reaction temperature. The reaction temperature, residence time, catalyst loading, and type of catalyst were varied to investigate the impact of pyrolysis parameters on the product's yields. The MSW was converted into organic vapor and gas. A preheater N₂ was employed to carry reaction products (vapor and gas) toward a condenser. Pyrolysis oil was collected from the condenser and the electrostatic precipitator and was analyzed using a Thermo Scientific Flash 2000 elemental analyzer to quantify the element content. Oxygen content in the liquid was obtained by subtracting the C, H, and N from the total mass. The oil was analyzed using a Hewlett-Packard HP 7890 Q2010 gas chromatograph-mass spectrometer (GC-MS) to analyze the oil composition. Analyzing the oil using GC-MS was explained in detail by [21]. The residence time of the reaction was counted from the first bio-oil drop into the condenser. After the experiment was conducted, the pyrolysis reactor was cooled to 25 °C. Then, the char yield was collected and calculated by subtracting the catalyst weight. The mass values of the bio-oil and char were measured, and the gas was calculated by subtracting the bio-oil and char yields from the total feed.

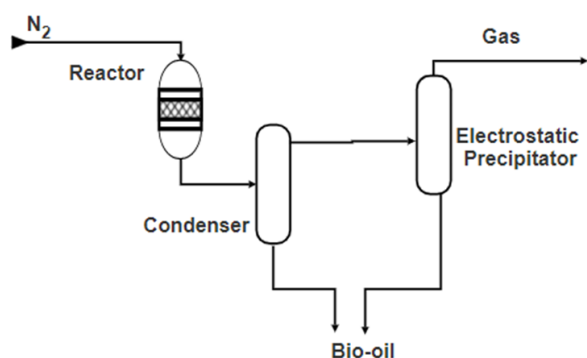


Figure 1. Pyrolysis process schematic.

Table 3. Textural properties of the catalysts.

	MgO content (wt%)	BET Surface Area (m ² /g)	Pore volume (cm ³ /g)
MgO	100	22	0.073
γ-Al ₂ O ₃	0	176	0.34
AC	0	547	0.78
MgO/γ-Al ₂ O ₃	40	68.64	0.19
MgO/AC	40	131.28	0.47

followed by γ - Al_2O_3 , MgO/AC , $\text{MgO}/\gamma\text{-Al}_2\text{O}_3$, and MgO , respectively. The BET surface area of MgO is $22 \text{ m}^2/\text{g}$. The AC BET surface area declined from 547 to $131 \text{ m}^2/\text{g}$ after adding MgO (40 wt%). The BET results suggest that adding MgO to AC and $\gamma\text{-Al}_2\text{O}_3$ decreased the support porosity because the pores of AC and $\gamma\text{-Al}_2\text{O}_3$ were filled with MgO . These results agree with those in the literature [35]. Penkova *et al.* [35] informed that the BET surface area of $\text{MgO}/\gamma\text{-Al}_2\text{O}_3$ declined from 137 to $65 \text{ m}^2/\text{g}$ when the MgO loading increased from 5 to 30 wt%, suggesting that the MgO aggregation rate increased with an increase in the loading of MgO [36]. Moreover, Cimino *et al.* [36] reported that increasing MgO loading from 10 to 30 wt% decreased the BET surface area of MgO/AC catalysts from 576 to $403 \text{ m}^2/\text{g}$, because the aggregation rate increased. This study and the literature indicate that adding MgO decreased the support porosity due to the aggregation of MgO particles, and the pores of the support were filled with MgO .

All catalysts were characterized using XRD to determine the crystalline phase. The XRD patterns of the catalysts are illustrated in Figure 2. The peaks (at $2\theta \cong 42.92^\circ$, 62.25° , and 77.82°) are very sharp for pure MgO , suggesting the crystallites are very large [36]. The XRD patterns for $\gamma\text{-Al}_2\text{O}_3$ demonstrated that the peaks appeared at $2\theta \cong 37.53^\circ$, 45.68° , and 66.69° . As depicted in Figure 2, no peak exists for AC, suggesting that AC is mostly amorphous. Adding MgO to $\gamma\text{-Al}_2\text{O}_3$ shifted the peaks of $\gamma\text{-Al}_2\text{O}_3$ and MgO to a lower angle due to the metal-metal interaction between MgO and $\gamma\text{-Al}_2\text{O}_3$ [35]. Also, the formation of a magnesium-defective spinel might cause the shift to lower angles [35]. Penkova *et al.* [35] reported

increasing the loading of MgO on $\gamma\text{-Al}_2\text{O}_3$ from 10 to 30 wt%, shifting the peaks of $\gamma\text{-Al}_2\text{O}_3$ from ($2\theta \cong 37.19^\circ$, 45.30° , and 65.87°) to lower angles ($2\theta \cong 36.89^\circ$, 45.00° , and 65.57°) due to the formation of the MgAl_2O_4 spinel layer. Despite the high BET surface area of AC, the XRD patterns of MgO/AC confirmed the presence of MgO , and the peaks were very sharp, reflecting that MgO presents as a large cluster on AC. These results agree with those in the literature [36]. Cimino *et al.* [36] reported that the intensity of MgO peaks and crystallite size increased with an increasing MgO load from 10 to 30 wt% for MgO/AC catalysts. In contrast, Zhang *et al.* [37] found that the MgO peak intensity was very low for 20 wt% MgO/AC owing to the high surface area of AC. For $\text{MgO}/\text{Al}_2\text{O}_3$ and MgO/AC catalysts, the MgO peaks are very sharp due to the high loading of MgO (40 wt%). The XRD results indicate that MgO is present in the catalyst surface, even though the support has a high surface area.

The TGA results illustrate that MSW decomposition started at 300°C and reached 71% decomposition at 500°C , as displayed in Figure 3. Increasing the temperature from 500 to 600°C improved the decomposition by just 6%. Thermal decay of MSW occurred in three stages. The first one occurred at ($200\text{--}310^\circ\text{C}$) and broke the substantial bonds into smaller bonds. Around 6% of MSW decays at this stage. The second stage occurred at ($310\text{--}500^\circ\text{C}$) and broke the small bonds into hot volatiles and gases. The decomposition of MSW at this stage is 65%. The final stage occurred ($500\text{--}800^\circ\text{C}$), which converts the volatiles into gases. The decomposition of MSW at this stage is 9%. The TGA results confirm the optimum temperature to convert the MSW to bio-oil, which is 500°C

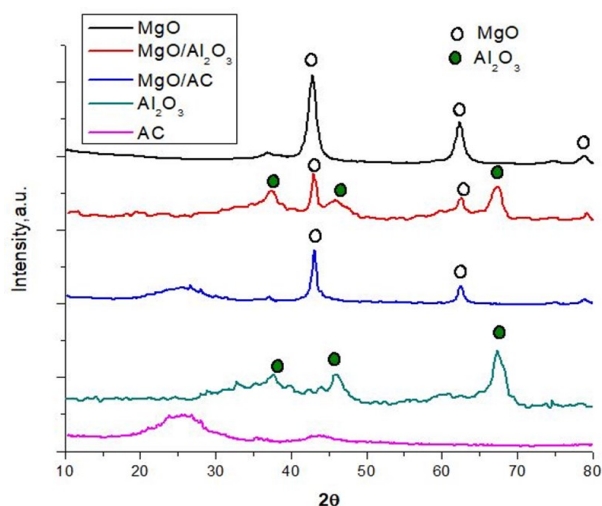


Figure 2. XRD patterns of the catalysts.

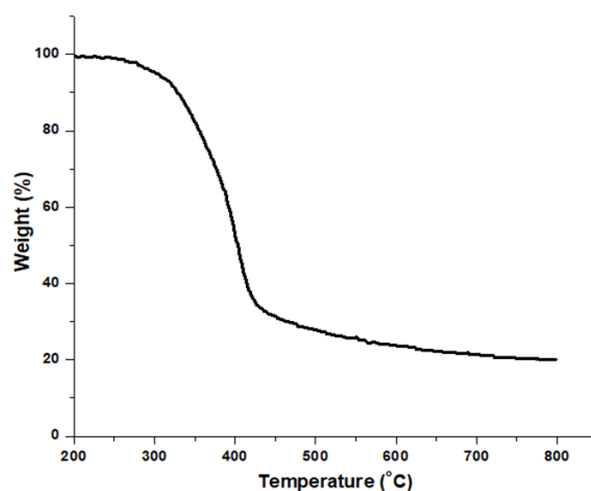


Figure 3. TGA analysis of MSW.

because more than 71% decomposition was attained at 500 °C, which consents with the results informed by Buah *et al.* [38]. They reported that the heating rate had not had a significant impact on the decomposition of MSW and that MSW started to decompose at 350 °C, reaching the maximum decomposition at 500 °C [38]. They stated that the ideal temperature for MSW pyrolysis is around 500 °C [38]. The TGA results demonstrate that the ideal temperature for MSW pyrolysis is 500 °C.

The reaction temperature was varied from 400 to 600 °C. As presented in Figure 4, for the noncatalytic pyrolysis experiment, as the reaction temperature increased, the gas yield improved, and char yield declined. The maximum liquid yield was 54 wt% at 500 °C. At 400 °C, the char yield was the highest (32 wt%) and decreased until reaching 18 wt% at 600 °C. In contrast, the gas yield increased from 17 to 29 wt% when the reaction temperature increased from 400 to 600 °C. The liquid yield increased with temperature until reaching the highest yield of 54 wt% at 500 °C. Then, the yield started to decline until reaching 48 wt% at 600 °C. The liquid yield declined with increased temperature because the cracking reaction rate increased with the temperature, leading to an increased gas yield and declined liquid yield, as explained by Lopez *et al.* [39]. They investigated the pyrolysis of plastic waste and found the cracking rate increased with temperature [39], and Miandad *et al.* [21] confirmed this phenomenon. Moreover, Buah *et al.* [38] examined the impact of the temperature on the bio-oil yield from MSW pyrolysis. They found that increasing the reaction temperature declined char yield and increased the gas yield, which agrees with the results of this study [38]. Additionally,

the feedstock type has a major impact on the yield of bio-oil. For instance, Horne and Williams [40] found the maximum bio-oil yield at 550 °C for biomass pyrolysis, which is higher than the optimum temperature found for this study. Also, pyrolysis MSW at low temperature (< 550 °C) is preferred to save energy and cost. These TGA and pyrolysis results demonstrate that the ideal temperature for pyrolysis of MSW is 500 °C.

The residence time effect on the product yield was investigated to obtain the optimum resistance time for pyrolysis. As illustrated in Figure 5, as the reaction time increased from 20 to 60 min, the char yield declined, and the gas yield increased. When the reaction time increased from 20 to 40 min, the liquid yield improved from 52 to 54 wt%, which is insignificant. The 40-min resistance time produced the highest liquid yield of 54 wt%. Similar outcomes were informed by Miandad *et al.* [21] and Lopez *et al.* [39]. Miandad *et al.* [21] examined the impact of reaction time on plastic waste pyrolysis product yield. The time varied from 60 to 120 min. The char yield declined from 9 wt% to 5 wt%, and the gas yield improved with an increase in the reaction time [21]. However, the reaction time did not have a major impact on the oil yield. The type of feedstock and reactor dimension influence the residence time of MSW pyrolysis, as informed by Jung *et al.* [17]. From the results of the presented study, the reaction time significantly influences the liquid yield and a minor effect on the char and gas yields.

Figure 6 and Table 4 present the impact of adding catalysts to the pyrolysis of MSW. For noncatalytic pyrolysis, the bio-oil contented 35 wt% of oxygen, and the HHV was 25 MJ/kg.

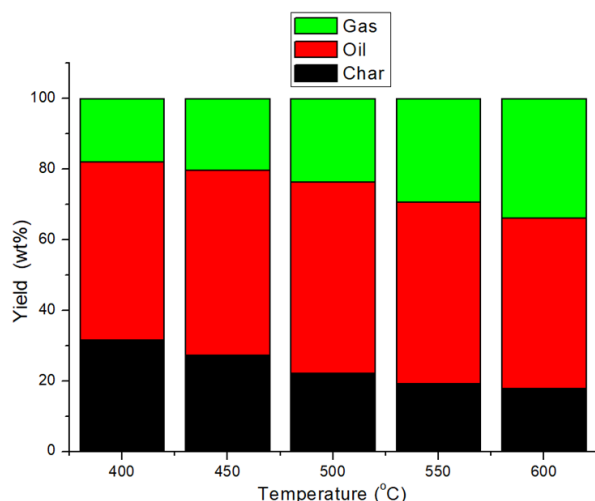


Figure 4. The effect of the temperature on the products yields.

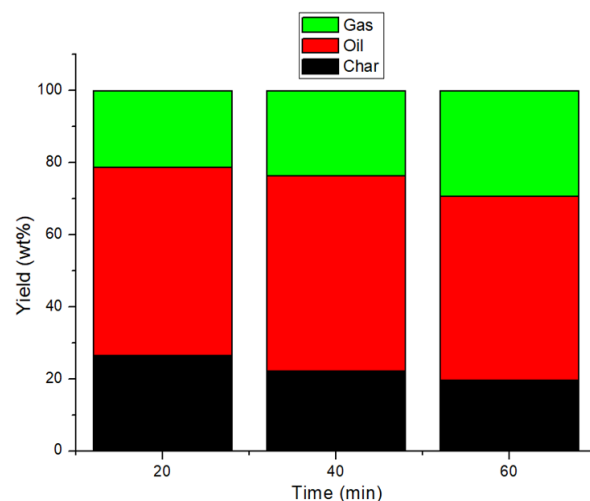


Figure 5. The effect of residence time on the products yields.

The high oxygen content in the bio-oil decreased the oil quality, making the oil upgrade stage more complicated, as reported by Case *et al.* [41]. They conducted a pyrolysis experiment on pine sawdust at 500 °C and found that the oxygen content in the bio-oil was more than 26 wt%. They stated that, as the oxygen content increased in the bio-oil, the bio-oil viscosity increased, which requires two steps to upgrade the bio-oil: stabilization and hydrotreatment [41]. For the catalytic pyrolysis, the catalyst load was 20 wt% of the feed. Adding pure MgO to the pyrolysis reactor increased the gas yield by 4% and decreased the bio-oil yield by 5%. Adding MgO improved the bio-oil quality by enhancing the deoxygenation rate, decreasing the oxygen content and oxygen-to-carbon ratio. This result agrees with that of Fang *et al.* [32] who investigated the impact of adding MgO to the reactor pyrolysis of MSW.

Adding MgO decreased the bio-oil yield and improved the gas yield because it decreased the activation energy for the reaction from 300 to 160 kJ/mol and increased the cracking rate [32]. Adding MgO increases the deoxygenation rate, decreasing the oxygen-to-carbon ratio of the bio-oil [32]. The char yield improved from 22 to 28 wt%, and the bio-oil yield declined from 54 to 47 wt% by adding MgO/Al₂O₃ to the

reactor. However, adding MgO/Al₂O₃ enhances the bio-oil quality because the MgO deposit on Al₂O₃ has a high surface area, increasing the reaction rate by increasing the contact between the catalysts and feedstock [27,42].

Adding MgO/Al₂O₃ improved the HHV of the bio-oil from 25 to 29 MJ/kg. The char yields increased because the coking rate increased from adding the catalysts [27,43,44]. Adding MgO/AC increased the gas yield from 24 to 39 wt% and declined the bio-oil yield from 54 to 40 wt%. The high surface area of MgO/AC increases the cracking rate, enhancing the bio-oil quality by decreasing the oxygen-to-carbon ratio and increasing the hydrogen-to-carbon ratio.

Adding pure Al₂O₃ does not significantly impact the reaction product's yields. However, adding Al₂O₃ enhances the bio-oil quality by decreasing the bio-oil oxygen content from 35 to 30 wt%. Li *et al.* [31] examined the role of adding Al₂O₃ to the pyrolysis of MSW. They found that the bio-oil yield (45 wt%) was attained at 500 °C, which is higher than the bio-oil yield attained in this study. They also found the Al₂O₃ improved the bio-oil quality by increasing the aromatic hydrocarbon content [31]. The difference between these results is because the reaction conditions and the MSW type are different. In contrast, adding pure AC decreased the bio-oil from 54 to 31 wt% and improved the gas yield by 10 wt% and the char yield by 12 wt% due to adding AC, enhancing the cracking and coking reactions [27,44]. Pure AC decreases the oxygen-to-carbon ratio because AC enhances the decarboxylation rate [27,32]. The high char amount is owing to the large pore size of AC, as reported by [20,33]. Based on the balance between the quality and yield of bio-oil in Figure 6 and Table 4, MgO/AC is the best catalyst to produce bio-oil from MSW because of the high surface area of the support and the MgO activity for deoxygenation. Furthermore, adding the MgO/AC catalysts improved the HHV of the bio-oil from 25 to 33 MJ/kg. This study demonstrated that adding catalysts (MgO, MgO/Al₂O₃, MgO/AC, Al₂O₃, and AC) to the pyrolysis reactor increas-

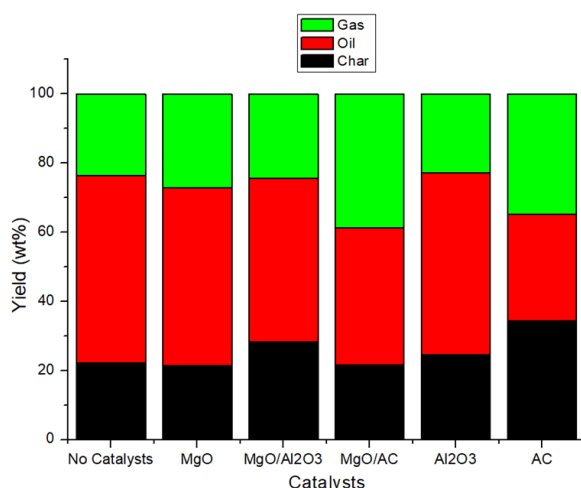


Figure 6. The effect of the catalysts on the products yields.

Table 4. The bio-oil element analysis.

	C%	H%	O%	O:C	H:C	HHV (MJ/kg)
No Catalysts	58.4	6.7	34.9	0.45	1.38	25
MgO	64.7	6.9	28.4	0.33	1.28	28
MgO/Al ₂ O ₃	67.1	7.1	25.8	0.29	1.27	29
MgO/AC	75.2	7.3	17.5	0.17	1.16	33
Al ₂ O ₃	62.5	6.6	30.9	0.37	1.27	26
AC	76.9	6.1	16.9	0.16	0.95	32

es the gas and char yields, declines the bio-oil yield, and improves the bio-oil quality.

Catalyst loading was investigated to determine the optimum load of MgO/AC, and the results are presented in Figure 7. As the catalysts load increased, the bio-oil declined, and the gas yield increased because adding the catalysts increased the cracking rate. When catalyst loading was 30 wt% of the feed, the char

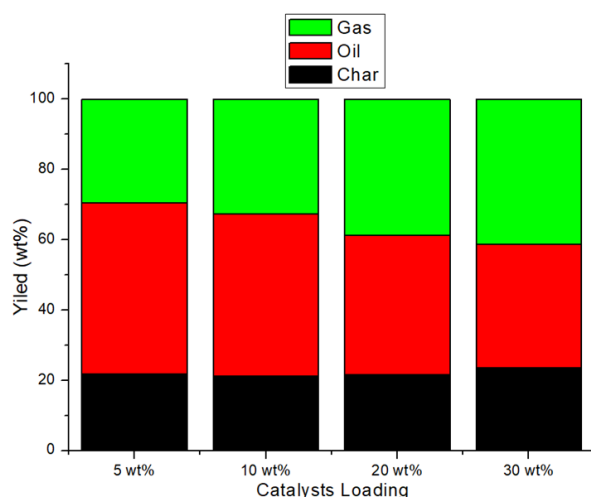


Figure 7. The effect of catalysts loading on the products yields.

yield increased because increasing the catalyst load leads to an increased coking rate. This result agrees with that of Aysu and Küçük [45], who investigated the impact of catalyst loading on the produced pyrolysis yields. They added Al_2O_3 and ZrO_2 to the pyrolysis reactor for different loadings [45]. For both catalysts, catalyst loading increased from 5 to 15 wt% of the feed, the bio-oil yield declined, and the gas yield improved. They stated that adding the catalysts enhances the rate of cracking and decreases the rate of polymerization [45]. Moreover, Garba *et al.* [22] found the same results for pyrolysis of bagasse using HZSM-5 at 500 °C. When the catalyst loading increased from 5 to 15 wt%, the liquid yield declined from 50 to 20 wt%, and the gas yield improved from 19 to 48 wt% [22]. They found that increasing the catalyst loading increases the cracking rate and aromatic bio-oil components [22]. Catalyst loading had no significant influence on the char yield because the coking rate was not enhanced by HZSM-5 [22]. In contrast, Pütün [20] studied the impact of catalyst loading on the product yields of pyrolysis biomass using MgO catalysts at 550 °C. As catalyst loading increased from 5 to 20 wt% of the feed, the char yield increased from 20 to 27 wt%, which

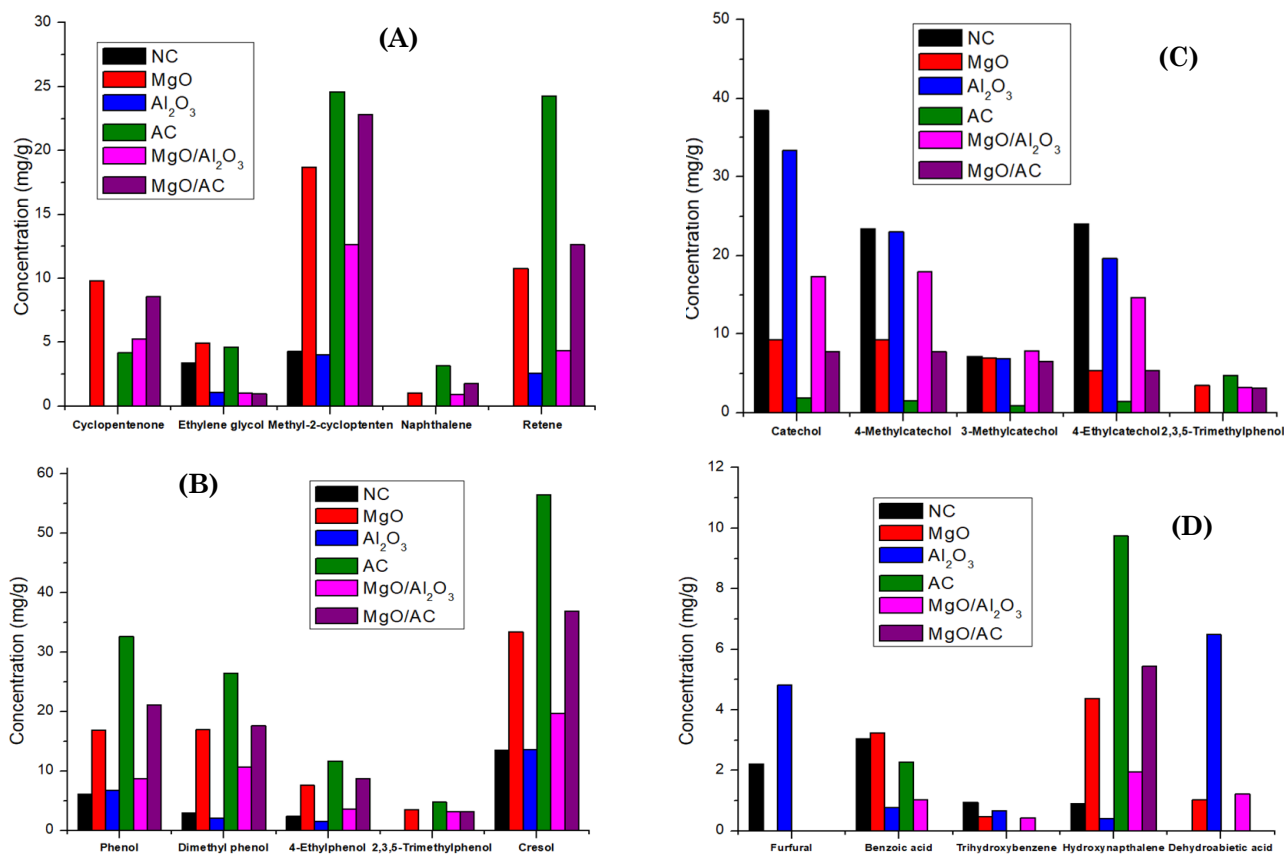


Figure 8. A-D The most significant compounds of bio-oil analyzed by GC-MC.

agrees with the results of this study [20]. Pütün stated that the increase of the MgO catalysts enhances the coking rate, which increases the char yield [20]. The results assert that catalyst loading highly influences the liquid and gas yields.

The most significant compounds analyzed by GC-MC are presented in Figure 8 A-D. Furfural is a typical biomass pyrolysis product produced using noncatalytic pyrolysis and Al_2O_3 , as depicted in Figure 8 D. When MgO, MgO/ Al_2O_3 , MgO/AC, and AC catalysts were added to the pyrolysis reactor, the furfural dispersed, and the cyclopentene and naphthalene concentrations increased. As illustrated in Figure 8A, adding MgO and MgO/AC catalysts increases the formation of cyclopentene and Methyl-2-cyclopentene due to the increased cracking rate caused by adding the catalysts [32]. These results are in agreement with those found by Case *et al.* [41], finding that adding CaO as catalysts to the pyrolysis of pine sawdust decreases the furfural formation and enhances the formation of cyclopentenones [41]. Another remarkable result is that AC catalysts increased the retene yield in the bio-oil because AC has a high surface area that promotes the cracking rate over the carboxylation rate [9,10]. Figure 8B illustrated that MgO, MgO/AC, and AC exhibit higher selectivity to phenols, indicating that acid compounds could be converted into phenols. Figure 8C reveals that these catalysts (MgO, MgO/AC, and AC) present lower selectivity to catechols because they can be converted into aromatic hydrocarbons through demethoxylation reactions. This result agrees with that by Ryu *et al.* [33], who reported that adding MgO/AC to the pyrolysis of lignin increases the aromatic hydrocarbon yield because MgO catalysts enhance the dihydroxylation rate and demethoxylation reactions [33]. Figure 8D demonstrates that MgO/AC catalysts decrease the selectivity of the reaction to benzoic acid because MgO enhances the deoxygenation reaction and increases the deoxygenated aromatic compounds, as displayed in Figure 8A. Therefore, adding MgO/ Al_2O_3 and MgO/AC increases the aromatic compound yield and improves the bio-oil quality.

4. Conclusions

The TGA results illustrate that MSW decomposition starts at 300 °C, reaching about 71% decomposition at 500 °C. The 40 min resistance time produces the highest liquid yield at 54 wt%. The liquid yields varied from 30% to 54% based on the experimental conditions. For the noncatalytic pyrolysis experiment, as the

temperature increases, the gas yield increases, and char yield decreases. The maximum liquid yield was 54% at 500 °C. The results indicated that adding MgO, MgO/ Al_2O_3 , and MgO/AC declines the oil yield and increases the gas yield. However, the catalysts exhibited significant deoxygenation activity, which enhances the quality of the oil. Of the catalysts that had high deoxygenation activity, MgO/AC had the highest relative yield. The loading of MgO/AC varied from 5 to 30 wt% of feed to the pyrolysis reactor. As catalyst loading increases, the liquid yield decreases, while the gas and char yields increase. The MgO/AC catalyst showed high activity, improved the oil's quality, and is inexpensive.

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