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Catalytic Pyrolysis Oil from Landfilled Plastics through Ni/HZSM-5 and Co/HZSM-5 Catalysts

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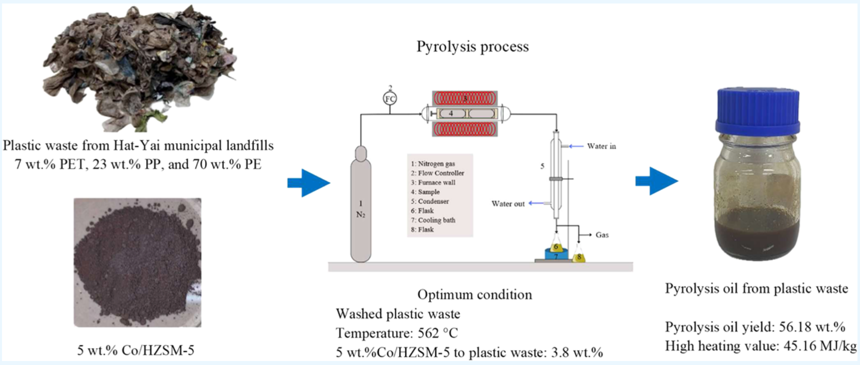

ABSTRACT: Plastic waste poses a significant environmental challenge. To address this issue, the pyrolysis process offers a promising solution to convert plastic waste into valuable products. This study investigated the pyrolysis of plastic waste sourced from a Hat Yai municipal landfill, aiming to optimize process conditions and characterize the resulting products. The plastic waste was classified into three primary types: polyethylene terephthalate (PET) (7 wt %), polypropylene (PP) (23 wt %), and polyethylene (PE) (70 wt %). Thermogravimetric analysis (TGA) revealed that the waste decomposed completely within the temperature range of 520−600 °C. To optimize pyrolysis conditions, experiments were conducted on both unwashed and water-washed plastic waste, varying particle size, catalyst type, and loading. Nickel- and cobalt-based zeolite catalysts (Ni/HZSM-5 and Co/HZSM-5) were employed to enhance the pyrolysis process. The results indicated that medium-sized, water-washed plastic waste, pyrolyzed at 560 °C with 5 wt % of 5 wt % Co/HZSM-5 catalyst, yielded the highest pyrolysis oil (47.42 ± 1.00 wt %) and a high heating value (HHV) of 38.06 ± 0.67 MJ/kg. To further optimize the process, central composite design (CCD) and response surface methodology (RSM) were utilized to investigate the effects of the temperature and catalyst loading on the pyrolysis oil yield and HHV. Optimal conditions were determined for both unwashed and washed plastic waste. Gas chromatography−mass spectrometry (GC-MS) analysis of the pyrolysis oil from both optimum conditions revealed a high proportion of hydrocarbon compounds similar to fossil fuels, including gasoline, jet fuel, and diesel. This study successfully optimized the catalytic pyrolysis of plastic waste, resulting in significant improvement in oil yield and product quality. The use of water-washed plastic waste and 5% Co/HZSM-5 catalyst proved to be effective in enhancing the pyrolysis process. These findings provide valuable insights into the sustainable management of plastic waste and the production of valuable resources.

1. INTRODUCTION

It is a known fact that more resources, energy, and food are consumed with increasing world's population creating significant waste problems, such as disposed plastic material.[1] As plastics are used widely in different applications encompassing packaging, bottles, construction, healthcare, automotive, industry, and among many others.[2,3] Especially during the outbreak of COVID-19, the amount of plastic waste generated worldwide increased by 1.6 million tons/day.[4] It is important to find ways to manage waste through various methods such as landfilling, waste incineration, and recycling.[5] However, waste management by incineration causes environmental pollution; on the other hand, recycling requires high operating costs. The most common and practical way to manage plastic waste is disposing in landfills.[6] Landfilling is a convenient method with a low operating cost. However, high volume of waste results in a possible shortage of landfills. Plastic waste is also creating an important environmental

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problem. Government agencies are trying to solve such issues from Hat-Yai municipal landfills, and pyrolysis process is considered as one of the alternative approaches.[7]

Pyrolysis of plastic waste is the process where long carbon chains are broken down by heat into shorter chains which changes the solid products into liquid fuels and gases, resulting in a higher heating value under conditions without oxygen gas. Pyrolysis of plastics produces oil, wax, char, and gas, all of which can be used in various applications.[8] Several previous studies showed that the pyrolysis process can be employed to convert plastic waste into energy so that consumption of fossil fuels is reduced. Thahir et al.[9] studied the effect of temperature on converting plastic waste (polypropylene (PP)) into alternative energy through a pyrolysis-catalytic cracking process. They used zeolite (ZSM-5) as a catalyst (1:10, Catalyst/PP ratio). It was found that the liquid yield was the highest at a temperature of 560 °C. The liquid product also had a high heating value (HHV) of 46.2 MJ/kg, which is similar to that of fossil fuels such as gasoline and kerosene.

The pyrolysis process usually occurs at high temperatures and uses a lot of energy. The catalyst helps run the reaction and offers a faster process at a temperature that is not high. In a past study, the use of natural catalysts for the pyrolysis process was investigated. Hendrawati et al.[10] to convert plastic waste into fuel oil through the pyrolysis process of packaging waste, which contains high-density polyethylene (HDPE) and polypropylene (PP), using natural zeolite as a catalyst at a temperature of 400 °C. They found that using natural zeolite reduced the reaction time, and operating at a lower temperature saved the overall processing cost. Additionally, the resulting product had hydrocarbon compounds with a good range, C5−C20, similar to those of gasoline and diesel. To improve the efficiency of catalysts for the pyrolysis process, researchers have incorporated metals into the catalyst. Akubo, Nahil, and Williams[11] studied pyrolysis-catalytic cracking process of high-density polyethylene (HDPE) using Y-zeolite impregnated with 1 and 5 wt % metal loading of Ni, Fe, Mo, Ga, Ru, and Co to determine the aromatic fuel composition at a temperature of 600 °C. They found that loading metal on Y-zeolite catalyst led to an increase in the hydrogen yield and higher production of single-ring aromatic hydrocarbons such as toluene, ethylbenzene, and xylene in the oil product.

Different types of plastics and landfills have varying chemical properties based on the lifestyle and dietary habits of local people and specific conditions of the environment and location, such as the climate, age, and size of the landfill. Pyrolysis process, which is considered to produce pyrolysis oil, has different properties, including HHV, density, viscosity, acidity, and organic composition. Therefore, it is important to study the properties of plastic waste from the local landfills before proceeding with pyrolysis process such as moisture content, fixed carbon, volatile matter, and ash content,[9] since plastic waste is mostly composed of carbon. Plastic waste from landfills often has a high contamination problem of impurities and organic matter, which directly affects the pyrolysis oil yield. Washing is one of the methods to reduce the amount of biological, inorganic, and impurities from plastic waste. Genuino et al.[12] investigated the effects of washing plastic waste for the pyrolysis process. They found that washing plastic waste effectively lowers the biogenic, inorganic, and halogen contents in plastic waste, which reduces the ash content in the pyrolysis product. Similarly, Borsodi et al.[13] reported that washing plastic waste before pyrolysis reduced impurities and contaminants significantly in pyrolysis products. This work studied the water-washing of plastic waste before entering the pyrolysis process to find the optimum conditions for converting plastic waste into value-added products.

Currently, there is limited data or information on pyrolysis of plastic waste from Hat-Yai municipal landfills. Therefore, the objective of the study was to investigate the optimum condition employing Central composite design (CCD) under the responses surface method (RSM) which specifies 2 variables, temperature and wt % catalysts to plastic waste. Also the results of using unwashed and washed plastic waste will be compared to each other within the perspective of the study.

2. MATERIALS AND METHODS

2.1. Plastic Waste Preparation. Plastic waste has been present in the Hat Yai municipal landfills for a period of two years. Siampoweroil Co., Ltd. is the supplier of this plastic waste material. The collected plastic waste was divided into two batches corresponding to the following washing procedures: (1) unwashed, (2) washed with water at room temperature, and dried up. Unwashed and washed plastic waste were cut into small pieces of three different sizes, namely, small (0.3−0.7 cm), medium (0.8−1.2 cm), and large (1.5−2.0 cm).

2.2. Catalyst Preparation. For pyrolysis experiments, four different catalysts were used comprising 5 wt %Ni/HZSM-5, 10 wt %Ni/HZSM-5, 5 wt %Co/HZSM-5, and 10 wt %Co/HZSM-5. The procedure for the preparation of catalyst was carried out in the initial preparation of zeolite (HZSM-5) into zeolite ammonium (ZSM-5). In the next step, ZSM-5 was dried in an oven at a temperature of 105 °C for 24 h to remove moisture and calcined at a temperature of 500 °C for 5 h.[14] Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 6H_2O$) and cobalt-(II) nitrate hexahydrate ($Co(NO_3)_2 6H_2O$) were prepared using a dry impregnation method, with 5 and 10 wt % on HZSM-5. HZSM-5-supported metal catalysts were dried in an oven at a temperature of 105 °C for 24 h to remove moisture. In the next step, the 5 and 10 wt %Ni/HZSM-5 catalysts were calcined at a temperature of 600 °C for 5 h, while the 5 and 10 wt %Co/HZSM-5 catalysts were calcined at a temperature of 500 °C for 6 h.

2.3. Characterization of Plastic Waste. The type of plastic waste from Hat-Yai municipal landfills was identified by using a Fourier transform infrared spectrometer (FT-IR) with the attenuated total reflectance (ATR) technique. Plastic waste was analyzed in a Bruker Vertex 70, which works by measuring the absorption of the middle infrared region (400−4000 cm^{-1}). To determine the appropriate temperature to decompose the plastic waste, thermogravimetric analysis (TGA) of the plastic waste was also performed, and 3−5 mg of plastic waste was heated within the range of 30−800 °C at a rate of 10 °C/min, with a nitrogen gas flow rate of 20 mL/min using a PerkinElmer TGA8000.

2.4. Characterization of Catalyst. The catalyst was analyzed to determine the metal content and dispersion of the transition metal by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). These analyses were performed on a Hitachi SU3900.

2.5. Experimental Procedures. A fixed-bed reactor made of stainless steel tube with dimensions of length, L: 48.00 cm and diameter, D: 6.35 cm, was used for the pyrolysis process, as illustrated in Figure 1. For each pyrolysis experiment of plastic waste, 50 g of plastic waste was used with a composition of 7

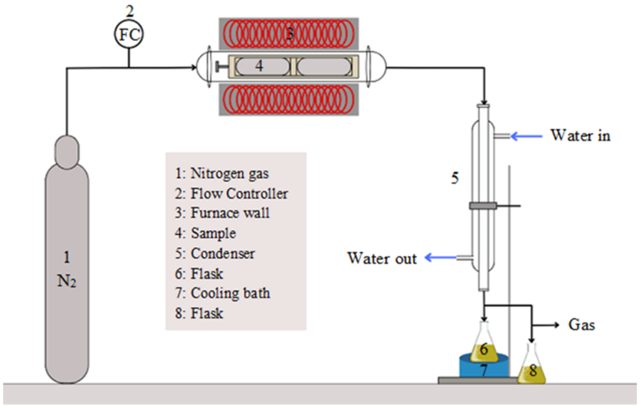

Figure 1. Diagram of the plastic waste pyrolysis system.

wt % PET, 23 wt % PP, and 70 wt % PE. Pyrolysis experiments were carried out at a temperature of 520, 540, 560, 580, and 600 °C, which were selected based on temperature levels of the decomposition of plastic waste using TGA. The catalysts used were 5 wt %Ni/HZSM-5, 10 wt %Ni/HZSM-5, 5 wt %Co/HZSM-5, and 10 wt %Co/HZSM-5 using 5, 10, 15, and 20 wt % catalysts to plastic waste. Before the experiment, the reactor was purged with nitrogen gas for 2−3 min to remove oxygen gas. Plastic waste was then heated from room temperature up to the required temperature at a rate of 10 °C/min, with a nitrogen gas flow rate of 100 mL/min. Nitrogen gas was used as the carrier gas for organic vapor products exiting the reactor. A condenser cooled with water at a temperature of 20 °C was used to transform the organic vapors into pyrolysis oil.

The effect of independent variables on the response of the pyrolysis oil yield and HHV was also analyzed. Central composite design (CCD) under the responses surface method (RSM) using a quadratic model was used to determine the design of the experiment (DOE), which specifies two variables, *A*: temperature, and *B*: 5 wt %Co/HZSM-5 to plastic waste (wt %) was also used to predict the experimental data to find optimum conditions to produce pyrolysis oil. The experiment was designed with 13 runs performed as suggested by the design-expert version 12 (Stat-Ease, Inc.) software, including five duplications at the central point to ensure reliable results. Data from unwashed and washed plastic waste were compared to each other to confirm the results of the study.

2.6. Products Analysis. The properties of the pyrolysis oil were analyzed as follows: HHV was determined using a bomb calorimeter (IKA C5000), viscosity was measured using a capillary viscometer, density was measured using a pycnometer, and acidity was measured using a pH meter.

Analyzing organic compounds in pyrolysis oil with a gas chromatograph−mass spectrometer (GC-MS), model GC7800B/MS5977B, Aligent brand. Typically, 400 ± 50 μg of the pyrolysis oil was used at a high heating rate of 20 °C/ms with pure helium (99.99%) as the carrier gas for the GC-MS system at a split ratio of 50:1. The organic compounds in pyrolysis oil were analyzed using an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The GC column oven was initially heated at a temperature of 40 °C for 1 min and then raised to a temperature of 280 °C at a rate of 10 °C/min.

Figure 2. Weight percentage of various plastic types in Hat-Yai municipal landfills.

Standardized data from the National Institute of Standards and Technology (NIST) library was used to identify organic compounds by matching with more than 85% of the system's database to analyze compound groups. The peak area percent was used to assess the relative composition. The experiment was performed three times and reported as mass averages and standard deviations.

The pyrolysis oil, wax, char, and gas yields were calculated using eqs 1-4.

$$\text{pyrolysis oil yield (wt \%)} = \frac{\text{pyrolysis oil (g)}}{\text{plastic waste feed (g)}} \times 100 \tag{1}$$

$$\text{wax yield (wt \%)} = \frac{\text{wax (g)}}{\text{plastic waste feed (g)}} \times 100 \tag{2}$$

$$\text{char yield (wt \%)} = \frac{\text{char (g)}}{\text{plastic waste feed (g)}} \times 100 \tag{3}$$

$$\text{gas yield (wt \%)} = 100 - \text{wt \% (pyrolysis oil yield + wax yield + char yield)} \tag{4}$$

3. RESULTS AND DISCUSSION

3.1. Characterization of Plastic Waste. The main plastic waste considered in this work includes plastic bottles (7 wt %), packaging bags (23 wt %), and plastic bags (70 wt %) illustrated in Figure 2. A sample of three types of plastic waste, namely, plastic bottles, packaging bags, and plastic bags, was used to analyze the characteristics of plastic waste using FT-IR, as depicted in Figure 3. The FT-IR spectra of plastic bottles exhibited transmittance peaks at 1722, 1245, 1097, and 728 cm^{-1} corresponding to the C═O stretch of the carbonyl group, C−O stretch of the alkyl-substituted ether, C−O stretch of the alkyl-substituted ether, and aromatic C−H out-of-plane bend, respectively, and plastic bottles were identified as polyethylene terephthalate (PET). The FT-IR spectra of packaging bags exhibited transmittance peaks at 2957, 2920, 1458, and 1378 cm^{-1} corresponding to methyl C−H asymmetric stretch, methylene C−H asymmetric stretch, methylene C−H bend, and methyl C−H symmetric bend, respectively, and packaging bags were identified as polypropylene (PP). The FT-IR spectra of plastic bags showed transmittance peaks at 2919, 2851, 1469, and 720 cm^{-1} corresponding to the methylene C−H asymmetric stretch, C−H methylene symmetric stretch, methylene C−H bend, and C−H long-chain methyl rock, respectively, and plastic bags were identified as polyethylene (PE). These transmittance peaks are similar to those reported by reliable sources.[15−17]

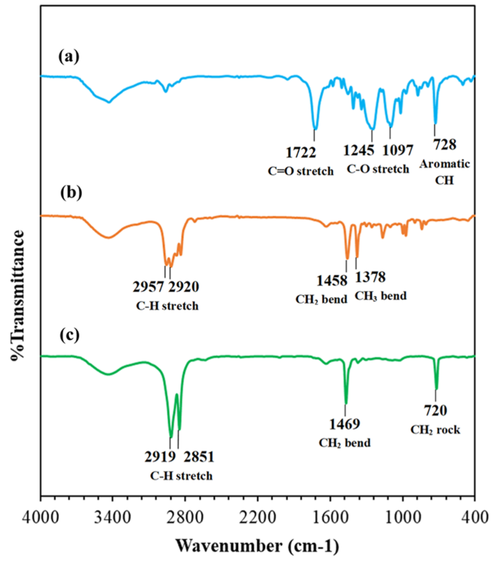

Figure 3. FT-IR spectra of the plastic waste: (a) PET, (b) PP, and (c) PE.

Proximate analysis of individual plastic waste is presented in Table 1. It shows that plastic waste is composed mainly of volatile matter (≥90.66 ± 2.59 wt %), alongside a minor fixed carbon (0.02 ± 0.01−2.45 ± 0.37 wt %), a relatively small ash content (0.82 ± 0.11−6.82 ± 1.21 wt %), and a negligible moisture content (≤0.10 ± 0.01 wt %). The experimental data closely aligns with the values reported by Martínez-Narro et al.[18]

Table 1. Proximate Analysis of Plastic Waste Samples (wt %)

plastic waste	proximate analysis (wt %)			
	moisture	ash	fixed carbon	volatile matter
This Study				
PET	0.02 ± 0.01	0.82 ± 0.11	0.02 ± 0.01	99.14 ± 1.78
PP	0.10 ± 0.01	2.48 ± 0.73	0.33 ± 0.18	97.09 ± 0.45
PE	0.07 ± 0.02	6.82 ± 1.21	2.45 ± 0.37	90.66 ± 2.59
Martínez-Narro et al.[18]				
PET	0.26 ± 0.13	0.70 ± 0.1	8.28 ± 1.74	91.03 ± 0.41
PP	0.15 ± 0.04	2.18 ± 0.12	0.21 ± 0.07	97.61 ± 0.38
LDPE	0.17 ± 0.08	6.12 ± 0.29	0.60 ± 0.25	93.28 ± 2.12
HDPE	0.04 ± 0.03	0.14 ± 0.06	0.22 ± 0.09	99.64 ± 0.52

The TGA was used to determine suitable pyrolysis process conditions for analyzing the temperature to decompose plastic waste due to different types of plastics having different temperatures to decompose depicted in Figure 4. There were three types of plastic waste comprising PET, PP, and PE. The results showed that all plastic waste contained negligible moisture because there was no change in the peak at the temperature range of 30−100 °C. Consider the start of

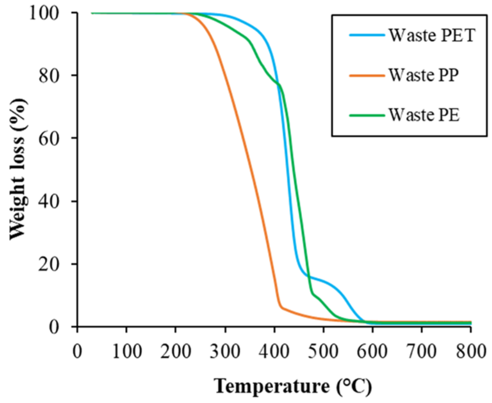

Figure 4. TGA results used to determine the optimum temperature for decomposing washed plastic waste.

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ACS Omega 2025, 10, 5744−5755

Table 2. SEM-EDS Analysis of the Catalyst Metal Composition

types of catalysts	O (wt %)	Al (wt %)	Si (wt %)	Ni (wt %)	Co (wt %)
5 wt %Ni/HZSM-5	57.29 ± 0.75	2.23 ± 0.07	35.54 ± 0.71	4.94 ± 0.13	
10 wt %Ni/HZSM-5	47.91 ± 1.01	2.46 ± 0.11	39.35 ± 1.15	10.28 ± 0.25	
5 wt %Co/HZSM-5	51.75 ± 0.03	2.55 ± 0.11	40.69 ± 0.19		5.01 ± 0.08
10 wt %Co/HZSM-5	48.32 ± 0.35	2.55 ± 0.10	39.16 ± 0.22		9.97 ± 0.13

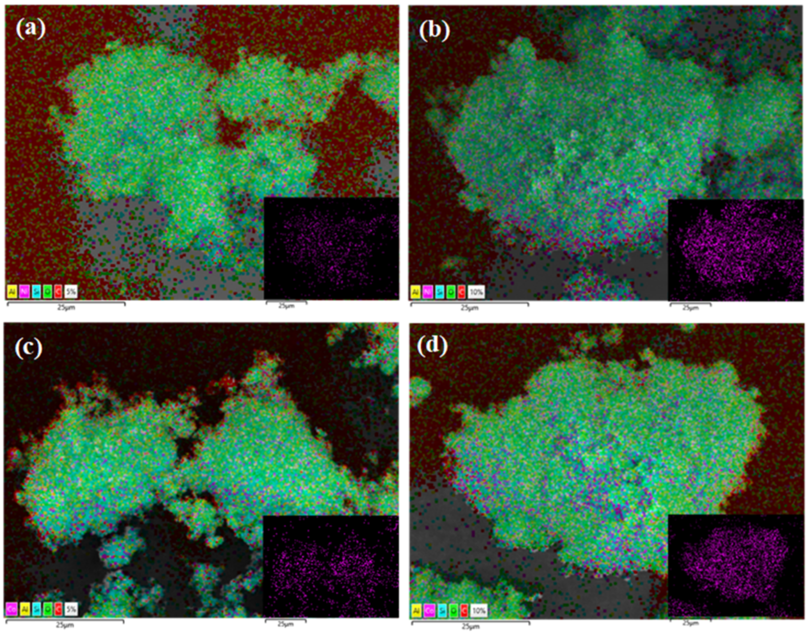

Figure 5. SEM-EDS results of the dispersion of the transition metal on catalysts (a) 5 wt %Ni/HZSM-5, (b) 10 wt %Ni/HZSM-5, (c) 5 wt %Co/HZSM-5, and (d) 10 wt %Co/HZSM-5.

Table 3. Effect of Size of Waste Material on the Pyrolysis Process

size of plastic waste	yield (wt %) pyrolysis oil	wax	char	gas	HHV (MJ/kg)
small (0.3−0.7 cm)	29.38 ± 0.62	3.32 ± 1.29	9.28 ± 0.71	58.02 ± 0.91	37.82 ± 0.67
medium (0.8−1.2 cm)	44.42 ± 0.94	4.02 ± 1.56	2.80 ± 0.21	48.76 ± 0.77	40.54 ± 0.71
large (1.5−2.0 cm)	28.00 ± 0.59	8.00 ± 3.11	5.28 ± 0.41	58.72 ± 0.93	32.34 ± 0.57

degradation at an initial mass loss of 1 wt %, in which waste PP began to decompose at temperatures that approximately 240 °C, slowly and with more residue product. This is a result of additives in the plastic,[19] which make it difficult to decompose. Waste PE began to decompose at a temperature of 260 °C, and waste PET began to decompose at a temperature of 300 °C, respectively. The partial decomposition of waste PET, PP, and PE occurs within the range of 300−500 °C. Complete degradation of all plastic waste occurred within the range of 520−600 °C, with a temperature of 600 °C a mass loss of 99 wt % of waste PET, 98 wt % of waste PP, and 99 wt % of waste PE. The TGA results in this study align with corresponding findings in previous research.[20] Therefore, the temperature used for this study occurred within the range of 520−600 °C.

3.2. Characterization of Catalyst. The SEM-EDS was employed to analyze the metal content and dispersion of the transition metals on four types of catalyst comprising 5 wt % Ni/HZSM-5, 10 wt %Ni/HZSM-5, 5 wt %Co/HZSM-5, and 10 wt %Co/HZSM-5. According to the SEM-EDS analysis shown in Table 2, the catalysts containing nickel and cobalt metals in proportions of 5 and 10 wt % impregnated onto the zeolite supports (HZSM-5) in the experiment had quantities approximate to the results obtained tests, which were 4.94 ± 0.13 wt %Ni/HZSM-5, 10.28 ± 0.25 wt %Ni/HZSM-5, 5.01 ± 0.08 wt %Co/HZSM-5, and 9.97 ± 0.13 wt %Co/HZSM-5. Other elements are composed of oxygen (O), silicon (Si), and aluminum (Al), confirming that zeolite is the source of silicon and aluminum, hence confirming the successful impregnation of nickel and cobalt metals onto zeolite. The distribution of nickel and cobalt metals on the surface of the zeolite can be seen on micrographs taken on the SEM as illustrated in Figure 5.

3.3. Pyrolysis of Plastic Waste. Three different sizes of washed plastic waste, including small (0.3−0.7 cm), medium (0.8−1.2 cm), and large (1.5−2.0 cm), at a temperature of 560 °C were considered without using a catalyst. Table 3 shows the increased production yield of pyrolysis oil from 29.38 ± 0.62 to 44.42 ± 0.94 wt % when plastic waste size was changed from small-sized to medium-sized, while the yield of the byproduct char and gas decreased. However, when plastic waste size was further increased from medium-sized to large-sized a decrease of pyrolysis oil yield to 28.00 ± 0.59 wt %, resulted while the yields of byproducts wax, char, and gas increased, which could be due to limitations in heat transfer at larger particles. The

Table 4. Effect of Type of Catalysts and Catalyst Loading on the Pyrolysis Process

		yield (wt %)				
type of catalysts	wt % catalyst to plastic waste (wt %)	pyrolysis oil	wax	char	gas	HHV (MJ/kg)
without a catalyst	0	44.42 ± 0.94	4.02 ± 1.56	2.80 ± 0.21	48.76 ± 0.77	40.54 ± 0.71
5 wt %Ni/HZSM-5	5	44.96 ± 0.95	0.82 ± 0.32	4.12 ± 0.32	50.10 ± 0.79	34.14 ± 0.60
	10	39.22 ± 0.83	1.06 ± 0.41	8.56 ± 0.66	51.16 ± 0.81	34.78 ± 0.61
	15	31.90 ± 0.67	2.24 ± 0.87	4.88 ± 0.37	60.98 ± 0.96	33.92 ± 0.60
5 wt %Co/HZSM-5	5	47.42 ± 1.00	0.44 ± 0.17	6.34 ± 0.49	45.80 ± 0.72	38.06 ± 0.67
	10	47.28 ± 1.00	1.58 ± 0.61	2.80 ± 0.21	48.34 ± 0.76	35.19 ± 0.62
	15	43.42 ± 0.92	1.26 ± 0.49	2.92 ± 0.22	52.40 ± 0.83	35.56 ± 0.63
10 wt %Ni/HZSM-5	5	42.20 ± 0.89	1.95 ± 0.76	6.47 ± 0.50	49.38 ± 0.78	35.00 ± 0.62
10 wt %Co/HZSM-5	5	37.16 ± 0.78	1.74 ± 0.68	5.99 ± 0.46	55.11 ± 0.87	37.87 ± 0.67

Table 5. CCD for Unwashed Plastic Waste Pyrolysis, the Corresponding Pyrolysis Oil Yield, and HHV

run	temperature (°C)	5 wt %Co/HZSM-5 to plastic waste (wt %)	pyrolysis oil yield (wt %)	HHV (MJ/kg)
1	520	5	23.96 ± 0.24	44.85 ± 2.06
2	540	10	26.98 ± 0.27	45.00 ± 2.06
3	540	15	25.56 ± 0.25	44.83 ± 2.05
4	560	5	34.84 ± 0.35	41.00 ± 1.88
5	560	20	30.12 ± 0.30	35.66 ± 1.63
6	560	5	33.90 ± 0.34	37.45 ± 1.72
7	560	5	34.42 ± 0.34	37.30 ± 1.71
8	560	0	38.88 ± 0.39	26.50 ± 1.21
9	560	5	34.20 ± 0.34	36.56 ± 1.68
10	560	5	34.26 ± 0.34	37.50 ± 1.72
11	580	15	33.20 ± 0.33	43.93 ± 2.01
12	580	10	32.82 ± 0.33	42.44 ± 1.95
13	600	5	31.74 ± 0.31	39.25 ± 1.80

experiment showed that both small-sized and large-sized plastic waste produced low amounts of pyrolysis oil yield, while medium-sized plastic waste produced significantly high pyrolysis oil yield. The results in this study agreed with the corresponding findings in previous research carried out by Dassi Djoukouo et al.,[21] who studied pyrolysis for converting plastic waste into fuels similar to gasoline and diesel. In the above study, it was also reported that the size of the pyrolysis plastic waste influences the pyrolysis oil yield, with increases of 12.5, 9.1, and 7% for LDPE, PS, and PP, respectively, when the particle size is changed from 3−7 to 1−3 cm. The smaller the particle, the shorter the reaction time and the higher the pyrolysis oil yield. Similarly, Faisal et al.[22] studied the effect of the size of mixed waste plastic (MWP) feedstock (5−45 mm) on pyrolysis oil yield. They found that the feedstock particle size was small (less than 20 mm) and too large (greater than 30 mm), resulting in a relative decrease in pyrolysis oil yield. Thus, the optimum size for producing the highest pyrolysis oil yield was approximately 23.99 mm. However, the larger the particle size, the lower the heat transfer, as the rate of heat and mass transfer to the feedstock is dependent on its shape, size, and homogeneity.

The results of HHV analysis on pyrolysis oil obtained from plastic waste. It was found that the plastic waste size affected HHV of pyrolysis oil: medium-sized (40.54 ± 0.71 MJ/kg) > small-sized (37.82 ± 0.67 MJ/kg) > large-sized (32.34 ± 0.57 MJ/kg). When the plastic waste size was too small or too large, it resulted in a decrease in the HHV of pyrolysis oil.

Therefore, the most suitable size of plastic waste for this study was medium-sized. This choice was based on several factors. First, it was convenient to prepare plastic waste before the experiment. Second, it produced high amounts of the pyrolysis oil yield. Finally, pyrolysis oil had a high HHV. All experiments from now on will use medium-sized plastic waste.

3.4. Effect of Type of Catalysts.

Washed plastic waste was performed at a temperature of 560 °C using 5 wt %Ni/HZSM-5, 10 wt %Ni/HZSM-5, 5 wt %Co/HZSM-5, and 10 wt %Co/HZSM-5 as a catalyst. The catalysts were used in amounts of 5, 10, and 15 wt % catalysts to plastic waste, as shown in Table 4.

The experimental results showed pyrolysis of plastic waste using a catalyst to provide a faster reaction at a lower temperature and shorter reaction time compared with without a catalyst. Particularly, the use of 5 wt % of 5 wt %Co/HZSM-5 as a catalyst showed the highest pyrolysis oil yield of 47.42 ± 1.00 wt % compared to the other catalysts and without a catalyst.

The results of the HHV analysis on the pyrolysis oil from plastic waste using 5 wt % of 5 wt %Co/HZSM-5 to plastic waste showed a high HHV of 38.06 ± 0.67 MJ/kg compared to other catalysts. However, when the amount of catalyst was increased to 10 and 15 wt % of catalyst to plastic waste, the pyrolysis oil yield tended to decrease, but the gas yield increased. Higher loading of metal on the HZSM-5 resulted in a lower pyrolysis oil yield and produced a high wax yield, while higher loading of cobalt metal from 5 to 10 wt % on the HZSM-5 resulted high gas yield from 45.80 ± 0.72 to 55.11 ± 0.87 wt %. Extreme high or low metal loading concentrations on HZSM-5 are not conducive to forming the desired hydrocarbon compound. Akubo, Nahil, and Williams[11] found that as the percentage of metal loading on the catalyst was increased from 1 to 5 wt %, more carbon was deposited on the catalyst, decreasing its efficiency and contributing to an increase in the gas yield. Sol and Muñoz-Batista[23] investigated

Table 6. CCD for Washed Plastic Waste Pyrolysis, the Corresponding Pyrolysis Oil Yield, and HHV

run	temperature (°C)	5 wt %Co/HZSM-5 to plastic waste (wt %)	pyrolysis oil yield (wt %)	HHV (MJ/kg)
1	520	5	31.62 ± 0.67	36.85 ± 0.65
2	540	10	40.68 ± 0.86	34.06 ± 0.60
3	540	15	36.86 ± 0.78	32.50 ± 0.57
4	560	5	45.28 ± 0.96	36.87 ± 0.65
5	560	20	31.44 ± 0.66	34.24 ± 0.60
6	560	5	46.72 ± 0.99	36.39 ± 0.64
7	560	5	47.42 ± 1.00	38.06 ± 0.67
8	560	0	44.42 ± 0.94	40.54 ± 0.71
9	560	5	47.68 ± 1.01	36.75 ± 0.65
10	560	5	47.50 ± 1.00	36.68 ± 0.65
11	580	15	33.74 ± 0.71	33.83 ± 0.60
12	580	10	39.66 ± 0.84	35.65 ± 0.63
13	600	5	33.70 ± 0.71	38.35 ± 0.67

Table 7. Analysis of Variation for Unwashed Plastic Waste Pyrolysis

source	sum of squares	df	mean square	*F*-value	*p*-value	remarks
Pyrolysis Oil Yield						
model	210.18	5	42.04	187.27	<0.0001	significant
A-temperature	70.23	1	70.23	312.87	<0.0001	
B-5 wt %Co/HZSM-5 to plastic waste	58.45	1	58.45	260.39	<0.0001	
AB	6.22	1	6.22	27.72	0.0012	
A^2	60.46	1	60.46	269.37	<0.0001	
B^2	8.84	1	8.84	39.38	0.0004	
residual	1.57	7	0.2245			
lack of fit	1.1	3	0.3655	3.08	0.1528	not significant
pure error	0.4747	4	0.1187			
cor total	211.75	12				
R^2 = 0.9926, adjusted R^2 = 0.9873, predicted R^2 = 0.9071, Adeq Precision = 44.9954						
HHV						
model	309.08	5	61.82	30.69	0.0001	significant
A-temperature	8.56	1	8.56	4.25	0.0782	
B-5 wt %Co/HZSM-5 to plastic waste	86.26	1	86.26	42.82	0.0003	
AB	1.26	1	1.26	0.6256	0.4549	
A^2	25.14	1	25.14	12.48	0.0096	
B^2	156.55	1	156.55	77.72	<0.0001	
residual	14.1	7	2.01			
lack of fit	1.99	3	0.6639	0.2193	0.8785	not significant
pure error	12.11	4	3.03			
cor total	323.18	12				
R^2 = 0.9564, adjusted R^2 = 0.9252, predicted R^2 = 0.8964, Adeq Precision = 19.5708						

the effects of metals loading on the catalytic pyrolysis of a real mixture of postconsumer plastic waste products with different nickel and cobalt loading (1 and 5 wt %) on HY and HZSM-5 and found that the loading of cobalt metal from 1 to 5 wt % on the HZSM-5 resulted in a high gas yield from 53.6 ± 2.0 to 57.1 ± 2.6 wt %. Therefore, the most suitable type of catalyst for this study was 5 wt %Co/HZSM-5. This is because it produces a high amount of pyrolysis oil yield and HHV.

3.5. RSM-CCD Model Validation. The RSM-CCD method quadratic was used to determine the optimum conditions of the pyrolysis of plastic waste. The model considered the effects of various parameters such as (*A*) temperature and (*B*) 5 wt %Co/HZSM-5 on plastic waste (wt %). Tables 5 and 6 display the results of 13 experiments comparing unwashed and washed plastic waste, respectively. These experiments were analyzed to determine the relationship between temperature and 5 wt %Co/HZSM-5 to plastic waste on pyrolysis oil yield and HHV.

The significance of the interaction effects and quadratic terms was determined using Analysis of variance (ANOVA) on the experimental results. The findings are presented in Tables 7 and 8. The significance of each term on the predicted data was evaluated using the *F*-value and *p*-value. A *p*-value of less than 0.05 was considered statistically significant at the 95% confidence level.[24] In addition, R^2, adjusted R^2, predicted R^2, and Adeq Precision values were used to predict the model's accuracy. Values close to 1 indicate that the mathematical model has a high level of adaptability.[25,26]

The coded equations are described in eqs 5-8. The sign of the coefficients determines whether a parameter has a positive or adverse effect on the response. High variable coefficients represent greater effects of the parameter on the variable being investigated.[27] In the case of model terms, the linear terms *A*, *B*, interactive terms *AB*, and quadratic terms A^2, B^2 are significant with *p*-value <0.05. Value with <95% level of confidence indicates that the model terms are not significant.[28,29]

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Table 8. Analysis of Variation for Washed Plastic Waste Pyrolysis

source	sum of squares	df	mean square	*F*-value	*p*-value	remarks
Pyrolysis Oil Yield						
model	484.56	5	96.91	88.79	<0.0001	significant
A-temperature	2.25	1	2.25	2.06	0.1942	
B-5 wt %Co/HZSM-5 to plastic waste	199.78	1	199.78	183.04	<0.0001	
AB	7.55	1	7.55	6.92	0.0339	
A^2	288.04	1	288.04	263.9	<0.0001	
B^2	42.27	1	42.27	38.73	0.0004	
residual	7.64	7	1.09			
lack of fit	3.75	3	1.25	1.28	0.3941	not significant
pure error	3.89	4	0.9734			
cor total	492.2	12				
R^2 = 0.9845, adjusted R^2 = 0.9734, predicted R^2 = 0.7852, Adeq Precision = 22.0636						
HHV						
model	53.89	5	10.78	30.24	0.0001	significant
A-temperature	2.88	1	2.88	8.08	0.025	
B-5 wt %Co/HZSM-5 to plastic waste	44.45	1	44.45	124.71	<0.0001	
AB	0.2377	1	0.2377	0.6669	0.441	
A^2	0.5772	1	0.5772	1.62	0.2438	
B^2	8.76	1	8.76	24.59	0.0016	
residual	2.5	7	0.3565			
lack of fit	0.8302	3	0.2767	0.6648	0.616	not significant
pure error	1.67	4	0.4163			
cor total	56.39	12				
R^2 = 0.9557, adjusted R^2 = 0.9241, predicted R^2 = 0.7245, Adeq Precision = 19.5314						

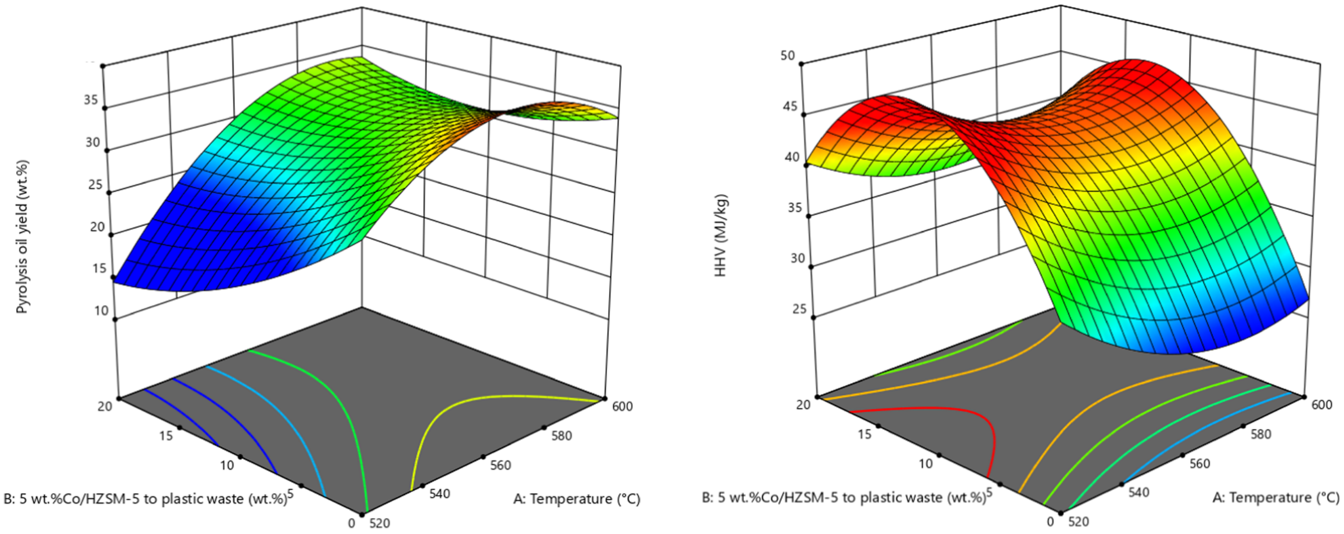

Figure 6. 3D response surface plots presenting the effect of temperature and 5 wt %Co/HZSM-5 on plastic waste (wt %) from unwashed plastic waste, pyrolysis oil yield and HHV.

Unwashed plastic waste

$$\text{pyrolysis oil yield (wt \%)} = +31.71 + 2.89A - 1.98B + 0.9429AB - 1.62A^2 + 0.7133B^2 \tag{5}$$

$$\text{HHV (MJ/kg)} = +43.29 + 2.40B + 1.04A^2 - 3.00B^2 \tag{6}$$

Washed plastic waste

$$\text{pyrolysis oilyield (wt \%)} = +44.41 - 3.66B - 1.04AB - 3.53A^2 - 1.56B^2 \tag{7}$$

$$\text{HHV (MJ/kg)} = +34.47 + 0.5855A - 1.73B + 0.7103B^2 \tag{8}$$

where A = temperature (°C)

B = 5 wt %Co/HZSM-5 to plastic waste (wt %)

From the three-dimensional (3D) response surface method effect of (*A*) temperature and (*B*) 5 wt %Co/HZSM-5 to plastic waste (wt %) on pyrolysis oil yield and HHV, Figures 6a and 7a demonstrate that washed plastic waste before pyrolysis resulted in a significantly higher pyrolysis oil yield compared to those of unwashed plastic waste due to the washing process lowers the biogenic, inorganic, and moisture content attached to plastic waste. As a result, pyrolysis oil yield

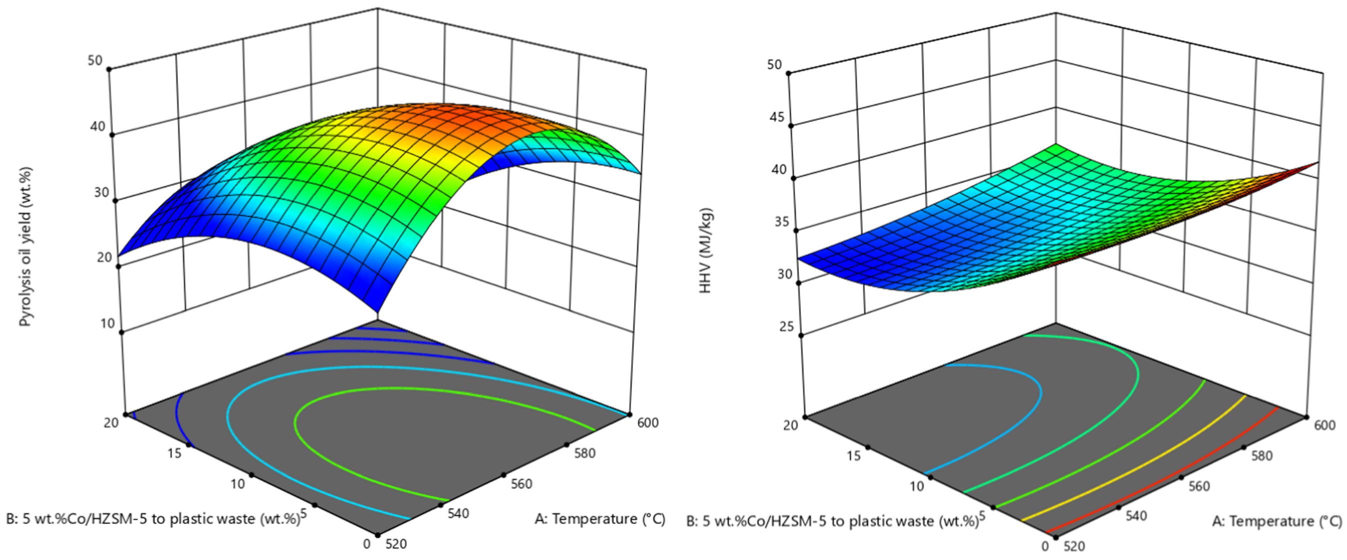

Figure 7. 3D response surface plots presenting the effect of temperature and 5 wt %Co/HZSM-5 on plastic waste (wt %) from washed plastic waste, pyrolysis oil yield and HHV.

Table 9. Optimum Conditions for Pyrolysis Process

			predict by RSM		experimental	
plastic waste	temperature (°C)	5 wt %Co/HZSM-5 to plastic waste (wt %)	pyrolysis oil yield (wt %)	HHV (MJ/kg)	pyrolysis oil yield (wt %)	HHV (MJ/kg)
unwashed	568	5.9	34.38	38.96	34.30 ± 0.34	45.11 ± 2.07
washed	562	3.8	46.59	37.75	56.18 ± 1.19	45.16 ± 0.79

contains other unwanted compounds such as chlorinated compounds that cause the pyrolysis oil properties to be unstable.[12] Lower moisture content in the plastic waste results in lower oxygen content in the pyrolysis oil. For pyrolysis of unwashed plastic waste, Figure 6b shows that HHV of the pyrolysis oil tends to decrease when the temperature and catalyst loading increase to a certain value. At a temperature of 540 °C using 10 wt % of 5 wt %Co/HZSM-5 to plastic waste results in the highest HHV of 45.00 ± 2.06 MJ/kg. However, using 5 wt % of 5 wt %Co/HZSM-5 catalyst at a temperature of 560 °C, the HHV was in the lower range of 36.56 ± 1.68–41.00 ± 1.88 MJ/kg. Similarly, pyrolysis without using a catalyst resulted in a lower HHV of 26.50 ± 1.21 MJ/kg. In Figure 7b, for pyrolysis of washed plastic waste, HHV increased with temperature up to a certain point. At a temperature of 520 °C using 5 wt % of 5 wt %Co/HZSM-5 to plastic waste, the HHV was 36.85 ± 0.65 MJ/kg, but when the temperature was increased to 560 °C (36.39 ± 0.64–38.06 ± 0.67 MJ/kg), the HHV tended to decrease gradually. It then gradually increased again when the temperature was raised to 600 °C (38.35 ± 0.67 MJ/kg). These results demonstrate the importance of using a catalyst in the pyrolysis process.

As the temperature and 5 wt %Co/HZSM-5 to plastic waste (wt %) increases, pyrolysis oil yield and HHV tend to decrease because the hydrocarbon in pyrolysis oil undergoes more effective thermal cracking and catalytic cracking, breaking down from the liquid phase (C7+) into the gas phase (C1–C4).[20]

3.6. Optimization of Process Variables by RSM-CCD.

Optimum conditions for the pyrolysis process are determined by the RSM-CCD method that affects pyrolysis oil yield and HHV by numerical optimization comparing the results of unwashed and washed plastic waste in Table 9. From the predictions, it was found that the optimum temperature for pyrolysis experiment was similar for both unwashed and washed plastic waste, at a temperature of 562 and 568 °C, respectively. However, the pyrolysis of unwashed plastic waste requires a higher amount of catalyst (5.9 wt %) compared to that of washed plastic waste (3.8 wt %). For pyrolysis of unwashed plastic waste, pyrolysis oil yield was 34.30 ± 0.34 wt %, which matched the prediction, and HHV was 45.11 ± 2.07 MJ/kg. An experiment on pyrolysis of washed plastic waste resulted in a pyrolysis oil yield of 56.18 ± 1.19 wt % and an HHV of 45.16 ± 0.79 MJ/kg, which was higher than the predicted values, similar to that of unwashed plastic waste.

The relative composition of the pyrolysis oil from plastic waste was determined using GC-MS and is presented in Figure 8. The pyrolysis oil from plastic waste composed of various chemical components was calculated using the relative peak area percentage and grouped hydrocarbon compounds, function groups such as alcohols, carboxylic acids, esters, ethers, halogen compounds, ketones, nitrogen compounds, and other compounds with more than one function group accordingly. Consider only hydrocarbon compounds, which are compounds composed only of carbon and hydrogen.[30] Pyrolysis oil produced without a catalyst, from unwashed plastic waste under optimum conditions (568 °C, 5.9 wt % of 5 wt %Co/HZSM-5 to plastic waste), and from washed plastic waste under optimum conditions (562 °C, 3.8 wt % of 5 wt % Co/HZSM-5 to plastic waste) contained 71.06, 68.64, and 63.65 wt % hydrocarbon compounds, respectively.

These hydrocarbon compounds can be categorized into gasoline (C6–C12), jet fuel (C13–C16), diesel (C17–C20), and others (C21+) based on previous studies.[31,32] From GC-MS results of pyrolysis oil, Figure 8, the hydrocarbon composition of pyrolysis oil produced without a catalyst was

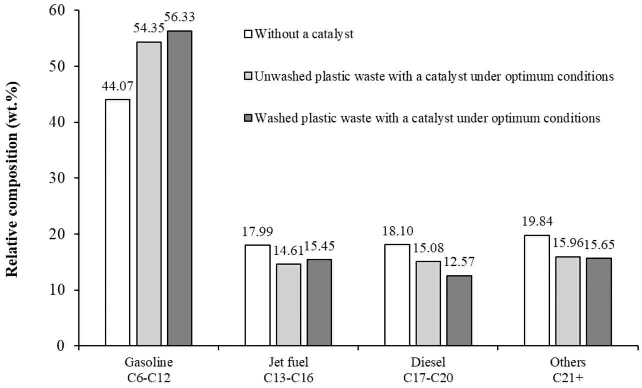

Figure 8. GC-MS analysis of hydrocarbon compounds in pyrolysis oils produced without a catalyst, from unwashed plastic waste, and from washed plastic waste under optimum conditions.

44.07 wt % gasoline, 17.99 wt % jet fuel, 18.10 wt % diesel, and 19.84 wt % others. Pyrolysis oil from unwashed plastic waste contained 54.35 wt % gasoline, 14.61 wt % jet fuel, 15.08 wt % diesel, and 15.96 wt % others. Finally, pyrolysis oil from washed plastic waste comprised 56.33 wt % gasoline, 15.45 wt % jet fuel, 12.57 wt % diesel, and 15.65 wt % others.

The use of 5 wt %Co/HZSM-5 as a catalyst during plastic waste pyrolysis demonstrated excellent performance. This is attributed to its strong acidic properties and porous crystal structure, which facilitate the cracking of larger molecules into smaller ones, resulting in a higher yield of gasoline (C6−C12) compared to thermal pyrolysis, as reported in the literature.[33] Similarly, Sol and Muñoz-Batista[23] reported the use of a 5 wt % Co/HZSM-5 catalyst for the pyrolysis of a mixture of postconsumer plastic waste at a temperature of 500 °C. It was found that the predominant product of pyrolysis oil was the gasoline range products (boiling points between 35 and 205 °C) as high as 48.2 ± 2.6 wt %. Importantly, pyrolysis oil from both unwashed and washed plastic wastes exhibited similar hydrocarbon compound distributions.

3.7. Physicochemical Properties of Pyrolysis Oil.

Table 10 presents the physicochemical properties of pyrolysis oil from unwashed and washed plastic waste under optimum conditions. The use of 5 wt %Co/HZSM-5 in pyrolysis of plastic waste resulted in a high HHV approximating that of gasoline, jet fuel, and diesel. Pyrolysis oil, both unwashed (pH = 4.73) and washed (pH = 5.00) which has a pH < 7 were therefore acidic. Upgrading pyrolysis oil with solvents and catalysts in optimum conditions was another way to reduce acidity in pyrolysis oil. Pyrolysis oil had a relative viscosity and density approximating that of jet fuel and diesel. Similarly, Ndiaye, Derkyi, and Amankwah[34] studied to convert A mixture of plastic waste (58 wt %PET: 20 wt % HDPE: 12 wt % LDPE: 7 wt % PP: 3 wt % PS) into diesel engine-grade oil using Y-Zeolite as a catalyst at 450 °C for 2 h. The HHV of pyrolysis oil from plastic waste was 43.18 MJ/kg, the viscosity was 4.34 cSt, and the density was 856 kg/m^3. The differences in the types of plastic waste affect the chemical properties of the pyrolysis oil.

4. CONCLUSIONS

This study was conducted to determine the optimum conditions for pyrolysis of plastic waste from Hat-Yai municipal landfills, considering the effect of the plastic waste size and type of catalysts. The experiments with pyrolysis-washed plastic waste at a temperature of 560 °C without using a catalyst determined that plastic waste size affects pyrolysis oil yield and HHV. Specifically, the medium-sized plastic waste (0.8−1.2 cm) resulted in a high pyrolysis oil yield of 44.42 ± 0.94 wt % and a high HHV of 40.54 ± 0.71 MJ/kg. 5 wt %Co/HZSM-5 was the most suitable type of catalyst for the plastic waste pyrolysis process. When using 5 wt % of 5 wt %Co/HZSM-5 to plastic waste produces a higher pyrolysis oil yield of 47.42 ± 1.00 wt % than without using a catalyst and a high HHV of 38.06 ± 0.67 MJ/kg compared to other catalysts. The optimum conditions for the pyrolysis process were determined using RSM-CCD to evaluate the effects of various parameters such as temperature (520−600 °C) and 5 wt % Co/HZSM-5 to plastic waste (0−20 wt %) to achieve high pyrolysis oil yield and high HHV. For optimum conditions of the pyrolysis process of unwashed plastic waste were at a temperature of 568 °C using 5.9 wt % of 5 wt %Co/HZSM-5 to plastic waste resulting in a high pyrolysis oil yield of 34.30 ± 0.34 wt % and HHV of 45.11 ± 2.07 MJ/kg. The optimum conditions for the pyrolysis of washed plastic waste were at a temperature of 562 °C using 3.8 wt % of 5 wt %Co/HZSM-5 to plastic waste resulting in a high pyrolysis oil yield of 56.18 ± 1.19 wt % and an HHVof 45.16 ± 0.79 MJ/kg. GC-MS analysis of the pyrolysis oil from both optimal conditions revealed high quantities of hydrocarbon compounds similar to fossil fuels, including gasoline (54.35−56.33 wt %), jet fuel (14.61−15.45 wt %), and diesel (12.57−15.08 wt %). The use of 5 wt %Co/HZSM-5 as a catalyst for pyrolysis plastic waste increases pyrolysis oil. Finally, pyrolysis of unwashed plastic waste

Table 10. Physicochemical Properties of Pyrolysis Oil and Fossil Fuels

material	wt % catalyst to plastic waste (wt %)	properties				source
		HHV (MJ/kg)	viscosity at 40 °C (cSt)	density (kg/m^3)	pH	
washed plastic waste	without a catalyst	40.54 ± 0.71	1.69	791	4.69	this study
unwashed plastic waste under optimum conditions	5.9 wt % of 5 wt %Co/HZSM-5	45.11 ± 2.07	2.14	821	4.73	this study
washed plastic waste under optimum conditions	3.8 wt % of 5 wt %Co/HZSM-5	45.16 ± 0.79	1.96	791	5.00	this study
plastic waste	10 wt % of Y-zeolite	43.18	4.34	856		34
Commercial Standard Value (ASTM)						
gasoline		44.94[a]	1.17	780		35
jet fuel		45.24[a]		775−840		36
diesel		45.44[a]	1.90−4.10	807		35

[a]HHV = LHV + 2.444 MJ/(kg-of-water), corresponding to the heat of vaporization of water at 25 °C.[37]

reduces process procedures for plastic waste preparation but requires a higher amount of catalyst compared with washed plastic waste. However, washed plastic waste before pyrolysis had a higher pyrolysis oil, and a smaller amount of catalyst was used.

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Notes

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■ NOMENCLATURE

ANOVA	analysis of variance
CCD	central composite design
EDS	energy-dispersive X-ray spectroscopy
FT-IR	Fourier transform infrared spectrometry
GS-MS	gas chromatography−mass spectrometry
HDPE	high-density polyethylene
HHV	high heating value
PE	polyethylene
PET	polyethylene terephthalate
PP	polypropylene
RSM	responses surface method
SEM	scanning electron microscopy
TGA	thermogravimetric analysis

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