

Selected Paper from the 6th International Thai Institute of Chemical Engineering and Applied Science Conference (ITICHe2016)

## Effects of MgO-ZSM-23 Zeolite Catalyst on the Pyrolysis of PET Bottle Waste

Pattra Kongsupakul and Kraipat Cheenkachorn

Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

Supak Tontisirin\*

Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

Center of Eco-Materials and Cleaner Technology, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

\* Corresponding author. E-mail: supak.t@eng.kmutnb.ac.th DOI: 10.14416/j.ijast.2017.08.004

Received: 9 February 2017; Accepted: 10 March 2017; Published online: 15 August 2017

© 2017 King Mongkut's University of Technology North Bangkok. All Rights Reserved.

### Abstract

The pyrolysis reaction of poly(ethylene terephthalate) or PET bottle waste was conducted comparatively in two cases: without catalyst and with MgO-ZSM-23 zeolite catalyst. The pyrolysis of PET was successfully decomposed to the product of liquid/wax, char, and gas (major product). Applying MgO-ZSM-23 catalyst, the product shows pronounced higher yield of gas (72.5 vs. 58.7 wt.%) and less yield of char solid (8 vs. 17.6 wt.%). The gas product shows less yield of CO<sub>2</sub> (75 vs. 98 wt.%) but gives higher hydrocarbon gas fractions of C1–C5 (25 vs. 2.1 wt.%). In liquid/wax products, the catalytic pyrolysis shifted the product spectrum from higher molecular weight, e.g., biphenyl, terphenyl to benzene derivatives, predominantly in “benzoic acid”.

**Keywords:** ZSM-23 zeolite, Catalytic pyrolysis, PET, Renewable energy, Fuel

### 1 Introduction

The continuous demand of plastics causes the plastic wastes accumulation in the landfill. This consumes a lot of spaces and results in environmental problem. The recovery of plastic wastes to fuel by pyrolysis process has great potential since to avoid negative effects and provide the new source of energy [1]. Certain types of plastic, e.g., PP, PE, PS can be pyrolysed to different product spectrum [2]–[4]. For pure poly(ethylene terephthalate) or PET plastic which is abundant waste as water drinking bottles and not biodegradable, its pyrolysis data is quite a few. The pyrolysis products of gas and solid were reported in different operating conditions. Pyrolysis in steam atmosphere yielded

terephthalic acid and oxygen-containing compounds, e.g., aldehyde and ester with suppressed carbonaceous residue [5]. Pyrolysis of several PET with and without fillers in fluidized bed reactor gave major solid yield of aromatic hydrocarbons, 38–49 wt.% of gases yield, and 5–40 wt.% of carbonaceous residue, which is strongly depends on the pyrolysis temperature [6]. Both works used virgin PET plastic from the companies. In this work, PET plastic from used drinking water bottles was applied in the pyrolysis tests. Moreover applying catalytic pyrolysis of PET plastic could be interesting and no work has been reported for this type of catalyst. Therefore this research will contribute the effects of MgO-ZSM-23 catalyst to the pyrolysis of pure PET bottle waste. ZSM-23 zeolite was selected as catalyst

Please cite this article as: P. Kongsupakul, K. Cheenkachorn and S. Tontisirin, “Effects of MgO-ZSM-23 zeolite catalyst on the pyrolysis of PET bottle waste,” *KMUTNB Int J Appl Sci Technol*, vol. 10, no. 3, pp. 205–211, Jul.–Sep. 2017.

support because of its excellent acidity and shape selective properties. Its unique structure of one-dimensional 10-member-ring window enhances the isomerization degree of long chain hydrocarbon. This could maximize the octane number and improve cold flow property of the pyrolysis product. ZSM-23 was first synthesized by Plank *et al.* [7]. This shape selective zeolite is active catalyst in hydroconversion of n-dodecane [8], isodewaxing process for lowering pour points of lubricants and diesel fuels [9], and catalytic cracking of mixed C4 alkene [10]. The incorporation of MgO can modify the acidity of the catalyst by increasing of weak Lewis acid site. This can avoid the excessive cracking and reduce undesired coke of the reaction [11].

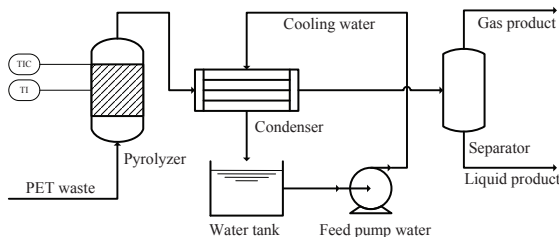
## 2 Experimental

### 2.1 Synthesis and preparation of MgO-ZSM-23 catalyst

ZSM-23 zeolite was synthesized with molar composition of  $110\text{SiO}_2$ :  $1.1\text{Al}_2\text{O}_3$ :  $50\text{C}_4\text{H}_9\text{N}$ :  $45\text{NaOH}$ :  $18\text{H}_2\text{SO}_4$ :  $5000\text{H}_2\text{O}$  at  $180^\circ\text{C}$  for 2 days by rotational reactor. It was calcined at  $580^\circ\text{C}$  in  $\text{N}_2$  and hold at this temperature for 3 hr in  $\text{O}_2$ . The calcined form was converted to protonate form by ion-exchanging with 1 M  $\text{NH}_4\text{NO}_3$  at  $65^\circ\text{C}$  for 4 times (each for 3 hr) and was calcined at  $450^\circ\text{C}$  for 3 hr. MgO-ZSM-23 catalyst (10 wt.% of MgO in zeolite) was prepared by wet impregnation using solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in ethanol (10 ml ethanol/1 g zeolite). It was stirred for 6 hr at  $40^\circ\text{C}$ . The solvent was removed by rotary evaporator and then the solid of MgO-ZSM-23 was obtained. The solid was dried at  $200^\circ\text{C}$  overnight and calcined at  $450^\circ\text{C}$  for 6 hr.

### 2.2 Characterizations

The materials were characterized by powder X-ray diffraction (XRD, BRUKER AXS model D8 Advance, Germany) operated at 40 kV and 30 mA. The measurement ran with angle from  $5^\circ$  to  $50^\circ$  of angle 2 theta with step size of  $0.02^\circ$  and scan speed of  $1^\circ/\text{min}$ . The surface characteristics of the materials were recorded using scanning electron microscope (FESEM, JEOL, model JSM-7610, Japan) operated at 15 kV. The chemical composition was determined by energy

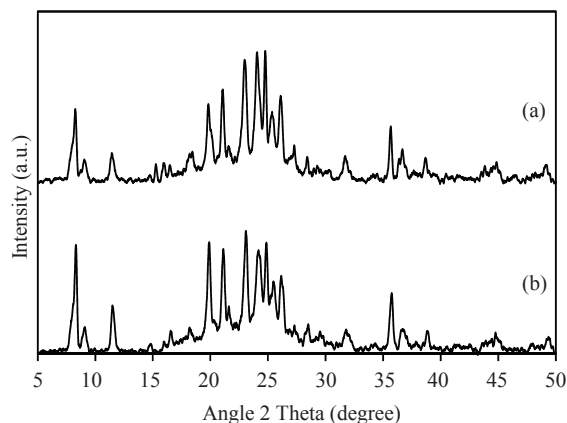


**Figure 1:** Process flow diagram of the pyrolysis.

dispersive X-ray spectroscopy (EDS, Oxford Instrument, X-MAX). The textural properties of the materials were determined by adsorption and desorption of  $\text{N}_2$  at  $-196^\circ\text{C}$  (BELSORP-max). Prior to determination of an adsorption isotherm, samples were pretreated at  $250^\circ\text{C}$  for 12 hr (BELSORP-flow). The specific surface area was calculated using the BET method and micropore volume was determined by the t-plot analysis.

### 2.3 Pyrolysis experiments

The pyrolysis experiments were conducted using 5L batch reactor equipped with gas product condenser and sampling points as shown in Figure 1. The reactor was heated by electrical furnace and the reaction temperature was measured in the pyrolysis zone. The reactor was loaded with 300 g of shred of PET bottle waste (in non-catalytic test). The test was carried out at  $440^\circ\text{C}$  with heating rate of  $5^\circ\text{C}/\text{min}$ . This temperature was maintained for 1 hr. Then the gas product was collected in sample bags for each 15 min interval until 60 min. The liquid/wax product was collected at one time in each test. In case of catalytic test, 10 g MgO-ZSM-23 was placed on top of the PET bottle waste inside the reactor. The gas product ( $\text{CO}_2$ ) was analyzed by Gas Chromatograph with Thermal Conductivity Detectors (GC-TCD) of Agilent 5973N with PoraPLOT Q column. Hydrocarbon gases (C1–C5) were analyzed by Gas Chromatograph with Flame Ionization Detector (GC-FID) of Agilent 6890N with PoraPLOT Q column. The result was calibrated with the standard gases. The product from liquid/wax was extracted by dichloromethane (0.017 g liquid/wax: 5.609 g  $\text{CH}_2\text{Cl}_2$ ). It was analyzed by using Gas Chromatography coupled with Mass Spectrometry (GC-MS) as a convenient method used in other studies [12]. The GC-MS with FID detector and column type DB-1MS of Agilent 6890 and Agilent 5973 was used.



**Figure 2:** XRD patterns of as-synthesized ZSM-23 (a) and calcined ZSM-23 (b).

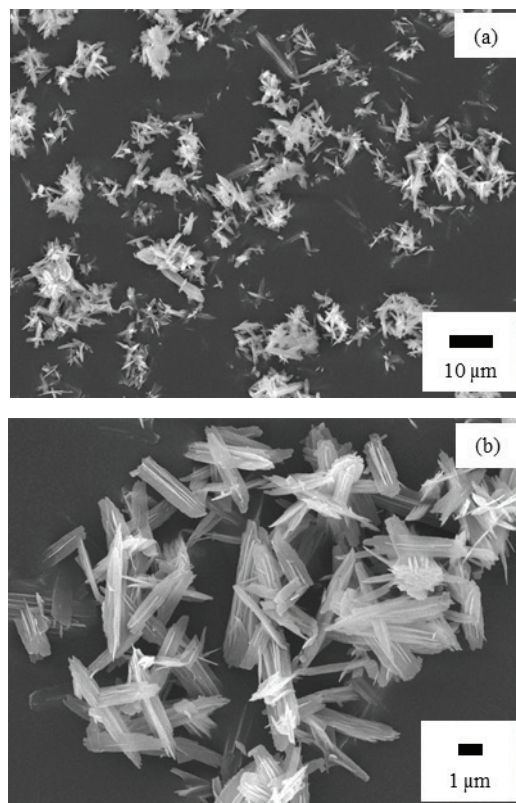
### 3 Results and Discussions

#### 3.1 Catalyst characterizations

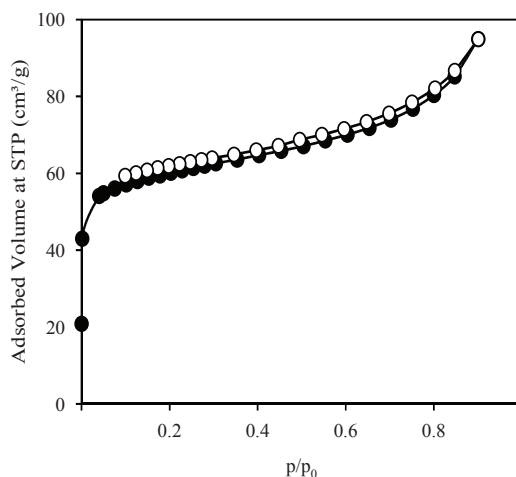
The XRD patterns of as-synthesized and calcined ZSM-23 zeolite are shown in Figure 2 (a) and (b). The peak positions at 2 theta around 8.26, 19.80, 21.08, 22.98, 26.10 and 35.66° are resembled to those of the reference of MTT framework [13]. This shows the pure phase of ZSM-23 zeolite. The calcined form shows relatively higher intensity of the main peaks in range of 2 theta between 5–23°. After calcination at high temperature to remove the organic template in the pore, the well preserved framework is still recognized.

The morphology of zeolite ZSM-23 is shown in Figure 3 (a) and (b) with different magnifications. Its crystal exhibits needle shape with approximately 6 μm long and 1.2 μm width. The needle crystals are intertwined and clustered.

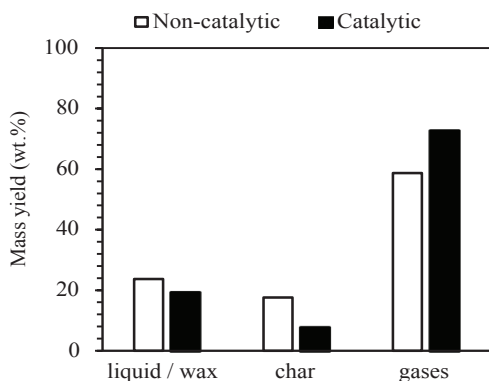
The N<sub>2</sub> adsorption/desorption isotherms of calcined ZSM-23 are presented in Figure 4. The isotherm shows characteristic of type II isotherm. This isotherm is attributed to monolayer adsorption at low relative pressure around 0.05 and multilayer adsorption after this point [14]. The micropore filling effect was observed at low relative pressure. This material possesses BET specific surface area of 193 m<sup>2</sup>/g, total pore volume of 0.15 cm<sup>3</sup>/g, and micropore volume of 0.067 cm<sup>3</sup>/g. The elementary analysis shows calcined ZSM-23 has Si/Al molar ratio of 50 which is similar to the Si/Al ratio of the synthesis gel.



**Figure 3:** Scanning electron micrographs of ZSM-23 zeolite with different magnifications at 1000x (a) and 5000x (b).



**Figure 4:** Nitrogen adsorption and desorption isotherms of calcined ZSM-23. Closed and open symbols denote adsorption and desorption, respectively.



**Figure 5:** Product yields distribution obtained in the pyrolysis tests.

### 3.2 Pyrolysis test

The product yields from the pyrolysis of PET bottle waste are shown in Figure 5. There are mainly three types of products (1) liquid/wax (2) char, and (3) non-condensable gases. Yellow liquid/wax occurred mostly out of the reactor, along the condenser and outlet. Char or carbonaceous residue occurred mostly inside the reactor. The gas fraction is the main product in both non-catalytic and catalytic pyrolysis. Applying MgO-ZSM-23 catalyst, it obviously increases gas yield (72.5 vs. 58.7 wt.%) and suppresses char product (8 vs. 17.6 wt.%).

#### 3.2.1 Pyrolysis gases

The gas product component obtained in non-catalytic pyrolysis by reaction time is presented in Table 1. CO<sub>2</sub> is the major product with yield ca. 97–98 wt.%. The second product is methane (C1) ca. 1.2–2.9 wt.%. Other hydrocarbon gases (C2–C5) were slightly detected. Table 2 shows gas product in catalytic pyrolysis. Contrastly, after 15 min, C1 is the major product with high yield of 73.2 wt.%. C5 is the secondary product of 11.8 wt.%. CO<sub>2</sub> shows relative low amount of 11.6 wt.%. C2–C4 occurred at relatively higher at this time. This indicates C1 and other hydrocarbon gases C2–C5 occurred predominantly at the early stage of the pyrolysis. CO<sub>2</sub> product dominated at later stage of the reaction. Table 3 summarizes the average values of gas products in one hour. In both cases, CO<sub>2</sub> and C1 are the main and secondary products, respectively. Applying MgO-ZSM-23 catalyst, the gas product gave more hydrocarbon gases of C1–C5 (25 vs. 2.1 wt.%)

and less CO<sub>2</sub> (75 vs. 98 wt.%) comparing to non-catalyst pyrolysis. These major hydrocarbon gas products of C1–C5 can be useful as fuel or chemical feed stocks for olefins and polymers production.

**Table 1:** Gas product yields obtained in non-catalytic pyrolysis test

Time (min)	Products (wt.%)					
	CO <sub>2</sub>	C1	C2	C3	C4	C5
0–15	97.2	2.85	0.00	0.00	0.00	0.00
15–30	98.4	1.47	0.03	0.01	0.12	0.00
30–45	98.7	1.16	0.03	0.01	0.10	0.05
45–60	97.5	1.77	0.04	0.02	0.67	0.00

**Table 2:** Gas product yields obtained in catalytic pyrolysis test

Time (min)	Products (wt.%)					
	CO <sub>2</sub>	C1	C2	C3	C4	C5
0–15	11.6	73.2	0.84	0.71	1.77	11.8
15–30	96.3	3.12	0.03	0.53	0.00	0.00
30–45	94.1	4.00	0.00	1.72	0.00	0.18
45–60	98.0	1.66	0.01	0.30	0.00	0.00

**Table 3:** Average gas product yields obtained in the pyrolysis tests

Condition	Products (wt.%)					
	CO <sub>2</sub>	C1	C2	C3	C4	C5
Non-catalytic	98.0	1.81	0.03	0.01	0.22	0.01
Catalytic	75.0	20.5	0.22	0.82	0.44	3.00

#### 3.2.2 Pyrolysis liquid/wax





















The components extracted from liquid/wax product using dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) in both non-catalytic and catalytic cases were summarized in groups as shown in Table 4. They are complex product spectrum of mainly aromatics with mono-, di-, and tri-benzene rings. This could be influenced by its parent plastic component which was derived from terephthalic acid and ethylene glycol [15]. The main product in both cases is benzoic acid which is as high as ca. 63 wt.% in each of their product distributions. In catalytic case, the second predominant product is benzoic acid derivatives, e.g., 2-propanoylbenzoic acid, 4-methylbenzoic acid, and 4-ethylbenzoic acid.

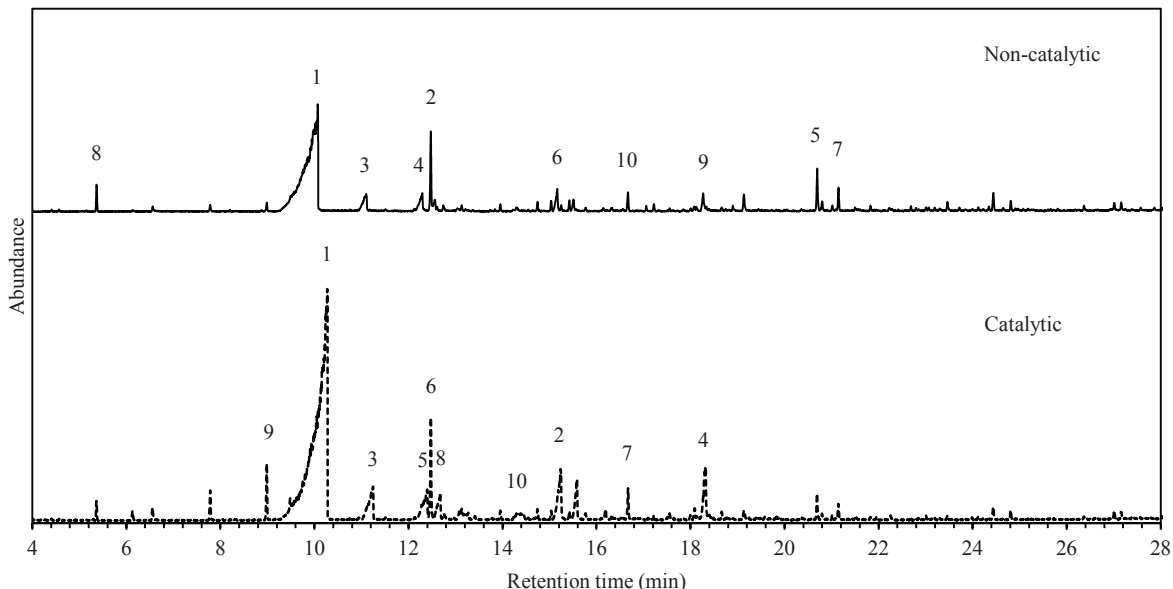
In non-catalytic case, the second predominant product is a group of biphenyl derivatives, e.g., biphenyl-4-carboxylic acid and 9-fluorenone. For clarification, Figure 6 and Table 5 present the GC-MS chromatograms and molecular structures with index of top-ten products. In summary, the results show catalytic pyrolysis using MgO-ZSM-23 catalyst affected product distribution of liquid/wax fraction by increasing benzoic acid and its derivatives (80 vs. 71.3 wt.%) but suppressing large molecules of biphenyl, terphenyl, and their derivatives (10.44 vs. 14.48 wt.%). The acid activity and shape selectivity of the MgO-ZSM-23 zeolite catalyst could play a role leading to cracking reaction in specific pattern. Higher yield of gas product in the catalytic case can support more intensive of the cracking reaction. The main product of benzoic acid (ca. 63 wt.%) is useful as industrial chemical. It can be used as preservatives in food industry, constituent of Whitfield's ointment for treatment of fungal skin diseases. Moreover, benzoic acid and some of its derivatives are also important precursor for the synthesis of many organic substances [16], [17].

**Table 4:** Components extracted from liquid/wax product from the pyrolysis tests

Components	Non-catalytic (wt.%)	Catalytic (wt.%)
<b>1. Mono-benzene Ring</b>		
Benzaldehyde	0	0.29
Phenol	0.39	0.38
Methyl Phenyl Ketone	0.44	0.84
Benzeneacetic Acid	0.56	1.40
Benzoic Acid	62.94	63.58
Benzoic Acid Derivatives	8.35	16.40
Allylquinol	3.05	0
<b>Total</b>	<b>75.73</b>	<b>82.89</b>
<b>2. Di-benzene Ring</b>		
Biphenyl	4.54	3.01
Biphenyl Derivatives	7.76	6.66
Naphthalene Derivatives	0	0.41
<b>Total</b>	<b>12.30</b>	<b>10.08</b>
<b>3. Tri-benzene Ring</b>		
Terphenyl	2.18	0.77
Phenanthrene	0.46	0.14
<b>Total</b>	<b>2.64</b>	<b>0.91</b>
<b>4. Long Chain</b>		
Hexadecanoic Acid	1.20	0.31
<b>5. Others</b>		
	<b>8.13</b>	<b>5.81</b>

**Table 5:** Top ten components extracted from liquid/wax product from the pyrolysis tests

No.	Non-catalytic	Catalytic
1	Benzoic acid  62.94 wt.%	Benzoic acid  63.58 wt.%
2	Biphenyl  4.54 wt.%	2-Propanoylbenzoic acid  4.24 wt.%
3	4-Methylbenzoic acid  3.40 wt.%	4-Methylbenzoic acid  3.91 wt.%
4	Allylquinol  3.05 wt.%	1,1'-Biphenyl-4-carboxylic acid  3.62 wt.%
5	N,N'-Dibenzoylhydrazine  2.63 wt.%	4-Ethylbenzoic acid  3.45 wt.%
6	2-Propanoylbenzoic acid  2.44 wt.%	Biphenyl  3.01 wt.%
7	m-Terphenyl  1.45 wt.%	4-Carboxybenzoic acid ethyl ester  2.36 wt.%
8	Tetrachloro-ethane  1.45 wt.%	4-Vinylbenzoic acid  2.11 wt.%
9	1,1'-Biphenyl-4-carboxylic acid  1.41 wt.%	Benzeneacetic acid  1.40 wt.%
10	9-Fluorenone  1.25 wt.%	1-Ethenyl-3-nitrobenzene  1.24 wt.%



**Figure 6:** GC-MS chromatograms of the components extracted from liquid/wax product from the pyrolysis tests.

#### 4 Conclusions

The pyrolysis of PET bottle waste was decomposed into three types of products: liquid/wax, char, and gas (major product). Comparing to non-catalytic pyrolysis, the MgO-ZSM-23 zeolite catalyst affected product distribution giving higher yield of gas and lower yield of char product. In gas product, it gave lower yield of CO<sub>2</sub> but higher hydrocarbon fraction of aliphatic C1–C5. These hydrocarbon products can be utilized as fuel and/or chemical feed stock for petrochemical industries. In liquid/wax product, highest yield of benzoic acid was obtained in both cases at about 63 wt.%. MgO-ZSM-23 catalyst can tailor the product distribution by increasing yield of benzoic acid and its derivatives but suppressing larger molecules of biphenyl, terphenyl, and their derivatives. High amount of benzoic acid and its derivatives can be potentially utilized as important feedstocks in various chemical industries.

#### Acknowledgments

The authors gratefully acknowledge the financial support from faculty of engineering, King Mongkut's University of Technology North Bangkok (KMUTNB) (contract no. 56-12-02-34) and the graduate school

of KMUTNB for master degree research fund. The authors would like to convey special appreciation to the academic committee of The 6th International Thai Institute of Chemical Engineering and Applied Science Conference (ITICHe2016) for providing the opportunity for this work to be published in this journal.

#### References

- [1] S. D. A. Sharuddin, F. Abnisa, W. M. A. W. Daud, and M. K. Aroua, "A review on pyrolysis of plastic wastes," *Energy Conversion and Management*, vol. 115, pp. 308–326, Feb. 2016.
- [2] I. Ahmad, M. I. Khan, H. Khan, M. Ishag, R. Tariq, K. Gul, and W. Ahmad, "Pyrolysis study of polypropylene and polyethylene into premium oil products," *International Journal of Green Energy*, vol. 12, no. 7, pp. 663–671, 2015.
- [3] S. H. Ng, H. Hesham, M. Stanciulescu, and Y. Sugimoto, "Conversion of polyethylene to transportation fuels through pyrolysis and catalytic cracking," *Energy Fuels*, vol. 9, pp. 735–742, 1995.
- [4] A. Karaduman, "Pyrolysis of polystyrene plastic wastes with some organic compounds for enhancing styrene yield," *Energy Resources*, vol. 24, no. 7, pp. 667–674, 2002.

- [5] T. Masuda, Y. Miwa, A. Tamagawa, S. R. Mukai, K. Hashimoto, and Y. Ikeda, "Degradation of waste poly(ethylene terephthalate) in a steam atmosphere to recover terephthalic acid and to minimize carbonaceous residue," *Polymer Degradation and Stability*, vol. 58, pp. 315–320, Jun. 1997.
- [6] T. Yoshioka, G. Grause, C. Eger, W. Kaminsky, and A. Okuwaki, "Pyrolysis of poly(ethylene terephthalate) in a fluidized bed plant," *Polymer Degradation and Stability*, vol. 86, pp. 499–504, Jun. 2004.
- [7] C. J. Plank, E. J. Rosinski, and M. K. Rubin, "Crystalline zeolite ZSM-23 and synthesis," *U.S. Patent 4 076 842*, Feb 28, 1978.
- [8] S. Ernst, G. T. Kokotailo, R. Kumar, and J. Weitkamp, "Shape selective catalysis in zeolites ZSM-22 and ZSM-23 influence of pore shapes on reaction selectivities," in *Proceedings 9th International Congress on Catalysis*, 1988, pp. 388–395.
- [9] D. N. Gerasimov, V. V. Fadeev, A. N. Loginova, and S. V. Lysenko, "Catalysts based on zeolite ZSM-23 for isodewaxing of a lubricant stock," *Catalysis in Industry*, vol. 5, pp. 123–132, Apr. 2013.
- [10] B. Wang, Q. Gao, J. Gao, D. Ji, X. Wang, and J. Suo, "Synthesis, characterization and catalytic C4 alkene cracking properties of zeolite ZSM-23," *Applied Catalysis*, vol. 274, pp. 167–172, 2004.
- [11] J. Feroso, H. Hernando, P. Jana, I. Moreno, J. Prech, C. Ochoa-Hernandez, P. Pizarro, J.M. Coronado, J. Cejka, and D. P. Serrano, "Lamellar and pillared ZSM-5 zeolites modified with MgO and ZnO for catalytic fast-pyrolysis of eucalyptus woodchips," *Catalysis Today*, vol. 277, part 1, pp. 171–181, Nov. 2016.
- [12] R. Yeetsorn, S. Tungkamani, and S. Yoshikazu, "Potential activity evaluation of CoMo/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts for hydrodesulfurization of coprocessing bio-oil," *KMUTNB Int J Appl Sci Technol*, vol. 7, no. 4, pp. 35–45, Sep. 2014.
- [13] M. M. J. Treacy and J. B. Higgins, *Collection of Simulated XRD Powder Patterns for Zeolites*, Amsterdam, Netherlands: Elsevier, 2007, pp. 298–299.
- [14] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez.-Reinoso, J. Rouquerol, and K. S. W. Sing, "Physisorption of gases with special reference to the evaluation of surface area and pore size distribution," *Pure and Applied Chemistry*, vol. 89, no. 9–10, pp. 1051–1069, 2015.
- [15] F. Welle, "Twenty years of PET bottle to bottle recycling-an overview," *Resources Conservation and Recycling*, vol. 55, pp. 865–875, 2011.
- [16] T. Maki and K. Takeda, "Benzoic acid and derivatives," in *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [17] A. Renzetti, H. Nakazawa, and C.-J. Li, "Rhodium-catalysed tandem dehydrogenative coupling-Michael addition: direct synthesis of phthalides from benzoic acids and alkenes," *RSC Advances*, vol. 6, pp. 40626–40630, 2016.

