

Pyrolysis of polyethylene terephthalate containing real waste plastics using Ni loaded zeolite catalysts

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Abstract. In this work the pyrolysis of polyethylene terephthalate (PET) containing real waste plastic was investigated using different Ni loaded catalysts: Ni/ZSM-5, Ni/ γ -zeolite, Ni/ β -zeolite and Ni/natural zeolite (clinoptilolite). Raw materials were pyrolyzed in a horizontal tubular reactor between 600 and 900 °C using 10% of catalysts. It was found, that both temperature increasing and catalysts presence can increase the gas yields, however owing to gasification reactions, the pyrolysis oil yield decreased with increasing temperature. Ni/ γ -zeolite catalyst had the most benefit in gas yield increasing at low temperature; however Ni/ZSM-5 showed advanced property in gas yield increasing at high temperature. Gases contained hydrogen, carbon oxides and hydrocarbons, which composition was significantly affected by catalysts. Ni loaded zeolites favoured to the formation of hydrogen and branched hydrocarbons; furthermore the concentrations of both CO and CO₂ were also increased as function of elevated temperature. That phenomenon was attributed to the further decomposition of PET, especially to the side chain scission reactions. Owing to the Boudouard reaction, the ratio of CO₂/CO can increased with temperature. Pyrolysis oils were the mixtures of n-saturated, n-unsaturated, branched, oxygen free aromatics and oxygenated hydrocarbons. Temperature increasing has a significant effect to the aromatization and isomerization reactions, while the catalysts can efficiently decreased the concentration of oxygen containing compounds.

1. Introduction

The environmental concern over waste plastic, especially polyethylene terephthalate (PET) and polyethylene (PE) is growing around the World. Regarding the plastic consumption, the PE and PET represent approximately 30% and 10% of the total market, respectively [1]. Mobility and fast moving people causes the increasing demand of the PE and PET for different purposes such as drinking water bottle, agriculture, constructional materials or even food packaging. On the other hand, serious environmental problems can be caused due to the dumping of these plastics in the landfill sites. Owing to the customer habits, selectively collected waste bins and waste islands containing vast amount of PE and PET. These plastics have chemical resistance and they are non-biodegradable. Therefore, they will accumulate in the landfill sites forever if no recycling process is carried out [2], [3]. It is also known, that the high efficient selective collection has high investment and labour cost. An average PET bottle contains approximately 10-15% polyethylene, such as cup, printed label, etc. and their type selective separation is difficult.

Nowadays, among the different methods used for waste plastic recycling, pyrolysis is considered as one of the environmentally friendly techniques for waste plastic conversion into valuable products [2],



[4]. During pyrolysis the long carbon chains of the polymers are cracked at elevated temperature (400-1000 °C) resulted in more valuable products, such as hydrocarbon gases, fuels, oils, chemicals, etc. The products of pyrolysis process are affected by many factors such as, type of catalyst and its amount [4], [5]. E.g. both the product yields and composition are significantly affected by different catalyst, such as synthetic or natural zeolites, alumina, silica-alumina, etc.. In high temperature pyrolysis process, catalysts play also important role to the gases [4]-[6]. In general, higher yields of gases can be found using catalysts [5], [6]. However, many catalysts have been used for the thermal decomposition of waste (PET and PE) in order to enhance and improve the waste plastics recycling and product selectivity. Wong et al. indicated that the pyrolysis product selectivity and coke formation are affected by the pore structure and acidity of the catalyst [7]. ZSM-5, γ -zeolite and other synthetic zeolite structures are widely investigated catalysts for promoting the decomposition reactions and affecting the product structure. Especially the aromatization and isomerization reactions can be enhanced and further cracking of aromatic derivate can be occurred over ZSM-5 and γ -zeolite [8]-[10]. Yuan et al. found that the aromatics yield was increased by pyrolysis of PET and PE due to the hydrogen transfer from polyethylene to polyethylene terephthalate while, the yield of solid residue was decreased for the same reason [5]. Hydrogen and other valuable products can be synthesized if transition metals are built into the structure of SiO_4 and AlO_4 - tetrahedral, which linked via common oxygen atoms containing ion-exchangeable mobile alkali atoms [10]-[12]. E.g. Ni, Fe or Zn resulted high hydrogen content in gases and high ratio of filamentous carbons in coked deposition on catalyst surface [12]-[15]. The goal of this work was the investigation of the pyrolysis of 50%/50% polyethylene and polyethylene terephthalate waste plastics at high temperature in tubular furnace using different Ni loaded zeolite catalyst, focussing to the effect of ZSM-5, γ -zeolite, β -zeolite and natural zeolite supporters on the pyrolysis process. Especially the product yields and the compositions of gaseous and pyrolysis oil fraction were discussed.

2. Experimental

2.1. Raw material

In this work scraps of real plastic waste were used: polyethylene terephthalate was obtained from waste mineral water bottles, while polyethylene wastes was obtained from packaging. Both raw materials were shredded and milled by laboratory grinder (Dipre GRS 183A9) into small particles (<5mm). The main properties of raw materials are listed in Table 1.

Table 1. Main properties of raw materials.

	Polyethylene	Polyethylene terephthalate
Polymer	$-(\text{CH}_2-\text{CH}_2)_n-$	$-(\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2)_n-$
Source	packaging	soft drink/mineral water bottles
Ash content^a, %	2.5	4.8
Humidity, %	1.02	1.44

^a combustion in air at 850 °C for 2hours

2.2. Catalysts

Mixtures of raw materials were pyrolyzed over different nickel loaded zeolite supported catalysts. They were synthesized using ZSM-5, γ -zeolite, β -zeolite and natural zeolite (clinoptilolite) catalysts according to the following method. Catalyst supporters were added into 1M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolution and continuously stirred for 2 hours at 85 °C. Then catalysts were dried for 10 hours at 110 °C, and each of them was conditioned at 650 °C for 4.5 hours in air. According to x-ray analysis, Ni/ZSM-5, Ni/ γ -zeolite, Ni/ β -zeolite and Ni/natural zeolite catalysts had nickel content of 10.4, 10.1, 10.3 and 10.7%, while they had 315, 610, 580, 205m²/g BET surface area, respectively.

2.3. Pyrolysis apparatus

Mixtures of 50% waste polyethylene and 50% polyethylene terephthalate were pyrolyzed in a tubular reactor in nitrogen flow at 600, 750 and 900 °C. Figure 1 demonstrates the layout of experimental rig. 10g of raw materials were weighted into the sample holder. In case of thermo-catalytic pyrolysis 10% of the synthesized catalysts were also added to the raw materials. Then nitrogen was continuously flushed through a quartz reactor tube during the experiments. Pyrolysis was taken at 600, 750 and 900 °C till 20 minutes. The reactor temperature was set and controlled by PID controller. Pyrolysis products were driven through a cooled glass container, where liquid fraction was condensed. Gases were taken from the container and further analysed. The temperature of the cooling water was 5 °C.

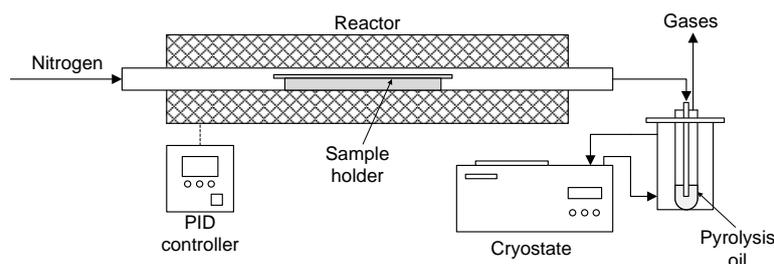


Figure 1. Layout of the pyrolysis process

2.4. Product analysis

The composition of gases was investigated by a DANI type GC instrument, which was fitted with programmed injector, flame ionized detector and Rtx PONA (100m x 0.25mm, surface thickness of 0.5 µm) and Rtx-5 PONA (100m x 0.25mm, surface thickness of 1 µm) columns. Sample analysis was taken using isotherm conditions (T=30 °C).

Hydrogen content of the gas products was measured by Shimadzu GC-2010 gas-chromatograph equipped with TCD detector (Carboxen™ 1006 PLOT column (30m × 0.53mm)). The temperature program was the following: from 35 °C (hold time 2 min) to 250 °C at 40 °C min⁻¹ heating rate, with the final temperature maintained for 5 min. The GC instrument was previously calibrated by mixture of defined composition of gases.

Pyrolysis oil was analysed by DANI GC, using Rtx 1 dimetil-polysiloxan capillary column (30m x 0.53mm, thickness of 0.25 µm). Sample was heated to 40 °C for 5 minutes, then the temperature was elevated by 8 °C/min till 340 °C and it was kept at 340 °C till 20min. Both the injector and detector temperature was 340 °C.

A TENSOR 27 type Fourier transformed infrared spectrometer (resolution: 2 cm⁻¹, illumination: SiC Globar light, monochromator: Littrow prism, detector: RT-DLaTGS (Deutero L-α-Alanine Triglycine-Sulphate) type detector with KBr window) was also used for pyrolysis oil analysis in wavenumber range of 400-4000cm⁻¹.

3. Result and discussion

3.1. Product yields

The yields of gases and pyrolysis oil obtained in the decomposition reactions are summarized in Figures 2 and 3. Results indicate that the yields of both gases and pyrolysis oil were much higher by the using of catalysts compared with without catalyst. It is well known, that pyrolysis needs lots of energy, which could be decreased by catalysts. E.g. the activation energy and the reaction time could be significantly decrease by catalysts, which led to decreasing in energy consumption [3]. For the pyrolysis process without catalyst, the results were 21.4, 35.2 and 48.3 for temperature of 600, 750 and 900 °C, respectively. It is well known, that the thermal stability of C-C bond decreases with increasing temperature. That is the cause for, that higher pyrolysis temperature can promote the more intensive cracking of C-C bond, leading to the dominant formation of gases. Figure 2 well illustrates that catalysts can also promote the more intensive cracking of C-C bonds, leading to significantly increase

in the yield of gaseous products in the temperature range of 600-900 °C. It can be seen that the gases yields over Ni/ZSM-5 catalyst was the highest when compared to the other three catalysts. Ni/ZSM-5 catalyst increases the gas yields with 42.4-69.2% depending on the reaction temperature. Natural zeolite supported Ni modified catalysts had the less effect to the decomposition reactions, because that catalysts can increase the gas yield only with 5.8-27.6%. It is important to remark, that the catalysts efficiency was different at 600 and 900 °C, because it was the order of Ni/Natural zeolite<Ni/β-zeolite<Ni/ZSM-5<Ni/γ-zeolite at 600 °C, however Ni/Natural zeolite<Ni/γ-zeolite<Ni/β-zeolite<Ni/ZSM-5 at 900 °C. The high cracking activity could be attributed to the high surface area of Ni/β-zeolite, Ni/γ-zeolite and Ni/ZSM-5 catalysts; Ni/natural zeolite catalysts had lower BET surface area.

The yields of pyrolysis oil for the four catalysts are shown in Figure 3, which were decreased by increasing temperature. The pyrolysis oil yields were 34.4, 21.6 and 11.4% at 600, 750 and 900 °C without catalyst, respectively. Ni/ZSM-5 catalyst had the highest activity in pyrolysis oil yield increasing at 600 °C with yield of 52.9%. β-zeolite showed also high activity in pyrolysis reactions resulted pyrolysis oils, however its activity rapidly decreased with increasing temperature. It was only 19.3% at 900 °C. Glancing result, it was concluded, that Ni/γ-zeolite catalyst had the slowest decreasing tendency. Comparing gas and pyrolysis oil yields, it is also clear, that basically the transformation of pyrolysis oil to gaseous product is the main reason to the decreasing tendency in pyrolysis oil yields as function of temperature. Higher temperature favours to the deeper cracking of primary decomposition products.

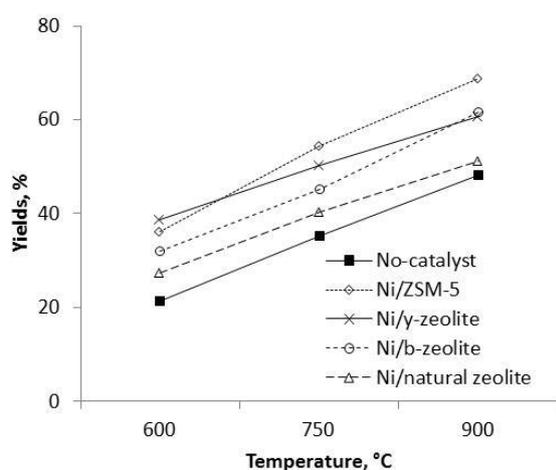


Figure 2. Yields of gases as function of temperature

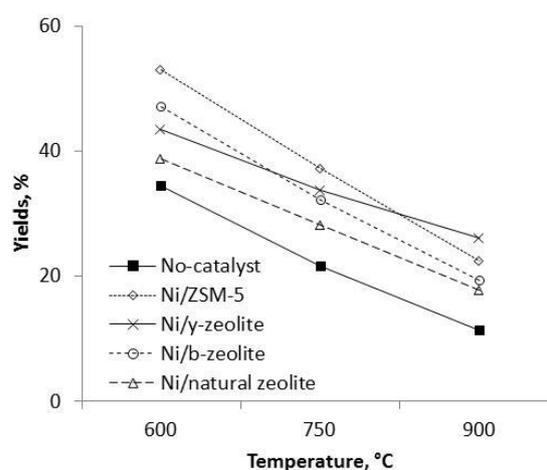


Figure 3. Yields of pyrolysis oil as function of temperature.

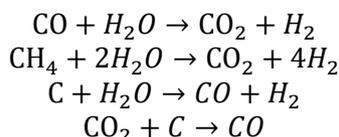
3.2. Gases

The compositions of gases are summarized in Figure 4, which shows the effect of catalyst and reaction temperature to the pyrolysis process with catalysts and without catalyst. Gases contain hydrogen, CO, CO₂, branched and non-branched hydrocarbons up to C₅. Regarding the effect of the pyrolysis temperature, it is well shown that the hydrogen yields could increase with increasing temperature, both absence and presence of catalysts. E.g. it was 4.0% at 600 °C and 14.1% at 900 °C without catalyst. Hydrocarbons resulted hydrogen and coke at high temperature as following reaction:



Higher temperature favours to the carbon and hydrogen production. Higher temperature favours to intramolecular hydrogen transfer reaction, which resulted higher yields of branched C₂-C₅ hydrocarbons with increasing temperature. CO and CO₂ in gases were the consequence of PET presence in raw materials. PET contains -(O-CO-C₆H₄-CO-O-CH₂-CH₂)- repeating unit in the polymer

macromolecule, which decomposition results significant carbon oxides. In general CO_2 had higher concentration than CO . In the most cases, the ratio of CO_2/CO increased with temperature, demonstrating the higher rate of Boudouard reaction at higher temperature. However, owing to PET structure, the water production and in-situ water-gas shift reaction or steam-methane reforming reaction in the produced water presence should be also the cause for CO_2 increasing. Regarding CO increasing the water-gas reaction could be also blamed.



The concentration of methane did not changed significantly with temperature, however it was highest a bit using higher process temperature. The increasing in methane concentration should be occurred by the methanization reaction: $\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$.

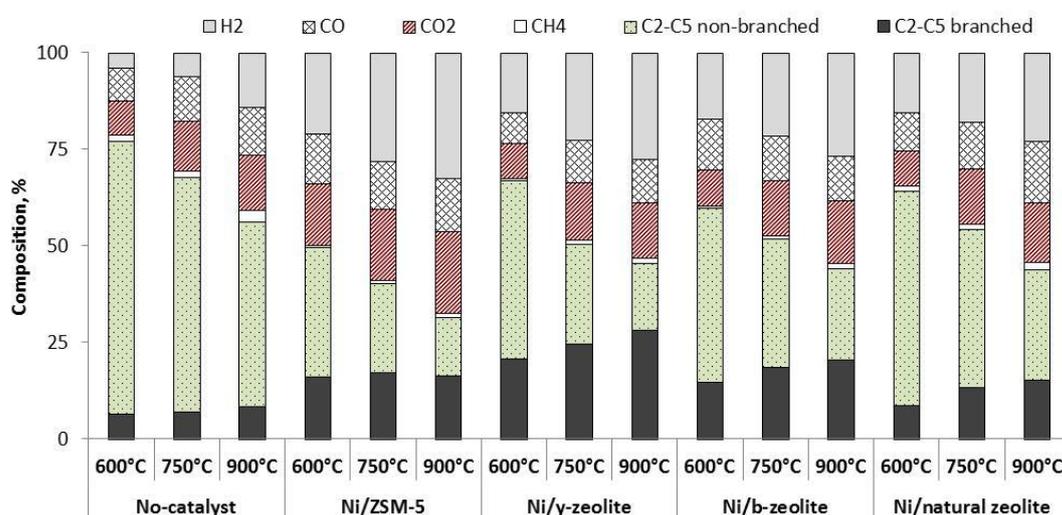


Figure 4. The composition of gases

Catalysts had also important effect to the composition of gaseous fractions. E.g. they can increase the yields of hydrogen and branched hydrocarbons and decreased the concentration of non-branched hydrocarbons. The increase in branched hydrocarbon was attributed to the intramolecular and intermolecular hydrogen transfer reactions over acidic zeolite catalyst supporters. Regarding isomerization, Ni/y-zeolite had the highest activity; the concentrations of branched hydrocarbons were 20.8, 24.5 and 28.1% at 600, 750 and 900 °C, respectively. However, Ni modified natural zeolite showed the less effect in branching reactions. Both CO and CO_2 had higher concentrations by the using of catalysts, which was the consequence of more intensive decomposition of PET, followed by the before listed secondary reactions. The most important effect of the catalyst was the increasing of hydrogen content. E.g. gases synthesised over Ni/ZSM-5 catalyst had 32.6% hydrogen at 900 °C. Presumably transition metal loaded zeolite can effectively increase the rate of reaction led to hydrogen formation; e.g. water-gas reaction, water-gas shift reaction or even decomposition of main carbon frame of polyethylene resulted coke, light hydrocarbons and hydrogen.

3.3. Pyrolysis oil

The compositions of pyrolysis oils are shown in Figure 5. Results indicate that the oil product contained n-olefins, n-paraffins, non-oxygenated aromatics, branched and oxygenated compounds. The main effect of the temperature increasing was the increasing in non-oxygenated aromatics and decreasing in oxygenated compounds. The concentrations of n-alkane, n-alkene did not change

significantly with temperature, however lower yields of n-olefins and n-paraffins were measured in pyrolysis oils obtained in thermo catalytic pyrolysis. N-olefins and n-paraffins were represented with concentrations of 31.9-33.3% and 23.3-24.3% without catalysts, while 20.2-27.0% and 15.4-21.7% in thermo-catalytic pyrolysis.

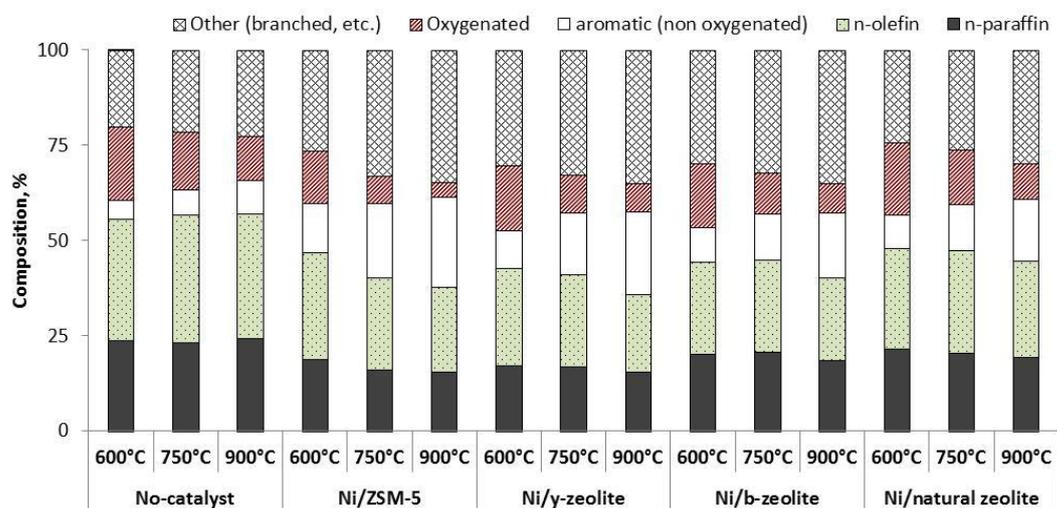
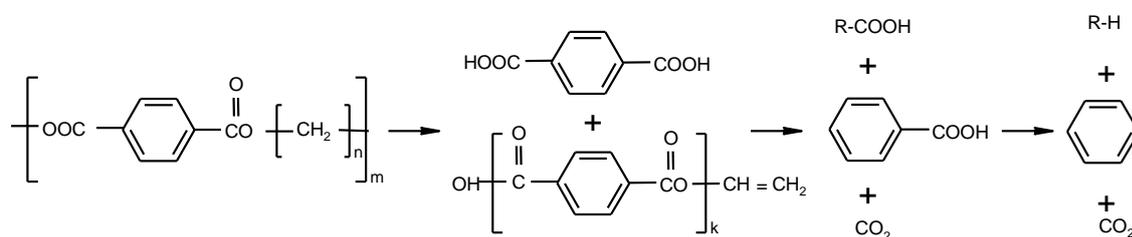
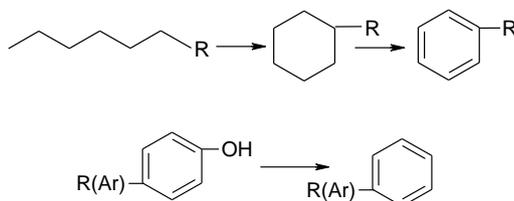


Figure 5. The composition of pyrolysis oils

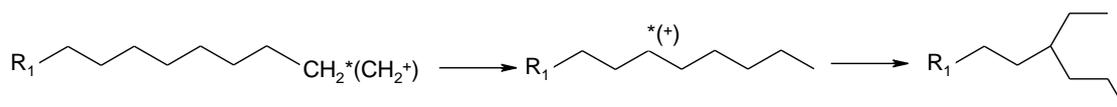
Based on FTIR result, oxygenated compounds were represented mainly in the form of carboxylic acids, esters, phenols and its derivatives according to the following reaction scheme:



It is also clear, that the temperature increases and catalyst presence favour to the further decomposition of carboxylic acids, such as terephthalic acid, acetic acid, benzoic acid, or oligomers of PET, resulting oxygen free aromatics and CO₂. Aromatization reactions and side broken reactions of phenol derivatives (especially from PET pyrolysis) could be also increased with temperature. Both the elevated temperature and presence of acidic catalysts are favoured for them.



As it was before mentioned, higher pyrolysis temperature favours to the intramolecular hydrogen transfer reactions, which lead to isomerisation reactions. That is why that higher concentration of branched hydrocarbons was obtained e.g. at 900 °C.



In pyrolysis reaction using catalysts, higher yield of branched compounds was achieved over Ni/ γ -zeolite and Ni/ β -zeolite, while the maximum yields of aromatic compounds was achieved over Ni/ZSM-5 which is.

4. Summary

In this work, the co-pyrolysis of waste polyethylene and polyethylene terephthalate was investigated using different Ni modified zeolite catalysts. Both gas and pyrolysis oily yields were significantly influenced by temperature and catalysts: temperature could increase the gas and decrease the pyrolysis oil yield. In gases H_2 , CO_2 , CO , CH_4 , branched and non-branched hydrocarbons up to C_5 , while in pyrolysis oil branched, oxygenated, aromatic, n-olefin and n-paraffin were mainly represented. Ni/ZSM-5 can effectively increase the amount of hydrogen. The maximum hydrogen production was achieved at high temperature therefore the high temperature is favoured for hydrogenation reaction. On the other hand the maximum oil product was achieved over Ni/ γ -zeolite and Ni/ β -zeolite. Owing to the side chain scission and secondary reactions, both catalysts and temperature increasing decreased the concentrations of oxygenated aromatic and increased the concentration non-oxygenated compounds or even CO_2 .

5. Acknowledgments

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6. References

- [1] <http://www.plasticseurope.org/Document/plastics---the-facts-2016-15787.aspx?FolID=2>
- [2] Z. Sun, B. Xu, A. H. Rony, S. Toan, K. A. M. Gasem, H. Adidharma, M. Fan, M. Xiang, *Energ Convers Manage*, 2017. **146** 182-194
- [3] N. Miskolczi, R. Nagy, *Fuel Proc Technol*, 2012. **104** 96-104
- [4] S. M. Al-Salem, A. Antelava, A. Constantinou, G. Manos, A. Dutta, *J Environ Manage*, 2017. **197** 177-198
- [5] X. Yuan, P. Johnston, X. Bai, *Energ Convers Manage*, 2017. **142** 441-451.
- [6] Miandad R, Barakat MA, Rehan M, Aburiazaiza AS, Ismail IMI, Nizami AS, *Waste Manage*, 2017. **69** 66-78
- [7] H. W. Wong, J. Peck, J. Assif, F. Panerai, F. Lachaud, N. N. Mansour, *J Anal Appl Pyrol*, 2016. **122** 258-267
- [8] S. Kumagai, R. Yamasakic, T. Kameda, Y. Saito, A. Watanabe, C. Watanabe, N. Teramae, T. Yoshioka. *Chem Eng J*, 2018. **332** 169-173
- [9] J. Chattopadhyay, T. S. Pathak, R. Srivastava, A. C. Singh, *Energy*, 2016, 103, 13-521
- [10] M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao, M. Plazar, *Ind Eng Chem Res*, 2013. **52**, 10637-10645.
- [11] A. R. Auxilio, W. L. Choo, I. Kohli, S. C. Srivatsa, S. Bhattacharya, *Waste Manage*, 2017. **67** 143-154
- [12] A. Ochoa, I. Barbarias, M. Artetxe, A. G. Gayubo, M. Olazar, J. Bilbao, P. Castaño, *Appl Catal B- Environ*, 2017. **209** 554-565
- [13] J. C. Acomb, C. Wu, P. T. Williams, *J Anal Appl Pyrol*, 2015. **113** 231-238
- [14] D. Yao, C. Wu, H. Yang, Y. Zhang, A. M. Nahil, Y. Chen, P. T. Williams, H. Chen, *Energ Convers Manage*, 2017. **148** 692-700
- [15] E. F. Iliopoulou, S. D. Stefanidis, K. G. Kalogiannis, A. Delimitis, A. A. Lappas, K. S. Triantafyllidis, *Appl Catal B- Environ*, 2012. **127** 281-290

