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Thermo-catalytic two-step pyrolysis of real waste plastics from end of life vehicle

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ABSTRACT

This work focuses to the thermo-catalytic pyrolysis of real plastic waste from End of Life Vehicle. Two-step batch reactor fitted with electric heating was used for pyrolysis. Zeolite catalysts (ZSM-5, β-zeolite and y-zeolite) was used in the first reactor at 425 °C and 485 °C, while the product yield and composition were further modified by the using of structured Ni/Mo–Al_2O_3 catalyst in the 2nd reactor at 380 °C. No water/steam was feed into the 2nd reactor. Gas-chromatography, high-pressure liquid chromatography, size exclusion chromatography and Fourier transformed infrared spectroscopy were used for identification of pyrolysis products, while the catalyst morphology was investigated by scanning electron microscopy. Catalysts in the 1st reactor had a significant effect to the product yields and decreased the time required for pyrolysis. ZSM-5 and y-zeolite catalysts had high activity in carbon frame isomerization. β-zeolite catalyst could crack the polymer main chain with high efficiency; however, its deactivation was the fastest. Structured Ni/Mo-Al_2O_3 in the 2nd reactor affected the gas/pyrolysis oil ratio, increased the hydrogen yield in gases, monoaromatic yield in pyrolysis oil and owing to the coke formation, its surface was fully covered by coke depositions after the pyrolysis. The hydrocarbon compositions of pyrolysis oils were favourable for further separation and refinery application.

1. Introduction

Due to their low weight, high chemical stability or even long service life, plastics are in all areas of life and the demand for plastics is significantly growing [1]. Fact, that the worldwide plastic production was 322 million tons, of which the European Union produced 58 million tons in 2015 [2]. On the other hand, the amount of polyolefins, as commodity plastics is used in the highest rate, which was nearly 24 million tons in 2015 in the EU [2]. It is also well known, that plastic wastes cause serious environmental problems. That is why the European Union has implemented various directives (e.g. 94/62/EC, 2000/53/EC) in order to reduce the amount of polymer waste mainly by recycling [3,4]. In 2014, in concern of the waste management, the EU28 + 2 could significantly increase the amount of recycled and decrease the landfilled waste polymers compared to 2006 [2].

Plastics have high energy content; therefore another driving force of the recycling is the energy recovery. The most common example for chemical recycling is the pyrolysis. Products could be utilized for energy-production, or as a feedstock for petrochemical and oil industry. In the refineries, after further quality improvement motor fuels may be obtained from them. Therefore the production of waste derived fuel-like pyrolysis oil is widely investigated in the last decade [5–9].

The composition of the products and their yields can be significantly influenced by reaction parameters [10–16]. For instance, both the gas and pyrolysis oil yields can be increased by increasing temperature [11,12], using of catalysts [13,14] or improvement in reactor construction [15,16]. During the waste plastic pyrolysis the following main reactions take place: cracking by β-scission, isomerization, oligomerization, cyclization and aromatization reactions [17]. The composition of raw materials, the catalyst concentration, the residence time, the heat transfer and the efficiency of the reaction are fundamentally depend on the reactor construction. Lab scale batch, semi-batch or continuous reactors are the mostly used for investigation of waste plastic pyrolysis. Continuous reactors have lower operating costs and can provide more consistent product quality compared to batch and semi-batch processes. Barbarias et al. [18] reported that the Ni supported Al_2O_3 catalyst showed high activity for hydrogen production with yield of 92.5% at 700 °C, in case of HDPE fast pyrolysis and in-line steam reforming in a continuous conical spouted bed reactor (CSBR). Arregi et al. stated that the hydrogen production increased lineally with HDPE content of the feed by the use of Ni containing reforming catalyst in a two-stage reaction system (CSBR and fluidized bed reactor, at 500 and

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700 °C, respectively) during the continuous pyrolysis and in-line catalytic reforming of pine wood waste and HDPE mixtures [19]. One stage batch reactors are also widely used for production of pyrolysis oil [20]. These reactors have some advantages opposite continuous technologies: simply design, advanced operation parameters, easy to control, total decomposition of raw material can be achieved. Regarding the two stage pyrolysis, most of the published papers are focused to the catalyst application exclusively in the second reactor. It means, that the thermal cracking occurs in the first reactor, and thermo-catalytic cracking or reforming reactions are taken place in the second one [5,21–23]. The two-stage pyrolysis is widely used for gasification [24,25] or steam-reforming reactions [26,27]. In that case, moderate temperature (400–500 °C) in the first reactor and high temperature (700–900 °C) in the second reactor is used. To ensure the reforming reactions, dominantly Ni-based catalysts together with steam are used in the second reactor [28,29]. When the pyrolysis oil is the main products, lower temperature must be used for second reactor (up to 600 °C). Regarding catalysts for plastics pyrolysis, especially ZSM-5 [30], y-zeolite [31], β-zeolite, FCC [32], silica alumina [33] or even MCM-41 [34] are used affecting the product properties [5,6].

Recently Y. Wang et al. investigated the effects of HZSM-5 catalyst producing vapours from pinewood by catalytic pyrolysis in a two stage, fix bed reactor. It was found that the HZSM-5 catalyst showed high selectivity for the formations of aromatic hydrocarbons and olefins at 550–600 °C [21]. Ratnasari et al. studied the gasoline-range hydrocarbons production by catalytic pyrolysis of waste high density polyethylene plastics in a two-stage reactor system using different ratios of polymer and catalysts (MCM-41 and ZSM-5) [5]. They concluded, that 1:2 polymer:catalyst ratio showed the best result. E.g. the pyrolysis oil had high yield of gasoline range hydrocarbons (C_8–C_{12}) and it had high yield of aromatics.

ZSM-5 and y-zeolite catalysts had high activity in aromatization. Bagri and Williams reported that the yield of aromatic compounds was increased in the pyrolysis oil in the presence of catalysts; however, higher concentrations of aromatic compounds could be measured with y-zeolite catalyst, than in the case of ZSM-5 zeolite [22]. Not only the concentration of aromatics, but also the branched compounds could be also increased by catalyst. Higher yield of aromatic, but lower yield of iso-paraffins and olefins was measured using nanosized HZSM-5 catalyst than Al-MCM-41 mesostructured material regarding the pyrolysis of low density polyethylene; however due to the weaker acid properties and larger pore dimensions, lower yield of gas and higher yield of gasoline type hydrocarbons was found over Al-MCM-41 [23].

This study focuses to the pyrolysis of End of Life Vehicle (ELV) waste plastics in a two-stage reactor system at 425 and 485 °C in the first reactor and 380 °C in the second reactor for production of mainly pyrolysis oil. The feedstock contained dominantly polyethylene and polypropylene. Catalyst was placed not only in the second, but also in the first reactor (Y-zeolite, ZSM-5, β-zeolite) as well, to investigate their effect to the polymer decomposition. For moderate increasing in gas yield and improving the product composition, Ni/Mo-catalyst was used in the second reactor, placed on Raschig ring packing. In one hand Ni/Mo catalyst is not typically used for waste pyrolysis, however Ni loaded catalyst is extensively used for hydrogen production at high temperature (over 600 °C) [18,19,24,35,36]. Our aim was the investigation of the effect of Ni/Mo-Al_2O_3 catalyst to the hydrogen production and aromatization using low temperature (380 °C). Transition metal loaded catalysts are used at higher temperature resulting vast amount of gases, however the dominancy of gaseous products and coke deposition (reducing the yield of pyrolysis oil) must to be avoided in current work. On the other hand, the amount of coke on catalyst surface was also investigated. The carbon deposition on the Ni/Mo-catalyst surface was further analysed by temperature programmed oxidation.

2. Experimental

2.1. Materials

The raw materials, used in this work, were large, easier removable plastic constituents of passenger cars; e.g. bumper, fuel tank, wheel rims, engine containers, etc. They could be easy to separate from the others and their selections do not need high labour cost. ELV waste had been shredded and then crashed by laboratory miller (Dipre GRS 183A9) into particles up to 3 mm. Fourier transformed infrared spectroscopy was used for identification of raw materials based on spectra comparison. Results show, that the ELV contains 41% HDPE, 42% PP and 17% LDPE. Besides that, raw material has 0.1% and 5.96% humidity and ash content (basically the glass fibre from reinforced plastic part), respectively. It is also fact, that owing to the surface impurities on the raw materials, their mechanical recycling is very difficult and needs extra cost, therefore their chemical recycling looks more attractive way for long term utilization.

Three different catalysts (ZSM-5, β-zeolite, y-zeolite) were used for increasing the volatile product yields and affect their properties in the 1st reactor and structured catalyst was also used for further modification of product properties (Ni/Mo-Al_2O_3) in the 2nd reactor. It is known, that Ni/Mo-Al_2O_3 catalyst is not generally used as cracking catalyst. On the other hand, the possibility for pyrolysis oil in-situ quality improving, hydrogen production and aromatization effect were studied using Ni/Mo-Al_2O_3 catalyst at low process temperature. The main properties of the applied catalysts are summarized in Table 1. Zeolite catalysts had average grain size of 20–30 μm; ZSM-5 was the smallest, while β-zeolite was the largest. Regarding surface area, y-zeolite had the highest (732m^2/g), while β-zeolite (320m^2/g) the lowest surface area. Acidity of the catalyst is key property for C-C cracking; in our case, catalyst had acidity as following: ZSM–5 > y-zeolite > β-zeolite.

2.2. Pyrolysis process

The pyrolysis of waste plastics was taken in a two stages pyrolysis reactor system. The main parts of the reactor are shown in Fig. 1. The pyrolysis process contains two reactors with independent temperature control. 50 g of the raw material together with 2.5 g of catalyst was placed in the 1st reactor, where pyrolysis reactions were taken in nitrogen atmosphere to avoid oxidation and unfavoured secondary reactions using 15dm^3/h flow rate. Plastic particles were mixed with catalysts before the pyrolysis by mechanically. Volatiles were driven through to the 2nd reactor by the using of a nitrogen flow, where 20 g of structured Ni/Mo-Al_2O_3 catalyst was placed over Raschig rings. The temperature in both reactors was controlled by computer, using PID controllers and data recorder unit. Regarding the 1st reactor, two temperatures were used: 425 and 485 °C; while 380 °C was applied in the 2nd reactor. The main reason for low temperature in 2nd reactor was, to avoid the significant increasing the yields of gases, because the

Table 1
The main properties of the used catalysts.

	ZSM-5	β-zeolite	y-zeolite	Ni/Mo–Al_2O_3
Appearance	White powder	White powder	White powder	Light green structure catalyst
Average grain size, μm	19.5	28.2	25.8	Structured catalyst
Surface area, m^2/g	355	320	732	125
Acidity, meqv. NH_3/g	0.74	0.58	0.61	0.10
Ni	–	–	–	11
Mo	–	–	–	76