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Recycling of ELV Waste Plastics by One-Stage and a Two-Stage Thermo-Catalytic Pyrolysis

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Due to the significant increasing in motorization, the long term sustainable utilization of End-of-Life Vehicles (ELV) wastes is in the focus of the waste management. In the European Union annually 8-9 Mt of ELV waste should be utilized. ELV contains mainly metals but its 15 - 20 % is plastics or rubber. According to the 2000/53/EC directive, from 1 January 2015, 95 % of the waste from vehicles have to be utilized; 85 % of the wastes by mechanical recycling and 10 % of the wastes by chemical recycling. The chemical recycling results valuable products from ELV plastic wastes, such as fuels, oil and hydrocarbon gases, which can be utilized as a feedstock for energy generation, for petrochemical processes or even in oil refinery.

Mixture of real ELV waste plastic was pyrolyzed in a one-stage and a two-stage reactor in the presence of zeolite catalysts at 425 °C in the first reactor. Different modified ZSM-5 catalysts were synthesized by wet impregnation and tested in the first reactor: H/ZSM-5, Fe(III)/ZSM-5, Ni/ZSM-5 and Cu/ZSM-5. In case of two-stage pyrolysis, Ni/Mo-Al_2O_3 was used in the second reactor. Due to avoid the formation of harmful by-products, the pyrolysis was taken under inert nitrogen atmosphere. The composition of gases was analysed by GC. Higher yield of gaseous products was measured using catalyst in the second reactor; furthermore the hydrogen yield was also higher. Pyrolysis oil was measured by GC, HPLC or even FTIR. Regarding pyrolysis oils, they contain non-branched, branched aliphatic hydrocarbons and aromatics compounds; and significant isomerization was concluded over catalysts.

1. Introduction

In our running world, the plastics yearly production is more than 300 Mt and the amount of waste plastics is increasing from year to year. Large portion of waste plastics is the End-of-Life Vehicles (ELV), from automobiles, trucks, buses, etc. at the end of their lifetime. Worldwide the number of vehicles reached the 1 billion in 2010 (Sousanis, 2011). In the European Union 8 - 9 Mt of ELV is generated yearly. The driving forces of the ELV recycling are the plastic waste recycling and different EU directives towards the environmental protection. For example according to the 2000/53/EC directive from 1 January 2015, 95 % of the waste coming from vehicles' construction material has to be utilized; 85 % by mechanical and 10 % by chemical recycling. An average car wreck contains mainly metals but its 15-20 % is plastic or rubber. Chemical recycling means that plastic waste is pyrolyzed and the obtained pyrolysis oil – after further conversion and quality improvement – may be used as fuel or chemical feedstock.

Pyrolysis is thermal decomposition of organic materials at high temperature in the absence of oxygen. Many factors affect for this process (Panda et al., 2010). For instance, the yield of the valuable volatile products (gas and pyrolysis oil) is increasing with temperature (Borsodi et al., 2011). Catalysts can be significantly influenced the products yields (Bagri and Williams, 2002) and compositions (Tian et al., 2015). Especially alumina silicate and zeolite-based catalysts are used (Marcilla et al., 2007). ZSM-5 is the most widely used catalyst, due to its strong acidity and shape selectivity (López et al., 2011).

The effect of ZSM-5 catalyst has been investigated by many researchers during the thermo-catalytic pyrolysis of plastic (Zhang et al., 2015). López et al. used ZSM-5 zeolite for the pyrolysis of mixed plastics waste. Conversion over 95 wt% and pyrolysis oil with high amount of aromatic compounds was found, like styrene and toluene, and mainly C_3-C_4 hydrocarbons in gases were concluded. The thermo-catalytic pyrolysis has

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been also investigated in the two-stage reactors (Choi et al., 2016). Aguado et al. found significant yield of gaseous products (over 74 wt%), which contains mainly olefins and the pyrolysis oil consisted of high proportion of aromatics and iso-paraffins in case of LDPE pyrolysis using nanosized n-HZSM-5 (Aguado et al., 2007).

In this work the thermo-catalytic pyrolysis of the real ELV waste plastic in a one-stage and a two-stage reactor system was investigated in the presence of modified ZSM-5 catalysts at 425 °C in the first reactor. In case of two-stage pyrolysis, Ni/Mo-Al_2O_3 had been also used in the second reactor. Basically the effects of zeolite-based and Ni/Mo catalysts on the yields and the composition of products were followed.

2. Experimental

2.1 Raw materials

In this work real ELV plastics were pyrolyzed. The composition of raw materials was obtained by identification of each particle using Fourier-transformed infrared apparatus based on spectrum comparison. According to results, the raw materials contained 41 % HDPE, 42 % PP and 17 % LDPE.

Because of to increase the yields of volatiles and affect the composition of gases and pyrolysis oil, different catalysts were used: H/ZSM-5, Fe(III)/ZSM-5, Ni/ZSM-5 and Cu/ZSM-5. Catalysts were synthesised by wet impregnation method using commercial ZSM-5 catalyst. For impregnation $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $CuSO_4{\cdot}5H_2O$ and 1 M NH_4NO_3 were used. In case of two-stage pyrolysis, Ni/Mo-Al_2O_3 was used in the second reactor. Catalysts were dried for 10 hours at 110 °C, and then each of them was calcined at 600 °C for 3 hours.

2.2 Apparatus for one- and two-stage pyrolysis

Pyrolysis of ELV wastes was carried out both in one-stage and two-stage stainless steel batch reactors. Figure 1 demonstrates the layout of the used reactors.

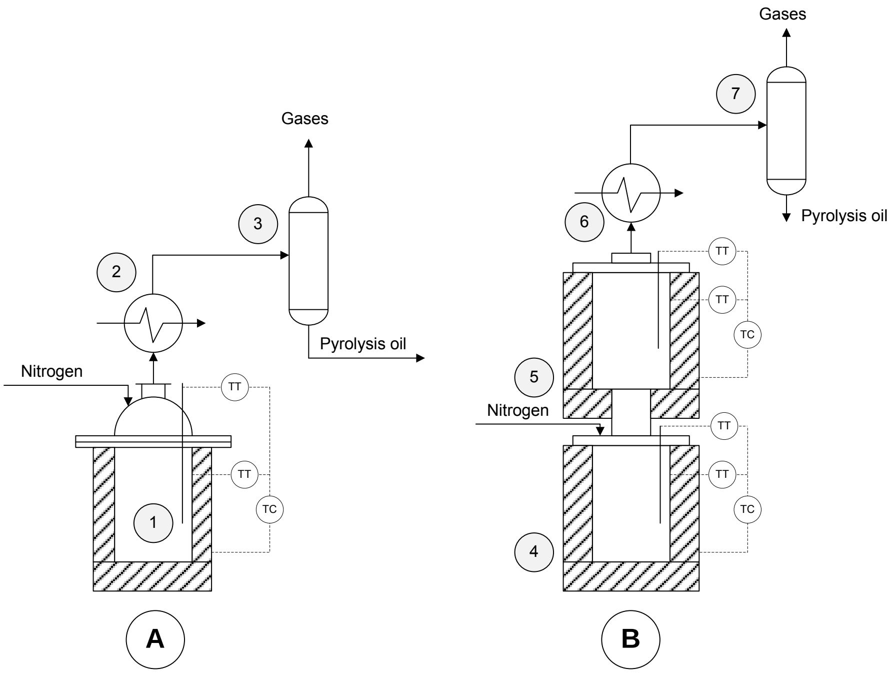

Figure 1: Simplified layout of the one-stage (A) and two-stage (B) batch pyrolysis reactors (1,4,5-reactor vessel fitted with electric heating system, 2,6-water cooled condenser, 3,7-phase separator)

50 g of raw materials were weighted into the 1st reactor (1 and 4) with 5 % catalysts. The reactor was fitted with electric heater and PID temperature controller. Firstly, raw material had been placed into the 1st reactor and the temperature was elevated to 425 °C then the reactor content was fully decomposed. Because of to avoid the undesired reactions, nitrogen was used with constant flow rate (11 dm^3/h). Regarding the one-stage pyrolysis, raw materials had decomposed in the 1st reactor and then volatiles were condensed in a water cooled heat exchanger. Then products were separated into gas fraction and pyrolysis oil in a phase separator.

The volume of the hydrocarbon gases was measured by gas flow meter and further analysed by GC. In case of two-stage pyrolysis, hot volatiles from the 1st reactor were driven through a fixed bed of Ni/Mo-Al_2O_3 catalyst placed in the 2nd reactor. The temperature of the 2nd reactor was 380 °C. Gases from the 2nd reactor was condensed also in a condenser and separated as it was previously mentioned, into gases and pyrolysis oil.

2.3 Methods for analysis

The composition of gaseous products was analysed by gas-chromatography (GC) (DANI type GC instrument, programmed injector, flame ionized detector) using Rtx-1 PONA column (100 m x 0.25 mm, surface thickness of 0.5 µm) and Rtx-5 PONA (5 m x 0.25 mm, surface thickness of 1 µm). Sample was analysed at isotherm conditions (T = 30 °C). The temperature of injector and detector were 240 °C.

Pyrolysis oil was analysed also by DANI GC, using Rtx-1 dimetil-polysiloxan capillary (30 m x 0.53 mm, thickness of 0.25 µm) using the following temperature program: 40 °C for 5 min, then the temperature was elevated by 8 °C/min till 340 °C and it was kept at 340 °C till 20 min. Both the injector and detector temperature were 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 used for identification of raw materials using spectrum comparison in wavenumber range of 4,000 - 400 cm^{-1}. The chemical structure of pyrolysis oils was also followed by FTIR spectroscopy.

3. Results and discussion

3.1 Pyrolysis yields

The quantity of the products from ELV decomposition is summarized in Figure 2. As it is well shown, waste decomposed manly into gases and pyrolysis oil. At the end of both one stage- and two-stage pyrolysis 6-7 wt% solid residues was remained in the bottom section of reactor vessel. In case of one-stage pyrolysis, the gas yield increased, while the yield of pyrolysis oil decreased following the order of H/ZSM-5 > Ni/ZSM-5 > Fe/ZSM-5 > Cu/ZSM-5 catalyst. However, the differences between the pyrolysis oil yield increasing effects of nickel and iron impregnated catalysts are slight. The maximum yield of pyrolysis oil and the minimum yield of gases generated over H/ZSM-5 were 67.9 wt% and 25.5 wt%. On the other hand, the lowest yield of pyrolysis oil and the highest yield of gas were found by the using of Cu/ZSM-5 catalyst, with yields of 39.1 wt% and 54.1 wt%, respectively.

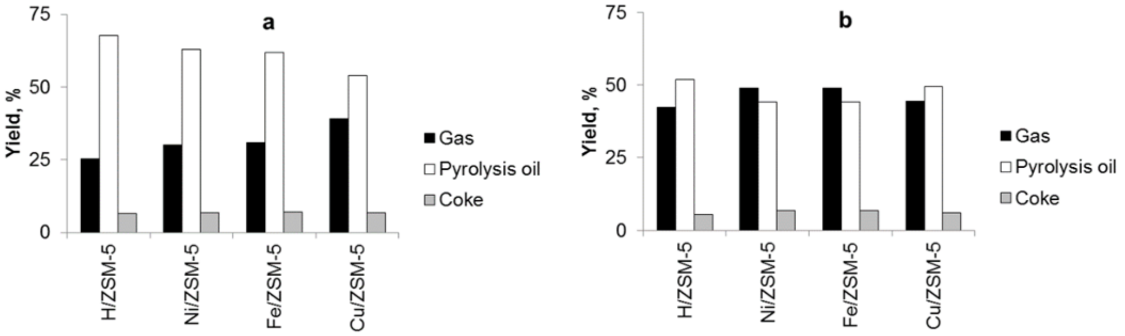

Figure 2: The yields of products (a, one-stage pyrolysis; b, two-stage pyrolysis)

In case of two-stage pyrolysis significantly higher yield of gases was found, than that of regarding one-stage pyrolysis, however, less pyrolysis oil yields was measured comparison to the one-stage pyrolysis. That phenomenon was attributed to the further cracking effect of the Ni/Mo-Al_2O_3 catalyst in the second reactor. The maximum growth of the gas yield was 66.3 wt% with using H form ZSM-5 catalyst, while the yield of the pyrolysis oil decreased with 23.4 wt%. When Cu/ZSM-5 catalyst was used, the effect of the two-stage pyrolysis for the yields was slight, namely the gas yield increased with 13.8 wt%, while the pyrolysis oil yield decreased with 8.5 wt%.

3.2 Gases

The hydrocarbon compositions of gases are shown in Figure 3. Gases contain mainly C_3-C_5 hydrocarbons with 81.2-91.8 wt% concentration. In addition, it contains C_1-C_2 (methane and ethane) and C_6 hydrocarbons, 5.4-15.6 wt% and 2.0-3.3 wt%. Gases principally consist of non-branched saturated and unsaturated hydrocarbons, and 28.9-35.1 wt% isomers. The most isomer was formed by using of modified ZSM-5 zeolite with copper during the one-stage and two-stage pyrolysis as well; 35.1 wt% and 34.8 wt%. The composition of gases did not significant change between the one-stage and two-stage processes. Although in case of two-stage pyrolysis the degree of cracking is slightly enhanced by Ni/Mo-Al_2O_3 catalyst, because the yields of methane and ethane increased due to the further cracking effect of Ni/Mo catalyst.

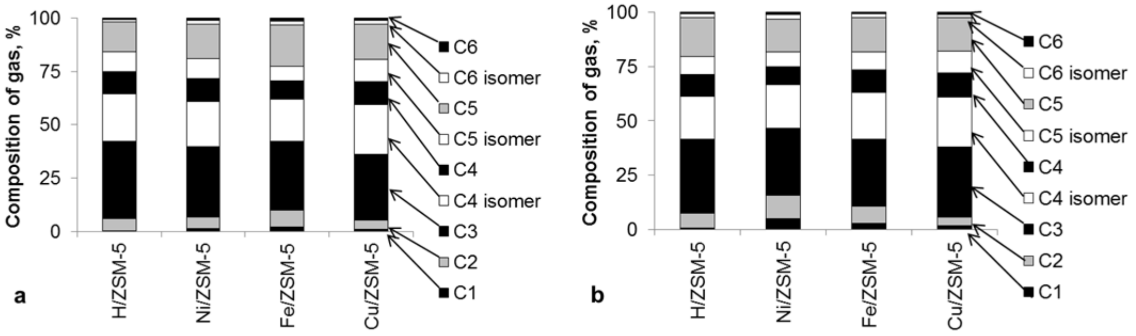

Figure 3: The hydrocarbon composition of the gas product (a, one-stage pyrolysis; b, two-stage pyrolysis)

3.3 Pyrolysis oil

The GC-FID results of the pyrolysis oil analysis are shown in Figure 4. Hydrocarbons in pyrolysis oils were defined between C_6-C_{40}. It is clear that the dominant part of the pyrolysis oil from both one-stage and two stage pyrolysis consisted C_6-C_{15} hydrocarbons, which ranged in concentration from 33.9 wt% to 49.2 wt%. According to the results from two-stage system, the concentration of C_6-C_{15} increased with 16.9-19.7 %, which effect can be attributed to the above mentioned further cracking impact of the Ni/Mo-Al_2O_3 catalyst. The concentration of the C_6-C_{15} fraction increased following the order of Cu/ZSM-5, Fe/ZSM-5, Ni/ZSM-5 and H/ZSM-5 catalyst, while the amount of C_{16}-C_{40} hydrocarbons decreased following same order. Cu/ZSM-5 catalyst showed the highest activity at 425 °C during both pyrolysis, because the highest increasing in C_6-C_{15} hydrocarbons could be found, when this catalyst was applied in the first reactor. Comparing results from one-stage and two-stage pyrolysis, it is well shown, that the concentration of C_6-C_{15} was higher in case of two-stage pyrolysis. This phenomenon can be attributed to the further cracking of C-C bonds over Ni/Mo-Al_2O_3 catalyst.

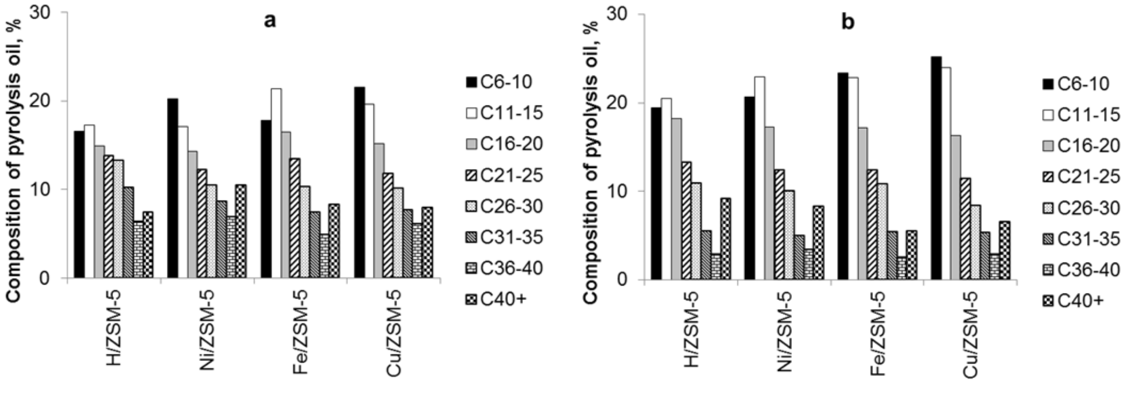

Figure 4: The carbon number distribution of the pyrolysis oil (a, one-stage pyrolysis; b, two-stage pyrolysis)

Figure 5 summarizes the composition of pyrolysis oils, such as n-saturated, n-unsaturated and other (branched and aromatics) compounds. According to results, higher n-paraffin was found in case of one-stage pyrolysis than that of two-stage pyrolysis. Regarding one-stage pyrolysis, the amount of the n-paraffins, α-olefins and other compounds were 20.2 - 23.2 wt%, 9.3 - 12.5 wt% and 65.7 - 70.5 wt%. However, 19.5-21.3 wt% n-paraffins, 8.0 - 10.9 wt% n-olefins and 67.9 - 72.6 wt% other compounds were found using two-stage reactors, respectively. It is important to remark, that the Ni/Mo-Al_2O_3 catalyst had slight effect to the formation of n-olefins and isomers. The maximum amount of the non-branched chain saturated hydrocarbon was 23.3 wt% using H/ZSM-5 catalyst, but this catalyst showed the less isomerisation effect. Regarding n-olefins, Fe(III)/ZSM-5 resulted the highest yield of n-unsaturated compounds using one-stage pyrolysis (12.5 wt%). The high concentration of branched hydrocarbon was also the consequence of the high ratio of PP (42 %) in raw material. The chemical structure of PP contains ramifications; therefore dominantly branched hydrocarbons could be formed from them.

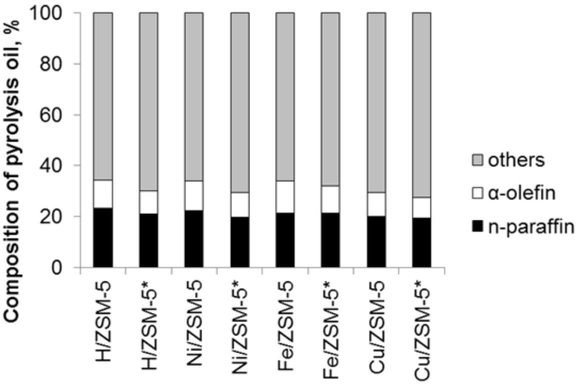

*Figure 5: The composition of the pyrolysis oil (*two-stage pyrolysis). Others means: isomers, cyclic- and aromatic hydrocarbons.*

Figure 6 and Figure 7 show the FTIR spectrums of pyrolysis oils in 4,000 - 400 cm^{-1} wave-number range. Well shown infrared activity was found in the range of 2,800 – 3,000 cm^{-1}, 1,300 – 1,500 cm^{-1} and 700 – 1,000 cm^{-1}.

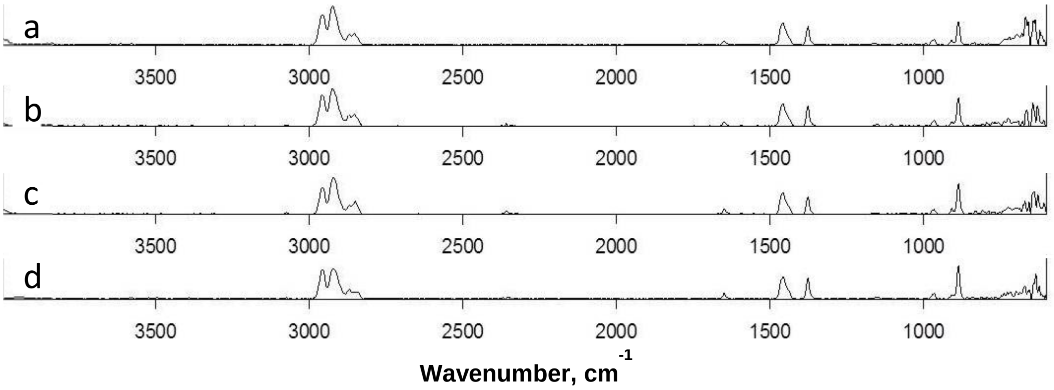

Figure 6: The FTIR spectra of the pyrolysis oil (a, H/ZSM-5; b, Ni/ZSM-5; c, Fe(III)/ZSM-5; d, Cu/ZSM-5)

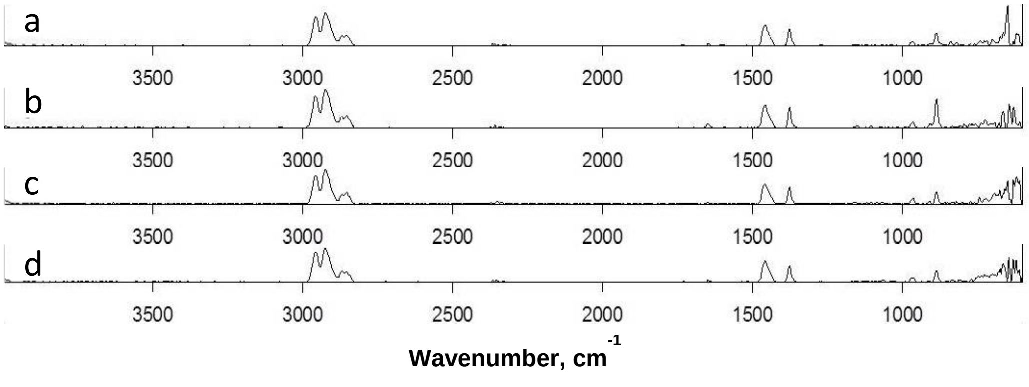

Figure 7: The FTIR spectra of the pyrolysis oil (a, H/ZSM-5/NiMo; b, Ni/ZSM-5/NiMo; c, Fe(III)/ZSM-5/NiMo; d, Cu/ZSM-5/NiMo)

Bands between 2,800 and 3,000 cm^{-1} could be attributed to the symmetric and asymmetric C–H stretching vibration of -CH_2- ($\nu_{as}CH_2$, ν_sCH_2, 2,926 cm^{-1} and 2,836 cm^{-1}) and -CH_3 ($\nu_{as}CH_3$, ν_sCH_3, 2,962 and 2,872 cm^{-1}) groups. Comparing spectrum, that higher intensity of bands belongs to methyl group and lower intensity of bands belongs to methylene groups were found using Ni/Mo-Al_2O_3 catalyst in the 2nd reactor. The infrared activity between 1,470 – 1,430 cm^{-1} and 1,400 – 1,350 cm^{-1} was the consequence of the asymmetric and symmetric deformation stretching of –CH_3 groups. Unsaturated hydrocarbons show infrared activity between 800 – 1,000 cm^{-1}; C–H stretching vibrations cause infrared bands. Results refers to the distribution of C = C bonds; vinyl, vinylidene and vinylene type double bonds result intensive adsorption bands at 910 and 990 cm^{-1}, at 890 cm^{-1} and at 956 cm^{-1}.

4. Conclusions

In our experimental work pyrolysis of real ELV waste plastic was carried out in a one-stage and a two-stage reactor system. According to the results, due to further cracking of hydrocarbons more light hydrocarbon and isomers were found in case of Ni/Mo-Al_2O_3 catalyst placed in the 2nd reactor. Gases contain especially C_3-C_5 hydrocarbons and the most isomer ratios were in case of Cu/ZSM-5 catalyst. Pyrolysis oil contains mostly C_6-C_{15} hydrocarbons, but the composition was affected by catalysts.

Acknowledgments

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