

Stability and Storage Properties of Hydrocarbons Obtained by Pilot Scale Pyrolysis of Real Waste HDPE-PVC in Tubular Reactor

Bahmed Fekhar, Norbert Miskolczi*

University of Pannonia, Faculty of Engineering, Institute of Chemical Engineering and Process Engineering, MOL
 Department of Hydrocarbon & Coal Processing, H-8200, Veszprém, Egyetem u. 10, Hungary; tel. +36 88 624 000
 mnorbert@almos.uni-pannon.hu

In this work the mixtures of real waste high-density polyethylene, low-density polyethylene, polypropylene and polyvinyl-chloride (PVC) were pyrolyzed in a pilot scale horizontal tubular reactor using different synthetic zeolite catalysts. Raw material was fed into the reactor through an electrically heated screw feeder, and then decomposed in the reactor. Products were separated into gases, pyrolysis oil and heavy fraction by atmospheric distillation. The yields of gases and pyrolysis oils can be significantly increased by using catalysts, but the catalyst properties were key parameter. For instance, Ni/ZSM-5 catalyst can increase the hydrogen content in gases and isomerize the carbon framework of hydrocarbons. Pyrolysis oils contained C5-C35 hydrocarbons; however their properties were modified by catalysts. An accelerated aging test was performed to follow the long term behavior of products. Pyrolysis oils were treated at 80 °C for 7 d, and then the stability of pyrolysis oils was assessed by evaluating the density, solid deposition and acid number. Unsaturated hydrocarbons in pyrolysis oils can agglomerate during the aging. On the other hand the catalysts can improve their properties. Pyrolysis oils obtained by thermo-catalytic pyrolysis resulted with less corrosion than in case of without catalysts.

1. Introduction

Plastics are widely used important materials. The plastic consumption has considerably increased in the last decade, which was about 60 Mt/y in Europe, yielding almost 27 Mt of plastic wastes in 2016. The majority of the plastics are landfilled and incinerated. At present, in Europe, about 40 % of the annual plastic wastes are valorized (especially incinerated); 60 % within the EU, while 40 % is outside of the EU, with and without energy recovery (Plastics Europe, 2017). In fact only partial quantity of plastic waste is recycled mechanically and chemically. It is known, that pyrolysis can be considered a sustainable way for chemical recycling but also a prospective method to obtain valuable liquid fuels from plastic wastes. In the pyrolysis process, the organic constituents of the material are decomposed to liquid and gaseous products, which can be used as fuels or sources of chemical syntheses. In general, waste plastic is contaminated on the surface and they are in mixed form. Therefore, the polyethylene and polypropylene with advanced chemical structure for chemical pyrolysis are available mixed with other sorts of plastics, such as polyvinyl chloride (PVC), polyethylene terephthalate (PET). The mixed and contaminated plastic waste is difficult to fully separate. For that reason, they cannot be mechanically recycled. It is also known, that contaminants in raw materials are moved to the products. Borsodi et al. (2011) concluded that, the unfavorable surface contaminations of waste plastics can be only partly reduced by pre-treating of real waste. PVC plays a crucial role, because chlorine from the polymer structure remains in the products, deteriorating the long-term properties of the pyrolysis oil. There are several references focusing on the thermal decomposition of PVC. It was concluded, that hydrogen chloride, toxic and corrosive compounds, are produced when PVC is moderately heated. Lopez et al. (2011) reported that the chlorine content of pyrolysis products obtained from the mixture of real plastics waste, PE, PP, PS, PVC, and PET could be effectively decreased by limestone. However, the properties of the pyrolysis products are affected by catalysts (Akaha et al., 2015). Yao and Ma (2017) concluded that the temperature was increasing during the hydrothermal carbonization, the chlorine content could be reduced and the carbon and hydrogen content augmented due to

the reaction of elimination and substitution. Organic chlorine is converted into inorganic chlorine in the form of hydrogen chloride. Yuan et al. (2014) considered that the pyrolysis of PVC takes place in two steps. The results showed that the dechlorination efficiency was only 81 % at the temperature of 280 °C because at lower temperature the C–H bonds in PVC did not break. When reaction temperature increased to 290 °C, the dechlorination efficiency increased to 96 %, without formation of hydrocarbons. Over 320 °C, lots of hydrocarbons emerge in the gas emitted together with the hydrogen chloride. Brebu et al. (2005) reported that iron-oxy-hydroxide and iron-carbon composite were found to be adequate catalysts in removing the organic bromine content with more than 90 % efficiency. However, the calcium-carbon composite and calcium carbonate showed the best results for chlorine removal.

In this work, the mixtures of real plastics waste LDPE, HDPE, PP and PVC were pyrolyzed in a pilot scale horizontal tubular reactor using different synthetic ZSM-5 zeolite catalysts. The composition of products and the stability of pyrolysis oil were investigated.

2. Raw materials and methods

2.1 Raw materials

In our current work, the mixtures of LDPE, HDPE, PP and PVC obtained by municipal plastic waste were used as raw materials. Waste plastics were shredded and mashed into suitable grain size. Pyrolysis reactions were enhanced. In addition, the possibility of in-situ quality upgrading of pyrolysis oil was investigated by using ZSM-5, Ca(OH)₂/ZSM-5, Ni/ZSM-5, and Ca(OH)₂-Ni/ZSM-5 catalysts.

2.2 Pyrolysis process

A horizontal tubular reactor was used for pyrolysis of raw materials the parts of this reactor is feeding zone, reactor zone and separation zone (Figure 1). 1.0 kg of raw material was fed hourly into the reactor through an electrically heated screw feeder. Raw materials have been decomposed in the reactor at 550 - 560 °C and the products were separated into gases, pyrolysis oil and heavy oil fraction by atmospheric distillation. In case of thermo-catalytic pyrolysis, 5 % of the catalyst was added right before the raw materials were pyrolyzed together.

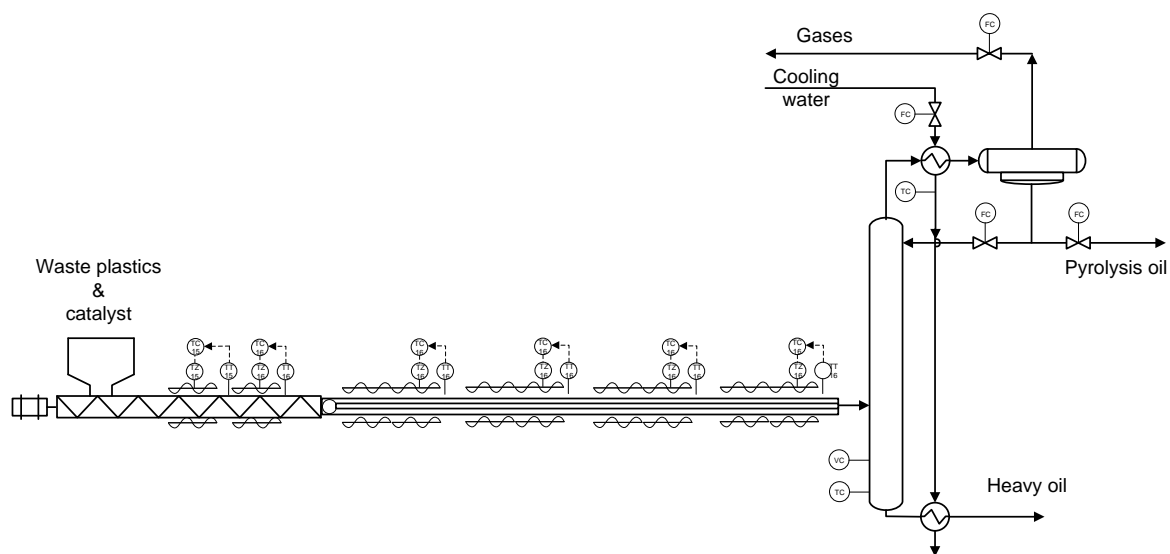


Figure 1: Horizontal tubular reactor system for waste pyrolysis

2.3 Product analysis

Gases were investigated by using a GC-FID (DANI GC) and Rtx PONA (100 m x 0.25 mm, using surface thickness of 0.5 µm) and Rtx-5 PONA (100m x 0.25 mm, using surface thickness of 1 µm) columns at isotherm conditions (T= 30 °C).

The hydrogen content in gases was measured using GC-TCD (Shimadzu GC-2010) with CarboxenTM 1006 PLOT column (30 m x 0.53 mm): 35 °C initial temperature (hold time 2 min), then it was elevated to 250 °C at 40 °C/min heating rate and the final temperature maintained for 5 min.

Pyrolysis oil was analysed by GC-FID (DANI GC), using Rtx 1 dimethyl-polysiloxane capillary column (30 m x 0.53 mm, thickness of 0.25 μm): 40 $^{\circ}\text{C}$ initial temperature for 5 minutes, then the temperature was elevated by 8 $^{\circ}\text{C}/\text{min}$ till 350 $^{\circ}\text{C}$ and it was kept at 350 $^{\circ}\text{C}$ for 20 min. Both the injector and detector temperature was 350 $^{\circ}\text{C}$. An accelerated aging was performed to investigate the long-term application of pyrolysis oil. Hydrocarbons were stored at 80 $^{\circ}\text{C}$ for 7 days in a drying cabinet, and then the stability of pyrolysis oils was examined by monitoring the following properties: density, solid deposition, acid number. It is important to note, that in general, standard tests, treating at 50 $^{\circ}\text{C}$ for 6 h is used for commercial fuels.

3. Result and discussion

3.1 Product yields

The yields of products obtained by the pyrolysis of real municipal plastic waste are shown in Figure 2. The product yields of thermo-catalytic run are compared with the results obtained by thermal pyrolysis (without using any catalyst). From the results, it seems that light oil was the predominant product in the presence of a catalyst. Without catalyst, the yield of light oil was 37.5 %, which increased to 50.5 % - 58.7 % in case of using catalyst. Regarding the gas yield, it could be increased from 8.1 % to 10.1 % - 17.4 % by catalysts. It means that ZSM-5 catalyst had a significant effect on the volatile yields, but there was a slight difference among the catalysts. The breaking of the C-C bonds was taken on catalyst active sites, while the presence of transition metal had no significant effect on the rate of decomposition. It is important to remark, that $\text{Ca}(\text{OH})_2$ presence can decrease the volatile yield increasing efficiency of both ZSM-5 and Ni/ZSM-5 catalysts: the summarized yields of gases and light oil was less in case of $\text{Ca}(\text{OH})_2\text{-Ni/ZSM-5}$ and $\text{Ca}(\text{OH})_2\text{-ZSM-5}$, than using ZSM-5 and Ni/ZSM-5.

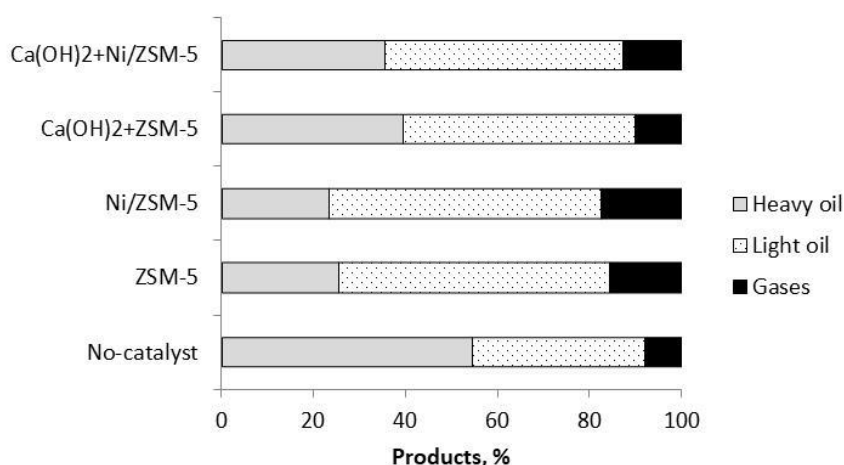


Figure 2: Yields of pyrolysis products obtained from horizontal tubular reactor at 550-560 $^{\circ}\text{C}$

3.2 Composition of gases and pyrolysis oil

In order to investigate the composition of gases GC-FID and GC-TCD were used. Table 1 summarizes the result of GC-FID analysis. Without catalyst, the propane, chloromethane, butene, butane, trans-2-butene, cis-2-butane, chloroethane, pentene and pentane were the predominant products. In general, catalysts favour the production of methane, ethene, ethane, i-butene; i-butane; dimethyl butane, and 2-methyl pentene. However, the propene and propane were the main products in case of without catalyst, while the ratio of the smaller molecules (such as methane, ethane and ethene) was higher in thermo-catalytic derived pyrolysis oils. Without catalyst 2.3 % methane and 12.9 % C₂-C₅ branched hydrocarbons can be detected in gases. The methane content could be increase to 4.2 % ($\text{Ca}(\text{OH})_2\text{-ZSM-5}$) - 6.4 % (Ni/ZSM-5), while the concentration of C₂-C₅ branched hydrocarbons changed to 32.1 % (ZSM-5 and $\text{Ca}(\text{OH})_2\text{-ZSM-5}$) - 33.1 % (Ni/ZSM-5) once using catalysts. Results well demonstrate that owing to the high Si/Al ratio in the ZSM-5 catalyst, it can isomerize the main carbon frame of products, and the zeolite structure had the key role. On the other hand, the incorporation of transition metals could significantly affect the composition of chlorine containing compounds. Regarding the branched hydrocarbons, the domination of the i-C₄ was concluded. The summarized concentration of i-C₄ was less than 10 % without catalysts, which increased to 21.1-22.4 % using catalysts. Comparing the ratio of i-butene and i-butane, it is important observation, that without transition metal on catalysts, the saturated isomer

had more domination, while the unsaturated isomer had higher concentration in pyrolysis oil obtained over Ni/ZSM-5 and Ca(OH)₂-Ni/ZSM-5 catalysts. That phenomenon can be attributed to the hydrogenation-dehydrogenation property of the nickel. The result is confirmed by the hydrogen content of gases; 11.1 % and 7.3 % hydrogen was measured by using Ni/ZSM-5 and Ca(OH)₂-Ni/ZSM-5 catalysts, respectively (Table 2). It is important to remark, that only trace amount of hydrogen was found without nickel (<0.9 %). Regarding the effect of the Ca(OH)₂, it can be concluded, that it deteriorated the advantageous property of the ZSM-5 and Ni/ZSM-5 catalysts; e.g. decreased the concentration of hydrogen, methane, ethane, ethene. But, this did not affect significantly the isomerization effect.

Table 1: The composition of gases by GC-FID (area, %)

	No-catalyst	ZSM-5	Ni/ZSM-5	Ca(OH) ₂ +ZSM-5	Ca(OH) ₂ +Ni/ZSM-5
methane	2.3	6.0	6.4	4.2	4.5
ethene	4.9	8.4	10.4	7.3	8.5
ethane	4.0	7.3	8.8	6.6	7.7
propene	10.3	6.8	7.1	6.5	6.2
propane	8.8	4.4	5.1	4.1	4.9
chloromethane	6.4	2.0	0.8	1.7	0.4
i-butene	3.8	8.5	14.2	8.8	17.1
i-butane	5.2	14.3	8.8	12.3	5.3
butene	7.0	4.2	5.0	6.7	5.4
butane	6.1	3.9	4.5	4.2	3.9
trans-2-butene	3.7	1.7	1.8	1.5	1.7
cis-2-butane	2.6	3.0	2.3	2.7	2.9
chloroethane	6.8	2.4	0.6	2.1	0.5
pentene	4.0	1.9	1.4	2.2	1.6
pentane	3.4	1.0	1.1	1.6	1.1
2,2 dimethyl butane	1.7	5.6	6.3	6.7	5.2
cyclopentane	2.3	0.7	0.5	1.1	0.8
2,3 dimethyl butane	1.5	2.2	2.4	2.7	2.7
2-methyl pentene	0.6	1.5	1.4	1.8	1.7
other	14.7	14.2	11.1	15.3	17.8

Table 2: The hydrogen content of gases by GC-TCD (vol %)

	No-catalyst	ZSM-5	Ni/ZSM-5	Ca(OH) ₂ +ZSM-5	Ca(OH) ₂ +Ni/ZSM-5
hydrogen	-	0.9	11.1	0.4	7.3

Pyrolysis oils contained C₅-C₃₅ hydrocarbons, but their properties were modified by catalysts. Figure 3 summarizes the composition of pyrolysis oil. By way of illustration, the thermal pyrolysis favors the production of n-olefin and n-paraffin with the proportion of 41.1 % and 39.8 %, respectively, but in the same time the thermal pyrolysis gives fewer amounts of branched compounds. In contrast, the catalyst free thermal pyrolysis does not produce any amount of aromatic compound. On the other hand the use of ZSM-5 catalyst has decreased the concentration of n-paraffin and n-olefin to 25.6 % and 30.1 %, respectively, but increased the concentration of the other compound (branched, etc.) to 34.9 %. It is well shown that the catalysts supports the production of aromatic compound in their different types of single ring hydrocarbons: benzene, toluene, chlorine-benzene, styrene, dichlorobenzene. 5.5 % benzene, 5.2 % toluene, 2.5 % chlorine-benzene, 2.9 % styrene, 1.3 % dichlorobenzene was obtained on neat ZSM-5 catalyst. This result was the consequence of the aromatization effect of the ZSM-5 zeolite structure. The aromatization effect of the ZSM-5 structured catalyst was confirmed by Ino et al. (2008), who demonstrated that the concentration of aromatics can significantly increase by using H-ZSM-5 zeolite-supported gallium oxides in case of polyolefin pyrolysis. On the contrary, the addition of nickel to the ZSM-5 catalysts shows different results. In all probability due to the hydrogenation-dehydrogenation property of nickel and owing to the local hydrogen overtake, the n-paraffin/n-olefin ratio was less than 1 in case of devoid using nickel, and was over 1 in case of Ni/ZSM-5 and Ca(OH)₂-Ni/ZSM-5 catalysts. Regarding the aromatics, the transition metal and Ca(OH)₂ presence in general can decrease the yield of aromatic compound. But it can significantly decrease the chlorinated aromatics amount. The dechlorination of aromatics by using catalysts is considered as an advantageous property for the long term utilization of products, because the corrosion property is the weakest issue regarding the pyrolysis oils obtained by PVC containing raw materials.

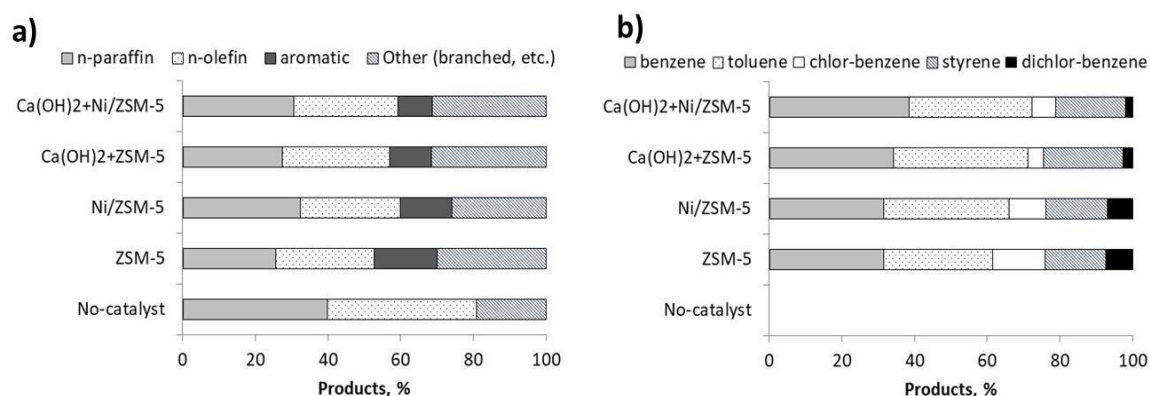


Figure 3: Product structure of pyrolysis oil (a) and the aromatics (b), area% by GC-FID

3.3 Stability of pyrolysis oils

In this study the stability of pyrolysis oil was performed in order to identify the factors responsible for it and determine how pyrolysis oil instability problems can be mitigated by using different catalytic agents was also investigated. Figure 4 summarized the density, the amount of the solid deposition and the acid number during the aging time. The stability was evaluated by accelerated aging, where the pyrolysis oils were treated at 80 °C for 7 days in the drying cabinet and its selected properties were measured in function of handling time.

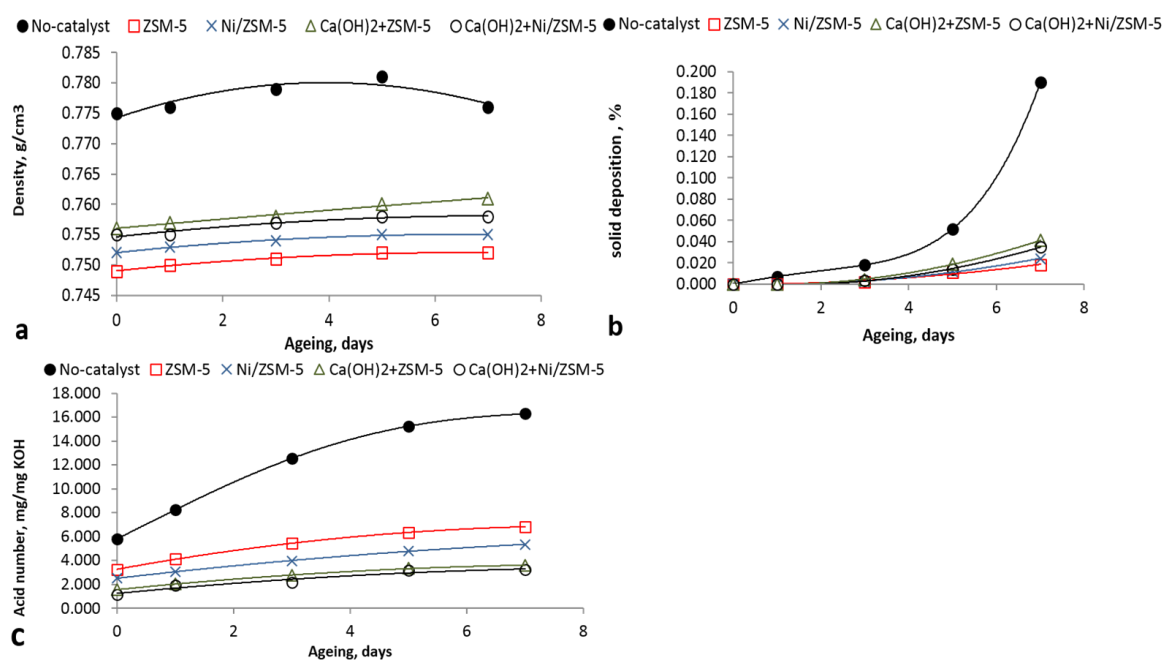


Figure 4: Density (a) solid deposition (b) and acid number (c) of light oil during aging at 80 °C

The density of the pyrolysis oil changed following the optimum relationship of aging time. In case of thermal pyrolysis, the density has been increased from 0.775 g/cm³ to 0.781 g/cm³ from the first day till the fifth day, after that, the density decreased to 0.776 g/cm³. This increasing trending was due to pyrolysis oils containing many reactive components that can form higher molecular weight during the aging. However, the heaviest molecule agglomerates still remain in liquid form. After five days of handling, the molecule agglomerates started to separate from the liquid phase, causing separation and decreasing in density. The phenomena was supported by the amount of the solid deposition, which showed increasing tendency by a turning point at 4-5 days aging, because the amount of the separated solid deposition suddenly increased after 5 days of handling from 0.052 % to 0.190 %. It is also clear, that the tested catalysts were advantageous to the stability of the pyrolysis oil. Catalysts can decrease the density of pyrolysis oil. Furthermore, they can significantly reduce the yield of solid

deposition. After 7 days of handling, the increase in the amount of the solid deposition was much less in comparison with the previous cases when the following catalysts: ZSM-5 (0.018 %), Ni/ZSM-5 (0.024 %), Ca(OH)₂-ZSM-5 (0.041 %), Ca(OH)₂-Ni/ZSM-5 (0.035 %) were used. The standard densities in case of naphtha or diesel oil are 0.776 and 0.86 g/cm³, respectively. Acid number corresponds to the amount of acidic compounds. Acid number of light oil obtained by thermo-catalytic pyrolysis was significantly less, than that of using catalysts. Due to the following reaction, the Ca(OH)₂ can also decrease the amount of acidic component: Ca(OH)₂+chlorinated compounds → Ca-chloride + chlorine free compounds.

4. Conclusions

In this paper the composition and stability of products obtained by thermal and thermo-catalytic pyrolysis of real waste LDPE, HDPE and PVC mixtures was investigated. ZSM-5 supported catalysts can increase the yields of gases and light oil. The combination of nickel with other catalyst slightly decreases the yields of gases and pyrolysis oil. However, significantly less volatiles was found using Ca(OH)₂ containing catalysts. Regarding gases, higher methane, ethene, ethane and branched hydrocarbons were obtained by the use of catalysts. However, Ni/ZSM-5 and Ca(OH)₂-Ni/ZSM-5 catalysts can increase the hydrogen yield and the unsaturated i-C4 had a higher concentration in pyrolysis oil obtained than saturated i-C4. Pyrolysis oils contained C5-C35 hydrocarbons; catalysts had aromatization and saturation property. Furthermore, the concentration of chlorinated monoaromatics were also decreased by using Ca(OH)₂ catalysts. Summarizing the stability tests, catalysts and Ca(OH)₂ catalysts showed benefits like decreasing in acidic compounds, reduction in density, and reduction in solid deposition. The forthcoming research should emphasize on the investigation of the effect of different catalyst supporters and combination of transition metal and surface active inorganic compound to the pyrolysis reactions and long-term product application.

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