

Catalytic Upgrading of Bio-oils Obtained from Different Sources

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This work focusses on the investigation of catalytic quality improvement of pyrolysis products. The yield of gases can increase significantly using Ni-Al₂O₃ and Ni-Al₂O₃/MoO₃/CeO₂ catalysts in case of both residential sewage sludge and farm waste sewage sludge raw materials (from 10.7-26.8% to 11.0-39.3%). It was found, that in addition to the oxygen content of the raw materials, the reaction conditions also greatly influenced the yield and properties of aqueous phase. The yield of aqueous phase was 9.7-17.9% without catalyst and that of 11.2-21.8% with catalyst. The amount of oxygen-containing organic substances in products (e.g. aldehyde, ketone and carboxylic acid) decreased significantly after the quality improvement. The efficiency of the catalysts was also influenced by the raw materials and temperatures in the 1st reactor. The hydrogen content and hydrocarbon distribution of the gas products changed favourably after the catalytic treatment, because less aldehyde, ketone, alcohols, carboxylic acids, phenols and its derivate were formed.

Keywords: waste, catalysts, pyrolysis, utilization, quality improving

1. Introduction

The further treatment and disposal of sewage sludge is an important challenge due to its increasing amount [Lee et al. 2021]. Currently, agricultural utilization and composting are mostly used for the further treatment of sewage sludge [Kiseley et al. 2019, Buta et al. 2021]. However, significant amount of the sewage sludge is still landfilled [Buta et al. 2021]. The main problem of the sewage sludge is that they contain significant amount of impurities, e.g. bacteria, pathogens, viruses, metals, phosphorus, nitrogen, sulfur, etc. [Buta et al. 2021, Wang et al. 2022]. Some of these get into the environment with current applications and contaminate that. Based on references, it was demonstrated, that the thermal treatment of sewage sludge looks prospective solution to these problems [Fonts et al. 2012, Gao et al. 2020]. The products of thermal processes are gases, bio-oil and char. The amount of products and their composition are significantly affected by the reaction parameters [Inguanzo et al. 2002]. At higher temperatures, more gas products should be obtained. The composition of bio-oil is also mostly influenced by the properties of raw materials. In many cases, catalysts are also used to increase the amount of more valuable products and to achieve more favorable product properties. Al₂O₃, synthetic zeolites (e.g. HZSM-5, γ -zeolite) and other oxides are used as catalysts [Gao et al. 2020, Inguanzo et al. 2002, Haghghat et al. 2020]. The combination of zeolites and other inorganic materials with transition metals proved to be beneficial for the in-situ bio-oil upgrading. Nickel-based catalysts are mostly used for this purpose. However, the advanced catalyst property can be further improved by promoters. Regarding the promoters mainly Ce, Cu, Fe, La, Mo or Zn are used to increase the hydrogen yield. Catalysts should be used by mixing them with raw material (in-situ quality improvement) or as catalyst to improve the property of pyrolysis product (post-situ quality improvement) in a separated reactor [Haghghat et al. 2020, Bai et al. 2022, Chen et al. 2021]. Catalysts can also reduce the amount of oxygen-containing compounds and polyaromatic hydrocarbons. Furthermore, the BET surface of the bio-char can be also effected by promoters of the catalysts. The amount of solid pyrolysis residue can also be reduced, if the catalysts are used in the mixed form with the raw material. In case of post-situ upgrading, mainly the yields of gases and liquid product is primarily changed. It is also known that the liquid products are the mixture of aqueous phase and hydrocarbons (bio-oil).

The hydrocarbon bio-oil is usually consisting of aldehydes, ketones, carboxylic acids, alcohols, phenols, and other hydrocarbons. Since oxygen-containing components have unfavorable properties regarding their further use, e.g. they have acidic character, or low transportation and storage stability. Therefore, the primary goal of both in-situ and post-situ upgrading is to decrease the concentration of oxygen-containing component [Chen et al. 2021]. The main aim of this work was the investigation of post-situ upgrading of bio-oils obtained from sewage sludge pyrolysis using different catalysts and reaction conditions.

2. Materials & methods

2.1 Raw material

Two different kinds of sewage sludge were used in this work; a residential sewage sludge (RSS) and farm waste sewage sludge (FW). The RSS had carbon of 39.1%, hydrogen of 5.9%, nitrogen of 4.8%, sulfur of 0.3%, while the FW had carbon of 29.8%, hydrogen of 3.9%, nitrogen of 1.6%, sulfur of 2.7%.

2.2 Catalyst

Nickel based catalysts had been used to modify the product yields and composition: Ni-Al₂O₃ and Ni-Al₂O₃/MoO₃/CeO₂. The nickel was coated on the supporter surface by wet impregnation. In case of Al₂O₃/MoO₃ supporter, the 70% γ -Al₂O₃, 20% MoO₃ and 10% CeO₂ was used.

2.3 Equipment

Raw materials had been pyrolyzed in a two-stage steel pyrolysis reactor; in the 1st reactor zone 400 and 600°C were used, while the temperature in the 2nd reactor was 600°C (Figure 1). In each case, 200g of raw material was placed in the 1st reactor. To investigate the fast pyrolysis of raw materials, the temperature in the 1st reactor was elevated by 100°C/min heating rate, while it was preliminary set in the 2nd reactor.

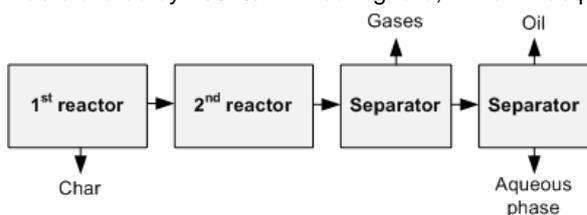


Figure 1: The pyrolysis process

Volatiles from the 1st reactor was driven through a 15g fixed bed of catalyst placed in the 2nd reactor, then it was cooled by a tubular heat exchanger, then the condensed liquid products (mixtures of aqueous phase and bio-oil) were separated from the gases and then further analyzed.

2.4 Product analysis

DANI gas chromatographs were used to investigate the composition of gases: a GC-FID (Rtx-1 PONA type 100 m long column with an internal diameter of 0.25 mm and film thickness of 0.5 μ m) and GC-TCD (CarboxenTM 1006 PLOT (30m \times 0.53mm) column). The chromatograms were evaluated using Clarity software.

The bio-oils were analyzed by DANI GC-FID (Rtx 1 dimetil-polysiloxan capillary column (30m \times 0.53 mm, thickness of 0.25 μ m)). Samples were dissolved in CS₂, and then injected to the instrument. Initial temperature of 40 °C for 5 min was used, then the temperature was elevated by 8 °C/min till 340 °C and it was kept at 340 °C till 20 min. The chromatograms were evaluated using Clarity software. The density, viscosity, acid number of bio-oils and the pH of water phase were followed by standardized methods.

3. Results & discussion

3.1 Product yield

Figure 2 summarizes the product yields. Based on the results, it is clear that the product yields changed significantly using different reaction parameters. In general, more volatiles could be obtained from the RSS raw material, than that of from the FW raw material. The amount of char remaining in the 1st reactor was ~60% at 400°C, while that of was ~47% at 600°C using FW raw material. Regarding the RSS raw material, the char yield was ~51% at 400°C and ~31% at 600°C. The liquid product of pyrolysis was the mixture of aqueous phase and hydrocarbons. During the pyrolysis, up to ~300°C, primarily the aqueous phase was formed, while more and more hydrocarbons produced by the further increase of the temperature.

Based on results, a bit more bio-oil could be obtained from the RSS raw material, than that of from the FW raw material. However, the bio-oil/water ratio was higher in case of FW raw material.

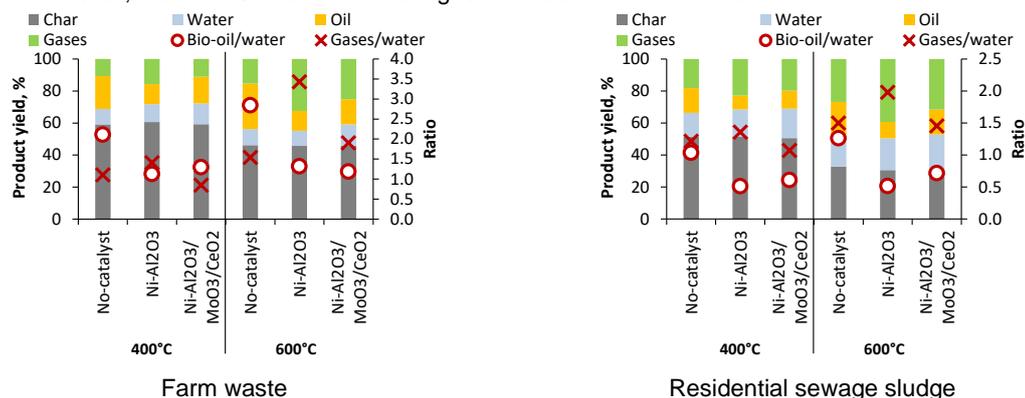


Figure 2: The yields of products

The amount of gases increased significantly using catalysts. Comparing the two catalysts, the Ni-Al₂O₃ catalyst can increase the yields of gases in higher proportion, than the Ni-Al₂O₃/MoO₃/CeO₂ catalyst. It was explained by the higher surface area of the Ni-Al₂O₃ catalyst. At higher temperature, more gas and liquid products were formed. Based on the results, it can also be seen that the catalysts increased the gas yield more significantly in case of 600°C catalyst temperature, than using 400°C. The reason for this was, that the smaller molecules produced at 600°C were better suited to the active sites of the catalyst, therefore their chemical bonds can be broken in higher degree. It is also important to mention, that more water was found in the presence of Ni-Al₂O₃/MoO₃/CeO₂ catalyst, which was the consequence of the dehydrogenation reactions of the oxygen-containing components.

3.2 Gases

The composition of gases are demonstrated in Figure 3. Based on the data, there were clearly visible differences between the gas composition using the FW and RSS raw materials.

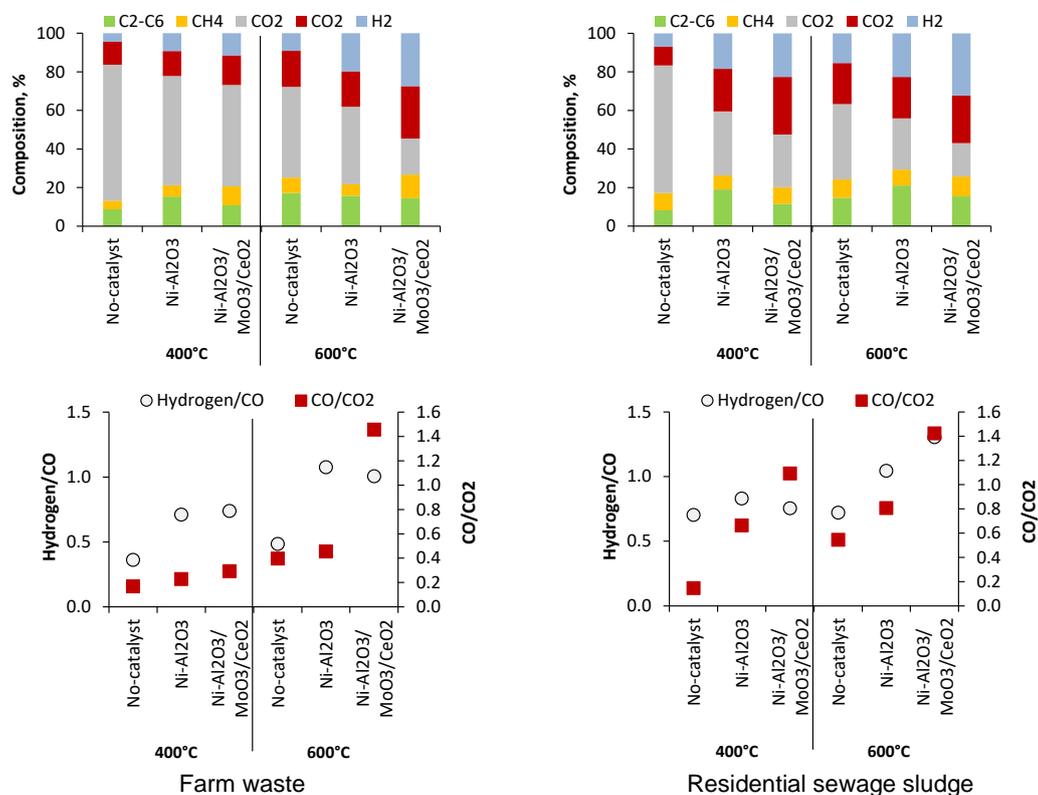


Figure 3: The composition of gases

Without catalysts, the concentration of CO₂ was high; 70.5% (FW) and 66.2% (RSS) in the case of 400°C 1st reactor temperature, while it decreased to 47.0% (FW) and 39.0% (RSS) using 600°C catalyst bed temperature. Furthermore more hydrogen, CO, methane and C₂-C₅ hydrocarbons was found at 600°C. The reason for this was that the macromolecules from the raw material degraded to greater extent at higher temperature. Regarding the effect of the catalysts, it is clear that they increase the amount of hydrogen, CO and methane, while the amount of CO₂ is reduced. At 400°C catalyst temperature using FW raw material, catalyst had significantly less effect to the gas composition, than that of using RSS raw material. More hydrogen and CO were produced using Ni-Al₂O₃/MoO₃ catalyst. Especially in case of 600°C 2nd reactor temperature. Regarding the hydrogen/CO ratio, higher value was found in the presence of catalysts, regardless of the raw materials and the temperature. This was the consequence of the hydrogenation-dehydrogenation property of the transition metals on the catalyst surface. Significantly higher values of hydrogen/CO ratio were obtained at higher temperature, than at the 400°C in case of thermo-catalytic pyrolysis of FW raw material. A similar increase was also observed in the CO/CO₂ ratio. The reason for this was a decrease in the amount of CO₂ rather than an increase in the concentration of CO. Both higher hydrogen/CO ratio and CO/CO₂ ratio was observed in Ni-Al₂O₃/MoO₃ catalyst.

3.3 Bio-oil

Bio-oils were black colour liquids with high density and viscosity. They were the mixtures of mainly hydrocarbons, aldehyde, ketone, carboxylic acids, alcohols and phenolic compounds. The composition of bio-oils are shown in Figure 4.

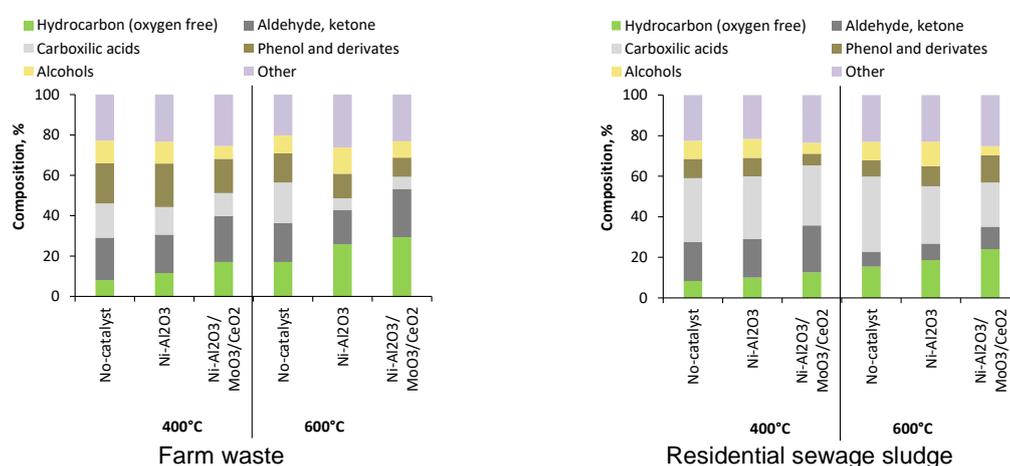


Figure 4: The composition of bio-oil

The composition of bio-oils show many differences depending on the reaction conditions. In case of farm waste raw material, the bio-oil contained significant amount of aldehyde, ketone and phenolic compounds, while the main components were the carboxylic acids in case of RSS raw material. Regarding the effect of temperature, it is clear, that a bit more oxygen free hydrocarbons and other undefined compounds were found at 600°C 1st reactor temperature. This was the consequence of more significant scission of chemical bonds containing oxygen. Catalysts can significantly reduce the concentration of oxygen containing compounds, therefore less aldehyde, ketone, carboxylic acid and phenolic compounds were found.

The chemical cause for this phenomenon is to be found in deoxygenation reactions. Compounds containing -OH, -CHO, -C=O or -COOH groups could be transformed by the escape of water to the compounds without oxygen by the use of transition metal-containing catalysts. This is also indicated by the fact that the water content of the products usually increased by 2-5% in the presence of catalysts. The amount of oxygen-free components was higher by the use of catalysts, than without them. In case of 600°C catalyst temperature, higher increase can be observed, than using 400°C. In particular, the amount of oxygen-free compounds increased with the use of Ni-Al₂O₃/MoO₃/CeO₂ catalyst.

In case of FW raw material, the Ni-Al₂O₃/MoO₃/CeO₂ catalyst showed significantly higher activity in reducing the amount of phenolic compounds and alcohols, than Ni-Al₂O₃. It is worth to mention, that the Ni-Al₂O₃ catalyst reduced the amount of aldehydes and ketones in more degree, although there was no significant difference between the two catalysts in this respect. It can be also said about both catalysts, that they showed high activity in reducing the amount of oxygen-containing groups primarily at 600°C. This was particularly noticeable with the FW raw material. In the case of the RSS raw material, the composition of the bio-oil changed only slightly at catalyst temperature of 400°C. However at 600°C, the amount of carboxylic acids decreased significantly. In case of Ni-Al₂O₃/MoO₃/CeO₂ catalyst, significantly less phenolic compounds were formed.

The acid number, viscosity and density are important for the long term utilization of bio-oils. Especially the corrosion properties, the transportation and storage stability can be deteriorated in case of high values of acid numbers. Table 1 shows the acid number, viscosity and density of bio-oils and the pH values of aqueous phase. Based on the results it is clear, that the bio-oils had relatively high acid numbers, which can be decreased by catalysts. Especially the Ni-Al₂O₃/MoO₃/CeO₂ catalyst had favourable property for acid number decreasing. Comparing the two raw material, RSS derived bio-oils has higher acid number, than farm waste derived. This was the consequence of the high carboxylic acid content of RSS derived bio-oils. Regarding the density and viscosity, the CeO₂ had unfavourable property, because higher density and viscosity can be measured in this presence. Presumably, the active centres of catalysts was partially blocked by CeO₂, which resulted less activity in C-C scission.

Table 1: The main properties of bio-oil and aqueous phase (FW raw material)

1 st reactor	400°C			600°C		
2 nd reactor	No-catalyst	Ni-Al ₂ O ₃	Ni-Al ₂ O ₃ /MoO ₃ /CeO ₂	No-catalyst	Ni-Al ₂ O ₃	Ni-Al ₂ O ₃ /MoO ₃ /CeO ₂
Density, g/cm ³	0.989	0.971	0.975	0.947	0.914	0.915
Viscosity, mPas	71.9	62.8	63.1	53.6	27.6	35.3
Acid number, mg KOH/g21.6		17.5	16.1	18.8	12.7	11.9
pH (aqueous phase)	8.7	8.9	9.1	9.0	9.1	9.2

Table 1: The main properties of bio-oil and aqueous phase (RSS raw material)

1 st reactor	400°C			600°C		
2 nd reactor	No-catalyst	Ni-Al ₂ O ₃	Ni-Al ₂ O ₃ /MoO ₃ /CeO ₂	No-catalyst	Ni-Al ₂ O ₃	Ni-Al ₂ O ₃ /MoO ₃ /CeO ₂
Density, g/cm ³	0.975	0.959	0.953	0.930	0.902	0.906
Viscosity, mPas	59.3	50.1	55.6	46.2	25.0	26.8
Acid number, mg KOH/g39.2		29.3	25.1	27.3	21.9	20.2
pH (aqueous phase)	8.9	9.1	9.3	9.1	9.3	9.5

The pH values of aqueous phase also refer to the acidity properties. The pH values were in the range of 8.7-9.5. It means, that the aqueous products had a bit alkaline characteristic. It was caused by the decomposition of nitrogen-containing compounds, which resulted ammonia and organic amines. Furthermore, alkali metals and alkali earth metal salts in the raw materials can transform to their hydroxyl derivatives with alkali character. The RSS raw material derived aqueous phase had a bit higher pH, while the presence of catalyst can also increase the pH values. Presumably the higher pH values refers to more ammonia and organic amines in water. This was the consequence of the more significant degradation of nitrogen containing compounds.

3.4 Catalysts

The catalyst activity is key parameter for pyrolysis reactions. However, the catalysts activity can be changed during their application. In general, coke depositions should be also formed during the pyrolysis reactions, which can block the catalysts active sites, result reduced catalyst activity. The carbon deposition on the surface of used catalysts is summarized in Figure 5.

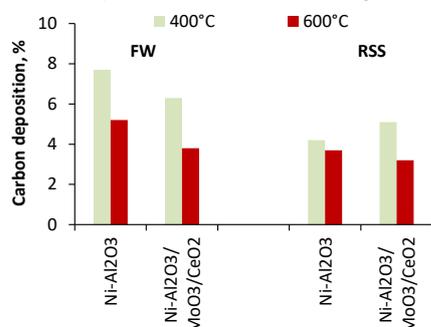


Figure 5: The carbon deposition on the used catalyst surface

It is clear, that coke was deposited on the catalyst surface. Comparing the two raw materials, the pyrolysis of farm waste resulted more coke on catalyst surface, than residential sewage sludge. On the other hand, more

coke was found on Ni-Al₂O₃ catalyst, which was the consequence of its higher activity in decomposition reactions. Regarding the temperature, less carbon deposition was formed at higher temperature, which was the consequence of the Boudouard reaction.

4. Conclusions

In this work, the thermo-catalytic pyrolysis of different sewage sludge and post situ product upgrading were investigated in a two stages laboratory scale batch reactor using Ni-Al₂O₃ and Ni-Al₂O₃/MoO₃/CeO₂ catalysts. It was found, that more volatiles were obtained at 600°C catalyst temperature and in the presence of catalysts. Due to the higher surface area of catalyst, the application of Ni-Al₂O₃ occurred more gases than Ni-Al₂O₃/MoO₃/CeO₂ catalyst. The catalyst activity was more significant at 600°C, however, it was affected by the raw materials. Less difference in catalyst activity was demonstrated in case of FW raw material, than RSS regarding gases. In general, the residential sewage sludge resulted more volatiles, than that of farm waste. Catalysts can decrease the formation of CO₂, and increase the concentration of hydrogen, CO and hydrocarbons in gases. The MoO₃ and CeO₂ in catalyst supporter seems favourable for more hydrogen and CO production. Bio-oils consisted of oxygen-containing hydrocarbons and oxygen free hydrocarbons. They were viscous, black colour liquid with high density. Comparing the two raw material, the RSS derived bio-oils had significantly more carboxylic acids, than FW derived. The main effect of the catalyst was the supporting of deoxygenation reactions, which resulted less oxygen-containing hydrocarbons in bio-oil and more CO₂ and aqueous phase. Especially, the Ni-Al₂O₃/MoO₃/CeO₂ catalyst showed high activity in these reactions at 600°C using RSS raw material. The bio-oil density and viscosity were in the range of 0.902-0.989g/cm³ and 25.0-71.9mPas, respectively. They acid number were between 11.9 and 39.2mgKOH/g. The Ni-Al₂O₃ catalyst can reduce the density and viscosity of bio-oil more significantly, however, the Ni-Al₂O₃/MoO₃/CeO₂ catalyst resulted products with less acidity. The aqueous phase had light alkali characteristic, which a bit was the dependence of raw materials and catalyst.

Acknowledgments

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