



OPEN Pyrolysis of municipal waste catalyzed with synthesized zeolite from steel making factory waste

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Bio-oil is lacking of many quality standards required for the engine fuel. Many types of catalysts have been used to upgrade the bio-oil. However, they deactivated quickly or had high price. In this study, the catalytic pyrolysis of wastewater treatment plant sludge, pine wood, municipal waste and their mixture over synthesized zeolite (A type) from steel factory waste was studied. The results indicated that zeolite led to the slight increase of the bio-oil yield (46.0 to 46.2 wt%) and improved the quality of the bio-oil. For instance, it reduced the content of oxygen (49.45 to 19.65 wt%) and acids in the bio-oil. However, it was partially deactivated by the formation of coke. To further improve the quality of the bio-oil and decline the formation of coke, Ni, Ce, Mg and Mo were loaded on the surface of the zeolite. The results of the mixture feedstock pyrolysis indicated that Ni enhanced the yield of bio-oil slightly, while the other metals did not change it significantly. Ni led to higher amount of cracking and deoxygenation of the acids. Ce enhanced the content of oxygen-containing species in the bio-oil. Mg resulted in the higher amount of –OH containing compounds. Mo increased the amounts of acids, aromatics and alcohols in the bio-oil. Due to the high tendency of Ni for cracking, the highest amount of hydrocarbons in the gas was measured for that. The highest deoxygenation of bio-oil was achieved by Mo. Mo/zeolite had the lowest content of carbon, which indicated the lowest amount of coke.

Keywords Pyrolysis, Water treatment sludge, Municipal waste, Synthesized zeolite, Modified zeolite

The decrease in the reserves of fossil fuel resources as well as the pollution associated with the use of fossil fuels have encouraged the scientists from all worldwide to develop the sustainable routes for the production of renewable and environmentally-friendly alternative fuels^{1,2}. The alternative resources of energy or fuels for the replacement of fossil fuels should be abundantly available, renewable and have low carbon footprint. Biomass meets these criteria and has become the interest of the energy research community.

There are many kinds of technologies for the conversion of biomass to highly valuable products, while pyrolysis is one of the most efficient routes for the transformation of solid biomass to combustible liquid, called bio-oil, with the yield of 60–75 wt% at a moderate temperature (~500 °C)³. Bio-oil was considered to replace the crude petroleum and be used in the production of petrol-like and diesel-like fuels⁴. However, it suffers from high content of oxygen-containing compounds such as water, acids, aldehydes, ketones, etc., which make the bio-oil non-stable, having low heating value, high acidity, quick aging, etc.⁴. Nevertheless, bio-oil cannot be directly used as an engine fuel due to its undesirable properties such as the high oxygen content, the high instability and correspondingly low heating value⁴.

To upgrade the properties of the bio-oil, different methods including hydrotreatment⁵, esterification⁶ and catalytic pyrolysis⁷ were used. Hydrotreatment suffers from the quick deactivation of the catalyst due to the formation of coke⁸. In addition, it is not economically feasible due to the high cost of hydrogen and catalyst⁹. Esterification improves the fuel properties of the bio-oil such as lowering the acid content and increasing its heating value⁶. However, the bio-oil obtained requires further upgrading of the properties to be considered as an engine fuel. The use of the catalyst during the pyrolysis (in-situ or ex-situ processes) can enhance the specifications of the bio-oil¹⁰. The disadvantages of the catalytic pyrolysis are the quick deactivation of the catalyst and the requirement for further upgrading by other processes such as hydrotreatment¹¹. Many catalysts including metal oxides¹², zeolites¹³, bimetallics¹⁴, etc. have been used to tackle these issues. However, still further fundamental studies are required to find the suitable catalyst for the pyrolysis of the biomass.

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Zeolites got the interest of the scientists due to their low price and their high tendency to produce aromatics^{15,16}. Although they were very active to crack down and stabilize the non-stable species, their efficiency reduced after few hours of the operation because of the high amount of coke formation^{17,18}. To improve the performance of the zeolites and to decline the formation of coke, metals such as Ni, Fe, etc. were loaded on the catalyst^{19,20}. Metals such as Ga and Ce led to the formation of less coke, while metals like Ga, Co and Ni produced higher amount of aromatics^{21,22}.

Steel slag contains considerable amount of alumina and silica, which are the components of the zeolites²³. As a result, zeolites can be produced from the steel slag by extracting the components of zeolites²³. So far, there have several studies, which used steel as the catalyst for the pyrolysis of the biomass^{24,25}. Additionally, the zeolites, which are produced from the steel slag, have been selected as catalyst in the pyrolysis of the biomass^{26,27}. Their results indicated that steel slag and zeolites prepared from the steel slag had high tendency to improve the fuel properties of the bio-oil such as the lowering of oxygen content, the increase of heating value, etc. However, still coke formation remained as the main obstacle.

To reduce the coke, a suitable catalyst should be developed. The cost of the catalyst and the practical procedure to make it should be also considered. This indicates that without the development of an appropriate catalyst, pyrolysis of biomass cannot lead to a fuel, which can replace fossil-based fuels. The high number of papers in the catalytic pyrolysis shows the fast growing investments of the research centres on the catalyst development. In this study, A type zeolite was produced from the steel factory waste and then it was modified by the metals including Ni, Ce, Mg and Mo. These catalysts were developed from cheap substances by the use of metal extraction from steel slag and impregnation of metals on the zeolite to control its activity for the upgrading of the bio-oil. The aim was to reduce the waste of steel factories and convert them into useful catalysts for the production of biofuel with better fuel properties compared to the bio-oil. Wastewater treatment sludge, pinewood and municipal waste were selected as feedstocks. Their mixture was also used as feedstock. The pyrolysis was conducted in the absence of the catalyst and over the synthesized zeolite and its modified forms in batch process. The results indicated that modified zeolite samples had better performances and less coke amounts were formed. For each experiment, the influence of the catalyst on the yield and composition of the products were studied.

Experimental methodology

Materials

Typical steel waste was collected from steel making factories in Catalonia. The chemicals, which were Ni ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Ce ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Mg ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, sodium aluminate, sodium hydroxide and hydrochloric acid were purchased from Sigma Aldrich. Poplar wood was collected from the farms in Manresa, Spain. Wastewater sludge and municipal waste were obtained from the Manresa Wastewater Treatment Company and Catalan Agency of Waste, respectfully. The feedstock was dried at 110 °C over night and then grounded and sieved into powder with the particle size of 2–3 mm.

Catalyst preparation

To prepare the catalyst, initially, the slag was ground and sieved. The composition of the steel slag is shown in Table S1. Typical procedure from literature was used to prepare the A type zeolite^{25–27}. The particles with size below 100 micron was used to produce A type zeolite to facilitate contact between the slag and the extracting agent. 100 g of the slag was fully dissolved in 2000 mL of HCl (3 M) under intense stirring at 100 °C for 2 h to fully pectize the Si component. The obtained suspension was separated into hydrated silica gel and leaching solution containing other elements by filtration using a Buchner funnel. In the next stage, the silica gel solid was washed with deionized water until reaching of pH of 7 in the solution. The hydrated silica gel, which was separated, was dried at overnight at 110 °C. It was calculated that 10 g of silica powder could be produced from 50 g of steel slag. Following this, alumina was loaded on silica with a certain ratio. To obtain type A zeolite, 6.92 g of Si powder was dissolved in 40 mL of NaOH (4 M) aqueous solution until homogenized. Then, 35.6 mL of aqueous solution containing 11.4 g of sodium aluminate was added dropwise. The obtained slurry was vigorously stirred for 1 h at room temperature and for another 1 h at 90 °C. The slurry was transferred into a Teflon bottle and aged in an oven at 100 °C for 6 h without stirring to achieve crystallization. The obtained suspension was filtered, washed with deionized water, and dried at 100 °C overnight. In the next stage, the material produced was grounded in an agate mortar and was dried for 4 additional hours to yield almost 15 g of A type zeolite. The analysis of the synthesized zeolite indicated that it had the mass of Si/Al : 0.83. The XRD analysis of the synthesized zeolite type A and commercial zeolite type A is shown in Figure S1.

The impregnation of different metals on the synthesized zeolite was carried out in the next stage. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as the precursor of Ni²⁸. The aim was to load 5 wt% of Ni on the zeolite. For this aim, 61.927 g of nickel nitrate hexahydrate was dissolved in a 100 mL distilled water. Then, gradually, zeolite and nickel nitrate hexahydrate solution were mixed until the solid part became wet. The substance obtained was dried at 110 °C over night. It was calcined for 7 h at 500 °C. In the final stage, the catalyst was activated at 500 °C in nitrogen environment for half an hour. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as the precursor of Ce²⁹. The aim was to load 5 wt% of Ce on the zeolite. To perform this, 38.737 g of cerium nitrate hexahydrate was dissolved in a 100 mL of distilled water. Then, gradually, zeolite A and cerium nitrate hexahydrate solution were mixed until the solid part was wet and it was dried overnight at 110 °C. Following this stage, it was be calcined for 7 h at 500 °C. Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was selected as the precursor of Mg³⁰. To load 5 wt% of Mg on Zeolite A, 131.871 g of magnesium nitrate hexahydrate was dissolved in a 100 mL of distilled water. Then, gradually, zeolite A and magnesium nitrate hexahydrate solution were mixed until the solid part became wet. Then, it was dried at 110 °C overnight and it was calcined at 500 °C for 7 h. Ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was used as the source of Mo³¹. The aim is to load 5 wt% of Mo on zeolite. 23.0 g of ammonium heptamolybdate tetrahydrate was dissolved in a 100

mL of distilled water. Then, gradually, zeolite A and ammonium heptamolybdate tetrahydrate solution were mixed until the solid part became wet. The substance obtained was dried at 110 °C followed by calcination for 7 h at 500 °C.

Pyrolysis experiments

Pyrolysis was carried out using a Mico-pyrolysis plant, which was located in Eurecat Centro Tecnológico de Catalunya. The pilot plant could be operated in the batch and continuous forms. For the experiments in this study, batch reactor was used. The reactor was made of AISI 310 and it was a fixed-bed reactor. It had the inlet diameter and length of 41.9 mm and 987.0 mm, respectively. The experiments were conducted at 500 °C. Initially, 150–200 g of feedstock was loaded to the reactor and the temperature enhanced to the target amount. The ramping rate of temperature was 10 °C/min. The experiment was kept for 30 min at 500 °C to convert the highest possible amount of feedstock into volatiles. Nitrogen gas with the flowrate of 1.5 NL/min was selected as carrier gas. The outlet flow of the reactors was passed through a filter to trap the possible escaped solid particles. A heat exchanger and two cold traps were used in series after the filter to condense the volatiles. The outlet of the pilot plant was connected to a Micro GC to analyze continuously the gas product. It should be noted that the yield of different products was calculated by dividing their weight to the weight of feedstock.

Analytical methods

X-ray diffraction (XRD)

Rigaku Ultima IV X-ray was used to characterize the catalysts before and after the pyrolysis experiments. The samples were scanned from 10 to 80° at the rate of 10°/min by using the radiation source of Cu, K.

GC-MS analysis

Bio-oil samples were analysed by Agilent GC-MS (a 6890 series gas chromatograph with a 5973 mass spectrometric detector). The instrument was equipped with a capillary column (HP-INNOWax), whose long was 30 m, the internal diameter was 0.25 mm and had film thickness, 0.25 µm of crosslinked polyethylene glycol. Each time, 0.5 µL of the bio-oil was transferred into the inlet of device, which had the temperature of 250 °C. The separation rate was 50:1. The GC oven was heated to 250 °C with the rate of 10 °C/min and kept the temperature for 5 min. Helium, as the carrier gas, had the velocity of 4.0 mL/min. The compound contained in the sample was identified by the standard spectra data basis (the NIST library).

Water content

The water content of liquid samples was measured by using Karl-Fischer titration (KF Titrand) from Metrohm. In each analysis, one drop of the liquid sample was injected into the glass container of the instrument, which had hydranal composite. The titration was conducted by hydranal ketonsolver.

Thermogravimetric analysis (TGA)

TGA (Mettler Toledo) was used to analyse the volatilities from the tar and the coke. The TG program was divided into two stages. In the first stage, the temperature was stable at room temperature for 10 min. During this period, nitrogen gas as the carrier gas (80 mL/min) was introduced to eliminate the air from the TG instrument. In the second stage, the temperature rose up to 850 °C at a rate of 15 °C/min.

Elemental analysis (EA)

The elemental composition (C, N, S and H) of the feedstocks, tar and char samples was measured by using an EuroEA3000-Single instrument analyser. 1–2 mg of the sample was weighted with a balance and wrapped in foil, and then was sent to the reactor (950 °C) for the full combustion in the atmosphere of O₂/He (100 mL/min). The gaseous products were passed through a column for separation and for further detection of the abundance by TCD.

FT-IR

The FT-IR characterization of used catalysts was acquired by using a Horiba Labram HR Evolution spectrometer. The samples were diluted with KBr to the concentration of 10 wt% to reduce the heating of the sample by laser.

Brunauer-Emmet-Teller (BET)

The surface area and pore channel of the fresh and used catalyst samples were measured by SSA-6000 instrument. Prior to the analysis, the samples were dried for 2 h at 120 °C.

X-ray fluorescence (XRF)

The XRF analysis of the fresh and used catalysts was performed by ZSX Primus II (Rigaku). During the analysis, the temperature of the samples was increased to 550 °C for 2 h and then heated to 850 °C for 4 h. This reason for this was to convert all metals to metal oxides. In the next stage, XRF samples were prepared by mixing 0.3 g of the obtained metal oxides with 6.7 g of flux. Following this, they melted at 1000 °C to make a glassdisk. Then, the samples were analyzed by the use of the XRF spectrometer.

Micro GC

The analysis of the gas was carried out in an online Micro GC Agilent 490 (p/n G3582A#110) during the experiment. It included dual channel cabinet including a 10-meter CP-Molsieve 5 A with argon as carrier gas. Column temperature was 80 °C and the injector temperature was 110 °C. Argon pressure was set at 200 kPa.

Results and discussion

The yields of the products

The yields of the products from the pyrolysis of different wastes and their mixture are shown in Table 1. The highest yield of the bio-oil (55.4 wt%) belonged to the pinewood, while the lowest yield of the bio-oil was calculated for the municipal waste (27.6 wt%). Municipal waste led to the highest yield of the biochar (66.8 wt%), which was showing the presence of the heavy materials. Comparison of the average of the yields of the products from single feedstocks and the yields from the non-catalytic pyrolysis of the mixture indicated that there was not a considerable deviation between the yield of the products. It showed that secondary reactions did not influence on the yields of the products^{32,33}. The presence of the different catalysts had different effects on the yields of the bio-oil and gas. Ni/zeolite followed by zeolite resulted in the highest yield of the bio-oil (45.3 wt% for Ni/zeolite and 42.8 wt% for zeolite). This indicated that these catalysts slightly enhanced the rate of the polymerization reactions of the volatiles. However, Ce/zeolite, Mg/zeolite and Mo/zeolite did not change significantly the yield of the bio-oil, which meant that these catalysts did not promote the condensation reactions considerably. It was expected that zeolite-based catalysts, especially zeolite with Ni would produce more gas due to their high tendency for the cracking reactions. It was shown in the previous study by Chaihad et al.³⁴ that Ni led to the formation of high gas and light compounds, which demonstrated the high rate of the cracking reactions. However, possibly the cracking and polymerization reactions occurred in parallel forms and the yield of the bio-oil did not reduce¹².

The analysis of the gas

The results of the gas analysis (concentration of the different gas compounds in the pilot plant gas exit line) for the single feedstocks and mixture are shown in Fig. 1. CO₂ had the highest concentration in all the experiment, but it had different concentrations. The lowest concentration of CO₂ (17 v% at the peak) was related to non-catalytic pyrolysis of the municipal waste, while the highest content of CO₂ (24 v% at the peak) belonged to the catalytic pyrolysis of mixture over Ni/zeolite, which could be due to the higher rate decarboxylation reactions of the volatiles by the catalyst^{12,35}. This was proved in our previous study¹², which studied the effect of the different metal oxides on the pyrolysis of the poplar wood. CO had different trend compared to CO₂. The highest amount of CO was produced from the pyrolysis of the pinewood, which was possibly due to the higher intensity of CO functionality in the woody biomass. Zeolite did not show high tendency for the change of the CO content, while the load of the metals on the zeolite reduced the content of CO. The increase of CO₂ and the decrease of CO content clarified that possibly the presence of the metals led to the higher rate of oxidation reaction of CO. Oxygen radicals were produced from the cleavage of O-H bond or possibly CO reacted with O-containing functional groups¹². Hydrocarbon gases including CH₄, C₂H₄, C₂H₆ and C₂H₂ were produced from the cracking of methyl and ethyl groups from aliphatic or aromatic compounds. The amount of CH₄ was slightly higher for municipal waste. The mixing of different feedstocks compared to the average of the results from the single feedstocks resulted in the slightly higher content of CH₄, which indicated the effect of the secondary reactions on the formation of the gaseous products^{32,33}. Ni/zeolite produced the highest amount of hydrocarbon gases demonstrating the high prone of Ni for cracking reactions. H₂ was produced from the breakage of C-H and O-H bonds and recombination of hydrogen radicals. Zeolite and Ni/zeolite did not change the content of H₂, while the metal loaded zeolite catalysts decreased the content of hydrogen in the gas phase, which might be due to their tendency for hydrogenation of non-saturated bonds in aromatics and aliphatics.

The analysis of tar

Water content

Clearly, water produced through several reactions such as dehydration, deoxygenation. The content of water for the bio-oil produced from mixture feedstock in the absence/presence of catalyst is presented in Table 2. The results indicated that Mg/zeolite led to the formation of the highest amount of water in the bio-oil (56.14 wt%), which indicated the high tendency of Mg for the deoxygenation reaction. On the other hand, Ni/zeolite produced the lowest content of water (32.84 wt%). The reason for this is the lower tendency of Ni compared

Feedstock	Catalyst	Biochar yield (wt%)	Bio-oil yield (wt%)	Gas yield (wt%)
Wastewater treatment plant sludge	–	42.6	38.0	19.4
Pinewood	–	26.5	55.4	18.1
Municipal waste	–	66.8	27.6	5.6
Mixture*	–	46.0	39.3	14.7
Mixture	Zeolite	46.2	42.8	11.0
Mixture	Ni/zeolite	46.1	45.3	8.6
Mixture	Ce/zeolite	45.7	41.4	12.9
Mixture	Mg/zeolite	45.8	39.9	14.3
Mixture	Mo/zeolite	45.3	39.6	15.1

Table 1. Yield of the products. Mixture included wastewater treatment sludge, pinewood chips and municipal waste from Catalan Agency of Waste with the same mass ratio. The experiments repeated several times and the most accurate data were selected and reported here. The standard deviation was below 5%.

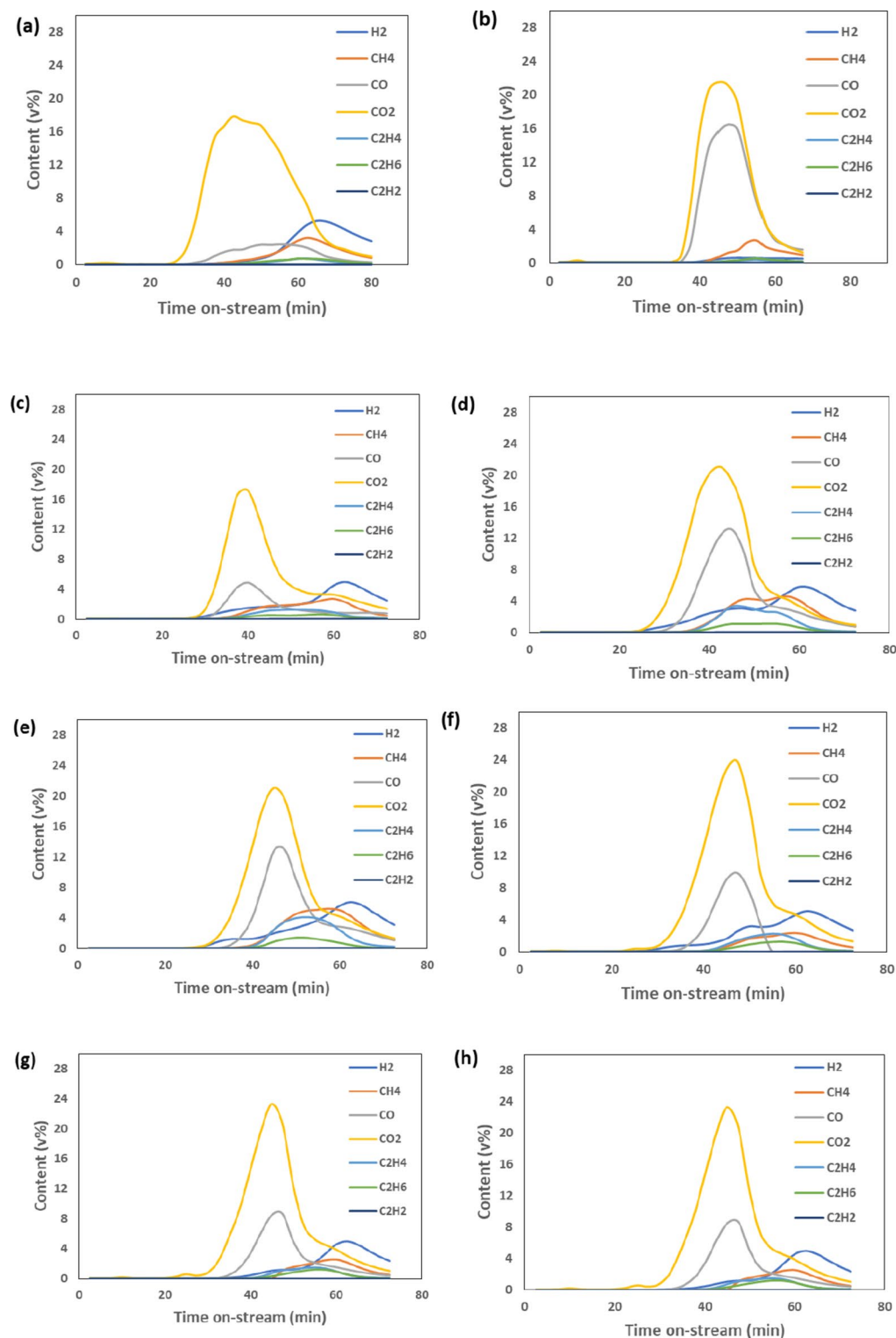


Fig. 1. Gas composition change during the experiments: (a) Non-catalytic pyrolysis of sludge (b) Non-catalytic pyrolysis of pinewood (c) Non-catalytic pyrolysis of municipal waste (d) Non-catalytic pyrolysis of mixture (e) Catalytic (zeolite) pyrolysis of mixture (f) Catalytic (Ni/zeolite) pyrolysis of mixture (g) Catalytic (Ce/zeolite) pyrolysis of mixture (h) Catalytic (Mg/zeolite) pyrolysis of mixture (i) Catalytic (Mo/zeolite) pyrolysis of mixture.

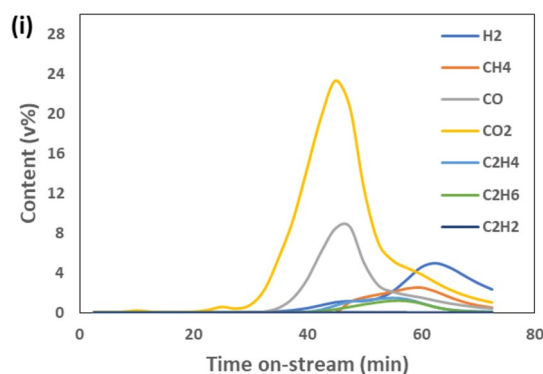


Figure 1. (continued)

Bio-oil in the presence of	Water content (wt%)
No catalyst	35.11
Zeolite	40.49
Ni/zeolite	32.84
Ce/zeolite	38.47
Mg/zeolite	56.14
Mo/zeolite	38.00

Table 2. Water content in the bio-oil samples. The analysis was repeated several times and the standard deviation was below 5%.

to other metals loaded on zeolite for deoxygenation reaction. Zeolite without loading any metals had higher activity for the production of water in comparison with Ce/zeolite and Mo/zeolite.

GC-MS analysis

In Fig. 2a-i, the normalised abundances of the main compounds in the bio-oil are shown. It should be noted that the liquid phase of the pyrolysis products is considered as bio-oil. The data in Fig. 2a show that the bio-oil produced from the pyrolysis of wastewater sludge had three phases. In addition, it had high content of aromatics such as benzene, xylene, phenol, naphthalene, etc. The reason for this was the high abundance of polyaromatics in the structure of the wastewater sludge³⁶. The data in Figure S2a showed that this phenomenon is correct. Light aromatics had higher intensity in the top phase, while in the middle phase the intensity of aliphatics was higher. The bottom phase included heavier aromatics and aliphatics such as benzene, 1,1'-(1,3-propanediyl) bis and hexadecanenitrile. The bio-oil obtained from pinewood (Figure S2b) included two phases. Aromatics and aliphatics were present in both phases. Some of them were the same, but with different intensities. For instance, the intensity of furfural in the top phase was 15.83%, while its amount in the bottom phase was 3.30%. Phenol, 4-ethyl-2-methoxy- had higher intensity in the bottom phase (9.44%). However, its abundance in the top phase was lower (93.71%). In Figure S2c, the result from the analysis of the bio-oil produced from the pyrolysis of municipal waste is shown. Clearly, municipal waste included different types of organics such as plastics, food, etc., which led to the formation of the bio-oil with different appearance and composition. The bio-oil obtained from the municipal waste included one phase. It had high content of the aromatics such as phenol (2.67%), naphthalene (2.52%), which might be related to the biomass waste and plastics with aromatic structure. It also included high content of acids and linear compounds such as octadecanoic acid (0.68%), n-Hexadecanoic acid (2.00%), 3-Penten-2-one, 4-methyl- (1.28%), etc., which might be related to the linear plastics such as polyethelene and biomass. The nitrogen containing compounds like Benzyl nitrile (0.47%), 5-Propyl-2 H-1,2,4-triazol-3-amine (0.75%), etc. were stemmed from the food residue.

Figure S2d-i present the effect of different catalysts on the composition of the bio-oil. Compared to the composition of the bio-oil from single feedstock, the bio-oil produced from the non-catalytic pyrolysis of mixture had similar compounds to the bio-oil from the single feedstocks, but with different intensities (Figure S2d). Other compounds such as myristamide, N-methyl-, Cholest-3-ene, (5.alpha.)-, etc. were produced, which were not present in the bio-oil of the single feedstocks. This was due to the secondary reactions between the compounds from single feedstocks during the pyrolysis and the transporting of the volatiles from the reactor to the other sections. Zeolite cracked down the large species in the municipal waste and smaller compounds were formed in the bio-oil (Figure S2e). As a result, the total concentration of the aromatics like phenol, naphthalene, cresol, xylene, etc. enhanced. In addition, light acids like acetic acid disappeared, which was due to the tendency of the zeolite catalyst for deoxygenation. Ni/zeolite changed the composition of the bio-oil (Figure S2f). The

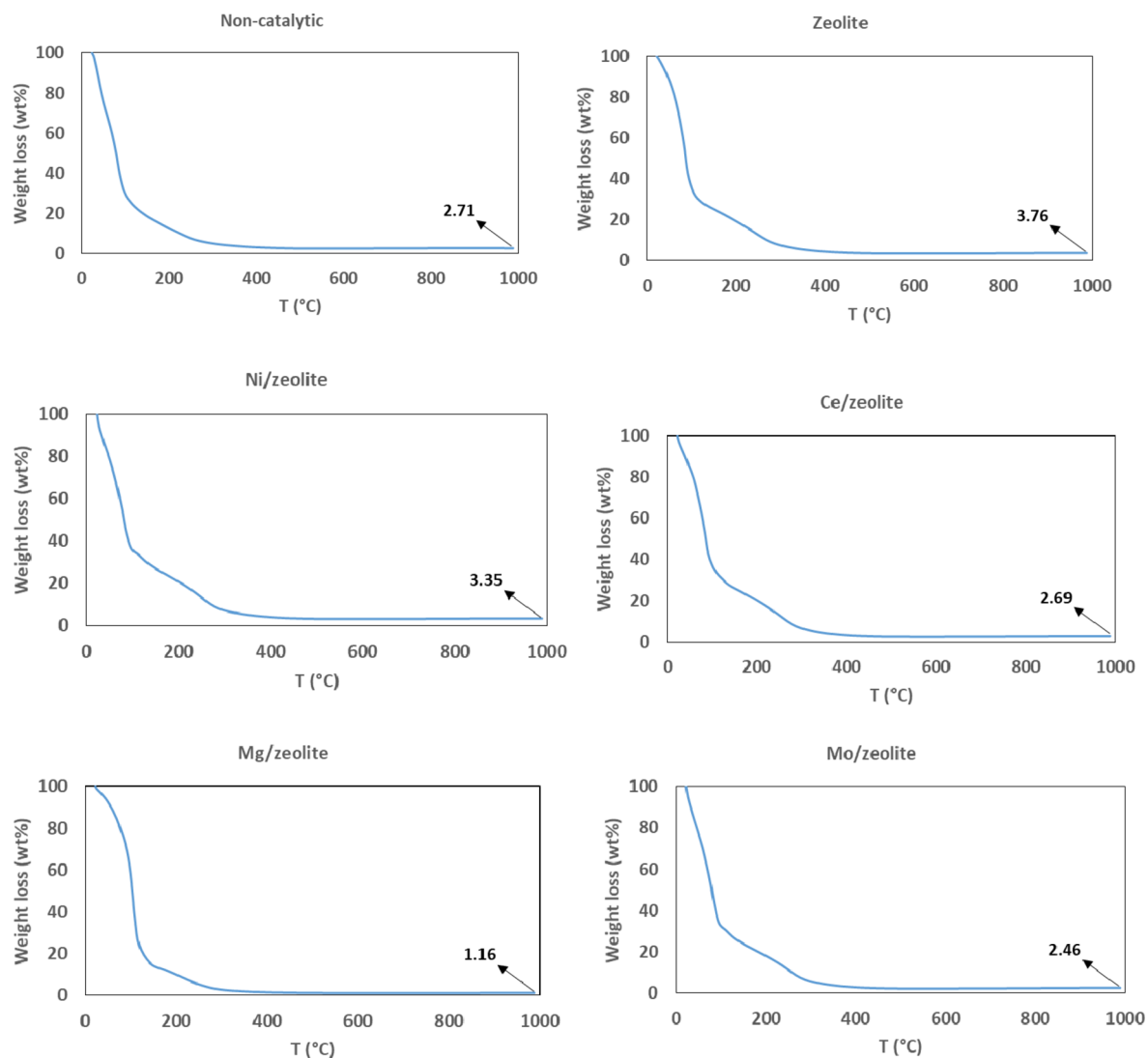


Fig. 2. TGA characterization of bio-oil obtained by pyrolysis of mixture waste with different no catalyst or catalysts.

lower amount of carboxylic acids such as n-hexadecanoic acid and phenolics like p-cresol and naphthalene were present in the bio-oil, which showed the higher rate of cracking and deoxygenation of acids reactions in the presence of Ni/zeolite compared to zeolite. Most of the compounds in the bio-oil with Ce/zeolite were the same as the compounds in the presence of Ni/zeolite. However, their abundances were different. Ce/zeolite resulted in higher content of aromatics compared to Ni/zeolite (Figure S2g). Ce-based catalysts are known for redox reactions²⁹, which led to the lower content of oxygen-containing compounds in the bio-oil. This can be seen in Table 4, which showed the oxygen content of 19.35 wt% for the bio-oil obtained in the presence of Ni/zeolite, while it was 15.93 wt% for the bio-oil produced with Ce/zeolite. In addition, high amount of compounds including 2-Cyclopenten-1-one, 2-hydroxy-3-methyl (2.9%), catechol (1.98%), o-methoxy- α -methylbenzyl alcohol (0.85%) and 1,3-Benzenediol, 4-ethyl- (1.01%) were formed. The influence of Mg/zeolite on the properties of the bio-oil composition is shown in Figure S2h. Magnesium is an active catalyst for hydroxylation reaction³⁷. As a result, the compounds including -OH bonds such as alcohols and carboxylic acids had higher intensities. For instance, benzoic acid (0.49%), n-hexadecanoic acid (0.51%), etc. were formed in the bio-oil. The influence of the Mo/zeolite catalyst on the composition of the bio-oil is shown in Figure S2i. Molybdenum is known a suitable catalyst for oxidation and hydrogenation reactions^{38,39}. Therefore, high content of acids like n-hexadecanoic acid (2.56%) from the oxidation reaction and cyclic compounds like 2-Cyclopenten-1-one, 2-hydroxy-3-methyl from possibly the hydrogenation reactions were formed. Furthermore, high content of aromatics and alcohols were also formed, which could be due to the tendency of Mo/zeolite as support for the cracking reactions.

Characterization with EA

Table 4 shows the results of the elemental analysis of bio-oil samples, which were produced at different conditions. In addition, the content of the elements for the feedstocks are presented in Table 4. Nitrogen was

present in the bio-oil samples of the wastewater treatment sludge and municipal waste, which were transferred from their feedstocks. The nitrogen in the wastewater sludge and municipal waste stems from human waste, food waste, soap, detergents, etc. The content of nitrogen in the bio-oil samples of mixture pyrolysis at different condition were similar for all the catalysts excluding Mg/zeolite, which might be related to the tendency of Mg for denitrogenation reaction⁴⁰. The effect of this phenomenon could be seen in Table 4. The bio-oil obtained in the presence of Mg/zeolite had the lowest N content (2.65 wt%), while the other bio-oil samples had the N content more than 3.0 wt%. There was some sulphur in the bio-oil, which was transformed from the sludge and municipal waste to the bio-oil. The bio-oil from non-catalytic experiment had the highest content of oxygen (49.45 wt%), which demonstrated the low rate of the deoxygenation reaction during the pyrolysis. It should be noted that municipal waste had the highest amount of oxygen (67.62 wt%) compared to pinewood and wastewater treatment sludge. The use of the catalyst led to the significant decline of the oxygen content in the bio-oil. The lowest amount of oxygen in the bio-oil (14.64 wt%) was obtained in the presence of Mo/zeolite, which was related to the higher rate of hydrogenation reaction by Mo. As a result, the highest content of carbon (71.53 wt%) was measured for the bio-oil produced by the use of Mo/zeolite. The highest content of oxygen (19.72 wt%) and hydrogen (11.01 wt%) were observed in the bio-oil when Mg/zeolite was used, which was due the higher rate of hydroxylation reaction by Mg.

TGA analysis

In Fig. 2, the results of TGA analysis of the bio-oil samples from the pyrolysis of mixture are shown. Similar trends of weight lost were recorded for all the bio-oil samples. Up to 400 °C, the majority of the bio-oil was decomposed and left the pan of the TGA. Slightly, the content of light volatiles, which evaporated prior to 150 °C, was higher for the bio-oil from the experiment used Mg/zeolite. This showed the slightly higher cracking of heavier species by Mg, which was confirmed by the less residue at 950 °C (1.16 wt%). The highest amount of heavy residue was measured for zeolite (3.76 wt%) and Ni/zeolite (3.35 wt%). The amount of the heavy species for the other catalysts was in the range of 2.5–2.7 wt%. Further investigations will be performed in the coming sections.

FT-IR analysis

The results of FT-IR analysis of the bio-oil samples are presented in Fig. 3. The broad peak, which was seen at 3000–3800 cm^{-1} was related to -OH stretching^{41,42}. All the catalysts excluding Mg/zeolite slightly reduced the intensity of the -OH functionality due to the higher rate of deoxygenation reactions of zeolite-based catalysts⁴², while Mg/zeolite enhanced significantly the amount of -OH. This was due to the high tendency of Mg to hydroxylation reaction³⁷, which was shown in the data of Figure S2 and Table 3. This phenomenon was in parallel with the results from GC-MS analysis (higher abundance of -OH containing compounds in the bio-oil of Mg/zeolite) and high content of oxygen in the bio-oil (19.72 wt%) with Mg/zeolite as the catalyst. C-H peak centred at 2900 cm^{-1} was assigned to symmetric and asymmetric mode of aliphatic functional groups and aromatics⁴¹. This peak was not observed in the presence of Mg/zeolite, while for the other catalysts, it showed similar intensities. The peak of C=C, which was showing aromatics appeared at 1700 cm^{-1} . The intensity of aromatics was the least for the bio-oil obtained in the presence of Mg/zeolite, while for the other bio-oil samples, similar intensities were recorded. The peak observed at 1250 cm^{-1} indicated -CH₃ functional group, which is related to alkyl groups and alkanes⁴¹. Its intensity was slightly lower for the Mg/zeolite bio-oil. C-O-C functionality, which was showing phenolics, was recorded at 1100 cm^{-1} . C-O-C intensity was similar for all the bio-oil samples except for the bio-oil produced in the presence of Mg/zeolite (its intensity was slightly lower). Ar-H of the aromatics was observed at 850 cm^{-1} with a weak peak for all the bio-oil samples.

Catalyst deactivation and coke formation

TGA and elemental analyses

The used catalysts for the upgrading of the bio-oil had difference colours. Ni/zeolite has the darkest colour, which could be due to high amount of coke formation on that. To understand the amount of coke and the nature of its composition on different catalysts, TGA and elemental analyses were conducted. The results from TGA are shown in Fig. 4. Different trends were recorded for different catalysts. From the comparison of fresh and used catalysts, the highest residue amount (4.96 wt%) at 1000 °C belonged to zeolite followed by Mg/zeolite (1.19 wt%). The other catalysts had weight losses more than fresh catalyst with the highest amount (8.32 wt%) was seen for Ce/zeolite and the lowest amount (5.59 wt%) for Ni/zeolite. The trends of weight loss for all the fresh and used catalysts indicated that there was a weight loss from initial stages of the heating up the samples up to almost 200 °C. This was related to the evaporation of the moisture and the evaporation/destruction of light compounds on the surface of the catalysts. Higher amount of the weight loss was recorded for all the used catalysts compared to fresh catalysts in this range. The highest weight loss up to 200 °C belonged to zeolite, which showed more contamination of the zeolite with light organics. Fresh Mg/zeolite had another sharp decrease of mass between 600 and 800 °C, which was due to the melting of Mg. Interestingly, this was not observed for the used Mg/zeolite, which was possibly due to the coverage of the surface of the catalyst with organic materials and preventing the Mg escape from the surface of the catalyst. Considering all the TGA graphs for the different catalysts, used in this study, revealed that the contamination on the catalysts could be categorized to three types. The first one is the light compounds, which were not polymerized and could be removed by washing the catalyst by the organic solvents such as acetone and ethanol. The second type was the coke with the weak bonds, which could be removed from the surface of the catalyst by heating up the catalyst in the oxygen-free environment. This type of coke could be obtained from the compounds, which stemmed from cellulose and hemicellulose. The last type of the coke was produced from the large aromatic species, which were obtain from the lignin oligomers.

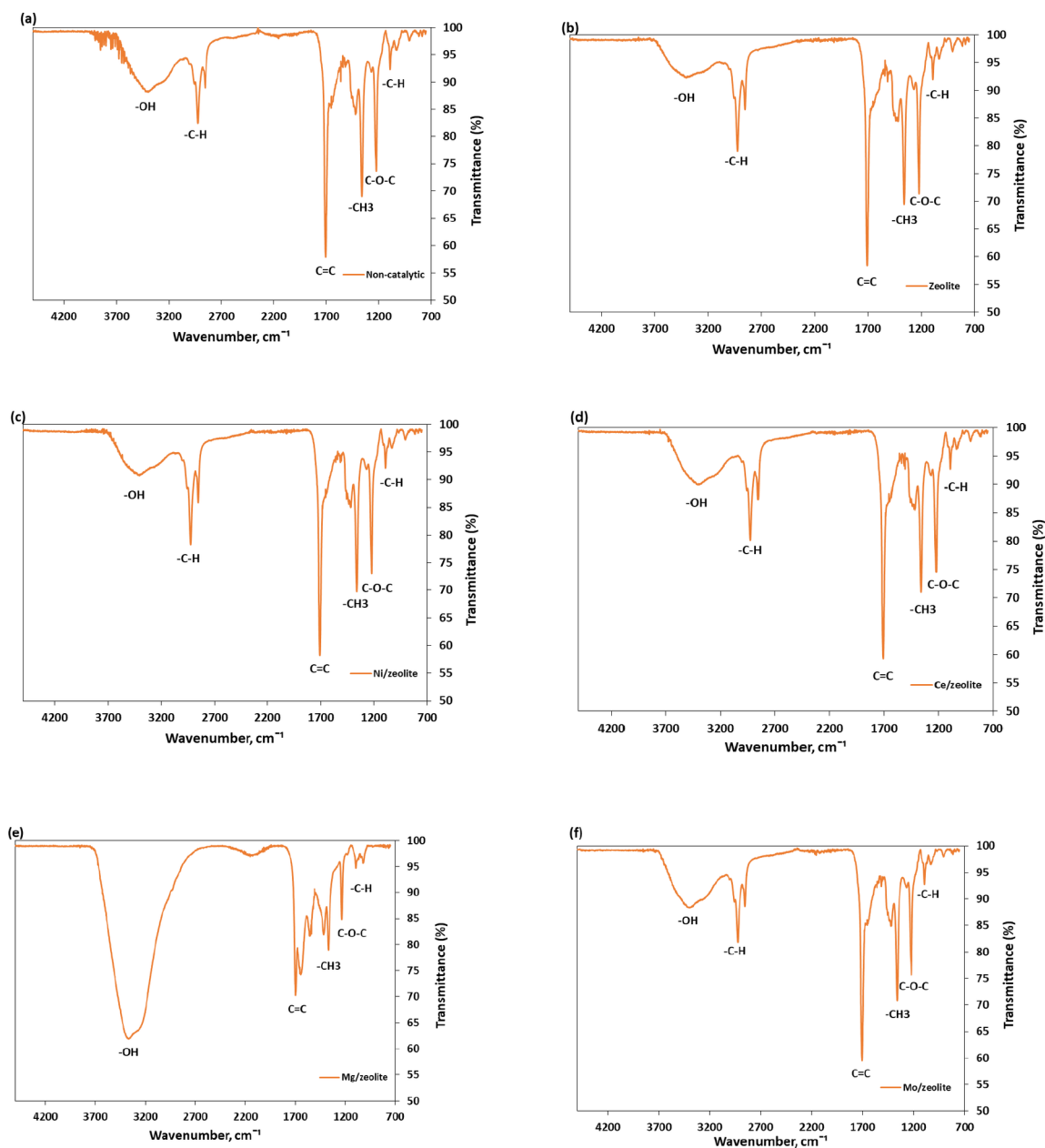


Fig. 3. FT-IR characterization of tar was obtained by pyrolysis of mixture waste with different catalysts including (a) non-catalytic (b) zeolite (c) Ni/zeolite (d) Ce/zeolite (e) Mg/zeolite (f) Mo/zeolite.

Depending on the type of the catalyst, TGA graphs showed that different contents of these types of coke were formed during the pyrolysis process.

The results from the elemental analysis of the catalyst samples are shown in Table 4. As expected from the visual inspection of Ni/zeolite (it was darker after use), it had the highest amount of carbon content increase (From 0.19 to 3.09 wt%). The lowest increase of the carbon content (from below 0.10 to 1.08 wt%) belonged to Mo/zeolite. This was in a good accordance with TGA graphs of the catalysts (Fig. 4). After 200 °C, by the increase of the temperature in the TGA oven, almost no weight change was recorded for Mo/zeolite, while for Ni/zeolite there was a slight decrease of weight. It was interesting to mention that visually the colour of fresh and used Mo/zeolite samples were the same, which indicated no coke/tiny amount of coke formation on the surface of the Mo/zeolite. The changes of the contents of H and S were ignorable. Slightly, the content of N in the used catalyst was higher in all the used catalysts, which was stemmed from the heavy compounds produced from the pyrolysis of sludge and municipal waste and remained on the surface of the catalyst as heavy residue/coke.

XRF analysis

To further understand the deactivation of the catalysts, the XRF analysis of the fresh and used catalysts was conducted. The results were shown in Table 5. In addition, the composition of the synthesized zeolite is

Sample	N (wt%)	C (wt%)	H (wt%)	S (wt%)	O (wt%)
Feedstock*					
Wastewater treatment plant sludge	4.59	40.08	5.97	0.90	48.46
Pinewood	< 0.10	44.76	6.36	< 0.10	48.88
Municipal waste	2.01	26.57	3.45	0.35	67.62
Bio-oil samples					
Mixture/thermal pyrolysis	3.24	37.93	9.15	0.23	49.45
Mixture (zeolite)	4.04	66.81	9.10	0.40	19.65
Mixture (Ni/zeolite)	3.43	67.33	9.59	0.30	19.35
Mixture (Ce/zeolite)	3.40	70.31	9.99	0.37	15.93
Mixture (Mg/zeolite)	2.65	66.62	11.01	< 0.10	19.72
Mixture (Mo/zeolite)	3.40	71.53	10.01	0.42	14.64

Table 3. The results of elemental analysis of the feedstocks and bio-oil samples. *The elemental analysis of the feedstock was performed on dry and ash-free basis.

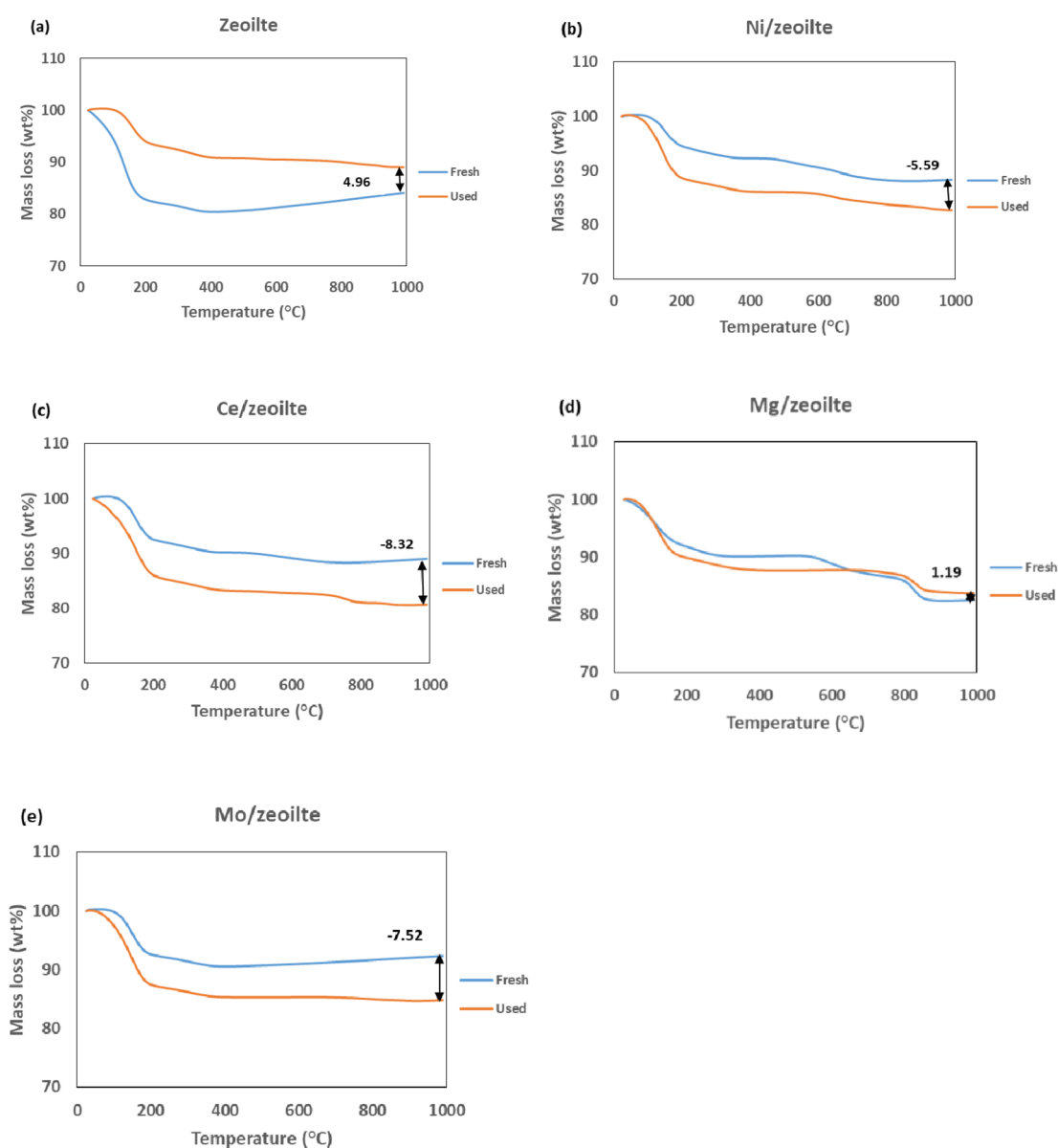


Fig. 4. The TG results of fresh and used catalysts in N_2 atmosphere.

Sample	N (wt%)	C (wt%)	H (wt%)	S (wt%)
Fresh zeolite	<0.10	0.19	2.14	<0.10
Used zeolite	0.23	2.18	2.12	<0.10
Fresh Ni/zeolite	1.39	<0.10	1.82	<0.10
Used Ni/zeolite	0.70	3.09	1.89	0.72
Fresh Ce/zeolite	0.71	<0.10	1.94	<0.10
Used Ce/zeolite	0.36	2.57	1.81	0.23
Fresh Mg/zeolite	2.47	0.10	1.23	<0.10
Used Mg/zeolite	1.12	1.89	1.34	0.24
Fresh Mo/zeolite	<0.10	<0.10	1.94	<0.10
Used Mo/zeolite	0.23	1.08	1.75	0.20

Table 4. The results of elemental analysis of the catalysts.

Sample	Metal (ppm)
Fresh Ni/zeolite	Ni: 74,754
Used Ni/zeolite	Ni: 68,135
Fresh Ce/zeolite	Ce: 15,969
Used Ce/zeolite	Ce: 15,824
Fresh Mg/zeolite	Mg: 52,509
Used Mg/zeolite	Mg: 53,408
Fresh Mo/zeolite	Mo: 46,266
Used Mo/zeolite	Mo: 39,575

Table 5. Loaded metal contents in fresh and used catalysts.

Elements	Concentration (ppm)
Al	197,295
Si	257,310
S	418
Ca	1406
Ti	521
Mn	245
Fe	821
Co	159
Ni	388
Cu	99
Zn	19
Sr	7
Zr	33
Nb	24
Th	74
U	18

Table 6. Different metals concentration in the zeolite synthesized.

presented in Table 6. The content Ni had the highest decline in the catalyst after the experiment (74754 to 68135 ppm). This might be related to the formation of the high amount of coke on the surface of the Ni/zeolite, which diluted significantly the content of Ni in the catalyst. This was in a good agreement with the results of TGA and elemental analysis of the fresh and used Ni/zeolite. The content of Mo in used Mo/zeolite was considerably lower in comparison with the fresh one (Mo content decreased from 46266 to 39575 ppm). This indicated that, considering the results from elemental analysis and TGA, very low amount of the coke was formed on the surface of the Mo/zeolite after the experiment. The decrease of Mo content could be due to the leaching of Mo by the volatiles/moisture during the pyrolysis. Ce/zeolite had a slight decrease of Ce content and Mg/zeolite had a slight increase of Mg content after the experiment. The composition of the synthesized zeolite indicated that Si and Al had the content with the mass ratio of Si : Al (1.3 : 1.0), which was in the range of low silica zeolite

Catalyst	BET surface area (m ² /g)	Total pore volume (cm ³ /g)
Fresh zeolite	5.2	0.009503
Used zeolite	2.8	0.009093
Fresh Ni/zeolite	23.7	0.064322
Used Ni/zeolite	15.0	0.037285
Fresh Ce/zeolite	6.7	0.020623
Used Ce/zeolite	6.0	0.017295
Fresh Mg/zeolite	15.0	0.014926
Used Mg/zeolite	3.1	0.007241
Fresh Mo/zeolite	3.3	0.008298
Used Mo/zeolite	2.8	0.008582

Table 7. The results from BET analysis of different synthesized catalysts.

(Si : Al of 1.0–2.0)⁴³. Other metals such as Ca, Fe, Ti, Ni, etc. and sulphur were available in the synthesized zeolite, which was transferred to the zeolite from the steel factor waste. The highest amounts belonged to Ca (1406 ppm) and Fe (821 ppm), while the lowest contents were related to Sr (7 ppm) and U (18 ppm). To further understand the change of the structure of the catalyst during the experiment, BET analysis of the fresh and used catalysts were performed and reported in the following section. To conclude, the formation of coke decreases the contact surface area of the volatiles and catalyst. In addition, the catalyst specifications could change during the pyrolysis. For instance, the metal loaded on the surface of the catalyst could be leached out by the species such as acids and in the continuous process and the activity of the catalyst reduced. The sintering of the catalyst particles could occur due to the process conditions such as high temperature of the pyrolysis. This can be seen in the SEM images of the fresh and used catalysts (Figure S3).

Coke analysis by BET

Table 7 shows the BET surface area, total volume of pores and micropores volume of the fresh and used catalyst samples. The BET surface area of all the catalysts used decreased after the experiment (See Figure S3, which is the SEM images of fresh and used catalysts). The highest surface area of the fresh catalysts belonged to Ni/zeolite. Its surface area reduced significantly after the experiment from 23.6614 to 15.0888 cm²/g. It should be noted that the highest decline of the BET surface area was measured for Mg/zeolite (from 15.0026 to 3.1251 cm²/g), which indicated the blockage of the pores, especially micropores (see Table 6). Synthesize zeolite had considerable decrease of the surface area from 5.2418 to 2.8443 cm²/g, which indicated the high amount of coke. Consequently, its pore volume decreased and all the micropores were filled by the coke. Ce/zeolite had a slight decrease of the BET surface area (it reduced from 6.6822 to 6.0202 cm²/g) due to the complete blockage of micropores. Mo/zeolite had a slight decrease of BET surface area from 3.3105 to 2.8331 cm²/g, which indicated the deactivation of the catalyst by the formation of coke or accumulation of heavy species on the surface of the catalyst.

Conclusions

In summary, the pyrolysis of wastewater treatment plant sludge, pinewood, municipal waste and their mixture with the same mass ratios were carried out. The results indicated that mixing the different types of the wastes did not result in linear averaging of the properties of the products properties obtained from the single feedstocks. To improve the quality of the bio-oil, A type zeolite was synthesized from the steel factory waste and used as a catalyst. The results indicated that the zeolite catalyst improved the quality of the bio-oil through the deoxygenation reaction. However, coke was formed on its surface. To further improve the quality of the bio-oil and reduce the amount of the coke, metals including Ni, Ce, Mg and Mo were loaded on the surface of the synthesized zeolite via impregnation method. The results showed that Ni led to the slight increase of the yield of bio-oil. It also enhanced the rate of cracking and deoxygenation of acids. Ce/zeolite reduced the content of oxygen in the bio-oil significantly. Higher amount of –OH containing compounds was recorded in the bio-oil in the presence of Mg/zeolite. Mo/zeolite had the highest tendency for deoxygenation reaction and produced the bio-oil with the lowest content of oxygen. The highest and lowest contents of carbon were measured for Ni/zeolite and Mo/zeolite, which indicated the higher life-time of Mo/zeolite. In summary, zeolite preparation from steel slag can reduce the waste from steel factories. However, the method used to obtain the zeolite could be expensive. The recycling of the chemicals such as acids is needed to reduce the cost. Techno-economic study of the zeolite production and its effect on the pyrolysis process is necessary. The loading of the metals on the zeolite surface enhanced the fuel properties of the bio-oil. The possibility of using of the other metals available in the steel slag should be evaluated to decrease the cost. Prior to the use in industrial scale, the regeneration of the catalyst and reuse of that would be a critical parameter.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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