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# Influence of catalyst support type on silver poplar pyrolysis vapors: a Py/GC-MS study

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## Abstract

This study aimed to investigate the effect of catalyst support material type on the pyrolysis products of biomass. For this purpose, ZSM-5 was selected as a commercial catalyst support material, while bio-char obtained from biomass was selected as a sustainable support material. Silver poplar (SP) was used in both bio-char production and pyrolysis reactions. Primarily, biomass characterization was performed. It was determined that carbon content of SP is suitable for the production of porous carbonaceous material as 52.4%wt. In addition, the high volatile matter content (75.48%wt.) and the low ash content (9.38%wt.) showed that SP was a suitable raw material for pyrolysis method. Cobalt loading to ZSM-5 and biochar was applied by dry impregnation method. Cobalt was successfully loaded onto the support material with the dry impregnation method, which was used for the first time for metal loading to biochar. Thus, Co/SPB catalyst was produced that was both inexpensive and provided less waste water production compared to other methods has been obtained. Commercially purchased ZSM-5, biochar obtained from SP and their 15%wt. cobalt loaded forms were characterized using BET, XRD and ICP-OES techniques. When cobalt was loaded to support materials, the specific surface area of biochar increased from 2.07 $m^2/g$ to 95.29 $m^2/g$, while the specific surface area of ZSM-5 decreased from 414.54 $m^2/g$ to 343.05 $m^2/g$. Also, it was seen that the pore size decreased if metal was loaded on the support materials. The pore size of the Co/SPB and Co/HZSM-5 samples were 6.5 nm and 2.2 nm, respectively. According to the XRD analysis results, it was specified that the cobalt onto the catalyst surface was in the $Co_3O_4$ crystal structure. The ICP-OES results were also showed that cobalt has been successfully loaded onto the catalysts. A significant increase in the amount of alcohol in the bio-oil was specified with using the Co/SPB catalyst in the pyrolysis of SP. The alcohol content increased as the amount of Co/SPB catalyst increased from 10 wt% to 20 wt%. According to this result, Co/SPB catalyst can be used in the production of bio-alcohol from biomass. While Co/HZSM5 catalyst was used in the pyrolysis reactions of SP, an increase in aromatic and aliphatic hydrocarbon content was determined. Co/HZSM5 catalyst can be utilized in the production of valuable chemicals, commercially. In addition, oxygenated compounds, which were undesirable products in the evaluation of bio-oil as a bio-fuel, were reduced in the bio-oil with catalytic performance.

**Keywords** Sustainability · Biomass · Biochar · ZSM-5 · Catalyst support · Py-GC/MS

## 1 Introduction

Renewable resources should be used for the sustainable development of the society by the reason of the increase in the need for energy due to the developing technology and the increasing population and the negative effects of this development on the environment [1].

Biomass, which benefits from solar energy through photosynthesis, has huge reserves in the world. It is also one of the renewable energy sources that can be converted into various types of energy sources. The fact that it is sustainable, renewable and carbon neutral, encourages researchers to study on biomass [2, 3]. Biomass is not only used as an energy resource, but also plays a key role in the production of carbonaceous and porous materials that can replace traditional synthetic carbon structures [4]. Carbonaceous materials have featured properties such as: high conductivity, good

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mechanical property, stability, porous structure, light weight etc. [5].

Carbonaceous material can be produced from biomass by different methods. These methods acan be listed as: Hydrothermal carbonization [6], pyrolysis [7, 8], carbonization [9], acid activation [10–12], alkaline activation [13, 14], physical activation + hydrothermal method [15] etc. In particular, the production of biochar by the pyrolysis method of biomass without the use of solvents is a very interesting subject as it is produced directly. It has also been specified that the use of biochar reduces the fabrication of the environmental footprint [4].

Biochar, which can be produced from a wide variety of biomass sources by thermal degradation/pyrolysis method, can be used in different application areas with its distinctive properties. The most important feature of biochar is that its physicochemical properties are tunable according to raw material and production conditions [1]. Due to this easily tunable surface functionality, large surface area and porosity, biochar is not only used as active carbon. In addition to these features, the abundance of functional groups (C – O, C = O, COOH, and OH, etc.) enables biochar to be used in different application areas. In the area of soil remediation [16], heavy metal removal from wastewater [17], dye removal [18], catalyst and catalyst support material [19] are only a few of the application areas of biochar.

Biochar can be used as catalyst or catalyst support material in photocatalytic, fine chemical production, pyrolysis, transesterification, gasification, catalytic cracking and electrochemical reactions and many more reactions [1, 20]. In literature, there was no sufficient study about catalytic pyrolysis of waste biomass with biochar supported catalyst. In this study, successfully synthesized biochar supported cobalt loaded catalyst was used in the pyrolysis of waste biomass from a furniture industry. It is aimed to complete the gap in the literature associated with the current experimental study, results and discussion.

Catalysts are one of the most important entries that are used in the chemical industry and increase the cost in the sector where they are used. Especially, in reactions where precious metals are used as catalysts, the use of catalyst support material is important to reduce the cost of the catalyst. Carbonaceous materials have been used for a long time in heterogeneous catalysis reactions because they provide the desired properties for catalyst support (good chemical, thermal and mechanical stability, wide porosity etc.), and it is important that these materials can be obtained from a sustainable and renewable source such as biomass [6].

Catalysts are also used in the reactions of producing valuable chemicals and fuel from biomass by pyrolysis method, to increase the yield of the desired product and to reduce the yield of undesired products. Studies in the literature show that zeolites are promising catalysts in catalytic upgrading of bio-oil due to shape selectivity. ZSM 5 is a zeolite type catalyst known for its strong surface acidity. When metal doped to ZSM 5, strong acidity of the surface is decreases and the different product selectivity increases [21]. In this study, cobalt loaded ZSM5 and biochar catalysts were used in waste biomass pyrolysis reactions. The results obtained from the catalytic pyrolysis experiments were given comparatively and contributed to the literature.

Pyrolysis reactions are developing using conventional methods in laboratory scale reactors. However, with the development of instrumental analysis, Pyrolysis–Gas Chromatography/Mass Spectrometry (Py-GC/MS) system has been successfully developed to determine the thermal degradation behavior and pyrolysis products of biomass in detail. The most important advantage of the system is the ability to separate complex pyrolysis product mixtures fast [22]. In addition, the system requires very little sample mass, ensure in situ derivation, and sample preparation is very easy [19, 23].

The main aim of this study is to investigate sustainable biochar as catalyst support material like ZSM-5. Another aim is to increase the desired product yield by loading cobalt on these support materials. For this purpose, biochar was produced from silver poplar sawdust (SP), which is a biomass source, by carbonization method. Then, the commercially purchased ZSM-5 and biochar was impregnated with cobalt 15%wt. Co doped biochar and ZSM-5 were tested as catalysts in the pyrolysis reactions of SP. The pyrolysis reactions were carried out in the PY-GC/MS system. In order to determine the effect of catalyst amount on pyrolysis products, SP: catalyst ratio was changed as 10% and 20% by mass. Experimental studies and the obtained results were given in the subsections in detailed.

## 2 Materials and methods

### 2.1 Materials

Silver poplar sawdust (SP) evaluated in this study was obtained as waste from a furniture industry in Eskişehir (Turkey). The raw material was dried at room conditions and kept in a closed container to be used in experimental studies. SP was utilized both in the production of carbonaceous catalyst support and as raw material in pyrolysis reactions. Commercially purchased $NH_4$-ZSM-5 (Alfa Aesar, LOT:T17B027, $SiO_2/Al_2O_3$ molar ratio = 80) was also used as catalyst support in catalytic pyrolysis experiments. Firstly, $NH_4$-ZSM-5 was converted to the HZSM-5 by the method described in the previous study [24]. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) (Merckmillipore, CAS No: 10026-22-9) was used as a metal source in the metal loading step of the catalysts.

## 2.2 Synthesis of SPB, Co/SPB and Co/HZSM-5 catalyst

The first step in cobalt doped carbon catalyst production was the production of carbonaceous support material. For this purpose, SP was placed in the muffle furnace with a tightly closed pot. Temperature was increased to 550 °C with the heating rate of 5 °C/min and kept at that temperature for 15 min. Then, it was cooled to room temperature with a cooling rate of 30 °C/min. This carbonized sample was named as SPB. Before the cobalt impregnation step, the acid activation process was carried out. 100 mL of 1.5 M $H_3PO_4$ was added to 5 g of SPB sample, and it was stirred at 70 °C for 2 h. Then, activated sample was dried in an oven at 100 °C for 12 h. After drying, the sample was calcined at 700 °C for 1 h under nitrogen atmosphere (100 mL/min) in a tubular furnace. Acid activated SPB and HZSM-5 were further promoted with 15 wt% Co via dry impregnation method using $Co(NO_3)_2.6H_2O$ salt [25]. This study contributed to the literature as the first study on the loading of Co into SP biochar using the dry impregnation method. Considering that biochar was hydrophobic, “dry impregnation” method was chosen by reason of being more efficient than other metal impregnation methods like “wet impregnation”. After Co impregnation, the produced catalysts were calcined at 600 °C for 5 h under air atmosphere in the tubular furnace. These catalysts, which were prepared for characterization studies, were named Co/SPB and Co/HZSM-5, respectively.

## 2.3 Characterization of SP and SPB

Since biochar would be obtained by applying the carbonization method to the biomass, firstly, thermogravimetric analysis (TGA) was performed to the SP sample. Thermogravimetric analyzer (SETARAM, LabSys evo) was operated both to examine the thermal degradation behavior and to decide on the carbonization temperature of SP. 10 mg sample was placed in an $Al_2O_3$ crucible and heated from ambient temperature to 950 °C with the heating rate of 10 °C/min. Nitrogen was flowed with the flow rate of 20 mL/min while TG and dTG curves were obtained. The carbonization temperature was decided from the TG curve of SP and SPB was obtained as described in the above section. Then, the weight fractions of moisture [26], ash [27] and volatile matter [28] contents of SP and SPB were determined. Carbon, hydrogen, nitrogen and oxygen contents of SP and SPB were specified with an elemental analyzer (LECO CHN628 Series). In order to determine the functional groups of the samples, FT-IR analyzer (Perkin Elmer Spectrum 100) were used.

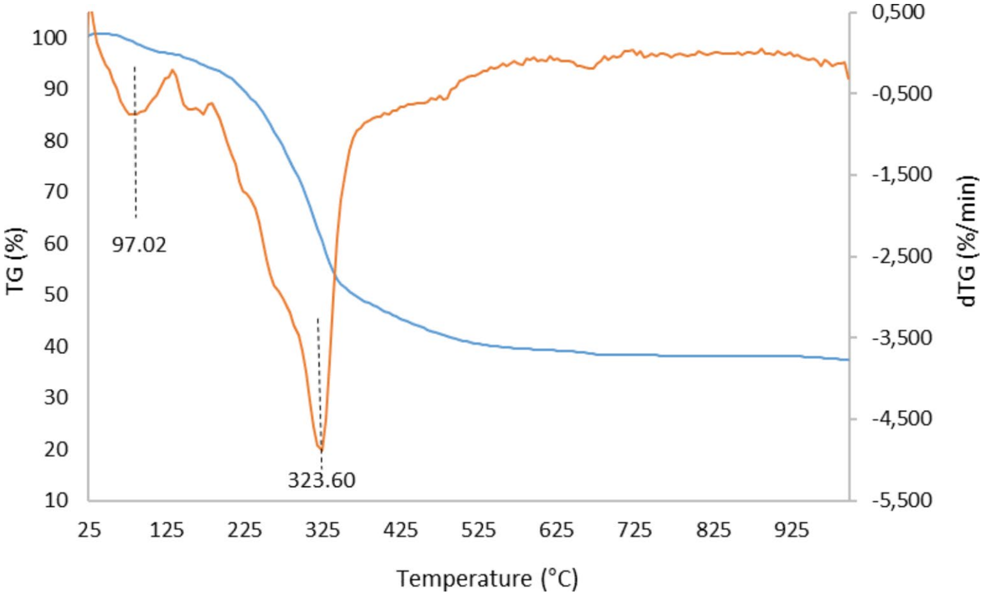
## 2.4 Characterization of Co/SPB and Co/ZSM-5 catalyst

The catalytic materials used for the pyrolysis experiments of SP were Co/SPB and Co/HZSM 5. The porosity characteristics of catalytic materials were determined by using Brunauer, Emmet and Teller surface area analyzer (BET, Micromeritics ASAP2020). SPB and HZSM-5 type catalysts were previously degassed 720 min at 360 °C under vacuum conditions. X-Ray diffraction (XRD) analyses were carried out to specify the crystal structures of the catalysts. XRD (PANalytical Empyrean) were employed CuKα radiation ($\lambda = 0.15405$ nm), in the range of 20–75° and 5–75° 2θ for SPB and HZSM-5 type catalyst, respectively. The scan rate was 2°/min. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Shimadzu ICPE 9000) were performed to determine whether the cobalt loaded on the SPB and HZSM-5 in the desired amount by weight.

## 2.5 Pyrolysis experiments

Pyrolysis experiments of SP were carried out in a pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) system (Frontier Py-2020is micro-pyrolyzer coupled Shimadzu QP 2010 GC/MS). Pyrolysis reactions were carried out as flash pyrolysis at 550 °C and in 10 min. While preparing the sample for the pyrolysis process, the sample without catalyst was SP, the samples containing 10%wt and 20%wt catalyst were named as SP + 10%Co/SPB, SP+%20Co/SPB, SP+%10Co/HZSM and SP+%20Co/HZSM-5 for both catalysts, respectively. Approximately 1 mg of sample was loaded into the microfurnace at 550 °C and volatilization reactions were occurred during 10 min. Frontier Ultra Alloy column (30 m×0.25 mm×0.25 µm film thickness) with the column temperature at 40 °C was used to chromatic separation of pyrolysis products. The GC oven was heated from 40 to 200 °C at the heating rate of 5 °C /min. It was held at this temperature at 2 min. Then it was heated to 300 °C with the heating rate of 20 °C /min and held at 300 °C for 11 min. The injection part temperature was 320 °C. The ultra-high purity grade helium (purity of 99.999%) was also used as carrier gas which flowed 1.0 mL/min. Mass spectra were recorded in electron ionization (EI) mode at 70 eV in the range of 20–500 m/z. The identification of the volatile pyrolysis products was done by using NIST mass spectral library. The identified products were grouped as aldehydes, alcohols, acids, phenols, aromatic HCs, aliphatic HCs, ketones, furans, PAHs, other oxygenates and unidentified (Chemical compounds that could not be identified by the

**Fig. 1** TG and dTG curves of SP



NIST mass spectral library). Pyrolysis experiments under the same conditions were performed three times to provide repeatability and determine the standard deviations.

## 3 Results and discussion

### 3.1 Characterization results of SP and SPB

At the beginning of the experimental studies, physicochemical properties of SP were determined by various methods. Since the pyrolysis method is the thermal decomposition process in an oxygen-free environment, the first characterization method applied is TG. Both the chemical structures SP contains and its thermal degradation profile were specified from TG and dTG curves (Fig. 1). The carbonization temperature to be used in the production of catalyst support material was also decided from this curve. According to the TG curve, it was observed that the weight loss occurs in three steps like the curve of a typical biomass [29]. The first step started at 25 °C, reached the highest mass loss rate at 97.02 °C and ended at 120 °C. The weight loss in this region was due to the evaporation of the water adsorbed to the surface [30, 31] and is about 9%wt. of the total mass. From the approximate analysis results (Table 1), it was determined that the moisture content of SP was 9.38%wt. The results obtained from these two analyzes were in the harmony. The second step in the TG curve with the highest weight loss was observed in the temperature range of about 220–400 °C (Active pyrolysis zone) [32]. SP loose about 45%wt. of its weight in active pyrolysis zone. The active pyrolysis region included sequential and small peaks on the dTG curve. Pyrolysis reactions of biomass involved many sequential and parallel chemical reactions due to the complex chemical structure of biomass [33]. This was the reason why small peaks were seen in the dTG curve in the active pyrolysis zone. The third step where weight loss was between 415 and 725 °C was called the passive pyrolysis zone. In this step, weight loss rate was very slow [32]. It was emphasized that the decomposition temperature intervals of hemicellulose, cellulose and lignin were 210–325 °C, 310–400 °C and 160–900 °C, respectively [34]. Accordingly, the peaks in the active pyrolysis region were due to the degradation of hemicellulose and cellulose. Lignin, on the other hand, begun to degrade in the active pyrolysis region and continued to degrade in the passive pyrolysis region. There was no significant weight loss after 550 °C. Major reactions such as decarboxylation, depolymerization, and cracking were completed before this temperature [35]. According to the degradation profile of SP, the optimum pyrolysis temperature required to produce SPB from SP was chosen as 550 °C.

**Table 1** Proximate analysis results of SP and SPB

| | SP | SPB |
|---|---|---|
| Moisture (%wt.) | 9.38 ± 0.50 | 2.23 ± 1.02 |
| Ash (%wt.) | 0.52 ± 0.03 | 8.27 ± 0.93 |
| Volatile matter (%wt.) | 75.48 ± 0.21 | 23.47 ± 0.57 |
| Fixed carbon* (%wt.) | 14.62 ± 0.97 | 66.03 ± 0.74 |

*Estimated by difference

Proximate analysis results of SP and SPB were given in Table 1. The amount of moisture and volatile matter content of SP were calculated as 85.31%wt. According to the TG curve, about 62%wt. of the SP was volatilized. In ASTM D 2016-74 method, the temperature of the sample was increased to 105 °C, then kept at this temperature to calculate moisture content. Volatile matter content was also

**Table 2** Ultimate analysis results of SP and SPB

| | SP | SPB |
|---|---|---|
| Carbon (%wt.) | 52.4 ± 3.22 | 85.9 ± 2.99 |
| Hydrogen (%wt.) | 3.65 ± 1.65 | 1.61 ± 0.13 |
| Nitrogen (%wt.) | 0.56 ± 0.02 | 0.20 ± 0.07 |
| Oxygen* (%wt.) | 43.39 ± 1.98 | 12.29 ± 1.55 |
| H/C | 0.84 | 0.23 |
| HHV (MJ/kg) | 15.16 | 29.16 |

*Estimated by difference

calculated via ASTM E-897-82 method, the sample was placed in a closed container, placed in the oven at 950 °C, and kept at this temperature for 7 min. In TG method, the biomass was heated from room temperature (25 °C) to 950 °C at a constant heating rate, then cooled to room temperature without waiting at 105 or 950 °C. In high temperatures, biomass volatilized with serial and parallel reactions at different temperature ranges due to its complex structure. Different reaction conditions such as temperature, heating rate, holding time and ambient were applied to SP in ASTM an TG methods. For this reason, temperature ranges and reactions occurring within these temperatures, and thus the amount of volatilization, may vary. The moisture and volatile matter content of rice husk, corn stalk, poplar wood and pine wood samples were calculated as 73.73, 83.05, 90.73 and 91.23%wt., respectively, by using Van Soest method. The same samples were volatilized about 62, 75, 73 and 72%wt. by TG method [36]. TG curves obtained by the camphor wood sample at different heating rates demonstrated that the heating rate was an important parameter while devolatilization of biomass. While the part that volatilizes via TG varies between 65–81%wt., it was calculated as 91.48%wt by mathematical methods [37]. Due to the alkyl functional groups on the SPB surface provided hydrophobic properties to the biochar, the moisture content of SP (9.38%wt.) decreased to 2.23%wt. in the SPB sample [38]. If the biomass is subjected to a pyrolysis reaction at low temperatures, it contains more aliphatic components in its surface and pores, which leads to obtain more hydrophobic biochar [39]. When the pyrolysis temperature increases, the number of aliphatic compounds in the surface and pores decreases and thus the hydrophobicity of biochar decreases [40]. Ash contents of SP and SPB samples were determined as 0.52% and 8.27% by mass, respectively. This increase could be explained by the removal of volatile matters from the SP structure by pyrolysis reactions and the relative increase in the number of inorganic components that constitutive the ash content in the SPB sample [41]. The removal of light volatile matters in the SP structure as a result of the pyrolysis reactions caused the decrease of volatile matter content from 75.48%wt. to 23.47%wt. in SPB. Accordingly, the fixed carbon amount in SP and SPB samples were calculated as 14.62% and 66.03% by mass, respectively.

Elemental analysis results and H/C ratios of SP and SPB samples were given in Table 2. As a result of the pyrolysis reactions of the biomass, the carbon content increased from 52.4 to 85.9%; hydrogen and oxygen contents decreased from 3.65 to 1.61% and from 43.39 to 12.29% by weight, respectively. The fact that the H/C ratio was higher in the SPB sample indicates that the aromatic structure has been developed in the SPB sample [42]. Higher heating values (HHV) of SP and SPB were determined from elemental analysis data by using Dulong's formula [43]. During the pyrolysis process, the HHV value increased from 15.16 MJ/kg to 29.16 MJ/kg with the increase of 63.9% oxygen content in the SPB.

FT-IR spectra showing the functional groups contained in SP and SPB samples were given in Fig. 2, comparatively. Since the pyrolysis process is a high temperature method, the functional groups decreased as a result of the leaving of volatile matters during biochar production. While -OH bonds showing stretching of alcoholic and phenolic groups in the 3325 $cm^{-1}$ regions were seen as a broad peak in the SP structure, it became negligible in SPB [44]. The two peaks belonging to C-H stretching in the region of 2850 $cm^{-1}$ and 2915 $cm^{-1}$ observed in the SP sample indicate the alkyl structure in the aliphatic group [45]. These two peaks have not seen in the SPB sample. The stretching vibration belonging to the C = O group, which demonstrated the ketone, aldehyde, carboxylic acid and ester in the SP structure, was observed in the 1733 $cm^{-1}$ region [46]. The peak in the 1397 $cm^{-1}$ region in the SPB sample showed the C-O vibration of the acetyl groups [47]. The peaks seen in the 1568 $cm^{-1}$ and 1612 $cm^{-1}$ regions belong to the C = O and C = C vibrations of aromatic rings and alkenes [48]. This peak, which became evident in SPB at 1612 $cm^{-1}$, indicated that aromatic structures were formed by the pyrolysis reactions. The peak, which was located in the 984 $cm^{-1}$ region and related to the C-O stretching vibration in the SP structure, belonged to the alcohol, ether and ester groups. In the biomass structure, completely disappeared in the SPB sample [16]. The peak seen at 874 $cm^{-1}$ and associated with the C-H vibration in the furan structure was seen in the SPB sample but not in the SP sample [49]. When results obtained from FT-IR analysis were compared, it was determined that SP contains single-bonded alkyl components like conventional biomass, while SPB has double-bond and aromatic ring structure.

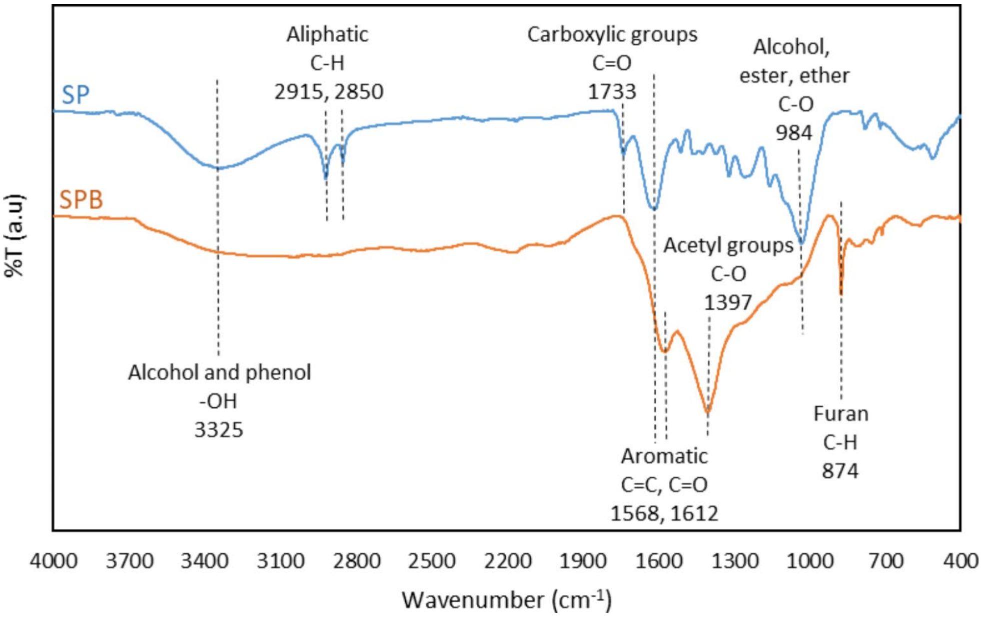


**Fig. 2** FT-IR spectrums of SP and SPB

**Table 3** Porosity characteristics of catalytic materials ($N_2$ porosimetry)

| | $S_{BET}$[a] ($m^2/g$) | Pore size[b] (nm) | $V_{micro}$[c] ($cm^3/g$) | $V_{meso/macro}$[d] ($cm^3/g$) |
|---|---|---|---|---|
| **SPB** | 2.07 | 27.3 | 0.001 | 0.009 |
| **Co/SPB** | 95.29 | 6.5 | 0.036 | 0.016 |
| **HZSM-5** | 417.54 | 3.1 | 0.126 | 0.122 |
| **Co/HZSM-5** | 343.05 | 2.2 | 0.113 | 0.067 |

[a] Multi point BET surface area.

[b] Determined by BJH method from nitrogen adsorption data.

[c] From V-t plot analysis.

[d] From the difference of total pore volume at $P/P_0 = 0.99$ minus the micropore volume.

$S_{BET}$: Specific BET surface area, ($m^2/g$)

$V_{micro}$: Specific micropore volume, ($cm^3/g$)

$V_{meso/macro}$: Specific meso/macro pore volume, ($cm^3/g$).

### 3.2 Characterization results of Co-Carbon and Co-ZSM-5 catalyst

The results of the characterization experiments which performed to determine the effect of metal loading on the physicochemical properties of SPB and HZSM-5 were given in this section. Specific BET surface area, pore size and micro-, meso- and macro- pore volume values of SPB, Co/SPB, HZSM-5 and Co/HZSM-5 were given in Table 3. Before metal loading to the SPB sample, acid activation and then high temperature treatment were applied to biochar. During to these additional treatments, the pore structure of the biochar improved. Despite metal loading to biochar, Co/SPB has higher surface area and well developed micro-meso-/macro-porosity than SPB. When the surface areas of ZSM 5 and Co/HZSM 5 samples were compared, a decrease in surface area was observed with metal loading. Moreover, meso/macropore volume of Co/HZSM-5 was remarkably reduced, in comparison of the micropore volume. This may be an indication of the deposition of cobalt particles onto surface of the HZSM-5 which caused the acidity reduction of the surface. The tentative acidity reducing has played an important role on the cracking of large biomass molecules during pyrolysis reactions. It was seen that the pore diameter decreases after metal loading in both support material types. The difference between the catalysts' average pore size and surface area after cobalt loading was expected owing to the cobalt particles blocking some of the catalyst pores.

XRD spectra of SPB, Co/SPB, ZSM-5 and Co/HZSM-5 samples were given in Fig. 3 (a) and 3 (b), respectively. A diffraction peak of amorphous carbon was observed at 22.3° and this result is in agreement with the results obtained from biochar samples in the literature [50]. Cobalt loading provides cubic $Co_3O_4$ structure on the biochar skeleton with the peaks appeared at 36.84°, 44.58° and 59.62°. According to previous studies, cobalt catalyzes the graphitization of carbon at high temperatures (500 °C). In the method that used in the study, heat treatment was applied (600 °C)

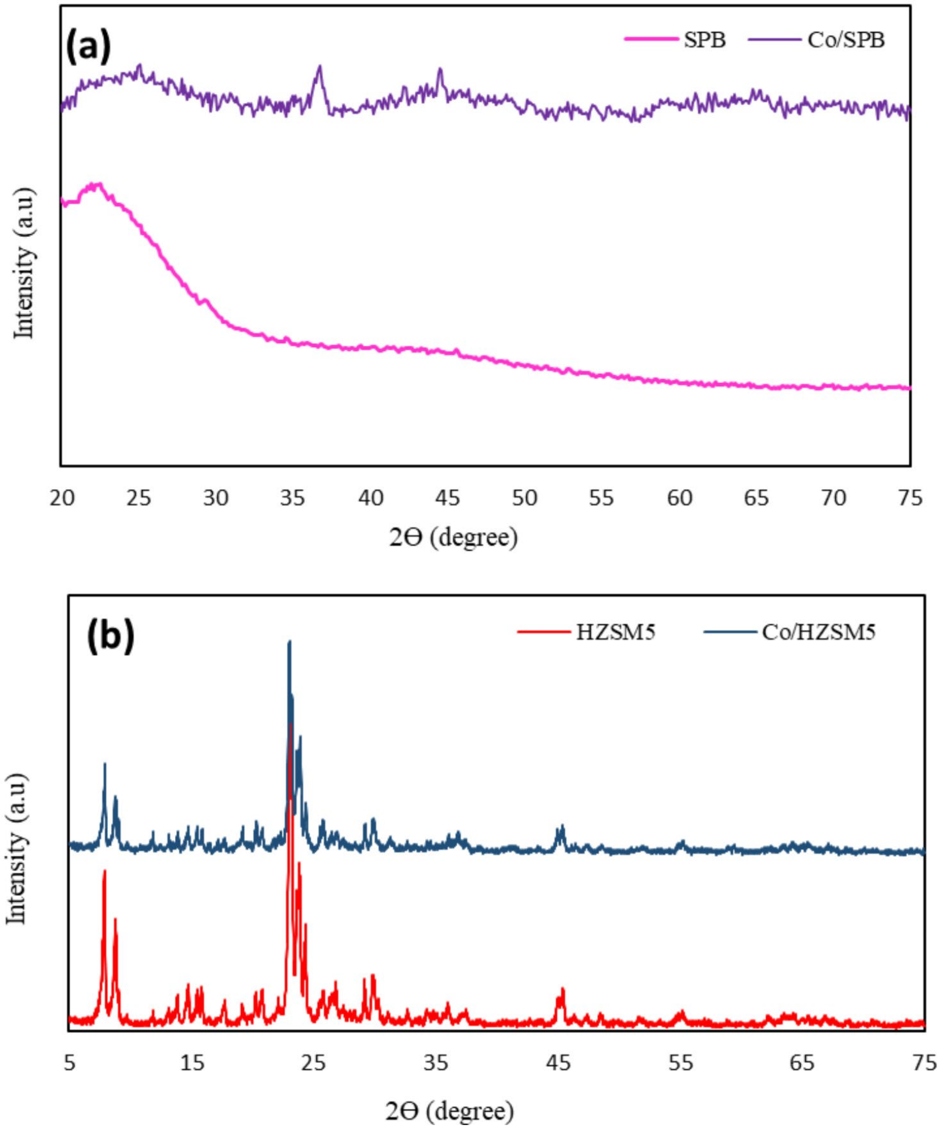


**Fig. 3** XRD patterns of catalytic materials

**Table 4** Co contents of catalytic materials (ICP-OES)

| Catalyst type | Nominal metal loading (%wt.) | Actual metal loading (%wt.) |
|---|---|---|
| **Co/SPB** | 15.0 | 13.9 ± 0.3 |
| **Co/HZSM-5** | 15.0 | 14.1 ± 0.2 |

after loading the cobalt to SPB. Accordingly, the decrease in the amorphous structure of Co/SPB can be attributed to graphitization [51]. According to Fig. 3(b), HZSM-5 has two peaks at ~8 and 23 like a typical Mobil-type five (MFI) zeolite [52]. This structure was also preserved when cobalt was loaded onto the HZSM-5. Previous studies have shown that at temperatures above 700 °C, $SiO_2$ interacts with cobalt, forming $Co_2Si$, CoSi, and $CoSi_2$ structures [53, 54]. The temperature was not exceeded to 600 °C during the production of the catalyst so the typical crystal structure of HZSM-5 was preserved. Co/HZMS5 showed the peaks of $Co_3O_4$ at 19°, 37° and 55° [25]. Since the SPB and HZSM-5 samples were calcined with air after cobalt loading, the CaO crystal structure was not detected on the catalyst surfaces.

ICP-OES results of Co/SPB and Co/HZSM-5 were given in Table 4. The analysis results confirmed that the catalytic materials were successfully impregnated with Co. It was an acceptable result that the actual metal loading was lower than the nominal metal loading. This difference was due to losses during the method applied when loading metal into the support materials [25].

## 3.3 Py-GC/MS experiments results

In order to examine the effect of catalyst support type on pyrolysis reaction product distribution, SP and catalysts

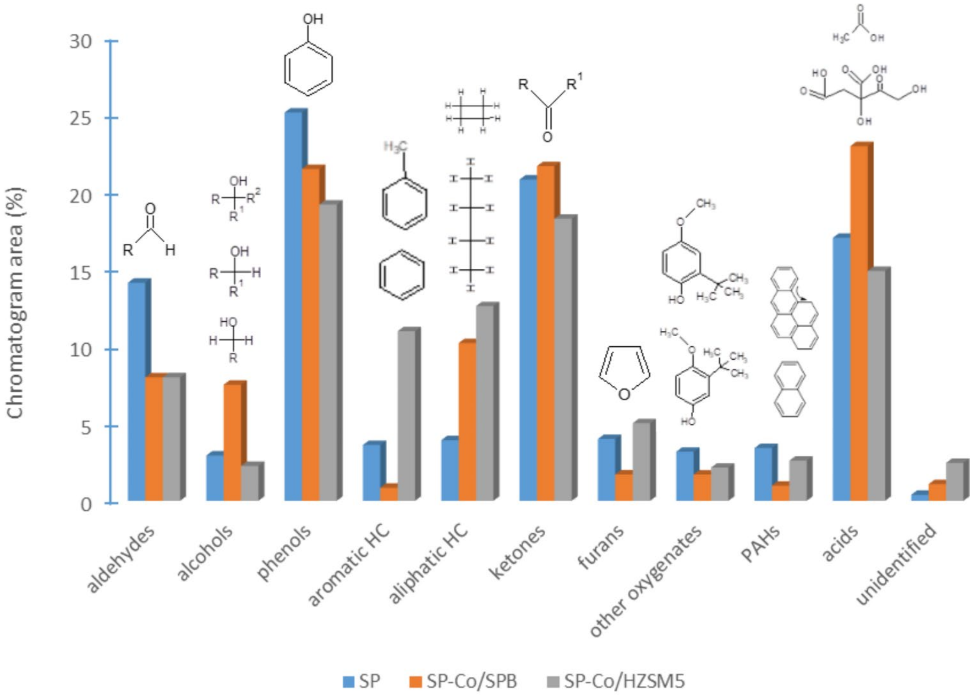


**Fig. 4** Py-GC/MS results of non-catalytic and catalytic pyrolysis of SP

were mixed at 10%wt. (catalyst:SP) and loaded into the Py-GC/MS system. The results obtained from these experimental studies were graded according to defined chemical groups and were given in Fig. 4. These chemical groups are classified as desirable and undesirable products depending on their commercial value and the effect of them on bio-oil properties, human health and the environment. Acids are undesired products due to their corrosive property. Aldehydes and ketones are reactive compounds therefore they decreased the stability of bio-oil. But ketones can also be used to produce valuable chemicals. Esters, ethers and oxygenates cause decreasing of heating value of bio-oil. PAH is also an undesired product and is harmful due to its carcinogenic property. The desired products in the pyrolysis liquid product can be listed as aliphatics, alcohols, aromatic hydrocarbons and phenols. While all these components are used in the production of valuable chemicals, phenolic and aliphatic compounds are also used in fuel production [19, 25]. The catalysts used in pyrolysis reactions is to reduce the yield of undesired product and to increase the yield of the desired product. The purpose Co/SPB and Co/HZSM 5 catalysts application was to determine which of the desired product yield increased by using Co and varying support material. As alcohols can be used in the production of value-added chemicals and aliphatics and aromatics can be used in fuel production, this laboratory study aimed to determine which catalyst can be used in which application area. Laboratory studies were important studies that should be execute initially for industrial production. According to the results obtained from this study, it was concluded that Co/SPB could be used in the production of value-added chemicals and bio-alcohol, since the amount of alcohol was increased in the bio-oil by applying Co/SPB catalyst. In addition to this, Co/HZSM5 catalyst could be used in the bio-fuel production in the industry as it increased the aromatic and aliphatic hydrocarbon content in bio-oil.

It was specified that the aldehyde, phenol and PAH yields decreased while the yield of aliphatics increased by performing the pyrolysis reactions in the presence of a catalyst. While cobalt loaded HZSM 5 was used, it was observed that phenols and PAHs decreased, and especially the percentage of aromatic hydrocarbons increased significantly. The decrease in the amount of phenols was explained by To and Resasco [55] as the adsorption of phenols on the catalyst surface, the formation of multiphenyl species by condensation and the production of water. It is known that the external surface of HZSM-5 zeolite is acidic [56]. This acidity provided the cracking of heavy molecules in the pyrolysis vapor, allowed these small molecules to enter the catalyst pores more easily, and increased aromatic hydrocarbon amount by catalyzing the aromatization reactions. Ma et al. [57] stated that two properties of the catalyst were very important in reactions involving the conversion of large molecules to small molecules: (i) acidity (ii) pore size. The reason why different results were obtained in this study, although the same metal impregnated via the same method to both catalyst support was that these two properties of these two catalysts were different from each other. Microporous catalysts such as HZSM-5 require higher temperatures for large molecules to enter their pores and convert to small

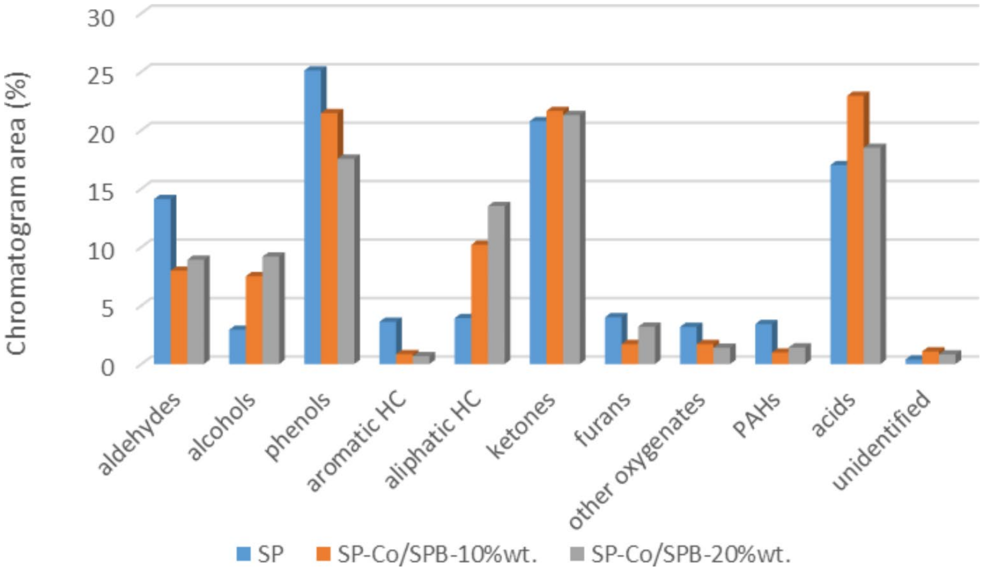


**Fig. 5** Py-GC/MS results of different Co/SPB:SP blending ratios

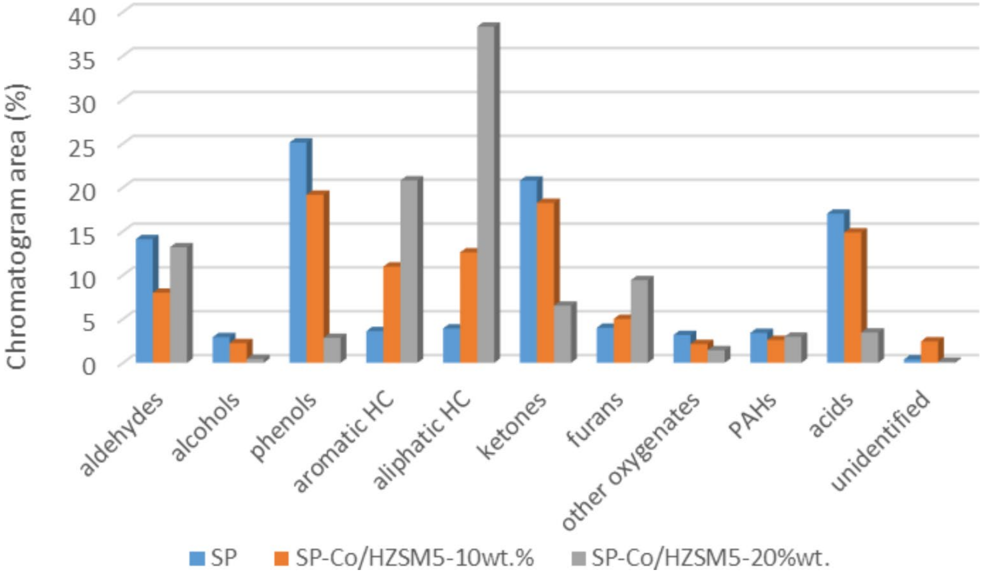


**Fig. 6** Py-GC/MS results of different Co/HZSM-5:SP blending ratios

molecules. At higher temperatures, the energy barrier of diffusion within the catalyst pores decreases. In this study, the obtained SPB and Co/SPB had a more suitable pore structure than HZSM-5 for the decomposition of large molecules to smaller molecules. However, the pH value of biochar can vary from acidic to basic depending on the production temperature [58]. Studies in the literature showed that the pH of biochar increased with higher pyrolysis temperatures [59]. Accordingly, Co/SPB, whose pore structure was suitable for the conversion of large molecules to small molecules, lacked acidity to efficiently convert or deoxygenate them.

In order to determine the effect of the amount of catalyst on the pyrolysis reaction products, pyrolysis reactions were carried out by blending the catalyst samples with SP at 10%wt. and 20%wt. The catalyst to biomass ratios were decided by literature survey. Although the catalyst ratios varied between 10%wt. and 100%wt., it was specified that the catalyst ratio used frequently in different studies is 20%wt. [60–63] and 10%wt. [61–64]. Considering that catalysts were the highest cost in the chemical industry, it was decided to blend biomass with the minimum amount of the catalyst. The graphs obtained by the grading of the obtained products for Co/SPB and Co/HZSM-5 catalysts were given in Figs. 5 and 6, respectively. Figure 5 showed that as the amount of catalyst increased, the alcohol content in the bio-oil increased. The amount of acid was obtained at the highest yield as a result of the experimental study with 10%wt. catalyst. During the thermal degradation of biomass, acids and alcohols are formed as a result of chain breaking reactions of hemicellulose and cellulose [22]. Hence, it was determined that the added catalyst promoted chain breaking reactions. According to the experimental results obtained, it was determined as the optimum catalyst ratio was 20%wt. since it increased the amount of alcohol, which was the desired product, and decreased the acid yield, which was the undesired product. As mentioned before, aromatic hydrocarbons are one of the important compounds that are desired to be present in bio-oil. The superior micropore structure of ZSM-5 supports the formation of aromatics within its pores. However, coke deposited on the pore surface reduces the catalyst efficiency [21]. The post-treatments applied to ZSM-5 significantly increased the amount of aromatic hydrocarbons obtained from different biomasses [65–68]. Especially when ZSM-5 is modified with metal, the surface acidity is adjusted and the yield of aromatic hydrocarbons obtained is also increased. As can be seen in Fig. 6, as the amount of Co/HZSM-5 added to the biomass increases, the amount of aromatic hydrocarbon obtained also increases. Additionally, no significant change was detected in the amount of PAH, an undesirable product. Acid content in bio-oil was decreased significantly when the catalyst ratio was 20%wt. In addition, aliphatic hydrocarbons, which were an important component in fuel production, also increased as the amount of catalyst increased. Hereby, it was decided that the Co/HZSM5:SP ratio was 20%wt.

## 4 Future perspective

It is very important to improve the quality as well as the yield of valuable chemicals and fuel obtained in pyrolysis reactions of biomass. This improvement is nowadays especially done by using solid heterogeneous catalysts. Solid heterogeneous catalysts are preferred because it is easy to separate from liquid bio-oil. Considering that catalyst is the most important entry that increases the production cost in the chemical industry, it is inevitable to use new, cheap and sustainable catalysts. In this study, the use of biochar produced by carbonization of biomass as a catalyst support material is very beneficial in terms of sustainable catalyst production. In the study, HZSM-5 catalyst, one of the most widely used catalysts in pyrolysis reactions, was also tested. The results showed that biochar supported cobalt catalyst has lower surface area and porosity than HZSM-5 supported cobalt catalyst. This property is undesirable for catalysts and future studies should be on improving the porosity of biochar. It was observed that aromatic hydrocarbons in the volatile products obtained in both catalysts increased, but phenols, another desired product, decreased. In future studies, bimetallic catalysts can be tested in pyrolysis reactions by loading metal/metals with high phenol selectivity into support materials besides cobalt. In addition, the disadvantage of the Py-GC/MS system used as a reactor is that the product distribution (solid, liquid, gas phase and water) cannot be determined. This study should be considered as an optimization study. The results obtained from this study will light the way on future laboratory and pilot scale real reactor studies.

## 5 Techno economic assessment

Py-GC/MS technique is a simultaneous technique involving pyrolysis and gas chromatography based on the co-determination of liquid and gaseous product. Quantitative analysis of gas and liquid pyrolysis product could not be specified, individually [22]. In order to analyze a full techno-economic analysis, it is necessary to determine amount of bio-oil obtained per unit mass of the raw material. Due to the yield could not be calculated in the Py-GC/MS system, a real technoeconomic analysis with numerical values was not possible, thus a general approach could be done. In a study in which walnut shell was used as a raw material, it was assumed that the average price of the raw material as 57 US$/ton. According to this assumption, the price of bio-oil was calculated as 771 US$/ton. Considering that walnut shell was a waste biomass resource, that had no commercial value, the price of bio-oil was calculated as 468 US$/ton [25]. It was considerably higher than the bio-oil price calculated in another study that the lignocellulosic biomass was used as raw material in [69]. The significant difference in prices was due to the higher bio-oil yield of lignocellulosic biomass than the bio-oil yield of walnut shell [25]. In this study, silver poplar sawdust was used as raw material. The raw material obtained from the furniture factory as waste had no commercial value. It significantly reduced the price of bio-oil since it was used both as a raw material for the pyrolysis reaction and as a raw material for the catalyst support material. The other catalyst support used in this study was ZSM-5. The price of ZSM-5 varies between 1.55 and 40 US$/kg depending on its $SiO_2$-to-$Al_2O_3$ ratio (SAR) value and purity. Considering that precious metal catalysts were expensive, it was important to reduce costs by using inexpensive and effective catalyst support materials. In addition, biochar was obtained from a sustainable biomass resource, which was very important in terms of providing both low cost and sustainability. Today, the chemical industry is experiencing one of the highest inflations in modern history, affecting both the energy and raw materials markets. W. R. Grace & Co, one of the world's largest catalyst manufacturers, announced a significant price increase, especially in the production costs of liquid phase cracking catalysts. Unusual levels of inflation for these catalysts affected raw materials such as alcohol, caustic soda, aluminum-derived chemicals and acids. In addition, energy price inflation has increased further due to the ongoing conflict in Eastern Europe. For this reason, catalyst prices have reached historical highs, seriously affecting the cost of chemical production [70]. For these reasons, synthesizing sustainable, effective and cheap catalysts instead of conventional expensive catalysts was very important in terms of the economic contribution of the study. This study was important not only in terms of the low cost of the catalyst, but also in terms of using waste biomass as raw material. For example, spend coffee ground [71] and corn stower [72, 73] were also superior raw materials that reduced the cost associated with of raw materials, saves the landfill area and promotes the bioeconomy. In addition, the pyrolysis method was a cheaper method to generate electricity with the compare with gasification, as the electricity obtained by the pyrolysis was 9.30 c/kWh and the electricity obtained by the gasification was 11.01 c/kWh. The main difference between pyrolysis and gasification was that the biomass conversion yields were different. The same biomass could be converted to 23.5% by gasification, while it could be converted to 29.8% by pyrolysis. The biomass conversion yield had the highest efficiency as 37.9% with the highest specific capital cost. While the highest specific capital cost was 2339 $/kWh in the pyrolysis method, it was 3869 $/kWh in the IGCC system [74]. As a result, performed techno-economic analyzes suggested that the utilization of waste biomass by catalytic pyrolysis method contributes to decrease of input costs, initial investment costs and operating costs.

## 6 Conclusion

The present study involves both catalyst preparation/characterization and aplication of these catalyst on the pyrolysis of SP. The successful loading of Co into commercially purchased ZSM-5 and SPB was proven by XRD and ICP-OES results. According to the Py-GC/MS results, although SPB and ZSM-5 were doped with the same metal, these catalysts had different effects on the components in bio-oil. This showed that the physicochemical properties of the support material as well as the loaded metal were effective on the product yields to be obtained. The interaction of the intermediate volatile components formed with the support material was very effective on the final product quality. For this reason, it should be decided in advance which product was desired as a result of the pyrolysis reaction of biomass and the support material should be selected accordingly. This study was also crucial in terms of the evaluation of waste biomass. Thus, it was concluded that catalyst support material, bio-fuel, bio-alcohol and value-added chemicals could be produced from a sustainable source instead of fossil sources. In addition, the use of raw materials as waste also contributed to waste management. The pyrolysis method was one of the clean energy conversion methods and did not cause water pollution. Considering the sustainable development goals (SDGs), this study contributed to the goals of clean water and sanitation, climate action, life below water and on land.

**Author Contribution** EY: conceptualization, methodology, validation, investigation, formal analysis, resources, writing—original draft.

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**Data Availability** Not applicable.

**Code Availability** Not applicable.

## Declarations

**Conflict of Interest** The author doesn't have any conflicts of interest.

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