Journal of Porous Materials (2022) 29:771–781
https://doi.org/10.1007/s10934-022-01207-3

Evaluation of bio-char as porous catalyst support in the pyrolysis of *Brassica napus* subsp. *napus* cake

Elif Yaman[1] · **Fatma Özge Gökmen**[1] · **Sinan Temel**[1] · **Nurgül Özbay**[2]

Accepted: 1 February 2022 / Published online: 15 February 2022

Abstract

It is very important to produce carbonaceous porous material from sustainable biomass resource and to investigate its different application areas. In this study, it was aimed to use fir wood sawdust as catalyst support material in precious metal catalysts and to evaluate this catalyst in pyrolysis reactions of *Brassica napus* subsp. *napus* cake. Fir wood sawdust, which have high carbon and volatile matter content, was a suitable raw material for the production of bio-char by carbonization of biomass. 1%, 3% and 5% platinum (Pt) and palladium (Pd) metal loading was applied to fir wood sawdust biochar (FB) and the obtained catalysts were characterized. Among the different metal-loaded catalysts, the catalysts with the highest BET surface area are 5%Pd-FB and 1%Pd-FB catalysts. TEM images showed that as the amount of metal was increased, the particle size of Pd metal was also increased. ICP-OES results verified that the used impregnation method was more efficient and the standard deviation proportion was lower at low metal ratios. Pyrolysis experiments of *B. napus* subsp. *napus* were carried out in analytical pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) system with and without catalyst. Pyrolysis products was mixture of organic compounds in the range of C_7–C_{29} carbons. With the application of catalytic pyrolysis, while the amount of alcohol, which was the desired product, was increased in the pyrolysis product, the amount of acid, which was the undesired product, was decreased. However, the amount of PAH, which was an undesirable product, increased with some catalyst applications, showed that bi-metallic catalyst applications can also be applied in future studies. Experimental results and discussions showed that the synthesis of carbon support material from biomass, which is a cheap and renewable resource, is a promising study.

Keywords Biomass conversion · Bio-char · Pd catalyst · Pt catalyst · Sustainable process

1 Introduction

The chemicals that are the raw materials of the basic requirements are generally produced from fossil fuels. Owing to the consuming of petroleum reserves and the environmental effects of fossil fuels, the search for alternative renewable sources for chemical raw material production is increasingly important [1]. Biomass-based chemicals production is become more of an issue as alternative against climate change and dependence on fossil fuels. Especially, in terms of being a global resource, growing in each country and waste conversion, biomass is an important raw material [2]. Lignocellulosic biomass is the most economical renewable carbon resource that could be utilized to obtain bio-chemicals and bio-fuels by carrying out suitable eco-friendly processes that achieve less greenhouse gas emissions [3].

There are three main categories Waste to Energy Technologies (WTE) to evaluate varied raw materials: thermochemical, physicochemical and biochemical technologies. Thermochemical conversion of waste biomass to value-added chemicals has gained attention for sustainability of waste management [4, 5]. Pyrolysis is one of the thermochemical processes that is economically profitable on a large scale due to its energy efficiency of 80%. In addition to that, pyrolysis reduces environmental concern, in particular waste utilization, carbon sequestration and value-added chemicals production [6]. Besides, with the development of instrumental systems, Py-GC/MS system has been improved to specify the thermal decomposition behavior and pyrolysis

---

✉ Elif Yaman
elif.yaman@bilecik.edu.tr

[1] Central Research Laboratory, Bilecik Şeyh Edebali University, Bilecik, Turkey

[2] Department of Chemical Engineering, Bilecik Şeyh Edebali University, Bilecik, Turkey

products of raw material in detail, successfully. The Py-GC/MS system is also used for the characterization of complex structures [7, 8]. The advantages of the system can be listed as being rapid, sensitive and having the ability to separate of complex pyrolysis product mixtures [9]. In addition to this, the system needs very little sample amount, provides in situ derivatization and sample preparation is so easy [10, 11].

The liquid product obtained by condensing volatile components in biomass pyrolysis contains polar and non-polar compounds with different molecular weights. Besides, it has undesirable properties such as low thermal and chemical stability, high oxygen content and high acid content [12]. These undesirable properties prevent the direct use of the liquid product in refineries, as it provides high corrosivity to the product [13, 14].

Performing the pyrolysis process with a catalyst provides advantages such as increasing energy efficiency and the desired product yield [15]. The catalytic pyrolysis process consists of two stages: (i) pyrolysis of biomass (ii) catalytic conversion of pyrolysis vapors. In the pyrolysis of biomass, liquid product, non-condensable gaseous product and biochar are formed when it is heated. In the second stage, the pyrolysis vapors contact the catalyst surface, where catalytic conversion takes place. On this surface, aromatics, aliphatics and alcohol are formed by the deoxygenation of oxygenated compounds [16]. By using a catalyst in the pyrolysis process, the quality and stability of the obtained liquid product is increased, and a product that is easier to process, use and transport is produced [17, 18]. According to Kobayashi et al. when Pt catalyst was used in the pyrolysis of wheat waste, the desired product yields such as sorbitol, xytol and other sugar alcohols in the liquid product increased [19]. Similarly, Yamaguchi et al. used pt catalyst to increase the yield of sorbitol, mannitol, galacticol, xylitol and arabitol in the liquid product. They also prepared ruthenium and platinum as bi-metallic catalysts and determined that this catalyst was more effective in the conversion of lignocellulosic biomass [20]. In addition, the superior properties of biochar, which is a solid product of the pyrolysis method, can be listed as being thermally stable, rich in carbon and porous [21]. Features such as high surface area, chemical, thermal and mechanical stability, homogeneous dispersion of metals on the surface are the desired properties of a catalyst support material [22]. Previous studies in the literature show that activated carbon [23], carbon nanotubes [24], and biochar [25, 26] can be used as catalyst support materials by means of their above discussed properties.

The use of waste lignocellulosic biomass in pyrolysis technologies is encouraged because it eliminates the competition against food. Forest wastes, which are among the sources of lignocellulosic biomass, are arisen in great abundance. Fir (Abies) is a coniferous species of the Abies genus of the Pinaceae family. It grows in the tierra templada regions of the northern hemisphere, in the high mountain areas and in North Africa, the Himalayas and Turkey. There are 213,652 hectares of fir forest in Turkey [27]. Since fir wood is used in the furniture sector, plenty of fir wood sawdust is produced in Turkey as both field waste and furniture industry waste. Not only woody biomass but also farm waste such as corn stalk, rice straw, wheat stem and *Brassica napus* subsp. *napus* (rapeseed) cake are renewable lignocellulosic resources. As a lignocellulosic biomass, these farm wastes can be feedstocks for the fuel or chemicals production [20]. *Brassica napus* subsp. *napus* cake is one of the lignocellulosic residues of the edible oil factory. In the world, approximately 68.9 million tonnes *B. napus* subsp. *napus* was produced in 2016. In addition, in 2019, *B. napus* subsp. *napus* production was approximately 250,000 tonnes in Turkey.

This study includes synthesis, processing, characterization and evaluation of biochar supported noble metal catalysts as a porous material. Firstly, biochar was produced from fir wood sawdust and the obtained biochar was evaluated as a catalyst support material. Biochar supported material loaded with Pt and Pd at different weight ratios was used as a catalyst in *B. napus* subsp. *napus* cake pyrolysis reactions. When the literature was analyzed, such a comprehensive study using the selected raw materials has not been found. The reactions were performed in Py-GC/MS system. The acquired results were targeted to promote towards the development of bio-based and sustainable bio-chemicals production.

2 Materials and methods

The raw materials which were used in this study are defined in this section. In addition to this, catalyst synthesis and characterization methods were described as well as the pyrolysis system.

2.1 Fir wood sawdust and *B. napus* subsp. *napus* cake

The moisture, volatile matter and carbon contents of the fir wood sawdust (F) used in the production of catalyst support material were 7.01 wt%; 80.74 wt% and 41.34 wt%, respectively [28]. Since the carbonization method is a thermal method, low moisture content is desired in the raw material in order to decrease the energy requirement. In addition, for the production of carbonaceous material, the raw material has a high carbon content is preferred. According to its high carbon content and low moisture content, F was a suitable raw material for the production of carbonaceous material by carbonization method. The weight percentage of carbon, hydrogen, nitrogen and oxygen of the *B. napus* subsp. *napus* cake (BNC) to be subjected to the pyrolysis process were 45.04%, 6.29%; 5.26% and 44.41%, respectively. BNC had a mid-calorific value (16.30 MJ/kg) and high volatile matter content (73.09 wt%) [29]. While compared to other energy crops, BNC was an appropriate raw material for the production of value added and fuel-derived chemicals by volatilization via pyrolysis method.

2.2 Synthesis and characterization of catalytic materials

The carbonization process of F was carried out in muffle furnace (Magma Therm). F sample was put in a closed pot and placed in the muffle furnace. Temperature was increased to 550 °C with a heating rate of 20 °C/min. The furnace was kept at 550 °C for 10 min. Then, it was cooled to room temperature. The sample taken from the muffle furnace was cooled in a desiccator until it reached room temperature and then stored in a moisture free environment. This carbonized sample was coded as FB.

For the preparation of carbon supported catalysts containing 1%, 3% and 5% Pd, firstly, FB, which will be used as the catalyst support material, was activated with 10% nitric acid (HNO_3) at 80 °C for 3 h. Activated catalyst support material dried at room temperature. Then, palladium(II) chloride ($PdCl_2$) salt was weighed as to be the palladium content of 1%, 3% and 5% and dissolved in 12 mL of 1 M hydrochloric acid (HCl) solution. 1 g of the activated support material was weighed and prepared Pd solutions were added drop by drop onto the solid. The mixture was kept at 30 °C for 20 h, and at the end of this period, 30 wt% sodium hydroxide (NaOH) solution was added until a basic pH (~ 8) was obtained. Stirring was continued for 3 h at 30 °C, then heated to 60 °C and 800 µL of 37% formaldehyde was added. The mixture, which was kept at 60 °C for 2 h, was filtered and washed 5 times with distilled water. The catalyst separated from the filtrate was dried at room temperature and ready for characterization [3, 30, 31]. The obtained catalysts were codded as 1Pd-FB, 3Pd-FB and 5Pd-FB, respectively.

The activation process for the preparation of Pt-loaded catalysts is the same as the Pd-loaded catalyst preparation method. Then, the tetraammineplatinum(II) nitrate ($[Pt(NH_3)_4](NO_3)_2$) salt was weighed as to be the platinum amount was 1%, 3% and 5% and dissolved in 10 mL of distilled water. 1 g of the activated support material was weighed and prepared Pt solutions were added drop by drop onto the solid at 50 °C. Then, 800 µL of 37% formaldehyde was added and kept at this temperature for 1 h. The solid separated from the solution by filtration was washed 5 times with distilled water and dried in an oven at 100 °C for 2 h [31–33]. The obtained catalysts were codded as 1Pt-FB, 3Pt-FB and 5Pt-FB, respectively.

Surface area measurement analyzes of the prepared catalysts were performed using the Brunauer, Emmet and Teller surface area analyzer (BET, Micromeritics-ASAP2020). BET surface areas (m^2/g), pore size (nm), micropore and meso-macropore volumes (cm^3/g) were determined by multi-point BET analysis. Degas conditions were 300 °C and 360 min.

Surface morphology of the catalysts were specified using the Scanning Electron Microscope (SEM, ZEISS SUPRA 40VP). Au/Pd coating process was applied to provide the conductivity of the catalysts. The coating thickness of the samples, which were coated for 1 min under the Au/Pd source in the coating device (Quorum, Q300 model), was approximately 100 nm. The parameters of the SEM analysis were 15 kV acceleration voltage (EHT), ~ 10 mm working distance (WD), different magnification ratios and secondary electron (SE) detector.

Transmission Electron Microscopy (TEM, JEOL-JEM 2100UHR) analysis of the catalysts was performed by taking images from different regions with resolutions ranging from 1000 to 10 nm.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Shimadzu ICPE 9000) were used to specify whether the Pt and Pd metals loaded on the catalysts were in the desired amount by mass.

2.3 Py-GC/MS experiments

A Py-GC/MS System (Frontier Py-2020is pyrolyzer, Shimadzu QP2010 GC/MS) was used for analytical pyrolysis of *B. napus* subsp. *napus* cake. Approximately 1.0 mg (± 0.050 mg) of raw material was loaded into a small size crucible, and then transferred to the microfurnace. Pyrolysis process was isothermal at 550 °C and reaction time was 10 min. The gas chromatograph equipped with a Frontier Ultra Alloy column (30 m × 0.25 mm × 0.25 µm film thickness) was used to chromatic separation of volatile products. The column and injection part temperature were 40 °C and 320 °C, respectively. The carrier gas was helium which flowed 1.0 mL/min. In the catalytic pyrolysis experiments, the catalyst:biomass ratio was set as 1:3 by weight. NIST library was used to identification of peaks from pyrolysis products. The defined chemical compounds were graded into 5 groups; alcohols, aromatics, acids, ketons and polyaromatic hydrocarbons (PAHs). Chemical compounds that could not be identified by the NIST library were named as unidentified. Py-GC/MS experiments were applied three times under the same conditions to make sure repeatability and the used values were average values from these experimental runs.

3 Results and discussion

In this section experimental results were presented and discussed.

3.1 Characterization of the catalysts

The moisture and ash content of the FB sample produced at 550 °C for 10 min were 1.21 wt% and 8.54 wt%, respectively. It was determined that the moisture content of the sample decreased by 82.74% after the carbonization process. True density and bulk density were specified as 1.41 g/cm^3 and 0.55 g/cm^3 in the previous work of the authors [21]. Difference between true density and bulk density verifies that the porosity increased with the carbonization and porous material was produced [34]. In accordance with the previous studies [35], as the porosity improves during the carbonization, the bulk density decreases.

The BET analysis results of the FB samples loaded with Pd and Pt metals in different weight ratios are given in Table 1. Pt and Pd loadings were contributed to decrease in the BET surface area as a consequence a significant pore blockage. This result is in a harmony with the literature. The authors specified the same results in Pt-loaded different catalyst types in previous studies [36, 37].

As the amount of metal increased, there was no significant change in the BET surface area of the Pd-loaded catalyst, while the BET surface area of the Pt-loaded catalyst decreased. This was sign to the metal accumulate in the pores gradually with the increasing metal ratio [38]. While both Pt and Pd metal were loaded on the carbon support, the micropore volume also decreased. It is evident that the loaded metal is located not only on the external surface of the biochar, but also inside the micropores. As it is known from the literature, a high micropore volume can both increase the adsorption ability of the catalyst and expand the active sites [39]. However, the presence of metal particles in the micropore in this study can increase the efficiency by acting as a favorable catalyst in the adsorbing of undesired products (acid and PAH) and their conversion to desired products (alcohol and aromatics). Among the different metal-loaded catalysts, the catalysts with the highest BET surface area are 5Pd-FB and 1Pt-FB catalysts. When these different types of catalysts were compared with each other, it was determined that both the BET surface areas and the micropore volume of the Pt loaded FB samples were higher.

Table 1 Porosity analysis results of the FB samples loaded with Pd and Pt metals in different weight ratios

	S_{BET}[a] (m^2/g)	Pore size[b] (nm)	V_{micro}[c] (cm^3/g)	$V_{meso/macro}$[d] (cm^3/g)
FB	36.140	6.99	0.0125	0.0072
1Pd-FB	0.4256	35.5	0.0003	0.0021
3Pd-FB	0.4946	49.8	0.0003	0.0004
5Pd- FB	0.8589	31.4	0.0002	0.0011
1Pt-FB	17.6335	47.50	0.0064	0.0037
3Pt-FB	12.4532	28.4	0.0067	0.0009
5Pt- FB	15.4984	42.7	0.0063	0.0027

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)

[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/P0 = 0.99 minus the micropore volume

SEM analysis results of FB samples loaded with 1%, 3% and 5% Pd metal by weight were given in Fig. 1 and SEM analysis results of FB samples loaded with 1%, 3% and 5% Pt metal by weight were given in Fig. 2. According to the SEM images obtained, it was determined that the increase in the amount of loaded metal did not damage the morphological structure of the catalysts in both Pd and Pt loaded catalysts. However, in some catalyst areas, it was seen that the metals were not homogeneously distributed on the support and the metals tended to accumulate, which was encountered with similar results in the literature [40].

TEM analysis results of FB samples loaded with 1%, 3% and 5% Pd and Pt metal by weight were given in Figs. 3 and 4, respectively. Due to the catalyst support was carbonaceous material, it was seen that the resolution is low in the images taken [41]. When the TEM images obtained from the Pd-loaded FB sample were examined, it was seen that the particle size distribution of the Pd metal is more apparent since the higher resolution. The images of the different samples showed that the Pd particle size was highly dependent on the amount of metal loaded. It has been determined that as the amount of loaded metal was increased, the particle size of Pd metal was also increased [3]. As seen in the TEM images in Fig. 4, Pt loaded biochar catalysts had multi-layer sheet structure.

ICP-OES analysis results of catalysts loaded with Pd and Pt at different weight ratios are given in Table 2. It was seen that the impregnation method used was more efficient and the standard deviation proportion is lower at low metal ratios. As can be seen from the table, generally the actual metal loading value was lower than the nominal metal loading value. The difference, which was especially in high metal impregnations, was due to the fact that metals were less soluble in the solvent and there was metal loss in the beaker, pipette and other laboratory equipment used during the impregnation method [42]. As it is known from the literature, the interaction of the metal and the carbon support depends on the nature of the oxygen groups on the carbon surface [43]. The basic oxygen regions on the carbon

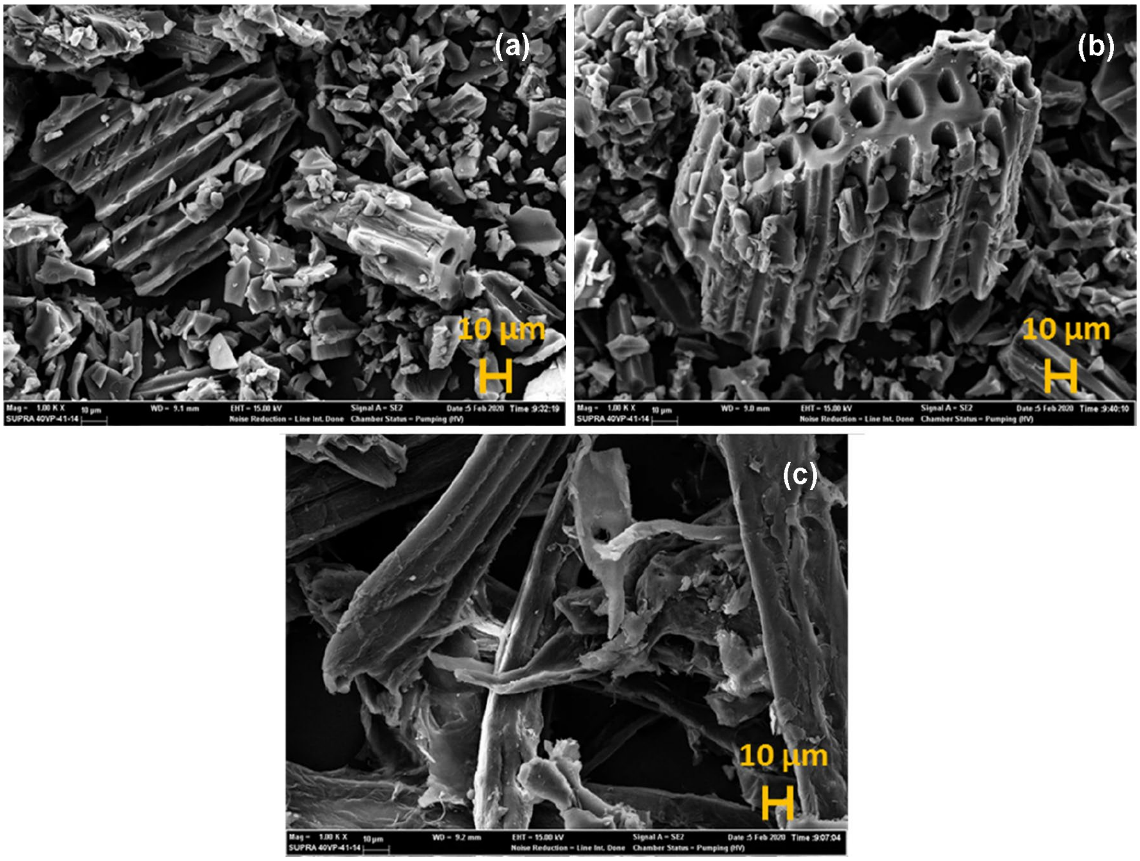


Fig. 1 SEM images of FB samples loaded with different amounts of Pd metal by weight **a** 1Pd-FB, **b** 3Pd-FB, **c** 5Pd-FB

support provide the formation of metal complexes between the metals and the carbon surface [44]. As seen in Table 2, it was specified that Pd was loaded on the carbon support with higher efficiency. In the experimental section, while Pd-carbon catalyst was synthesized, adjusting the basic pH with NaOH provided the formation of metal complexes on the Pd-carbon surface and thus the increase in metal loading efficiency.

3.2 Pyrolysis of *B. napus* subsp. *napus* cake

The qualitative composition data of the *B. napus* subsp. *napus* cake volatile components' from Py-GC-MS analysis are given in Fig. 5. These results showed that the pyrolysis products obtained through *B. napus* subsp. *napus* cake was a mixture of organic compounds in the range of C_7–C_{29} carbons. But the main product was acids which can be classified as undesired product, because it leads to increase of the corrosivity of bio-oil. PAHs were also undesired products due to their carcinogenic potential. In other respects, alcohols, ketones and aromatic hydrocarbons are desired products that can be used for the production of valuable chemicals such as fuels and bio-alcohol [41]. The peak area of alcohol was determined as 23.02%. While this quantity was an acceptable ratio to produce alcohol from *B. napus* subsp. *napus* cake, the peak area of acids (36.94%) as undesired product in the pyrolysis product should be reduced. Acids and alcohols were produced from hemicellulose and cellulose by chain breaking reactions during the pyrolysis process of the biomass [9]. It can be performed the pyrolysis process catalytically with noble metal loaded catalyst in order to reduce the acid yield, which was the undesired product, and to increase the yield of alcohol as desired product [20]. According to the above discussions, a possible reaction scheme for the pyrolysis of *B. napus* subsp. *napus* cake is presented in Fig. 6.

3.3 Catalytic pyrolysis of *B. napus* subsp. *napus* cake

Catalytic pyrolysis experiments were carried out in the presence of Pd and Pt loaded carbon support catalyst in order to reduce the amount of acid, which is an undesirable product in the pyrolysis of *B. napus* subsp. *napus* cake. In addition to this, it is aimed to increase the yield of alcohol and aromatics, which are the desired products.

The results obtained by grading the volatile components obtained from the Py-GC/MS experiments using the

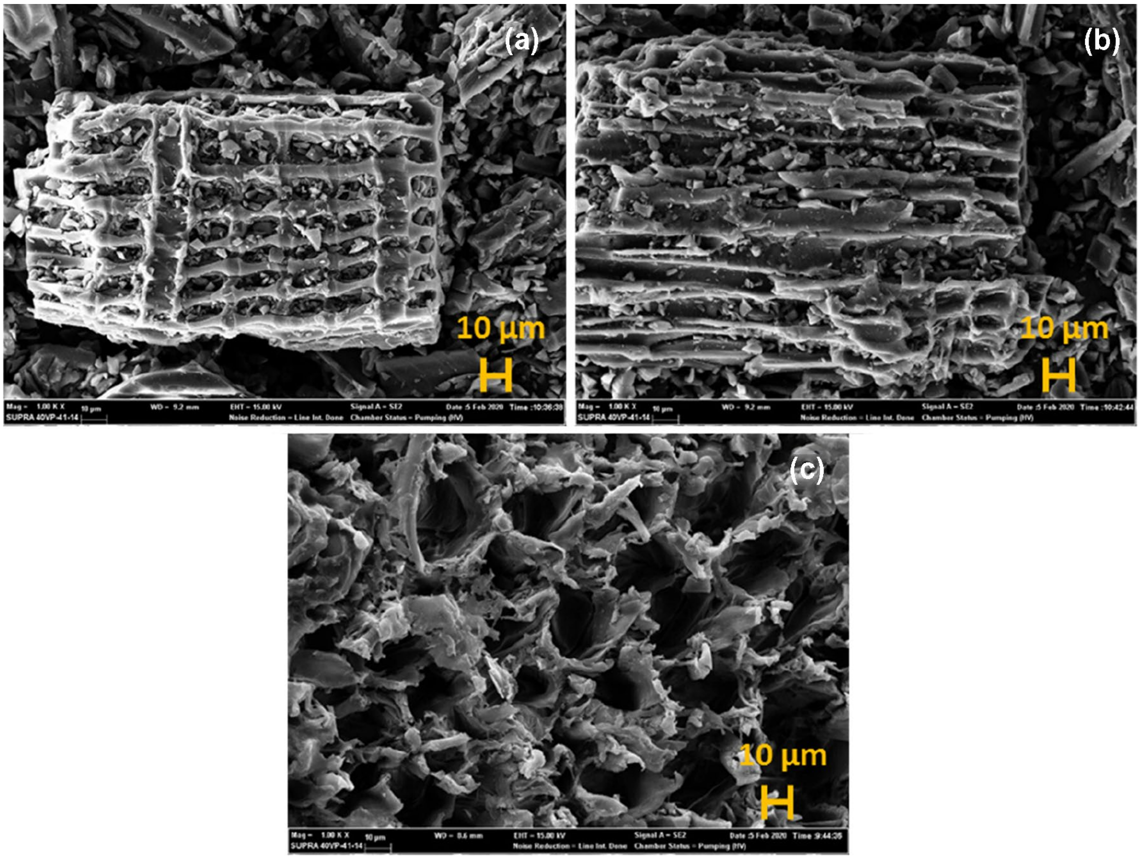


Fig. 2 SEM images of FB samples loaded with different amounts of Pt metal by weight **a** 1Pt-FB, **b** 3Pt-FB, **c** 5Pt-FB

catalysts obtained by loading the FB sample with 1% Pd, 3% Pd and 5% Pd were given in Fig. 7. The catalyst that reduced the amount of acid, which was the undesired product, is the 1 wt% Pd loaded FB catalyst. As the amount of metal loaded on the support material increases, the number of compounds that cannot be detected by the library also increased. Cassoni et al. [3] stated that in the conversion of furan derivatives to alcohol, furfural was converted to furfuryl alcohol by catalytic hydrogenation reaction on Pd-carbon catalyst. The increase in alcohol yield in pyrolysis reactions performed with Pd-loaded biochar compared to the pyrolysis reactions applied without catalyst could be explained by this reaction pathway.

The results obtained by grading the volatile components obtained from the Py-GC/MS experiments using the catalysts obtained by loading the FB sample with 1% Pt, 3% Pt and 5% Pt are given in Fig. 8. The peak area of the highest alcohol content was obtained as 31.02% with 1 wt% Pt loaded catalyst. Yamaguchi et al. [20] stated that sugar alcohols were produced by the hydrogenation reaction of sugar components in the presence of Pt/C catalyst. According to this, higher alcohol yield was obtained by hydrogenation reaction of sugar components hemicellulose and cellulose.

When the effects of Pt and Pd metals on the volatile products were compared, the catalyst that increase the alcohol content the most was the catalyst 1Pd-FB with a peak area of 32.58%. Hydrogenation reactions for catalytic upgrading of volatiles suggest the following reaction sequence: (i) sugar → sugar alcohol (ii) ketone and aldehyde → alcohols (iii) carboxylic acid → alcohols. According to this sequence, the amount of acid obtained as a result of catalytic pyrolysis reactions using precious metals was also reduced. The catalyst that reduced the amount of acid in the volatiles the most was the catalyst with 1 wt% Pd load with a peak area of 18.24%. Also, Wang et al. [45] stated that the chemical composition of the bio-oil changed as a result of the hydrogenation reactions catalyzed by the precious Ru metal catalyst. The yield of aromatics, another desired product was also increased with the deoxygenation of lignin oligomers over Pd and Pt loaded biochar catalyst. However, metal-loaded catalysts caused an increase in one of the undesirable products, PAH. Only 5Pt-FB catalyst slightly reduced the amount of PAH. Possible reaction pathways for alcohol and aromatics production according to the explanations clarified above were given in Fig. 9.

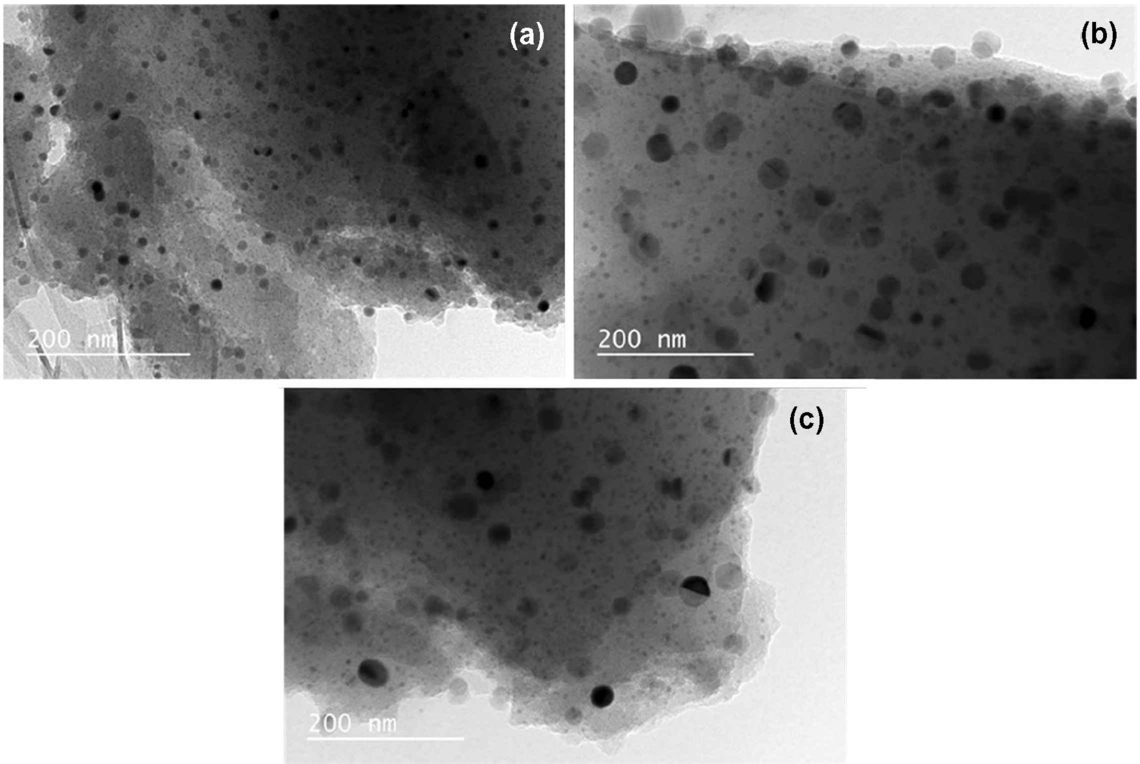


Fig. 3 TEM images of FB samples loaded with different amounts of Pd metal by weight **a** 1Pd-FB, **b** 3Pd-FB, **c** 5Pd-FB

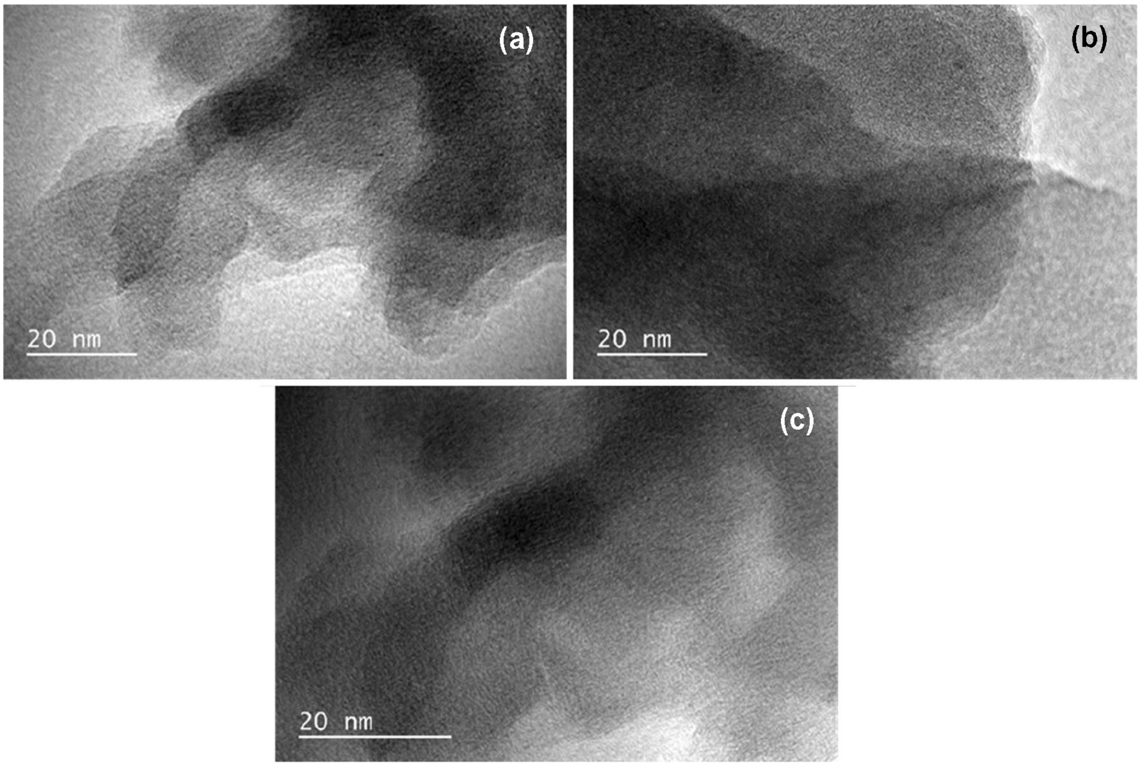


Fig. 4 TEM images of FB samples loaded with different amounts of Pt metal by weight **a** 1Pt-FB, **b** 3Pt-FB, **c** 5Pt-FB

Table 2 ICP-OES results of the FB samples loaded with Pd and Pt metals in different weight ratios

	Pd		Pt (%)	
	Nominal metal loading (%)	Actual metal loading (%)	Nominal metal loading (%)	Actual metal loading (%)
1Pd-BC	1.0	1.03 ± 0.05		–
3Pd-BC	3.0	2.94 ± 0.07		–
5Pd-BC	5.0	4.59 ± 0.09		–
1Pt-BC		–	1.0	1.06 ± 0.05
3Pt-BC		–	3.0	2.52 ± 0.07
5Pt-BC		–	5.0	4.21 ± 0.10

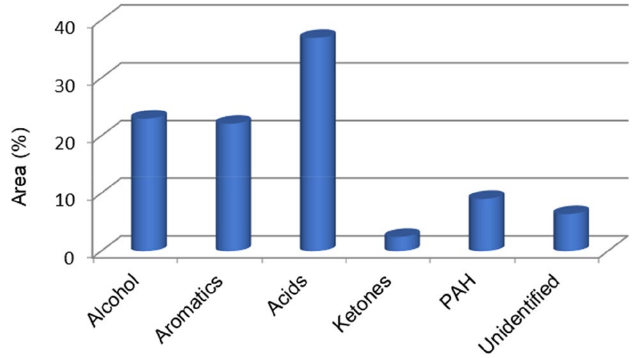


Fig. 5 Chemical composition of *B. napus* subsp. *napus* cake pyrolysis products (unidentified: chemical compounds that could not be identified by the NIST library)

3.4 Future perspective

In studies on the pyrolysis of biomass, it is very important to increase the desired product yield and to use the by-product efficiently. In this study, while valuable chemicals are obtained from biomass by pyrolysis method, biochar, which is produced as a by-product, was also evaluated as a catalyst support material. Considering that catalysts are the highest cost in the chemical industry, the importance of this study is clear in terms of cheap catalyst support material production. In the results obtained, it was determined that the surface areas were not very high and the metals agglomerated in some regions. These problems should be eliminated in future studies. However, when the synthesized catalysts are used, the yield of acids, which is one of the undesirable products, is reduced and the yield of alcohols and aromatics, which are the desired products, is increased. In addition to this, PAHs as another undesired product yields were increased. Therefore, it could be aimed to reduce the amount of PAH by bi-metallic catalyst applications in future studies. As can be seen, the catalyst support material obtained from biochar is very important as it is obtained from both a renewable and sustainable source and can be made available on a larger scale with additional studies.

4 Conclusion

Characterization of physicochemical properties of a biomass is an important point to specify whether it is suitable for pyrolysis. According to the characterization results, *B. napus* subsp. *napus* cake is suitable raw material for pyrolysis due to its high volatile matter content, low ash content, high carbon content and higher heating value. Analytical pyrolysis experiments were executed pyrolysis coupled to GC/MS system which is a useful tool to detect pyrolysis vapors. As indicated above, the main components of pyrolysis products determined were alcohols, aromatics, acids, ketones and PAHs. Thermal degradation mechanism of *B. napus* subsp. *napus* cake was also suggested that depolymerisation and chain scission to levoglucosane derivatives, alcohols, acids, aldehites, ketons and furan derivatives for cellulose and hemicelluloses, while thermal degradation to form aromatic hydrocarbons such as guaiacol, syringol derivatives and lignin oligomers for lignin. According to the Py-GC/MS results, *B. napus* subsp. *napus* cake is a suitable feedstock for production of bio-chemicals. By performing pyrolysis reactions with Pd-BC and Pt-BC catalysts, the yield of acid (undesired product) yield decreased while alcohol and aromatic hydrocarbon (desired product) yield increased. This results showed that the production of carbon support material from biomass, which is a cheap and renewable resource, is a promising study.

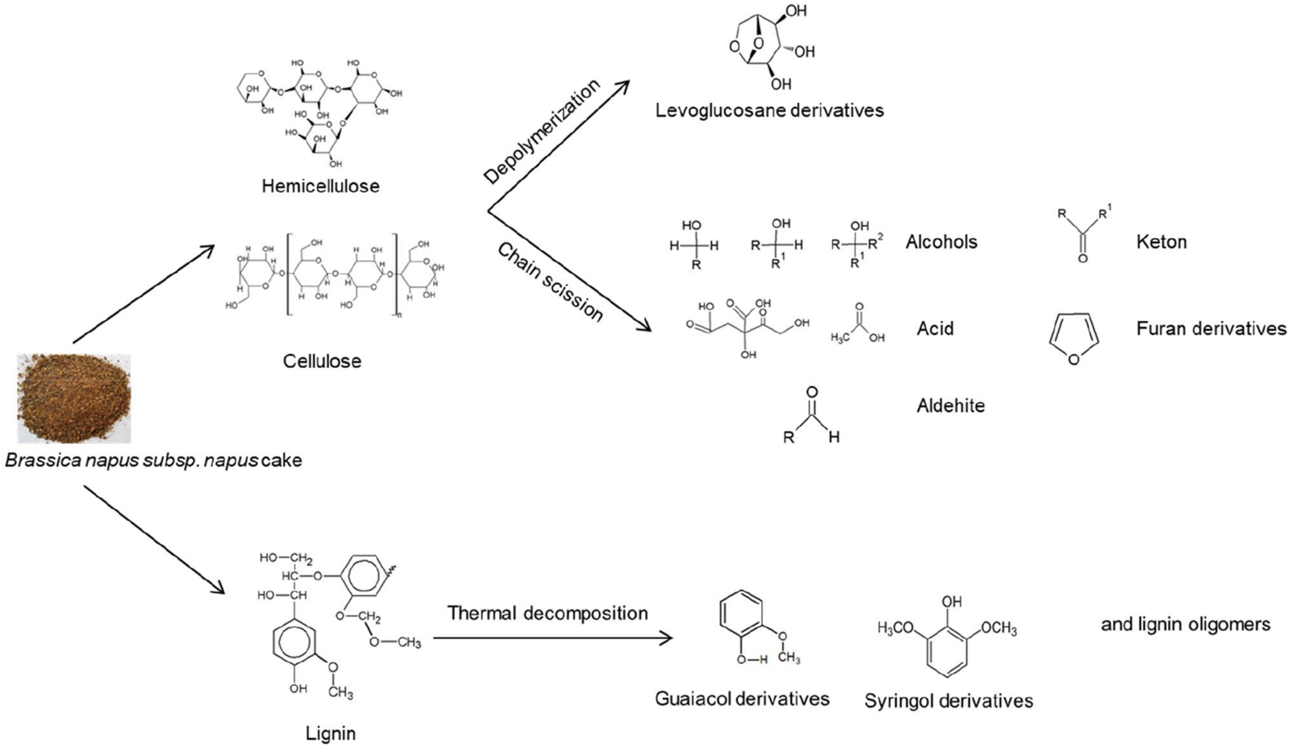
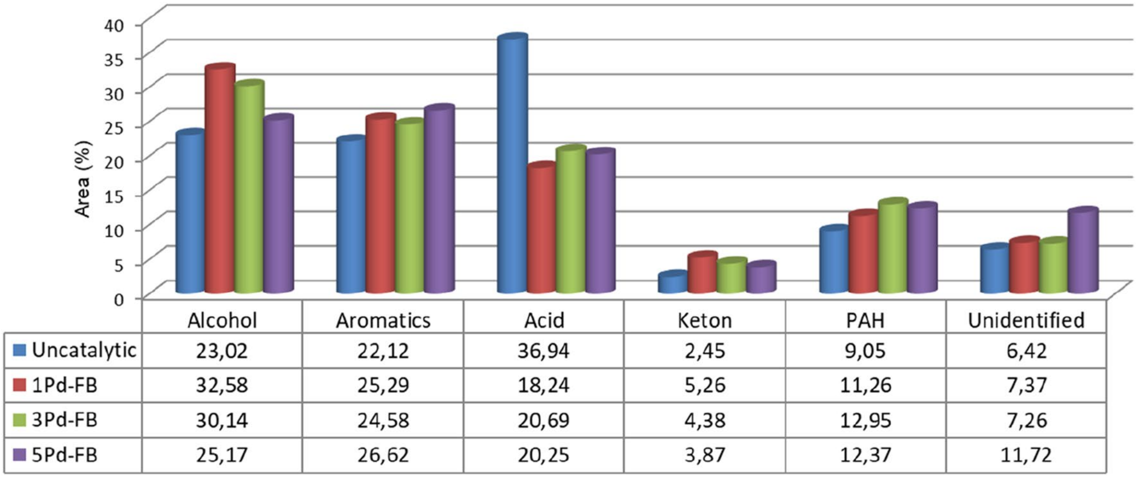
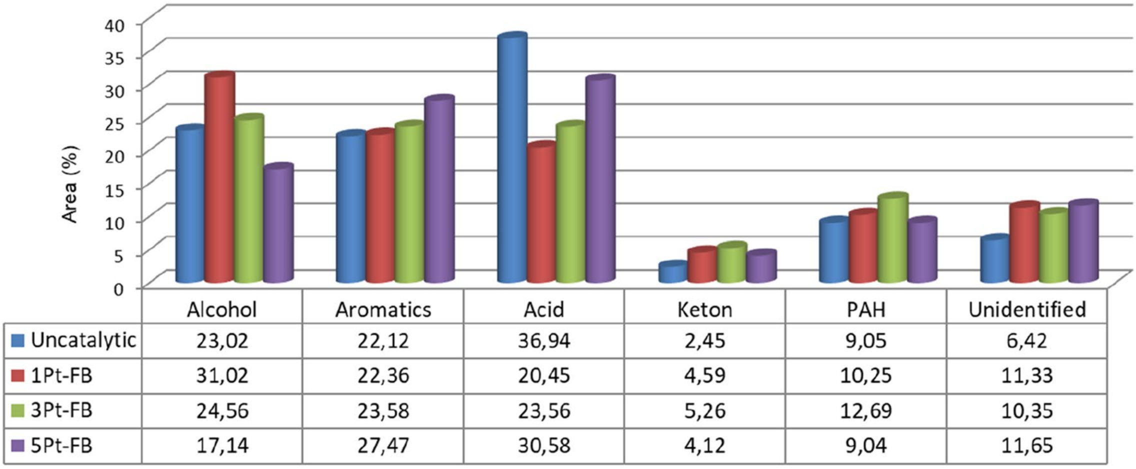


Fig. 6 Reaction scheme for the pyrolysis of *B. napus* subsp. *napus* cake



	Alcohol	Aromatics	Acid	Keton	PAH	Unidentified
🟦 Uncatalytic	23,02	22,12	36,94	2,45	9,05	6,42
🟥 1Pd-FB	32,58	25,29	18,24	5,26	11,26	7,37
🟩 3Pd-FB	30,14	24,58	20,69	4,38	12,95	7,26
🟪 5Pd-FB	25,17	26,62	20,25	3,87	12,37	11,72

Fig. 7 Py-GC/MS results using Pd loaded bio-char catalyst (unidentified: chemical compounds that could not be identified by the NIST library)



	Alcohol	Aromatics	Acid	Keton	PAH	Unidentified
🟦 Uncatalytic	23,02	22,12	36,94	2,45	9,05	6,42
🟥 1Pt-FB	31,02	22,36	20,45	4,59	10,25	11,33
🟩 3Pt-FB	24,56	23,58	23,56	5,26	12,69	10,35
🟪 5Pt-FB	17,14	27,47	30,58	4,12	9,04	11,65

Fig. 8 Py-GC/MS results using Pt loaded bio-char catalyst (unidentified: chemical compounds that could not be identified by the NIST library)

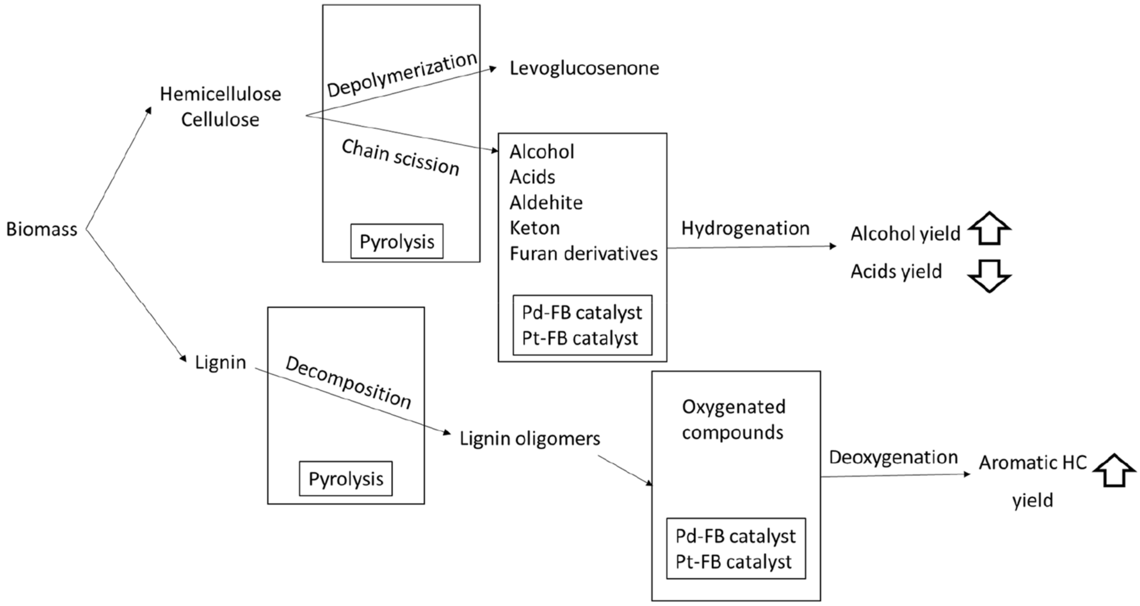


Fig. 9 Possible reaction pathways for alcohol and aromatics production

Author contributions EY: conceptualization, methodology, writing—original draft. FÖG: validation, investigation, writing—review & editing. ST: formal analysis, resources. NÖ: project administration.

Funding Scientific Research Project Commission of Bilecik Seyh Edebali University supported this work financially (Project Number is 2018-02.BŞEÜ.28-01).

Data availability Not applicable.

Code availability Not applicable.

Declarations

Conflict of interest The authors don't have any conflicts of interest.

References

1. Y. Zhu, Z. Li, J. Chen, Green Energy Environ. (2019). https://doi.org/10.1016/j.gee.2019.01.003
2. S. Papari, K. Hawboldt, P. Fransham, Fuel (2019). https://doi.org/10.1016/j.fuel.2019.02.055
3. A. Casoni, P.M. Hoch, M.A. Volpe, V.S. Gutierrez, J. Clean. Prod. (2018). https://doi.org/10.1016/j.jclepro.2018.01.031

4. A. Corma, S. Iborra, A. Velty, Chem. Rev. (2007). https://doi.org/10.1021/cr050989d
5. J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew. Chem. Int. Ed. (2007). https://doi.org/10.1002/anie.200604274
6. A. Higman, S. Tam, Chem. Rev. (2014). https://doi.org/10.1021/cr400202m
7. G. Sribala, H.H. Carstensen, K.M. Van Geem, G.B. Marin, Wiley Interdiscip. Rev. Energy Environ. (2019). https://doi.org/10.1002/wene.326
8. M. Mattonai, A. Watanabe, E. Ribechini, Microchem. J. (2020). https://doi.org/10.1016/j.microc.2020.105321
9. X. Gu, X. Ma, L. Li, C. Liu, K. Cheng, Z. Li, J. Anal. Appl. Pyrolysis (2013). https://doi.org/10.1016/j.jaap.2013.04.009
10. D. Fabbri, G. Chiavari, Anal. Chim. Acta (2001). https://doi.org/10.1016/S0003-2670(01)01359-9
11. M. Mattonai, E.J. Ribechini, Anal. Appl. Pyrolysis (2018). https://doi.org/10.1016/j.jaap.2018.08.029
12. R.V. Silva, N.S. Tessarolo, V.B. Pereira, V.L. Ximenes, F.L. Mendes, M.B. de Almeida, D.A. Azevedo, Talanta (2017). https://doi.org/10.1016/j.talanta.2016.11.005
13. D.C. Elliott, Curr. Opin. Chem. Eng. (2015). https://doi.org/10.1016/j.coche.2015.08.008
14. V.O. Nunes, R.V. Silva, G.A. Romeiro, D.A. Azevedo, Microchem. J. (2020). https://doi.org/10.1016/j.microc.2019.104514
15. M. Peiyong, S. Yadong, X. Xianjun, L. Hui, L. Tao, H. Yunlong, Energy Proc. (2015). https://doi.org/10.1016/j.egypro.2015.02.059
16. T. Aysu, Bioresour. Technol. (2015). https://doi.org/10.1016/j.biortech.2015.05.037
17. Y.H. Chan, K.V. Dang, S. Yusup, M.T. Lim, A.M. Zain, Y. Uemura, J. Energy Inst. (2014). https://doi.org/10.1016/j.joei.2014.03.008
18. N. Ozbay, A.S. Yargic, R.Z.Y. Sahin, E. Yaman, E. Renew, Energy (2019). https://doi.org/10.1016/j.renene.2019.03.071
19. H. Kobayashi, Y. Yamakoshi, Y. Hosaka, M. Yabushita, A. Fukuoka, Catal Today (2014). https://doi.org/10.1016/j.cattod.2013.09.057
20. A. Yamaguchi, O. Sato, N. Mimura, M. Shirai, Catalysis (2016). https://doi.org/10.1016/j.cattod.2015.08.026
21. E. Yaman, T.C. Ulu, N. Özbay, Biomass Convers. Biorefin. (2021). https://doi.org/10.1007/s13399-021-01812-3
22. N. Kaewtrakulchai, R. Kaewmeesri, V. Itthibenchapong, A. Eiad-Ua, K. Faungnawakij, Catalysts (2020). https://doi.org/10.3390/catal10060694
23. J.D.B.D. Moreira, D.B. de Rezende, V.M.D. Pasa, Fuel (2020). https://doi.org/10.1016/j.fuel.2020.117253
24. G. Abdulkareem-Alsultan, N. Asikin-Mijan, H.V. Lee, U. Rashid, A. Islam, Y.H. Taufiq-Yap, Catalysts (2019). https://doi.org/10.3390/catal9040350
25. H. Li, Y.F. Qiu, X.L. Wang, J. Yang, Y.J. Yu, Y.Q. Chen, Chemosphere (2017). https://doi.org/10.1016/j.chemosphere.2016.11.117
26. C.C. Tran, D. Akmach, S. Kaliaguine, Green Chem. (2020). https://doi.org/10.1039/D0GC00680G
27. R. Anşin, Tohumlu Bitkiler Gymnospermae (Açık tohumlular) (1994). https://www.ktu.edu.tr/dosyalar/ormanbotanigi_8ce92.pdf
28. E. Yaman, F.Ö. Gökmen, S. Temel, N. Özbay, G. Özsin, Avr. Bil. Tek. Dergisi (2021). https://doi.org/10.31590/ejosat.858676
29. E. Yaman, A. Ulusal, B.B. Uzun, SN Appl. Sci. (2021). https://doi.org/10.1007/s42452-020-04040-y
30. T. Kubota, H. Ogawa, Y. Okamoto, T. Misaki, T. Sugimura, Appl. Cat. A (2012). https://doi.org/10.1016/j.apcata.2012.06.008
31. M.R.A. Arcanjo, I.J. Silva Jr., E. Rodríguez-Castellón, A. Infantes-Molina, R.S. Vieira, Catal. Today (2017). https://doi.org/10.1016/j.cattod.2016.02.01
32. S. He, C. Sun, H. Du, X. Dai, B. Wang, Chem. Eng. J. (2008). https://doi.org/10.1016/j.cej.2007.12.036
33. D. Liang, J. Gao, J. Wang, P. Chen, Z. Hou, X. Zheng, Catal. Commun. (2009). https://doi.org/10.1016/j.catcom.2009.04.023
34. L. Leng, Q. Xiong, L. Yang, H. Li, Y. Zhou, W. Zhang, H. Huang, Sci. Total Environ. (2020). https://doi.org/10.1016/j.scitotenv.2020.144204
35. S. Joseph, J. Lehmann, *Biochar for environmental management: science and technology*, 1st edn. (GB Earthscan, London, 2009)
36. C.K. Cheng, M.R. Derahman, M.R. Khan, J. Environ. Chem. Eng. (2015). https://doi.org/10.1016/j.jece.2014.10.016
37. C. Zhang, H. He, K.I. Tanaka, Appl. Catal. B (2006). https://doi.org/10.1016/j.apcatb.2005.12.010
38. A.K. Aboul-Gheit, F.K. Gad, G.M. Abdel-Aleem, D.S. El-Desouki, S.M. Abdel-Hamid, S.A. Ghoneim, A.H. Ibrahim, Egypt. J. Pet. (2014). https://doi.org/10.1016/j.ejpe.2014.08.006
39. Y. Bai, C. Wu, F. Wu, B. Yi, Mater. Lett. (2006). https://doi.org/10.1016/j.matlet.2005.12.119
40. A. Fuente-Hernández, R. Lee, N. Béland, I. Zamboni, J.M. Lavoie, Energies (2017). https://doi.org/10.3390/en10030286
41. L. Johnson, W. Thielemans, D.A. Walsh, Green Chem. (2011). https://doi.org/10.1039/C0GC00881H
42. E. Yaman, A.S. Yargic, N. Ozbay, B.B. Uzun, K.G. Kalogiannis, S.D. Stefanidis, A.A. Lappas, J. Clean Prod. (2018). https://doi.org/10.1016/j.jclepro.2018.03.033
43. J.L. Santos, L.F. Bobadilla, M.A. Centeno, J.A. Odriozola, J. Carbon Res. (2018). https://doi.org/10.3390/c4030047
44. M.A. Fraga, E. Jordão, M.J. Mendes, M.M.A. Freitas, J.L. Faria, J.L. Figueiredo, J. Catal. (2002). https://doi.org/10.1006/jcat.2002.3637
45. H. Wang, S.J. Lee, M.V. Olarte, A.H. Zacher, ACS Sustain. Chem. Eng. (2016). https://doi.org/10.1021/acssuschemeng.6b01270