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Upgraded bio-oil production with catalytic co-pyrolysis of spruce sawdust

Ladin talaşının katalitik kopiroliziyle geliştirilmiş biyo-yağ üretimi

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Abstract

This paper aimed to upgrade the bio-oils with the catalytic co-pyrolysis of spruce sawdust. A bubble-fluidized bed pyrolysis reactor was used in the experiments. The effects of the different mixing ratios of spruce sawdust with glycerol (10, 20, and 30 wt%), the usage of different catalysts (HZSM-5 and dolomite), and pyrolysis temperatures (400°C, 450 °C, 500 °C, 550 °C and 600 °C) on the yields and quality of obtained bio-oils were examined. The experimental results revealed that the bio-oil yield improved with an additive of glycerol at all mixing ratios. The highest bio-oil yield (46.4 wt%) was received at a 20 wt% mixing ratio of glycerol and a pyrolysis temperature of 550 °C with a dolomite catalyst. The results of GC-MS indicated that the pyrolysis oil included a high proportion of ketones, phenols, and alcohols, which supported the potential of the catalytic co-pyrolysis of spruce sawdust with glycerol for bio-oil upgrading. The pyrolysis oil from spruce sawdust pyrolysis consisted of a ratio of 4.81% (GC-MS peak area) of unoxygenated hydrocarbons. Furthermore, the unoxygenated components were found to be 8.02% in the bio-oil produced by co-pyrolysis with glycerol. The number of unoxygenated hydrocarbons increased significantly during ex-situ catalytic co-pyrolysis. The unoxygenated hydrocarbons in the bio-oils produced by catalytic co-pyrolysis with HZSM-5 and dolomite were found to be 19.10% and 22.24%, respectively. The co-pyrolysis and catalytic co-pyrolysis results also revealed that the average carbon number of the compounds in the bio-oils depends on the chosen methods and catalysts. Using the catalyst in the reactor resulted in the formation of low-carbon number hydrocarbons. However, when used outside the reactor, the catalysts were observed to be more effective for deoxygenation.

Keywords: Catalytic co-pyrolysis, Biomass, Glycerol, HZSM-5, Dolomite

Öz

Bu makale, ladin talaşının katalitik ko-pirolizi ile biyo-yağların yükseltilmesini amaçlamaktadır. Deneylerde kabarcıklı akışkan yataklı piroliz reaktörü kullanılmıştır. Ladin talaşının gliserol ile farklı karıştırma oranlarının (%10, 20 ve 30 ağırlık), farklı katalizörlerin (HZSM-5 ve dolomit) kullanımının ve piroliz sıcaklıklarının (400 °C, 450 °C, 500 °C, 550 °C ve 600 °C) elde edilen biyo-yağların verimi ve kalitesi üzerindeki etkileri incelenmiştir. Deneysel sonuçlar, biyo-yağ veriminin tüm karıştırma oranlarında gliserol katkı maddesiyle arttığını ortaya koymuştur. En yüksek biyo-yağ verimi (%46.4 ağırlıkça), %20 gliserol karıştırma oranında ve dolomit katalizörüyle 550 °C'lik bir piroliz sıcaklığında elde edilmiştir. GC-MS sonuçları, piroliz yağının yüksek oranda keton, fenol ve alkol içerdiğini göstermiştir; bu da biyo-yağ iyileştirmesi için gliserol ile ladin talaşının katalitik eş-pirolizinin potansiyelini desteklemektedir. Ladin talaşı pirolizinden elde edilen piroliz yağı, %4.81 oranında (GC-MS pik alanı) oksijensiz hidrokarbonlardan oluşmuştur. Ayrıca, gliserol ile eş-pirolizle üretilen biyo-yağda oksijensiz bileşenlerin %8.02 olduğu bulunmuştur. Ex-situ katalitik eş-piroliz sırasında oksijensiz hidrokarbonların sayısı önemli ölçüde arttı. HZSM-5 ve dolomit ile katalitik eş-pirolizle üretilen biyo-yağlardaki oksijensiz hidrokarbonların sırasıyla %19.10 ve %22.24 olduğu bulundu. Eş-piroliz ve katalitik eş-piroliz sonuçları ayrıca biyo-yağlardaki bileşiklerin ortalama karbon sayısının seçilen yöntem ve katalizörlere bağlı olduğunu ortaya koydu. Reaktörde katalizörün kullanılması düşük karbon sayılı hidrokarbonların oluşumuyla sonuçlandı. Ancak katalizörlerin reaktör dışında kullanıldığında oksijensizleştirme için daha etkili olduğu görülmüştür.

Anahtar Kelimeler: Katalitik kopiroliz, Biyokütle, Gliserol, HZSM-5, Dolomit

1 Introduction

It is essential to meet the energy needs of the increasing population with clean and renewable energy sources. Energy consumption and environmental pollution are increasing because of the rise in human population. Therefore, just meeting the energy demand is not enough. Clean, sustainable energy resources that meet the increasing need should be created [1-3]. Bioenergy is promising as an alternative to clean and renewable energy. Bioenergy is valuable because it is renewable, meets multiple needs, and does not harm the environment during production. It is essential to balance the carbon footprint created by the increasing population by recycling waste biomass. [4, 5].

The fact that biomass to be chosen as an energy source serves more than one purpose makes this resource valuable. In addition, there are some disadvantages to chemicals and fuels obtained from biomass. Biomass has a complex structure and high oxygen content, which makes it difficult to control chemical reactions and maintain product quality. Problems such as high acidity, high oxygen content, and low calorific value are encountered in fuels obtained from biomass [6, 7]. However, when considered an energy source, its abundance, easy production, cleanliness, and cheapness make it attractive for research on this subject [8]. There are many different ways to obtain energy from biomass. Some of them are hydrolysis, biophotolysis, pyrolysis, fermentation, combustion, and gasification [9]. Among the various biomass conversion technologies, pyrolysis has garnered substantial interest. Hydrolysis can transform Organic compounds into valuable products such as bio-oil, biochar, and bio-gas. A diverse array of feedstocks, including agricultural residues, forestry by-products, and dedicated energy crops, can be utilized for pyrolysis.

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The main product, bio-oil formed due to pyrolysis, has yield values that can reach up to 70 % by weight, depending on various factors (reactor operating conditions, holding time, biomass properties, etc.).[10]. Most fossil fuels are considered gasoline, diesel, aviation, and jet fuel in the transportation sector. Crude bio-oil obtained through pyrolysis has properties such as high viscosity, acidity, and chemical instability that make it unsuitable for use as fuel. For this reason, bio-oil properties need to be improved for direct use. One obstacle to using bio-oils as a renewable alternative to fossil fuels is their significantly high oxygen content of approximately 50 % by weight. Pyrolysis oil is a complex structure consisting of various oxygenated components such as ketones, aldehydes, phenols, and sugars. The possibilities of using methods used in oil refining processes to obtain high-value-added petroleum products from bio-oil are also being investigated. However, it has disadvantages in fluidized bed pyrolysis and hydrothermal processes. When large quantities of bio-oil are directly processed using fluidized bed pyrolysis, a high amount of coke is formed, decreasing liquid yield. Studies on hydrothermal processes with bio-oil can provide higher degrees of deoxygenation than studies conducted with fluidized beds. In addition, hydrogen creating high partial pressure has increased process costs [11].

Many studies have been carried out on pyrolysis and co-pyrolysis [12-14]. Moreover, co-pyrolysis or catalytic pyrolysis methods have been used to reduce the oxygen content and decrease the C/H ratio of pyrolysis oil. The purpose of co-pyrolysis or catalytic pyrolysis is to remove the oxygen contained in the bio-oil by converting it into CO_2, CO, etc. gases or to ensure that the carbons in the structure bind excess Hydrogen. Rotliwala and Parikh studied the co-pyrolysis of high-density polyethylene (HDPE) with defatted Jatropha cake (JK) in a batch reactor. The co-pyrolysis process was carried out in nitrogen flow at atmospheric pressure and a temperature of 450 °C. The bio-oil yield obtained from co-pyrolysis was determined to be 63 %. Bio-oils obtained from co-pyrolysis were examined using analysis of GC-MS and ASTM D86 standards. The co-pyrolysis of HDPE with JK significantly increased the proportion of components with a gasoline-like carbon range (C6-C12) by up to 45 % compared to when HDPE was pyrolyzed alone [15]. Solak et al. [16, 17] obtained the highest bio-oil yield of 79.5 % from the co-pyrolysis of cellulose and polyethylene at 500 °C. Brebu et al. [18, 19] investigated the pyrolysis of lignin with polymers such as PE, PP, PS, and PC. He stated that the liquid yield obtained only reached 53.2-62.7 % by weight. In addition, they reported that they co-pyrolyzed pine cones with synthetic polymers and found that they gave a liquid yield of 63.9-69.7 % by weight. When biodiesel is produced by transesterification of grease, glycerin is released as a significant by-product. Mihalcik et al. [20] utilized pyrolysis coupled with gas chromatography-mass spectrometry (Py/GC-MS) to investigate the catalytic fast pyrolysis of lignocellulosic biomass, including oak, corn cob, corn stover, and switchgrass, along with the primary biomass components: cellulose, hemicellulose, and lignin. The various catalysts were tested in their study. The HZSM-5 exhibited the highest efficiency in producing aromatic hydrocarbons from the pyrolytic vapors.

Pan et al. [21] investigated the catalytic pyrolysis of Nannochloropsis sp. (a green microalgae residue) with an HZSM-5 catalyst in a fixed-bed reactor. Their findings revealed that the bio-oil obtained via pyrolysis had an oxygen content of 30.1wt% and a heating value of 24.6 MJ/kg. The bio-oil produced via catalytic pyrolysis had a significantly lower oxygen content (19.5 wt%) and a higher heating value (32.7 MJ/kg) than the bio-oil from non-catalytic pyrolysis. Bio-oil from direct pyrolysis primarily consists of long-chain carbon compounds. On the other hand, the bio-oil obtained via catalytic pyrolysis products were predominantly aromatic hydrocarbons.

The boiling point of glycerol is 290 °C, and when higher temperatures are reached in pyrolysis, components such as CO, H_2, CO_2, CH_4, etc. are formed. In this case, Glycerol becomes a usable material in co-pyrolysis for hydrogen enrichment and deoxygenation. Carmines et al. [22] analyzed by adding different amounts of glycerol (5 %, 10 %, and 15 %) to tobacco and collecting the products of pyrolysis and particulate matter from the pyrolysis gas during the co-pyrolysis of the mixture. The results showed that glycerol diluted the smoke and increased the humidity. They also found that co-pyrolysis of tobacco with 10% and 15% glycerol increased acrolein content in the smoke. Nicotine, aromatic amine, acetaldehyde, propanol, phenols, N-nitrosamines, and other compounds have also been shown to be reduced. Skoulou et al. [23] prepared hydrogen-enriched fuel via co-pyrolysis using glycerin and olive stone in their study. They revealed that the hydrogen content in the gas obtained from pyrolysis increased by 11.6 % in the mixture of olive stone with 25 % glycerol.

This study aims to investigate the catalytic co-pyrolysis of spruce sawdust and glycerol with HZSM-5 and dolomite. It also seeks to elucidate the synergistic effects of glycerol on the co-pyrolysis with woody biomass. In this context, direct and catalytic fast pyrolysis of spruce sawdust was examined by a fluidized bed reactor at different temperatures between 400 °C and 600 °C. In experimental studies, HZSM-5 was used as a commercial catalyst, and dolomite was chosen as a natural catalyst. Catalytic co-pyrolysis trials were conducted as in-situ and ex-situ. TGA and elemental analyses of spruce sawdust were performed. GC-MS and FT-IR analyses were performed to examine the quality of bio-oil. The yields of the products obtained from the pyrolysis process performed at 3 different temperatures were compared. The effect of the catalyst on the obtained bio-oil was examined.

2 Material and method

2.1 Materials

Furniture manufacturers operating in Samsun province of Turkey supplied spruce sawdust used in experimental studies. The spruce sawdust were sieved to be 0.75-1.2 mm. The drying process was carried out by keeping it in an oven at 75 °C for 12 hours. Vario Cube Elemental Analyzer was used for elemental analyses. Muffle and convection furnaces performed a proximate analysis of spruce sawdust samples. The samples were air-dried at 105 °C by the ASTM E871-92 standard and waited in the oven until they reached a constant weight. The samples placed in the lidded porcelain container were heated in a muffle furnace at 850 °C for 70 minutes. After the process, the remaining samples were cooled, and their weights were measured. For ash determination according to the ASTM D1102-84 standard, the samples were heated in lidless porcelain containers at 950 °C for 2 hours. The amount of fixed carbon was calculated by subtracting the sum of the resulting ash, moisture, and volatile substances from the initial mass. Glycerol (99.7%) used in the studies was purchased by Beyanlab Laboratory Products Industry Trade Limited Company. Glycerol was mechanically mixed with spruce sawdust at 10 wt%, 15 wt%, and 20 wt%.

2.2 Catalyst

The dolomite catalyst was provided by Ataman Chemicals. It was then ground and passed through an 80-mesh sieve. The dolomite with the appropriate size was taken in an oven for drying at 105 °C for 18 hours. The surface area of the dolomite catalyst as a result of Brunauer-Emmett-Teller (BET) analysis was determined as 3.975 m^2/g. The HZSM-5 catalyst was supplied by ACS Material. In the study of the catalyst made by the seller, the SiO_2/Al_2O_2 molar ratio was stated as 26. Crystal size, H_2O, and BET surface area values of HZSM-5 were specified as 800 nm, <5 wt%, and 362 m^2/g, respectively. Catalysts were used in ex-situ experiments as 4 g to ensure that the pyrolysis vapor passing through the metal container wholly passed through the catalyst. In the in-situ experiments, 4 g was added to raw materials with a total weight of 40 g and mixed to form a homogeneous mixture.

2.3 Thermogravimetric analysis (TGA)

TA Instruments SDTQ600 device was used in thermogravimetric analysis to determine the thermal behavior of spruce sawdust and temperature-dependent mass losses. The sample mass for the experiment was 2 mg. The initial temperature of experiments was set at room temperature. In analyses performed up to 800 °C, the heating rate was set as 10 °C/min. Nitrogen gas flow was set at 50 ml/min as a carrier gas, providing an inert atmosphere in the analyses. Furthermore, TGA analysis was performed twice to minimize the experimental error.

2.4 Characterization of bio-oil

The molecular bonds in the pyrolysis oil produced from spruce sawdust were identified via FTIR analysis. Bruker Tensor 27 IR analyzer, which measures in the range of 400-4000 cm^{-1}, was used in the analyses. Gas Chromatography-Mass Spectrometry analysis was performed using the Shimadzu GCMS-QP2020 plus device to determine the compounds contained in the bio-oil. The bio-oils to be analyzed were diluted with Methanol at the HPLC level at a ratio of 1/100 by volume. 2 µl of the sample was used for each injection. Restek Rxi-5ms (30m x 0.25 mm, 0.25 µm Film thickness) column was used in GC-MS analyses. Helium was used as a carrier gas in the sample analysis, and the injector temperature was determined as 250 °C; the program was adjusted to start from 50 °C, reach 280 °C at a speed of 10 °C/min, and wait for 1 minute at 280 °C.

2.5 Experimental setup

The experimental system established to obtain bio-oil from spruce sawdusts by pyrolysis is given in Figure 1. The raw material was fed into the bubble-fluidized bed pyrolysis reactor from the top at a constant rate of 0.1 g/s into the reaction zone. The reactor, which had an inner diameter of 50 mm and a length of 400 mm, was heated only with electrical heaters. Nitrogen (N) gas was used to carrier gas and provide an inert environment during the experiments. Nitrogen gas was connected to the reactor from the bottom, and the flow was provided at a constant flow rate of 100 ml/min (the flow rate was standardized for 0 °C and 1 atm conditions). Temperatures were measured with 7 thermocouples inside and outside the reactor. Silica sand was used as the bedding material in all experimental studies carried out at different temperatures. Pyrolysis was performed with 40 g of sample in each experimental set. The reactor's gases were passed through the condenser at 0 °C. A second cooler and, finally, a gas washing chamber were used to increase the condensation of the gases. Since the amount of usable, helpful liquid was prioritized when calculating the total liquid yield, the liquid products in the glass containers were weighed to determine the total mass. The obtained products were filtered using filter paper and separated from solid particles.

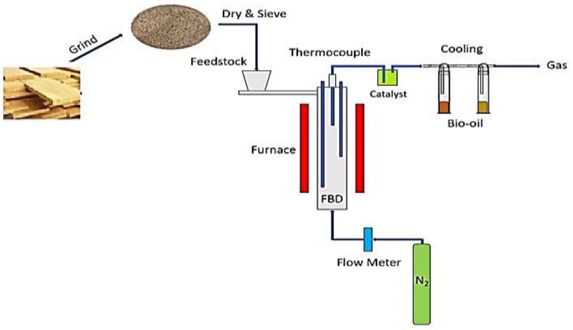

Figure 1. Schematic view of the pyrolysis system.

3 Results

The sample homogeneity was ensured to avoid errors related to particle size during the thermal and experimental analysis of spruce sawdust. Proximate and ultimate analyses are crucial for controlling and understanding the pyrolysis reactions because of the complex structure of woody biomass. These analysis results are shown in Table 1. The fixed carbon, ash, moisture, and volatile matter contents of the spruce sawdust were found to be 19.96 wt%, 5.49 wt%, 9.99 wt%, and 75.54 wt%, respectively. Excessive humidity may cause adverse effects such as high heat requirement for evaporation [24]. It is seen that the hydrogen, carbon, oxygen, and nitrogen contents of spruce sawdusts are 6.07 wt%, 50.44 wt%, 43.19 wt%, and 0.3 wt%, respectively. It can be seen that spruce sawdust alone cannot provide the desired H/C ratio to obtain diesel fuel-like bio-oil. In addition, the high oxygen content indicates that the pyrolysis oil will be rich in oxygen and might contain acid, alcohol, and ketone-like structures. For this reason, bio-oil should be enriched with hydrogen and oxygen removed. It is known that the quality of pyrolysis oil increases, its calorific value increases, and its oxygen content decreases thanks to co-pyrolysis [25-28]. Compared to enriching bio-oils with hydrogen at high pressure, co-pyrolysis is a safer and easier way to produce quality bio-oil [13, 29-31].

Table 1. Proximate and ultimate analysis of spruce sawdust.

	Compound	wt%
Ultimate analysis	C	50.44
	H	6.07
	N	0.3
	O	43.19
Proximate analysis	Fixed Carbon	19.96
	Moisture	9.99
	Volatiles	75.54
	Ash	5.49

The curves obtained from thermogravimetric analysis applied to spruce sawdust are presented in Figure 2. The mass loss started with the increase in temperature and gave the first peak at approximately 63 °C. As a result of the evaporation of moisture at temperatures up to 207 °C, the spruce saw dust lose approximately 9 % mass. Subsequently, with the increase in temperature, the decomposition of hemicellulose began rapidly. It reached its maximum mass loss rate at 345 °C, where hemicellulose and cellulose decompose. At 390 °C, where the curve started to become linear, the total mass loss was observed to be 70 %. When the temperature reached 500 °C, the passive pyrolysis zone was entered. The lignin degrades slowly in this region [32].

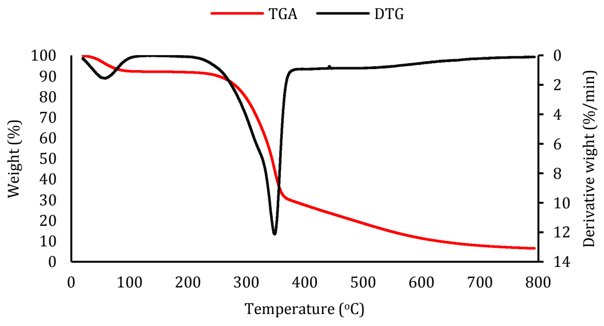

Figure 2. TGA and DTG curves of spruce sawdust.

In the pyrolysis of spruce sawdust carried out at different temperatures, the highest liquid product yield was obtained at 550 °C. While the temperature increased the liquid and gas product yield, it caused the biochar yield to decrease. Heating rates were kept constant for all temperatures. In addition, feed rates and carrier gas flow rates were kept constant. It was not expected to see a difference at the desired level in product conversion when increasing the temperature above 600 °C. For this reason, this temperature was not exceeded. The pyrolysis product yields of spruce sawdust at different temperatures are given in Figure 3.

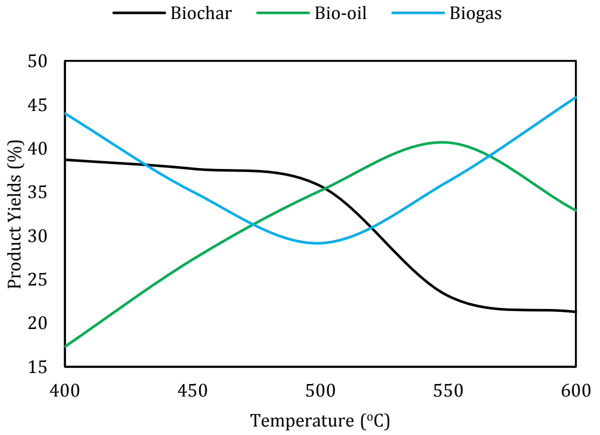

Figure 3. Product yields in pyrolysis of spruce saw dusts at different temperatures.

In pyrolysis at 400 °C, the product yields of bio-oil, bio-char, and biogas were determined as 17.32 wt%, 38.69 wt%, and 43.99 wt%, respectively. The biochar, bio-oil, and biogas yields in pyrolysis at 600 °C were obtained as 21.28 wt%, 32.89 wt%, and 45.83 wt%, respectively. The pyrolysis oil yield increased significantly at 550 C temperature, and the highest pyrolysis oil yield was obtained at 40.66 wt%. The co-pyrolysis and catalytic co-pyrolysis experiments were conducted at 550 °C temperature because the highest bio-oil yield of pyrolysis was obtained at this temperature. Co-pyrolysis is a well-known method to improve bio-oil quality obtained from pyrolysis [22, 23, 28, 33]. In co-pyrolysis, choosing materials that are compatible with each other and will create a synergistic effect is important. Co-pyrolysis with glycerol was evaluated to obtain high-quality bio-oil from spruce sawdust. It is known in many studies that glycerol has positive effects on bio-oil. Three different mixture ratios were used in the experiments with glycerol. The yields of the products obtained from the co-pyrolysis of spruce sawdust with glycerol at different rates are given in Figure 4. When the liquid product amounts obtained from each mixture ratio were evaluated, it was seen that the 20% mixture amount gave the highest liquid yield. The liquid product yields obtained for 10 wt%, 20 wt%, and 30 wt% mixing ratios at 550 °C are 40.17 wt%, 44.11 wt%, and 43.59 wt%, respectively. Biochar yield decreased with increasing mixing ratio. It was observed that more liquid and gaseous products were formed with the increase in the mixing ratio. The results of co-pyrolysis revealed that the glycerol positively impacted the formation of both liquid and gaseous products in the co-pyrolysis reactions. However, increasing the rate of glycerol, the second component of co-pyrolysis, can enhance the conversion to gas product. In addition, it might evaporate before the pyrolysis and condense in the condensation zone. The experimental studies focused on the highest liquid product yield. The experiments of catalytic co-pyrolysis were conducted with a 20 wt% glycerol mixing ratio.

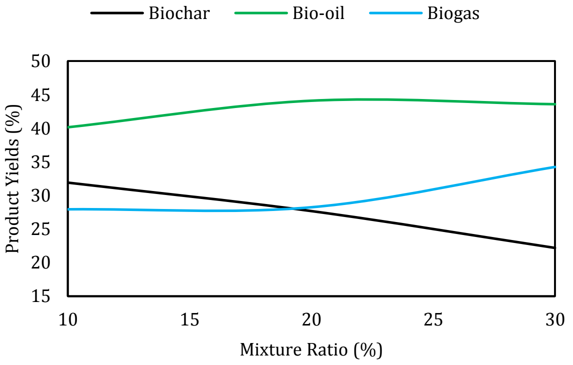

Figure 4. Product yields in co-pyrolysis of spruce saw dusts with glycerol at different mixing ratios.

The HZSM-5 catalyst was used as an acidic and commercial catalyst. The dolomite catalyst was used as an alkaline and natural catalyst. Catalytic co-pyrolysis experiments were carried out in two stages: in-situ and ex-situ. The catalysts were mixed with the raw material in the in-situ catalytic co-pyrolysis of spruce sawdust mixed with glycerol. In ex-situ experiments, the pyrolysis vapor exiting the reactor was passed through a metal enclosed, including the catalyst. The yields of the products obtained from catalytic co-pyrolysis experiments are given in Figure 5. In all experiments, bio-char yields decreased in co-pyrolysis experiments using the HZSM-5 catalyst. Biogas yields increased with HZSM-5. The structure of the catalyst used for pyrolysis generally affects product yields slightly. However, when acidic zeolitic catalysts are used, the chemical composition of the bio-oil may differ considerably [8]. The HZSM-5 catalyst reduced the amount of biochar with in-situ experiments compared to ex-situ experiments. However, the HZSM-5 showed greater efficiency and raised the gas product yield in ex-situ experiments. The HZSM-5 catalyst is less effective when used in the reactor, which may be caused by the temperature triggering irreversible deactivation or by contamination of the catalyst that limits its effectiveness [33-36]. The catalyst can be used for a long time and remains clear at ex-situ catalytic pyrolysis [37-39].

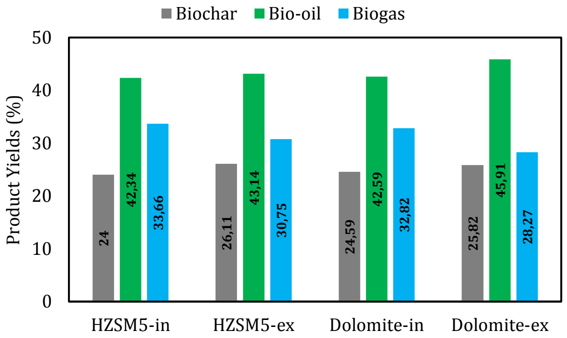

Figure 5. Product yields in co-pyrolysis of spruce sawdust and glycerol (20 wt.%) with different catalysts.

The dolomite catalyst increased biochar yields with in-situ experiments. However, the dolomite catalyst slightly increased the liquid product yield with ex-situ experiments. The dolomite catalyst decreased biogas yields in both situations. In addition, bio-oil yield decreased by 1.52 % with in-situ experiments. A dolomite catalyst is often used to gasify biomass. Dolomite usually contains calcium and magnesium. Due to dolomite structure, it reduces tar production by breaking down and re-forming high molecular weight components and increases the amount of gas products [40, 41]. The dolomite catalyst increased the gas product yield in both cases. The dolomite used was not subjected to the calcination process. It was observed that the gas product yield of some independently calcined dolomite was increased [42-44]. Calcined dolomite consists of mixtures of CaO and MgO. MgO reduces the acid composition of bio-oil and promotes ketonization [45]. CaO catalyzes decarboxylation reactions and increases hydrocarbon formation [46]. In the experiments, partial calcination of the dolomite used in the reactor with the rising temperature may have caused the liquid product yield to increase while the gas product yield to decrease. The curves obtained from the FTIR analysis performed to determine the functional groups of the components in bio-oils are given in Figure 6. Since a diesel-like bio-oil is targeted, oxygen-containing compounds should not be in the liquid product. However, when the curves for all cases were examined, the peaks between the wavelengths of 3200-3700 cm^{-1}, which showed O-H stretching vibrations, showed that there were oxygen-bonded compounds in all the bio-oils. It appears that there are a lot of oxygenated components in the bio-oil obtained with the pyrolysis of spruce sawdust.

The co-pyrolysis results with catalysts showed that oxygen-containing components decreased. It can be said that O-H bonded carboxylic acid and alcohol structures exist in bio-oils. C-H stretching vibrations in the band gap of 2695-3333 cm^{-1} and C-H bending vibrations in the band gap of 1350-1475 cm^{-1} showed the presence of alkane and aldehyde structures in the bio-oil. Similar peaks at a wavelength of 1700 cm^{-1} in all structures indicated C-O bonds, indicating the presence of ketones, carboxylic acids, and aldehydes in the bio-oils. In addition, C-O stretching vibrations between 950-1300 cm^{-1} showed that alcohol and ester structures may be among the compounds [47, 48].

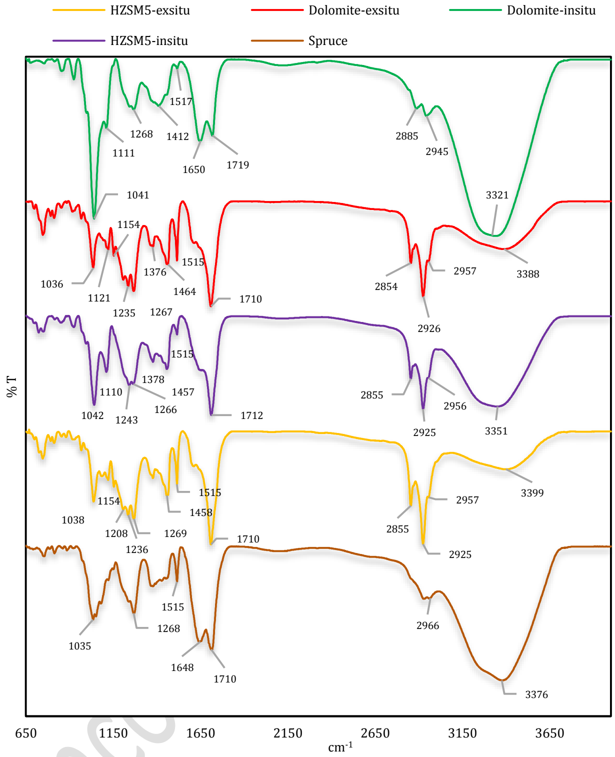

Figure 6. FTIR curves of bio-oil obtained from catalytic co-pyrolysis with HZSM-5 and dolomite.

Catalysts such as HZSM-5 and dolomite enhance decarboxylation and decarbonylation reactions, facilitating the conversion of oxygenated compounds in biomass into gases such as carbon dioxide (CO_2) and carbon monoxide (CO). These processes significantly contribute to the reduction of oxygen content in bio-oil. The strong acidic structure of HZSM-5 promotes the decomposition of oxygenated compounds, enabling the removal of oxygen atoms from hydrocarbon chains. These oxygen atoms are subsequently converted into water (H_2O) or other volatile oxygenated compounds, decreasing the residual oxygen content in the bio-oil. Additionally, the high aromatization capacity of HZSM-5 facilitates the breakdown of oxygenated compounds, leading to the formation of more stable, low-oxygen aromatic hydrocarbons [49]. As a dual-function catalyst, Dolomite exhibits both acidic and basic properties, enabling the selective removal of oxygenated compounds. Furthermore, dolomite's ability to capture carbon dioxide contributes indirectly to reducing oxygen content in the bio-oil [50].

GC-MS analysis was performed to get specific results about the contents of the bio-oils obtained from the experiments. The data obtained from the GC-MS are given in Table 2 for the best results. The commentary about FTIR analysis results was confirmed by GC-MS results. The bio-oil obtained from the pyrolysis of spruce sawdust contained mainly oxygenated hydrocarbons. The broad O-H peak seen in the FTIR analysis supported this situation. The GC-MS results revealed that furan, aldehyde, alcohol, and phenol compounds comprised the majority. The number of oxygen-free hydrocarbons was determined as 4.81 % (peak area). Benzene, alcohol, and aliphatic hydrocarbons were primarily seen in bio-oil obtained from co-pyrolysis. The oxygen-free hydrocarbons increased with glycerol at 8.02%. Although the increase is significant, it is not sufficient for use as a diesel fuel. The oxygen-free hydrocarbons peak areas in the pyrolysis oils produced from catalytic co-pyrolysis experiments were determined as 8.46 %, 19.10 %, 10.28 % and 22.24 % for HZSM5-insitu, HZSM5-exsitu, dolomite-insitu and dolomite-exsitu, respectively. The highest amount of aliphatic hydrocarbon was observed in the co-pyrolysis of dolomite-exsitu. The highest deoxygenation was obtained using a dolomite catalyst compared to other catalytic co-pyrolysis experiments. With many features of the HZSM-5 catalyst, such as its three-dimensional pore structure, acidic characteristics, and ion exchange capacity, reduces the number of oxygenated components. It causes an increase in the number of aromatic hydrocarbons [8].

The bio-oil compounds derived from spruce pyrolysis exhibit shorter carbon chains than those obtained through catalytic co-pyrolysis. The average carbon chain length was calculated based on the composition of the bio-oils. The average carbon chain lengths for spruce, HZSM5-ex situ, and dolomite-ex situ bio-oils were 7.12, 10.76, and 10.98, respectively, indicating that HZSM-5 and dolomite catalysts facilitated the formation of longer carbon chains. The carbon chain distributions in the bio-oils were compared to the carbon ranges of fossil fuels. The carbon ranges for diesel, kerosene, and gasoline were determined as C_8–C_{21}, C_6–C_{16}, and C_4–C_{12}, respectively. The similarity of the bio-oils to the diesel fuel carbon range was found to be 42.45%, 76.80%, and 76.07% for spruce, HZSM-5-ex situ, and dolomite-ex situ, respectively. The diesel fuel carbon range of the HZSM-5-ex situ and dolomite-ex situ bio-oils was similar. Among the samples, the dolomite-ex situ bio-oil exhibited the closest structural resemblance to diesel fuel.

This study similarly promoted the formation of aromatic and aliphatic hydrocarbons, as well as a decrease in the number of oxygenated compounds. However, the HZSM-5 catalyst did not show the desired effect on catalytic co-pyrolysis compared to dolomite. Dolomite catalyst increases the formation of smaller hydrocarbon structures by promoting catalytic cracking in bio-oil. In particular, it converts carboxylic acid structures into ketones by ketonization. In addition, it contributes to the transformation of lignin-derived oligomers into aromatic and oxygenated phenol structures [41, 51, 52]. The results showed that dolomite is more effective than HZSM-5 in catalytic co-pyrolysis.

Table 2. GC-MS results of pyrolysis oils produced from catalytic co-pyrolysis.

	Spruce		*HZSM5-exsitu*		*Dolomite-exsitu*	
Peak	Area %	Name	Area%	Name	Area %	Name
1	2,39	Glycerol	1,27	2,2-Dimethoxybutane	0,35	N-Propyl Acetate
2	4,81	N-Methyl-N-(Methyl-D3)Aminoheptane	1,84	Furfural	1,77	2,2-Dimethoxybutane
3	0,78	1-Hydroxy-2-Butanone	0,86	Furfuryl Alcohol	1,91	Furfural
4	0,83	Methyl Pyruvate	0,50	1,2-Epoxy-3-Propyl Acetate	1,01	Furfuryl Alcohol
5	6,28	Furfural	0,71	2-Methyl-2-Cyclopentenone	0,75	2-Methyl-2-Cyclopentenone
6	4,52	Furfuryl Alcohol	0,50	5-Methyl-2-Furfural	0,55	2-Furancarboxaldehyde, 5-Methyl-
7	1,37	1,2-Epoxy-3-Propyl Acetate	1,07	4-Methyl-5h-Furan-2-One	0,92	Xylose
8	1,20	2-Methyl-2-Cyclopentenone	0,54	Phenol	0,64	Phenol
9	0,88	1-(3h-Imıdazol-4-Yl)-Ethanone	2,23	1,2-Cyclopentanedione, 3-Methyl-	0,55	N-Tetradecane
10	1,72	2(5h)-Furanone	0,51	2,3-Dimethyl-2-Cyclopenten-1-One	2,10	Corylon
11	3,07	1,2-Cyclopentanedıone	1,45	O-Cresol	0,57	2,3-Dimethyl-2-Cyclopenten-1-One
12	0,62	N-Propyl Acetate	0,87	N-Butylbenzene	2,65	O-Cresol
13	1,68	5-Methyl-2-Furfural	2,52	O-Cresol	2,65	Phenol, 2-Methyl-
14	0,85	4-Methyl-5h-Furan-2-One	4,36	Mequinol	4,63	Mequinol
15	0,61	Phenol	2,83	1-Acetoxy-2,3-Dıhydrox	3,44	1-Acetoxy-2,3-Dıhydrox
16	1,09	2,2-Diethyl-3-Methyloxazolidine	0,44	Dodecane, 4,6-Dimethyl-	0,56	Dodecane, 4,6-Dimethyl-
17	4,05	Corylon	0,51	3-Ethyl-2-Hydroxy-2-Cyclopenten-1-One	0,93	3,5-Xylenol
18	1,19		1,35	Phenol, 2,6-Dimethyl-	0,79	P-Methylbenzyl Alcohol
19	0,74	O-Cresol	1,13	Pentylbenzene	1,17	Benzene, Pentyl-
20	0,83	M-Cresol	0,72	P-Methylbenzyl Alcohol	1,02	P-Methylbenzyl Alcohol
21	0,53	4-Hydroxy-2,5-Dımethyl-3(2h)-Furanone	1,15	Octanoic Acid	0,49	Caprylic Acid
22	5,83	Guaiacol	10,64	2-Methoxy-4-Methylphenol	1,17	M-Cresol, 2-Methoxy-
23	0,91	Maltol	0,93	Pyrocatechol	11,01	2-Methoxy-4-Methylphenol
24	0,56	2-Cyclopenten-1-One, 3-Ethyl-2-Hydroxy-	0,74	2,3-Dimethoxytoluene	0,90	Nonane, 3-Methyl-5-Propyl
25	0,58	2,2'-Bioxepane	2,46	Bıcyclo[6.4.0]Dodeca-9,11-Dıen	2,07	Bıcyclo[6.4.0]Dodeca-9,11-Dıen
26	0,69	Carvomenthol	1,28	Nonoic Acid	1,23	Satın Aldehyde
27	8,61	Phenol, 4-Methoxy-3-Methyl-	6,86	Phenol, 4-Ethyl-2-Methoxy-	6,69	Guaiacol <4-Ethyl->
28	0,56	Butyrıc Acıd, 1-Propylpentyl Ester	0,59	1,2-Benzenediol, 3-Methyl-	3,16	Phenol, 4-Ethenyl-2-Methoxy-
29	2,89	Pyrocatechol	3,87	Phenol, 4-Ethenyl-2-Methoxy-	1,16	M-XHQ
30	1,11	Ethyl Cyclopropanecarboxylate	1,54	1,4-Benzenediol, 2,6-Dimethyl-	2,35	Eugenol
31	4,11	HMF	2,67	Eugenol	1,79	1-Phenylheptane
32	0,60	2-(2-Hydroxy-2-P-Chlorophenylethyl)-3,5,6-Trımet	1,90	1-Phenylheptane	2,61	Eugenol
33	1,24	1,2-Benzenediol, 3-Methyl-	2,74	Euganol	0,44	Cyclotetradecane
34	3,11	Guaiacol <4-Ethyl->	0,89	M-Cresol, 2-Methoxy	1,06	Isoeugenol
35	1,54	1,2-Benzenediol, 3-Methyl-	1,25	3-Allyl-6-Methoxyphenol	7,89	Isoeugenol
36	1,72	Guaiacol <4-Vinyl->	9,34	Isoeugenol	0,48	1-Phenyloctane
37	0,59	M-XHQ	1,72	Heptadecane	2,47	N-Hexadecane
38	1,08	Eugenol	0,72	2-Propanone, 1-(4-Hydroxy-3-Methoxyphenyl)-	0,63	Heneicosane
39	0,81	4-Ethylresorcinol	0,51	Benzene, Nonyl-	0,55	5-Heptadecene, 1-Bromo
40	1,14	Vanillin	0,87	Benzeneacetic Acid, 4-Hydroxy-3-Methoxy-	2,93	9-Eicosene, (E)-
41	0,55	Eugenol	0,92	5-Heptadecene, 1-Bromo-	3,19	9-Octadecene, (E)-
42	5,17	1,6-Anhydro-Beta-D-Glucopyranose (Levoglucosa	3,36	9-Eicosene, (E)-	2,62	N-Hexadecane
43	4,52	Isoeugenol	2,86	9-Eicosene, (E)-	1,23	2-PHENYLUNDECANE
44	0,66	Eugenol	1,88	N-Hexadecane	0,66	2-PHENYLUNDECANE
45	1,44	Acetovanillone	1,05	4-PHENYL-4-METHY	0,54	2,3-Benzocyclododecenedımethanol,
46	2,45	2-Propanone, 1-(4-Hydroxy-3-Methoxyphenyl)-	2,37	Methyl Palmitate	2,61	Methyl Palmitate
47	2,30	Heptyl Acetate	1,56	ALLYL OCTADECAN	1,14	ALLYL OCTADECAN
48	0,92	N-(5-Oxo-Tetrahydro-Furan-2-Ylmethyl)-Acetamı	1,50	9,12-Octadecadienoic Acid (Z,Z)-, Methyl Ester	1,24	9,12-Octadecadienoic Acid (Z,Z)-, Methyl
49	2,57	Methyl-(2-Hydoxy-3-Ethoxy-Benzyl)Ether	4,81	Methyl Oleate	4,49	Methyl Oleate
50	1,69	3-(P-Hydroxy-M-Methoxyphenyl)-2-Propenal	0,83	Methyl Oleate	2,25	Methyl Cis-7-Octadecenoate

4 Conclusion

In this study, the spruce sawdust was catalytic co-pyrolyzed with glycerol using HZSM-5 and dolomite catalysts in a one-stage reactor to generate an improved and upgraded bio-oil. The main findings can be summarized as follows:

1. In spruce sawdust pyrolysis performed at different temperatures, the highest liquid product yield was recorded as 40.66 wt% at 550 ^{o}C.
2. In co-pyrolysis made with glycerol in different ratios (10 wt%, 20 wt%, 30 wt%) to increase the yield and quality of the pyrolysis oil, the highest liquid product

yield in all experiments was obtained to be 44.11 wt% at mixture ratio with 20 wt%.

3. In catalytic co-pyrolysis of spruce sawdust with HZSM5 and dolomite increased the yield and quality of the pyrolysis oil, the highest bio-oil yield was found to be 45.91 wt% with dolomite-exsitu experiments.
4. It was observed that co-pyrolysis with glycerol also made significant improvements in the liquid product content. The amount of oxygen-free component, which was 4.81% (GC-MS peak area) in spruce sawdust pyrolysis, was determined as 8.02 % due to co-pyrolysis with glycerol. When the effects of using HZSM-5 and dolomite catalysts inside and outside the reactor on the liquid product were examined, it was seen that the HZSM-5 catalyst reduced the number of oxygenated components.
5. The dolomite catalyst gave the closest results to the diesel-like bio-oil target. The oxygen-free component amounts of the bio-oils obtained from Dolomite-exsitu and HZSM5-exsitu were determined as 22.24% and 19.10 %, respectively. The number of oxygenated compounds in the pyrolysis oil decreased but the ketone, furan, phenol, and alcohol structures continued to exist in the bio-oil. 2-Furancarboxaldehyde, Phenol, 4-methoxy-3-methyl-, HMF, and 1,6-Anhydro-Beta-D-Glucopyranose structures were primarily found in the pyrolysis bio-oil obtained from spruce sawdust. As a result of dolomite-exsitu experiments, mostly Phenol, 4-ethyl-2-methoxy- 9-Eicosene, 2-methoxy-4-methylphenol, and Methyl oleate structures were found in the bio-oil.

Catalytic co-pyrolysis of spruce sawdust gave positive results in obtaining clean, sustainable, and easily producible liquid fuel. The high oxygen content and presence of reactive components in bio-oils produced from biomass are their main disadvantages compared to fossil fuels. In future studies, the use of HZSM-5 and dolomite catalysts at different rates can be investigated to increase the quality of pyrolysis oil. In addition, the bio-oils obtained after catalytic co-pyrolysis can be further improved by catalytic cracking reactions. Better results can be obtained using plastic materials rich in hydrogen and low in oxygen in the co-pyrolysis of spruce sawdust.

5 Author contribution statement

Author 1: Investigation, Conceptualization, Visualization, Formal analysis, Methodology, Writing–original draft; Author 2: Data curation, Supervision, Funding acquisition, Resources, Methodology, Project administration, Validation, Visualization, Writing–review & editing.

6 Ethics committee approval and conflict of interest declaration

There is no need for ethics committee approval for the prepared article. There is no conflict of interest with any person/institution in the prepared article.

7 References

[1] Bhoi P, Ouedraogo A, Soloiu V, Quirino R. “Recent advances on catalysts for improving hydrocarbon compounds in bio-oil of biomass catalytic pyrolysis”. *Renewable and Sustainable Energy Reviews*, 121, 2020.

[2] Chia SR, Kit Wayne C, Show P-L, Ong HC, Phang S-M, Ling T, Nagarajan D, Lee D-J, Chang J-S. “Sustainable approaches for algae utilization in bioenergy production”. *Renewable Energy*, 2017.

[3] Leong YK, Show PL, Ooi CW, Ling TC, Lan JC. “Current trends in polyhydroxyalkanoates (PHAs) biosynthesis: insights from the recombinant Escherichia coli”. *Journal of Biotechnology*, 180, 52-65, 2014.

[4] Koyande A, Kit Wayne C, K R, Tao Y, Show P-L. “Microalgae: A potential alternative to health supplementation for humans”. *Food Science and Human Wellness*, 8, 2019.

[5] Tan S, Zhang Z, Sun J, Wang Q. “Recent progress of catalytic pyrolysis of biomass by HZSM-5”. *Chinese Journal of Catalysis*, 34, 641-650, 2013.

[6] Panwar NL, Paul A. “An overview of recent development in bio-oil upgrading and separation techniques”. *Environmental Engineering Research*, 26, 2020.

[7] Gupta S, Mondal P. “Advances in upgradation of pyrolysis bio-oil and biochar towards improvement in bio-refinery economics: A comprehensive review”. *Environmental Technology & Innovation*, 21, 2021.

[8] Gayathiri M, Pulingam T, Lee KT, Sudesh K. “Activated carbon from biomass waste precursors: Factors affecting production and adsorption mechanism”. *Chemosphere*, 294, 133-764, 2022.

[9] Kapluhan E. “Enerji coğrafyası açısından bir inceleme: biyokütle enerjisinin dünyadaki ve türkiye’deki kullanım durumu”. *Marmara coğrafya dergisi*, 30, 97-125, 2014.

[10] Bridgwater AV. “Review of fast pyrolysis of biomass and product upgrading”. *Biomass and Bioenergy*, 38, 68-94, 2012.

[11] Han Y, Gholizadeh M, Tran C-C, Kaliaguine S, Li C-Z, Olarte M, Garcia-Perez M. “Hydrotreatment of pyrolysis bio-oil: A review”. *Fuel Processing Technology*, 195, 106140, 2019.

[12] Taşar Ş, Kaya F, Özer A. “A Study on the Pyrolysis of Peanut Shells at Different Isothermal Conditions and Determination of the Kinetic Parameters”. *Pamukkale University Journal of Engineering Sciences*, 21, 7, 306-313,2015.

[13] Merdun H, Sezgin Vİ, Güzelçiftçi B. “Evaluation of bio-oil compounds of catalytic fast pyrolysis by multivariate analysis”. *Pamukkale University Journal of Engineering Sciences,* 25, 3, 297-303, 2019.

[14] Özdemir A, Özkan A, Günkaya Z, Banar M. “Kentsel katı atıkların ve kentsel atıksu arıtma çamurlarının birlikte pirolizi ve sıvı ürün karakterizasyonu”. *Pamukkale University Journal of Engineering Sciences,* 28, 6, 920-928, 2022.

[15] Rotliwala Y, Parikh P. “Thermal Coprocessing of High Density Polyethylene with Coal, Fly Ashes, and Biomass: Characterization of Liquid Products”. *Energy Sources Part A-recovery Utilization and Environmental Effects*, 34, 1055-1066, 2012

[16] Solak A, Rutkowski P. “Bio-oil production by fast pyrolysis of cellulose/polyethylene mixtures in the presence of metal chloride”. *Journal of Material Cycles and Waste Management*, 16, 2013.

[17] Solak A, Rutkowski P. “The effect of clay catalyst on the chemical composition of bio-oil obtained by co-pyrolysis of cellulose and polyethylene”. *Waste management*, 34, 2013.

[18] Brebu M, Uçar S, Vasile C, Yanik J. “Co-pyrolysis of pine cone with synthetic polymers”. Fuel, 89, 1911-1918, 2010.

[19] Brebu M, Spiridon I. “Co-pyrolysis of LignoBoost Ò lignin with synthetic polymers”. *Polymer Degradation and Stability*, 97, 2104-2109, 2012.

[20] David J. Mihalcik, Charles A. Mullen, Akwasi A. Boateng. “ Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components”. *Journal of Analytical and Applied Pyrolysis*, 92, 224-232, 2011.

[21] Pan Pan, Changwei Hu, Wenyan Yang, Yuesong Li, Linlin Dong, Liangfang Zhu, Dongmei Tong, Renwei Qing, Yong Fan. “The direct pyrolysis and catalytic pyrolysis of Nannochloropsis sp. residue for renewable bio-oils”. *Bioresource Technology*, 101, 4593-4599, 2010.

[22] Carmines E, Gaworski CL. “Toxicological evaluation of glycerin as a cigarette ingredient”. *Food and chemical toxicology : an international journal published for the British Industrial Biological Research Association*, 43, 1521-1539, 2005.

[23] Skoulou V, Manara P, Zabaniotou A. “H2 enriched fuels from co-pyrolysis of crude glycerol with biomass”. *Journal of Analytical and Applied Pyrolysis*, 97, 198–204, 2012.

[24] Kumar P, Singh VP, Tagade A, Sawarkar AN. “Thermochemical characterization of post-phytoremediated vetiver (Vetiveria zizanioides (L.) Nash) root and shoot for their prospective bioenergy potential”. *Industrial Crops and Products*, 191, 115964, 2023.

[25] Uçar S, Karagöz S. “Co-pyrolysis of pine nut shells with scrap tires”. *Fuel*, 137, 85-93, 2014.

[26] Anuar Sharuddin SD, Abnisa F, Wan Daud WMA, Aroua MK. “A review on pyrolysis of plastic wastes”. *Energy Conversion and Management*, 115, 308-326, 2016.

[27] Uzoejinwa BB, He X, Wang S, El-Fatah Abomohra A, Hu Y, Wang Q. “Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide”. *Energy Conversion and Management*, 163, 468-492, 2018.

[28] Prakash R, Siddharth R, Gunasekar N. “Chapter 10 - Cracking of Toxic Waste. In: Barik D (ed) Energy from Toxic Organic Waste for Heat and Power Generation”. *Woodhead Publishing*, 139-149, 2019.

[29] Kuppens T, Cornelissen T, Carleer R, Yperman J, Schreurs S, Jans M, Thewys T. “Economic assessment of flash co-pyrolysis of short rotation coppice and biopolymer waste streams”. *Journal of Environmental Management*, 91 , 2736-2747, 2010.

[30] Han B, Chen Y, Wu Y, Hua D, Chen Z, Feng W, Yang M, Xie Q. “Co-pyrolysis behaviors and kinetics of plastics–biomass blends through thermogravimetric analysis. *Journal of Thermal Analysis and Calorimetry*, 115, 227-235, 2014.

[31] Yaman E, Ulusal A, Uzun BB. “Co-pyrolysis of lignite and rapeseed cake: a comparative study on the thermal decomposition behavior and pyrolysis kinetics”. *Applied Sciences*, 3, 97, 2021.

[32] Slopiecka K, Bartocci P, Fantozzi F. “Thermogravimetric analysis and Kinetic study of poplar wood pyrolysis”. *Applied Energy*, 97, 491–497, 2012.

[33] Fantozzi F, Frassoldati A, Bartocci P, Cinti G, Quagliarini F, Bidini G, Ranzi EM. “An experimental and kinetic modeling study of glycerol pyrolysis”. *Applied Energy*, 184, 68-76, 2016.

[34] de Lucas A, Canizares P, Durán A, Carrero A. “Dealumination of HZSM-5 zeolites: Effect of steaming on acidity and aromatization activity”. *Applied Catalysis A: General*, 154, 221-240, 1997.

[35] Adjaye JD, Sharma RK, Bakhshi NN. “Catalytic Upgrading of Wood Derived Bio-Oil over HZSM-5 Catalyst: Effect of Co-Feeding Steam”. *Advances in Thermochemical Biomass Conversion*, 1032-1046, 1993.

[36] Valle B, Gayubo AG, Alonso A, Aguayo AT, Bilbao J. “Hydrothermally stable HZSM-5 zeolite catalysts for the transformation of crude bio-oil into hydrocarbons”. *Applied Catalysis B: Environmental*, 100, 318-327, 2010.

[37] Oudejans JC, Van Den Oosterkamp PF, Van Bekkum H. “Conversion of ethanol over zeolite h-zsm-5 in the presence of water”. *Applied Catalysis*, 3, 109-115, 1982.

[38] Sharma RK, Bakhshi NN. “Catalytic conversion of crude tall oil to fuels and chemicals over HZSM-5: Effect of co-feeding steam”. *Fuel Processing Technology*, 27, 113-130, 1991.

[39] Katikaneni SPR, Adjaye JD, Bakhshi NN. “Studies on the Catalytic Conversion of Canola Oil to Hydrocarbons: Influence of Hybrid Catalysts and Steam”. *Energy & Fuels*, 9, 599-609, 1995.

[40] Al-Obaidi MM, Ishak NS, Ali S, Arifin NA, Raja Shahruzzaman RM, Wan Abdul Karim Ghani WA, Yun Hin T-Y, Shamsuddin AH. “H2-Rich and Tar-Free Downstream Gasification Reaction of EFB by Using the Malaysian Dolomite as a Secondary Catalyst”. *Catalysts*, 11, 2021.

[41] Harith N, Hafriz RSRM, Arifin NA, Tan ES, Salmiaton A, Shamsuddin AH. “Catalytic co-pyrolysis of blended biomass – plastic mixture using synthesized metal oxide(MO)-dolomite based catalyst”. *Journal of Analytical and Applied Pyrolysis*, 168, 105776, 2022.

[42] Charusiri W, Vitidsant T. “Upgrading bio-oil produced from the catalytic pyrolysis of sugarcane (Saccharum officinarum L) straw using calcined dolomite”. *Sustainable Chemistry and Pharmacy*, 6, 114-123, 2017.

[43] Islam MW. “A review of dolomite catalyst for biomass gasification tar removal”. *Fuel*, 267, 117095, 2020.

[44] Wu Q, Ke L, Wang Y, Zhou N, Li H, Yang Q, Xu J, Dai L, Zou R, Liu Y, Ruan R. “Pulse pyrolysis of waste cooking oil over CaO: Exploration of catalyst deactivation pathway based on feedstock characteristics”. *Applied Catalysis B: Environmental*, 304, 120968, 2022.

[45] Valle B, García-Gómez N, Remiro A, Gayubo AG, Bilbao J. “Cost-effective upgrading of biomass pyrolysis oil using activated dolomite as a basic catalyst”. *Fuel Processing Technology*, 195, 106142, 2019.

[46] Chen X, Chen Y, Yang H, Wang X, Che Q, Chen W, Chen H. “Catalytic fast pyrolysis of biomass: Selective deoxygenation to balance the quality and yield of bio-oil”. *Bioresource Technology*, 273, 153-158, 2019.

[47] Onay O, Koçkar O. “Fixed-bed pyrolysis of rapeseed (Brassica napus L.)”. *Biomass & Bioenergy*, 26, 289-299, 2004.

[48] Zhou L, Yang H, Wu H, Wang M, Cheng D. “Catalytic pyrolysis of rice husk by mixing with zinc oxide: Characterization of bio-oil and its rheological behavior”. *Fuel Processing Technology*, 106, 385–391, 2013.

[49] Nuttapan P, Nuwong C, Adisak P. “Effect of low-temperature hydrothermal treatment of HZSM-5 extrudates on the production of deeply-deoxygenated bio-oil via ex-situ catalytic fast pyrolysis of biomass”. *Fuel*, 324, 124627, 2022.

[50] Praserttaweeporn K,Vitidsant T, Charusiri W. “Ni-modified dolomite for the catalytic deoxygenation of pyrolyzed softwood and non-wood to produce bio-oil”. *Results in Engineering*, 14, 100461, 2022.

[51] Raja Shahruzzaman RMH, Ali S, Yunus R, Yun-Hin TY. "Green Biofuel Production via Catalytic Pyrolysis of Waste Cooking Oil using Malaysian Dolomite Catalyst". *Bulletin of chemical reactıon engineering and catalysis*, 13, 2018.

[52] Hafriz RSRM, Nor Shafizah I, Arifin NA, Maisarah AH, Salmiaton A, Shamsuddin AH. "Comparative, reusability and regeneration study of potassium oxide-based catalyst in deoxygenation reaction of WCO". *Energy Conversion and Management*, 13, 100173, 2022.