SYNTHESIS OF Fe/Al_2O_3 CATALYST USING CO-PRECIPITATION METHOD AND ITS USE IN Py-GC/MS SYSTEM

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ABSTRACT

Biomass is one of the most important renewable energy sources with the potential to replace petroleum-derived polymers and fuels. Due to environmental problems, the use of cleaner fuels and chemicals is increasing worldwide. Catalytic pyrolysis is one of the most important methods in biofuel production. The liquid product obtained by catalytic pyrolysis is both a potential source of biofuel and chemical raw materials for a sustainable energy system. In this study, sugar beet pulp was used as a biomass source to produce bio-oil. In the first part of the study, Fe/Al_2O_3 (5%wt) catalyst to be utilized in pyrolysis was synthesized by the co-precipitation method, and the catalyst was characterized by using SEM, BET, XRD, and FTIR methods. In the second part, catalytic pyrolysis experiments of sugar beet pulp at 550 °C were carried out by Py-GC/MS system with a heating rate of 10 °C/min. According to catalytic pyrolysis results, it has been observed that valuable chemical raw materials such as phenolic compounds can be obtained from sugar beet pulp pyrolysis. Eventually; it is recommended to synthesize catalysts that have economic advantages over commercial catalysts and to use them in the production of liquid products equivalent to petroleum from biomass.

Keywords: Bio-fuel, characterization, catalytic pyrolysis, $Fe–Al_2O_3$.

INTRODUCTION

The increase in world energy demand, environmental concern and the shortage of fossil fuels have driven interest in alternative energy sources. Biomass is such an alternative and renewable energy source. Among the various type of renewable energy, biomass is considered a promising alternative and renewable resource to petroleum because high value-added fuels and/or chemicals can be obtained from biomass using the proper conversion technologies, such as fermentation, gasification, and pyrolysis (Stefanidis et al., 2016).

Pyrolysis is an endothermic decomposition process implemented in oxygen-deficient and high-temperature environments to yield bio-oil, syngas, and biochar. The bio-oil is a complex mixture of oxygenated compounds (i.e. ketones, phenolics, furans, acids, aldehydes, etc.) derived from the thermal degradation of the holocellulose and lignin fractions in the biomass. Bio-oil or pyrolysis oil has a low calorific value and thermal stability as well as high corrosivity and viscosity (Ozbay et al., 2019), which restrict the direct bio-oil application to alternative transportation fuels. To resolve this issue, the upgrading method to remove oxygen from bio-oils should be developed (Kim et al., 2016).

The use of catalysts to improve the properties of biomass pyrolysis products is also one of the most commonly used methods. Catalyst is favorable for pyrolysis intermediates and accelerates the secondary reactions towards specific chemicals, thereby improving the selectivity of target components in the bio-oil (Özbay et al., 2018). Various catalytic systems or catalysts can support suitable reactions to obtain desirable chemicals. Different catalyst types such as alkali metals, transition metals, and alkaline earth metals, molecular sieves have been investigated to optimize the efficiency and performance of bio-oil and value-added chemical products, many metals and their oxides have shown exclusive characteristics among them (Dai et al., 2020). But it is worth noting that most studies only use one kind of effective metal or one kind of effective metal which was supported on another porous metal support (such as γ-

Al_2O_3). The most active surface sites on the alumina are on turning, edges, and the oxide structure lack, the sites located on surface plates being likely fewer reactive. Over the gappy sites, the deposited groups would interact firstly, while at higher coverage they also hold down fewer reactive sites. Research on effective metals and detecting the interaction between the two is extremely scarce (Farahmandjou et al., 2020).

Among the numerous types of waste from agricultural production, sugar beet pulp plays an essential role. Beet pulp is a waste product from beet sugar production. Turkey has an important position among the countries producing sugar from beet, and ranks fifth in the world after the USA, Russia, France, and Germany, and ranks fourth in the European Continent after Russia, Germany, and France. Sugar beet pulp can be used as only animal feed and as a raw material in cosmetic and paper industries (TürkŞeker, 2020). It can also be used as a raw material for catalytic pyrolysis reactions.

Pyrolysis and on-line gas chromatography and mass spectroscopy (Py-GC/MS) has been announced as a direct method to investigate the pyrolytic performance of biomass and its volatile product characterization. It has gained excessive attention in recent years, as it permits identifying all pyrolytic products with superior efficiency than in GC/MS of condensable products (liquid fraction), whose identification under several operating conditions needs full condensation (Bensidhom et al., 2021). This present work focuses on two aspects; *i)* to synthesized Fe-Al_2O_3 catalysts via co-precipitation method and characterized by using SEM, BET, XRD, and FTIR analytical technics, *ii)* to ınvestigate the effects of catalytic pyrolysis of sugar beet pulp by using Py-GC/MS technique for production of high value-added bio-oil and chemical raw material.

MATERIALS AND METHODS

In this section, preparation and characterization techniques of Fe-Al_2O_3 catalysts, and Py-GC/MS experiments were given in detail. In addition, the properties of biomass feedstock that was used in this study were determined.

Biomass Feedstock

The sugar beet pulp for this study was taken from sugar factories around Eskişehir located in Central Anatolia. Prior to use pulp samples were ground to have an average particle size. Proximate analysis was applied on sugar beet pulp to detect the weight fractions of volatile matter, ash, moisture, and fixed carbon. The ultimate analysis was performed using an elemental analyzer (Leco CNH628 S628).

Preparation and Characterization of Catalyst

The co-precipitation method was used to prepare 5 wt.% of iron-containing Fe-Al_2O_3 catalysts. Through the synthesis of catalysts, aqueous solutions containing the needed quantity of $Fe(NO_3)_2.9H_2O$ and $Al(NO_3)_3.9H_2O$ with a concentration of 0.1 N each were simultaneously precipitated using an aqueous solution containing 0.25 N KOH. The co-precipitated catalyst was entirely washed, filtered, and dried at 110 °C for 12 h in the air at room temperatures. After that, the catalyst was calcined in a tubular furnace at 900 °C for 6 h in an air atmosphere.

The x-ray diffraction measurements (XRD, PANalytical Empyrean diffractometer) were performed to determine crystal structure by employing CuKα radiation (λ=0.15405 nm, running at 45 kV and 40 mA). The XRD patterns were accumulated in the range of 2θ= 10-90 degrees every 0.02 degree (2θ) with a counting time of 2 s per step. N_2 adsorption/desorption experiments were conducted at -196°C, using an automatic volumetric sorption analyzer for the determination of surface area, pore-volume, and pore size. The samples were previously outgassed for 300 min at 360 °C. The surface area of catalyst was calculated from N_2 adsorption/desorption isotherms by using the BET (Brunauer–Emmett–Teller) method with Quantachrome NovaWin analyzer. SEM images of the catalysts were obtained by using a Zeiss Supra VP40 scanning electron microscope. Samples were placed on carbon bands and coated with a platinum thin layer in an argon atmosphere using Quorum Q150RESDC Sputter Coater. Fourier transform infrared spectroscopy (FT-IR) analysis of catalyst was carried out using a Perkin Elmer Spectrum 100 to identify structural groups in the range of 4000-400 cm^{-1} wavenumber by using the ATR technique.

Py-GC/MS Experiments

A Py-GC/MS system (Frontier Py-2020 pyrolyzer, Shimadzu QP2010 GC/MS) was used to pyrolyze sugar beet pulp. Approximately 1.0 mg raw material was loaded into a small size crucible, and then transferred to the micro-furnace. The pyrolysis process was isothermal at 550 °C and the reaction time was 10 min. The column and injection part temperatures were 40 °C and 320 °C, respectively. The carrier gas was helium which flowed 1.0 mL/min.

RESULTS AND DISCUSSION

Properties of Biomass Sample

Proximate analysis of sugar beet pulp gave 9.9% moisture, 74.5% volatile matter (dry basis), 4.2% ash (dry basis), 11.4% fixed carbon (dry basis), respectively. Elemental analysis (wt.%, dry basis) gave 41.2% C, 6.7% H, 1.3% N, and 50.8% O for sugar beet pulp, respectively.

Catalyst Characterization

The surface area of the catalyst was measured through the conventional Brunauer, Emmett, and Teller (BET) method. The properties of Fe-Al_2O_3 catalysts were given in Table 1. The surface area and total pore volume of the 5% Fe-Al_2O_3 catalysts were 13.218 m^2/g and 0.4173 cm^3/g, respectively. As seen in Table 1 pore size and the pore volume data, the catalyst was highly macroporous with textural and structural defects that caused the observed limited micro- or mesoporosity.

Table 1. Surface Properties of Fe-Al_2O_3 catalysts

Catalyst type	**Surface Area (m^2/g)**	**Pore size (nm)**	**V_{total} (cm^3/g)**
5% Fe-Al_2O_3	13.218	63.14	0,4173

Figure 1 showed XRD patterns of 5% Fe-Al_2O_3. As it could be seen in Figure 1, peaks formed at 2θ angles of 33.41° and 37.51° represented α-Fe_2O_3. The detection of the α-Fe_2O_3 phase indicated that only a certain amount of Fe^{3+} could incorporate into the crystal lattice of γ-Al_2O_3. Moreover, peaks obtained at 39.52°, 46.03°, 60.59°, and 66.71° indicated γ-Al_2O_3-Fe_2O_3 and the intensities of these peaks were bigger than that of Fe_2O_3. No peaks of Al_2O_3 were observed. It was evident that iron was diffused in the catalyst surface while preparing the catalyst, acquisition in the formation of γ-Al_2O_3-Fe_2O_3 structures.

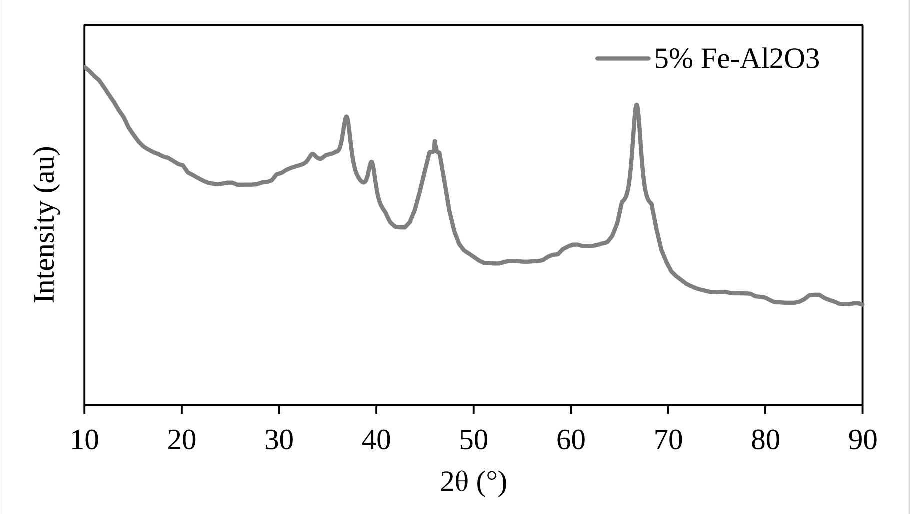

Figure 1. XRD Pattern of 5% Fe-Al_2O_3

Figure 2 showed the surface morphology of 5 wt.% Fe-loaded Al_2O_3 taken at 1000 magnification. According to SEM images (Figure 2), catalyst particles had an angular morphology with a large size range.

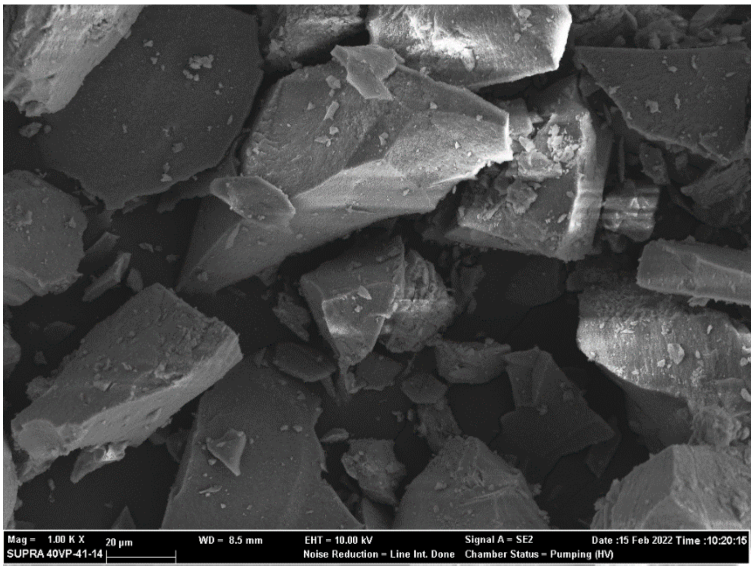

Figure 2. SEM image of 5% Fe-Al_2O_3

Fourier-transform infrared spectroscopy (FT-IR) analysis was applied to determine the functional groups and vibrational bond (Figure 3). According to the FT-IR result, a broad peak in the wavenumber of 3387 cm^{-1} was associated with the hydroxyl vibrational bond. This peak corresponded to the stretching vibrations of the O-H group. The absorption peak observed in the wavenumber of 2161 cm^{-1} was related to the C-H vibrational bond, the peak generated in the wavenumber of 1586 cm^{-1} was related to the tensile vibrational bond C=C, and the vibrational peaks generated in the sample in the wavenumber of 850 and 510 cm^{-1} were related to the tetrahedral and Octo-Al_2O_3 groups, respectively.

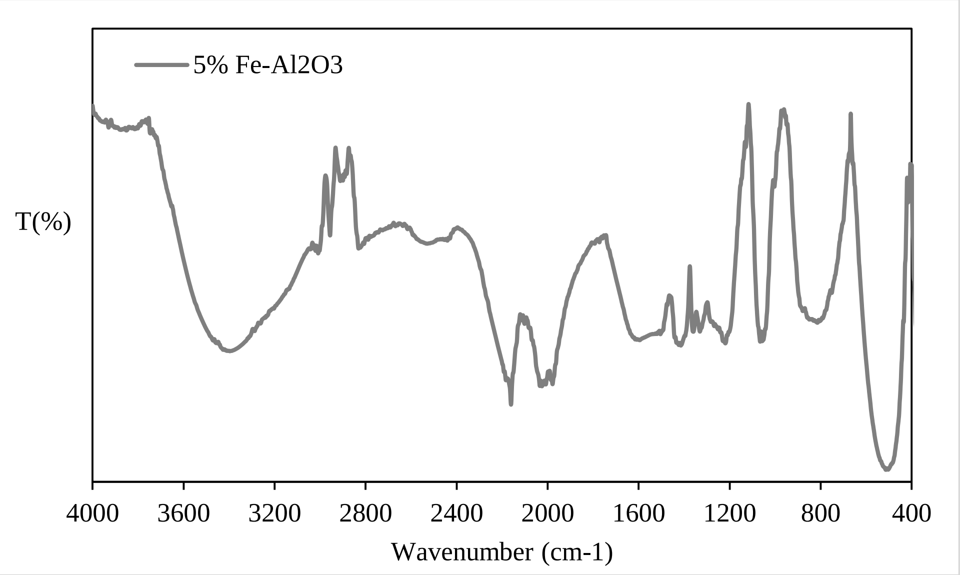

Figure 3. FTIR spectra of 5% Fe-Al_2O_3

Py-GC/MS Results

Figure 4 showed the catalytic Py-GC/MS spectra of sugar beet pulp. According to the results, the catalytic pyrolysis products were a mixture of organic compounds in the range of C_6–C_{29} carbons. The aliphatics groups consisted of n-alkanes, alkenes, and branched hydrocarbons. While considering the result of GC/MS detailed analysis, the total amounts of hydrocarbons were %15.28. In order to determine the distribution of volatile components obtained from the catalytic Py-GC/MS experiments, a semi-quantitative study was made by means of the percentage of the area of chromatographic peaks. As shown in Figure 5, the highest peak area was obtained in aromatic compounds at 23%. The peak areas of other value-added chemical products were obtained as 25%, 15%, and 10% as alcohol, acid, and ketone, respectively,

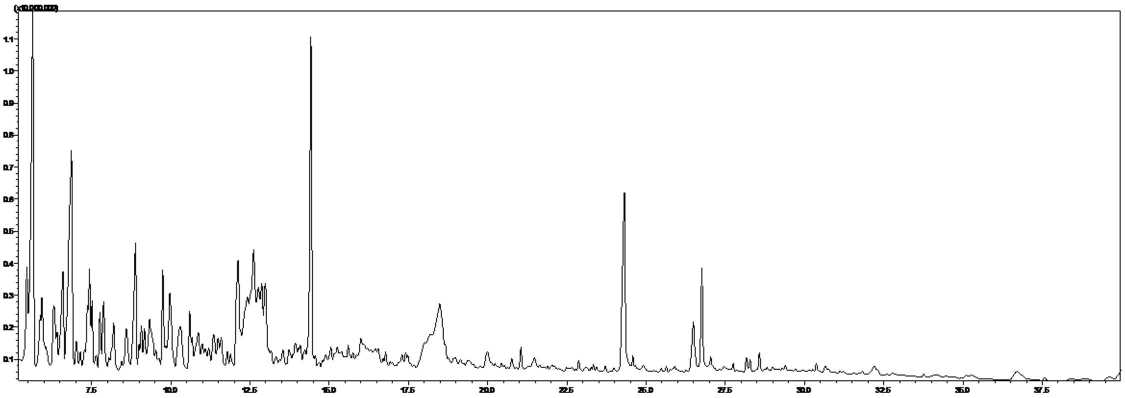

Figure 4. GC/MS chromatogram catalytic Py/GC-MS spectra of sugar beet pulp

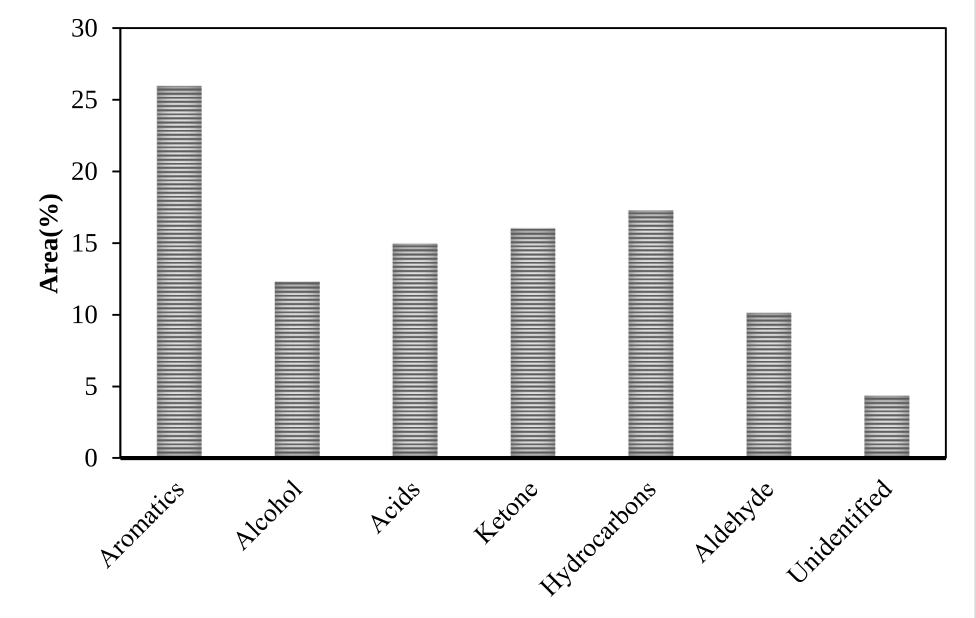

Figure 5. Chemical composition from Py-GC/MS spectra of sugar beet pulp

CONCLUSION

In this study, Fe-doped Al_2O_3 were successfully synthesized with iron percentages of 5% using the co-precipitation method. Catalytic pyrolysis was carried out using the Py-GC/MS method, which was an advantageous method for detecting pyrolysis vapors. This study showed that precise chemicals, such as aromatics, alcohols, and hydrocarbons, could be produced in the presence of Fe/Al_2O_3 catalyst.

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