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Hydrogen Production from Sawdust Pyrolysis Catalysed by TiO_2 Impregnated Al_2O_3 Nanoparticles

Songül KASKUN ERGANİ[1*]

[1]*Department of Environmental Engineering, Engineering Faculty, Karabuk University, 78050 Karabuk/Turkey*

(ORCID: 0000-0002-2760-2218)

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Abstract
In the present study, the hydrogen production of wood sawdust pyrolysis catalysed by TiO_2 impregnated Al_2O_3 (TiO_2/Al_2O_3) was investigated under temperatures of 600, 700 and 800 °C. The catalyst preparation was made by wet impregnation method for enhanced hydrogen-rich gas production from catalytic pyrolysis of sawdust. Characterization and morphology of TiO_2 doped Al_2O_3 nanoparticles were performed using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and the gas product was analysed by gas chromatography. The presented TiO_2 doped Al_2O_3 catalyst showed the highest H_2 yield in sawdust pyrolysis as 17.04 mol/kg, and gas productivity 0.72 Nm^3/kg biomass at temperatures of 800 °C. Furthermore, the carbon conversion rate of the sawdust pyrolysis was detected as 53.6% with the TiO_2 doped Al_2O_3 catalyst. It was observed that TiO_2 doped Al_2O_3 nanoparticles supplementation approximately 50% increased the hydrogen production of sawdust pyrolysis, compared to non-catalytic experiment of sawdust pyrolysis.

1. Introduction

The growing use of fossil fuels resulting in global warming and environmental pollution have made it necessary to use more alternative and renewable energy sources. Hydrogen energy is known the 21st century promising alternative energy resource and can be used in industry, buildings, and transport with huge energy density and zero carbon emissions [1]. Hydrogen can be produced from raw materials including fossil fuels, biomass and water electrolysis in environmentally friendly way for its large scale utilization [2].

Biomass is renewable, and eco-friendly energy resources due to its basic and clean structure. Different type of biomass differs in chemical composition, ash, and moisture content. Recent years, there has been huge interest to degrade biomass by thermo-chemical methods because of their ease of use and fastness to economically produce hydrogen [3-5].

Biomass pyrolysis is a complicated process that numerous chemical reactions occur in the gas and the condensed phase. Bio-oil, bio-crude and CO, CO_2, H_2 and light hydrocarbon gases are produced by the pyrolysis process. Many studies have also been reported to obtain hydrogen with high efficiency from pyrolysis of biomass with catalysts [6-8].

Sol-gel, hydrothermal, chemical vapor deposition, and wet impregnation methods are used to prepare catalysts. The preparation methods of the catalysts and doping catalyst with some nanoparticles are applied to increase the catalytic activity [9]. Catalyst support materials such as titanium dioxide (TiO_2), aluminium oxide (Al_2O_3), silicon dioxide (SiO_2), carbon nanotubes, prevent agglomeration by allowing the catalyst to be easily dispersed on the support material, resulting in increased catalytic activity [10,11]. Increasing the catalytic activity also increases the active site of the catalyst. Furthermore, the active part of the catalyst

[*]Corresponding author: *songulkaskun@karabuk.edu.tr*
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which is used in hydrogen production allows for higher hydrogen production. Therefore, the development of catalysts used in hydrogen production is of great importance in this field [12]. Pyrolysis of biomass is expressed as following:

Biomass→ H_2 + CO + CO_2 + HC (gases) + Tar + Char

Ji et al. depicted the hybrid-functional material Ni-CaO-Ca_2SiO_4 enhanced hydrogen production by sawdust decomposition. They found that 20 wt.% Nickel (Ni) loading generated the most H_2 yield compared to 0, 5, 10, 15, 25, 30 wt. % Ni loading on Ni-CaO-Ca_2SiO_4 catalyst. Also, 20 wt. % Ni loading sample showed the highest BET surface area of 56.948 m^2/g. However, all catalyst that they produced with different Ni loading on Ni-CaO-Ca_2SiO_4 catalyst showed decreasing hydrogen production after 15 cycles. Moreover, H_2 gas purity decreased after 15 cycles approximately 25%. In summary of their study, 20 wt.% Nickel (Ni) loading showed 626 mL H_2 yield with 68% H_2 purity under pressure of 1 atm and at room temperature [13].

Liu et al. investigated the catalytic effect of Aluminium (Al) dross on H_2 yield of pine sawdust pyrolysis. In the study, aluminium dross was used as catalyst to pyrolysis of pine sawdust. They showed that, the amount of H_2 produced by pine sawdust pyrolysis increased from 98.97 ml/g to 131.86 ml/g with aluminium dross catalyst [14]. Additionally, it was investigated that aluminium dross makes catalytic transformation of CH_4 to H_2 easy by breaking the covalent bonds in pine.

Yang et al, investigated the H_2 yield of sawdust pyrolysis with the various Iron (Fe) based catalysts. They observed the highest H_2 yield as 217 mL/g biomass with the carbon conversion (ηc) rate of 2.5 using Al deposited Fe catalyst, compared to Mg deposited Fe catalyst and Ca deposited Fe based catalyst. Moreover, Al increased the reducibility of iron, providing more efficient active sites which inducing more catalytic conversions during biomass pyrolysis [15].

Zhao et al. studied the influence of Na_2ZrO_3, Li_4SiO_4, and Li_2ZrO_3 as bifunctional catalyst to enhance hydrogen production during biomass pyrolysis. They pointed out that the highest H_2 yield was observed with Li_4SiO_4 catalyst as 15.85 mmol/g and the lowest H_2 yield was observed as 8.87 mmol/g while the H_2 yield was detected as 5.73 mmol/g without catalyst. Also, it was depicted that the conversion of carbon dioxide (CO_2) and coke into carbon monoxide (CO) supported by potassium, sodium, and lithium (K, Na, and Li) catalysts at temperatures below 750 ℃ [16].

In summary, hydrogen is the most important energy carrier and biomass-derived hydrogen has attracted many researchers to reduce fossil fuel consumption [17-19]. However, there is still room for further investigation on hydrogen production efficiency of sawdust pyrolysis with catalysts. This study is proposed to investigate the influence of the TiO_2 impregnated Al_2O_3 (TiO_2/Al_2O_3) catalyst on hydrogen production of sawdust pyrolysis under temperatures of 600, 700 and 800 ℃. The TiO_2 impregnated Al_2O_3 catalyst shows a good catalytic activity in the pyrolysis process of sawdust to produce hydrogen-rich gas under the temperature of 800 ℃.

2. Material and Method

The wood sawdust was obtained from Ankara wood pellets, Ankara, Turkey. Before experiments, sawdust was dried at 105 °C for overnight, ground and sieved to mesh size of 0.25 mm.

2.1. Catalyst Preparation

$Ti_2(SO_4)_3$, H_2SO_4 (99% purity) and Al_2O_3 nanoparticles were provided from Sigma Aldrich. The TiO_2/Al_2O_3 catalyst was prepared by the wet impregnation method. Desired amount of Al_2O_3 was mixed into a saturated solution of Ti(III) sulfate and H_2SO_4 with a magnetic stirrer for 6 h at 70 ℃. The pH values of the solution were adjusted to 8-9 with NaOH solution. Then, the nanoparticles were separated from the solution by filtration, washed with distilled water and dried at 105 °C for overnight. The impregnated alumina was calcinated in an air gas stream for 4 h at 750 ℃ with a heating rate of 1 min^{-1} in static air. The obtained TiO_2 doped Al_2O_3 catalyst was labelled as TiO_2/Al_2O_3 [20]. The Zeiss Ultra Plus field emission gun scanning electron microscopy (FESEM) and Rigaku Ultima IV X-ray diffraction (XRD) using Cu Kα radiation was used to analyse the morphology and characterization of the TiO_2/Al_2O_3 catalyst. Analysis results were consistent with the data in the literature and TiO_2 impregnation on Al_2O_3 nanoparticles was obtained successfully.

2.2. Pyrolysis Experiment

The sawdust pyrolysis catalysed by TiO_2/Al_2O_3 nanoparticles was performed in a fixed-bed pyrolysis tube furnace. The schematic representation of pyrolysis system was shown in Figure 1. The pyrolysis reactor system consists of reactor, tube furnace, liquid-gas phase separator, liquid product container, particle trap filter, moisture trap filter, thermo-couple, nitrogen tube, power supply, controller and Tedlar™ bag. The reactor, which was made of stainless steel, with dimensions of 6 cm diameter and 20 cm height was used.

In the pyrolysis experiment, a high temperature tube furnace was performed at the pyrolysis temperature of 600 °C, 700 °C, 800 °C. The temperature of tube furnace was measured by K-type thermocouple. 10 gr amount of sample was put the reactor at the inception of the pyrolysis. While the amount of sawdust declined, the gas increased gradually which was collected by Tedlar™ gas sample bag. When the pyrolysis process of sawdust with the catalyst was completed, the tube furnace cooled down to room temperature. The Tedlar™ gas sample bag was analysed by gas chromatography (GC). In pyrolysis experiment, nitrogen was used as carrier gas (99.99% purity) at a flow rate of 50 mL/min.

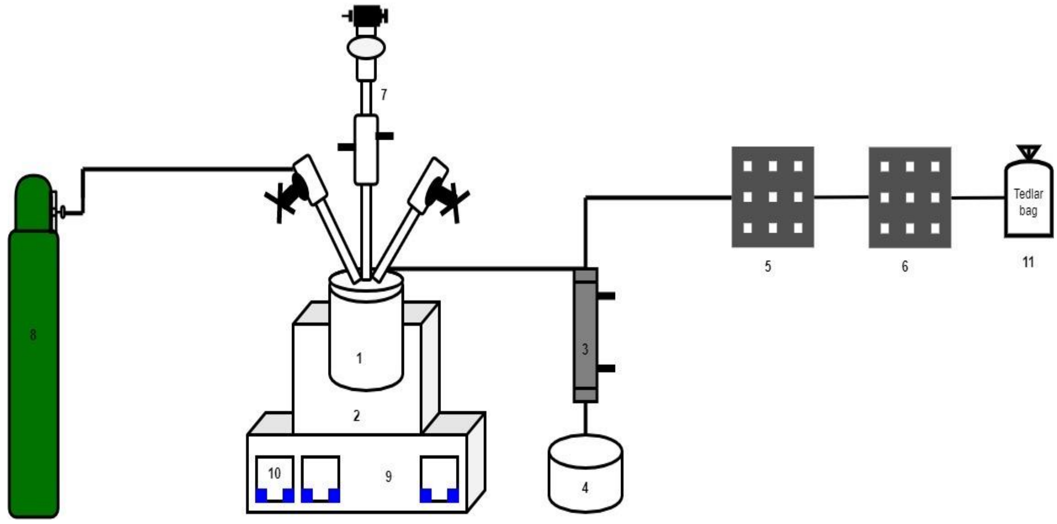

Figure 1. Schematic representation of the pyrolysis system 1- Reactor, 2- Tube furnace, 3-Liquid-gas phase separator, 4-Liquid product container, 5- Particle trap filter, 6-Moisture trap filter, 7-Thermo-couple, 8-Nitrogen tube, 9-Power supply, 10-Controller 11- Tedlar™ Bag

Tedlar™ Bag was used to collect non-condensed gases approximately 30 min to make sure the reaction completed. All experiments were repeated 3 times to ensure the reliability of the results. The obtained catalyst was mixed with sawdust in constant mass ratio 1:2, and the mixed complex was decomposed at a ramping rate of 50 ºC min^{-1} to 800 ºC under the nitrogen at 50 ml min^{-1}. It was revealed that the volume of hydrogen produced by the pyrolysis of sawdust is increasing by increasing the temperature to 800 °C degree [21].

3. Results and Discussion

3.1. Morphology Characterization of TiO_2 Impregnated Al_2O_3 Catalyst

The morphology and the characterization of the present TiO_2/Al_2O_3 catalyst were investigated by SEM and XRD analyses. The SEM images of the synthesized catalyst is shown in Figure 2 with varied sizes. It is clearly seen from the SEM images that TiO_2 nanoparticles impregnation on Al_2O_3 was well dispersed. The nanoparticles have higher surface area and smaller particle size. Also, the anatase phase was revealed because of the spherical shape of TiO_2 nanoparticles on Al_2O_3 nanoparticles.

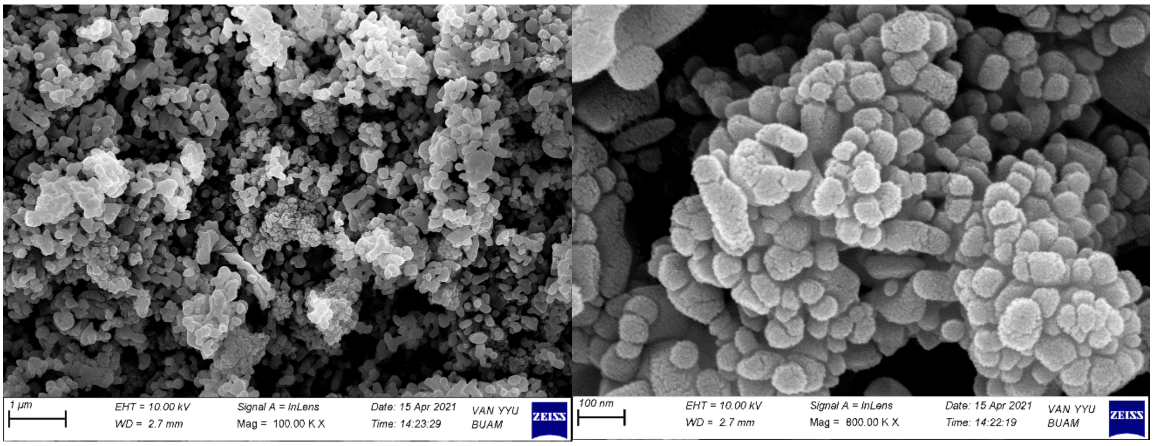

Figure 2. The SEM images of TiO_2/Al_2O_3 catalyst

The XRD analysis result of TiO_2/Al_2O_3 is presented in Figure 3. The strong diffraction peaks at 38.6°, 44.8°, 65.2° can be clearly indexed (311), (400), (440) peak intensity ratios from Al_2O_3 [Joint Committee on Powder Diffraction Standards (JCPDS)] [22]. No characteristic peaks were observed for rutile phase and no peaks of impurities were detected. The diffraction peaks of XRD pattern corresponding to (311) is in good agreement with the standard XRD peaks of TiO_2 (JCPDS Card No. 040477 [23]. All diffraction peaks were well indexed to purely anatase phase Al_2O_3 according to standard JCPDS card No. 00-010-0425). From the analysis of XRD, it could be finalized that TiO_2 nanoparticles have been efficaciously embedded into Al_2O_3 nanoparticles by wet chemical method.

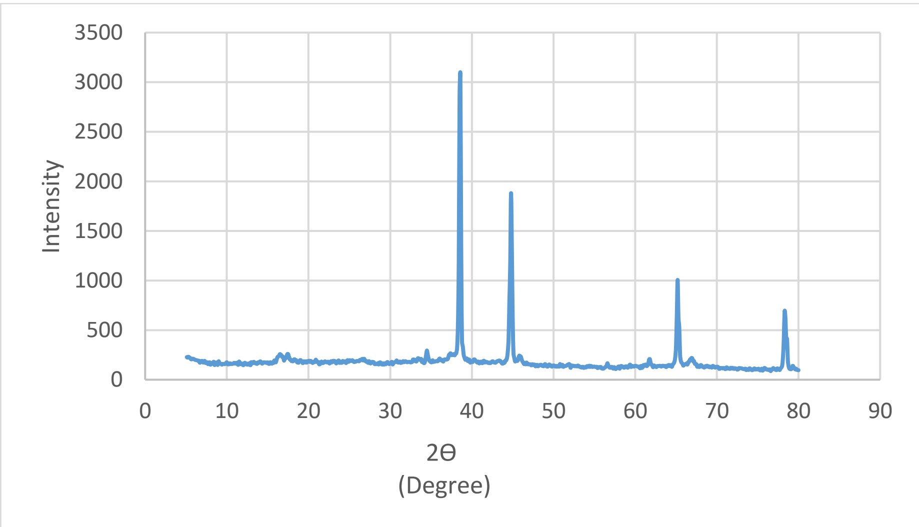

Figure 3. X-Ray Diffraction (XRD) pattern of TiO_2/Al_2O_3 catalyst

3.2. Catalytic Pyrolysis of Sawdust by TiO_2 Impregnated Al_2O_3 Catalyst

H_2, CO and N_2 were analysed with Agilent 6890 GC on a Alltech, Hayesep D 80–100 mesh column. Nitrogen was used as carrier gas with a flow rate of 20 ml/min. 40, 100 and 150 °C were set for oven, injector, and detector temperatures, respectively.

Elemental analysis of the sawdust was determined by using elemental analyzer (Leco CHNS-932). Table 1 presents the chemical components of the wood sawdust which consists of 48.7% Carbon, 44.1% Oxygen, 6.9% Hydrogen and 0.3% Nitrogen.

Table 1. Chemical components of the wood sawdust

Carbon (C) %	Hydrogen (H) %	Oxygen (O) %	Nitrogen (N) %
48.7	6.9	44.1	0.3

It is necessary to use a catalyst to increase the hydrogen-rich gas production from sawdust. The catalyst used allows the syngas to form higher amounts and higher purity of hydrogen [24-25]. The main feature of the catalyst to be used is that it has high ability to break C-C and C-O bonds, provides low char and tar formation, and has thermal and mechanical stability. The material of the catalyst support as well as the catalyst material is very important because the catalyst support material must offer better catalytic activity to prevent coke formation.

Table 2 presents the yields of sawdust pyrolysis at different temperatures without catalyst. In the case of no catalyst, gas yield was low, but tar yield was relatively high. Moreover, the maximum hydrogen yield and the minimum tar yield of sawdust pyrolysis was seen at 800 ℃ without catalyst. Furthermore, the low pyrolysis temperatures resulting in the low yield of gas and high yield of tar on sawdust pyrolysis.

Table 2. Yields of sawdust pyrolysis at different temperatures without catalyst

Temperature (℃)	Gas Yield (Nm^3/kg biomass)	Tar yield (g/Nm^3)	H_2 yield (mol H_2/kg biomass)	ηc (%)
600 ℃	0.26	24.62	5.12	30.4
700 ℃	0.31	21.31	5.31	34.8
800 ℃	0.37	19.71	5.79	41.2

The influence of TiO_2/Al_2O_3 catalyst on sawdust pyrolysis at different temperatures is shown in Table 3. It was seen that the presented catalyst drastically enhanced the gas yield of sawdust pyrolysis at different temperatures. Contrary to the increase in gas yield, tar yield decreased from 0.27 to 0.21 (g/Nm^3). Moreover, there was a significant increase in H_2 yield from 11.54 mol H_2/kg biomass at 600 ℃ to 17.04 mol H_2/kg biomass at 800 ℃. This is due to the high surface area of Al_2O_3, which is the catalyst support, and its ability to bind more effectively to the active sites in biomass. Additionally, the carbon conversion rate was enhanced from 43.8% to 53.6% by increasing the temperature from 600 to 800 ℃.

Table 3. Yields of sawdust pyrolysis at different temperatures with TiO_2/Al_2O_3 catalyst

Temperature (℃)	Gas Yield (Nm^3/kg biomass)	Tar yield (g/Nm^3)	H_2 yield (mol H_2/kg biomass)	ηc (%)
600 ℃	0.59	0.27	11.54	43.8
700 ℃	0.69	0.23	15.03	48.1
800 ℃	0.72	0.21	17.04	53.6

The maximum difference between hydrogen yield and tar yield was observed in sawdust pyrolysis at 800 ℃ with and without the catalyst. The maximum H_2 yield of sawdust pyrolysis was observed to be 17.04 mol H_2/kg biomass with catalyst and 5.79 mol H_2/kg biomass without catalyst at 800 ℃. Also, the presented catalyst decreased very significantly the tar yield compared to without catalyst from 19.71 to 0.21 g/Nm^3 at 800 ℃.

The CO amount was drastically inhibited with the TiO_2/Al_2O_3 catalyst, as the amount of hydrogen significantly increased. This situation may be occurred the secondary cracking of covalent bonds to produce hydrogen [26]. In one step process catalytic pyrolysis, water-gas-shift reaction doesn't take please easily because no water is added to reactor. The appearance of a beneficial H_2/CO ratio, although no water is added as an extra hydrogen source to the pyrolysis, indicates a Fischer Tropsch or methanol process [27].

According to the results of this experimental study, TiO_2/Al_2O_3 catalyst obviously influence hydrogen-rich gas production in sawdust pyrolysis at temperatures of 600, 700 and 800 ℃. Hence, the maximum hydrogen yield was measured as 17.04 mol H_2/kg biomass on sawdust pyrolysis with TiO_2/Al_2O_3 catalyst at 800 ℃. This finding was confirmed by repeated experiments.

4. Conclusions

TiO_2 nanoparticles are homogeneously doped to Al_2O_3 supporting powder by wet impregnation method and was used for catalytic biomass pyrolysis in this study. It was observed that TiO_2/Al_2O_3 catalyst supplementation to sawdust pyrolysis drastically enhanced the hydrogen production in gas mixture. The structure of the presented catalysts inducted catalytic cracking of covalent bonds in sawdust to release more hydrogen gases. The highest H_2 yield 17.04 mol/kg biomass and the highest gas productivity of 0.72 Nm^3/kg biomass were obtained with the presented TiO_2/Al_2O_3 catalyst at pyrolysis temperature of 800 °C. It was also revealed that, the higher temperatures make lower char yield, higher catalytic performance as well as hydrogen rich gas production on sawdust pyrolysis. Whereas carbon conversion rate of sawdust pyrolysis was observed as 41.2% without catalyst, it was significantly increased to 53.6% with the presented catalyst at 800 °C. Therefore, the maximum hydrogen production was obtained in the presence of the TiO_2/Al_2O_3 catalyst in sawdust pyrolysis under the temperature of 800 °C. For future studies, the TiO_2/Al_2O_3 catalyst can be further developed for applications on hydrogen production of sawdust pyrolysis.

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Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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