Hydrogen Production from Agricultural Waste Using Bentonite-Supported Catalyst

Elif Ece Çağlı¹ , Nezihe Ayas^{1,*}

¹Eskisehir Technical University, Engineering Faculty, Department of Chemical Engineering, 2 Eylül Campus, 26555 Eskisehir, Turkey.

Article History

Received 30 June 2021

Accepted 20 September 2021

First Online 15 November 2021

Corresponding Author

Tel.: +902223213550

E-mail: nazcan@eskisehir.edu.tr

Keywords

Biomass

Catalyst

Gasification

Hydrogen

Abstract

Agricultural wastes have a high commercial potential for being utilized as a raw material to generate energy and they are proposed as an alternative energy source for fossil-based fuels. In this study, the biomass mixture (the mixture of sunflower seed pulp, tea, and tobacco waste) was gasified using Ni-based bentonite supported catalysts. The catalysts were synthesized via the impregnation method by loading different amounts (10 and 20 wt%) Ni over bentonite then analyzed by XRF, XRD, and FT-IR. The biomass gasification was performed by using an updraft gasifier with a constant biomass/catalyst ratio (5/1) in the presence of air atmosphere as a gasification agent, at 650°C and for 15 min. The highest hydrogen yield was obtained as 5.31 mol/kg biomass at 650°C, for 15 min by using 20 wt% of Ni/Bentonite.

Introduction

The majority of global energy demands are met through fossil-based fuels however it pollutes the environment and causes emissions of SO_x, NO_x, and CO₂. The utilization of cleaner fuels can avoid environmental problems and climate change. Renewable energy sources are the ultimate solution for dealing with global warming which has a less environmental impact (Abbasi & Abbasi, 2011).

Hydrogen is a clean energy carrier and has the highest energy content per mass than conventional fuels. Renewable energy sources such as biomass, solar, hydropower, and wind power can be harnessed for producing hydrogen (Christopher & Dimitrios, 2012). Biomass is a sustainable alternative renewable energy source that has net zero CO₂ emissions. (Min et al., 2011). Biomass sources could be classified into six groups: forestry waste, agricultural waste, animal waste, industrial waste, municipal solid waste, and sewage

(Tursi, 2019). Wood, herbaceous materials, and agricultural waste, in particular, at a rate of approximately 64 million tons per year in Turkey, making it a significant source of waste for energy production (Türkiye Biyokütle Enerjisi Potansiyeli Atlası (BEPA), 2021). Agricultural wastes are attractive energy sources as they are cost-effective and renewable. Thermal (such as combustion, pyrolysis, gasification, liquefaction, etc.) and biological (such as direct biophotolysis, indirect biophotolysis, biological water–gas shift reaction, photo-fermentation, and dark-fermentation, etc.) methods are available for hydrogen production from biomass (Chang et al., 2011). Gasification is one of the promising technology for converting biomass to syngas which can be used in order to obtain heat, power, and chemicals (Lopez et al., 2016).

During the biomass gasification process, organic materials are converted into syngas (combustible gas), tar, and char in the presence of a limited oxidation

atmosphere (air, oxygen, steam, etc.). The main issue of gasification is tar formation which poses operating and technical issues that deactivates the catalyst. There are several tar removal methods, which could be divided into two main groups; post-gasification reduction and tar reduction in situ. Post-gasification reduction includes physical methods by using different equipment such as cyclones, electrostatic precipitators, or chemical methods by thermal and catalytic processes, and partial oxidation. In-situ reduction is accomplished by adding additives or catalysts during gasification. Reducing tar formation by directly adding catalyst or additives in the gasifiers improves the yield of the syngas and high conversion efficiency as well. In addition to reducing tar formation, catalysts are used in order to obtain high-quality syngas at lower reaction temperatures (Rios et al., 2018; Wu & Williams, 2011).

Many researchers have been investigated several catalytic materials such as natural clay-based catalysts (Hervy et al., 2019), Ni-based catalysts (Srinakruang et al., 2005), noble metal-based catalysts (Mazumder & de Lasa, 2015), and alkaline catalysts (Jiang et al., 2015) and they are widely employed in the gasification process. Natural catalysts are more preferable due to being less expensive and abundant (Islam, 2020). Bentonite is a natural clay that is composed of volcanic ash. It contains a type of smectic group minerals including montmorillonite, beidellite, nontronite, saponite, sauconite, wolchonskoite, and hectorite. One or several minerals can be presented in the clay (Oliveira et al., 2016). Bentonite has various applications and is mostly used as an adsorbent (Hamid et al., 2017), in wastewater treatment (Huang et al., 2017), drilling muds (Abdou et al., 2013), etc. Apart from them, bentonite was used directly as a catalyst in the biomass gasification studies reviewed in the literature. The study of biomass gasification has not been found in the literature survey in which bentonite is used as a support material by loading Ni metal.

Hamidi et al. (2018) investigated the effect of bentonite through the gasification of oil palm waste on hydrogen and methane gas yield. Bentonite increased the hydrogen and methane gas yield while decreasing carbon dioxide.

Aprianti et al. (2021) gasified oil palm empty fruit bunch (OPEFB) at various reaction temperatures (350–550°C) in an updraft gasifier. The highest hydrogen and carbon monoxide amounts were achieved at 27.74% and 20.43% at 550°C, respectively.

The purpose of the study is to evaluate different agricultural wastes and the effect of calcined-bentonite and synthesized Ni/Bentonite catalysts on gas composition. The different Ni content of bentonite-based catalysts was prepared by the impregnation method and analyzed by using XRF, XRD, and FT-IR techniques. The experiments were carried out at 650 °C, for 15 min, in an updraft tubular reactor in the presence of calcined-bentonite and synthesized catalysts.

Materials and Methods

Materials

Sunflower seed pulp, tea waste, and tobacco waste were provided by different factories, which are all located in Turkey. Sunflower seed pulp was the residue part of the oil extraction process. The part of tea and tobacco waste were obtained before processing. Nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ was purchased from Sigma-Aldrich and used as a Ni precursor. Bentonite was supplied from a factory in Turkey.

Catalysts Preparation

Bentonite has high moisture (24 wt%), therefore it was dried at 105°C and for 24 h. The catalysts were prepared via the impregnation method. Bentonite was used as a support material. Nickel nitrate hexahydrate as a Ni precursor and distilled water was dissolved and then added into bentonite. The aqueous solution was stirred at 70°C and for 3 h. It was aged at room temperature overnight. After aging, the sample was dried at 105°C and for 24 h. Finally, the catalysts were calcined at 400°C for 2 h in the presence of air atmosphere.

Catalyst Characterization

The compositional analysis of bentonite and catalysts was performed on the X-ray fluorescence (XRF) instrument, Rigaku ZSX. The crystal structure of bentonite and catalysts were recorded on X-ray diffraction (XRD) with a Rigaku Rint 2200 instrument by using the radiation of Cu-K α at 40 kV and 30 mA at $2\theta=5-85^\circ$ at a rate of $2^\circ/\text{min}$. Fourier transform infrared spectroscopy (FTIR) was performed using Thermo Science Nicolet IS10 brand which is the range of spectra from 650 to 4000 cm^{-1} in order to identify the functional groups of the materials.

Experimental System

The experimental system mainly includes an updraft tubular reactor, ceramic insulator, gas-liquid separator, particle-moisture filter, airflow meter, electrical supply, and controller. The stainless steel (316) updraft tubular reactor has a height of 90 cm and an inner diameter of 1 cm. A schematic drawing of the experimental system is shown in Figure 1.

Experimental Procedure

Experiments were performed at 650 °C reaction temperature, for 15 min reaction time, and in the presence of various catalysts. At least all experiments were repeated 3 times and obtained similar results. The experimental error was calculated according to the following formula in Eq. 1 and the standard deviation

values were varied between 0.01-0.9 (Azcan & Danisman, 2008).

$$\delta = \sqrt{\frac{\sum_{i=1}^n (X_i - X_{avg})^2}{n-1}} \quad (1)$$

Biomass materials were milled using a rotary cutter mill device and at a speed of 8000 RPM. The equal amount of sunflower seed pulp, tea waste, and tobacco waste was thoroughly blended. The biomass/catalyst weight ratio was constant at 5/1. Prior to gasification, the catalysts were reduced at 800°C for 30 min under H₂/N₂ mixture (20 (v/v% of H₂) flow. Biomass mixture (sunflower seed pulp, tea waste, and tobacco waste) and the catalyst were placed into a gasifier. The reactor was located in a ceramic insulator for the insulation of heat. High purity air as a gasification agent was fed into the bottom of the tubular reactor and adjusted by a flow meter. The gas sampling bag was used in order to collect the product gas and analyzed by using micro-gas chromatography. The liquid product was collected from a gas-liquid separator with dichloromethane as a solvent and the solvent was evaporated from the liquid product

using the rotary evaporator. The solid product was obtained from the reactor and then the solid product was dried at 105°C for 24 h. Finally, both products were weighed as tar and char.

Syngas Analysis

The composition of the product gas was determined by SRA Technologies Micro Gas Chromatograph instrument (μ-GC) (T-3000 series) equipped with MS5A (Molecular sieves 5 Å) and PPQ (PolarPlot Q) columns coupled to a thermal conductivity detector (TCD).

Results and Discussion

Catalysts Characterization

The chemical compositions of bentonite, calcined bentonite 10 wt% of Ni/Bentonite and 20 wt% of Ni/Bentonite catalysts are given in Table 1.

Table 1 shows that the dominant components in bentonite are silica oxide and alumina that are used as

Figure 1. Schematic drawing of the experimental system; (1) tubular gasifier, (2) ceramic insulator, (3) thermocouple, (4) gas-liquid separator, (5) particle filter, (6) moisture filter, (7) high purity air, (8) electrical supply, (9) controller

Table 1. XRF analysis results of catalysts

	Catalysts			
	Bentonite	Calcined Bentonite	10 wt.% Ni/Bentonite	20 wt.% Ni/Bentonite
NiO	-	-	13.38	22.61
Na ₂ O	0.85	0.85	0.82	0.72
MgO	1.74	1.35	1.34	1.21
Al ₂ O ₃	13.48	12.5	11.57	10.03
SiO ₂	70.72	74.1	62.31	56.12
P ₂ O ₅	0.04	0.03	0.03	0.03
SO ₃	0.05	0.04	0.05	0.05
K ₂ O	1.37	1.44	1.20	1.06
CaO	2.41	2.95	1.90	1.28
TiO ₂	0.12	0.13	0.11	0.11
Fe ₂ O ₃	1.34	0.72	1.01	0.65
LOI*	7.86	5.73	6.27	5.68

*LOI: Loss on ignition

support materials of catalysts. Alumina provides a reduction of tar during biomass gasification (Erkiaga et al., 2013). Since the results of XRF analysis are given as NiO, its amount is higher than the calculated Ni loading. This represents that the Ni metal into bentonite is appropriately loaded.

The XRD patterns of bentonite, calcined bentonite, 10 wt% of Ni/Bentonite, and 20 wt% of Ni/Bentonite are shown in Figure 2.

Figure 2. indicates that bentonite mainly includes montmorillonite minerals with characteristic peaks. The peaks of montmorillonite found at 2θ ($^\circ$)=19°, 24°, 35-37°, 61°. The peaks of quartz found at 2θ ($^\circ$)=21°, 26°, 27°. The existence of SiO₂ can be seen from the XRD pattern of bentonite, which supported the results of XRF analysis as well. The intensity of the montmorillonite peaks decreases with the increasing Ni amount in the catalysts (Zhirong et al., 2011).

Figure 3. illustrates the FT-IR spectrum of bentonite, calcined bentonite, 10 wt% of Ni/Bentonite, and 20 wt% of Ni/Bentonite. The band at 3650 cm⁻¹ is observed with the stretching vibrations of OH groups in the bentonite. The absorption band at 914 cm⁻¹ indicates Al-Al-OH stretching. The sharp band corresponding to Si-O bending vibration is observed in the range of 997-1010 cm⁻¹ (Zhirong et al., 2011).

Activity Tests of Catalysts

In order to determine the activity of catalysts, the gasification of biomass mixture was carried out at 650°C reaction temperature, 15 min reaction time, with and without catalyst.

Figure 4. shows that the effect of the catalysts and their nickel loading ratio (0, 10, 20 wt%) on the gas composition yield distribution. The hydrogen yield was obtained as 3.08 mol/kg biomass without using any catalyst. The hydrogen yield slightly increased from 4.45 to 5.31 mol/kg biomass when the Ni loading ratio increased from 0 to 20 wt%. The highest hydrogen yield was achieved as 5.31 mol/kg biomass in the presence of 20 wt% of Ni/Bentonite. Since bentonite is mainly composed of SiO₂ (Tomishige et al. 2004) and Al₂O₃ (Farooq et al., 2021), it has a good catalytic effect without nickel loading. SiO₂ (Tomishige et al., 2004), Al₂O₃ (Farooq et al., 2021), and both of them (Keller et al., 2016) is used widely as a catalyst support material in the gasification process. The amount of hydrogen increases as Ni content affects shifting steam reforming and water-gas shift reactions thus improving hydrogen yield (Chan & Tanksale, 2014). While methane yield improved with the increasing Ni loading ratio, carbon dioxide decreased from 14.49 mol/kg biomass to 13.01

Figure 2. XRD patterns of bentonite, calcined bentonite, 10Ni/Bentonite and 20Ni/Bentonite (Montmorillonite:●, Quartz:▲, NiO:■)

Figure 3. FT-IR spectrum of bentonite, calcined bentonite, 10 wt.% Ni/Bentonite and 20 wt.% Ni/Bentonite

mol/kg biomass, and carbon monoxide significantly increased as well.

As it is seen in Figure 5, the gas product percentage increases from 40 to 55 wt% by using calcined-bentonite. The highest gas product percentage was observed as 67 wt% in the presence of 20 wt% of Ni/Bentonite catalyst. The tar concentration considerably decreased when the gas product increased. Ni improved tar elimination, which is a significant problem during the gasification that caused plugging, fouling, and coking. The amount of Ni has a positive effect on the tar cracking reaction (Chen et al., 2019). According to a literature survey, several researchers have found that tar formation was eliminated by using Ni-based catalysts in their studies (Arauzo et al., 1997; Inaba et al., 2006; Sato et al., 2006).

Conclusion

In this study, the effect of calcined bentonite and the synthesized catalysts on the gas product distribution were investigated. Bentonite, calcined bentonite, and the synthesized catalysts were synthesized and then analyzed by XRD, XRF, FTIR.

The activity tests of catalysts were performed in the gasification of biomass mixture. The highest

hydrogen yield was obtained as 5.31 mol/kg biomass mixture at 650°C for 15 min and using a 20 wt% of Ni/Bentonite catalyst with a constant biomass/catalyst (wt/wt) ratio of 5/1. The hydrogen yield increased while the tar formation decreased. It observed that there is no significant difference when comparing the results of calcined bentonite and 20 wt% of Ni/Bentonite. It is effective directly used as a catalyst and economically suitable as well.

As a result of experiments, bentonite can be used as a support material by loading Ni metal that improved the hydrogen gas yield and tar removal. The mixture of biomass waste (sunflower seed pulp, tea waste, and tobacco waste) was a suitable feedstock in order to evaluate for hydrogen-rich gas production.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Acknowledgements

This study was financially supported within "The project of sustainable use of biomass to assist the

Figure 4. The Effect of catalysts on gas composition yield distribution (650°C, 15 min, with a biomass/catalyst: 5/1)

Figure 5. The product yield distribution (650°C, 15 min, with a biomass/catalyst: 5/1)

development of Turkey's economy towards green growth" by the Republic of Turkey Ministry of Agriculture and Forestry General Directorate of Agricultural Research and Policies, United Nations Industrial Development Organization, and Global Environment Facility.

References

- Abbasi, T., & Abbasi, S. (2011). 'Renewable' hydrogen: Prospects and challenges. *Renewable and Sustainable Energy Reviews*, 15(6), 3034–3040. <https://doi.org/10.1016/j.rser.2011.02.026>
- Abdou, M., Al-sabagh, A., & Dardir, M. (2013). Evaluation of Egyptian bentonite and nano-bentonite as drilling mud. *Egyptian Journal of Petroleum*, 22(1), 53–59. <https://doi.org/10.1016/j.ejpe.2012.07.002>
- Aprianti, N., Faizal, M., Said, M., & Nasir, S. (2021). Catalytic gasification of oil palm empty fruit bunch by using Indonesian bentonite as the catalyst. *Journal of Applied Engineering Science*, 19(2), 334–343. <https://doi.org/10.5937/jaes0-28781>
- Arauzo, J., Radlein, D., Piskorz, J., & Scott, D.S. (1997). Catalytic pyrogasification of biomass. Evaluation of modified nickel catalysts. *Industrial & Engineering Chemistry Research*, 36(1), 67–75. <https://doi.org/10.1021/ie950271w>
- Azcan, N., & Danisman, A. (2008). Microwave assisted transesterification of rapeseed oil. *Fuel*, 87(10–11), 1781–1788. <https://doi.org/10.1016/j.fuel.2007.12.004>
- Chan, F.L., & Tanksale, A. (2014). Review of recent developments in Ni-based catalysts for biomass gasification. *Renewable and Sustainable Energy Reviews*, 38, 428–438. <https://doi.org/10.1016/j.rser.2014.06.011>
- Chang, A.C.C., Chang, H.F., Lin, F.J., Lin, K.H., & Chen, C.H. (2011). Biomass gasification for hydrogen production. *International Journal of Hydrogen Energy*, 36(21), 14252–14260. <https://doi.org/10.1016/j.ijhydene.2011.05.105>
- Chen, G., Li, J., Liu, C., Yan, B., Cheng, Z., Ma, W., Yao, J., & Zhang, H. (2019). Low-temperature catalytic cracking of biomass gasification tar over Ni/HZSM-5. *Waste and Biomass Valorization*, 10, 1013–1020. <https://doi.org/10.1007/s12649-017-0107-7>
- Christopher, K., & Dimitrios, R. (2012). A review on exergy comparison of hydrogen production methods from renewable energy sources. *Energy & Environmental Science*, 5, 6640–6651. <https://doi.org/10.1039/c2ee01098d>
- De Oliveira, C.I.R., Rocha, M.C.G., Da Silva, A.L.N., & Bertolino, L.C. (2016). Characterization of bentonite clays from Cubati, Paraíba (Northeast of Brazil). *Cerâmica*, 62(363), 272–277. <https://doi.org/10.1590/0366-69132016623631970>
- Erkiaga, A., Lopez, G., Amutio, M., Bilbao, J., & Olazar, M. (2013). Steam gasification of biomass in a conical spouted bed reactor with olivine and γ -alumina as primary catalysts. *Fuel Processing Technology*, 116, 292–299. <https://doi.org/10.1016/j.fuproc.2013.07.008>
- Farooq, A., Song, H., Park, Y.K., & Rhee, G.H. (2021). Effects of different Al_2O_3 support on HDPE gasification for enhanced hydrogen generation using Ni-based catalysts. *International Journal of Hydrogen Energy*, 46(34), 18085–18092. <https://doi.org/10.1016/j.ijhydene.2020.05.199>
- Hamid, S.A., Shahadat, M., & Ismail, S. (2017). Development of cost effective bentonite adsorbent coating for the removal of organic pollutant. *Applied Clay Science*, 149, 79–86. <https://doi.org/10.1016/j.clay.2017.07.022>
- Hamidi, N., Purnami, & Juliyono, A.R. (2018). The effect of natural bentonite and temperature on gasification of oil palm shell. *AIP Conference Proceedings*, 1983(1), 020017. <https://doi.org/10.1063/1.5046213>
- Hervy, M., Olcese, R., Bettahar, M.M., Mallet, M., Renard, A., Maldonado, L., Remy, D., Mauviel, G., & Dufour, A. (2019). Evolution of dolomite composition and reactivity during biomass gasification. *Applied Catalysis A: General*, 572, 97–106. <https://doi.org/10.1016/j.apcata.2018.12.014>
- Huang, Z., Li, Y., Chen, W., Shi, J., Zhang, N., Wang, X., Li, Z., Gao, L., & Zhang, Y. (2017). Modified bentonite adsorption of organic pollutants of dye wastewater. *Materials Chemistry and Physics*, 202, 266–276. <https://doi.org/10.1016/j.matchemphys.2017.09.028>
- Inaba, M., Murata, K., Saito, M., & Takahara, I. (2006). Hydrogen production by gasification of cellulose over Ni catalysts supported on zeolites. *Energy & Fuels*, 20(2), 432–438. <https://doi.org/10.1021/ef050283m>
- Islam, M.W. (2020). A review of dolomite catalyst for biomass gasification tar removal. *Fuel*, 267, 117095. <https://doi.org/10.1016/j.fuel.2020.117095>
- Jiang, L., Hu, S., Wang, Y., Su, S., Sun, L., Xu, B., He, L., & Xiang, J. (2015). Catalytic effects of inherent alkali and alkaline earth metallic species on steam gasification of biomass. *International Journal of Hydrogen Energy*, 40(45), 15460–15469. <https://doi.org/10.1016/j.ijhydene.2015.08.111>
- Keller, M., Fung, J., Leion, H., & Mattisson, T. (2016). Cu-impregnated alumina/silica bed materials for chemical looping reforming of biomass gasification gas. *Fuel*, 180, 448–456. <https://doi.org/10.1016/j.fuel.2016.04.024>
- Lopez, G., Alvarez, J., Amutio, M., Arregi, A., Bilbao, J., & Olazar, M. (2016). Assessment of steam gasification kinetics of the char from lignocellulosic biomass in a conical spouted bed reactor. *Energy*, 107, 493–501. <https://doi.org/10.1016/j.energy.2016.04.040>
- Mazumder, J., & de Lasa, H.I. (2015). Fluidizable La_2O_3 promoted Ni/ γ - Al_2O_3 catalyst for steam gasification of biomass: Effect of catalyst preparation conditions. *Applied Catalysis B: Environmental*, 168–169, 250–265. <https://doi.org/10.1016/j.apcatb.2014.12.009>
- Min, F., Zhang, M., Zhang, Y., Cao, Y., & Pan, W.P. (2011). An experimental investigation into the gasification reactivity and structure of agricultural waste chars. *Journal of Analytical and Applied Pyrolysis*, 92(1), 250–257. <https://doi.org/10.1016/j.jaap.2011.06.005>
- Sato, T., Furusawa, T., Ishiyama, Y., Sugito, H., Miura, Y., Sato, M., Suzuki, N., & Itoh, N. (2006). Effect of water density on the gasification of lignin with magnesium oxide supported nickel catalysts in supercritical water. *Industrial & Engineering Chemistry Research*, 45(2), 615–622. <https://doi.org/10.1021/ie0510270>
- Srinakruang, J., Sato, K., Vitidsant, T., & Fujimoto, K. (2005). A highly efficient catalyst for tar gasification with steam. *Catalysis Communications*, 6(6), 437–440. <https://doi.org/10.1016/j.catcom.2005.03.014>

- Tomishige, K., Asadullah, M., & Kunitomi, K. (2004). Syngas production by biomass gasification using Rh/CeO₂/SiO₂ catalysts and fluidized bed reactor. *Catalysis Today*, 89(4), 389–403. <https://doi.org/10.1016/j.cattod.2004.01.002>
- Türkiye Biyokütle Enerjisi Potansiyeli Atlası (BEPA) [Turkey Biomass Potential Energy Map]. (2021). Enerji İşleri Genel Müdürlüğü. <https://bepa.enerji.gov.tr/>
- Tursi, A. (2019). A review on biomass: importance, chemistry, classification, and conversion. *Biofuel Research Journal*, 6(2), 962–979. <https://doi.org/10.18331/brj2019.6.2.3>
- Rios, M.L.V., González, A.M., Lora, E.E.S., & Almazán Del Olmo, O.A. (2018). Reduction of tar generated during biomass gasification: A review. *Biomass and Bioenergy*, 108, 345–370. <https://doi.org/10.1016/j.biombioe.2017.12.002>
- Wu, C., & Williams, P.T. (2011). Nickel-based catalysts for tar reduction in biomass gasification. *Biofuels*, 2(4), 451–464. <https://doi.org/10.4155/bfs.11.113>
- Zhirong, L., Uddin, M.A., & Zhanxue, S. (2011). FT-IR and XRD analysis of natural Na-bentonite and Cu(II)-loaded Na-bentonite. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 79(5), 1013–1016. <https://doi.org/10.1016/j.saa.2011.04.013>