

Catalytic decomposition of tar derived from wood waste pyrolysis using Indonesian low grade iron ore as catalyst

Doni Rahmat Wicakso, Sutijan, Rochmadi, and Arief Budiman

Citation: [AIP Conference Proceedings](#) **1737**, 060009 (2016); doi: 10.1063/1.4949316

View online: <http://dx.doi.org/10.1063/1.4949316>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1737?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Co-pyrolysis of biomass tar and iron ore fines for the production of direct reduced iron](#)

J. Renewable Sustainable Energy **7**, 043131 (2015); 10.1063/1.4928948

[Pyrolysis characteristics and kinetics of lignin derived from three agricultural wastes](#)

J. Renewable Sustainable Energy **5**, 063119 (2013); 10.1063/1.4841215

[Catalytic hydrorefining of tar to liquid fuel over multi-metals \(W-Mo-Ni\) catalysts](#)

J. Renewable Sustainable Energy **5**, 053114 (2013); 10.1063/1.4822050

[Catalytic pyrolysis of peat with additions of oil-slime and polymeric waste](#)

AIP Conf. Proc. **1482**, 595 (2012); 10.1063/1.4757541

[Production of Hydrogen from Bio-oil Using Low-temperature Electrochemical Catalytic Reforming Approach over CoZnAl Catalyst](#)

Chin. J. Chem. Phys. **23**, 451 (2010); 10.1088/1674-0068/23/04/451-458

Catalytic Decomposition of Tar Derived from Wood Waste Pyrolysis using Indonesian Low Grade Iron Ore as Catalyst

Doni Rahmat Wicakso^{1,2}, Sutijan², Rochmadi², and Arief Budiman^{2,3*}

¹ *Chemical Engineering Department, Faculty of Engineering, Lambung Mangkurat University, Jalan A. Yani KM. 36 Banjarbaru, 70714, South Kalimantan, Indonesia*

² *Chemical Engineering Department, Faculty of Engineering, Gadjah Mada University, Jalan Grafika No. 2 Bulaksumur, Yogyakarta, 55281, Indonesia*

³ *Center for Energy Studies, Gadjah Mada University, Sekip K1A, Yogyakarta, 55281, Indonesia.*

* Corresponding author Tel.: +62-274-902171; fax: +62-274-902170.

E-mail address: abudiman@ugm.ac.id

Abstract. Low grade iron ore can be used as an alternative catalyst for bio-tar decomposition. Compared to other catalysts, such as Ni, Rd, Ru, Pd and Pt, iron ore is cheaper. The objective of this research was to investigate the effect of using low grade iron ore as catalyst for tar catalytic decomposition in fixed bed reactor. Tar used in this experiment was pyrolysis product of wood waste while the catalyst was Indonesian low grade iron ore. The variables studied were temperatures between 500 – 600 °C and catalyst weight between 0 – 40 gram. The first step, tar was evaporated at 450 °C to produce tar vapor. Then, tar vapor was flowed to fixed bed reactor filled low grade iron ore. Gas and tar vapor from reactor was cooled, then the liquid and uncondensable gas were analyzed by GC/MS. The catalyst, after experiment, was weighed to calculate total carbon deposited into catalyst pores. The results showed that the tar components that were heavy and light hydrocarbon were decomposed and cracked within the iron ore pores to from gases, light hydrocarbon (bio-oil) and carbon, thus decreasing content tar in bio-oil and increasing the total gas product. In conclusion, the more low grade iron ore used as catalyst, the tar content in the liquid decrease, the H₂ productivity increased and calorimetric value of bio-oil increased.

Keywords: iron ore, catalytic decomposition, pyrolysis, hydrogen.

INTRODUCTION

Many power plants across the world burn fossil fuels to generate energy. Coal is the remains of ancient plants and trees that grew over 200 millions of years ago. Oil and gas is made up of the remains of microscopic plankton. Over millions of years these remains become the carbon-rich coal, oil and gas we can use as fuel. When fossil fuels are burned, they release carbon dioxide into the atmosphere which contributes to global warming. Using fossil fuels to generate energy also releases pollutants into the atmosphere [1]. Even, fossil fuels provide the main source of energy for our global economy however their stocks are limited and renewable fuels need to be found [2]. One of the renewable resources that are promising for substitution of fossil fuel in the future is biofuel.

Biofuels are fuels produced directly or indirectly from organic material, including plant materials and animal waste. Among the various biofuels type, biodiesel is widely studied by adopting esterification and transesterification reactions [3]. Several studies reported on biodiesel production performed in batch-stirred reactors from crude palm oil (CPO), cooking oil and palm fatty acid distillate [4,5]. Moreover, the continuous process of reactive distillation column is more popular due to low energy consumption [5-7]. However, biodiesel has poor cold-flow properties, which can be problem for engine performance and the oxygen content in the biodiesel is responsible for the low

heating value and the weakness of stability [8,9]. So, some researcher studied thermal conversion including gasification and pyrolysis processes.

Several studies reported on gasification process with the raw material of sugarcane bagasse and oil palm empty fruit bunches and showed promising result for producing bio-syngas [1,10]. However, the gasification process needs much higher energy compared to pyrolysis. Pyrolysis process has several advantages such as simple reactor configuration, faster reaction time, more liquid products (less energy for product separation) and adaptive to several of biomass [11]. Pyrolysis process produces gas, char and tar [12]. Char is the main product used as reducing agent, while tar and gas are by-product containing carbon and substantial energy [13]. In pyrolysis, tar is an undesired byproduct because it causes operational problems such as the contamination of the inner wall of a reactor, blockages in pipes, corrosion and formation of tar aerosols [14-16] and is also carcinogenic [17]. Therefore, it is necessary to take steps for removing tar or decomposing tar into fuel gas (bio-syngas) and other compounds that are more useful. There are three options to remove or decompose tar including physics, non-catalytic and catalytic processes [18]. However, the last process are the most promising economically and technically [19].

Several studies of tar decomposition using alkali metal catalysts such as Ni, Pt, Rh and Pd have been conducted [20-22]. The performance of the catalyst was Rh > Pt > Pd > Ni = Ru [23]. The most important problem in catalytic tar decomposition was catalyst deactivation due to the accumulation of carbon in the pores of the catalyst [24]. Recently, Fe-based catalyst has attracted attention some researchers. Besides its ability to reduce tar, it could be integrated in the iron-making process [25-26]. It has been reported that Fe added in the catalyst Ni / PG had better result than the Mg, Mn and Ce [27] and the Fe / olivine for tar decomposition process of biomass gasification in fluidized bed. It was concluded that the Fe / olivine could reduce tar and increase the production of bio-syngas [28]. The existence of Fe is believed to make the catalyst more active for producing clean bio-syngas. And usually, the material of Fe can be extracted from high-grade iron ore (total Fe > 60 mass %).

High-grade iron ore is used in the iron making process to produce high grade iron and steel [24]. However, it is limited in availability [29]. In contrast, low grade iron ore (total Fe <60% mass) is still available abundantly. Direct utilization of low grade iron ore in steel-making industries is thermally disadvantageous because it's requires high energy consumption compared to commercial high grade ore due to large content of combined water [24,25]. As compared to high grade iron ore, low grade iron ores contain more gangue minerals and combined water because main component is goethite, FeO.OH [26]. So when heated, the specific surface area of ore increases due to thermal decomposition effects on iron ore porosity. This process needs extra thermal energy in steel-making which makes the utilization of low grade iron ore less energy efficient. By using low grade iron ore as catalyst of tar decomposition, carbon in the form of tar will fill the pores of the iron ore. The deposited carbon within pores of the iron ore can act as reducing agents. Compared to conventional processes (processes in the blast furnace), the distance between carbon and iron atoms was very close so this process resulted in high reduction rate, low reduction temperature and low energy consumption [24]. Fig.1 shows the additional process of tar decomposition to produce energy (fuel). The additional process could also improve the quality of low grade iron ore that can be used as raw material in iron and steel-making industries.

The objective of this research was to investigate the effect of using Indonesian low grade iron ore as catalyst for tar catalytic decomposition in a fixed bed reactor. Yields of product, compositions of syngas and quality bio-oil were studied.

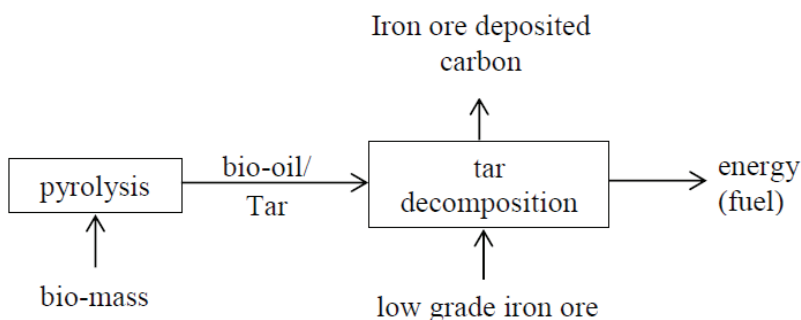


FIGURE 1. Scheme of tar decomposition process using low grade iron ore

MATERIALS AND METHODS

Materials

Tar used in this study was derived from pyrolysis of wood waste with heating value 28.77 MJ/kg and density 1.0358 gr/cm³. While low grade iron ore was obtained from PT. SILO (Sebuku Iiril Laterit) in Sebuku Island, Kotabaru, South Kalimantan, Indonesia. The compositions of low grade iron ore were 51.41 % of Total Fe, 7.214 % of Al₂O₃, 3.042 % of SiO₂ and 0.4803 % of NiO.

Methods

Fig. 2 shows the experimental equipment for tar decomposition. The experiment were carried out at temperature of 500 and 600 °C in a fixed bed reactor filled with catalyst range of 0 – 40 gram. The apparatus was equipped with vaporizer to ensure the oil enters the reactor in the vapor phase.

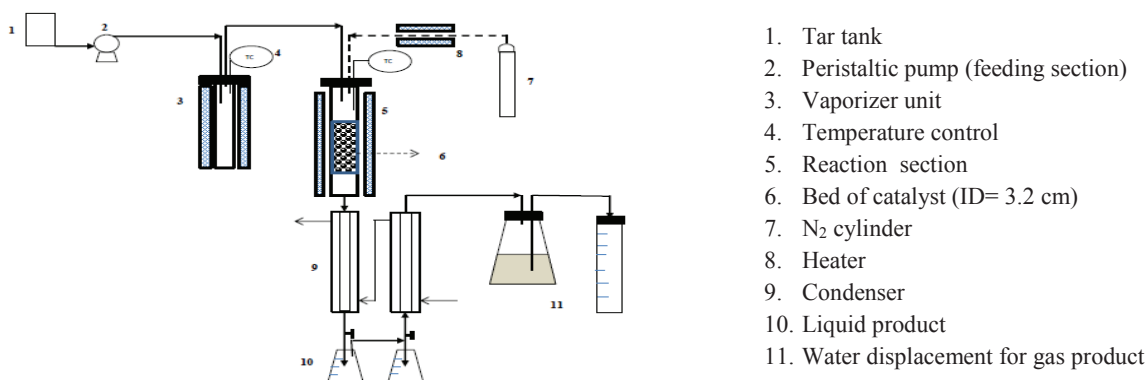


FIGURE 2. Experiment apparatus for tar decomposition

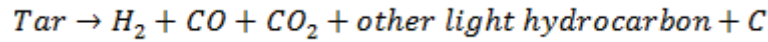
Prior to start the experiments, nitrogen was passed through the reactor and preheater to remove oxygen. The reactor and vaporizer were heated by an electric heating system and the temperature was controlled by a digital temperature controller. Once the temperature inside the reactor and vaporizer has reached steady condition at specified temperature, the tar was flowed into the vaporizer to vaporize the tar. Then, the vapor will pass through the catalytic bed and resulting in catalytic reaction. Subsequently, the vapor left the reactor and entering the cooling system. There are two phases which obtained from the condenser, the aqueous and the organic liquid phase. Besides product in the liquid phase, the cracking reactions also produce gas which its volume is measured by the displacement volume of water. The reaction was continued until no more liquid product was condensed. The composition of the liquid and gas product was analyzed using Gas Chromatography and GC-MS. The effectiveness of catalyst was evaluated by performing the experiments with various ratio of catalysts to oil and temperature of reaction.

RESULT AND DISCUSSION

Effect of Catalyst Weight on Yield of Product

The catalyst has a very important role in the reaction process because it can reduce the activation energy. By decreasing the activation energy, the reaction will proceed more rapidly to achieve the optimum conversion which will reduce the energy needed. In this experiment, a preliminary study was conducted for studying the performance of Indonesian low grade iron ore on the produced yields.

Fig. 3 shows the effect of weight of iron ore catalyst on the distribution of tar decomposition product including bio-oil, bio-char, gas and aqueous at 500 and 600 °C. It shows that gas and bio-char yield increased by increasing the catalyst weight, but bio-oil and aqueous yield decreased. It indicated that the iron ore has catalytic activity for tar decomposition. The introduction of iron ore to catalytic decomposition caused cracking tar as follow:



The tar components, heavy and light hydrocarbon, were decomposed and cracked within the iron ore pores into gases, light hydrocarbon (bio-oil) and carbon, resulting in decreased tar content in bio-oil and increased the total gas product. Simultaneously by tar decomposition, the carbon product of tar also infiltrated and deposited within the pores of the iron ore. Bio-char is amount of char product including deposited carbon. This data agreed with the result reported Uddin et al. that iron oxide promoted catalytic tar decomposition [16]. The existence Fe on catalyst is believed to make the catalyst more active, prevent the formation of stable chemical structures and decrease the activation energy [28,30].

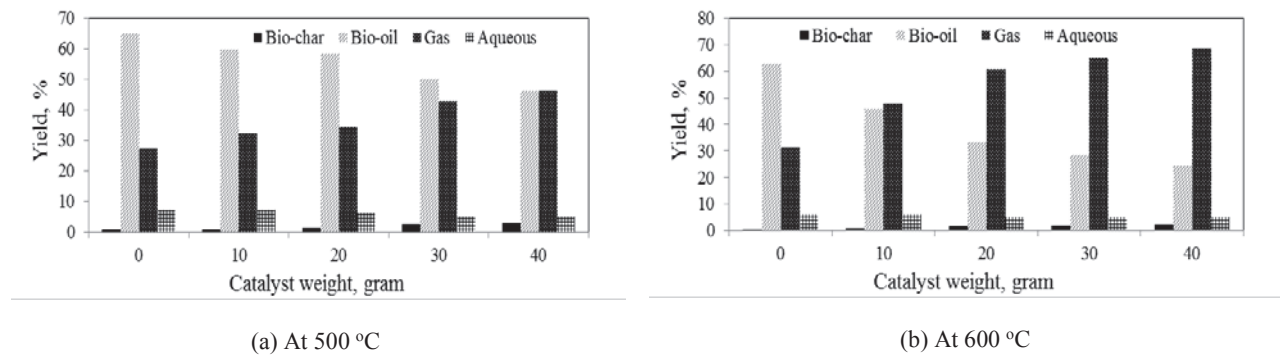


FIGURE 3. Effect of catalyst weight on yield of product

Effect of Catalyst Weight on Composition of Gas Product

The main gas components resulted to tar catalytic decomposition were CO, CO₂, H₂ and CH₄. Fig. 4 shows composition of gas product from this process. The results show that content of hydrogen and carbon dioxide increased while catalyst weight increased. Meanwhile, content of methane and carbon monoxide tend to decrease when catalyst weigh of tar decomposition increase. Decreasing CO and increasing H₂ as well as CO₂ were probably due to increasing in the water-gas shift reaction, where steam was produced to break deoxygenated reaction into hydrocarbon. However, this trend was not observed in the present work. From Fig. 4, we also identified that increasing catalyst weight of tar decomposition gave the better quality of syngas. This data agreed with the result reported Virgine et al. that Fe catalyst can improve syngas quality [33].

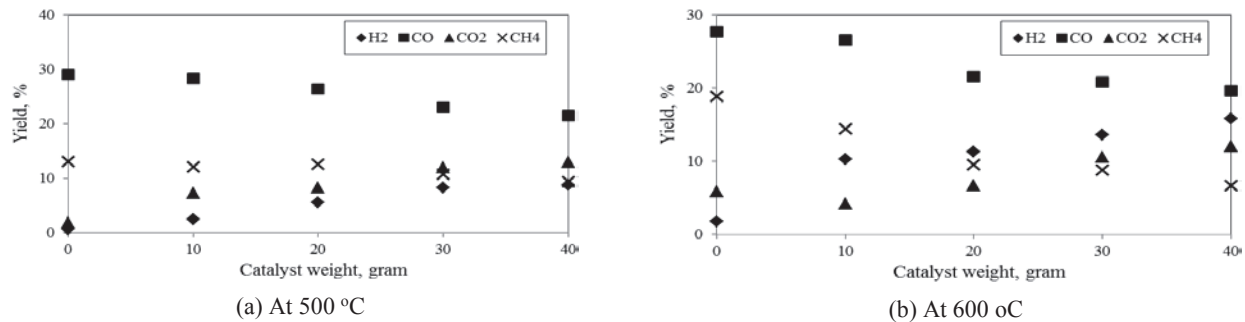


FIGURE 4. Content of syn-gas at various catalyst weight of tar decomposition

Effect of Catalyst Weight on Quality of Bio-Oil

Fig. 5 shows effect of catalyst weight on heating value of bio-oil. We may see that heating value of bio-oil increased when catalyst weight increased. This means that the presence of catalyst is easier to deoxygenation of oxygenated compounds in the tar into hydrocarbon compounds. From this figure, we also identified that the heating value of bio-oil at 600 °C was higher than the heating value at 500 °C.

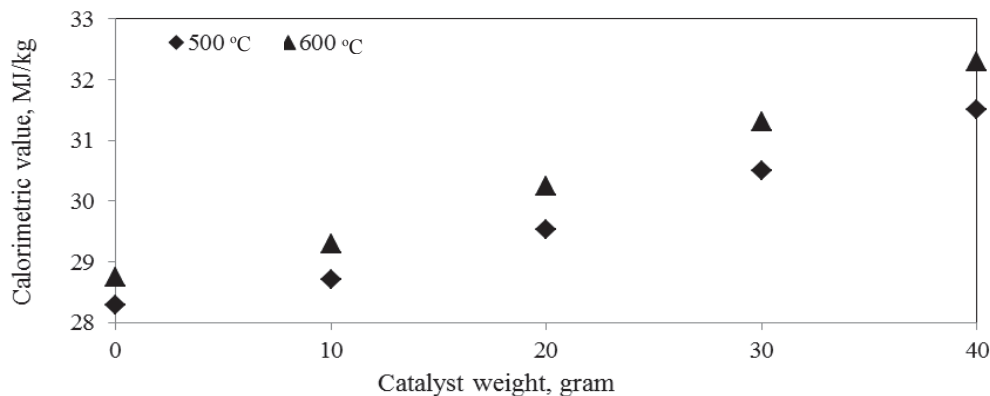


FIGURE 5. Effect catalyst weight on heating value of bio-oil

CONCLUSION

Effective utilization of Indonesian low grade iron ore was proposed as catalyst of tar decomposition. The main results can be summarized as follows.

1. The iron ore has good performance for tar decomposition. With the increasing of catalyst weight, gas product increased but bio-oil and bio-char decreased.
2. The iron ore also had influence on composition of gas product on tar catalytic decomposition. With the increasing of catalyst weight, content of hydrogen and carbon dioxide tends to increase while carbon monoxide and methane decrease.
3. Heating value of bio-oil increased when catalyst weight and temperature increased.

REFERENCE

1. Daniyanto, Sutijan, Deendarlianto, and A. Budiman, *Energy Proc.* **68**, 157-166 (2015).
2. W.H. Chen, C.J. Chen, C.I. Hung, C.H. Shen, and H.W. Hsu, *Appl. Energy*. **112**, 421-430 (2013).
3. S.K. Saxena and N. Viswanadham, *Fuel Process Technol.* **119**, 158 – 165 (2014).
4. W.A. Kawentar and A. Budiman, *Energy Proc.* **32**, 190-199 (2013).
5. A. Budiman, Sutijan, and D.R. Sawitri, *Int. J. Exergy*. **8** (4), 477-493 (2011).
6. A. Budiman and M. Ishida, *J. Chem. Eng. Japan* **30** (5), 966-969 (1997).
7. R.D. Kusumaningtyas, Rochmadi, S. Purwono, and A. Budiman, *Int. J. Exergy* **1** (4), 447-467 (2014).
8. J.A. Botas, D.P. Serrano, A. Garcia, and R. Ramos, *Appl. Catal. B: Environ.* **145**, 205-215 (2014).
9. G. Ramya, R. Sudhakar, J.A.I. Joice, R. Ramakrishnan, and T. Sivakumar, *Appl. Catal. A: Gen* **433-434**, 170-178 (2012).
10. Y.S. Pradana and A. Budiman, *JESTEC* **10** (8), 1-8 (2015)
11. S. Kudo, K. Norinaga, and J. Hayashi, *Journal of Novel Carbon Resource Sciences* **6**, 1-8 (2012).
12. R.C. Brown, *Thermochemical Processing of Biomass*, Wiley Series in Renewable Resources, United Kingdom, 124–127 (2011).
13. R.B. Cahyono, N. Yasuda, T. Nomura, T. Nomura, and T. Akiyama, 2014, *Fuel Process Technol.* **119**, 272 – 277 (2014).
14. J. Corella, A. Orio, and P. Aznar, *Ind. Eng. Chem.* **37**, 4617 – 4624 (1998).

15. L. Devi, K.J. Ptasinski, F.J.J.G Janssen, V.B. Sander, van Paasen, P.C.A. Bergman, and J.H.A. Kiel, [Renew. Energ.](#) **30**, 565-587 (2005).
16. M.A. Uddin, H. Tsuda, S. Wu., and E. Sasaoka, [Fuel](#) **87**, 451- 459 (2008).
17. Y. Shen and K. Yoshikawa, [Renew. Sust. Rev.](#) **21**, 371 – 392 (2013).
18. Z.A. El-Rub, E.A. Bramer, and G. Brem, [Ind. Eng. Chem](#) **43**, 6911 – 6977 (2004).
19. S. Schmidt, S. Giesa, A. Drochner, and H. Vogel, [Catal. Today](#) **175**, 442 – 449 (2011).
20. R. Zhang, R.B. Brown, A. Suby, and K. Cummer, [Energ. Convers. Manage](#) **45**, 995 – 1014 (2004).
21. P. Lu, Z. Yuan, L. Wu, L. Ma, Y. Chen, and N. Tsubaki, [Energ. Convers. Manage.](#) **48**, 1132 – 1139 (2007).
22. M. Asadullah, T. Miyazawa, S.I. Ito, K. Kunimori, M. Yamada, and K. Tomishige, [Appl. Catal. A-Gen](#) **267**, 95 – 102 (2004).
23. K. Tomishige, M. Asadullah, and K. Kunimori, 2004, [Catal. Today](#) **89**, 389–403 (2004).
24. R.B. Cahyono, A.N. Rozhan, N. Yasuda, T. Nomura, S. Hosokai, Y. Kashiwaya and T. Akiyama, [Fuel Process Technol.](#) **113**, 84 – 89 (2013).
25. Y. Hata, H. Purwanto, S. Hosokai, J. Hayashi, Y. Kashikawa, and T. Akiyama, [Energ. Fuel](#) **23**, 1128-1131 (2009).
26. A.N. Rozhan, R.B. Cahyono, N. Yasuda, T. Nomura, S. Hosokai, H. Purwanto, and T. Akiyama, 2012, [Energ. Fuel](#) **26**, 7340 – 7346 (2012).
27. H. Liu, C.H. Chen, X.L. Zhang, J.H. Li, D.Y. Chang, and L. Song, [Chinese J. Catalyst](#) **31**, 409 – 414 (2010).
28. M. Virginie, J. Ada'nez, C. Courson, L.F. de Diego, F. Garcí'a-Labiano, and D. Niznansky, [Appl. Catal. B: Environ.](#) **121–122**, 214–222 (2012).
29. M. Yellishetty, P.G. Ranjith, A. Tarumarajah, [Resources, Conservation and Recycling](#) **54**, 1084-1094(2010).
30. B.X. Shen and L. Qin, [Energ. Convers. and Manage.](#) **47** 1429–1437 (2006).