UTILIZATION OF NATURAL IRON ORE FOR CATALYTIC REACTION OF Pyroligneous Acid DERIVED FROM PALM KERNEL SHELLS

PEMANFAATAN BIJIH BESI SEBAGAI KATALIS PADA PROSES REAKSI KATALITIK Pyroligneous acid YANG BERASAL DARI CANGKANG KELAPA SAWIT

Muhammad Arifuddin Fitriady^{1,*}, Dieni Mansur¹, and Sabar Pangihutan Simanungkalit¹

¹⁻³Pusat Penelitian Kimia, Lembaga Ilmu Pengetahuan Indonesia, Kawasan Puspiptek Serpong, Tangerang Selatan, Indonesia

*E-mail: dienilipi@gmail.com

ARTICLE INFO

Article history

Received date:

3 May 2016

Received in revised form date:

23 June 2016

Accepted date:

1 August 2016

Available online date:

30 November 2016

Abstrak

Kebutuhan energi dan penurunan bahan bakar fosil bersamaan dengan munculnya kesadaran tentang kerusakan lingkungan menyiratkan bahwa pasokan energi masa depan harus berasal dari sumber energi terbarukan. Salah satu sumber energi terbarukan yang utama adalah biomassa. Pirolisa adalah dekomposisi yang cepat dari material organik tanpa adanya gas oksigen yang menghasilkan produk *pyrolysis oil*, gas, dan arang. Kandungan air yang tinggi dan ketidakstabilannya; seperti perubahan viskositas dan pemisahan fasa adalah masalah utama dari *pyrolysis oil* sebagai sumber dari bahan kimia yang berguna. *Pyrolysis oil* terpisah menjadi fasa minyak dan *pyroligneous acid*. *Pyroligneous acid* tersebut mengandung banyak bahan kimia, oleh karena itu *pyroligneous acid* tidak dapat dibuang secara langsung ke lingkungan karena akan mencemari lingkungan. Selanjutnya, *pyroligneous acid* perlu diolah untuk mendapatkan bahan kimia yang berguna. Reaksi katalitik dari *pyroligneous acid* yang didapat dari proses pirolisa dari cangkang kelapa sawit, telah dilakukan dengan menggunakan katalis bijih besi pada suhu 350 °C dengan W/F [W: massa tumpukan katalis (gram) dan F : laju alir umpan (g·h⁻¹)] sebesar 0,5 h. Hasil analisis menunjukkan bahwa bijih besi yang diberi pelakuan dengan kalsinasi pada suhu 285 °C memiliki kemampuan yang lebih tinggi untuk reaksi ketonisasi dari asam karboksilat dibandingkan dengan katalis lain. Walaupun begitu, baik kalsinasi hingga suhu 500 °C maupun perlakuan steam pada biji besi tidak dapat meningkatkan aktivitas dari katalis untuk reaksi ketonisasi secara signifikan meskipun luas permukaan BET dari katalis meningkat.

Kata kunci: Bijih besi, Reaksi katalitik, *Pyroligneous acid*, Pirolisa, Cangkang kelapa sawit.

Keywords:

Iron ores

Catalytic reaction

Pyroligneous acid

Pyrolysis

Palm kernel shells

Abstract

The energy demand and depletion of fossil fuels along with emerging consciousness about environmental degradation imply that the future energy supply has to come from renewable sources of energy. One of the major renewable energy sources is biomass. Pyrolysis is a rapid decomposition of organic materials in the absence of oxygen resulting in *pyrolysis oil*, gas, and charcoal products. High water contents and instabilities such as *viscosity* increase and phase separation are the main problems of *pyrolysis oil* as a source of useful chemicals. The *pyrolysis oil* is separated into the oil phase and the *pyroligneous acid*. The *pyroligneous acid* contains a lot of chemical substances, that prohibit removal to the environment as a waste due to environmental pollution. Furthermore, *pyroligneous acid* needs to be treated to obtain the useful chemical. In this study, catalytic reaction of the *pyroligneous acid*, derived from pyrolysis process of palm kernel shells, was carried out over natural iron ores catalyst at 350 °C with W/F [W: the amount of catalyst bed (g) and F: the flow rate of feed (g h⁻¹)] of 0.5 h. The analysis result showed that iron ores that treated by calcination at 285 °C had a higher ability for ketonization reaction of carboxylic acid compared to other catalysts. Even so, neither calcination up to 500 °C nor steam treatment of natural iron ores can significantly increase the activity of the catalyst for the ketonization reaction even though the BET surface area of the catalyst increased.

INTRODUCTION

Nowadays, the industrial and domestic energy needs of the society are fulfilled generally by the petroleum products. The demand for energy is increasing due to the rising growth of world population. The energy demand and depletion of fossil fuels along with emerging the awareness about environmental degradation imply that the future energy supply has to come from renewable sources of energy (Demirbas et al. 2001). One of the major renewable energy sources is biomass. Biomass is considered as a clean energy resource because it contains negligible amounts of nitrogen, sulfur, and ash compared to conventional fossil fuels, which results lower emissions of SO_2 , NO_x , and soot than the conventional fossil fuels (Q. Zhang et al. 2006; Börjesson 1996). In addition, CO_2 released from biomass is overcome by plants photosynthesis (Sembiring et al. 2015). Biomass can be used directly or indirectly by converting it into a gaseous or liquid fuel (LeValley et al. 2014).

Biomass can be converted to various forms of energy mainly by two types of processes: thermochemical, and biochemical (Dincer 2011). Biochemical processes decompose the biomass into biofuels by the action of the living organisms or their products. Biochemical processes produce a large amount of hydrogen in comparison with the other processes (Das et al. 2001). However, the efficiency of the biochemical process makes them less attractive for industries (Shweta et al. 2016).

Meanwhile, thermochemical conversion processes allowed biomass to break down into its constituents as bio-fuels, gasses, and chemicals by applying heat and pressure. Combustion, gasification, pyrolysis, and liquefaction are the four different types of thermochemical processes. Combustion can be defined as a complete oxidation of the fuel. The hot gasses

coming from the combustion can be used for direct heating purposes. A solid fuel combustion process will always begin with drying and pyrolysis/gasification (Sjaak van et al. 2008).

The gasification is a thermochemical conversion process in which biomass is heated at high temperatures and produces combustible gasses. Air, steam, or oxygen can be used as a gasification agent to increase energy value (Kalinci et al 2009). The syngas produced is a gas mixture of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2), and hydrocarbons. However, undesirable gasses such as hydrosulphuric (H_2S) and hydrochloric acid (HCl), or inert gasses such as nitrogen (N_2), can also be present in the syngas. (Molino et al. 2016).

Hydrothermal liquefaction can be determined as a conversion of biomass into liquid fuels by processing in a pressurized water environment to break down the solid biopolymeric structure to liquid components. Hydrothermal liquefaction was usually conducted in range temperature from 247°C to 374°C . This process aimed to remove oxygen in order to make the product has higher energy density than raw material (Elliott et al. 2015).

Pyrolysis is a rapid decomposition of organic materials in the absence of oxygen which results in the production of liquid, gaseous and charcoal products. It is a promising thermal approach that can be used to convert biomass into energy in the forms of pyrolysis oil, solid charcoal, and syngas composed of H_2 , CO , CO_2 , and hydrocarbon gasses. The drastic reduction of solid residue volume is the important advantage of pyrolysis compared to other energy conversion process (Sembiring et al. 2015). High water contents and instabilities such as viscosity increase and phase separation were the main problems of pyrolysis oil as a source of useful

chemicals. Pyrolysis oil was separated into the oil phase and pyroligneous acid (Mansur et al. 2014; Bridgwater 2011).

The oil phase product, after some treatment, can be used as a fuel blend oil. However, the pyroligneous acid contains a lot of chemical substances, which causes it cannot be discarded to the environment as a waste due to environmental pollution. Furthermore pyroligneous acid needs to be treated to obtain the useful chemical (Mansur et al. 2013).

There are many previous studies about the treatment of pyroligneous acid such as its antioxidant capability from the walnut shell (Wei et al. 2010), mangrove plant (Loo et al. 2007), and pineapple (Mathew et al. 2015). All of the pyroligneous acids can be used as an alternative natural antioxidant. Sumanatrakul et al. (2015) reported that pyroligneous acid derived from *Asper Backer* bamboo was capable of being used as an alternative antifungal and coagulating agent in a rubber sheet production process. Moreover, Möbius et al. (2012) studied about the usage of supercritical water gasification (SCWG) in gasification of pyroligneous acid which consists mainly of formic acid, glycolaldehyde, glycolic acid, and phenol. Temperature, residence time, TOC-concentration of feed, and usage of potassium carbonate as the catalyst were the variable of the study. It is reported that a higher gasification efficiency was achieved at high-temperature process condition and moderate residence times using low TOC-concentration of feed with the addition of potassium carbonate as catalyst (Möbius et al. 2012).

There are also many previous studies about iron oxide which used as a catalyst either to decompose plastic or upgrade bio oil. Zhang et al. (2014) reported that the Fe(III)/CaO catalyst can reduce the number of oxygenated compounds in the upgrading process of biomass fast

pyrolysis vapor. The catalyst has the ability to produce light phenols from heavy phenols without any methoxyl group and unsaturated C-C bonds on the side chain. Furthermore, the catalyst greatly decreased the yield of aldehydes and ketones and also completely eliminated the acids while significantly increase the yield of furans, light and aromatic hydrocarbons. It is reported that the zirconia-supporting iron oxide catalysts were capable of converting hydrocarbons contained in the product of hydrothermally liquefied sewage sludge to a mixture containing primarily acetone without any carbonaceous residue (Fumoto et al. 2006). The process was conducted at one atmospheric pressure and superheating steam atmosphere. Our previous study reported that the utilization of $\text{ZrO}_2\text{-FeO}_x$ catalyst in the catalytic reaction can convert hydroxyacetone and carboxylic acids (acetic and propionic acids) contained in the pyroligneous acid into aliphatic ketones (acetone and 2-butanone) via ketonization reaction (Mansur et al. 2013).

In this study, we try to utilize natural iron ore to enhance its usability as a catalyst to replace zirconia-supporting iron oxide catalyst. Natural iron ore was treated to a potential catalyst and its activities was tested in catalytic reaction of the pyroligneous acid.

MATERIALS AND METHODS

Materials

The Palm Kernel Shells (PKS) were obtained from a palm oil mills of PTPN-IV located in Tombatu (North Sumatera-Indonesia). The shells were reduced in size using a size reducer (crusher 5HP) operating at 2800 rpm min⁻¹, dried in an oven at 100 °C overnight and then sieved to obtain chips between 0.84 and 4 mm in length. The cellulose, hemicellulose, lignin, ash, and

moisture were analyzed using NREL methods and found to be 21.17, 16.13, 45.06, 1.87, and 15.77 wt% respectively (Hyman et al. 2008; Sluiter et al. 2008; Sluiter et al. 2008; Sluiter and Sluiter 2008). Moreover, the C, H, N, and O content were analyzed using CHN 628 (Leco Corporation) and found to be 48.6, 6.29, 0.48, and 44.63 wt% respectively. This carbon content value was used as the basis for calculation of the total carbon yield of products after the pyrolysis process.

Thermal Gravimetric Analysis of Iron Ore

Iron ore was weighed about 11-12 mg into a crucible and placed in sampling chamber. The sample was heated from 50 – 600 °C with the heating rate of 10 °C min⁻¹ in nitrogen condition. The nitrogen gas flow rate was 50 ml min⁻¹ as the carrier gas. At 600 °C the temperature was held for 5 min (isothermic) and then the heating was continued up to 950 °C in oxygen condition under the same flow rate and heating rate with nitrogen gas. The analysis was carried out using Netzsch TG 209 F3 Tarsus.

XRD, SEM, and EDX Analysis of Iron Ore

X-Ray analysis of iron ore was carried out in Research Centre for Physics, Indonesian Institute of Sciences using X-ray diffractometer, SmartLab, Rigaku. The microstructure of iron ore was analyzed by Scanning Electron Microscopy (SEM) type SU3500, Hitachi and point analysis was conducted by EDX X-max, Horiba that also located in the Research Centre of Physics.

Pretreatment of Natural Iron Ore for Catalyst

The natural iron ores were obtained from Lampung, Indonesia and treated in order to be able to used as a catalyst, the iron ores were treated in several ways to increase surface area. The treatments of iron ores were as follows:

1. Natural iron ore was crushed using porcelain mortar crusher then sieved to obtain 300 - 850 µm of grains catalyst. This catalyst was used as the base catalyst to make other treated catalysts.
2. The grains catalyst were calcined at 285 °C under heating and cooling rate of 10 °C min⁻¹ and holding time of two hours.
3. The grains catalyst were calcined at 500 °C under heating and cooling rate of 2 °C min⁻¹ and holding time of two hours.
4. The grains catalyst were treated by steam at 500 °C for an hour and then dried using drying oven at 120 °C overnight.
5. The grains catalyst were treated as the same as treatment no. 4, and continued by calcination at 500 °C for two hours.

Figure 1. Natural iron ore treatment for the catalyst

According to the natural iron ores treatment, there were five types of catalyst that used in this study. Simply, the catalyst and their symbols for pyroligneous acid catalytic reaction can be seen in Figure 1.

Calcination of natural iron ores was carried out in a high-temperature furnace (Thermolyne 46200). Moreover, the steam treatment was conducted in a fixed bed stainless steel reactor. The grains catalyst were placed in the reactor and heated up to 500 °C. The dosing pump was switched on to supply water with the flows rate of 10 ml min⁻¹. The water flow into the reactor and gradually becomes steam as the temperature increased. After contacting with catalyst, steam was discharged from the bottom of the reactor into the cold water trap. The process was maintained for an hour. A schematic diagram of the apparatus is shown in Figure 2.

Figure 2. A schematic diagram of the apparatus for steam treatment of natural iron ore.

Pyrolysis Process

The pyrolysis experiments were carried out in a fixed-bed stainless steel flow reactor. The length and inner diameter of the pyroly-

zer were 59.69 cm and 2.54 cm, respectively. About 20 g of PKS chips were placed in the pyrolyzer. Nitrogen as a sweeping gas was passed through the pyrolyzer to remove air/oxygen. The nitrogen flow rate was set to 20 cm³ min⁻¹. The process was maintained at temperature 550 °C for 50 min. The temperature was measured using a thermocouple located just below the bed. Three stages of the condenser (0 °C) were installed to capture the vapor/liquid product, and non-condensable gasses were trapped in the water trap before it was released to the environment. A schematic diagram of the pyrolysis apparatus is given in Figure 3.

Figure 3. A schematic diagram of the pyrolysis apparatus

The heat of the pyrolyzer was terminated when the desired reaction time was reached, and the system was allowed to cool to room temperature. The pyrolyzer, and all condenser, including all of the connections tubes, were carefully removed from the system and weighed. Char remained on the bed after pyrolysis. Pyrolysis oil obtained in condenser then to be united in one condenser and let settled. The

pyroligneous acid was removed from oil phase using a pipette and used as feedstock in the catalytic reaction.

Catalytic Reaction of Pyroligneous Acid

The catalytic reaction of pyroligneous acid over the iron ore catalyst was carried out in a fixed bed stainless steel flow reactor for two hours under atmospheric conditions at 350 °C. Two concentrations of pyroligneous acid: were produced, and 50% diluted in distilled water, hereafter called as 100% feed and 50% feed of pyroligneous acid respectively, were fed into the reactor as the variable process. Nitrogen gas (15 cm³ min⁻¹) used as the carrier gas. W/F [W: Amount of catalyst bed (g) and F: Flow rate of feed (g h⁻¹)] was 0,5 h. A schematic diagram of the apparatus for the catalytic reaction is shown in Figure 4.

After the catalytic reaction, gas and liquid products were collected in a gas pack and a condenser (0 °C) respectively.

Figure 4. A schematic diagram of catalytic reaction of pyroligneous acid apparatus

The liquid product was analyzed by GCMS (Agilent Technologies 5977A

MSD) using DB-Wax column. The calculation of product composition was based on peak area of GC-MS. The n-butanol was added to the sample as the internal standard. The calculation based on peak area of GC-MS. Area of the component was compared with the n-butanol area to calculate mol and carbon mol (C-mol) of the component based on mol and C-mol of n-butanol. C-mol of the component was divided by C-mol of pyroligneous acid and then multiplied by 100% to find C-mol% of group chemicals. C-mol of pyroligneous acid was calculated according to its carbon content of elemental analysis.

C-mol% of component in the product was subtracted by C-mol% of component in pyroligneous acid to get the changes of yield for each group of chemicals (C-mol%).

The amount of coke-like residue deposited on the catalyst was measured by an elemental analyzer (Leco CHN 682). Product yields of the catalytic reaction were calculated based on the carbon contents of feed (pyroligneous acid).

RESULTS AND DISCUSSION

Chemical Composition of Pyroligneous Acid

During pyrolysis, there are several chemical reactions occurred and produced solid, water vapor, tar, volatiles, and gaseous products (Mansur et al. 2013). Water vapor, tar, and volatiles were condensed using three stages condensers with the same temperature of 0 °C. The uncondensable vapor and gaseous products were trapped in the water trap before released to the environment.

The pyrolysis oil was separated into the oil phase and the pyroligneous acid. The pyroligneous acid was mainly derived from pyrolysis of cellulose and hemicellu-

lose in PKS (Mansur et al. 2013). In this study, the pyroligneous acid, which was an organic-containing water solution, used as the feedstock for the catalytic reaction. Based on data from GCMS analysis, the chemical compounds in the pyroligneous acid were grouped into aliphatic ketones, cyclic ketones, furans, heterocyclic organic compounds, carboxylic acids, phenols, and benzenediols. The yields of chemical composition are shown in Table 1.

Table 1. The chemical composition of pyroligneous acid

Components	Composition [C mol%]
Aliphatic ketones	2.38
Cyclic ketones	3.50
Furans	6.78
Heterocyclic organic compounds	1.32
Carboxylic acids	38.24
Phenols	43.50
Benzenediols	2.77
Others	1.51

Characterization of Iron Ores Catalyst

In an application of iron ores as a natural mineral product for catalyst in the catalytic reaction of the pyroligneous acid, some analysis were needed such as TGA, XRD, SEM, and EDX. Thermal Gravimetric Analysis (TGA) and Differential Thermo-gravimetric (DTG) curves were needed in the selection of thermal treatment of the iron ores for catalyst purpose. The TGA and DTG curves of the iron ore are shown in Figure 5.

According to Figure 5, thermal degradation of iron ore took place within a wide range from 150 to 550 °C which consisted of two distinct decomposition regions: 150–400 °C and 400–550 °C. Around temperatures of 600–700 °C, there were peaks that correspond to change in carrier gas from nitrogen to oxygen during analysis. In decomposition region of 150–400 °C, it was predicted that moisture

Figure 5. TGA and DTG curves of iron ore

content of iron ores was vaporized. This prediction was confirmed by XRD analysis using two samples of iron ores that heated at 200 °C and 400 °C that represent prior to and after the decomposition region. XRD patterns of the iron ores can be seen in Figure 6.

Based on Figure 6, XRD patterns of both of the iron ores were the same that peaks of Fe_2O_3 and SiO_2 appeared in the same position. Therefore, by heating treatment at 200 °C and 400 °C, there were changes in crystallography of the iron ores. Referred to XRD analysis, it was found that crystal system of Fe_2O_3 was rhombohedral and SiO_2 was hexagonal with their

Figure 6. XRD analysis of iron ore after heating at 200 °C and 400 °C

fraction volume were 48.4% and 51.6%, respectively.

Moreover, the iron ores were also analyzed by SEM + EDX to show their microstructure and composition of elements and the results are shown in Figure 7. The microstructure of the iron ores was not uniform and maximum around 20 μm . In EDX analysis, three representing spectrums were analyzed to give the atomic ratio for each element and the atomic ratios for each element were different. According to the atomic ratio, the spectrum 1 and spectrum 2 can be considered as SiO_2 and Fe_2O_3 , respectively. On the other hands, spectrum 3 consisted of a mixture of oxides (Al_2O_3 , SiO_2 , and Fe_2O_3). Therefore, the iron ores were not only iron oxide (Fe_2O_3) but also containing other oxides.

Figure 7. SEM and EDX analysis of iron ore

Before used as a catalyst, the iron ores were treated in several ways as shown in

Figure 1. The treatments were aimed to increase the surface area of the ore prior to use as the catalyst. The catalyst was analyzed using surface area analyzer (Micromeritic tristar II) to identify BET surface area. The BET surface area of the catalyst is shown in Table 2.

Table 2. Catalyst surface area

Catalyst	BET Surface Area (m^2g^{-1})
Catalyst no. 1	3.78
Catalyst no. 2	18.77
Catalyst no. 3	19.90
Catalyst no. 4	19.33
Catalyst no. 5	11.33

According to Table 2, iron ores after calcination at 500 $^{\circ}\text{C}$ (catalyst no. 3) had a higher BET surface area than others. It was suggested that calcination at 500 $^{\circ}\text{C}$ allowed volatile which trapped between molecules to evaporate. It caused empty pores between the iron ore's molecules lead to increase the surface area of the catalyst.

Catalytic Reaction of Pyroligneous Acid over Natural Iron Ores Catalyst

Catalytic reaction of pyroligneous acid was conducted to investigate the activity of natural iron ores as the catalyst for ketonization reaction. Five types of the catalysts as listed in Figure 1 or Table 2 were used for the catalytic reaction of two concentrations of pyroligneous acid; the pyroligneous acid used as produced and 50% diluted in distilled water, hereafter called as 100% feed and 50% feed of pyroligneous acid, respectively.

The yield of the catalytic reaction of 50% feed of pyroligneous acid over natural iron ores catalyst is shown in Figure 8. Moreover, the changes of yield for each

group of chemicals compared to feed are shown in Table 3.

According to Figure 8 and Table 3, ketonization reaction occurred over natural

iron ores catalysts because the yield of aliphatic ketones increased while carboxylic acid decreased.

Table 3. The changes of yield for each group of chemicals over natural iron ores catalyst using 50% feed of pyroligneous acid

Group of Chemicals \ Catalysts	Changes of Chemicals Over the Catalyst [C-mol %]				
	1	2	3	4	5
Aliphatic ketones	0.80	1.88	0.64	0.39	0.12
Cyclic ketones	4.18	3.54	0.88	-0.96	0.75
Furans	-0.12	-0.17	-1.49	-0.66	-0.22
Heterocyclic organic compound	1.17	0.80	-0.25	-0.70	-0.40
Carboxylic acids	-2.69	-3.32	-1.89	-0.25	-0.02
Phenols	-7.75	-7.09	0.26	0.99	-2.05
Benzenediols	3.52	2.38	1.22	-0.51	0.87
Others	-0.53	-1.33	-1.21	-1.46	-1.34

Positive values mean increase in yield
Negative values mean decrease in yield

Figure 8. Yield of 50% w/w pyroligneous acid catalytic reaction process result

As it is explained before that keto-nization is a reaction of two molecules of carboxylic acids to form a molecule of aliphatic ketones and a molecule of CO_2 (Mansur et al. 2013). The increase in yield of aliphatic ketones was higher over iron ores catalyst calcinated at 285°C (catalyst no. 2) than other catalysts. In point of view of ketonization reaction, natural iron ores that can be used as catalyst and calcination at 285°C was good enough for the catalyst treatment although BET surface area of catalyst calcined at 500°C for two hours (catalyst no. 3) and steam treatment at 500°C for 1 hour (catalyst no. 4) were higher than catalyst no. 2. Catalyst no. 2 can increase the yield of aliphatic ketones as 2 C-mol% based on feed. The increasing yield was low compared to $\text{ZrO}_2\text{-FeO}_x$ catalyst that reached about 26 C-mol%.

It was predicted that the increase of aliphatic ketones yields over catalyst no. 2 will be higher if operated in W/F of 4 as well as the $\text{ZrO}_2\text{-FeO}_x$ catalyst.

Figure 8 and Table 3 were also shown the yield of phenols and benzenediols. Some of the phenols decreased followed by increasing benzenediols. It was caused by oxidation of phenols to form benzenediols (Greenhill-hooper et al. 2008).

Moreover, some of the phenols yields also increased that caused by the reaction of guaiacol via benzenediols (Amen-chen et al. 2001).

The yield of the catalytic reaction of 100% feed of pyroligneous acid over natural iron ores catalyst is shown in Figure 9 and the changes of the yield that calculated based on chemicals in the feed are shown in Table 4.

Table 4. The changes of yield for each group of chemicals over natural iron ores catalyst using 100% feed of pyroligneous acid

Group of Chemicals \ Catalysts	Changes of Chemicals Over the Catalyst				
	[C-mol %]				
	1	2	3	4	5
Aliphatic ketones	0.54	-1.38	-0.93	-1.64	-1.41
Cyclic ketones	3.06	0.17	0.31	0.35	1.35
Furans	1.84	-1.12	-0.97	1.13	1.02
Heterocyclic organic compounds	0.78	-0.33	-0.90	-0.50	-0.53
Carboxylic acids	-8.61	-0.31	2.48	-1.70	-3.03
Phenols	-10.38	-0.72	-2.46	-2.91	-3.91
Benzenediols	2.02	-0.32	-1.62	1.08	1.59
Others	2.94	-1.24	-0.66	0.00	0.76

Positive values mean increase in yield
Negative values mean decrease in yield

Figure 9. Yield of 100% w/w feed of pyroligneous acid catalytic reaction process result

According to Figure 9 and Table 4, ketonization reaction only occurred over fresh natural iron ores catalyst (catalyst no. 1) because of the increase of aliphatic ketones and the decrease of carboxylic acids. While catalytic reactions of 100% feed of pyroligneous acid over catalyst no. 2 to 5 were shown a decrease in yield of aliphatic ketones. It was caused by the high concentration of feed and low selectivity of the catalyst for ketonization reaction. Therefore, the formation of gas as decomposition of pyroligneous acid was high at high temperature.

Over catalyst no.1 (natural iron ore) oxidation of phenols into benzenediols also occurred because of the decrease of phenol yield as well as increasing benzenediols yield. It was suggested that 100% feed of pyroligneous acid was not so suitable for investigation activity of natural iron ores catalyst in ketonization reaction.

CONCLUSIONS

After some treatments, iron ores can be used as a catalyst for ketonization reaction. Iron ores contain not only iron oxide (Fe_2O_3) but also other oxides such as SiO_2 and Al_2O_3 . The iron ores which calcined at 285°C showed a higher activity than other catalysts in this study.

It can increase the yield of aliphatic ketones by about 2 C-mol% during the catalytic reaction with 50% feed of pyroligneous acid as the raw material. In this case, neither calcination up to 500°C nor steam treatment can increase the activity of natural iron ores as the catalyst for ketonization reaction even though the BET surface area increased.

ACKNOWLEDGEMENTS

This work was supported by Research Center for Chemistry, Indonesian Institute of Sciences. We acknowledge Ir. M. Yunus,

MTA form Research Unit for Mineral Technology in Lampung for sending us the natural iron ore.

REFERENCES

- Amen-chen, Carlos, Hooshang Pakdel, and Christian Roy. 2001. "Production of Monomeric Phenols by Thermochemical Conversion of Biomass : A Review." *Biore* 79: 277–99.
- BÖRJESSON, P.I.I. 1996. "Emissions of CO₂ from Biomass Production and Transportation in Agriculture and Forestry." *Energy Conversion and Management* 37 (95): 1235–40.
- Bridgwater, A V. 2011. "Review of Fast Pyrolysis of Biomass and Product Upgrading." *Biomass and Bioenergy* 38. Elsevier Ltd: 68–94. doi:10.1016/j.biombioe.2011.01.048.
- Das, Debabrata, and T Nejat Veziroä. 2001. "Hydrogen Production by Biological Processes: A Survey of Literature." *International Journal of Hydrogen Energy* 26: 13–28.
- Demirbas, Ayhan, and Gönenç Arin. 2001. "An Overview of Biomass Pyrolysis." *Energy Source* 24: 471–82.
- Dincer, Ibrahim. 2011. "Green Methods for Hydrogen Production." *International Journal of Hydrogen Energy* 37 (2). Elsevier Ltd: 1954–71. doi:10.1016/j.ijhydene.2011.03.173.
- Elliott, Douglas C, Patrick Biller, Andrew B Ross, Andrew J Schmidt, and Susanne B Jones. 2015. "Bioresource Technology Hydrothermal Liquefaction of Biomass: Developments from Batch to Continuous Process." *Bioresource Technology* 178. Elsevier Ltd: 147–56. doi:10.1016/j.biortech.2014.09.132.
- Fumoto, Eri, Yosuke Mizutani, Teruoki Tago, and Takao Masuda. 2006. "Production of Ketones from Sewage Sludge over Zirconia-Supporting Iron Oxide Catalysts in a Steam Atmosphere." *Applied Catalysis B: Environmental* 68: 154–59. doi:10.1016/j.apcatb.2006.08.006.
- Greenhill-hooper, Michael John, Robert Raja, and John Meurig-Thomas. 2008. "Selective Oxidation of Organic Compounds." united states. <http://patentimages.storage.googleapis.com/pdfs/US20080227984.pdf>.
- Hyman, D, A Sluiter, D Crocker, D Johnson, J Sluiter, S Black, and C Scarlata Nrel. 2008. *Determination of Acid Soluble Lignin Concentration Curve by UV-Vis Spectroscopy. National Renewable Energy Laboratory*.
- Kalinci, Yildiz, Arif Hepbasli, and Ibrahim Dincer. 2009. "Biomass-Based Hydrogen Production: A Review and Analysis." *International Journal of Hydrogen Energy* 34 (21). Elsevier Ltd: 8799–8817. doi:10.1016/j.ijhydene.2009.08.078.
- LeValley, Trevor L, Anthony R Richard, and Maohong Fan. 2014. "The Progress in Water Gas Shift and Steam Reforming Hydrogen Production Technologies - A Review." *International Journal of Hydrogen Energy* 39 (30). Elsevier Ltd: 16983–0. doi:10.1016/j.ijhydene.2014.08.041.
- Loo, A Y, K Jain, and I Darah. 2007. "Food Chemistry Antioxidant and Radical Scavenging Activities of the Pyroligneous Acid from a Mangrove Plant, Rhizophora Apiculata" 104: 300–307. doi:10.1016/j.food-chem.2006.11.048.
- Mansur, Dieni, Teruoki Tago, Takao Masuda, and Haznan Abimanyu. 2014. "Conversion of Cacao Pod Husks by Pyrolysis and Catalytic Reaction to Produce Useful Chemicals." *Biomass and Bioenergy* 66. Elsevier Ltd: 275–85. doi:10.1016/j.biombioe.2014.03.065.

- Mansur, Dieni, Takuya Yoshikawa, Koyo Norinaga, Jun-ichiro Hayashi, and Teruoki Tago. 2013. "Production of Ketones from Pyrolygneous Acid of Woody Biomass Pyrolysis over an Iron-Oxide Catalyst." *Fuel* 103. Elsevier Ltd: 130–34. doi:10.1016/j.fuel.2011.04.003.
- Mathew, Sindhu, Zainul Akmar Zakaria, and Nur Fashya Musa. 2015. "Antioxidant Property and Chemical Profile of Pyrolygneous Acid from Pineapple Plant Waste Biomass." *Process Biochemistry* 50 (11). Elsevier Ltd: 1985–92. doi:10.1016/j.procbio.2015.07.007.
- Möbius, Anja, Nikolaos Boukis, Ulrich Galla, and Eckhard Dinjus. 2012. "Gasification of Pyrolygneous Acid in Supercritical Water" 94: 395–400. doi:10.1016/j.fuel.2011.11.023.
- Molino, Antonio, Simeone Chianese, and Dino Musmarra. 2016. "Biomass Gasification Technology : The State of the Art Overview." *Journal of Energy Chemistry* 25 (1). Elsevier B.V.: 10–25. doi:10.1016/j.jechem.2015.11.005.
- Sembiring, Kiky C, Nino Rinaldi, and Sabar P Simanungkalit. 2015. "Bio Oil from Fast Pyrolysis of Empty Fruit Bunch at Various Temperature." *Energy Procedia* 65. Elsevier B.V.: 162–69. doi:10.1016/j.egypro.2015.01.052.
- Shweta, Sharma, and Pratik N Sheth. 2016. "Air – Steam Biomass Gasification: Experiments, Modeling and Simulation." *Energy Conversion and Management* 110. Elsevier Ltd: 307–18. doi:10.1016/j.enconman.2015.12.030.
- Sjaak van, Loo, and Koppejan Jaap, eds. 2008. *The Handbook of Biomass Combustion & Co-Firing*. Earthscan.
- Sluiter, A, B Hames, R Ruiz, C Scarlata, J Sluiter, and D Templeton. 2008. *Determination of Ash in Biomass*.
- Sluiter, A, D Hyman, C Payne, and J Wolfe. 2008. *Determination of Insoluble Solids in Pretreated Biomass Material*.
- Sluiter, A, and J Sluiter. 2008. *Determination of Starch in Solid Biomass Samples by HPLC*.
- Sumanatrakul, Panita, Panita Kongsune, Lakana Chotitham, and Unwena Sukto. 2015. *Utilization of Dendrocalamus Asper Backer Bamboo Charcoal and Pyrolygneous Acid*. *Energy Procedia*. Vol. 79. Elsevier B.V. doi:10.1016/j.egypro.2015.11.558.
- Wei, Qin, Xihan Ma, Zhong Zhao, Shanshan Zhang, and Shengchen Liu. 2010. "Journal of Analytical and Applied Pyrolysis Antioxidant Activities and Chemical Profiles of Pyrolygneous Acids from Walnut." *Journal of Analytical and Applied Pyrolysis* 88 (2). Elsevier B.V.: 149–54. doi:10.1016/j.jaap.2010.03.008.
- Zhang, Qi, Jie Chang, Tiejun Wang, and Ying Xu. 2006. "Upgrading Bio-Oil over Different Solid Catalysts." *Energy & Fuels* 20 (9): 2717–20.
- Zhang, Xiaodong, Laizhi Sun, Lei Chen, Xinping Xie, Baofeng Zhao, Hongyu Si, and Meng Guangfan. 2014. "Comparison of Catalytic Upgrading of Biomass Fast Pyrolysis Vapors over CaO and Fe (III)/ CaO Catalysts." *Journal of Analytical and Applied Pyrolysis* 108. Elsevier B.V.: 35–40. doi:10.1016/j.jaap.2014.05.020.