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Research Article

Utilization of Modified Zeolite as Catalyst for Steam Gasification of Palm Kernel Shell

Joko Waluyo[1,*], Petric Marc Ruya[2], Dwi Hantoko[3], Jenny Rizkiana[2], I.G.B.N. Makertihartha[2], Mi Yan[3], Herri Susanto[2]

[1]*Department of Chemical Engineering, Universitas Sebelas Maret, Surakarta, Indonesia.*
[2]*Department of Chemical Engineering, Institut Teknologi Bandung, Bandung, Indonesia.*
[3]*Institute of Energy and Power Engineering, Zhejiang University of Technology, Hangzhou, China.*

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Abstract

Syngas from biomass gasification is being developed for alternative feedstock in the chemical industry. Palm kernel shell which is generated from palm oil industry can be potentially used as raw material for gasification process. The purpose of this study was to investigate the use of modified natural zeolite catalysts in steam gasification of palm kernel shells. Mordenite type zeolite was modified by acid leaching to be used as a tar cracking catalyst. Steam gasification was conducted at the temperature range of 750–850 °C and the steam to biomass ratio was in the range of 0–2.25. The result showed that steam gasification of palm kernel shell with the addition of zeolite catalyst at 750 °C and steam to biomass ratio 2.25 could reduce tar content up to 98% or became 0.7 g/Nm^3. In this study, gasification of palm kernel shells produced syngas with the hydrogen concentration in the range of 52–64% and H_2/CO ratio of 2.7–5.7.

Keywords: Gasification; Tar Removal; Clean Syngas; Mordenite; Palm Kernel Shells

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1. Introduction

Biomass gasification is a thermochemical conversion technology that converts biomass into combustible gases by the use of gasifying agents such as air, steam, O_2, CO_2 or its combination. The product gas can be used for electricity production, and also as a raw material for the chemical synthesis, such as ammonia, methanol, Fischer Tropsch Fuels, and dimethyl ether [1]. However, product gas from gasification process contains contaminant, such as tar, particulate, ammonia, hydrogen sulphide, *etc.* [2]. Thus, the syngas cleaning is needed before the application of syngas. Tar is one of the contaminants that requires more attention on the biomass gasification derived gas.

Tar from the gasification process can cause plugging at lower temperature and also poison catalyst used during chemicals synthesis, which results in various problems during the operation and maintenance of the gasification process [3,4]. Therefore, there is a need for the attempt to reduce or eliminate the presence of tar. Tar is conventionally removed by physical treatment such as a wet scrubber where syngas temperature decreases and cause considerable wastewater. This could reduce the energy efficiency of the gasification process [5]. Thus, the

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* Corresponding Author.
Email: jokowaluyo@staff.uns.ac.id (J. Waluyo);
Telp: +62-271-632112, Fax: +62-271-632112

proposed tar removal process should be designed not only to eliminate tar, but also to convert tar into syngas, so the negative impact of the waste on the environment could be minimized. Catalytic steam reforming is predicted to be a suitable process in regards to achieve the previously mentioned results.

Twin fluidized bed has been claimed to be capable of producing syngas with low tar and high hydrogen content [6,7]. Twin fluidized bed with steam as gasifying agent produces H_2/CO ratio >1 and H_2 concentration more than 50%. Updraft gasifiers generally produce the largest amounts of tar, approximately 30-150 gram/Nm^3, followed by a downdraft and fluidized bed gasifier, at 0.01-6 gram/Nm^3 and 4-20 gram/Nm^3, respectively [8]. The fluidized bed gasification technology utilizes sand as the heating medium. Utilization of silica sand results in relatively high tar content in the product gas, and thus another material, preferably also functioning as tar cracking catalyst should be adopted. One way of achieving the desired process would be to use natural minerals that can be utilized as tar cracking catalyst. The development of natural mineral based catalyst is currently being carried out by several researchers, among which dolomite, olivine, ilminite, limonite, calcite, polygorskite, perovskite, which are adjusted with the available minerals in the respective region [9-15]. Dolomite achieves high activity in tar conversion but is a fragile material, while olivine has high attrition resistance but lower catalytic activity compared to dolomite [16]. Zeolite is an alumina-silica mineral that has been widely used as a cracking catalyst and adsorbent [17]. Besides having high activity in cracking, zeolites can be obtained synthetically or naturally. Natural zeolites have disadvantages because they have some impurities and low surface area. Therefore, natural zeolites need to be modified to increase their activity [18]. Natural zeolites contain some impurities which can be removed by ion exchange and acid leaching. Acid leaching is also used to increase the Si/Al ratio of zeolites, so more active and increase resistance.

The current study concerns the development of natural zeolite-based catalyst. Natural zeolite possesses various crystalline phases; among which mordenite, clinoptilolite, and mesolite are the more commonly applied types for catalysis purpose [19,20]. In a previous study, natural zeolite activity was tested in toluene steam reforming as a tar model and gave high activity results [21,22]. In the current study, zeolites are used for catalytic steam gasification of palm kernel shells. Increasing world palm oil production, palm kernel shells will be predicted to become significant solid waste in the future [23,24]. This research provides novel results and information regarding the conversion of palm kernel shells to syngas with a high H_2/CO ratio and low tar content using natural zeolites as a catalyst. The natural zeolite was modified to improve its catalyst activity. Furthermore, the natural catalyst is directly applied in the gasification of palm kernel shells to lower the tar content in syngas, which is closer to the actual or real condition of biomass gasification. The application of natural catalyst for catalytic cracking of tar derived from gasification is also much beneficial compared to the catalytic cracking of model tar. In addition to investigating the effect of modified zeolite catalyst, this study also investigates the effect of the steam to biomass ratio, temperature of gasification on the syngas concentration, tar conversion and carbon conversion.

2. Materials and Methods

2.1 Catalyst Modification and Characterization

Natural zeolite which is used as raw material is obtained from Wonosari - Indonesia, with a size of 5 – 10 mesh. NH_4NO_3 and HNO_3 solutions are used as ion exchange and acid leaching agents to remove some impurities. NH_4NO_3 and HNO_3 were purchased from Merck. Natural zeolites are washed and then dried. Modification was done in 2 steps, ion exchange and acid leaching. In ion exchange, every 1 gram of sample was stirred and refluxed with 10 mL 2 M NH_4NO_3 at 90 °C for 2 hours. The sample was then washed and followed by calcination at 550 °C for 12 hours to remove NH_3. Acid leaching was carried out by reflux using 6 M HNO_3 at 90 °C for 6 hours (ZA-66). At the end of the modification, the sample was washed and calcined at 550 °C for 12 hours. Ni/Zeolite (ZNi-665 and ZNi-6610) catalyst was prepared by impregnation of modified zeolite with solution of $Ni(NO_3)_2.6H_2O$ in an appropriate concentration to obtain a contents of 5 or 10 wt% of NiO. After impregnation, the catalysts were dried at 105 °C for 6 hours and continued to be calcined at 550 °C for 3 hours using temperature increasing rate 5 °C/min.

The sample pulverized into powder to characterized morphology structure and pore structure. The diffraction pattern of the catalyst was measured by XRD 6000 (Shimadzu, Japan) and recorded over 2θ ranged from 5°-60° with speed of 76.8°/minutes and step size of 0.019. The Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX, FEI

Quanta 200 ESEM FEG) (Oxford instruments Inc., Abingdon, United Kingdom) and X-ray fluorescence (XRF, Epsilon 3, United Kingdom) were used to quantify the elemental component and Si/Al ratio of modified zeolite. For surface and pore structure, liquid nitrogen absorption was measured at 77.35 K using Nova 3200e, United States. The Brunauer-Emmet-Teller (BET) method used to measure surface area and pore volume.

Table 1. Proximate and ultimate analysis of palm kernel shell.

Characterization of palm kernel shell		
1	Proximate analysis (adb) (%wt)	
	Moisture	8.19
	Volatile matter	70.45
	Fixed Carbon	18.89
	Ash	2.47
2	Ultimate Analysis (adb) (%wt)	
	Carbon	48.25
	Hydrogen	6.41
	Oxygen	42.69
	Nitrogen	0.15
	Sulfur	0.03
3	Heating value (kJ/kg)	19,820

2.2 Biomass Gasification

Palm kernel shell was obtained from a palm oil mill located in Lampung, Indonesia. The proximate and ultimate of palm kernel shell are presented in Table 1. The palm kernel shell goes through size reduction to the size of about 5 mm. The palm kernel shell was dried in the oven at 105 °C for 6 hours to remove unbounded air. The modified zeolite catalyst was prepared by ion exchange and acid washing. The detailed explanation can be found in our previous study [21,22]. The properties of modified zeolite catalyst are presented in Table 2.

Biomass gasification was conducted under atmospheric pressure in tubular furnace. The experimental set up is shown in Figure 1. In each experiment, 4 grams of palm kernel shell was loaded with the ratio of biomass to catalyst of 1:1. The flow rate of N_2 was set at 200

Table 2. Modified Natural Zeolite.

Catalyst	Acid leaching Conc. HNO_3 (M)	Leaching time (hr)	Ni Impregnation	Si/Al ratio*	Surface area (m^2/g)
ZA0	-	-	-	5.09	16
ZA66	6	6	-	5.61	161.8
ZNi-665	6	6	5%	5.31	73.5
ZNi-6610	6	6	10%	5.25	51.4

*analyzed by XRF

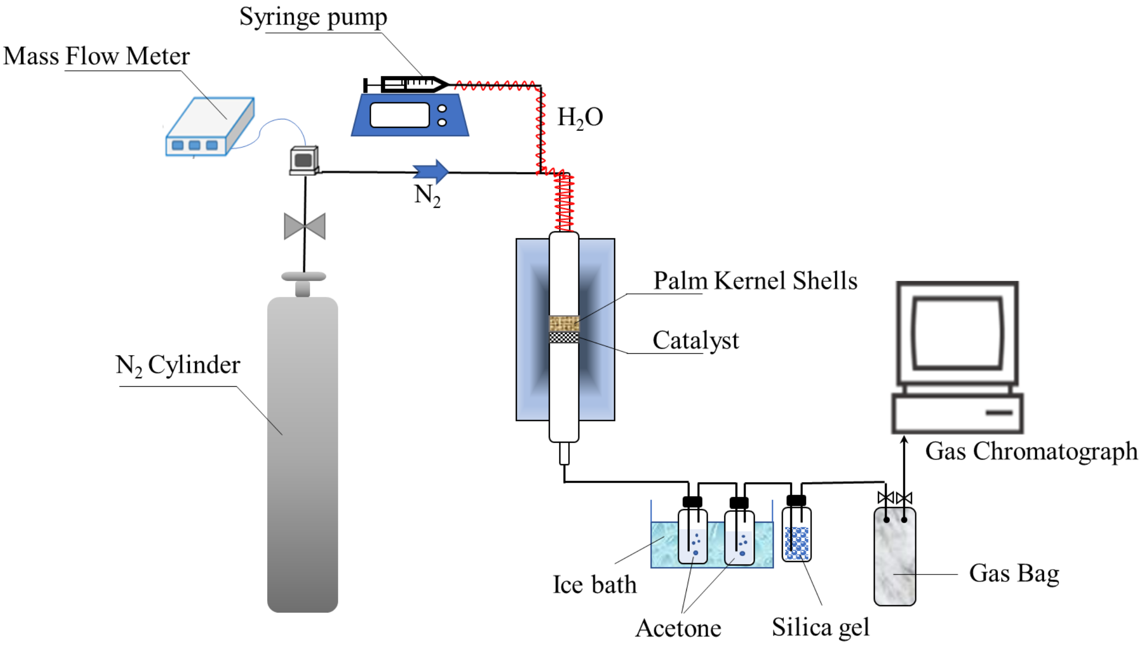

Figure 1. Experimental setup of steam gasification.

mL/min (at atmospheric condition). Electric heater was used to heat the reactor with the heating rate of 75 °C/min. When the temperature of the reactor has reached 400 °C, steam was injected into the reactor until the desired temperature has been reached (750 °C, 800 °C, 850 °C). Upon achieving the desired temperature, the temperature was kept for 30 minutes. Gasification derived tar was cooled down and then dissolved into acetone, while the gas produced was collected inside gas bag (capacity 10 Liter). Gravimetric analysis was used to determine the concentration of tar in syngas trapped in acetone. The composition/concentration of the pyrolysis and gasification product gas was analyzed using gas chromatograph (GV 2014A Shimadzu, Japan) with 2 columns (MS5A and Porapak-Q). The sample was analyzed using TCD (Thermal Conductivity Detector) at the temperature of 150 °C.

Yield of the pyrolysis products (tar, char and gas) are defined as follows:

$$Y_{tar} = \frac{w_{tar}}{w_{biomass}} \tag{1}$$

Yield of the gasification product, particularly hydrogen is defined as:

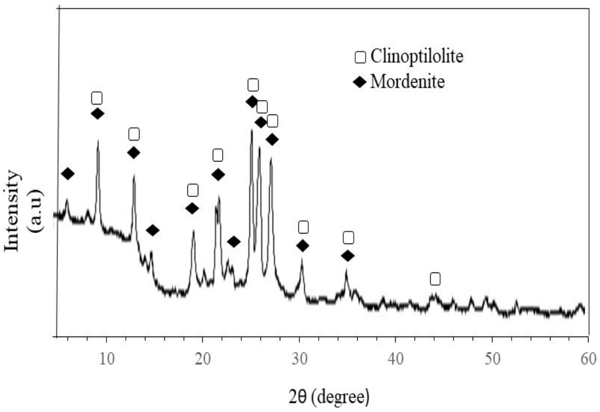

Figure 2. Natural zeolite structure.

$$Y_{H_2} = \frac{n_{H_2}}{w_{biomass}} \tag{2}$$

Mol of H_2 was calculated by using the following equation

$$n_{H_2} = \frac{\begin{bmatrix} \text{Flowrate of} \\ \text{Nitrogen} \end{bmatrix} \times \begin{bmatrix} \text{Collection} \\ \text{time} \end{bmatrix}}{\begin{bmatrix} \text{Concentration of} \\ \text{Nitrogen} \end{bmatrix}} \times \begin{bmatrix} \text{Concentration of} \\ \text{Hydrogen} \end{bmatrix} \tag{3}$$

For mol of CO, CO_2, CH_4 follow the Equation (3) by substituting the appropriate gas concentration.

Meanwhile, the potential yield of H_2 that can be obtained from the presence of CO from the composition of syngas. This may be due to the water gas shift reaction involving CO that is mild exothermic and relatively easy to perform:

$$Y_{H_2+CO} = \frac{n_{(H_2+CO)}}{w_{biomass}} \tag{4}$$

Biomass carbon conversion is defined as:

$$X_C = \frac{n_{(CO+CO_2+CH_4)}}{n_{Carbon\ in\ biomass}} \times 100\% \tag{5}$$

3. Results and Discussion

The composition and yield of syngas from biomass conversion is affected by several factors, namely temperature and the ratio of steam/biomass. Aside from the yield, carbon conversion will also be discussed in this section. The carbon conversion is the number of gaseous products obtained from CO, CO_2, and CH_4 as compared to the carbon (C) from biomass. The presence of catalyst on the gasification process can improve the carbon conversion with regard to the increase in the CO, CO_2 and CH_4 concentration (obtained due to the conversion of gasification derived tar into smaller component/syngas). In this sub-chapter characterization of catalyst, effect of catalyst type, ra-

Table 3. Zeolite composition as determined using EDX analysis.

No	Element	Fresh Zeolite	After acid leaching (ZA-66)	After impregnation Ni 5%	After impregnation Ni 10%
1	C	0	5.68	4.24	3.84
2	O	55.02	51.21	50.2	45.53
3	Na	0.72	0.22	0.19	0.32
4	Mg	0.87	0.53	0.36	0.36
5	Al	7.09	7.23	6.30	6.28
6	Si	30.47	31.48	31.01	30.61
7	K	0.65	0	0	0
8	Ca	3.06	1.72	1.65	1.67
9	Ti	0.27	0.27	0	0.19
10	Fe	2.57	1.65	0.72	1.36
11	Ni	0	0	5.34	9.82

tio of steam/biomass along with the gasification temperature on the composition and yield of tar is discussed.

3.1 Characterization of Catalyst

XRD results (Figure 2) show that Indonesia's natural zeolites consist of mordenite and clinoptilolite as the main components. The stage comparison is based on the ICDD (International Center for Diffraction Data) database. The diffraction results also showed that natural zeolites still contained impurities, in line with the results of component analysis using SEM-EDX (Table 3). Some of the impurities contained are alkaline and alkaline earth metals, such as: Na, K, Mg, Ca. These impurities can cover the pores and active sites of zeolites which can reduce zeolite activity. After modification by acid washing some of these impurities were reduced (Table 3 and Figure 3). In this study, the zeolite from acid washing was further modified with Ni impregnation to determine the effect of the addition of Ni on the zeolite on catalyst activity.

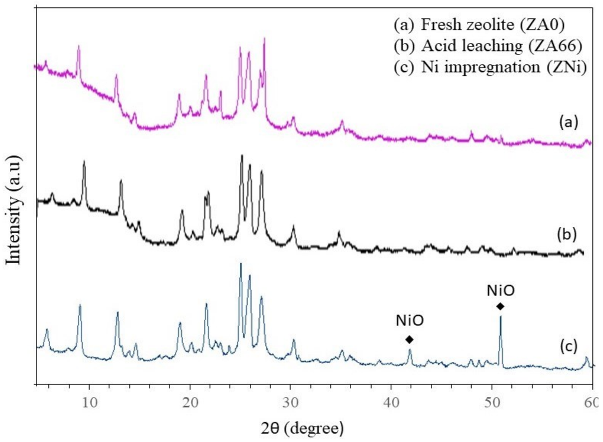

Figure 3. XRD pattern of modified zeolite.

The dealumination of natural zeolites using acid leaching generally had a negligible effect on the crystallinity as the characteristic peaks remain unchanged unless a small reduction in intensity. Figure 3 shows that small peaks at 2θ of 23°, 26.5°, and 29.5° have declined in intensity. The zeolite modification by acid leaching apart from reducing impurities also increased the Si/Al ratio and increased the surface area.

3.2 Effect of Catalyst Type

In previous studies, zeolites from Wonosari are mordenite type zeolite and after modification by ion exchange and acid leaching, impurities in zeolites such as Na, K, Mg can be removed. Impurity loss also has a positive impact on increasing surface area and pore volume [21]. In this study, the catalysts employed were the previously developed catalysts which has been tested using tar model component [22]. The modified zeolite catalyst was tested to determine the effect of catalyst to the syngas concentration, the yield of each syngas component, as well as carbon conversion, which represents the amount of reacted biomass and also the amount of reacted tar. The test was conducted at 750 °C, the ratio of catalyst to biomass is taken as 1:1, the ratio of steam to biomass taken as 1.5:1, and the flowrate of N_2 of 200 mL/hour.

The presence of catalyst did not affect the syngas composition significantly (Figure 4), however tar concentration decreased from 4.6 g/Nm³ to 1.9 g/Nm³ with the presence of ZA66 catalyst. In other words, the application of ZA66 catalyst reduced the tar content by 57%. When the gasification was conducted for 30 minutes, the effect of the catalyst on the syngas yield and carbon conversion can be ob-

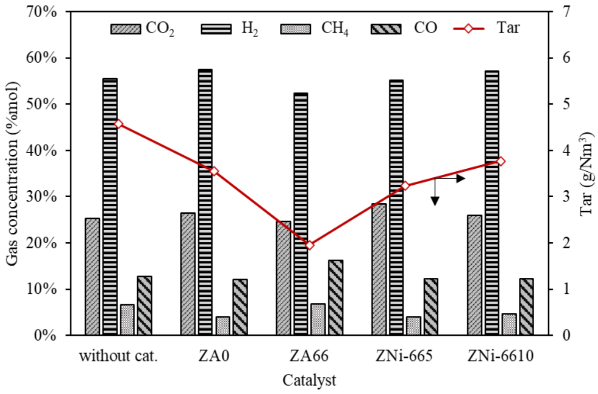

Figure 4. Effect of catalyst on syngas and tar concentration at 750 °C and steam/biomass ratio of 1.5.

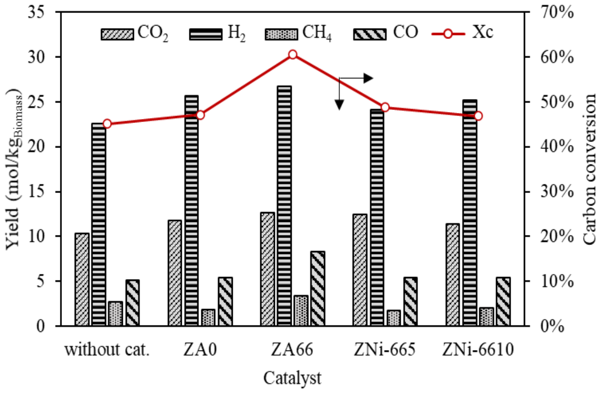

Figure 5. Effect of catalyst on the syngas yield and carbon conversion at 750 °C and steam/biomass ratio of 1.5.

served. From Figure 5, the presence of the modified zeolite catalyst ZA66 increased the syngas yield as compared to when unmodified zeolite, without the addition of Nickel active phase, was used. This was due to the ZA66 catalyst having the largest surface area as compared to other catalysts. This is in line with the results of XRD and EDX that the acid leaching process has reduced impurities, such as: Na, K, Ca, and Mg, thereby increasing the activity of the catalyst. The nickel (NiO) impregnated zeolite catalyst remains inactivate/unreduced due to the short gasification time (30 minutes). This was different with the experiment that used toluene as tar model where the reaction was conducted for 8 hours and nickel oxide has been reduced [22]. The usage of nickel doped catalyst is not suitable as both catalyst and heating media on twin fluidized bed gasifier. The nickel catalyst is only suitable to be used on secondary tar reaction mode (steam reforming reactor on a separate unit after the gasifier).

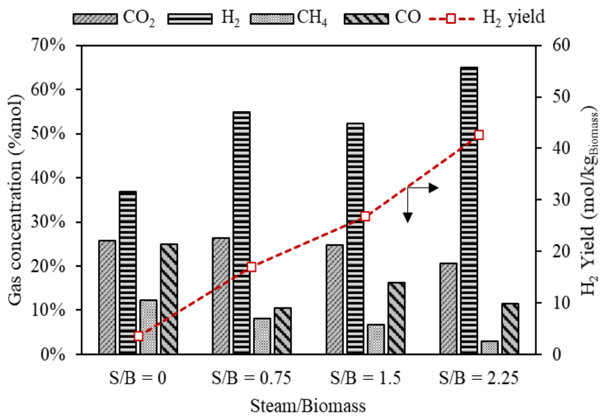

Figure 6. Effect of steam to biomass ratio on H_2 concentration and H_2 yield at 750 °C with the addition of ZA66 catalyst.

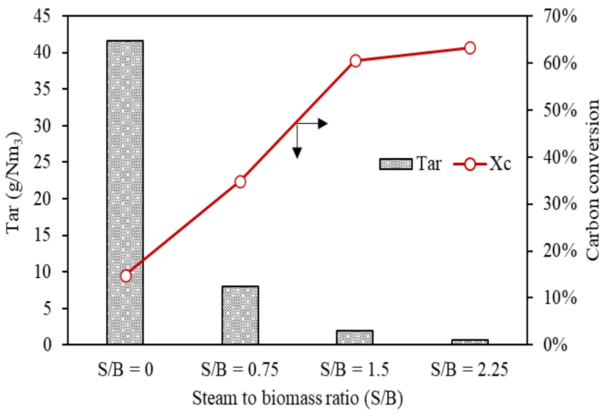

Figure 7. Effect of steam to biomass ratio on tar concentration and carbon conversion at 750 °C with the addition of ZA66 catalyst.

The utilization of ZA66 could increase the syngas yield from a total of 41 mol/kg$_{biomass}$ to 51 mol/kg$_{biomass}$. The carbon conversion also increased from 45% to 61%. The increase in syngas yield and carbon conversion indicated that tar underwent cracking or reforming reaction to produce syngas. On the subsequent experiments to observe the effect of steam to biomass ratio and gasification temperature, ZA66 catalyst was used.

3.3 The Effect of Steam to Biomass Ratio

Gasification with steam medium is required in the production of H_2 rich syngas. In this study, the ratio of steam to biomass was varied in the range of 0 to 2.25 as presented in Figure 6. When the steam to biomass ratio was 0.75, the H_2 concentration increased by 18% mol (54.9% mol) and H_2 yield increased 4.9-fold (17 mol/kg$_{biomass}$) as compared to when no steam (pyrolysis with ZA66 catalyst). The highest H_2 concentration and yield was obtained when the steam to biomass ratio was 2.25 with the H_2 concentration of 65% and H_2 yield of 42.6 mol/kg biomass. On the process without steam (pyrolysis with ZA66 catalyst), the tar concentration was 41.7 N/m^3, while when the steam to biomass (S/B) ratio was 2.25, the tar concentration was 0.72 g/Nm^3 (98% tar conversion upon increasing the steam flowrate), as presented in Figure 7.

As the steam to biomass ratio increased, the concentration of H_2 also increased, while the concentration of CH_4 decreased. This indicated the occurrence of steam reforming reaction on tar and light hydrocarbons (CH_4), and water gas shift. Aside from that, the operating condition will be more profitable if the concentration of H_2 was high and the concentration of CO_2

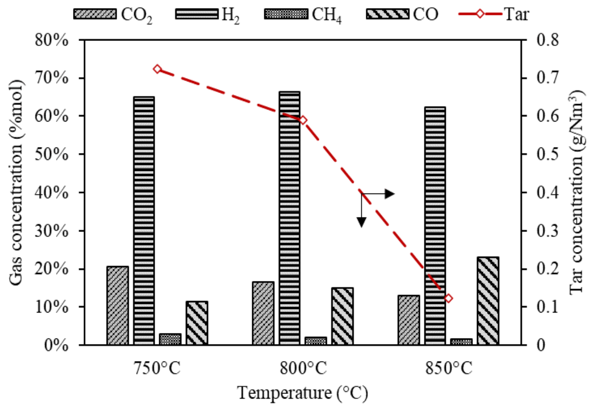

Figure 8. Effect of temperature on the gas concentration and tar concentration at S/B of 2.25 with the addition of ZA66 catalyst.

was kept as low as possible. This was acquired at the steam to biomass ratio of 2.5. Therefore, the variation of reaction temperature used the steam to biomass ratio of 2.5. The disadvantage of increasing steam utilization would be the increased requirement for energy.

3.4 Effect of Gasification Temperature

The H_2 concentration as well as the H_2/CO ratio on the gasification process is affected by the gasification temperature. Palm kernel shell gasification was conducted at the temperature varied from 750 to 850 °C using the ZA66 catalyst. The steam to biomass ratio used was 2.25 and the gasification was conducted for 30 minutes. The effect of gasification temperature on the syngas composition is presented on Figure 8 and Table 4.

In the palm kernel shell biomass gasification as the temperature increased, the yield of H_2 and its potential yield also increased. This was due to the main gasification reactions, such as water gas (6–7), Boudouard (8), and steam reforming (9) being endothermic reaction, which is favored at higher temperature. The CO yield and carbon conversion increased with increasing temperature, while the CO_2 yield decreased. This was due to the water gas and Boudouard reaction, both of which were endothermic reaction, being more dominant at higher temperature.

Water gas:
$$C + H_2O \leftrightarrow H_2 + CO \qquad +131\ \text{kJ/mol} \tag{6}$$
Water gas:
$$C + 2H_2O \leftrightarrow 2H_2 + CO_2 \qquad +90\ \text{kJ/mol} \tag{7}$$
Boudouard:
$$C + CO_2 \leftrightarrow 2CO \qquad +172\ \text{kJ/mol} \tag{8}$$
Steam reforming:
$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad +206\ \text{kJ/mol} \tag{9}$$

Biomass gasification with ZA66 catalyst at steam to biomass ratio of 2.25 resulted in relatively high H_2 concentration which was around 64 mol% and increasing the temperature from 750 °C to 850 °C could increase the carbon conversion from 63.3% to 83.8%. Comparatively,

Table 4. Effect of gasification temperature using ZA66 catalyst on S/B of 2.25.

No	Parameter	Temperature (°C)		
		750	800	850
1	Gas composition (%mol)			
	H_2	65.02	66.27	62.37
	CO	11.40	14.97	22.95
	CH_4	2.94	2.09	1.71
	CO_2	20.65	16.67	12.97
2	Tar concentration (g/Nm^3)	0.72	0.59	0.12
3	Heating value (MJ/Nm^3)	10.89	11.17	11.52
4	H_2/CO ratio (mol/mol)	5.71	4.43	2.72
5	H_2/CO_2 ratio (mol/mol)	3.15	3.98	4.81
6	Syngas yield (mol/kg biomass)			
	H_2	42.60	51.11	55.85
	CO	8.30	11.54	20.55
	CH_4	2.14	1.61	1.53
	CO_2	15.03	12.85	11.61
7	Yield potential (*yield* H_2+CO)	50.90	62.66	76.40
8	Carbon conversion (%)	63.3	64.7	83.8

Table 5. Comparison of the effect of different catalyst on syngas composition.

Parameter	Yusup *et al.* [25]	Chiodo [26]	Kimbauer *et al.* [27]	Zhang *et al.* [28]	Udomsirichakom *et al.* [29]	This Study
Biomass	Palm kernel shell	Orange Peel	Wood pellet	Ficus lacor leaves	Pine wood sawdust	Palm kernel shell
S/B[1] Ratio	1.5-2.5	1.5	1.6	0.5-2.5	3.41	0.75-2.25
Catalyst	CaO	Dolomite	Olivine	CaO/MgO	Silica sand and CaO	Natural zeolite
Temperature	600-700 °C		750-875 °C		550-700 °C	750-850 °C
H_2 (%mol)	78-86%	45%	38-43%	45%	45-63%	52-64%
H_2/CO	-	2.5-4.5	1.8	2.5-4.5	4	2.7-5.7
Tar (g/Nm^3)	-	-	0.9-3		3-100	0.1-8

[1] Steam to biomass ratio

biomass gasification with ZA66 catalyst at the steam to biomass ratio of 1.5 and temperature of 750 °C increased the yield of gas with H_2 composition of 52%-mol. This is in accordance to the requirement, such as pure hydrogen utilization (fuel cell, ammonia synthesis) or syngas with a certain H_2/CO ratio (methanol synthesis, dimethyl ether, Fischer Tropsch, *etc.*)

Compared to the previous work on biomass gasification, utilization of natural material, namely the natural zeolite on palm shell gasification yielded satisfactory results with regards to H_2 concentration, as well as H_2/CO ratio as can be seen on Table 5. The use of CaO in biomass gasification can increase the concentration of H_2 in syngas because it can be used as a CO_2 adsorbent, but the tar concentration is still high. While the use of olivine, tar concentration is quite low but also produces low hydrogen concentrations. The use of zeolite can improve the quality of syngas by increasing hydrogen concentration and eliminating tar in syngas.

4. Conclusions

Activation of natural zeolite by acid leaching was capable to increase zeolite activity in catalytic tar cracking. Gasification of palm kernel shells with modified natural zeolite catalyst could produce clean syngas with tar content reached 0.12 g/Nm^3 and the ratio of H_2/CO syngas ranging from 2.7–5.7. Increasing the gasification temperature could increase the yield of hydrogen and reduce the tar concentration in syngas, but also decrease the H_2/CO ratio. The syngas produced at 850 °C and steam to biomass ratio of 2.25 can be used as feedstock in chemical industry. Future studies are planned for testing the strength of the catalyst against catalyst abrasion and deactivation.

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