

Investigation of biomass gasification using indonesian clay as catalyst

SD Sumbogo Murti¹, Yuta SUDO², SUN Yan², Adiarso¹ and Reiji NODA²

¹Center for Technology Energy Resources and Chemical Industry, BPPT, Energy Building 625, PUSPIPTK Area, Serpong, South Tangerang, Banten 15314, Indonesia

²Chemical and Environmental Engineering, Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu-shi, Gunma 376-8515, Japan

Email: sd.sumbogo@bppt.go.id

Abstract. Gasification is one of the technologies to process biomass as a renewable alternative energy source. Steam biomass gasification using various clays derived from Indonesia was carried out with laboratory scale fluidized bed reactor to evaluate the activities of clay as catalysts. At the same time to elucidated the relationship between material bed characteristics and gasification process activity. Tar capturing ability was compared for activated clay, silica sand and clay minerals derived from Indonesia by using a laboratory scale fluidized bed reactor. Even raw clay minerals were found to reduce heavy tar and water-soluble species emissions and increased carbonaceous materials deposited on the bed materials compared to activated clay. Activity of some Indonesian clay revealed high performance on the biomass gasification due to the amount of acid center.

1. Introduction

Indonesia is the largest producer of palm oil in the world [1]. Production of palm oil in Indonesia has recorded a phenomenal increase from 157, 000 tons in 1964 to 33.5 million tons in 2014 [2]. Production of crude palm oil (CPO) generates a large amount of residues (solid waste) which recently becomes an issue due to its environmental impact [3]. The process of fresh fruit bunches (FFBs) into CPO results in biomass wastes in large amount of empty fruit bunch fiber (EFBs) [4] As for the production of palm oil, almost same weight of EFB is left as waste [5]. These wastes can be used to generate power. From 1 tons of EFB is possible to produce power of 1.330 kWh [5]. However, the utilization rate of palm oil residues in Indonesia is still very low [6].

As the environmental issue such as global warming increases in severity, the promotion of energy conservation and the introduction of renewable energy has become a global challenge. Biomass is one of the renewable and potentially sustainable energy sources. It is a carbon neutral energy that does not increase CO₂ in the atmosphere, and international research into biomass energy is currently moving forward. Biomass has been mentioned to be the fourth largest energy resource in the world, after coal, petroleum and natural gas [7]. Biomass gasification converts biomass into combustible gas that can be used for power and heat production. The product gas also can be upgraded to other valuable products such as FT liquids, SNG, hydrogen, or chemical.



The main technical obstacle of the biomass gasification is the efficient elimination of tar from the producer gas [8,9]. The objective of this research is to study tar reduction by using clay catalyst in the fluidized bed biomass gasification and to elucidate the relation between characteristics of bed material and activity of gasification process.

2. Material and Methods

2.1. Experimental setup and Bed material

In this research, steam gasification tests were carried out with a laboratory-scale fluidized bed reactor in a batch experiment to achieve these objectives. A comparison of various bed materials, such as Na-Bentonite and Ca-bentonite [10] derived from Indonesia with steam gasification was carried out. Silica sand and activated clay also carried out to compare these activities. A schematic diagram of the fluidized bed gasification reactor used in this research is shown in figure 1.

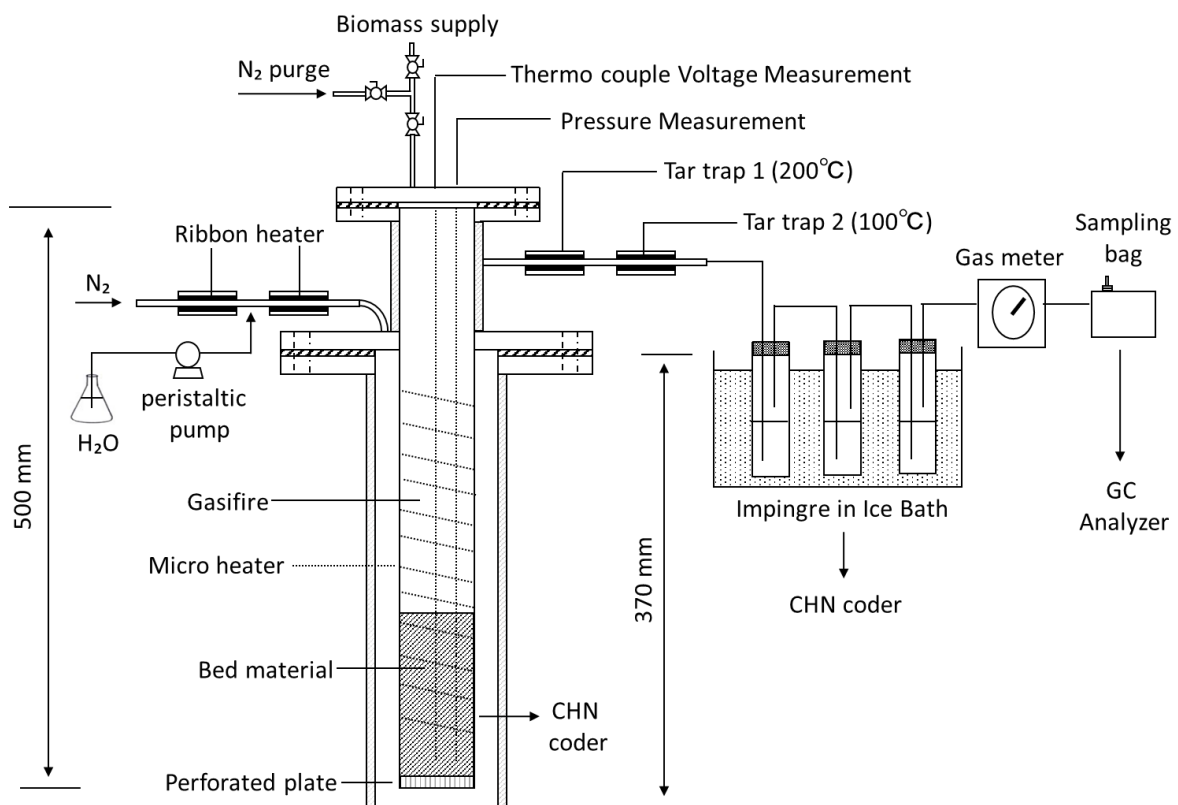


Figure 1. Experimental setup

Biomass sample is fed to the gasifier with feeding port pressured by nitrogen slightly. Products of synthetic gas in the reactor are introduced into a tar trap at 200°C and 100°C, to separate heavy tar. Small steel balls put inside the pipe can be used to trap the tar. Then, after tar trapping, products gas are flew through sampling line and quenched in three impingers cooled by ice bath, to separate water and water soluble organic compounds from gas products. The products of synthetic gas are collected into sampling bags. In experiments, cellulose is used as feedstock and clay derived from Indonesia as bed materials. Table 1 shows the basic chemical composition of cellulose. Table 2 shows information of clay as bed materials. There are 9 types of clay that have been collected from Java Island in Indonesia. Steam gasification of cellulose is performed in a fluidized bed gasifier at atmospheric pressure. Table 3 shows experimental conditions in this study.

Table 1. Ultimate analysis of cellulose as biomass

Components	Cellulose	
	Powder	Capsule
Ash (wt%-dry)	0	0
C (wt%-daf)	40.7	39.5
H (wt%-daf)	5.9	6.3
N (wt%-daf)	0.3	0.1

Table 2. Clay mineral derived from Indonesia as Bed material

No	Place of Origin	Note
1	Jampang (Banten)	
2	Pacitan (East Jawa)	Ca-Bentonite
3	Pacitan (East Jawa)	Na-Bentonite
4	Pacitan (East Jawa)	Na-Bentonite
5	Pacitan (East Jawa)	Ca-Bentonite
6	Bogor (West Jawa)	Ca-Bentonite
7	Blitar (East Jawa)	Ca-Bentonite
8	Blitar (East Jawa)	Na-Bentonite
9	Trenggalek, Tulungagung, Pacitan (East Jawa)	Ca-Bentonite

Table 3. Experimental Conditions

Condition	Unit	
Bed Material	-	Clay Samples
Biomass	-	Cellulose
Temperature	°C	650
Sample Weight	g	1
Gas Sampling Time	min	40
Bed Height	mm	80
Size of Bed Material	µm	75-150
U_0 - U_{mf}	cm/s	2.5
Steam Concentration	%	85
Nitrogen Concentration	%	15 (Balance)

2.2. Analytical methods

After the experiment, product gas was analyzed by TCD Gas Chromatography (GC, 2014 SHIMADZU) after measured volume with gas meter and collected in sample bag to determine the carbon in each tar. Tar is trapped step wisely. The outlet pipe from the gasifier is covered by heater to trap tar condensable in the temperature more than 100°C [11]. The collected tar in each tar trap were burned in air to collect the combustion gas [12]. The condensed water that is collected by impingers is analyzed by CHN (LECO 628) analyzer to determine total carbon in solution. Char is separated from bed material by sieving with standard sieve of 150 µm opening. Total carbon remaining in the bed is determined by ultimate (CHN) analysis. After reaction process, the reactor was cleaned by nitrogen and cooled down the equipment.

2.3. Amount of acid center

The amount of acid center and its acidity were determined by the method developed by Benesi^{13,14,15)}, where 0.1 g of bed material sample was put in 5ml of benzene and a predetermined quantity of butylamine-benzene solution. Four indicators benzalacetoph-enon (transparent to yellow): $pK_a=-5.6$, dicinnamalacetone (yellow to red): $pK_a=-3.0$, phenylazonaphthylamine (purple to yellow): $pK_a=+1.5$, Methyl Red (yellow to red): $pK_a=+4.8$ were applied to the titration by which amounts of butylamine adsorbed on acid centers were determined. If the addition of butylamine is less than the amount of acid center below pK_a of the indicator applied, the color of the indicator does not change. Butylamine was added until each indicator changes its color to determine the amount acid center corresponding to the indicator.

3. Result and Discussion

3.1. Result of gasification

To confirm reproducibility two gasification runs were carried out in the same condition for 9 kinds of clay material. All of products could be recovered in the experiment, carbon recovery of the twice experiment were almost same, therefore reproducibility had been confirmed. As can be seen in figure 2, in the case of silica sand, carbon in the cellulose sample was gasified into around 35% gas, leaving 13% in residual solid (including char and carbonaceous materials trapped by particles), 11.7% in tar trap at 373K+473K (hereinafter, referred to as heavy tar), and 31.4% in water-soluble organics. The carbon fraction in each product are synthesis gas, in bed residue (char), trapped on bed materials (clay), heavy tar and water soluble. The total carbon recovery reached to around 90% for all sample. Figure 2 and table 4 show the carbon distribution of the fluidized gasification using Silica sand and activated clay. Markedly different things of this result are in trapped on bed material, heavy tar and water soluble. Result of silica sand which heavy tar is more than 10 times, water soluble is around 3 times compared with activated clay. In case of using silica sand, tar production is very high against activated clay. Amount of trapped on bed material using activated clay is around 3.5 times than silica sand. This result found to reduce heavy tar and water-soluble species emissions, and to increase trapped on bed materials than porous silica sand. Char, tar and carbonaceous materials in condensed water were decreased significantly while the amount of carbonaceous materials in bed material was greatly increased by applying clay beds. Therefore, activated clay has catalytic activity. Activated clay showed significantly higher energy conversion to gas by gasification of captured carbonaceous materials.

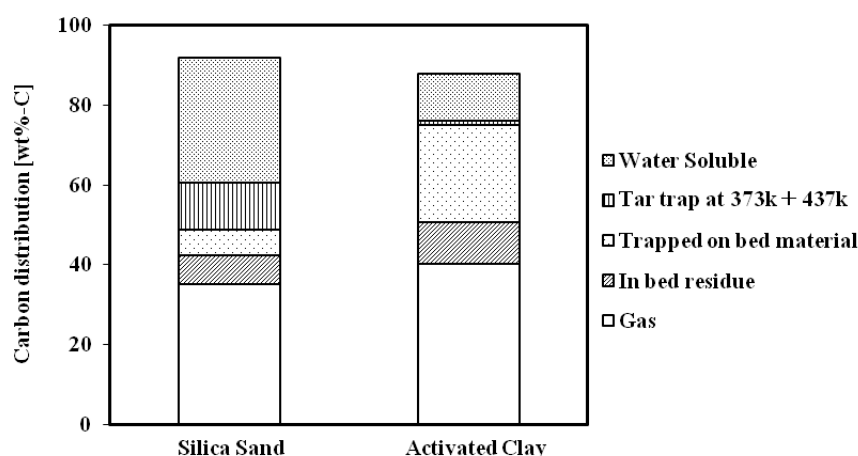


Figure 2. Result of Gasification using Silica sand and activated clay

Result of carbon distribution of the fluidized gasification using clay from Java Island in Indonesia is given in figure 3 and table 5. The carbon fraction in each product was resembles except for the case of silica sand. The different types of bentonite are each named for their respective dominant element, such as potassium (K), sodium (Na), calcium (Ca), and aluminium (Al) [16]. These clay samples can separate Ca-bentonite (No2, 5, 6, 7, 9.) and Na bentonite (No3, 4, 8.). Gas production of each sample is 35 to 41 wt%-C. A mount of tar production such as heavy tar and water soluble is smaller using Ca-bentonite. As shown on the table 5 that the best quality of the clay catalyst for biomass gasification process is the clay samples No. 2, type of Ca-bentonite. This is shown from the distribution of gasification products that produce relatively high product gas (syngas) and tar which can be captured by the highest catalyst / bed material compared to others catalyst types. Because one of the parameters for assessing the quality of the catalyst used in the gasification process is the ability of the catalyst to capture the tar, so the resulting syngas product is relatively more abundant and cleaner. A clay catalyst that can be selected based on the result of gasification is that has the ability to reduce emissions of heavy tar and water soluble species and can increased carbonaceous materials deposit on the bed material. Based on the results, Clay No. 2 and 6 produce very small tar of 0.88% and 0.68%, smaller than the tar produced by active clay. And increased carbonaceous materials deposited on the bed material to the value of 38.7% and 32% greater than using activated clay.

Table 4. Result of Gasification using Silica sand and activated clay

Products Yields	Silica	Activated
Gas	35.1	40
In bed residu	7.03	10.6
Trapped on bed material	6.6	24.3
Tar trap at 373k+437k	11.7	1.07
Water Soluble	31.4	11.7
Total Cabon	91.8	87.7

wt%-C

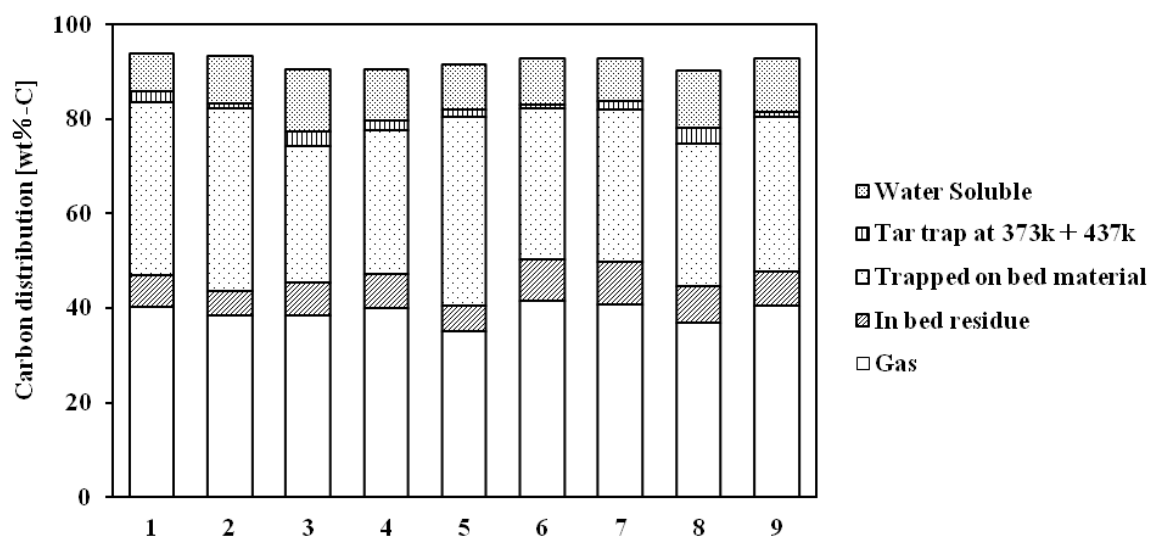


Figure 3. Result of Gasification using clay from Indonesia

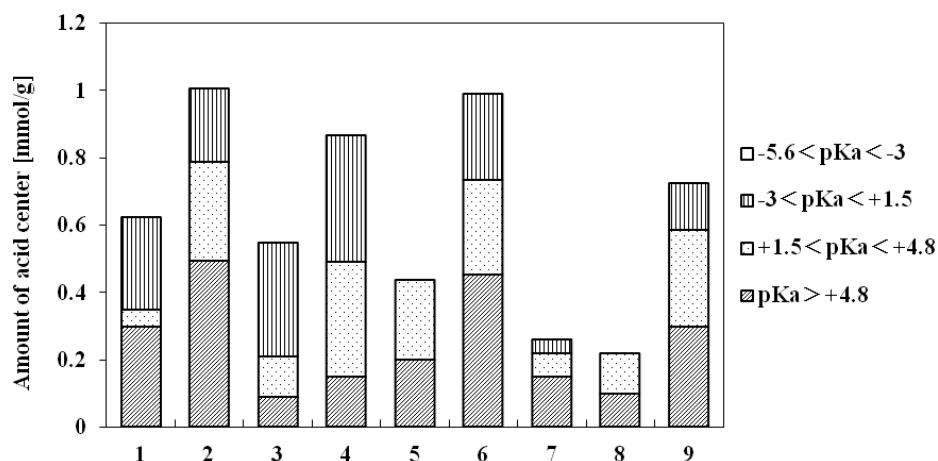
Table 5. Result of Gasification using clay from Indonesia

Products Yields	1	2	3	4	5	6	7	8	9
Gas	40.2	38.5	38.5	40	35.2	41.6	40.8	36.8	40.5
In bed residu	6.6	5.1	7	7.1	5.4	8.6	8.9	7.7	7.3
Trapped on bed material	36.6	38.7	28.8	30.4	39.9	32	32.3	30.2	32.6
Tar trap at 373k+437k	2.5	0.9	3.1	2.2	1.5	0.7	1.66	3.5	1
Water Soluble	7.8	10.1	13	10.7	9.6	9.9	9.1	11.9	11.4
Total carbon	93.8	93.3	90.5	90.1	91.7	92.9	92.8	90.1	92.8
Wt%-C									

3.2. Characterization of Clay

In this study, the amount of acid was analyzed to elucidate relation between characteristics of bed material and activity of gasification process. Fig.4 shows evaluation of acid center. Amounts of relatively strong acid are No.2, 4, 6, 9 (1.0, 0.87, 0.98, 0.72 mmol/g). On the other hand 7 and 8 are quite small (0.25, 0.22 mmol/g). No.1, 2, 3, 4, 6, 7, 9 are similar acid center ($-3 < pK_a < +4.8$). No.5, 8 are weak acid center ($+1.5 < pK_a < +4.8$) existed on the surface.

According to this result, amounts of strong acid are good conditions for gasification process. Because if using No.2, 6, 9 tar production such as heavy tar is smaller than others.

**Figure. 4** Evaluation of Acid Center Conclusion

4. Conclusion

Biomass gasification using Indonesian clay as catalyst was conducted and succeeded reducing tar production. In the case of using active clay as catalyst, the carbon in the cellulose sample was gasified producing about 40% gas, leaving 10.6% solids residual (including char and carbon trapped by particles), 1.07% tar and 11.7% organic soluble in water. Activity of Indonesian Clay No 2 and 6 showed the higher performance due higher of acid center.

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