BIS ENERGY AND ENGINEERING

Volume 1 2024 | DOI: 10.31603/biseeng.41
5th Borobudur International Symposium on Science and Technology (BIS-STE) 2023

UNIMMA PRESS
UNIVERSITAS MUHAMMADIYAH MAGELANG

Effectiveness of using limestone (CaO) as a syngas durch traps

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Abstract

This research aims to determine the effect of using CaO as an adsorbent to produce environmentally friendly combustible gas using biomass waste material. The technology for producing combustible gas or syngas is an updraft gasification system using an air gasification agent. To produce syngas that are not polluted with tar or other impurities, a CaO adsorbent is used. CaO is obtained from mountains in the form of small, irregular granules research is carried out using experimental study methods. CaO is installed in the syngas outlet before the cyclone. CaO is not heated separately but uses heat from the gasification reactor. The raw materials used were rice husks and wood, a mixture composition of 100% rice husks, 75% rice husks and 25% sawdust, 50% rice husks and 50% sawdust, 25% rice husks and 75% sawdust and 100% sawdust wood. The results of this research showed that a mixture of 50% rice husk + 50% sawdust wood produced gas with a high H_2 concentration and low CO where the highest H_2 concentration that could be achieved was 38.95%, and the H_2 content was 24.18% without using CaO absorbent materials. A high increase in H_2 concentration was obtained by adsorbing CaO. The mechanism for CO_2 adsorption by CaO was a heterogeneous reaction to produce $CaCO_3$.

Keyword

Limestone, CaO, Combustible gas

Introduction

The main energy currently comes from fossils, almost 80% of transportation equipment and industrial machines use fossil fuels in 2020. Nearly 25% of energy originating from fossils is used as transportation fuel and is the largest contributor to air pollution [1]. The weakness of fossil fuels is that they cannot be renewed and will eventually run out. It is predicted that fossil fuels will be scarce in the next few years [2]. Therefore, it is a challenge for researchers to develop renewable fuels that can replace fossil fuels [3]. Biomass has the potential to be developed into a renewable energy source [4]. Indonesia is an agricultural country that has many provinces, one of which is capable of producing rice production of 2.40 million tons in 2022 and 20% of this weight is rice husks [5]. Rice husks weigh around 20% of the weight of rice [6]. Rice husks are rice husks and

Published: October 20, 2024

Selection and Peer-review under the responsibility of the 5th BIS-STE 2023 Committee

have not been used optimally [7]. Indonesia is located in a tropical area and has forest products in the form of wood, this wood is processed for furniture or houses [8]. The wood production process also produces waste [9] which has the potential to be processed into alternative fuels [10]. By looking at the interrelated needs between food and energy, the use of rice husks as an environmentally friendly energy source is very interesting to develop [11]. One way to convert biomass into biofuel is by gasification [12]. Gasification can be classified based on the gasification agent, including air, steam, steam-oxygen, and air-steam [13]. Air gasification can obtain a producer gas calorific value of 4-6 MJ/m^3 with a hydrogen content of 8-14 vol% [14]. The temperature of the gasification agent [15], the gasification agent, and the material being gasified greatly influence the gasification results, namely volume, the heating value of the syngas, and gas content [16]. Syngas resulting from gasification using air agents has a low heating value (4-6 MJ/m^3) [17]. In a gasification reactor, there are several zones, in each zone a chemical reaction occurs, and the drying zone occurs at a temperature between 25°C-150°C. In the drying zone, the water content in the biomass evaporates, and no chemical reactions occur. After passing through the drying zone, the biomass then enters the pyrolysis or devolatilization zone. In the pyrolysis process, slow pyrolysis occurs if the process temperature is below 3500C or fast pyrolysis if the temperature is above 8000C. The pyrolysis process produces products, namely syngas (H_2, CO, CO_2, H_2O, and CH_4), tar, and charcoal [18]. In general, the reaction that occurs in pyrolysis and its products is Biomass → charcoal + water vapor + gas + and tar. Charcoal, tar, pyrolysis oil, the resulting gas will then be oxidized by oxygen from the air. This event occurs in the oxidation or combustion zone [19]. The heat produced from this reaction is used for the drying process and other endothermic reactions. The reactions that occur in the combustion process are as follows:

$$C + O2 \rightarrow CO_2 \tag{1}$$

In the combustion zone, the oxidation of hydrogen contained in biomass also takes place. The reaction is as follows:

$$H2 + \tfrac{1}{2}\, O2 \rightarrow H2O \tag{2}$$

In the reduction zone, endothermic events occur and require heat produced from the combustion reaction. The products produced in this process are fuel gases, such as H2, CO, and CH4. The following reactions are four reactions commonly involved in gasification.

$$C + CO_2 \leftrightarrow 2\,CO \quad \text{(Boudouard reaction)} \tag{3}$$

$$C + H_2O \leftrightarrow CO + H_2 \quad \text{(Steam-carbon reaction)} \tag{4}$$

$$CO + H_2O \leftrightarrow CO2 + H_2 \quad \text{(Water-gas shift reaction)} \tag{5}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \text{(CO methanation)} \tag{6}$$

In the gasification process, there is a water gas shift (WGS) reaction which converts carbon monoxide and water vapor into hydrogen and carbon dioxide. Carbon dioxide can reduce the hydrogen concentration in the producer gas, and water vapor comes from the biomass itself. An interesting method used to reduce the amount of carbon dioxide in producer gas is the carbonation reaction where calcium oxide (CaO) is used as a reactant to react with carbon dioxide (CO2) to form calcium carbonate ($CaCO_3$) by releasing energy for the reaction [20]. The carbonation reaction can be seen in equation 7 [21].

$$CaO + CO_2 \leftrightarrow CaCO_3 \qquad \Delta H = -178{,}9\ kJ/mol \tag{7}$$

The carbonation reaction can proceed both forward and backward. The reverse reaction is a decarbonization or calcination reaction. This reaction, which can run in both directions, can convert CaO into calcium carbonate ($CaCO_3$) but requires heat. The carbonation reaction depends on temperature, the higher the temperature, the higher the partial pressure of carbon dioxide. So, if the temperature is high, the partial pressure of carbon dioxide required to react with CaO to form $CaCO_3$ is higher (Figure 1).

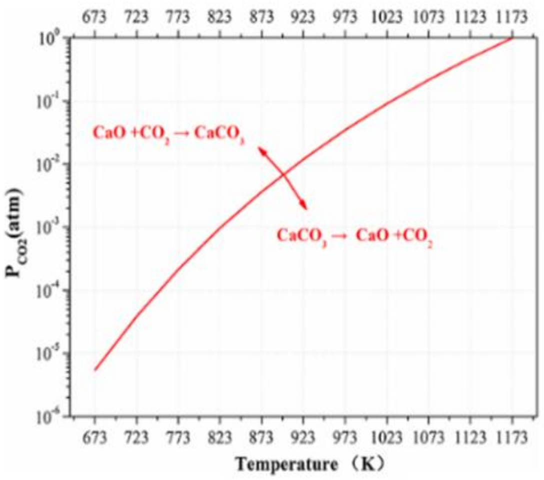


Figure 1. Equilibrium partial pressure of CO_2 on CaO as a function of temperature [22]

By adding CaO it is hoped that it can reduce the carbon dioxide concentration by 93.33% when compared to gasification without CaO [23].

1. Hydration events (H2O absorption), take place at temperatures below 3000C

$$CaO + H_2O \blacktriangledown \quad Ca(OH)_2 + \text{High temperature} \tag{8}$$

2. Dehydration event, takes place at a temperature of 400°C – 650°C

$$Ca(OH)_2 \blacktriangledown \quad CaO + H_2O \tag{9}$$

3. The carbonation event takes place at a temperature of 400°C – 650°C

$$CaO + CO_2 \blacktriangledown \quad CaCO_3 \tag{10}$$

4. Calcination event, takes place above a temperature of 6500C

$$CaCO_3 + \text{high temperature} \blacktriangledown \quad CaO + CO_2 \tag{11}$$

Methods

Raw materials and equipment

This research utilizes agricultural waste in the form of rice husks, the type of rice is not specified. The water content of rice husks is 11%, and the size of the rice husks is negligible. Sawn wood is in powder form and has a water content of 11%, screened 20 - 40 mesh. Both raw materials are dried by drying them under the hot rays of the sun. CO_2 Adsorb uses CaO which is installed in the gas channel resulting from gasification, CaO weighing 50 grams in granule form. The gasification reactor is an updraft fixed bed reactor with a capacity of 1.8 kg using air as a gasification agent (Figure 2).

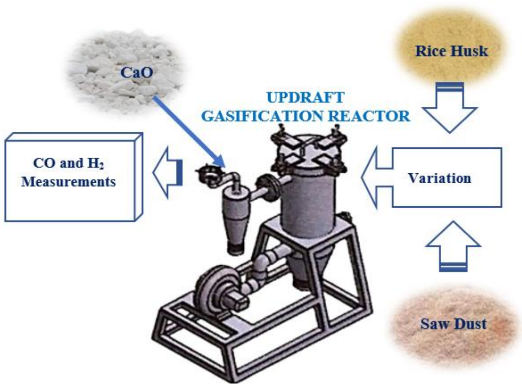


Figure 2. Gasification test

Thermoreaders and thermocouples are used to measure environmental temperature, the temperature in the reactor, heater temperature, and producer gas temperature leaving the reactor. One H_2 and CO gas analyzer unit is used to measure the H_2 and CO gas content (Figure 2). The raw materials for gasification were weighed at 1.8 kg, variations of raw materials for testing were100% rice husks, 75% rice husks + 25% sawdust, 50% rice husks + 50% sawdust, 25% rice husks + 75% sawdust, 100% sawdust.

Research testing steps

The raw materials for gasification, namely rice husks and sawn wood, are weighed according to variations in the raw materials tested, and mixed until homogeneous. Weigh 1.8 kg of gasification raw materials, and put them in the reactor. Light the fire in the reactor without using oil. Close the cover, turn on the air blower, and set the blower air speed to 0.04 – 0.05 l/minute. Place 50 grams of CaO in the syngas exhaust channel, the CaO used is in granule form. The syngas resulting from gasification are passed through the channel to adsorbing impurities by CaO. After the combustible gas comes out of the exhaust outlet, the gas is burned with a flame [24]. If the gas ignites, carry out a test with a tool to determine the content in the syngas, especially the H_2 and CO content [25].

Result and discussion

Gasification tests that have been carried out, obtained the following data. Figure 3 explains the syn gas resulting from gasification, namely the concentration of H_2 in each material variation. The test is carried out by passing syn gas for each variation of raw material to a CaO trap or not passing it. From the test results for each variation, the concentration of H_2 that CaO passes is better than that that CaO does not pass. The highest concentration of H_2 that the syn gas produced through CaO passes through is a mixture of 50% rice husk + 50% sawdust at 32.4%. Data from H_2 concentration testing results using a raw material mixture of 50% rice husks + 50% sawdust where syngas was not passed through CaO obtained an H2 concentration of 12.7%. Meanwhile, the 100% rice husk material where syngas was passed through CaO as an adsorbent produced an H_2 concentration of 26.9%, while syngas was not passed through CaO and obtained an H_2 concentration of 13.7%. A mixture of 75% husk + 25% sawdust syn gas is passed through a CaO trap resulting in an H_2 concentration of 23.2%, if Syn gas is not passed through CaO the H_2 concentration is 12.7% with the same variation of ingredients. A mixture of 25% husk + 75% sawdust syn gas is passed through CaO as a trap producing an H_2 concentration of 23.7%, if CaO is not passed the H_2 concentration is 13.5%. The material is 100% sawdust, where syn gas is passed through CaO to produce an H2 concentration of 16.5%, and when syn gas is not passed through CaO, the H_2 concentration is 11.1%.

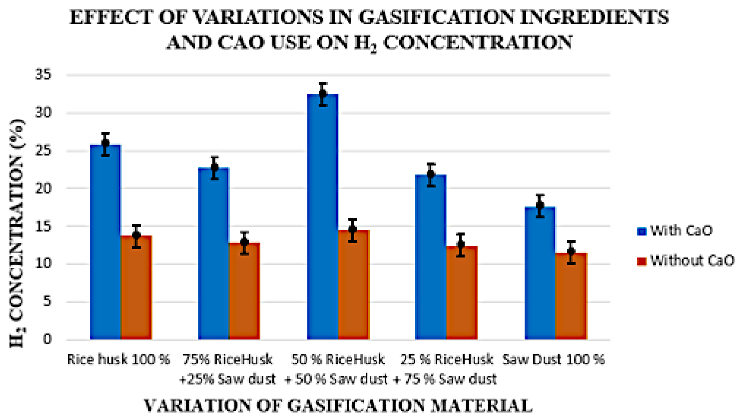


Figure 3. Test results for H_2 concentration in each variation of gasification raw materials

Several previous studies have obtained data that the adsorption of CO_2 using CaO in syn gas can increase the H2 content, but if the carbonization temperature exceeds 650°C, the H_2 will decrease. CO_2 adsorption to increase H_2 content is very effective at stable temperatures [26]. The novelty of this research is the use of CaO which is not mixed into the gasification material but CaO is placed in the syngas flue channel so that the temperature can be stabilized and the absorption of CO_2 and other impurities can be maximized.

Figure 4 is the result of CO concentration testing for each variation of gasification raw materials. Syn gas from the gasification results is passed through CaO which functions as a trap or not for each variation of gasification raw material. The test results showed that the highest CO concentration was obtained from a mixture of 25% rice husk + and 75% sawdust. In this variation, the CO concentration was obtained as much as 7.3%, where the syn gas was passed through CaO, and where CaO was not passed, the CO concentration was 6.01%. The CO concentration in the mixture variation of 50% rice husk + 50% sawdust where the syngas is passed through CaO is 4.4% and CaO is not passed at 4.1%. Variations in the mixture of 75% rice husk + 25% sawdust where the syngas is passed through CaO with a CO concentration of 5.1% and which is not passed CaO has a concentration of 4.9%. The raw material is 100% rice husk where the syngas are passed through CaO, obtained at 6.2% and where CaO is not passed, the CO concentration is

5.6%. The 100% sawdust raw material where the syngas was passed through CaO was found to be 5.2% and where CaO was not passed, the CO concentration was 4.9% in the same raw material variation. Figure 3 and Figure 4 show the effect of using a CaO trap on variations in gasification raw materials on H_2 and CO concentrations. CaO comes from nature and is very effective as an adsorbent for dirt carried by syn gas resulting from gasification so that the H_2 and CO produced are higher than without passing through CaO. CaO also functions to adsorb CO_2, with CaO expected to increase the concentration of combustible gas. Syngas enters the CaO reactor so that CO_2 adsorption occurs, an increase in the concentration of hydrogen and carbon monoxide gas (Table 1).

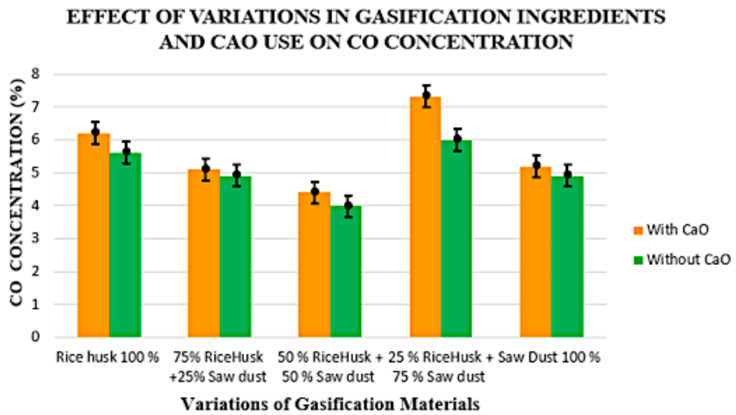


Figure 4. Test results for CO concentration in each variation of gasification raw materials

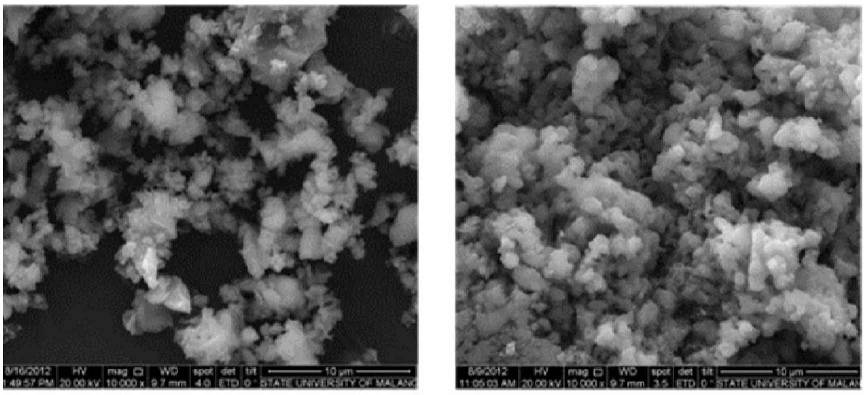
Table 1. Percentage of CaO content

Chemical Elements	CaO
C	6,38%
O	30,68%
Ca	61,03%
Al	0,48%
Si	0,53%

Increasing the high concentration of H_2 by flowing syngas into the CaO adsorbent causes a CO_2 adsorption mechanism on the CaO surface, resulting in $CaCO_3$. The white $CaCO_3$ can be seen sticking to the surface of the CaO, so it can be seen that the CaO after being used as an adsorbent has a denser surface than before it was used. CaO surface after CO_2 adsorption process for 30 minutes. It needs to be explained here that CaO and $CaCO_3$ each have the same basic color, namely white, so from the SEM analysis in Figure 5 it is still somewhat difficult to distinguish that the white color after the adsorption process is CaCO3. For this reason, the EDX test was carried out before and after the adsorption process, as can be seen in Table 2. It can be seen that the concentration of C and O in CaO after the adsorption process increased, while the concentration of Ca decreased, indicating that the reaction between CaO and CO_2 produced $CaCO_3$, where the mass percentage of O in $CaCO_3$ theoretically is 48%.

From the results of the BET test on the initial CaO, it was obtained that the pore surface area of CaO was 2.89 m^2/g with a pore radius of 115.4 Å. Hydrogen concentration in CaO.

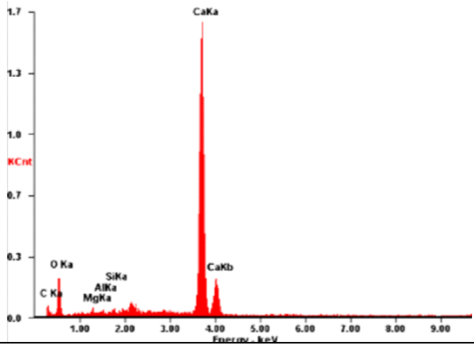
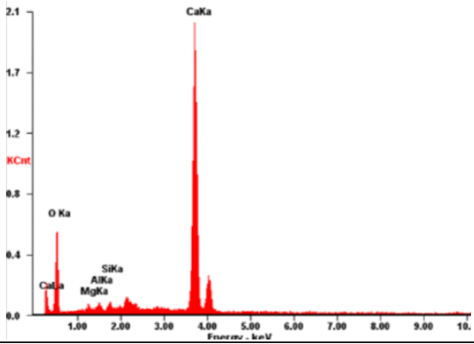
From this test, it can also be seen that the highest H2 concentration can be achieved amounting to 32.4% when gasifying 50% rice husk + 50% sawdust using CaO as the trap.



(a) CaO Before Use For Research (b) CaO After Use For Research

Figure 5. SEM of CaO before and after being used as a CO_2 adsorbent

Table 2. Results of EDX analysis of CaO before and after being used for adsorption

Item	CaO Before Use for Research	CaO After Use for Research
C	6.38%	12.20%
O	30.68%	47.37%
Ca	61.03%	38.20%
Energy Spectrum		

The CaO adsorption reaction with CO_2 occurs exotherm (ΔH= -178 kJ/mol) while the reaction between C and CO_2 occurs endotherm (ΔH= 131.4 kJ/mol).

Conclusion

Gasification using rice husks and sawdust as raw materials produces environmentally friendly combustible gas using waste materials. The technology for producing combustible gas or syngas is an updraft gasification system, using an air gasification agent. To produce syngas that are not polluted with tar or other impurities, a CaO trap is used. CaO is installed in the syngas outlet before the cyclone. CaO is not heated separately but uses heat from the gasification reactor. The raw materials used are rice husks and wood, a mixture composition of 100% rice husks, 75% rice husks and 25% sawdust, 50% rice husks and 50% sawdust, 25% rice husks and 75% sawdust and 100% sawdust. The results of this research, a mixture of 50% rice husk + 50% sawdust produces gas with a high H_2 concentration and low CO where the highest H_2 concentration that can be achieved is 32.4%, the H_2 content is 14.6% without using a CaO absorber. A high increase in H_2 concentration was obtained by adsorbing CaO. The mechanism for CO_2 adsorption by CaO is a heterogeneous reaction to produce $CaCO_3$.

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