

The Effect of K_2CO_3 and $Ca(OH)_2$ Catalysts on The Yield of Syngas Products and Tar Production on Tobacco Waste Gasification with Downdraft Gasifier Type

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ABSTRACT

Nowadays tobacco waste from cigarette production has not been managed properly, only used as fuel on direct combustion process that caused air pollution. To resolve it, indirect combustion method or gasification can be used. Gasification is a thermochemical process that converts solid fuel into a gas capable of fuel known as Synthesis Gas by a combustion process using limited oxygen. Fuel gases and synthesis gases produced by the gasification is used as power generation, heating, chemical products, etc. However, gasification processes also generated condensable organic compounds, so called "tar". As the processing method, using the catalytic tar decomposition has been widely studied. The purposes of this study is to determine the effect of catalysts K_2CO_3 and $Ca(OH)_2$ on increasing the composition of synthesis gas produced and decreasing the amount of tar produced. As for the steps of this research are preparation of raw materials, gasification process and analyzing the composition of the syngas. The experimental results show that alkali metal compound (K_2CO_3) and alkaline earth metal compound ($Ca(OH)_2$) have a catalytic effect to decompose tar contents, to enhance gaseous production. The largest syngas composition produced by the use of $Ca(OH)_2$ catalyst with $H_2 = 10,20\%v$; $CO = 21,81\%v$; dan $CH_4 = 2,02\%v$. On tar reduction, $Ca(OH)_2$ catalyst was better than K_2CO_3 catalyst with tar production reduced by $34,04\%v$.

Keywords: *catalyst, gasification, tar reduction, tobacco waste.*

1. INTRODUCTION

The use of renewable energy as an alternative energy is a must as petroleum reserves in Indonesia are running low. One alternative to meet the needs of the alternative energy sources that can be developed is the biomass energy from tobacco waste which very abundant. Tobacco production in Indonesia reached ± 190 thousand tons/year and in 2015 period January – May, national cigarette industries production reached 129,3 billion cigarettes [kemenperin, 2015]. Currently the waste from cigarette production can not be managed properly, only sold to farmers to be used as compost and partly to produce pesticides by taking nicotine contained in it or

directly used as fuel in the direct combustion process that cause air pollution.

To handle this, indirect combustion or gasification may be used. Gasification is a thermochemical process that converts solid fuel into a gas capable of fuel known as Synthesis Gas (CO , H_2 , CH_4 , O_2 , N_2) by a combustion process using limited oxygen.

In addition to producing gas producers or syngas, the biomass gasification process also produces tar in the form of a problem in the downstream processes of gas utilization. In general, tar removal can be done by primary and secondary methods. The primary method is the removal of the tar content in the gasifier reactor or before the gas exits the gasifier, i.e by the selection of gasification operating conditions, gasifier modification,

and the use of catalyst in the gasifier. The secondary method is the removal of tar outside the chemical gasification reactor such as catalytic and thermal cracking, as well as physically such as cyclone, baffle filter, wet scrubber, wet electrostatic precipitator, etc [Devi, 2005].

The tar removal effort has been largely done by adding catalysts. According to Wang [2013], research using cellulosic feedstock and the addition of catalysts K_2CO_3 and $Ca(OH)_2$. From their research, the total molar amount of hydrocarbons increased by approximately 6,1 % dan 42,2% by using K_2CO_3 and $Ca(OH)_2$ catalysts.. Pei [2009], did research using peanut raw material and found comparative results of several catalysts used.

Based on the these researches, tar reduction efforts become the foundation in this study, by choosing the primary method of tar reduction which is the addition of catalysts to determine the effect on syngas produced on the tobacco waste gasification.

2. THEORETICAL BASIS

Gasification is the process of converting carbonaceous materials such as coal, petroleum, and biomass into carbon monoxide (CO) and hydrogen (H₂) by reacting the raw materials used at high temperatures to the amount of oxygen regulated and producing syngas (CO, H₂, CH₄) through the combustion process.

Gasification generally consists of four processes, namely drying, pyrolysis, oxidation, and reduction. The process that takes place on the gasifier can be observed from the temperature range of each process, which is as follows [Vidian, 2008]:

- Drying: $T > 150\text{ }^\circ\text{C}$
- Pyrolysis: $150\text{ }^\circ\text{C} < T < 800\text{ }^\circ\text{C}$
- Oxidation: $800\text{ }^\circ\text{C} < T < 1400\text{ }^\circ\text{C}$
- Reduction: $600\text{ }^\circ\text{C} < T < 900\text{ }^\circ\text{C}$

Fuel gas and synthesis gas generated by gasification are used as power plants, heating, chemical products, etc. However, the gasification process also produces a condensable organic compound called tar. Visually, we can see tar in black and viscous. The content of primary tar is as follows:

Table 1. Content of Tar.

Components	Weights (%)
Benzene	37.9
Toluene	14.3
Other 1-ring aromaticHydrocarbons	13.9
Napthalene	9.6
Other 2-ring aromaticHydrocarbons	7.8
3-ring aromaticHydrocarbons	3.6
4-ring aromaticHydrocarbons	0.8
Phenolic Compounds	4.6
Heterocyclic Compounds	6.3
Others	1.0

The process of tar formation depends on two factors. These factors are temperature and high of reactor.

When temperatures are low (below 500°C), tar production initially increases, then tar production decreases with increasing temperature. It can be concluded that the higher the temperature, the tar production will decrease. This is because at high temperatures, tar will experience cracking process. The cracking process is the process by which the tar turns into a gas like O₂, CO, CO₂, and H₂O [Nurtanio, 2012]. This can be seen in Figure 1.

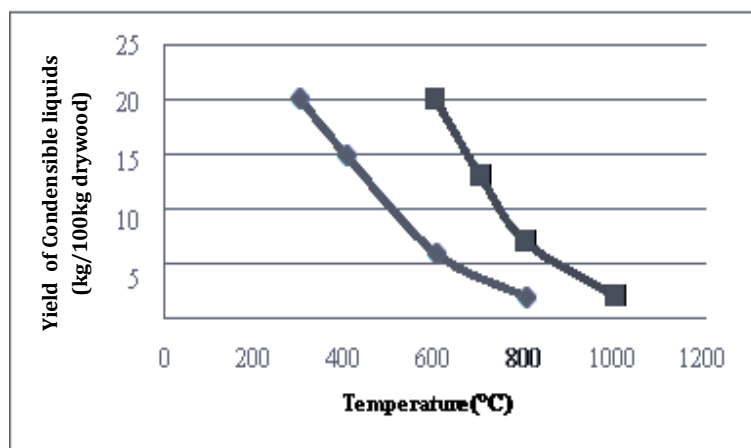


Figure 1. Graph of Temperature Comparison with Tar Mass.

The efforts to eliminate tar has been largely done by previous research. In general, tar removal can be done by two methods, which are:

- Primary Method: is the removal of the tar content in the gasifier or before the gas exits the gasifier, ie by the choice of gasification operating conditions,

gasifier modification, and the use of additive or catalyst in the gasifier.

- Secondary Method: is a tar removal outside the gasification reactor either chemically such as thermal cracking, or physically as such cyclone, baffle filter,

wet scrubber, wet electrostatic precipitator, etc. [Devi, 2005].

It has been mentioned that one of the methods of tar reduction is the addition of a catalyst to the gasification process. The catalyst is defined as a substance which can accelerate the reaction rate toward the equilibrium, without the consumed catalyst in the process. The catalyst can not change the equilibrium limit determined by thermodynamics, its role is limited to accelerate the reaction rate toward equilibrium.

A good catalyst which can be used for gasification processes is a catalyst containing elements of the alkaline and alkaline earth groups in the form of their oxides or carbonates as well as the transition groups in their oxide form. Calcium hydroxide is one of the compounds that can be used as a catalyst of biomass gasification reaction with carbon dioxide gas, while potassium catalyst is effective in gasification process. The catalysts commonly used in the gasification process are as follows:

- a. Elements of the alkaline group: Ca(OH)_2 , CaCO_3 and NaCO_3
- b. Element of the alkaline earth group: Mg(OH)_2
- c. Elements of the metal oxide group: In_2O_3 , Fe_2O_3 and ZnO
- d. Elements of the alkali metal group: KOH , K_2CO_3 , NaOH , Na_2CO_3 and NiCO_3

Potassium carbonate (K_2CO_3) has been known as a good catalyst for biomass gasification [Pei, 2009]. In addition, the price tends to be cheap and can be

regenerated, making this catalyst very suitable for addition to the gasification process. Research on calcium hydroxide (Ca(OH)_2) is not very popular compared to research on potassium carbonate catalyst, but Wang et al in 2013 have proved that the addition of calcium hydroxide in the gasification process significantly improves the quality of syngas products and can reduce tar production when compared to using potassium carbonate catalyst.

3. MATERIAL AND METHODS

3.1 Preparation of Raw Materials.

In this step, the tobacco waste is soaked with water for 3 days and dried for 5 days with sunlight. The tobacco waste that has been dried and then inserted into the crusher for process of reducing the size. After that, a screening process of 2 - 3 mm. The tobacco waste that has been through the screening process, then weighed each as much as 2 kg for use on the process of gasification. After that, weighing the K_2CO_3 and Ca(OH)_2 catalysts each by 3% of the weight of the raw materials of tobacco waste or as much as 60 grams.

3.2 Gasification Process

Before the gasification process begins, first prepare a series of gasification tools that are used and prepare the fuel used in the process of gasification which is charcoal. Then charcoal is burned using kerosene. The series of gasification tools are shown in Fig. 2.

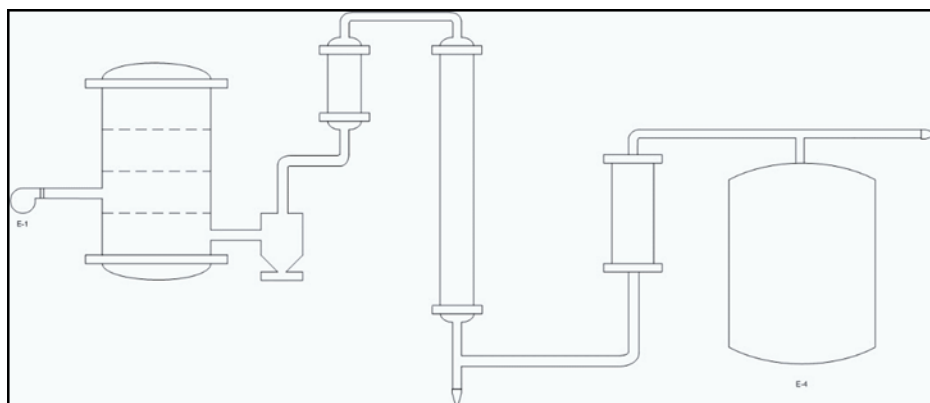


Fig 2. Schematics of Experimental Set-Up.

1. Blower
2. Gasifier Reactor
3. Cyclone
4. Condenser
5. Filter
6. Tank

The gasification process begins by loading the raw material and catalyst until the gasifier is filled $\frac{3}{4}$ of gasifier's capacity. Then enter the already-burned charcoal followed by the raw material until the gasifier is fully charged. Then adjust the desired air flow rate by adjusting the air intake valve on the blower until a

predetermined airflow rate is obtained with an air flow rate of $1.33 \text{ m}^3/\text{h}$.

During the gasification process, observation every 5 minutes at each thermocouple point for 120 minutes. Then take the sample of gases using a sample bottle at 50 to 80 minutes with a 10 minute interval adjusted from the calibration process. After the gasification process is complete, the inlet air duct is closed and turn of the blower. After that, take the tar sample at the bottom output of the condenser. Then analyze the gas sample using Gas Chromatography.

4. RESULT

In the process of gasification, observed temperature distribution is affected by time. The results of syngas obtained in this research is influenced by the addition of K_2CO_3 and $Ca(OH)_2$ catalysts. The use of catalysts also affects the amount of by-product in the form of tar.

4.1 The Effect of Gasification Process Time to Temperature of Each Zone of Gasification.

Fig. 3 shows the temperature profiles contained in the gasification reactor. In Fig. 3, the thermocouple 1 (T_1) has a temperature range of 30,8- 97,5 °C. Thermocouple 1

indicates that the process is in the drying zone ($T = 25 - 150$ °C). In thermocouple 2 (T_2) shows a temperature range of 30,5-134,2°C, these results indicate that T_2 is in the pyrolysis zone ($150^\circ C < T < 800^\circ C$). While at thermocouple 3 (T_3), optimum temperature reached in this zone is 898,5 °C. The zone in the thermocouple 3 shows the oxidation zone, where in this zone an exothermic reaction occurs ($800^\circ C < T < 1400^\circ C$). In thermocouple 4 (T_4) has a temperature range of 29,9 – 393 °C which indicates that T_4 is in the reduction zone (600 °C < $T < 900^\circ C$). Based on data obtained from the graph of the effect of time on temperature, indicating that the condition of the gasification process is in the steady state.

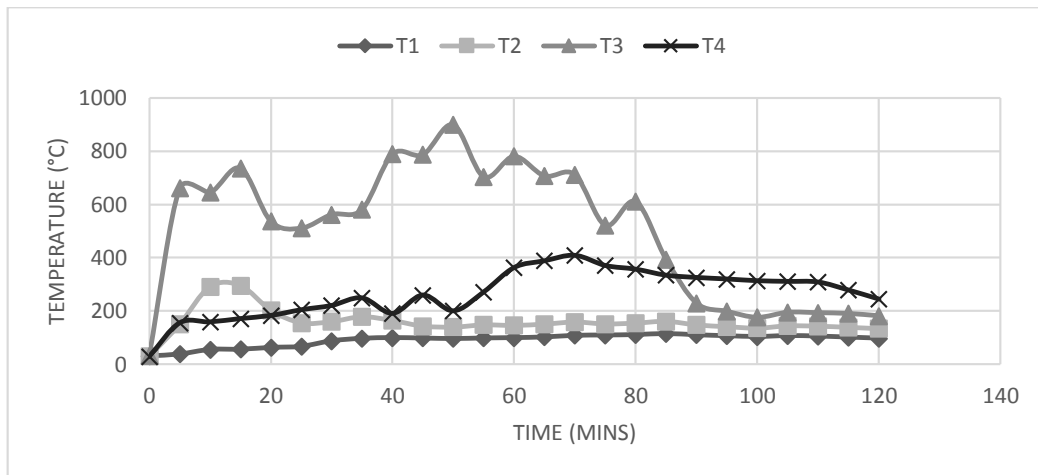


Fig 3. The Effect of Gasification Process Time to Temperature of Each Zone of Gasification

4.2 The Effect of Catalysts on Syngas Production.

The catalyst is one of the factors that influence the gasification process. The use of K_2CO_3 and $Ca(OH)_2$

catalysts in this study showed an effect on the syngas results compared to without the use of a catalyst, as shown in Fig 4.

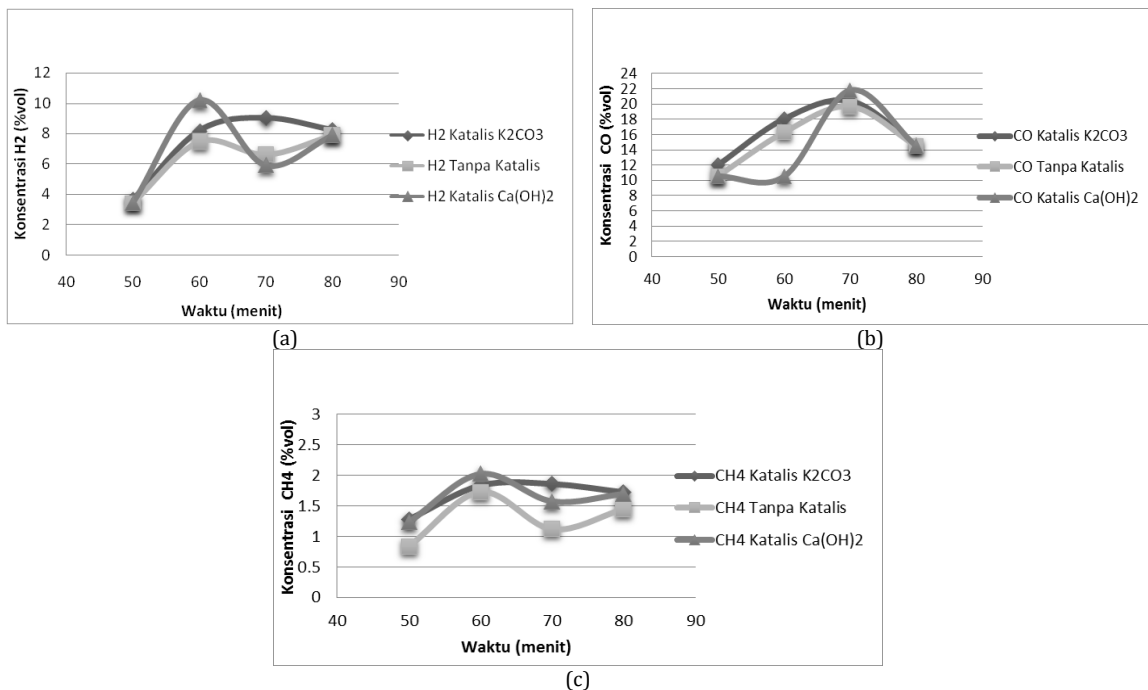


Fig 4. The Effect of Catalysts on Syngas Production, (a) H_2 , (b) CO , (c) CH_4

Fig 4 shows The Effect of Catalysts on Syngas Production (H₂, CO, CH₄). From the Fig 4, it is seen that the use of catalyst can increase the concentration of syngas (H₂, CO, CH₄). The largest concentration of syngas (H₂, CO, CH₄) is at the time of use of the Ca(OH)₂. At the time of use Ca(OH)₂, the largest formed Hydrogen (H₂) was 10,201 %vol, concentration of Carbon Monoxide (CO) was 21,813 %vol, and concentration of Methane (CH₄) was 2,023 %vol. Figure 4 shows that the largest condition of syngas concentration exists between minute 60 and 70. This is because the temperature of gasifier at minute 60 and 70 is in optimum condition. At the time of gasification process of tobacco waste without catalyst, optimum temperature were at minute 60 and 70, which were 854,1 °C and 802,9 °C with concentration of H₂, CO and CH₄ were 7,46 %v, 19,68 %v and 1,72 %v. At the time of use of the K₂CO₃ catalyst, the optimum temperature was at 70 minutes, which was 884,6 °C with concentration of H₂, CO and CH₄ were 9,03 %v, 20,41 %v dan 1,85 %v. At the time of use of the Ca(OH)₂ catalyst, the optimum temperature were at minute 60 and 70 with temperature were 898,5 °C and 780,6 °C with concentration of H₂, CO and CH₄ were 10,20 %v, 21,81 %v dan 2,02 %v. The largest condition of syngas concentration in each variable with optimum time is shown in Figure 5.

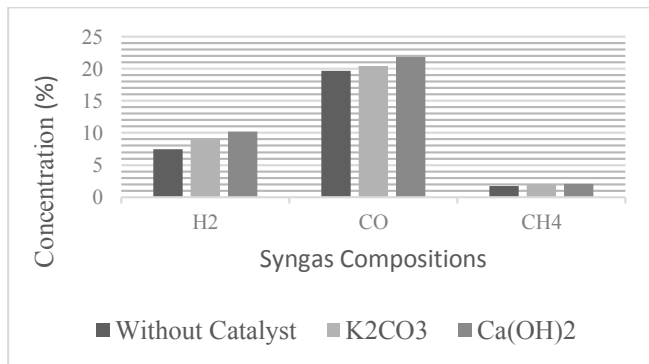
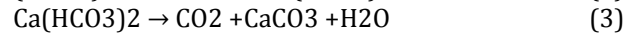
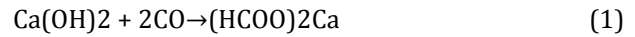


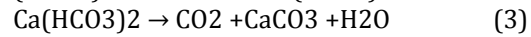
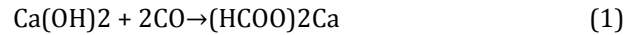
Fig 5. The Optimum Condition of Syngas Concentration in Each Variable

The optimum temperature will be used in the oxidation process, which will produce syngas products (H₂, CO, CH₄), so the syngas concentration produced on the Ca(OH)₂ catalyst is greater than that produce by the addition of the K₂CO₃ catalyst. As stated in Wang research in 2013, using microcrystalline cellulose and using the same catalysts, which are Ca(OH)₂ and K₂CO₃, produced syngas of: CO = 5,059 mmol/g ; H₂ = 1,892mmol/g ; CH₄ = 1,114 mmol/g without catalysts, CO = 6,088 mmol/g ; H₂ = 2,033 mmol/g ; CH₄ = 1,244 mmol/g with K₂CO₃ catalyst and CO = 8,116 mmol/g ; H₂ = 3,359 mmol/g ; CH₄ = 1,626 mmol/g with Ca(OH)₂ catalyst, and the temperature was 700 °C. While at the temperature was 800 °C, increased syngas concentration of: CO = 6,411 mmol/g ; H₂ = 3,638mmol/g ; CH₄ = 1,454 mmol/g without catalysts, CO = 6,487 mmol/g ; H₂ = 4,665mmol/g ; CH₄ = 1,590 mmol/g with K₂CO₃ catalyst and CO = 9,691 mmol/g ; H₂ = 5,294 mmol/g ; CH₄ = 2,040 mmol/g with Ca(OH)₂ catalyst. This shows that the addition of the catalyst can increase the concentration of syngas (H₂, CO, CH₄). When the two catalysts are

compared, the Ca(OH)₂ catalyst was better at producing the syngas than the K₂CO₃ catalyst. This is because the Ca(OH) catalyst function is different than K₂CO₃ catalyst in its catalytic mechanism [Pei, 2009].



The amount of CO₂ decreases when compared to the reaction without the catalysts. This happened because CO₂ is absorbed by a basic catalyst such as Ca(OH)₂ to carbonate [Tingyu, 2000].



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4.3 The Effect of Catalysts on Tar Production.

Fuel gas and synthesis gas generated by gasification are used as power plants, heating, chemical products, etc. However, the gasification process also produces a condensable organic compound called tar. Most of the tar content is present in the gas at high temperatures. However, when the temperature is cooled lower than its boiling point, it will make the black oily liquid causing the failure of the process equipment. Figure 6 shows the effect of K₂CO₃ and Ca(OH)₂ catalysts on the decrease of tar production.

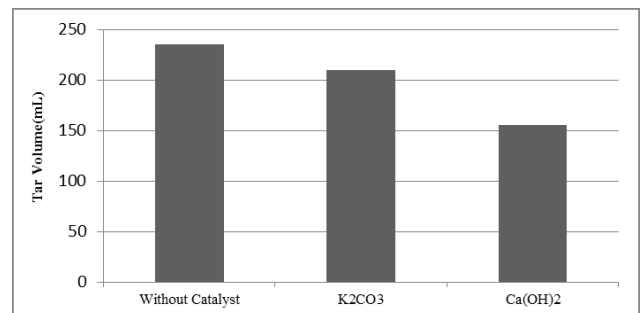


Fig 6. The Effect of Catalysts on Tar Production

The tar sample is taken when the gasification process has been completed. At the time of tar sampling without the use of a catalyst, the amount is very large, which amounted to 235 ml. At the time of sampling after using K₂CO₃ and Ca(OH)₂ catalysts the amount of tar decomposed to 210 ml and 155 ml consecutively. On the use of K₂CO₃ catalyst, tar reduction amounted of 10,63 %v while on the use of Ca(OH)₂ catalyst, tar reduction amounted of 34,04 %v.

As was done in Wang's research in 2013, with the same treatment, the first experiment was carried out at the temperature of 800 °C, tar content: 38 %wt for tar without catalyst, 36 %wt using K₂CO₃ catalyst and 28 %wt after using Ca(OH)₂ catalyst. While in the second experiment

with temperature of 700°C, the tar content formed was: 42 %wt without using a catalyst, 40 %wt after using K₂CO₃ catalyst and 32 %wt after using Ca(OH)₂ catalyst.

This happened because the operating temperatures of the reactor affect the quantity of tar. As temperature increases, the number 1- and 2- aromatic rings together with the substituents will decrease, but the 3- and 4- aromatic rings are increased. The aromatic compounds without substituents (naphthalene, benzene, etc) are preferred at high temperatures, the naphthalene and benzene content increases with temperature. High temperatures also reduce the ammonia content in gases and increase charcoal changes, but have the negative effect of reducing the useful heat value of the product gas [Nurtanio, 2012].

In comparison to the use of the catalyst against tar decomposition the effect of using Ca(OH)₂ catalyst is better than using K₂CO₃ catalyst. This occurred because in experiments using Ca(OH)₂ catalyst, the highest temperature values are obtained so that Ca(OH)₂ is in a CaO state, tar is attached to the CaO surface. In addition, the polarity of the active parts of CaO may affect the π -electron stability of the condensed aromatic compound, and the CaO itself has an active cracking section on the inside and outside surfaces [Tingyu, 2000].

5. CONCLUSION

Based on the result of the research, it can be concluded that K₂CO₃ and Ca(OH)₂ catalysts can reduce the amount of tar to increase syngas production. The largest syngas composition was produced by the use of Ca(OH)₂ catalyst with H₂ = 10,20 %v; CO = 21,81 %v; dan CH₄ = 2,02 %v. In the reduction of tar, the use of Ca(OH)₂ catalyst is also better than the use of K₂CO₃ catalyst by producing tar only as much as 155 ml or 34,04 %v, whereas by using K₂CO₃ catalyst, produces tar as much as 210 ml or 10,63 %v.

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