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Syngas Production by the Gasification of Bayah's Coal over $Ca(OH)_2$ and Na_2CO_3 catalyst

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ABSTRACT

Official data of Indonesia's coal reserve provided by government in 2014 approximately reached 104.8 billion tonnes. Bayah as a part of South Banten region has been stored quite amount of coal. Gasification is one solution to utilize Bayah's coal potential. Coal Gasification is a conversion process of solid phase coal into synthetic gas mixture (CO, H_2). Main reaction of the process involves Boudouard and Water-Gas-Shift reaction. The aim of experiment was to observes influence of several variables such as : Air Fuel Ratio (AFR), Temperature, and Catalyst at particular condition. Gasification process becomes beneficial when ratio of synthetic gas mixture (H_2/CO) exhibits 2.0. Synthetic gas mixtures were analyzed by using gas chromatograph method. 300 grams of Bayah's coal (14 – 18 mesh) were gasified in updraft type of fixed bed reactor using steam injection under Air Fuel Ratio varied between 1.5, 2.0, 2.5, temperature of 600°C, 700°C, 800°C and catalyst of $Ca(OH)_2$ and Na_2CO_3 . Air Fuel Ratio of 1.5 and 800 with the help $Ca(OH)_2$ catalyst tended to produce the optimum result for H_2/CO ratio which obtained a value of 1.98. Synthetic gas composition at this variation reached 33.8% for Hydrogen and 17.1% for Carbon Monoxide.

Keywords: *Synthetic Gas, Fixed Bed Reactor, Steam, Air Fuel Ratio.*

1. INTRODUCTION

Coal is the second high networth of energy resources after Oil and Gas. Cheaper cost than Oil and Gas is the main cause of many industry utilized coal. Between 2004 – 2014 Indonesia's coal consumption has multipled near 4 times from 13,177,000 tonnes skyrocketed to 52,533,000 tonnes. Unlike Oil and Gas that produced for domestic purposes, local utilization of coal only reached 27% of total production whilst the rest production was exported (Kurniawan, 2012). Many minerals including coal lies abundatnly under South Banten region, specifically at a place named Bayah. An observation taken at 2006 by Coal Indonesian Study Team (ESDM, 2006) found that about 13.31 millions tonnes of coal stored in Bayah. Coal can be main resource of synthetic gas (H_2, CO, CO_2, CH_4) production which has good industrial utilization. Hidrogen, in particular, is useful on many purposes like Ammonia and Methanol production, startup material for oil and gas hydrocracking treatment, hydrogenation, and also become an alternative fuel.

The gasification is a thermochemical conversion process of solid phase fuel into gas phase products, with consumption slightly under combustion process. Common medium for gasification process is Water and Air. Products of gasification process discrete into three parts : (1) Solid phase (Tar), (2) Liquid phase, and (3) Permanent Gas. Combustible gas that produced includes : CO, H_2, and CH_4. The gases can be directly used for several purposes such as : Synthetic process or other chemical treatment.

Incereasing of Air velocity causes the gasification was changed to combustion. Other researchs has analyzed the influence between air velocity and raw material mass reduction which later called an Air Fuel Ratio. Air Fuel Ratio equation described as :

$$AFR = \frac{\rho \cdot v}{m}. \qquad (1)$$

Gasification is done cored in through pyrolysis process under temperature varied between 150 – 900°C followed by oxidation of produced gas at 900 – 1400°C and reduction process at 600 – 900°C. Coal gasification can be classified by reactor type involving : Fixed Bed, Fluidized Bed, and Entrained Flow.

Gasification lies under high temperature with limited air and oxygen changing solid phase material into gas phase products such as : Hydrogen (H_2), Carbon monoxide (CO), and Carbon Dioxide (CO_2). Several reactions take impart of whole process as represent in equations (Highman, 2007) below :

$$C + \tfrac{1}{2}O_2 \leftrightarrow CO \qquad (2)$$
$$C + CO_2 \leftrightarrow 2CO \qquad (3)$$
$$C + H_2O \leftrightarrow CO + H_2 \qquad (4)$$
$$C + 2H_2 \leftrightarrow CH_4 \qquad (5)$$

In this work, the effect of air fuel ratio, temperature and catalyst has been evaluated on product distribution of syngas such as hydrogen and carbon monoxide gases.

2. METHODS

Table 1 showed typical characteristics of Bayah's coal. Bayah's Coal was grinded into particle size of 14 – 18 mesh by using ball mill crasher and then it was screened to get material with homogenous size of 14 mesh. The coal samples has been pulverized by screener 14 mesh.

Table 1. Ultimate And Proximate Analysis Of Bayah's Coal

Element / Compound	Value
Ash Content	41.17 wt%
Volatile Matter	27.46 wt%
Fixed Carbon	26.36 wt%
Gross Calorific Value	42.08 Kcal/Kg
Total Sulphur	5.00 wt%
Carbon (C)	42.11 wt%
Hydrogen (H)	3.71 wt%
Nitrogen (N)	0.98 wt%
Oxygen (O)	7.02 wt%

As much as 300 g of screened Bayah's coal were then gasified along with Air Fuel Ratio 1.5 and steam injection ratio 1:1 (v/v% of air) at 700°C for 1 h operation as initial experiment into fixed bed reactor (11 cm diameter and 25 cm heights) with updraft module. Sample of produced gas was stored in bottle for every 15 minutes for analysis. The gasification was evaluated in fix bed reactor. The syngas product during the gasification experiment were analyzed by gas chromatography Shimadzu in Laboratory Chemical Engineering University of Indonesia, Depok. The experiment repeated for variation of Air Fuel Ratio (2 and 2.5). Further observation of gasification process was done through mixed up 300 grams of coal and 9 grams of applied catalyst ($Ca(OH)_2$ and Na_2CO_3) into the reactor with fixed Air Fuel Ratio of 1.5 for 45 minutes operation under different temperatures (600°C, 700°C, and 800°C). Sample of produced gas also was stored in bottle for every 15 minutes for further analysis. For every sample produced gas, the analysis was conducted by using gas chromatograph method. 4. The brand of GC used is Shimadzu GC 8A and the type of detector is Thermal Conductivity Detector (TCD) and stainless steel column with Molecular Sieve. The result of analysis displayed a percent volume of particular chemical compared to total volume gas of sample. Desirable gas results (H_2 and CO) were propotioned and converted into chart.

3. RESULTS AND DISCUSSION

3.1 Influence of Air Fuel Ratio (AFR)

The syngas production (CO and H_2) influenced at various Air Fuel Ratio was depicted in **Fig.1** and **Fig.2.**

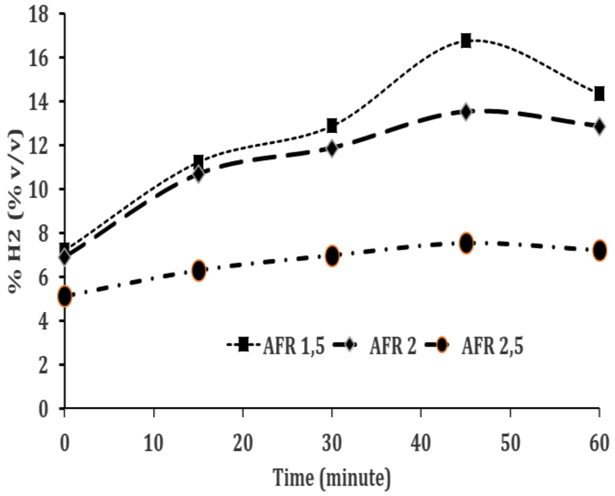

Fig.1. Production of hydrogen at different air fuel ratio

Fig. 1 explain a significant trend of hydrogen gas production. The graph showed that Hydrogen gas volume decreased along with increasing Air Fuel Ratio. The increasing amount of Hydrogen mainly was caused from steam injection which stimulated water gas and water gas shift reaction that was subscribed in the equation :

Water gas

$$C + H_2O \leftrightarrow CO + H_2 \; \Delta H = +131.3 kj/mol \qquad (6)$$

Water gas shift

$$CO + H_2O \leftrightarrow CO_2 + H_2 \Delta H = -41.2 kj/mol \qquad (7)$$

By this term, it was clear that water gas required more energy rather than the water gas shift reaction provided. This condition caused the process temperature and thermodynamic decreased so the production of syngas was inhibited[4]. Furthermore, increasing air fuel ratio altered the number of water contacted to the process. Prior to Bernaulli's equation about relationship between velocity and pressure with vapor – liquid equilibrium of reaction, higher air velocity impacted the decreasing vapor water pressure whilst switching water gas and water gas shift reaction was back to initial gases (Tristantini, 2014). Produced sythentic gas then became limited.

The Production of syngas from Bayah's coal gasification increased per amount of operation time. At 45 minutes' operation (**Fig. 1** and **Fig. 2**), the amount of synthetic gas (syngas) either hydrogen and carbon monoxide significantly increased and tended to be optimum time of experiment. Bayah's coal diminished along with operation time. That explained the cause of decreasing amount of synthetic gas after 45 minutes where presumably due to a little number of coal left to be gasified. This trend aligned with the other research that has proved that maximum amount of coal to produce synthetic gas was is about 70% of coal total mass (Hantoko, 2011).

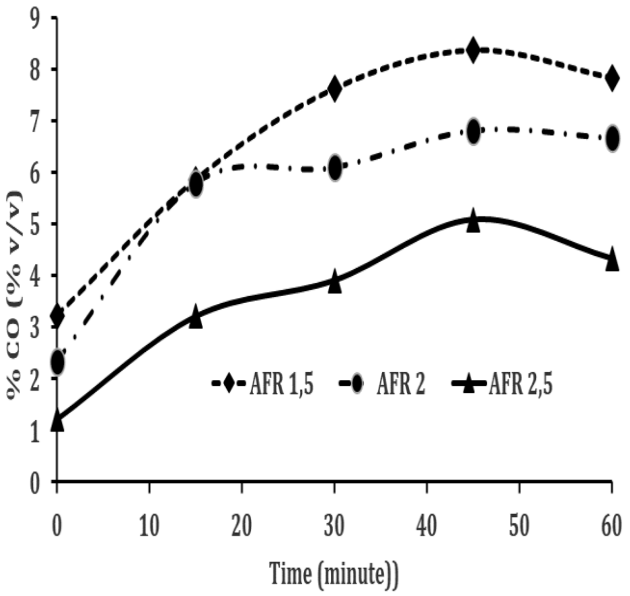

Fig.2. Percent of Carbon Monoxide Produced at 700°C

3.2 Catalyst Influenced

Additional catalyst indeed will initiated reaction process faster than normal process. Generally, coal gasification process using an alkali compound in form of oxide derivatives or carbonates molecule. Calcium Hydroxide ($Ca(OH)_2$) and Na_2CO_3 are common catalysts that have been used for coal gasification. Boundouard reaction was taken at coal gasification with $Ca(OH)_2$ catalyst 3% of raw material used under steam injection as described below :

$$Ca(OH)_2\,(s) + H_2O\,(g) + C\,(s) \rightarrow CaO_2(s) + CO\,(g) + H_2(g) \quad (8)$$

The influence of various temperature for production hydrogen gas and CO gas production through gasification Bayah coals were presented **in Fig. 3 – 4.** The higher of temperature process was taken the more the hydrogen will be produced. The trend occured due to catalyst role by which deactivate acid mineral within coal will prevent gasification process (Alexis, 2005).

The experiment proved that at temperature of 800°C, production for both synthetic gas exhibited the highest percent amount from total composition produced gas. At temperature of 800°C, Hydrogen gas produced peaks at 15 minutes operation which achieved 33.8% of total produced gas where at the same time, Carbon Monoxide gas produced achieves 17.1%. The trend of percent composition slightly got down because of a few amount catalyst were carried over during process by produced gas.

Aligned with the use of $Ca(OH)_2$ catalyst, the trend of Na_2CO_3 catalyst occured similarity result. Despite of fastening reaction process, aimed of Na_2CO_3 performed a good inhibitor for lowering side product such as Sulphur derivatives inside Bayah's coal. Reaction of gasification process using Na_2CO_3 catalyst represents as Eq. 9.

$$Na_2CO_{3(s)} + 2C_{(s)} + H_2O_{(g)} \rightarrow Na_2O_{(s)} + 3CO_{(g)} + H_{2(g)} \quad (9)$$

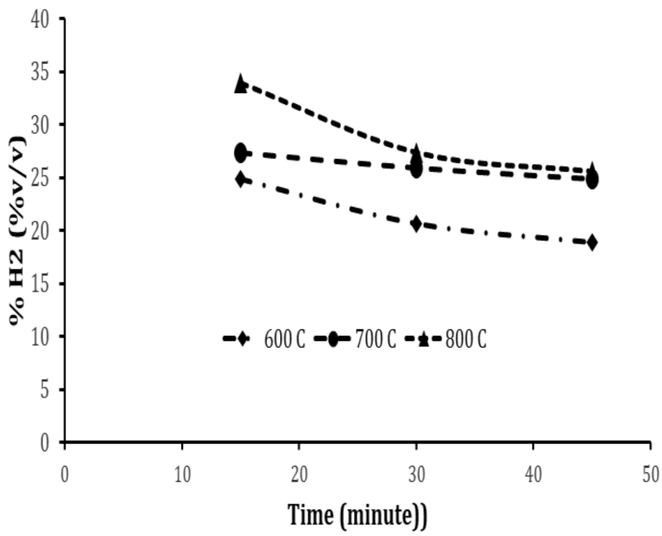

Fig. 3. Hydrogen Production by gasification Bayah coal at different temperature over ($Ca(OH)_2$)

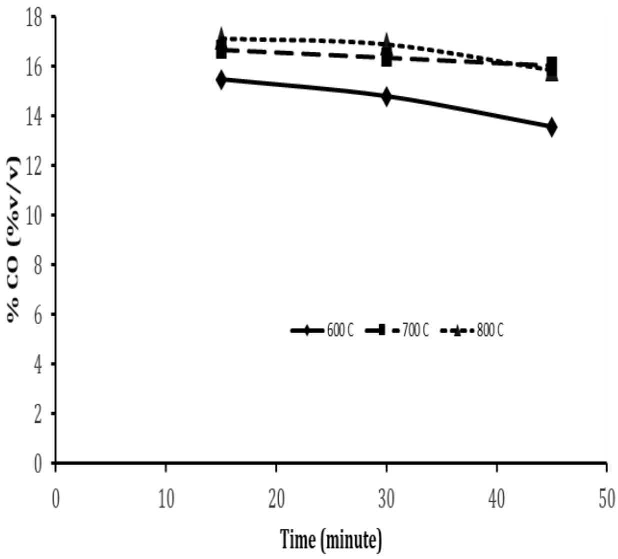

Fig. 4. Carbon Monoxide Production by gasification Bayah coal at different temperature over ($Ca(OH)_2$)

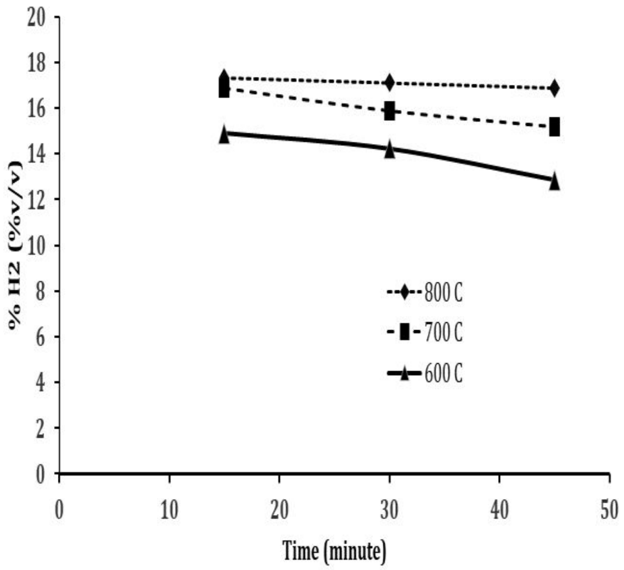

Fig. 5.Hydrogen Production by gasification Bayah Coal at different temperature over (Na_2CO_3)

Fig. 5 and **Fig. 6** captured percent volume of produced gas at 45 minutes operation. The highest amount of percent volume Hydrogen produced gas (approximately 25%) was reached at 15 minutes operation for temperature of 800°C. Thus, for CO produced gas, highest amount of percent volume achieved 25% from total volume gas composition also at 15 minutes operation and 800 ^{0}C temperature Nevertheless, the profile trend for syngas production over Na_2CO_3 catalyst provide a similarity over $Ca(OH)_2$ catalyst.

In contrast of trend of data, the total percent volume of CO gas produced from gasification process using Na_2CO_3 catalyst exhibited higher than $Ca(OH)_2$ catalyst. The phenomenon occured due to reactivity of catalyst. As for equilibria reaction, since Na_2CO_3 had C and O content, Carbon and Oxygen within catalyst helped reaction to produce more CO gas rather than hydrogen gas (Tsai, 2006).

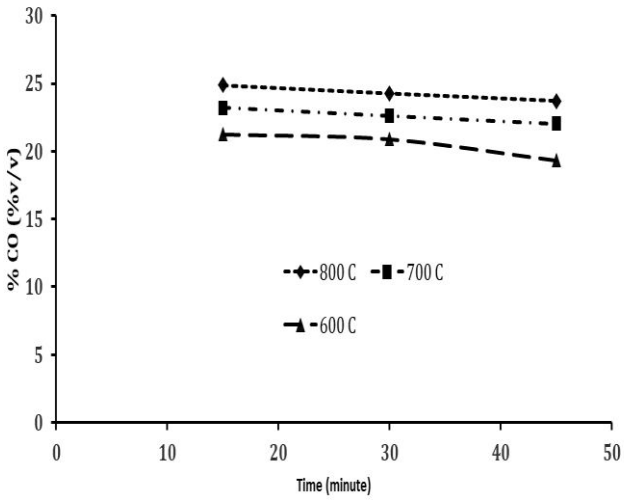

Fig. 6. Carbon Monoxide Production by gasification Bayah Coal at different temperature over (Na_2CO_3)

Presumably, catalyst will optimize gasification process. The comparison of each particular process (using catalyst or without catalyst intake) showed in **Fig. 7** (% volume of Hydrogen gas) and **Fig. 8** (% volume of CO gas). Operation was taken at temperature 700°C with Air Fuel Ratio of 1.5 for 45 minutes operation.

The optimization production of hydrogen over $Ca(OH)_2$ catalyst and the production of CO over Na2CO3 catalyst. As in generally, using catalyst showed an improvement of gasification process to alter both Hydrogen gas and CO gas production. At 45 minutes operation, gasification process using Na_2CO_3 catalyst produced less Hydrogen than a process without catalyst intake. The carbonate compound helped the conversion of CO gas production rather than hydrogen gas (Shen, 2012).

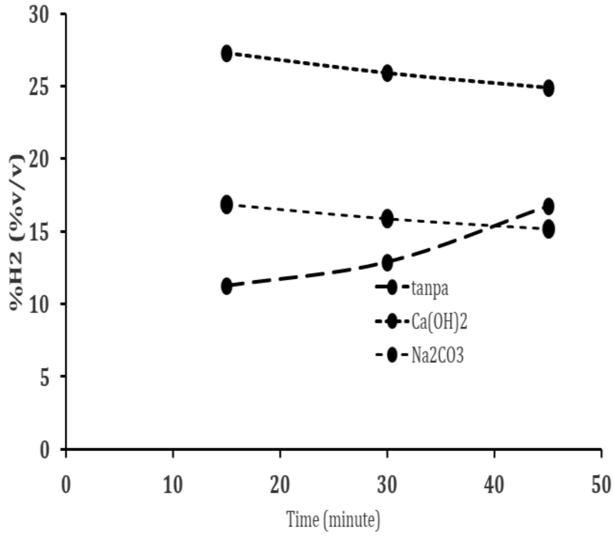

Fig. 7. Hydrogen Production by gasification Bayah coal at different catalyst

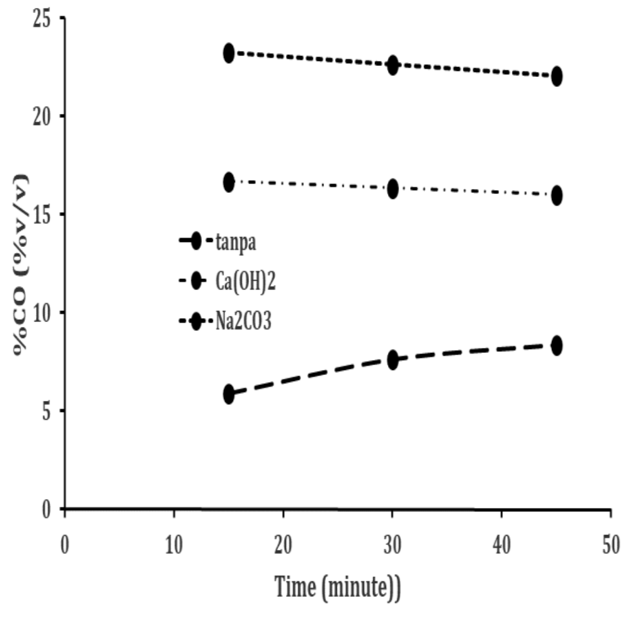

Fig. 8. Carbon Monoxide Production by gasification Bayah coal at different catalyst.

3.3 H_2/CO ratio

The percent of H_2/CO at different air fuel ratio was presented in Figure 9. The figure reported that increasing the amount of Air Fuel Ratio and the ratio of H_2/CO production is decreased. **Fig. 9** explained the highest ratio of H_2/CO established at the lowest Air Fuel Ratio (1.5), this is due to smaller amount of water vapor from air taken into reaction process. The content of water vapor decreased the conversion of steam rate to hydrogen gas and the pressure of water vapor decreases too. This condition caused the equilibrium of water gas and water gas shift reaction was shifted, it caused the syngas production is lower.

Equation (8) showed a theoretical evidence in which $Ca(OH)_2$ catalyst improved Hydrogen production gas whereas Equation (9) represented a highly impact of Na_2CO_3 into CO gas.

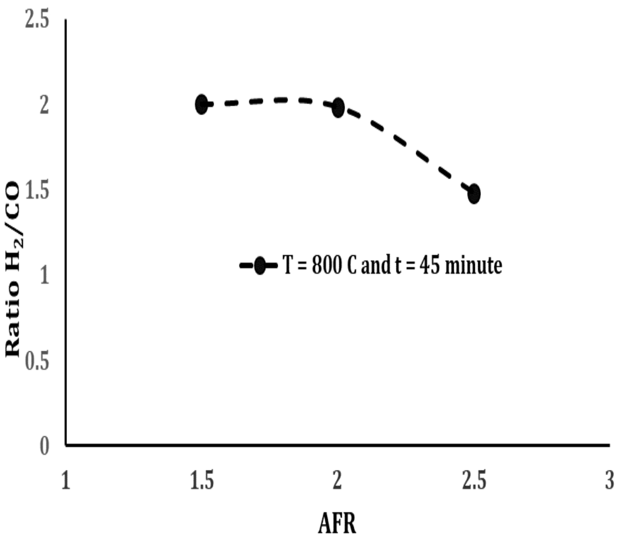

Fig. 9. H_2/CO ratio (T = 800°C, t = 45 minutes)

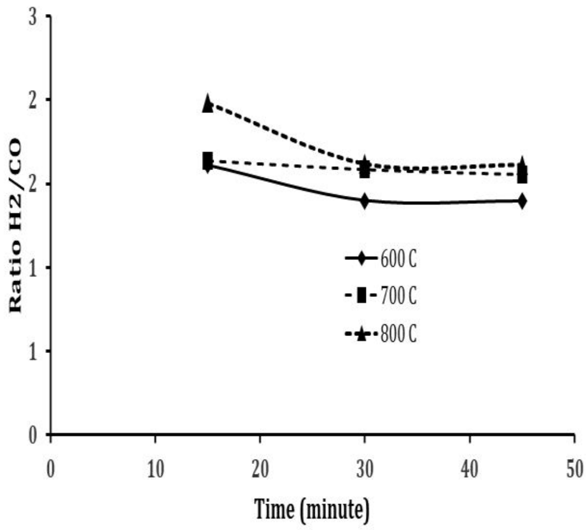

Fig. 10. H_2/CO ratio at AFR = 1.5 and $Ca(OH)_2$

Figure 10 and **Fig. 11** displayed the comparison of ratio H_2/CO gas overtime for any particular temperature. Bayah's coal gasification using $Ca(OH)_2$ catalyst (**Fig. 10**) achieved a good value of H_2/CO gas ratio better than Na_2CO_3 catalyst (**Fig. 11**). This result agreed as per thermodynamic theory shown in Equation (9) and Equation (10) in which $Ca(OH)_2$ will produce more Hydrogen gas than CO gas. Conversely, Na_2CO_3 catalyst produced more CO gas rather than Hydrogen gas.

The gasification process reached a better result at higher temperature. Increasing H_2/CO gas ratio at higher temperature could be caused by its change of Gibbs' energy which later decided how spontaneous reaction taken. Details of increasing H_2/CO gas ratio produced had been investigated at particular temperature as represents in Table 2.

Table 2. Gibbs' Energy At Several Temperature[9]

Reaction	ΔG (Kj/mol)		
	600°C	700°C	800°C
Water Gas $C + H_2O \rightleftharpoons CO + H_2$	10.417	-4.167	-18.750
Boudouard $C + CO_2 \rightleftharpoons 2CO$	16.667	0	-14.583
Water Gas-shift $CO + H_2O \rightleftharpoons CO_2 + H_2$	-8.333	-4.167	0

If the change of Gibbs' Energy below the value of zero then reaction will occure spontaneously. Furthermore, reducing the change of Gibb's Energy impacted the value of equilibrium constant for each reaction. Low value of Gibbs' Energy changes indicated high value of equilibrium constant. Therefore, the reaction of process will take immediately after moles of reactant reach standard value to be reacted (Anis, 2009).

At 600°C, the Boudouard reaction and water gas reaction were not spontaneously happened. Thus indication signed there were no addition of H_2 and CO molecules compound produced immediately. On the contrary, the result of the study showed that H_2 and CO gas yet still can be produced at 600°C. The phenomena could be cause by overlapping during start-up process. When heating process continued from ambient temperature to established required temperature, there were a little parts of coal which had been converted into synthetic gas. Thus, produced gas effected overall thermodynamic equilibrium of gas phase and made some gases detected on sample.

At 15 minutes operation, gasification process using $Ca(OH)_2$ catalyst at 800°C temperature with Air Fuel Ratio of 1.5, H_2/CO gas ratio obtained a value of 1.98 which near of minimum standard for further industrial purposes. Furthermore, in order to provide strong support for the performance catalyst on coal gasification in this work, we compared type of catalyst and reaction condition. The result as presented in Table 3.

Base on the Table 3, the catalyst is important role on product of hydrogen and monoxide increases. The increase in the rate of gasification process, caused by the addition of a catalytic additives. The addition of 0.85 wt. % of potassium significantly increased the share of the resulting CO, but also reduced the amount of hydrogen. The carbon conversion degrees achieved during the coal gasification with the addition of calcium are much more coal gasification. The addition of catalyst caused the varied than the results achieved during the gasification with the addition of potassium. The catalytic activity of calcium and potassium metals which accelerated the formation rate of carbon monoxide and hydrogen during the process, resulting in their increased yields in the post reaction gas.

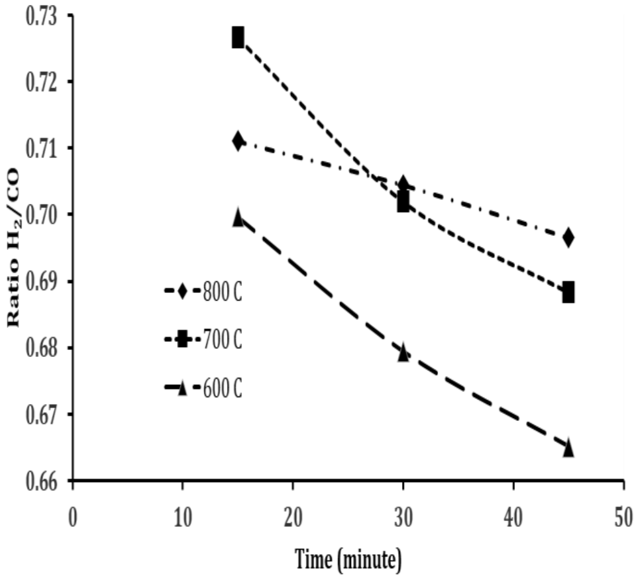

Fig. 11. H_2/CO at AFR = 1.5 and Na_2CO_3

Table 3. Comparison of catalyst on performance of coal gasification

Catalyst	Reaction condition	Result	Reference
Calcium and potassium	Temperature 600, 700 and 800 ^{0}C and Air Fuel Ratio : 1.5, 2.0, 2.5	Air Fuel Ratio of 1.5 and 800 with the help $Ca(OH)_2$ catalyst tended to produce the optimum result for H_2/CO ratio which obtained a value of 1.98. Synthetic gas composition at this variation reached 33.8% for hydrogen and 17.1% for carbon monoxide	Present
Potassium and calcium	Temperature 900 ^{0}C and pressure 2Mpa	The addition of potassium nitrate added due to the formation rate of hydrogen and carbon monoxide was increased.	(Porada, 2016)
$FeCO_3$	Temperature: 700, 800 and 900 ^{0}C and pressure 75kPa	The addition of iron carbonate as a catalyst is beneficial to gasification of coal in terms of increased coal conversion rate and tar mitigation as well as H_2 productions at low temperatures.	(Popa, 2013)
KOH, $KHCO_3$ and K_2CO_3	Temperature 800 – 900 ^{0}C	With addition of catalyst, H_2 and CO_2 content in producer gas increases up to 13 and 11 vol. %, respectively. This result is attributed to synergistic effects at coal/biomass weight ratio of 60:40% at ER = 0.29 due to presence of alkali and alkaline minerals in biomass that enhances gasification of char and tar.	(Mallick, 2020)

4. CONCLUSION

Both of catalysts in this study exhibited a good result of producing synthetic gas (CO and H_2). $Ca(OH)_2$ catalyst was the most likely to produce more H_2 gas whilst Na_2CO_3 catalyst significantly impacted CO gas production. $Ca(OH)_2$ catalyst provided a better conversion for gasification process interm of H_2/CO gas ratio. The Optimization of H2/CO gas ratio is 1.98. It was achived from gasification process over 3% $Ca(OH)_2$ (w/w%) catalyst of coal at 800°C temperature and air fuel ratio is 1.5.

5. ACKNOWLEDGMENT

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