INTRODUCTION

The use of carbon resources to produce clean fuel is desired to overcome fossil fuel depletion and the resulting environmental problems. In the process of converting a carbon material into energy, minimization of the CO₂ emissions must be considered properly. According to the Ministry of Energy and Mineral Resources of Republic Indonesia (2018), the total amount of coal resources in Indonesia is estimated to reach 105 billion tons, about 21 billion tons of which is reserve; 60% of the reserve coal in Indonesia consists of low rank coal sub-bituminous with the calories content less than 6100 cal/gram. Coal mining in Indonesia, which adopts an open pit mining system, cannot prevent fine coal waste from the production unit and is exposed to the air, watershed and land (Adiansyah et al., 2017; Zhang et al., 2018). This fine material from low-rank coal is very promising for use in the production of environmentally friendly synthetic gases. The synthetic gas from gasification is a mixture of CO, H₂, CH₄, CO₂, and other gases. Syngas can be converted easily into environmentally friendly fuel and used as raw material to produce other useful chemical products.

CO₂ is a by-product of the gasification process, which can contribute to the emissions to the atmosphere. The reduced CO₂ continuously encourages carbon gasification and methane reform and shifts the water gas reaction to the product side so that the syngas is rich in hydrogen (Chen et al., 2020; Chen and Chen, 2020). The heat released from the carbonation process makes up most of the heat supply for the gasification process. The gasification process, producing syngas with low CO₂ emission involves absorbing or capturing...
CO₂ in the syngas. Carbon capture and storage are economical and efficient strategies for reducing CO₂ (Ghaemi and Behroozi, 2020; Wu et al., 2020). The Ca-based sorbent is very attractive for use as a CO₂ absorber at high temperatures, apart from being abundant, environmentally friendly, and inexpensive. It is also because of its appropriate kinetics and CO₂ absorption capacity (Soleimanisalim et al., 2016). Calcium oxide plays an essential role in removing CO₂ in syngas through the absorption process in the gasification process. The water-gas shift reaction takes place more dominantly after CO₂ is absorbed so that the purity of syngas, especially H₂, increases (Dou et al., 2016). However, inorganic or dissolved organic calcium compounds derived from limestone are preferred to manufacture synthetic Ca-based absorbers (Soleimanisalim et al., 2017).

The fixation of CO₂ through the production of insoluble carbonate salts, such as through the carbonation of an acidic solution that absorbs CO₂, is another option for capturing CO₂. The aqueous solution of Ca(OH)₂ is used as an effective solvent to absorb CO₂ because of its various beneficial features. CaCO₃ is formed after CO₂ has been successfully absorbed in the gasifier and can be regenerated (Hafner, Schmid, and Scheffknecht, 2021). Precipitation of CaCO₃ from the carbonation of a Ca(OH)₂ solution is a widespread reaction, commonly observed in nature. Considering that the cost and stock of the CaO sources in Indonesia are abundant and promising, so the absorption of CO₂ in the gasification process is very relevant for studying. CaO-enhanced gasification is a promising technology for the production of hydrogen-rich synthetic gas (Mostafavi et al., 2016; Sun and Wu, 2019).

The studies on absorption using Ca(OH)₂ both as an absorbent and as a catalyst have been carried out by Soomro et al. (2018); Kumar et al. (2019); Kim, Jo, and Kim (2020). The research by Li et al. (2017) found that calcined CaO acts as an absorbent and a catalyst in the water-gas shift reaction in corn stalk gasification. Furthermore, in coal gasification, Ca(OH)₂ acts as an active catalyst that decomposes tar to increase the gas yield and hydrogen concentration, which correlates with CO₂ absorption (Shuai et al., 2015; Jia et al., 2018). Although several studies have been submitted regarding the absorption of CO₂ using CaO or Ca(OH)₂ in the gasification process, the research on CO₂ absorption in syngas from the fine coal gasification process using Ca(OH)₂ has not been intensively studied by researchers. Therefore, this study aimed to produce syngas with minimal CO₂ in a specific temperature range using hydrated CaO. The gas composition was evaluated to determine the role and synergy between the gasification temperature and the absorbent. The following reactions (R1–4) are occurring within the gasifier in the gasification and purification process:

\[
C(s) + CO_2(g) \leftrightarrow 2CO(g) \quad \text{(R1)} \\
C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g) \quad \text{(R2)} \\
CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \quad \text{(R3)} \\
CaO(s) + H_2O(g) \rightarrow Ca(OH)_2(s) \quad \text{(R4)} \\
Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(g) \quad \text{(R5)}
\]

**MATERIALS AND METHODS**

**Raw materials**

The fine coal used in this research having the size below 3 mm, was supplied by a coal mining at Sumatera Selatan. The proximate and ultimate analyses of the fine coal are shown in Table 1 in order to investigate the characteristics of fine coal. The gasifier used was a fixed bed type made of stainless steel. Air was used as the gasification agent in this process. The condition inside gasifier was temperature 450°C, 550°C, 650°C and 700°C. The gasifier was isolated to prevent heat release and gas leakage, as well as the two pipes of input stream for gasification agent and output stream for gas product. A flowmeter was installed to measure the flowrate of gasification agent needed. The flow diagram of the gasification process refers to the previous work (Aprianti et al., 2020). CaO was used in the form hydrated by H₂O becoming calcium hydroxide (Ca(OH)₂) (R4).
Gasification procedure

The samples were placed into the gasifier and the coal was ignited to 450–700°C, then the mixture of oxygen and air was supplied continuously as the agents of gasification to sustain the gasification process. In this research, the fine coal gasification was carried out under different temperature. The syngas produced then accumulated into gas samplers to be analysed by gas chromatography.

Gas analysis

The syngas produced accumulated into gas sampler bag to analyse by Perkin Elmer Clarus 680 Gas Chromatography equipped flame ionization detector (FID). The success of the gasification process and the quality of syngas are evaluated through the gas ratio and heating value of syngas (Eq. 1–2).

\[
HHV_{\text{gas}} = \left( (30.18 \times CO) + (30.52 \times H_2) + (95 \times CH_4) \right) \times 4.1868 \ (MJ/\text{NM}^3)
\]

\[
LHV_{\text{gas}} = \left( (30 \times CO) + (25.7 \times H_2) + (85.4 \times CH_4) \right) \times 4.2 \ (MJ/\text{NM}^3)
\]

RESULTS AND DISCUSSION

Fine coal characteristics by proximate and ultimate analysis

The proximate, ultimate, and calorific analyses in Table 1 provide important insights regarding the chemical properties of fine coal materials. Proximate analysis of fine coal was carried out to identify its composition in moisture, which was later found to be 16.77%. The volatile material of fine coal burning into gas in the nitrogen atmosphere was 40.74%, while the inorganic material in fine coal (ash) was 4.13%. Fine coal is expected to have high gasification efficiency with risks such as clogging, slag, and minor dirt due to low ash. Fine coal contains 38.37% fixed carbon. This result is relatively low compared to raw coal in similar studies (Yan et al., 2021; Vega, Diaz-Faes, and Barriocanal, 2021). The moisture content in fine coal will affect the gasification process. When the water content is high, some of the heat energy will be used to evaporate water in the drying zone. Increasing the volatile matter can result in greater gas conversion yields (Aprianti et al., 2021). Fine coal is mostly composed of minerals. The calorific value of fine coal is relatively high because classified as a sub-bituminous coal type. The high calorific value expected to make the syngas produced also has a high calorific value.

The ultimate fine coal analysis consists of carbon, hydrogen, oxygen, nitrogen and sulphur. The carbon composition in fine coal was 69.04%, which contributes to the CO formation in syngas and a high calorific value. Meanwhile, the H\textsubscript{2} and O\textsubscript{2} content in the material causes a decrease in the calorific value. In fine coal, H\textsubscript{2} was found only 4.78%. N\textsubscript{2} was around 0.97%, because it is an inert gas and is not flammable. The portion of sulphur in this coal type was 0.45%. Oxidized sulphur can later cause air pollution and contribute to the formation of detrimental acid rain. The low nitrogen and sulphur content in fine coal minimise the possibility of NO\textsubscript{x} and SO\textsubscript{x} formation along the updraft gasification process. Thus, it can be predicted that the resulting syngas is highly desirable for fuel, chemical synthesis and methanol (Mansur et al., 2020).

Effect of reaction temperature on syngas production

Figure 1 shows the synthetic gas after the absorption process at different temperatures. The CO\textsubscript{2} concentration has decreased with increasing gasification temperature from 450°C to 700°C. This situation is due to the fact that the CO\textsubscript{2}

| Parameter             | Unit  | Air dry basis |
|-----------------------|-------|---------------|
| Total moisture        | %     | 16.77         |
| Ash content           | %     | 4.13          |
| Volatile matter       | %     | 40.74         |
| Fixed carbon          | %     | 38.37         |
| Total sulphur         | %     | 0.21          |
| Gross Calorific Value | MJ/kg | 21.54         |
| Carbon                | %     | 69.04         |
| Hydrogen              | %     | 4.78          |
| Oxygen                | %     | 13.62         |
| Nitrogen              | %     | 0.97          |
| Sulphur               | %     | 0.45          |

Table 1. Proximate and ultimate analyses of sub-bituminous fine coal
content in the synthetic gas exiting the gasifier before purification shows an identical trend, where the CO₂ content decreases if the gasification temperature is increased. This can be possible when the CO₂ content in synthetic gas decreases, then the opportunity for the absorption process will easily occur. Hydrogen has increased significantly after the gasification temperature was raised, while methane in syngas tends to decrease. The CO content increases slowly with a range of 20–30 mole% at 450–650°C. When the gasification temperature reaches 700°C, the CO concentration is reduced by 6.5 mole% to 19 mole% at the end of the process. The reaction temperature is an important parameter in the gasification process which significantly affects the equilibrium of the reaction and the resulting syngas (Aprianti et al., 2020).

The effect of CO₂ absorption by Ca(OH)₂ on gas composition

The syngas production rate for fine coal gasification with and without absorption is a maximum at a reaction temperature of 700°C. The percentages of H₂ without and with absorption were 42.6 and 48.8 mole%, respectively. This result shows that the CO₂ produced without the absorption process inhibits the chemical reactions shown by R1 and R2, while the absorption of CO₂ using Ca(OH)₂ encourages the reaction. Ca(OH)₂ has increased the H₂ concentration effectively and decreased the gasification equilibrium temperature (Xiong et al., 2020). The H₂ concentration can be improved with the addition of Ca(OH)₂, and the H₂ concentration is more sensitive to temperature by the incorporation of Ca(OH)₂.

The carbon monoxide content was observed to increase at 450–550°C, but after passing through this phase, CO decreased when the temperature is increased to 700°C with a final yield of 19 mole%. This is possible because the water-gas shift reaction also increases hydrogen (R3). During the gasification process, methane is consumed through the methane dry reforming reaction. The two reactions are associated with each other and occur in the reduction zone (Kumari and Vairakannu, 2018). Regardless of whether absorption using Ca(OH)₂ was applied or not, the amount of methane that fell was not much different (19.5 mole% and 18 mole%) at maximum temperature.

**Figure 1.** Composition of gas from gasification (a) before and (b) after purification
By adding Ca(OH)$_2$, the higher hydrogen concentration will be obtained under sufficient reaction conditions. In addition, the percentage of gas volume is found to be lower when the gasification process is carried out without the addition of Ca(OH)$_2$. Calcium hydroxide, together with the availability of steam, actively absorbed carbon dioxide. Furthermore, the volume of CO$_2$ and CO is decreased whilst H$_2$ is more dominant in syngas by Ca(OH)$_2$. Syngas purification is more likely to occur in gasification after CO$_2$ has been removed. At the stage between 550–650°C, the addition of Ca(OH)$_2$ only contributes slightly to the decrease in CO$_2$, but then the performance increases again at 700°C. This is possible because Ca(OH)$_2$ has decreased its ability to absorb CO$_2$ under these conditions.

CO$_2$ reduced by Ca(OH)$_2$ is shown in Figure 2. The highest reduction in CO$_2$ occurs at the initial gasification temperature (450°C). The highest CO$_2$ content (21.8 mole%) was successfully reduced by 4.9 mole% in this initial state. Ca(OH)$_2$ reduced 22.48% of the total CO$_2$ in syngas at 450°C. CO$_2$ remained at the end of the gasification process in a small volume of 3.9 mole%. The absorption of CO$_2$ in syngas referred to as the carbonation reaction of Ca(OH)$_2$ in gasification. At higher temperatures, the calcination reaction is preferred in the absorption of CO$_2$. At high temperatures, the Ca(OH)$_2$ particles decompose to become CaO just before CO$_2$ is absorbed (Li et al., 2015; Yanase, Sasaki, and Kobayashi, 2017). The absorption of CO$_2$ reduces its percentage volume in the syngas, leading to the formation of H$_2$, preferably in this state according to the water-gas shift reaction. Hydrogen increases along with temperature and Ca(OH)$_2$ addition. Hydrogen increased by 6.2 mole% while CH$_4$ slightly decreased after the absorbent application. These results indicate that the absorption of CO$_2$ by Ca(OH)$_2$ affects the rate of H$_2$ production. This situation has been reported in several previous studies (Hwang, Kobayashi, and Kawamoto, 2014; Chen et al., 2017; Lazzarotto et al., 2020). The reaction between Ca(OH)$_2$ and CO$_2$ formed CaCO$_3$ according to the Ca(OH)$_2$ carbonation reaction (R5).

Gas ratio and heating value of syngas from fine coal

The gas ratio from fine coal gasification is evaluated by the H$_2$/CO and CG/NCG ratio. The H$_2$/CO ratio determines the usefulness of the syngas produced (Figure 3). The highest H$_2$/CO ratio was achieved at 700°C at 2.23. The H$_2$/CO ratio increases along with temperature. The high H$_2$/CO ratio is in line with the facts in the previous section that there has been an increase in H$_2$. As well as the CG/NCG ratio, the CO$_2$ content that continues to decline coupled with the increase in other combustible gases causes the CG/NCG ratio to continue to increase. In order to see the role of Ca(OH)$_2$ as an absorber, gasification has been carried out at the same temperature range. The results show that Ca(OH)$_2$ has increased the H$_2$/CO ratio for almost all temperatures except at 650°C. The highest H$_2$/CO ratio occurred for the gasification process with the absorption of 2.57. The CG/NCG ratio after application of Ca(OH)$_2$ shows a positive effect at each reaction temperature. The CG/NCG ratio before using the absorbent reached 4.83, whereas after using the absorbent it increased to 7.40 at 700°C.

The heating value represents the chemical energy contained in syngas. Humidity affects the heating value of syngas. The pattern of HHV and LHV results obtained between absorption with

![Figure 2. Absorbed CO$_2$ in syngas by Ca(OH)$_2$ solution](image1)

![Figure 3. Gas ratio of syngas](image2)
and without absorption has a way similar to temperature changes, as illustrated by Figure 4. The highest HHV and LHV were achieved at 450°C with the Ca(OH)$_2$ absorbent of 17.34 MJ/Nm$^3$ and 15.72 MJ/Nm$^3$. CH$_4$ decreases rapidly when the temperature is increased from 450°C to 700°C, which also has a large effect on the concentration of HHV and LHV syngas. The results show that there has been a significant decrease in HHV from 17.34 to 15.8 MJ/Nm$^3$. Although the H$_2$ concentration appears to increase over 450–700°C, its heating value is much lower than that of CH$_4$ so that the HHV and LHV syngas gradually decrease.

CONCLUSIONS

The experimental results demonstrate that the gasification of fine coal with Ca(OH)$_2$ sorbent have a significant impact on syngas producing at the temperature range of 450–700°C. The gas analysis reveal that Ca(OH)$_2$ absorbs the CO$_2$ content throughout the temperature rise. Additionally, H$_2$ increased significantly at 700°C from 42.6 mole% to 48.8 mole%. This trend also applies to the H$_2$/CO ratio, which consistently rises to reach a ratio of 2.57.

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