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Process analysis of biomass gasification and sorption-enhanced water gas shift coupled with CO2 utilization via reforming for hydrogen production

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The development of bio-based products for substituting petroleum-based products has received much attention due to environmental concerns. Hydrogen is an important chemical feedstock and energy carrier that can be derived from agricultural residue. Gasification is a thermochemical process that can convert biomass into syngas (H2+CO), while sorption-enhanced water gas shift (SEWGS) is a promising technology used to produce H2 and simultaneously separate CO2 in the same time. However, high energy is required for CO2 compression and storage. This study proposes the integration of biomass gasification and SEWGS coupled with CO2 utilization via reforming. The effect of key technical parameters, i.e., reforming reactors and percentage of recycled CO2, on H2 yield, system energy efficiency and H2/CO ratio of synthesis gas generated from reformers, are investigated. The correlation between key parameters and process performance is modeled through Aspen Plus process simulation program. Parametric analysis indicates key factors affecting syngas yield and overall energy efficiency with enhanced CO2 utilization. A performance comparison between gasification-SEWGS coupled with two different types of reforming (dry reforming and tri-reforming) using CO2 as a co-reactant is discussed, indicating the process with the highest H2 purity and overall energy efficiency.

* 1. Introduction

Due to the global warming issue, renewable resources, especially biomass, have become important raw material for generating clean chemicals and energy. Biomass gasification (BG) is a promising technology that converts biomass into synthesis gas (H2 and CO) with a higher heating value. This synthesis gas serves as an essential intermediate for chemical and fuel production. For hydrogen production applications, raw syngas from biomass gasification requires multiple separation steps for gas cleaning and conditioning to produce high-purity H2. Many researchers have proposed sorption enhanced water gas shift (SEWGS) technology to simultaneously increase H2 yield through the water-gas shift reaction and remove CO2 from the product, thereby overcoming the limitation of the water gas shift (WGS) reaction (Stevens Jr et al., 2010). In addition to producing high-purity H2, this technology generates CO2 as a byproduct. However, capturing CO2 requires significant energy for compression and storage. Consequently, converting CO2 into additional syngas is an efficient method to increase product yield and energy efficiency, while providing environmental benefits.

Many studies investigated CO2 utilization captured from SEWGS. For example, Qian et al. (2015) evaluated technical and economic performance of coal gasification and SEWGS integrated with tri-reformer for H2 and methanol production. Yang et al. (2021) analyzed thermochemical and economic efficiency of gasification integrated with tri-refomer to convert CO2 into additional syngas, which was used as a reactant of ethylene glycol production. Al-Rowaili et al. (2024) studied the technical and economic performance of vacuum residue gasification and SEWGS coupled with CO2 utilization through dry reformer for methanol synthesis. Liu et al. (2025) compared the performance of two CO2 utilization methods—reverse Boudouard reaction, and dry reforming—using CO2 captured from BG integrated with SEWGS for CO2 utilization. Based on these studies, many researchers have focused on CO2 utilization technologies to convert CO2 into high-value chemicals. Dry reforming and tri-reforming are two potential technologies for converting CO2 to syngas, an important intermediate chemical. However, there is limited research comparing the technical performance of these two technologies when integrated with BG and SEWGS for CO2 utilization.

Consequently, this study proposes a comparative analysis of BG and SEWGS integrated with two different reforming technologies: dry reforming and tri-reforming, through process simulation using the Aspen Plus program. The effects of reforming temperature and percentage of recycled CO2 on process performance including overall H2 yield, energy efficiency, and H2/CO ratio of syngas generated from the reformers, will be analyzed and discussed.

* 1. Process description

In this study, cassava rhizome was utilized as a biomass feedstock for gasification and SEWGS, coupled with two different types of reforming reactors: dry reformer and tri-reformer. The ultimate and proximate analyses of cassava rhizome are presented in Table 1.

2.1 BG and SEWGS coupled with CO2 utilization process

Figure 1 shows the schematic diagram of the BG and SEWGS process, coupled with a dry reformer (DR) (a) and a tri-reformer (TR) (b), as modeled in the in Aspen Plus program. The process consists of two sections: BG-SEWGS, which produce high-purity H2 and CO2 utilization through dry or tri- reforming to generate additional synthesis gas. The Peng-Robinson equation of state was selected as the property method to calculate the physical properties of gas components.

In the first section, dry biomass was fed into a gasifier to produce syngas, simulated by a fluidized-bed gasifier. The gasifier comprises three reaction zones; pyrolysis; combustion, and reduction zones. The pyrolysis zone was simulated using an RStoic reactor (PYRO), incorporating the yield of products reported in the literature, which biochar yield calculated based on mass balance. The outlet gas from the pyrolysis zone was then fed into the combustion zone, while biochar; considered a non-conventional component, was separated from the pyrolysis gas and decomposed to conventional components (N2, O2, H2, S, C, and ash) using RYield reactor (DECOMP). These components were subsequently introduced to combustion zone, simulated using an RPlug reactor (OXY). After combustion, the outlet gas was fed into the reduction section, modeled by RPlug reactor (RED). The reactions and kinetic rates occurring in the OXY and RED reactors are included in Table 2. The raw syngas from gasifier including H2, CO, CO2, CH4, and other impurity, was then fed into SEWGS system for gas cleaning and conditioning. The SEWGS technology shifts CO and H2O into H2 and CO2 as a byproduct, while simultaneously removing CO2, resulting in the production of high purity H2. The captured CO2 was released from the CaO adsorbent in a calciner, modeled by an RGibb reactor, and the CaO was subsequently recycled for reuse in the process (Detchusananard et al., 2024).

For CO2 utilization, two process configurations of BG-SEWGS with different types of reforming reactors were compared to produce additional synthesis gas. In the dry reforming reactor, 50 % of the captured CO2 was used as feedstock for the dry reforming reaction, where it reacted with CH4 at an S/C ratio of 1 and a temperature of 850 ºC. The tri-reformer (Figure 1b) operated at the same temperature as BG-SEWGS-DR with a CH4/CO2/H2O/O2 molar ratio of 1:1:1:1. The SEWGS, calciner and reformers (both dry and tri reformers) were simulated using RGibb reactor to calculate gas composition by minimizing Gibb Free energy. The operating conditions used in these processes, BG-SEWGS-DR and BG-SEWGS-TR, are shown in Table 3.

2.2 Technical analysis

In this study, the effect of temperature and the CO2/CH4 ratio (%CO2 recycle) on performance of different reforming reactors coupled with BG-SEWGS were compared using the following criteria: overall H2 production generated from BG-SEWGS and reformers, overall energy efficiency, and the H2/CO ratio of syngas produced through different reformers. The overall energy efficiency was calculated using Eq(1)

|  |  |
| --- | --- |
|  | (1) |

Table 1: Ultimate and proximate analyses of cassava rhizome (Pattiya et al., 2007)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Ultimate Analysis (%wt dry basis) | | | | | Proximate analysis (%wt dry basis) | | | | LHV |
| C | H | N | O | S | Volatile matter | Fixed carbon | Ash | Moisture |
| 51.59 | 6.69 | 1.27 | 40.45 | <0.1 | 77.75 | 18.20 | 4.05 | 8.31 | 18.47 |

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**(b)**

*Figure 1 The schematic diagram of biomass gasification (BG) and sorption enhanced water-gas shift (SEWGS) coupled with dry reformer (DR) (a) and tri-reformer (TR) (b) in Aspen Plus program*

* 1. Results and discussion

3.1 Effect of reforming temperature on overall H2 yield, H2/CO ratio and energy efficiency

This work proposed a comparison of the utilization of CO2 in two configurations: BG-SEWGS-DR and BG-SEWGS-TR. Figure 2 shows the effect of reforming temperature on the overall H2 yield and H2/CO molar ratio of BG-SEWGS systems with different types of reformers; a dry reformer (Figure 1a) and a tri-reformer (Figure 1b). As the temperature increases, both processes produce the same H2 yield from BG-SEWGS units. In CO2 utilization section, additional syngas was produced through the dry reforming or tri-reforming unit, with production increasing as the temperature rises. This results in an overall increase in H2 yield, peaking at 800 ºC (65.91 kmol/h) for BG-SEWGS-DR and at 700 ºC (61.62 kmol/h) for BG-SEWGS-TR before gradually declining. The increase in yield is attributed to the favorability of the endothermic steam and dry reforming reactions at higher temperature in the tri-reformer. However, in BG-SEWGS-TR, this also limits the exothermic water-gas shift reaction. Additionally, some H2 is consumed through combustion with O2.

When comparing the H2/CO molar ratio of syngas produced by the dry reformer and tri-reformer using internally captured CO2, the results indicated that the H2/CO in both cases decreased with increasing temperature due to the limitations rise in CO production at higher temperatures. However, the H2/CO ratio of BG-SEWGS-TR is lower than BG-SEWGS-DR at temperatures between 400-600 ºC, but becomes higher at temperatures above 600 ºC. This is because the combustion reaction, which consumed H2 produced by the steam and dry reforming reaction, is more favorable at lower temperatures. Conversely, the steam reforming reaction in BG-SEWGS-TR is more favorable at high temperatures.

Regarding the energy efficiency of the two configurations (Figure 3), the process with the dry reformer exhibits higher system energy efficiency at temperature above 600 ºC. This is because BG-SEWGS-TR produces less H2 yield and requires more energy for the steam and oxygen feed streams. Table 4 shows the energy consumption in each unit of two process configurations.

Table 2: Reactions and kinetic rates used in gasifier model (Detchusananard et al.,2024; Eikeland et al.,2015).

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction |  | Reaction rates (mol m-3s-1) |  |
| Pyrolysis zone |  |  |
|  |  |  |
| Combustion zone |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
| Reduction zone |  |  |
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Table 3: Base case operating conditions in the process simulations

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Value | | |
| Gasifier temperature (ºC) | 700 | | |
| S/C molar ratio in gasifier | 3 | | |
| SEWGS temperature (ºC) | 650 | | |
| S/C molar ratio in SEWGS | 1.5 | | |
| CaO/C molar ratio | 0.7 | | |
| Calciner (ºC) | 850 | | |
| CO2 recycle (%) | 50 | | |
| BG-SEWGS-DR | Value | BG-SEWGS-TR | Value |
| Dry reforming temperature (ºC) | 850 | Tri-reforming temperature (ºC) | 850 |
| S/C molar ratio | 1 | CH4/CO2/H2O/O2 ratio | 1:1:1:1 |

3.2 Effect of percentage of recycled CO2 on overall H2 yield, H2/CO ratio, and energy efficiency

The effect of the percentage of recycled CO2 (CO2/CH4 ratio) on overall H2 yield, the H2/CO molar ratio, and energy efficiency is shown in Figures 4 and 5. As illustrated in Figure 4, an increase in CO2 recycling raises the CO2/CH4 ratio, which is not beneficial for H2 production in either process. This is because higher CO2 levels favor the reverse side reaction in BG-SEWGS-DR and reverse WGS reaction in BG-SEWGS-TR, slightly reducing the amount of H2 produced.

When comparing the overall H2 yield between the BG-SEWGS-DR and BG-SEWGS-TR processes at the same CO2 recycling percentage, the BG-SEWGS-TR process results in a lower H2 yield because methane is partly consumed in the oxidation reaction. However, both processes exhibit the same decreasing trend in H2 yield with increasing CO2 recycling. Consequently, the H2/CO ratio in both processes decreases with increasing CO2 recycling due to increased CO generation. Nevertheless, the H2/CO ratio of the BG-SEWGS-TR remains higher than that in the BG-SEWGS-DR process, as the presence of steam promotes the forward WGS reaction.

Additionally, the system energy efficiency of BG-SEWGS DR process increases, reaching a maximum of 66.42 % at 60 % CO2 recycling (Figure 5). This improvement may be attributed to the higher heating value of syngas, which contains more CO from the reverse side reaction. In contrast, the energy efficiency of the BG-SEWGS-TR process shows only a slight increase with CO2 recycling, reaching at 34.41 % at 60 % CO2 recycling, due to the higher CO content from the reverse WGS reaction.

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| --- | --- |
|  |  |
| Figure 2 Effect of temperature on overall H2 yield and H2/CO molar ratio of BG-SEWGS-DR and BG-SEWGS-TR | Figure 3 Effect of temperature on energy efficiency of BG-SEWGS-DR and BG-SEWGS-TR |
|  |  | |
| Figure 4 Effect of percentage of recycled CO2 on overall H2 yield and H2/CO molar ratio of BG-SEWGS-DR and BG-SEWGS-TR | Figure 5 Effect of percentage of recycled CO2 on energy efficiency of BG-SEWGS-DR and BG-SEWGS-TR | |

Table 4: Energy consumption in each unit of BG-SEWGS-DR and BG-SEWGS-TR under the base case

|  |  |  |
| --- | --- | --- |
|  | BG-SEWGS-DR (kW) | BG-SEWGS-TR (kW) |
| Gasifier | 1065.51 | 1199.6 |
| Heater 1 | 1199.60 | 1199.60 |
| Heater 2 | 617.75 | 617.75 |
| Cooler 1 | -60.55 | -60.55 |
| SEWGS | -385.27 | -385.27 |
| Calciner | 4284.34 | 4284.34 |
| Cooler 2 | -61.00 | -534.67 |
| Cooler 3 | -385.30 | -385.30 |
| Dry/Tri-reformer | 658.73 | -582.426 |
| Heater 3 | - | 248.26 |
| Cooler 4 | 53.11 | -53.11 |
| Cooler 5 | -229.60 | -1844.66 |
| Cooler 6 | -6.86 | -6.86 |

* 1. Conclusions

This study proposed a comparative analysis of the BG-SEWGS process integrated with two different types of reformers: a dry reformer and a tri reformer, for CO2 utilization. The effects of key parameters; reforming temperature and percentage of recycled CO2, on process performance (i.e., H2 yield, H2/CO molar ratio, and energy efficiency) were investigated. The results showed that increasing the reforming temperature enhanced H2 yield in both technologies. However, BG-SEWGS-DR demonstrated superior performance, achieving a maximum H2 yield of 65.91 kmol/h and a system energy efficiency of 61.46 % at reforming temperature of 800 ºC. This represented increases of 8.61 % and 82.97 %, respectively, compared to the BG-SEWGS-TR. Regarding the effect of CO2 recycling, it was found that increasing CO2 recycling elevated the CO2/CH4 ratio in dry and tri reformers. This favoured the inverse WGS reaction, which increased CO generation in the tri-reformer and reduced the total H2 yield. However, the presence of steam in the tri-reformer promoted the WGS reaction in the BG-SEWGS-TR, resulting in higher H2/CO ratio comparing to the BG-SEWGS-DR. In terms of system energy efficiency, the BG-SEWGS-TR required additional energy for preheating steam and O2, which lowered its efficiency relative to the BG-SEWGS-DR.

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