Syngas Production for Fischer–Tropsch Synthesis from Rubber Wood Pellets and Eucalyptus Wood Chips in a Pilot Horizontal Gasifier with CaO as a Tar Removal Catalyst

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ABSTRACT: This research aims to investigate steam biomass gasification in a pilot horizontal gasifier using rubber wood pellets (RWPs) and eucalyptus wood chips (EWCs) for producing syngas with an H₂/CO ratio range of 1.8 to 2.3 for Fischer–Tropsch synthesis. The study was divided into two parts. One was carried out in a lab-scale reactor to determine the effect of temperature and CaO on the gas product composition and the efficiency of tar removal. Another part was determined by investigating the effect of the steam/biomass (S/B) ratio on the produced H₂/CO ratios in the pilot horizontal gasifier, which used the optimum conditions of temperature and % loading of CaO for tar removal according to the optimal conditions from the lab-scale gasifier. The lab-scale gasifier results showed that H₂ and CO increased with temperature due to primary and secondary water gas reactions and hydrocarbon reforming reactions. The water gas shift and hydrocarbon reforming reaction depressed the CO and CH₄ contents with increasing temperature, respectively. The optimum gasifying temperature was 900 °C, which obtained H₂/CO ratios of 1.8 for both RWPs and EWCs. The tar yield decreased with increasing temperature and was less than 0.2 wt % when using CaO as a tar-cracking catalyst. The operation of the pilot horizontal gasifier at the operating condition of 900 °C and a S/B ratio of 0.5 using 0.2 wt % loading of CaO for tar removal also produced a H₂/CO ratio of 2.0. The supply of an external heat source stabilized the gasifying temperature, resulting in a stable syngas composition and production rate of 2.5 and 2.7 kg/h with H₂/CO ratios of 1.8 and 1.9 for the RWPs and EWCs, respectively. In summary, the horizontal gasifier is another effective designed gasifier that showed high-performance operation.

1. INTRODUCTION

With the progress of economic and social development, the rapid increase in global energy demand raises the serious problem of energy supply, whereas the consumption of traditional fossil fuels released from electricity generation, industrial manufacturing, and other activities using fossil fuel is a major impact on greenhouse gas emissions and the global warming phenomenon. The development of super clean alternative renewable energy to replace conventional fossil fuels has attracted more attention and sustainability challenges to reduce greenhouse gas emissions while meeting the rapidly increasing world energy demand. Among the alternative renewable fuels, biomass has attracted attention as a potential carbon-neutral and abundant energy resource, providing clean fuels to achieve the ambition of negative CO₂ emissions.

Gasification of biomass is a promising prominent thermochemical technology that converts a carbonaceous material into a CO and H₂-rich gas at small and medium scales used for energy and chemical applications that can be increasingly considered for power generation or further conversion into valuable chemicals such as substitutes for natural gas, biohydrogen, or Fischer–Tropsch (FT) biofuel.

Generally, the direct supply of gas to internal combustion engines is its main advantage. Among all utilizations of biomass, gasification has been presented as a possible process for fuel gas production, synthetic fuels, and chemicals because it has a low investment cost and high rate of gas production.

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The principal reactions during the gasification of biomass, coal, or their blends are presented as the following chemical reactions:\(^5\)\(^–\)\(^7\)

**Boudouard**

\[
C + CO_2 \rightarrow 2CO \quad \Delta H = 172.5 \text{ kJ/mol} \quad (1)
\]

**Primary water gas**

\[
C + H_2O \rightarrow CO + H_2 \quad \Delta H = 131.3 \text{ kJ/mol} \quad (2)
\]

**Secondary water gas**

\[
C + 2H_2O \rightleftharpoons CO_2 + 2H_2 \quad \Delta H = 90.2 \text{ kJ/mol} \quad (3)
\]

**Methanation**

\[
C + 2H_2 \rightarrow CH_4 \quad \Delta H = -74.9 \text{ kJ/mol} \quad (4)
\]

**Water gas shift**

\[
CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41.2 \text{ kJ/mol} \quad (5)
\]

**Steam reforming**

\[
CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H = 206.2 \text{ kJ/mol} \quad (6)
\]

**Dry reforming**

\[
CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H = 247.4 \text{ kJ/mol} \quad (7)
\]

The syngas composition normally depends on the biomass feedstock, the gasifier type, the type of oxidizing agent, the temperature, and the residence time in the gasifier.\(^8\) Gasification reactors can be classified into three types: fixed beds, fluidized beds, and entrain beds.\(^5\)\(^–\)\(^10\) A fixed bed consists of three configurations: updraft, downdraft, and cross draft.\(^11\) Downdraft gasifiers are used the most for small power plants using internal combustion engines.\(^12\) However, there are some problems when low bulk density biomass is used as the feedstock.\(^13\) A large difference in the temperature profile inside the reactor is one disadvantage of the downdraft reactor because the reaction rate is not uniform over the area.\(^14\) It is difficult to control the feed rate of the feedstock, which is operated in batches instead of continuous feeding. Furthermore, there are potential difficulties with ash fusion and the necessity to have feedstock with a moisture content less than 25%, and the ash discharge rate is another problem as well.\(^15\) Some of these disadvantages were solved by designing a horizontal reactor system, which can be used with biomass feedstocks that contain moisture up to 30% and has the effective process for syngas production in the appropriate H\(_2\)/CO ratio for further FT synthesis. However, the instability of temperature inside the reactor is still a problem; thus, this research attempts to supply the external heat source to control the temperature. The tar formation problem during biomass gasification is the major challenge in current thermal gasification. Tar may condense and tend to form polymers with a more complex structure, such as phenolics, mono- and polyaromatics, heterocyclic aldehydes, and alkyl derivatives of aromatics,\(^19\) which are a serious drawback for the use of syngas for biofuel synthesis or chemicals. For steam gasification, experiments have reported that increasing the steam/biomass (S/B) ratio reduces the tar yield due to an enhanced steam reforming reaction.\(^20\)\(^–\)\(^22\) Moreover, at high temperatures, above 800 °C, higher S/B decreases all tar species. In the case of steam gasification, reported experimental results have shown that increasing the S/B ratio reduces the tar yield due to enhanced steam reforming reactions.\(^21\)\(^–\)\(^26\) although the effect on the tar composition depends on the operational temperature. At sufficiently high temperatures, above 800 °C, all tar species decrease with the S/B ratio, but below 750 °C, the increase in the S/B ratio diminishes secondary tars but increases light aromatic tars.\(^24\)

The catalysts that were reported to have high performance in removing tars from the producer gas were classified into three groups: (1) natural catalysts, such as CaO from CaCO\(_3\) and CaO and MgO from dolomite; (2) alkali-based catalysts, such as Li, Na, and K; and (3) metal-based catalysts, such as nickel catalysts.\(^23\)\(^–\)\(^30\) In this work, CaO was used as the catalyst. CaO not only acts as a CO\(_2\) sorbent but also as a tar-reforming catalyst.\(^31\)\(^–\)\(^32\) Mahishi and Goswami\(^33\) reported the use of CaO for increasing H\(_2\) and decreasing CO\(_2\) from steam gasification of southern pine bark in a batch-type gasifier and showed the effect of CaO as bed material on produced gas: CO\(_2\) decreased from 28.4 to 26.7 vol %, while H\(_2\) increased from 62.0 to 65.5 vol % at 700 °C.

This research aims to investigate the use of rubber wood pellets (RWPs) and eucalyptus wood chips (EWCs) for biomass gasification in a pilot horizontal gasifier connected with tar removal using CaO as a tar-reforming catalyst. The gasifier, which was designed specifically for FT syngas production, was created in the horizontal rotary vessel, in which the shape was similar to the rotary kiln with a slight degree of inclination.\(^12\)\(^,\)\(^16\)\(^–\)\(^17\) The advantages of this custom-built pilot horizontal gasification system allowed for the control of the H\(_2\)/CO ratio in the required range of the downstream FT synthesis process. All equipment and operation procedures were designed to ensure that syngas production, which focused on the productivity and quality of produced syngas with high purity and high heating value in long-term operation, was conducted for at least 7 days for each operation sequence. In the first step, gasification at the lab scale is carried out, followed by tar removal to determine the optimum temperature, which provides a H\(_2\)/CO range of 1.8–2.3 and the lowest tar presented. The gasification temperature of the pilot horizontal gasifier is used from the lab-scale reactor result. The effect of the biomass/steam ratio on the H\(_2\)/CO ratio and average gas product composition is investigated. The stability of the operation was also investigated and discussed.

2. METHODS

2.1. Biomass Feedstock. The lab-scale and pilot horizontal gasifier units were operated with two different types of biomasses, which were rubber wood and eucalyptus wood. The lab-scale reactor used fine particles of both raw materials, while the pilot reactor used RWPs and dried EWCs. The wood pellet was cylinder shaped and 8 mm in diameter and 30–80 mm in length. The size and shape of wood chips were proven by testing the behavior of biomass in the feed system, including channeling formation and movement downward in the hopper and obstruction in the screw feeder. Sieving should help control the size and shape of wood chips and is beneficial for homogeneous biomass. The average size of the wood chips used was 5–10 mm. The physical and chemical properties of the biomass feedstock were analyzed, as shown in Table 1. The biomass characteristics and proximate and ultimate analyses were determined using the ASTM D3172-
3175 standard procedure method. Ultimate analysis was measured using a LECO CHN-628 instrument (LECO Corporation, USA) following the ASTM D5373 standard procedure method, and the heating value was determined using a LECO AC-500 (LECO Corporation, USA) according to ASTM D5868.

2.2. Experimental Procedure. This research aims to investigate the operation of a pilot horizontal gasifier using RWPs and EWCs for producing syngas with a specific $\text{H}_2/\text{CO}$ ratio. The study was divided into two parts. The first experiment was a set of experiments, which were carried out in a custom-built lab-scale reactor to determine the effects of temperature on the gas product composition and tar fraction. The second part was the investigation of the operation of the pilot horizontal gasifier, which was specifically set up for the appropriate gasification temperature received from the first part.

2.2.1. Lab-Scale Reactor. Biomass particles of rubber wood and eucalyptus wood were air dried and ground, and both biomasses were subjected to moisture reduction, milled in an SW-2 high-speed rotary cutting mill (Hsiangtai, the People’s Republic of China), sieved into a size distribution of 0.5–0.7 mm and used as feedstocks in this test. The custom-built gasifier reactor comprised a steam generator, flow controller, electric furnace, and ice trap, as shown in Figure 1. The custom-built gasifier reactor was a stainless-steel tube with an inner diameter of 27 mm and length of 893 mm. The reactor was heated using an electric furnace and supplied with steam from a steam generator. The flow controller was used to adjust the $\text{N}_2$ flow rate as the carrier gas at 100 mL/min. Tar from the experiment was collected by a series of three ice traps to confirm that entire tar was completely condensed.

Approximately 10 g of the biomass sample was filled into biomass storage, which was placed on the top of the gasifier outside the heater zone. $\text{N}_2$ was fed into the reactor continuously. When the temperature reached the desired level (600, 800, 900, and 1000 °C), the valve of biomass storage was opened, and then biomass dropped into the gasifier immediately at the same time as steam at 0.5 g/min, which was fed continuously into the gasifier with concurrent flow with biomass sample. The complete reaction time was approximately 10 min. The last experiment was carried out to observe tar removal by using CaO, which was packed into separate layers after being operated at 900 °C. Gas production was collected in a sampling bag from the gas drier unit and analyzed by an Agilent GC7820A gas chromatograph coupled with a thermal conductivity detector (Agilent Technologies, USA). Tar was collected in ice traps, while solid biochar weight was classified as solid yield in percent by weight.

| Characteristics of Biomass<sup>a</sup> | rubber wood pellets | eucalyptus wood chips |
|--------------------------------------|---------------------|----------------------|
| moisture content (wt %), d.b.        | 8.5                 | 8.0                  |
| proximate analysis (wt %), d.b.      |                     |                      |
| volatile matter (wt %), d.b.         | 79.5                | 81.4                 |
| fixed carbon (wt %), d.b.            | 18.0                | 17.9                 |
| ash (wt %), d.b.                     | 2.5                 | 0.7                  |
| ultimate analysis (wt %), d.b.       | C 49.7              | 47.8                 |
|                                      | H 6.0               | 5.8                  |
|                                      | N 0.3               | 0.3                  |
|                                      | O<sup>b</sup> 44.0  | 46.1                 |
|                                      | H/C 1.4             | 1.5                  |
|                                      | O/C 0.7             | 0.7                  |
| heating value, MJ/kg, LHV, d.b.      | 18.4                | 18.4                 |

<sup>a</sup>d.b.: dry basis. <sup>b</sup>By difference.

Figure 1. Schematic diagram of the custom-built gasifier at the lab scale.
2.2.2. **Pilot Horizontal Gasifier.** The pilot horizontal gasification unit and facilities were installed at the Center of Fuel and Energy from Biomass, Chulalongkorn University, Saraburi Province, Thailand. Figure 2 illustrates a schematic view of the gasification unit. It consists of a feeding system, gasifier, steam generator, tar reformer (TR), gas purification unit, gas compression unit, and gas storage.

Biomass gasification was carried out in a pilot horizontal gasifier system consisting of the three zones of the gasifier reactor related to the three heaters to provide a constant temperature of 900 °C. The size of the gasifier is 2.5 m in length, 20 cm in diameter, and a 2° decline. The pilot custom-built gasifier system is a horizontal cylindrical shape and has a 1.0 m diameter quipped with insulation to prevent heat loss from the reactor, including several joint connectors, since the feedstock hopper has a capacity of 4 kg/h until the tar-reforming unit at the end of the gasification system.

The tar-reforming unit operating during the gasification stage to limit tars formation or to convert tars in the gasification reactor and which operate downstream of gasification with various purification processes was conducted at the operating temperature of 900 °C. CaO (12 kg) was used as the catalyst within the TR, which performed as a CaO-fluidized bed type. CaO enhanced the tar-reforming reaction to totally remove tar as the syngas moved up from the bottom to the top.

Tar-less syngas was sent to the cleaning part, then syngas and reduced the temperature, and the tar was condensed at the water scrubber. Fresh water was supplied to the water scrubber, and a conventional water treatment system was used to treat tar with cooling water. A gas cooler and mist separator were installed next to the water scrubber to remove water that might come from the gasifier process and water scrubber. Although there was a very low sulfur content in the biomass feedstock,\(^{32-35}\) the DS unit was still necessary because sulfur is an FT catalyst poison. The DS unit was placed after the mist separator unit and connected with a first induced draft (ID) fan that used to control the syn gas flow and balance the pressure in the system. Because the downstream process is an FT process, which is an exothermic and pressurized process, the oxygen content in syngas is a serious safety concern. Hence, the oxygen remover (OR) was applied and placed. Cleaned syngas was compressed and kept in a set of buffer tanks in two steps of compression. First, syngas was flowed by a second ID fan from the OR to the first compressor, which was used to build gas pressure and keep in a receiver tank. An automatic control valve was placed after the buffer tank to tank, syngas still undergoes a final purification process via a gas chromatography unit every 30 min.

### 2.3. Gasification Procedure

After purging with N\(_2\) to remove air in the gasification system and heating the gasifier, biomass was manually fed into the hopper, and the screw-type feeder placed under the hopper was used to control the feed rate into the gasifier. Four load cells were installed at the hopper to measure the feed rate. The superheated steam generator with a feed controller was placed to supply steam as a gasifier agent into the gasifier. Gas produced from the gasifier flowed to the TR unit 85 cm in diameter and 155 cm in height and was then sent to the gas cleaning unit. Eventually, biochar fell into the char box at the outlet of the gasifier. The TR produced gas, including tar vapor, that flowed through the bubble bed of CaO. Tar was converted to syngas in this part. Tar-less syngas was sent to the cleaning part, then syngas and reduced the temperature, and the tar was condensed at the water scrubber. Fresh water was supplied to the water scrubber, and a conventional water treatment system was used to treat tar with cooling water. A gas cooler and mist separator were installed next to the water scrubber to remove water that might come from the gasifier process and water scrubber. Although there was a very low sulfur content in the biomass feedstock,\(^{32-35}\) the DS unit was still necessary because sulfur is an FT catalyst poison. The DS unit was placed after the mist separator unit and connected with a first induced draft (ID) fan that used to control the syn gas flow and balance the pressure in the system. Because the downstream process is an FT process, which is an exothermic and pressurized process, the oxygen content in syngas is a serious safety concern. Hence, the oxygen remover (OR) was applied and placed. Cleaned syngas was compressed and kept in a set of buffer tanks in two steps of compression. First, syngas was flowed by a second ID fan from the OR to the first compressor, which was used to build gas pressure and keep in a receiver tank. An automatic control valve was placed after the buffer tank to
control the pressure in the buffer tank, which remained constant at 0.8 MPa and was steady stored before being sent to the second step of compression. Before reaching the second compressor unit, syngas with 0.8 MPa of pressure could become moist by water saturation at a high pressure, so a H₂O remover using a molecular sieves was placed to absorb that moisture, and the dry gas was analyzed in real time for the gas humidity by a dewpoint measurement (Michell Instrument) and gas composition by Agilent 490 Micro-GC (Agilent Technologies, USA). At the second gas compressor, middle high-pressure gas was compressed to fill the buffer tank at 12 MPa. This gas was ready to use in the downstream unit. The temperature of the gasifier and its downstream unit was monitored by K-type thermocouples. The pressure at each point was measured and is shown in the main monitor. All data and parameters were stored in a computer with A/D convertors. To achieve the production of syngas at the desired H₂/CO ratio range of 1.8–2.3 in pilot horizontal gas, two variables, the S/B (RWPs) ratio and gasification temperature, were investigated. The two S/B ratios of 0.5 and 1.4 were set up to gasify for 5 h in a continuous operation. The appropriate gasification temperature received from the lab-scale and S/B ratio were considered to operate syngas for 10 days of continuous production. Both operations of the gas composition were analyzed every 30 min.

2.4. Data Analysis and Calculation. To evaluate the performance of this gasification system, common gasification indexes were calculated. Therefore, the total mole and composition of the produced gas were precisely known, and the calculation of gas yield, carbon conversion, and gas efficiency were determined based on mass basis, which can be seen from eqs 8–11 as follows

\[
\text{Gas yield, wt %} = \frac{\text{total mass of produced gas}}{\text{total mass of fed biomass}} \times 100 \tag{8}
\]

\[
\text{Carbon conversion, wt %} = \frac{\text{mass of carbon in produced gas}}{\text{mass of carbon in total fed biomass}} \times 100 \tag{9}
\]

\[
\text{Gas/Biomass} = \frac{\text{total mass of produced gas}}{\text{total mass of fed biomass}} \tag{10}
\]

\[
\text{Cold gas efficiency, } \eta_{\text{cold}} = \frac{M_{\text{syngas}} \times \text{LHV}_{\text{syngas}}}{M_{\text{biomass}} \times \text{LHV}_{\text{biomass}}} \times 100
\tag{11}
\]

where \( M_{\text{syngas}} = \text{total mass of produced gas, kg} \); \( M_{\text{biomass}} = \text{total mass of fed biomass, kg} \); \( \text{LHV}_{\text{syngas}} = \text{lower heating value of produced gas, MJ/kg} \); and \( \text{LHV}_{\text{biomass}} = \text{lower heating value of biomass feedstock, MJ/kg} \).

3. RESULTS AND DISCUSSION

3.1. Feed Stock Characterization. Table 1 illustrates the biomass proximate analysis, including the ultimate analysis and low heating value (LHV) of the RWPs and EWCs. Although there were different milling processes of both biomass feedstocks, the chemical and some physical properties appeared to be similar on a dry basis. For example, the LHV of RWPs was 18.4 MJ/kg, which was close to the EWCs of 18.4 MJ/kg for dry basis also. In addition, similar properties might affect similar gasification results. However, the major differences in these biomass feedstocks were in shape and moisture content. The shape of the biomass feedstock influenced the bulk density, which could be affected in transportation and storage facilities.36 For moisture content, the biomass milling process causes the difference in the moisture content in feedstock and results in a variety of biomass feedstock qualities.37 In other words, for the wood pellet milling process, there must be a drying process in its production process. Thus, wood pellets are always less moist (8–10 wt % moisture). On the other hand, the wood chips milling process is a simple milling process of biomass conversion or biomass size reduction that only reduces the size of biomass from wood logs to small chips without any drying process. Normally, wood chips have a high moisture content similar to a fresh log.24,38 In this test, wood chips were air dried to be subjected to a moisture reduction before use due to the limitation of the gasification unit and to maintain the efficiency of gasification processes.

3.2. Influence of Temperature on the Tar Yield in the Lab-Scale Reactor. This study aimed to investigate the influence of gasification temperature on tar yield by using a powder of rubber wood and eucalyptus as raw materials. The temperature ranged from 600 to 1000 °C with excess water vapor. The results of the produced yield and gas composition are illustrated in Table 2. Tar decreased with increasing temperature to obtain solid char, while gaseous yield increased for rubber and eucalyptus wood. Tar decreased from 19.6 to 1.0% and 26.6 to 2.0% for RWPs and EWCs, respectively. In

Table 2. Product Yields and Gas Compositions of Variation Temperatures

| biomass | temp. (°C) | product yield (wt %) | gas composition (vol %) |
|---------|-----------|----------------------|------------------------|
|         |           | tar | char | gas | CH₄ | CO₂ | H₂ | CO | H₂/CO |
| RWPs    | 600       | 19.6 | 18.0 | 62.4 | 17.3 | 9.6 | n.d. | 73.1 | n.c. |
|         | 800       | 12.7 | 12.7 | 74.6 | 14.6 | 10.3 | 38.7 | 36.4 | 1.1  |
|         | 900       | 3.8  | 10.3 | 85.9 | 10.4 | 11.6 | 51.7 | 30.3 | 1.7  |
|         | 1000      | 1.0  | 8.3  | 90.7 | 1.3  | 11.9 | 60.0 | 26.8 | 2.2  |
|         | 900°      | 0.0  | 9.2  | 90.8 | 8.4  | 9.5  | 52.9 | 29.2 | 1.8  |
| EWCs    | 600       | 26.6 | 18.7 | 54.7 | 18.8 | 9.11 | n.d. | 72.1 | n.c. |
|         | 800       | 16.0 | 11.4 | 72.6 | 12.4 | 10.5 | 39.1 | 38.0 | 1.0  |
|         | 900       | 5.5  | 9.7  | 85.0 | 8.1  | 10.3 | 52.7 | 28.9 | 1.8  |
|         | 1000      | 2.0  | 3.5  | 94.6 | 4.0  | 11.1 | 59.9 | 28.0 | 2.1  |
|         | 900°      | 0.0  | 8.8  | 91.2 | 8.0  | 9.2  | 53.2 | 29.6 | 1.8  |

*C. tar removal using CaO. b.n.d.—not detected. *n.c.—not calculated.

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particular, there was a shape decreasing between 800 and 900 °C from 12.6 to 3.8% and 16.0 to 5.3% for RWPs and EWCs, respectively.

The components of the gas product as a function of temperature were examined. A higher temperature favors the primary and secondary water gas reactions, secondary cracking, and reforming of heavy hydrocarbons or tars, which are endothermic reactions and increase the formation of H$_2$.

While CO decreased with higher temperature, Franco et al. reported that during biomass gasification using holm-oak and eucalyptus in a temperature range of 730 to 830 °C, lower CO was produced due to the water gas shift reaction. While the CH$_4$ content decreased with increasing temperature due to further cracking and reforming reactions, the CO$_2$ content was slightly increased according to the dominancy of secondary water gasification than the water gas shift that was also observed. It has also been reported that the effect of temperature on methane consumption is highly dependent on gasifying agents such as steam.

CO and H$_2$ are important in the gas product, which requires an H$_2$/CO ratio range of 1.8–2.3 for FT synthesis. The operating conditions of syngas production to obtain the H$_2$/CO ratio of both RWPs and EWCs feedstocks are carried out at temperatures of 900 and 1000 °C. Tar removal by using CaO also operated at 900 °C, and the efficiency of CaO for tar removal was investigated under these conditions. The tar composition in both raw materials was less than 0.2 wt %. Tar reforming (eq 12) and hydrocarbon reforming (eq 13) were the principal reactions for tar removal. The catalytic reforming of tar in this experiment not only reduces the tar amount in the product gas but also enhances the hydrogen and CO content, as reported by Tanksale et al. and Balat et al. However, the tar yield was investigated at the operating temperature of 900 °C from both types of raw material which was also an appropriate condition to produce syngas for the target ratio. In this study, the operating temperature in the gasifier and tar reforming of 900 °C was used to operate the pilot horizontal gasifier system.

Tar reforming

\[ \text{Tar} + \text{H}_2\text{O} + \text{CaO} \rightarrow \text{Ca(OH)}_2 + \text{CO} + \text{hydrocarbons} \]  

(eq 12)

Hydrocarbon reforming

\[ \text{Hydrocarbons} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 + \text{CO} \]  

(eq 13)

3.3. Influence of the S/B Ratio on the H$_2$/CO Ratio in the Pilot Horizontal Gasifier. The effect of S/B ratios of 0.5 and 1.4 on the H$_2$/CO ratio by using RWPs was examined in the pilot horizontal gasifier at 900 °C for 5 days of operation. The results of this operation are presented in Table 3. It revealed that the increasing S/B ratio promoted a higher content of hydrogen from 50.0 to 56.7 vol % by primary, secondary water gasification, water-gas shift, and methane steam reforming.

However, although H$_2$ was consumed by the methanation reaction. CO$_2$ was increased from 14.7 to 16.8 vol % with a higher S/B ratio by secondary water gasification and water gas shift reactions. The water gas shift reaction was responsible for maintaining the equilibrium between CO and CO$_2$ contents and found a decrease in CO with increasing S/B ratios. CH$_4$ was decreased (11.2 to 9.4 vol %) due to a strong methane steam reforming reaction. Xiao et al. reported the influence of the S/B ratio on the gas product composition, as mentioned in this study. However, the S/B ratio of 0.5 gave the desired H$_2$/CO of 2.1, which is in the target range of 1.8–2.3. Thus, for the next continuous operation, the temperature was 900 °C, and the S/B ratio was approximately 0.5.

3.4. Investigation of Long-Term Operation Gasification. The pilot horizontal gasifier operation was carried out for 7 days to produce syngas for storage in 77 gas cylinders, in which syngas was used as the reactant for FT synthesis. The appropriate parameters were a gasifying temperature of 900 °C and a S/B ratio of 0.5, whereas RWPs and EWCs were used as raw materials. The target of this operation was to produce syngas with a H$_2$/CO ratio range of 1.8–2.3.

3.4.1. Temperature Profile. The temperature of the horizontal gasifier was kept at 900 °C using a controlled external heater. The temperature profiles of the gasifier and outlet gas for EWCs and RWPs gasification are represented in Figures 3 and 4, respectively. Although the net heat of gasification was exothermic, an external heat source was needed to keep the temperature constant at the desired high temperature. The constant temperature was 900 °C during operation for 7 days. The gasifier temperature was constant, resulting in a constant temperature of the outlet gas at 600 °C. Then, the gas outlet from the gasifier was purified by tar removal in a TR. For the TR, Figure 3 shows the temperature profile. The tar-reforming reaction with the CaO catalyst took place in zone 1, where the temperature was kept at 900 °C. After the reaction, the temperature dropped to 800 °C and 500 °C in zone 2 and zone 3 of the TR, respectively. The stability of the temperature profile in the TR was observed for 7 days of operation.

3.4.2. Average Syngas Composition and H$_2$/CO Ratio. The composition of the product gas from pilot horizontal gasifier operation for 7 days of RWPs and EWCs is shown in Figures 5 and 6, respectively. Under these operating conditions, the average S/B ratio was 0.5 and 0.6 for the RWPs and EWCs, respectively, and the gasifying temperature was 900 °C. Figure 5 illustrates the composition profile of the gas product for RWPs as a raw material. All gas compositions were almost stable during operation; the average H$_2$, CO, CO$_2$, and CH$_4$ were 48.4, 27.7, 15.2, and 8.7 vol %, respectively, as shown in Table 3, and the H$_2$/CO ratio was 1.8. The average gas compositions of H$_2$, CO, CO$_2$, and CH$_4$ were 48.0, 25.4, 18.6, and 8.0 vol %, respectively, and the H$_2$/CO ratio was 1.9 for EWC, as shown in Figure 6. The higher S/B ratio of the EWCs resulted in an increase in CO$_2$ (15.2 to 18.5 vol %) due to the water gas shift reaction and a decrease in CH$_4$ (8.7 to 8.0 vol %) due to the reverse methane steam reforming reaction.

| Table 3. Gasification Results for Two Differences in S/B at 900 °C |
|-----------------|-----------------|-----------------|-----------------|
|                | experiment 1    | experiment 2    |
| operating time, h | 5               | 5               |
| biomass feed rate, kg/h | 4.0            | 1.7             |
| steam feed rate, kg/h   | 2.1            | 2.3             |
| steam/biomass, kg/kg   | 0.5            | 1.4             |
| gas compositions       |                |                |
| H$_2$                | 50.0           | 56.7            |
| CO                   | 24.1           | 17.1            |
| CO$_2$               | 14.7           | 16.9            |
| CH$_4$               | 11.2           | 9.4             |
| H$_2$/CO, mole/mole   | 2.1            | 3.3             |
This phenomenon was also observed, as in the former study of the effect of the S/B ratio on the gas composition. In addition, the H₂/CO ratio in both raw materials was the range of this target.

3.4.3. Material Balance of Syngas Production. The syngas production for the 7 days of operation was mentioned above to fill seven sets of buffer tanks, including 11 cylinders, or each set was filled per day. Figure 7 illustrates the pressure development during syngas filling in one set of buffer tanks, and the desired pressure was 120 MPa. The material balance was realized on the basis of 1 day of operation with buffer volumes of 0.9 m³, 120 MPa, and 30 °C. Table 4 summarizes all of the data, including the operating conditions, gas yield, average gas composition, LHV, and carbon conversion for the RWPs and EWCs. The production gas rate and produced gas/biomass ratio were 2.5 kg/h and 0.5 kg/kg for RWPs, respectively, while the production gas rate and produced gas/biomass ratio from EWCs were 2.7 kg/h and 0.7 kg/kg, respectively. The biomass feed rates of these tests were 4.3 and 3.9 kg/h for RWPs and EWCs, respectively, whereas the steam feed rate of 2.0 kg/h for RWP's was less than that of 2.3 kg/h for EWCs. It seemed that the higher CO₂ and lower CO content in the gas product for EWCs promoted by the water gas shift reaction played an important role in increasing the production gas rate and decreasing the LHV. The LHV from the calculation was 12.9 and 11.7 MJ/Nm³ for RWPs and EWCs, respectively.

In addition, the carbon conversion in the gas product was 49.5 vol % for RWPs, which was higher than the value of approximately 45.0 vol % for EWCs. However, both raw materials did not give much difference in the product gas property, especially the cold gas efficiency, which was approximately 47−48 wt % for both raw feedstocks.

One of the byproducts was solid biochar, which could be collected after gasifying termination. Carbon in char was approximately half of the total carbon in feed that was observed for RWPs and EWCs. High carbon contents of 83.1 and 88.8 wt % were found for the RWPs and EWCs, respectively, as shown in Table 5.

The solid biochar behaves as activated carbon, which has Brunauer–Emmett–Teller (BET) surface areas of 464.7 and 497.3 m²/g for RWPs and EWCs, respectively. The BET surface area of EWCs activated carbon was higher than that of RWPs due to the higher steam feed rate, which was the activating gas.

4. CONCLUSIONS

This research aimed to operate a pilot horizontal gasifier of RWPs and EWCs to produce syngas with a H₂/CO ratio range
of 1.8–2.3 for FT synthesis. A lab-scale gasifier was conducted with both raw biomass feedstocks to determine the optimum gasifying temperature as 900 °C, and the tar yield was less than 0.2 wt % using CaO as a tar-reforming catalyst. The temperature was 900 °C, and CaO was used in the pilot horizontal gasifier. The pilot gasifier comprised a tar removal system, gas purification system, and gas pressurized buffer tank system. The S/B ratio affects the gas product composition and

Figure 4. Temperature profile of RWP gasification: (a) gasifier zone and (b) reformer zone.

Figure 5. Gas composition and H₂/CO ratio of RWP gasification for 7 days of operation.
H₂/CO ratio. The results revealed that a S/B ratio of 0.5–0.6 gave an H₂/CO ratio in the range of 1.8–2.3. The stability of syngas production and gas composition of both raw materials for 7 days were determined. The gas production rates were 2.5 and 2.7 kg/h with H₂/CO ratios of 1.8 and 1.9 for the RWPs and EWCs, respectively. The supply of an external heat source stabilized the gasifying temperature, resulting in a stable gas composition. In summary, the horizontal gasifier is another effective designed gasifier that showed high-performance operation.

Table 4. Summary of Gasification Conditions and Results for Two Types of Biomasses

| operating parameters                  | RWPs       | EWCs       |
|---------------------------------------|------------|------------|
| operating time, h                     | 30.5       | 27.8       |
| biomass feed rate, kg/h               | 4.3        | 3.9        |
| steam feed rate, kg/h                 | 2.0        | 2.3        |
| steam/biomass, kg/kg                  | 0.5        | 0.6        |
| gas yield at constant volume of 0.9071 m³ | 2.5        | 2.7        |
| produced gas rate, kg/h               | 2.5        | 2.7        |
| gas/biomass, kg/kg                    | 0.6        | 0.7        |
| H₂/CO, mole/mole                      | 1.8        | 1.9        |
| gas compositions                      |            |            |
| H₂                                    | 48.4       | 48.0       |
| CO                                    | 27.7       | 25.4       |
| CO₂                                   | 15.2       | 18.6       |
| CH₄                                   | 8.7        | 8.0        |
| low heating value, LHV                |            |            |
| MJ/Nm³                                | 12.9       | 11.7       |
| carbon balance, kg                    |            |            |
| feed stock                            | 47.7       | 55.3       |
| produced gas                          | 23.6       | 24.9       |
| char (solid)                          | 24.1       | 30.4       |
| cold gas efficiency, η⁰cold            | 47.8       | 48.1       |
| carbon conversion in gas product, wt %, η⁰carbon | 49.5       | 45.0       |

Table 5. Characteristics of Biochar

| biochar from RWPs | biochar from EWCs |
|-------------------|-------------------|
| moisture content  | 13.5              | 13.9              |
| proximate analysis (wt %), d.b. |            |                |
| volatile matter   | 3.5               | 3.6               |
| fixed carbon*     | 83.1              | 88.8              |
| Ash               | 13.4              | 7.6               |
| ultimate analysis (wt %), d.b. |            |                |
| C                 | 82.1              | 89.6              |
| H                 | 1.0               | 1.0               |
| N                 | 0.3               | 0.4               |
| O*                | 16.6              | 9.0               |
| BET (m²/g)        | 464.7             | 497.3             |

*d.b.: dry basis, * by difference.
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Notes

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