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Cogeneration System of Power and H_2 from Black Liquor Through Gasification and Syngas Chemical Looping

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One of the strategies to improve environmentally friendly energy harvesting can be realized by using biomass as a primary energy source for generating electricity and H_2. In addition, high energy efficiency can be achieved by minimizing the exergy loss through process integration and exergy recovery. As an implementation, this study proposes a cogeneration system for black liquor (BL) to co-produce electricity and H_2. The system primarily comprises of BL drying, circulating fluidized bed gasification, syngas chemical looping (SCL), and power generation. The Aspen Plus V8.8 software package is used for modelling and performing calculations of the proposed integrated system. Furthermore, thermodynamic analysis of gasification is performed by employing Gibbs energy minimization. The effects of target solid content on the required total work and compressor outlet pressure during drying and gasification with different steam-to-fuel ratios are evaluated. Moreover, the SCL process adopts three reactors, namely, the reducer, oxidizer, and combustor. Compared to the conventional processes, the integrated drying-gasification-SCL processes are significantly cleaner and more energy efficient. The proposed integrated system can achieve a net energy efficiency of about 70 %, with almost 100 % carbon capture.

1. Introduction

In the future, hydrogen (H_2) will be an important energy carrier due to its favourable characteristics, namely cleanliness, various production technologies and high efficiency (Aziz et al., 2016). Hydrogen utilization will lead to zero carbon emission on use (Kumar, 2015). Despite the beneficial character of the energy carrier, H_2 is available on earth mostly in its oxidized state (water). Many conversion technologies are actively being developed to generate hydrogen at large and small scales with technologies such as gas reforming (Mulewa et al., 2017), oil reforming, biomass gasification (Gong et al., 2017), and water splitting by electrolysis.

Black liquor (BL) from the pulp and paper industry is considered as a potential alternative energy source. The conversion of this biomass through gasification is a promising technology that have fast reaction rate and high conversion efficiency. Naqvi et al. (2012) reported the synthetic natural gas production performance from BL gasification with direct causticization utilizing a circulating fluidized bed (CFB) gasifier. Unfortunately, their study did not further investigate on the energy circulation and the recovery in the system. Ferreira et al. (2015) provided the study of BL gasification and the integration of combined cycle (BLGCC) with and without CO_2 capture. However, the study did not focus on the system innovation and energy efficiency improvement, it focused on the exergetic and economic analyses. Darmawan et al. (2017) conducted study on the integration of BL to produce electricity while utilizing entrained flow gasifier. Unfortunately, this type of gasifier is high in cost and rather difficult to operate and complex in material handling. Additionally, Andersson and Harvey (2006) reported the performance of conventional BL gasification system to produce H_2 with emphasize on the CO_2 emission. Nonetheless, there was no effort to improve the system from the energy efficiency standpoint.

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Via a keyword search in Scopus and Google Scholar that yields no documents, there is no study emphasizing on the energy efficiency improvement of a H_2 and power generation system from BL. This study proposes an integrated system that comprises of BL drying, CFB gasification, syngas chemical looping (SCL), and power generation. After the conversion of BL using gasification, SCL is utilized to efficiently produce H_2 and power. Owing to the multiple reactor nature of SCL, H_2 and CO_2 will be produced in different reactors and therefore, additional CO_2 separation procedure could be avoided (Darmawan et al., 2017a). Besides that, process integration and exergy recovery are adopted to integrate and improve the energy efficiency of the system.

2. Proposed integrated system

A high energy efficiency can be achieved in the system by employing process integration and exergy recovery in the system itself. This method had already been studied before and could significantly reduce the exergy losses (Aziz et al., 2017), and it has been evaluated in many types of system, namely biomass-based power generation (Aziz, 2016 a, b), coal based power generation (Darmawan et al., 2017b) and H_2 production (Zaini et al., 2017). Figure 1 shows the simplified flow diagram of the whole proposed cogeneration system. As mentioned in the previous section, this system comprises of BL drying, CFB gasification, SCL and power generation. The solid lines represent material, dashed lines represent heat and dotted lines represent electricity. A detailed explanation of the system is further elaborated in the next section.

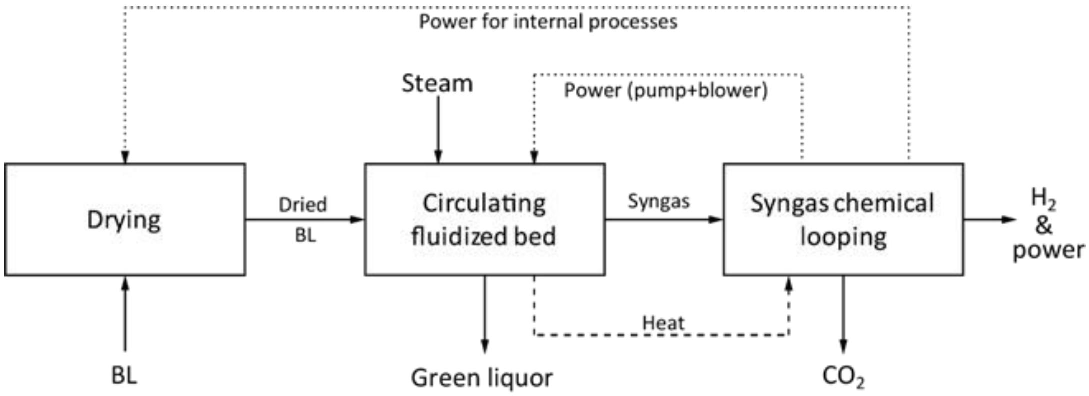

Figure 1: Simple flow diagram of the proposed cogeneration system

3. Process modelling and calculation

3.1 General conditions

For modelling and calculation regarding the energy and mass balances in the proposed system, Aspen Plus V8.8 (Aspen Technology, Inc.) process simulator software is used. Considering a pulp production rate of 730 t d^{-1}, the flow rate of the weak BL entering the drying module is set at 348.12 t h^{-1}.

Table 1: Composition of BL used

Properties	Value
Total solids (wt.% wb)	15
Water content (wt.% wb)	85
Components (wt.% db) [22]	C: 27.50; H: 3.75; O: 39.35; N: 0.07; Cl: 0.16; Na: 19.85; K: 3.12, S: 6.20
LHV (MJ kg^{-1}, db)	12.4

3.2 BL drying system

Presently, existing Kraft pulp mills uses multiple effect evaporator (MEE) to reduce moisture content of BL. In this technology, prior to entering the boiler, the BL must be in concentrated condition to improve the combustion and energy efficiency. Among other modules in the Kraft pulp mill, the MEE would consume the highest amount of steam. Regarding to the steam contact types, MEE is divided into direct and indirect contact.

Process flow diagram of the drying system is showed in Figure 2. The drying system consists of several stages: preheating, drying and steam superheating. Darmawan et al. (2017a) initially proposed this system which utilizes exergy recovery method. This drying system is adopted for this study due to its high energy efficiency.

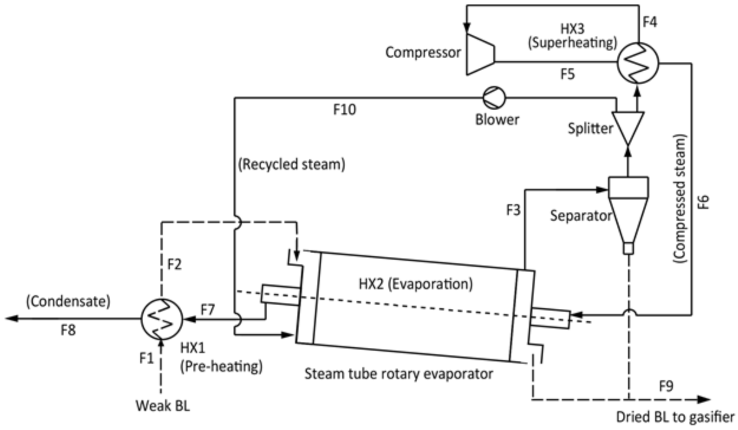

Figure 2: Process flow diagram of proposed BL drying system (adopted from (Darmawan et al., 2017))

3.3 CFB gasification

Gasification utilizing CFB technology is done to partially oxidize the fuel to provide heat required for the process. This gasifier operates at a temperature range of 750 to 850 °C (Shen et al., 2007) which is being influenced by steam-to-fuel ratio or air-to-fuel ratio. The CFB gasifier were chosen due to its better characteristics, namely its higher carbon conversion efficiency and excellent heat transfer performance (Ju et al., 2010) compared to traditional bubbling bed gasifier. The gasification process is performed after the concentrated BL (80 wt.% wb dry solids) completed its drying process. Gasification is done at a high temperature to produce syngas containing H_2, CO and CH_4. Tar and other hydrocarbons species are also expected to form. On the other hand, because BL contains high amounts of catalytically active Na, hydrocarbon content will be lower compared to another biomass (Carlsson et al., 2010). Afterwards, the high temperature syngas will be used to generate steam for the gasification due to the presence of water. The temperature of syngas is also being maintained over 300°C to avoid condensation.

3.4 SCL and power generation system

In this module, syngas is being reacted to produce power and H_2 by cyclic operation inside an iron oxide reaction medium. The operation itself consists of 3 reactors, specifically reduction, oxidation and combustion reactors in an interconnected fashion as shown in Figure 3. The reduction and oxidation reactors utilize a counter-current moving bed reactor and the combustion reactor adopted the entrained bed type. The module operates by utilizing iron oxide oxygen carrier (OC) as a facilitator for the reduction and oxidation reactions. The solids circulated in the SCL system is assumed to have a mass fraction of 70 % Fe_2O_3, 15 % SiC, and 15 % Al_2O_3, as suggested by Fan (2010). At the start of operation, after gas cleaning, syngas enters the reduction reactor, where it reacts with O_2 carried by Fe_2O_3. In this reactor, a high pressure (up to 3.5 MPa) is suggested to increase the reaction kinetics and to reach the maximum gas-solid conversion, which favorably leads to smaller reactor size (Gupta et al., 2007). Besides that, the operation is conducted at a minimal temperature of 900 °C, and the syngas is completely converted to steam and CO_2 (Fan et al., 2010). The implications of the equilibrium concentrations of gases should be considered when doing calculations (Fan et al., 2010). Later on, in the oxidation stage, the reduced gasses will react with steam to produce H_2-rich gas stream, which flows out along with the remaining steam. Furthermore, after the steam is condensed, pure H_2 is be obtained. Afterwards, the Fe_3O_4 produced in the oxidation reactor will react with O_2 to convert it back to Fe_2O_3. The assumptions and conditions regarding the SCL module are as follows:

Table 2: Assumptions and conditions associated with the SCL process

Parameters	Value
Reducer temperature (°C)	930
Oxidizer temperature (°C)	820
Combustor temperature (°C)	1,000
SCL pressure condition (MPa)	2–3.5
Compressor isentropic efficiency (%)	90
Pump efficiency (%)	85
Mass fraction of circulated solid material	70 % Fe_2O_3, 15 % Al_2O_3, 15 % SiC

3.5 Enhanced process integration and performance evaluation

Figure 3 shows the overall system process flow diagram the gasification and SCL modules, as the drying part has already been explained in previous section. After gas cleaning, the syngas is compressed to 2–3.5 MPa to increase its exergy and reduction performance (Zaini et al., 2017). Furthermore, the steam and CO_2 streams are utilized to preheat the syngas in the HX-7 heat exchanger and then, subsequently, the power will be generated in the expander (EXP-1); afterwards, H_2O (HX-6) is preheated before it flows to the condenser. Moreover, the produced steam containing steam and high-pressure H_2 is then expanded in EXP-2 to produce additional power. On the other hand, the combustor is operated at a pressure of 0.2 MPa higher than the reducer and oxidizer (Zaini et al., 2017). Likewise, the heat carried by the hot gas stream from the combustor is utilized to increase the exergy rate in the air inlet stream and the remaining energy is recovered to generate more power in EXP-3. To evaluate the system performance, the total net energy efficiency is calculated as follows:

$$\eta_{net} = \frac{P_{output} - P_{internal}}{P_{input}} \tag{1}$$

where, P_{output} , $P_{internal}$, and P_{input} are total produced H_2 and generated power, internal power consumption, and total energy input (the BL input (MW)), respectively. The internal power consumption represents the work done by compressor and blower for drying, pump and compressor in the gasification and the SCL modules. Likewise, the integrated system is evaluated at different steam-to-fuel ratios of the gasifier and the SCL modules to examine the effects of different operating parameters on the energy efficiency.

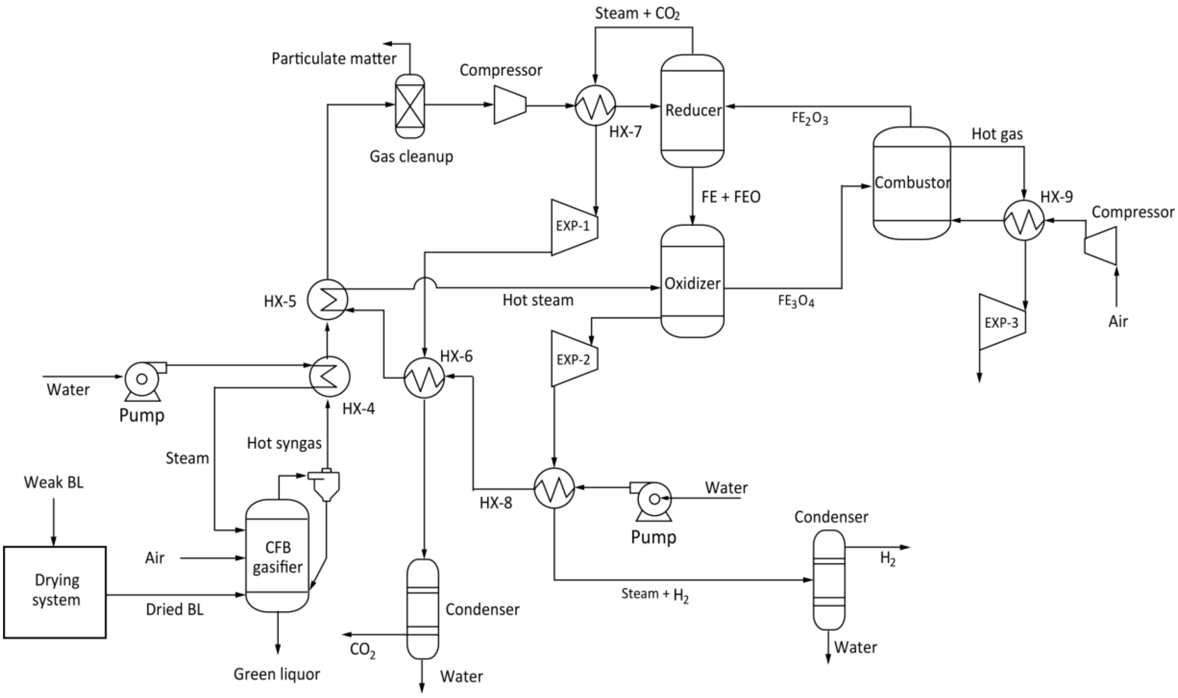

Figure 3: Process flow diagram of gasification and SCL modules

4. Results and discussion

Figure 4(a) shows the effect of varying steam-to-fuel ratio to the composition syngas and the cold gas efficiency. Cold gas efficiency is the ratio of the flow of energy in the gas to the energy contained in the BL. Generally, increasing the steam-to-fuel ratio will increase H_2 and CO_2 amounts produced in the syngas, adding more steam to the reactor would decrease the CO concentration as the steam-to-fuel ratio increases, which, in turn would decrease the cold gas efficiency. Moreover, to maintain a steady gasification temperature of 800 °C, higher steam-to-fuel ratio is required as the reactor requires more heat supplied from steam generated from carbon combustion. By doing so, the CO_2 concentration will increase and consequently decrease the gasification efficiency. This is verified by Ju et al. (2010); their research affirms that increasing the amount of air will lead to less valuable gas yield in the gasifier due to the endothermic reaction of steam. It can be concluded that the amount of air and steam entering the gasifier will influence the gasification performance. Figure 4(b) shows the effect of steam-to-fuel ratio to the total energy efficiency in the system. It was observed that changing the steam-to-fuel ratio from 0.1 to 0.8 will increase the internal energy consumption by 4.61 %. Increasing the steam-to-fuel ratio will decrease the total energy efficiency (power and H_2 production) from 69.16 % to 56.74 %. The internal consumption is dominated by compressor work (more than 90 %), most notably in the drying and SCL processes. In the drying system alone, the compressor consumes as much as 7.6 MW, which equals to 28 % of the total energy internal consumed.

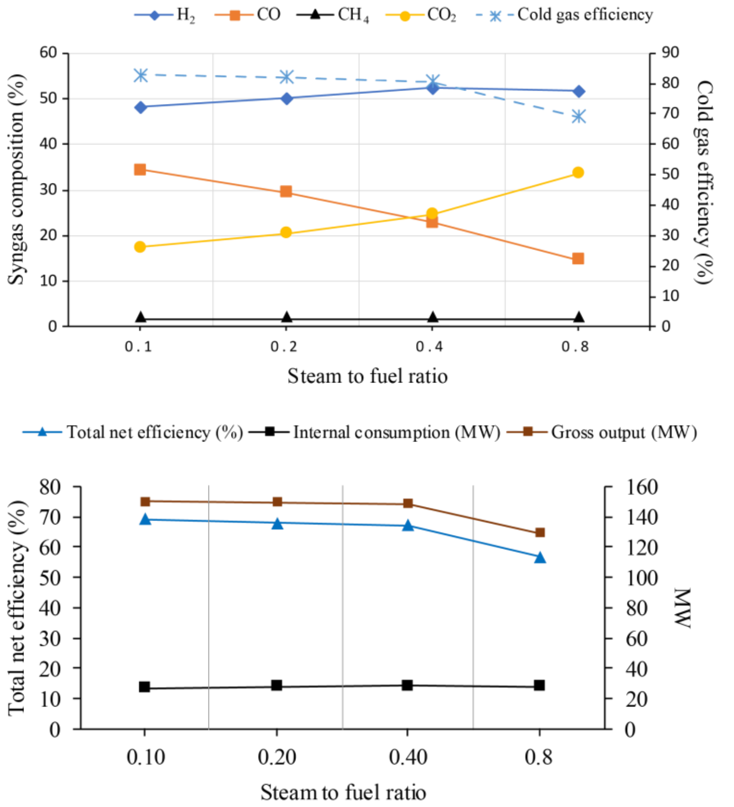

Figure 4: Effects of steam/fuel ratio during gasification on (a) the composition of produced syngas composition and cold gas efficiency, and (b) the performance of the proposed system

The performance of the overall integrated system at different SCL operating pressures is described in Figure 5. As shown, the increase of SCL operating pressure has no significant outcome on the total energy efficiency. Nonetheless, the net produced power is increasing as the pressure increases from 2 to 3.5 MPa, which is promoted by the slight increase of power produced from EXP-2.

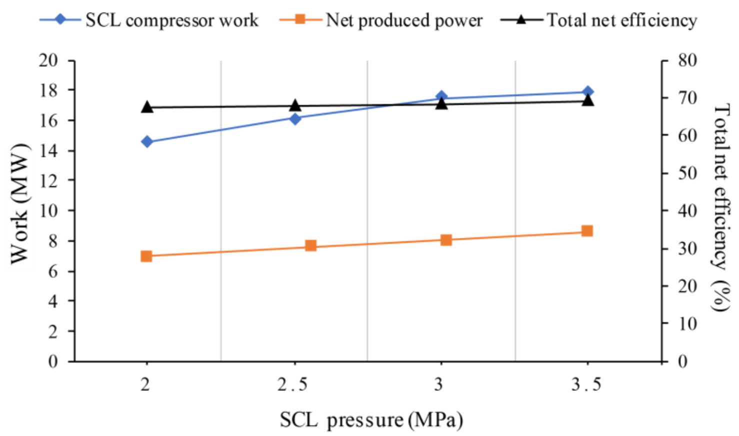

Figure 5: Effects of SCL pressure on the system performance

5. Conclusion

An integrated system was proposed to effectively utilize BL for the cogeneration of H_2 and power. The proposed system can achieve a total net energy efficiency of nearly 70 % by employing process integration and exergy recovery technologies. These technologies can utilize the unrecovered exergy in any process; therefore, a high total energy efficiency could be achieved. Compared to other BL recovery systems, the integrated system which consists of drying, gasification, and SCL seems to be very promising. Furthermore, a concentrated CO_2 stream can be obtained from the SCL process directly. Thus, eliminating additional energy for CO_2 separation for CCS. It can be concluded that the proposed integrated system provides a cleaner and more efficient BL usage.

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