Energy-Efficient Co-production of Hydrogen and Power from Brown Coal Employing Direct Chemical Looping

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An integrated system for co-production of H₂ and power from brown coal having high energy efficiency is proposed. The integrated system consists of drying, coal direct chemical looping, hydrogenation, and power generation. To minimize the exergy destruction occurs throughout the integrated system, enhanced process integration technology is applied, first in each single process, and second among the involved processes to recover the unrecoverable energy/heat from any single process. Coal direct chemical looping is adopted to convert the brown coal to H₂ and CO₂, and the rest of produced heat is recovered for power generation through gas and steam turbines. The produced hydrogen is then hydrogenated with toluene producing methyl cyclohexane which is ready for storage and transportation. The effects of target moisture content in drying and carbon conversion in reduction to H₂ production, power generation, and total energy efficiencies are evaluated. From modelling and process calculation, the proposed integrated system shows very high values of the above mentioned efficiencies, which are about 68.9, 21.0 and 90.0 %, respectively. Although higher carbon conversion in reduction leads to lower power generation, higher H₂ production efficiency and higher total energy efficiency can be achieved. In addition, no significant influence of target moisture content in drying to each efficiency could be observed.

1. Introduction

Hydrogen (H₂) is very chemically stable, non-toxic, and has very high energy density per weight, which is about 120 MJ/kg (LHV). It doesn’t contribute to climate change because water is produced during oxidation. H₂ is believed to act as an essential secondary energy source in the future. Unfortunately, the development of H₂ still faces some challenging problems including its production, conversion, storage and transportation (Orhan et al., 2012). H₂ has very low energy density per volume, which is 3 Wh L⁻¹ (under ambient conditions), leading to difficulties in its storage and transportation. Some H₂ storage technologies are proposed including high compression, liquefaction, metal and liquid hydrides.

As one of the very potential fuels, brown coal is categorized as low rank coal having some characteristics of high moisture content, low calorific value, sulphur and ash contents (Aziz et al., 2014a). In addition, compared to other types of coal, brown coal has relatively large reserve but its utilization is still limited. Advanced utilization of brown coal is demanded in the future to increase its utilization and reduce its environmental impacts. Therefore, conversion of brown coal to H₂ is believed as an excellent solution. Some conversion technologies of coal to H₂ are available today, such as gasification, pyrolysis, shift reaction, and chemical looping. Among those technologies, chemical looping is considered as the most advanced and promising technology which is able to convert the fuel and separate CO₂ with relatively low energy and cost penalties (Cormos et al., 2014).

The production of H₂ from coal faces some constraints due to coal mining location and environmental problems. An in situ conversion is considered as the most efficient way in terms of production cost and transportation. In addition, among the available storage technologies, liquid organic hydrogen carrier (LOHC) is considered as an excellent method due to its stability, storage capacity, safety, and handling (Aziz, 2016a). In LOHC, aromatic hydrocarbons, such as toluene and benzene, are converted to organic hydrides, such as...
methyl cyclohexane (MCH) and cyclohexane, when they are reacting with H₂. Moreover, the bound H₂ can be released from organic hydrides through dehydrogenation.

An integrated in-situ system which can convert brown coal to H₂ with high energy efficiency and low environmental impact is demanded. Fan et al. (2008) have studied H₂ and power production from coal employing CDCL with conversion efficiency of about 80%. Zeng et al. (2012) has developed a reactor model for CDCL using ASPEN plus and found that the developed reactor and process can convert coal to hydrogen with thermal efficiency of about 78%. Unfortunately, their developed processes only deals with the conversion (gasification) process without considering the other processes including drying and storage. In addition, no effort has been taken to minimize the exergy destruction.

This study focuses mainly on the effort to propose an integrated system to co-produce H₂ and power with high total energy efficiency. The proposed system consists of coal drying, CDCL, power generation, and storage. To minimize the exergy destruction, as well as improve the energy efficiency, an enhanced process integration (EPI) technology is adopted. Some operating conditions are evaluated including target moisture content in drying and carbon conversion in reduction (CDCL) in relationships to H₂ production, power generation and total energy efficiencies.

2. Modelling of the proposed system

2.1 Overall concept of the integrated system

Figure 1 shows the conceptual diagram of the proposed co-production system of H₂ and power from brown coal. The integrated system consists of four continuous modules: coal drying, CDCL, power generation, and hydrogenation. The as-mined brown coal is initially dried in drying module to decrease its moisture content, hence higher calorific value of brown coal can be earned. The dried brown coal is then converted to H₂ and CO₂ in CDCL module. CDCL module consists of three circulated processes: reduction, oxidation and combustion. The produced H₂ is going to hydrogenation module for being chemically bound with toluene producing MCH. The heat generated in CDCL and hydrogenation is then recovered for power generation utilizing gas and steam turbines.

The integration is performed based on the principle of EPI technology in which heat circulation and process integration are combined (Aziz, 2016b). Heat circulation is initially employed in each single module to circulate the energy/heat involved in the same module. In addition, the unrecoverable energy/heat is then utilized to other modules through process integration of the whole processes. The concept of EPI, especially heat circulation, has been studied thermodynamically by Kansha et al. (2013) and it is application has been evaluated further in algae drying (Aziz et al., 2014b) and power generation (Aziz, 2015).

2.2 Process flow of each module

Figure 2 shows the detailed process flow diagram of the integrated system. In this study, a moving bed is adopted as both reducer and oxidizer, while an entrained bed is employed for combustor. Wet brown coal is preheated in HE1 and HE2 before entering fluidized bed dryer, FBD. The exhausted steam from FBD is split to fluidizing and compressed steam. The compressed steam is utilized to provide the required heat for drying which is supplied to the heat exchanger, HE3, immersed inside fluidized bed dryer. Dried brown coal is fed using feeder, FDR, and mixed with a part of produced CO₂ to reducer, RED.

Brown coal reacts with the iron particles, Fe₂O₃, forming CO₂, Fe, FeO, and moisture (Eq(1)). The produced CO₂ and moisture are exhausted and going to gas turbine, EX1, for expansion and power generation. On the other hand, Fe, FeO and the rest of Fe₂O₃ particles are moving to the oxidizer, OXD, to be reacted with steam.
to produce $H_2$. The reactions following this oxidation are shown in Eqs(2, 3). The produced $H_2$ and steam are exhausted to the gas turbine, EX2, for additional power generation. Furthermore, they are flowing to condenser, CD2, for phase and material separations. $Fe_3O_4$ and the rest of $Fe_2O_3$ particles are flowing to the combustor, COM, for oxidation with oxygen (Eqs(4, 5)). This combustion is important to provide the heat required for reduction, as well as to recover the used iron particles to their initial form, $Fe_2O_3$. The flue gas which is rich of $N_2$ is then flowing to gas turbine, EX3, for expansion. In addition, the rest of heat from flue gas is recuperated to generate steam for steam turbine, EX4.

**Figure 2: Process flow diagram of the whole integrated system.**

$$\begin{align*}
CH_{0.84}O_{0.29} + Fe_2O_3 &\rightarrow CO_2 + 0.42 H_2O + 1.13 Fe + 0.87 FeO \\
Fe + H_2O &\rightarrow FeO + H_2 \\
3FeO + H_2O &\rightarrow Fe_3O_4 + H_2 \\
4Fe_3O_4 + O_2 &\rightarrow 6Fe_2O_3 \\
C + O_2 &\rightarrow CO_2 \\
C + H_2 &+ 3H_2 \rightarrow C + H_14
\end{align*}$$

The produced $H_2$ from reducer is flowing to the hydrogenation module for storage. It is mixed with toluene and preheated before being catalytically reacted in hydrogenator, HYD. The reaction during hydrogenation is shown in Eq(6). As hydrogenation is exothermic reaction, the produced heat can be recovered for superheating the steam for steam turbine, EX4. In hydrogenation, $H_2$ is chemically bound with toluene producing MCH and the produced MCH is ready for transportation.

### 3. Process analysis

Process calculation of the proposed integrated system is conducted in terms of the influences of target moisture content in drying and carbon conversion in reduction to the $H_2$ production, power generation and total efficiencies. Table 1 shows the properties of used brown coal and assumed parameters in each module. A steady-state process simulator SimSci Pro/II (Schneider Electric Software, LLC.) is used for process calculation. The energy inputs of the system include brown coal and the reaction heat during hydrogenation. Each of $H_2$ production efficiency, $\eta_{H_2}$, power generation efficiency, $\eta_{power}$, and total efficiency, $\eta_{tot}$, are calculated based on Eqs(7–10). In this study, four target moisture contents in drying are evaluated: 5, 10, 15, and 20 wt% wb. In addition, four carbon conversions in reduction are also observed: 80, 85, 90, and 95 %.
\[ \eta_{\text{tot}} = \eta_{H2} + \eta_{\text{power}} \]  
\[ \eta_{H2} = \frac{m_{H2} CV_{H2}}{m_{bc} CV_{bc} + \Delta H_{\text{H2O}} \frac{m_{H2}}{3 M_{H2}}} \]  
\[ \eta_{\text{power}} = \frac{W_{\text{net}} t}{m_{bc} CV_{bc} + \Delta H_{\text{H2O}} \frac{m_{H2}}{3 M_{H2}}} \]

### Table 1: Brown coal properties and assumed conditions in each corresponding module

<table>
<thead>
<tr>
<th>Item</th>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown coal properties</td>
<td>Ultimate analysis (wt% db)</td>
<td>C: 66.7; H: 4.7; O: 26.0; N: 0.6; S: 0.3</td>
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<tr>
<td></td>
<td>Proximate analysis (wt% wb)</td>
<td>VM: 33.82; FC: 4.51; Ash: 1.67; Moisture: 60</td>
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<tr>
<td>Drying</td>
<td>Flow rate (t h(^{-1}))</td>
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<tr>
<td></td>
<td>Fluidization velocity ( \frac{U}{U_{mf}} )</td>
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<tr>
<td>CDCL</td>
<td>Reduction temperature (°C)</td>
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<tr>
<td></td>
<td>Average particle size of Fe(_2)O(_3) (mm)</td>
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<tr>
<td></td>
<td>Feeding CO(_2) amount (t h(^{-1}))</td>
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<td></td>
<td>Operating pressure (MPa)</td>
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<td>Power generation</td>
<td>Maximum gas turbines inlet temperature (°C)</td>
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<td></td>
<td>Maximum steam turbine inlet temperature (°C)</td>
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<tr>
<td></td>
<td>Polytrophic efficiency (%)</td>
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<td></td>
<td>Steam turbine inlet pressure (MPa)</td>
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<td>Hydrogenation</td>
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<td></td>
<td>Reaction pressure (kPa)</td>
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<tr>
<td></td>
<td>Catalyst</td>
<td>Pt/TiO(_2)-SiO(_2)</td>
</tr>
</tbody>
</table>

### 4. Results and discussion

#### 4.1 Target moisture content in drying

Figures 3 and 4 show the influence of target moisture content in drying to each efficiency, power and duties, respectively. In drying, changes in target moisture content affect mainly the amount of exhausted steam from fluidized bed dryer and drying temperature. Drying temperature increases following the decrease of target moisture content due to high driving force for water removal, especially the chemically bound moisture inside the particles. As the results of process calculation, in general, high H\(_2\) production, power generation and total energy efficiencies are achieved. In addition, although higher target moisture content shows higher power generation and total energy efficiencies, there is no significant influence of target moisture content in drying to the above mentioned efficiencies. The highest H\(_2\) production, power generation, and total energy efficiencies are achieved at target moisture content of 20 wt% wb which are 68.95, 21.07, and 90.02 %, respectively.

![Figure 3: Influences of target moisture content in drying to power, duty and efficiencies.](image-url)
As target moisture content in drying decreases, the compressor outlet pressure and compressor duty increases accordingly. The outlet pressure increases from 122 to 184 kPa when the target moisture content is reduced from 20 to 5 wt% wb. In addition, the blower work for fluidizing steam also increases due to higher temperature of inlet steam.

4.2 Carbon conversion in reduction

Figure 5 shows the calculation results evaluating the effects of carbon conversion in reduction to the amount of produced H\textsubscript{2} and MCH, and H\textsubscript{2} production efficiency. Higher carbon conversion leads to higher H\textsubscript{2} production amount and its efficiency. Numerically, the produced H\textsubscript{2} increases from 6.6 t h\textsuperscript{-1} (production efficiency 64.0 %) to 7.6 t h\textsuperscript{-1} (production efficiency 71.4 %) in case of carbon conversion is increased from 80 to 95 %, respectively. In addition, the increase of produced H\textsubscript{2} results in the increase of MCH storing H\textsubscript{2}. The amount of produced MCH for carbon conversion of 80 and 95 % are 108.2 and 123.7 t h\textsuperscript{-1}, respectively.

Figure 6 shows the effects of carbon conversion in reduction to the generated power, required duties, net power, power generation efficiency and total energy efficiency. Higher carbon conversion in reduction led to lower generated and net power. Therefore, the power generation efficiency decreases accordingly. The net power which are achieved under carbon conversions of 80 and 95 % are 81.4 MW (generation efficiency 23.4 %) and 70.8 MW (generation efficiency 19.8 %), respectively. Higher carbon conversion in reduction means lower amount of remaining carbon which can be burned during combustion with oxygen. It results in lower amount of energy which can be recovered by gas turbine after combustion. However, there is no significant change in the total energy efficiency due to the production of H\textsubscript{2} in reduction.

In addition, the amount of circulated Fe\textsubscript{2}O\textsubscript{3} increases following the increase of carbon conversion in reduction. This is because of larger amount of heat which is required for reduction (endothermic) as the amount of converted carbon increases.
Figure 6: Effects of carbon conversion in reduction to generated power, required duties, net power, power generation efficiency and total energy efficiency.

5. Conclusions
An integrated system for co-production of H$_2$ and power from brown coal has been well developed with the aim of high total energy efficiency. The application of EPI technology, covering heat circulation and process integration technologies, is able to minimize the exergy destruction throughout the integrated system. Therefore, high H$_2$ production, power generation and total energy efficiencies can be achieved. This proposed system is considered suitable for in-situ energy conversion system which is able to convert brown coal to cleaner energy, hence significantly low environmental impact can be realized.

Reference