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Clean Hydrogen Production from Low Rank Coal: Novel Integration of Drying, Gasification, Chemical Looping, and Hydrogenation

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State-of-the-art integrated processes for hydrogen production from low rank coal (LRC) consisting of drying, gasification, chemical looping, and hydrogenation is proposed based on enhanced process integration (EPI). This paper focuses mainly on the performance of drying module, especially related to energy efficiency during drying. EPI, which is a combination of exergy recovery and process integration, in developed in order to minimize the total exergy destruction throughout the integrated processes. Each process module is designed initially based on exergy recovery to maximize the recirculated heat amount in each process module. Furthermore, the developed process modules are integrated based on process integration, hence the exergy destruction throughout the integrated processes can be minimized. LRC is initially dried in drying module employing exergy recovery and utilizing steam as drying medium. Hot dried-LRC is fed directly to gasification module for conversion producing syngas. The produced syngas is then flowing to chemical looping module to produce hydrogen, CO_2 and power. Finally, the produced hydrogen is then stored in liquid organic hydrogen carrier (toluene-methylcyclohexane). On the other hand, the separated CO_2 can be sequestered to achieve a clean coal conversion. From process calculation, the proposed drying module shows very high energy efficiency, which is about one sixth to which is required in drying with conventional heat recovery.

1. Introduction

Hydrogen is considered as a potential secondary energy source due to some advantages of cleanliness, high efficiency and high variety of production and utilization technologies. Hence, hydrogen is expected to have an important role in the future energy system. Unfortunately, at present, the utilization of hydrogen is still far from its expectation due to some challenging problems covering production, transportation, storage, and energy conversion (Orhan et al., 2012).

Hydrogen is currently produced mainly from natural gas, oil reforming, coal gasification, and water electrolysis (Dincer, 2012). In addition, among the fossil energy resources, low rank coal (LRC) is believed to have relatively large reserve, almost the half of the total worldwide coal reserve. LRC has some advantages including low ash content, possibility for open-cut mining and low production cost. Unfortunately, LRC also has disadvantages especially on its low calorific value, high moisture content, high risk of spontaneous combustion, and larger CO_2 emission in its utilization (Aziz et al., 2011). The moisture content of just-mined LRC is ranging from 40 to 65 wt% on wet basis (wb). Therefore, drying becomes a compulsory process to solve these disadvantages. Unfortunately, LRC drying is a very energy intensive process. In addition, recently, the trend to convert and decarbonize LRC to secondary clean energy resources, including hydrogen, increases significantly.

Under ambient pressure, although the energy density of hydrogen by weight is high (33 kWh kg^{-1}), its energy density by volume at ambient state is very low (3 Wh l^{-1}). This leads to some difficulties in its storage and transportation. A liquid organic hydrogen carrier (LOHC) is one of the promising hydrogen storage because of high safety, storage capacity, long storage time, and reversibility (Jiang et al., 2014). In

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LOHC, hydrogen is covalently bound to LOHC through hydrogenation. Furthermore, the bound hydrogen can be released from LOHC through dehydrogenation. Among available LOHCs, toluene (C_7H_8)-methylcyclohexane (C_7H_{14}, MCH) is considered to be well-established and promising because it is relatively cheap, stable, and easy to store/transport. In addition, a successful demonstration test has been achieved by Chiyoda Corporation in Japan (Okada and Shimura, 2013).

In addition, in currently available conversion processes, the conversion of LRC to hydrogen has relatively low total energy efficiency due to limitation in their energy conservation and unintegrated multiple processes. For example, an integrated system including coal hydrogasification, power generation, and electrolysis to produce synthetic natural gas has been proposed by Minutillo and Perma (2010). Unfortunately, their proposed processes were designed based on conventional process integration technology, hence still large amount of exergy destruction is generated. Furthermore, a huge amount of CO_2 will be emitted leading to some environmental problems.

Research and development of innovative method and design of the well-integrated processes are urgently demanded. This paper discusses and proposes a novel integration of hydrogen production from LRC, including drying, gasification, chemical looping, combined cycle, and hydrogenation based on enhanced process integration (EPI) to achieve high total energy efficiency. Furthermore, a detailed evaluation of drying module related to energy efficiency is performed.

2. Proposed integrated processes

To minimize the total exergy destruction in the overall integrated processes, EPI has been proposed and evaluated in several applications processes including algae drying (Aziz et al., 2014), empty fruit bunch-based power generation (Aziz et al., 2015) and algae-based power generation (Aziz, 2015). EPI mainly consists of two core technologies: exergy recovery and process integration. Different to conventional process integration, in EPI, process intensification in term of energy efficiency is performed initially in each single process through exergy recovery to recover thoroughly the energy involved in that process. Exergy recovery can be achieved through exergy elevation and effective heat coupling (Liu et al., 2012). Unfortunately, although each single process has been intensified through exergy recovery, at the last, there is still energy that cannot be recovered due to some limitations in heat exchange, etc. To minimize this unrecoverable energy, the idea of process integration is adopted. Hence, the total exergy destruction throughout the integrated processes can be minimized leading to higher energy efficiency.

Figure 1 shows the proposed integrated-processes of LRC conversion to hydrogen including drying, gasification, chemical looping, combined cycle, and hydrogenation. Solid and dotted lines represent material/heat and electricity. The as-mined LRC is fed initially to drying module to remove its moisture, as well as increasing its calorific value. Next, the dried LRC is converted to syngas through gasification which is also involving air and steam. The produced syngas is flowing to chemical looping module for co-production into hydrogen, CO_2, and heat. The produced hydrogen is then flowing to hydrogenation module to be covalently bound to toluene producing MCH. On the other hand, the separated CO_2 is sequestered leading to clean energy conversion. In addition, the produced heat from chemical looping module is utilized to produce electricity through combined cycle module. The produced electricity is distributed to the involved integrated-processes and the excess power could be sold to the grid as an additional economic benefit.

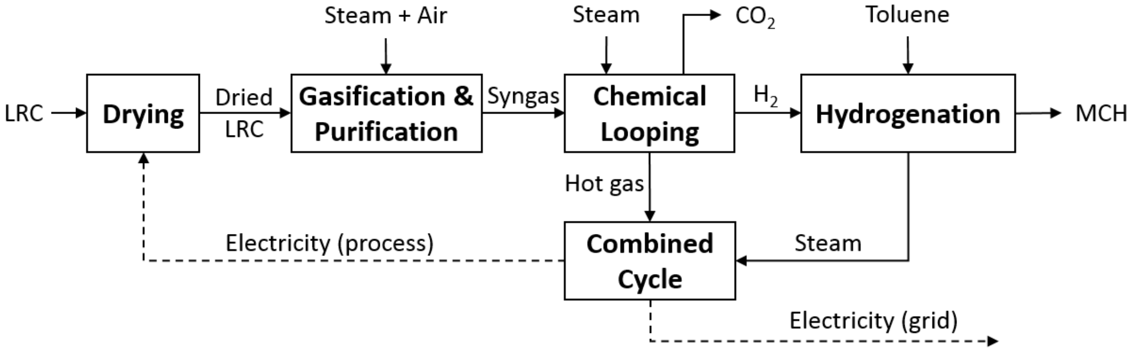


Figure 1: Basic schematic diagram of the proposed integrated-processes of LRC conversion to hydrogen.

2.1 Drying and gasification modules

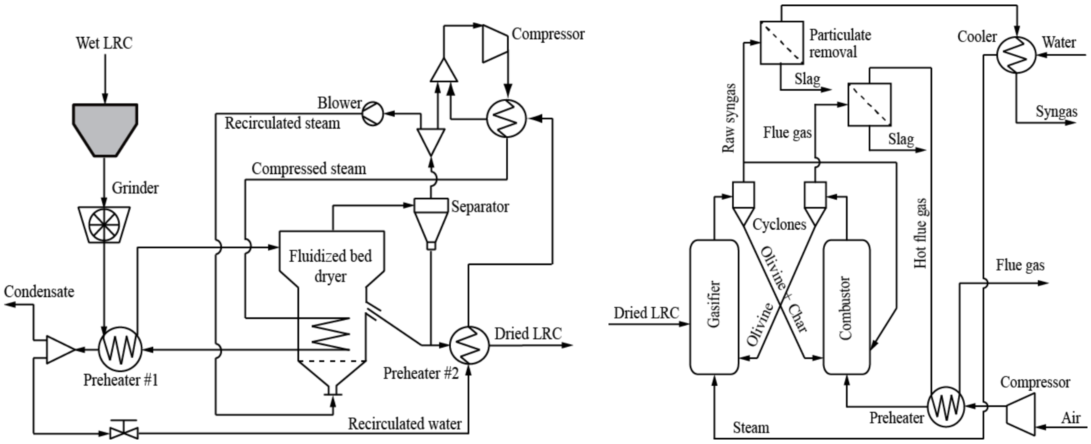


Figure 2: Process flow diagrams: (a) drying module, (b) gasification module

Figure 2(a) shows the proposed drying module which is developed based on EPI. Drying is a moisture removal which is influenced strongly by its surrounding conditions leading to the concept of equilibrium moisture content. Superheated stem is adopted as drying medium due to its advantages, especially related to the possibility for high energy recovery.

A fluidized bed with immersed heat exchanger is selected as the dryer due to its advantages on good particle mixing, uniform temperature distribution, and rapid moisture and heat transfer (Aziz et al., 2012). To realize the exergy recovery in drying, the evaporated steam is compressed to certain pressure depending on the performance of heat coupling afterward. As its pressure increases, the exergy rate of steam increases leading to the possibility of self-heat exchange. The exhausted steam from fluidized bed dryer is split to recirculated steam (for fluidization) and compressed steam. The compressed steam from dryer which is mixed with the superheated recirculated-water is compressed and utilized as heat source for subsequent drying. This leads to self-heat exchange inside the drying module.

Furthermore, Figure 2(b) shows the proposed gasification module in where dual circulating fluidized beds of gasifier is adopted due to its higher carbon conversion efficiency and conversion rate. Hot dried LRC is fed directly to the first gasification reactor where the pyrolysis and gasification take place. The unreacted char leaves together with inert material (such as silica sand) to the second gasification reactor for combustion. Furthermore, the inert material is recirculated to the first reactor transporting the heat for pyrolysis and gasification. Next, the produced syngas is filtered by particulate remover eliminating the ash or slag. A ceramic particulate removal is considered as the best candidate due to its removal capability under high temperature condition.

2.2 Chemical looping, combined cycle, and hydrogenation modules

Figure 3 shows the process flow diagram for integrated chemical looping, combined cycle, and hydrogenation. Chemical looping of produced syngas from gasification is adopted in this study converting syngas to hydrogen and CO_2, and also producing the heat. In chemical looping, iron-based metal oxide is utilized as an oxygen carrier transferring the oxygen from combustion to the fuel because it does not involve catalytically and it has high conversion of syngas. Therefore, there is no direct contact between oxygen (air) and fuel. The advantages of chemical looping include high purity of separate CO_2 leading to clean and efficient energy conversion.

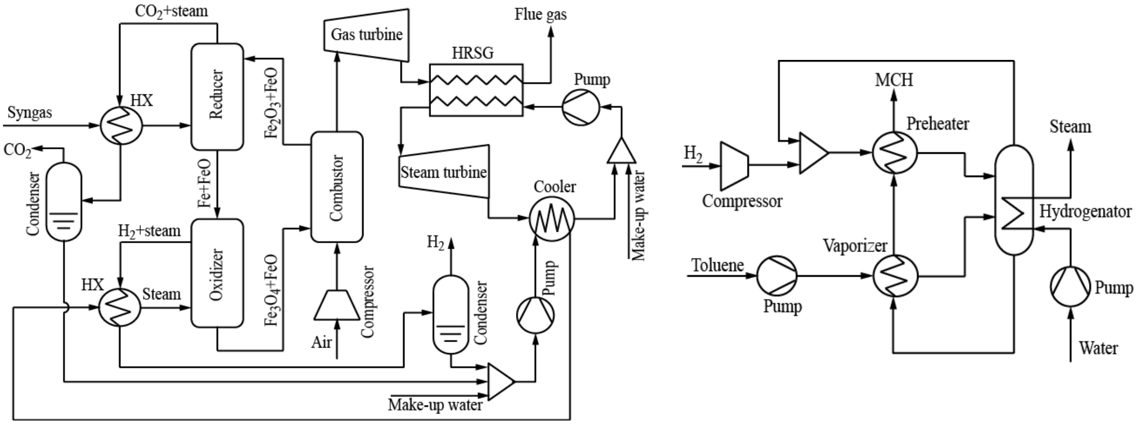
In chemical looping, there are three main fluidized bed type reactors involved: reducer, oxidizer, and combustor. In reducer, the produced syngas is utilized directly as fluidizing gas and the following reactions occur:

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \qquad \Delta H = -2.8\ \text{kJ mol}^{-1} \qquad (1)$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad \Delta H = -11\ \text{kJ mol}^{-1} \qquad (2)$$

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O \qquad \Delta H = 38.4\ \text{kJ mol}^{-1} \qquad (3)$$

$$FeO + H_2 \rightarrow Fe + H_2O \qquad \Delta H = 30.2\ \text{kJ mol}^{-1} \qquad (4)$$



(a) (b)

Figure 3: Process flow diagrams: (a) chemical looping and combine cycle modules, (b) hydrogenation module

As the product of reduction reaction, CO_2, together with steam, is produced which is further cooled down for separation. The remainders are going to oxidizer to produce high purity of hydrogen. Following reactions are considered take place in the oxidizer:

$$Fe + H_2O \rightarrow FeO + H_2 \qquad \Delta H = -30.2 \text{ kJ mol}^{-1} \tag{5}$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad \Delta H = -60.6 \text{ kJ mol}^{-1} \tag{6}$$

The produced hydrogen together with steam are exhausted from oxidizer and cooled down to achieve high purity of hydrogen. The separated hydrogen is then flowing to hydrogenation module for storage. In addition, in combustor, the following reaction occurs:

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \qquad \Delta H = -471.6 \text{ kJ mol}^{-1} \tag{7}$$

As combustion is very exothermic reaction, its produced heat is utilized to cover the heat required in reducer and the excess heat is used to generate steam in combined cycle module generating electricity.
The separated hydrogen is reacted with toluene producing MCH. The following reaction occurs in hydrogenation module:

$$C_7H_8 + 3H_2 \rightarrow C_7H_{14} \qquad \Delta H = -205 \text{ kJ mol}^{-1} \tag{8}$$

3. Process analysis for drying module

The current study focuses mainly on the evaluation of the proposed drying module developed based on EPI in term of energy efficiency. To perform this analysis including material and energy balances, process modelling and calculation are conducted using SimSci Pro/II (Schneider Electric Software, LLC.). Related to LRC drying, the correlation between the vapour pressure, p/p_o, to the equilibrium moisture content, M_{eq}, can be approximated as follows (Chen et al., 2001):

$$\frac{p}{p_o} = 1 - \exp\left[-2.53 \left(T_b - 273\right)^{0.47} \left(M_{eq} \Big/ \left(100 - M_{eq}\right) \right)^{1.58} \right] \tag{9}$$

where T_b is mean temperature of the fluidized bed during drying (K). Furthermore, the minimum fluidization velocity, U_{mf}, for LRC particles are approximated as fluidization velocity for coarse particle with consideration of correction factor for wet coal particles. It can be presented as follows:

$$U_{mf} = \mu_s \left\{ \left[(28.7)^2 + 0.0494 Ar \right]^{1/2} - 28.7 \right\} \Bigg/ \left\{ \rho_s \left[1.182 d_p - 5.65 \times 10^{-4} + \frac{7.413 \times 10^{-2}}{M^{1.58}} \right] \right\} \tag{10}$$

where, μ_s, Ar, ρ_s, d_p, and M are dynamic viscosity of steam (Pa s), Archimedes number (-), steam density (kg m^{-3}), average diameter of LRC particle (m), and moisture content (wt% wb).
Table 1 shows the detailed drying conditions. The flow rate of LRC is 100 t h^{-1}. The heat exchangers are considered as counter current, and the temperature approach during heat exchange is fixed at 10 K. The

ambient temperature and pressure are 25 °C and 101.25 kPa. In this study, the effect of target moisture content to the total required energy input is calculated and compared to one with conventional heat recovery. Three target moisture contents are evaluated: 5, 10 and 15 wt% wb.

Table 1: Drying and gasification conditions

Component	Value
Drying conditions	
Initial moisture content (wt% wb)	60
Mean particle diameter (mm)	1.5
Bulk density (kg m^{-3})	900
Particle density (kg m^{-3})	1,470
Sphericity (-)	0.6
LRC ultimate analysis (wt% db)	
Carbon	64.06
Hydrogen	4.54
Nitrogen	0.26
Oxygen	24.5
Sulphur	0.25
Ash	6.39

4. Results and discussion

The performance of developed drying module is evaluated in term of energy consumption for each target moisture content. In addition, the comparison to the drying which employs a conventional heat recovery is performed. Figure 4(a) shows the total energy consumption of the proposed drying module compared to the conventional one for each target moisture content. The proposed drying module shows significant lower energy consumption up to 1/6 to which required in drying with conventional heat recovery.

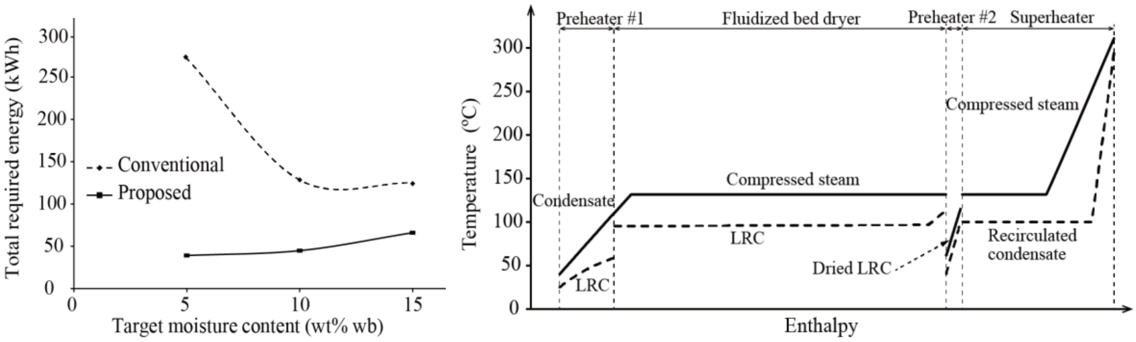


Figure 4: Simulation results: (a) total energy input required for drying in different target moisture contents, (b) temperature-enthalpy diagram of the developed drying module (target moisture content of 10 wt% wb)

Table 2: Detailed simulation results of LRC drying for each target moisture content

Component	Target moisture content		
	5 (wt% wb)	10 (wt% wb)	15 (wt% wb)
Recirculated water (t h^{-1})	5	20	70
Outlet pressure (kPa)	326	283	199
Compressor work (MW)	4.509	4.896	6.293
Blower work (MW)	0.65	0.615	0.606
Total required work (MW)	5.159	5.511	6.569
Preheater #1 duty (MW)	0.294	0.527	0.899
Dryer duty (MW)	2.061	3.236	2.813
Superheater duty (MW)	0.111	0.14	0.209
Preheater #2 duty (MW)	1.918	1.47	5.596
Dried LRC temperature (ºC)	101.1	61.94	66.55

In addition, different to conventional heat recovery-based drying, in the developed drying module the total required energy decreases for lower target moisture content. Lower target moisture content means a larger flow rate of evaporated water from LRC. As the result, more effective heat coupling and recovery, especially in dryer and preheater #1, can be achieved due to better material balance. Drying to lower moisture content can minimize the compression work which is the largest duty in the drying module. On the other hand, drying to higher target moisture content leads to less amount of evaporated. Hence, the heat required for drying is provided by the sensible heat of the compressed steam and recirculated steam. As the result, the compressor works excessively and acts as a heater rather than its main purpose which is elevating the exergy rate of steam for heat coupling.

For each target moisture content, there is an optimum amount of recirculated water used as fluidizing gas to achieve the minimum total required energy. Water recirculation leads to better heat recovery and coupling. A higher target moisture content demands larger flow rate of recirculated water to cover the material balance and also recover the heat of the dried LRC.

Figure 4(b) shows the temperature-enthalpy diagram in the proposed drying module in case of target moisture content of 10 wt% wb. Solid and dotted line represent hot and cold streams. It is clear that almost the heat can be recovered effectively leading to small exergy destruction (hot and cold streams are almost parallel to each other). Generally, the largest amount of heat exchange occurs in the fluidized bed dryer

5. Conclusions

Integrated processes to convert LRC to hydrogen covering drying, gasification, chemical looping, combined cycle, and hydrogenation has been proposed and discussed. EPI consisting of exergy recovery and process integration is adopted to achieve high total energy efficiency of the integrated processes. In addition, detailed evaluation on proposed drying module has been conducted and significantly high energy efficiency can be achieved. Furthermore, it is believed that the proposed integrated processes developed based on EPI can achieve high total energy efficiency.

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