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Efficient Hydrogen Production from Algae and its Conversion to Methylcyclohexane

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Herein, the supercritical water gasification (SCWG) of microalgae combined with syngas chemical looping (SCL) for H_2 production and storage employing liquid organic H_2 carrier (LOHC) system have been proposed and analysed in terms of energy efficiency. Microalgae are converted to syngas in the SCWG module and then introduced into the SCL module to produce high-purity of H_2 and a separated CO_2 stream. H_2 storage is achieved via the hydrogenation reaction using toluene to produce methylcyclohexane (MCH). The heat released from the exothermic hydrogenation reaction is exploited to generate steam for sustaining the SCWG reaction. Simulations were performed using Aspen Plus™ considering the feed concentration and SCWG temperature as the system variables. The simulation results show that the SCWG reaction can be energetically self-sustained using the proposed configuration. Based on the process modelling and calculations, the proposed integrated system exhibited of approximately 13.3 %, 42.5 %, and 55.8 % for power generation, H_2 production, and total energy efficiency.

1. Introduction

Hydrogen (H_2) has been considered as a versatile and environmentally friendly energy carrier for the future. H_2 offers high flexibility because it is easily converted to electricity in fuel cells, has a very high gravimetric energy density (120 MJ/kg), and generates no air pollutants (Zaini et al., 2017). Currently, industrial production of H_2 relies on the fossil fuel feedstocks (Shahlan et al., 2017). The processing of fossil fuels for H_2 production may represent a more efficient route but releases significant amounts of CO_2 in the process. H_2 produced through a range of renewable primary energy sources such as biomass is ideal for gradually replacing fossil fuels.
Among various biomasses, microalgae are a promising alternative energy source due to the fast-growing rate (Aziz, 2016a), require no arable soil, capable of using a variety of different water sources (fresh, brackish, saline, and waste water), and can absorb waste CO_2 as a nutrient (Aziz, 2015). Microalgae can be converted into secondary energy sources, such as H_2, via several conversion routes including pyrolysis, liquefaction, gasification, combustion, and anaerobic digestion. Among conversion methods, gasification is considered as well established, most cost-effective, and efficient for biomass conversion to bioenergy (Sikarwar et al., 2017). Gasification has been considered as a feasible option for producing renewable H_2 in highly efficient and clean large-scale plants (Udomsirichakorn and Salam, 2014).
For converting high-moisture biomass such as microalgae, conventional gasification technologies have low thermal efficiency due to the high-energy requirement for drying. Supercritical water gasification (SCWG) is considered as the most promising method for wet biomass conversion. This process employs water above its critical point (T: 374 °C, P: 221 bar) which in this state, water has a gas-like viscosity and liquid-like density enhancing mass transfer and solvation properties (Basu and Mettanant, 2009).
To obtain high-purity of H_2 from syngas, various routes can be selected, including H_2 separation, conventional steam-reforming processes, and syngas chemical looping (SCL). Membrane separation is relatively simple and low-cost process, yet the H_2 production is not optimum. SCL is high temperature cyclic redox reactions of solid

oxygen carriers between two or more reactors (reducer, combustor, and oxidizer) for the conversion of fuel to generate electricity and/or H_2 (Deshpande et al., 2015). This process has advantages that it can perform various functions conducted in the traditional gasification process such as water-gas shift (WGS), CO_2 separation, and H_2 purification. Thus, the overall energy conversion from syngas to pure H_2 is significantly simplified compared with the traditional process (Fan, 2010). This technology offers a much less energy-intensive method for CO_2 separation compared to the conventional carbon capture and storage (CCS) technology (Lyngfelt et al., 2001).
H_2 has a low energy per unit volume due to the low ambient temperature density which is a challenge for the H_2 storage (Aziz et al., 2016b). Among the available storage technologies, liquid organic H_2 carrier (LOHC) is considered as an excellent method due to its stability, storage capacity, safety, and handling (Aziz, 2016b). In this method, H_2 is fixed to aromatic compounds such as toluene by exothermic hydrogenation reaction to produce methylcyclohexane (MCH).
To date, most studies on microalgae utilization have focused on experimental work, while the design and optimization of the entire process have been relatively less investigated. Several process simulation studies on the conversion of microalgae to H_2 and/or electricity have been previously reported. Yao et al. (Yao et al., 2017) proposed an integrated system including steam gasification, WGS, and pressure swing adsorption for the production of H_2 from biomass. However, no significant effort was devoted to achieving the optimum energy conversion efficiency in that study, and the system was designed for the biomass with relatively low moisture content. Aziz (2015) studied an integrated system, including SCWG, H_2 separation, and combined cycle, for the production of H_2 and power from algae. However, the amount of produced H_2 is very low because the system employs very simple membrane separation without any H_2 enrichment. The integration of SCWG, an SCL, and hydrogenation for MCH production from microalgae is worth to be studied. In the present work, an efficiency evaluation of the H_2 production from microalgae and its conversion to MCH via the proposed routes is investigated to seek the viability of the process.

2. Methodology

2.1 Basic concept of the integrated system

Figure 1 shows the conceptual diagram of the proposed co-production system of MCH and power from microalgae. The integrated system consists of four continuous modules: SCWG, SCL, power generation, and hydrogenation.

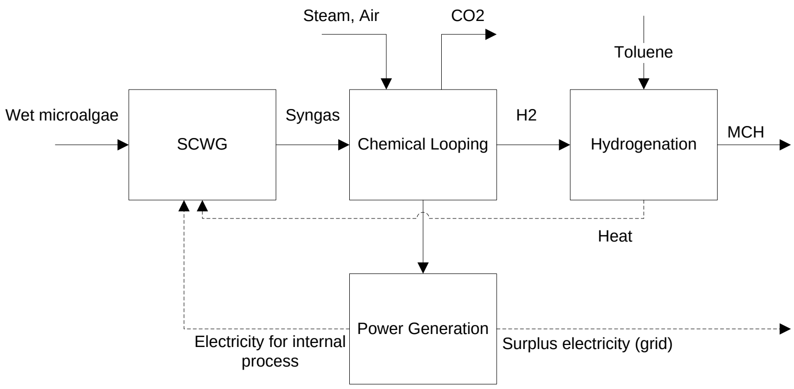

Figure 1: Schematic of the proposed system

The algae slurry with certain moisture content is fed to the SCWG reactor wherein they are converted to syngas. The produced syngas then enters the SCL module. SCL module consists of three reactors: reducer, oxidizer, and combustor. The produced H_2 is going to hydrogenation module for being reacted with toluene producing MCH. The heat generated in SCL and hydrogenation is then recovered for power generation utilizing gas and steam turbines.

2.2 System modeling

Figure 2 shows the detailed process flow diagram of the integrated system.

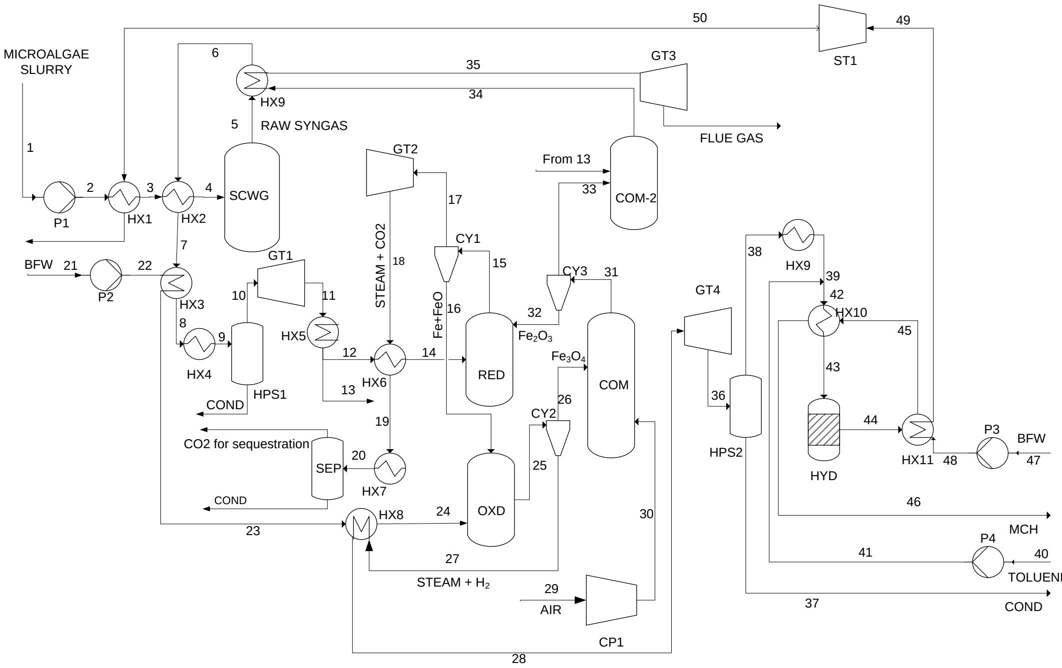

Figure 2: Process flow diagram of the SCWG, SCL, and hydrogenation systems

The simulations are performed in steady-state conditions by using the Aspen Plus™ software package (version 8.8; Aspen Technology, Inc.). The used equations of state are PRMHV2 for the SCWG module and Peng-Robinson for the remaining modules. Using Aspen Plus™, simulations are performed at various algae concentration and SCWG temperature. The selected algae species, operating condition of SCWG, the carbon gas efficiency, and the product gas composition is based on experimental work by Elsayed et al. (2016) (Elsayed et al., 2016). In this study, the mass flow rate of wet microalgae used for producing MCH and power is 1,000 t h^{-1}. Table 2 summarizes the operating conditions and several assumptions used in the simulations.

Table 2: Composition of the selected microalgae (Acutodesmus obliquus) and assumed conditions in each corresponding module

Parameter	Assumption	Ref./Note
Ultimate analysis (wt% db)	C: 54.59; H: 7.37; N: 9.03; S: 0.73; O: 0.02; Cl: 28.3 Ash: 10.0; HHV = 23.3 MJ kg^{-1}	(Elsayed et al., 2016)
SCWG	600 °C, 620°C, 650 °C, 690 °C (Pressure 28 MPa), catalyst K_2CO_3 Carbon gas efficiency: 70.0-96.4 %	(Elsayed et al., 2016)
SCL	Reducer (900 °C, 3 MPa), oxidizer (900 °C, 3 MPa), combustor (1000 °C, 3.2 MPa)	
LOHC system	270 °C, 200 kPa, catalyst Pt/TiO2–SiO2	
Power generation system	Pump, compressor, and expander isentropic efficiency = 85% Max. gas turbine inlet temperature: 1500 °C Max. gas turbine inlet temperature: 600 °C Minimum vapor quality: 0.9	
Heat exchangers	ΔTmin: 10 °C (exc, $\Delta T_{min,HX1}$: 5°C)	

Microalgae slurry is pressurized up to 28 MPa is preheated in HX1 and HX2. The HX1 and HX2 block exchanges the heat from the hot stream exiting the hydrogenation module and SCWG reactor (syngas), respectively. The SCWG reactor is modeled using the Ryield and RGibbs reactors. The Ryield block is required to decompose the algae as a non-conventional solid material into its basic components, simulating a devolatilization process. In the model simulation, a Q-SCWG thermal flux is defined as the net energy from the Ryield reactor and the RGibbs reactor. Q-SCWG represents the value of the energy required to sustain the SCWG reactor. In all cases, Q-SCWG is kept at zero by adjusting the temperature of the preheated feed. In the SCWG reactor, microalgae are mainly converted to syngas containing H_2, CO_2, CH_4, and C_2H_6. The composition of the syngas is taken from the experimental result which depends on the experimental conditions. The produced syngas is heated by the flue gas stream coming from the COM-2. After the heat exchange in HX1, the syngas is cooled and undergo water separation.

The SCL consists of three main reactors, namely, a reducer, an oxidizer, and a combustor. These reactors are modeled using the RGibbs reactor based on the minimization of the Gibbs free energy. Fe-based OCs are selected in this simulation due to their low cost and non-toxic nature; they also show sufficiently high reaction rates as well as good thermal and mechanical properties. Syngas reacts with the iron particles, Fe_2O_3, in the reducer, RED, forming CO_2, Fe, FeO, and moisture Eq(1) to Eq(5). The produced CO_2 and moisture are going to gas turbine, GT2, for expansion and power generation. On the other hand, Fe, FeO and the rest of Fe_2O_3 and alumina 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(6, 7). The produced H_2 and steam are firstly used for preheating the feed steam then flows to the gas turbine, GT4, for additional power generation. Fe_3O_4 particles are flowing to the combustor, COM, for oxidation with oxygen Eq(8). The flue gas is then flowing to COM-2 to react further with a part of syngas (combustion). The flue gas exiting COM-2 has a high temperature (> 1,500 ˚C) which provides sufficient heat exchange required in the SCWG process.

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \quad (1)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (2)$$

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O \quad (3)$$

$$FeO + H_2 \rightarrow Fe + H_2O \quad (4)$$

$$4Fe_2O_3 + 3CH_4 \rightarrow 8Fe + 3CO_2 + 6H_2O \quad (5)$$

$$Fe + H_2O(g) \rightarrow FeO + H_2 \quad (6)$$

$$3FeO + H_2O(g) \rightarrow Fe_3O_4 + H_2 \quad (7)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad . \quad (8)$$

$$C_7H_8 + 3H_2 \rightarrow C_7H_{14} \quad (9)$$

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(9). As hydrogenation is an exothermic reaction, the produced heat can be recovered for superheating the steam for the steam turbine, ST1.

2.3 Performance evaluation

To evaluate the system performance, three energy efficiencies are defined: the H_2 production efficiency η_{H_2}, the power generation efficiency η_{power}, and the total energy efficiency η_{total}. The η_{total} is calculated according to the following equation:

$$\eta_{total} = \eta_{power} + \eta_{H_2} \quad (10)$$

$$\eta_{power} = \frac{W_{net}}{m_{dried\ algae} \cdot HHV_{dried\ algae}} \quad (11)$$

$$\eta_{H_2} = \frac{m_{H_2} \cdot HHV_{H_2}}{m_{dried\ algae} \cdot HHV_{dried\ algae}} \quad (12)$$

$$W_{net} = \sum W_{GT} + \sum W_{ST} - \sum W_{CP} - \sum W_{PM} \quad (13)$$

Here, W_{net} is the net generated power by the system (kW), $m_{dried\ algae}$ is the mass flow of the dried algae (kg/s), $HHV_{dried\ algae}$ is the HHV of the dried algae (kJ/kg), m_{H_2} is the mass flow of H_2 produced in the oxidizer (kg/s), and HHV_{H_2} is the HHV of H_2 (kJ/kg). W represents the generated power or duty (MW), GT is the gas turbine, ST is the steam turbine, CP is the compressor, and PM is the pump.

3. Result and discussion

3.1 Effect of the algae concentration

Based on the experimental work by Elsayed et al. (2016), it was found that at an SCWG temperature of 690 ˚C, complete gasification is not achieved represented by the CGE less than 100 %. The CGE increased from 82.0 to 96.4 % as the algae concentration decrease from 20 to 2.5 wt% dry matter - DM (Elsayed et al., 2016). As the feed concentration increases, the amount of H_2 in the syngas decreases while CH_4 increases accordingly (data not shown). According to the thermodynamics equilibrium, a higher amount of water favors the forward direction of the water-gas shift reaction, increasing the H_2 and CO_2 yields. The equilibrium of the carbon methanation reaction then shifts in the backward direction, increasing the methane gas production.

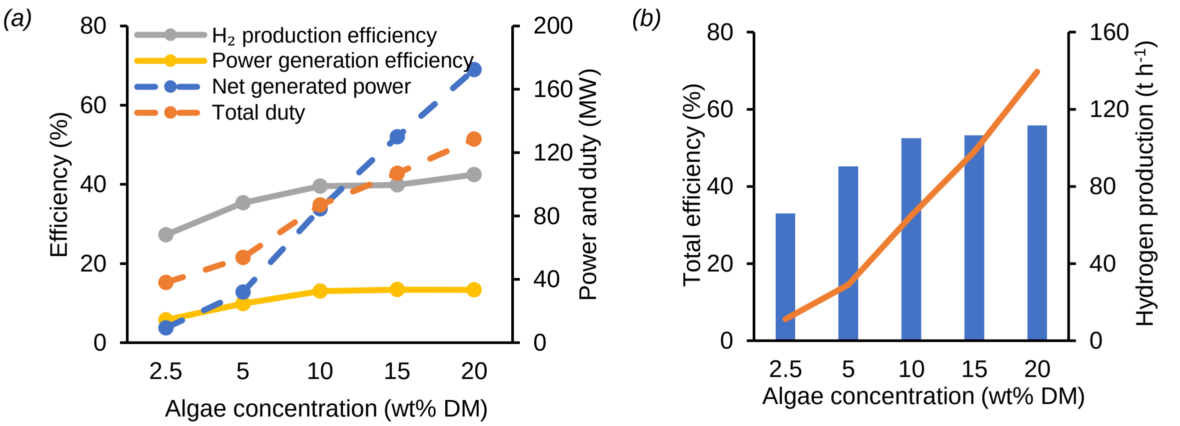

Figure 3: Effect of the algae concentration on a) power, duty, and efficiencies (T_{SCWG} = 690 ˚C), and b) the total efficiency (T_{SCWG} = 690 ˚C)

Figure 3 shows the performance of the system. The net generated power, duty, and power generation efficiency increases as the algae concentration increases. The total efficiency increases from 33 % to 55.8 % when the algae concentration increases from 2.5 to 20 wt%. This phenomenon is mainly resulted from the rise of syngas and H_2 production at a higher algae concentration. Due to the higher syngas flow rate, the generated power in all expanders as well as the duty for compression increases accordingly. At an algae concentration of 20 % and SCWG temperature of 690 ˚C, the system had the highest total efficiency (55.8 %). At this condition, around 0.07 kg H_2/ kg DM is produced and converted to 1.1 kg MCH/ kg DM.

3.2 Effect of the SCWG operating condition

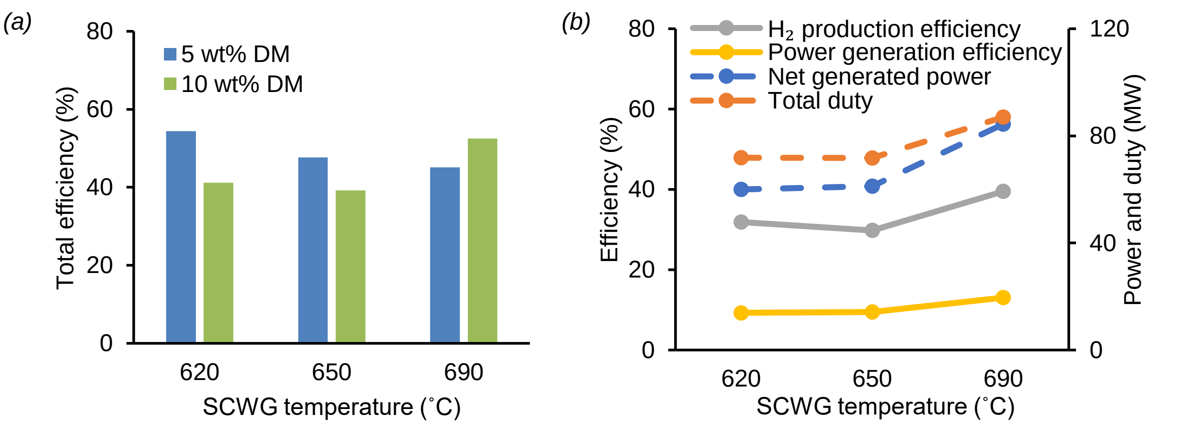

Figure 4: Effect of the temperature on a) total efficiency (T_{SCWG} = 690 ˚C), and b) power, duty, and efficiency (T_{SCWG} = 690 ˚C, 10 % DM)

Figure 4 shows the dependence of the efficiency on the SCWG temperature and algae concentration. It can be seen that at a lower temperature, a lower algae concentration is more favorable to achieve higher efficiency (54.4 %). At 5 wt% DM, the total efficiency decreases as the temperature increases. An increase in temperature and algae concentration lead to a rise in the reaction heat duty which give an impact on efficiency. However, at 10 wt% DM, the highest SCWG temperature gives higher efficiency value. This phenomenon can be explained by two related parameters: the SCWG heat requirement and the calorific value (CV) of the produced syngas. To cover the SCWG heat duty, the syngas is partly combusted at COM-2 to provide additional heat required which finally reduces the syngas flow to the SCL module. In addition, at a higher temperature, the H_2 content in the syngas reduces while methane content increases. It is known that the energy density of methane is higher than H_2. Therefore, CV of syngas is influenced by temperature and algae concentration. The syngas produced at 690 ˚C and 10 wt% DM has the highest CV. The SCWG heat duty and CV of syngas, both influence on the amount of syngas need to be combusted which finally influences the power, duty, and efficiencies.

4. Conclusions

An integrated system for co-production of MCH and power from microalgae has been well developed with the aim to evaluate the total energy efficiency. SCWG operated around 600–690 °C with the algae concentration less than 20 wt% can be energetically sustained with the need to combust certain amount of the produced syngas. Considering the use of high moisture content microalgae as the feedstock, the proposed system offers relatively high efficiency and an environmentally friendly energy production route which makes the production of H_2 from microalgae more likely to be developed.

Acknowledgments

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