

# Highly Energy-Efficient Combination of Dehydrogenation of Methylcyclohexane and Hydrogen-Based Power Generation

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Hydrogen, H<sub>2</sub>, has been well known as one of potential energy storages in utilization of renewable energy with its intermittent characteristic. However, H<sub>2</sub>, which is in gas phase at standard pressure and temperature, has challenging problem of storage, transportation, and low volumetric energy density. As one of the solution, H<sub>2</sub> storage in (C<sub>7</sub>H<sub>8</sub>)/methylcyclohexane (MCH, C<sub>7</sub>H<sub>14</sub>) cycle is one of the effective and reversible methods. In this study, an integrated power generation cycle is investigated, including the the dehydrogenation process and the combined cycle power generation. Comprehensive analysis on heat circulation was performed through an enhanced process integration to ensure the high energy-efficiency system. Thermal energy required for highly endothermic dehydrogenation reaction was supplied from air-fuel combustion to ensure the effective heat recovery of the system. The performance of proposed system is compared to the Graz cycle-based system, one of the cycle of power generation cycle from H<sub>2</sub>. The comparison result shows that the proposed integrated system has a significantly higher power-generating efficiency. Additionally, with dehydrogenation included in the system, the proposed system showed a system efficiency of 53.7 %, compared with the Graz cycle based system at 22.7 % under the same operating condition.

## 1. Introduction

Despite increasing trends of renewable energy utilization in many countries, there are several challenges related to the power grid operation, including intermittent output and mismatch between supply and demand (Mitani et al., 2017), resulting in the grid instability and wasted energy during oversupply period (Quan et al., 2015). Chemical storage of electrical energy has been widely studied and applied, such as batteries, CH<sub>4</sub>, and H<sub>2</sub>. Among those chemical storages, H<sub>2</sub> has the best ratio of valence electron to the protons, therefore, the energy gain per electron is very high (Schlapbach et al., 2001). Moreover, number of studies on H<sub>2</sub> production methods have been reported, such as decarbonization of fossil fuels and conversion of biomasses (Zaini et al., 2017). The specific chemical energy of H<sub>2</sub> (142 MJ kg<sup>-1</sup>) is at significantly higher than that of gasoline (44 MJ kg<sup>-1</sup>) (Schlapbach et al., 2001). H<sub>2</sub> is one of the most abundant element on earth, and it has high potential as the energy storage or energy carrier, therefore, the role of H<sub>2</sub> is believed to increase in the future (Gong et al., 2017). However, H<sub>2</sub> is in gas phase at standard pressure and temperature, which has challenging problem of storage and transportation, due to the low volumetric energy density, which is only 3 Wh/L (Aziz et al., 2016). H<sub>2</sub> storage by compression is one of the basic technology to increase the volumetric energy density (Graetz, 2009). H<sub>2</sub> gas is compressed up to 200–450 bar in high-pressure tanks. However, high-pressure compression has safety risk of pressurized H<sub>2</sub> and requires additional pressure control during depressurization process. Liquefaction is another method of H<sub>2</sub> storage by condensing the gas to liquid (Baker et al., 1978) or even solid phase (Bracha et al., 1994). However, due to the intrinsic property of H<sub>2</sub>, which has very low condensation temperature (-252 °C at 1 bar), high energy input is required for cryogenic technology.

Number of studies have been reported on chemical storage of H<sub>2</sub> (Aziz et al., 2017). Chemical storage of H<sub>2</sub> can be applied by binding H<sub>2</sub> to produce H<sub>2</sub>-rich molecules in a hydrogenation reaction (Preuster et al., 2017). The sustainable cycle of H<sub>2</sub> storage system, requires at two processes of hydrogenation and dehydrogenation. Numerous molecules are applicable in H<sub>2</sub> chemical storage, which can be categorized into: (1) natural H<sub>2</sub>-lean molecules that can be extracted from an exhaust gas mixture such as CO<sub>2</sub> or N<sub>2</sub>, and (2) a H<sub>2</sub>-lean organic

liquid, known as liquid organic H<sub>2</sub> storage (LOHC), which allows a fully reversible cycle of hydrogenation/dehydrogenation. Among available LOHCs, toluene (C<sub>7</sub>H<sub>8</sub>)/methylcyclohexane (MCH, C<sub>7</sub>H<sub>14</sub>) cycle has been evaluated and demonstrated well (Aziz et al., 2015). H<sub>2</sub> gas is bonded to toluene molecules through hydrogenation process with liquid MCH as the product of the reaction (Li et al., 2013). High boiling point of MCH allows wide range of storage condition under liquid phase for easier transportation and storage. In addition, MCH has high H<sub>2</sub> content up to 6–8 wt%, or 60–62 kg m<sup>-3</sup> (volume based under ambient condition) (Hatim et al., 2013). Toluene has been widely produced and utilized industrially, providing low cost material for large scale process (Hatim et al., 2013). In industrial scale, the large-scale H<sub>2</sub> storage and delivery system has been constructed by Chiyoda Corporation in 2013 (Okada et al., 2013). Therefore, toluene-MCH cycle is theoretically promising as H<sub>2</sub> carrier, and practically applicable in industrial scale.

H<sub>2</sub> is firstly separated from toluene through dehydrogenation process, before converted to electrical energy through thermal power generation (combined cycle) or chemical energy (fuel cell). Scherer et al. (1998) developed a seasonal electricity generation from MCH by employing solid oxide fuel cells (SOFC). However, SOFC, despite exhibiting high energy efficiency, has very fragile characteristics due to the reformation-based H<sub>2</sub> used for the fuel. According to the studies, inability to provide large power output is one of have a common challenging factor of have a common challenging factor of fuel cell (Turco et al., 2016). Number of cycles for thermal power generation of H<sub>2</sub> were investigated and achieved 60 % of energy efficiency (Milewski, 2015). Among these cycles, Graz cycle has been developed furthermore with net efficiency above 65 % (Sanz et al., 2016). However, most of combined cycles, including Graz cycle, employ pure O<sub>2</sub>, resulting in additional utilities and energy consumed for O<sub>2</sub> separation from the air, leading to high cost plant and efficiency drop to nearly 61 % (Sanz et al., 2016). Moreover, the above studies assumed that the H<sub>2</sub> feed is in the pure phase, which is very difficult in real operation. Regarding the large scale production of MCH, Aziz et al. (2017) delivered novel integrated concepts of large-scale MCH production from low-rank coal and brown coal by applying a chemical looping and hydrogenation using toluene. The delivered concepts achieved high values of H<sub>2</sub> production while maintaining clean technology to the environment.

In this study, the concept of electricity generation plant is proposed, including the dehydrogenation and combined cycle power generation. Dehydrogenation of MCH is integrated with hydro-fuel combined cycle, which employs ambient air for combustion. Therefore, the proposed system is more realistic with comprehensive energy balance analysis of the cycle. Adequate analysis of the heat circulation is performed by employing enhanced process integration (EPI) to ensure high energy efficiency of the proposed system (Darmawan et al., 2017).

## 2. Methodology

### 2.1 Conceptual model

Figure 1 shows the conceptual diagram of the proposed integrated-system. The system consists of three combined modules: MCH dehydrogenation, H<sub>2</sub> combustion, and combined cycle power generation. The solid, dotted, and dashed line represent the material, heat, and electricity flows, respectively. MCH for dehydrogenation process is supplied from the hydrogenation plant. Thermal energy for highly endothermic dehydrogenation process is supplied mainly from recovered heat through pre-heating and fuel gas from combustion module before it is converted to electrical energy through combined cycle module.

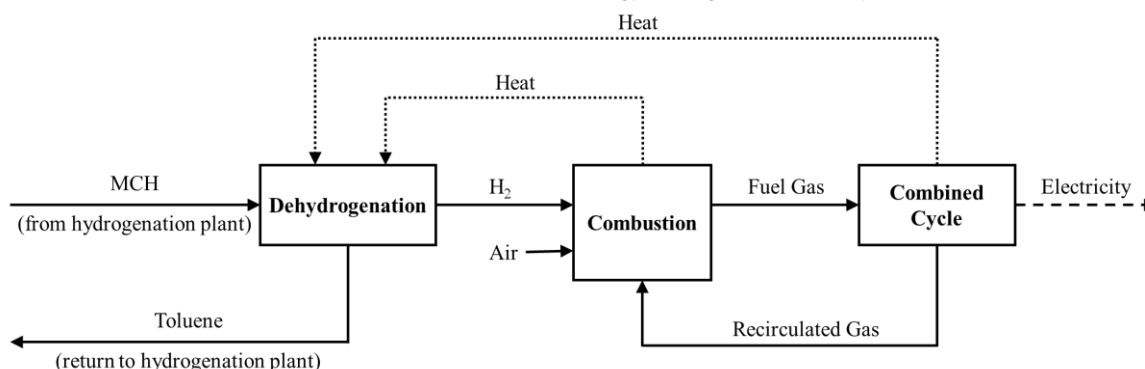


Figure 1: Conceptual diagram of proposed integrated system

## 2.2 Detailed system

The proposed system is evaluated by theoretical calculation and software modeling using Aspen HYSYS ver. 8.8 (Aspen Technology, Inc.). To establish the model of the system, the following additional assumptions are employed for simulation:

- (i) The rated flow rate of MCH is  $100 \text{ t h}^{-1}$ .
- (ii) Heat exchangers, including HRSG, are a counter-flow type.
- (iii) The ambient pressure and temperature are 101.33 kPa and  $25 \text{ }^\circ\text{C}$ , respectively.
- (iv) The kinetic and potential energy losses are negligible.
- (v) Air consists of 79 mol%  $\text{N}_2$  and 21 mol%  $\text{O}_2$ .
- (vi) The adiabatic efficiency of the pump and compressor is 90 %.
- (vii) The pressure drop in the heat exchanger is 2 %.
- (viii) The minimum approach temperature in the heat exchanger is  $10 \text{ }^\circ\text{C}$ .
- (ix) There are no external heat losses.

Dehydrogenation module employs packed bed reactor with catalyst to improve the following reaction.



Among various hydrogenation catalysts, number of studies have been reported on Pt catalyst with both theoretically and experimentally demonstrated that  $\text{Pt}/\text{Al}_2\text{O}_3$  is considered the best catalysts for MCH dehydrogenation (Alhumaidan et al., 2011) in terms of activity, selectivity, and stability (Li et al., 2013). Thermal energy required for dehydrogenation is supplied through self-heat exchange between the cold stream (process stream, F3) and hot stream (combustion flue gas, F9). Toluene, as  $\text{H}_2$  carrier, is returned to hydrogenation plant (F17) for another cycle.

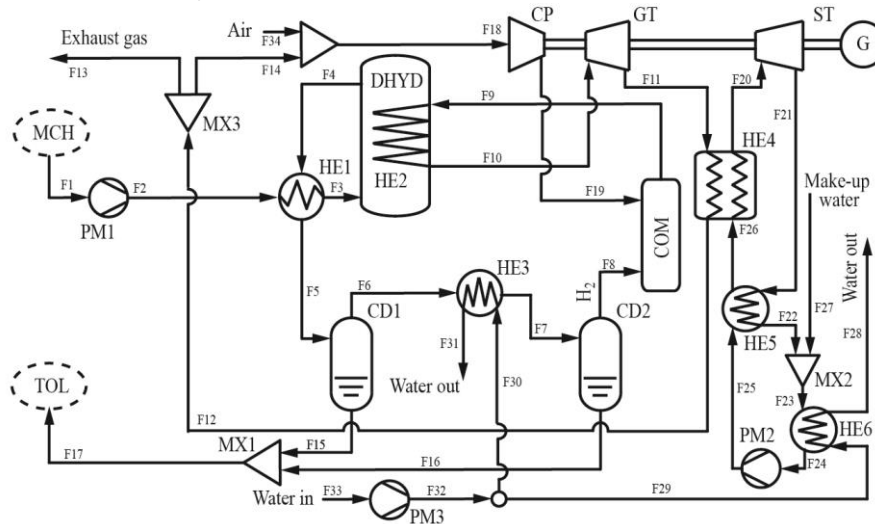
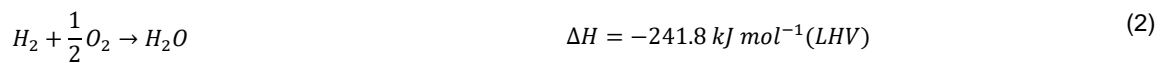


Figure 2: Arrangement and process flow diagram of the proposed integrated-system

$\text{H}_2$  is converted to the thermal energy in combustion chamber by combustion reaction with  $\text{O}_2$  (included in air). The hydro-fuel combustion reaction is a carbon-free reaction, therefore, there is no emission of carbon dioxide ( $\text{CO}_2$ ), as shown in reaction Eq. (2). After dehydrogenation, gaseous  $\text{H}_2$  and liquid toluene is separated in separators (CD1, CD2) and cooled by water cooling (F30). Due to extremely different boiling temperature,  $\text{H}_2$  is discharged in the gas phase, while Toluene is discharged in the liquid phase. However, there are small portion of toluene in gas phase remains and mixed with  $\text{H}_2$ , flow into combustion chamber. Therefore, very small portion of  $\text{CO}_2$  production may occur, as shown in reaction, Eq. (3).



Combined cycle consists of three main components: gas turbine (GT), steam turbine (ST), and heat recovery steam generator (HRSG). Table 1 summarizes the conditions and assumptions for each module of dehydrogenation and combined cycle.

In this study, the combined cycle is employed with the flue gas and steam from HRSG (F14) is partially returned to the combustion chamber for cooling, as well as to improve the energy density owing to the high heat capacity of water. Graz cycle utilizes high-pressure steam from a high-pressure steam turbine for combustion chamber cooling (Sanz et al. 2004; 2016). However, in this study, the gas and steam exhausted from the HRSG outlet is used instead of high-pressure steam, leaving the steam expansion process in the ST for optimum electrical generation. Effective cooling in combustion chamber can be achieved due to the lower temperature at HRSG outlet.

Table 1: Assumed conditions for each module of dehydrogenation and combined cycle.

Parameter	Value	Symbol (refer to Fig. 2)
<i>Dehydrogenation (DHYD)</i>		
Reactor temperature (°C)	450	F4
Internal pressure (kPa)	120–150	DHYD
Catalyst	Pt/Al <sub>2</sub> O <sub>3</sub>	-
Minimum toluene discharge ratio	90 %	F17
<i>Power generation – Gas turbine (GT)</i>		
Isentropic efficiency (%)	90	-
Inlet temperature (°C)	1400–1600	F11
Inlet pressure (MPa)	2.8–4.0	F11
<i>Power generation – Steam turbine (ST)</i>		
Isentropic efficiency (%)	90	-
Inlet pressure (MPa)	10	F20
Steam turbine inlet temperature (°C)	522–581	F20
Minimum vapor quality	0.9	-

### 3. Result and discussion

Performance of the proposed integrated-system is evaluated by determining the system efficiency ( $\eta_{\text{system}}$ ) and power generation efficiency as follows:

$$\eta_{\text{system}}[\%] = \frac{W_{\text{net}}[\text{MW}]}{(\dot{m}_{\text{MCH}}[\text{kg}/\text{h}] \times \text{LHV}_{\text{MCH}}[\text{MWh}/\text{kg}] - \dot{m}_{\text{Toluene}}[\text{kg}/\text{h}] \times \text{LHV}_{\text{Toluene}}[\text{MWh}/\text{kg}])} \quad (4)$$

$$\eta_{\text{power}}[\%] = \frac{W_{\text{net}}[\text{MW}]}{(\dot{m}_{\text{H}_2}[\text{kg}/\text{h}] \times \text{LHV}_{\text{H}_2}[\text{MJ}/\text{kg}])} \quad (5)$$

where  $\dot{m}_{\text{MCH}}$ ,  $\dot{m}_{\text{Toluene}}$ ,  $\dot{m}_{\text{H}_2}$ ,  $\text{LHV}_{\text{MCH}}$ ,  $\text{LHV}_{\text{Toluene}}$ , and  $\text{LHV}_{\text{H}_2}$  are mass flow rate and LHV of MCH, toluene, and H<sub>2</sub>, respectively. Net power ( $W_{\text{net}}$ ) is calculated based on the total power generated by GT ( $W_{\text{GT}}$ ) and ST ( $W_{\text{ST}}$ ) with consideration of power consumed by auxiliaries ( $W_{\text{Aux}}$ ), shown as follows:

$$W_{\text{net}}[\text{MW}] = W_{\text{GT}}[\text{MW}] + W_{\text{ST}}[\text{MW}] - W_{\text{Aux}}[\text{MW}] \quad (6)$$

#### 3.1 Performance comparison with Graz cycle-based power generation

System performance of the proposed integrated system is compared with the Graz cycle, which is equipped with dehydrogenation process for comprehensive analysis. Table 2 shows the main parameters of each system for details performance. The dehydrogenation process in the Graz cycle-based system is calculated through a stoichiometric reaction shown in Equation (1). Moreover, the energy required for the endothermic reaction of dehydrogenation was calculated under the assumption that the dehydrogenation system was designed based on conventional heat recovery technology for minimum exergy loss. The amount of MCH and toluene are calculated based on the H<sub>2</sub> mass flow rate, with a toluene discharge ratio of 0.9. Additional power consumption of 24.3 MW is required for O<sub>2</sub> separation in air separation unit (ASU) and compression process. Therefore, additional power consumption of 24.3 MW is supplied from the generated power. The proposed system utilizes air-combustion, eliminating the requirement of ASU and additional compression system.

Table 2: Main parameters and integrated system performance comparison of Graz cycle based system (Sanz et al., 2016) and proposed integrated-system

	Graz cycle-based system	Proposed system	Unit
Combustor outlet temperature	1,500	1,722	°C
GT inlet temperature	1,500	1,500	°C
GT inlet pressure	4	4	MPa
ST inlet pressure	17	20	MPa
Condenser pressure	0.0025	0.035	MPa
Minimum steam quality	0.893	0.9	
GT power output	231.8	235.4	MW
ST power output	52.2	41.7	MW
Auxiliary power (pumps, etc.)	78.6	146.4	MW
ASU+O <sub>2</sub> compression	24.3	0 <sup>a</sup>	MW
Net power	205.4	130.7	MW
Hydrogen LHV	120	120	MJ/kg
Hydrogen mass flow	2.5	1.71	kg/s
Power generation efficiency	60.37 %	63.7 %	
<i>Dehydrogenation</i>			
MCH mass flow	147,000	100,000	kg/h
MCH LHV	43.38	43.38	MJ/kg
Toluene mass flow	124,150.5	85,170	kg/h
Toluene LHV	40.59	40.59	MJ/kg
Energy required for dehydrogenation	99.87 <sup>b</sup>	0 <sup>b</sup>	MW

<sup>a</sup> ASU and O<sub>2</sub> is not required, due to air-fuel combustion type in the proposed model

<sup>b</sup> Dehydrogenation process for Graz cycle was calculated based on stoichiometric reaction, with conservative heat recovery system

The integrated system proposed in this study shows a  $\eta_{power}$  of 63.7 %, compared to the Graz cycle-based system with a  $\eta_{power}$  of 60.37 %. This implies that an air–fuel combustion cycle is more efficient than an oxy–fuel combustion cycle due to the excessive power consumption of ASU. In addition, air–fuel combustion has been well applied in a typical combined cycle plant with fewer components, providing a low initial power plant cost. In terms of system efficiency ( $\eta_{system}$ ), the proposed integrated system has a significantly higher efficiency of 53.7 % compared to the Graz cycle-based system, at 23 %. Extensive energy demand for dehydrogenation reduce the system performance significantly. In addition, in the proposed integrated-system, the hot flue gas after combustion (F9) has a higher temperature (1,722 °C) than that of the Graz cycle-based system (1,500 °C). High-temperature gas is used as the thermal energy source for a reaction, reducing the exergy loss from the system, and thereby increasing the overall system efficiency.

#### 4. Conclusion

An integrated system of dehydrogenation and power generation process is proposed to gain energy from chemically bonded H<sub>2</sub> in MCH. MCH/toluene has been well reported as promising H<sub>2</sub> storage system and practically applied in industrial scale. Highly endothermic dehydrogenation reaction is covered by the thermal energy generated from air-fuel combustion of H<sub>2</sub>. Moreover, the remaining heat is supplied to the combined cycle plant, optimized with EPI to reduce the exergy loss, leading to highly-efficient system.

The comparison between the proposed integrated-system and Graz cycle based system is carried out to evaluate the overall system performance. The results show that the proposed integrated-system can provide energy for dehydrogenation process while maintaining highly efficient combined cycle as power generation system. Power generation efficiency of the proposed integrated-system is higher than of Graz cycle based system, mainly due to air-fuel combustion, which requires less energy and less component. With a higher combustion temperature and heat recovery optimization, the proposed integrated system has a significantly high system efficiency of 53.7 %, compared to that of the Graz cycle based-system, at 23 %.

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