Techno-Economic Analysis of Hydrogen Production from Dehydrogenation and Steam Reforming of Ethanol for Carbon Dioxide Conversion to Methanol

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การวิเคราะห์เชิงเทคนิคและเศรษฐศาสตร์ของกระบวนการผลิตไฮโดรเจนจากดีไฮโดรจีเนชั่นและรีฟอร์มมิ่งด้วยไอน้ำของเอทานอลเพื่อการเปลี่ยนคาร์บอนไดออกไซด์ให้เป็นเมทานอล

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ในการลดการปลดปล่อยคาร์บอนไดออกไซด์โดยการเปลี่ยนเป็นผลิตภัณฑ์ที่มีมูลค่าต่างๆ ถูกให้ความสนใจ ซึ่งในงานวิจัยฉบับนี้สนใจการลดการปลดปล่อยคาร์บอนไดออกไซด์ไปเป็นเมทานอล โดยไฮโดรเจนจึงเป็นสาระสำคัญในการเปลี่ยนคาร์บอนไดออกไซด์เป็นเมทานอล ทำให้ราคาและกระบวนการผลิตของไฮโดรเจนจะส่งผลต่อการเปลี่ยนคาร์บอนไดออกไซด์เป็นเมทานอล ดังนั้นงานวิจัยฉบับนี้จะศึกษาในส่วนของกระบวนการผลิตไฮโดรเจนจากเอทานอล โดยทำการเปรียบเทียบกระบวนการผลิตไฮโดรเจนจากรีฟอร์มมิ่งด้วยไอน้ำของเอทานอล และดีไฮโดรจิเนชั่นของเอทานอลที่ได้ผลิตภัณฑ์ที่มีมูลค่าสูง ประกอบด้วยเอทิลอะซิเตทและอะเซตัลดีไฮด์ จากงานวิจัยนี้พบว่ารีฟอร์มมิ่งด้วยไอน้ำของเอทานอลมีราคาของไฮโดรเจนที่ผลิตจากกระบวนการนี้ถูกที่สุดเท่ากับ 1.90 ดอลลาร์ต่อกิโลกรัมของไฮโดรเจน ในขณะที่ราคาของไฮโดรเจนจากกระบวนการดีไฮโดรจิเนชั่นของเอทานอลเป็นเอทิลอะซิเตท และกระบวนการดีไฮโดรจิเนชั่นของเอทานอลเป็นอะเซตัลดีไฮด์ เท่ากับ 3.57 และ 3.40 ดอลลาร์ต่อกิโลกรัมของไฮโดรเจน ตามลำดับ ถึงแม้ว่าราคาของไฮโดรเจนจากกระบวนการรีฟอร์มมิ่งด้วยไอน้ำของเอทานอลมีราคาถูกที่สุดจากทั้ง 3 กระบวนการแต่เมื่อพิจารณาจากผลรวมของการปลดปล่อยคาร์บอนไดออกไซด์ของทั้งกระบวนการผลิตไฮโดรเจนและกระบวนการเปลี่ยนคาร์บอนไดออกไซด์เป็นเมทานอลยังแสดงผลรวมเป็นบวก ตรงกันข้ามกับกระบวนการดีไฮโดรจิเนชั่นของเอทานอลเป็นเอทิลอะซิเตท และกระบวนการดีไฮโดรจิเนชั่นของเอทานอลเป็นอะเซตัลดีไฮด์ที่แสดงผลรวมของการปลดปล่อยคาร์บอนไดออกไซด์เป็นลบเท่ากับ -253.33 กิโลกรัมต่อตันของเมทานอล และ -5.55 กิโลกรัมต่อตันของเมทานอล ตามลำดับ ในงานวิจัยนี้จึงสรุปได้ว่าผลรวมของการปลดปล่อยคาร์บอนไดออกไซด์จะมีค่าลดลง เมื่อราคาของไฮโดรเจนมีราคาที่สูงขึ้น

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Decreasing carbon dioxide (CO_2) emission by converting to higher-valued product has become of interest. Hydrogen (H_2) is an important feedstock required in thermochemical conversion of CO_2 to chemicals such as methanol. The cost and availability of H_2 affect the cost of CO_2 conversion. This study is focused on the process simulation of H_2 production from ethanol feedstock. Steam reforming of ethanol is compared with dehydrogenation of ethanol to H_2 with valued products including ethyl acetate and acetaldehyde. Form this study, steam reforming of ethanol presents the lowest cost of H_2 production at 1.90 USD/kg H_2 while dehydrogenation of ethanol presents the cost at 3.57 and 3.40 USD/kg H_2, respectively. Although presenting the lowest cost, steam reforming of ethanol provides a net positive CO_2 emission in the overall CO_2 conversion to methanol process. In contrast, ethanol dehydrogenation to H_2 and byproducts, ethyl acetate and acetaldehyde, promotes a net negative CO_2 emission of -253.33 kg/ton methanol and -5.55 kg /ton methanol, respectively. The results present a decreasing CO_2 emission with an increasing cost of H_2 production.

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CHAPTER 1

Introduction

1.1 Research background

Nowadays, carbon dioxide (CO_2) emission is the main factor affecting the environment because CO_2 emissions from industrial activities and the burning of fossil fuels will pump an estimated 36.8 billion metric tons of carbon dioxide into the atmosphere. And total carbon emissions from all human activities, including agriculture and land use, will likely cap off at about 43.1 billion tons in 2019 [1, 2]. Therefore, mitigation of carbon dioxide (CO_2) emission has been a worldwide concern due to CO_2 emissions is a key contributing factor to the high emissions of green-house gases (GHG) globally. The report was presented that 76.7% of GHG emissions emanate from emissions of CO_2 [3-5].

The decreasing of CO_2 emission into the atmosphere is arguably the most challenging. One of the strategies for minimizing anthropogenic CO_2 emission is utilization or conversion of CO_2 [6]. The CO_2 utilization as a raw material in the synthesis of the important chemicals such as synthesis of cyclic carbonate from CO_2 and epoxide, reaction of CO_2 and propylene glycol, CO_2 dehydrogenation to methanol [7, 8].

Methanol is a versatile chemical. It is important intermediate in manufacturing many other chemicals such as formaldehyde and acetic acid, both of which are important feed stocks for the polymer industry [9, 10]. Moreover, methanol can be converted into dimethyl ether (DME) which serves as a replacement for liquefied petroleum gas (LPG) or compressed natural gas (CNG) [11-14]. However, for each ton of methanol produced from syngas generates 0.6 -1 tons of CO_2. CO_2 can react with hydrogen (H_2) to form methanol [15]. Therefore, conversion of CO_2 into methanol can be a promising way to mitigate CO_2 emission. For conventional H_2 production, steam reforming of methane, which is non-renewable source, is the most widely used technique and covers over 50% of the world's H_2 production. Steam reforming of methane requires high operating temperatures (700-1100 °C) and still promotes CO_2 emission [16-19]. Therefore, H_2 source and availability is one among barriers of CO_2 conversion. For CO_2 conversion to higher-valued produce, H_2 must be obtained from renewable sources. This H_2 is normally relatively more expensive. It was reported that the H_2 fed methanol production from CO_2 plant is still uneconomically feasible [16, 20]. Therefore, the renewable sources were considered for H_2 production. Bio-based chemicals *e.g.* bioethanol as renewable source for H_2 production process has become interesting. The use of ethanol for this purpose represents an opportunity to produce H_2 from renewable sources.

Bioethanol takes the widest slice of the production of biofuels worldwide. It is derived from the fermentation of polysaccharides, obtained from the processing of certain agricultural products, almost exclusively from sugar cane and corn [21]. In 2018, bioethanol is becoming over supply in Thailand. Ethanol consumption growth is expected to slow down due to increasing of electricity's involvement in the transport. To maintain bioethanol consumption, bioethanol can be used to produce H_2 through ethanol steam reforming process [22, 23].

The steam reforming of ethanol:

$$C_2H_5OH + 3H_2O \leftrightarrow 6H_2 + 2CO_2 \qquad \Delta H_0 = +174 \text{ kJ/mol} \qquad (1)$$

As presented in Eq. (1), although steam reforming of ethanol generates CO_2, it was reported that biomass energy and carbon capture and storage (CSS) lead to a net removal of atmospheric CO_2 [23, 24]. Alternative to steam reforming of ethanol was ethanol dehydrogenation for H_2 production. Dehydrogenation of ethanol not only generates H_2 without CO_2 emission but also ethyl acetate or acetaldehyde [25, 26], which are valued chemicals, as presented in Eqs. (2)-(3) respectively.

The dehydrogenation of ethanol to acetaldehyde:

$$C_2H_5OH \longrightarrow CH_3CHO + H_2 \qquad \Delta H_0 = +16.45 \text{ kcal/mol} \qquad (2)$$

The dehydrogenation of ethanol to ethyl acetate:

$$2C_2H_5OH \longrightarrow CH_3COOCH_2CH_3 + 2H_2 \qquad \Delta H_0 = +5.98 \text{ kcal/mol} \qquad (3)$$

In this study, different methods of hydrogen productions from ethanol for supplying to methanol plants. Steam reforming of ethanol is compared with dehydrogenation of ethanol. Techno-economic analysis of the H_2 production process combined methanol production process is carried out in term of H_2 productivity, net CO_2 emission, energy consumption and cost. Capital investment and operating cost are estimated as well as process profitability index is reported.

The study was based on the amount of H_2 available to convert CO_2 to methanol on conventional process of methanol synthesis.

1.2 Research objective

To compare H_2 production from ethanol processes in terms of process performance and cost analysis.

1.3 Research scopes

1.3.1 A comparative study on hydrogen production processes between ethanol steam reforming reaction and ethanol dehydrogenation reaction was performed using Aspen PLUS V10.

1.3.2 The H_2 production from ethanol processes is divided into 3 cases:

- Ethanol steam reforming (Case I)
- Ethanol dehydrogenation to ethyl acetate (Case II)
- Ethanol dehydrogenation to acetaldehyde (Case III)

1.3.3 The capacity of the H_2 synthesis unit is based on the amount of H_2 (approximately 1,665.47 t/y) which is available for CO_2 conversion to methanol in conventional process of methanol synthesis (7,427 t/y methanol productivity based on medium scale methanol production). This capacity is correlated to the work of *Khunathorncharoenwong et al.* [27].

1.3.4 The process performance is reported in term of H_2 productivity, net CO_2 emission, and energy consumption, respectively.

1.3.5 The process cost analysis is reported in term of fixed capital investment and manufacturing cost of the process.

CHAPTER 2

Theory and literature review

2.1 Process for H_2 production

Hydrogen (H_2) is a flammable, odorless, tasteless, colorless and very clean chemical fuel. The H_2 is an energy carrier in the stationary power, transportation, industrial, and commercial chemical for conversion with other chemicals to value products [19]. The global demand of H_2 energy has been grown in 2020 with 8% of global energy demand (GED). The demand of H_2 being widely used for 51% of ammonia production, 31% of oil refining, 10% of methanol production and 8% of other uses [28] as shown in Figure 2.1.

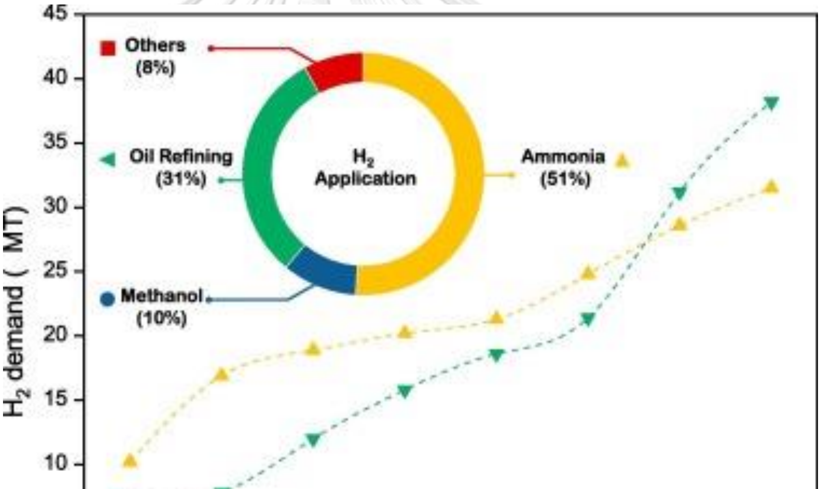

Figure 2.1 Demand of H_2 with share on various applications [28]

The H_2 economy can help the significantly reduce greenhouse gases emission if H_2 is produced from renewable energy resources [29, 30]. Although H_2 can be generated from both renewable energy and non-renewable source as shown in Figure 2.2. At present, the largest market for H_2 production process is in the refining of petroleum from using the current steam methane reforming (SMR) as non-renewable source. Even though the H_2 can be produced from various technologies [18]. Currently, the major H_2 production processes are steam methane reforming and electrolysis. On the other hand, the other technologies are developed as new methods from alternative renewable energy resources to be a long term solution to reduce a major source of greenhouse gases emission (i.e. CO_2, CH_4 and CO) which affect climate change and global warming [31]. Up to date, Department of Energy (DOE) is focused on developing H_2 production methods from renewable energy sources with significantly reduce greenhouse gases emission aiming to produce H_2 at the target cost of <4 USD/kg of H_2 [32] while conventional methods retain their dominant role in H_2 production with costs in the range of 1.34–2.27 USD/kg of H_2 [33].

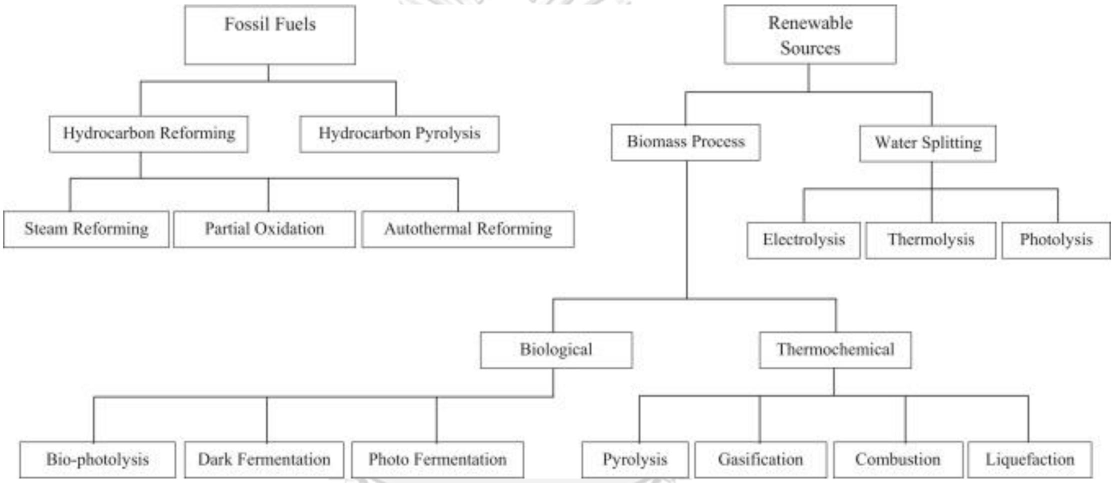

Figure 2.2 H_2 production methods [33]

The major of conventional technology which is steam reforming of methane for H_2 production as a hydrocarbon reforming as shown in figure 2.3.

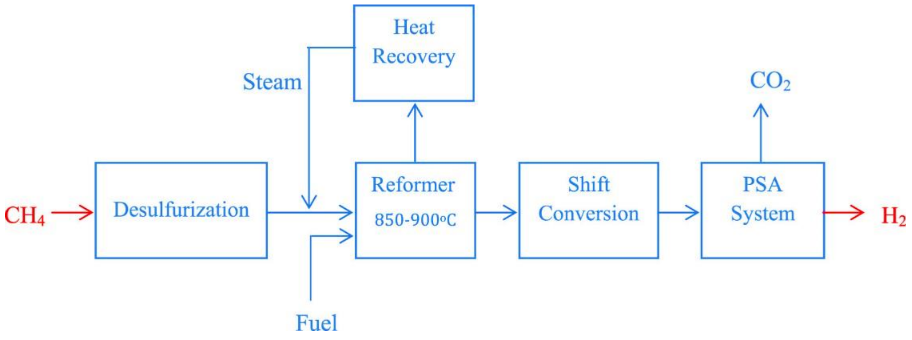

Figure 2.3 Steam reforming of methane to H_2 production [33]

This process involves a catalytic conversion to H_2 and CO_2 and consist of 2 main reactions as shown in Eqs.(4)-(5) of steam reforming and water gas shift.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_0 = +203 \text{ kJ/mol} \qquad (4)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_0 = -41.2 \text{ kJ/mol} \qquad (5)$$

The steam reforming of methane requires high operating temperature (at 850-900 ℃). After steam reformer, the mixed gas fed into a water gas shift reactor due to CO out of the steam reforming reaction reacts with steam to H_2 addition [33]. For purification of H_2, the residual CO and CO_2 in the H_2 stream fed into a CO_2 removal and methanation, or into a pressure swing adsorption. The H_2 purity is approximately 97-98% [34] .

Table 2.1 Various H_2 production methods based on non-renewable energy sources

Technology	**Advantages**	**Disadvantage**	**Ref.**
Hydrocarbon pyrolysis	● The energy requirement per mole of H_2 produced (37.6 kJ/mol) less than that for hydrocarbon reforming as the steam methane reforming method (63.3 kJ/mol) ● Hydrocarbon pyrolysis does not include water gas shift (WGS) and CO_2 removal step	● H_2 separation weakness due to the low H_2 partial pressures in the reaction mixture and membrane durability is affected by high temperatures needed for the de-carbonization equilibrium ● Catalyst deactivation will occur	[19, 33, 35]

Table 2.2 Various H_2 production methods based on non-renewable energy sources (continue)

Technology	Advantages	Disadvantage	Ref.
Hydrocarbon reforming			
○ Steam methane reforming	● Most developed industrial sector ● No O_2 requirement ● Lowest manufacturing cost per kg of H_2	● Highest CO_2 emission ● This process is sensitive to natural gas qualities	[18, 33, 36, 37]
○ Partial oxidation	● Low methane slip ● No catalyst requirement ● Reduction of desulfurization requirement	● Very high operating temperature ● Low H_2 to CO ratio ● Pure O_2 requirement	
○ Auto-thermal reforming	● Low methane slip ● Requirement of O_2 less than partial oxidation	● Limited commercial experience	
Coal gasification	● No catalyst requirement	● A large amount of byproduct ash ● Cost of manufacturing more expensive than hydrocarbon reforming due to additional handing of un-reacted solid feedstock ● High operating temperature	[35]

The H_2 production methods from non-renewable sources uses hydrocarbon as current main feedstock such as fossil fuel that leads to greenhouse emission. So, the alternative method for long term solution is introduced to shift towards carbon free technology to dominate over the traditional method of H_2 production. There are many processes for H_2 production from renewable sources by following the biomass and water spitting processes as presented in Table 2.2. For biomass process, H_2 can be produced by thermochemical and biological technologies. The following water spitting method is accompanied by passage of an electric current. This method is a cleaner and relatively more environmentally friendly.

Table 2.3 Various H_2 production methods based on renewable energy sources [17]

Technology	Advantages	Disadvantage
Biomass		
○ Thermochemical	● Higher conversion can be achieved	● Gas conditioning and tar removal is to be done
○ Biological	● Low energy intensive ● Normal operating conditions	● The requirement of large surface area to collect sufficient light
Water splitting		
○ Electrolysis	● Cleanest technology	● This technology costs around 80% of the operating cost of H_2 production that is very expensive cost of manufacturing per ton of H_2
○ Thermochemical	● Good H_2 yield	● High temperature water splitting process in the range of 500-2000 ℃.
○ Photo-electrolysis	● This technology is uncomplicated.	● This method is limited visible light absorption efficiency of the semiconductor electrode

The electrolysis can be used to produce H_2 with the cleanest technology but it needs most power sources [38]. Thus, H_2 production from electrolysis technology still presents relatively highest the H_2 production cost (see section 2.4). Nowadays, most research on the H_2 production from biomass sources focus on catalytic reforming of alcohol for a future H_2 economy and renewable way which have less environmental impact than non-renewable source. The alcohol such as ethanol is used as feedstock because ethanol as the reforming fuel has its potential in large availability, low-cost and low toxicity [39-41]. Moreover, ethanol has no sulfur containing thus it will not cause catalyst poisoning [42]. H_2 can be produced from steam reforming reaction and has been widely studied by following in the next section [43, 44].

2.2 Steam reforming of ethanol to H_2 synthesis model

The steam reforming method basically involves a catalytic conversion and consists of the main steps of steam reforming and water gas shift, respectively. Steam reforming was favored by high temperature, while water gas shift reactor is favored at low temperature. In general, H_2 is produced from a variety of feedstocks which are fossil fuel and non-fossil fuel [45]. Recently most of the developed research widely focus on the ethanol steam reforming.

The steam reforming of feedstock to produce H_2 is normally done in 3 steps as shown in Figure 2.4. Moreover, Tripodi et al. [46] simulated the H_2 production by steam reforming of ethanol. The system was constituted by 3 reactors connected in series for H_2 production with share on chemical applications i.e. steam reformer, high-temperature water gas shift reactor and low-temperature water gas shift reactor. For steam reformer, modelled as a multitubular reactor with catalyst packed inside the tubes. The catalyst of the steam reformer affected the conversion of ethanol, the H_2 yield and the undesirable products. Then, water gas shift reactors consisted of high-temperature and low-temperature water gas shift reactor, were operated at 350 ℃ and 280 ℃ at atmospheric pressure, respectively. The water gas shift reaction was an exothermic for the reaction between CO and steam to produce CO_2 and H_2. Decreasing temperatures in both reactors helped improving the CO_2 concentration [47].

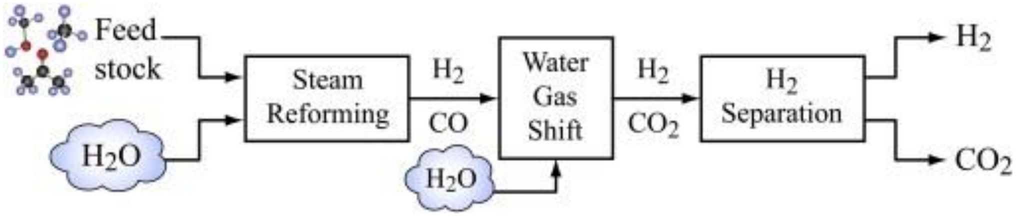

Figure 2.4 Diagram showing the multiple stages for H_2 production with steam reforming [47]

In addition, Hajjaji et al. [48] investigated the H_2 production via ethanol steam reforming. They simulated the process of reforming section coupled with the CO clean-up section as shown in figure 2.5. The first section of H_2 production was ethanol steam reforming process involving reaction between ethanol and steam. The simulation of this work was performed under condition as follows: water and ethanol fed to the process at temperature of 25 ℃ and pressure of 1 bar; and, the operating temperature of high-temperature and low-temperature water gas shift operated at 300 ℃ and 200 ℃, respectively. The product out of the water gas shift was fed to the CO preferential oxidation reactors since this work was adjusted to obtain a molar CO concentration lower than 10 ppm at which improved the conversion of ethanol at 1%.

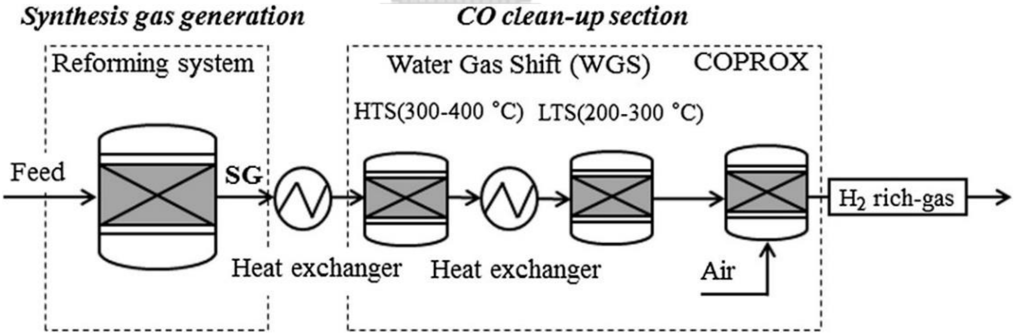

Figure 2.5 A simplified flow diagram of H_2 production process [48]

Vita et al. [49] analyzed the energy requirements and the efficiencies of steam reforming of ethanol. The simulation was performed in Aspen HYSYS using the Non-Random Two Liquid (NRTL) properties, partial oxidation and autothermal reforming of ethanol to produce high-grade H_2 following ISO FDIS 14687-2. They found that the performance of steam reforming of ethanol process provided the lowest thermal efficiency. For ethanol steam reforming, they assumed that the feed in and the product out of the process was under the standard state (at 25 ℃, 1 bar) and the steam to ethanol molar ratio was 1.5. Thus, they explained the ethanol steam reforming as shown in Figure 2.6 that showed a first steam reformer of process aims with conversion of ethanol to increasing H_2 yield under operating at 706.85 °C, followed by high-temperature water gas shift reactor (at 350-400 °C) was exothermic reaction which converted CO to CO_2 and higher H_2 yield. For the third reactor, low-temperature water gas shift reactor (at 170-200 °C) worked at decreasing temperature to abate CO concentration for specifications of the fuel cell below 20 ppm [23]. Next, the final step separated H_2 from the synthesis gas thought the purification unit.

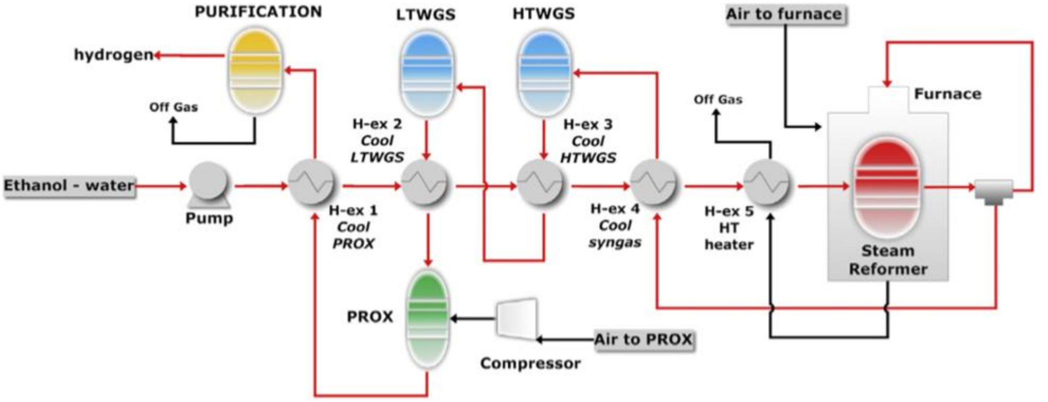

Figure 2.6 Detailed flow sheet of ethanol steam reforming process [49]

The H_2 production from ethanol through ethanol steam reforming has been widely reported in terms of the technical and economic feasibility of production by using different catalysts. In the application to catalysts, the catalysts that use in H_2 production from ethanol steam reforming must be capable of breaking down the C-C and C-H bonds efficiently [43, 50, 51]. Thus, the noble metal catalysts are Rh, Ru, Pd, Pt and Ir catalyst and the non-noble metal catalysts is Ni, and Co with different metallic oxide as supports (i.e. Al_2O_3, CeO_2, MgO, ZnO, SiO_2) in ethanol steam reforming for H_2 production [52]. For the non-noble catalyst, Ni is the best choice for H_2 production by catalytic steam reforming of ethanol [51]. From the noble metal catalysts, the Rh catalysts are the most active. Nevertheless, expensive noble metal catalysts are unsuitable for industrial H_2 production [52]. Ni is widely used in industry because of low cost and high activity of breaking C-C bond, although it is known to has coke formation and sintering problem, leading to low catalyst performance [53]. Additionally, Aupretre et al. [54] compared the conversion of ethanol steam reforming at 600 °C between using Rh and Ni supported on Al_2O_3. In case of Rh/Al_2O_3, they found that the selectivity of H_2 was 73.5% $Rh/Al_2O_3$for while the selectivity of H_2 over the Ni/Al_2O_3 catalyst was 76% with 100% conversion at the same temperature. Although, Rh and Ni were the best catalytic performance in steam reforming of ethanol but it was more selectivity of CO than selectivity of CO_2. Platinum (Pt) is considered for ethanol steam reforming because the activity of Pt increased in water gas shift reaction. Moreover, Pt provided the higher H_2 productivity and less coke formation [55].

Palma et al. [56] studied a kinetic rate by using bimetallic catalyst based on Pt and Ni with supported on CeO_2 which was prepared by impregnation. For the activity test, steam to ethanol molar ratio of 6 was introduced. Moreover, they studied the operating temperature for ethanol steam reforming as shown in Figure 2.7.

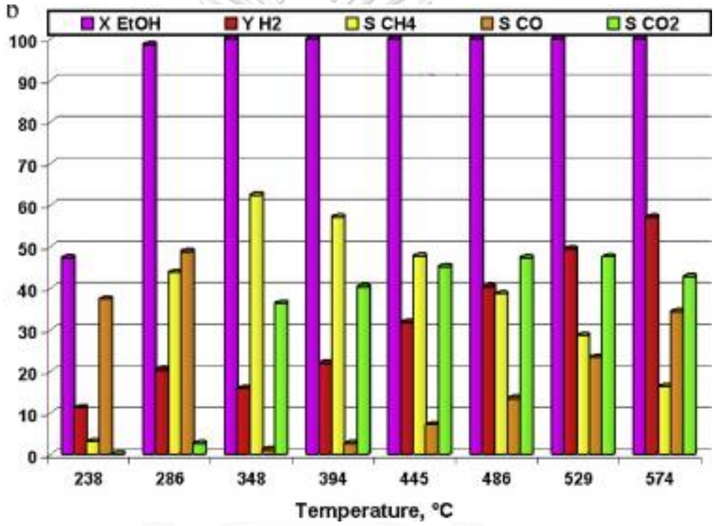

Figure 2.7 Ethanol conversion ($X_{C_2H_5OH}$), H_2 yield (Y_{H_2}) and product selectivity (S_{CH_4}, S_{CO}, S_{CO_2}) as a function of temperature for Pt/Ni supported on CeO_2 catalyst [56]

In Figure 2.7, it was found that the results in term of ethanol conversion was completely converted at 348 °C, but the undesirable CH_4 showed the highest of selectivity. Additionally, the H_2 yield increased with operating temperature and the trend of CO and CO_2 selectivity increased while the trend of CH_4 selectivity decreased with operating temperature. Moreover, Palma et al. [57] studied the ethanol steam reforming to H_2 production via bimetallic Pt-Ni/CeO_2-ZrO_2 catalyst as shown in Figure 2.8. They investigated the effect of different operative temperature in the range of 400-500 °C via steam to ethanol ratio in feed at 6, and it was found that the results of temperature that showed conversion of steam was decreased with temperatures. On the contrary, the selectivity of H_2, CO, CO_2 and CH_4 increased with temperatures.

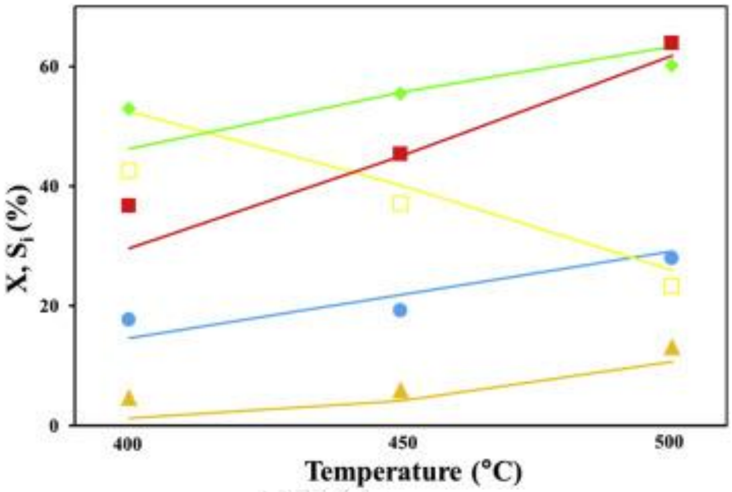

Figure 2.8 Influence of temperature on water conversion (circle) and products selectivities (triangle CO, diamond CO_2, filled square H_2, empty square CH_4) [57]

2.3 Dehydrogenation of ethanol to H_2 synthesis model

Nowadays, alternative technologies for H_2, requires minimization of CO_2 emission while conventional technology for H_2 production, which is steam reforming of natural gas feedstock, promotes relative higher CO_2 emission [58, 59]. Ethanol could be one of the future feedstocks of the chemical industry because the annual amount of ethanol produced exceeds 50 million tons [60]. In recent year that, electric vehicle is significantly increasing. Therefore, ethanol consumption mixing fuel application is likely to decrease. Catalytic ethanol dehydrogenation has been proposed as an alternative method to produce H_2 without CO and CO_2 emission from reaction [61]. Moreover, it not only generates H_2 but by-product such as ethyl acetate, acetaldehyde and others. Dehydrogenation of ethanol reaction is presented in Eqs. (2)-(3).

The dehydrogenation of ethanol to acetaldehyde:

$$C_2H_5OH \longrightarrow CH_3CHO + H_2 \qquad \Delta H_0 = +16.45 \text{ kcal/mol} \qquad (2)$$

The dehydrogenation of ethanol to ethyl acetate:

$$2C_2H_5OH \longrightarrow CH_3COOCH_2CH_3 + 2H_2 \qquad \Delta H_0 = +5.98 \text{ kcal/mol} \qquad (3)$$

For Eqs. (2)-(3), ethanol can be converted to acetaldehyde and ethyl acetate formation by an exothermic process [61, 62].

2.3.1 Dehydrogenation of ethanol to H_2 and ethyl acetate

The synthesis route of ethyl acetate from ethanol dehydrogenation became an attractive process due to this process needs only ethanol for feedstock without steam. Several catalytic processes have been developed in recent years to convert ethanol to H_2 by different routes, The commercial catalyst for ethanol dehydrogenation is Cu-based catalysts due to their basic characteristics, which favor ethanol dehydrogenation but inhibit dehydration. Cu metal can be supported by different oxides such as Al_2O_3, Cr_2O_3, ZnO, ZrO_2 and SiO_2. Cu-Cr_2O_3 containing catalysts has been deeply investigated by several researchers.

Carotenuto et al. [25] explained the formation of ethyl acetate as Eqs. (6)-(7) with the production of acetaldehyde as an intermediate step.

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2 \tag{6}$$

$$CH_3CH_2OH + CH_3CHO \longrightarrow CH_3COOCH_2CH_3 + H_2 \tag{7}$$

Franckaerts et. al. [63] studied the ethanol conversion to ethyl acetate which was the dehydrogenation pathway with Cu/Cr_2O_3 catalyst in the catalyst conversion reactor as shown in Eq. (3). In this study, they used the operating temperature in range of 225 - 285 ℃ and pressure at 10 atm and it was found that the temperature of 250 ℃ can be used to convert ethanol to higher H_2 and ethyl acetate selectivity than other temperatures. In addition, Santacesaria et al. [64] investigated the ethanol dehydrogenation by using Cu/Cu-Cr_2O_3 catalyst in packed-bed tubular reactor to convert ethanol to form ethyl acetate in one step reaction as shown in Figure 2.9. The reaction was operated at 200, 220, 240 and 260 ℃ with a pressure range of 10, 20 and 30 bars. In this study, the results demonstrated that the best performance of ethanol dehydrogenation to form ethyl acetate and H_2 was operated at 240 ℃ and 20 bars. In this condition, they found that a conversion at 64.83% with a selectivity of ethyl acetate and H_2 of 99.58%.

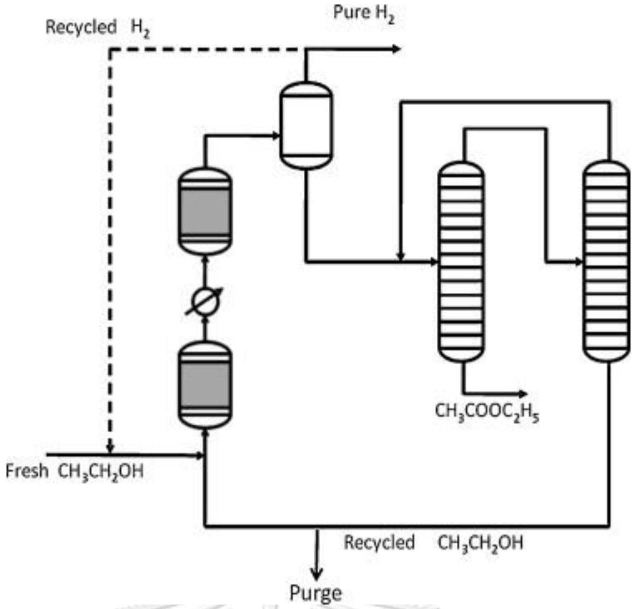

Figure 2.9 A simplified scheme of the process based on the use of a new Cu/Cu-Cr_2O_3 commercial catalyst [64]

2.3.2 Dehydrogenation of ethanol to H_2 and acetaldehyde

Acetaldehyde was widely used as the intermediate for synthesis of many industrial chemicals [65]. The selection of catalysts affected the activity of the reaction in term of conversion and selectivity as shown in Table 2.3 thus the Cu-based catalyst promoted high activity and selectivity for ethanol dehydrogenation to acetaldehyde and H_2. For the support catalysts, Sato et al. [66] found that SiO_2 was more suitable supports for Cu for dehydrogenation of ethanol to form acetaldehyde and H_2 than ZrO_2 since Cu/ZrO_2 tended to promote ethyl acetate formation.

Table 2.4 Summary of previous experimental studies of ESR

Catalyst	**Temp. (℃)**	**Conv. %**	**Sel. %**	**Deactivation**	**Ref.**
Cu-Ni alloy	250	26	100	Sintering	[65]
Cu/ZrO_2	300	56.9	54.1	Sintering	[67]
Cu/Rice husk ash (SiO_2)	275	77	100	Sintering	[68]
CuO-Cr_2O_3/Al_2O_3	300	50	55	Sintering	[69]

Table 2.5 Summary of previous experimental studies of ESR (continue)

Catalyst	Temp. (°C)	Conv. %	Sel. %	Deactivation	Ref.
Cu/MgAlOx (hydrotalcite)	300	75	99	Coke deposition	[70]
Cu/ZrO_2	275	80.7	15	Sintering	[60]
Cu/SiO_2	280	90	98	Sintering	[71]

2.4 Cost estimate and CO_2 emission of various H_2 production methods

Different technologies for H_2 production with varying cost of H_2 and CO_2 emission are widely investigated by extensive researchers. Consequently, the challenge of H_2 production is to reduce the price of H_2 with significantly reduce greenhouse gases emission form the process. There has extensive research to show the relationship between environmental issue in term of CO_2 emission and economical issue in term of cost of manufacturing per ton of H_2.

Numerous studies have demonstrated the cost estimate of H_2 with different alternative H_2 production technologies. Konda et al. [72] investigated the production technologies that could be operated on commercial scale. They studied capital cost of different H_2 production technologies which included steam methane reforming, coal gasification, biomass gasification and water electrolysis as shown in the capital cost in Table 2.4.

Table 2.6 H_2 production capital cost as a function of plant capacity (ton/d) [72]

Production technology	Capital cost ($\times 10^6$ USD)
Steam methane reforming	$134 \times (\text{Capacity}/150)^{0.75}$
Coal gasification	$352 \times (\text{Capacity}/150)^{0.77}$
Biomass gasification	$360 \times (\text{Capacity}/150)^{0.75}$
Water electrolysis	$598 \times (\text{Capacity}/150)^{0.85}$

The results from Table 2.4 demonstrated that steam methane reforming has the lowest capital cost compared to other technologies. In contrast, water electrolysis gave the highest capital cost at the same plant capacity. In addition, Simbeck et al. [73] showed the capital and variable costs for H_2 production in Table 2.5 with four different technologies, which are steam methane reforming, electrolysis, methanol steam reforming and gasoline reforming. They assumed that each unit that was designed to produce 329 kg/d of H_2.

Table 2.7 The capital and variable cost of alternative H_2 production methods [73]

Production technology	**Capital costs ($ millions)**	**Variable cost ($/kg of H_2)**
Steam methane reforming	1.63	1.28
Electrolysis	4.15	4.18
Methanol steam reforming	1.57	1.51
Gasoline reforming	1.78	1.59

Table 2.5 listed the capital and variable cost including raw material and utility used in H_2 production plants. It was found that the electrolysis process promoted the highest capital, followed by gasoline reforming, steam methane reforming and methanol steam reforming, respectively. For the variable cost, electrolysis still promoted the highest variable cost per kg of H_2. In contrast, the steam reforming of methane provided the lowest the variable cost per kg of H_2. Thus, the H_2 production from electrolysis exhibited the highest cost of manufacturing per kg of H_2.

Currently, steam reforming of methane and electrolysis are major H_2 production technology. Although steam reforming of methane gave the lowest production cost, it promoted the high CO_2 emission [74]. Electrolysis technologies generated H_2 production from renewable sources and is stated as a clean technology. The cost of electrolysis technology is strongly dependent on the electrolyzer capital cost and extensive electrical energy requirement (40 kWh/kg of H_2) [75]. However, in term of global warming potential (GWP) as shown in Figure 2.10, the electrolysis with grid can has negative impact [76].

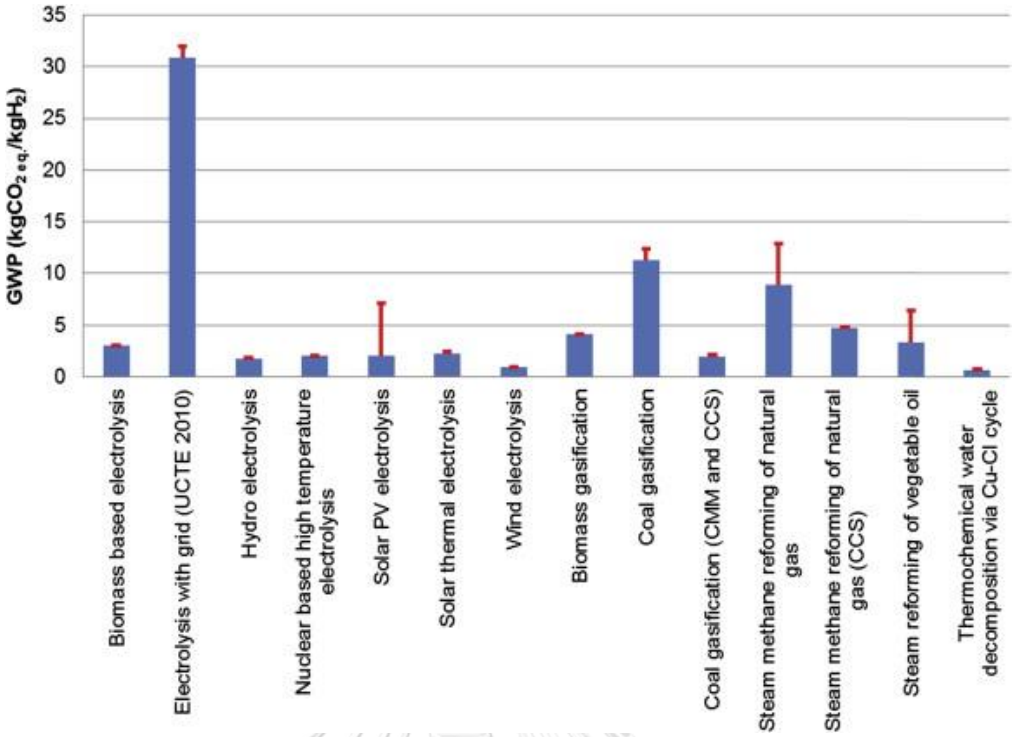

Figure 2.10 GWP values of different hydrogen production technologies [76]

Moreover, Acar et. al. [77] presented eight of H_2 production methods from renewable and non-renewable sources with comparative environmental impact in term of global warming potential (GWP) and acidification potential (AP), and they compared the ranking range with ideal case (0 emissions, 0 cost, 100% efficiency) as shown in Figure 2.11. They found all of electrolysis methods had close to ideal case ranking because the electrolysis method for H_2 production promoted lower emissions. Moreover, Dincer et. al. [78] demonstrated that the electrolysis method promoted the highest H_2 generation efficiency.

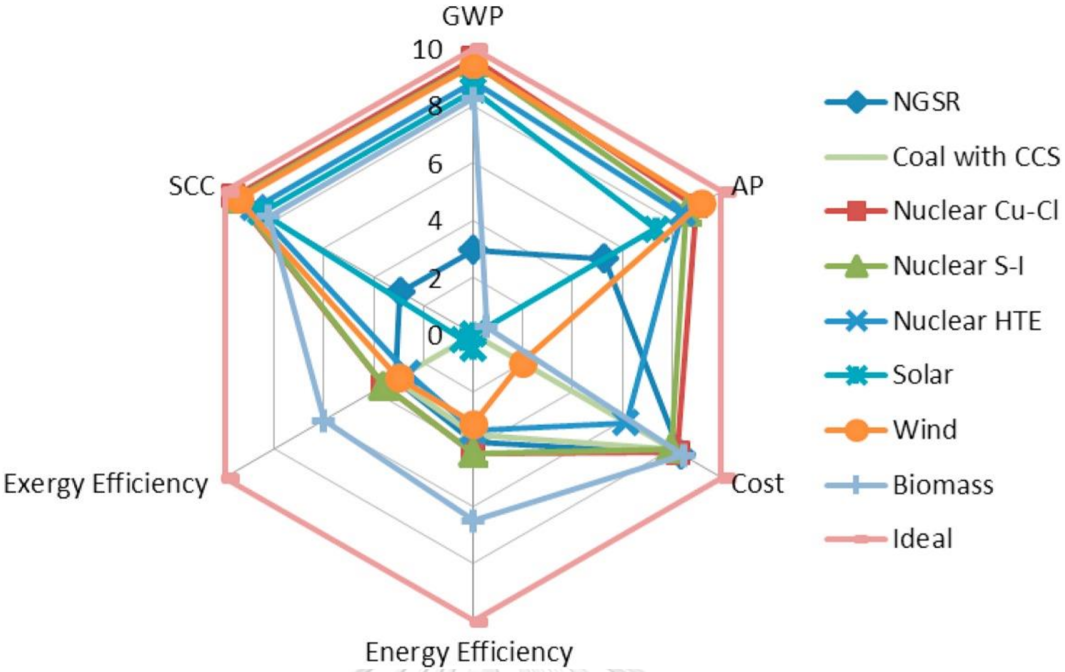

Figure 2.11 Overall comparison of selected H_2 production processes [77]

Numerous research have interested to produce H_2 via ethanol steam reforming. Thus, ethanol steam reforming is widely reported as the cost of manufacturing and CO_2 emission. Lorena Mosca and her team [79] compared the CO_2 emission in function of utility and reforming reaction between steam methane reforming and ethanol steam reforming. They found the results as shown in Table 2.6 that promoted lower CO_2 emission of ethanol steam reforming than steam methane reforming method.

Table 2.8 Comparative process utility and CO_2 emissions [79]

Feedstock	Unit	Production technology	
		Steam reforming of methane	Steam reforming of ethanol
Fuel (Natural gas)	MW	176.2	46.8
HP steam	Ton/hr	35.4	38.6
Electric power	MW	2.15	0.74
CO_2 emission	kg/ Nm^3 of H_2	0.869	0.228

In addition, Noureddine Hajjaji et. al. [48] compared various H_2 production process including steam methane reforming, ethanol steam reforming and the other processes in term of GWP impact as a CO_2 emission in Figure 2.12. As observed in the figure, ethanol steam reforming method was found to emit the CO_2 about half of steam methane reforming.

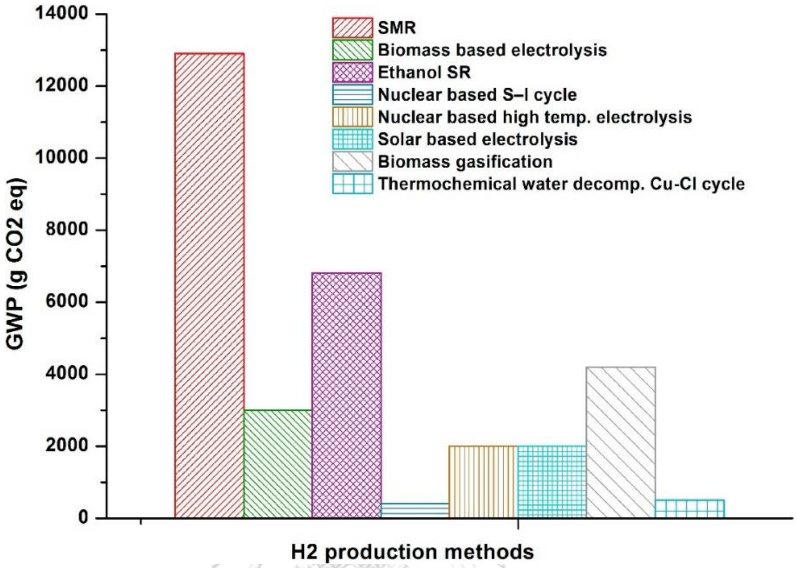

Figure 2.12 Relative comparison of the GWP impact of the bioethanol steam reforming system and other alternative routes for H_2 production [48]

Currently, one of the most challenges for H_2 production was the process with low production cost and environmentally friendly with minimum CO_2 emission. There had extensive research to promoted cost of H_2 and CO_2 emission in Table 2.7.

Table 2.9 H_2 production technologies considered in term of H_2 production cost and CO_2 emission

Technology	**Input material**	**H_2 production cost ($/kg H_2)**	**CO_2 emission (kg CO_2/kg H_2)**	**Reference**
Steam methane reforming	Natural gas	1.26	12.40	[58]
Steam methane reforming with CCS	Natural gas	1.88	4.30	[58]
Coal gasification	Coal	1.38	19.14	[72]
Coal gasification with CCS	Coal	2.17	1.80	[80]
Methane pyrolysis	Natural gas	1.75	3.72	[81]
Biomass gasification	Biomass	2.24	2.60	[82]
Biomass gasification with CCS	Biomass	2.27	n/a	[83]
Electrolysis – wind	Water	5.24	1.34	[58]
Electrolysis – solar	Water	8.87	4.47	[58]
Electrolysis – nuclear	Water	4.63	1.65	[58]
Glycerol steam reforming	Glycerol	4.46	n/a	[84]
Methanol steam reforming	Methanol	3.47	n/a	[85]

CHAPTER 3

Experiments

3.1 Process modelling and simulation

A comparative study on hydrogen production from ethanol processes (ethanol steam reforming and ethanol dehydrogenation) was performed using Aspen PLUS V10. The ethanol dehydrogenation was divided into 2 processes. Two different processes of ethanol dehydrogenation reaction were described in 2 main products as follows: ethanol dehydrogenation to acetaldehyde with hydrogen production and ethanol dehydrogenation to ethyl acetate with hydrogen production. The modelling for simulation using properties database was used along with the Non-Random Two Liquid (NRTL) fluid package and henry's law involved in supercritical components. This model has been applied to a full set of experimental data with a good accuracy for ethanol steam reforming process (case I) [23, 56]. However, NRTL model could not suitable predict high pressure (P >10 bar) in ethanol dehydrogenation processes (case II and case III). The Predictive Redlich-Kwong-Soave (PSRK) equation of state provides very satisfactory predictions of the ethanol dehydrogenation at high temperature and pressure [25].

3.2 Process chemistry

3.2.1 Ethanol steam reforming (Case I)

For H_2 production process through ethanol steam reforming, the kinetic models used in the reformer was based on power-rate law expression (Eq. (8)). The ethanol steam reforming on CeO_2-supported Pt/Ni catalyst in a fixed bed reactor has been proposed by *Vincenzo Palma et al.* [56]. Table 3.1 presents the main possible reactions to describe the steam reforming of ethanol, suggesting a set of reactions as in Eqs. (1), (9)-(11) with an activation of energy and kinetic constant.

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{8}$$

The rate expression was reported at constant temperature of 527 ℃ under atmospheric pressure for use in case I.

Table 3.1 Parameters for equilibrium constant using in the ethanol steam reforming reaction [56]

Reaction		Activation energy, E_a (kJ mol^{-1})	Kinetic constant, k (m^3 $kmol^{-1}$ s^{-1})
$C_2H_5OH + 3H_2O \leftrightarrow 6H_2 + 2CO_2$	(1)	17	21.2
$C_2H_5OH \leftrightarrow C_2H_4O + H_2$	(9)	74	45,231
$C_2H_4O \leftrightarrow CH_4 + CO$	(10)	181	6,781
$CO + H_2O \leftrightarrow H_2 + CO_2$	(11)	74	5,132

The product out of the steam reforming reactor was purified in a high temperature water gas shift reactor following a low temperature water gas shift reactor. The water gas shift reactor was operated at 350 and 280 ℃ respectively. All these reactors were modelled as equilibrium reactors.

3.2.2 Ethanol dehydrogenation to ethyl acetate (Case II)

In this study, the results from Carotenuto et al. [25] was used to describe the ethanol dehydrogenation to ethyl acetate on a copper/copper-chromite based catalyst with isothermal conditions. The involving reactions are reported as presented in Eqs. (6)-(7),(12). The endothermic reaction (ΔH_0 = +5.98 kJ/mol) in gas phase was based on a constant temperature of 240 ℃ and a pressure of 20 bar. All the kinetic constants and adsorption constants determined by regression analysis was reported on table 3.2-3, respectively.

Table 3.2 Kinetic parameter of Langmuir Hinshelwood Hougen Watson dual site model using in the ethanol dehydrogenation to ethyl acetate reaction [25]

Reaction		Kinetic constant, k_i (mol g_{cat}^{-1} h^{-1} atm^{-2})	Activation energy, E_a (kcal/mol)
$C_2H_5OH \longrightarrow CH_3CHO + H_2$	(6)	97.100	32.25
$C_2H_5OH + CH_3CHO \longrightarrow CH_3COOCH_2CH_3 + H_2$	(7)	0.089	12.95
$2CH_3CHO \longrightarrow$ Other products	(12)	0.001	1.60×10^{-4}

Table 3.3 Adsorption parameters using in the ethanol dehydrogenation to ethyl acetate Reaction [25]

Adsorption parameter	Adsorption constant, (atm^{-1})	Adsorption enthalpy, (J mol^{-1})
$b_{C_2H_5OH}$	10.4	-25.53
b_{CH_3CHO}	98.4	-7.02
$b_{CH_3COOCH_2CH_3}$	41.2	-13.91
b_{H_2}	2.5 x 10^{-4}	-13.34

Based on a Langmuir Hinshelwood Hougen Watson dual site model approach, described mechanisms of ethanol dehydrogenation to ethyl acetate. The following kinetic rate laws can be derived on Eqs.(13)-(15).

$$r_6=\frac{k_6 b_{C_2H_5OH}\left[p_{C_2H_5OH}\right]\left[1-\frac{1}{K_{e_6}}\frac{\left[p_{CH_3CHO}\right]\left[p_{H_2}\right]}{\left[p_{C_2H_5OH}\right]}\right]}{\left[1+b_{C_2H_5OH}\left[p_{C_2H_5OH}\right]+b_{CH_3CHO}\left[p_{CH_3CHO}\right]+b_{H_2}\left[p_{H_2}\right]+b_{CH_3COOCH_2CH_3}\left[p_{CH_3COOCH_2CH_3}\right]\right]^2} \quad (13)$$

$$r_7=\frac{k_7 b_{C_2H_5OH} b_{CH_3CHO}\left[p_{C_2H_5OH}\right]\left[p_{CH_3CHO}\right]\left[1-\frac{1}{K_{e_7}}\frac{\left[p_{CH_3COOCH_2CH_3}\right]\left[p_{H_2}\right]}{\left[p_{C_2H_5OH}\right]\left[p_{CH_3CHO}\right]}\right]}{\left[1+b_{C_2H_5OH}\left[p_{C_2H_5OH}\right]+b_{CH_3CHO}\left[p_{CH_3CHO}\right]+b_{H_2}\left[p_{H_2}\right]+b_{CH_3COOCH_2CH_3}\left[p_{CH_3COOCH_2CH_3}\right]\right]^2} \quad (14)$$

$$r_{12}=k_{12}[p_{CH_3CHO}]^2 \quad (15)$$

The separation of ethyl acetate and ethanol with azeotropic mixture, as boiling points at 78.31 and 77.20 ℃ respectively. The technology in the separation of azeotropic mixture is extractive distillation by addition of a dimethyl sulfoxide as a solvent [86].

3.2.3 Ethanol dehydrogenation to acetaldehyde (Case III)

At present, there are not the study about the reaction rate of the ethanol dehydrogenation to acetaldehyde. Therefore, the conversion data of this case was related with the experimental data of Hongwei Zhang et. al. [71]. who reported the conversion and the selectivity of the ethanol dehydrogenation to acetaldehyde and H_2. The reaction was done over 10 wt% Cu/SiO$_2$ catalyst with the isothermal condition. The conversion of ethanol was reported at 90% while the selectivity of ethanol to acetaldehyde and H_2 was reported at 98%. Ethanol dehydrogenation proceeded at reaction temperature of 280 ℃ and atmospheric pressure.

3.3 Process description

3.3.1 Ethanol steam reforming (Case I)

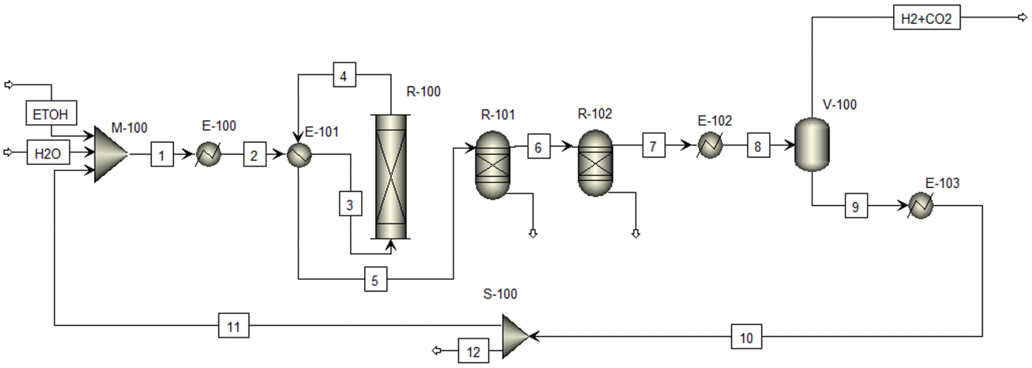

Figure 3. 1 Process flow diagram of ethanol steam reforming

As presented in Figure 3.1, the ethanol feed stream and the H_2O feed stream were mixed with the recycled gas (M-100) and preheated to 200 °C by the heat exchanger (E-100) using high pressure (HP) steam. Before entering reactor, the feed stream was preheated by exchanging heat duty with the product stream from the reactor. The feed gas was fed to the isothermal fixed-bed reactor operated at 527 °C (R-100). The product stream was then further cooled (E-101) to 250 °C by cooling water. After that, the stream was fed to the high-temperature water gas shift reactor (R-101) and the low-temperature water gas shift reactor (R-102) which was operated at 250 and 180 °C, respectively. The stream outlet of the low-temperature water gas shift reactor was condensed for phase splitting at the flash vessel (V-100). The vapor product from the top of the flash vessel was H_2 mixed with other products (mainly CO_2 and trace amount of CO and CH_4). This stream of the H_2 product had 82.73% purity.

3.3.2 Ethanol dehydrogenation to ethyl acetate (Case II)

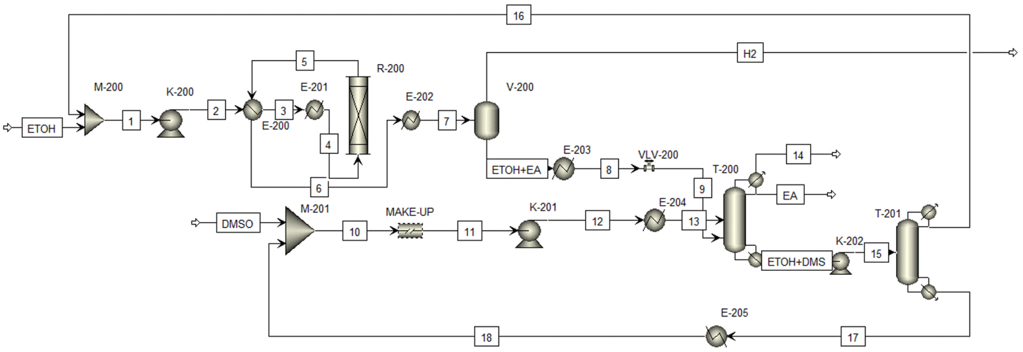

Figure 3.2 Process flow diagram of ethanol dehydrogenation to ethyl acetate

As presented in Figure 3.2, the ethanol feed was pumped to 20 bar and preheated to 161.58 °C (E-200) by exchanging heat duty with the product stream from the reactor. After that, the steam was preheated to 240 °C by HP steam before the stream was fed to isothermal fixed bed reactor (R-200). The operating condition inside the reactor was maintained at 240 °C and 20 bar. The unreacted ethanol together with H_2 and ethyl acetate were removed from the reactor to cooler (E-202). The product stream was cooled to 35 °C (E-202) by cooling water. The majority of the ethyl acetate and unreacted ethanol were then separated from H_2 product in flash vessel (V-200). The stream of H_2 production had 98.87 % purity. Ethyl acetate mixed with unreacted ethanol from the bottom stage. Ethyl acetate and ethanol are azeotrope mixture and can be separated using the extractive distillation column. Dimethyl sulfoxide (DMSO), the solvent currently used in the extractive distillation, was fed at the molar flowrate ratio of solvent to feed (ETOH+EA) at 1.25. The extractive distillation with 48 theoretical trays (T-200) was done to separate 99.64 wt% of ethyl acetate from ethanol, based on industrial purity requirement (ethyl acetate > 99.5 wt% with ethanol < 0.2 wt%). After that, the stream outlet of the reboiler was fed to simple distillation with 10 theoretical trays (T-201). This distillation column was used to separate ethanol and dimethyl sulfoxide solvent for recycle purpose. The dimethyl sulfoxide solvent make-up stream was 0.078 kg/h.

3.3.3 Ethanol dehydrogenation to acetaldehyde (Case III)

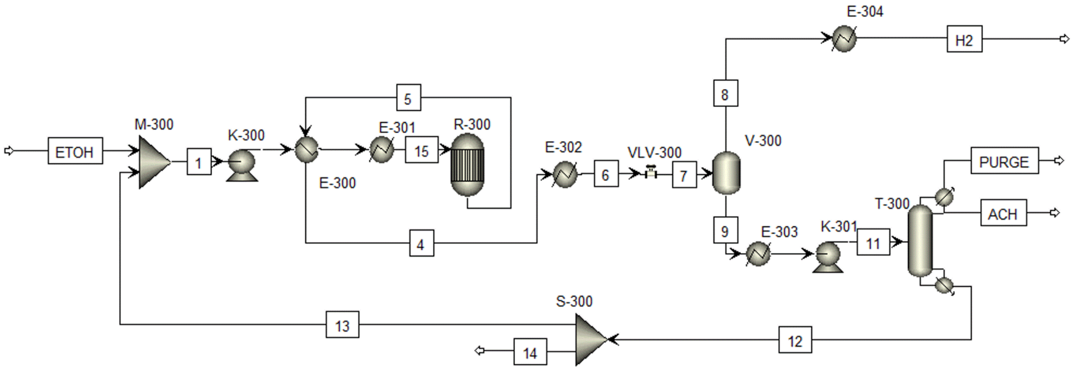

Figure 3. 3 Process flow diagram of ethanol dehydrogenation to acetaldehyde

As presented in Figure 3.3, the ethanol feed was mixed with the recycle ethanol in mixer (M-300). The mixed feed was pumped to 37.42 bar and was preheated to 201.89 by exchanging heat duty with the product stream from the reactor. After, the steam out of heat exchanger was preheated to 280 °C by heat exchanger (E-300) with HP steam. The feed was fed to conversion reactor operated at 280 °C and 37.42 bar. Product stream was cooled to 50 °C (E-301) with cooling water and the pressure was reduced to 2 bar through the valve (VLV-300). After that, the H_2 product was separated from acetaldehyde and unreacted ethanol by the flash vessel (V-300). H_2 was removed from the top of the column, while acetaldehyde and unreacted ethanol were removed from the bottom. The mixture of acetaldehyde and unreacted ethanol from the bottom stage was fed to a distillation column. The atmospheric column with 17 theoretical trays (T-300) was used to separate 99.46 wt% acetaldehyde from ethanol.

3.3.4 Methanol process

For case I-III, the H_2 product (approximately 1,600 t/y) was fed to methanol synthesis through the CO_2 hydrogenation process. As presented in Figure 4.2, the H_2 product was compressed to 50 bar and preheat to 250 °C before feeding to the methanol reactor. The conditions was based on the work of Khunathorncharoenwong et.al [40].

In case I, the H_2 product stream was mixed with CO_2. The mixed-gas stream was compressed to 50 bar through 3 stages of compressors (K-101, K-102, K-103) at 6, 17.5, 50 bar, respectively, with 2 intercoolers at 60 ℃. After that, the feed stream was mixed (M-101) with the recycle stream and preheat to 250 ℃.

In case II, the H_2 stream from the ethanol dehydrogenation was at rather high pressure of 20 bar. The H_2 stream was further compressed to 50 bar through 1 stage compressor (K-204). Case II and III required external CO_2 feedstock. Therefore the CO_2 feed in case II and II were compressed to 50 bar through 3 stages with 2 intercoolers, in similar manner to case I. In case III, H_2 stream was compressed to 50 bar and preheat to 250 ℃, in similar manner to case I.

3.4 Economic analysis

The following section shows the cost analysis related to H_2 production processes. The cost of the processes was estimated based on the capital and the operating costs.

3.4.1 Total capital investment (TCI)

The capital cost of H_2 production process was estimated by using the Module costing technique. The sizing of equipment for the estimation was obtained the simulation data from Aspen Plus V10 software. The bare module cost (C_{BM}) was calculated from the purchased equipment and installation costs. The chemical engineering plant cost index (CEPCI) was used to accommodate inflation rate. Working capital was assumed at 15% of total capital investment [87]. Fixed cost investment and total capital investment are presented in Eqs. (16) and (17), respectively.

Fixed cost investment (FCI):

$$\mathrm{FCI} = 1.18 \sum_{i=1}^{n} C_{BM,i} \qquad (16)$$

Total capital investment (TCI):

$$\mathrm{TCI} = \frac{100}{85}\mathrm{FCI} \qquad (17)$$

3.4.2 Cost of manufacturing (COM)

The overall of H_2 production process, including the cost of manufacturing without depreciation (COM_d) was calculated by fixed cost investment, operating labor cost (C_{OL}), utility cost (C_{UT}), waste treatment (C_{WT}) and raw material cost (C_{RM}) by using Eqs. (18).

$$COM_d = 0.180\mathrm{FCI} + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \qquad (18)$$

The raw material cost of ethanol anhydrous was in 0.431 USD/l [88]. This price was based on 99.5 wt% of ethanol. Other raw material cost of solvent for purification of azeotropic mixture was used dimethyl sulfoxide in case 2 was 3069.4 USD/l [88]. The utility cost was presented in Table 3.4.

Table 3.4 Utility cost [87]

Utility	**Unit**	**Cost of utility**
Cooling Water	USD/t	0.0148
LP steam (5 bar, 160 ℃)	USD/t	29.29
MP steam (10 bar, 184 ℃)	USD/t	29.59
HP steam (41 bar, 254 ℃)	USD/t	29.97
Electricity	USD/kWh	0.06

The CO_2 emission factor for electricity production plants was listed in table for using in the H_2 production processes. Electricity was generated in a power plant based on different fuel: natural gas and coal which releases different amount of CO_2 during electricity generation. For natural gas, the CO_2 emission was estimated at 0.450 kg/kWh during electricity generation process. On the contrary, for electricity generation using coal as fuel, CO_2 was released at 1.142 kg/kWh as shown in table 3.5.

Table 3.5 CO_2 emission factor for electricity production with different fuels

Fuel	**CO_2 emission factor (kg-CO_2/kWh)**	**Reference**
Coal	1.142	[89]
Natural gas	0.450	[90]

The operating labor cost was assumed at 5,700 USD/y with a single operator works 49 weeks/y, 6 shifts/week and 8 h/shift. The operating labor rate was the rate in Thailand. It should be noted that the labor rate can be significantly different in other countries. The number of operating labors (N_{OL}) can be determined using Eq. (19) :

$$N_{OL} = (6.29 + 0.23N_{np})^{0.5} \tag{19}$$

where N_{np} is the number of equipment such as compressors, reactors, heat exchangers and towers.

3.4.3 Revenues

H_2 price of 4,872.88 USD/t (1.15 USD/ 100 SCF) [88] was assumed in the cost. This revenues of H_2 can reduce the cost of raw materials for methanol synthesis. For the value product, acetaldehyde price was 1,005.30 USD/t and ethyl acetate price was 1,110.00 USD/t [88] on industrial requirement (Ethyl acetate > 99.5 wt% and ethanol < 0.2 wt%). The value product can sell to decrease the cost of manufacturing per ton of H_2.

3.4.4 H_2 production cost and sensitivity analysis

Based on process simulation results, economic analysis was performed in term itemized cost estimation and sensitivity analysis of net present value (NPV). For itemized cost estimation per unit of H_2 production, the calculation was done by the total annual costs and the annual H_2 production as shown in Eq. (20):

$$H_2 \text{ production cost (USD/kg of } H_2) = \frac{\text{Total annual cost } (\text{USD}/\text{y})}{\text{Annual } H_2 \text{ production } (\text{kg of } H_2/\text{y})} \qquad (20)$$

The total annual costs were summation of the annualized capital costs and the annual operating costs.

The sensitivity analysis was used to study the effect of uncertainties on input parameters which were raw material cost, utility cost, total capital investment and selling price of H_2. The input parameters impacted on the output NPV of the processes. Each input parameter was varied from ±10% to ±40% while other parameters were kept at constant values. The NPV is cumulative discounted cash flow at the end of the project. In this study the NPV was based on a 10-year plant life and internal rate of return of 10%. The NPV was calculated using Eq. (21):

$$\text{NPV} = \sum_{n=0}^{10} \frac{\text{net cash flow at year n}}{(1+0.10)^{n}} \qquad (21)$$

CHAPTER 4

Results and discussion

The techno-economic analysis of the proposed H_2 production processes from ethanol were performed in term of performance and economic analysis with simulation models developed in Aspen PLUS. The process for comparison study mainly consists of 2 process: H_2 production process from ethanol and CO_2 hydrogenation to methanol process. The conventional CO_2 hydrogenation process have been described clearly in the work of Khunathorncharoenwong et.al [40].

4.1 Performance analysis

The performance of the proposed H_2 production processes were compared amount of ethanol requirement and CO_2 emission from both of reaction and utility (low-pressure steam (LP), medium-pressure steam (MP), high-pressure steam (HP) and electricity).

4.1.1 Comparison of required ethanol feed

The difference of H_2 production reaction contributed a significant amount of required ethanol feed due to the conversion of reaction. The amount of ethanol affected mainly the operating cost which provided cost of H_2 production.

Based on mass balance, ethanol feed was determined in order to produce H_2 at 1,663-1,693 t/y which was available for CO_2 conversion to methanol at 7,427 t/y. The ethanol feed to each process is shown in Figure 4.1. The result can be showed that dehydrogenation required much more ethanol feed than the steam reforming process since the steam reforming reaction provides the highest stoichiometric H_2 as presented on Eqs. (1)-(3).

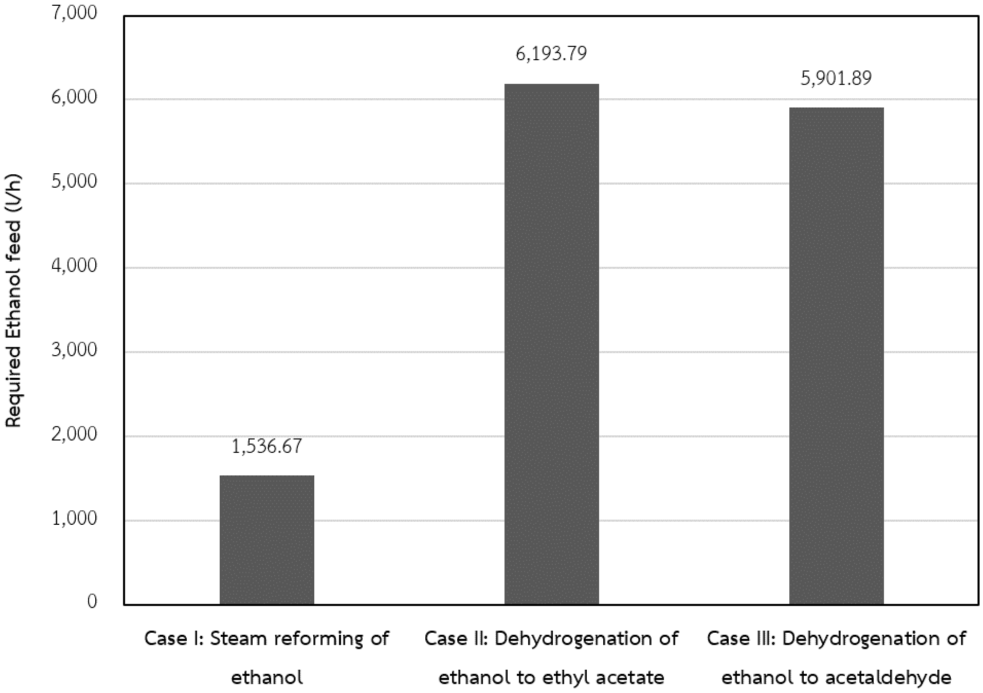

Figure 4.1 Required ethanol feed for ethanol steam reforming and ethanol dehydrogenation

Then, H_2 production for all cases was fed to CO_2 hydrogenation to methanol process as presented in Fig. 4.2. In Case I, the H_2 production from ethanol steam reforming promoted CO_2 emission from reaction at 4,784 kg/h, which was equivalent to 7,392 ton of CO_2/ton of H_2. Produced H_2 and CO_2 in the H_2 plant were fed to the methanol plant. Although CO_2 produced in the reaction of case I can be converted with produced H_2 to methanol, the H_2 production through ethanol steam reforming was not suitable for CO_2 conversion to methanol process since the process did not consume CO_2 from external source but rather utilized CO_2 produced from ethanol steam reforming. In other word, it was a conversion from ethanol to methanol. On the other hand, case II and case III consumed CO_2 from external feedstock about 28.640 kg of CO_2/h and 28.058 kg of CO_2/h, respectively.

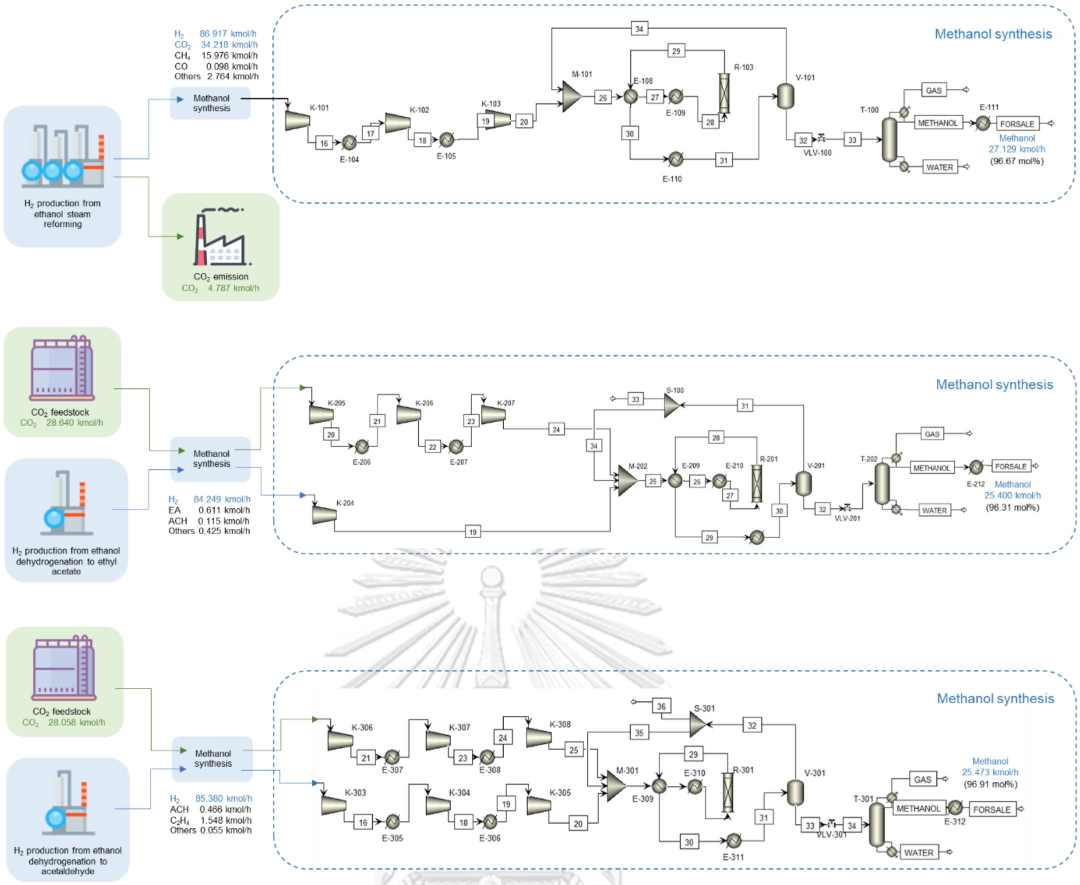

Figure 4.2 Schematic diagram of hydrogen production processes: (a) ethanol steam reforming process (case I); (b) ethanol dehydrogenation process to ethyl acetate (case II); and, (c) ethanol dehydrogenation process to acetaldehyde (case III), for used in CO_2 conversion to methanol

4.1.2 Comparison of net CO_2 emission

For the table 2.7, the results showed the H_2 production cost and CO_2 emission that the CO_2 emission from H_2 production process decreased with increasing the H_2 production cost. However, the range of both objective functions were limited the H_2 production cost via the DOE [32] aims at the target cost below 4 USD/kg of H_2, which indicated that the net CO_2 emission as less as possible.

Figure 4.3 presents the net CO_2 emission in H_2 production process and CO_2 conversion to methanol process. The CO_2 emission was divided into 2 sections: CO_2 emission from the reaction and utility (low-pressure steam (LP), medium-pressure steam (MP), high-pressure steam (HP) and electricity). It is known that reforming of bio-based raw material can counted as carbon natural.

However, CO_2 produced in ethanol steam reforming reaction was used as feedstock for methanol synthesis in this study. In case I, the stream of H_2 production was mixed with CO_2 which was byproduct from the reaction at the H_2/CO_2 molar ratio of 2.54. The remaining CO_2 in case I was separated by three-stage hybrid hydrate-membrane separation process [91] before fed to methanol synthesis. Then, product stream of ethanol steam reforming contained H_2 with 12,515.90 t/y of CO_2 which further reacted with the H_2 for methanol synthesis. Consequently, H_2 from ethanol steam reforming presented net positive CO_2 emission from the reaction and the utility at 2,792.79 kg CO_2 per ton of methanol. In contrast, the ethanol dehydrogenation in case II and III can produce H_2 without CO_2 releasing from the reactions and consumed CO_2 from external sources in methanol synthesis. Although the CO_2 emission was promoted by utility in the ethanol dehydrogenation processes, case II and III presented net negative CO_2 emission of -253.33 and -5.55 kg per ton of methanol, respectively - case II provided the highest CO_2 consumption.

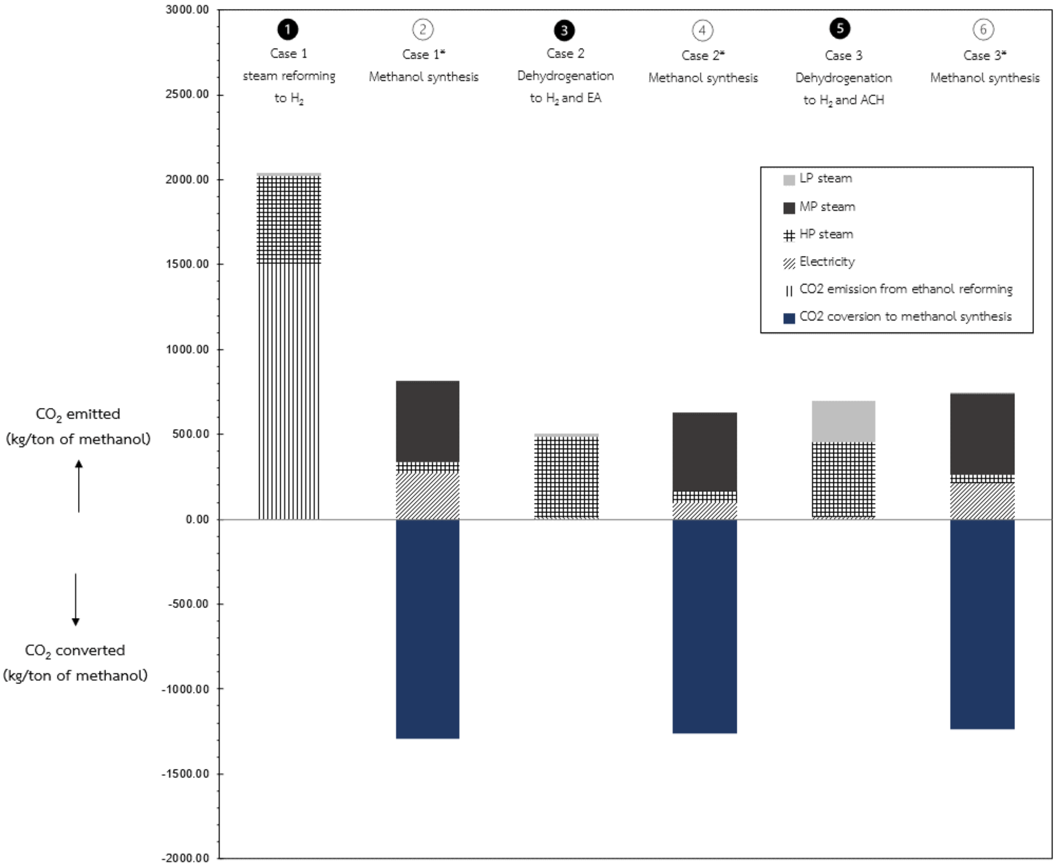

Figure 4.3 Net CO_2 emission of H_2 production combined CO_2 hydrogenation to methanol process

4.2 Economic analysis

The overall cost of H_2 production process was consisted of capital investment and the annualized cost of manufacturing. The capital investment of different processes is shown in Table 4.1 while the cost of manufacturing without depreciation (COM_d) is shown in Table 4.2.

As presented in Table 4.1 and 4.2, case I presented the lowest FCI and cost of manufacturing while case II was relatively most expensive. Ethyl acetate and ethanol are azeotrope and cannot be easily separated using a simple distillation column. Ethyl acetate and ethanol can be separated by an extractive distillation, requiring addition of the solvent which was dimethyl sulfoxide in this study. For case III, although acetaldehyde could be separated, the price of acetaldehyde is relative cheaper than ethyl acetate in case II. Acetaldehyde price is 1,005.30 USD/t [88] while ethyl acetate price is 1,110.00 USD/t [88]). The cost of manufacturing was deducted from the revenue of selling byproducts (ethyl acetate and acetaldehyde) is shown in Table 4.2.

Table 4.1 Capital investment costs of ethanol steam reforming and ethanol dehydrogenation process

Parameters	Unit	case I	case II	case III
H_2 Productivity	t/y	1,693.04	1,664.77	1,663.85
Fixed capital investment (FCI)	USD	1,536,656.87	5,438,713.20	1,691,695.97
Total capital investment (TCI)	USD	1,807,831.61	6,398,486.12	1,990,230.55

Table 4.2 Cost of manufacturing (COM_d) of H_2 production from ethanol steam reforming and ethanol dehydrogenation process

Parameters	Unit	case I	case II	case III
Raw material:				
Ethanol	USD/y	1,557,740.82	6,278,719.25	5,732,954.30
Process water	USD/y	197.13	-	-
Dimethyl sulfoxide	USD/y	-	1,924.51	-
Total raw materials costs		1,557,937.95	6,280,643.76	5,732,954.30

Table 4.2 Cost of manufacturing (COM_d) of H_2 production from ethanol steam reforming and ethanol dehydrogenation process (continue)

Parameters	Unit	case I	case II	case III
Utility:				
Cooling Water	USD/y	10,325.00	93,728.80	110,408.00
LP steam	USD/y	28,501.07	33,363.33	459,191.05
MP steam	USD/y	-	740,457.20	-
HP steam	USD/y	1,327,044.63	1,702,649.65	2,360,590.05
Electricity	USD/y	-	8,923.92	19,037.28
Total utility costs	USD/y	1,365,870.70	2,579,122.89	2,949,226.38
Operating labor	USD/y	74,100.00	79,800.00	79,800.00
Total cost of manufacturing	USD/y	4,077,621.19	11,119,810.99	9,543,516.92
Cost of manufacturing per ton of Hydrogen	USD/t	2,408.46	6,679.49	5,735.80
Revenue of selling value products per ton of Hydrogen	USD/t	-	2,278.22	2,014.18
Total cost of manufacturing per ton of Hydrogen (Deduct from Revenue of selling value products)	USD/t	2,408.46	4,401.27	3,721.63

As presented in Table 4.2, case I presents the lowest cost of manufacturing per ton of H_2. However, CO_2 emission in case I was relatively highest and must be handled. The carbon capture and storage (CCS) with post-combustion amine scrubbing technology using monoethanolamine (MEA) can capture CO_2 with the cost of 164.6 USD/t of CO_2 avoided [92]. Therefore, if taken carbon capture into account, CO_2 emission in case I increased the cost of manufacturing per ton of H_2 at 2,606.38 USD with CCS.

As presented in Table 4.3, the itemized cost estimation of H_2 production for each case was calculated from the annual capital cost, the annual operating cost and the annual revenue of selling byproducts. The results showed the lowest unit H_2 production cost of 1.90 USD/kg of H_2 in case I. In case I, the lowest amount of ethanol was consumed as the raw material. Moreover, case I was operated at atmospheric pressure while case II and III were operated at the higher pressure, affecting the energy consumption. Ethanol dehydrogenation in case II and III presented the H_2 production cost of 3.57 USD/kg of H_2 and 3.40 USD/kg of H_2, respectively.

Table 4.3 Itemized cost estimation for a unit H_2 production cost of (a) case I, (b) case II and (c) case III

Items	**(a) case I** Annual cost (USD/y)	**(b) case II** Annual cost (USD/y)	**(c) case III** Annual cost (USD/y)
1.Capital cost	180,783.16	639,848.61	199,023.06
2.Operating cost			
Raw materials	1,557,937.95	6,280,643.76	5,732,954.30
Utility	1,365,870.70	2,579,122.89	2,949,226.38
Labor	74,100.00	79,800.00	79,800.00
Maintenance*	30,733.14	108,774.26	33,833.92
Other costs**	15,366.57	54,387.13	16,916.96
3.Revenue of selling byproducts	0.00	-3,792,714.60	-3,351,290.24
Total costs	3,224,791.52	5,949,862.06	5,660,464.38
H_2 production cost (USD/kg)	1.90	3.57	3.40
H_2 production cost (USD/kg) with CCS	2.10	3.62	3.47

*2% of FCI, **1% of FCI

For methanol synthesis based on H_2 stream from case I-III were compared with the work of Khunathorncharoenwong et.al [40] as presented on Table 4.4. The raw material of CO_2 price in case I was determined. In case I, CO_2 was released from H_2 production process and the cost of carbon capture and storage (CCS) with post-combustion amine scrubbing technology using MEA was applied. The captured CO_2 costs 164.6 USD/t of CO_2 avoided [92]. In case II and III, CO_2 feed was required and the price was 9.53 USD/t. In addition, H_2 price for case I-III was shown in Table 4.3. For the work of Khunathorncharoenwong et.al [40], the H_2 price was 4.20 USD/kg (produced using renewable source). The results showed the highest the CO_2 cost in case I corresponding to high the CCS cost for captured CO_2. On the contrary, Case I was presented lowest the COM per ton of methanol at 959 USD/t followed by case II, case III and the work of Khunathorncharoenwong et.al.

Table 4.4 Cost of manufacturing (COM_d) of CO_2 conversion with H_2 from ethanol steam reforming and ethanol dehydrogenation process steam reforming and ethanol dehydrogenation process

Parameters	Unit	Case I	Case II	Case III	[40]
Raw material:					
• CO_2	USD/y	300,153.04	105,225.02	103,087.92	110,221
• H_2 (cost of H_2 based on table 4.3)	USD/y	3,224,791.52	5,949,862.06	5,660,464.38	6,342,000
Total raw materials costs	USD/y	3,524,944.55	6,055,087.08	5,763,552.29	6,452,221
Total utility costs	USD/y	1,519,800.80	1,343,445.09	1,483,815.09	2,177,582
Operating labor	USD/y	85,500.00	85,500.00	85,500.00	85,500.00
Total cost of manufacturing	USD/y	6,879,180.18	9,746,838.49	9,693,739.37	13,112,669
Cost of manufacturing per ton of Methanol	USD/t	959.41	1,296.49	1,346.99	1,756

NPV as shown in Figure 4.4 for all case presented 21,470, 3,779 and 6,662 (x10^3 USD), respectively. Although, the economic analysis of H_2 production in case I presents best alternative for conversion of CO_2 to methanol due to low H_2 price and high NPV, in part of desire to reduce CO_2 emission case I is not require CO_2 feedstock for feed into methanol synthesis

Sensitivity analysis (SA) was performed to investigate the impact of input parameters on the NPV of the H_2 production processes, as shown in Figure 4.4. The SA showed the selling price of H_2 as the most significantly sensitive parameter for all cases. In case I, II and III, the selling price of H_2 presented the NPV in the range of 3,993 to 38,947; -13,407 to 20,964; and, -10,514 to 23,838 (x10^3 USD), respectively. In case I, the utility presented NPV in the range of 18,113 to 24,827 (x10^3 USD) The sensitive parameters of case II and III was in the order of H_2 selling price, raw material cost, utility cost and TCI. It should be noted that the NPV was negative in case II and III when the selling price of H_2 decreased lower than 10%.

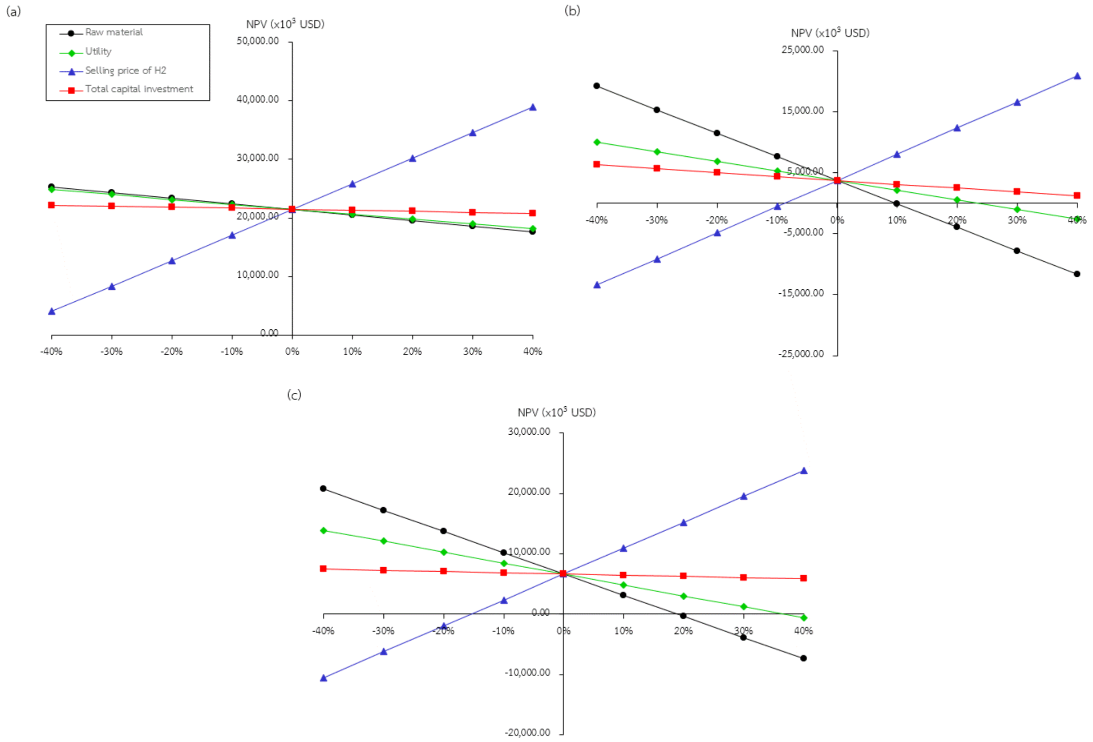

Figure 4.4 Sensitivity analysis (SA) in terms of net present value (NPV) of the H_2 production process: (a) case I, (b) case II and (c) case III

CHAPTER 5

Conclusion

5.1 Conclusion

Techno-economic analysis of H_2 production from ethanol was performed, comparing between ethanol steam reforming and ethanol dehydrogenation. Performance analysis included required ethanol feed and net CO_2 emission. Cost analysis included capital investment, product cost and sensitivity analysis. For the performance analysis, the required amount of ethanol feed was compared to achieve H_2 production at 1,663-1,693 t/y which was available for CO_2 conversion to methanol at 7,427 t/y. Ethanol steam reforming process (case I) required the lowest ethanol feed, followed by ethanol dehydrogenation to ethyl acetate process (case II) and ethanol dehydrogenation to acetaldehyde process (case III), respectively.

The steam reforming of ethanol process also showed that the lowest fixed capital investment and cost of manufacturing. However, the process presented significant amount of CO_2 emission from the reaction and the utility usage. In contrast, dehydrogenation of ethanol not only generated H_2 without CO_2 emission from the reaction but also ethyl acetate or acetaldehyde which were valued chemicals.

Net CO_2 emission from the H_2 production process combined methanol production process was also negative at -253.33 and -5.55 kg per ton of methanol produced in case II and III, respectively. The cost of H_2 production was 1.90, 3.57 and 3.40 USD per kg for case I, II and III, respectively. However, if carbon capture was considered, the cost of manufacturing per ton of H_2 was 2.10 USD per kg in case I. Dehydrogenation of ethanol to H_2 and acetaldehyde showed the best potential in term of the H_2 cost competitiveness to steam reforming process while dehydrogenation of ethanol to H_2 and ethyl acetate consumed relative largest amount of CO_2 in overall processes of H_2 production and CO_2 conversion to methanol. The results of this study showed that although the cost of H_2 produced by steam reforming of ethanol was relatively lowest and CO_2 emitted from H_2 process could be utilized as a raw material in methanol synthesis, CO_2 emission was still net positive.

5.2 Suggestion for future work

5.2.1 Due to the lowest cost of H_2 via ethanol steam reforming as case I, the ethanol steam reforming can be further developed to mitigate CO_2 emission. For example, catalyst development for this reaction can be done.

5.2.2 The type of ethanol as a raw material used in this study was based on anhydrous ethanol with 99.5 wt% of ethanol (the price at 0.431 USD/L [88]). The cost of ethanol is fluctuated and can be decreased in hydrous ethanol. Using hydrous ethanol may not affect the steam reforming reaction.

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APPENDIX A

Process flow diagram and flow summary table for H_2 production for CO_2 conversion

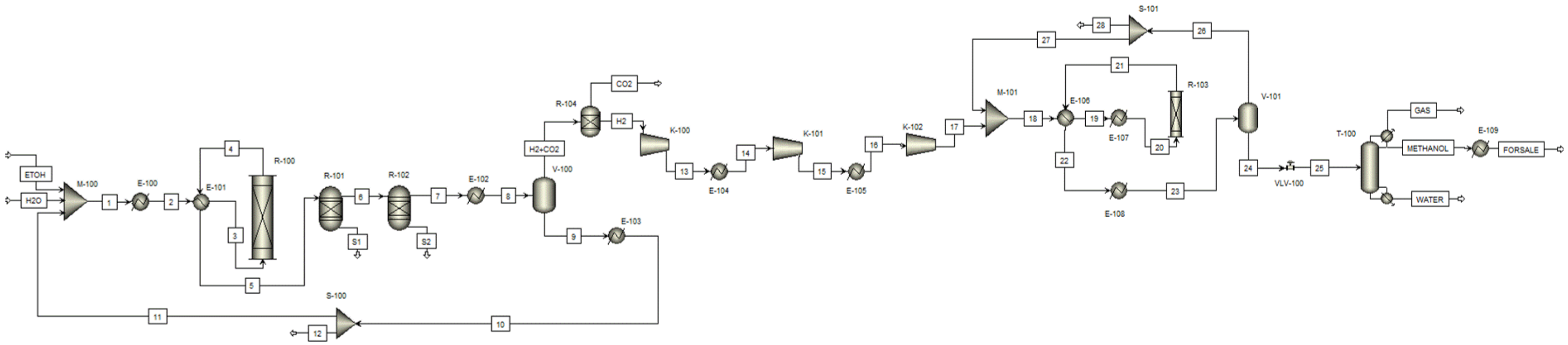

Figure A.1 Process flow diagram of H_2 production for CO_2 conversion via ethanol steam reforming (case I)

Table A.1 Flow summary table of H_2 production for CO_2 conversion via ethanol steam reforming (case I)

Stream number	**ETOH**	**H2O**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature (℃)	45.00	45.00	47.44	200.00	517.00	527.00	229.74	250.00	180.00	45.00
Pressure (bar)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Vapor fraction	0	0	0	1	1	1	1	1	1	1
Mass flow (kg/h)	1190.88	1378.46	3686.33	3686.33	3686.33	3686.33	3686.33	3686.33	3686.33	3686.33
Mole flow (kmol/h)	25.85	76.52	159.13	159.13	1591.13	220.60	220.60	220.60	220.60	220.60
Component flowrates (kmol/h)										
C_2H_5OH	1.00	0.00	0.18	0.18	0.18	0.03	0.03	0.03	0.03	0.03
H_2O	0.00	1.00	0.82	0.82	0.82	0.48	0.48	0.48	0.41	0.41
H_2	0.00	0.00	0.00	0.00	0.00	0.29	0.29	0.29	0.35	0.35
CO_2	0.00	0.00	0.00	0.00	0.00	0.08	0.08	0.08	0.14	0.14
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.06	0.06	0.06
CO	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.06	0.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.1 Flow summary table of H_2 production for CO_2 conversion via ethanol steam reforming (case I) (continue)

Stream number	**9**	**10**	**11**	**12**	**H2+CO2**	**CO2**	**H2**	**13**	**14**	**15**
Temperature (℃)	15.00	45.00	45.00	45.00	15.00	15.00	15.00	237.54	60.00	199.64
Pressure (bar)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	6.00	6.00	17.50
Vapor fraction	0	0	0	0	1	1	1	1	1	1
Mass flow (kg/h)	1861.65	1861.65	1116.99	744.66	1824.68	188.72	1635.97	1635.97	1635.97	1635.97
Mole flow (kmol/h)	94.61	94.61	56.77	37.85	125.98	4.29	121.70	121.70	121.70	121.70
Component flowrates (kmol/h)										
C_2H_5OH	0.06	0.06	0.06	0.06	0.01	0.00	0.01	0.01	0.01	0.01
H_2O	0.94	0.94	0.94	0.94	0.02	0.00	0.02	0.02	0.02	0.02
H_2	0.00	0.00	0.00	0.00	0.62	0.00	0.64	0.64	0.64	0.64
CO_2	0.00	0.00	0.00	0.00	0.24	1.00	0.22	0.22	0.22	0.22
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.00	0.00	0.00	0.00	0.11	0.00	0.12	0.12	0.12	0.12
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.1 Flow summary table of H_2 production for CO_2 conversion via ethanol steam reforming (case I) (continue)

Stream number	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Temperature (℃)	60.00	196.69	190.53	240.00	250.00	250.00	212.89	59.00	59.00	57.53
Pressure (bar)	17.50	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	4.00
Vapor fraction	1	1	1	1	1	1	1	0	0	0
Mass flow (kg/h)	1635.97	1635.97	1716.83	1716.83	1716.83	1716.83	1716.83	1716.83	1364.77	1364.77
Mole flow (kmol/h)	121.70	121.70	126.74	126.74	126.74	76.15	76.15	76.15	54.20	54.20
Component flowrates (kmol/h)										
C_2H_5OH	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
H_2O	0.02	0.02	0.02	0.02	0.02	0.36	0.36	0.36	0.50	0.50
H_2	0.64	0.64	0.62	0.62	0.62	0.03	0.03	0.03	0.00	0.00
CO_2	0.22	0.22	0.21	0.21	0.21	0.02	0.02	0.02	0.00	0.00
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.12	0.12	0.15	0.15	0.15	0.24	0.24	0.24	0.01	0.01
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.33	0.33	0.33	0.46	0.46

Table A.1 Flow summary table of H_2 production for CO_2 conversion via ethanol steam reforming (case I) (continue)

Stream number	**26**	**27**	**28**	GAS	WATER	METHANOL	FORSALE
Temperature (℃)	59.00	59.00	59.00	78.02		28.46	50.00
Pressure (bar)	50.00	50.00	50.00	2.80		2.80	2.80
Vapor fraction	1	1	1	1		0	0
Mass flow (kg/h)	352.06	80.79	271.09	42.59	436.78	885.40	885.40
Mole flow (kmol/h)	21.95	5.05	16.90	1.50	24.24	28.46	28.46
Component flowrates (kmol/h)							
C_2H_5OH	0.00	0.00	0.00	0.02	0.00	0.04	0.04
H_2O	0.00	0.00	0.00	0.03	1.00	0.10	0.10
H_2	0.12	0.12	0.12	0.02	0.00	0.00	0.00
CO_2	0.05	0.05	0.05	0.14	0.00	0.00	0.00
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.82	0.82	0.82	0.29	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.01	0.01	0.01	0.52	0.00	0.86	0.86

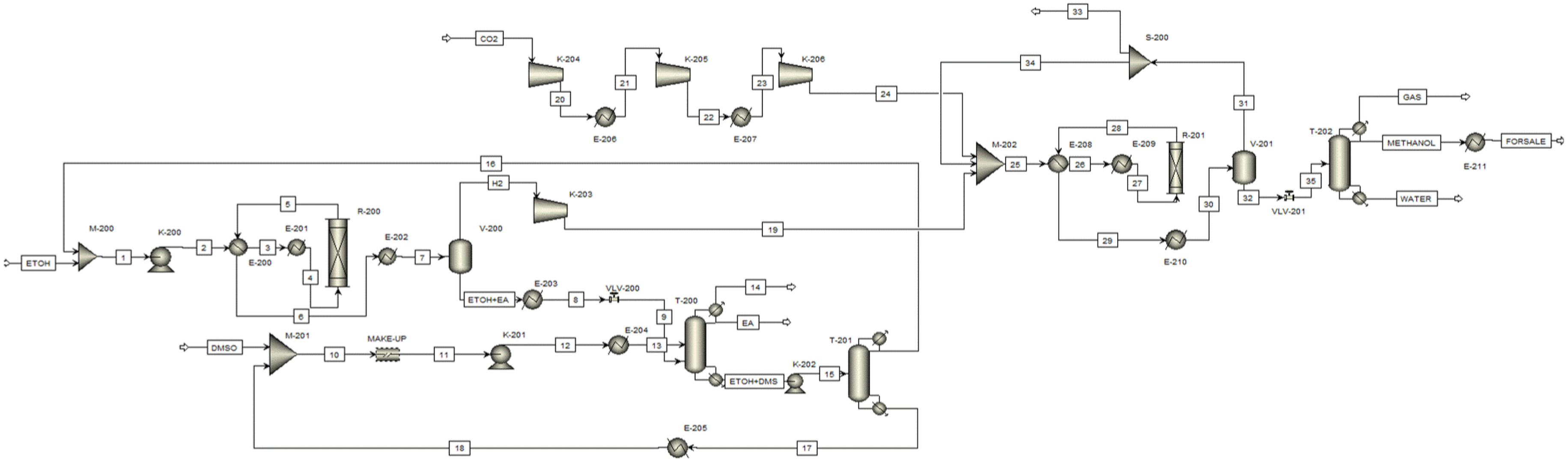

Figure A.2 Process flow diagram of H_2 production for CO_2 conversion via ethanol dehydrogenation to ethyl acetate (case II)

Table A.2 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to ethyl acetate (case II)

Stream number	**ETOH**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**ETOH+EA**	**8**
Temperature (℃)	25.00	37.04	38.81	161.58	220.00	240.00	134.90	50.00	45.00	47.56
Pressure (bar)	1.00	0.50	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Vapor fraction	0	0	0	0	1	1	0.77235	0.508435	0	0
Mass flow (kg/h)	4050.85	6129.84	6129.84	6129.84	6130.07	6130.07	6130.07	6130.07	5833.63	5833.63
Mole flow (kmol/h)	87.93	130.62	130.62	130.62	130.62	174.25	174.25	174.25	86.06	86.06
Component flowrates (kmol/h)										
C_2H_5OH	1.00	0.98	0.98	0.98	0.98	0.23	0.23	0.23	0.46	0.46
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	0.00	0.00	0.00	0.00	0.00	0.50	0.50	0.50	0.01	0.01
$CH_3COOC_2H_5$	0.00	0.01	0.01	0.01	0.01	0.26	0.26	0.26	0.51	0.51
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$(CH_3)_2SO$	0.00	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.2 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to ethyl acetate (case II) (continue)

Stream number	**9**	**DMSO**	**10**	**11**	**12**	**13**	**14**	**EA**	**ETOH+DMS**	**15**
Temperature (℃)	47.88	25.00	35.09	35.09	35.28	47.00	52.81	52.81	151.37	151.63
Pressure (bar)	1.50	1.00	1.00	1.00	3.00	3.00	0.50	0.50	2.00	5.00
Vapor fraction	0.0089426	0	0	0	0	0	1	0	0	0
Mass flow (kg/h)	5833.63	0.08	10016.50	10016.50	10016.50	10016.50	326.29	3428.12	12095.40	12065.40
Mole flow (kmol/h)	86.06	0.00	128.20	128.20	128.20	128.20	4.37	39.03	170.88	170.88
Component flowrates (kmol/h)										
C_2H_5OH	0.46	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.23	0.23
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
H_2	0.01	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00
$CH_3COOC_2H_5$	0.51	0.00	0.00	0.00	0.00	0.00	0.84	0.99	0.01	0.01
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$(CH_3)_2SO$	0.02	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.76	0.76
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.2 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to ethyl acetate (case II) (continue)

Stream number	**16**	**17**	**18**	**H2**	**19**	**CO2**	**20**	**21**	**22**	**23**
Temperature (℃)	60.98	229.34	35.00	45.00	170.01	25.00	208.23	60.00	173.12	60.00
Pressure (bar)	0.50	2.50	2.50	20.00	50.00	1.00	6.00	6.00	17.50	17.50
Vapor fraction	0	0	0	1	1	1	1	1	1	1
Mass flow (kg/h)	2078.99	10016.40	10016.40	296.44	296.44	1260.44	1260.44	1260.44	1260.44	1260.44
Mole flow (kmol/h)	42.69	128.16	128.16	88.19	88.19	28.64	28.64	28.64	28.64	28.64
Component flowrates (kmol/h)										
C_2H_5OH	0.93	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	0.00	0.00	0.00	0.98	0.98	0.00	0.00	0.00	0.00	0.00
$CH_3COOC_2H_5$	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$(CH_3)_2SO$	0.05	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.2 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to ethyl acetate (case II) (continue)

Stream number	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**
Temperature (°C)	172.44	166.98	220.00	250.00	250.00	217.69	59.00	59.00	59.00	59.00
Pressure (bar)	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Vapor fraction	1	1	1	1	1	0.951299	0.164617	1	0	1
Mass flow (kg/h)	1260.44	1597.43	1597.43	1597.43	1597.43	1597.43	1597.43	106.53	1490.90	66.04
Mole flow (kmol/h)	28.64	121.08	121.08	121.08	67.70	67.70	67.70	11.14	56.55	6.91
Component flowrates (kmol/h)										
C_2H_5OH	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	0.00	0.74	0.74	0.74	0.13	0.13	0.13	0.78	0.01	0.78
$CH_3COOC_2H_5$	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.02	0.00
H_2O	0.00	0.00	0.00	0.00	0.40	0.40	0.40	0.00	0.48	0.00
$(CH_3)_2SO$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.08	0.00	0.08
CO_2	1.00	0.24	0.24	0.24	0.03	0.03	0.03	0.11	0.01	0.11
CH_3OH	0.00	0.00	0.00	0.00	0.39	0.39	0.39	0.01	0.47	0.01

Table A.2 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to ethyl acetate (case II) (continue)

Stream number	**34**	**35**	**GAS**	**WATER**	**METHANOL**	**FORSALE**
Temperature (℃)	59.00	58.94	66.93	141.45	66.93	50.00
Pressure (bar)	50.00	4.00	2.80	4.80	2.80	2.80
Vapor fraction	1	0.0152829	1	0	0	0
Mass flow (kg/h)	40.48	1490.90	41.01	546.52	903.37	903.37
Mole flow (kmol/h)	4.23	56.55	1.39	28.79	26.37	26.37
Component flowrates (kmol/h)						
C_2H_5OH	0.00	0.01	0.00	0.02	0.01	0.01
CH_3CHO	0.00	0.00	0.00	0.00	0.00	0.00
H_2	0.78	0.01	0.25	0.00	0.00	0.00
$CH_3COOC_2H_5$	0.00	0.02	0.02	0.00	0.04	0.04
H_2O	0.00	0.48	0.00	0.95	0.00	0.00
$(CH_3)_2SO$	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.08	0.00	0.03	0.00	0.00	0.00
CO_2	0.11	0.01	0.31	0.00	0.00	0.00
CH_3OH	0.01	0.47	0.39	0.04	0.95	0.95

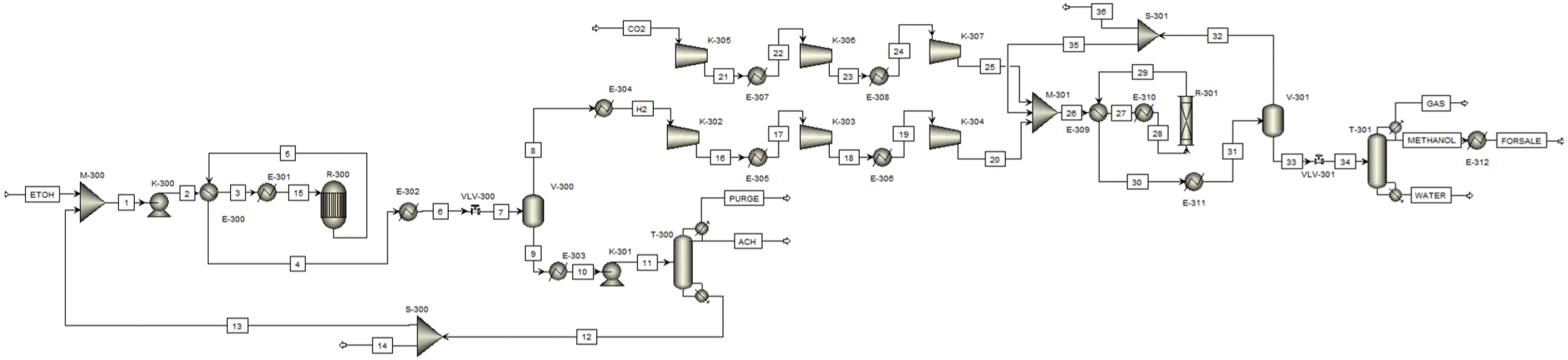

Figure A.3 Process flow diagram of H_2 production for CO_2 conversion via ethanol dehydrogenation to acetaldehyde (case III)

Table A.3 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to acetaldehyde (case III)

Stream number	**ETOH**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature (℃)	25.00	86.17	89.04	201.89	161.00	280.00	50.00	34.98	-22.00	-22.00
Pressure (bar)	2.00	2.00	37.42	37.42	37.42	37.42	37.45	2.01	2.01	2.01
Vapor fraction	0	0	0	0.13255	0.49486	1	0.238956	0.312903	1	0
Mass flow (kg/h)	4712.03	12294.70	12294.70	12294.70	12294.70	12294.70	12294.70	12294.70	239.13	12055.60
Mole flow (kmol/h)	102.28	273.36	273.36	273.36	360.52	360.52	360.52	360.52	87.43	273.10
Component flowrates (kmol/h)										
C_2H_5OH	1.00	0.93	0.93	0.93	0.46	0.46	0.46	0.46	0.00	0.61
CH_3CHO	0.00	0.03	0.03	0.03	0.26	0.26	0.26	0.26	0.01	0.34
H_2	0.00	0.00	0.00	0.00	0.24	0.24	0.24	0.24	0.98	0.00
C_2H_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
H_2O	0.00	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.00	0.04
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.3 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to acetaldehyde (case III) (continue)

Stream number	**10**	**11**	**12**	**13**	**14**	**ACH**	**PURGE**	**H2**	**CO2**	**15**
Temperature (℃)	50.00	50.19	115.18	115.18	115.18	39.21	39.21	25.00	25.00	239.00
Pressure (bar)	2.01	5.00	5.00	5.00	5.00	2.00	2.00	2.00	2.00	37.42
Vapor fraction	0	0	0	0	0	0	1	1	1	1
Mass flow (kg/h)	12055.60	12055.60	8332.63	7582.70	749.94	3350.68	372.30	239.13	28.06	12294.70
Mole flow (kmol/h)	273.10	273.10	188.00	171.08	16.92	76.51	8.59	87.43	1234.84	273.36
Component flowrates (kmol/h)										
C_2H_5OH	0.61	0.61	0.89	0.89	0.89	0.00	0.00	0.00	0.00	0.93
CH_3CHO	0.34	0.34	0.05	0.05	0.05	0.99	0.97	0.01	0.00	0.03
H_2	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.98	0.00	0.00
C_2H_4	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00
H_2O	0.04	0.04	0.06	0.06	0.06	0.01	0.01	0.00	0.00	0.04
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.3 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to acetaldehyde (case III) (continue)

Stream number	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Temperature (℃)	173.25	60.00	220.66	60.00	217.13	207.67	60.00	171.96	60.00	169.68
Pressure (bar)	6.00	6.00	17.50	17.50	50.00	6.00	6.00	17.50	17.50	50.00
Vapor fraction	1	1	1	1	1	1	1	1	1	1
Mass flow (kg/h)	239.13	239.13	239.13	239.13	239.13	1234.84	1234.84	1234.84	1234.84	1234.84
Mole flow (kmol/h)	87.43	87.43	87.43	87.43	87.43	28.06	28.06	28.06	28.06	28.06
Component flowrates (kmol/h)										
C_2H_5OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3CHO	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
H_2	0.98	0.98	0.98	0.98	0.98	0.00	0.00	0.00	0.00	0.00
C_2H_4	0.02	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.3 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to acetaldehyde (case III) (continue)

Stream number	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**
Temperature (℃)	192.14	240.00	250.00	250.00	217.80	59.00	59.00	59.00	57.53	59.00
Pressure (bar)	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	4.00	50.00
Vapor fraction	1	1	1	1	0.954511	0.19162	1	0	0.0180485	1
Mass flow (kg/h)	1549.95	1549.95	1549.95	1549.95	1549.95	1549.95	111.74	1438.20	1438.20	75.99
Mole flow (kmol/h)	124.66	124.66	124.66	70.40	70.40	70.40	13.49	56.91	56.91	9.17
Component flowrates (kmol/h)										
C_2H_5OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3CHO	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.00
H_2	0.74	0.74	0.74	0.16	0.16	0.16	0.80	0.00	0.00	0.80
C_2H_4	0.02	0.02	0.02	0.03	0.03	0.03	0.05	0.02	0.02	0.05
H_2O	0.00	0.00	0.00	0.39	0.39	0.39	0.00	0.48	0.48	0.00
CO	0.00	0.00	0.00	0.01	0.01	0.01	0.06	0.00	0.00	0.06
CO_2	0.23	0.23	0.23	0.02	0.02	0.02	0.07	0.01	0.01	0.07
CH_3OH	0.00	0.00	0.00	0.39	0.39	0.39	0.01	0.48	0.48	0.01

Table A.3 Flow summary table of H_2 production for CO_2 conversion via ethanol dehydrogenation to acetaldehyde (case III) (continue)

Stream number	**36**	GAS	WATER	METHANOL	FORSALE
Temperature (℃)	59.00	32.98	140.69	32.98	50.00
Pressure (bar)	50.00	2.80	4.80	2.80	2.80
Vapor fraction	1	1	0	0	0
Mass flow (kg/h)	35.76	39.13	543.32	855.76	855.76
Mole flow (kmol/h)	4.32	1.40	28.95	26.56	26.56
Component flowrates (kmol/h)					
C_2H_5OH	0.00	0.00	0.00	0.00	0.00
CH_3CHO	0.00	0.01	0.00	0.02	0.02
H_2	0.80	0.13	0.00	0.00	0.00
C_2H_4	0.05	0.58	0.00	0.02	0.02
H_2O	0.00	0.00	0.95	0.00	0.00
CO	0.06	0.02	0.00	0.00	0.00
CO_2	0.07	0.18	0.00	0.00	0.00
CH_3OH	0.01	0.09	0.05	0.96	0.96

APPENDIX B

Utility and CO_2 consumption

Table B.1 Utility and CO_2 usage from ethanol steam reforming for CO_2 conversion

Process	Symbol	Equipment	Utility	Unit	Utility consumption	CO_2 emission (kg/h)
H_2 process (case I)	E-100	Heat exchanger	HP steam	t/y	44,279.10	518.02
	E-101		Process exchanger		-	-
	E-102		Cooling water	t/y	697,635.00	-
	E-103		LP steam	t/y	973.07	14.52
	R-101	Reactor	Cooling water	t/y	58,527.00	-
	R-102				89,121.00	-
Methanol process	K-100	Compressor	Electricity	kW	254.63	88.33
	K-101				159.67	55.39
	K-102				156.18	54.18
	E-104	Heat exchanger	Cooling water	t/y	113,837.00	-
	E-105				88,738.30	-
	E-106		Process exchanger		-	-
	E-107		HP steam	t/y	4,901.86	57.35
	E-108		Cooling water	t/y	393,382.00	-
	E-109				13,542.00	-
	T-100	Condenser	Cooling water	t/y	1,103,710.00	-
		Reboiler	MP steam	t/y	35,406.90	490.24
Total water consumption				t/y	2,558,492.30	-
Total LP steam consumption				t/y	973.07	14.52
Total MP steam consumption				t/y	35,406.90	490.24
Total HP steam consumption				t/y	49,180.96	575.36
Total electricity consumption				kWh	4,997,439.84	197.90

Table B.2 Utility and CO_2 usage from ethanol dehydrogenation to ethyl acetate for CO_2 conversion

Process	Symbol	Equipment	Utility	Unit	Utility consumption	CO_2 emission (kg/h)
H_2 process (case II)	K-200	Pump	Electricity	kW	12.40	4.30
	K-201				1.59	0.55
	K-202				2.98	1.03
	E-200	Heat exchanger	Process exchanger		-	-
	E-201		HP steam	t/y	25,931.60	303.37
	E-202		Cooling water	t/y	1,314,690.00	-
	E-203		LP steam	t/y	159.07	2.37
	E-204				980.00	14.62
	E-205		Cooling water	t/y	1,921,166.00	-
	T-200	Condenser	Cooling water	t/y	1,153,746.00	-
		Reboiler	HP steam	t/y	15,696.69	183.63
	T-201	Condenser	Cooling water	t/y	1,943,425.00	-
		Reboiler	HP steam	t/y	15,183.46	177.63
Methanol process	K-203	Compressor	Electricity	kW	95.32	33.07
	K-204				59.45	20.62
	K-205				36.02	12.50
	K-206				34.04	11.81
	E-206	Heat exchanger	Cooling water	t/y	83,611.00	-
	E-207				65,598.00	-
	E-208		Process exchanger		-	-
	E-209		HP steam	t/y	5,795.40	67.80
	E-210		Cooling water	t/y	1,104,224.00	-
	E-211				20,636.50	-
	T-202	Condenser	Cooling water	t/y	3,141,719.00	-
		Reboiler	MP steam	t/y	33,329.90	461.48
Total water consumption				t/y	10,748,815.50	-
Total LP steam consumption				t/y	1,139.07	17.00
Total MP steam consumption				t/y	49,026.59	645.11
Total HP steam consumption				t/y	46,910.46	548.80
Total electricity consumption				kWh	2,118,257.61	83.88

Table B.3 Utility and CO_2 usage from ethanol dehydrogenation to acetaldehyde for CO_2 conversion

Process	Symbol	Equipment	Utility	Unit	Utility consumption	CO_2 emission (kg/h)
H_2 process (case III)	K-300	Pump	Electricity	kW	33.60	11.66
	K-301				2.69	0.93
	E-300	Heat exchanger	Process exchanger		-	-
	E-301		HP steam	t/y	18,908.02	221.22
	E-302		Cooling water	t/y	3,935,010.00	-
	E-303		LP steam	t/y	15,768.10	235.18
	E-304				524.94	7.83
	T-300	Condenser	Cooling water	t/y	1,671,519.00	-
		Reboiler	HP steam	t/y	18,640.58	218.10
Methanol process	K-302	Compressor	Electricity	kW	106.87	37.07
	K-303				116.61	40.45
	K-304				114.02	39.56
	K-305				58.49	20.29
	K-306				35.94	12.47
	K-307				35.17	12.20
	E-305	Heat exchanger	Cooling water	t/y	136,535.00	-
	E-306				194,319.00	-
	E-307				80,140.40	-
	E-308				59,888.60	-
	E-309		Process exchanger		-	-
	E-310		HP steam	t/y	4,520.58	52.89
	E-311		Cooling water	t/y	1,179,144.00	-
	E-312		LP steam	t/y	203.00	3.03
	T-301	Condenser	Cooling water	t/y	3,295,921.00	-
		Reboiler	MP steam	t/y	34,595.30	479.00
Total water consumption				t/y	10,552,477.00	-
Total LP steam consumption				t/y	16,496.04	1,135.31
Total MP steam consumption				t/y	34,595.30	97.79
Total HP steam consumption				t/y	42,069.17	1,507.66
Total electricity consumption				kWh	503.41	611.36

Table B.4 Net CO_2 consumption from different H_2 production processes

Scenario	1	1*	2	2*	3	3*
Reaction						
CO_2 emission from H_2 plant	1505.94	0	0	0	0	0
CO_2 conversion to methanol plant	0	-1295.26	0	-1260.44	0	-1234.84
Utilities						
Electricity	0	276.37	5.89	98.64	12.59	210.25
LP steam	14.52	0	17.00	0	243.01	3.03
MP steam	0	478.80	0.00	461.48	0	479.00
HP steam	518.02	57.35	481.00	67.80	439.32	52.89
Ton of methanol per h	1.00	1.00	0.90	0.90	0.90	0.90
CO_2 emitted (kg/ton of methanol)	2034.98	0	561.67	0.00	772.37	0.00
CO_2 avoided (kg/ton of methanol)	0	-757.81	0	-815.01	0	-777.92
Net CO_2 emitted (kg/ton of methanol)	2792.79		-253.33		-5.55	

APPENDIX C

Cost estimation

Table C.1 Total COM from ethanol steam reforming (case I) to methanol

Process	Symbol	Equipment	Specifications (A)	Unit	C_{BM} (USD)
H_2 Process (case I)	E-100	Heat exchanger	18.43	m^2	94,015.29
	E-101		45.82		101,286.90
	E-102		52.75		104,584.76
	E-103		0.60		556,843.50
	R-100	Reactor (Fixed bed)	3.79	m^3	147,871.12
	R-101		3.50		136,473.55
	R-102		3.50		136,473.55
	V-100	Flash vessel	2.403		24,702.90
Methanol Process	K-100	Compressor	183.33	kW	293,058.62
	K-101		114.96		191,089.61
	K-102		112.45		187,168.27
	E-104	Heat exchanger	11.68	m^2	98,730.25
	E-105		6.85		112,483.72
	E-106		3.00		107,665.66
	E-107		46.20		101,462.35
	E-108		29.60		94,970.37
	E-109		0.90		379,509.73
	R-103	Reactor	0.15	m^3	5,848.87
	V-101	Flash vessel	0.98		15,940.20
	T-100	Vessel	16.93		103,090.42
		Sieve tray	0.95(21)	m^2	95,682.14
		Condenser	17.49		94,532.34
		Reboiler	33.20		193,759.87
Fixed capital investment (FCI)	H_2 process				1,536,656.87
	Methanol process				2,448,491.05
Total capital investment (TCI)	H_2 process				1,807,831.61
	Methanol process				2,880,577.70

Table C.2 Total COM from ethanol dehydrogenation to ethyl acetate (case II) to methanol

Process	Symbol	Equipment	Specifications (A)	Unit	C_{BM}
H_2 Process (case II)	K-200	Pump	12.40	kW	21,680.21
	K-201		1.59		12,663.10
	K-202		2.98		13,979.30
	E-200	Heat exchanger	12.67	m^2	98,943.45
	E-201		31.49		96,977.29
	E-202		10.41		102,411.58
	E-203		0.18		2,306,176.95
	E-204		1.48		257,121.48
	R-200	Reactor (Fixed bed)	3.27	m^3	81,764.89
	V-200	Flash vessel	3.27		29,661.78
	T-200	Vessel	67.52		301,983.17
		Sieve tray	1.37(49)	m^2	114,633.59
		Condenser	28.57		94,958.16
		Reboiler	56.42		290,928.29
	T-201	Vessel	14.94	m^3	94,362.53
		Sieve tray	1.37(10)	m^2	114,633.59
		Condenser	25.17		94,245.50
		Reboiler	96.03		481,954.09
Methanol Process	K-203	Compressor	68.63	kW	116,446.56
	K-204		42.80		72,477.34
	K-205		25.94		42,883.79
	K-206		24.51		40,351.62
	E-206	Heat exchanger	2.15	m^2	195,769.70
	E-207		1.27		285,131.32
	E-208		7.94		107,665.66
	E-209		46.20		101,462.35
	E-210		29.60		94,970.37
	E-211		0.90		379,509.73
	R-201	Reactor (Fixed bed)	0.15	m^3	5,848.87
	V-201	Flash vessel	0.98		15,940.20
	T-202	Vessel	16.93		103,090.42
		Sieve tray	0.95(21)	m^2	95,682.14
		Condenser	17.49		94,532.34
		Reboiler	33.20		193,759.87
Fixed capital investment (FCI)	H_2 process				5,438,713.20
	Methanol process				2,295,716.26
Total capital investment (TCI)	H_2 process				6,398,486.12
	Methanol process				2,700,842.66

Table C.3 Total COM from ethanol dehydrogenation to acetaldehyde (case III) to methanol

Process	Symbol	Equipment	Specifications (A)	Unit	C_{BM}
H_2 Process (case III)	K-300	Pump	33.60	kW	34,075.74
	K-301		2.69		15,589.68
	E-300	Heat exchanger	97.59	m^2	128,640.43
	E-301		95.30		128,948.02
	E-302		42.05		101,103.89
	E-303		14.85		95,795.24
	E-304		1.97		208,274.50
	R-300	Reactor (Fixed bed)	5.41	m^3	210,994.61
	V-300	Flash vessel	4.27		34,275.48
	T-300	Vessel	11.72		79,812.95
		Sieve tray	2.06	m^2	147,883.59
		Condenser	74.08		115,880.28
		Reboiler	16.78		132,366.25
Methanol Process	K-302	Compressor	76.95	kW	130,224.54
	K-303		83.96		141,716.46
	K-304		82.10		138,674.34
	K-305		42.11		71,279.34
	K-306		25.88		42,776.58
	K-307		25.32		41,797.78
	E-305	Heat exchanger	4.00	m^2	138,953.25
	E-306		3.17		156,104.80
	E-307		2.07		200,943.27
	E-308		1.16		315,983.40
	E-309		7.94		107,665.66
	E-310		46.20		101,462.35
	E-311		29.60		94,970.37
	E-312		0.90		379,509.73
	R-301	Reactor (Fixed bed)	0.15	m^3	5,848.87
	V-301	Flash vessel	0.98		15,940.20
	T-301	Vessel	16.93		103,090.42
		Sieve tray	0.95(21)	m^2	95,682.14
		Condenser	17.49		94,532.34
		Reboiler	33.20		193,759.87
Fixed capital investment (FCI)	H_2 process				1,691,695.97
	Methanol process				3,033,680.53
Total capital investment (TCI)	H_2 process				1,990,230.55
	Methanol process				3,569,035.92

APPENDIX D

Sensitivity analysis

Table D.1 Sensitivity analysis (SA) in terms of net present value (NPV) of the H_2 production process

sensitivity analysis	NPV ($\times 10^3$) USD											
	Raw material			Utility			Selling price of H_2			Total capital investment		
	Case I	Case II	Case III	Case I	Case II	Case III	Case I	Case II	Case III	Case I	Case II	Case III
-40%	25,299.42	19,215.28	20,752.43	24,827.36	10,117.59	13,910.50	3,993.25	-13,406.66	-10,513.89	22,193.42	6,337.94	7,457.91
-30%	24,342.14	15,356.10	17,229.77	23,988.09	8,532.83	12,098.33	8,362.51	-9,110.36	-6,219.97	22,012.63	5,698.10	7,258.89
-20%	23,384.85	11,496.92	13,707.12	23,148.82	6,948.07	10,286.16	12,731.76	-4,814.05	-1,926.04	21,831.85	5,058.25	7,059.86
-10%	22,427.57	7,637.73	10,184.47	22,309.55	5,363.31	8,473.99	17,101.02	-517.75	2,367.89	21,651.07	4,418.40	6,860.84
0%	21,470.28	3,778.55	6,661.82	21,470.28	3,778.55	6,661.82	21,470.28	3,778.55	6,661.82	21,470.28	3,778.55	6,661.82
10%	20,513.00	-80.63	3,139.16	20,631.01	2,193.79	4,849.65	25,839.54	8,074.85	10,955.75	21,289.50	3,138.70	6,462.79
20%	19,555.71	-3,939.82	-383.49	19,791.75	609.03	3,037.47	30,208.80	12,371.15	15,249.67	21,108.72	2,498.85	6,263.77
30%	18,598.43	-7,799.00	-3,906.14	18,952.48	-975.73	1,225.30	34,578.06	16,667.46	19,543.60	20,927.93	1,859.00	6,064.75
40%	17,641.14	-11,658.19	-7,428.79	18,113.21	-2,560.49	-586.87	38,947.32	20,963.76	23,837.53	20,747.15	1,219.16	5,865.72

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