Integrative Carbon Capture and Utilization Process: Aqueous Penta-Ethylene Hexamine System for CO_2 Capture and Hydrogenation to Methanol

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Abstract

In this study, integration of CO_2 capture process with CO_2 conversion to methanol process was simulated. Penta-ethylene hexamine (PEHA) was used in absorber to capture CO_2 and then CO_2-rich amine was used directly as feedstock for CO_2 conversion to methanol. The PEHA could capture CO_2 at 11 mmol CO_2/ g PEHA when the unit is operated at 70 ˚C with 1.013 bar pressure of CO_2 and the amine-based was soluble in water. The CO_2-rich amine was then directly hydrogenated at 145 ˚C with hydrogen at 80 bar using a homogeneous catalyst. The homogeneous catalyst was a metal complex catalyst soluble in an organic solvent (2-MTHF). Process simulation was carried out to evaluate the performance of CO_2-rich amine conversion to methanol. The comparative study between conventional methanol production process (case I) and conversion CO_2-rich amine to methanol production process (case II) was carried out. The conversion CO_2-rich amine to methanol production process increased CO_2 conversion to methanol and reduced energy consumption in the CO_2 capture section and in the methanol synthesis section. However, the solvent recovery and product separation caused high heat duty demand in the purification section. Thus, high energy consumption in the purification section of case II remained challenging.

Keywords: CO_2 capture, Carbon capture and utilization, Hydrogenation, Methanol, Penta-ethylene hexamine, Amine

1. Introduction

Global warming has become a serious problem. The increase of global temperature results in climate change and extreme weather. Carbon dioxide (CO_2), which is a major cause of global warming, has been extensively and increasingly emitted to atmosphere (Alper and Orhan, 2017). A carbon capture and utilization (CCU) is a process to capture CO_2 and convert it into high-value products such as methane (CH_3), methanol (CH_3OH) and formic acid ($HCOOH$) (Aresta and Dibenedetto, 2007; Dibenedetto et al., 2014). The CCU has been widely considered as a method to help reduce the CO_2 emission. Currently, an amine-based absorption technology is extensively used for capturing CO_2 (Kierzkowska-Pawlak et al., 2014). However, the major drawback of the CO_2 capture process is the high energy consumption for amine regeneration (Amann, 2007). The CH_3OH can be normally produced from hydrogenation of CO_2 using heterogeneous catalysts such as $Cu/ZnO/Al_2O_3$ (Behrens

et al., 2012). On the other hand, CO_2 can also be hydrogenated to CH_3OH at mild temperatures using metal-base homogeneous catalysts. Many researches have reported using various metal complexes for direct conversion of captured CO_2 to CH_3OH. Homogeneous catalysts are used for one-step CO_2 capture and hydrogenation to CH_3OH. In this study, the one-step CO_2 capture and hydrogenation to CH_3OH is called conversion of CO_2-rich amine to methanol production process. The homogeneous catalyst is a metal complex catalyst solute in an organic solvent or water (Rezayee and Huff, 2015; Kothandaraman et al., 2016; Kar et al., 2018). After the hydrogenation step, the solution is considered to be two layers that consisted of an aqueous layer and an organic layer. Therefore, the amine and catalyst can be easily separated and recycle from the aqueous and the organic layer (Kar et al., 2018) as represented in Fig. 1.
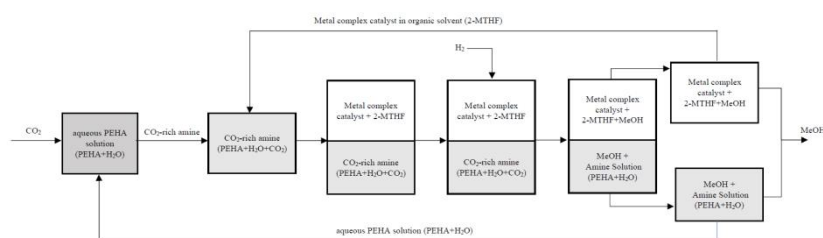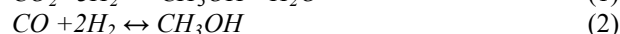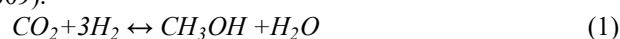

Fig. 1 The biphasic CO_2 to methanol process with recyclable organic solvent (2-MTHF) and aqueous PEHA solution.

This research aims to reduce energy consumption of amine regeneration in CO_2 capture process by integrating CO_2 capture process with CO_2 conversion process. The performance of the integrative process is compared with the conventional process with solvent recovery unit. Penta-ethylene hexamine (PEHA) is a polyamine used for CO_2 absorption in this research. The amine presents rather high CO_2 capacity and reaction rate for capturing CO_2 and recently demonstrates the possibility of direct conversion of captured CO_2 in the amine into methanol. Methanol purification process is also studied. Process simulation is carried out to evaluate the performance of the conversion of CO_2-rich amine to methanol, comparing with conventional process.

2. Property model and Process chemistry

A comparative study between conventional methanol production process (case I) and conversion CO_2-rich amine to methanol production process (case II) was simulated using Aspen Plus V.8.8 process simulator. The process feed was the stoichiometric ratio with 30 kgmol/h of CO_2 and 90 kgmol/h of H_2. The feed of PEHA was 11 kgmol/h. Conventional methanol process (case I) was based on CO_2 hydrogenation with Cu/ZnO catalyst at high temperature and temperature (250 ˚C and 49.5 bar). There were 3 main equilibrium reactions, includes CO_2-rich methanol synthesis reaction, CO-rich methanol synthesis reaction, and reverse water gas shift reaction (Lim et al., 2009). The equilibrium reactions represented in equation 1 – 3, respectively. High pressure was required for increasing CO_2 equilibrium conversion (Lim et al., 2009).

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad (1)$$
$$CO + 2H_2 \leftrightarrow CH_3OH \qquad (2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad\qquad (3)$$

At temperature 250 ˚C and 49.5 bar, Equilibrium constant of equation 1-3 were validated using experimental data of (Graff et al., 1986) and (Sakurai et al., 1993). The equilibrium constants of these equations are represented in Table 1. In the conventional methanol production process, the Redlich-Kwong-Soave equation of state (SRK) was used to calculate thermodynamic properties in equipment which operated at more than 10 bar. On the other side, the equipment which operated at pressure less than 10 bar used NRTL-PR to calculate the thermodynamic properties (Van-dal and Bouallou, 2012).

Table 1 Equilibrium constants were used in the conventional methanol process.

Reaction	Equilibrium constant
(1)	2.37×10^{-5}
(2)	2.15×10^{-3}
(3)	1.10×10^{-2}

For the conversion of CO_2-rich amine to methanol production process (case II), PEHA was a polyamine used for CO_2 absorption. The CO_2 captured in PEHA amine solution (CO_2-rich amine) was then directly hydrogenated at 145 ˚C with hydrogen at 80 bar using a homogeneous catalyst. The homogeneous catalyst consisted of a metal complex catalyst (Ru-MACHO-BH) soluble in 2-Methyltetrahydrofuran (2-MTHF). The 2-MTHF is an organic solvent. The reaction of conversion directly CO_2 capture to CH_3OH represents in Fig. 2. It also is hydrogenated in high yield (95%) to methanol (Kar et al., 2018). Moreover, ENRTL-RK was used to calculate the thermodynamic properties of the amine-based process (Pinto et al., 2013).
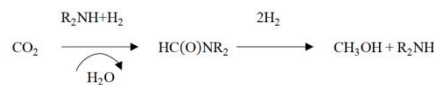

Fig.2 Amine assisted CO_2 hydrogenation to CH_3OH (Rezayee and Huff, 2015).

3. CO₂ to methanol production process design

In this study, there are 2 difference processes for methanol production. The first process (case I) was conventional methanol process which was based on CO_2 hydrogenation with Cu/ZnO catalyst at high temperature and temperature (250 ˚C and 49.5 bar). The process flow diagram of the case I is represented in Fig. 3. In Fig. 3, The process feed was the stoichiometric ratio with 30 kgmol/h of CO_2 and 90 kgmol/h of H_2. The CO_2 and H_2 feed stream were compressed to 49.5 bar though 3 stages of compressors (COM1 - COM6) with 2 intercoolers (H-1 – H-4). The two gases were mixed (MIX1) with a recycle stream before preheating. Before entering a reactor, the stream was preheating by exchanging heat duty with the product stream at heat exchanger (HX1) and heated to 250 ˚C (H-5). After that, the stream injected into an equilibrium reactor. The product stream from the reactor was cooled down to 61.29 ˚C with 49.2 bar of pressure. Then it was split into the liquid-vapor phase by a flash vessel (FLASH1). Vapor outlet from the vessel was the unreacted gases that moved to the recycle unit using a compressor (COM7) and mixed fresh feed streams at the mixer (MIX1). As for liquid outlet, it went to the purification unit passes pressure control valve (VALVE1). Pressure was let down to 4 bar. A distillation column with

21 theoretical trays (DIS1) was used to purify liquid methanol to the top stream and excess water was drawn at the bottom. Moreover, the methanol 99.85 wt% was obtained at the top of the distillation column and the temperature of the distillate was reduced to 50 ˚C by intercooler (H-7). The other process is conversion CO_2-rich amine to methanol production process (case II). PEHA was a polyamine used for CO_2 absorption. PEHA could capture CO_2 at 11 mmol CO_2/ g PEHA when the unit was operated on 70 ˚C with 1.013 bar pressure of CO_2 and the amine was soluble in water. The CO_2 captured in PEHA amine solution (CO_2-rich amine) was then directly hydrogenated at 145 ˚C with hydrogen at 80 bar using homogeneous Ru-MACHO-BH metal complex catalyst soluble in 2-Methyltetrahydrofuran (2-MTHF) which is an organic solvent (Kar et al., 2018). The process flow diagram of case II is represented in Fig. 4.
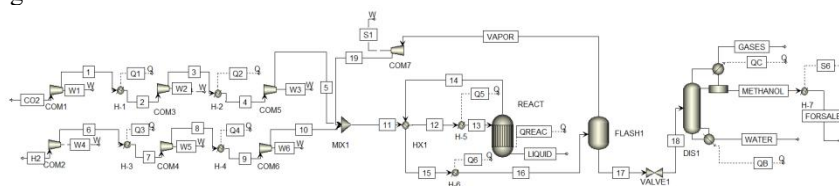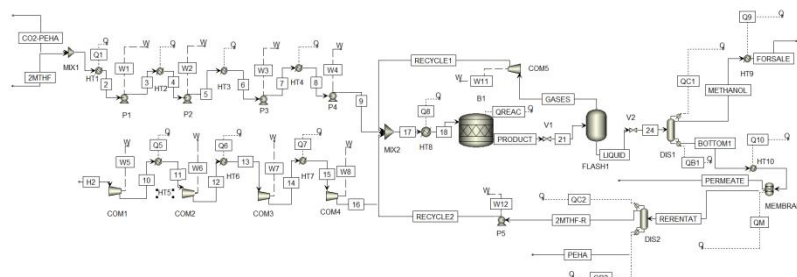

Fig.3 Conventional methanol process flow diagram

Fig.4 Conversion CO_2-rich amine to methanol process flow diagram

In Fig. 4, the CO_2-rich amine feed stream contained 30 kgmol/h CO_2, 11 kgmol/h PEHA and 138.85 kgmol/h H_2O at 70 ˚C with 1.013 bar, representing conditions after the abosrber. The 2-MTHF feed was 0.1305 kgmol/h at 1.013 bar and 25 ˚C. After that, the CO_2-rich amine feed and the 2-MTHF feed were mixed at a mixer (MIX1) and preheated (HT1). The mixed feed stream was compressed to 80 bar though 4 stages of pumps (P1 – P4) with 3 intercoolers (HT2 – HT4). The H_2 feed stream also was compressed to 80 bar though 4 stages of compressors (COM1 – COM4) with 3 intercoolers (HT5 – HT7). The mixed feed stream and the H_2 feed stream were mixed (MIX2) with recycle streams before preheating. Before entering a reactor, the stream was heated to 145 ˚C (HT8). After that, the stream was injected into a stoichiometry reactor. The pressure of the product stream from the reactor was reduced to 40 bar through passes pressure control valve (V1). Then the product stream was split into the liquid-vapor phase by a flash vessel (FLASH1). Vapor outlet from the vessel was the unreacted gases that were recycled using a compressor (COM5) and mixed with the feed streams at the mixer (MIX2). As for liquid outlet, it went to the purification unit passes a pressure control valve (V1) and it was decreased pressure to 4 bar. A distillation column with 20 theoretical trays (DIS1) was used to purify liquid methanol. The excess PEHA solution and homogeneous catalyst (2-MTHF) were drawn at the

bottom. Moreover, the methanol 98.60 wt% was obtained at the top of the distillation column and temperature of the distillate was reduced to to 50 ˚C by a intercooler (HT9). For the bottom product stream, temperature was reduced to 60 ˚C (HT10) to remove water at the membrane separator unit (MEMBRANE). The PESU membrane module (MEMBRANE) was installed to remove water from the liquid stream using the pervaporation technique at 60 ˚C and transmembrane pressure at 4 bar. Xu et al. (2016) reported that the mass fraction of methanol in the permeate stream was measured (0.56 wt%) for the H-PESU membrane at 60 ˚C and 0.001 bar. Thus, the remaining stream (RERENTAT) included 2-MTHF and PEHA. The RERENTAT stream was purified a homogeneous catalyst (2-MTHF) and PEHA through the distillation column with 16 theoretical trays (DIS2). The top stream was the homogeneous catalyst (2-MTHF) at 4 bar. It was moved to the recycle unit using a pump (P5) and then mixed fresh feed streams at the mixer (MIX2). The PEHA was drawn at the bottom with pressure of 4 bar.

4. Comparative study

A comparative study between conventional methanol production process (case I) and conversion CO_2-rich amine to methanol production process (case II) was carried out. The simulation results of methanol productivity and energy consumption are represented in Tables 2. Methanol production of both processes could be divided into 3 sections; CO_2 capture section, methanol synthesis unit and purification section. In case I, energy consumption in CO_2 capture unit was assumed at 1.936 kW/kgmol CO_2 for the compression of fuel gas and 20.2 kW/kgmol for the regeneration of CO_2-rich amine (Amann, 2007). In case II, energy consumption was assumed only for the compression of fuel gas in CO_2 capture unit which is 1.936 kW/kgmol CO_2 (Amann, 2007). Electrical heating energy consumption was required for all the streams of hot water leaving the heater and heat exchanger

Table 3 Comparison of methanol productivity and energy consumption

	Operation	Unit	Case I Amount	Case II Amount
CO_2 capture section	Compressing fuel gas	kW	58.08 (Amann, 2007)	58.08 (Amann, 2007)
	Regeneration column	kW	606.0 (Amann, 2007)	
Methanol synthesis section		kW	3,042.9	3,022.6
Purification section		kW	8,702.5	11,820
Overall energy		kW	12,410	14,901
Methanol productivity		ton/year	80,177	81,982

In the table 2, It was found that methanol productivity in case II is 81,982 ton per year and it was higher than case I which produced 80,177 ton per year. Moreover, the methanol yield of case II was 0.974 kgmol methanol/kgmol CO_2 feed and was higher than case I (0.952 kgmol methanol/kgmol CO_2 feed). The CO_2 conversion in case II was also significantly higher than case I. According to (Kar et al., 2018), the CO_2-rich amine can be directly hydrogenated with hydrogen using homogeneous Ru-MACHO-BH metal complex catalyst soluble in 2-MTHF, providing rather high methanol yield (95%). It was also observed that the energy consumptions of case I in the CO_2 capture section (664.08 kW) and the methanol synthesis section (3,042.91 kW) were higher than case II due to amine recovery and higher reaction temperature (250 ˚C), respectively. Although the energy consumptions of case II in the purification section (8,702.52 kW) was higher than case I, case II required energy consumption in product

purification up to 79.32 % of the overall energy consumption. High energy consumption in product purification was because 2 distillation columns and 1 membrane separator were used for solvent recovery in case II.

5. Conclusions

The CO_2 to methanol production processes: conventional methanol production (case I) and conversion CO_2-rich amine to methanol production (case II), were simulated using Aspen Plus V.8.8. The methanol productivity showed that the two processes could convert a large amount of CO_2 to methanol. Methanol productivity of case I was 80,177 ton/year while it was 81,982 ton/year in case II. The overall energy consumption was 12,410 kW and 3,942 kW for case I and case II, respectively. A comparative study between case I case II showed that case II could reduce energy consumption in the CO_2 capture and the methanol synthesis section. Water which was generated as by-product could be separated and PEHA and homogeneous catalyst could be recovered. However, most of energy consumption of case I and case II was used in the product purification session up to 70 - 80 % of the overall energy consumption. Thus, reducing energy consumption in product purification section remained challenging.

6. References

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