

Liquid Phase CO₂ Hydrogenation to Synthesize Methanol: Solvent Screening, Process Design and Techno-Economic Evaluation

Dongliang Wang*, Yun Du

School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou, 730050, China
 wangdl@lut.edu.cn

With the global shift towards low-carbon and environmentally friendly energy sources, converting CO₂ into methanol through hydrogenation is seen as an optional solution to reduce reliance on fossil fuels and promote the efficient utilization of renewable energy. However, the CO₂ methanol synthesis reaction is limited by thermodynamic equilibrium, which results in low single-pass conversion of CO₂ and high recycling of reaction gases. In this paper, a process for synthesizing methanol through liquid-phase hydrogenation is developed. This process relies on liquid-phase solvents to remove the reaction products water and methanol, affecting the reaction equilibrium and breaking the thermodynamic limit. Based on Aspen Plus software, the binary interaction parameters were regressed using gas-liquid equilibrium data, and the solvent's capacity to enhance the reaction system was assessed. The polar solvent tetraethylene glycol dimethyl ether (TEGDME) was selected as the liquid-phase medium for the process. A liquid-phase CO₂ synthesis process was developed to achieve a high single-pass CO₂ conversion rate of 98.42 % and a methanol yield of 99.82 %.

1. Introduction

Fossil energy combustion and industrial processes emit large amounts of carbon dioxide, contributing to a steady rise in global average temperatures and exacerbating the greenhouse effect. The development of clean energy can significantly reduce carbon emissions. However, renewable energy faces challenges of intermittency, volatility, and stochasticity. The H₂ from clean energy production and CO₂ into a stable storage medium like methanol has become an important approach to effectively utilizing clean energy. D'Amore et al. (2022) utilized CO₂ emissions from refineries in combination with green hydrogen to convert them into methanol. For the CO₂ hydrogenation process to synthesize methanol, the primary reactions considered are represented by Eq (1), (2), and (3). The CO₂ methanol synthesis reaction is limited by thermodynamic equilibrium, resulting in low single-pass conversion of CO₂ and high recycling of reaction gases (Zhong et al., 2020). In the CO₂ synthesis of methanol, the conversion of CO₂ ranged from 1.5 % to 25.9 % (Saeidi et al., 2014). Wang et al. (2023) proposed a full-cycle process and constructed a process with near-zero carbon emissions after analyzing the catalyst and process conditions. In the study, the total CO₂ utilization reached 99.88 %.



The liquid-phase method was considered for constructing the methanol synthesis process. Nieminen et al. (2019) employed n-butanol as a liquid-phase solvent in the CO₂ hydrogenation reaction for methanol synthesis. The novel reaction pathway enhanced methanol yield. However, the involvement of the solvent added complexity to the synthesis process. The high volatility of alcohols and the formation of azeotropes raised the cost of separation. Nevertheless, this approach offered valuable insights for further consideration. Without altering the reaction pathway for methanol synthesis, Ghosh and Seethamraju (2021) employed TEGDME

solvent and Cu/ZnO/Al₂O₃ catalyst and implemented a reactive distillation process to enhance the methanol synthesis reaction. This approach led to a 12.5 % increase in the conversion of methanol from syngas and in their work, it was shown that the liquid single-pass phase methanol synthesis process using CO₂-rich syngas feed may be more favorable than the gas-phase method. The liquid-phase CO₂ hydrotreating process for methanol synthesis is expected to address the issues of low single-pass conversion and high raw gas recovery in the gas-phase process. The principle of liquid-phase methanol synthesis is illustrated in Figure 1. This method involves introducing liquid-phase solvents into methanol synthesis. These solvents have good solubility properties for methanol or water, which helps reduce the concentration of the product, shifting the reaction equilibrium. Additionally, the liquid-phase medium efficiently controls the temperature of the exothermic synthesis reaction.

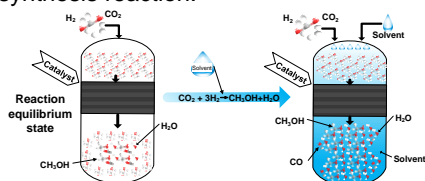


Figure 1: Principle of liquid phase synthesis of methanol

In this study, regression analysis of gas-liquid equilibrium data was conducted using the Aspen Plus software to accurately determine the binary interaction parameters of the Soave-Redlich-Kwong (SRK) equation among the components in the system. The effect of solvents on promoting the equilibrium reaction were investigated through experimental tests. Based on these experimental data, the favorable solvents were identified, and an efficient process for the liquid-phase synthesis of methanol from CO₂ was developed accordingly. In order to further enhance process performance, the process underwent a thorough optimization of process conditions. By adjusting the operating parameters and optimizing the reaction conditions, the conversion of CO₂ and the yield of methanol were improved. In addition, an energy integration and economic analysis of the process was conducted to assess its economic viability and environmental sustainability in practical production.

2. Solvent screening

The solvent plays a crucial role in the liquid phase method, serving as a core component that significantly enhances the conversion of CO₂ and the yield of methanol. Khosla et al. (1991) investigated the gas-liquid equilibrium data between different components and solvents in methanol synthesis systems. They obtained the optimal binary interaction parameter by minimizing the bubble point pressure prediction error based on the SRK equation of state and demonstrated that SRKEOS predictions agree well with the experimental results.

2.1 Binary interactive parametric regression

Using vapor-liquid equilibrium data from the database and literature, the binary interaction parameters were obtained through regression using Aspen Plus software, as depicted in Table 1.

Table 1: Binary interaction parameters of SRK equation based on regression of vapor-liquid equilibrium data

	H ₂	H ₂ O	CO	CH ₃ OH	CO ₂
H ₂	0	-2.36297	0.067231	-0.07255	-0.25127
H ₂ O	-2.36297	0	-0.79021	-0.07255	-0.04242
CO	0.067231	-0.79021	0	-0.1652	-0.06752
CH ₃ OH	-0.07255	-0.07255	-0.1652	0	-0.2235
CO ₂	-0.25127	-0.04242	-0.06752	-0.2235	0
Tetraglyme	3.7983	-0.396	0.050428	0.012947	-0.02732
Dimethylformamide	0.824242	-0.20379	0.22477	-0.04479	0.04613
Dimethylacetamide	10.13355	-0.28113	-0.11899	-0.05818	0.013165
Squalane	0.584	0.287	0.119	0.11	0.018
N-octane	1.394302	0.234333	-0.00232	0.078618	0.135503
Decalin	0.257031	0.437245	0.102397	0.18456	-0.17139
Dodecane	-0.09201	0.545813	0.116471	0.000889	0.099273

2.2 Effect of solvent on reaction equilibrium

CO₂ single-pass conversion and methanol yield serve as indicators of the efficiency of liquid-phase solvent-enhanced CO₂ synthesis for methanol reactions. The impact of the solvent on the reaction equilibrium of methanol synthesis through the hydrogenation of CO₂ was examined using the REquil reactor model in Aspen Plus software. Experimental conditions: temperature 250 °C, pressure 50 bar, feed 3 kmol/h H₂, 1 kmol/h CO₂. In the absence of a solvent, When the reaction reached equilibrium, the conversion of CO₂ was 26.77 %, and the methanol yield was 19.16 %. The experimental results are shown in Figure 2.

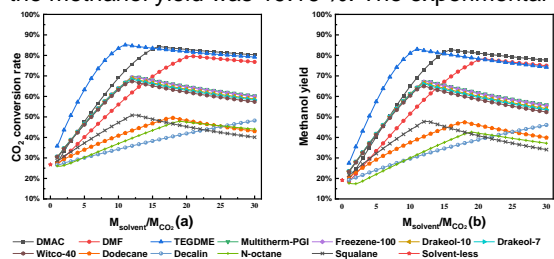


Figure 2: Effect of solvent: (a) carbon dioxide conversion; (b) methanol yield

Among the alternative solvents, TEGDME promoted the methanol synthesis reaction with CO₂ most significantly. The CO₂ conversion reached 85.11 %, and the methanol yield reached 82.98 % when the mole ratio of solvent to CO₂ was 11. The use of TEGDME as a liquid-phase medium for the process of liquid-phase CO₂ hydrogenation to synthesize methanol.

3. Process Design

The power-law kinetic model reported by Ghosh and Seethamraju (2019) was used. The reactor was simulated using the RCSRT model in Aspen Plus, while the distillation section was designed using the RadFrac model to create a process capable of producing 100 kt of methanol annually. The process flow without recycling (Process 1) for the synthesis of methanol through liquid-phase CO₂ hydrogenation is shown in Figure 3.

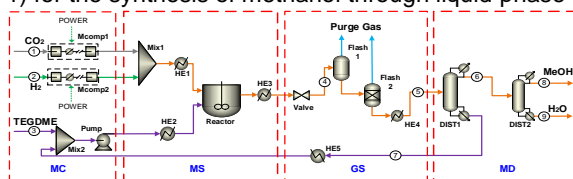


Figure 3: Liquid-phase synthesis of methanol without recycling process flow (Process 1)

In process 1, the feed gas and solvent are pressurized and preheated to a reaction temperature of 250 °C and a pressure of 50 bar. After the feedstock passes through the reaction section, the temperature and pressure of the material are reduced to 30 °C and 25 bar. It then enters the gas separation section, where it passes through Flash1 high-pressure flash tanks and Flash2 low-pressure flash tanks. The unreacted gas is released through Flash1 high-pressure flash tank and Flash2 low-pressure flash tank, while the liquid phase stream is preheated to 240 °C before entering the methanol distillation section. The methanol distillation section includes the DIST1 solvent separation tower and the DIST2 methanol distillation tower. The DIST1 solvent separation tower separates the solvent in the system from the bottom of the tower, achieving a solvent purity of 99.0 %. The material from the top outflow of DIST1 tower is transferred to the DIST2 methanol distillation tower for further distillation to obtain refined methanol with a purity of 99.9 %. CO₂ conversion rate of 98.27 % and final methanol production of 100.15 kt/y.

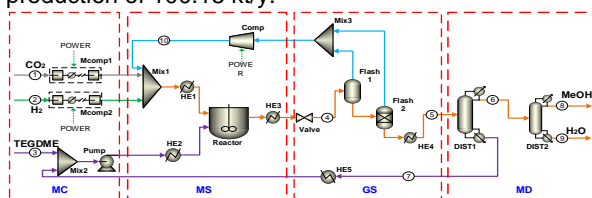


Figure 4: Liquid-phase synthesis of methanol cycle process flow (Process 2)

The cyclic process flow (Process 2) for the synthesis of methanol through liquid-phase CO₂ hydrogenation is illustrated in Figure 4. To enhance the efficiency of utilizing the feedstock, the unreacted gases separated from Flash1 and Flash2 were recirculated into the reactor through a recirculation compressor after pressurization.

Simultaneously, optimizing critical process parameters. The material balance data for Process 2 is shown in Table 2. The methanol yield of the recirculation process was 100.41 kt/y with a purity of 99.90 % and an overall CO₂ conversion of 99.82 %.

Table 2: Material balance data for Process 2

	S1	S2	S3	S4	S5	S7	S8	S10
Phase	Vapor	Vapor	Liquid	—	Liquid	Liquid	Liquid	Vapor
Temperature, °C	40	40	40	32.00	240.00	283.23	64.23	171.1
Pressure, bar	1	1	1	15.00	15.00	1.30	1.00	50.00
Vapor Fraction	1	1	0	0.03	0.00	0.00	0.00	1.00
Liquid Fraction	0	0	1	0.97	1.00	1.00	1.00	0.00
Enthalpy Flow, Gcal/hr	-36.80	0.12	-0.37	-435.40	-389.31	-334.74	-21.96	-1.12
Mole Flows, kmol/h	392.11	1176.3	1.60	2542.58	2444.21	1658.40	392.00	98.37
Mole Fractions								
H ₂	0.0000	1.0000	0.0000	0.0270	0.0000	0.0000	0.0000	0.6982
CO ₂	1.0000	0.0000	0.0000	0.0025	0.0000	0.0000	0.0000	0.0642
CO	0.0000	0.0000	0.0000	0.0090	0.0000	0.0000	0.0000	0.2327
H ₂ O	0.0000	0.0000	0.0000	0.1542	0.1604	0.0000	0.0018	0.0003
CH ₃ OH	0.0000	0.0000	0.0000	0.1544	0.1604	0.0000	0.9982	0.0046
TEGDME	0.0000	0.0000	1.0000	0.6529	0.6792	1.0000	0.0000	0.0000

4. Results and discussion

4.1 Influence of process conditions

The effects of process conditions, such as catalyst dosage, solvent dosage, reaction temperature, and pressure, on methanol yields were systematically analyzed by Process 1. The relationship between the amount of catalyst, solvent, and methanol production is being tested. The amounts of catalyst and solvent are plotted against methanol production. The mass of catalyst ranges from 100,000 to 120,000 kg on the X-axis, the amount of solvent ranges from 1,500 to 2,000 kmol/h on the Y-axis, and methanol production is represented on the Z-axis. The results are shown in Figure 5a. The maximum methanol production of 397.0 kmol/h was obtained.

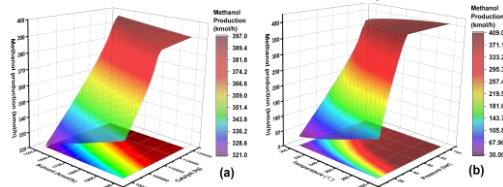


Figure 5: Effect of (a) catalyst–solvent and (b) temperature–pressure on methanol yields

The graph of T–P–Y_{CH₃OH} is shown in Figure 5b, where the X-axis represents the temperature T (200–300 °C), the Y-axis represents the pressure P (10–100 bar), and the Z-axis represents the methanol production. The results indicate that as the pressure increases, the methanol production also increases and then stabilizes after reaching a turning point. And the higher the temperature, the lower the pressure needed to reach the turning point, and the higher the methanol production obtained.

4.2 Techno-economic evaluation

The vapor-phase process studied by Wang et al. (2023) was referenced. The performance of the various processes in relation to energy efficiency and production cost was assessed through a comparative analysis, where energy efficiency is defined as the ratio of the sum of product energy, raw material energy, and process energy, defined in Eq (4). Where, $E_{product}$ is the energy of output product, $E_{feedstock}$ is the energy of input raw material, and $E_{utilities}$ is the consumption of utilities in the whole process.

$$\eta = \frac{E_{product}}{E_{feedstock} + E_{utilities}} \quad (4)$$

According to the data in Table 3, the single-pass conversion rate of CO₂ in the liquid-phase method has significantly increased, attributed to the enhancement effect of the liquid-phase solvent. Analysis of the process

revealed that the introduction of solvents increased the complexity of product separation. In the separation section, additional energy is required to separate the product and solvent, leading to lower energy efficiency.

Table 3: Key performance indicators and consumption results for CO₂ hydrogenation to methanol

Parameter	Unit	Process 1	Process 2	Process W.
CH ₃ OH production rate	kt/y	100.15	100.41	100.12
Recycle to feed ratio	mol/mol	—	0.06	4.99
H ₂ : CO ₂ ratio (feed/reactor inlet)	mol/mol	3/3	3/3.12	3/3.92
CO ₂ conversion (per pass)	%	98.27	98.42	22.99
Utilization efficiency of CO ₂	%	92.13	99.82	99.89
Utilization efficiency of H ₂	%	61.42	66.53	66.59
CH ₃ OH yield (overall process)	%	91.81	99.82	99.89
Power of recycle compressor	kW	—	137.95	793.04
Heat generated in the reactor	kW	-11,179.8	-11,293.6	-5,759.7
Pure CO ₂ use (per unit of CH ₃ OH product)	kg/kg	1.49	1.3749	1.3767
Pure H ₂ use (per unit of CH ₃ OH product)	kg/kg	0.2055	0.1889	0.1877
Process energy efficiency	%	73.25	79.23	90.54

Table 4: Ratio factors for fixed capital investment (Yang et al.,2020)

Item	Range (%)	Basis (%)	Cost (1·10 ⁶ \$)	
			Process1.	Process2.
(1) Direct costs				
(1.1) Equipment and Installation Costs	15–55	40	13.06	12.30
(1.2) Instrumentation and control	2–8	4	1.31	1.23
(1.3) Pipes	3–20	8	2.61	2.46
(1.4) Electrical appliances	2–10	4	1.31	1.23
(1.5) Land and construction	3–20	14	4.57	4.31
(2) Indirect costs				
(2.1) Engineering and supervision costs	4–21	10	3.27	3.08
(2.2) Construction costs	4–16	9	2.94	2.77
(2.3) Contract costs	2–6	4	1.31	1.23
(2.4) Unforeseen costs	5–15	7	2.29	2.15
(3) Investment in fixed assets	(1)+(2)	100	32.66	30.76
(4) Operating investment	15–20	20	6.53	6.15
(5) Total investment	(3)+(4)	120	39.19	36.91

Table 5: Assumptions for the estimation of total product cost (Wang et al.,2021)

Component	Basis & Units	Cost (1·10 ⁶ \$)	
		Process1.	Process2.
(1) Raw material			
H ₂	3.13 \$/kg	64.36	59.38
CO ₂	21.43 \$/t	3.21	2.96
Solvent	526.99 \$/t	1.52	1.50
(2) Utilities			
Cooling water	1.81·10 ⁻⁶ \$/kJ	0.14	0.14
HP steam	16.55·10 ⁻⁶ \$/kJ	9.45	9.19
Electricity	29.28·10 ⁻⁶ \$/kJ	1.30	0.94
(3) Operating & Maintenance		1.49	1.45
(4) Depreciation	Life period 20y, salvage value 4 %	1.57	1.48
(5) Plant overhead cost	5 % (3.1+3.2+3.3)	1.19	1.16
(6) Administrative cost	2 % of product cost	1.75	1.63
(7) Distribution and selling cost	2 % of product cost	1.75	1.63
(8) Product cost	(1)+(2)+(3)+(4)+(5)+(6)+(7)	87.74	81.43
Cost per ton of methanol	(8) / CH ₃ OH production rate	876.07 \$/t	811.04 \$/t

Production cost (PC) is an important indicator for evaluating the economics of a process, including the fixed capital investment (FCI) and the working capital, which is the cost of purchasing equipment and installation costs, and the operating capital, which is needed to maintain the normal operation of the project. Its data economic analysis is shown in Table 4 and Table 5. In addition, the calculation process is based on an annual operating time of 8,000 h/y.

5. Conclusions

The thermodynamic equilibrium limitation was successfully overcome by screening advantageous solvents and incorporating them into the reaction system to enhance the reaction. Enhancing the single-pass conversion of CO₂ and boosting methanol yield.

In Process 2, the single-pass conversion of CO₂ was 98.42 %, the element utilization rates for carbon and hydrogen were 99.82 % and 66.53 %, respectively, and the methanol yield was 99.82 %. The energy efficiencies of Process 1 and Process 2 are 73.52 % and 79.23 %, while the costs per ton of methanol are 876.07 \$/t-CH₃OH and 811.04 \$/t-CH₃OH. The findings indicate that solvents help to facilitate the reaction, but the act of isolating and purifying solvents requires extra energy. Additionally, incorporating solvents adds complexity to the synthesis procedure. On the other hand, the raw materials for Process 1 and Process 2 accounted for 78.74 % and 78.39 % of the production cost, respectively. This was attributed to the price of hydrogen production from renewable energy sources at 3.13 \$/kg. Therefore, the cost of the process is relatively high. When the price of electricity is reduced to 0.1 CNY/kW·h, the production cost of each process is 362.74 \$/t-CH₃OH and 340.91 \$/t-CH₃OH. This cost is economically viable for the hydrogenation of CO₂ to methanol.

In summary, the liquid-phase process is expected to achieve a more efficient and environmentally friendly CO₂ methanol synthesis process in the future through further optimization and improvement.

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