

PROCESS DEVELOPMENT AND ECONOMIC ANALYSIS OF CARBON DIOXIDE TO DIMETHYL CARBONATE

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ABSTRACT

This study developed a strategy for production of dimethyl carbonate from flue gas. In this strategy, Carbon dioxide is captured from flue gas by using monoethanolamine-based carbon dioxide absorption/desorption subsystems. Then, captured carbon dioxide is converted to dimethyl carbonate over a CeO_2 catalyst. This study designed a heat exchanger network for reducing energy requirements of our process. The techno-economic evaluation of this study shows that the integrated process strategy results in a minimum selling price of US\$2.06 per kg.

1. INTRODUCTION

Carbon dioxide (CO_2) is one of the most influential greenhouse gases associated with climate change. So the industrial utilization of CO_2 as a feedstock for chemicals has obtained significant attention. We develop the integrated process for production of dimethyl carbonate (DMC) using CO_2 which is captured from flue gas (FG) released from power plants. The DMC is widely used as electrolytes in lithium ion batteries and as aprotic polar solvent. In the process, CO_2 is first captured from FG by monoethanolamine (MEA)-based CO_2 absorption/desorption subsystem [1, 2]. The captured CO_2 with methanol is then converted to DMC over a CeO_2 catalyst [3-6]. Here, 2-cyanopyridine is used as a recyclable dehydration agent to increase yields of DMC [3-6]. The reaction mixture passes finally through separation subsystems to obtain a high purity of DMC. The simulation models of CO_2 -to-DMC process are developed using ASPEN Plus simulator [7]. Moreover, we performed heat integration of the process using Aspen Energy Analyzer to minimize the total process energy requirements [2].

We expect that CO_2 -to-DMC process concepts can be further applied to economic process development of various value-added chemicals from CO_2 .

ABBREVIATION

CO_2	Carbon dioxide
MEA	Monoethanolamine
DMC	Dimethyl carbonate
FG	Flue gas
VG	Vent gas
MPS	Minimum selling price

2. TECHNOLOGY OVERVIEW

We develop an integrated process for production of DMC using CO_2 in the process, CO_2 is first captured from FG by MEA based CO_2 absorption/desorption subsystems. The captured CO_2 with methanol is then converted to DMC over a CeO_2 catalyst.

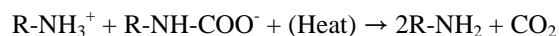
2.1 CO_2 CAPTURE

The MEA-based absorption/desorption subsystems consist of CO_2 absorption and MEA regeneration:

1. CO_2 absorption:



2. MEA regeneration:



Before CO_2 capture, FG including soluble toxic and/or corrosive gases should be first pretreated by wet scrubbing. Then, the pretreated FG enters to the bottom of the absorber and flows upward, while the aqueous solution of MEA enters to the top of the absorber and flows downward as countercurrent to the FG flow. The absorption/desorption occurs at 40°C and 121kpa [8, 9], resulting in capturing 85 % CO_2 from the FG and leaving CO_2 -rich solution at the bottom and CO_2 -lean gas (containing N_2 , O_2 and remaining CO_2) at the top [8, 9]. After CO_2 capture, CO_2 -rich solution flows to the regenerator to obtain a high purity of CO_2 . At the regenerator, 99.9% of MEA is recovered to the bottom stream at 394K and 200kpa [8, 9] and it is reused flowing to the absorber, while 99.9wt% of CO_2 is obtained at the top stream at 313K and 200kpa [8, 9]. The captured CO_2 flows then to DMC production process.

2.2 DMC PRODUCTION

The captured CO_2 is mixed with methanol and is then sent to a continuous flow fixed bed reactor based on CeO_2 catalyst. Here, 2-cyanopyridine ($\text{C}_6\text{H}_4\text{N}_2$) is used as a recyclable dehydration agent to increase yields of DMC. The DMC production reaction is as follows.

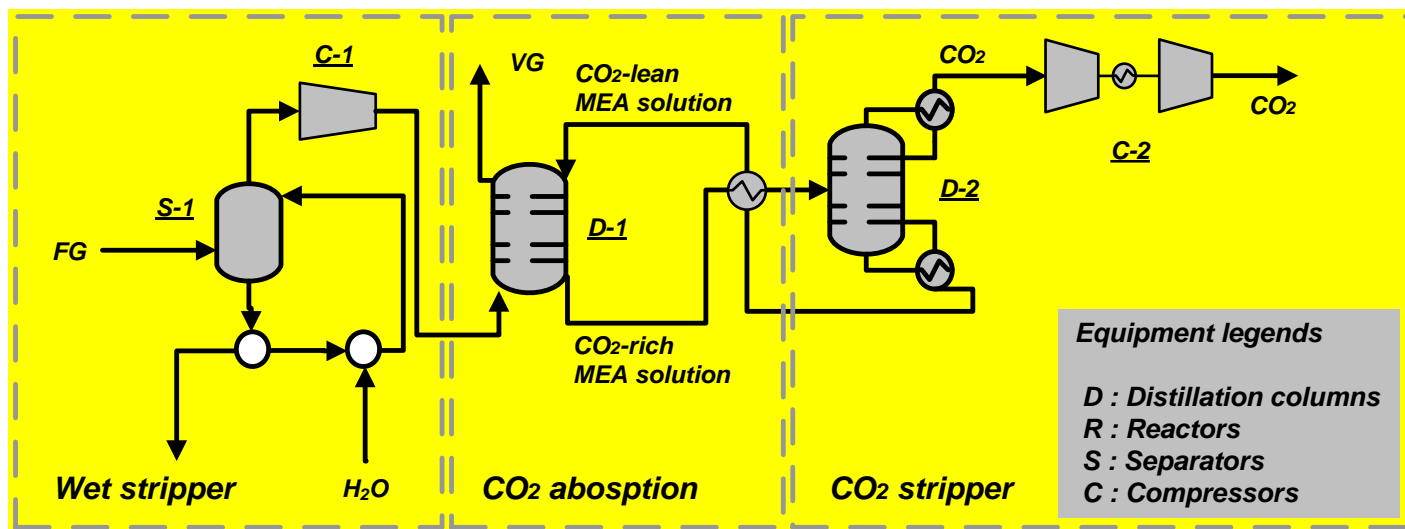
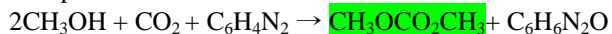


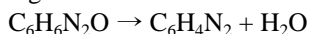
Figure 1 CO₂ capture subprocesses

3. DMC production:



The reaction leads to a high yield (95mol% of methanol conversion and 99mol% DMC selectivity) over CeO₂ catalyst at 30bar and 393K[3]. The reaction mixture then passes through separation subsystems to separate picolinamide (C₆H₆N₂O) and produced DMC using hexane solvents. The produced DMC mixture passes through the extraction and distillation to obtain high purities of DMC and hexane solvents. The separated picolinamide pass through the several subsystems to finally regenerate cyanopyridine. First, picolinamide is sent to an evaporation unit using acetone solvents, resulting in catalyst regeneration and separation of solid picolinamide while acetone recycling. The solid state of picolinamide with the extra acetone solvents goes through a regeneration reaction using mesitylene solvents to regenerate cyanopyridine. The regeneration reaction is as follows.

4. Cyanopyridine regeneration reaction:



The regeneration reaction occurs over CsO₂ catalyst at 438K and 1atm (45mol% of picolinamide conversion and 99mol% of cyanopyridine selectivity)[5]. The mesitylene solvents passed through several distillations and decanters for being recycled. The unconverted picolinamide flows to the reactor again. The converted cyanopyridine is then recycled as a reactant to reduce its makeup.

3. PROCESS DEVELOPMENT

This study decided the amount of FG emitted from power plants to capture about 100,000Mt CO₂ per year when the process is operated 333days per year and CO₂ capture efficiency is 85%. The processing capacity of FG is 570,000Mt per year (71.2Mt per hours). The overall process this study developed consists of CO₂ capture and DMC production process.

3.1 PROCESS SYNTHESIS

First, CO₂ capture sub-process consists of three subsystems including wet scrubber, CO₂ absorption and CO₂ desorber. FG

emitted from power plants is used as a feed stream of the process. With the processing capacity as this study have just explained, toxic and/or corrosive gases in FG are first removed by wet scrubbing. The CO₂ is absorbed by MEA solution at CO₂ absorber at 120kpa and steady state [8]. The amount of absorbed CO₂-rich solution is 12.5Mt per hours. The CO₂-rich solution is separated from MEA solution at the CO₂ desorber. After the CO₂ separation from FG, a high purity of CO₂ is sent to the DMC production process.

DMC production sub-process consists of DMC production, DMC purification, hexane recycle, catalyst regeneration & acetone recovery, cyanopyridine regeneration and mesitylene recovery. First, DMC production is a continuous catalyst reaction over CeO₂ catalyst[3]. Considering feed streams, CO₂ is supplied as molar 2.5 times of methanol[3]. Cyanopyridine used as dehydration agents is supplied (molar ratio 1:2 = cyanopyridine : methanol)[3]. Here, methanol with CO₂ is converted to DMC at molar yield of 95% at 373K and 30bar[3]. The unreacted CO₂ is recycled back to the reactors after passing through several heat exchangers, valves and flash tanks. As a result, the CO₂ recovery rate is 97.5wt% and the loss ratio of DMC is less than 2wt%.

The CO₂ is removed from the product mixture and then DMC-rich solution is then separated from picolinamide containing catalysts using hexane solvents. This is because the picolinamide doesn't dissolve at hexane solvent[6]. Hexane solution containing DMC is separated at distillation as DMC solution and hexane solution containing some unreacted methanol. After adding water, this hexane solution is separated as a pure hexane solution (99.3wt% of hexane) and water by liquid-liquid equilibrium separation[10]. The hexane solution is recycled back while, the DMC solution is distilled again, resulting in a high purity of DMC (99.9wt%). After distillation, the residues are used as fuel for sales.

The picolinamide containing catalyst separated from hexane solution is separated by acetone solvent as picolinamide and CeO₂ catalyst. This is because the catalyst doesn't dissolve at acetone solvent. The picolinamide dissolved in acetone is separated as the solid state of picolinamide and acetone solution

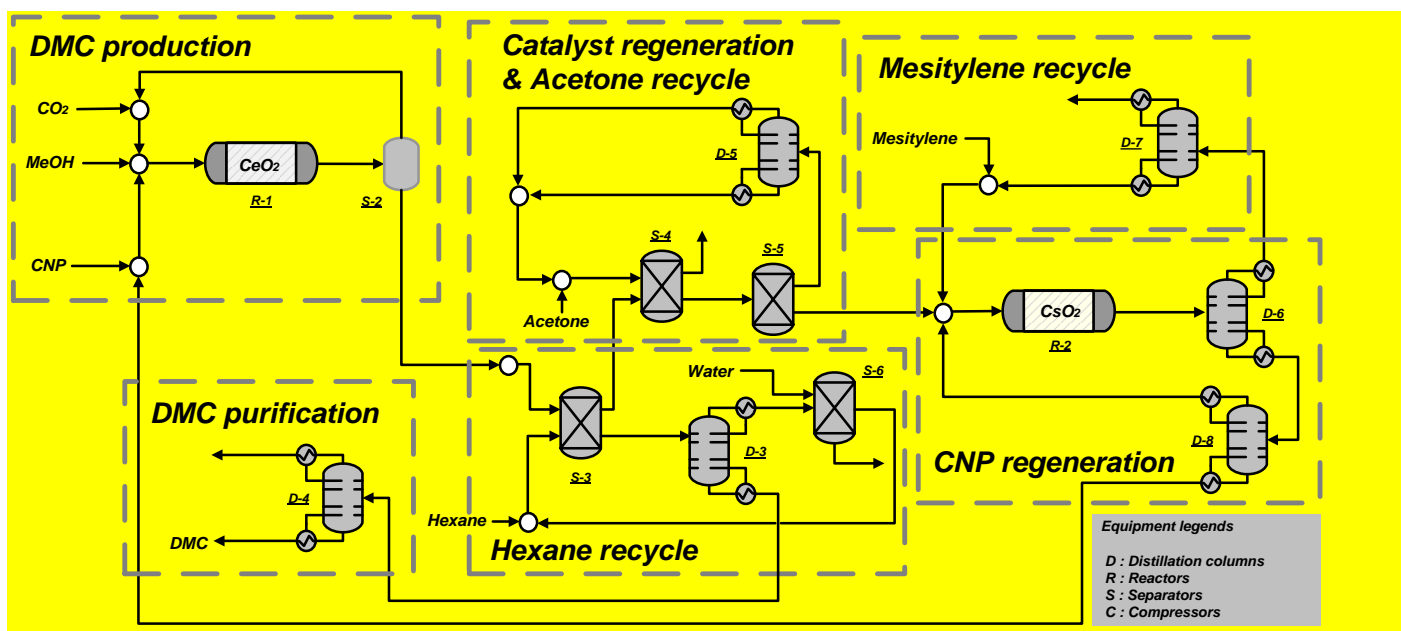


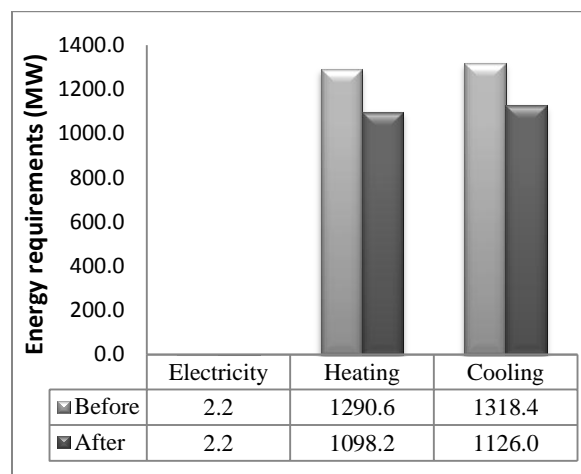
Figure 2 DMC production subprocesses

by evaporation. Then, the picolinamide flows to regeneration reactors of cyanopyridine while the acetone flows to separator back. Picolinamide regeneration reaction proceeds with mesitylene solvents and CeO_2 catalyst at 438K and 1atm[5]. The amount of mesitylene is supplied as a molar ratio for 143 times of picolinamide[5]. At this reaction, picolinamide is converted to cyanopyridine (45mol% conversion of picolinamide)[5]. After the reaction, the unreacted picolinamide is recycled back after passing several distillations, while the converted cyanopyridine flows to reactor R-1. The mesitylene also flows to reactor R-2 after passing several distillations and a decanter.

3.2 HEAT INTEGRATION

In the strategy of this study, the heat requirement of overall integrated process for DMC production is 1290.6MW. Among them, as the heat demand of CO_2 capture process is 16.8MW, it occupied small part. But as the heat demand of DMC process is 1273.9MW, it occupied the most part of whole heat demand. The heat demand of DMC process is composed of DMC production (18.7MW), DMC purification (7.7MW), hexane recycle (69.9MW), acetone recycle (77.3MW), cyanopyridine regeneration (1038.7MW) and mesitylene recycle (61.6MW). As the heat demand of cyanopyridine regeneration is 1038.7MW, it occupied 80% of overall heat demand. As this study mentions in section 4, this section is very important and should be necessary included. So this study includes all system and performs heat integration including integration between hot and cold process streams to reduce the energy demands. After heat integration, it recovers about 192.4MW of heat. As a result, the reduced heating requirement of the overall process is 1098.2MW.

Figure 3 summary of heat requirements



4. TECHNOECONOMIC EVALUATION.

4.1 DESIGN BASIS AND ASSUMPTIONS

This study developed a simulation model using the ASPEN Plus Process Simulator[7]. It estimated equipment costs of CO_2 capture and DMC production systems using Aspen Process Economic Analyzer on the basis of the experimental data and simulation results[2]. And some parts (DMC production, cyanopyridine regeneration and mesitylene recycle) of reactor and decanter are estimated using an exponential scaling expression on the basis of the equipment size and cost data in literature. It also estimated the equipment and utility costs of the heat exchange network using Aspen energy analyzer[2].

4.2 CAPITAL AND OPERATING COSTS.

This study estimated capital and operating costs for integrated process, as shown in Table 2. The total capital cost of the process is estimated to US\$394.9 million per year and total operating cost is estimated to 123.4 million per year. Among the capital costs, the costs of mesitylene recycle and cyanopyridine regeneration section occupied most portions (each of them is US\$117.1 million and US\$114.2 million per year). This is because the excess of solvent is used demanding a large equipment. Among the operating costs, the cost of DMC production section occupied most portions (US\$101.7 million per year). This is because the excess of methanol is used and also try to reduce cyanopyridine makeup through cyanopyridine regeneration and also the price of cyanopyridine is so expensive. Thus, cyanopyridine regeneration section is considered that although it occupied expensive equipment cost and so much heat requirement, because the price of cyanopyridine is so expensive, this section should be necessary included. And also utility cost is estimated to US\$199.1 million per year. This great cost is because heat requirement of cyanopyridine regeneration section. But, as this study has mentioned before, this section is imperative considering overall costs.

Table 1 summary of annualized capital and operating costs (US\$ million per year)

CO ₂ capture and DMC production process			
Annualized capital cost		Operating cost	
Conversion and separation	48.61	Raw materials cost	123.12
Waste water treatment	0.64	Electricity cost	1.04
Storage	0.32	Utility cost	199.13
Heat exchanger	3.21	Fixed operating cost	2.08
Total capital cost	52.78	Total operating cost	325.37
Total production cost	378.14		

4.3 MINIMUM SELLING PRICE (MSP)

This study determined a minimum selling price (MSP) of DMC for a net present value equal to zero by analyzing a discounted cash flow based on the capital and operating costs. The major portion of MSP was operating cost (32.7%) and utility cost (53.3%). As it have mentioned before, this is because utility cost for overall heat requirement is very big and the cost of raw material (cyanopyridine: US\$9450 per Mt) is expensive[11]. But, in numbers, utility cost is largest portion of MSP. As a result, the MSP of DMC is US\$2.06 per kg. Detailed prices of raw materials and steam are based on the literatures [11-13].

5. CONCLUSION

In this study, it developed integrated process for producing the DMC from FG. CO₂ capture method from FG uses the MEA-

based CO₂ absorption/desorption subsystems. The method to produce DMC used catalyst (CeO₂) conversion process. We adopted a process that captures 100,000 Mt per year assuming that this process operates 333 day per year. It finally developed the process that produces 184,000 Mt per year of DMC.

Energy analysis of this study showed that very important part of our process is cyanopyridine regeneration section. As it have mentioned continuously, this is because the cost of cyanopyridine used as important agent of reaction is so expensive and heat requirement of this section occupies 80% of all. Also, this cause the utility cost occupied largest portion of MSP. As a result, the MSP of DMC was determined to US\$2.06 per kg, as compared to market price of DMC (US\$0.8~1.8 per kg)[11], it is confirmed with little expensive. It identified more research necessity about cyanopyridine regeneration. To the current research, the amount of mesitylene used as solvent is so much and cyanopyridine yield with proper reaction time isn't also high. Although it reduce the makeup of cyanopyridine to 40 times of initial stream by recycling, increasing separation cost (utility cost) have a considerable effect on overall cost. If the proper amount of solvent is used at cyanopyridine regeneration section, the MSP of DMC of our process will be proper at market price.

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