Capturing and Using CO_2 as Feedstock for Clean Chemical Process Technologies

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ABSTRACT

Chemical-looping technologies for capturing CO_2 are discussed with critical assessments of the circulating fluidized bed systems and the packed bed reactor with periodic switching of the feed streams of fuel and air. Beside, some industrial chemical processes, we have developed, for converting CO_2 into value added chemicals are discussed. The first process uses 137.31 tonne/day CO_2 and hydrogen to produce 100.0 tonne/day of methanol. Electrolysis of water using the electricity from wind power supplies the hydrogen and helps store the electricity in the form of methanol. The second process is the production of propylene carbonate (200,226,816 lb/year) and polypropylene carbonate (200 million lb/year) from propylene oxide and CO_2 by using 9990.2 lb/hr and 12762.8 lb/hr CO_2, respectively. Another process uses 1652.97 kg/hr of bioglycerol and 273.74 kg/hr of CO_2 to produces 670.9 kg/hr bioglycerol carbonate by direct carboxylation. CO_2 can also be converted to formic acid, methanol, and hydrogen by using zero-valent metal/metal oxide redox cycles under hydrothermal conditions. The oxidized metal can be regenerated by glycerin, which is converted to lactic acid. These case studies emphasize the sustainability and feasibility of chemical process technologies and positive impact of converting CO_2 to useful chemicals on global warming.

Keywords: carbon capture, methanol production, propylene carbonate production, glycerol carbonate production, hydrothermal process

1 INTRODUCTION

Chemical-looping is an emerging carbon capture technology [1,2]. Hydrogen produced by electrolyzing water would be valuable feedstock [3]. Hydrogen can be used to synthesize methanol using CO2 and/or as energy storage [4-6]. Methanol can easily be converted to H_2 at relatively low temperature and to electricity efficiently in a direct methanol fuel cell. Propylene carbonate can be manufactured from CO_2 and propylene oxide. The copolymerization of CO_2 and epoxides is possible by using a heterogeneous catalyst derived from diethyl zinc and water [7-10]. The CO_2 may be supplied, preferably, from a nearby bioethanol plant. Carboxylation of epoxides holds obvious advantages, especially in instances where the epoxides are derived from renewable resources. Another process uses bioglycerol and CO_2 to produce bioglycerol carbonate by direct carboxylation [11,12]. CO_2 can also be converted to formic acid, methanol, and hydrogen by using zero-valent metal/metal oxide redox cycles under hydrothermal conditions. The oxidized metal can be regenerated by glycerol, which is converted to lactic acid [13,14].

Production of various chemicals from CO_2 can have a positive but only marginal impact on the global carbon balance; worldwide, we add 3500 million tons carbon dioxide annually, while we use only 110 million tons of the CO_2 to produce other chemicals (mainly urea); this is only around 3% usage of CO_2 as feedstock. On the other hand, the utilization of CO_2 in the fuel production or as a chemical storage of energy, such as methanol, could make a significantly larger impact as only 16.8% of the world oil consumption was used in 2007 for nonenergy purposes. If nonrenewable, energy usage affects environment adversly. Sustainability has environmental, economic, and social dimensions and requires the responsible use of resources such as energy and reduction in CO_2 emission. [15,16]. This study discusses CO_2 conversion processes.

2 CHEMICAL-LOOPING TECHNOLOGY

Chemical-looping technology uses an oxygen carrier (OC) to transfers O_2 from the air to the fuel preventing direct contact between them. OC is composed of a metal oxide and alternately oxidized and reduced within the circulating fluidized bed system (Fig. 1a). The fuel may be solid or gaseous. The product gas contains mainly CO_2 and water undiluted with N_2, and without the production of nitrogen oxides (NO_x) as the high temperatures associated with the use of flame is avoided. The oxidation of the OC carrier is strongly exothermic and hence can be used to heat air flow to high temperatures and can drive a gas turbine. Two models consist of fluidized bed system with circulating metal oxides and stationary bed [1,2].
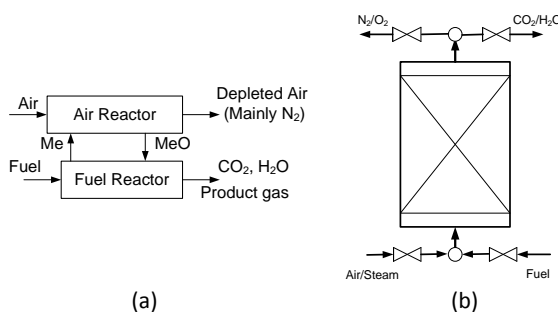

Figure 1: Schematic of chemical-looping: (a) fluidized bed; (b) Periodically operated packed bed system.

An alternative to fluidized bed systems is based on packed bed chemical-looping reactor systems that contain the stationary OC particles alternately exposed to reducing and oxidizing conditions by periodic switching of the fuel feed (generally natural gas) and air streams (Fig. 1b). In this packed bed reactor technology, the circulation and separation of gas and the OC particles are avoided. This may lead to better utilization of OC with more efficient oxidation/reduction cycles. For solid fuel like coal and biomass, *in situ* or separate gasification will be required.

3 HYDROGEN PRODUCTION

Hydrogen needed for methanol synthesis can be produced by electrolytic process. If the cost of electricity is 6 cents/kWh for new installed wind turbine, the cost for H_2 production is about \$3.50/kg H_2. The DOE target is \$3.00 /kg H_2 (4 to 5 cents /kWh). The largest electrolyzer units, using aqueous solution of potassium hydroxide, produce about 380,000 kg of H_2 per year requiring approximately 2.3 MW of electricity. A large alkaline electrolyzer unit is the Norsk Hydro Atmospheric Type No. 5040, which can produce 1046 kg H_2/day. The typical gas output streams are 99.9 for H_2 and 99.2 for O_2. Electricity cost is typically 70 to 80% of the total cost of H_2 production [3,15].

4 METHANOL PRODUCTION PLANT

Methanol is synthesized using a catalyst $Cu/ZnO/Al_2O_3$ at high pressure: $CO_2 + 3H_2 = CH_3OH + H_2O$ $\Delta G^o(298 K) = -4.1$ kcal/mol. The RKS method is used. The plant uses 18.868 MT/day hydrogen and 137.310 MT/day carbon dioxide, and produces 100.061 MT/day (~33,000 gallons/day) 99.7-wt% of methanol and 56.114 MT/day water. The plant requires 786.193 kg/hr H_2 and 5721.274 kg/hr CO_2. Figure 2 presents a basic process flow diagram for the methanol plant. In Unit 100 the H_2 and CO2 are compressed to 50 bar and mixed with the recycle stream S3 in mixer M101. In Unit 200 methanol synthesis takes place in reactor R201 operating at 50 bar and 250°C. In Unit 300, liquid output of F301 is conditioned in E303 and sent into the distillation column T301. The tower has 40 equilibrium stages including condenser and reboiler. The tower operates near atmospheric pressure. The distillate stream 'METHANOL' contains 99.7-wt% of methanol, while the bottoms flow 'WATER' contains 99.7 wt% of water. Table 1 shows the sustainability metrics for the RadFrac-distillation column T301 to separate the methanol [4-6].
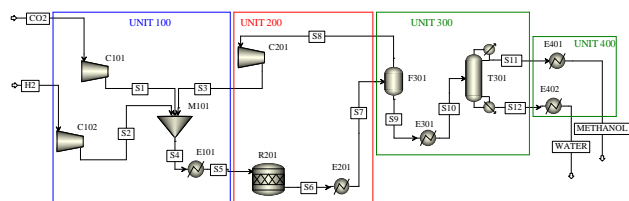

Figure 2: Process flow diagram of the methanol plant.

Total heating duty, Gcal/hr	+4.958
Total cooling duty, Gcal/hr/hr	+9.236
Total heating cost, \$/hr	274.46
Total cooling cost, \$/hr	66.17
Net cost (heating + cooling), \$/hr	340.62
Net stream CO_2, kg/hr	−5718.3
Utility CO_2, kg/hr	+1261.0
Total CO_2, kg/hr	−4457.2
Net carbon fee/tax, \$/hr	−4.4

*US-EPA-Rule-E9-5711; natural gas; carbon fee: \$2/tonne

Table 1: Sustainability metrics for the methanol plant*

If we can lower the cost of H_2 from \$3.5/kg to \$1.499/kg and hence the cost of methanol production from \$49.84 10^6 to \$33.35 10^6 the net present value becomes zero, which may make the investment. Also, if the revenue of methanol increases from \$1.0/kg to \$1.464/kg then the net present value becomes zero with the hydrogen cost of \$3.5/kg.

5 PRODUCTION OF PROPYLENE CARBONATE

Cyclic propylene carbonate (PC) is an intermediate in the production of drugs and pesticides and frequently used in lithium batteries. The reaction between PO and CO_2 needs expensive salen or ionic liquid catalysts, which may impede the commercialization of these routes. We used the kinetics by Hue et al [10]: $k = 61267 \exp(-61024.76 / RT)$ where R is the gas constant in 8.314 kJ/kmol K [7-9]. In this study ionic liquid-1-n-ethyl-3-methylimidazolium chloride is used as catalyst in a stirred tank reactor at 212 ^{o}F and 114.7 psi. Figure 3 shows a possible PFD for PC production from PO and CO_2. The CO_2 supplied, (from a nearby bioethanol plant), is compressed to 114.7 psi in compressor C101 and heated to 212 ^{o}F. The catalyst is dispersed in the PO within the reactor. Separator SEP101 separates the catalyst. Unused CO_2 and PO are recycled to compressor C101, and eventually to reactor R101. Stream S7 containing almost pure PC is cooled and stored at 68 ^{o}F. Table 2 shows the sustainability metrics. The SRK is used.
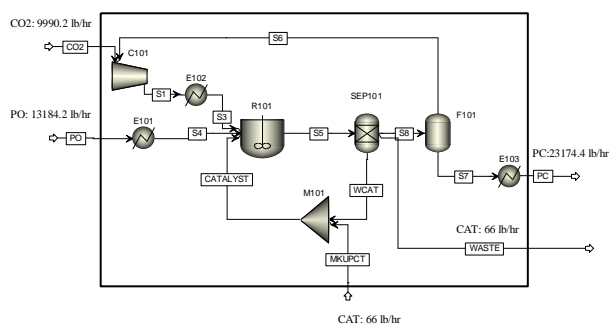

Figure 3: Process flow diagram for PC.

Total heating duty, Btu/hr	$+2.67857 \times 10^6$
Total cooling duty, Btu/hr	$+1.58213 \times 10^7$
Total heating cost, \$/hr	40.98
Total cooling cost, \$/hr	3.54
Net cost (heating + cooling), \$/hr	44.52
Net stream CO_2, lb/hr	-9976.82
Utility CO_2, lb/hr	$+2587.81$
PC CO_2, lb/hr	$+13.40$
Total CO_2, lb/hr	-7389.01
Net carbon fee/tax, \$/hr	-6.70

*US-EPA-Rule-E9-5711; natural gas; carbon fee: \$2/tonne

Table 2: Sustainability metrics for PC.

For a capacity of 200, 226, 816 lb PC the economic analysis resulted in the values of NPV, PBP, and ROR of \$17.97 10^6, 3.5 years, and 33 %, respectively when the selling price of PC was \$0.72/lb. Therefore, the process seems feasible under the current economic data, available technology, and catalyst utilized.

6 PRODUCTION OF POLY(PROPYLENE) CARBONATE

Poly(propylene) carbonate (PPC) is soluble in polar solvents, biologically degradable polymer, and substitutes of thermoplastic polymers. This process uses (salen)CrIIICl complex as catalyst with the kinetic data: $k = 17452614 \exp(-67600.00 / RT)$ [7-10]. The reaction takes place at 850 psi and 86 ^{o}F and produces a small amount of a cyclic PC. The reaction initially forms segments from CO_2 and PO and then proceeds in the copolymerization of these segments as the repeating units to form the polymer. Figure 4 shows the PFD; Table 3 display the sustainability metrics. The CO_2 is compressed to 850 psi in compressor C101 and its temperature is adjusted to 86 ^{o}F before it is fed into the reactor R101. SEP101 separates the catalyst. Stream S7, containing the unused CO_2, PO, and produced PC and PPC, is flashed at around 5 psi in the F101 and most of the unused CO_2 and PO are recycled to to reactor R101 after cooling down in E102. Stream S10 is separated in SEP103 and the remaining unused CO_2 and PO are recycled back to compressor C102, while PC is stored. This design uses the NRT model.

The values of NPV, PBP, and ROR are \$12.55 10^6, 8 years, and 11.5 %, respectively when the selling price of PPC was \$0.98/lb. Therefore, the process was deemed feasible under the current economic data, available technology, and catalyst utilized.

7 CARBOXYLATIONOF GLYCEROL

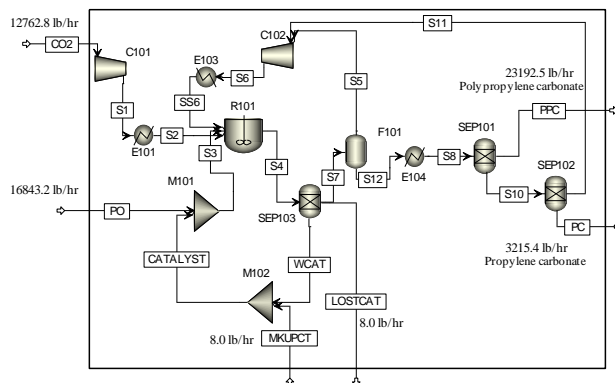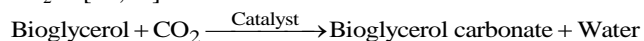Synthesis of glycerol carbonate from bioglycerol and CO_2 is [11,12]:

$$\text{Bioglycerol} + CO_2 \xrightarrow{\text{Catalyst}} \text{Bioglycerol carbonate} + \text{Water}$$

Figure 4: PFD to produce poyl(propylene) carbonate.

Total heating duty, Btu/hr	3.37161×10^7
Total cooling duty, Btu/hr	2.67199×10^7
Total heating cost, \$/hr	237.0
Total cooling cost, \$/hr	5.9
Net cost (heating+cooling), \$/hr	243.0
Net stream CO2, lb/hr	-14523.2
Utility CO2, lb/hr	+4861.2
PC CO2, lb/hr	+0.030
Total CO2, lb/hr	-9662.0
Net carbon fee/tax, \$/hr	-8.76

*US-EPA-Rule-E9-5711; natural gas; carbon fee: \$2/tonne

Table 3: Sustainability metrics for the PPC.

Direct carboxylation of bioglycerol and CO_2 is the quickest and simplest route for synthesis of glycerol carbonate. A recent study shows that 35% conversion is possible at 80 ^{o}C and 3.5 MPa using 1 mol% of n-dibutyltin(IV)oxide (n-Bu$_2$SnO) as catalyst and methanol as solvent. However, Direct carboxylation of glycerol and CO_2 is thermodynamically limited. So, indirect use of CO_2 by another reaction may be considered [11,12].

Figure 5 shows the plant for glycerol carbonate production. Stream BY-PROD contains, by mass, 2.77% of methanol and 96.40% of glycerol. CO_2 is compressed to 35 bars in compressor COM201 before it is fed to reactor R201. The carboxylation reaction takes place at 80 ^{o}C and 3.5 MPa of CO_2 using methanol as a solvent and 1 mole percent of n-dibutyltin(IV)oxide as catalyst. The methanol/glycerol molar ratio of 11.22 (in stream S3) is used in this simulation. However, only 25% conversion is assumed in this simulation because of the ongoing research on the level of conversion achievable with the catalyst n-dibutyltin(IV)oxide. Separator SEP201 is used to separate the catalyst from the reactor outlet with 50% of recovered, treated, and recycled to the reactor. Flash drum F201 removes excess CO_2 operating at an absolute pressure of 0.2 bar. The bottom product of F201, stream S7, is pressurized to 1 bar in pump P202 upon entering flash drum F202 to separate water and methanol from glycerol and

glycerol carbonate. The top product of flash drum F202, stream S9, containing methanol and water is fed to distillation column T201 to at stage 4. Column T201 operates with 8 equilibrium stages with a kettle reboiler and a partial vapor-liquid condenser. The reboiler and condenser duties are 14,542.01 kW and 17,168.59 kW, respectively. The UNIF-DMD model is used to predict the phase-equilibrium in distillation column T201. The distillate of column T201, stream S13, contains high concentration of methanol is split and recycled to both sections. The bottom product of flash drum F202, stream S10, is preheated to 240°C, and fed to stage 10 of distillation column T202. The column T202 has 16 stages. The distillate, stream R3, contains mostly glycerol, which is recycled. The bottom product, stream S12, with a flow rate of 670.89 kg/hr and 92.94% on the weight basis is the glycerol carbonate. Glycerol carbonate properties are approximated based on the structural information obtained using the group contribution model of UNIF-DMD. The glycerol carbonate production section (Section 2) utilizes 273.74 kg/hr of carbon dioxide, 266.78 kg/hr of methanol and the byproduct of the Section 1 to produce 649.69 kg/hr of glycerol carbonate and 209.51 kg/hr [11].
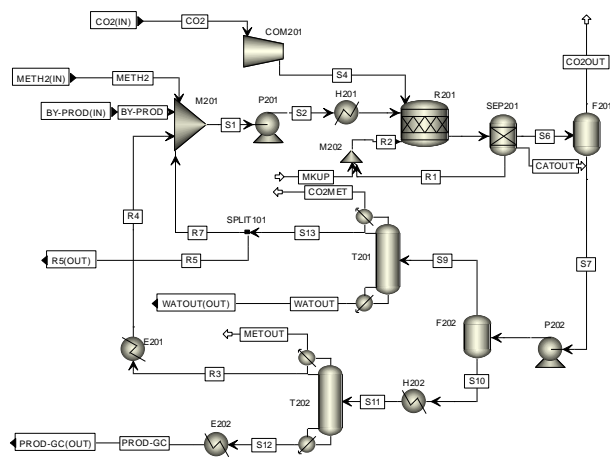

Figure 5: Glycerocarbonate by direct carboxylation.

8 HYDROTHERMAL METHANOL

Highest yield of methanol at hydrothermal conditions using Cu (12 mmol) as catalyst in the presence of Al (4.4 mmol) is about 30.4%. The reaction takes place at 300 °C with a reaction time of 9 hours. Methanol may be formed by the synthesis of CO_2 and H_2 from the decomposition of formic acid. This shows that there is possibility of converting CO_2 to methanol directly starting with CO_2 in a packed bed chemical-looping system. By combining the chemical-looping combustion and the hydrothermal process of converting CO_2 to formic acid as shown in Fig. 6, we may have an integral process converting a fuel to methanol [13,14] and producing power and other chemicals.
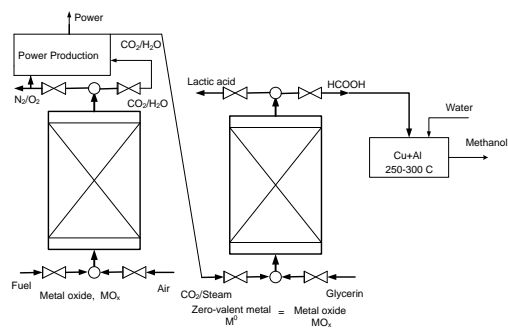

Figure 6: Chemical-looping hydrothermal process of converting CO_2 to methanol.

9 CONCLUSIONS

Chemical-looping is a promising technology for CO_2 capture. Engineering and economic analyses of industrial scale processes for the manufacturing of methanol, cyclic PC and PPC from H_2, CO_2, and PO indicate that processes using CO_2 as feedstock would be feasible. They are also valuable for sustainability. Glycerol can also be directly carboxylated with CO_2. In hydrothermal processes with zero valent metals, formic acid and methanol production is another emerging field. The existing publications for the synthesis of intermediates and chemical from carbon dioxide appear promising.

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