Post-Combustion CO2 Capture from Exhaust Gas by Amines and Membranes

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Post-Combustion CO_2 Capture from Exhaust Gas by Chemical Absorption and Membrane: Review

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Abstract. There is a necessity to reduce GHG emission because climate change may have critical consequences in many places the world. The main gas which causes climate change is CO_2 which is released into atmosphere by industries and vehicles. This research aims to compare two technologies for CO_2 capture: absorption with amines and membrane, and to present hybrid processes using these. A review of the state of art for CO_2 capture is used in this research. The capture by absorption with amines is the state of the art for post-combustion because it produces CO_2 with higher purity and is cheaper. However, the energy and installation cost is high which does not encourage its applicability. Membrane for CO_2 capture from natural gas is promissory because of this. Thus, researchers have studied other technologies for CO_2 to replace or add through hybrid processes. Capture by membrane is a promising technology for this, provided that it presents appropriate selectivity and permeability. This paper presents a comparison between CO_2 capture by absorption with amines and by membranes. The goal is to discuss hybrid processes with these two technologies in series.

Introduction

CO_2 capture from exhaust gas is studied because of society's uneasiness about climate change and its environmental impact on future generations. Climate changes have occurred on Earth since geological eras because of the increase in the Earth's temperature. However, researchers have found evidence that human activity has caused global warming because some gases have the capacity to absorb ultraviolet rays. Consequently, the emission of such gases causes a phenomenon that retains heat in the air, increasing the global temperature. This phenomenon is called the greenhouse effect [11].

There are four main gases which cause the increase in temperature. These gases are CH_4, N_2, CO_2 and freons. Freons are compounds consisting of fluor, chlorine and carbon. CO_2 is the most impactful gas in global warming because it is produced by many reactions, though mainly fossil fuel combustion. . Table 1 shows data regarding greenhouse gases. The freon CHF_3 is included in this Table because it is the Freon with the most warming potential.

There are three options for capturing CO_2 from exhaust gas: post-combustion, pre-combustion, and oxy-combustion. Fig. 1 shows how post-combustion occurs; Fig. 2 shows how pre-combustion occurs; Fig. 3 shows how oxy-combustion occurs. The technologies studied for capture of CO_2 are in Tables 2 and 3 [10].

Table 1. Greenhouse gases data [21].

Compound	Concentration before industry [ppmv]	Concentration in 2011 [ppmv]	Lifetime in the atmosphere [years]	Main Human Activity	Global Warming Potential
CO_2	280	388.5	~100	Fossil fuel burning.	1
CH_4	0.715	1.87 / 1.784	12	Fossil fuel, Rice agriculture , landfill, livestock.	25
NO_2	0.27	0.323	114	Fertilizers and industrial combustion processes.	298
CHF_3	0	0.000018	279	Electronics and refrigerators	11 700

Table 2. CO_2 capture from gas natural and exhaust gas by post-combustion process [10].

Separation Task	Process Stream		Post-Combustion	
	CO_2/CH_4		CO_2/N_2	
Capture Technologies	Current	Emerging	Current	Emerging
Absorption	Physical Solvents	Improved Solvents	Chemical Solvents	Improved Solvents
	Chemical Solvents	Novel Contacting Equipment		Novel Contacting Equipment
		Improved Design of Processes		Improved design of processes
Membrane	Polymeric	Ceramic	Polymeric	Ceramic
		Facilitated Transport		Facilitated Transport
		Carbon		Carbon
		Contactor		Contactor
Solid Sorbents	Zeolite	-	Zeolite	Carbonate
	Activated Carbon		Activated Carbon	Carbon Based Sorbents
Cryogenic	Ryan-Homes Processo	-	Liquefaction	Hybrid Processes

Table 3. CO_2 capture from exhaust gas by oxy-combustion and pre-combustion processes [10].

Separation Task	Oxy-Combustion		Pre-Combustion	
	O_2/N_2		CO_2/H_2	
Capture Technologies	Current	Emerging	Current	Emerging
Absorption	-	Biomimetic Solvents, e.g. Hemoglobinederivatives	Physical Solvents	Improved Solvents
			Chemical Solvents	Novel Contacting Equipment
				Improved Design of Processes
Membrane	Polymeric	Ion Transport Membranes	Polymeric	Ceramic
				Palladium
		Facilitated Transport		Reactors
				Contactors
Solid Sorbents	Zeolite	Adsorbents for O_2/N_2	Zeolite	Carbonates Hydrotalcites
	Activated Carbon	Oxygen Chemical Looping	Activated Carbon	
			Alumina	Silicates
Cryogenic	Distillation	Improved distillation	Liquefaction	Hybrid Processes

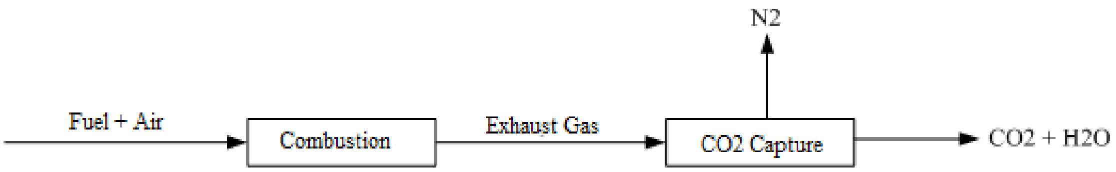

Fig. 1. Post-Combustion CO_2 capture [10].

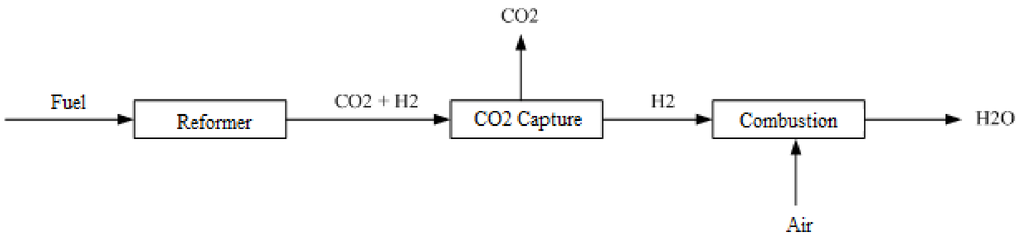

Fig. 2. Pre-Combustion CO_2 capture [10].

This paper shows the state of art for the post-combustion CO_2 capture by membrane and absorption with amines, and compares these processes. Our aim is to further study post-combustion CO_2 capture. According to the IPCC in 2005 it is commercially applicable in the chemical and petrochemical industry. One example of applicability is CO_2 injection for recovery of oil from wells [23].

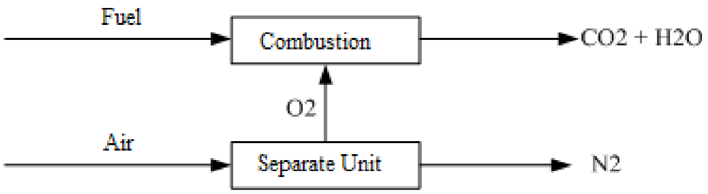

Fig. 3. Oxy-Combustion CO_2 capture [10].

Chemical Absorption

Chemical absorption is the oldest CO_2 capture processes from exhaust gas. Three companies have already evaluated the cost of this technology: Lummus; Fluor Daniel, and Mitsubishi. Lummus has used monoethanolamine 15 to 20% wt aqueous; Fluor Daniel has used monoethanolamine 30% wt aqueous; and Mitsubishi has used three solvents aqueous with monoethanolamine [10]. Table 4 shows Fluor Daniel consumes less energy. Eq. 1 describes the neutralization reaction between CO_2 and MEA. CO_2 reacts with all other amines by the same equation; however, they change the cation [1]. Fig. 4 shows this process flowchart. Below, amines except for monoethanolamine studied for CO_2 capture are shown [13].

- N, N-Dimethylethanolamine, DMAE
- N-Methylethanolamine, MDEA
- N-Methylethanolamine, MAE
- Diethanolamine, DEA
- 2-Amino-2-Methylpropan-1-ol, AMP
- N-(2-Hydroxymethyl) Ethylenediamine, HEEDA
- N, N-Dimethylpiperazine, DMF
- N, N, N ', N'-Tetramethylethylenediamine, TMEDA
- N, N, N'-Trimethylethylenediamine, N, N, N'-triMEDA
- N, N, Dimethylethylenediamine, N, N-Dimeda
- Dimeletilenodiamina N-N'-N, N'-Dimeda.

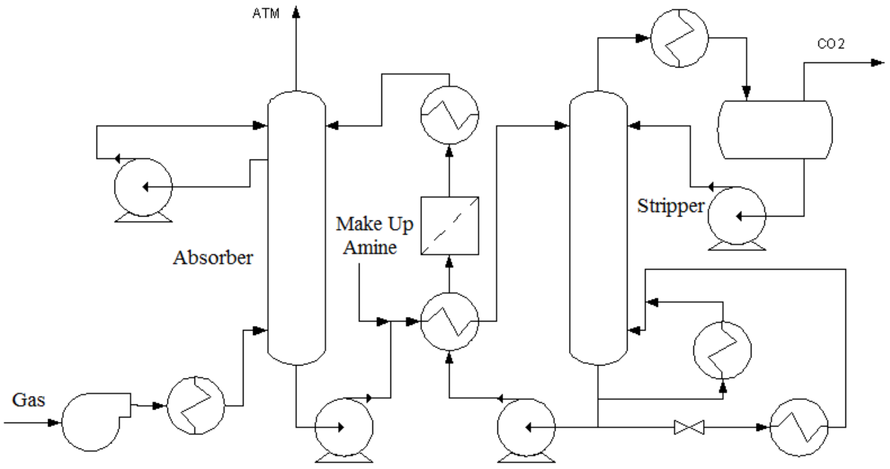

Fig. 4. CO_2 Capture by Absorption flowchart [10].

Because of corrosion problems caused by amines, there are studies using amino acids or ammonia for this technology. Amino acids do not volatilize, have high surface tension and are more chemically resistant than amines, however, their performance decreases in the presence of oxygen. Ammonia does not degrade in the presence of oxygen, it does not corrode, it requires less energy in the stripper than amines, and it is also cheaper. However, a reaction between CO_2 and ammonia is explosive in a high CO_2 concentration and it can cause operational problems [21].

Table 4. CO_2 capture by absorption with amines, plant data [18].

	Unit	Lummus	Fluor Daniel	Mitsubish
CO_2 mole fraction in exhaust gas	%	13.3	13.2	15
Electricity consumption per CO_2 captured	kWh/tCO_2	119	91.5	118.84
Heat consumption per CO_2 captured	GJ/tCO_2	2.76	3.95	

$$2HO(CH_2)_2NH_2 + CO_2 \leftrightarrow HO(CH_2)_2NHCOO^{-}H_3N^{+}(CH_2)_2OH$$
(1)

Absorption is a separation process by liquid-vapour equilibrium whose compounds in gas form are absorbed by a liquid solvent. There are two kinds of absorption: physical absorption and chemical absorption. The difference between these is the presence of a chemical reaction in chemical absorption. However, physical absorption modeling can be used for chemical absorption modeling if reaction equilibrium constants are considered. The hydraulic calc for Column absorption and stripping can be simulated using the distillation simulator. Furthermore, distillation, absorption and striping column can be plated or packaged [16].

In the flowchart of equipment shown in Fig. 4, the two columns function in the specific temperature range because of chemical and physical properties. If MEA is used, the temperature range absorption is 40 to 60°C, and temperature range stripping is 100 to 140°C. The pressure is near 1 atm for both columns [10]. The energy consumed in the CO_2 capture process stripper is 3.88 GJ/tCO_2 if the exhaust gas is from natural gas [5].

Because of the high energy consumption for capture using this process, the percentage of CO_2 capture used in one of the economic studies is 65%. An example of this is exhaust gas from natural gas. One research aimed to produce 690 tonnes of CO_2 [18]. The cost of this process was € 60.58/tCO_2, considering $3.58x10^6$ tonnes CO_2 by year. This cost corresponds to US$ 80.80 according to data in *Portal do Brazil* web [17].

Membrane

Membrane is a promising technology studied to decrease the cost of CO_2 capture using absorption with amines [10]. The advantages are simpler installation. This is leads to lower maintenance costs [3]. The membrane is studied for hybrid technologies. Cellulose acetate is the state of art for membrane material in this process because it is cheaper. Rather than capturing CO_2 only using membrane, researchers have been studied hybrid technology using absorption with amine [10].

Because of the high energy consumption and high cost of installing absorption plants, there are other CO_2 capture processes studies. The use of membranes is one of these. They operate by partial pressure difference, according to eq. 2 [15]. In this equation, Ji is the component i flow (kmol/s), Pi is the component i permeability [kmol.m/(s.m^2.bar)], δ is the membrane thickness (m), Am is the membrane mass transfer area (m^2), xi and yi are tube stream and permeate stream component i mole fraction respectively, and Pf and Pp are tube stream and permeate stream pressure respectively [9]. Membrane technology is more appropriate for CO_2 capture from natural gas because the pressure is high, 20 bar [20].

$$J_i = \frac{P_i}{\delta} Am(x_i P_f - y_i P_p) = \frac{P_i}{\delta} Am\Delta P$$
(2)

The pressure difference can be created in two ways: compression system in upstream or in a vacuum system downstream [3], [9] and [8]. Both are shown in Fig. 5. Studies have shown that a membrane to separate CO_2 capture from exhaust gas by vacuum system is cheaper than a compression system, in spite of bigger membrane separation equipment. This is because the energy consumption defines the cheaper technology [9]. Studies have shown that it is impossible to capture CO_2 90% from exhaust gas with CO_2 mole fraction less than 10% using only one membrane stage specifying CO_2 for injection for recovery of oil [4]. This information is in Fig. 6 where xin is CO_2 mole fraction in exhaust gas, and α is membrane selectivity [2]. The recommended materials to make membrane separating equipment are polymers, as shown in Table 5 below.

Table 5. Polymeric membranes data [15].

Polymer	H_2 Permeability [Barrer]	N_2 Permeability [Barrer]	O_2 Permeability [Barrer]	CH_4 Permeability [Barrer]	CO_2 Permeability [Barrer]
Cellulose Acetate	2.63	0.21	0.59	0.21	6.3
Ethyl Cellulose	87	8.4	26.5	19	26.5
Polycarbonate. Brominated		0.18	1.36	0.13	4.23
Polidimetilsiloxane	550	250	500	800	2700
Polyamide	28.1	0.32	2.13	0.25	10.7
Polidimetilpenteno	125	6.7	27	14.9	84.7
Polyphenyl oxide	113	3.81	16.8	11	75.8
Polisulfone	14	0.25	1.4	0.25	5.6

Barrer = $10^{-10}.cm^3.cm/(cm^2.s.cmHg)$.

In spite of polymeric membranes in Table 5 being state of art for current process and post-combustion, zeolite ZSM-5 offers better conditions for CO_2 capture because of its higher permeability and selectivity. The CO_2 permeability is 1 140 Barrer and the CO_2/N_2 selectivity is 54.5 in zeolite ZSM-5 at 25°C. These properties will be obtained if this material is supported with polymeric silica to avoid aluminum ions leaching. These properties can decrease without this support because the gas can pass by empty surface between crystals. Another advantage is its hydrophobic characteristic [19]. However, the material with the greatest selectivity is PVBTAF. Polyvinyl benzyl trimethyl [7] and [21].

The most promise CO_2 capture technology for hybrid process is membrane [10]. The absorption with membrane modules is the hybrid process whose it studies is the most forward. In this process, the solvent should go in the absorption column in higher pressure than gas for avoid bubble. The fig. 7 shows how liquid and vapour interact them in the column [14]. Other process has membrane module using vacuum in the stripper. This aims decreasing energy consumption in the reboiler. The material used for membrane in it study was polypropylene because it is hydrophobic [24]. The other possibility for hybrid technology is membrane before the other separation. The fig. 8 shows the flowchart using absorption after membrane.

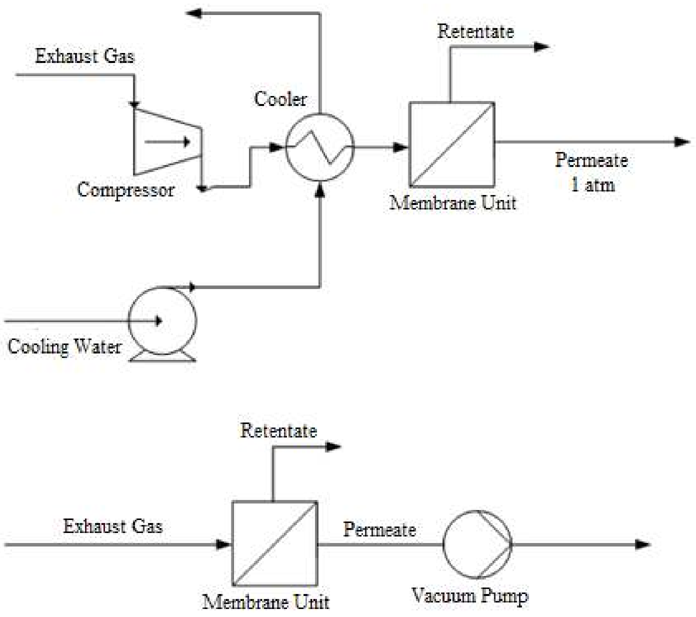

Fig. 5. Membrane Separate Processes Flowchart [8].

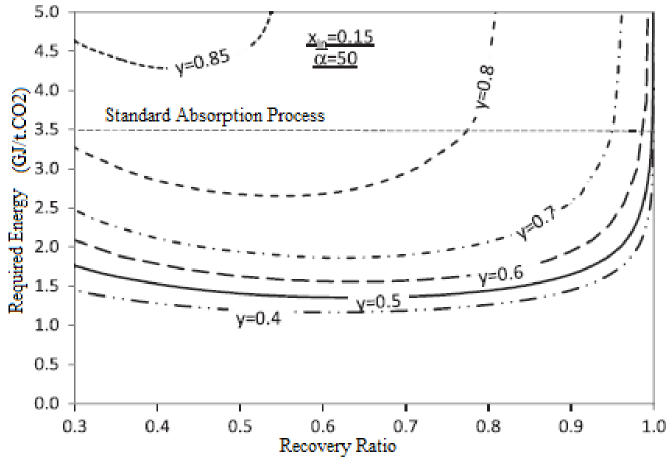

Fig 6. Post-Combustion CO_2 capture by membrane simulation graph [2].

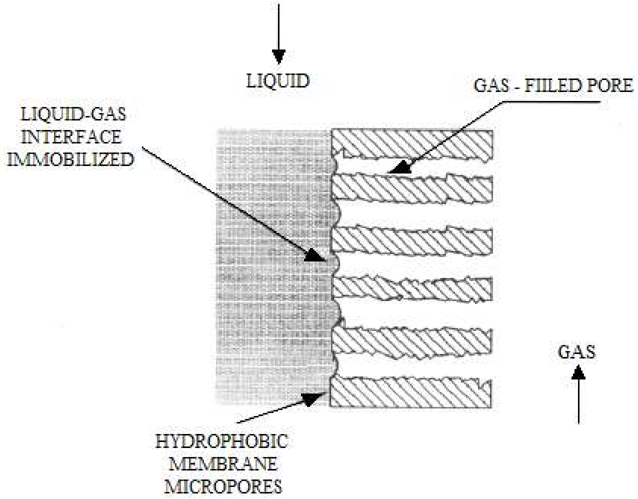

Fig. 7. Absorption with membrane module [14].

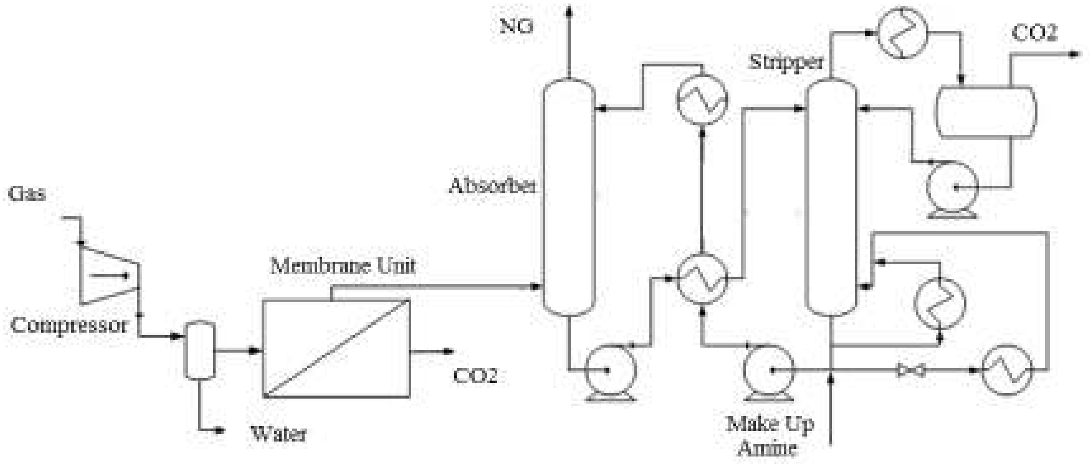

Fig. 8. Hybrid technology in serie using membrane flowchart [20].

Comparing between CO_2 Capture by Chemical Absorption and Membranes

In spite of difficult for specify CO_2 by membrane, it is promissory for hybrid processes. The advantage is less installation cost and less energy consumption. These occur if it produces CO_2 not specified [10] and [6]. Economic studies shown in this paper indicate these advantages using membrane. It is because the absorption with MEA cost was US$ 80.88 / t [18]. CO_2 while membrane vacuum cost was US$ 54 / t CO_2 [9]. However, CO_2 captured by membrane does not attend specifying condition for industrial applicable.

Table 6. Quantitative comparing between membrane and absorption from exhaust gas.

Paper	[18]	[9]	[9]
Process	Absorption with MEA	Membrane	Membrane with Vacuum
Knowing level	Advanced	Novelty	Novelty
CO_2 Specifying [%]	97	43	45
Energy Penalty [%]	37	52	28
Annual Total Cost [US$/t$CO_2$]	81	82	54

Table 7. Quantitative comparing between membrane and absorption from natural gas [20].

CO_2 Removal Technology		Chemical Absorption			Membrane	Hybrid
		MEA	MDEA	MEA+MDEA		MEA
Recovery	CH_4	98,76	98,51	98,50	96,21	94,73
(%)	CO_2	99,28	91,57	95,77	90,68	99,01
CAPEX [milhões de US$]		26	43	31	50	27
OPEX [milhões de US$]		58	69	116	6,7	19

In order to join both processes advantages, it was developed hybrid technologies. However, hybrid process in series using vacuum membrane is not promissory because the absorption column pressure is 1 atm. One date that it shows difficult capturing CO_2 by membrane without vacuum pump is cost US$ 82 / t. CO_2 [9]. In spite of this, it cost refers polyphenyl membrane, which cost US$ 10 / m^2, while cellulose acetate, the most indicated material, cost US$ 0.1/ft^2 or US$ 1.0 m^2 [22]. The tables 6 to 8 show comparatives information about membrane and absorption with amine.

Table 8. Qualitative comparing between membrane and absorption [21].

Process	Advantages	Disadvantages
Absorption with Amines	1 – Fast reaction 2 – Higher Selectivity 3 – More flesible	1 – Equipments corrosion 2 – Higher instaliings
Membrane	Simper and cleaner	Higher energy for exhaust gas in compression system

Discussion and Conclusion

The table 6 shows it is possible reducing cost increasing energy plants efficiencies by hybrid processes for post-combustion if it will use vacuum system in membrane. One example used vacuum system in membrane module [24]. The table 7 shows that CO_2 capture from natural gas by hybrid process investment is cheapest of the plant studied. Other papers proposed different hybrid processes using vacuum system in membrane. There is study hybrid process using membrane with adsorption, too [12]. In this table too, there are dates which it causes study CO_2 capture by hybrid process using fig. 8 changing adsorption to absorption are the less energy penalty and less CO_2 capture cost if it will use vacuum system.

It is noted, too that CO_2 capture by absorption as membrane studies have many compounds developed to improve energy efficiencies. There are many amines for absorption however MEA has been more indicated yet because of it price. MDEA and DEA are other amines in advanced stage of study, too. About membrane, although cellulose acetate is more indicated because of it price, many materials offering better conditions have already studied. Zeolite ZSM-5and polyvinyl benzyl trimethyl are examples [21].

In this paper, the conclusions are: Elevated installing cost for building CO_2 capture process plant by absorption arouses necessity to find other developing other technologies for it substitutes or builds hybrid processes [21]. It is not possible producing CO_2 specified more 90% mole capture more 90% CO_2 mole from exhaust gas with only one membrane stage. This is if the exhaust has less CO_2 10% mole. This fact does not preclude specifying CO_2 in these conditions with too many stages [2].

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