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Hydrogenation of Carbon Dioxide for Methanol Production

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A process for the hydrogenation of CO_2 to methanol with a capacity of 10 kt/y methanol is designed in a systematic way. The challenge will be to obtain a process with a high net CO_2 conversion. From initially four conceptual designs the most feasible is selected and designed in more detail. The feeds are purified, heated to 250 °C and fed to a fluidized bed membrane reactor equipped with a $Cu/ZnO/Al_2O_3$ catalyst. Zeolite membranes mainly remove the methanol and shift the equilibrium reaction towards methanol. A yield of 25 % per pass is obtained. The permeate and the water-methanol mixture from the phase separator is finally separated in a distillation column. In the final design 15.4 kt/y of carbon dioxide is needed in order to produce 10 kt/y methanol. The net CO_2 reduction is about 2/3, which is significant. The process is technical but currently not economically feasible.

1. Introduction

Converting CO_2 to valuable products becomes increasingly interesting as CO_2 emissions are restricted and penalties have to be paid for every ton of CO_2 that is exhausted. One possible route for conversion of CO_2 is the hydrogenation to methanol. In this project different processes for the production of methanol are evaluated and a systematic design is made for the most promising concepts. The goal is to produce 10 kt methanol per year. A typical flue gas stream containing 12 mol% CO_2 is used as the source of CO_2. A mixture of 75 mol% H_2/ 25 mol% CH_4 at a pressure level of 30 bar, the light ends byproduct stream of a cracker, is the source of hydrogen.

2. Literature

A process design project starts with a systematic literature search to find general and specific data about the conversion of CO_2 to methanol. It resulted in a state-of-the-art overview for catalysts and processes investigated and applied.
For the hydrogenation of carbon dioxide to methanol two main reactions need to occur in the reactor. Assuming a pure feed of CO_2 and H_2 the reactions are given by the reverse water gas shift reaction and the methanol reaction, Eq. 1 and 2 respectively.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H_{r,300K} = 41.2 \text{ kJ/mol} \qquad (1)$$

$$CO + 2\,H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{r,300K} = -90.8 \text{ kJ/mol} \qquad (2)$$

The overall reaction to produce methanol is given by Eq. 3.

$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{r,300K} = -49.2 \text{ kJ/mol} \qquad (3)$$

The most promising processes are summarized in Table 1.

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Table 1: Selected CO_2 hydrogenation processes available in literature and their characteristics

Authors	Feed (ratio $CO_2/H_2/Ar$)	Products	Process Conditions	Catalyst	Conv. to CO_2 / Sel. to CH_3OH (%)	Type reactor
Borodko et al. (1999)	CO_2, H_2 (1/3)	Methanol, CO, H_2O	T: 498–548 K P: 5 MPa Capacity: 50 kg/day	$Cu/ZnO/Al_2O_3$	12 / 36	Packed bed tubular reactor (pilot scale)
Liu et al. (2007)	CO_2, H_2, Ar (26/72/2)	Methanol, CO, H_2O, methylformate	T: 443 K P: 3 MPa	$Cu/ZnO/Al_2O_3$	17 / 71 26 / 73 16 / 79	Semi-batch autoclave (lab scale)
Toyir et al. (2001)	CO_2, H_2, CH_4, C_2H_6 (1/3)	Methanol, CO, Methylformate, CH_4/C_2H_6	T: 523–543 K P: 2 MPa φ_v: 18000 l/kgcat*h	Cu-Ga/ZnO Cu-Zn-Ga/SiO_2	5 / 85 3 / 97	Fixed bed continuous reactor

Selection criteria like maturity of the process, commercially available catalyst, conversion and selectivity towards methanol lead to the preference for the $Cu/ZnO/Al_2O_3$ system. Which has the best conversion (±20 %) and selectivity (±80 %) towards methanol according to recent data reported by Liu et al. (2007). CO_2 and H_2 can be fed directly to a reactor with a $Cu/ZnO/Al_2O_3$ catalyst, but Uhm et al. (1996) reported in their patent that the process performance can be improved if the CO_2 and H_2 feed is first partially converted to CO and water with a MoO_3/Alumina catalyst. After this reaction step water is separated from the gas and the gas is partially recycled. The remaining gas is fed to the $Cu/ZnO/Al_2O_3$ catalyst reactor. This process can be advantageous since water suppresses the reaction to methanol. Another interesting option is to shift the reaction equilibrium to the right by in-situ removal of the water or methanol from the reactor.

3. Methodology

The process of CO_2 to methanol is designed in a systematic way according to the method discussed e.g. by Seider et al. (2010). It starts with a process analysis and an overall process approach. A tree diagram is used to visualize the relationship between input variables and objectives or goals. All process design steps have been documented, including decisions and loops in the design activities. Next to the process overall, the concept of process functions required to convert raw materials into products is the basis to create process alternatives. This is followed by a further development of the functional block diagrams into preliminary process flow sheets using new and conventional technologies. In line with Seider et al. (2010) it is stated that each process operation can be viewed as having a role in eliminating one or more of the property differences between the raw materials and the products. The first step is to eliminate differences in molecular type; this is done by chemical reaction in the function of a reactor, the heart of a chemical process. Raw material is seldom-converted 100% into the desired product. So besides a reactor, one or more separation functions are needed. Selection is needed as not all alternatives can be developed in detail. According to the methods developed by Douglas (1988) the focus is on the rejection of less attractive alternatives. Usually there are several process design steps between the generation and the selection. The project is finalized with a detailed design of the units, heat integration, safety analysis and a technical en economical evaluation. To master the method described is an essential part of the process design course in our MSc curriculum. This multi-step conceptual design method is described in more detail by Van den Berg (2001).

4. Results and discussion

The process can be divided in several functions that are presented in Figure 1. The reactants are first purified to reduce the load on the main process, heated and then fed to the reaction system and the product finally purified. In the reactor methanol and water are produced according to the overall reaction shown in Eq. 3.

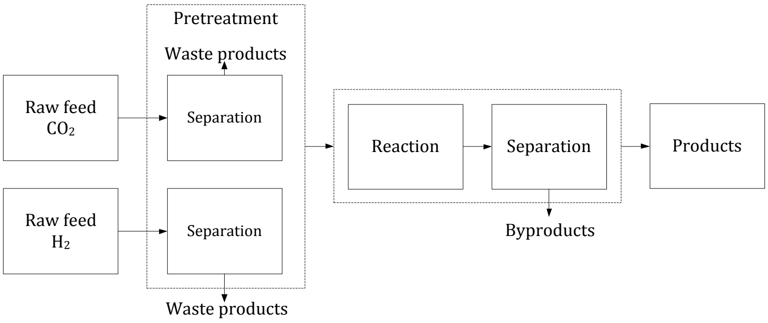

Figure 1: Functional process scheme for CO_2 hydrogenation

The CO_2 is purified from the flue gas by a MEA scrubbing system; the hydrogen is purified by a PSA or membrane system. The design methodology resulted in four conceptual designs of which two are evaluated in more detail. The first (see Figure 2) has two separate reactors in which a reverse water gas shift and the conversion of CO_2/CO towards methanol take place respectively in the first and second reactor. The catalysts used are MoO_3 on alumina for the reverse water gas shift reaction and Cu/ZnO/Al_2O_3 for the conversion towards methanol. This design is in agreement with the patent of Uhm et al. (1996).

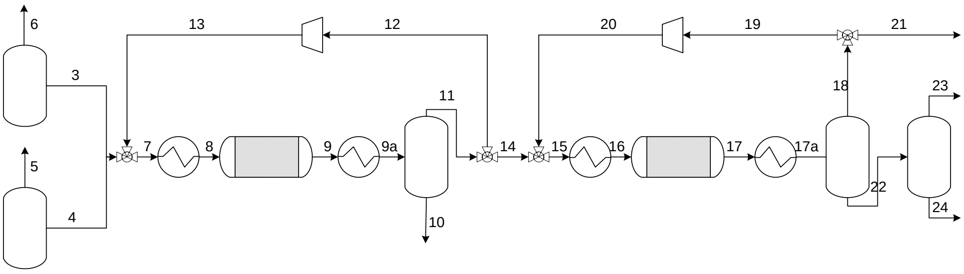

Figure 2: conceptual flowsheet of design 1

The second design (see Figure 3) has only one reactor having an integrated separator unit in which CO_2 is converted to methanol. The catalyst used in this reactor is a Cu/ZnO/Al_2O_3 catalyst with a CO_2 conversion of 20% and a selectivity to methanol of 80 % as described by Liu et al. (2007). The reactor evaluated in more detail is equipped with a membrane. In this reactor methanol and water are produced and at the same time a major part of methanol is removed to shift the reaction toward methanol. In both designs the unconverted reactants are recycled after a flash drum separation in which the remaining water and methanol are separated from the lights. The water-CH_3OH mixture is finally separated by distillation. Both options are compared in Table 2 and finally design 2 was selected for further detailing.

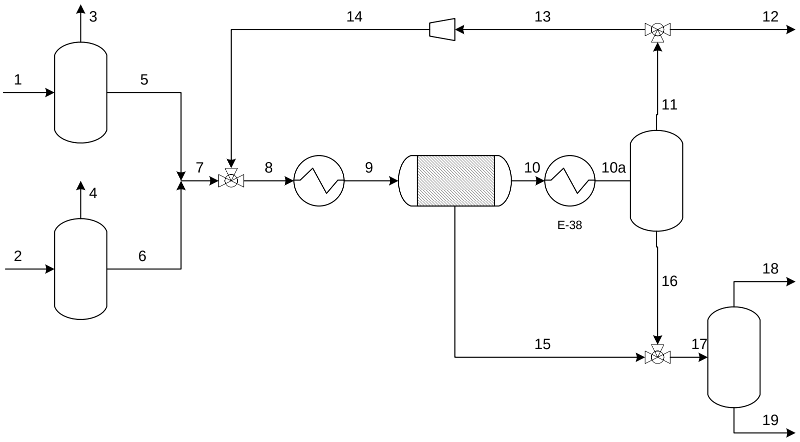

Figure 3: conceptual flowsheet of design 2

Table 2: Comparison of conceptual design 1 and 2

Conceptual	design 1		design 2	
	Value	Rating	Value	Rating
Energy before HI	14 MW	-	4.3 MW	+
Energy after HI	1 MW	±	0.8 MW	+
Energy saving	13 MW	±	3.5 MW	±
Mass balance	81 % Carbon-eff.	-	89 % Carbon-eff.	+
Recycle (relative to feed)	R1: 4.2 R2: 5.8	-	R: 4.0	+
Separations	5 units	±	4 units	±
Reactor design	2 conv. reactors	+	membrane reactor	-
Heat exchangers	13	-	11	+
Functional units	22	-	16	+

Table 3: Parameters of the CO_2 hydrogenation process for design 2

Parameters	Value
H_2 feed required (kt/y)	2.3
CO_2 feed required (kt/y)	15.4
CH_3OH produced (kt/y)	10
Overall carbon efficiency (-)	0.89
Recycle ratio (recycle/feed) (-)	4
Purge (% of gas outlet of flash vessel)	3
Conversion in reactor towards methanol (single pass) (-)	0.26
Selectivity in reactor towards methanol (single pass) (-)	0.96
Yield towards methanol (single pass) (-)	0.25
Energy reduction by HI (% of heat in steam/coolant)	82
Total electricity required [MW]	1.56
Total heat required (steam 8 bar) (MW)	1.02
Yearly profit (M$)	-0.27

Detailed mass and energy balances were calculated using the process simulator UniSim®. The main equipment is designed in detail up to the level necessary for cost estimation. Flowsheet calculations showed a methanol yield of 25 % per pass. The process has an overall carbon efficiency of 89 %. A fraction of 3 % of the recycle is purged to avoid build-up of inerts in the system. More calculation results are presented in Table 3. To maintain the process 1.6 MW of electricity and 1.0 MW of heat (steam) is required. By heat integration an energy reduction of 82 % is obtained in heating and cooling. The heat integration is concentrated around the reactor system and does not cover the pre-treatment separation steps. In the final design 15.4 kt/y of carbon dioxide is needed in order to produce 10 kt/y methanol. The net CO_2 reduction is about 2/3, which is significant.

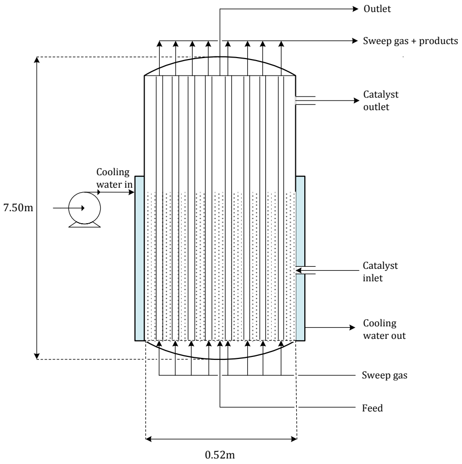

Figure 4: schematic representation of wall-cooled fluidized bed membrane reactor

Table 4: reactor specifications

Reactor property	Value	Unit
Operating conditions		
Temperature	523	[K]
Pressure	3	[MPa]
Hydrodynamic regime	bubbling turbulent fluidization	
Initial gas velocity	1.0	[m/s]
Process	Continuous	
Membrane module dimensions		
Specific surface area	125	$[m^2/m^3]$
Tube diameter	0.01	[m]
Number of tubes	855	
Total membrane surface area	200	$[m^2]$
Pressure difference membrane	2.9	[MPa]
Catalyst properties		
Distribution	Uniform	
Material	$Cu/ZnO\text{-}Al_2O_3$	
Height	3	[mm]
Diameter	3	[mm]
Regeneration	Continuous	

5. Reactor design

One of the main issues is deactivation of the catalyst due to the water produced in the reaction and the exothermic nature of the reaction. A systematic procedure, described by Krishna and Sie (1994), is used for the design of a suitable reactor. Their approach starts with the design of a proper catalyst followed by the selection of type of injection and dispersion of the feed material, ending with the selection of the hydrodynamic flow regime. Based on this a wall-cooled fluidized bed reactor has been selected with the advantage that the catalyst can easily be removed and regenerated.

Additionally a zeolite membrane is introduced for selective removal of the methanol and water and for shifting the reaction to the product side. These membranes are operated at 250 °C. Higher temperatures will destruct the membrane while lower temperatures will result in low fluxes. Isothermal control of the reactor is therefore required. This resulted in the selection and design of a wall-cooled fluidized bed membrane reactor as described by Galluci et al. (2004). The permeate stream is mixed with the liquid stream of the phase separator and separated in the final CH_3OH/H_2O distillation column (see Figure 3). The necessary kinetics of the $Cu/ZnO\text{-}Al_2O_3$ catalysed CO_2 hydrogenation reaction is taken from Hori et al. (2001). In order to design the reactor a suitable model has to be selected. In this case the Kunii-Levenspiel model is applied which describes a bubbling fluidized bed fairly well.

Figure 4 shows a schematic representation of the reactor and Table 4 shows the results of the model calculations.

6. Evaluation

Technically the process is feasible as shown above with a high net CO_2 reduction. However, the economic analysis shows a profit of -0.3 M$/y. Which means the process is not economically feasible at this moment, but might become so in the future when methanol prices (used 389 $/t) and the emission taxes for CO_2-emission (used 21 $/t) increase. Based on the analysis data and the economy of scale (current design capacity is only 10 kt/y which is relatively small compared to current methanol plants of 2000 kt/y and higher) it might become feasible for higher capacities. Critical process items in the design presented are the energy needed for hydrogen compression and the CO_2 separation; and the membrane technology selected.

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