A comparative analysis of methanol production routes: synthesis gas versus CO2 hydrogenation

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Abstract

The two processes are proposed to meet the demand for methanol production with focus in the reduction of carbon dioxide (CO_2) emission and operating costs. The first is the conventional process of methanol synthesis from syngas. The new process is the hydrogenation of CO_2 for methanol production. This new process can be considered a green chemical process because it uses CO_2 as raw material contributing to the mitigation of CO_2 (major greenhouse gas). The simulation of this processes were carried out using the Aspen Hysys V7.3 software to assess energy consumption and CO_2 emissions in addition to process conditions. The influence of various process conditions as pressure, H_2/CO_2 ratio and $(H_2\text{-}CO_2)/(CO_2+CO)$ were analyzed from different parameters as selectivity to methanol, CO and CO_2conversion, methanol production. In all cases studied the processes were evaluated at 245 °C to produce 465 kta of methanol for define the behavior of the operation conditional, to compare the energy consumption and the CO_2 emission of the two process.

Keywords

Methanol, Carbon Dioxide, Synthesis gas, Process simulation, CO_2 emission

1. Introduction

One of the most important chemical feedstock used in the chemical industry is methanol (MeOH), with a worldwide demand of approximately 50 MTA (Behrens et al. 2012). Methanol is used extensively in the plastics industry, as solvents in the pharmaceutical industry and on extraction of animal and plant products (as in the preparation of vitamins, cholesterol and hormones). In organic synthesis, methanol is used as precursor of various chemical intermediates, mainly in the manufacture of formaldehyde. Additionally, it is considered as an excellent alternative energy resource.

For instance, more recently, methanol has been considered as an alternative fuel when blended with gasoline, and through the transesterification of triglycerides to produce Biodiesel that reduce greenhouse gas emissions (Olah, 2005). It was also found that methanol can be converted into olefins in the MTO (methanol-to-olefins) process (Patent 5 191 141), into propylene in the MTP (methanol–to-propylene) process (Koempel and Liebner, 2007), and in turn, hydrocarbon fuels can be produced through these olefins. Futhermore, the MTG and MTGD, processes (methanol-to-gasoline and methanol-to-gasoline/distillate, respectively), one produce hydrocarbons (Keil, 1999). DMC (Dimethyl carbonate) synthesis and DME (Di-methyl ether) synthesis are other promising application of methanol.

Another aspect of environmental relevance is the mitigation of industrial emissions of carbon dioxide (CO_2) through of CO_2 capture by one process of hydrogenation. Hydrogenation of CO_2 reduces the major man-made cause of global warming. However, it is worth noting that renderingeffectiveCO_2 reduction requires the use of low CO_2 emitting sources of energy (e.q., solar energy, hydro energy, nuclear energy, or biomass). The CTM (CO_2 to Methanol) Process stands as a promising alternative to CO_2 reutilization due to the expanding of methanol.

In this direction, several heterogeneous catalysts for conversion of CO_2 to methanol by catalytic partial hydrogenation have been investigated (Highfield, 1995). Based on reported reaction mechanisms of the $CO/CO_2/H_2$ conversion to methanol, three overall reactions (Bussche and Froment, 1996) occur over $Cu/ZnO/Al_2O_3$ catalysts:
Methanol decomposition:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298} = -\ 90.8\ \frac{kJ}{mol} \tag{1}$$

Water gas shift:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298} = -\ 49.2\ \frac{kJ}{mol} \tag{2}$$

Methanol steam reforming:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298} = +\ 41.2\frac{kJ}{mol} \tag{3}$$

In addition to reactions (1), (2) and (3), other two reactions may occur (Eliasson et al., 1998):

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{4}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{5}$$

Reactions (4) and (5) indicate that methane formation is the main obstacle limiting the production methanol. In other words, methanation is the main competitive reaction for methanol formation. Typical additional byproducts include DME, higher alcohols, oxygenates, acids and aldehydes.

In reaction (1), methanol is produced by conversion of CO_2 in an exothermic process. The resulting temperature increase enhances the rate of reaction. On the other hand, the resulting high temperature enhances the deteriorating effect of equilibrium conversion, resulting in the net methanol production decreasing.

Hence the aim of present work is to the analysis of two CTM processes: production of methanol by hydrogenation of CO_2 (direct CTM, d-CTM) and production of methanol from synthesis gas (sg-CTM). Sg-CTM is the conventional industrial process used in large scale worldwide. Operational conditions are evaluated to determine the influence of process parameters on methanol yield, such as pressure, inlet gas composition H_2/CO and H_2/CO_2(N) ratios. Aspen Hysys was employed to simulate the two CTM processes, to compare the energy consumption and to indicate the behavior of operation conditional with the parameters listed above.

2. Process Simulation

To assess technical and economic feasibility of sg-CTM and d-CTM processes, material and energy balances were performed using Aspen Hysys V7.3 (Aspen Technology, Inc.) process simulator. As process design premises, reaction was assumed to occur at a temperature of 245 °C because the process should have a reasonable temperature in order to the methanol steam reforming occurs, and plant capacity were fixed at 464ktaand the feed streams does not have impurities.

2.1 Reaction Kinetics

Different kinetic expressions have been proposed for CO_2 and CO hydrogenation to produce methanol. Graaf et al. (1988) studied and developed the following model which has been used in this study:
Methanol decomposition:

$$r_1 = \frac{K_1 K_{CO}\left(f_{CO} f_{H2}^{1.5} - \frac{f_{CH3OH}}{f_{H2}^{0.5} K°_{P1}}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO2} f_{CO2}\right)\left(f_{H2}^{0.5} + \left(\frac{K_{H2O}}{K_{H2}^{0.5}}\right) f_{H2O}\right)} \tag{6}$$

Water gas shift:

$$r_2 = \frac{K_2 K_{CO2}\left(f_{CO2} f_{H2} - \frac{f_{H2O} f_{CO}}{K°_{P2}}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO2} f_{CO2}\right)\left(f_{H2}^{0.5} + \left(\frac{K_{H2O}}{K_{H2}^{0.5}}\right) f_{H2O}\right)} \tag{7}$$

Methanol steam reforming:

$$r_3 = \frac{K_3 K_{CO2}\left(f_{CO2} f_{H2}^{0.5} - \frac{f_{CH3OH} f_{H2O}}{f_{H2}^{0.5} K°_{P3}}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO2} f_{CO2}\right)\left(f_{H2}^{0.5} + \left(\frac{K_{H2O}}{K_{H2}^{0.5}}\right) f_{H2O}\right)} \tag{8}$$

The parameters for the Eqs. (6) – (8) are given in Table 1. $K°_{p1}$, $K°_{p2}$, $K°_{p3}$ are the equilibrium constants for the Eqs. (1) – (3). The synthesis of methanol is generally catalyzed by Cu-Zn-Al or Cu-Zn-Cr mixed oxides. Important factors in studying this process are values of the equilibrium constants of the reactions (1), (2) and (3) because the literature data on the methanol equilibrium are numerous but conflicting. To ensure kinetic reliability, the values of the equilibrium constants were calculed on the work of Graff et al. (1986) Where the equilibrium constants were calculated and well described using thermo chemical data assuming ideal gas behavior and correcting for non-ideal gas behavior by Soave-Redlich-Kwong equation of state (SRK) in the reaction (1) and (2) and $K^{\circ}_{p3}=K^{\circ}_{p1}*K^{\circ}_{p2}$ because the stoichiometric sum of reaction (1) and (2) is equal the reaction (3) (Graff et al. 1988). It is worth noting that methanol is produced industrially from synthesis gas (syngas) mixtures ($H_2/CO_2/CO$) at elevated pressures P (50 to 100 bar) and temperatures in the range of 200° to 300°C, but for this study the temperature has been fixed in 245 °C (Behrens et al., 2013). The catalyst density (ρ_{cat}) and sphericity (ε) were needed to adjust the reaction rates unit (r_1, r_2 and r_3), as shows in the Table 2.

Table 1: Parameter for kinetic rate expressions for Hydrogenation of CO2 and CO (Graff et al. 1986 and 1988)

Parameter	Expression
K°_{P1} (bar^{-2})	2.4685×10^{-13}exp (98268.98/RT)
K°_{P2}	106.7 exp (-39640.32/RT)
K°_{P3}	2.6338×10^{-11}exp (58628.66/RT)
K_1	2.69×10^{7}exp(- 109,900/RT)
K_2	7.31×10^{8}exp(- 123,400/RT)
K_3	4.36×10^{2}exp(- 65,200/RT)
K_{CO}	7.99×10^{-7}exp(- 58,100/RT)
K_{CO2}	1.02×10^{-7}exp(- 67,400/RT)
$K_{H2O}/K^{0.5}_{H2}$	4.13×10^{-11}exp(- 104,500/RT)

Table 2: Catalyst density and sphericity of Commercial $Cu/ZnO/Al_2O_3$ Catalyst

Parameter	value
ρ_{cat}	1775 kg/m^3 (Bussche and Froment 1996)
ε	0.39 (Lim et al. 2010)

2.2 Thermodynamic model

The Peng-Robinson equation of state was used for the gas phase and Wilson solution model was employed for the liquid phase in the simulation done Aspen Hysys. The Wilson Model has been used due to the need to deal with non-ideal phase polar liquid in the distillation column. The equation of state Peng-Robinson was chosen to predict relevant thermodynamic properties since it can be applied to polar, nonelectrolytes at high pressures.

2.3 Processes' Description

The sg-CTM process flowsheet is presented in the Figure 1. The temperature of the reactor was fixed at 245°C and the reactor's pressure was investigated. The syngas feed stream was set at 25 °C and 5 bar with molar composition of $H_2/CO/CO_2$ as H_2/CO_2. The syngas fed was compressed to reactor pressure and heated to 245 °C before entering the reactor (PFR-101). The flowsheet is composed of a compression section, a loop of reaction, and a purification section. In the first section, the syngas (101-synthesis gas) is compressed to pressure reaction pressure, and then heated in a heat integration exchanger before entering the reactor. The reaction occurs in the PFR-101, a fixed bed reactor with cooling between tubes by medium pressure steam. The heat exchangers E-103 and E-105 perform energy integration and cooling temperature was set to maximize recovery of methanol in the separation vessel V-101 following to a low pressure vessel (V-102).

The gas phase with low methanol content is recycled to the reaction´s loop where a purge is calibrated appropriately. The recycle increases the reaction conversion and yield of, but should be considered carefully due to the costs associated to the recycle. The liquid phase rich in methanol follows to the third methanol purification section. Simulated conditions are needed only one distillation column to fulfills the separation requirements for water, light components and methanol whose specification was set at 99.8 wt% (T-101). The bottom product from the T-101 is mainly of water. The distillate from the T-101 is cooled in the E-108 and decompression to 1 bar generates the final product stream. The overhead vapor is formed by light gases, which were discarding for the process. In this work, do not considerate presence of byproduct as methane and nitrogen, for d-CTM process, and water and carbon, for sg-CTM process. These simplifications make the simulation less complex in the reaction loop and separation section, but comparison between two processes is still valid.

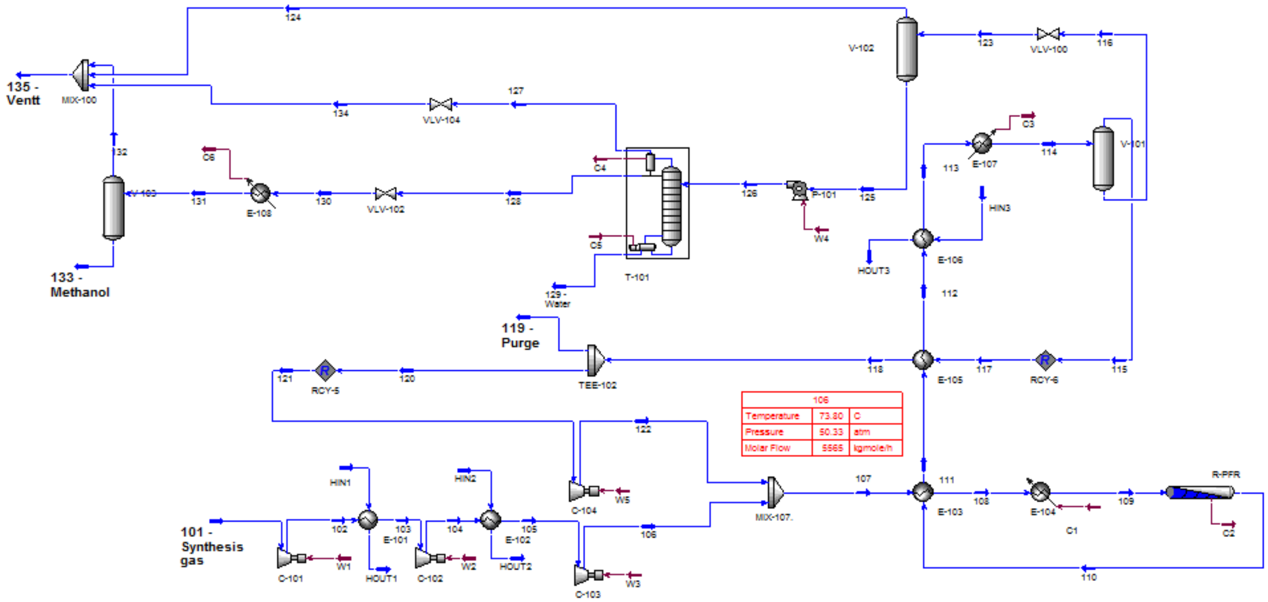


Figure 1: Process flowsheet for sg-CTM Process

The flowsheet for the d-CTM is presented in the Figure 2. There are some differences in the operation conditions of both processes. The major difference is used of two train of compression of feed streams, *101-Carbon Dioxide* and *107-Hydrogen*. This is necessary because the compression of the mixture feed streams (with CO_2 and H_2) forms condensates. These are not desired because the reaction occurs in the gas phase.

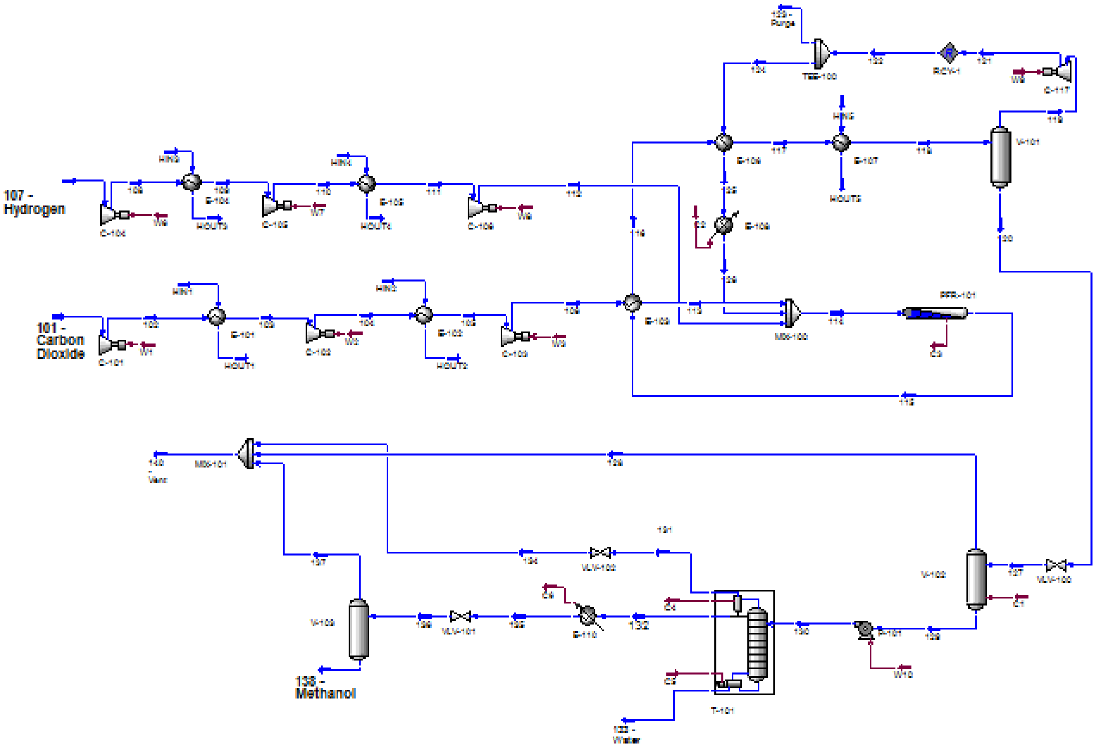


Figure 2: Process flowsheet for d-CTM Process

3. Results and Discussion

Table 3 presents simulation results concerning the utilities consumption per ton of methanol. The consumption of utilities is considerably higher for the d-CTM process. This is due the differences at the operation conditions which were simulation for the two processes renders economically unfeasible the application industrial of technology CO_2 hydrogenation (d-CTM).

Table 3: Comparative analysis of Utilities Consumption the CTM processes

Consumption/tonofmethanol	d-CTM	sg-CTM
Vapor (ton/ton)	1.26	0.30
Cooling water (m^3/ton)	101.18	67.93
Eletricity (GJ/ton)	3.36	1.34

Reactor conditions: T = 245 °C, P = 80 bar,
Feed conditions: H_2/CO_2=4, M=2.1 (sg-CTM)

Table 4 shows the relevant factors of production for the comparison of the d-CTM and sg-CTM processes as methanol yield, consumption of H_2 and CO_2 to d-CTM, consumption of syngas to sg-CTM and CO_2 emission. The CO_2 emission was calculated using 80.09 ton of CO_2 equivalent per TJ of electricity consumption and 55.37 ton of CO_2 equivalent per TJ of vapor consumption (Source: City of New York, Inventory of New York City Greenhouse Gas Emissions, December 2012).

Considering a thermal power plant as source of CO_2, the material cost is considerably inferior to the price of the syngas. However, hydrogen has a higher cost making its consumption a critical point for feasibility of the d-CTM process. Furthermore, other factor shows the disadvantage of the d-CTM process. As can be seen in the Table 4, the d-CTM process emits 19.02 tonCO_2eq/h while the corresponding value for sg-CTM process is inferior. The electric consumption for the compressors and pumps and thermal energy consumption for the vapor in the d-CTM process were superior to the energy expenses of the sg-CTM process.

Table 4: Methanol production, CO_2, H_2 and syngas consumption, and CO_2 emissions

Factor	d-CTM	sg-CTM
MethanolProdution	464kta	464kta
H_2 Consumption	99.04kta	-
CO_2Consumption	664.8 kta	-
syngasConsumption	-	536kta
CO_2emission	19.02 tonCO_2eq/h	15.56 tonCO_2eq/h

Reactor conditions: T = 245 °C, P=80 bar
Feed conditions: H_2/CO_2=4 (d-CTM), M=2.1 (sg-CTM)

In order to obtain a study about process conditions some important parameters were evaluated for each case, sg-CTM and d-CTM.

3.1 Case sg-CTM

The M parameter is defined in the Equation (9) where H_2 molar fraction was fixed at 0.7. Table 5 shows the CO and the CO_2 molar fractions calculated for the fixed M parameter in each case. Considering reaction (1) as the major source for the methanol production in the sg-CTM process, the stoichiometric ratio of the syngas is 2:1(H_2:CO) for the synthesis of methanol and M parameter must be equal to 2. Note that, M is a simple stoichiometric relationship commonly used for characterizing the methanol production by syngas process. Other important property of this process is the CO/CO_2 ratio. A high CO/CO_2 ratio increases the conversion and the reaction rate. Moreover, an important point is the catalyst deactivation rate, which decreases due to the formation of water in high CO/CO_2 ratio (Aasberg-Petersen et al. 2013).

$$M = \frac{(H_2 - CO_2)}{(CO + CO_2)} \tag{9}$$

In order to identify the influence of pressure and M parameter to determine the suitability of the syngas for the synthesis of methanol, the following parameters were investigated: (1) Methanol production in kg/h (stream *“133 – Methanol*” in the sg-CTM process), which is the desired product . Its impact on the revenue should be evaluated from an economic stand point. (2) CO_2 and CO conversion. These parameters were calculated through the Equations

(10) and (11). (3)Selectivity to MeOH, which was calculated as on Equation (11). (4)CO/CO_2 ratio, an important parameter which influences the conversion. (5) Water production in kg/h, the main byproduct.

$$CO_2 conversion\ (\%) = \left(\frac{(CO_2in - CO_2out)}{CO_2in}\right) * 100 \tag{10}$$

$$COconversion\ (\%) = \left(\frac{(COin - COout)}{COin}\right) * 100 \tag{11}$$

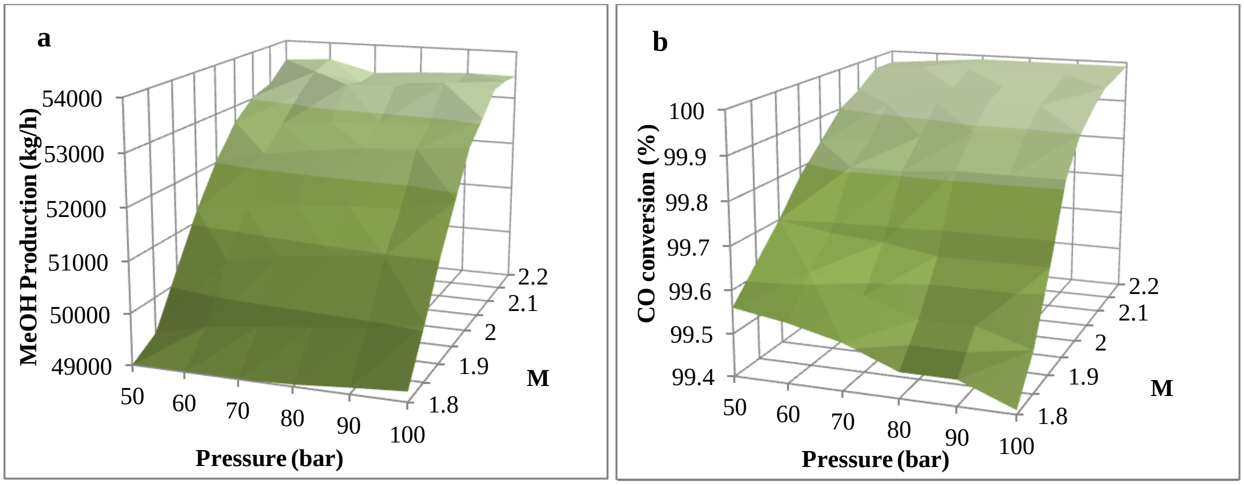
$$MeOH\ selectivity(\%) = \left(\frac{MeOHprod}{((CO+CO_2)in - (CO+CO_2)\ out)}\right) * 100 \tag{12}$$

Table 5: Variation of M parameter and CO/CO_2on the feed stream of sg-CTM

	Feed Composition (molar fraction)			
M	CO/CO_2	H_2	CO_2	CO
1.8	0.875	0.7	0.16	0.14
1.85	1.069	0.7	0.145	0.155
1.9	1.308	0.7	0.13	0.17
1.95	1.609	0.7	0.115	0.185
2	2	0.7	0.1	0.2
2.05	2.529	0.7	0.085	0.215
2.1	3.286	0.7	0.07	0.23
2.15	4.454	0.7	0.055	0.245
2.2	6.5	0.7	0.04	0.26

The results relating to the MeOH production, CO conversion, MeOH selectivity and CO_2 conversion as function of pressure and M parameter are shown in Figure 3 (3D surfaces). As can be seen in Figure 3(a), the production of methanol is high at high M parameter but with the increase of pressure the production of methanol remains practically unchanged. The conversion of CO and CO_2 were approximately the same profile. The conversion of CO_2 is lower than conversion of CO most of the range because feed molar fraction with lower M parameter has CO/CO_2 ratio lower than 2 whereas the stoichiometric ratio of the syngas equal 2 is more favorable for the methanol decomposition reaction (Eqs. (1)). The selectivity to methanol is very high at high M parameter. This occurs because M parameter is greater than 2, whereas molar fraction of CO is greater than molar fraction of CO_2. Therefore, the methanol decomposition reaction is more favored, increasing the selectivity to methanol.

Table 6 shows the differences in the behavior of CO conversion, CO_2 conversion, MeOH selectivity and MEOH production in sg-CTM process for pressure varying in the range of 50 – 100 bar and for M parameter between 1.8 – 2.2, in order to obtain the most favorable process condition.



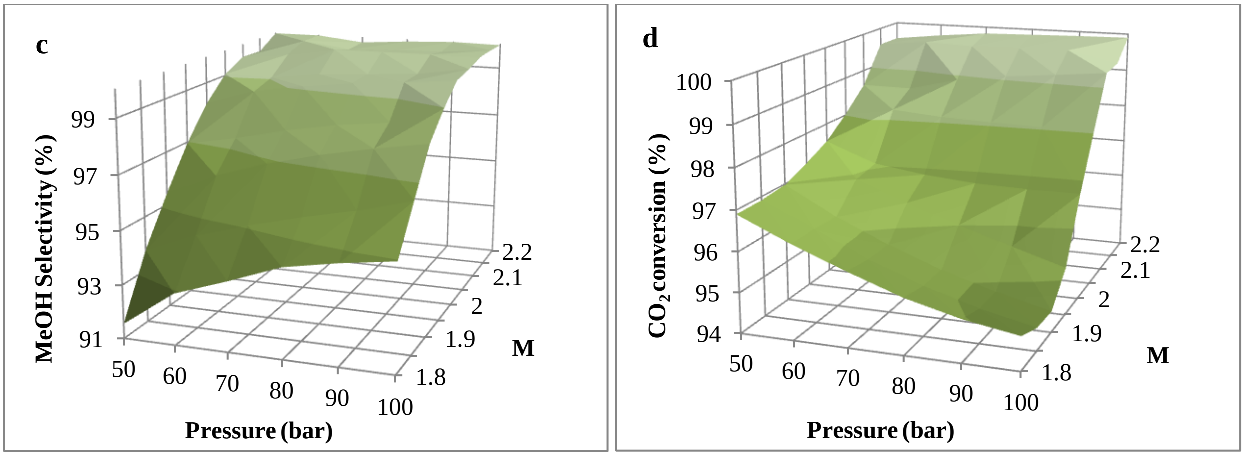


Figure3: Results for methanol production (a), CO conversion (b), methanol selectivity (c) and CO_2 conversion (d)

Table 6: Behavior of CO conversion, CO_2 conversion, MeOH selectivity and MeOH production due the variation of pressure and M parameter of the sg-CTM process

	MEOH production (kg/h)						CO conversion (%)					
M/Pressure (bar)	50	60	70	80	90	100	50	60	70	80	90	100
1.8	48122	47787	48801	49041	49125	49197	99.56	99.54	99.51	99.46	99.46	99.41
1.85	49295	49544	49672	49786	49898	50084	99.63	99.62	99.58	99.54	99.54	99.5
1.9	50284	50561	50744	50875	50974	51067	99.7	99.68	99.67	99.65	99.65	99.65
1.95	51245	51376	51509	51594	51627	51884	99.78	99.81	99.81	99.82	99.82	99.82
2	52041	52262	52405	52518	52590	52698	99.84	99.85	99.87	99.89	99.89	99.9
2.05	52665	52692	52802	52852	52917	53072	99.9	99.92	99.93	99.94	99.94	99.94
2.1	53038	53150	53429	53426	53575	53496	99.93	99.94	99.95	99.96	99.96	99.97
2.15	53173	53497	53325	53361	53384	53517	99.97	99.98	99.98	99.98	99.98	99.98
2.2	53575	53632	53378	53446	53489	53470	99.97	99.98	99.99	99.99	99.99	99.99
	MeOH selectivity (%)						CO_2 conversion (%)					
M/Pressure (bar)	50	60	70	80	90	100	50	60	70	80	90	100
1.8	91.55	92.92	93.59	94.32	94.68	94.96	96.9	96.33	95.83	95.37	95.04	94.82
1.85	93.75	94.52	95.08	95.57	96	96.53	96.91	96.33	95.73	95.24	94.85	94.56
1.9	95.43	96.27	96.89	97.37	97.75	98.08	96.98	96.29	95.72	95.23	94.84	94.52
1.95	96.96	97.31	97.76	98.1	98.33	98.98	97.24	96.93	96.45	96.01	95.6	95.2
2	98.18	98.77	99.1	99.34	99.49	99.69	97.54	97.05	96.87	96.76	96.73	96.73
2.05	99.06	99.03	99.27	99.38	99.51	99.81	98.03	98.23	98.13	98.08	98.05	98.04
2.1	99.49	99.7	100	100	100	100	98.6	98.59	98.91	99.08	99.2	99.33
2.15	99.46	100	99.74	99.81	99.85	100	99.55	99.68	99.63	99.65	99.67	99.38
2.2	100	100	99.79	99.92	100	99.96	99.55	99.7	99.82	99.85	99.88	99.9

H_2 Molar fraction = 0.7, T = 245°C

3.2Case d-CTM

In this case, the influence of pressure and H_2/CO_2 (N ratio) on the following parameters were investigated: (1) Methanol production in kg/h (stream*"133 – Methanol*" in the process d-CTM). (2) CO_2 conversion as show on Equation (10). (3) Selectivity to MeOH as show on Equation (11). (4) N ratio. (5) Water production in kg/h.

Figure 4 shows different behaviors of selectivity to MeOH, CO_2 conversion, MeOH production and water production for a set of N ratios and pressures. Conversion of CO_2decreases slightly as pressure increases and at the low N ratio possibly due to the reverse water gas shift whereas the selectivity of methanol is more affected by these operation conditions, mainly due to the high pressure. In the water gas shift reaction, the number of moles remains unchanged. As can be seen, the production of water is high N ratio and the difference between production of water at 50 and 100 bar greater as the N ratio increases. This is mainly due to the excess of hydrogen in the feed because high N ratio displaces the equilibrium producing more water. Pressure has a greater influence in the production of methanol probably due to the increasing in the moles of reactions. A similar situation occurs in the production of methanol, which is high at high pressure and high N ratio. Methanol decomposition (Eqs.(1)) and methanol steam reforming (Eqs.(2)) at high pressure increase the production of MeOH, as shown in the Figure 4(c). Table 7 shows in details the influence of pressure and N parameter on the behavior of the following parameters methanol yield, selectivity to methanol, CO_2 conversion and production of water for the d-CTM process.

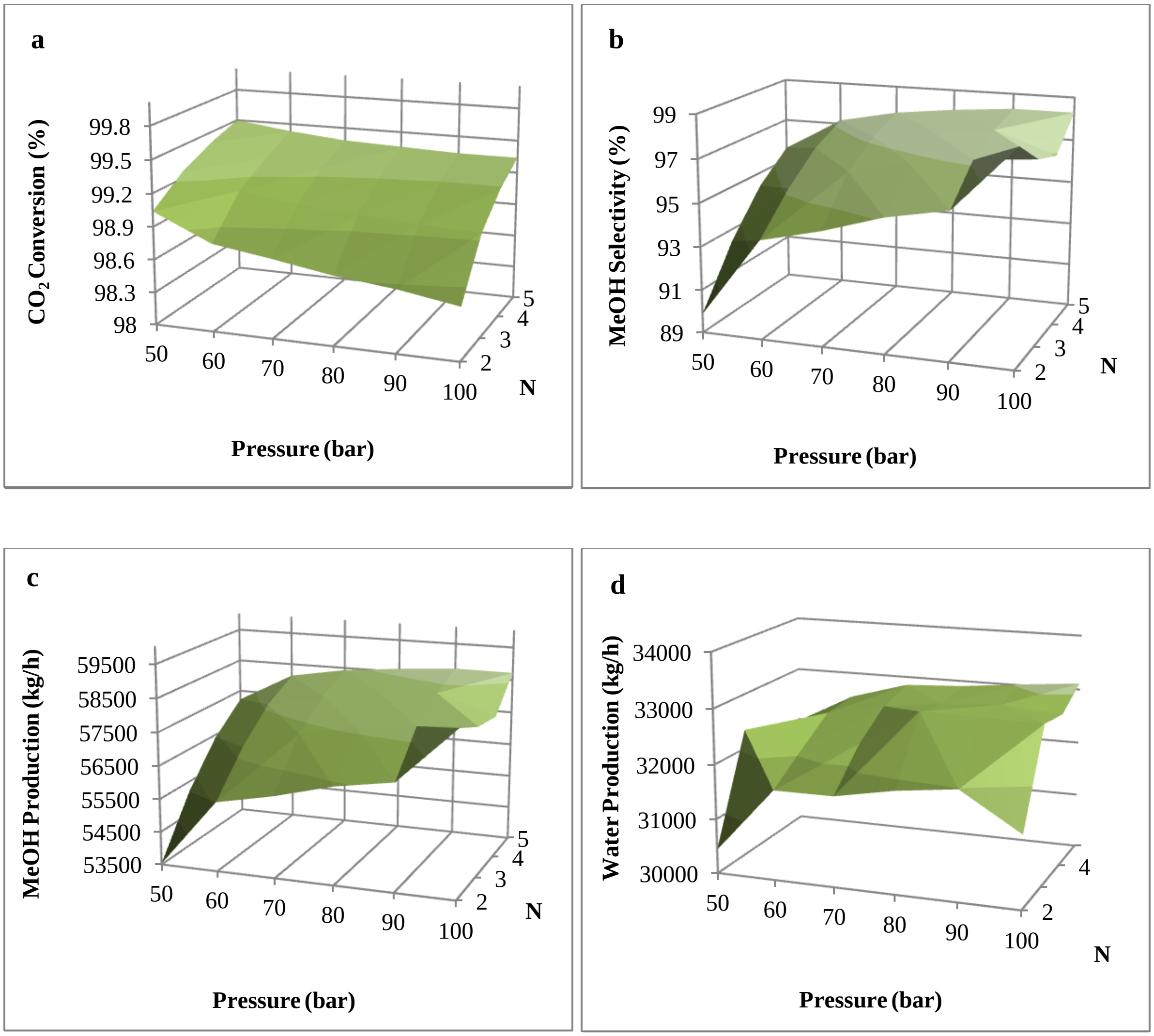


Figure 4: Results for methanol selectivity (a), CO_2 conversion (b), methanol production (c) and water production (d)

Table 7: Behavior of MeOH production, MeOH selectivity, CO_2 conversion and water production due the variation of pressure and N parameter of the d-CTM process

	CO_2 conversion (%)						MeOH selectivity (%)					
N/Pressão (bar)	50	60	70	80	90	100	50	60	70	80	90	100
2	99.04	98.8	98.72	98.63	98.57	98.48	89.87	93.58	94.26	95.13	95.68	98.61
3	99.26	99.13	99.05	99	98.97	98.95	92.44	95.19	96.2	96.77	97.17	97.41
4	99.4	99.3	99.25	99.21	99.19	99.19	94.37	96.44	97.18	97.6	97.88	96.91
5	99.5	99.43	99.38	99.36	99.34	99.34	95.59	97.17	97.74	98.06	98.29	98.29
	MEOH production (kg/h)						Water production (kg/h)					
N/Pressão (bar)	50	60	70	80	90	100	50	60	70	80	90	100
2	53530	55590	55950	56410	56700	58380	30435	31638	31642	31849	31983	31317
3	55190	56750	57300	57610	57830	57960	32342	32069	32274	32947	32924	32909
4	56420	57610	58010	58230	58380	57810	31883	32479	32694	32814	32894	32803
5	57220	58130	58430	58600	58730	58720	31976	32536	32847	32903	33016	33112

4. Conclusions

This work shows that there are at least two differences in the paths for methanol synthesis using syngas or a mixture of H_2 and CO_2 as raw material. The analysis carried out in this work has revealed that, d-CTM process presents more consumption of utilities as vapor, cooling water and electricity per ton of methanol production. Moreover, d-CTM process emits 19.02 ton CO_2 equivalent per hour against an emission of 15.56 ton CO_2 equivalent per hour for sg-CTM.

Regarding the consumption of raw material, d-CTM process is more demanding because of the high stroichiometry ratio, which requires a high H_2/CO_2 ratio. The production of methanol through the sg-CTM process is maximized at high M parameter but in the studied pressure range remains unchanged. The CO and CO_2conversion is also maximized at high M parameter and pressure has not great influence. The selectivity to methanol is very high at high M parameter. The use of the M parameter with different value from stoichiometric proportion affects the operation conditional. In the d-CTM process, the most suitable process conditions for methanol production are pressure higher than 80 bar and high value N parameter, but these values must be adjusted for economic viability. Therefore, the d-CTM process still requires more study about process condition in order minimize electric energy and thermal energy expenses, and to reduce pressure requirements as low as the economics of the process allows. This will reduce operating costs improving process economics.

Acknowledgements

The authors acknowledgethe support provided by PRH41 - ANP / MCTI (the Program in Environmental Engineering Petroleum Industry, Gas and Biofuels) of the Polytechnic School and School of Chemistry of the UFRJ, for scholarship to Camila Machado.

References

Arakawa, H., Dubois, J. L.,Sayama, K.,*Selective conversion of CO2 to methanol by catalytic hydrogenation over promoted copper catalyst*, Energy Converts, Manage, 33, 521, 1992.

Aasberg-Petersen K., Nielsen C. S.,Dybkjær,Perregaard J.,*Large Scale Methanol Production from Natural Gas*, Available: http://www.topsoe.com/business_areas/methanol/~/media/PDF%20files/Methanol/Topsoe_large_scale_methanol_prod_paper.ashx, July 9, 2013.

Behrens M., Felix, Kasatkin I., Kühl S., Hävecker M., Abild-Pedersen F., Zander S., Girgsdies F., Kurr P.,Kniep B., Tovar M., Fischer R. W.,Nørskov J. K.,Schlögl R.,*The Active Site of Methanol Synthesis over Cu/ZnO/Al2O3*, Industrial Catalysts, vol. 336, 18 may, 2012.

Barger P.T., Wilson S.T.,Holmgren J.S.,*Process for converting methanol to olefins using an improved metal aluminophosphate catalyst*, US Patent 5 191 141, 1993.

Campbell, J.M.,*Gas conditioning and processing. In: The Equipment Modules*, eighth ed., vol. 2. John M. Campbell and Company, USA, 2004.

Chinchen, G. C., Mansfield, K., Spencer, M. S.,*The methanol synthesis: How does it work*? CHEMTECH, 20, 692, 1990.

Eliasson, B.,Kogelschatz, U.,Xue, B., Zhou, L. M.,*Application of dielectric-barrier discharges to the decomposition and utilisation of greenhouse gases*, 13th International Symposium on Plasma Chemistry, Beijing, Vol. IV, p 1784, 1997.

Eliasson, B.,Kogelschatz, U.,Xue, B., Zhou, L. M. Hi., *Hydrogenation of Carbon Dioxide to Methanol with a Discharge-Activated Catalyst*, ABB Corporate Research Ltd., 5405 Baden, Switzerland, Ind. Eng. Chem. Res., 37, 3350-3357,1998.

Eliasson, B.,Egli, W.,Kogelschatz, U., *Modelling of dielectric barrier discharge chemistry,* Pure Appl. Chem., 66, 1275,1994.

Vanden B. K. M and Froment G. F., *A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3 Catalyst*,JOURNAL OF CATALYSIS 161, 1–10, ARTICLE NO. 0156, 1996.

Fujiwara, M., Ando, H., Tanaka, M., Souma, Y., *Hydrogenation of carbon dioxide over Cu-Zn-Cr oxide catalysts* ,Bull. Chem. Soc. Jpn., 67, 546, 1994.

Office of Mobile Source, *An Analysis of the Economic and Environmental Effect of Methanol as an Automotive Fuel*, EPA Report No. 0730 (NTIS PB 90-225806) Motor Vehicle Emissions Laboratory, 1989.

Olah, George A. Beyond, *Oil and Gas:The Methanol Economy*,Angew.Chem., Int. Ed., 44, 2005.

Highfield, J. G. *The central role of catalysis in a future energy cycle based on renewable hydrogen and carbon dioxide as "liquefier"*,Trends Phys. Chem., 5, 91,1995.

Keil, F. J., Methanol-to-hydrocarbons: process technology (Review),Microporous and Mesoporous Materials 29 (1999) 49–66.

Kogelschatz, U.,Eliasson, B. Greenhouse Gas Plasma Chemistry in Silent Discharges.Hakone V, International Symposium on High Pressure and Low Temperature Plasma Chemistry, Milovy, Czech Republic, Sept 1996, p 47.

Koempel, H.,Liebner, W.,Lurgi's Methanol To Propylene (MTP®) Report on a successful commercialization. Lurgi AG, Germany. Natural Gas Conversion VIII, 2007 Published by Elsevier B.V.

Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A., 2009. Analysis, Synthesis, and Design of Chemical Processes, third ed. Prentice Hall, Upper Saddle River, New Jersey.