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Analysis of a process for methanol production by CO_2 hydrogenation and reactor design

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Highlights

- Validation by means of literature data of a computational tool for simulation of methanol plant.
- Comparison of two processes for methanol production in terms of reaction efficiency.
- Detailed design of the methanol packed bed reactor to evaluate different operating conditions.

1. Introduction

Methanol is one of the most valuable chemicals with a variety of uses either as fuel or as building block for the synthesis of other chemicals. In the last years, there is increasing interest in the production of methanol from CO_2, based on the so called "Power-to-Fuel" concept.

2. Methods

Two schemes for the methanol production by hydrogenation of CO_2 reported in the literature by Perez-Fortes et al. [1] and Kiss et al. [2] are analyzed. In the second scheme, a recycle of the product stream of the reactor is used to enhance the productivity. Simulations of the two schemes are carried out by ChemCad software. For the methanol reactor, the SRK thermodynamic model is used, while for the distillation section the NRTL model is set. The reactions involved are the following (see Eq. 1-3):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^0_{298} = 41.2\ kJ/mol_{CO_2} \qquad (1)$$

$$CO + 2 \cdot H_2 \leftrightarrow CH_3OH \qquad \Delta H^0_{298} = -90.7\ kJ/mol_{CO} \qquad (2)$$

$$CO_2 + 3 \cdot H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^0_{298} = -49.5\ kJ/mol_{CO_2} \qquad (3)$$

The reactor is modelled according to the kinetics of Graaf et al. [3]. It is an adiabatic ideal plug flow reactor using the $Cu/ZnO/Al_2O_3$ commercial catalyst. The density of catalyst is equal to 1775 kg_{cat}/m^3_{cat}, the fixed bed porosity is 0.5, the pellet diameter is 5.5 mm [4]. Figure 1a and 1b show the two process schemes.

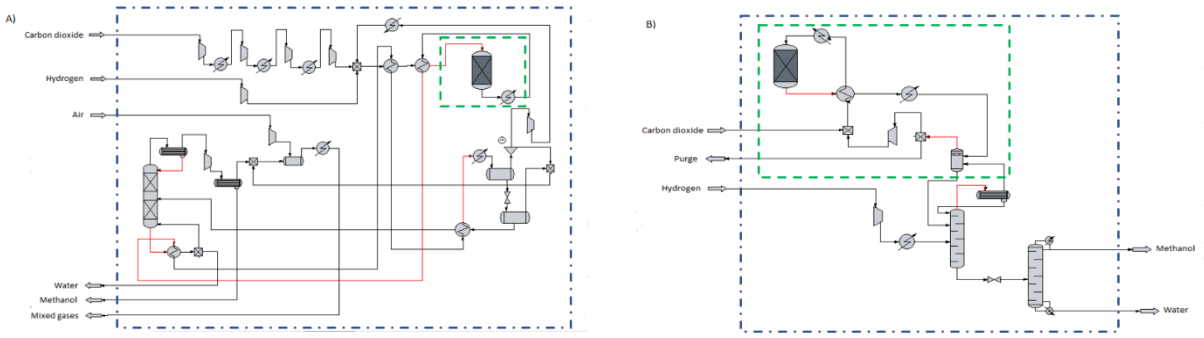

Figure 1. Process scheme for methanol production according: a) Perez-Fortes et al. [1], b) Kiss et al. [2] (green dashed line: boundaries of the reactor section; blue dashed line: boundaries of the plant section).

A mathematical model of the methanol reactor is also developed in MATLAB, comparing the reaction kinetics of Graaf et al. [3] and Bussche and Froment [5].

3. Results and discussion

The two processes are reproduced in ChemCad software and a validation of the tool is obtained comparing the obtained data with the literature data, as shown in table 1.

Table 1 Comparison of the simulation and literature data for the two analyzed process schemes.

	Perez-Fortes et al. [1]	Kiss et al. [2]	Perez-Fortes et al. [1] -ChemCad	Kiss et al. [2] -ChemCad
Methanol production (kg/h)	55100	12507	51711	12294
Water production (kg/h)	31700	7346	31293	6014
CO_2 conversion (%)	21.97	17.20	21.99	17.13
Gross CO_2 used (kg/kgCH_3OH)	1.37	1.38	1.56	1.40
Heat of reaction (kW)	-23339	-4449	-17333	-5000

Results shows that the tool implemented in ChemCad is positively validated against literature calculations. A comparison of the two schemes considering some efficiency parameters is made in table 2.

Table 2 Comparison of the two analyzed process schemes

	Kiss et al. [2]	Perez-Fortes et al. [1]
Stochiometric efficiency, CH_3OH:CO_2	1.00	1.00
CO_2 reaction conversion (%)	17.13	21.99
$CH_3OH/CO_{2,reacted}$ selectivity (%)	99.75	98.50
$CH_3OH/CO_{2,input}$ yield (%)	17.21	21.66
Plant efficiency, CH_3OH:$CO_{2,consumed}$ (%)	97.14	98.61
CO_2 plant conversion (%)	100	90.51

The recycle of the product stream allows to have a higher selectivity and CO_2 plant conversion but lower values for the other parameters. However, a higher methanol productivity is ensured by the process of Perez-Fortes et al. [1], due to the higher conversion of carbon dioxide in the reaction.

4. Conclusions

More work will be done regarding the design and analysis of the methanol reactor by means of a detailed numerical model in MATLAB; the results will be presented at the conference.

References

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Keywords
Methanol production; Mathematical model; Process simulation; Reactor design;