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Dimethyl ether production from CO₂ rich feedstocks in a one-step process: Thermodynamic evaluation and reactor simulation



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HIGHLIGHTS

• Thermodynamic study of DME production in a one-step process from syngas.

• CO2 rich feedstock for DME production.

- Packed bed reactor simulation and operating conditions analysis.
- The study is based on one-dimensional pseudo-homogeneous model.
- DME yields within wide ranges of operating conditions are quantified.

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ABSTRACT

The dimethyl ether (DME) direct production from CO₂-rich feedstock has been evaluated from thermodynamic and fixed bed reactor simulation perspectives, in order to evaluate the potentialities of using CO₂ as reagent in one-step DME synthesis. The thermodynamic model has been applied to perform a detailed sensitive analysis of DME synthesis process at temperature within the range 200–275 °C, pressures of 20– 70 bar and inlet composition of H₂/CO = 1–3 and CO₂/CO = 0–2.5. The results show a stringent thermodynamics threshold in DME yield (DME yield < 30%), when the CO₂/CO ratio is greater than 2 in the fed to the synthesis reactor. The results have been confirmed by the kinetic mathematical model and reactor simulation, which includes chemical reactions, heat transfer and pressure drop along the fixed bed reactor. The performed simulations point out the role of cooling fluid temperature and reactor pressure. Furthermore, the kinetic modeling, in agreement with the thermodynamic approach, evidences the negative effect of water formed during CO₂ conversion and further steps. The proposed thermodynamic and kinetic insight states that water removal during CO₂ conversion, for example by hydrophilic membrane, is a mandatory element to enable industrial production of DME in the framework of CO₂ valorization. © 2016 Elsevier B.V. All rights reserved.

1. Introduction

DME (dimethyl ether) plays a key role in the future energy and chemical production scenario [1–5] and for this reason many companies, among which Topsoe, Mitsubishi Co. and Total, are actively promoting its development. DME is a clean burning synthetic fuel that can be a substituted for liquefied petroleum gas (LPG) or blended in fuel mix [6,7]. It has excellent combustion characteristics due to a low auto-ignition temperature. With a cetane number of 55–60, DME can be used as a substitute for diesel fuel in a diesel engine, which would need only slight modifications. DME in diesel engines burns without soot and, as oxygenated fuel additive, it

* Corresponding author. Tel.: +39 347 6809041. *E-mail address:* m.defalco@unicampus.it (M. De Falco). promotes a favorable fuel/air-mixture and consequently prevents soot formation. DME shows also an excellent thermal efficiency among all syngas-to-products.

Markets for DME include aerosol (main current market), LPG (commercial alternative), diesel (emerging market), power generation and fuel cells (development stage) and petrochemical feedstock [8]. DME conversion to hydrocarbons is a relevant emerging market [9]: the series of processes indicated with the general terms methanol-to-hydrocarbons (MTH, which include olefin – MTO, propylene – MTP, gasoline – MTG, aromatics – MTA, etc.) are most effective when starting from DME rather than from methanol. Currently, there are various MTO/MTP facilities in China, while many other projects are advancing toward completion. Fourteen to fifteen facilities are expected to be operational by 2016. The MTO/MTP sector is projected to



Nomenclature

$\begin{array}{c} A_i \\ A_0 \\ c_p \end{array}$ $\begin{array}{c} D_0 \\ D_i \\ d_p \\ F \\ F_j \end{array}$	inside area of the tube, m^2 outside area of the tube, m^2 specific heat of the gaseous mixture at constant pres- sure, J mol ⁻¹ tube outside diameter, m tube inside diameter, m particle diameter, m mole flux of gas phase, kmol/(m ² s) mole flux of species <i>j</i> , kmol/(m ² s)	P_j r_i R S_j T T_{ν} y_j Y_j U	partial pressure of species j in fixed bed side, Pa reaction rate, kmol/(kg s) ideal gas constant selectivity of compound j temperature, °C steam temperature in the shell, °C mole fraction of species j yield of species j overall heat transfer coefficient between pipe and shell,
h _i h _o k k	heat transfer coefficient between the gas and the wall, $W/(m^2 K)$ heat transfer coefficient outside of the tube, $W/(m^2 K)$ thermal conductivity, $W/(m K)$ wall thermal conductivity $W/(m K)$	X _j v z	W/(m ² K) conversion of compound <i>j</i> superficial velocity of gas phase in fixed bed side, m/s axial coordinate, m
$ar{K}_{i}$ $ar{K}_{j}$ $ar{K}_{eq}$ $ar{L}$ P P_{O} P_{a}	reaction rate constant adsorption equilibrium constant, Pa ⁻¹ equilibrium constant, Pa ³ reactor length, m reactor pressure in fixed bed side, Pa pressure in the shell side, bar atmospheric pressure, bar	Greek Le α ε μ ρ ρ _{sc}	tters stoichiometric coefficient void fraction gas phase dynamic viscosity, kg/(m s) density of gas phase, kg/m ³ catalyst bed density, kg/m ³

grow from just under one million metric tons in 2013 to almost eleven million metric tons in 2023, experiencing a 27% annual growth rate. Methanol-to-Gasoline (MTG) is also an emerging demand segment: today, six plants use the ExxonMobil's MTG two-steps technology (DME as intermediate). Dalian Institute of Chemical Physics (DICP) MTO technology, at the basis of most of the plants in China and of the world's first MTO unit, uses the acronym DMTO (dimethyl ether and methanol-to-olefin) to remark that, even when starting from methanol, DME is the reaction intermediate.

DME could be obtained by dehydration of methanol in a separate or integrated step [10,11], but a valuable alternative is to synthetize directly DME from the syngas (CO/H₂ mixtures with a eventual amount of CO₂, typically below 3%) [12–16] produced both from fossil fuels (methane or coal, the latter in rapid expansion in China) and non-fossil-fuel sources (residue/biomass/renewable). DME is thus an important and versatile platform chemical for chemical industry, but also a key element in the transformation to a sustainable energy future [17].

The most interesting studies on innovative processes to synthetize DME are focused on the use of alternative raw materials such as CO₂ [18–27]. The direct (one-step) or indirect (via methanol production) production of DME from syngas is relatively well established, with a number of companies proposing the direct (Topsoe, JFE Ho., Korea Gas Co., Air products, NKK) or indirect (Toyo, MGC, Lurgi, Udhe) processes [2]. MegaDME process, for example, is essentially the combination of Lurgi MegaMethanol and Dehydration Plants: a single-train production with capacities of 5000 t/d (1.7 Mt/a) and more. The use of CO₂ (or CO₂-rich streams, as those deriving from coal conversion or biomass transformation) as raw material, on the contrary, is less developed [28,29]. Although starting from CO₂ rather than syngas introduces only an additional step (the reversible water gas shift - rWGS - reaction, refer to reactions scheme Eqs. (1-5)) in an already multistep process involving different type of catalytic functionalities [11,30,31], the presence of this additional (reversible) step significantly influences the performances. For example, water forms in the rWGS reaction, influencing both the rate of methanol intermediate formation and the reversible reaction of methanol dehydration to DME. Diban et al. [32] used a zeolite membrane for the in situ H₂O removal in a packed-bed membrane reactor evidencing with simulation models that the transformation of CO_2 into DME is promoted, although yields and conversions were highly dependent on membrane transport characteristics. Iliuta et al. [33] also discussed the potential and limits of in situ removal of water under DME synthesis conditions in a fixed-bed membrane reactor, on the basis of simulation studies. Dadgar et al. [34] very recently showed that combining methanol synthesis and dehydration (i.e. the reaction of methanol to DME, also forming water as product of reaction) has a negative effect on the methanol formation kinetics.

A further difference in starting from CO_2 rather than syngas is related to the higher oxidation power of CO_2 has with respect to $CO. CO_2$ -only or CO_2 -rich feed thus influence the active state of the catalyst for methanol synthesis, influencing the rate of formation of methanol [35]. Therefore, there is a strong influence of the reaction conditions on the overall catalytic behavior and the need to develop appropriate kinetic models to describe the overall synthesis. This is the basis for a proper modeling of the process and its optimization.

Various authors have investigated the use of different bifunctional catalyst for CO₂ to DME reaction, based typically on the combination of a methanol synthesis component (Cu/ZnO-based) and an acid (zeolite or alumina) catalyst [21,36–43]. Many researches also involved deeper insight of reactor configuration and fluid dynamics [28,43-46]. More limited, on the contrary, are the studies which have analyzed in detail the thermodynamic of the system, that may significantly influence the possible industrial use of the process, given the many reversible reactions present, particularly starting from CO₂. Clausen et al. [47] has reported a thermodynamic analysis of DME and methanol synthesis plants, but starting from syngas deriving from wood gasification. In addition, limited results have been reported on the reactor simulation in direct CO₂ conversion to DME, which in combination with the thermodynamic analysis allow identifying better the boundary conditions for process development. Clausen et al. [48] have modeled DME fuel production plant using syngas generated by gasification of torrefied woody biomass. Hayer et al. [49] have made a simulation of micro-channel reactor in DME synthesis from syngas. Vakili et al. [50] have modeled DME synthesis in a thermally-coupled heat exchanger reactor, but also starting from syngas.

Given the relevance of the direct DME synthesis from CO_2 and its role in the valorisation of CO_2 stream producing high addedvalue products [51,52], there is thus the need to analyze better this process from a thermodynamic and kinetic perspective. In this work, the one-step DME synthesis with a feedstock poor in H₂ (with respect to CO and CO_2) is assessed in order to evaluate the CO_2 potentialities as reagent in DME production processes. Starting from the thermodynamics analysis, the reactions are then simulated in a packed-bed configuration.

Overall reactions involved in DME direct synthesis from CO₂ are quite exothermic so the tubes containing the catalyst are commonly surrounded by a jacket with a cooling fluid. The coupling of heat exchange with the chemical reactions in one dimensional model has been studied in deep by research group in Shiraz (Iran) [50,53–55]. They studied several technological solutions in order to quench the reactor and, at the same time, exploiting the heat of reaction to increase the overall process efficiency. Vakili et al. [53] proposed to use a double reactor implementing the heat generated by the DME synthesis to support the endothermic reaction of propane dehydrogenation. The same group studied the hydrogen production from cyclohexane dehydrogenation in a multi-functional auto-thermal reactor (DME and hydrogen production) [54]. In this work, the reactor configuration as depicted in Fig. 1, similar to the pipe shell reactor implemented by KOGAS [56] and described by Hu et al. [57], has been assumed.

2. Mathematical modeling

2.1. Thermodynamics modeling

The first step to develop the DME direct synthesis thermodynamic model is the definition of the independent reactions composing the process. The main reactions involved are [58]:

 $\begin{array}{ll} \mbox{CO}_2 \mbox{ hydrogenation}: & \mbox{CO}_2 + 3 \mbox{H}_2 \rightleftharpoons \mbox{CH}_3 \mbox{OH} + \mbox{H}_2 \mbox{O} \\ \mbox{\Delta H}_o = -49.4 \mbox{ kJ/mol} \end{array} \tag{1}$

CO hydrogenation : $CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H_o = -90.4 \text{ kJ/mol}$ (2)



Fig. 1. Pipe-shell fixed bed reactor for DME synthesis directly from syngas [54].

Water-gas shift :
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 $\Delta H_o = -41.0 \text{ kJ/mol}$
(3)

$$Overall reaction: 3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2$$

$$\Delta H_0 = -258.3 \text{ kJ/mol}$$
(5)

Among the 5 reactions, only 3 are independent. The reactions scheme imposed in this work is composed by CO_2 hydrogenation (1), water–gas shift (3) and methanol dehydration (4). It is a worth noting that all the reactions are exothermic and thermodynamically feasible at low temperature. Concerning with the operating pressure, the reaction (1) is promoted at high pressure, while reactions (3) and (4) are not influenced.

The thermodynamics model is based on the solution of a set of 3 equations of the reactions (1), (3) and (4) equilibrium constants as a function of the reactions conversions. The equilibrium constants are defined according the well-known Van't Hoff equation:

$$\left(\frac{\partial K_{eq}}{\partial T}\right)_{p} = \frac{\Delta H_{0}}{RT^{2}} \tag{6}$$

where ΔH_0 is the standard reaction heat, *R* the gas constant and K_{eq} is the equilibrium constant.

The Eq. (6) is integrated imposing a reference temperature T_0 , obtaining:

$$\ln K_{eq}(T) = \ln K_{eq}(T_0) + \int_{T_0}^T \frac{\Delta H_0}{RT^2} dT$$
(7)

where the term ΔH_0 is calculated by the following equation:

$$\left(\frac{\partial\Delta H_0}{\partial T}\right)_p = \Delta c_p \tag{8}$$

$$\Delta c_p = \sum_{i=1}^{c} \alpha_i c_{p,i}^0 \tag{9}$$

where $c_{p,i}^0$ is the specific heat of the component *i* involved in the reaction at the reference state (gas/vapor, pure component) and α_i is the corresponding stoichiometric coefficient. The specific heats are calculated by means of empirical equations in function of the temperature:

$$c_{p,i} = A_i + B_i T + C_i T^2 + D_i T^3$$
(10)

The coefficient of the Eq. (10) are reported in Table 1 [59]. Therefore, the term Δc_p is calculated according to:

$$\Delta c_p = \Delta A + \Delta B \cdot T + \Delta C \cdot T^2 + \Delta D \cdot T^3$$
(11)

where

$$\Delta A = \sum_{i=1}^{C} \alpha_i A_i$$

$$\Delta B = \sum_{i=1}^{C} \alpha_i B_i$$

$$\Delta C = \sum_{i=1}^{C} \alpha_i C_i$$

$$\Delta D = \sum_{i=1}^{C} \alpha_i D_i$$

(12)

Solving Eq. (8) introducing Eq. (11) and, then, solving Eq. (7), the equilibrium constants are calculated from:

Table 1Coefficients for the specific heat quantification in Eq. (10).

	А	В	С	D
H ₂ O CH ₃ OH H ₂ CO ₂ CH ₃ OCH ₃	35.553 37.068 23.365 99.215 19.846 20.582	-0.0206 -0.0429 0.033 0.1416 0.1552 0.0108	6E-05 3E-04 -6E-05 -2E-04 1E-05	-3E-08 -2E-07 4E-08 1E-07 -5E-08
co	0.000	-0.0100	11-05	-JL-00

$$\ln K_{eq}(T) = A_2 + \frac{B_2}{T} + C_2 + D_2 T + E_2 T^2 + F_2 T^3$$
(13)

where

$$A_{2} = \ln K_{eq}(T_{0}) + \frac{1}{R} \left(A_{1}T_{0}^{-1} - B_{1} \ln T_{0} - C_{1}T_{0} - \frac{D_{1}}{2}T_{0}^{2} - \frac{E_{1}}{3}T_{0}^{3} \right)$$

$$B_{2} = -A_{1}$$

$$C_{2} = B_{1}$$

$$D_{2} = C_{1}$$

$$E_{2} = \frac{D_{1}}{2}$$

$$F_{2} = \frac{E_{1}}{3}$$
(14)

The coefficient A_1 , B_1 , C_1 , D_1 and E_1 are reported in Table 2.

As the equilibrium constants of the 3 reactions are calculated according Eq. (13), the dependence of K_{eq} from the progress grade of the reaction has to be defined according to the following equation:

$$K_{eq}(T) = \prod_{i=1}^{c} \varphi_i^{\alpha_i}(P, T, y_i) \cdot \prod_{i=1}^{c} y_i^{\alpha_i} \cdot P^{\Sigma \alpha_i}$$
(15)

where φ_i are the fugacity coefficient of the component *i* involved in the reaction, calculated according to the Tsonopoulos correlation [60], efficient for polar components, and y_i is the molar fraction of the component *i*, which have to be calculated in function of the reactions progress grades:

$$y_{CH_{3}OH} = \frac{F_{in,CH_{3}OH} + \xi_{1} - 2\xi_{3}}{F_{in,tot} - 2\xi_{1}}$$

$$y_{CH_{3}OCH_{3}} = \frac{F_{in,CH_{3}OCH_{3}} + \xi_{3}}{F_{in,tot} - 2\xi_{1}}$$

$$y_{H_{2}} = \frac{F_{in,H_{2}} - 3\xi_{1} + \xi_{2}}{F_{in,tot} - 2\xi_{1}}$$

$$y_{CO} = \frac{F_{in,CO} - \xi_{2}}{F_{in,tot} - 2\xi_{1}}$$

$$y_{CO_{2}} = \frac{F_{in,CO_{2}} - \xi_{1} + \xi_{2}}{F_{in,tot} - 2\xi_{1}}$$

$$y_{H_{2}O} = \frac{F_{in,H_{2}O} + \xi_{1} - \xi_{2} + \xi_{3}}{F_{in,tot} - 2\xi_{1}}$$
(16)

where F_{in} are the inlet molar flow-rate and ξ_1, ξ_2, ξ_3 are the progress grade of reactions (1), (3) and (4), respectively. Imposing Eq. (16) in Eq. (15) and fixing the inlet flow-rates, the temperature and the

Table 2 Coefficient A_1 , B_1 , C_1 , D_1 and E_1 for K_{eq} calculation.

A_1	$\Delta H_0(T_0) - (\Delta A \cdot T_0 + \Delta B/2 \cdot T_0^2 + \Delta C/3 \cdot T_0^3 + \Delta D/4 \cdot T_0^4)$
B_1	ΔA
<i>C</i> ₁	$\Delta B/2$
D_1	$\Delta C/3$
E_1	$\Delta D/4$

pressure, it is possible to calculate the progress grades by numerically solving a set of 3 equations. Then, the components outlet flow-rates are calculated as follow:

$$F_{out,CH_{3}OH} = F_{in,CH_{3}OH} + \xi_{1} - 2\xi_{3}$$

$$F_{out,CH_{3}OCH_{3}} = F_{in,CH_{3}OCH_{3}} + \xi_{3}$$

$$F_{out,H_{2}} = F_{in,H_{2}} - 3\xi_{1} + \xi_{2}$$

$$F_{out,CO} = F_{in,CO} - \xi_{2}$$

$$F_{out,CO_{2}} = F_{in,CO_{2}} - \xi_{1} + \xi_{2}$$

$$F_{out,H_{2}O} = F_{in,H_{2}O} + \xi_{1} - \xi_{2} + \xi_{3}$$
(17)

The thermodynamic performance is assessed by calculating the CO and H_2 conversion, the DME yield and the DME selectivity:

$$X_{\rm CO} = \frac{F_{in,\rm CO} - F_{out,\rm CO}}{F_{in,\rm CO}} \quad \text{CO conversion}$$
(18)

$$X_{\rm H_2} = \frac{F_{in,\rm H_2} - F_{out,\rm H_2}}{F_{in,\rm H_2}} \quad \rm H_2 \ conversion \tag{19}$$

$$Y_{\text{CH}_{3}\text{OCH}_{3}} = \frac{2F_{out,\text{CH}_{3}\text{OCH}_{3}}}{F_{in,\text{CO}} + F_{in,\text{CO}_{2}}} \quad \text{DME yield}$$
(20)

$$S_{\text{CH}_{3}\text{OCH}_{3}} = \frac{2F_{out,\text{CH}_{3}\text{OCH}_{3}}}{2F_{out,\text{CH}_{3}\text{OCH}_{3}} + F_{out,\text{CH}_{3}\text{OH}}} \quad \text{DME selectivity}$$
(21)

2.2. Reactor modeling

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The steady-state mass, energy and momentum balance equations for the fixed-bed reactor are formulated assuming a onedimensional plug-flow (axial mass and heat dispersion negligible, L/d > 30). The reactor is packed with bifunctional catalytic particles of Cu–ZnO–Al₂O₃/HZSM-5, in which any inactivation phenomena is neglected, and the solid–gas phases are described through pseudo-homogeneous modeling, by which the gas and solid inside the reactor are considered as a one single phase. The mass balances of the six components are expressed by Eqs. (22–27):

$$\varepsilon \frac{dF_{\rm H_2O}}{dz} = \rho_{\rm sc}(r_1 - r_2 + r_3) \tag{22}$$

$$\varepsilon \frac{dF_{\rm H_2}}{dz} = -\rho_{\rm sc}(3r_1 - r_2)$$
(23)

$$\varepsilon \frac{d\dot{F}_{\rm CO}}{dz} = -\rho_{\rm sc}(r_2) \tag{24}$$

$$\varepsilon \frac{d\dot{F}_{\rm CO_2}}{dz} = -\rho_{\rm sc}(r_1 - r_2) \tag{25}$$

$$\varepsilon \frac{d\dot{F}_{\rm CH_3OH}}{dz} = -\rho_{sc}(2r_3 - r_1) \tag{26}$$

$$\varepsilon \frac{d\dot{F}_{\rm CH_3O}}{dz} = \rho_{\rm sc}(r_3) \tag{27}$$

where ρ_{sc} is the ratio of mass catalyst on the reaction volume, r_1 , r_2 , r_3 are the rates of the reactions and ε is the void fraction in the catalyst bed. The final reaction rates for methanol synthesis (Cu–ZnO–Al₂O₃) and for methanol dehydration (Cu–ZnO–HZSM-5) are described by Eqs. (28–30) [33] neglecting the absorption of water and methanol:

$$r_{1} = \bar{K}_{1} \frac{P_{\text{CO}_{2}} P_{\text{H}_{2}} (1 - P_{\text{CH3OH}} P_{\text{W}} / K_{eq1} P_{\text{CO}_{2}} P_{\text{H}_{2}}^{3})}{\left(1 + K_{\text{CO}_{2}} P_{\text{CO}_{2}} + K_{\text{CO}} P_{\text{CO}} + \sqrt{(K_{\text{H}_{2}} P_{\text{H}_{2}})}\right)^{3}}$$
(28)

$$r_{2} = \bar{K}_{2} \frac{P_{W} - P_{CO_{2}}P_{H_{2}}/K_{eq2}P_{CO}}{\left(1 + K_{CO_{2}}P_{CO_{2}} + K_{CO}P_{CO} + \sqrt{(K_{H_{2}}P_{H_{2}})}\right)}$$
(29)

$$r_3 = \bar{K}_3 \left(\frac{P_{\text{CH3OH}}^2}{P_{\text{W}}} - \frac{P_{\text{CH3OCH3}}}{K_{eq3}} \right)$$
(30)

where P_j represents the partial pressures of the *j*th component (*j* = H₂O, H₂, CO, CO₂, DME, MeOH) in the gaseous mixture, \bar{K}_1 , \bar{K}_2 and \bar{K}_3 are the kinetic constants and K_j the Langmuir adsorption kinetic constants of the respective compounds on the catalyst [61,62] calculated in function of the operating temperature according to the Arrhenius' law:

$$K_j = A \, \exp\left(-\frac{B}{RT}\right) \tag{31}$$

The coefficients appearing in (31) are reported in Table 3.

The reactor configuration as depicted in Fig. 1 is considered in this work. The kinetic approach does not include the presence of deactivation to simplify the approach. The cooling of the catalytic tubes takes place by means of natural circulation of boiling water between the steam drum and the reactor. The exit stream is sent to the DME and methanol purification section and the system allows to exploit the enthalpy of exothermic reactions by producing high pressure steam also used for the feed pretreatment (e.g. steam reforming of natural gas). The heat balance inside the reactor is written through Eq. (32):

$$\left(\sum_{j=1}^{nc}\dot{F}_{j}c_{p_{j}}\right)\frac{dT}{dz} = \rho_{sc}\sum_{i=1}^{nr}\left(-\Delta H_{i}^{r}(T)\right)r_{i} - \frac{\pi D_{i}}{A_{0}}U(T-T_{\nu})$$
(32)

where dT/dz is the temperature gradient along the reactor abscissa z (varying from 0 to L) and ΔH_i^r is the heat of reaction. The heat flux toward the shell is evaluated considering an overall heat transfer coefficient U and the temperature difference between the interior of the reactor at T and the external vapor at T_v according to Eq. (33) [50,53,54]:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{A_i \ln(D_0/D_i)}{2\pi L k_w} + \frac{A_i}{A_0} \frac{1}{h_0}$$
(33)

which introduces a rigorous calculation of the lobal coefficient considering the dependence on the operating conditions, through the evaluation of the physical quantities of the gaseous mixture, and on the geometry of the system, where k_w is the wall conductivity, *L* the reactor length, D_0 and D_i the external and internal pipe diameter and A_0 and *Ai* the cross flow area. The heat transfer coefficient between the gaseous phase and the tube wall h_i is calculated through Eq. (34) from Smith et al. [63]:

$$\frac{h_i}{c_p\rho\mu} \left(\frac{c_p\mu}{k}\right)^{2/3} = \frac{0.458}{\varepsilon} \left(\frac{\rho v d_p}{\mu}\right)^{-0.407}$$
(34)

where ρ is the gas density, c_p the specific heat, k the thermal conductivity and μ the gas viscosity, d_p the catalyst diameter and v is the superficial velocity.

 Table 3

 Coefficient A and B for the calculation of kinetic and adsorption constant according to (31) [59,60].

	А	В
\bar{K}_1	35.450	$1.7069\cdot 10^4$
\bar{K}_2	7.3976	$2.0463\cdot 10^4$
\bar{K}_3	8.2894	$5.2940 \cdot 10^4$
K _{H2}	0.2490	$-3.4394\cdot10^4$
K _{CO2}	$1.02 \cdot 10^{-7}$	$-6.7400 \cdot 10^4$
K _{co}	$7.99 \cdot 10^{-7}$	$-5.2940\cdot10^4$

The heat transfer coefficient in the shell side is expressed by Eq. (35) [64]:

$$h_0 = 7.96(T - T_v)^3 \left(\frac{P_0}{P_a}\right)^{0.4}$$
(35)

where P_0 is the outside pressure (in the shell side) and P_a the atmospheric pressure.

The reactor modeling is completed with Eq. (36) by including the balance of momentum based on the characteristics of the mixture, the geometry of the reactor and the catalytic bed in order to evaluate the pressure drop resulting from the Ergun equation for spherical particles [65]:

$$\frac{dP}{dz} = \frac{150\mu(1-\varepsilon)^2 v}{\varepsilon^2 d_p^2} + \frac{1.75(1-\varepsilon)\rho v^2}{\varepsilon^3 d_p}$$
(36)

The physical properties of the gaseous mixture (viscosity, the density, the specific heat and the thermal conductivity) were calculated via the methods of Reid et al. [66]. The set of ODEs (22–27, 32, 36) has been solved through the Runge–Kutta–Fehlberg method for the simulation of the fixed-bed reactor defining the reactor configuration and the initial condition at z = 0. The overall code has been developed in MatLab R2012a environment.

3. Results and discussion

3.1. Thermodynamic analysis

The thermodynamic model has been validated reproducing the results reported in a similar work [67], where the variables (18–21) are calculated imposing an inlet stream composed only by CO and H₂. Then, the model has been applied for the sensitivity analysis including the effect of the main process parameters: the operating temperature, the operating pressure, the ratio between H₂ and CO (H₂/CO) and the ratio between CO₂ and CO (CO₂/CO) in the inlet stream.

Figs. 2 and 3 show the effect of the inlet stream composition defined by H_2/CO and CO_2/CO . Increasing H_2 and reducing CO_2 content in the feedstock improve the CO conversion. The X_{H2} is positively affected by a reduction of H_2/CO while the effect of CO_2 is negative when H_2/CO is low, negligible with H_2/CO equal to 2 and 3. The DME selectivity is slightly influenced by the CO_2 content, while increasing H_2 has a significant negative effect ($S_{DME} = 95.8\%$ at $H_2/CO = 1$, $S_{DME} = 89.7\%$ at $H_2/CO = 1$ when CO_2/CO is fixed at 2). DME yield is positively affected by H_2/CO , while the CO_2 content has a strong negative impact ($Y_{DME} = 69.2\%$



Fig. 2. CO and H₂ conversion vs. CO₂/CO varying H₂/CO (temperature = 250 °C, pressure = 50 bar).



Fig. 3. DME yield and selectivity vs. CO₂/CO varying H₂/CO (temperature = 250 °C, pressure = 50 bar).

at $CO_2/CO = 0$, $Y_{DME} = 17.6\%$ at $CO_2/CO = 2.5$ with H_2/CO fixed at 2), since increasing the CO_2 composition in the inlet stream promotes the reverse water–gas shift reaction, thus increasing the H_2O production with a detrimental effect on reactions (1) and (4).

Figs. 4 and 5 show the effect of operating temperature, always changing the inlet CO_2/CO ratio. Since the reactions are exothermic, the temperature has a negative effect on both X_{CO} and X_{H2} . The effect on the selectivity is negligible (S_{DME} is equal to 94.4% and 90.4% at 200°C and 275°C respectively, fixing $CO_2/CO = 2$), while the Y_{DME} is significantly reduced increasing the temperature.

Finally, Figs. 6 and 7 illustrate the effect of the pressure, which is positive for the conversions due to the reduction of mixture volume associated to reaction (1). Although the selectivity is not significantly affected, the DME yield increases with the pressure since the promotion of reaction (1), and the resulting increase of methanol production, also supports the methanol dehydration (4).

Globally, focusing the attention on the DME production, which is the scope of the process, the thermodynamics analysis leads to the following main results:

- DME selectivity is always high, within the range 89.6% (T = 250 °C, P = 50 bar, $H_2/\text{CO} = 3$, $\text{CO}_2/\text{CO} = 2.5$) and 98.6% (T = 250 °C, P = 50 bar, $H_2/\text{CO} = 1$, $\text{CO}_2/\text{CO} = 0$), even if it is slightly reduced by a increase of CO₂ inlet composition, of the operating temperature and of the H₂ content.
- DME yield is negatively influenced by the CO₂ content in the reactor feedstock and by the temperature, while the pressure has a positive effect. Y_{DME} values vary from 10.9% (*T* = 250 °C, *P* = 20 bar, H₂/CO = 2, CO₂/CO = 2.5) to 79.1% (*T* = 200 °C, *P* = 50 bar, H₂/CO = 2, CO₂/CO = 0).



Fig. 4. CO and H_2 conversion vs. CO_2/CO varying the operating temperature ($H_2/CO = 2$, pressure = 50 bar).



Fig. 5. DME yield and selectivity vs. CO_2/CO varying the operating temperature ($H_2/CO = 2$, pressure = 50 bar).



Fig. 6. CO and H_2 conversion vs. CO_2/CO varying the operating pressure ($H_2/CO = 2$, temperature = 250°C).



Fig. 7. DME yield and selectivity vs. CO₂/CO varying the operating pressure (H₂/CO = 2, temperature = 250 °C).

The main conclusion is that, if the DME is produced starting from a CO_2 rich mixture (40 %vol. at least), the values of selectivity and yield are low and a strong process optimization effort is required.

3.2. Reactor simulation

The DME synthesis reactor simulation have been made using the model described in the previous paragraph using the initial values and the main operating parameters as reported in Table 4. This simulation is complementary to the thermodynamic analysis and allows investigating the process kinetics through a sensitivity study. These calculations consider CO_2 -rich feeds ($CO_2/CO > 1$) that could be characteristic of a gaseous stream produced by the purification and steam reforming of biogas or coal bed methane. The thermodynamics of DME synthesis in the investigated range of working conditions stated that the yield is the most sensible parameter while the selectivity and conversion, although very important from and industrial point of view, are slight influenced by the CO2 content. Consequently, for the kinetic study, only DME yield is considered as objective function for the performance evaluation.

The reproduction of the thermodynamic results has been checked by simulating the effect of the gas hour space velocity (GHSV) on the DME yield. Results are reported in Fig. 8 where the inlet ratio H_2 /CO varies within the range $2 \div 3$, the inlet pressure is 50 bar and the inlet temperature 200 °C. The simulations validate the thermodynamic results: the equilibrium is reached when GHSV is <10,000 h⁻¹ for the studied range at different H_2 /CO ratio. However, the maximum achievable yield is higher than in the case of the previous isothermal simulations. In this case, the first part of the reactor is the most thermally stressed wherein the mixture reaches temperatures of ~300 °C; along the reactor, the temperature decreases since the heat removed is greater than that generated by the reaction: at the exit of the reactor, the temperature of the mixture approaches the fluid coolant one of 230 °C.

Fig. 9 shows this phenomenon at different GHSV. Due to the rapid quenching of the reactor that occurs with an overall transport coefficient higher than 500 W/m² K and only for high GHSV (at the top of the investigated range, 15,000–20,000 h⁻¹), the gas temperature does not reach T_{v} until the end of the reactor. These results do not vary at different inlet gas and coolant temperatures, suggesting that T_{v} will have an influence on the efficiency of the reactor much more evident than the initial temperature of the feedstock.

Fig. 10 shows the effect of cooling water temperature and reactor inlet pressure over the DME yield. This simulation spans the range of 50–70 bar for the pressure inside the pipe and $T_v = 200-230 \,^{\circ}$ C. The pressure profile calculated in such simulations has a modest monotonically decrease, with a pressure drop along the reactor of $\Delta P = 0.01$ bars. A maximum DME yield of 32.5% can be reached if the H₂/CO is 3 and CO₂/CO is 2 at $T_v = 200 \,^{\circ}$ C and P = 70 bar. As assessed by the thermodynamics, increasing temperature decreases both the equilibrium conversion and the DME yield (in accordance with the exothermicity of the reactions of methanol formation and dehydration methanol). By increasing the pressure, the conversion of the reactants increases constantly since the reaction of the methanol synthesis takes place with decrease in the number of moles (while the methanol dehydration and the WGS do not present changes in the number of moles).

Table 4

Operation conditions and properties of conventional DME fixed bed reactor for the parametric study.

Variable	Value
Reactor diameter	0.038 m
Bed length	1 m
Catalyst density	1200 kg/m ³
Void fraction of the bed	0.39
Catalyst particle diameter	0.002 m
Inlet gas temperature	200–250 °C
Inlet pressure	50-70 bar
CO ₂ /CO	2
H ₂ /CO	2-4



Fig. 8. Influence of the GHSV on the DME yield ($T = 200 \degree$ C; P = 50 bar; $CO_2/CO = 2$).



Fig. 9. Reactor temperature profile at GHSV spanning the range 2000–20,000 h^{-1} ; *P* = 50 bar; fluid coolant temperature = 230 °C.



Fig. 10. DME yield vs. reactor pressure *P* and the water temperature T_v (at CO₂/ CO = 2; H₂/CO = 3. GHSV = 3500 h⁻¹).

The convenience of working at low temperature of the coolant water has to be assessed not only on the basis of the evaluations related to the thickness of the tube (which must withstand higher pressure differences), but also depending on the pressure of the produced steam that influences the overall process efficiency. Therefore, the maximum differential pressure as well as the maximum heat flux achievable between tubes and shell limit the value the steam temperature T_{v} .

The carbon conversion is among the most important performance parameters as long as we consider the DME production in



Fig. 11. Conversion of CO_2 and $CO_2 + CO$ (indicated as CO_x) versus the hydrogen initial concentration (GHSV = 3500 h⁻¹).

the framework of CO₂ valorization processes. In Fig. 11 the conversion of CO_2 + CO and CO_2 versus the initial hydrogen content in the syngas, calculated as $H_2/(CO + CO_2)$, is reported. The simulations are repeated for two level of pressure and three level of shell temperature T_{v} . The thermodynamics states that, for low values of the ratio $H_2/(CO + CO_2)$, hydrogen is the limiting reagent and the WGS reaction plays an important role in adjusting the ratio between the reagents for the synthesis of methanol. Instead, increasing the ratio $H_2/(CO + CO_2)$, the limiting reagent becomes progressively the CO and, although it considerably decreases the conversion of H₂ at equilibrium, it is possible to obtain higher CO₂ conversion and DME yields (through the reaction of rWGS and the reaction of methanol synthesis from CO₂). The kinetic results confirm the mentioned consideration. Moreover, it must be noted that, if the H₂ content approaches 1.1, the CO₂ conversion is approximately zero at any investigated condition.

This phenomenon, due to the promotion of reverse WGS by CO₂, causes H₂O accumulation and limits the effective removal of water via WGS and methanol dehydration. As long as the synergy between the WGS reaction and the reactions of methanol and DME synthesis is limited (due to high CO₂ in the feed), the water gradually accumulates in the reactor up to the attainment of equilibrium conditions. This phenomenon can be observed in Fig. 12: the amount of water produced inside the reactor increases as the fraction of CO₂ increases at fixed H₂/(CO + CO₂) ratio. The higher the content of CO₂ in the feed, the faster the equilibrium condition



Fig. 12. Water mole fraction along the reactor as function of CO₂/CO; P = 50 bar, $T_v = 230$ °C. (GHSV = 3500 h⁻¹).

is achieved causing the equilibrium to move towards the inlet of the reactor.

In conclusion, the CO_2 rich feeds promote reverse WGS causing H_2O accumulation and limits the effective removal of water via WGS and methanol dehydration causing the high fractions of unconverted methanol and the low DME yields. In addition, one must consider that the actual industrial process is characterized by some negative phenomena not included in this work, such as the deposition of coke on the metal components [36,68], which, causing the catalyst deactivation, further lower the performances of the process.

4. Conclusions

The thermodynamic fundamentals of DME synthesis in the onestep process is reported together with the chemical engineering model of the process in a fixed bed with bifunctional catalysis for the evaluation of the performances in case of CO₂-rich feeds. The inlet temperature spans the range 200–275 °C and the inlet pressure varies from 20 to 70 bar. Thermodynamically, the DME selectivity is always high, within the range 89.6% (*T* = 250 °C, *P* = 50 bar, H₂/CO = 3, CO₂/CO = 2.5) and 98.6% (*T* = 250 °C, *P* = 50 bar, H₂/CO = 1, CO₂/CO = 0). On the contrary, DME yield is negatively influenced by the CO₂ content in the reactor feedstock and by the temperature, while the pressure has a positive effect. Y_{DME} values vary from 10.9% (*T* = 250 °C, *P* = 20 bar, H₂/CO = 2, CO₂/ CO = 2.5) to 79.1% (*T* = 200 °C, *P* = 50 bar, H₂/CO = 2, CO₂/CO = 0).

The study has been extended to an actual fixed bed configuration by fixing the $CO_2/CO = 2$ and investigating the effect of pressure and temperature of the cooling fluid. In order to optimize the DME production, it is convenient to increase the pressure and to decrease the shell temperature as long as it is compatible with the materials and the operating cost. Globally, the calculated DME yields are very low (in the range 25-32%) as well as the CO₂ conversion obtained in this configuration. The CO₂ rich feeds promote reverse WGS causing H₂O accumulation and limit the effective removal of water via WGS and methanol dehydration resulting into high fractions of unconverted methanol. In addition, one must consider that the actual industrial process is characterized by some negative phenomena not included in this work, such as the deposition of coke on the metal components, which, causing the catalyst deactivation, further lower the performances of the process. Moreover, the hot spot occurring in the first centimeters of the reactor (Fig. 9) because of the exothermic nature of the reactions, may result in lower effectiveness factor and in catalyst deactivation [36].

Thus, in situ H_2O removal is the only way to overcome the thermodynamic limit of CO_2 conversion since it can accelerate the reverse WGS of CO_2 towards H_2 and CO improving DME production. In this framework, CO_2 can be utilized as a syngas constituent in the DME synthesis only in reactors coupled with hydrophilic membranes [32,33]. These can accelerate the methanol production by reducing the kinetic inhibition (shifting WGS to CO formation) and by increasing the reactant partial pressures. These applications, in membrane reactors as well as in multi stage processes, will be object of further studies with the aim to legitimate the extension of the membrane-based syngas catalysis from Fischer– Tropsch to DME synthesis.

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