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An analysis of dimethyl ether synthesis from syngas

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Abstract. The dimethyl ether (DME) is an environmentally friendly fuel, that can replace successfully the petroleum Diesel in engines, or the LPG fuel. In the last period, the world production of DME was steadily rising, with annual rates of 5-8%. The actual commercial technologies producing DME are based on the methanol etherification (the two-step process). An important research effort was expensed in last decennia, in the development of technologies transforming directly the synthesis gas into DME, without separation of the intermediary methanol (the direct or one-step process). This work presents data related to the direct DME synthesis technologies from synthesis gas, thermodynamic particularities of the chemical process and design issues of multi-tubular fixed bed catalytic reactor for gas phase DME synthesis. It is proposed a new constructive solution of the synthesis reactor, with the reactor divided in multiple zones, having distinct catalyst compositions and cooling characteristics. The simulation calculations evidenced the important increase in DME production that can be achieved by this constructive solution, as consequence of an improved control of process evolution along the catalytic reactor.

Key words: synthesis gas, methanol, process thermodynamics, catalyst, fixed bed reactor, process modelling, reactor design.

1. Introduction

Dimethyl ether (DME) has attracted a high interest in recent decades, as an alternative to petroleum fuels, due to its interesting combustion properties, characterized by low CO, NO_x and SO_x emissions. DME has a high cetane number (~ 60) and an ignition point that recommends it as a Diesel fuel, superior to that derived from petroleum. From a physical point of view, it is in gaseous state under ambient conditions, liquefying at 6 bar and 25 °C, like the LPG. Thus, DME can be mixed with LPG and used as domestic fuel (for heating and cooking); a mixture LPG-DME that contains up to 20% DME in volumes can be used as a fuel, without

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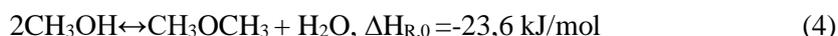
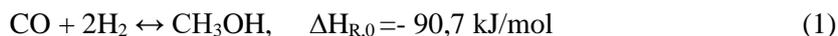
the need to change distribution and combustion plants. It is also used as a spraying agent and as a refrigerant. In the chemical industry, DME is an intermediate product in the synthesis of some organic compounds (acetic acid, methyl acetate, olefins, aromatic hydrocarbons).

Due to its increasing use as vehicle and domestic fuel, it is expected that the production of DME will accelerate in the next period. World DME production rose to about \$ 4.7 billion in 2017, with sales reaching about \$ 9 billion by 2025. Europe remains a net importer of DME worldwide. Asia Pacific region, especially China, dominates DME production and sales by over 80%, North America is the second largest producer of DME, and Europe is expected to become the third largest market for production and sales (particularly Great Britain, Germany and France) [1].

The starting raw material for DME manufacturing is the mixture of carbon oxides (CO, CO₂) and H₂, called synthesis gas, or 'syngas', in turn obtained from hydrocarbons, fossil fuels or vegetal origin materials. The manufacturing process involves, as a first step, the formation of MeOH as an intermediate product. This is further dehydrated to DME. Depending on the source of MeOH, DME can be manufactured by two processes:

a) *The two-step process*, which is using the methanol synthesized in a plant distinct of that for DME synthesis. In this process, MeOH is transformed into DME in presence of acid catalysts, according to the chemical equation (4) below.

b) *The one-step process (or direct DME synthesis)* in which DME is obtained directly from the synthesis gas, in a single manufacturing stage (reactor), which includes both the MeOH synthesis and its etherification, according to equations (1) to (4):



There are two main advantages of the one-step process for DME synthesis, as compared with the two-step process: (i) the overall process of CO_x conversion to DME is favored thermodynamically, leading to higher CO_x conversions at a single pass through the catalytic bed; (ii) lower manufacturing costs, representing about 2/3 of those related to the two-stage process [2].

Nevertheless, from reasons of production flexibility, there are industrial plants producing both MeOH and DME, but in different reactors. Thus, Toyo has developed a DME manufacturing technology, complementary to the existing methanol synthesis process (based on a multi-bed MeOH synthesis reactor, with radial circulation and indirect inter-bed cooling), having the capacity of 3500 tons DME/day (www.toyo-eng.com/jp/en/products/energy/dme). A similar process was developed by Lurgi, which likewise, completes its very high-capacity MeOH

(MegaMethanol) synthesis technology. In 2005, the company reported a capacity of 5000 tons DME/day, at an estimated production cost of 93 USD/t [3].

2. Thermodynamics of the gas phase DME production from syngas

In the design of catalytic reactors, it is important to know the composition at the chemical equilibrium state, which represents the maximum limit of the chemical transformation, in given working conditions. In what follows, there are presented calculated equilibrium compositions, obtained from synthesis gas, according to reactions (1), (2) and (4), based on the equilibrium constants values (the equation (3) is not included in calculation, being dependent on the other ones). To this end, we used physical-chemical data and thermodynamic relationships published by Poling et al. [4]. The fugacity coefficients of chemical species were calculated using the relationships based on the Soave Redlich Kwong equation of state. From the equilibrium constants defined in fugacities ($K_{f,i}$), there were calculated the equilibrium constants in molar fractions ($K_{y,i}$), using the relations:

$$\ln K_{f,i,0} = \frac{-\Delta G_{R,i,0}}{RT_0}; \quad \frac{d \ln K_{f,i}(T)}{dT} = \frac{\Delta H_{R,i}(T)}{RT^2}, \quad i = 1, 2, 3 \quad (5)$$

$$\Delta H_{R,i}(T) = \Delta H_{R,i,0} + \int_{T_0}^T \Delta C_{p,i}(T) dT \quad (6)$$

$$K_{f,i} = K_{y,i} K_{\phi,i} P^{\Delta v_i}; \quad K_{f,i} = \prod_{j=1}^s f_j^{v_{i,j}}; \quad K_{y,i} = \prod_{j=1}^s y_j^{v_{i,j}}; \quad K_{\phi,i} = \prod_{j=1}^s \phi_j^{v_{i,j}}; \quad (7)$$

$$\Delta X_i = \sum_{j=1}^s v_{i,j} X_j; \quad X = G, H, C_p; \quad \Delta v_i = \sum_{j=1}^s v_{i,j} \quad (8)$$

In the relations (5) to (8): H-enthalpy; G-Gibbs free energy; C_p -molar heat capacity; f_j , ϕ_j , y_j , fugacity, fugacity coefficient and molar fraction of the species j ; R- gas constant; T-working temperature; P- working pressure.

In the selection of the temperature interval, there was considered the recommendation to operate the methanol synthesis reaction at temperatures below 280-290 °C, to limit the catalyst deactivation [5]. As can be observed from the figures 1 and 2, on the temperature range specific to MeOH synthesis, the equilibrium constant of MeOH etherification ($K_{y,4}$) is significantly higher than that of MeOH synthesis ($K_{y,1}$). Consequently, the MeOH synthesis reaction represents the limitation step (the bottleneck) of the global DME synthesis process. Therefore, when reactions (1) and (4) occur in the same reaction volume, the conversion of CO into MeOH is favored by the presence of reaction (4). Furthermore, when CO₂ concentration in syngas is low, the reactions (1), (2) and (4) have also a synergistic effect, favorable to the conversion of CO into DME. The methanol formed in the reaction (1) is consumed by the reaction (4), generating DME and water (thus

favoring the reaction (1)). Water consumption in reaction (2) favors the formation of DME in reaction (4) and generates hydrogen, which is also beneficial for reaction (1) (sacrificing in the same time a part of CO present in the mixture). However, when CO₂ concentration is significant, the reaction (2) may occur in reverse direction (consumption of CO₂ and water generation), this having a certain limiting effect on the methanol etherification. These particularities assure yield values for the equilibrium transformation of carbon oxides into DME, in a single step (in the same catalytic bed), higher than that achievable by the two-step process (in identical working conditions).

The transformation is characterized by the DME yield, defined as the fraction of carbon oxides, present in the syngas, which were transformed into DME. Figures 3 and 4 show the transformation yields of the carbon oxides into DME and MeOH respectively, at equilibrium, starting from a typical synthesis gas composition: 10 % CO₂, 18 % CO, 69 % H₂ and 3 % CH₄ (mole) [5].

As expected, the DME yield increases with pressure, as a result of the favorable pressure effect on the MeOH synthesis reaction, the limiting step of the process. The increase of the temperature leads to the diminution of the yield, since the reactions (1) and (4) are disadvantaged, both being exothermic. Note that, the chemical equilibrium composition includes also significant concentrations of untransformed MeOH. For example, at 270 °C and 60 bar, typical working conditions, the yield of transformation in DME is 50% and that in MeOH is 6.2%. Fig. 4 shows the temperature dependence of the DME yield at different concentrations of CO₂ in the synthesis gas (total concentration of carbon oxides and molar ratio hydrogen/carbon oxides being kept constant).

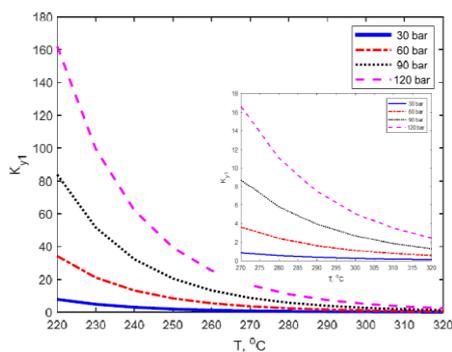


Fig. 1. Temperature and pressure dependencies of the equilibrium constant for the methanol synthesis reaction (1).

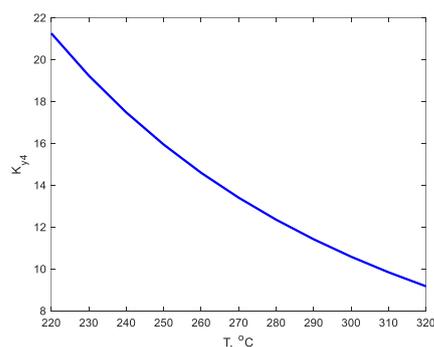


Fig. 2. Temperature dependence of the equilibrium constant for the methanol etherification reaction (4).

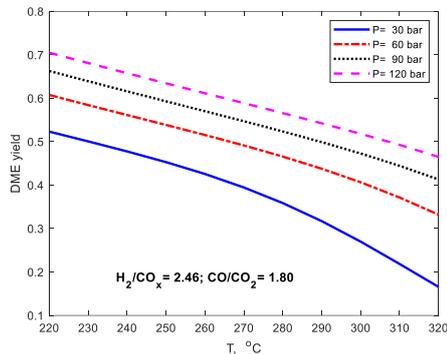


Fig. 3. Temperature and pressure influences on DME yield at chemical equilibrium.

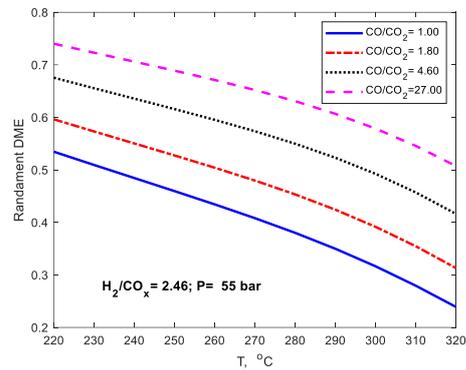


Fig. 4. Influence of the CO/CO₂ molar ratio in the syngas, on the DME yield at chemical equilibrium.

The increase of the CO₂ concentration in the synthesis gas leads to the decrease of DME yield. The explanation is the inhibition of water consumption by the reaction (2), at high CO₂ concentrations, leading to the accumulation of water in the mixture, which limits the progress of the etherification reaction (4). Also, increasing the CO₂ concentration, at total concentration of carbon oxides constant (i.e. at the expense of CO concentration), has as consequence a decrease in the amount of MeOH formed in the reaction (1).

3. Catalysts and catalytic reactors used for direct DME synthesis

Catalysts

The direct conversion of the syngas in DME involves the use of two catalysts, one for methanol synthesis and the other for methanol etherification. For syngas conversion to MeOH, the most used catalyst is Cu-ZnO/Al₂O₃, promoted with different compounds [5]. Studies on laboratory facilities evidenced high performances of some catalysts, where Al₂O₃ or ZnO are partially or totally replaced with other metal oxides, such as MnO, ZrO₂ or La₂O₃ [6]. The etherification step of MeOH is conducted in presence of solid acid catalysts. The most preferred catalyst for this step, due to its accessibility and selectivity is γ -Al₂O₃. However, it presents also some shortcomings: instability in the presence of water vapor and limited catalytic activity, over the temperature window required by MeOH synthesis. Published studies have also evidenced interesting catalytic properties of some zeolites and mesoporous materials for MeOH etherification [7,8,9]. Usually, the one-step DME synthesis working conditions overlap on those specific for methanol synthesis (temperature below 280-290 °C and pressure between 40-100 bar). Under these conditions, one of the most effective candidates to replace γ -Al₂O₃ appears to be the H-ZSM-5 zeolite, which features catalytic activity and stability in the presence of water vapor (hydrophobicity), higher than

those of γ -Al₂O₃. Furthermore, the strength of the acidic centers and the hydrophobicity of this zeolite can be controlled by an adequate selection of the preparation conditions [9,10,11].

A first approach in the calculation of the overall kinetics of syngas conversion to DME was based on the combination of the kinetic model for MeOH formation from syngas, with a kinetic model for the methanol etherification stage. Among the kinetic models proposed for MeOH synthesis from syngas, the most used are those published by Graaf et al. [12] and Vanden Busshe & Froment [13] respectively. For the MeOH etherification over γ -Al₂O₃, the most widely used is the one published by Bercic, and Levec [14]. Kinetic calculations of the direct DME synthesis, based on the prediction models derived separately for the two process steps, are adequate only when the two catalysts are used as individual pellets. However, this procedure is not recommended in situations where there are used pellets of bifunctional catalyst (i.e. when the two active components are mixed in the same pellet, during the catalyst preparation stage), as it does not take into account possible interactions that may occur between the two active components inside the catalyst pellet. More reliable kinetic models were developed based on direct synthesis experiments, which integrate both process stages [15, 16].

Catalytic reactors used in the one-step DME synthesis

The published studies are reporting performances of both vapor and liquid phase DME synthesis reactors, successful tested on pilot plants at semi-industrial scale. The design and operation objectives of the synthesis reactor is to maximize DME yield, simultaneously with an efficient recovery of the heat generated in the chemical process.

i) Fixed bed reactors (FBR). Presenting the advantages of relatively low investment costs, low degree of gas mixing and the existence of technical means for temperature control, the FBR are frequently used in different constructive and functional alternatives: series of adiabatic beds with intermediate cooling and multi-tubular (heat exchanger type) reactors (MTFBR). The use, in the DME synthesis, of a unit consisting of two MTFBRs interconnected on the principle of the 'Johnson Matthey Combi' loop, which ensures the recovery of the reaction heat, was analyzed by Vakili and Eslamloueyan [17]. In 2008, the Korea Gas Corporation commissioned a single-stage DME synthetic gas plant with a capacity of 10 t/day DME, using a MTFBR, cooled with water under pressure. Based on the data obtained from this pilot plant, it was estimated that a plant having the capacity of 3000 t/day DME can be designed with 4 such reactors, arranged in parallel [18].

ii) Fluidized bed reactors. Presents the possibility to continuously refresh the catalyst in the bed, to compensate for the effect of deactivation. An experimental study conducted on a laboratory scale reactor was published by Lu et al. [19]. Interestingly, the authors report CO conversions and productivity in DME, higher than that obtainable in fixed-bed reactors. The use of fluidized-bed reactors in DME synthesis is still in incipient stage, limited to laboratory-scale, with industrial-scale feasibility not yet demonstrated [8].

iii) *Three-phase slurry reactors*. In these reactors, the fine particles of catalyst are dispersed in a liquid solvent, through which it is bubbled the syngas. These present several advantages: better use of catalyst (high internal effectiveness factor), lower intensity of deactivation (as compared with the vapor phase process), better control of the temperature and a lower working pressure. The shortcomings consist in a relatively low intensity of the gas-liquid mass transfer, the complexity of the installation (including a section of separation and recirculation of the catalyst) and a certain loss of catalyst respectively. Such reactors have been successfully tested in DME synthesis, at the level of semi-industrial pilot plants [8,17,20].

4. Simulation of a catalytic reactor for DME synthesis

To emphasize the main particularities of the direct DME synthesis process, there will be presented the main results obtained by numerical simulation of a multi-tubular fixed bed reactor, having the structure close to that of Lurgi reactor for methanol synthesis (Fig. 6). The tubes are cooled with liquid water under pressure, generating saturated steam. The catalyst inside the tubes, is a mechanical mixture of Cu-ZnO/Al₂O₃ pellets and pellets of H-ZSM5 zeolite in a matrix of γ -alumina (60% zeolite concentration, by weight). The chemical transformation is described by the reactions (1) to (4). The rate expressions of these reactions are those published in references [9] and [12]. A one-dimensional mathematical model of the catalytic reactor, assuming plug flow of the gas mixture, was used to describe the DME synthesis process inside the catalyst bed [22]. The influence of internal diffusion on the process kinetics is taken into consideration by the intermediate of the effectiveness factors calculated individually for the 4 reactions [9, 22, 23]. The catalyst pellets were considered isothermal and the external concentration and temperature gradients were neglected. The process performances are characterized by the DME yield, CO conversion and selectivities of CO transformation in DME, MeOH and CO₂ [22]:

$$X_{CO} = \frac{F_{CO,0} - F_{CO}}{F_{CO,0}}; \quad \eta_{DME} = \frac{2(F_{DME} - F_{DME,0})}{F_{CO,0} + F_{CO_2,0}}$$

$$\sigma_{DME} = \frac{2(F_{DME} - F_{DME,0})}{F_{CO,0} - F_{CO}}; \quad \sigma_J = \frac{F_J - F_{J,0}}{F_{CO,0} - F_{CO}}; \quad J = MeOH, CO_2 \quad (9)$$

In the expressions above: X_{CO} - CO conversion; F_{J0} , F_J - molar flow rate of species J, in the feed and along the reactor respectively; η_{DME} - the yield of carbon oxides conversion into DME; σ_k - the selectivity of CO conversion into the product k.

The most important variables of the catalytic process are the temperature, pressure, specific mass flow rate, ratio of the two catalysts in the bed, as well as the diameter of the tube in which the catalyst is located. As mentioned above, to limit the phenomenon of catalyst deactivation, the maximum working temperature is

recommended to be limited to 290 °C. A first information regarding the potential of the temperature increase along the reactor is the maximum adiabatic temperature increase. In the case of the analyzed process, this correspond to the hypothetical case when both carbon oxides would be totally converted to DME, and is calculated from the relation:

$$\Delta T_{\text{ad}} = - \frac{y_{\text{CO}}^{(0)}(2\Delta H_{\text{R1}} + \Delta H_{\text{R4}}) + y_{\text{CO}_2}^{(0)}(2\Delta H_{\text{R3}} + \Delta H_{\text{R4}})}{\bar{C}_p} \quad (10)$$

ΔH_{Ri} - the enthalpy variation in the reaction 'i'; $y_{\text{CO}_x}^{(0)}$ the molar fraction of corresponding carbon oxide; \bar{C}_p - the molar heat capacity of the reaction mixture.

The values of the main operating parameters of the reactor are presented in Table 1. For the feed composition given in the table, corresponds an adiabatic temperature increase of approximately 2000 K. This value indicates a high potential of temperature rise along the reactor. The factors influencing directly the temperature rise along the reactors tubes are the feed temperature, the cooling agent temperature and the specific flow rate (or equivalently, the velocity) of the reaction mixture. Besides, the DME yield is strongly dependent on the concentrations of the two catalysts in the reactor tubes. Generally, the most practiced thermal regime for the cooled multi-tubular fixed bed reactors corresponds to an axial temperature evolution presenting a maximum. In the selection of the operating parameters, the goal is to maximize the DME yield and DME production, fulfilling the upper limit imposed on the reaction temperature. Identifying the most convenient set of operating parameters for highly exothermic processes, like the DME synthesis, is a rather challenging task.

In the figures 7 and 8 are presented the calculated evolutions of the DME yield and temperature along a catalyst bed with constant catalyst bed composition (methanol synthesis catalyst volume fraction, 0.9) for the feed temperature 254 °C, cooling water temperature 256 °C and specific flow rate of reaction mixture, 2.3 kg m⁻² s⁻¹. As can be seen, a relatively good yield of DME transformation (~ 41.8%) can be obtained, with the maximum temperature kept within the prescribed limits. These parameters were identified by several successive simulations, not being the result of an optimization study. Note that, the DME yield could be further increased by decreasing the specific flow rate. However, this would decrease the gas-solid mass and heat transfer coefficients, which is detrimental to overall process kinetics.

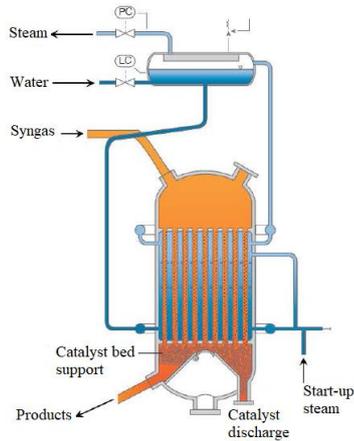


Fig. 6. The Lurgi type reactor [21].

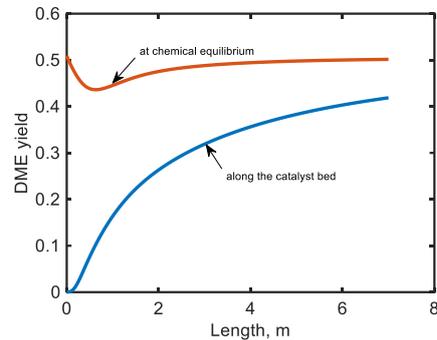


Fig. 7. The DME yield along the reactor axis.

Table 1 Constructive and operating parameters of the catalytic reactor

Parameter	value
Length of the tubes	7 m
Inner diameter of the tube	0.0254 m
Diameter of catalyst pellets (spherical)	0.004 m
Inlet pressure	54 bar
Feed composition (molar fractions): CO ₂ :0.08; H ₂ :0.665; H ₂ O:0.006; CH ₃ OH:0.0038; CO:0.215; DME:0.0002; CH ₄ :0.03.	

It is also important to notice that the simulation calculations revealed a relatively high sensitivity of the temperature in respect with the feed temperature and the temperature of the cooling agent respectively.

The calculation tests evidenced that improved performances can be obtained by dividing the catalytic reactor in multiple sections (zones), with distinct catalytic bed compositions and cooling water having distinct temperatures on each section. The figures 9 and 10 show the evolutions of the DME yield and temperature, calculated for a reactor with 4 distinct zones having the lengths of 1 m, 2 m, 2 m and 2 m respectively, the first one being operated adiabatically and the other three cooled with water. The selected volume fractions of the methanol synthesis catalyst in the four zones were 0.95, 0.90, 0.90 and 0.80 respectively. The synthesis gas is fed in the first zone with a temperature of 224 °C and the cooling water temperatures on the last three zones are respectively 260, 270 and 278 °C.

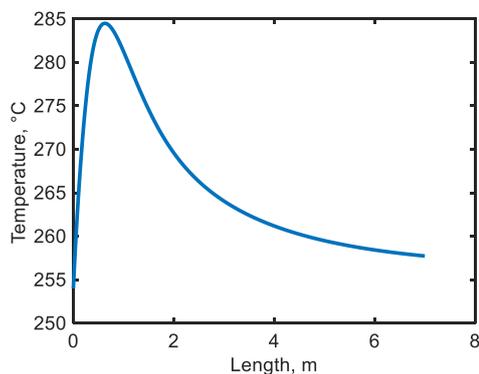


Fig. 8. The temperature along the reactor axis.

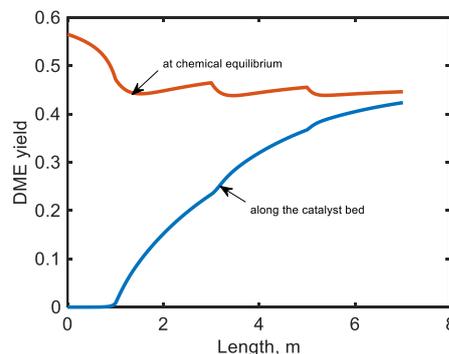


Fig. 9. DME yield evolution along the reactor divided in 4 zones.

The possibility of modifying the cooling temperature and the composition of the catalyst bed on the four zones along the reactor permits an increase of the specific flow rate of reaction mixture to $3.3 \text{ kg m}^{-2} \text{ s}^{-1}$, keeping the DME yield at the same level of $\sim 42 \%$. This corresponds to approximately 43 % increase in DME production as compared with previous constructive solution (a single zone along the reactor).

The evolutions of CO conversion and CO transformation selectivities in respect with DME, MeOH and CO_2 , are depicted in Fig. 11. The CO conversion at the exit of reactor ($\sim 81 \%$) is lower with approximately 5 % than in the classical reactor structure, mainly due to the values of the specific flow rate. However, the DME selectivity is higher (71.7 % as compared with 67 %) and MeOH selectivity lower (6.85 % as compared with 12.8 %). Another advantage of the zoned reactor is a lower feed temperature, as result of the adiabatic operation of the first section. As seen from Fig. 11, the CO_2 selectivity presents an initial interval of negative values. These are explained by the consumption of CO_2 in reaction (3) with an intensity higher than that of CO_2 formation from reaction (2), over this reactor zone.

These constructive and operating characteristics are selected similarly, after few preliminary reactor simulations, not being the results of a systematic optimization study.

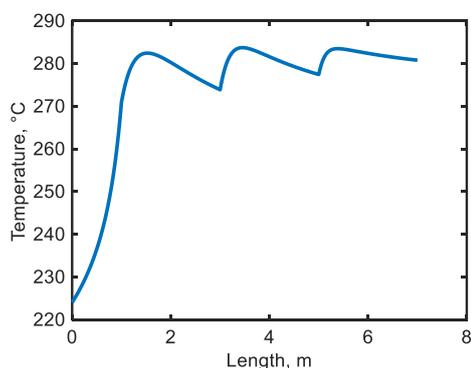


Fig. 10. The temperature evolution along the reactor divided in 4 zones.

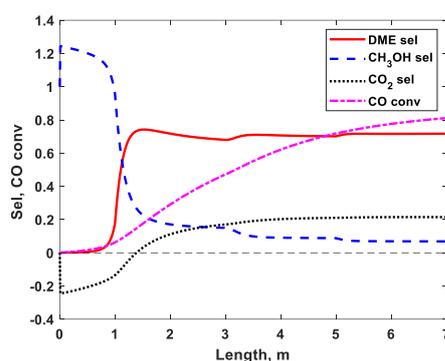


Fig. 11. The product selectivities and CO conversion along the reactor divided in 4 zones.

5. Conclusions

Although currently obtained from the etherification of methanol (the two-step process), the DME can be manufactured directly from the synthesis gas (single-step process), the technology being already developed at the semi-industrial pilot level. Compared with the two-stage process, the direct DME synthesis (one-step process) is advantageous both from the investment cost and thermodynamics points of view. A particularity of the direct DME one step process is the relatively high exothermicity and a high sensitivity of temperature and composition in respect with the operating parameters. Based on numerical simulations using published data, a new reactor structure is proposed, which is dividing the multitubular space of the catalytic reactor into multiple sections with distinct catalytic bed compositions and cooling water feeds. This structure permits an important increase of DME production, as compared to the classical construction, at a higher DME selectivity and a lower MeOH selectivity. Nevertheless, the construction and operation of this reactor structure being more costly than the classical one, there are necessary further studies in order to validate its effectiveness.

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