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ADVANCED PROCESS MODELLING OF TAME INDUSTRIAL SYNTHESIS IN gPROMS®

Elena Cătălina UDREA, Valentin PLEȘU*, Costin Sorin BÎLDEA

University POLITEHNICA of Bucharest, Department of Chemical and Biochemical Engineering, str. Gh. Polizu 1-7, RO-011061, Bucharest Romania

Abstract

Tert-amyl methyl ether (TAME), widely used as gasoline additive, is obtained by the etherification of isoamylenes with methanol. This study develops a mathematical model simulating the behavior of two fixed-bed catalytic reactors for TAME synthesis in an industrial plant. Each reactor consists in a fixed bed of acidic catalyst (Amberlyst 35 wet) of 7.6 m height and 2 m diameter, which is operated adiabatically. The model includes dynamic, one-dimensional mass and energy balance equations, together with appropriate initial and boundary conditions. For numerical integration, the axial coordinate is discretized by the backwards finite difference (BFDM) method. The model is used to predict the transient profiles of molar concentration and temperature along the reactor beds. The model is implemented in gPROMS® ModelBuilder, with physical properties calculations supported by SIMULIS®. Comparison with industrial data shows good agreement.

Key words: Fixed-bed reactor, dynamic modelling, numerical integration, gPROMS

1. Introduction

The octane rating indicates the performance of the gasoline and aviation fuels, more precisely the maximum compression ratio at which a particular fuel can be utilized in an engine without „knocking” of the fuel / air mixture. Gasoline with high octane number is used in high performance engines that require high compression ratios. Tetraethyl lead, used in the past as octane enhancer, was forbidden because of its toxicity and it was replaced by other octane boosters, as light ethers. Amongst them, the methyl-tert-butyl ether (MTBE) - employed on large scale in the 1990s – was phased out because polluting the ground water. Currently, MTBE is replaced by the more environmentally-friendly tert-amyl methyl ether (TAME) and ethyl-tert-butyl ether (ETBE). TAME is mostly used as an oxygenate additive to gasoline, enhancing the octane number, raising the

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* Corresponding author: Email address: v_plesu@chim.upb.ro

oxygen contents, and reducing the exhaust emissions of volatile organic compounds.

Figure 1 shows the general scheme of a Fluid Catalytic Cracking (FCC) unit together with the downstream process. The reactor effluent is separated in the Main Column. The overhead, containing mainly C1-C5 hydrocarbons is further processed in the Gas Concentration (GASCON) unit. The heavy product of the GASCON unit is hydro-desulphurized. The heavier components (HCN) are sent to the gasoline pool. The lighter isoamylene-rich fraction (LCN) is used for production of tert-amyl methyl ether (TAME).

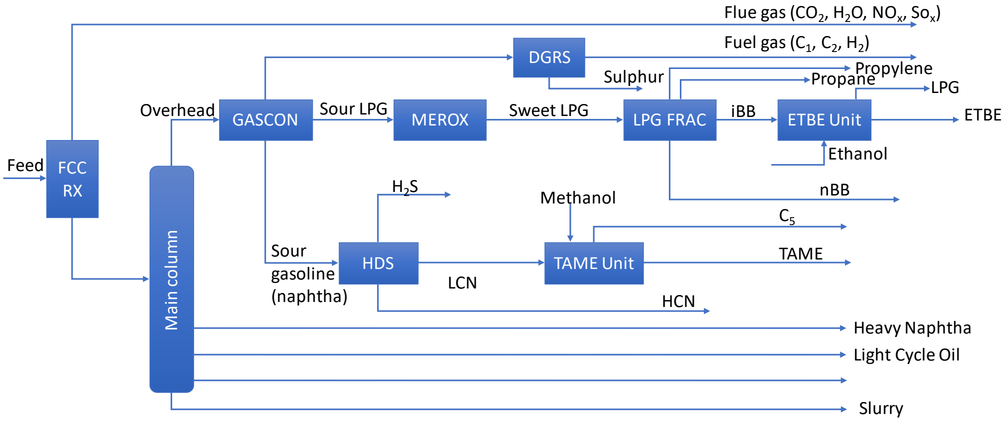

Fig 1. Fluid Catalytic Cracking plant

TAME is obtained by the reaction of methanol with the isoamylenes (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B) from the Light Cracking Naphtha (LCN) fraction. The main reactions of the TAME process are the etherification reactions of isoamylenes with methanol and the isomerization reaction between the two isoamylenes (Figure 2). The reactions take place in liquid phase in the presence of a catalyst: ion exchange resin like Amberlyst 35 wet. In addition to the three main reaction, secondary reactions such as dimerization of isoamylenes, dehydration of methanol, etc. occur.

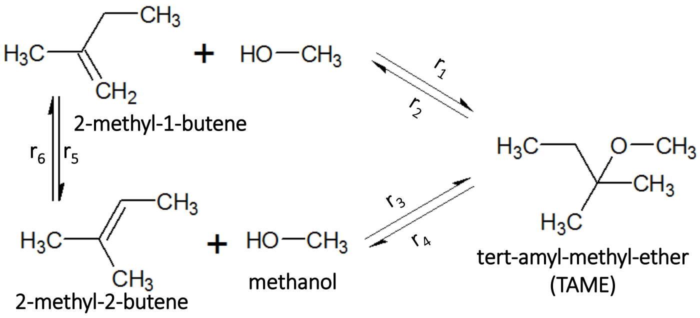

Fig 2. TAME reaction system

Figure 3 shows the flowsheet of the TAME process. The gasoline and methanol (fresh and recycled) are mixed and preheated to reaction temperature. The reaction takes place in a series of two adiabatic, fixed-bed tubular reactors, with intermediate cooling. The effluent contains, besides the TAME product, the unreacted isoamylenes, the inert C5 alkanes (iC5) and the excess of methanol. A distillation column separates TAME concentrate from the C5 – methanol mixture. The latter may be further processed in third reactor, for completing the reaction. Finally, the unreacted methanol is separated by extraction with water. The raffinate is etherified gasoline with a small amount of methanol, while the extract contains the excess of methanol which is recovered by distillation and recycled.

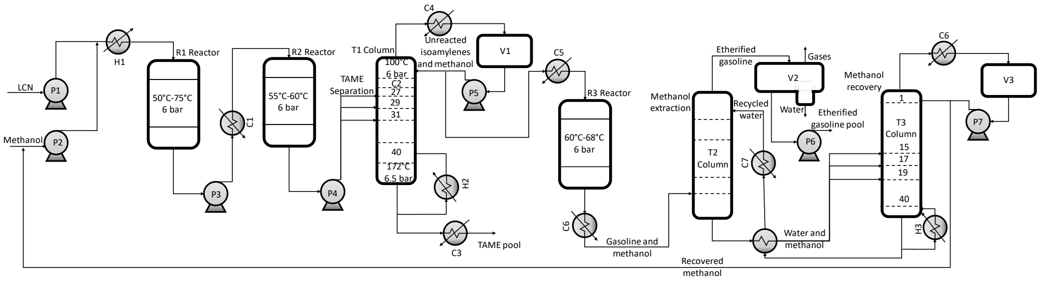

Fig 3. Process flowsheet diagram of TAME reaction and separation section [1]

In this work, the mathematical model of the first two reactors (R1 and R2) is developed. The specifications, shown in Table 1, are similar to industrial processes.

Table 1

TAME synthesis reactor operating conditions

Plant capacity / [$t_{gasoline}$ /yr]	175,000		
Internal diameter, D_i / [m]	2		
Packing height, H / [m]	7.6		
Molar ratio alcohol: reactive olefins	1.3		
Feed composition (wt.%)	iC5	2M2B	2M1B
	80.22	13.27	6.51

2. Reactors modelling

In this section, the mathematical model of the industrial reactors for TAME synthesis is presented. The model implemented in gPROMS® includes the mass and energy balance equations with appropriate initial and boundary conditions. The model is complemented by constitutive equations which allow calculation of the reaction rate and physical properties.

Assumptions

The assumptions of the mathematical model are:

- The reaction mixture contains the following compounds specific to LCN fraction: inerts, grouped as isopentane; methanol; 2-methyl-1-butene; 2-methyl-2-butene; TAME.
- The behavior of the tubular reactor is suitably described by a one-dimensional pseudo-homogeneous model.
- The fluid velocity is constant in a cross section of the reactor (plug-flow).
- The liquid phase and the catalyst particles have the same temperature.

The model unknowns are the component concentrations $C_i(z,t)$, $\mathrm{i} \in COMP = \{\text{2M2B, MeOH, TAME, 2M1B, iC5}\}$ and temperature $T(z,t)$, which are distributed along the axial coordinate *z* and are changing during the time *t*. The significance of the other variables is presented in the ***Notation*** section, together with typical value.

Balance equations

The model consists of mass balance equations for each component, and energy balance.

a. Component mass balance

The first term of the equation is the transient term, namely the evolution of concentration in time, while the right-hand side is contains convective, axial dispersion and reaction terms.

$$\varepsilon \cdot \frac{\partial C_i}{\partial t} = -\mathrm{v}_s \cdot \frac{\partial C_i}{\partial z} + \varepsilon \cdot D_z \cdot \frac{\partial^2 C_i}{\partial z^2} + \rho_b \cdot \sum_{j \in REAC} \nu_{i,j} \cdot r_j, \quad z \in (0,H),\ \mathrm{i} \in COMP \tag{1}$$

In distributed parameter models, the initial and boundary conditions are extremely important. In order to have a well-developed model, the specification of the initial conditions for the time-dependent equations and the corresponding boundary conditions to establish the equation domain are significant [2], [3].

At the ***reactor inlet*** (z = 0), the Robbins-type condition considers a perfectly mixed feed and ensures flow continuity. The incoming fluid is mixed with the liquid inside the reactor.

$$v \cdot C_{tot,in} \cdot x_{in,i} = v \cdot C_i\left(t,0\right) - \varepsilon \cdot D_z \cdot \frac{\partial C_i}{\partial z}\left(t,0\right),\ i \in COMP \tag{2}$$

At the ***reactor outlet*** (z = H), the Neumann-type condition specifies that the reaction does not takes place outside the reactor.

$$\frac{\partial C_i}{\partial z}\left(t,H\right) = 0,\ \ i \in COMP \tag{3}$$

b. Energy balance

The energy balance follows the same structure as the mass balance, this time the partial differential terms being for temperature. The first term is the accumulation (transient) term. Then, the convective and diffusion terms (defined by effective thermal conductivity) follow. Finally, the reaction term contains the enthalpy of the reaction.

$$\begin{aligned}&\left(\varepsilon \cdot \rho_f \cdot C_{pf} + \left(1-\varepsilon\right) \cdot \rho_{solid} \cdot C_{ps}\right) \cdot \frac{\partial T}{\partial t} = -\rho_f \cdot C_{pf} \cdot \mathrm{v}_s \cdot \frac{\partial T}{\partial z} + \lambda_z \cdot \frac{\partial^2 T}{\partial z^2} + \\ &+\rho_b \cdot \sum_{j \in REAC} r_j \cdot \left(-\Delta H_j\right),\ z \in \left(0,H\right)\end{aligned} \tag{4}$$

The differential equations is completed with Robbins- and Neumann-type conditions, for reactor inlet and outlet, respectively.

$$v \cdot T^{feed} = \rho_f \cdot C_{pf} \cdot \mathrm{v} \cdot T\left(t,0\right) - \lambda_z \cdot \frac{\partial T}{\partial z}\left(t,0\right) \tag{5}$$

$$\frac{\partial T}{\partial z}\left(t,H\right) = 0 \tag{6}$$

The **initial conditions** set the values of the time-dependent variables at the initial moment (t = 0) inside the reactor.

$$C_i\left(0,z\right) \ = \ C_i^*\left(z\right) \tag{7}$$

$$T\left(0,z\right) \ = \ T^*\left(z\right) \tag{8}$$

Reaction rate

The kinetic model based on activities [4] follows the Eley-Rideal mechanism [5]. Considering 2 active centers and assuming that methanol is the only species adsorbed on the catalyst surface, the expressions of the reaction rates are:

R1: MeOH + 2M1B ⇔ TAME

$$r_1 = L^2 \frac{k_{ap,1} \cdot K_M^2 \left(a_{1B} \cdot a_M - \dfrac{a_T}{K_{eq1}} \right)}{\left(1 + K_M \cdot a_M\right)^2} \tag{9}$$

R3: MeOH + 2M2B ⇔ TAME

$$r_3 = L^2 \frac{k_{ap,2} \cdot K_M^2 \left(a_{2B} \cdot a_M - \dfrac{a_T}{K_{eq2}} \right)}{\left(1 + K_M \cdot a_M\right)^2} \tag{10}$$

R5: 2M1B ⇔ 2M2B

$$r_5 = L \frac{k_{ap,3} \cdot K_M \left(a_{1B} - \dfrac{a_{2B}}{K_{eq3}} \right)}{1 + K_M \cdot a_M} \tag{11}$$

Considering an Arrhenius-type expression for the temperature-dependent kinetic and adsorption equilibrium constants, as presented in the equations below, the model has the following parameters.

$$k_{ap,j} = k_{0,ap,j} \cdot \exp\left(-\frac{E_{a,j}}{R \cdot T} \right) \tag{12}$$

Table 2

Parameters of apparent kinetic constant

Kinetic constant	$k_{0ap,j}$ (kmol/(kg$_{cat}$·h)	$E_{a,j}$ (kJ/kmol)
$k_{ap,1}$	$5.4 \cdot 10^{13}$	$1.06 \cdot 10^{5}$
$k_{ap,3}$	$2.03 \cdot 10^{11}$	$9.2 \cdot 10^{4}$
$k_{ap,5}$	$1.16 \cdot 10^{10}$	$8.2 \cdot 10^{4}$

$$K_M = K_{0,M} \cdot \exp\left(-\frac{\Delta H_M^{ads}}{R \cdot T} \right) \tag{13}$$

Table 3

Parameters of adsorption constant

M	ΔH_M^{ads}(kJ/kmol)	$K_{0,M}$
Methanol	-10,000	8.34×10^{-2}

The expressions of temperature-dependent equilibrium constants are taken from [6].

R1:MeOH + 2M1B ⇔ TAME $$K_{eq1} = \exp\left(-8,3881 + \frac{4041,2}{T}\right) \quad (14)$$

R3:MeOH + 2M2B ⇔ TAME $$K_{eq3} = \exp\left(-8,2473 + \frac{3225,3}{T}\right) \quad (15)$$

R5:2M1B ⇔ 2M2B $$K_{eq5} = \exp\left(-0,1880 + \frac{833,3}{T}\right) \quad (16)$$

Liquid phase properties

The reaction mixture presents a strong non-ideal behavior induced by the high polarity of methanol as compared to other components. The non-ideality of the liquid phase is described by the NRTL model. Physical properties (molar density, liquid dynamic viscosity, molar heat capacity, etc.) are estimated with relationships and parameters taken from Simulis® [7]. More details are given in reference [8].

3. Results and discussions

Once the model is defined and correctly implemented in gPROMS, the process is simulated. The numerical method discretizes the axial coordinate by the backward finite differences method (BFDM) and integrates in time the resulting set of ordinary differential equations (ODEs). A study was conducted to determine the number of discretization steps. As can be seen, from Fig. 3, 80 axial discretization steps are enough as practically there no change of the temperature and concentration profiles when the number of steps is doubled.

Figure 4 shows steady-state concentration and temperature profiles along the two fixed-bed adiabatic reactors. The reactants are consumed, and the TAME product is formed. The temperature increases due to the exothermic character of the etherification reaction. The temperature difference between the two reactors is due to the intermediate the cooling.

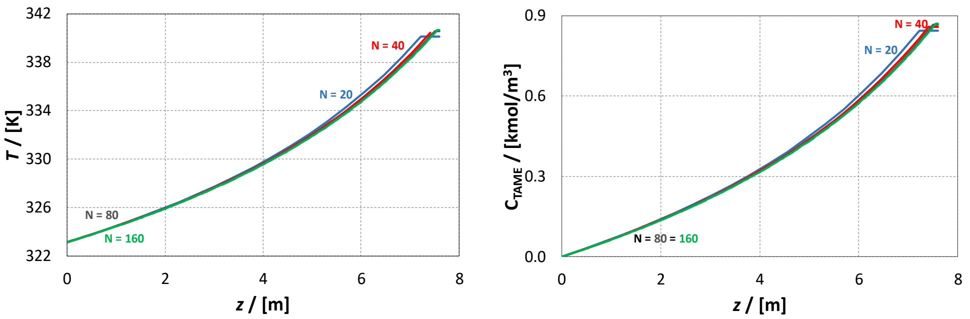

Fig. 3. Effect of the number of discretization steps on the axial temperature and concentration profile along the first reactor

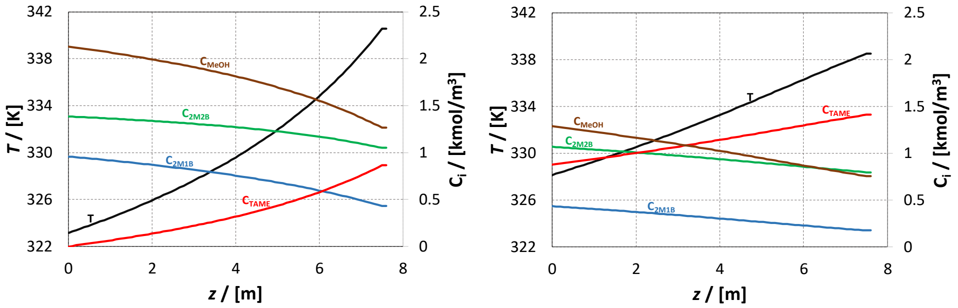

Fig. 4. Evolution of the temperature and concentrations of the reaction systems components along the reactors R1 (left side) and R2 (right side)

Figure 5 shows the dynamic behavior of the system, when the inlet temperature is increased by 10°C.

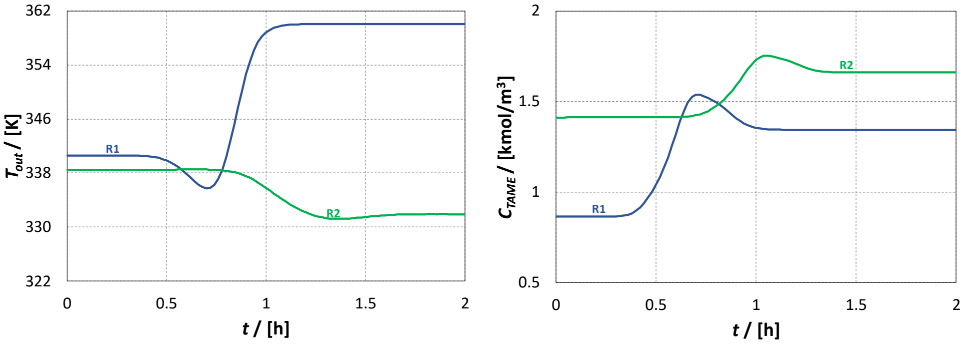

Fig 5. The response of temperature and TAME concentration at the exit of the two reactors at the addition of 10°C to the inlet temperature in the R1 reactor

In figure 5 it is noticed that the reactor outlet temperature begins to change after 0.4 hours, corresponding to the residence time for R1 reactor. The temperature at R2 reactor outlet begins to change for another 0.4 hour (0.8 hour).

In the mass and energy balance equations, it can be observed that concentration and temperature time-derivatives are multiplied by different factors. This means that the concentration and temperature changes will propagate at different speeds along the catalytic layer. In particular, the concentration disturbances move with the flow rate. On the other hand, the temperature changes propagate at a lower speed due to the inertia of the catalyst bed. After increasing the inlet temperature, the reaction rate increases in the first part of the reactor. As the reactants are consumed, towards the reactor-exit the reactants concentration decreases. Less heat is generated and therefore the temperature decreases. After a while, the increase of temperature at the reactor inlet affects the temperature at the end of catalyst bed.

Figure 6 illustrates the temperature and concentration profiles of the reactants and the product throughout the reactors, at different times.

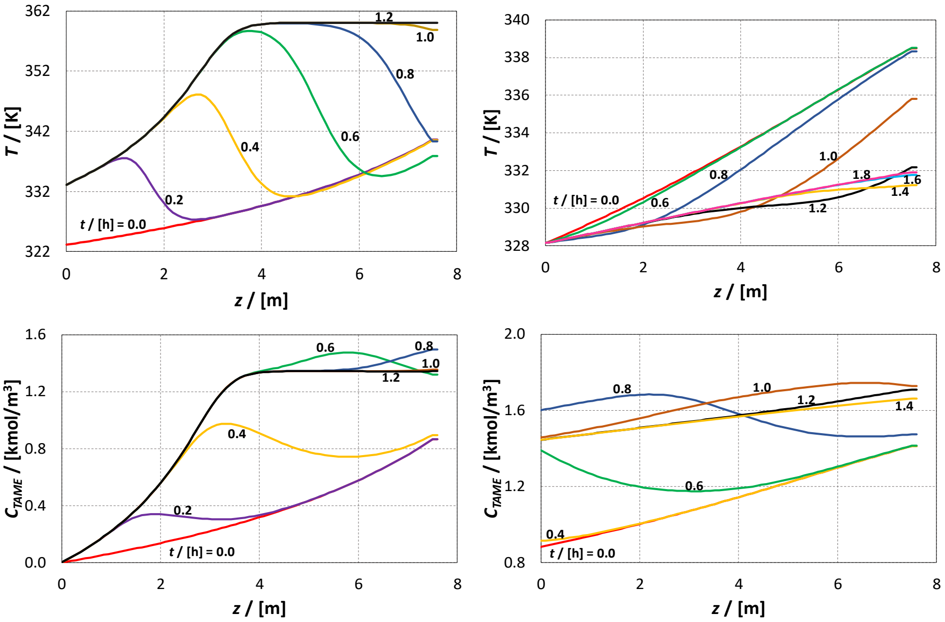

Fig 6. The temperature and TAME concentration profiles along the R1 (left side, up and down) and R2 (right side, up and down) reactors and at different time points

It can be observed in Figure 6 that temperature, following the introduction of the perturbation, reaches the stationary state after 1.2 hours in the first reactor and after 1.8 hours in the second reactor. In the case of concentration profiles, regardless of the compound, the concentrations reach the stationary state after about 1.2 hours in the first reactor and after 1.4 hours in the second reactor.

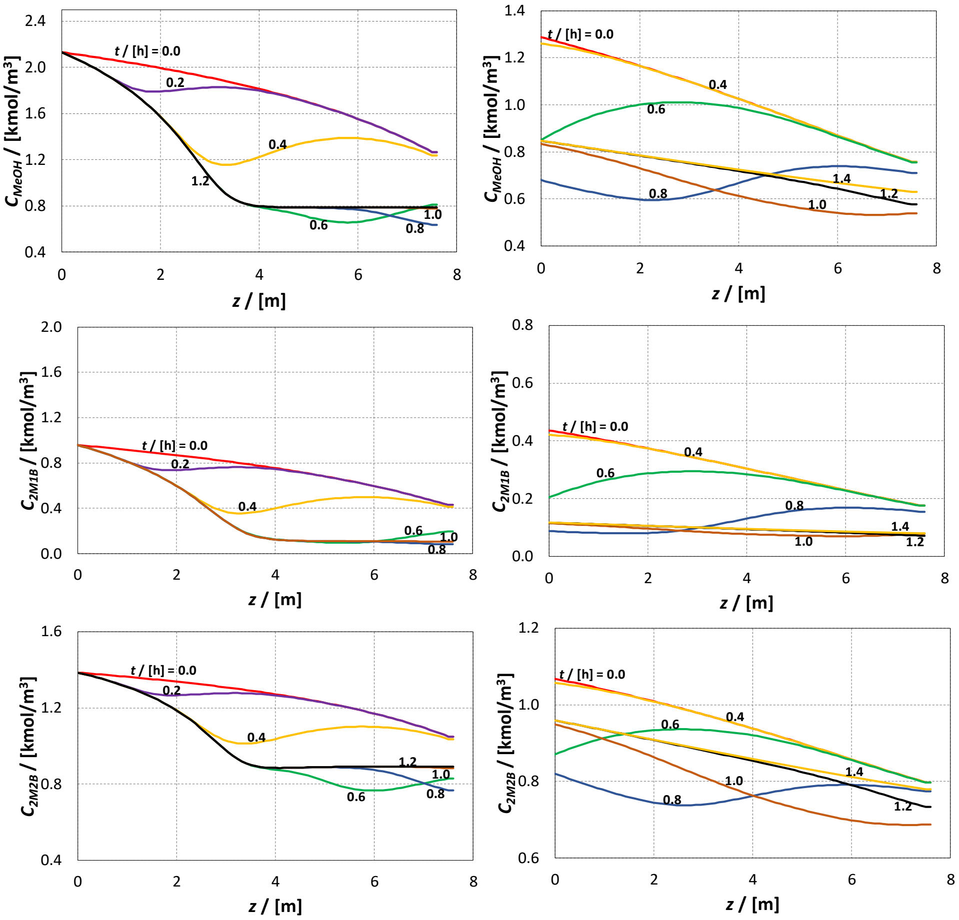

Fig 7. Concentration profile of methanol (top), 2M1B (middle) and 2M2B (bottom) along the R1 (left side) and R2 (right side) reactors at different time points

6. Conclusions

gPROMS® is a suitable environment for advanced process modelling. Detailed mathematical model is proposed for component mass balance and energy balance supported by adequate thermodynamic and kinetic models for reactors. Time and space profiles for temperature and concentrations are presented. Time profiles show that the steady state conditions are reached quite quickly. The model developed in this study proved to describe well the industrial scale reactors. Model solution results give detailed information about the behavior of both reactors. These results can assist the process engineer in decision making on correct process operation.

Table 4

The concentrations (mass fractions) obtained at the R2 reactor outlet in gPROMS® presented in comparison with the industrial results

Components	gPROMS® results	Industrial data
TAME	0.209	0.1873
Isoamylenes	0.099	0.0632
Methanol	0.035	0.0384
Inert	0.657	0.6985

Notation

a_i – liquid-phase activity of component i
$K_{eq,j}$ – thermodynamic equilibrium constant of reaction j
$k_{ap,j}$ – apparent kinetic constant of reaction j, (kmol/kg$_{cat}$/h)
K_M – adsorption equilibrium constant of component M (methanol) on the active center,
ΔH_M^{ads} – heat of adsorption of component M (methanol), (kJ/kmol)
L – concentration of active sites on the catalyst (5.2)
$E_{a,j}$ – activation energy of reaction j, (kJ/kmol)
$k_{0ap,j}$ – preexponential factor of apparent kinetic constant of reaction j, (kmol/kg$_{cat}$/h)
$K_{0,M}$ – preexponential factor of adsorption equilibrium constant of component M (methanol,
i – component identification, (2M2B, MeOH, TAME, 2M1B, iC5)
j – reaction number (R1, R3, R5)
ρ_b – bulk density (800 kg$_{cat}$/m^3_f)
ρ_s – solid density (2000 kg$_{cat}$/m^3_f)
ρ_f – fluid density (9.06… 10.96 kmol/m^3_f)
C_{pf} – fluid specific heat capacity (154 … 192 kJ/kg$_f$/K)
C_{ps}– solid specific heat capacity (1.518 kJ/kg$_s$/K)
D_z – axial diffusivity (0.002 … 0.003 m^3_f/m$_{cat}$/h)
λ_z – axial thermal conductivity (0.6 … 0.9 W/m$_r$/K)
ε – bed voidage fraction (0.6 m^3_f/m^3_r)
ΔH_j – enthalpy of reaction j, (R1: -36140.7 kJ/kmol; R2: -28909.9 kJ/kmol; R3: -7230.87 kJ/kmol)
R – ideal gas constant (kJ/kmol/K)
$v_{i,j}$ – stoichiometry of component i in reaction j
t – time variable
z – axial direction
$C_i(t,z)$ – molar concentration of component i, (1.385 …0.81 2M2B, 2.13 …0.77 MeOH, 0.9 … 1.4 TAME, 0.95 …0.18 2M1B, 6.17…6.3 iC5 kmol/m^3_f)

$C_{tot,in}$ – inlet total concentration, (1.38 2M2B, 2.13 MeOH, 0.9 TAME, 0.95 2M1B, 6.17 iC5 kmol/ m^3_f)

$x_i(t,z)$- molar fraction of component i

$x_{in,i}(z)$- inlet molar fraction of component i (0.13 2M2B, 0.2 MeOH, 0 TAME, 0.09 2M1B, 0.58 iC5)

$T(t,z)$ – reactor temperature

T^{feed} – feed temperature (323.15 K)

v_s – superficial velocity (1.546 $m^3_f/m^3_r/h$)

$r_j(z)$ – rate of reaction j

$F_{v,,in}$ – inlet volumetric flowrate (3.247 MeOH, 33.65 LCN m^3/h)

v_r – reactor volume (23.86 m^3)

Indices: M – methanol, 1B – 2M1B (2-methyl-1-butene), 2B – 2M2B (2-methyl-2-butene), T – TAME.

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