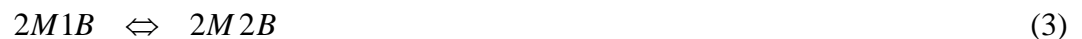


TAME synthesis problem

Tert-Amyl Methyl Ether (TAME) is an oxygenated additive for green gasolines. Besides its use as an octane enhancer, it also improves the combustion of gasoline and reduces the CO and HC (and, in a smaller extent, the NO_x) automobile exhaust emissions. Due to the environmental concerns related to those emissions, this and other ethers (MTBE, ETBE, TAEE) have been lately studied intensively.

TAME is currently catalytically produced in the liquid phase by the reaction of methanol (MeOH) and the isoamylenes 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B). There are three simultaneous equilibrium reactions in the formation and splitting of TAME: the two etherification reactions and the isomerization between the isoamylenes:



These reactions are to be carried out in a plug flow reactor and a membrane reactor in which MeOH is fed uniformly through the sides.

For isothermal operation:

- Plot the concentration profiles for a 10 m³ PFR.
- Vary the entering temperature, T_0 , and plot the exit concentrations as a function of T_0 .

For a reactor with heat exchange ($U = 10 \text{ J.m}^{-2}.\text{s}^{-1}.\text{K}^{-1}$):

- Plot the temperature and concentration profiles for an entering temperature of 353 K
- Repeat (a) through (c) for a membrane reactor.

NOTE: To simplify the problem, consider the solution density and heat capacity constant (evaluate them for the entering temperature and the feed mole fractions) and consider the solution as ideal: $a_i = x_i$ in the rate expressions.

A new and improved kinetic model, including the non-ideal character of the reacting solution, can be found in “Number of Active Sites in TAME Synthesis: Mechanism and Kinetic Modeling”, Manuela V. Ferreira and José M. Loureiro, *Ind. Eng. Chem. Res.* **43** (2004) 5156-5165.

Additional information for solving the problem

- Thermodynamic equilibrium constants, activity based (Vilarinho Ferreira and Loureiro, 2001)

$$Keq_1 = \exp\left(\frac{5.0166 \times 10^3}{T} - 10.839\right) \quad (I.1)$$

$$Keq_2 = \exp\left(\frac{3.7264 \times 10^3}{T} - 9.6367\right) \quad (I.2)$$

$$Keq_3 = \frac{Keq_1}{Keq_2} \quad (I.3)$$

with: T in Kelvin

- Kinetic constants for the direct reactions (Kiviranta-Pääkkönen et al., 1998)

$$k_1 = 3.2870 \times 10^{10} \exp\left(-\frac{76.8 \times 10^3}{RT}\right) \quad (I.4)$$

$$k_2 = 3.9682 \times 10^{13} \exp\left(-\frac{99.7 \times 10^3}{RT}\right) \quad (I.5)$$

$$k_3 = 7.4767 \times 10^{10} \exp\left(-\frac{81.7 \times 10^3}{RT}\right) \quad (I.6)$$

with: k in $\text{mol. kg}_{cat}^{-1} \cdot \text{s}^{-1}$

T in Kelvin

$R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

- Adsorption constants for each component, activity based (calculated and adapted from Oktar et al., 1999)

$$K_{1B} = \exp\left(\frac{4.6825 \times 10^3}{T} - 10.157\right), 1B = 2M1B \quad (I.7)$$

$$K_{2B} = \exp\left(\frac{3.4420 \times 10^3}{T} - 6.5849\right), 2B = 2M2B \quad (I.8)$$

$$K_M = \exp\left(\frac{1.0014 \times 10^3}{T} + 4.7496\right), M = \text{MeOH} \quad (I.9)$$

$$K_T = \exp\left(\frac{2.3934 \times 10^3}{T} - 3.5736\right), T = \text{TAME} \quad (I.10)$$

with: T in Kelvin

- Heat of reaction (Vilarinho Ferreira and Loureiro, 2001)

$$\Delta H_1^R = - 41.708 \text{ kJ.mol}^{-1}$$

$$\Delta H_2^R = - 30.981 \text{ kJ.mol}^{-1}$$

$$\Delta H_3^R = - 10.727 \text{ kJ.mol}^{-1}$$

- Bulk density and bed porosity

The PFR is filled with a macroreticular strong cation ion-exchange resin in hydrogen form (Amberlyst 15 Wet, Rohm & Haas).

The bulk density is: $\rho_b = 770 \text{ g/L}$

The bed porosity is: $\varepsilon = 0.4$

- Rate equations for the formation of each component (Vilarinho Ferreira and Loureiro, 2001)

$$r_{1B} = \frac{k_1 K_M K_{1B} a_M a_{1B} \left(\frac{1}{Keq_1} \frac{a_T}{a_M a_{1B}} - 1 \right)}{\left(1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T \right)^2} + \frac{k_3 K_{1B} a_{1B} \left(\frac{1}{Keq_3} \frac{a_{2B}}{a_{1B}} - 1 \right)}{\left(1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T \right)} \quad (\text{I.11})$$

$$r_{2B} = \frac{k_2 K_M K_{2B} a_M a_{1B} \left(\frac{1}{Keq_2} \frac{a_T}{a_M a_{2B}} - 1 \right)}{\left(1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T \right)^2} - \frac{k_3 K_{1B} a_{1B} \left(\frac{1}{Keq_3} \frac{a_{2B}}{a_{1B}} - 1 \right)}{\left(1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T \right)} \quad (\text{I.12})$$

$$r_M = r_{1B} + r_{2B} \quad (\text{I.13})$$

$$r_T = - r_M \quad (\text{I.14})$$

with: r in $\text{mol.kg}_{cat}^{-1}.\text{s}^{-1}$

a_i stands for the activity of component i in the liquid phase, and since we are considering the solution as ideal:

$$a_i = x_i \quad (\text{I.15})$$

where x_i is the mole fraction of component i in the liquid phase.

We can also define the rate of each reaction:

$$r_1 = \frac{k_1 K_M K_{1B} a_M a_{1B} \left(\frac{1}{Keq_1} \frac{a_T}{a_M a_{1B}} - 1 \right)}{(1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T)^2} \quad (\text{I.16})$$

$$r_2 = \frac{k_2 K_M K_{2B} a_M a_{1B} \left(\frac{1}{Keq_2} \frac{a_T}{a_M a_{2B}} - 1 \right)}{(1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T)^2} \quad (\text{I.17})$$

$$r_3 = \frac{k_3 K_{1B} a_{1B} \left(\frac{1}{Keq_3} \frac{a_{2B}}{a_{1B}} - 1 \right)}{1 + K_{1B} a_{1B} + K_{2B} a_{2B} + K_M a_M + K_T a_T} \quad (\text{I.18})$$

- Heat capacity of each component

$$Cp_i = a_i + b_i T + c_i T^2 + d_i T^3 \quad (\text{I.19})$$

with: Cp in $\text{kJ.mol}^{-1}.\text{K}^{-1}$

T in Kelvin

component i	$10 a_i$	$10^4 b_i$	$10^7 c_i$	$10^{10} d_i$
MeOH^a	0.077	1.62	2.06	2.87
2M1B^b	1.27	-0.609	5.08	1.69
2M2B^b	1.33	-1.48	7.51	-0.882
TAME^c	1.73	2.29	-6.00	20.0

^aZhang and Datta, 1995; ^bKitchaiya and Datta, 1995; ^cEstimated by the Missenard method (Reid et al., 1987)

To simplify the problem we are going to consider the heat capacity of each component constant and equal to its value at the entry conditions: $T = T_0$.

The solution heat capacity will also be considered constant and equal to its value at the entry conditions:

$$Cp = \sum_{i=1}^4 Cp_i x_i^{IN} \quad (\text{I.20})$$

where x_i^{IN} is the feed mole fraction of component i.

- Density of each component (Perry and Green, 1997)

$$\rho_i = \frac{C_{1,i} M_i}{C_{2,i} \left[1 + \left(1 - \frac{T}{c_{3,i}} \right)^{c_{4,i}} \right]} \quad (\text{I.21})$$

with ρ in g.L^{-1}

T in Kelvin

M in g.mol^{-1}

component i	M_i	$C_{1,i}$	$C_{2,i}$	$C_{3,i}$	$C_{4,i}$
MeOH	32.042	2.288	0.2685	512.64	0.2453
2M1B	70.135	0.91619	0.26752	465	0.28164
2M2B	70.135	0.93322	0.27251	471	0.26031
TAME	102.177	*	*	*	*

* as there is no data available for TAME, we will consider its density constant and equal to its value at 293 K: $\rho_{TAME} = 770 \text{ g/L}$

To simplify the problem we are going to consider the heat capacity of each component constant and equal to its value at the entry conditions: $T = T_0$.

The solution density will also be considered constant and equal to its value at the entry conditions:

$$\rho = \sum_{i=1}^4 \rho_i x_i^{IN} \quad (\text{I.22})$$

Starting solving the problem

① Writing mass and energy balances

In the figure is a representation of a PFR filled with a catalyst.

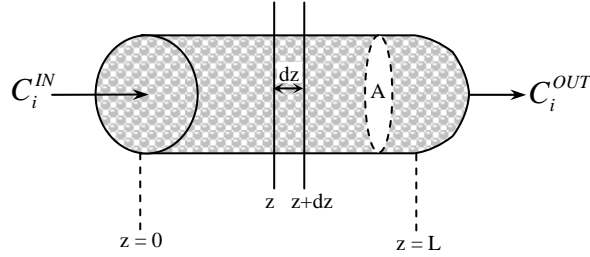


Fig. 1:Representaion of a PFR filled with catalyst.

A. Steady state mass balance

For the steady state mass balance of component i, in the volume element of length dz, we can write:

$$\text{Total Flux IN}\Big|_z = \text{Total Flux OUT}\Big|_{z+dz} - \text{What is formed by Chemical Reaction} \quad (\text{A.1})$$

If ε is the bed porosity, the area, A , available for the catalyst particles is $[(1-\varepsilon) A]$ and the area available for the fluid is $[\varepsilon A]$. Equation (A.1) becomes:

$$(\varepsilon A) \varphi_{i,z} = (\varepsilon A) \varphi_{i,z+dz} - \rho_b r_i A dz \quad (\text{A.2})$$

where φ_i is the molar flux of component i, ρ_b is the bulk density and r_i is the rate of formation of component i.

Re-writing equation (A.2):

$$\frac{\varphi_{i,z+dz} - \varphi_{i,z}}{dz} - \frac{\rho_b}{\varepsilon} r_i = 0 \quad (\text{A.3})$$

$$\frac{d\varphi_i}{dz} - \frac{\rho_b}{\varepsilon} r_i = 0 \quad (\text{A.4})$$

Considering a plug flow with axial dispersion, the molar flux is given by:

$$\varphi_i = u_i C_i - D_{ax} \frac{dC_i}{dz} \quad (\text{A.5})$$

where u_i is the interstitial velocity of the fluid, C_i is the concentration of component i in the fluid and D_{ax} is the axial dispersion coefficient.

$$u_i \frac{dC_i}{dz} - D_{ax} \frac{d^2 C_i}{dz^2} - \frac{\rho_b}{\varepsilon} r_i = 0 \quad (\text{A.6})$$

Normalizing some of the variables: $X = \frac{z}{L}$ (L is the PFR length), $f_i = \frac{C_i}{C_{total}^{IN}}$ ($C_{total}^{IN} = \sum_i C_i^{IN}$ where C_i^{IN} is the feed concentration of component i),

$$\frac{u_i}{L} C_{total}^{IN} \frac{df_i}{dX} - \frac{D_{ax}}{L^2} C_{total}^{IN} \frac{d^2 f_i}{dX^2} - \frac{\rho_b}{\varepsilon} r_i = 0 \quad (\text{A.7})$$

dividing by $\frac{u_i}{L} C_{total}^{IN}$, equation (A.7) becomes:

$$\frac{df_i}{dX} - \frac{1}{Pe} \frac{d^2 f_i}{dX^2} - \frac{\rho_b}{\varepsilon C_{total}^{IN}} \tau r_i = 0 \quad (\text{A.8})$$

where Pe is the dimensionless Peclet number given by $\frac{u_i L}{D_{ax}}$, and τ is the space-time given by $\frac{L}{u_i}$.

Grouping the term $\frac{\rho_b}{\varepsilon C_{total}^{IN}} \tau r_i$ as a reaction term represented by \mathfrak{R}_i , the steady state mass balance of component i becomes:

$$\boxed{\frac{df_i}{dX} - \frac{1}{Pe} \frac{d^2 f_i}{dX^2} - \mathfrak{R}_i = 0} \quad (\text{A.9})$$

In the limiting case of **absence of dispersion** $\left(\frac{1}{Pe} \rightarrow 0\right)$, equation (A.9) becomes:

$$\boxed{\frac{df_i}{dX} - \mathfrak{R}_i = 0} \quad (\text{A.10})$$

B. Steady state energy balance

For the steady state energy balance in the volume element of length dz , considering no dispersion, we can write:

$$\text{Total Flux IN}|_z + \frac{\text{heat produced by}}{\text{Chemical Reaction}} = \text{Total Flux OUT}|_{z+dz} + \frac{\text{heat losses through}}{\text{reactor walls}} \quad (\text{B.1})$$

$$(\varepsilon A) \varphi_z^h + \rho_b \sum_{j=1}^{M \text{ reactions}} (\Delta H_j^R r_j) A dz = (\varepsilon A) \varphi_{z+dz}^h + A_{lat} U (T - T_w) \quad (\text{B.2})$$

where φ^h is the heat flux, ΔH_j^R is the heat of reaction j , r_j is the rate of reaction j , A_{lat} is the lateral area of the volume element, U is the overall heat-transfer coefficient, T is the reactor temperature and T_w is the reactor wall temperature.

Re-writing equation (B.2):

$$\varepsilon \frac{\varphi_{z+dz}^h - \varphi_z^h}{dz} - \rho_b \sum_{j=1}^{M \text{ reactions}} (\Delta H_j^R r_j) + \frac{A_{lat}}{A} U (T - T_w) = 0 \quad (\text{B.3})$$

The heat flux can be given by:

$$\varphi^h = u_i \rho C_p T \quad (\text{B.4})$$

where ρ is the solution density and C_p is the solution heat capacity.

If R_0 is the reactor radius, the lateral area of the volume element of length dz is:

$$A_{lat} = 2\pi R_0 dz \quad (\text{B.5})$$

and its sectional area is:

$$A = \pi R_0^2 \quad (\text{B.6})$$

leading to:

$$\frac{A_{lat}}{A dz} = \frac{2}{R_0} \quad (\text{B.7})$$

Substituting into equation (B.3):

$$\varepsilon u_i \rho C_p \frac{dT}{dz} - \rho_b \sum_{j=1}^{M \text{ reactions}} (\Delta H_j^R r_j) + \frac{2}{R_0} U (T - T_w) = 0 \quad (\text{B.8})$$

Normalizing the space variable: $X = \frac{z}{L}$, remembering the space-time definition $\left(\tau = \frac{L}{u_i} \right)$ and rearranging equation (B.8):

$$\varepsilon \frac{dT}{dX} - \frac{\rho_b \tau}{\rho C_p} \sum_{j=1}^{M \text{ reactions}} (\Delta H_j^R r_j) + \frac{2U \tau}{\rho C_p R_0} (T - T_w) = 0 \quad (\text{B.9})$$

The term $\frac{2U \tau}{\rho C_p R_0}$ is dimensionless and is referred as NTU (number of heat transfer units).

Finally, the steady state energy balance becomes:

$$\boxed{\varepsilon \frac{dT}{dX} - \frac{\rho_b \tau}{\rho C_p} \sum_{j=1}^{M \text{ reactions}} (\Delta H_j^R r_j) + NTU (T - T_w) = 0} \quad (\text{B.10})$$

C. Boundary Conditions

In the absence of dispersion, we only need one boundary condition:

$$X = 0 \Rightarrow \begin{cases} f_i = \frac{C_i^{IN}}{C_{total}^{IN}} \\ T = T_0 \end{cases} \quad (\text{C.1})$$

where T_0 is the initial reactor temperature.

② Algorithm to solve the problem

We have a non-linear system of Ordinary Differential Equations (ODE) to solve:

$$\begin{cases} \frac{df_{1B}}{dX} - \mathfrak{R}_{1B} = 0 \\ \frac{df_{2B}}{dX} - \mathfrak{R}_{2B} = 0 \\ \frac{df_M}{dX} - \mathfrak{R}_M = 0 \\ \frac{df_T}{dX} - \mathfrak{R}_T = 0 \\ \varepsilon \frac{dT}{dX} - \frac{\rho_b \tau}{\rho Cp} \sum_{j=1}^3 (\Delta H_j^R r_j) + NTU (T - T_w) = 0 \end{cases} \quad (1)$$

The program we developed uses subroutine DDASSL (Brenan et al., 1989) to solve this system. This code solves a system of differential/algebraic equations of the form $\delta(t, y, yprime)=0$, with $\delta(i) = yprime(i) - y(i)$, using the backward differentiation formulas of orders one through five. t is the current value of the independent variable (in our case $t = X$), y is the array that contains the solution components at t (in our case we have: $y(i) = f(i)$, $i=1,4$ and $y(5) = T$) and $yprime$ is the array that contains the derivatives of the solution components at t .

The program solves the system from t to $tout$ and it is easy to continue the solution to get results at additional $tout$. In our case, we are going to get results at different values of X , between 0 and 1.

This problem is rather complex because most of the other variables depend on y_i : the kinetic, adsorption and thermodynamic equilibrium “constants” depend on T (y_5), the reaction rate and the components rate of formation depend on y_i (f_i ($i=1,4$) and T), as the activity coefficients.

In Figure 2 is the algorithm to solve our problem.

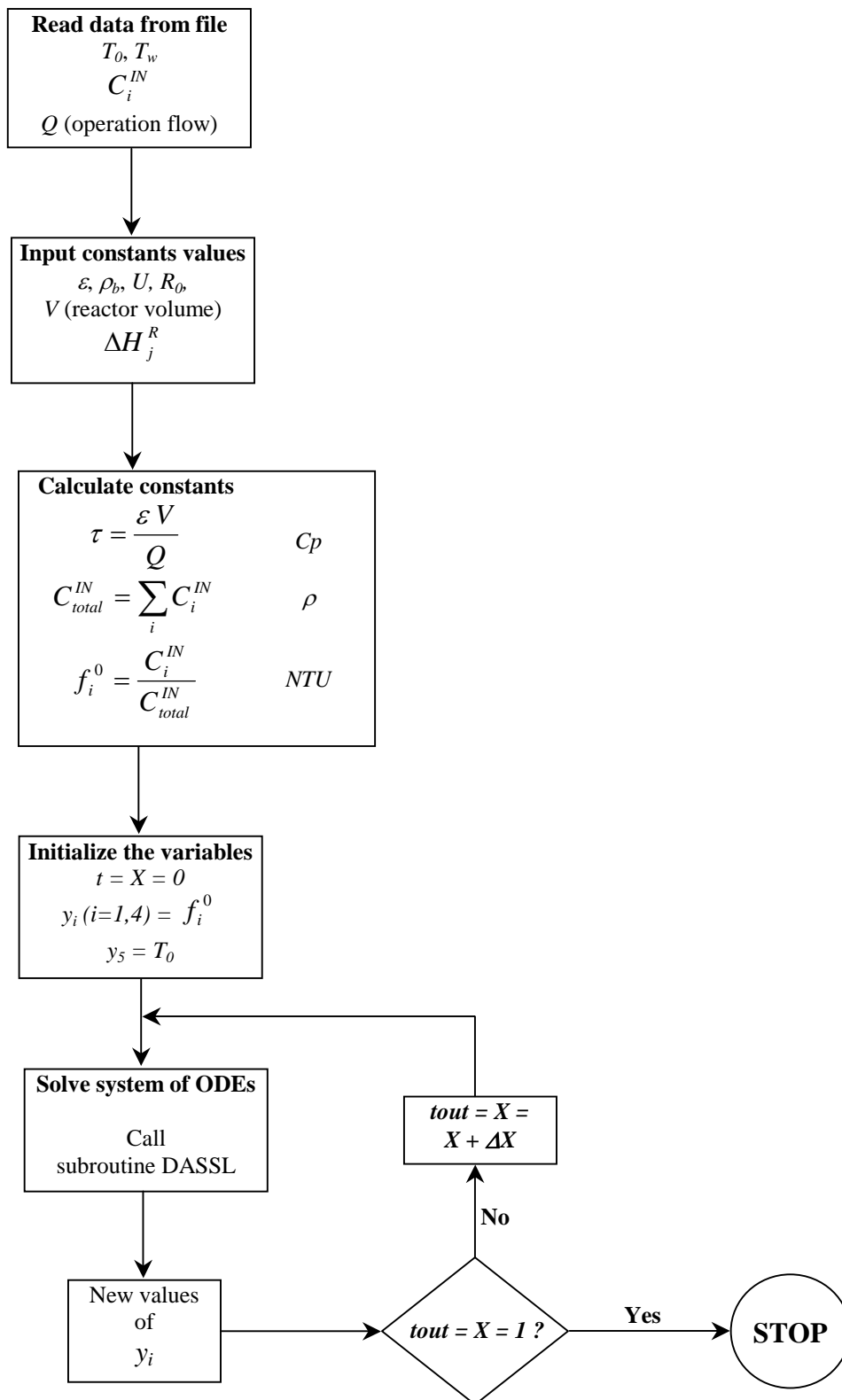


Fig. 2: Algorithm to solve the problem.

Some results

For both cases, isothermal and non-isothermal, the feed concentrations were the same:

$$C_{2M1B}^{IN} = 3.33 \text{ mol/L}$$

$$C_{2M2B}^{IN} = 3.33 \text{ mol/L}$$

$$C_{MeOH}^{IN} = 6.66 \text{ mol/L}$$

$$C_{TAME}^{IN} = 0$$

These concentrations lead to a feed mole ratio MeOH/isoamylenes, $R_{M/IA}$, of 1.0.

a) Figures R.1, R.2 and R.3 represent the concentration profiles for a 10 m^3 isothermal PFR, operating at 323 K, 343 K and 363 K, and a flow of 40 L/min.

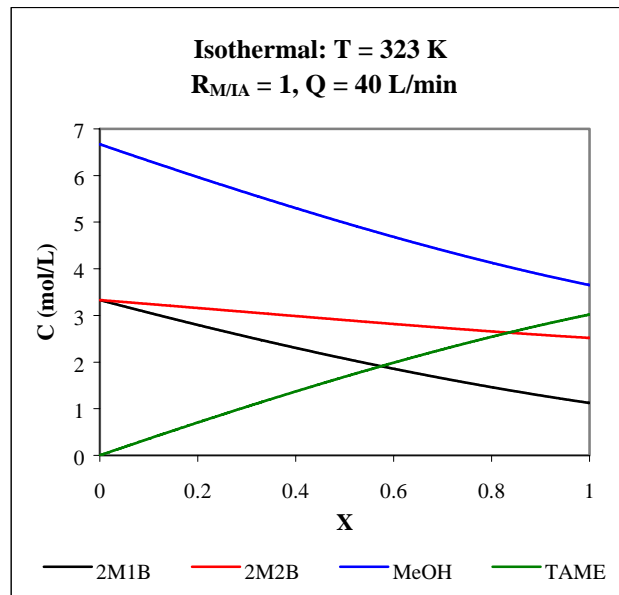


Fig. R.1: Concentration profiles for a 10 m^3 isothermal PFR operating at 323 K.

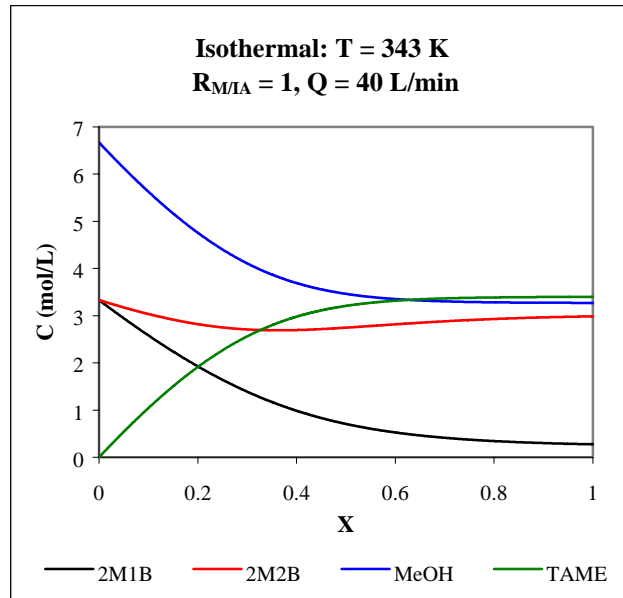


Fig. R.2: Concentration profiles for a 10 m³ isothermal PFR operating at 343 K.

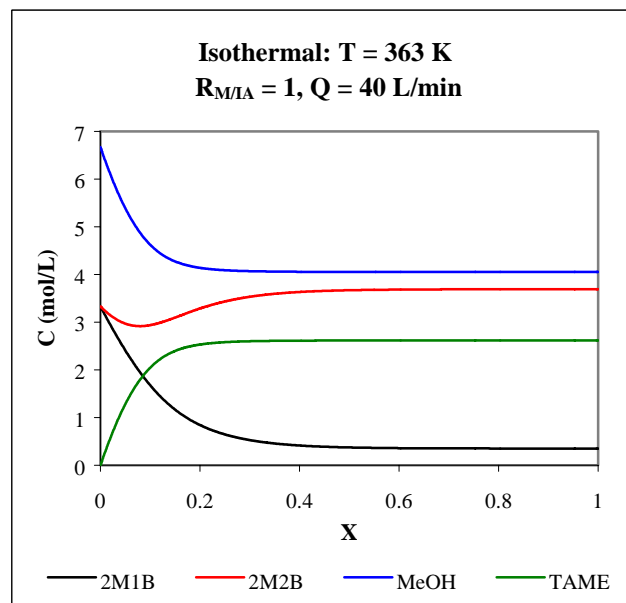


Fig. R.3: Concentration profiles for a 10 m³ isothermal PFR operating at 363 K.

As the temperature increases, the reactions are faster, favoring TAME production, but the chemical equilibrium is moved to the opposite direction: for an operating temperature of 363 K, the equilibrium concentration of TAME is reached faster than for 343 K, but its value is lower.

b) Figure R.4 represents the exit concentrations as a function of the entering temperature, T_0 , for a 10 m³ isothermal PFR operating with a flow of 40 L/min.

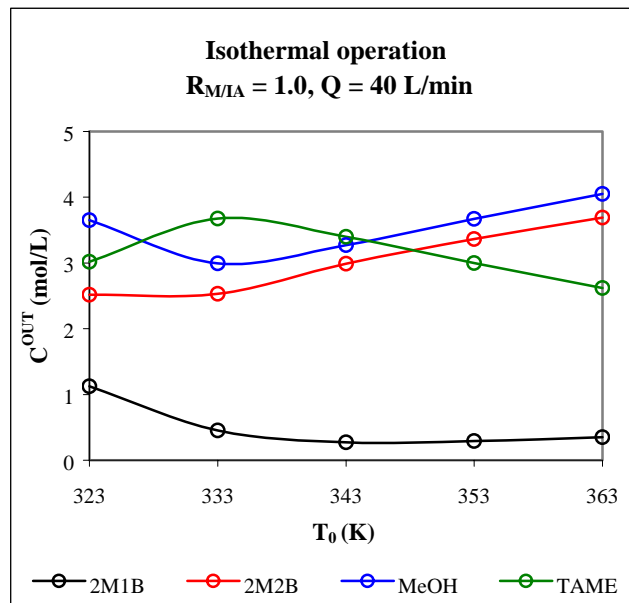


Fig. R.4: Exit concentrations as function of T_0 , for a 10 m³ isothermal PFR

Figure R.4 shows that there is an **optimum operating temperature around 333 K** that leads to a maximum exit concentration for TAME. It is due to the fact that we have a system with competition between kinetics and equilibrium, as we are going to see for the non-isothermal PFR

c) We chose a reactor diameter of 1 m (for a volume of 10 m³ it leads to a reactor length of 12.7 m approximately) and for the wall temperature, we decided to use room temperature: 298 K. The entering temperature is 353 K.

It is important to notice that the catalyst used in TAME production is a macroreticular strong cation ion-exchange resin in hydrogen form (Amberlyst 15 Wet, Rohm & Haas) that has a maximum operating temperature of 393 K.

Figure R.5 represents the concentration (a) and temperature (b) profiles for an operating flow of 200 L/min.

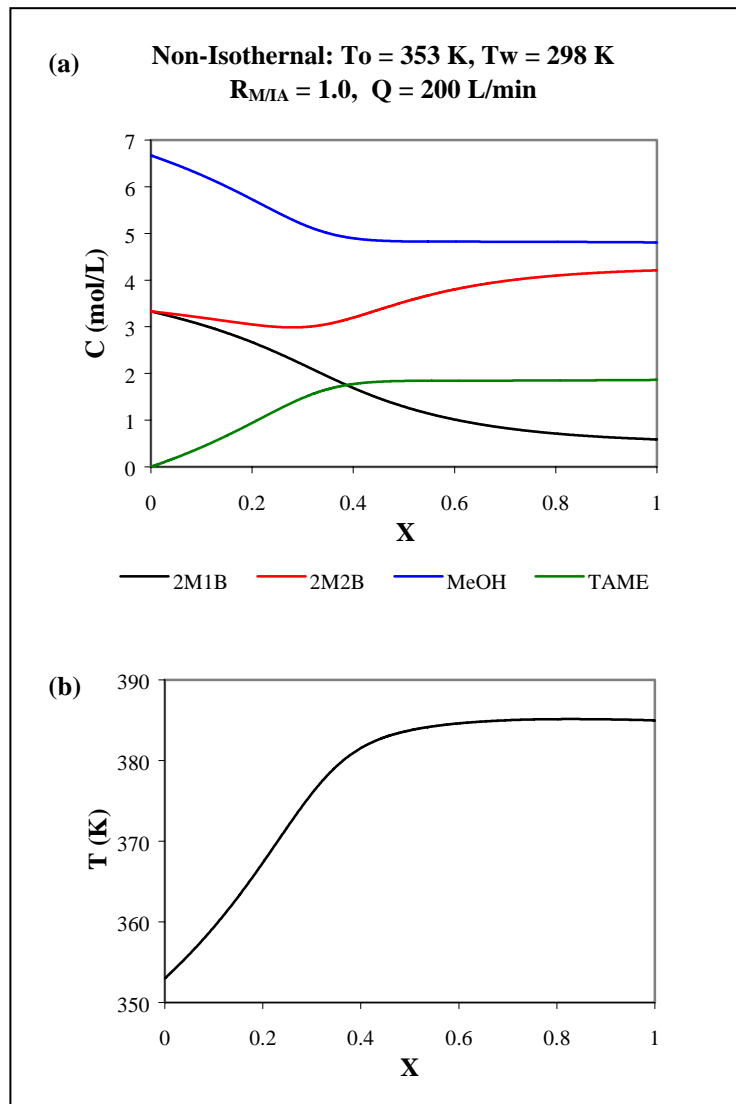


Fig. R.5: Non-isothermal PFR: (a) concentration profiles; (b) temperature profile.

Figure R.5(a) shows the competition between the three reactions: first, 2M1B and 2M2B react with MeOH to produce TAME and the reactants concentrations decrease and TAME concentration increases; but then, although MeOH and TAME concentrations are almost constant, 2M1B is still decreasing and 2M2B starts to increase: the third reaction, the isomerization, is now more evident.

The temperature profile (Fig. R.5(b)) shows that the reactor seems to be almost adiabatic (no heat losses through the reactor walls) since the reactor temperature is always increasing. This close to adiabatic behavior was expected since the reactor diameter is rather large: 1 m. **But the temperature reaches a value that is very close to the catalyst limit:** remember that its maximum operating temperature is 393 K and the reactor is reaching 385 K.

To see what is the maximum temperature that the reactor reaches, we can make it adiabatic setting the overall heat-transfer coefficient equal to zero: $U = 0$. In Figure R.6 are the results for the adiabatic reactor.

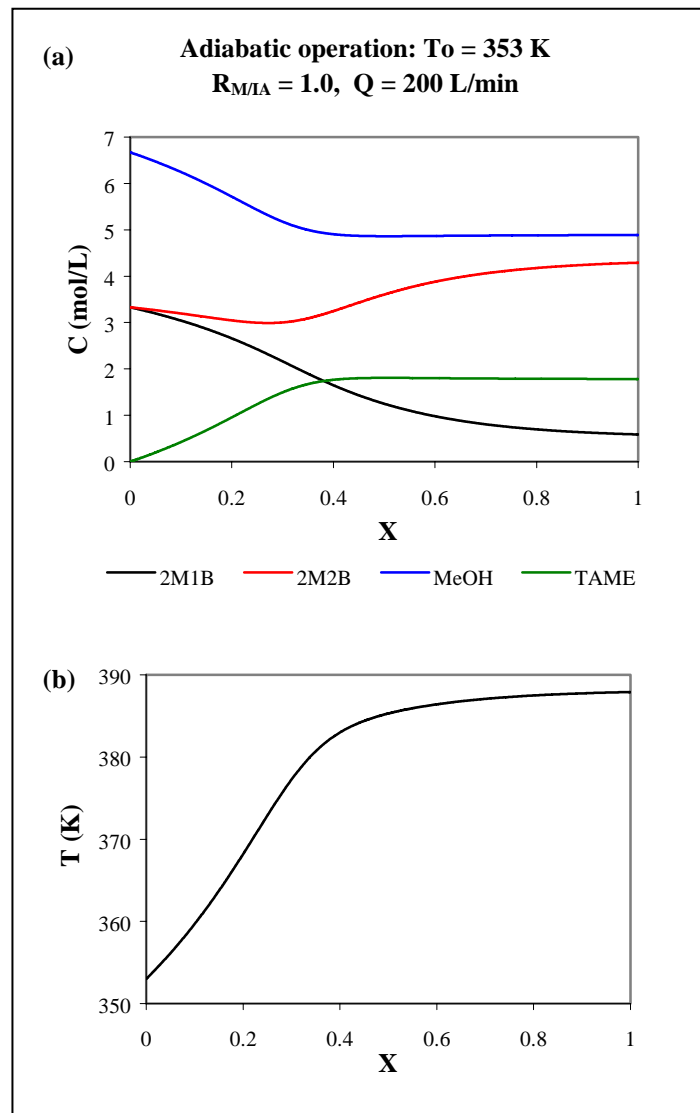


Fig. R.6: Adiabatic PFR: (a) concentration profiles; (b) temperature profile.

The maximum temperature reached by the reactor is 388 K. Comparing Figures R.5 and R.6 it is easy to see that the non-isothermal 1m diameter PFR can be considered adiabatic: the concentration and temperature profiles are almost the same.

To improve the reactor production, i.e., to reach higher exit concentrations of TAME, we can use a multi-tubular reactor. Lets think of a reactor composed of 4000 tubes (each one considered as a PFR)

with a diameter of 1'' each. To have a total reactor volume of 10 m^3 , each tube has a length of 5 m. In order to compare the results of the multi-tubular reactor with the ones obtained with the 1 m diameter PFR (Fig. R.5), we have to choose similar operating conditions: to have a total operating flow of 200 L/min, the equivalent flow in each tube is 0.05 L/min; since the reactor is now really cooled, we will choose the “best” temperature for the cooling fluid (333 K, as seen with the isothermal behavior runs). Figure R.7 shows the results for one of this tubes operating in the above conditions.

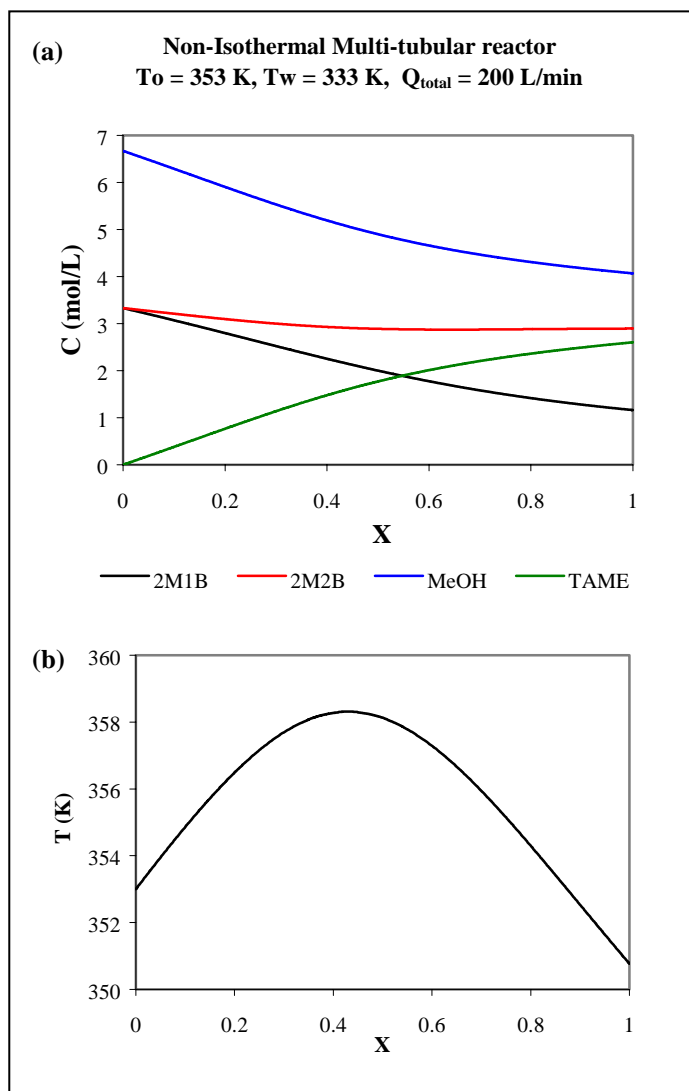


Fig. R.7: Multi-tubular reactor: (a) concentration profiles; (b) temperature profile.

The maximum temperature reached is 358 K - in this case there are no problems with the catalyst - and the exit concentration of TAME is higher: 2.603 mol/L against 1.862 mol/L for the PFR in Figure R.5, which represents an increase of 28.5 %.

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