Modelling Heat and Mass Transfer in Microreactor for Methanol to Hydrocarbons

P. A. Delou[*1,2] and V. Degirmenci[2,3]

[1]Universidade Federal do Rio de Janeiro, Escola de Química, Rio de Janeiro, RJ, Brazil.
[2]Queen's University Belfast, School of Chemistry and Chemical Engineering, Belfast, United Kingdom.
[3]University of Warwick, School of Engineering, Coventry, United Kingdom.
*Corresponding author: pedrodelou@gmail.com

Abstract: Recently, increasing availability of natural gas, due to the shale gas, raises the attention to the conversion of methane. Methanol-to-Hydrocarbons reaction (MTH) is the important step in this route where methanol synthesized through syngas is converted into hydrocarbons, such as gasoline. However, cost effective scalable technologies are not mature due to the difficulties in controlling the product selectivity. In this study heat and mass transfer in a microreactor for MTH reaction is investigated. A kinetic model and the heat and mass transfer in a porous media flow for the Methanol conversion was modelled. Simulation was carried out using COMSOL Multiphysics®. The results pointed the appropriate initial concentration required to achieve the maximum conversion to Gasoline. In addition, it proved that the process is suitable to changing the final product to Light Olefins. Finally, the uniform temperature profile clarifies the unnecessity of a heat transfer jacket for the microreactor.

Key words: synfuel, ZSM-5, Gasoline, Methanol-to-Hydrocarbons.

1. Introduction

The demand for oil in 70s over exceeded the rate of discovery of new reservoirs, causing the oil prices to peak. Rapidly, several studies pointed that the world would be running out of oil in the early 90s. These crises led to the development of a new technology to convert Methanol into Gasoline (MTG) over zeolite ZSM-5 [7]. When fed with a stream of Methanol and inert gas (to adjust the partial pressure required), the catalyst has several acid sites that triggers a series of hydrocarbons reactions, which later turned out to proceed through hydrocarbon pool mechanism. ZSM-5 has shape selectivity that limits the size of hydrocarbons produced inside the catalyst pore. Producing a high quality Gasoline with no sulphur content and high octane number.

The reaction in the MTG process is exothermic and have a theoretical adiabatic temperature rise around 600°C. A simplified reaction scheme is presented below [7].

$$2CH_2OH \leftrightarrow DME + H_2O$$
$$DME \rightarrow Light\ Olefins(LO) + H_2O$$
$$LO + DME \rightarrow Heavy\ Olefins(HO) + H_2O$$
$$HO \rightarrow Aromatics + Paraffins$$
$$Aromatics + DME \rightarrow Higher\ Aromatics + H_2O$$

The first reaction is the dehydration of methanol. It is generally assumed an equilibrium reaction. After that, DME is converted into light olefins, mostly propene and butenes. The consumption of DME disturbs the equilibrium of the first reaction, which leads to more dehydration of methanol. DME and light olefins reaction also produces higher olefins, which than reacts with each other to form aromatics and paraffins. Residual DME alkylates those aromatics to higher carbon numbers [7]. The mixture of Aromatics and Paraffins is the Gasoline itself.

The reaction scheme suggests that depending on the reaction conditions two products can be obtained, Light Olefins and Gasoline. This flexibility increases the economical attractiveness of the MTH reactions, as it can follow the market demands. This study will show that just by changing the initial concentration of Methanol it is possible to manage which product will be produced.

Heat management is the critical issue of the process as the reaction is very exothermic, its heat of reaction is about 1.74 MJ/(kg methanol) [5]. The process developer defined a maximum and a minimum temperature limits, 415°C and 360°C respectively, in order to balance reactor cost, time of cycle and catalyst life. A gas recycle system is used to control the catalyst temperature and the reaction pressure of 21 bar [7].

For exothermic reactions such as MTH reactions, the effect of heat releasing within the catalyst pellets can improve the reaction rate. However, for practical terms, there is a limit temperature to guarantee a good overall conversion and insure that the catalyst do not suffer with thermal harmful effects and lose its proprieties irreversibly. Therefore, the heat generation is a critical variable that must be controlled. The present work will show that, for the microreactor used, the heat generation is not a significant issue considering the scale of the process.

The aim of this work is to evaluate heat and mass transfer in a packed bed microreactor over ZSM-5, through simulation of a porous reactive flow using COMSOL Multiphysics®.

2. Use of COMSOL Multiphysics

The model is a single specie gaseous flow in a cylindrical tube, where reaction takes place in a porous media and the products leaves by the outlet tube. The developed model is based on "carbon deposition in heterogeneous catalysis" example in COMSOL model library.

Three physics were used: **Transport of Diluted Species**, **Heat Transfer in Porous Media** and **Free and Porous Media Flow**. In order to describe the Mass, Energy and Momentum balances in the system, respectively. The details of the used model in order to describe the system satisfactorily are as follows:

- The use of the 0D Reaction Engineering interface with posteriorly generation of a Space-Dependent produces valuable information about the reaction's ideal behavior. However, it increases the complexity of the model and leads to a higher processing requirement. This physics was not used without effecting the model.

- The physics Heat Transfer in Porous Media was coupled to the model in order to get information about heat transfers during the reaction.

2.1. Reaction Kinetics

Schipper and Krambeck (1986) proposed the adopted reaction scheme of the Methanol conversion to Gasoline [1]:

$$MeOH/DME\ (A) \xrightarrow{K_1} Light\ Olefins\ (C)$$
$$2C \xrightarrow{K_2} Gasoline\ (D)$$
$$A + D \xrightarrow{K_3} D$$
$$C + D \xrightarrow{K_4} D$$

It is an autocatalytic scheme, in other words, the product is a catalyst to the formation of itself. Where A is considered hypothetical species formed by the equilibrium between Methanol and Dimethyl Ether, C are light olefins and D is Gasoline, the desired product. The kinetic lumped model adopted were proposed by Benito *et al.* [1], which is valid using ZSM-5 as catalyst in a temperature range from 300 to 375°C. The reaction rates are:

$$r_1 = k_1 * X_A * a$$
$$r_2 = k_2 * X_C^2 * a$$
$$r_3 = k_3 * X_A * X_D * a$$
$$r_4 = k_4 * X_C * X_D * a$$

Therefore, rates for each component are:

$$\frac{dC_A}{dt} = -k_1 * X_A * a - k_3 * X_A * X_D * a$$
$$\frac{dC_C}{dt} = -k_1 * X_A * a - k_2 * X_C^2 * a - k_4 * X_C * X_D * a$$
$$\frac{dC_D}{dt} = k_2 * X_C^2 * a$$

The difference of a lumped model from the regular is that the reaction rates are functions of the mass fractions instead of concentrations. The standard concentration can be easily converted to mass fraction by the following expression:

$$X_i = \frac{C_i \cdot M_{Wi}}{\sum C_{0,i} \cdot M_{Wi}} \qquad for\ i = A, C\ or\ D$$

Where C_i is the concentration of specie i (mol/m^3), M_{wi} is the molecular weight of specie i (kg/mol) and $C_{0,i}$ is the concentration of specie i in the inflow stream (mol/m^3). The kinetic constants for each reaction are calculated by the Arrhenius expression:

$$k_n = k_{0,n} \cdot exp\left(-\frac{E_{a,n}}{R_g T}\right) \qquad for\ n = 1, 2, 3\ or\ 4$$

The values for $k_{0,n}$ and $E_{a,n}$ are given in table 1:

Table 1. Kinetic constants [1]

n	$k_{0,n}$ (h^{-1})	$E_{a,n}$ (cal/mol)
1	$0.733 \cdot 10^{13}$	33358
2	$0.127 \cdot 10^{8}$	17633
3	$0.204 \cdot 10^{12}$	27987
4	$0.634 \cdot 10^{6}$	15855

The activity (a) is calculated by the deactivation rate by carbon deposition in the catalyst surface during the reaction:

$$-\frac{da}{dt} = (k_{dA} * X_A + k_{dC} * X_C + k_{dD} * X_D) * a$$

The deactivation constants are calculated by the Arrenius expression, where $k_{0,i}$ and $E_{a,i}$ are in presented in table 2:

Table 2. Deactivation constants [1]

i	$k_{0,i}$ (h^{-1})	$E_{a,i}$ (cal/mol)
dA	$0.461 \cdot 10^{9}$	26700
dC	$0.139 \cdot 10^{10}$	31600
dD	$0.129 \cdot 10^{13}$	38100

The microreactor geometry, boundary conditions and each physics used in the model will be described in the next sub-sections.

2.2. Geometry and Boundary conditions

The specific microreactor considered has a channel section where many tubes are disposed in series and each of them are packed with the catalyst. In this model one tube were modelled using an axial-symmetric 2D geometry (Figure 1). The porous domain has 0.25 mm of radius and 25 mm of length.

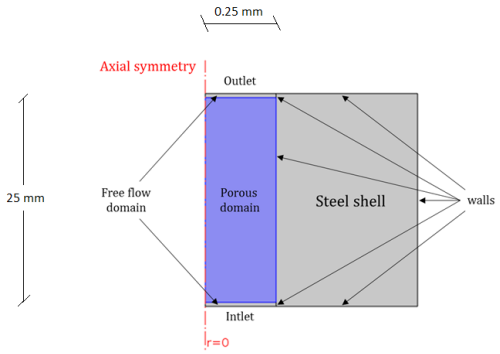

Figure 1. Tubular reactor geometry and boundary conditions.

It is noteworthy that the steel shell walls are adiabatic, in other words it does not change heat with the environment. Three materials were used from the Material Library: Nitrogen to approximate the gaseous behavior during the reaction; Alumina was taken to represent the ZSM-5 catalyst; and High-strength alloy steel to represent the heat proprieties of the steel shell.

2.3. Transport of Diluted Species

Four species were selected: A, C, D and I. They are, respectively, a hypothetical species to represent the equilibrium between Methanol and DME, light olefins, gasoline and an inert gas to adjust the partial pressure of the feed.

Two Convection and Diffusion nodes were used, one for the porous domain and other for the free flow domain. In the porous domain, it was assumed that Knudsen diffusion ruled the species flux to calculate the Diffusion coefficients:

Table 3. Diffusion coefficients in the porous media

Species	Diffusion coefficient value
A	$3.1 \cdot 10^{-9}$ m^2/s
C	$3.3 \cdot 10^{-9}$ m^2/s
D	$2.5 \cdot 10^{-9}$ m^2/s
I	$3.8 \cdot 10^{-9}$ m^2/s

For the free flow domain, these coefficients were assumed 10 times greater.

The inlet stream is a mixture of 30% Methanol (A) and 70% Nitrogen (I), the initial concentrations fitted for the maximum production of gasoline are:

Table 4. Initial concentrations

Specie	Initial concentration value ($\mu mol/m^3$)
A	1.0
C	0
D	0
I	2.33

A reaction node was added to the porous domain and the reaction rate for each specie was defined as described in section 2.1.

2.4. Heat Transfer in Porous Media and Free

A Heat Transfer in Porous Media node was selected to porous and free flow domain, where the fluid material is Nitrogen and the solid material is Alumina. All proprieties of this node were taken from materials, but Porous Matrix density, that was used 1280 kg/m^3 [3].

The initial temperature and inlet temperature is 623K.

A Heat source node was added to the porous domain in order to represent the heat produced by the reaction. In the heat source node, General source were chosen and the expression was typed was the sum of the heat of reaction times the rate for each reaction.

Table 5. Heat of reactions

i	Heat of reaction (J/mol)
1	1x10^8
2	9.2x10^4
3	1x10^8
4	6x10^4

The heat of each reaction was calculated separately from COMSOL, by taking the mean heat capacities of A, C and D from Reklaitis [8]. To do that, A is a mixture of Methanol and Dimethyl Ether, C is Ethylene and Propylene and D was considered to be a mixture of n-Butane, n-Pentane and n-Hexane. The heat of reaction is given by:

$$H_i^r = H_i^f + \int_{298}^{623} \nabla C_{pi} dT \qquad for\ i = 1,2,3\ or\ 4$$

A Heat Transfer in Solids node was added to the steel shell domain and all the proprieties were taken from material.

2.5. Porous Media Flow

The momentum balance just occurs in the porous and free flow domain. A compressible flow (Ma<0.3) was selected. In the Fluid proprieties flow, Temperature and Pressure were selected from previous physics and fluid material is Nitrogen (Density and Dynamic viscosity were taken from material).

In the initial values node, the velocity field was 0.18189 m/s in z direction and the pressure follows the expression: R_const*T*(cAin+cIin). In the inlet node, normal inflow velocity was chosen and U_0 is 0.18189 m/s. The outlet pressure is 0 and the Supress backflow option was marked.

Finally, a Porous Matrix Proprieties node was added to the porous domain, the porosity was defined as 0.405 and the Permeability as 10^{-9}m^2 [3].

3. Results

The simulation was carried out for a series of times until 10 hours of continuous reaction. The results for product and temperature profile did not show significant variations. So, these results are presented as a profile along the z-direction of the reactor for 10 hours of reaction. The flow rate used was 30 ml/min and the residence time was 0.01 s. For the microreactor used, the maximum production of Gasoline happens with an initial concentration of Methanol of 1 µmol/m^3. Its product profile along the z-direction of the reactor is given in Figure 2. It presented a typical autocatalytic configuration, where the reactant Methanol rapidly disappear forming Light Olefins, which is gradually consumed forming Gasoline, very similar to the ideal case. Methanol is completely consumed after 2.5 mm of the reactor length, the maximum of production of Light Olefins is around 2 mm and the maximum of Gasoline is achieved after 15 mm, with total consumption of C after 25 mm. The maximum conversion is around 30%.

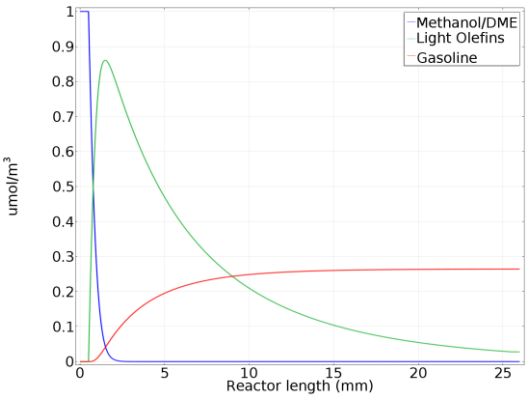

Figure 2. Product distribution along the microreactor after 10h of reaction and 1 µmol/m^3 of Methanol.

The above picture shows that the process is very suitable considering the desired product, over ZSM-5 as the catalyst, by varying the initial

concentration of Methanol. The next figure shows the product profile along the z-direction of the catalyst for 30 µmol/m^3 of Methanol in the feed and 10 hours of reaction, aiming to maximize the production of Light Olefins.

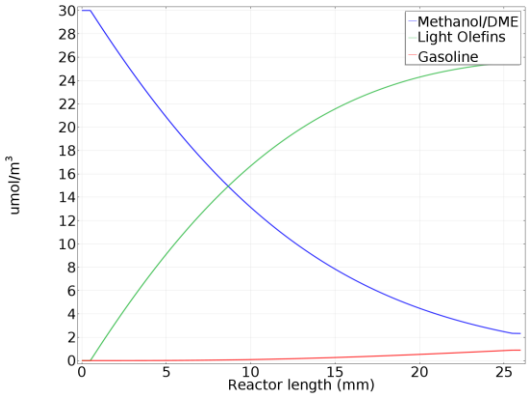

Figure 3. Product distribution along the microreactor for 10h of reaction and 30 µmol/m^3 of Methanol.

The temperature profile was evaluated with three cut lines along the reactor (Figure 3), one in the centre of the reactor tube, the second between the centre and the wall and the last near the wall. By comparison of the temperature profile in three points along the radial direction of the reactor it can be concluded that temperature can be considered uniform in the microreactor, where the maximum raise is only 0.015 K. Figure 4 shows the temperature profile along the z-direction of the reactor after 10 hours of reaction and 1 µmol/m^3 of Methanol in the feed.

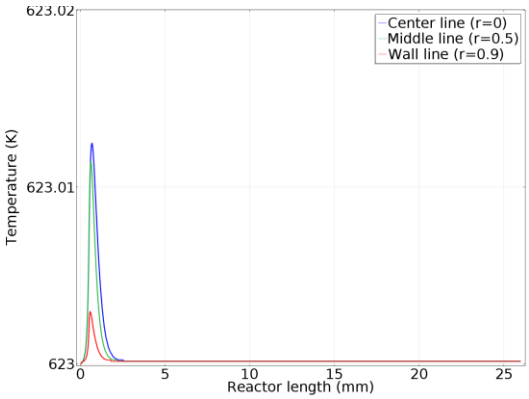

Figure 4. Temperature distribution along the z-direction of the microreactor for 10h of reaction and 1 µmol/m^3 of Methanol.

The activity is an important variable to measure the performance of the catalyst along the reactor and the reaction. While the reaction takes place, the catalyst performance suffers with coke deposition, which is an impurity produced in consequence of the reaction mechanism inside the zeolite pore. In addition, it will directly affect the catalyst along the reactor. How most of the reaction occurs at the initial region of the reactor, the catalyst disposed at this space will be the most affected by deactivation.

Figure 5 shows the activity profile along the reactor, after 1 hour (blue line) and 10 hours (green line) of reaction. As expected, the activity fall is greater at the very beginning of the reactor. This fall matches with the full consumption of Methanol. Therefore, Methanol consumption is the important step that reduces the catalyst activity, while the conversion of Light Olefins to Gasoline is a milder coke deposition step. After 10 hours of reaction, despite the activity fall to less than 0.6 before 1 mm, major part of the reactor is over 0.9. Literature suggest that just after 200 hours regeneration needs to take place in order to keep a high conversion [9].

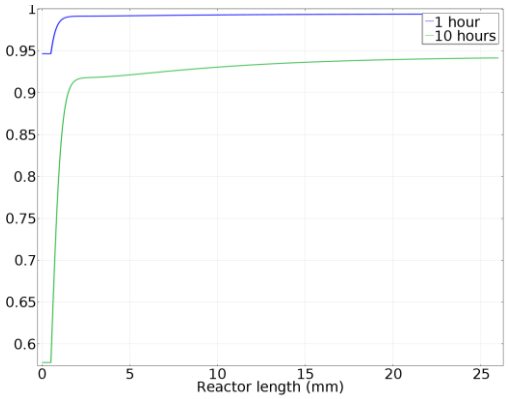

Figure 5. Activity profile along z-direction of the microreactor for 1 µmol/m^3 of Methanol.

4. Conclusions

The model successfully provided the appropriate initial concentration required to achieve the maximum production of Gasoline. In addition, it proved that the process is suitable to change the final product to Light Olefins, by varying the reactor length or rising the initial concentration to 30 µmol/m^3. This flexibility provides a better adaptation to the market demands, which increases the economic attractiveness of the process. The temperature

profile clarifies the unnecessity of a heat transfer jacket for the microreactor. For a laboratory scale, the activity fall is not a problem. However, to an industrial scale, further studies need to be carried out and this model can be used as a framework for scale up processes.

5. References

1. Benito, P. L. et al., Concentration-Dependent Kinetic Model for Catalyst Deactivation in the MTG Process, *Industrial and Engineering Chemistry Research*, **Volume 35**, pp. 81-89 (1996)

2. Bjorgen, M., Lillerud, K. -P., Olsbye, U. & Svelle, S., Conversion of methanol to hydrocarbons: Hints to rational catalyst design from fundamental mechanistic studies on H-ZSM-5, *Studies in Surface Science and Catalysis*, **Volume 167**, pp. 463-468 (2007)

3. Guo, W., Xiao, W. & Luo, M., Comparison among monolithic and randomly packed reactors for metanol-to-propylene process, *Chemical Engineering Journal*, **Volume 207-208**, pp. 734-735 (2012)

4. Guisnet, M. & Ramôa Ribeiro, F., Zeólitos: Um nanomundo a serviço da catálise. Lisboa: Fundação Calouste Gulbenkian. (2004)

5. Keil, F. J., Methanol-to-hydrocarbons: process technology, *Microporous and Mesoporous Materials*, **Volume 29**, pp. 49-66 (1999)

6. Lesthaeghe, D. et al., Theoretical Insights on Methylbenzene Side-Chain Growth in ZSM-5 Zeolites for Methanol-to-Olefin Conversion, *Chemistry - A European Journal*, **Volume 15**, p. 10803 – 10808 (2009)

7. MacDougall, L. V., Methanol to Fuels routes - the achievements and remaining problems, *Catalysis Today*, pp. 337-369 (1991)

8. Reklaitis, G. V., *Introduction to Material and Energy Balances*, 1st edn., New York: John Wiley & Sons (1983)

9. Stöcker, M., Methanol-to-hydrocarbons: Catalytic materials and their behavior, *Microporous and Mesoporous Materials*, **Volume 29**, pp. 3-48 (1999)