METHYL-*TERT*-BUTYL-ETHER SYNTHESIS REACTOR MODELLING AND OPTIMIZATION USING AN ASPEN CUSTOM MODELER

ZEESHAN NAWAZ

SABIC Technology & Innovation, PO Box 42503, Saudi Basic Industries Corporation (SABIC), Riyadh, 11551, SAUDI ARABIA

A pseudo-homogeneous model of methyl-*tert*-butyl-ether (MTBE) synthesis in a multi-tubular packed-bed reactor has been developed using an Aspen Custom Modeler (ACM) for selecting optimum operating strategies, for the maximization and enhancement of MTBE production, and isobutylene consumption, respectively. The model accounts for mass, energy and momentum balances; and the effectiveness factor is evaluated in a one-dimensional pseudo-homogeneous model. The kinetic investigation contains kinetic rate expressions as given by the effectiveness factor for accounting the resistance of pellets in terms of mass and heat transfer. An activity coefficient can be used in order to systematically obtain a new steady-state solution. The model used literature-based correlations for the estimation of heat transfer coefficients. The value of the coefficient for gas-coolant heat transfer can be adjusted by using a tuning coefficient in order to enrich the process data. Reasonable agreement was found between model predictions and data under similar conditions. The studies concerning model sensitivity compute the optimum temperature, pressure, feed flow rate, methanol/isobutylene ratio, heat removal rate, etc. of the reactor and suggest optimum operating conditions of the reactor.

Keywords: methyl-*tert*-butyl-ether (MTBE) synthesis, lead reactor, multi-tubular packed-bed, Aspen Custom Modeler (ACM), isobutylene

1. Introduction

Methyl-*tert*-butyl-ether (MTBE) is of importance among petrochemicals due to its physicochemical properties and as an additive in gasoline. It contributes to the gradual elimination of lead-based additives, increasing the octane number (as an octane booster) and serves as a volume extender [1]. It is formed by the etherification reaction of an alcohol with a tertiary olefin. Ethers are preferable over alcohols due to their lower sensitivity values, i.e. the difference between the RON (Research Octane Number) and MON (Motor Octane Number) [2]. Today, standard (Huls AG) and Ethermax are the known processes commercialized by Snamprogetti, CDTech, Universal Oil Products (UOP), Axens, Fortum, Arco, Phillips, BP-Intevep, Sinopec, Sumitomo, etc. These are similar processes to each other. In this study a Snamprogetti-lead reactor is modelled to maximize its productivity.
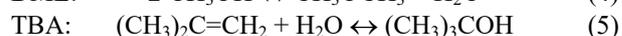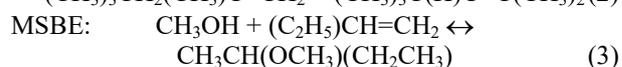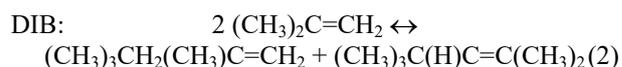
2. Experimental Conditions Considered

2.1. Reaction Chemistry

The following five reactions (*Eqs.(1-5)*) are involved in MTBE synthesis when isobutylene reacts with methanol

(MeOH). MTBE synthesis is an exothermic liquid-phase reversible reaction catalysed by a cationic ion-exchange resin (sulphonated macroporous polystyrene). For each mole of isobutylene converted, ~37.7 kJ of heat is released and the thermodynamic equilibrium determines the extent of conversion [1-2].

MTBE: $CH_3OH + (CH_3)_2C=CH_2 \leftrightarrow (CH_3)_3COCH_3$ (1)
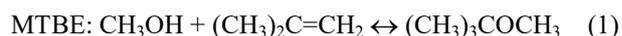
However, undesirable side reactions may take place such as the dimerization of isobutylene to diisobutenes (DIB), 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2); and the formation of methyl sec-butyl ether (MSBE), dimethyl ether (DME) and tert-butyl alcohol (TBA). The water produced during the formation of DME may react with isobutylene to form tert-butyl alcohol (TBA) and its blending octane number is lower than that of MTBE. On the other hand, the presence of water reduces the acidity of the catalyst (reducing activity) and therefore a higher reaction temperature is required.

DIB: $2 (CH_3)_2C=CH_2 \leftrightarrow$
$(CH_3)_3CH_2(CH_3)C=CH_2 + (CH_3)_3C(H)C=C(CH_3)_2$ (2)
MSBE: $CH_3OH + (C_2H_5)CH=CH_2 \leftrightarrow$
$CH_3CH(OCH_3)(CH_2CH_3)$ (3)
DME: $2 CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ (4)
TBA: $(CH_3)_2C=CH_2 + H_2O \leftrightarrow (CH_3)_3COH$ (5)

---

*Correspondence: zeeshan@sabic.com
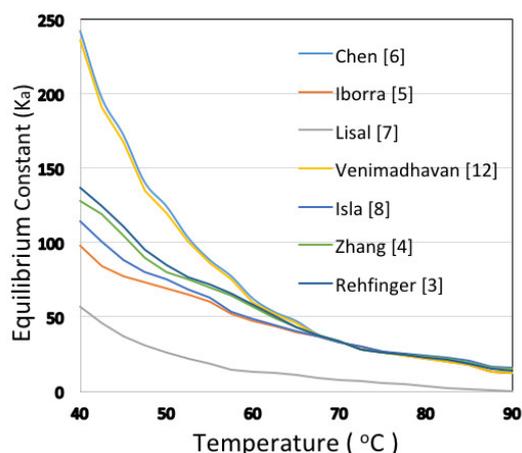
Figure 1. Values of the equilibrium constant K_a as a function of temperature.

Table 1. Properties of the catalyst Amberlyst-15.

Properties	Specifications
Porosity of Catalyst (ε_p)	0.31-0.39
Tortuosity of Catalyst (t)	0.7-1.7
Density of catalyst (kg m^{-3})	~2000
Physical Shape	spherical beads
Ionic Form	hydrogen
Moisture Content (g/g %)	~50
Particle Size (mm)	0.3-1.5
Functional Group	RSO$_3$H
Surface Area (m^2 g^{-1})	~45
Pore Diameter (Å)	~250
Acid Sites (eq(H$^+$) kg^{-1})	4.6-5.2

2.2. Thermodynamics

Etherification is an exothermic equilibrium reaction between a primary alcohol and an *iso*-olefin containing a double bond on a tertiary carbon atom (such as isobutene (iBu) under the operating temperature and pressure. Owing to the non-ideality of liquid mixtures due to their disparate polarities and equilibria, the kinetic rate expressions for the synthesis of MTBE are generally given in terms of component activities. Equilibrium and rate equations based on activities were first proposed by Rehfinger *et al.* [3] and kinetic (including the effectiveness factor) and equilibrium data from an isothermal packed-bed reactor using the catalyst Amberlyst-15 were discussed by Zhang *et al.* [4]. The activity-based equilibrium constant is expressed as:

$$K_a = \left[\frac{a_{\text{MTBE}}}{a_{\text{iBu}} \cdot a_{\text{MeOH}}}\right]_{\text{eq.}} = \left[\frac{\gamma_{\text{MTBE}}}{\gamma_{\text{iBu}} \cdot \gamma_{\text{MeOH}}} \cdot \frac{x_{\text{MTBE}}}{x_{\text{iBu}} \cdot x_{\text{MeOH}}}\right]_{\text{eq.}} \quad (6)$$

where a_{MeOH}, a_{iBu}, and a_{MTBE} are the activities of methanol, isobutene, and MTBE, respectively, while γ and x are the activity coefficients and mole fractions of these components, respectively.

The values of the equilibrium constant (K_a) published in the literature vary significantly (*Fig.1*) as a function of temperature [3-10]. Deviations may stem from the different bases used for the evaluation of the activity coefficient as well as from the operating temperature of the reactor, for example, employing primary reactors or reactive distillation columns.

2.3. Catalysis and Kinetics

The acidic cation exchange macroporous resin catalysts used commercially for the synthesis of MTBE are provided by Bayer, Dow Chemical (Rohm & Haas), Purolite, Kairui, etc. The resins are prepared by the suspension of styrene in the presence of an appropriate cross-linking agent (divinylbenzene (DVB)) for polymerization functionalized by means of sulphonation

with sulphuric or chlorosulphonic acid [11]. A reduction in volume of ~20-30% is observed because of the shift of the resin from the hydrated form (as it is generally charged in water) to a more contracted form due to a much less polar-reacting medium (a hydrocarbon/methanol mixture). The usability of the catalyst largely depends upon the process conditions, namely the type of reactor, e.g. a reactor receiving thermal support is better than adiabatic and thermal degradation with breakage of the carbon-sulphur bond (therefore, temperatures below 130 °C are recommended) and feed impurities (cations, e.g. Na, Ca, Fe, Al, Cr, Si, etc., strong N-bases like ammonia and amines, weak N-bases like acetonitrile and propionitrile, and dienes).

The rate expressions, essential kinetic parameters and thermodynamic data such as the activation energy, effectiveness of the catalyst, heat of reaction, equilibrium constant and so forth have been selected from the literature [3-14]. The rate of reaction depends substantially on two parameters: acidity (type and number of acidic sites) and accessibility (porosity, content, particle diameter and treating medium). In the homogeneous model (in the absence of the diffusion phenomena), the reaction rate can be described in terms of confined catalyst pores, where the reactant concentration is in a partition equilibrium with the corresponding concentrations in the external solution. The rate-determining step was estimated to be the surface reaction between protonated adsorbed methanol and isobutylene [3-13]. This simplifies the rate of consumption for isobutylene after assuming that polar methanol molecules are preferentially adsorbed onto the ion-exchange resin catalyst (*Table 1*) and the fraction of unoccupied sites over the catalyst surface was small as follows [4]:

$$-r_{\text{iBu}} = a_0 \cdot e^{-\frac{E_a}{RT}} \cdot \left(\frac{a_{\text{iBu}}}{a_{\text{MeOH}}} - \frac{1}{K_a} \cdot \frac{a_{\text{MTBE}}}{a_{\text{MeOH}}^2}\right) \quad (7)$$

where r_{iBu} is the rate constant of the reaction, R is the universal gas constant, E_a is the activation energy of 85.4 kJ mol^{-1} (for Amberlyst-15 this value varies between 71 and 93 kJ mol^{-1} and is influenced by not

Specification	Units	Value
Reactor Length	m	~8
Reactor Diameter	m	~3.5
LHSV	h^{-1}	~2-9
Porosity	-	~0.35
Feed Inlet Temperature	^{o}C	~40
i-C_4/MeOH Ratio	molar	~1.1
Pressure	bar	~10
Recycling Ratio	%	~15

only the type of catalyst but also by the composition of the reaction mixture); and $a_0 = 6.3 \times 10^{12}$ mol h^{-1} g^{-1}.

The effective diffusion coefficient and activation energy of methanol over Amberlyst-15 at 60 ^{o}C was estimated to be $2.3 \cdot 10^{-9}$ m^2 s^{-1} and ~35.4 kJ mol^{-1}, respectively [4]. The given value of the effective diffusion coefficient is slightly lower than the one Rehfinger and Hoffmann reported ($3.5 \cdot 10^{-9}$ m^2 s^{-1}) [3]. The catalysts Kastel CS 381 and Amberlyst CSP used in the synthesis of MTBE possess similar rate constants to Amberlyst-15, whereas Amberlyst XE 307 and Duolite ES 276 have significantly higher; and Duolite C16P and Duolite C26 have substantially lower values for their rate constants [3-15]. Every resin undergoes deactivation, if sodium ions are exchanged for their protons. Due to the acidic nature of resins, the activity is strongly reduced by the presence of basic substances and/or salts in the reaction mixture. The heat of reaction, ΔH^o(MTBE), in the liquid phase at 25 ^{o}C was reviewed by Iborra *et al.* and found to be within the range of -34 to -40 kJ mol^{-1} [5].

The rate for dimerization of isobutene (DIB formation) [4, 10] can be calculated as follows:

$$r_{DIB} = k_0 \cdot e^{\frac{-66.7kJ/mol}{R}\left(\frac{1}{T} - \frac{1}{333}\right)} \cdot \frac{a_{iBu}^2}{K_{ad} \cdot a_{MeOH} + a_{iBu}} \quad (8)$$

where the unit of r_{DIB} is mmol s^{-1} eq^{-1}, K_{ad} is the ratio of adsorption equilibrium constants, and k_0 is the frequency factor of the kinetic constant.

2.4. Reactor and Process

Generally, the multi-tubular packed-bed reactor is used exclusively as a front-end for the reactor performing the synthesis of MTBE, where the catalyst is lodged in the tubes (~10,000 tubes of diameter ~30 mm, length ~6 m, $\varepsilon = 0.4$). The cooling water flows in the shell side and can either flow co- or counter-current. The reactor column is used solely for finishing and exploits the principle of catalytic distillation possessing the normal fractionation trays with reactive trays (where the catalyst is packed) [2, 16]. Therefore, the maximum degree of isobutene conversion was achieved and reactants were separated from the product simultaneously, as MTBE has a much higher boiling temperature. Reactor parameters used for the modelling are given in *Table 2*. Almost all the commercial

etherification technologies use similar sections with regard to operation and separation, but are different in terms of type of reactors, numbers and process schemes [16-17]. The MTBE plant consists of a multi-tubular packed-bed reactor, and reactive distillation and methanol recovery sections. There are two separation towers after each reactor that recover the C_4/methanol azeotrope from the top and MTBE from the bottom, followed by the washing tower where water removes the methanol from the C_4, and then a distillation tower to separate water and methanol.

3. Reactor Modelling

Classical models of multi-tubular packed-bed reactors (pseudo-homogeneous one-dimensional) have been extensively discussed in the literature [1, 3-5]. In this study, a custom model of an MTBE water-cooled multi-tubular packed-bed reactor was built using an Aspen-based platform (ACM) with the ultimate objective of developing a complete process flow-sheet using the same method as in Refs. [18-19]. Model equations have been developed based on the following assumptions:

- steady-state operation;
- plug flow with no axial mixing;
- one dimensional as no temperature and composition gradients exist in a radial direction (perfect radial mixing);
- pseudo-homogeneous conditions for fluid - solid phase interactions: transport limitations in terms of catalyst particles are taken into account by using the concept of an effectiveness factor;
- heat transfer coefficient of the liquid phase to coolant (constant value along the reactor axis) is implemented as a sub-model. The heat transfer coefficient was evaluated under various changeable process parameters as defined the coolant inlet temperature, inlet flow rate, inlet pressure and inlet composition;
- pressure drops according to the Ergun equation in the model.

3.1. Mass and Energy Balance

The steady-state material balance in the liquid phase expressed in terms of vectors of the molar flow rates of the components in z direction is

$$\frac{d\mathbf{f}}{dz} = A\mathbf{r} \quad \text{and} \quad \mathbf{r} = \rho_b \cdot \mathbf{S}^T \cdot \mathbf{r}_{kef} \quad (9)$$

where $\mathbf{r}$ is the vector of the rate of production or consumption per unit volume of a component, $\mathbf{S}$ is the stoichiometric matrix, $\mathbf{r}_{kef}$ is the vector of effective reaction rates, A is the cross-sectional area of the reactor, $\mathbf{f}$ is a molar flow rate vector of the component, and ρ_b the bulk density of the catalyst.

The liquid side of the heat balance equation under steady-state conditions is as follows:
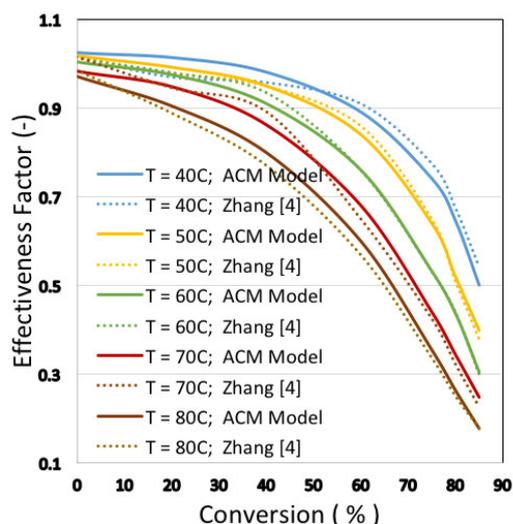
Figure 2. Effectiveness factor for the MTBE synthesis reaction based on data from Ref. [4].

$$\frac{dT}{dz} = \frac{\left| \left(\Delta \mathbf{h}_R \right)^T \cdot \mathbf{r}_{kef} \right| A - h_{fc} \pi D_t \left(T - T_c \right)}{\mathbf{f}^T \cdot \mathbf{c}_p} \quad (10)$$

where $\Delta \mathbf{h}_R$ is the vector concerning the heat of reaction, $\mathbf{c}_p$ is the vector concerning the molar specific heat of a component, T and T_c are the liquid phase and coolant absolute temperatures, respectively, h_{fc} is the liquid-to-coolant heat transfer coefficient, and D_t is the diameter of the reactor tube.

The shell side of the heat balance equation under steady-state conditions is as follows:

$$\frac{dT_c}{dz} = \pm \frac{h_{fc} \cdot \pi \cdot D_t \left(T - T_c \right)}{F_{Vcool} \cdot \rho_{cool} \cdot c_{s,cool}} \quad (11)$$

where F_{Vcool} is the volumetric flow rate of the coolant, ρ_{cool} is the density of the coolant, and $c_{s,cool}$ is the specific heat capacity of the coolant. In terms of modelling, the negative sign stands for the counter-current and the positive sign for the co-current.

The boundary conditions at the inlet of the reactor in terms of the material and energy balance differential equations are $z = 0$, $F_i(0) = F_{0,i}$, $T(0) = T_0$, $T_c(0) = T_{cool,in}$ and $T_c(R_L) = T_{cool,in}$.

3.2. Effectiveness Factor

The effectiveness factor for the synthesis of MTBE has been evaluated on the basis of data concerning the generalized Thiele modulus (ϕ_g) [3]:

$$\eta = \tanh(\phi_g) / \phi_g . \quad (12)$$

In terms of the pseudo-homogeneous model, the effectiveness factor is expressed as a function of temperature and conversion:

$$\eta = \frac{1}{x_1 \cdot e^{\frac{-x_2}{RT}} \cdot \left(1.1 - \left(\frac{\text{conversion \%}}{100} \right)^{x_3} + x_4 \right)} . \quad (13)$$

The parameters $x_1 - x_4$ have been evaluated by minimizing the absolute error between evaluations by Zhang *et al.* [4] and the values predicted by *Eq. 13*. The accuracy of the prediction is shown in *Fig.2*.

3.3. Overall Heat Transfer Coefficient

The overall heat transfer coefficient, taking into account the small value of the wall thickness, is evaluated as follows:

$$h_{fc} = \frac{1}{\left[\frac{1}{h_{fw}} + \frac{D_{te} - D_{ti}}{2 \cdot \lambda_{pipe}} + r_{fouling} + \frac{1}{h_{shell}} \right]} \quad (14)$$

where D_{ti} and D_{te} are the internal and external diameters of the reactor tube, respectively, λ_{pipe} is the thermal conductivity of the reactor tube, h_{fw} is the fluid-to-wall heat transfer coefficient, h_{shell} is the shell side (wall-to-cooling water) heat transfer coefficient, and $r_{fouling}$ is the fouling factor.

The evaluation of the fluid-to-wall heat transfer coefficient was conducted on the basis of a newly proposed correlation for the estimation of the total (wall and effective thermal conductivity effects) heat transfer coefficient [16]:

$$\text{Nu}_f = \left[3.87 - 3.77 \cdot \exp \left(\frac{-1.37}{D_{ti} / d_p} \right) \right] \cdot \text{Re}_f^{0.643} \cdot \text{Pr}_f^{0.333} . \quad (15)$$

In this case, both Nu_f and Re_f are expressed based on particle diameters. The heat transfer coefficient of the shell side is expressed as a function of Nu and Re and are both based on the external diameter of the tube, where ε_ϕ stands for a correction factor accounting for the angle between the coolant stream and reactor tubes:

$$\text{Nu}_s = 0.4 \cdot \varepsilon_\phi \cdot \text{Re}_s^{0.6} \cdot \text{Pr}_s^{0.333} . \quad (16)$$

3.4. ACM Property Estimations

The physical properties of components and mixtures like viscosity, density and specific heat, were estimated by Aspen Properties (using UNIFAC - Dortmund property package). The ".appdf" file prepared by Aspen Properties is the one called in ACM for seamless transfer of properties. The kinetic sub-model helps in terms of the calculation of reaction heats using the Aspen Properties database.

Table 3. Typical base-case operating conditions and results for the primary reactor.

Specification	Units	Value
tube length	m	6
tube diameter (ID)	mm	21
number of tubes	-	10,000
porosity	-	0.33
feed inlet temperature	ºC	50
isobutene/MeOH ratio	molar	1.1
pressure	bar	8
coolant inlet temperature	ºC	45
feed flow rate	kmol h^{-1}	2,000
isobutene mole fraction	-	0.35
ΔP	bar	0.723
conversion	%	84.7
MTBE selectivity	%	97.86

3.5. Performance Parameters

Reactor performance is evaluated by the following equations:

$$\text{Conversion}(z) = \frac{F_0^{\text{key\_reactant}} - F_z^{\text{key\_reactant}}}{F_0^{\text{key\_reactant}}} \qquad (17)$$

$$\text{Selectivity}(z) = \frac{F_z^{\text{key\_product}} - F_0^{\text{key\_product}}}{F_0^{\text{key\_reactant}} - F_z^{\text{key\_reactant}}} \qquad (18)$$

$$\text{Yield}(z) = \text{Conversion}(z) \cdot \text{Selectivity}(z) \qquad (19)$$

where z stands for the axial coordinate.

4. Model Predictions and Analysis

ACM is the preferred choice for robust reactor modelling. Its equation-oriented modelling platform can be easily exported to Aspen Plus process flow-sheets. The coding of a multi-tubular packed-bed reactor in terms of the synthesis of MTBE was conducted in a modular form. The main reactor model defines the constitutive equations in the bulk phase and sub-models
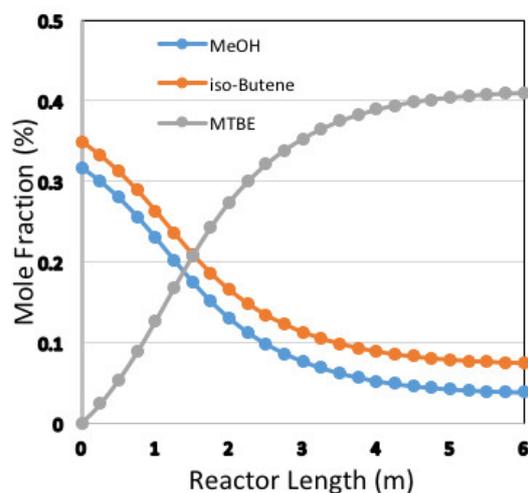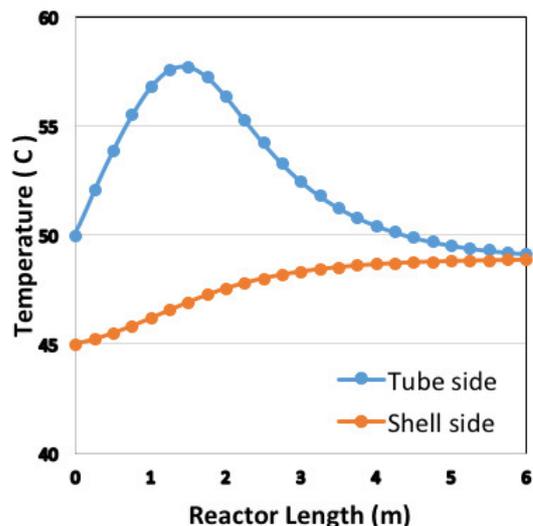
Figure 4. Temperature profiles of the reactor and coolant.

in terms of the reaction kinetics, the estimation of the heat transfer coefficient, and the development of the pellet design. The normal operating conditions for the primary reactor were selected as the base case in terms of modelling (Table 3), where MTBE productivity is ~50 T h^{-1}. The molar concentration profile of the reactants and product along the axis of the reactor is shown in Fig.3. The full length of the reactor is used for the synthesis of MTBE. Fig.4 shows the temperature profiles of the reactor and coolant.

The temperature sensitivity is controlled by keeping the temperature difference between the coolant and feed temperatures constant (Fig.5). It was observed that due to the exothermic nature of the reaction, the maximum temperature increased significantly with the

Figure 3. Molar concentration profile along the length of the reactor.
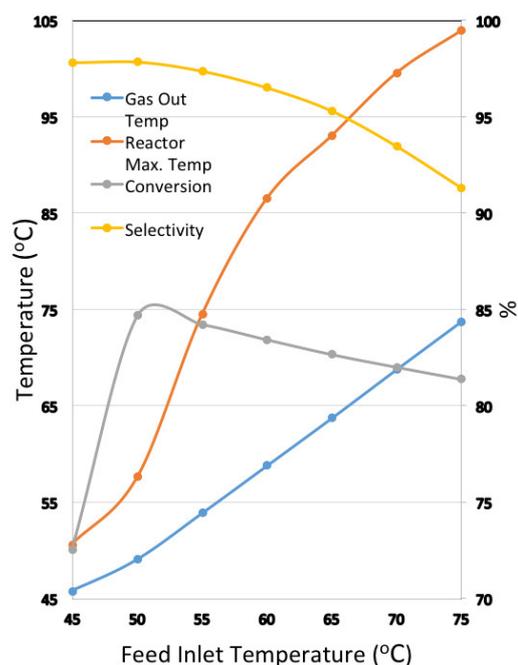
Figure 5. Temperature sensitivity by varying the feed temperature and keeping constant the temperature difference between the coolant and feed temperatures.

Table 4. Dependence of conversion (%), selectivity (%) and the maximum temperature of the reactor (T_{max}) on the isobutene/methanol molar ratio (iBu/MeOH).

iBu/MeOH	0.8	0.9	1.0	1.1	1.2	1.3
conversion	84.7	85.4	85.5	84.6	80.7	76.7
selectivity	98.1	98.1	98.1	97.9	97.1	95.4
T_{max}, ºC	56.1	56.5	56.9	57.7	59.5	62.0

increase in reaction temperature. At a constant pressure and feed flow rate, the increase in the reaction temperature led to an outer mass transfer limitation that strongly affects the rate of conversion. At the same time the selectivity also decreased due to a significant increase in the maximum temperature of the reactor (product degradation) and the maximum rate of conversion was achieved in almost ~30% of the reactor. The isobutylene/methanol molar ratio is one of the key operating parameters and is always kept higher than its stoichiometric value. *Table 4* shows that by deviating from the stoichiometric ratio the effect on the rate of conversion and selectivity also decreases with the increase in the isobutylene/methanol molar ratio.

The predictions according to reactor modelling were found to be in good agreement with data from the literature. The reaction must reach an equilibrium at the rear end of the lead reactor. The estimated effectiveness factor is 0.75 which was also used in the model. The possible explanation for the occurrence of minor discrepancies could be the use of a different catalyst or errors in terms of experimental measurements. It was observed that the maximum degree of productivity corresponded to an isobutene/MeOH molar ratio of close to 1 and a feed inlet temperature of between 50 and 55 ºC. However, it is necessary to synchronize this with the secondary reactor and other unit operations.

5. Conclusion

An ACM-based pseudo-homogeneous model with regard to the synthesis of MTBE using an industrial multi-tubular packed-bed (methyl-*tert*-butyl-ether) reactor has been developed for enhancing operation strategies. The UNIFAC - Dortmund property package was used for reactor modelling. The effectiveness factor was implemented as a function of the reaction temperature. The model was validated using data from the literature. Various sensitivity evaluations were conducted to determine the operational optimization and maximization of MTBE production under different operating parameters. The model was able to predict reaction behaviour and produce temperature and concentration profiles along the length of the reactor. Sensitivity studies were able to calculate the optimum temperature, feed flow rate, methanol/isobutylene ratio as well as heat removal rate of the reactor and thus provide insights into a reasonable operational strategy.

SYMBOLS

A	cross-sectional area of the reactor
a	activity
$a_{MeOH}, a_{iBu}, a_{MTBE}, a_{inert}$	
	activities of methanol, isobutene, MTBE and inert isobutane, respectively
a_0	6.3×10^{12} mol h^{-1} g^{-1}
$\mathbf{c}_p$	molar specific heat vector of a component
$c_{s,cool}$	specific heat capacity of the coolant
D_t	diameter of the reactor tube
D_{ti}, D_{te}	internal and external diameters of the reactor tube, respectively
E_a	activation energy in kJ mol^{-1}
F_{Vcool}	volumetric flow rate of the coolant
$\mathbf{f}$	molar flow rate vector of a component
h_{fc}	liquid-to-coolant heat transfer coefficient
h_{fw}	fluid-to-wall heat transfer coefficient
h_{shell}	shell side (wall-to-cooling water) heat transfer coefficient
$\Delta \mathbf{h}_R$	heat of reaction vector
γ	activity coefficient
K_a	equilibrium constant (based on activities)
K_{ad}	ratio of adsorption equilibrium constants
$K_{MeOH}, K_{iBu}, K_{MTBE}, K_{inert}$	
	adsorption equilibrium constants for methanol, isobutene, MTBE and inert isobutane, respectively
k_0	frequency factor of the kinetic constant
k_r	reaction rate constant
λ_{pipe}	thermal conductivity of the reactor tube
R	universal gas constant
$\mathbf{r}$	vector of the rate of production or consumption per unit volume of a component
$\mathbf{r}_{kef}$	vector of effective reaction rates
$r_{fouling}$	fouling factor
ρ_b	bulk density of the catalyst
ρ_{cool}	density of the coolant
$\mathbf{S}$	stoichiometric matrix
T, T_c	absolute temperatures of the liquid phase and coolant, respectively
x	mole fraction

Acknowledgement

REFERENCES

[1] Nawaz, Z.: Light alkane dehydrogenation to light olefin technologies: A comprehensive review, *Rev. Chem. Engng.*, 2015 **31**(5), 413–436 DOI 10.1515/revce-2015-0012

[2] DiGirolamo, M.; Sanfilippo, D.: Etherification: Process to improve the quality of distillates, in Beccari M.; Romano, U.; eds. Encyclopaedia of hydrocarbons (ENI S.p.A and Istituto della Enciclopedia Italiana fondata da Giovanni Treccani S.p.A, Roma, Italy) 2006 Vol. II. pp. 193–209

[3] Rehfinger, A.; Hoffmann, U.: Kinetics of MTBE liquid phase synthesis catalyzed by ion-exchange resin. I. Intrinsic rate expression in liquid phase activities, *Chem. Eng. Sci.*, 1990 **45**(6), 1605–1617 DOI 10.1016/0009-2509(90)80014-6

[4] Zhang, T.; Datta, R.: Integral analysis of MTBE synthesis kinetics, *Ind. Eng. Chem. Res.*, 1995 **34**, 730–740 DOI 10.1021/ie00042a004

[5] Iborra, M.; Tejero, J.; Ben El-Fassi, M.; Cunill, F.; Izquierdo, J.F.; Fite, C.: Experimental study of the liquid phase simultaneous synthesis of MTBE and TBA, *Ind. Eng. Chem. Res.*, 2002 **41**, 5359–5365 DOI 10.1021/ie010640q

[6] Chen, F.; Huss, R.S.; Doherty, M.F.; Malone, M.F.: Multiple steady-states in reactive distillation: kinetic effects, *Comp. Chem. Engng.*, 2002 **26**, 81–93 DOI 10.1016/S0098-1354(01)00750-5

[7] Lisal, M.; Smith, W.R.; Nezbeda, I.: Molecular simulation of multicomponent reaction and phase equilibria in MTBE ternary system, *AIChE J.*, 2000 **46**(4), 867–875 DOI 10.1002/aic.690460419

[8] Isla, M.; Irazoqui, H.: Modeling, analysis and simulation of MTBE reactive distillation column, *Ind. Eng. Chem. Res.*, 1996 **35**, 2696–2708 DOI 10.1021/ie9505930

[9] Venimadhavan, G.; Malone, M.F.; Doherty, M.F.: Bifurcation study of kinetic effects in reactive distillation, *AIChE J.*, 1999 **45**(3), 546–556 DOI 10.1002/aic.690450311

[10] Oktar, N.; Murtezaoglu, K.; Dogu, T.; Dogu, G.: Dynamic analysis of adsorption equilibrium and rate parameters of reactants and products in MTBE, ETBE and TAME production, *Can. J. Chem. Eng.*, 1999 **77**, 406–412 DOI 10.1002/cjce.5450770229

[11] Girolamo, M.; Tagliabue, L.: MTBE and alkylate co-production: fundamentals and operating experience, *Catal. Today*, 1999 **52**, 307–319 DOI 10.1016/S0920-5861(99)00084-X

[12] Ancilotti, F.; Fattore, V.: Oxygenate fuels: Market expansion and catalytic aspect of synthesis, *Fuel Proc. Technol.*, 1998 **57**, 163-194 DOI 10.1016/S0378-3820(98)00081-2

[13] Girolamo, M.; Lami, M.; Marchionna, M.; Pescarollo, E.; Tagliabue, L.; Ancilotti, F.: Liquid phase etherification/dimerization of isobutene over sulfonic acid resins, *Ind. Eng. Chem. Res.*, 1997 **36**, 4452–4458 DOI 10.1021/ie9700932

[14] Miracca, I.; Tagliabue, L.; Trotta, R.: Multitubular reactors for etherifications, *Chem. Engng. Science*, 1996 **51**, 2349–2358 DOI 10.1016/0009-2509(96)00091-7

[15] Panneman, H.J.; Beenackers, A.: Influence of the isobutene/methanol ratio and of the MTBE content on the reaction rate of the synthesis of MTBE, *Ind. Eng. Chem. Res.*, 1995 **34**, 3817–3825 DOI 10.1021/ie00038a019

[16] Mariani, N.J.; Martinez, O.M.; Barreto, G.F.: Evaluation of heat transfer parameters in packed beds with cocurrent downflow of liquid and gas, *Chem. Engng. Science*, 2001 **56**, 5995–6001 DOI 10.1016/S0009-2509(01)00225-1

[17] Elkanzi, E.M.: Optimization of MTBE synthesis in a packed-bed reactor system, *Chem. Engng. Proc.*, 1996 **35**, 131–139 DOI 10.1016/0255-2701(95)04122-2

[18] Nawaz, Z.: Dynamic modeling of CATOFIN® packed-bed isobutane dehydrogenation reactor for operational optimization, *Int. J. Chem. Reactor Engng.*, 2016 **14**(1), 491–515 DOI 10.1515/ijcre-2015-0087

[19] Nawaz, Z.: Heterogeneous reactor modeling of an industrial multitubular packed-bed ethylene oxide reactor, *Chem. Engng. Technol.*, 2016 **39**(10), 1845–1857 DOI 10.1002/ceat.201500603