Comparison of hydrocarbons synthesis mathematical models for dimethyl ether catalytic transformation process

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Abstract. A comparison of mathematical models applicable for hydrocarbons formation process by catalytic transformation of dimethyl ether is discussed in the article. Dimethyl transformation is complex catalytic process used for aliphatic, aromatic hydrocarbons and olefins formation. The process can be realized for transformation of renewable and waste organic resources into fuel range hydrocarbons. Proper mathematical modelling for this complex process can play a driver role for process productivity intensification. A mathematical models proposed by different authors are discussed and compared to self-developed Eley-Rideal based model. Advantages and models limitations are discussed in the article.

1. Introduction

Mathematical modeling of complex chemical processes can be considered as key factor to provide process optimization and increasing of products yields [1-4]. Dimethyl ether transformation to hydrocarbons is one of the chemical engineering processes that allow to utilize biomass, wastes and other organic and inorganic carbon containing feed stocks to produce valuable hydrocarbons (Figure 1).

Figure 1. Biomass, wastes and other carbon containing feed stock processing in hydrocarbons via dimethyl ether transformation process

However process complexity does not allow wide application of this process due to different technological and economic problems [3-6]. To overcome this difficulties application of reliable process mathematical models is needed. The reaction of dimethyl ether transformation contains more than one hundred reaction species taking part in process, however, only several groups are taken in to account due to their high rate of accumulation [6]. Typically dimethyl transformation process includes following reactions: a) formation of light olefins, b) formation of benzene, toluene, xylene (BTX)
fraction c) formation of polymethylbenzenes, d) formation of polyaromatic hydrocarbons, c) formation of aliphatic hydrocarbons (Figure 2).

Figure 2. Dimethyl ether transformation scheme

Mathematic modeling of dimethyl ether transformation process typically provides by application two different models types: a) simplified models using products lumps, b) kinetics mathematical models taking into account individual reaction steps. Lumped models characterized by application simplicity and short duration of calculations, however lack of physical meaning for obtained reaction rate constants is obvious disadvantage of this model types [7-9]. From the other side large kinetics models taking in to account individual steps are more precise, however much more time needed for calculations.
The objective of this paper is to evaluate precision of most frequently used mathematical lumped models of dimethyl ether to hydrocarbons transformation processes and to compare results with self-developed lumped model using the same experimental data for experiments.

2. Methodology

2.1. Dimethyl ether transformation to hydrocarbons methodology

On the first step of the investigation catalytic dimethyl ether transformation experiments were performed. Experiments were made in laboratory fixed-bed reactor set-up presented on figure 3. Methanol was fed with a flow rate of 0.01-0.3 ml/min by pump 7 forming a vapor mixture in the mixer 6 filled with glass beads, where flow was heated to 350 °C temperature. A gas mixture of methanol and nitrogen enters the dimethyl ether forming reactor 8, also heated to 350 °C, filled with aluminum oxide (6.4 g). Dimethyl ether which was separated from water and methanol in the condenser 9 enters in the hydrocarbons synthesis reactor 10 where flow was heated to the reaction temperature (350, 400, 450, 500 °C). The reactor was filled with zeolite H-ZSM-5 (HKC corp, Hong-Kong) (6.4 g). Gas samples were taken once per hour by an automatic sampling valve and injected in chromatograph 2000M (Russia). Liquid samples were taken every 12 hours, the sample mass and hydrocarbons concentrations were determined. The analysis of liquid hydrocarbons was performed using a Shimadzu HPMS2010 gas mass spectrometer and gas chromatographs 4000M (Russia) in accordance with ISO R 52714-2007. Determined products concentrations were used for mathematic modeling.

![Figure 3. Scheme of reaction set-up for obtaining data for dimethyl ether to liquid hydrocarbons transformation.](image)

2.2. Methodology for mathematical modeling of dimethyl ether transformation

To find model parameters it is needed to solve mass conservation equation for each reaction. The mass conservation equation can be calculated according to formula 1.

\[
\frac{dX_i}{d\xi} = \frac{Z(1-\varepsilon)}{u_e} \rho \frac{RT}{pM} \frac{m_f}{m_{v}} \tau_{10} - \frac{X_i \, du}{U \, d\xi}
\]  

(1)
For solving system of ordinary differential equations a Mat Lab software was used. The gas linear velocity at various reactor positions was calculated by finite $\Delta u/\Delta \xi$ increments between two very close positions in the reactor. The model calculations were provided using objective function (2) [2, 5, 6, 9].

\[
OF = \frac{\Sigma_{i=1}^{n} \Sigma_{j=1}^{\text{exp}} (x_{i,j} - x_{i,\text{calc},j})^2}{n_{\text{exp}}}
\]  

Objective function was minimized as square of deviations between experimental and calculated values of lumps concentrations.

3. Results and discussion

Several models were used for mathematical modeling of dimethyl ether catalytic conversion to hydrocarbons, including the most frequently used model developed by prof. Chen and Reagan. This model of dimethyl ether transformation includes the sums of the initial oxygen-containing substances, as well as reaction products (3).

\[
\text{CH}_3\text{OCH}_3 \xrightarrow{k_1} \text{Light olefins} \xrightarrow{k_2} \text{Aromatic and aliphatic hydrocarbons}
\]  

The professor Chen and Reagan model explains the increase in the rate of dimethyl ether consumption during the accumulation of hydrocarbons. This model can be expressed by the system of equations 4.

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
A + B & \xrightarrow{k_2} B \\
B & \xrightarrow{k_3} C
\end{align*}
\]  

Where A is the mass fraction of CH$_3$OCH$_3$, wt. %
B is the mass fraction of light olefins with the number of carbon atoms of 1-4, wt. %
C is the mass fraction of aromatic and aliphatic compounds.

The system of equations consists of two differential equations and one algebraic equation 5-6 can describe this mathematical model.

\[
\begin{align*}
\frac{dA}{dt} &= -k_1A - k_2AB \\
\frac{dB}{dt} &= k_1A - k_3AB \\
C &= 1 - A - B
\end{align*}
\]  

The determination of the constants of the system of equations (Table 1) was carried out by the method described in previous section. The evaluation of the results was carried out by calculating constant deviation and plotting of the model and experiments results (Figure 5).

| №  | Constants | Units | Values | Value deviations |
|----|-----------|-------|--------|------------------|
| 1  | $k_1$     | h$^{-1}$ | 15.2   | ±0.9             |
| 2  | $k_2$     | h$^{-1}$ | 137.0  | ±18.2            |
| 3  | $k_3$     | h$^{-1}$ | 16.4   | ±4.1             |
| 4  | $E_1$     | kJ/mol | 142.4  | ±12.4            |
| 5  | $E_2$     | kJ/mol | 182.1  | ±20.1            |
| 6  | $E_3$     | kJ/mol | -5.4   | ±45.6            |

To develop a more reliable model of dimethyl ether into hydrocarbons catalytic transformation process, the equations of the cycle mechanism - “hydrocarbon pool” were used. A system of equations was obtained (8). The model takes into account the following components: A - dimethyl ether and
methanol, B - ethylene, C - propylene, D - butene, E - the sum of saturated hydrocarbons with the number of carbon atoms from two to four, I - polymethylbenzenes, G - the sum of hydrocarbons with the number of carbon atoms more than four.

\[ \begin{align*}
A & \xrightarrow{k_1} I \\
I & \xrightarrow{k_2} B \\
I & \xrightarrow{k_3} C \\
A + C & \xrightarrow{k_4} D \\
C & \xrightarrow{k_5} E \\
D & \xrightarrow{k_6} E \\
A + D & \xrightarrow{k_8} G \\
C + C & \xrightarrow{k_9} G \\
C + D & \xrightarrow{k_8} G \\
D + D & \xrightarrow{k_6} G
\end{align*} \]  

The following system of differential equations can be formed (9-16).

\[ \begin{align*}
\frac{dA}{d\tau} &= -k_1A - k_2AC - k_6AD \\
\frac{dB}{d\tau} &= \frac{k_1k_2A}{k_2 + k_3} \\
\frac{dC}{d\tau} &= \frac{k_1k_3A}{k_2 + k_3} - k_4AC - k_5C - k_6C^2 - k_6CD \\
\frac{dD}{d\tau} &= k_4AC - k_5D - k_6AD - k_6CD - k_6D^2 \\
\frac{dE}{d\tau} &= k_5C + k_5D \\
\frac{dI}{d\tau} &= k_1A - k_2I - k_3I = 0 \\
I &= \frac{k_1A}{k_2 + k_3} \\
G &= 1 - A - B - C - D - E
\end{align*} \]

The determination of equations system constants (Table 2) was carried out by the method described in previous section.

| №  | Constants | Units | Values | Value deviations |
|----|-----------|-------|--------|------------------|
| 1  | $k_1$     | h$^{-1}$ | 20.4   | ±0.8             |
| 2  | $k_2$     | h$^{-1}$ | 0.7    | ±0.1             |
| 3  | $k_3$     | h$^{-1}$ | 2.1    | ±0.5             |
| 4  | $k_4$     | h$^{-1}$ | 154.3  | ±15.4            |
| 5  | $k_5$     | h$^{-1}$ | 32.5   | ±4.2             |
| 6  | $k_6$     | h$^{-1}$ | 124.3  | ±21.4            |
| 7  | $E_1$     | kJ/mol  | 175.4  | ±10.2            |
| 8  | $E_2$     | kJ/mol  | 45.2   | ±4.2             |
| 9  | $E_3$     | kJ/mol  | 87.3   | ±16.4            |
| 10 | $E_4$     | kJ/mol  | 125.6  | ±24.1            |
| 11 | $E_5$     | kJ/mol  | 79.5   | ±20.5            |
| 12 | $E_6$     | kJ/mol  | 88.9   | ±17.4            |
Self-developed model represents extended lumped kinetic model of dimethyl ether to hydrocarbons transformation process based on Eley-Rideal catalytic mechanism derivation [1]. Developed model (Figure 4) includes nineteen reactions, ten of them can take place utilizing dimethyl ether or methanol as reaction feed stock. Reaction rate constants $k_1$-$k_6$ are responsible for olefins formation rates, reaction rate constants $k_{1.1}$-$k_{8.2}$ are responsible for aliphatic hydrocarbons formation rate and $k_7$-$k_{11}$ are responsible for aromatic hydrocarbons formation rates. Substrate absorbance constants $Q_1$-$Q_6$ are responsible for olefins dimethyl ether and olefins adsorption over catalysts surface over, adsorption constants $Q_{7.1}$-$Q_{8.1}$ are responsible aromatic adsorption over catalysts surface.

![Figure 4. Kinetics scheme of dimethyl ether transformation into hydrocarbons (k – reaction rates constant, Q – substrate adsorption constants)](image)

The kinetic equation for dimethyl ether transformation rate can be denoted as equation containing eleven rate and adsorption constants. Resolving of this equation can be done by numerical modeling and optimization. The kinetic equation for liquid hydrocarbons formation rate can be denoted as equation 2 containing seven rate and three adsorption constants.

\[
\frac{d(\text{Hydr. carb})}{dt} = k_5 \frac{Q_5[C_5H_{10}][CH_3OCH_3]}{1 + Q_5[C_5H_{10}]} - k'_5 \frac{Q_5[C_6H_{12}][CH_3OH]}{1 + Q_5[C_6H_{12}]}
\]

\[
+ k_{5.2} \frac{Q_5[C_5H_{10}]}{1 + Q_5[C_5H_{10}]} - k_{6.1} \frac{Q_6[C_6H_{12}]}{1 + Q_6[C_6H_{12}]} + k_{6.2} \frac{Q_6[C_6H_{12}]}{1 + Q_6[C_6H_{12}]}
\]

\[
+ k_{10} \frac{Q_{10}[C_6H_4(CH_3)_2][CH_3OCH_3]}{1 + Q_{10}[C_6H_4(CH_3)_2]} - k'_{10} \frac{Q_{10}[C_6H_4(CH_3)_2][CH_3OH]}{1 + Q_{10}[C_6H_4(CH_3)_2]} (17)
\]

Calculated rate constants and adsorption constants are presented in table 1, the relative constant deviation doesn’t exceed ten percent that can be considered as reliable value. Providing kinetics modeling for dimethyl ether to hydrocarbons transformation process in temperature range 350-500°C
allowed to calculate apparent activation energy and preexponential factors for Arrhenius equation (Table 3).

**Table 3.** Calculated apparent activation energies, rate, adsorption constants and their deviations for dimethyl ether transformation to hydrocarbons processes

| Constant | Constant dimension | Constant value | Constant deviation | Apparent activation energy, kJ/mol | Apparent activation energy deviation |
|----------|--------------------|----------------|--------------------|-------------------------------------|--------------------------------------|
| k₁       | h⁻¹                | 359.8          | 17.99              | 46.3                                | 2.315                                |
| k₁₁      | h⁻¹                | 6.4            | 0.32               | 38.2                                | 1.91                                 |
| Q₁       | h⁻¹                | 0.24           | 0.012              | 4.1                                 | 0.205                                |
| k₂       | h⁻¹                | 21405.0        | 1070.25            | 62.6                                | 3.13                                 |
| k₂’      | h⁻¹                | 14247.2        | 712.36             | 57.9                                | 2.895                                |
| k₃,₁     | h⁻¹                | 2335.6         | 116.78             | 64.1                                | 3.205                                |
| Q₂       | h⁻¹                | 0.16           | 0.008              | 2.3                                 | 0.115                                |
| k₃       | h⁻¹                | 1169.9         | 58.495             | 48.6                                | 2.43                                 |
| k₃’      | h⁻¹                | 1079.3         | 53.965             | 32.7                                | 1.635                                |
| k₄,₁     | h⁻¹                | 257.6          | 12.88              | 24.9                                | 1.245                                |
| Q₃       | h⁻¹                | 1.10           | 0.055              | 3.8                                 | 0.19                                 |
| k₄       | h⁻¹                | 3415.5         | 170.775            | 54.2                                | 2.71                                 |
| k₄’      | h⁻¹                | 21822.4        | 1091.12            | 62.7                                | 3.135                                |
| k₅,₁     | h⁻¹                | 486.4          | 24.32              | 28.6                                | 1.43                                 |
| Q₄       | h⁻¹                | 0.40           | 0.02               | 2.6                                 | 0.13                                 |
| k₅       | h⁻¹                | 11.3           | 0.565              | 24.9                                | 1.245                                |
| k₅’      | h⁻¹                | 1890.0         | 94.5               | 35.6                                | 1.78                                 |
| k₆,₁     | h⁻¹                | 8336.4         | 416.82             | 42.9                                | 2.145                                |
| k₆,₂     | h⁻¹                | 2229.7         | 111.485            | 52.1                                | 2.605                                |
| Q₅       | h⁻¹                | 5.0            | 0.25               | 4.9                                 | 0.245                                |
| k₆       | h⁻¹                | 11.3           | 0.565              | 24.9                                | 1.245                                |
| k₆’      | h⁻¹                | 70.49          | 3.5245             | 18.6                                | 0.93                                 |
| k₇,₁     | h⁻¹                | 2941.2         | 147.06             | 53.7                                | 2.685                                |
| k₇,₂     | h⁻¹                | 3861.9         | 193.095            | 36.9                                | 1.845                                |
| Q₆       | h⁻¹                | 5.73           | 0.2865             | 5.2                                 | 0.26                                 |
| k₇       | h⁻¹                | 9.9            | 0.495              | 24.1                                | 1.205                                |
| k₇’      | h⁻¹                | 83.7           | 4.185              | 19.4                                | 0.97                                 |
| Q₇       | h⁻¹                | 2.52           | 0.126              | 1.6                                 | 0.08                                 |
| k₈,₁     | h⁻¹                | 40.5           | 2.025              | 15.2                                | 0.76                                 |
| k₈,₂     | h⁻¹                | 15.8           | 0.79               | 25.7                                | 1.285                                |
| Q₈       | h⁻¹                | 4.1            | 0.205              | 4.1                                 | 0.205                                |
| k₉       | h⁻¹                | 719.6          | 35.98              | 46.3                                | 2.315                                |
| k₉’      | h⁻¹                | 807.8          | 40.39              | 31.2                                | 1.56                                 |
| Q₉       | h⁻¹                | 3.47           | 0.1735             | 2.9                                 | 0.145                                |
| k₁₀      | h⁻¹                | 1548.7         | 77.435             | 62.3                                | 3.115                                |
| k₁₀’     | h⁻¹                | 239.2          | 11.96              | 53.1                                | 2.655                                |
| Q₁₀      | h⁻¹                | 4.04           | 0.202              | 3.8                                 | 0.19                                 |
| k₁₁      | h⁻¹                | 1311.8         | 65.59              | 62.1                                | 3.105                                |
| k₁₁’     | h⁻¹                | 2156.6         | 107.83             | 35.9                                | 1.795                                |
| Q₁₁      | h⁻¹                | 0.25           | 0.0125             | 4.7                                 | 0.235                                |

k – reaction rates constant, Q – substrate adsorption constants
To compare experimental data of liquid hydrocarbons formation rate on contact time of catalysts and dimethyl ether and values obtained during modeling a figure 5 was plotted.

![Figure 5. Comparison of Chen and Reagan, hydrocarbon-pool and self-developed Eley-Rideal based model for correlation of liquid hydrocarbons formation rate on contact time for catalyst and dimethyl ether.](image)

Calculated objective function for Chen and Reagan model was found to be 0.15% and showed less accuracy compare to “hydrocarbon pool” model where objective function was found to be 0.04% and Eley-Rideal based model where objective function was found to be 0.03%. Comparison of hydrocarbon pool” and Eley-Rideal based models shows that Eley-Rideal model characterized by slightly lower deviation from experimental plots. However Eley-Rideal model reaction rate and adsorption coefficients have physical meaning that can be attributed to exact reaction groups and adsorption of reaction species over surface of active sites.

4. Conclusions

Chen and Reagan, “hydrocarbon pool” and Eley-Rideal based models were compared in mathematical modeling of dimethyl ether to hydrocarbons transformation process. Sufficient reliability of compared models was found. However Eley-Rideal based model is more accurate and characterized by presence of physical meaning for found reaction rate constants. Proposed Eley-Rideal based model includes main transformation steps taking part during transformation. Application of this model allows to calculate apparent activation energy and preexponential factors values for main groups of chemical processes taking place during dimethyl ether transformation process.

5. Appendix A: Nomenclature

- M – average molecular weight of water-free products, (kg/kmol),
- P – partial pressure of water free products (Pa),
- \( r_{o} \) – hydrocarbons lump reaction rate at zero time on steam, \((g(lump \ i)g(total \ mass))/(g(Cat)g(water \ free \ products)h))\),
- R – gas constant \((J/(mol \ K))\),
- \( X_{i} \) – weight fraction of lump \( i \) on water free basis,
T – process temperature (K),

\( u \) – gas linear velocity (m/h)

\( \epsilon \) – bulk porosity

\( \xi \) – longitudinal coordinate,

\( \rho \) – catalyst density (kg/m\(^3\)),

\( \tau \) – contact time, (kg(Cat)\(*h/kg(DME)

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