

Mathematical model of dimethyl ether catalytic transformation to liquid hydrocarbons process

Valentin Doluda, Adel Latypova, and Olga Lefedova

Abstract—Catalytic transformation of dimethyl ether to liquid hydrocarbons is process of special interest for industry and scientific community. This process can be applied for liquid hydrocarbons production from biomass or waste organic products by consecutive biomass transformation to syngas, further methanol and dimethyl ether synthesis and dimethyl catalytic transformation to hydrocarbons. The process is characterized by high complexity therefore development of its model is of great interest as for increasing of target products yield as for reactor modelling and heat management. The article is devoted to the development of extended lumped kinetic model of dimethyl ether to hydrocarbons transformation based on Eley-Rideal catalytic mechanism derivation. A series of differential equations were developed and numerically solved using Levenberg Marquardt algorithm. Model includes carbon chain and carbon cycle forming. Developed kinetic model allowed to determined specific activation energies and exponentials factors for lumped reactions. The relative deviation of found specific activation energy and preexponential factors varies from 5 to 12% depends on calculations accuracy and components concentrations. Developed model characterize by not high consumption of computational time and its applicability for reactor modelling and heat management.

Keywords—dimethyl ether, transformation, mathematic, model, kinetics.

I. INTRODUCTION

DIMETHYL ether catalytic transformation is a complex chemical process consist of series consecutive and parallel reactions results in formation of olefins, aromatic and aliphatic hydrocarbons. Dimethyl ether catalytic transformation to liquid hydrocarbons can be considered as promising way for biomass conversion into valuable substances through biomass gasification into syngas, further methanol synthesis from syngas, methanol transformation to dimethyl ether and final dimethyl ether transformation into liquid hydrocarbons¹. Complexity of dimethyl ether catalytic transformation process requires development of appropriate

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kinetic model to increase liquid hydrocarbons yield^{2, 3}. Development of proper kinetic model can serve a good base for process intensification and increasing products yield⁴. Beside developed kinetic model should be suitable for reactor set-up modeling to determine heat release and transfer along catalyst bed⁵. Today there are two approaches to develop kinetic model of dimethyl ether to hydrocarbons transformation process the first one is formation of short lumped model, taking in to account only main joint hydrocarbons fractions and the second approaches includes development of exhaustive model taking in to account all possible chemical reactions⁶. The first approach is applicable for optimization of target products yield, however it is practically impossible to use such models for reactor set-ups modeling especially in terms of reactor heat management. On the contrary exhaustive models are suitable for this purpose, however, this type of models require a lot of computational time. Therefore development of extended lumped kinetic models applicable for reactor heat management and characterized by short computational time is in focus of scientific community.

II. METHODOLOGY

Kinetic experiments were provided in laboratory tube reactor set-up presented on figure 1. 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 and enters in the hydrocarbons synthesis reactor 10 where flow was heated to the desired 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 was taken at a frequency of once per hour by an automatic sampling chromatograph. Liquid samples were taken every 12 hours, the mass, the hydrocarbons concentration was determined. The analysis of liquid hydrocarbons was carried out using a Shimadzu HPMS2010 gas chromatography mass spectrometer, crystal chromatograph 4000M and crystal 2000M in accordance with ISO R 52714-2007. Determined products concentrations were used for Kinetics calculations were provided using MatLab software. Levenberg-Marquardt algorithm was used to determine reaction rate constants. Apparent activation energies

and reaction rates pre-exponential factors were calculated using Arrhenius equation.

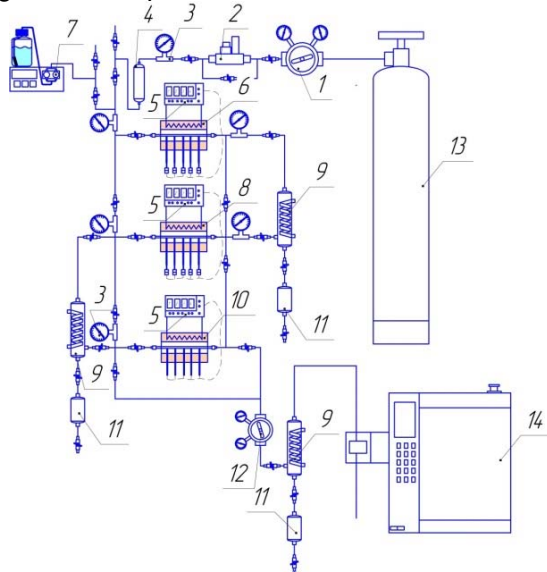


Figure 1: Scheme of reaction set-up for obtaining kinetics data on dimethyl ether to liquid hydrocarbons transformation. (1 – pressure reducer of nitrogen, 2 – mass-flow controller for nitrogen dosage, 3 – manometer, 4 – buffer tank, 5 – temperature controller, 6 – mixer-evaporator, 7 – pump for methanol feeding, 8 – reactor for dimethyl ether synthesis, 9 – condenser, 10 – hydrocarbons synthesis reactor, 11 – fraction collector, 12 – pressure regulator, 13 – nitrogen tank, 14 – gas chromatograph)

The mass conservation equation can be calculated according to formula 1.

$$\frac{dX_i}{d\xi} = \frac{Z(1-\epsilon)}{u\epsilon} \rho \frac{RT}{pM} \frac{m}{m_T} r_{io} - \frac{X_i}{U} \frac{du}{d\xi} \quad (1)$$

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).

$$OF = \frac{\sum_{i=1}^n \sum_{j=1}^{n_{exp}} (X_{i,j} - X_{i(calc),j})^2}{n_{exp}} \quad (2)$$

Objective function was minimized as square of deviations between experimental and calculated values of lumps concentrations⁵⁻⁸.

III. RESULTS AND DISCUSSIONS

Olefins, aliphatic and aromatic hydrocarbons were found to be main products of catalytic dimethyl ether transformation process, also formation of methanol, hydrogen, carbon oxide and carbon monoxide was noticed. Olefins fraction consist mainly from ethylene, propylene and butylene⁹. Aliphatic fraction of hydrocarbons consist of methane, ethane, propane, butane, i-butane, C5 and C6 aliphatic isomers of hydrocarbons. Fraction of aromatic hydrocarbons consist of benzene, toluene, methylbenzene, xylenes, polymethylbenzenes and traces of naphthalene and anthracite.

Product distribution and previously developed kinetic models allows to create extended lumped kinetic scheme (Figure 2).

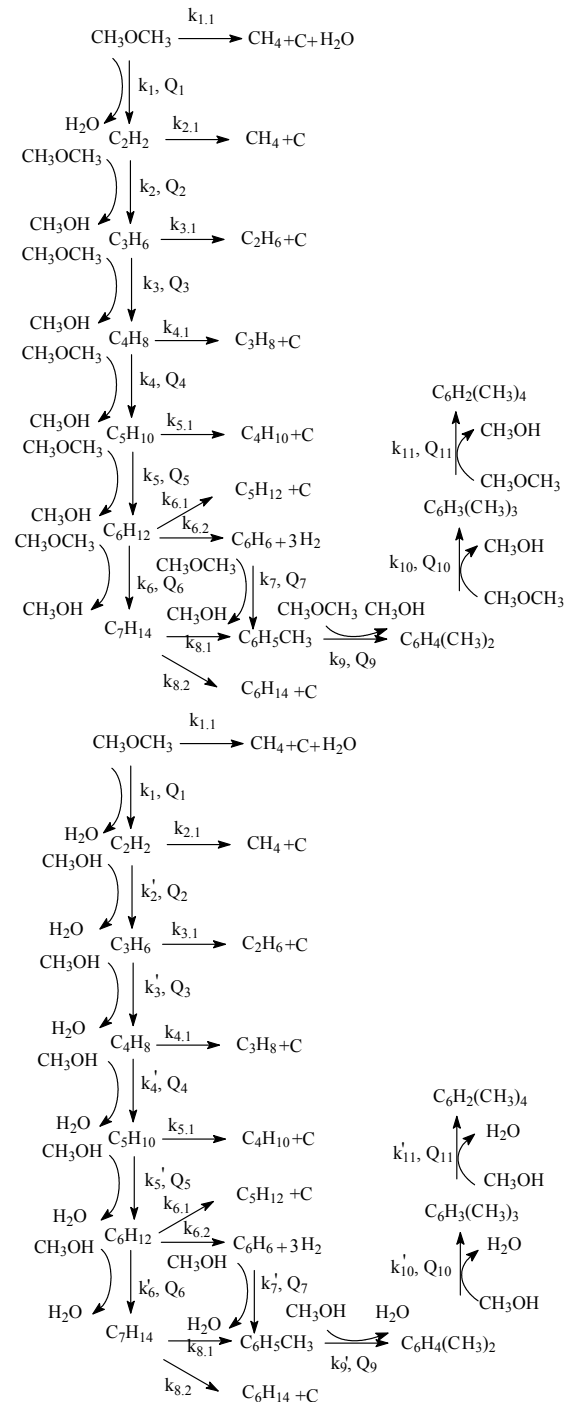


Figure 2: Kinetics scheme of dimethyl ether transformation into hydrocarbons (k – reaction rates constant, Q – substrate adsorption constants)

Dimethyl transformation starts from with formation of ethylene that after consecutive reactions with dimethyl ether or/and with methanol forms olefin fraction consist of propylene, butylene, pentene and hexane¹⁰. Aliphatic hydrocarbons fraction forms by catalytic cracking of

appropriate olefins over zeolite surface with carbon formation over the catalyst surface.

Benzene formation occurs by hexane aromatization. Further methylation of benzene by methanol be dimethyl ether or/and methanol results in formation of toluene, xylenes and polymethylbenzenes.

Reaction rate constants k1-k6 are responsible for olefins formation rates, reaction rate constants k1.1-k8.2 are responsible for aliphatic hydrocarbons formation rate and k7-k11 are responsible for aromatic hydrocarbons formation rates. Substrate adsorbance constants Q1-Q6 are responsible for olefins dimethyl ether and olefins adsorption over catalysts surface over, adsorption constants Q7-Q8 are responsible aromatic adsorption over catalysts surface.

The kinetic equation for dimethyl ether transformation rate can be denoted as equation 3 containing eleven rate and adsorption constants. Resolving of this equation can be done by numerical modeling and optimization.

$$\begin{aligned} \frac{d(CH_3OCH_3)}{dt} = & -k_1 \frac{Q_1[CH_3OCH_3]^2}{1 + Q_1[CH_3OCH_3]} - \\ & -k_2 \frac{Q_2[C_2H_4][CH_3OCH_3]}{1 + Q_2[C_2H_4]} - k_3 \frac{Q_3[C_3H_6][CH_3OCH_3]}{1 + Q_3[C_3H_6]} - \\ & -k_4 \frac{Q_4[C_4H_8][CH_3OCH_3]}{1 + Q_4[C_4H_8]} - k_5 \frac{Q_5[C_5H_{10}][CH_3OCH_3]}{1 + Q_5[C_5H_{10}]} - \\ & -k_6 \frac{Q_6[C_6H_{12}][CH_3OCH_3]}{1 + Q_6[C_6H_{12}]} - k_7 \frac{Q_7[C_6H_6][CH_3OCH_3]}{1 + Q_7[C_6H_6]} - \\ & -k_9 \frac{Q_9[C_6H_5CH_3][CH_3OCH_3]}{1 + Q_9[C_6H_5CH_3]} - \\ & -k_{10} \frac{Q_{10}[C_6H_4(CH_3)_2][CH_3OCH_3]}{1 + Q_{10}[C_6H_4(CH_3)_2]} - \\ & -k_{11} \frac{Q_{11}[C_6H_3(CH_3)_3][CH_3OCH_3]}{1 + Q_{11}[C_6H_3(CH_3)_3]} \end{aligned} \quad (3)$$

The kinetic equation for liquid hydrocarbons formation rate can be denoted as equation 4 containing seven rate and three adsorption constants.

$$\begin{aligned} \frac{d(hyd. carb)}{dt} = & k_5 \frac{Q_5[C_5H_{10}][CH_3OCH_3]}{1 + Q_5[C_5H_{10}]} + \\ & + k'_{5.1} \frac{Q_5[C_5H_{10}][CH_3OH]}{1 + Q_5[C_5H_{10}]} + k_{5.2} \frac{Q_5[C_5H_{10}]}{1 + Q_5[C_5H_{10}]} - \\ & -k_{6.1} \frac{Q_6[C_6H_{12}]}{1 + Q_6[C_6H_{12}]} + k_{6.2} \frac{Q_6[C_6H_{12}]}{1 + Q_6[C_6H_{12}]} + \\ & + k_{10} \frac{Q_{10}[C_6H_4(CH_3)_2][CH_3OCH_3]}{1 + Q_{10}[C_6H_4(CH_3)_2]} \\ & - k'_{10} \frac{Q_{10}[C_6H_4(CH_3)_2][CH_3OH]}{1 + Q_{10}[C_6H_4(CH_3)_2]} \end{aligned} \quad (4)$$

Parity plots of model and experimental relative concentrations for determined kinetic equation is presented on

figure 3 and 4. The deviation of model and experimental concentration do not exceed twelve percent that can be considered as good correlation for such complicated process.

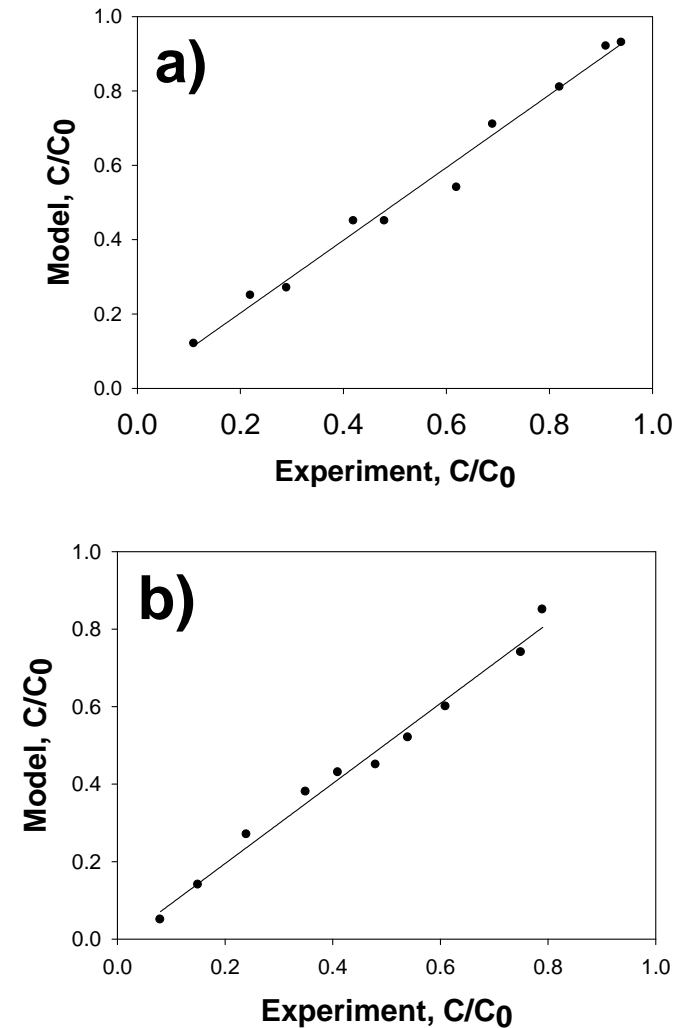


Figure 3: Parity plots of model and experimental relative concentrations for a) dimethyl ether, b) liquid hydrocarbons sum

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 modelling for dimethyl ether to hydrocarbons transformation process in temperature range 350-5000C allowed to calculate apparent activation energy and preexponential factors for Arrhenius equation (Table 1).

Calculated apparent activation energy correlates with activation energies founded for separate reaction taking place in dimethyl ether catalytic transformation to hydrocarbons presented in the literature¹¹⁻¹³. As it is well known formation of carbon deposits on catalysts surface can be considered as the main reason of H-ZSM-5 zeolite deactivation, therefore

developed model contains carbon formation steps over the catalyst surface (Figure 2). Formation of carbon deposits can be evaluated using equation 5.

Table 1. Calculated parameters of dimethyl ether to hydrocarbons transformation process

Constant	Constant dimension	Constant value	Constant deviation	Apparent activation energy, kJ/mol	Apparent activation energy deviation
k ₁	h ⁻¹	359.8	17.99	46.3	2.315
k _{1.1}	h ⁻¹	6.4	0.32	38.2	1.91
Q ₁	h ⁻¹	0.24	0.012	4.1	0.205
k ₂	h ⁻¹	21405.0	1070.25	62.6	3.13
k _{2'}	h ⁻¹	14247.2	712.36	57.9	2.895
k _{2.1}	h ⁻¹	2335.6	116.78	64.1	3.205
Q ₂	h ⁻¹	0.16	0.008	2.3	0.115
k ₃	h ⁻¹	1169.9	58.495	48.6	2.43
k _{3'}	h ⁻¹	1079.3	53.965	32.7	1.635
k _{3.1}	h ⁻¹	257.6	12.88	24.9	1.245
Q ₃	h ⁻¹	1.10	0.055	3.8	0.19
k ₄	h ⁻¹	3415.5	170.775	54.2	2.71
k _{4'}	h ⁻¹	21822.4	1091.12	62.7	3.135
k _{4.1}	h ⁻¹	486.4	24.32	28.6	1.43
Q ₄	h ⁻¹	0.40	0.02	2.6	0.13
k ₅	h ⁻¹	11.3	0.565	24.9	1.245
k _{5'}	h ⁻¹	1890.0	94.5	35.6	1.78
k _{5.1}	h ⁻¹	8336.4	416.82	42.9	2.145
k _{5.2}	h ⁻¹	2229.7	111.485	52.1	2.605
Q ₅	h ⁻¹	5.0	0.25	4.9	0.245
k ₆	h ⁻¹	11.3	0.565	24.9	1.245
k _{6'}	h ⁻¹	70.49	3.5245	18.6	0.93
k _{6.1}	h ⁻¹	2941.2	147.06	53.7	2.685
k _{6.2}	h ⁻¹	3861.9	193.095	36.9	1.845
Q ₆	h ⁻¹	5.73	0.2865	5.2	0.26
k ₇	h ⁻¹	9.9	0.495	24.1	1.205
k _{7'}	h ⁻¹	83.7	4.185	19.4	0.97
Q ₇	h ⁻¹	2.52	0.126	1.6	0.08
k _{8.1}	h ⁻¹	40.5	2.025	15.2	0.76
k _{8.2}	h ⁻¹	15.8	0.79	25.7	1.285
Q ₈	h ⁻¹	4.1	0.205	4.1	0.205
k ₉	h ⁻¹	719.6	35.98	46.3	2.315
k _{9'}	h ⁻¹	807.8	40.39	31.2	1.56
Q ₉	h ⁻¹	3.47	0.1735	2.9	0.145
k ₁₀	h ⁻¹	1548.7	77.435	62.3	3.115
k _{10'}	h ⁻¹	239.2	11.96	53.1	2.655
Q ₁₀	h ⁻¹	4.04	0.202	3.8	0.19
k ₁₁	h ⁻¹	1311.8	65.59	62.1	3.105
k _{11'}	h ⁻¹	2156.6	107.83	35.9	1.795
Q ₁₁	h ⁻¹	0.25	0.0125	4.7	0.235

k – reaction rates constant, Q – substrate adsorption constants

$$\begin{aligned} \frac{d(C)}{dt} = & k_{1.1} \frac{[CH_3OCH_3]}{1 + Q_1[CH_3OCH_3]} + k_{2.1} \frac{[C_2H_4]}{1 + Q_2[C_2H_4]} + \\ & + k_{3.1} \frac{[C_3H_6]}{1 + Q_3[C_3H_6]} + k_{4.1} \frac{[C_4H_8]}{1 + Q_4[C_4H_8]} + \\ & + k_{5.1} \frac{[C_5H_{10}]}{1 + Q_5[C_5H_{10}]} + k_{6.1} \frac{[C_6H_{12}]}{1 + Q_6[C_6H_{12}]} + \\ & + k_{8.2} \frac{[C_7H_{14}]}{1 + Q_8[C_7H_{14}]} \end{aligned} \quad (5)$$

Decreasing of active sites quantity can be calculated according to equation 6, taking into account initial concentration of active sites Θ_0 and effective constant of carbon deposits adsorption^{14, 15}.

$$\frac{d(\Theta)}{dt} = \Theta_0(1 - Q_{ads}[C]) \quad (6)$$

Comparison of experimental and model data on decreasing of dimethyl ether transformation rate and carbon deposits concentration increase versus time on stream (Figure 5) shows suitable correlation.

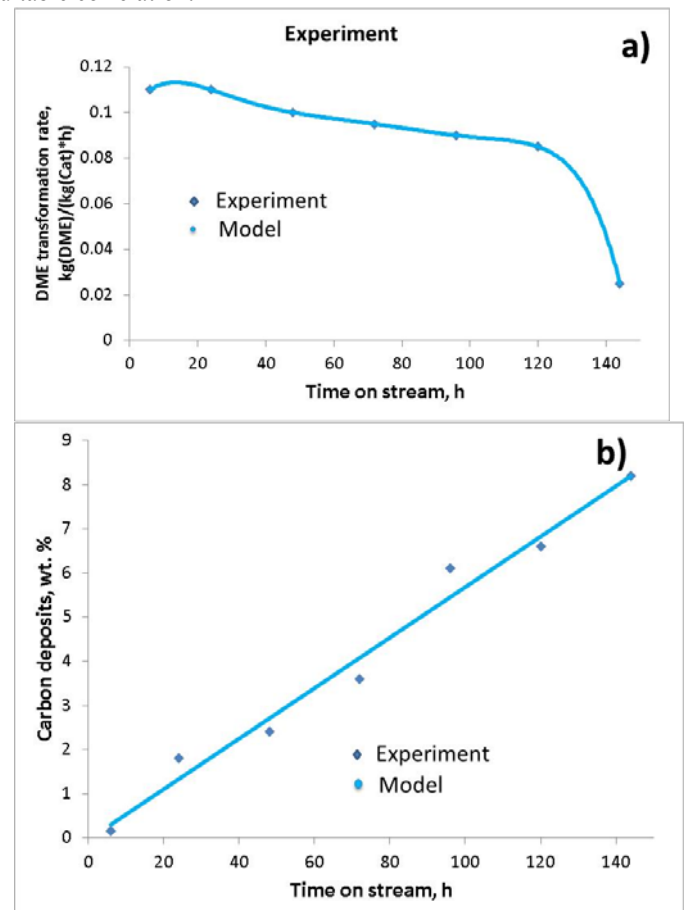


Figure 5: Comparison of model and experimental data for a) dimethyl ether transformation rate, b) carbon deposits concentration on the catalysts versus time on stream (experiment conditions: $t=350^{\circ}\text{C}$, $W(\text{DME})=0.38$ kg(DME)/(kg(Cat)*h))

IV. CONCLUSIONS

A reliable model of dimethyl ether to liquid hydrocarbons transformation was propounded. Proposed model includes main transformation steps, can be attributed to semilumped models and use Eley-Rideal concept for evaluation of surface catalytic processes. Model application allowed to calculate apparent activation energy values for developed process and to evaluate catalyst deactivation. Relative deviation of found specific activation energy and preexponential factors varies from 5 to 12% depends that can be considered as reliable results for lumped models.

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M – average molecular weight of water-free products, (kg/kmol),

P – partial pressure of water free products (Pa),

r_{i0} – 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)

ϵ – bulk porosity

ξ – longitudinal coordinate,

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