
Modeling of the Oxidative Dehydrogenation of Isomers Methyl Cyclopentene Into Methylcyclopentadiene

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Abstract

The article deals on modeling of the oxidative of isomers methyl cyclopentene into methylcyclopentadiene. The rate constants of the routes included in model were calculated by least squares method. The mathematical model has been constructed and the study has been carried out taking into account the convective and diffusive heat and mass transport on a granule of the oxidic catalyst. Estimate the concentration and thermal diffusive boundary beds effect on the chemical process.

Key words: *oxidative dehydrogenation, reaction mechanism, kinetic model, diffusion coefficients*

Introduction

The experimental researches on estimation of the convective heat- and mass transport rate in granular bed of commercial oxidic catalyst have been carried out. The mathematical model of oxidative dehydrogenation (OD) isomers methyl cyclopentene MCP into methylcyclopentadiene (MCPD) has been constructed and studied taking into account the convective and diffusive transfer of substance and heat inside a granule (of catalyst bed).

The convective transport plays an essential role on the catalyst spherical granules and in reactors that has been insufficiently neglected until now both in the choice of the procedure for catalysts test and in the process of mathematical modeling in reactors for its stable operation.

The researches were conducted in several directions:

1. The effective values of heat and mass transport coefficients were experimentally defined.
2. The mathematical model of MCP OD kinetics has been constructed and the study has been carried out taking into account the convective and diffusive heat and mass transport on a granule (in a reactor) of the oxidic catalyst and in a reactor.

For describing the heat-and mass transport processes in porous catalysts the diffusion effective coefficients were found as a result of the reverse task solution from assumption for use of diffusion and heat conduction equations with allowance for chemical reactions. The given method drawback should be noted to be an equivocal definition of the obtained values of effective diffusion coefficients.

1. THE STATEMENT OF THE PROBLEM

For determination of concentration and thermal profiles taking into account the convective heat and mass transport there have been considered the set of the second-order equations of parabolic type and with allowance for the mathematical model of oxidative dehydrogenation isomers methyl cyclopentene MCP into methylcyclopentadiene MCPD has been constructed of the following form:

$$\frac{\partial P_i}{\partial \tau} = D_{i\vartheta} \left(\frac{\partial^2 P_i}{\partial r^2} + \frac{1}{r} \frac{\partial P_i}{\partial r} \right) + w_i(P_i, T) \quad (1)$$

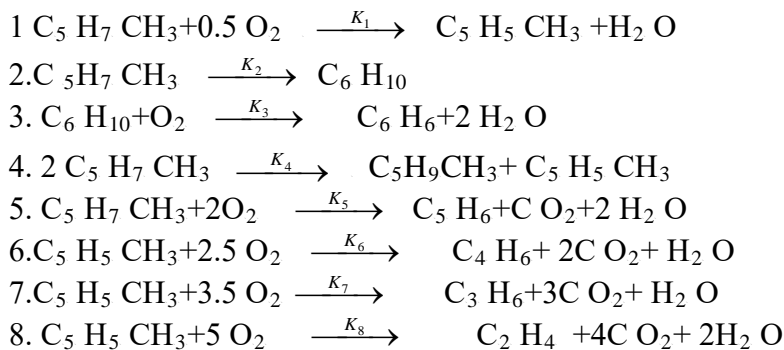
$$c_p \rho \frac{\partial T}{\partial \tau} = \lambda_{ef} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \sum_{j=1}^n h_j r_{ji}(P_i, T)$$

where: i, j-numbers of key components and participants in the considered routes of reaction, respectively, with initial and boundary conditions for the case when the convective heat-and mass exchange occurs at the boundary:

$$\begin{aligned} \tau = 0 \quad & P_i(0, r) = P_{i,0}(r); \quad T(0, r) = T_0(r) \\ \tau > 0 \quad & \frac{\partial P_i}{\partial r} = \frac{\partial T}{\partial r} = 0 \\ r = R \quad & -D_{i\vartheta} \frac{\partial P_i}{\partial r} = \beta_i (P_i - P_{i,n}) \\ & -\lambda_{ef} \frac{\partial T}{\partial r} = \alpha_{ef} F_{ef} (T - T_n) \end{aligned} \quad (2)$$

The model (2) solution was defined in the region D $[0 \leq r \leq R, 0 \leq \tau \leq \tau_k]$

Experimental data obtained in fairly wide ranges of process parameters demonstrated that the mechanism of the oxidative dehydrogenation (OD) process of isomers methyl cyclopentene (MCP) has a form:



With this reaction mechanism, the rates of the disappearance of the initial compounds and the rates of accumulation of the reaction products are given by the following set of differential equations:

$$\omega_{C_5 H_7 CH_3} = -r_1 - r_2 - 2r_4 - r_5 \quad (3)$$

$$\omega_{C_6H_{10}} = r_2 - r_3 \quad (4)$$

$$\omega_{C_5H_5CH_3} = r_1 + r_4 - 3r_6 \quad (5)$$

$$\omega_{C_5H_9CH_3} = r_4 \quad (6)$$

$$\omega_{C_6H_6} = r_3 \quad (7)$$

$$\omega_{C_5H_6} = r_5 \quad (8)$$

$$\omega_{C_2-C_4} = 3r_6 \quad (9)$$

$$\omega_{CO_2} = r_5 + 9r_6 \quad (10)$$

$$\omega_{C_5H_7CH_3} = \omega_{51-CH_7CH_3} + \omega_{3-C_5H_7CH_3}$$

$$r_1 = k_1 \cdot P_{C_5H_7CH_3} \cdot P_{O_2}^{0.5} \quad r_2 = k_2 \cdot P_{C_5H_7CH_3} \quad r_3 = k_3 \cdot P_{C_6H_{10}} \cdot P_{O_2} \quad r_4 = k_4 \cdot P_{C_5H_7CH_3}^2$$

$$r_5 = k_5 \cdot P_{C_5H_7CH_3} \cdot P_{O_2} / 1 + k_\alpha \cdot P_{C_5H_7CH_3}^{0.5} \quad r_6 = r_7 = r_8 = k_6 \cdot P_{C_5H_5CH_3} \cdot P_{O_2} / 1 + k_\beta \cdot P_{C_5H_5CH_3}^{0.5}$$

where: P_i -partial pressure of the key components ($i=1,6$): 1- sum isomers of methyl cyclopentene MCP P_{MCP} ; 2- sum isomers methylcyclopentadiene MCPD P_{MCPD} ; 3- tsiklogeksen TG P_{TG} ; 4 - benzol B P_B ; 5 - cyclopentadiene CPD P_{CPD} ; 6 – oxygen O_2 ; $T_1 - T_x$ -a gas temperature in a reaction zone and on a surface of a granule (of a reactor); C_p ; P -volume specific heat and bulk density of a catalyst; F_{eff} -specific surface of heat removal.

The rate constants of the routes included in model were calculated by least squares in terms of the deviations between the rate of the overall reaction calculated for this model and the observed reaction rate and have the following values:

$$\begin{aligned} r_1 &= 14389 \exp(-80770/RT) && 1/[l \text{ (cat) s kPa}^{1.5}] \\ r_2 &= 85179 \exp(-77870/RT) && 1/[l \text{ (cat) s kPa}^{1.5}] \\ r_3 &= 604.3 \exp(-46710/RT) && 1/[l \text{ (cat) s kPa}^2] \\ r_4 &= 0.912 \exp(-3550/RT) && 1/[l \text{ (cat) s kPa}^2] \\ r_5 &= 5.112 \exp(-30370/RT) && 1/[l \text{ (cat) s kPa}^2] \\ r_6 &= r_7 = 1.12 \cdot 10^7 \exp(-110000/RT) && 1/[l \text{ (cat) s kPa}^2] \end{aligned} \quad (11)$$

where R -a gas constant.

The thermal effects have the following values [5]:

$$H_i = 1286; 1107.15; 4415.4; 6481.8; 17387.9; 19709.5 \text{ cal/l (cat)} \quad (12)$$

The effective coefficient of heat transfer =18.7 cal/m².h.c and specific surface of heat removal of oxidic catalyst F_{eff}=1640 m²/m³ have been obtained by the estimated method, in this case the dimension of bed was taken ε=0.4.

The researches were conducted in the following region of variable parameters:

P₁₀ [2.6-19.6] kPa; P₆₀ [1.5-47] kPa; T(τ) ∈ [623-723] K_i at volumetric rates by MCP ∈ [62.9-426.2] h⁻¹, i.e. the contact time τ ∈ [0-1.5] s.

Based upon the kinetic theory of gases, for Knudsen diffusion in straight cylindrical pore for determination of the effective diffusion coefficient the following relationship was used.

$$D_{ef} = 19400 \frac{\theta^2}{\delta_m S_{swt} \rho_h} \sqrt{T/M_i} \quad i = \overline{1,4} \quad (13)$$

where: δ_m=2.6; θ=0.38; specific surface of particles S_{sp}=160-180m²/gr; P₃=1620 kg/m³; the region of reaction temperature change T ∈ [623-723] K.

$$D_i = 0.00359; 0.00362; 0.00368; 0.00585 \text{ sm}^2 / \text{s} \quad (14)$$

The following effective diffusion coefficients were obtained for key components 1-MCP; 2-MCPD; 3-CPD and 4-O₂ at temperature T=623⁰K. Reynolds numbers were determined by formula:

$$\text{Re}=4\theta p_c u D / (6(1-\theta)\mu)=2.1 \quad (15)$$

where: P_m=0.84 kg/m³-density of mixture; u=0.2 m/s-linear rate of mixture; D=(0.5-1.7) 10⁻³ m-diameter of particles; μ=3.2/0⁻⁵ kg (mc)-dynamic viscosity of mixture.

Schmidt criterion has a form:

$$Sc_i = \mu / [\rho_h D_{i,ef}] \quad i = \overline{1,4} \quad (16)$$

The numerical values of which are:

$$S_{ci}=52.43; 51.99; 51.15; 32.18$$

for MCP; MCPD; CPD and O₂ respectively.

In accordance with the experimental relationship.

$$Sh_i \text{Re}^{-1/2} S_{c,i}^{-1/3} = 093[\theta - 0.75(1 - \theta)]^{-1/2} \quad (17)$$

According to [9] Sherwood criterion has the following form:

$$Sh_i = 1.75 \text{Re}^{-1/2} S_{c,i}^{-1/3} = k_{i,g} D_3 / D_{i,ef} \quad (18)$$

from which mass transfer coefficients k_{i,g} for D₃=0.002 m, have the following values:

$$k_{i,g} = 0.00255 : 0.002579 : 0.002622 : 0.004168 \text{ m/s} \quad (19)$$

for - MCP; MCPD, CPD and O₂, respectively.

The coefficient of mass transfer from catalyst granule to the flow has been defined by Cober-lyand Marshall method [10]:

$$\lambda = (0.268 + 0.0145DG / \mu) = 0.297 \text{ kcal } (m \text{ s } K) \quad (20)$$

The numerical values of the coefficient of heat transfer from a granule to flow have been defined by the known Frosling formula:

$$\frac{\alpha D}{\lambda} = 2 + 0.6 \left(\frac{C_p \mu}{\lambda} \right)^{\frac{1}{3}} \left(\frac{Du_p S}{\mu} \right)^{\frac{1}{2}} = 3.24 \quad (21)$$

from which: $\alpha = 13.61 \cdot 10^2 \text{ kcal}/(\text{m}^2 \text{ s } K)$.

2. ALGORITHM OF SOLUTION

The solution of set partial differential equations (1), (2) has been made by the modified differential method using Runge-Kutta numerical method with constant pitch by contact time and radius of a catalyst granule (and a reactor).

The algorithm of solution of a parabolic differential equation is presented as a differential operator and considering the approximation of derivatives has a form [12]:

$$\frac{dP_{i,j}}{d\tau} = D_{i,ef} \left[\frac{P_{i,(j+1)} - 2P_{i,j} + P_{i,(j-1)}}{\Delta r^2} + \frac{1}{\Delta r} \frac{P_{i,(j+1)} - P_{i,(j-i)}}{2\Delta r} \right] + w_{i,j}(P_{i,j} T_j)$$

$$\frac{dT_j}{d\tau} = \frac{\lambda_{ef}}{C_p \rho} D_{i,ef} \left[\frac{T_{i,(j+1)} - 2T_{i,j} + T_{i,(j-1)}}{\Delta r^2} + \frac{1}{\Delta r} \frac{T_{i,(j+1)} - T_{i,(j-i)}}{2\Delta r} \right] + \sum_{i,j=1}^{m,n} h_i T_i (P_{i,j} : T_j)$$

where: $P_{i,j}, T_{i,j}$ - partial pressure and temperature in j -radial section at the following initials:

$$\tau = 0 \quad P_{i,j}(r) = P_{i,0}(r) : \quad T_j(0, r) = T_{0j}(r) \quad i = \overline{1, m} : j = \overline{1, n}$$

$$\tau > 0 \quad \frac{\partial P_{i,j}}{\partial r} = \frac{\partial T_i}{\partial r} = 0$$

$$r = 0 \quad D_{i,ef} = \lambda_{ef} = 0$$

$$r=R \quad -\frac{dP_{i,m}}{dr} = \frac{\beta_i}{D_{i,ef}} (P_{i,m-1} - P_{i,m})$$

$$-\frac{dT_n}{dr} = \frac{\alpha_{ef} F_{ef}}{\lambda_{ef}} (T_n - T_x) \quad (22)$$

where: $P_{i,n}$, T_n , $T_{x,i}$, partial pressure and temperature through flow at the boundary of a granule and a cooling agent, $\Delta_r = \frac{r}{n}$ - grid of splitting by radius.

In this case it was assumed that in a granule care (and on a reactor symmetry axis) of a catalyst ($r=0$), a purely kinetic region involves, not complicated by diffusion ($D_{i,ef}=\lambda_{ef}=0$ at $r=0$).

The difference of the modified programmer module developed, solution of a task of convective heat – and mass transport is that the set of second-order partial non-linear differential equations of parabolic type with allowance for the differential transformations is scanned in each section of radial distribution.

The numerical modified method, according to the standard procedure for choice of integration step by contact time peculiar to Runge-Kutta method allows solving a system taking into account the limitations (22).

In spite of increasing a rank of model matrix by $(m \times n)$ times the procedure of task solution is simplified and resolved to the standard Runge-Kutta numerical method.

3.RESULTS IN A CATALYST GRANULR

The numerical solution of a mathematical model of MCP (15) OD process kinetics with allowance for boundary conditions (22) permitted to determine the concentration and thermal profiles in a reactor for different contact times.

The radial concentration and temperature profiles in a catalyst granule for different contact times are presented in Figure 1.

As is seen from Figure 1, the value of adiabatic heating- $\Delta T=55^0K$ and then temperature at the reactor outlet begins sharply to reduce and if at the distance of 0.75 min to the catalyst surface it is 723^0K , at the surface of bed granule the temperature drops to the value 723^0C and at the distance as early as Δr from the granule surface it is equal to the flow temperature.

The researches carried our allowed to assume that granule heating occurs mainly at the expense of deeper oxidation of C_1-C_4 hydrocarbons molecules penetrating sufficiently deeply into the pores of catalyst granule and cyclones are formed essentially at the catalyst surface and in its external pores.

The idea of a degree of conformity of estimation results by one-dimensional model to the actual values gives Bio criterion:

$$B_i = \frac{r_p \cdot \alpha \delta}{\alpha_{ef}} = \frac{0.45 \cdot 8.74 \cdot 10^{-3}}{0.87 \cdot 10^{-3}} = 4.5$$

As criterion $B_i \gg S$, then in this case the resistance of heat transfer inside the granular bed surpasses significantly the resistance of heat transfer from flow to the reactor wall.

In this case the boundary conditions take on a value $T(r_k) = T_c$ -the wall temperature.

The Bio criterion also shows the considerable cross drops of temperature and approximation by “one – dimensional” reactors is unused.

The numerical experiment carried out allowed analyzing an equation of reagent transport in a reactor with finely dispersed oxidic catalyst on external and partially inside surface of which the complex, highly exothermal process is proceeding with parallel-sequential mechanism of reaction.

The relative error of MCP removal from the unit of catalyst volume calculated by one-dimensional model didn't exceed 10% with suspect to the corresponding removal calculated by the mathematical model taking into account the radial heat and mass transport.

One can assume that the limiting stage is the act of chemical reaction itself and not adsorption-desorption processes in a catalyst granule and the estimate of MCP OD process to cyclones MCP, MCPD may be carried out on one-dimensional model of ideal displacement without loss of total confidence.

The mathematical model developed for a granule of oxidic catalyst allows to forecast the process proceeding in tubular reactors.

With the aim of estimation of the concentration and thermal diffusive boundary beds effect on the chemical process itself, the additional researches have been performed.

3. ESTIMATION OF THE THICKNESS OF THERMAL AND CONCENTRATION DIFFUSIVE BOUNDARY BEDS.

As a result of transforming equations characterizing the boundary conditions (22) criterion dependences of material and thermal balances have been obtained by gas diffusing through boundary bed of catalyst granule with flow which after some transformations for key components have a form:

Thickness of concentration

$$\delta_i = d_3 / [0.25 \cdot \text{Re}(\tau) \cdot S_{ci} + A_i(\tau) S_{hi}] \quad (23)$$

and thermal boundary beds

$$\delta_T = d_3 / [0.25 \cdot \text{Re}(\tau) P_{ri} + B(\tau) \cdot N_{ui}] \quad (24)$$

$$A_i(\tau) = (P_{i,n} - P_{i,o}) / (P_{i,n-1} - P_{i,n})$$

$$B(\tau) = [T_n - T^o] / [T_{n-1} - T_n]$$

Criteria: of Hutceld- $N_4 = B_i \cdot l / D_i$, ef. and

of. Prandte- $P_2 = C_p \mu / \alpha$, and $\text{Re}(\tau)$, S_{ci} and S_{hi} -are determined above)

The solution of mathematical model and modified boundary conditions (22) allowed to define the profiles of thermal and concentration diffusive boundary beds.

It follows from the numerical experiment, that with increasing the rate of gas mixture movement (i.e. with reducing contact time- δ) the concentration and thermal profiles remain practically flat and then beginning at certain distance apart the catalyst surface, they sharply change. The basic drop of concentrations and temperature from their established value takes place in the concentration and thermal boundary beds δ_p and δ_T .

In spite of the comparatively slight thickness of a boundary bed, the latter plays the main role in the processes of heat-and mass exchange of gas phase from granule surface.

The gaseous reagent prior to adsorbing at the catalyst surface passes through boundary bed and then through the pores diffuses to the catalyst active surface.

Hydrocarbons OD processes refer to the class of very fast reactions for which the coefficient of the granule inner part is rather small, therefore the role of a boundary bed is impossible to be neglected.

The procedure developed allows to estimate the role of resistance rendered by heat-and mass transfer in boundary beds and to draw conclusions that different radial sections of a reaction zone and temperature distribution have different thickness of boundary beds being a function of contact time. In this case the assumption is needed that the constancy of a boundary bed thickness is supposed along all the spherical coordinates; a boundary bed thickness is a function of contact time; a boundary bed doesn't give up a granule surface. And it is also supposed that laminar flow-round of a particle by gas flow occurs and that in a rather narrow surface bed of catalyst at the boundary with heat-removing gas flow $P_i, n_{\tau, r} = P_i^0(0, r)$.

The researches carried out on an acidic catalyst granule allowed also to estimate the influence of concentration and thermal diffusive boundary beds on the chemical process itself.

The curves complex nature is evidently explained by the peculiarities of hydrocarbons OD processes, in particular, their high exothermicity, complexity and multi-route sequential-parallel mechanism of reaction, occurrence of competing reactions(oxidative and conventional dehydrogenation).

As it follows from Figure 2 with increasing contact time the thickness of diffusive boundary beds of the reaction products is extended and that of the starting components becomes narrower that is mainly explained by the lack of the reaction products and excess of the starting components in a gas flow. With increasing contact time the thickness of thermal boundary bed also becomes narrower and at the end of boundary bed approaches to the temperature of flow. In the region of competing processes proceeding (at: $E=0.6-1.0 \Delta$) the thickness of boundary beds slightly changes.

4. CONCLUSION. The mathematical model developed for a granule of oxidic catalyst allows to forecast the process proceeding in tubular reactors. The researches performed on a granular bed of oxidic catalyst of MCP OD permit to estimate at design stage the mutual influence of the thickness of thermal and diffusive

boundary beds on a reaction itself that is rather important for intensification of the processes under development.

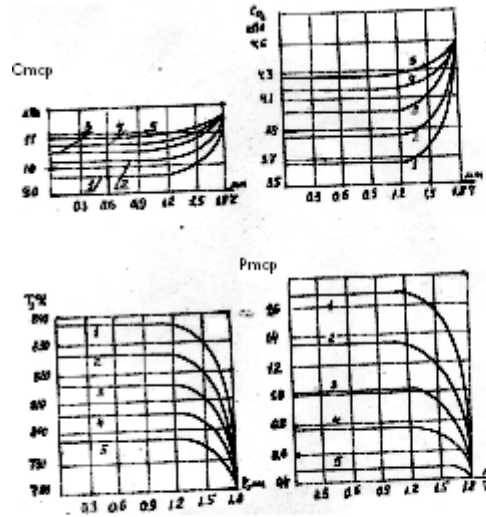


Figure 1: Radial profiles of temperature concentrations for different contact times of MCP OD MCPD process on a granule of oxidic catalyst at $C_{MCP}^o = 11,4 \text{ kPa}$, $C_{O_2}^o = 4,6 \text{ kPa}$; $T_0 = 783^0 \text{ K}$

1-1,2s, 2-1,0s, 3-0,8s, 4-0,6 s, 5-0,4s.

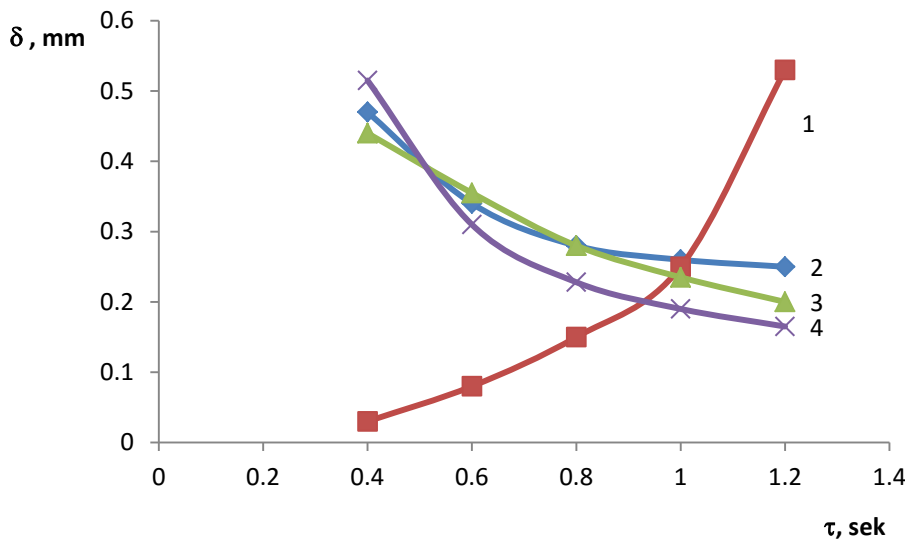


Figure 2: Profiles of thermal and concentration boundary beds of MCP OD process at

$$C_1^0 = 11,4 \text{ kPa}, C_4^0 = 4,6 \text{ kPa}, T^0 = 783^0 \text{ K. /1-MCP, 2-MCPD, 3-T, 4-oxygen/}$$

CONVENTIONAL NOTATION

v- flow velocity, m/s ;

β - mass-exchange coefficient

D- diffusion coefficient, m^2/S ;

α - heat-exchange coefficient, $\text{Y}/(\text{m}^2\text{s}^0\text{K})$;

r, R- radia, m.i

λ - heat-transfer coefficient, $\text{Y}/(\text{m c}^0\text{K})$;

c ρ c g- volume specific heat, $\text{Y}/(\text{m}^3^0\text{K})$;

F- heat removal surface m^2/m^3 ;

τ - contact time, s;

T- temperature, (0 K)

P- partial pressures, k Pa

Δ - coefficient of pores convolution

Indices:

c-cooling agent:

f-flow:

g-granule of catalyst:

g/f- granule/flow:

r- reactor:

ef- effective coefficient:

sp. – specific surface:

i=1.m-key components:

j=grid of splitting

l=1.1- number of stages:

K=l,m- key sections of reaction:

Sp. –specific:

m- mixture

S- surface of particle, m^2/g .

V-volume of charge, cm^3

W-volume rate m^3/s

θ -average volume of pores, resp.

M-polymeric mass.

μ -dynamic viscosity, kg/ (m,s)

c-mass-transfer coefficient

Y-mass rate. kg/ (m².h)

δ - coefficient of heat conduction, cal/(m.h.k)

g-apparent density

Criteria :

Reynolds Re

Schmidt: Sc⁻

Sherwood: Shi

Huteld:

Prandtl:

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