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Kinetic model of uncatalyzed oxidation of cyclohexane

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ABSTRACT

A model of uncatalyzed oxidation of cyclohexane in the liquid phase, including both kinetics and mass transfer, is presented. The reaction rate constants as well as the activation energies were determined on the basis of the experimental results obtained in a laboratory reactor with carefully passivated inner surface. A mathematical model of an industrial reactor for the cyclohexane oxidation is also presented. The results of the uncatalyzed cyclohexane oxidation simulations are compared with the data from the industrial reactor. The results of the present work have been used for modernization of the Polish CYCLOPOL process, and enabled the development of CYCLOPOL-bis [Gruszka, M., Krzysztoforski, A., Moniuk, W., Oczkowicz, S., Pohorecki, R., Wierzchowski, P.T. and Żyliński, M., 2005, CYCLOPOL-bis – the second youth of the Polish process for oxidation of cyclohexane, Przemysł Chemiczny (Chem Ind), 84: 493–502 (in Polish)].

Keywords: Kinetics; Mathematical modelling; Multiphase reactors; Reaction engineering

1. Introduction

The process of cyclohexane oxidation is widespread in chemical industries all over the world, mostly to get cyclohexanone and cyclohexanol, being in turn processed into caprolactam, adipic acid, and – subsequently – polyamide fibers and plastics (as nylon 6, nylon 66).

Practically all of the adipic acid and about 63% of the caprolactam produced in the world in 1990 used cyclohexane oxidation as the first step (Suresh et al., 2000).

The amount of cyclohexane oxidized this way exceeds 4 millions t/year.

The process is a relatively difficult one, since the desired products (i.e., cyclohexanone and cyclohexanol) are intermediates in a sequence of reactions, and the overoxidation results easily in a number of useless (or hardly recuperable) by-products.

Cyclohexane oxidation is a two-phase process, carried out in a gas–liquid system. The course of the process may be affected both by chemical kinetics and by hydrodynamic factors.

One of the processes commercially employed to oxidize cyclohexane is the Polish CYCLOPOL process. In order to keep pace with other leading companies, the owners of the CYCLOPOL process continue to carry on research and development work, aimed at increasing productivity and selectivity of the process.

One of the ways to increase the selectivity is to carry out the oxidation process without (or with very small amount of) the catalyst to obtain possibly high concentration of cyclohexyl hydroperoxide and subsequently to conduct catalyzed transformation of the hydroperoxide to cyclohexanol and cyclohexanone.

In order to design properly such two-step process, a deeper quantitative knowledge of the uncatalyzed oxidation kinetics is necessary. The aim of this work was to develop a mathematical model of the uncatalyzed cyclohexane oxidation process, and to verify this model in the conditions of an industrial process.

2. Model of uncatalyzed cyclohexane oxidation

The mechanism of cyclohexane oxidation is a complicated, multistage, free-radical chain reaction with degenerated chain, comprising different chain inhibition, chain propagation and chain termination steps. A reaction scheme comprising up to 154 reactions has been developed by Tolman

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Nomenclature

a	interfacial area per unit volume of liquid, m^2/m^3
B	break-up rate, $1/m^3$ s
C	coalescence rate, $1/m^3$ s
C'	constant in Eq. (A14)
D	reactive by-products in the liquid phase
d	column diameter, m
D'	non-reactive by-products in the gas phase
D_A	oxygen diffusivity in the liquid, m^2/s
d_b	bubble diameter, m
d_{32}	Sauter bubble diameter, m
F	external body force per unit volume, N/m^3
G	generation function, $1/m^3$ s
g	gravity acceleration, m/s^2
H	Henry's constant, $kmol/m^3$ MPa
Ha	Hatta number definied by Eq. (A27)
H_L	clear liquid height, m
k	pseudo-first order reaction rate constant, 1/s
k_i	reaction rate constants, m^3/kmol s, 1/s (Table 3)
k_L	physical mass transfer coefficient in the liquid phase, m/s
n	bubble concentration per unit volume, $1/m^3$
P	pressure, MPa
r	reaction rate, $kmol/m^3$ s
RH	cyclohexane
RO	cyclohexanone
ROH	cyclohexanol
ROOH	cyclohexyl hydroperoxide
t	time, s
T	temperature, °C
u	velocity, m/s
u_r	bubble rise velocity, m/s
x	spatial coordinate
y	mole fraction in the gas phase
[ ]	concentration, $kmol/m^3$

Greek letters

ε	gas holdup
μ	viscosity, Pa s
ρ	density, kg/m^3
υ	bubble volume, m^3

Sub- and superscripts

0	reactor inlet
D	diffusion variable
i	coordinate index
j	coordinate index
k	phase index
m	mixture variable
n	number of phases
s	secondary phase

(1997), but was never published (at least not in the open literature).

A number of simplified kinetic models for both catalytic and noncatalytic oxidation have been described in our earlier paper (Pohorecki et al., 2001a).

An early model of noncatalytic cyclohexane oxidation was presented by Kharkova et al. (1989). The model was based both on the literature data and the author's own experiments. The model comprises 19 reactions, but for some of them only the ranges of values of the reactions rate constants were given, which renders it useless for detailed design purposes.

On the basis of that model and our own experimental data we formulated a new, modified kinetic model shown in Table 1.

In comparison to the Kharkova et al. model, the changes are as follows:

- stoichiometric equations of reactions (11) and (18) are corrected (Hursan et al., 1990);
- three new reactions (20), (21) and (22) are added (Table 1).

The reason of adding the new reactions was to differentiate reactive liquid phase by-products from the non-reactive gas phase (volatile) by-products. This differentiation is important from the design point of view.

The rates of the individual reactions are as follows:

$$\begin{aligned}
r_1 &= k_1[\mathrm{RH}][\mathrm{O_2}];\;\; r_2 = k_2[\mathrm{R^*}][\mathrm{O_2}];\;\; r_3 = k_3[\mathrm{RH}][\mathrm{RO_2^*}];\\
r_4 &= k_4[\mathrm{RH}][\mathrm{RO^*}];\;\; r_5 = k_5[\mathrm{ROOH}];\;\; r_6 = k_6[\mathrm{ROOH}][\mathrm{ROH}];\\
r_7 &= k_7[\mathrm{ROOH}][\mathrm{RO}];\;\; r_8{=}k_8[\mathrm{ROOH}][\mathrm{RH}];\;\; r_9{=}k_9[\mathrm{ROOH}][\mathrm{RO^*}];\\
r_{10} &= k_{10}[\mathrm{ROOH}][\mathrm{RO_2^*}];\;\; r_{11} = k_{11}[\mathrm{ROH}][\mathrm{RO_2^*}];\\
r_{12} &= k_{12}[\mathrm{RO}][\mathrm{RO_2^*}];\;\; r_{13}{=}k_{13}[\mathrm{ROOH}][\mathrm{R^*}];\;\; r_{14}{=}k_{14}[\mathrm{ROOH}][\mathrm{R^*}];\\
r_{15} &= k_{15}[\mathrm{RO_2^*}]2;\;\; r_{16} = k_{16}[\mathrm{ROOH}][\mathrm{D}];\;\; r_{17} = k_{17}[\mathrm{ROH}][\mathrm{D}];\\
r_{18} &= k_{18}[\mathrm{RO_2^*}]^2;\;\; r_{19} = k_{19}[\mathrm{RH}][\mathrm{OH^*}];\;\; r_{20} = k_{20}[\mathrm{RO^*}][\mathrm{RH}];\\
r_{21} &= k_{21}[\mathrm{RH}][\mathrm{RO^*}];\;\; r_{22} = k_{22}[\mathrm{D}] \qquad (1)
\end{aligned}$$

A detailed analysis of the balance equations, describing the changes of the concentrations of the reaction species involved, as well as the assumptions made in the calculation of the reaction rate constants, is given in Appendix A.

3. Experiments

In order to determine the reaction rate constants in Eq. (1), measurements of the kinetics of the cyclohexane oxidation were performed. Experiments were carried out in a stainless steel PARR reactor with capacity $1 \times 10^{-3}\,m^3$, with carefully passivated inner surface. The passivation of the inner surface of the laboratory reactor was performed using 4% aqueous solution of sodium pyrophosphate. The solution was applied twice at 100 °C, each time for 1 h. It was checked experimentally that this procedure ensured complete passivation of the surface.

The scheme of the experimental apparatus is shown in Fig. 1. The gas (air or N_2/air) from the gas cylinders (7, 8) was supplied through the pressure reducing valves and flow-stabilising tubes and flow meters (4) to the gas sparger (10) below the stirrer (2).

The process parameters were varied in the following ranges: temperature: 150–170 °C; pressure: 1.0–1.2 MPa; stirring rate: 300–600 rpm; gas flow rate: 2×10^{-5}–$5 \times 10^{-5}\,m^3/s$; concentration of oxygen in gas inlet: 5.3–20.7 vol%. A detailed description of the experimental apparatus is presented in our earlier paper (Moniuk et al., 1997a).

During the experiments, samples of liquid were drawn through a cooler 9. The liquid samples ($3 \times 10^{-6}\,m^3$) were analyzed by the chromatographic method (Wierzchowski and Zatorski, 2000; Polish Patent, 2005). The concentrations of the