

Mathematical Modeling and Optimization of Technological Schemes for Oxidation of Organics in Supercritical Water

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Technological scheme for the oxidation of organic wastes in SCW has been proposed. Mathematical models of all apparatuses in the scheme (heat exchangers, chemical reactor, separator) consider specific properties of chemical processes realized in supercritical water (alteration of heat capacity, enthalpy and critical parameters of mixture with changing pressure, temperature and composition). Non-ideal thermodynamic methods have been used to calculate the properties of two-phase multi-component mixtures. Detailed numerical analysis and optimization of the proposed scheme for the oxidation of acetic acid and phenol by oxygen in SCW have been carried out.

INTRODUCTION

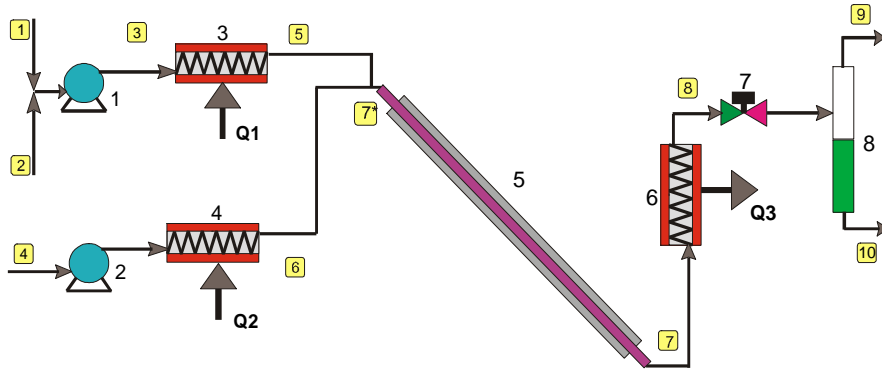
Oxidation processes in supercritical water (SCWO) have been considered for a long time as an efficient method for destruction and utilization of organics, toxic wastes, including those dissolved in water in trace concentrations, conversion of toxic agents and wastes, propellants and explosives into ecologically safe products. Numerous research works prove high efficiency and encouraging potentials of SCWO technologies [1,2]. Intensive studies during almost two decades accumulated a great deal of information on fundamental aspects of the reactions in supercritical fluids. Modeling of the SCWO processes will help to optimize process parameters and increase the energetic efficiency, i.e. to overcome the factors, which hamper wide application of SCWO technologies. The aim of the present work was to develop approaches to mathematical modeling of the SCWO processes, design a model and to calculate the main parameters of a pilot-plant.

PROCESS DESCRIPTION

In the present work we analyze an alternative process flow diagram, Fig. 1, which implies the oxidation of acetic acid and phenol by hydrogen peroxide in SCW and may be considered as a pilot-plant prototype. As a rule, oxidation of acetic acid, which is a target or intermediate compound at the decomposition of numerous organic compounds, is the limiting stage of the whole process. In our work, methanol was the fuel, hydrogen peroxide – the oxidant. Note that the alteration of reagents, fuel or oxidant caused no principal variations of the process and apparatus models.

In the tubular flow reactor (5) methanol and organic admixtures are oxidized in SCW to give CO₂ and H₂O. Besides, hydrogen peroxide, which survived heat-exchanger, undergoes conversion in the reactor. The input oxidant/fuel/reagent ratio α is usually set in excesses against the oxidation reaction stoichiometry. The reactor operates in an adiabatic mode. The heat is released by fuel and reagent oxidation and by hydrogen peroxide decomposition. As a

result, the temperature of the reactor effluent (flow 7) may attain 850-950K. The temperature of the reaction mixture is controlled by the amount of fed methanol and by the temperature of the heat-exchangers effluents. In the case of complete oxidation of reagent and fuel in the



reactor, flow 7 consists of water, CO₂ and unreacted oxygen.

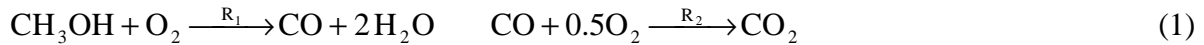
Fig. 1. Process flow diagram for the oxidation of organic compounds in SCW: 1, 2 – pumps, 3, 4 – heat-exchangers, 5 – reactor, 6 – condenser, 7 – back pressure reducer, 8 – separator.

PROCESS MODEL

Process model consists of mathematical models of constituent units connected by material and heat flows.

Chemical reactions proceeded in the system

It is assumed that the process of methanol oxidation by oxygen resulted from hydrogen peroxide decomposition proceeds by two reactions:



Besides, acetic acid is oxidized in the reactor by reaction:



Kinetics of reactions (1) – (2) and hydrogen peroxide decomposition in SCW were calculated by equations taken from the literature [3-5].

REACTOR MODEL

The model was developed on the assumption of an ideal plug flow reactor. The model equations can be presented in the following form:

$$\frac{dy_i}{dt} = \frac{1}{g} \left[q_i - y_i \frac{dg}{dt} \right] \quad i=1,2,\dots,N \quad (3)$$

$$\frac{dT}{d\tau} = \frac{1}{\gamma \bar{c}_p} \left[- \sum_{i=1}^N (q_i H_i) - \bar{c}_p T \frac{d\gamma}{d\tau} \right] \quad (4)$$

$$\frac{dg}{dt} = \sum_{i=1}^N q_i \quad (5)$$

Initial conditions

$$t = 0: F = F^0, \quad g = 1, \quad y_i = y_i^0, \quad T = T^0 \quad \bar{c}_p = \bar{c}_p(T^0) \quad (6)$$

where F^0, T^0, y_i^0 - characteristics of flow at the reactor input; $g \equiv F/F^0$ - coefficient to account molar flow variation resulted from chemical reaction; $t \equiv V/F^0$ - residence time l·s/gmol; F - mass flow, gmol/s; y_i - molar fraction of i -th component, $q_i = \sum_{j=1}^{N_r} Z_{ji} R_j$ - conversion rate of i -th component, gmol/l/s; Z_{ji} - an element of j -th line and i -th column in a matrix of stoichiometric coefficients of reactions; N, N_r - number of chemical components and number of chemical reactions, respectively ($N = 7, N_r = 4$); V - reactor volume; \bar{c}_p - mixture thermal capacity, cal/mol/K; H_i - enthalpy of i -th component, cal/mol.

Model of heat-exchanger

In heat-exchanger 4 flow 4 is heated by external source and by the heat of exothermic reaction of hydrogen peroxide decomposition. Mathematical model of heat-exchanger 4 differs from the reactor model (3)-(6) only by that the heat balance equation contains additional term $Q_{\text{inp}}^{(2)}$ (cal/l/s), which accounts for the heater power density. The $Q_{\text{inp}}^{(2)}$ value is specified; this is the process control parameter. Mathematical model of heat-exchanger 4 includes equation (3) and the modified heat balance equation:

$$\frac{dT}{d\tau} = \frac{1}{\gamma \bar{c}_p} \left[\sum_{i=1}^N - (q_i H_i) + Q_{\text{inp}}^{(2)} - \bar{c}_p T \frac{d\gamma}{d\tau} \right], \quad (7)$$

with initial conditions (6).

Model of separator

In the separator, the reaction products, cooled in the heat-exchanger (6) to 300K, are separated under atmospheric pressure into two equilibrium phases - gas and liquid. Mathematical model of this process is based on the equality of fugacities of both phases. Detailed description of the method and algorithm for the solution of this task can be found in [8].

Thermodynamic calculations

It is known that in critical state the thermal physical properties of water vary considerably at slight temperature and pressure/density alterations. For example, thermal capacity or thermal conductivity of water in sub- or supercritical state displays anomalous behavior, which appears in a form of extremum functions of temperature or pressure, Fig.2. Anomalous fluid properties must affect the course of the process in the reactor. Therefore, calculation of alteration of the fluid properties in supercritical state is the necessary condition for the modeling of the reactor and apparatuses.

The mixture thermal capacity \bar{c}_p and molar enthalpy H , which display strong fluctuations near critical point, is determined in the above model by the additivity rules. To calculate thermal capacity and enthalpy of individual compounds we used the methods of non-ideal thermodynamics. The physical properties of mixture were calculated using the partial molar values of individual components, e.g. Fig. 3.

Non-ideal character of individual components was accounted by thermodynamic functions connecting free Gibbs energy, enthalpy, entropy and fugacity:

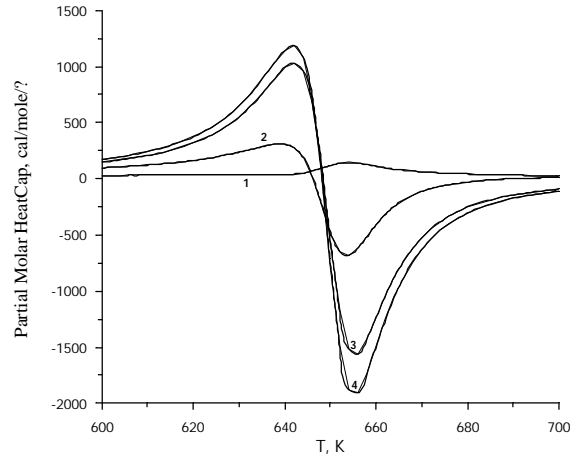
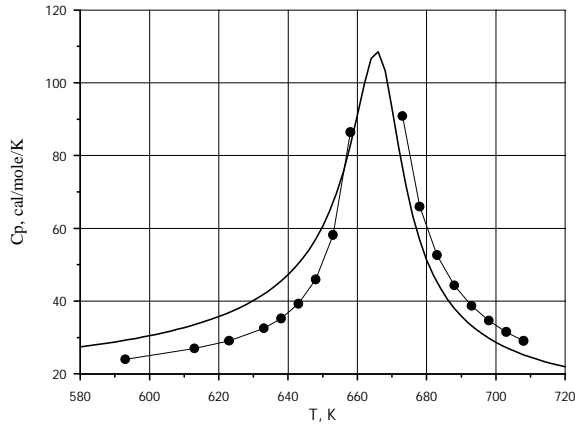


Figure 2. Heat capacity of water depending on temperature. $P = 27$. MPa. Solid line – the calculation by equation (8), dots with points – the tabular data [11].

Figure 3. Partial molar heat capacity of individual components and heat capacity of mixture vs. temperature. $P = 27$ MPa. 1- H_2O ; 2- CH_3OH ; 3- O_2 ; 4 – CO ; 5 – mixture.

$$G_i - G_i^0 = RT \ln \bar{f}_i,$$

$$\bar{S}_i(T, P, \mathbf{y}) = S_i^0(T, 1) - R \ln \bar{f}_i(T, P, \mathbf{y}) - \left(RT \frac{\partial \ln \bar{f}_i(T, P, \mathbf{y})}{\partial T} \right)_{P, \mathbf{y}}$$

$$\bar{C}_{pi}(T, P, \mathbf{y}) = C_{pi}^0(T, 1) - RT \left(2 \frac{\partial \ln \bar{f}_i(T, P, \mathbf{y})}{\partial T} + T \frac{\partial^2 \ln \bar{f}_i(T, P, \mathbf{y})}{\partial T^2} \right)_{P, \mathbf{y}} \quad (8)$$

$$\bar{H}_i(T, P, \mathbf{y}) = H_i^0(T, 1) - RT^2 \left(\frac{\partial \ln \bar{f}_i(T, P, \mathbf{y})}{\partial T} \right)_{P, \mathbf{y}} \quad (9)$$

$$Q^{eq}(T, P) = - \left(\sum_i n_i^{eq} \bar{H}_i(T, P, \mathbf{y}^{eq}) - \sum_i n_i^0 \bar{H}_i(T, P, \mathbf{y}^0) \right)$$

Here, $f_i = P y_i \Phi_i(T, P, \mathbf{y})$, $\Phi_i(T, P, \mathbf{y})$ - fugacity and fugacity coefficient of i -th component of the mixture.

In the above equations \mathbf{y} stands for the vector of molar composition; subscript “0” indicates respective thermodynamic values for ideal gas, calculated at $P = 0.1$ MPa at process temperature T . These values were obtained from tabular data by tenth order polynomial approximation on T . The fugacity coefficients were calculated by the RKS equation of state [7]. Heat efficiency of chemical reaction in SCF calculated by (9) differs from the heat efficiency in ideal approach, Fig. 4.

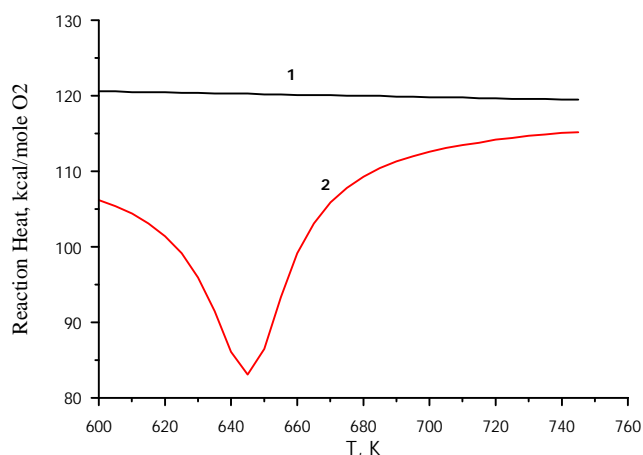


Figure 4. Heat efficiency of equilibrium chemical conversion of model mixture vs. temperature. $P = 27.0$ MPa: 1 – Calculation in ideal-gas approach, 2 – Calculation in non-ideality of mixture

CALCULATION RESULTS

Below, the modeling results are presented in order to demonstrate some important features of running chemical reactions in SCW. The flow rate and reagent concentrations used for the calculations were equal to real values. Indeed, flow 1 was fed at a rate of 35 kg/h, it contained 1.5 wt.% acetic acid; the rate of flow 2 was 7 kg/h, methanol content in flow 2 was 30 wt.%. Mass fraction of hydrogen peroxide in flow 4 was 0.3 that corresponded to molar fraction 0.185. The rate of flow 4 was set based on the stoichiometry of reactions and assuming oxygen excess $\alpha=1.2$.

Heat-exchanger. Calculation of heat-exchanger (4) was performed using the following parameters: pressure 30.0 MPa, input temperature 300K, outlet temperature 680K, external heat density $Q_{\text{inp}}^{(2)} = 5000 \text{ kcal/h/l}$. Fig. 5 presents the temperature and thermal capacity profiles of the reaction mixture along the heat-exchanger dimensionless length $L = t/t_{\text{max}}$, where t_{max} - a finite residence time sufficient to reach the specified temperature. It is seen that at the two-third part of L the feed temperature increases linearly due to external heating, whereas the thermal capacity profile remains unchanged. The above calculation results prove obvious specific character of reaction mixture heating in the heat-exchanger (4) in near-critical region.

Chemical reactor. Analysis of the proposed mathematical model of SCWO process allows to find the optimal flow of fuel by given concentration of oxidized compound and input reagent temperature. One may decline from feeding fuel to the reactor when concentration of oxidized organics is high. Since the processes in the reactor are highly sensitive to the input parameters, the calculation results represent extremely massive data files. Let us report only several results. Figure 6 illustrates the distribution of reagent concentrations along the reactor. Calculations showed that the feed temperature at the reactor entry part increased considerably due to exothermal reactions of methanol oxidation and hydrogen peroxide decomposition, whereas thermal capacity decreased down, because feed parameters progressively moved away from critical values.

Both methanol and hydrogen peroxide convert substantially at this entry part; the CO concentration proceeds through the maximum. The oxidation of acetic acid is a slow reaction; its concentration decreases almost linearly along the reactor length, Fig. 6. While the feed concentration of acetic acid is low, the increase of adiabatic temperature in reactor due to oxidation of acetic acid is insignificant (~15K). Thus, the role of methanol as the fuel is to provide sufficient temperature for the acetic acid oxidation at relatively short initial part of the reactor. Variation of fed methanol and organic wastes concentration allows controlling the temperature in the reactor.

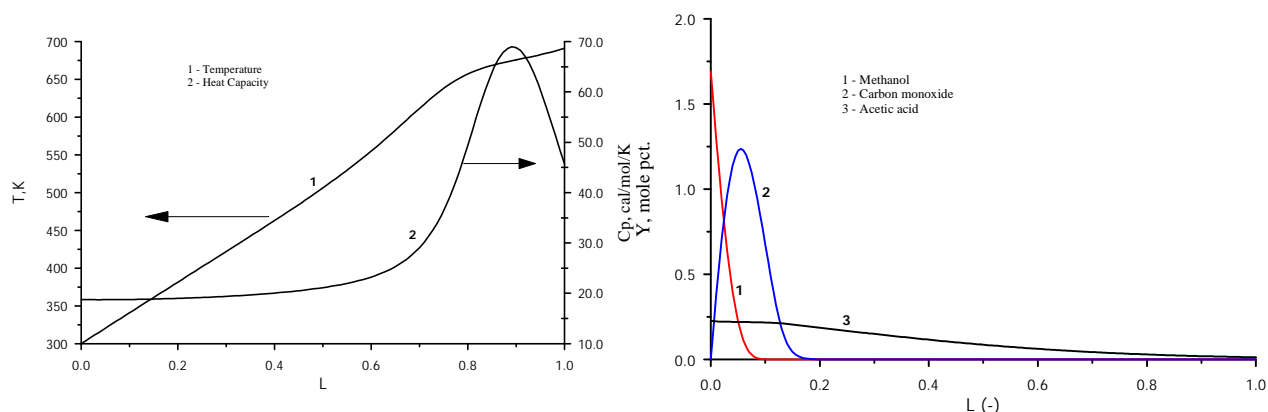


Figure 5. Variation of temperature (curve 1) and thermal capacity (curve 2) along the heat-exchanger.

Figure 6. Variation of concentrations of methanol (curve 1), carbon monoxide (curve 2) and acetic acid (curve 3) along the reactor.

CONCLUSION

The performed calculations of simplified SCWO process prove that the supercritical fluid properties affect essentially the chemical and thermal physical processes in the reactor. The proposed mathematical and thermodynamic models of individual process units can form basis for the calculation of a whole class of chemical processes in supercritical state. Currently, primary data for the designing of a pilot plant for SCWO of nitro-compounds are calculated based on the proposed models. The pilot-plant is planned to be multi-functional, and suitable for oxidation and decomposition of diverse organic compounds in SCW.

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