

# COMBUSTION OF HYDROCARBONS IN SUPERCRITICAL WATER

**Vostrikov A.A.\*, Psarov S.A. and Dubov D.Yu.**

E-mail: vostrikov@itp.nsc.ru. Fax: +7 (3832) 343094.

We have studied the kinetics of benzene, naphthalene, and heavy oil residue combustion in an aqueous solution at supercritical temperatures ( $663 \text{ K} \leq T \leq 1200 \text{ K}$ ) and pressures ( $28 \text{ MPa} \leq P \leq 90 \text{ MPa}$ ). The oxidative combustion exhibits an explosive character and can develop according to either thermal or branched-chain mechanisms. The corresponding kinetic constants for fuels are determined and conditions for these mechanisms of benzene are established.

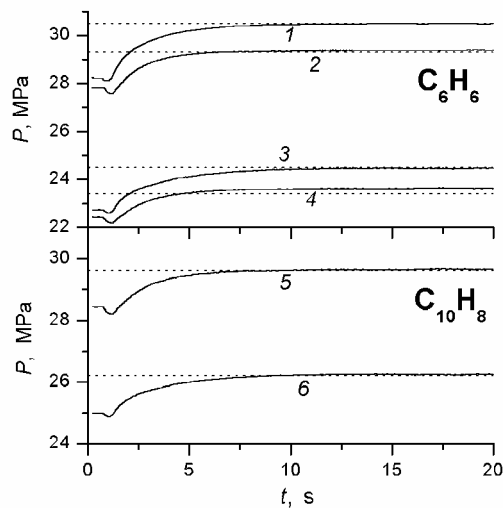
## INTRODUCTION

In recent years, basic principles have been extensively developed for use of the unique properties of water under supercritical pressures ( $P > 22.1 \text{ MPa}$ ) and temperatures ( $T > 647 \text{ K}$ ) in essentially new, ecologically safe technologies for the conversion of organic matter (OM) of low-grade fuel, and various wastes into valuable hydrocarbons, fuel, and thermal energy [1–8]. In particular, it was suggested to use the process of combustion of a low-grade fuel directly in supercritical water (SCW), thus obtaining a high-enthalpy vapor-gas working body for thermal power plants. The unique property of SCW consists in that this is a universal solvent for both OM and oxygen, while partly retaining the properties of liquid water. For example, the SCW at  $T = 663 \text{ K}$  and  $P = 30 \text{ MPa}$  has a density of  $\rho = 0.47 \text{ g/cm}^3$  [9] and a static permittivity of  $\varepsilon = 12$  [10]. The free radical mechanism of the OM conversion in SCW and relatively low temperatures ( $T < 1000 \text{ K}$ ) required for these reactions exclude the formation of oxygen-containing organic compounds and harmful oxides, while heteroatoms such as Cl, S, and P are converted into inorganic substances [11].

## I – MATERIALS AND METHODS

In this study, we have measured for the first time the kinetics of the explosive oxidation (combustion) of benzene, naphthalene, and heavy oil residue (HOR) dissolved in SCW with  $\text{O}_2$ , established mechanisms, and determined the kinetic constants of the oxidation process. The experiments consisted in automated continuous monitoring of the solution pressure in a reactor before and after fuel injection into SCW or an SCW– $\text{O}_2$  mixture. Fuel was injected along the reactor axis via a plunger valve at a pressure of 90 MPa and a temperature of 500 K. The reactor channel had a diameter of 10 mm and a volume of  $10.3 \text{ cm}^3$ . The pressure was measured with a fast-response (10-kHz) membrane strain gauge [6]. After termination of the combustion process, the composition of reaction products was analyzed using a quadrupole mass spectrometer.

In preliminary experiments, we studied the rate of benzene and naphthalene dissolution after injection into the reactor with SCW. Figure 1 shows how the solution pressure varies with the time  $t$  after injection. Curves 1–4 refer to the temperatures  $T = 673, 674, 654,$  and  $651 \text{ K}$  and the concentrations of benzene 0.6, 0.6, 0.37, and 0.27 mol/l and water 15.1, 13.5,

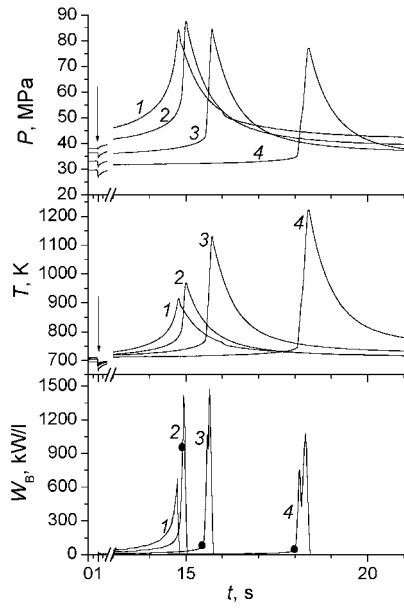


**Figure 1** : Time variation of the pressure  $P$  for the benzene and naphthalene solution in SCW. The drops on the curves 1–6 at  $t = 1$  s refer to the moment of cold fuel injection into the reactor with SCW.

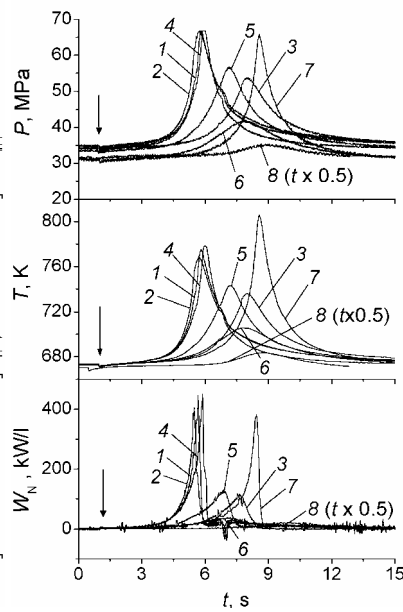
15.1, and 15.1 mol/l, respectively. Curves 5, 6 refer to the temperatures  $T = 663.7$  and  $651$  K and the concentrations of naphthalene 0.227, 0.297 mol/l and water 11.7, 15.2 mol/l. As can be seen from these kinetic curves, the pressure  $P$  quite rapidly attains a stationary level. The stationary pressure values are well described by the Redlich-Kwong equation written assuming the classical mixing rule [12] (dashed lines in Fig. 1). It should be noted that the same equation adequately described the  $P(T)$  curves for SCW mixtures with  $O_2$  and  $CO_2$  (oxidation product) in the range of oxidation parameters studied. The reaction products predominantly (>97%) consisted of  $CO_2$  and  $H_2O$  (the remainder including  $CH_4$ ,  $CO$ ,  $H_2$ ,  $C_7H_8$ , and  $C_8H_{10}$ ). This ensured reliable determination of a heat capacity of the mixture and of the thermal effect  $H(T)$  of the oxidation reaction based on the tabulated data [13]. Under these conditions, the  $P(T)$  curves measured in the course of oxidation could be used for determining the temperature in the reactor  $T(t)$ . Using the  $T(t)$  curves, we also determined the amount of heat  $Q(t)$  corresponding to the mixture temperature variations in the reactor. The heat losses  $Q_r(T)$  through the reactor wall were determined using the right-hand branches of the  $T(t)$  curves corresponding to cooling of the reaction mixture after termination of the combustion process. As a result, we determined the heat evolution with time  $Q_c(t) = Q(t) + Q_r(T(t))$ . Using the  $Q_c(t)$  values, it is easy to calculate the heat evolution rate of fuel oxidation in SCW as  $W(t) = dQ_c(t)/dt$  by numerical differentiation and concentration of reagents at time  $t$  as  $x(t) = x_0 - \nu Q_c(t)/H(T)$ . Here,  $\nu$  is stoichiometric coefficient of given reagent in the reaction of total oxidation of a particular fuel. In this study, the  $W(t)$  curves were calculated for 15 sets of initial conditions for benzene, 8 - for naphthalene, and 6 - for HOR.

## II – RESULTS AND DISCUSSION

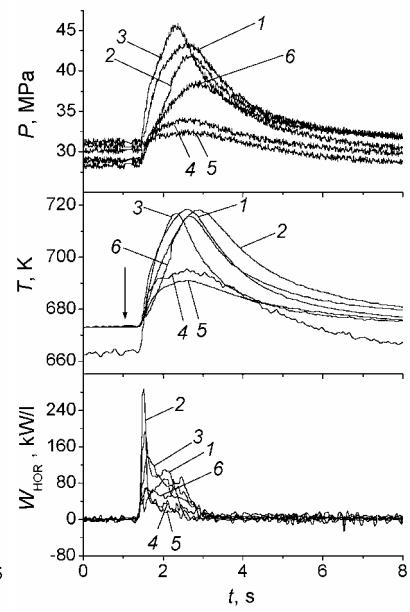
Figures 2, 3, and 4 present  $P(t)$ ,  $T(t)$ , and  $W(t)$  for benzene, naphthalene, and HOR combustion in SCW– $O_2$  mixture correspondingly. Initial concentrations of reagents are shown in Table 1. HOR examined in this work has the gross formula  $C_{10}H_{14.3}S_{0.015}$ . For convenience, we present HOR in mol of substance  $C_{10}H_{14.3}S_{0.015}$ .



**Fig. 2**



**Fig. 3**



**Fig. 4**

**Figure 2, 3, 4** : Time variation of the pressure  $P$ , temperature  $T$ , and heat evolution rate  $W$  during the explosive oxidation of benzene (Fig. 2), naphthalene (Fig. 3), and HOR (Fig. 4) by oxygen in SCW.

**Table 1** : Initial concentrations of reagents

Reagent, mol/l	Number of curve on Figures							
	1	2	3	4	5	6	7	8
$C_6H_6$	0.183	0.349	0.360	0.360				
$O_2$	0.838	0.691	0.591	0.607				
$H_2O$	13.49	12.50	8.35	6.79				
$C_{10}H_8$	0.118	0.092	0.053	0.145	0.092	0.152	0.092	0.092
$O_2$	0.855	0.833	0.777	0.757	0.573	0.249	0.922	0.097
$H_2O$	19.95	19.95	19.95	19.95	19.95	19.95	16.18	16.18
HOR ( $C_{10}H_{14.3}S_{0.15}$ )	0.051	0.032	0.173	0.051	0.173	0.051		
$O_2$	0.339	0.320	0.291	0.206	0.242	0.272		
$H_2O$	19.95	19.95	19.95	19.95	18.87	13.48		

An analysis showed that some of the  $W_B(t)$  curves contain break points related to the jumps in  $W$ . The positions of the first jump are indicated by black circles in Fig. 2. These features in the behavior of  $W_B(t)$  are related to a change in the mechanism of benzene oxidation in SCW, by analogy with the changes observed for the hydrocarbon oxidation in the gas phase [14, 15]. In the region of mixture parameters for the time before the first jump in  $W$ , the behavior of  $W_B(t)$  is determined primarily by the oxidation of fuel via the reaction with  $O_2$  (stationary oxidation regime). This regime has been also observed for naphthalene and HOR oxidation in SCW- $O_2$  mixture. A more involved shape of the  $W_{HOR}(t)$  profile is explained by the more complex composition of this fuel. Apparently, various HOR components are characterized by different oxidation rates. In addition, heavier components may slower dissolve in SCW.

In the regime of slow oxidation of fuel by oxygen, the oxidation rate  $W(t)$  is described in terms of a global reaction equation in the form [2] taking into account the influence of the nonideality of SCW on the reaction activation energy:

$$W = A \exp\left(-\frac{E_0 - E(\varepsilon)}{RT}\right) \prod_i [n_i]^{\Theta_i}. \quad (1)$$

Here,  $E_a = E_0 - E(\varepsilon)$  is the activation energy,  $[n_i]$  is the concentration of the  $i$ -th reagent, and  $\Theta_i$  is the reaction order with respect to the  $i$ -th reagent. The quantity  $E(\varepsilon)$  allows for a change in the energy of the activated complex in the reaction of fuel oxidation by oxygen in SCW, which is related to manifestations of the polar properties of water. The  $E(\varepsilon)$  value was determined by the formula [16]:

$$E(\varepsilon) = \alpha \frac{\varepsilon - 1}{2\varepsilon + 1}, \quad (2)$$

where  $\alpha = \mu^2 / r^3$ ,  $\mu$  is the dipole moment of the activated complex and  $r$  is the effective radius of the activated complex in solution. The coefficient  $\alpha$  was used as a fitting parameter, and the values of  $\varepsilon$  for various  $T$  and  $\rho$  were taken from reference data [10].

The results of fitting by least squares showed that the experimental curves of  $W(t)$  for the times corresponding to oxidation of benzene, naphthalene, and HOR in the stationary regime are most adequately described by the following expressions:

$$\begin{aligned} W_B &= 10^{15.5 \pm 0.3} \exp\left(-\frac{205 \pm 4}{RT} + \frac{55 \pm 3}{RT} \frac{\varepsilon - 1}{2\varepsilon + 1}\right) [C_6H_6]^{0.16 \pm 0.03} [O_2]^{0.94 \pm 0.07} \\ W_N &= 10^{15.2 \pm 0.3} \exp\left(-\frac{194 \pm 5}{RT} + \frac{59 \pm 4}{RT} \frac{\varepsilon - 1}{2\varepsilon + 1}\right) [C_{10}H_8]^{0.44 \pm 0.01} [O_2]^{0.62 \pm 0.02} \\ W_{HOR} &= 10^{14.9 \pm 0.4} \exp\left(-\frac{188 \pm 4}{RT} + \frac{24 \pm 3}{RT} \frac{\varepsilon - 1}{2\varepsilon + 1}\right) [C_{10}H_{14.3}]^{0.67 \pm 0.04} [O_2]^{0.12 \pm 0.02} \end{aligned} \quad (3)$$

In Eqs. (1)–(3), the oxidation rate  $W$  is expressed in [kW/l], the concentrations of reactants in [mol/l], and the activation energy  $E_a$  in [kJ/mol].

The results of mass-spectrometry analysis of benzene oxidation products in SCW for curves 1 and 4 on Fig. 2 are given in Table 2. In Table 2, the amount of carbon atoms in every carbon-bearing product is normalized to the total amount of carbon atoms in products of benzene partial oxidation.

**Table 2** : Products of benzene oxidation in SCW–O<sub>2</sub> fluid, %

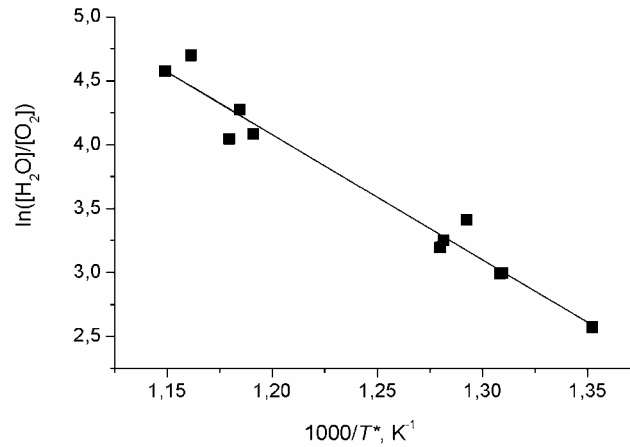
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8</sub> H <sub>10</sub>	CO	CO <sub>2</sub>
1	0.11	0.07	0.09	0.01	1.10	98.62
4	0.70	0.12	0.10	0.00	3.40	95.68

Analysis of outcome products demonstrated that the molar fraction of incompletely oxidized reaction products was lower than 5% and it decreases with the concentration of water in the reactor. This means that the rest of benzene molecules kept after act of reaction of C<sub>6</sub>H<sub>6</sub> with O<sub>2</sub>, is swiftly after-oxidized down to CO<sub>2</sub> and H<sub>2</sub>O. However, the rate of after-oxidation decreases with increasing water concentration. The reason, as we demonstrate below, is a change in mechanism of C<sub>6</sub>H<sub>6</sub> oxidation in mixture SCW–O<sub>2</sub>. The jumps in  $W_B(t)$  indicated by the black circles in Fig. 2 is related to the transition from a slow oxidation of benzene by oxygen to a faster, nonstationary, oxidation of C<sub>6</sub>H<sub>6</sub> by active species in the reaction medium. These species, formed in the reactions of oxygen with intermediate

oxidation products, are capable of initiating oxidation according to the branched-chain mechanism [14, 15]. A boundary condition for the passage from stationary to nonstationary regime of oxidation is the equality of the branching rate  $k_+$  and the chain termination rate  $k_-$  [14]. Since the active species are formed in the reactions involving  $O_2$  [15], in the excess of  $C_6H_6$  we may assume that  $k_+ = A_+ \exp(-E_+/RT)[O_2]$ . Then, taking into account that quenching of the active species is an activationless process ( $E_- = 0$ ) determined by the pair collisions with  $H_2O$  molecules, we can assume that  $k_- = A_-[H_2O]$ . Taking the logarithms of these expressions and using the condition of their equality, we eventually obtain

$$\ln(A^*) - \frac{E_+}{RT^*} = \ln\left(\frac{[H_2O]}{[O_2]}\right), \quad (4)$$

where  $A^* = A_+/A_-$  and  $T^*$  is the temperature of the transition from stationary to nonstationary oxidation regime. Dependence of  $\ln([H_2O]/[O_2])$  on the temperature  $T^*$  is show on Fig. 5.



**Figure 5** : Dependency of relative concentration  $[H_2O]/[O_2]$  on the temperature  $T^*$ .

Applying the least squares method to the experimental data corresponding to black circles on the  $W_B(t)$  curves in Fig. 5, we obtained the following values of the kinetic constants:  $A^* = 10^{6.8 \pm 0.3}$  and  $E_+ = 80 \pm 3$  kJ/mol. It should be noted that the energy  $E_+$  of the partial oxidation of  $C_6H_6$  in SCW falls within the region of vales reported previously, 90 kJ/mol [14] and 75–87 kJ/mol [15], for the gas phase oxidation of benzene under the conditions corresponding to the first jump in  $W_B(t)$ .

Substituting the above values of  $A^*$  and  $E_+$  into Eq. (4), we may readily the dependence of  $T^*$  on the relative concentration  $[H_2O]/[O_2]$  for the partial oxidation of benzene with oxygen in SCW. Using the kinetic constants determined in this study, it is possible to calculate the energy parameters of a stationary combustion process and to determine conditions for the passage to nonstationary benzene combustion in SCW.

## CONCLUSION

Obtained in this work kinetic constants of heat evolution during combustion of benzene, naphthalene, and HOR in SCW permit to calculate energy parameters of stationary combustion regime of examined hydrocarbons and transition conditions to nonstationary oxidation of benzene.

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