Pyrolysis of Eicosane, Naphthalene and Thiophene in Supercritical Water

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Kinetics of eicosane, naphthalene, and thiophene (fuel) pyrolysis in an aqueous solution at supercritical temperatures ($400^{o}C \leq T \leq 750^{o}C$) and pressure $P = 30$ MPa has been studied. Using the first order kinetics of fuel pyrolysis the corresponding kinetic constants are determined.

INTRODUCTION

The progress in using water under supercritical conditions ($T > 374°C$, $P > 22.1$ MPa) as an active medium for partial oxidation of organic compounds in order to convert them into more useful or safe products has stimulated fundamental and applied investigations of the properties of supercritical water (SCW) [1]. Some parameters such as density, dielectric constant, and ionic dissociation constant change by orders of magnitude following an increase in P and T, thus inducing changes in the mechanisms and kinetics of reactions performed in SCW. Under supercritical conditions, water can dissolve any amounts of oxygen and of weakly polar or nonpolar organic substances [2]. The sharp decrease in the ionic dissociation constant for SCW (eg., to about $2\cdot10^{-20}$ at $T = 500°C$ and $P = 25$ MPa) [2] results in ionic reaction mechanisms being replaced by free radical mechanisms. The conversions of hydrocarbon under these conditions yield weakly polar and nonpolar substances such as methane, ethane, benzene, hydrogen, and carbon oxides as the major products [3]. The purpose of this work is to study experimentally the pyrolysis of eicosane, naphthalene, and thiophene in SCW. This makes possible understanding of the role of SCW in pyrolysis of the heavy organic substances.

I – MATERIALS AND METHODS

The investigations were conducted in a cylindrical batch reactor made of the stainlesssteel. The setup was described in detail previously [4]; hence, only the functional diagram is given here (Fig. 1). The amount of molecular oxygen (β) in SCW varied from 0 to 2.5 moles per mole of the fuel. The fuel : H_2O molar ratio in the reactor was controlled by adding a definite amount of the fuel; the density of SCW was taken from a handbook [5]. The reaction time (t) was measured starting from the instant of completion of fuel feeding into the reactor and ending at the instant the reaction mixture was removed from the reactor into a trap cooled with liquid nitrogen. Supercritical water (either neat or mixed with oxygen) was supplied from a pre-reactor to the evacuated reactor heated to the working temperature. Since the pre-reactor volume was 30 times as large as the reactor volume, the temperature change was insignificant. During the reaction, the pre-reactor damped the increase in the reactor pressure. The specified amount of the fuel was injected into the reactor using a piston, which plugged the reactor inlet. The fuel was injected into the upper section of the reactor arranged vertically. The fast dissolution of to be ~1 s was promoted by free convective stirring with downward migration of the denser fuel. Both the reactor and the pre-reactor were maintained

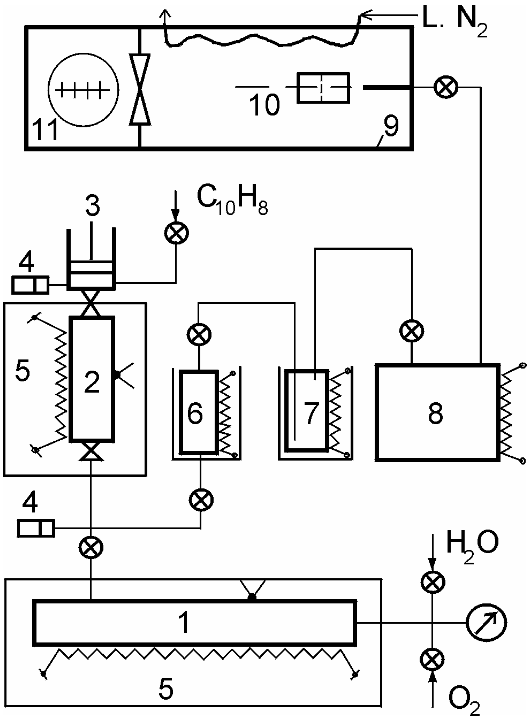

Figure 1 : Schematic diagram of the setup: (1) pre-rector; (2) reactor; (3) piston; (4) strain transducer; (5) thermostats; (6) trap; (7) separator; (8) receiver for the gaseous products; (9) vacuum chamber; (10) ion source of a quadrupole mass spectrometer; (11) turbo-molecular pump.

at a reaction temperature. The temperature was measured by thermocouples. The pressure was measured with diaphragm strain transducers in the 1–40 MPa range with an accuracy of 0.25%. The reaction products were analyzed using a MS-7303 quadrupole mass spectrometer located in a high-vacuum chamber. The reaction products traveled to the mass analyzer via the following route: reactor – trap – cryogenic separator – receiver – vacuum chamber – ion source of the mass spectrometer. The gases under analysis flew out of the heated receiver (≈120°C) into the high-vacuum chamber. A molecular beam was formed from the gas stream by diaphragms [6]; the beam crossed the ion source of the mass spectrometer. The quantitative composition of the reaction products was determined from the mass spectra after normalizing to the ionization cross section (taking into account the dissociative ionization) for each gaseous component [3,4].

II – RESULTS AND DISCUSSION

Eicosane ($C_{20}H_{42}$). The dependences of the molar ratio (*N*) of CH_4 (curves 1), CO_2 (2), CO (3), H_2 (4), and eicosane (5) in the products of eicosane pyrolysis on temperature and on reaction time measured at $P = 30$ MPa and an $H_2O : C_{20}H_{42}$ mass ratio of 1 : 0.5 are shown in Figs. 2 and 3. The number of moles of each substance was normalized to the initial number of eicosane moles corresponding to the reaction temperature. The dependences shown by curves 5 were derived from measurements of the amount of unreacted eicosane in the products of pyrolysis. The amount of unreacted eicosane in the pyrolysis without water ("dry" pyrolysis) was measured for comparison. By analogy with [7], the kinetics of "dry" pyrolysis of heavy hydrocarbons was described using a first-order equation:

$$\frac{dL}{dt} = -kL, \tag{1}$$

where *L* is the amount of the compound studied, *k* is the rate constant of the reaction described by the Arrhenius dependence

$$k(T) = A\exp\left(\frac{-E}{RT}\right), \tag{2}$$

where *E* is an activation energy, *R* is the universal gas constant. The values obtained for the "dry" pyrolysis of eicosane were $E = 241\pm1$ kJ/mol and $A = 10^{14.5\pm0.5}$ s^{-1}; these are consistent with data [7]. Since the amount of water in the reactor virtually does not change during eicosane pyrolysis in SCW, the kinetics of this process was also described using the equation (1) and (2). This gave $E = 266\pm16$ kJ/mol and $A = 10^{16.5\pm0.5}$ s^{-1}, i.e ., the rate of pyrolysis is higher in SCW. For example, at $T = 500°C$, the effective rate constant for "dry" pyrolysis is $k = 1.8 \cdot 10^{-2}$ s^{-1}, while that for the pyrolysis in SCW is $k = 3.8 \cdot 10^{-2}$ s^{-1}. Eicosane pyrolysis goes to completion at $T < 500°C$ (see Fig. 2) giving rise to a complex mixture of lighter hydrocarbons.

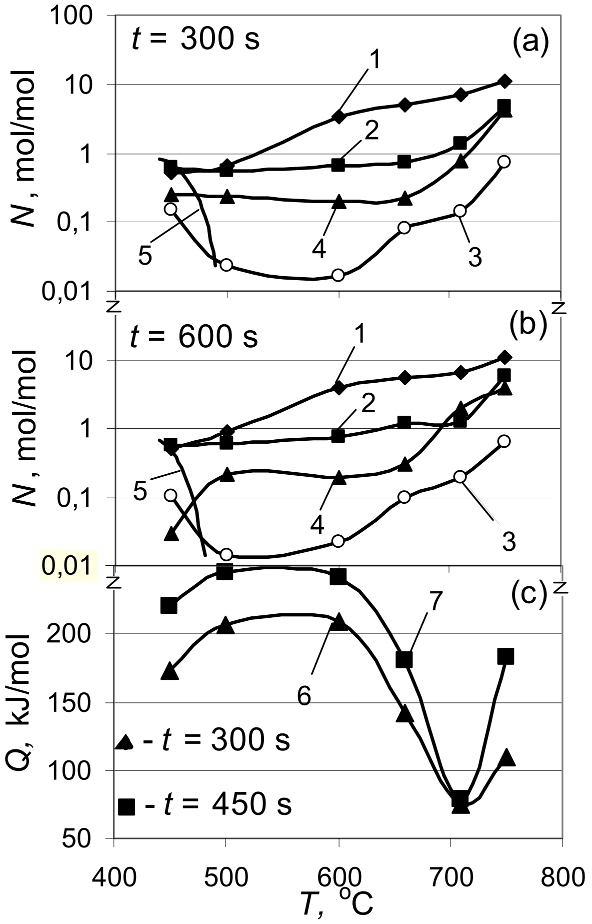

Figure 2 : Proportions (N) of CH_4 (1), CO_2 (2), CO (3), H_2 (4), and $C_{20}H_{42}$ (5) in the products of eicosane pyrolysis in SCW (a, b) and heat of the reaction (Q) (c) vs. T at different t.

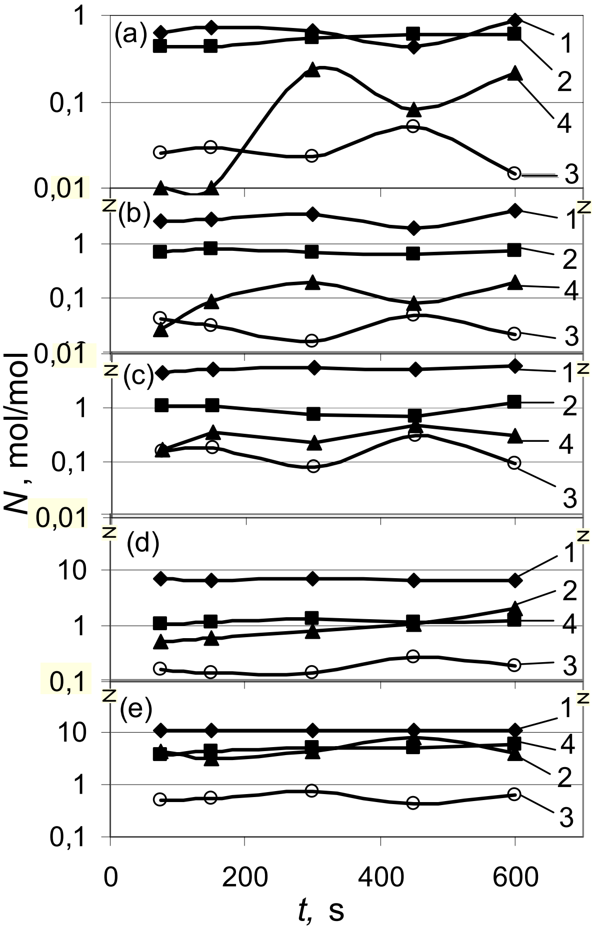

Figure 3 : Proportions (N) of CH_4 (1), CO_2 (2), CO (3), H_2 (4), and $C_{20}H_{42}$ (5) in the products of eicosane pyrolysis in SCW vs. t for different T. T, °C: (a) 500, (b) 600, (c) 660, (d) 710, (e) 750.

Mass-spectrometric measurements of the quantitative composition of the reaction products in SCW provided the possibility of calculating the heat of the reaction (Q). The variation of Q vs. T is shown in Fig. 2 (c) for t = 300 and 450 s (curves 6 and 7). It can be seen that the energy consumption (heat) of the reaction increases with an increase in T to ~550°C. The increase in the energy consumption is due to the destruction of eicosane molecules and decrease in the molecular masses of the fragments (see Fig. 2 (a), (b)). The pattern of the $Q(T)$ dependence changes in kind at $T > 550°C$. This is caused by energy evolution during oxidation and hydrogenation of hydrocarbons by H_2O molecules (see. Fig. 2, curves 1–3).

It was found that the experimental time and temperature dependences of the number of H_2 molecules in the reaction obey first-order kinetics with the rate constant k and the concentration of H_2 at $t = \infty$ as variable parameters. With the assumption of applicability of the Arrhenius $k(T)$ dependence, this gave $E = 530 \pm 30$ kJ/mol, $A = 10^{25 \pm 0.8}$ s^{-1}.

It can be seen from Fig. 2 and 3 that the CO : CO_2 ratio is << 1 over the whole temperature range studied. This means that the rates of formation of CO and CO_2 are close. A general equation for CO oxidation in SCW has been derived [8]. This equation implies that the observed CO : CO_2 ratio is established, for example, at $T \geq 710°C$ over the period $t \approx 60$ s.

Naphthalene ($C_{10}H_8$). The analysis of the gaseous products formed upon naphthalene pyrolysis in SCW showed the presence of a narrow range of compounds, namely CH_4, benzene and toluene (a very small amount), H_2, carbon oxides, and unreacted naphthalene. Determination of the quantitative composition posed no difficulties because the molecular ion peaks of these compounds do not overlap and the ionization cross-sections are known.

After removal of the vapor–gas mixture and cooling, the reactor was freed. The elemental composition of the solid residue after reaction was determined by weighing the products of complete combustion of this material in an O_2 flow in a quartz reactor. The C : H molar ratio in the residue was about ~2. (Hereinafter, carbon in the residue will be referred to as soot and, for a more convenient comparison of soot with other reaction products, its amount will be conventionally expressed in moles of the C_{10} cluster.) The experiments were carried out within a time interval $t = 90–600$ s.

Some of the results of analysis of the products of naphthalene conversion in SCW are plotted as dependences of the proportion of each component (N) on the proportion (β) of O_2 in SCW at 710°C, $t = 600$ s (Fig. 4) and on the reaction temperature for $\beta = 2.1$ at $t = 600$ s (Fig. 5). The molar amount of each substance is referred to the molar amount of naphthalene injected into the reactor. The change in the amount of water due to the reaction was calculated from the oxygen balance before and after the reaction.

Figure 4 demonstrates that for $\beta = 0$, i.e., in the absence of O_2 , the reaction products contain carbon oxides. This implies that water acts as the source of oxygen atoms, that is, it chemically participates in the pyrolysis of naphthalene. Interestingly, the amount of CO does not depend on β, while the amounts of CO_2 and H_2O increase with an increase in the content of O_2 in the reactor. Hence, in the absence of O_2, carbon dioxide is formed in the reaction of CO with H_2O. Apparently, at $T \leq 660°C$, the conversion of naphthalene in SCW mainly advances via complete oxidation of some of naphthalene by oxygen. As the temperature increases, pyrolysis is accelerated and other compounds appear in the conversion products, in addition to CO_2 and H_2O.

The rate of pyrolysis was described by the first-order kinetic equation (1). The experimental $L(t)$ dependence at 710°C is described satisfactorily by this equation with $k = 4.0 \pm 0.6 \cdot 10^{-4}$ s^{-1}. The data were processed using the least-squares method. The resulting temperature dependence $k(T)$ is described adequately by the Arrhenius relation (2) with the constant $A = 10^{12.3 \pm 0.2}$ s^{-1} and with the activation energy $E = 294 \pm 4$ kJ/mol. The common expression for $k(T)$ is $k = 10^{12.5 \pm 0.2} \exp[-(294 \pm 4)/RT]$.

The dependences of the heat of reaction (Q) on β (see Fig. 4) and on T (see Fig. 5) were elucidated from the quantitative composition of the products of naphthalene conversion in SCW. The Q values were calculated from the differences between the heats of formation of the final and initial substances at the reaction temperature [9]. The Q values presented in Figs. 4 and 5 are referred to the amount of naphthalene decomposed. It can be seen from Fig. 4 that even at $\beta = 0$, the conversion of naphthalene in SCW is an exothermic reaction.

Under certain conditions, the heat evolved in the conversion of naphthalene in SCW can raise significantly the temperature of the mixture in the reactor. The calculated dependences of the temperature increments (ΔT) on β and T, related to the heat of reaction in pure SCW, are also presented in Figs. 4 and 5. The ΔT values were found in the adiabatic approximation using reference data on the temperature dependences of the enthalpy of SCW [5].

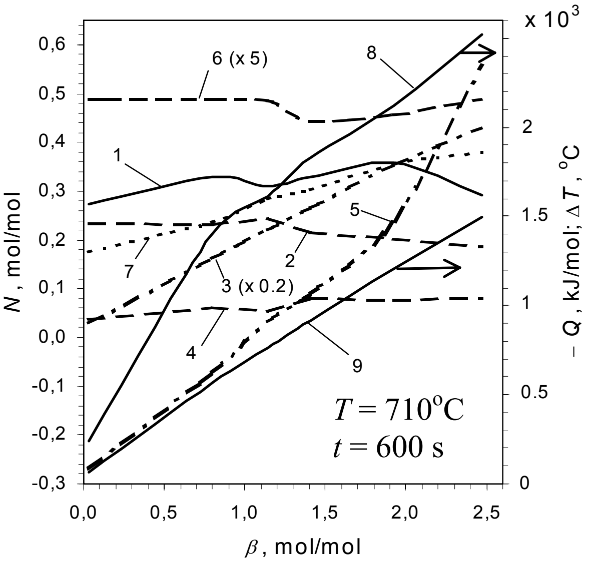

Figure 4 : Effect of the amount of molecular oxygen in the reactor on the proportions of some products of naphthalene pyrolysis: CO_2 (1), CO (2), H_2O (3), soot (4), H_2 (5), CH_4 (6), $C_{10}H_8$ (7); heat of the reaction *Q* (8); increment of the temperature of water ΔT (9).

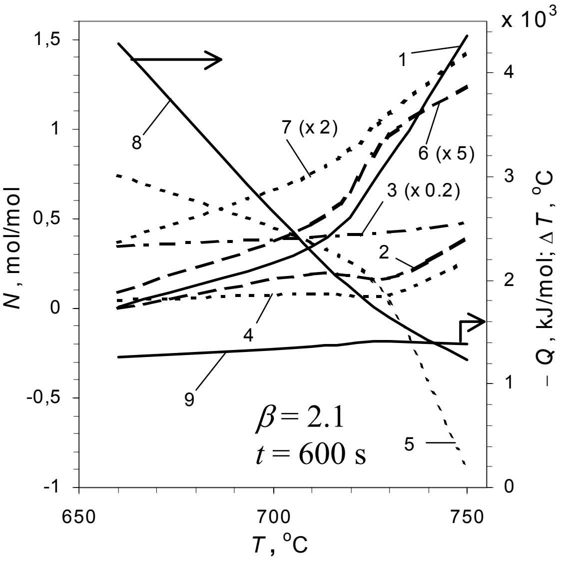

Figure 5 : Effect of the reactor temperature on the proportions of some products of naphthalene pyrolysis: CO_2 (1), CO (2), H_2O (3), soot (4), H_2 (5), CH_4 (6), $C_{10}H_8$ (7); heat of the reaction *Q* (8); increment of the temperature of water ΔT (9).

Generally, our investigation showed that at $T \geq 660°C$, water having supercritical parameters participates chemically in the conversion of naphthalene in the absence of molecular oxygen. The introduction of O_2 does not influence the chemical composition of the reaction products because oxygen is consumed rapidly and almost completely for oxidation of some of naphthalene to CO_2 and H_2O. The quantitative composition of the products of naphthalene conversion even in the absence of molecular oxygen implies an exothermic reaction.

Thiophene (C_4H_4S). With two initial substances (H_2O и C_4H_4S) at $T = 750^oC$, we observe in mass-spectrum the products of oxidation: CO, CO_2, COS. The existence of oxygen-containing products indicated that water participates in decomposition of thiophene. The total balance in elements H, C, and O for reagents and products is kept, indicating that no soot formation occurs. It was no soot when we opened the reactor. The relative concentrations of reaction products at $T = 750^oC$ and $t = 600$ s corresponds to the brutto-formula of reaction: $C_4H_4S + 3.23H_2O \rightarrow 1.95H_2 + 1.52CH_4 + 0.71CO + 1.26CO_2 + 0.087C_6H_6$ (+S). The rate constant for thiophene pyrolysis in SCW $k = 10^{4.0\pm0.4} \exp[-(120\pm8)/RT]$ s^{-1}, where *R* has dimention of [kJ/(mol·K)].

Thiophene decomposition with oxygen for the mixture with mass ratio $H_2O : C_4H_4S : O_2 = 2 : 1 : \beta$ increased up to 90 % at $T = 750^oC$, $t = 600$ s, and $\beta = 1.46$. The balance of C, H and O is kept, that is no soot formation. The brutto-formula for decomposition: $C_4H_4S + 3.83O_2 \rightarrow 0.31H_2 + 0.28CH_4 + 0.45CO + 3.08CO_2 + 0.031C_6H_6 + 1.04H_2O$ (+S).

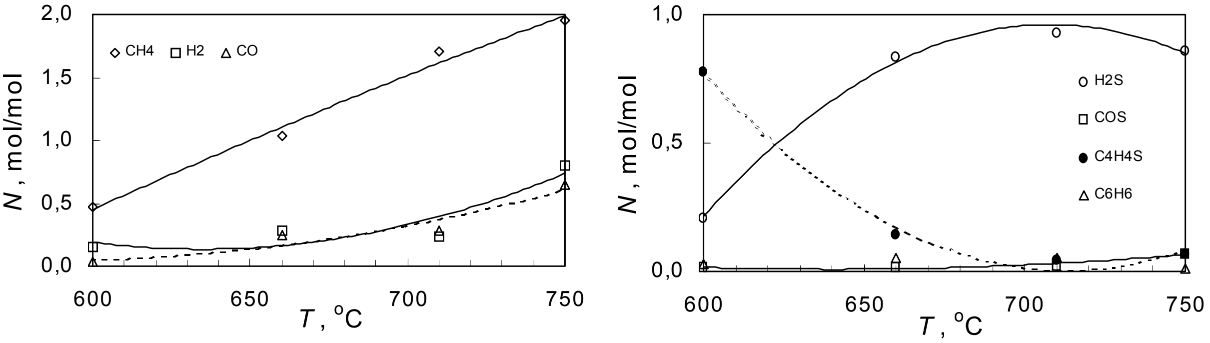

Figure 6 : Gaseous products of the thiophene pyrolysis depending on the reacion temperature at $t = 600$ s, $H_2O : C_4H_4S : O_2 = 1 : 1 : 0.5$.

The temperature dependence of gaseous products for thiophene pyrolysis at mass ratio $H_2O : C_4H_4S : O_2 = 1 : 1 : 0.5$ is shown in Fig. 6. This data was obtained from mass-spectra after normalizing to the molar content of S in spectra (that is, normalization on C_4H_4S amount in the reactor for every specific *T*).

CONCLUSION

Thus, it can be concluded that SCW chemically participates in the conversion of hydrocarbons. The major products of a redox process in SCW include hydrogenated hydrocarbons, H_2, CO_2, and CO. The formation of CO_2, CO, and H_2 is sharply accelerated at $T > 660$°C. As this takes place, the proportion of CO remains relatively low, and the $H_2 : CO_2$ ratio increases.

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