Brief Communications

Pyrolysis of eicosane in supercritical water

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Pyrolysis of eicosane and redox reactions of the pyrolysis products in supercritical water (SCW) were studied in a batch reactor at 30 MPa, in the temperature range from 450 to 750 °C and with reaction times ranging from 75 to 600 s. The rate constants for eicosane pyrolysis ($k' = 10^{16.5\pm0.5}\exp[-(32000\pm2000)/T]\ \mathrm{s}^{-1}$) and for the formation of H_2 ($k'' = 10^{25\pm0.8}\exp[-(64000\pm4000)/T]\ \mathrm{s}^{-1}$) were determined. The time and temperature dependences of the heat of reaction were elucidated. Water accelerates pyrolysis and participates in the subsequent transformations of the pyrolysis products. The yield of H_2 sharply increases for $T > 700$ °C.

Key words: supercritical water, eicosane, partial oxidation, hydrogenation, batch reactor, mass spectrometric analysis.

Supercritical water (SCW) at $T > 374$ °C and $P > 22.1$ MPa is a suitable medium for the conversion of organic compounds to give valuable products, or to produce heat upon oxidation (combustion) of low-grade fuels, or to destroy toxic substances.[1] The high solubility of organic compounds and oxygen in SCW[2] ensures the homogeneity of the reaction medium and, as a consequence, high rates of reactions.

In this work, we studied the pyrolysis of *n*-eicosane in SCW and transformations of the products of pyrolysis to give hydrocarbons, H_2, and carbon oxides.

Experimental

The studies were carried out in a constant-volume reactor[3] ($V = 10$ cm^3) at a constant pressure of 30 MPa in the 450—750 °C temperature range. The residence time (*t*) in the reactor (reaction time), which was measured starting from the instant the reactor was filled with the compound, was varied from 75 to 600 s. Supercritical water was fed into the reactor, preliminary evacuated and heated to the working temperature, from a pre-reactor at 450 °C and ~30 MPa. The pre-reactor volume was 30 times as large as the reactor volume (thus the pre-reactor damped the pressure increase in the reactor during the process). The specified reaction temperature was established over a period of ≤12 s. The required amount of *n*-eicosane was fed with the SCW flow entering the reactor. The reactor, pre-reactor, and other components of the setup were made of the 12X18H10T stainless-steel. The reaction products were analyzed using a MS-7303 quadrupole mass spectrometer. The products traveled to the mass analyzer *via* the following route: reactor → cryogenic sorption separator → receiver → vacuum chamber → the ion source of the mass spectrometer. The gases to be analyzed flew out of the heated

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receiver (~120 °C) to a high-vacuum chamber in a continuous mode. A molecular beam was formed from the axial part of the stream by diaphragms and crossed the ion source of the mass spectrometer. The current of the beam molecules ionized by the electron impact was measured by the MS-7303 mass spectrometer. After corrections for the ionization cross-sections and fragmentation, the quantitative composition of the reaction products was calculated from the mass spectrum.[3,4]

Results and Discussion

The dependences of the proportions (*N*) of CH_4 (curves *1*), CO_2 (*2*), CO (*3*), H_2 (*4*), and *n*-eicosane (*5*) in the products of *n*-eicosane conversion on temperature for reaction times of 300 and 600 s and on reaction time for a temperature of 500—750 °C measured at 30 MPa and an $H_2O : C_{20}H_{42}$ mass ratio of 1 : 0.5 are shown in Figs. 1 and 2. The data on the density of water as functions of *T* and *P* were taken from the literature.[5] The number of moles of each substance was normalized to the initial number of *n*-eicosane moles corresponding to the reaction temperature. The dependences shown by curves *5* were derived from measurements of the amount of unreacted *n*-eicosane in the products of pyrolysis. The amount of unreacted *n*-eicosane in the pyrolysis without water ("dry" pyrolysis) was measured for comparison. By analogy with the published study,[6] the kinetics of "dry" pyrolysis of heavy hydrocarbons was described using a first-order equation: $dL/dt = -kL$, where *L* is the amount of the compound studied, *k* is the rate constant of the reaction described by the Arrhenius dependence $k(T) = A\exp(-E/RT)$. The values obtained for the "dry" pyrolysis of *n*-eicosane were $E = 241\pm12$ kJ mol^{-1} and $A = 10^{14.5\pm0.5}$ s^{-1}; these are consistent with published data[6] (see also the references in the study cited). Since the amount of water in the reactor virtually does not change during *n*-eicosane pyrolysis in SCW, the kinetics of this process was also described using the first-order equation. This gave

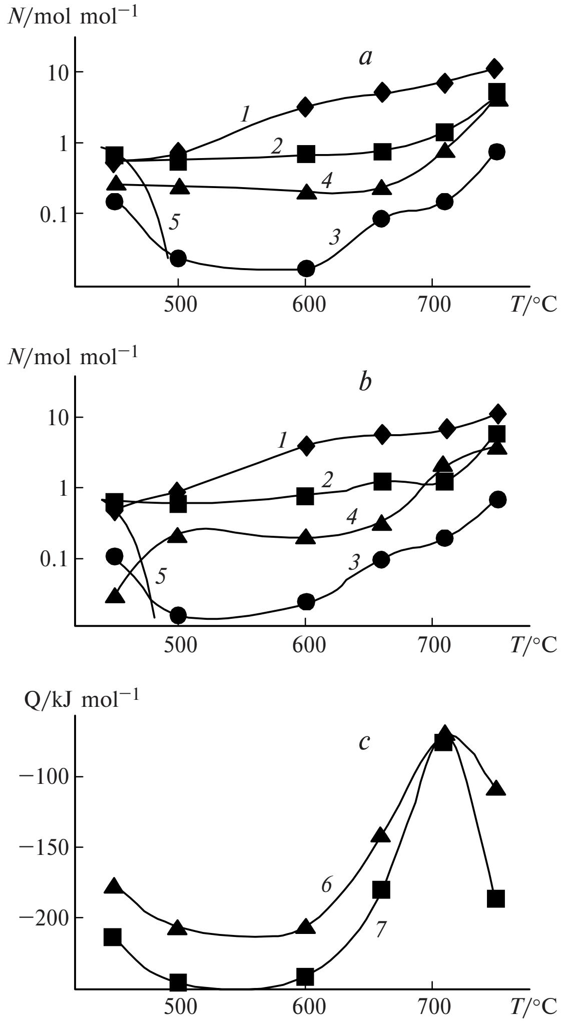

Fig. 1. Proportions (*N*) of CH_4 (*1*), CO_2 (*2*), CO (*3*), H_2 (*4*), and $C_{20}H_{42}$ (*5*) in the products of *n*-eicosane conversion in SCW (*a*, *b*) and heat of the reaction at 300 (*6*) and 600 s (*7*) (*c*) *vs.* temperature at different reaction times. Time of conversion/s: *a*, 300; *b*, 600.

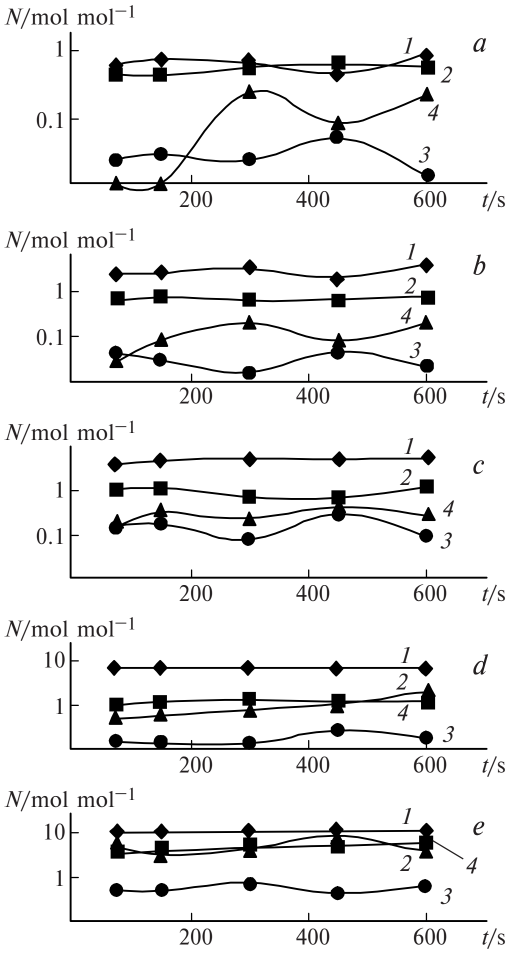

Fig. 2. Proportions (*N*) of CH_4 (*1*), CO_2 (*2*), CO (*3*), and H_2 (*4*) in the products of *n*-eicosane conversion in SCW *vs.* reaction time for different temperatures. Conversion temperature/°C: (*a*) 500; (*b*) 600; (*c*) 660; (*d*) 710; (*e*) 750.

$E' = 266\pm16$ kJ mol^{-1} and $A' = 10^{16.5\pm0.5}$ s^{-1}, *i.e.*, the rate of pyrolysis is higher in SCW. For example, at 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. 1) giving rise to a complex mixture of lighter hydrocarbons.

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. 1 for $t = 300$ and 600 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 *n*-eicosane molecules and decrease in the molecular masses of the fragments (see Fig. 1, curves *1—5*). 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. 1, curves *1—3*). For example, the Q values for the exothermal reaction

$$C_iH_j + \frac{4i-j}{4}H_2O = \frac{4i-j}{8}CO_2 + \frac{4i+j}{8}CH_4 + Q$$

with *n*-eicosane, naphthalene, benzene, and ethane at $T = 0$ K are equal to 246.2, 238.7, 159.7, and 24 kJ mol^{-1}, respectively.

The destruction of the main bulk of saturated and unsaturated $C_{n>1}$ hydrocarbons becomes almost complete at $T \approx 700$ °C. This can be seen from comparison of the number of carbon atoms in the initial compound and in the final products. As a consequence, hydrogenation is retarded, which affects the pattern of the $Q(T)$ dependence. The retardation of hydrogenation at higher temperatures results in a higher content of H_2 in the reaction products (see Fig. 1, curves *4*). The formation of a CO_2 molecule is accompanied by liberation of four hydrogen atoms from water. 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 given 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 $E'' = 530\pm30$ kJ mol^{-1}, $A'' = 10^{25\pm0.8}$ s^{-1}.

The dependences shown in Figs. 1 and 2 make it possible to distinguish three characteristic temperature ranges for *n*-eicosane conversion in SCW. Below 500 °C, *n*-eicosane pyrolysis predominates. At $T > 500$ °C, the concentrations of lighter hydrocarbons and methane increase continuously with an increase in T. Methanation of the reaction products does not result from the dissociation of water molecules alone. This conclusion follows from the fact that at $T < 660$ °C, the content of CO_2 virtually does not depend on the temperature or reaction time, while the amount of CH_4 increases with an increase in T and t. For $T > 660$ °C, the concentration of CH_4 does not virtually depend on t, while CO_2 and H_2 are accumulated as the temperature increases. Analysis of the mass spectra of the hydrocarbon-type reaction products showed that an increase in the temperature in the $500 < T < 660$ °C range entails aromatization of the products and a decrease in their molecular weights, while at $T \approx 660$ °C, dearomatization starts.

During the conversion of *n*-eicosane in SCW, the rate of decomposition of water molecules to give CO, CO_2, and H_2 at $T < 660$ °C is relatively low (see Figs. 1 and 2). 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.[7] This equation implies that the observed CO : CO_2 ratio (see Fig. 1) is established, for example, at $T \geq 710$ °C over the period $t \approx 60$ s.

Thus, it can be concluded that water 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.

References

1. P. E. Savage, S. Gopalan, T. I. Mizan, C. J. Martino, and E. E. Brock, *AIChE J.*, 1995, **41**(7), 1723.
2. J. W. Tester, H. R. Holgate, F. J. Armellini, P. A. Webley, G. T. Hong, and H. E. Barner, in *Emerging Technologies in Hazardous Waste Management III, ACS Symposium Series*, Eds. D. W. Tedder and F. G. Pohland, American Chemical Society, Washington, DC, 1993, **518**, 35.
3. A. A. Vostrikov, D. Yu. Dubov, and S. A. Psarov, in *Khimiya Nefti i Gaza* [*Oil and Gas Chemistry*], Izd-vo STT, Tomsk, 2000, **2**, 492 pp. (in Russian).
4. V. A. Galichin, S. V. Drozdov, D. Yu. Dubov, V. V. Mikhailin, S. A. Psarov, and A. A. Vostrikov, in *Aktual'nye Voprosy Teplofiziki i Fizicheskoi Gidrogazodinamiki* [*Topical Items of Thermal Physics and Physical Hydraulic Gas Dynamics*], In-t teplofiziki SO RAN, Novosibirsk, 1998, 268 pp. (in Russian).
5. M. P. Vukalovich, *Tablitsy termodinamicheskikh svoistv vody i vodyanogo para* [*Tables of Thermodynamic Properties of Water and Water Vapor*], Energiya, Moscow, 1965, 400 pp. (in Russian).
6. J. Yu and S. Eser, *Ind. Eng. Chem. Res.*, 1997, **36**, 574.
7. H. R. Holgate, P. A. Webley, J. W. Tester, and R. K. Helling, *Energy and Fuels*, 1992, **6**, 586.

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