



# Heavy oil upgrading at oxidation of activated carbon by supercritical water-oxygen fluid



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## ABSTRACT

In this paper, we have investigated for the first time heavy oil conversion under the conditions of activated carbon (AC) oxidation by supercritical water-oxygen (SCW/O<sub>2</sub>) fluid at temperature 723 K, pressure 30 MPa, constant flow rate of water and oil (6 and 4 g/min, respectively), and variable flow rate of oxygen (0–3.5 g/min). The experiment was performed by supplying the oil (from the top) and SCW/O<sub>2</sub> fluid (from the bottom) into a vertically located tubular reactor packed with AC. The obtained time dependences of the reactor wall temperature and the power of resistance heaters allowed revealing that due to heat generation during the combustion of AC and oil high-molecular components in SCW/O<sub>2</sub> fluid the conversion process occurs in autothermal mode. The overall yield of volatile combustibles and liquid products of oil conversion amounted to 24.0 and 59.5 wt.%, respectively. It is shown that the involvement of water in redox reactions with AC and oil high-molecular components accumulated in the AC bed, contributes to the enrichment of conversion products with hydrogen (the portion of H<sub>2</sub> and CH<sub>4</sub> in the volatile combustible products is >60 mol.%). We detected a significant decline in the fractions of asphaltene and resin, as well as the content of vanadium (V) and nickel (Ni) in the liquid products compared to crude oil due to their accumulation in the AC bed. It follows from the results of IR and <sup>1</sup>H NMR spectroscopy that a significant increase in the content of aromatic compounds in the liquid products occurs only at the increase in oxygen flow rate up to 3.5 g/min.

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## 1. Introduction

Increased consumption of motor fuels [1] and exhaustion of natural reserves of light crude oils [2] inspire the search for alternative sources of hydrocarbons and the development of new energy efficient and ecologically safe ways of their processing. Currently, much attention is paid to the processing of highly viscous heavy oils and bitumens having a low hydrogen content and high content of high-molecular components (asphaltene and resin) as well as heteroatomic compounds including vanadyl- and nickel-porphyrins [3]. Conversion in a supercritical water ( $T_{cr} = 647$  K,  $P_{cr} = 22.1$  MPa, and  $\rho_{cr} = 0.322$  g/cm<sup>3</sup>) as the cheapest and most environmentally friendly reaction medium can be one of the processing technologies of such hydrocarbon feedstocks (HCF). The possibility of using supercritical water (SCW) for the conversion of HCF is due to its unique properties, such as low viscosity, low dielectric constant, high density, the ability to dissolve non-polar organic substances

and participate in redox reactions [4–7]. Close temperatures of the transition of water into the supercritical state and the decomposition interval of the bulk of HCFs (623–723 K) due to the thermolysis of aliphatic C–S, C–O, and C–C bonds (the bond energy equals to ≈300, 350, and 370 kJ/mol, respectively [8]) provide the possibility of effective use of SCW for processing of HCF. Significant progress in this direction has been achieved in the last decade [9–11].

The SCW conversion of hydrocarbons feedstocks was studied in a series of papers [12–19], in which a greater yield of hydrocarbon (HC) fractions with the H/C atomic ratio higher than that of raw HCF has been obtained. The major part of these studies was performed in the autoclaves without stirrers. The drawback of the autoclave conversion is a slow diffusive dissolution of the HCF high-molecular components in SCW [14]. We have studied the HCF conversion under various modes and process conditions: pumping of SCW through the HCF layer in isothermal conditions [20,21] and at a uniform temperature increase [22]; supplying of HCF into a counter SCW flow under isothermal conditions [22] and the temperature gradient along the axis of the vertically located tubular reactor [23,24]. The latter method, which is an analog of the distillation column, appeared to be the most effective. Thus, during the

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residence time of the reactants in the reactor of about 5 min, the yield of volatile and liquid hydrocarbons was  $\approx 70\%$  relative to the weight of HCF supplied into the reactor [23,24]. However, in all the cases we noted accumulation of residue, which was formed from the HCF high-molecular components insoluble in SCW. According to the SCW based mechanisms of HCF conversion proposed in [14,15], asphaltene serve the precursors of this residue, while its formation results from recombination of the high molecular radicals, generated upon thermolysis, and the subsequent reactions of dealkylation, dehydrogenation, and cyclization.

The H/C atomic ratio in the residue decreases from 1.45 [20] to 0.29 [22] with increasing temperature of SCW conversion from 673 to 973 K. In the first case, the residue is a highly viscous liquid, while in the second case, it is solid with a specific surface of  $\approx 220 \text{ m}^2/\text{g}$ . Obviously due to a significant reduction in the H/C atomic ratio in the residue, its further conversion into low-boiling HCs without additional hydrogenation is impossible. In our opinion, more rational is the combustion of the residue in SCW/O<sub>2</sub> fluid flow, which will ensure both the continuity of the conversion and compensate for heat expenditure on its implementation. In [25,26], at conversion of brown coal supplied as a coal-water slurry into SCW/O<sub>2</sub> fluid counter-flow (the temperature gradient along the reactor axis: at the top – 673 K and at the bottom – 873 K, 30 MPa), it was revealed that in case of the lack of O<sub>2</sub>, the oxidation of the portion of coal not only compensates partially for the conversion heat expenditure, but also increases the yield of products enriched with hydrogen. A similar result was obtained in [27] at conversion of tar in SCW/O<sub>2</sub> fluid counter-flow (the starting temperature of 723 K, 30 MPa). It was stated that the conversion is accompanied by the adhesion of the layer, formed by the tar high-molecular sediment components, to the reactor wall, and this layer was moved up in the reactor due to burning-out of these tar components from the bottom and refill from the top.

Carrying out the present work, we were the first to implement the SCW conversion of the heavy oil supplied from the top into a vertically located tubular reactor packed with activated carbon (AC), where the SCW/O<sub>2</sub> fluid was pumped through the AC bed. On the one hand, this process technology aimed at ensuring the generation of CO *in situ* through partial oxidation of activated carbon by SCW/O<sub>2</sub> fluid (at low concentrations of O<sub>2</sub>), and, on the other hand, to implement autothermal process conditions due to the heat generation at oxidation of the AC and the oil conversion residue with increasing concentrations of O<sub>2</sub>. In [28–30], studying SCW conversion of bitumen (autoclave, 623–753 K) it was revealed that in the presence of CO the decomposition of asphaltene and the yield of low-boiling HCs increase and the coke formation is suppressed, as a result of active hydrogen generation in the water-gas shift reaction:



In addition, when studying the SCW conversion of model compounds (semi-batch reactor, 873 K, 34.5 MPa) [31] and organic wastes (autoclave, 673 K, 25 MPa) [32], it was shown that AC catalytically influences their gasification and oxidation.

## 2. Experimental investigation

### 2.1. Reagents and experimental procedure

The objects of our investigation were heavy oil (gross-formula CH<sub>1.59</sub>N<sub>0.01</sub>S<sub>0.020</sub>O<sub>0.01</sub>) enriched with resin-asphaltene components of Ashal'chinskoe oilfield (Tatarstan, Russia) and granulated activated carbon (produced from birch wood, the average particle size of 2 × 3 × 5 mm). Contents of asphaltene, resin, oil, vanadium, and nickel in crude oil are given in Table 1. Moisture content W,

ash content per dry basis A<sup>d</sup>, elemental composition and specific surface S of activated carbon are listed in Table 2.

Fig. 1 shows a scheme of the experimental setup, where the key element is a tubular reactor (internal diameter  $d_{\text{in}} = 24 \text{ mm}$ , length  $L = 70 \text{ cm}$ ) made of stainless steel. Heating of the reactor (1) was provided by three resistance heaters  $H_1-H_3$  with power controlled via a multi-channel thermo-programmer and three chromel-alumel thermocouples  $T_1-T_3$ . The water temperature at the inlet of the reactor was maintained at a constant level by resistance heater  $H_4$ , paired with a chromel-alumel thermocouple  $T_4$ . Time dependences of  $H_1-H_3$  heaters power and the reactor temperatures  $T_1-T_3$  were recorded in digital form using analog-to-digital converter with a frequency of 10 Hz.

The water and oxygen were supplied into the reactor through its lower end, while crude oil was supplied through the upper end. The water was supplied to the reactor by means of the plunger high-pressure pump (15) through the damping vessels (14). The water flow rate was regulated by the valve (12) and measured by a differential pressure gauge (13). The oxygen was supplied to the reactor from a cylindrical vessel ( $d_{\text{in}} = 40 \text{ mm}$ ,  $L = 199 \text{ cm}$ ), which after evacuation was filled with O<sub>2</sub> from a standard cylinder (8). The additional compression of O<sub>2</sub> in the vessel (7) was carried out by the piston (6) under pressure of the water supplied from the damping vessels (14). The oxygen flow rate was regulated by a Bronkhorst flowmeter (9). Mixing of water and oxygen occurred in the reactor lower part under the plate made of porous stainless steel (3) installed at a height of 65 mm from its lower end. This plate ensured uniform distribution of water and oxygen along the reactor cross section. Crude oil was supplied to the reactor from cylindrical vessel ( $d_{\text{in}} = 24 \text{ mm}$ ,  $L = 132 \text{ cm}$ ) under pressure of water fed below the piston (6) through a differential pressure gauge (13). To reduce the oil viscosity, vessel (5) was heated up to  $\approx 350 \text{ K}$ . Oil flow to the reactor was regulated by a valve (4) installed between the reactor and the oil vessel (5). To increase the residence time of the oil components in the reactor, a hollow cylindrical pipe ( $d_{\text{in}} = 4 \text{ mm}$ ,  $L = 27 \text{ cm}$ ) was mounted in the top end of the oil supply duct.

Before the experiment, the reactor was packed with a certain amount of AC (Table 2). At the bulk density  $\rho_{\text{AC}} = 0.226 \text{ g/cm}^3$ , the AC bed height in the reactor was about  $h_0 \approx 60 \text{ cm}$ . The reactor was started with a vacuum pumping to remove air. Then, according to a given program, we carried out heating and stabilization of the operating reactor temperatures  $T_1 = 673 \text{ K}$ ,  $T_2 = T_3 = 723 \text{ K}$  and the water temperature at the inlet of the reactor,  $T_4 = 723 \text{ K}$ . After that, the reactor was filled with water to the operation pressure of 30 MPa. At the same time, the cylindrical vessels with oxygen (7) and crude oil (5) were overpressurized to  $\approx 33 \text{ MPa}$  that ensured their subsequent supplying into the reactor. At the beginning of supplying the reagents, valve (17) controlling the reactants flow from the reactor to one of the samplers (with a volume of  $\approx 1.4 \text{ dm}^3$ ), was opened to the extent that ensured maintenance of the pressure in the reactor at  $30.0 \pm 0.5 \text{ MPa}$ . Reactants were collected employing Samplers S1–S5 equipped with a membrane pressure gauge (18) and shut-off valves.

The experimental procedure was as follows. At the stage I, SCW/O<sub>2</sub> fluid was pumped through the AC bed at a flow rate of water  $G_w = 6 \text{ g/min}$  and oxygen  $G_{\text{ox}} = 1.4 \text{ g/min}$  over the time  $t_{\text{ox}} = 10 \text{ min}$  (Table 3). Then the supply of O<sub>2</sub> into the reactor was stopped, while the water was pumped at the same flow rate for another  $t_w = 10 \text{ min}$  (Table 3) to remove the AC conversion products from the reactor, the products together with SCW flowing down into Sampler 1. The value of  $t_w$  is chosen based on the estimation of the SCW residence time ( $\tau_w = V_R \cdot \rho_w / G_w \approx 5 \text{ min}$ ) in the reactor at  $T = 723 \text{ K}$ ,  $P = 30 \text{ MPa}$ ,  $\rho_w = 0.148 \text{ g/cm}^3$ , and the reactor volume  $V_R \approx 200 \text{ cm}^3$  (excluding the volume of AC particles). At the stage II, the crude oil was supplied at a flow rate  $G_{\text{oil}} = 4 \text{ g/min}$  into

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