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Effect of temperature on bitumen conversion in a supercritical water flow

Oxana N. Fedyaeva, Anna V. Shatrova, Anatoly A. Vostrikov*

Kutateladze Institute of Thermophysics SB RAS, 1, Acad. Lavrentiev Av. 1, Novosibirsk 630090, Russia

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ABSTRACT

This article deals with a study of bitumen conversion (the gross-formula $CH_{1.47}N_{0.01}S_{0.007}$) in a supercritical water (SCW) flow continuously supplied at the bottom of the vertically located tubular reactor. At the first stage, bitumen was continuously supplied from the top of the reactor into a counter-current SCW flow (400 °C, 30 MPa) for 60 min. At the second stage (after ceasing the supply of bitumen into the reactor), SCW was pumped through the layer of bitumen residue at uniform (2.5 °C/min) temperature increase from 400 to 700 °C at 30 MPa. The amount and composition of the liquid and volatile conversion products were measured. It is revealed that during bitumen supply into the reactor and subsequent pumping of SCW through the layer of bitumen residue in the temperature increasing mode from 400 to 500 °C, the yields of liquid conversion products are equal to 26.9 and 45.4%, respectively, relative to the weight of bitumen supplied into the reactor. Oils are the major components of these liquid products. Participation of H_2O molecules in redox reactions became evident due to the formation of CO and CO_2 even at 400 °C. A significant increase in the yields of H_2, CH_4, and CO_2 are detected at $T > 600$ °C. Based on the sulfur balance, it can be stated that the degree of bitumen desulfurization at 400–700 °C due to sulphur removal in form of H_2S accounts for 21.6 wt.% A solid carbonaceous bitumen residue, obtained after SCW conversion, is characterized by high specific surface (224 m^2/g).

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1. Introduction

Continuous increase in energy consumption [1] and exhaustion of natural reserves of light oils contribute to both the searching for alternative sources of hydrocarbons and the development of new energy-efficient and environmentally friendly methods of upgrading. Recently, much attention has been paid to the involvement of heavy oil and bitumen with high viscosity, high asphaltene and heteroatom content [2] into the energy production and petrochemical synthesis. One of the ways to upgrade the hydrocarbon feedstocks (HCFs) is their conversion in supercritical water ($T > 374$ °C, $P > 22.1$ MPa). This is due to the unique properties of supercritical water (SCW), such as low viscosity, low dielectric constant and high density at rather high temperatures. At $T > 374$ °C, a hydrogen-bond net characteristic of liquid water breaks down and does not restore under any powerful compression, i.e. water passes into a gaseous state where it becomes an effective solvent for organic substances and gases [3–6]. When temperature rises, H_2O molecules become active participants of redox reactions.

Numerous studies have been carried out on the SCW conversion of hydrocarbon feedstocks, such as bitumen [7,8], oil sand bitumen [9,10], asphalt [11], asphaltite [12–14], vacuum residue [15–17], high-temperature coal tar [18], petroleum [19,20] and coal-tar [21] asphaltenes. A greater yield of light hydrocarbon fractions with the H/C atomic ratio higher than that of raw HCF has been obtained. However, as it follows from the results of the studies [7–21], the yield of the conversion products depends not only on H/C atomic ratio in raw HCF and conversion conditions (temperature and density of SCW), but also on the process mode.

The major part of the results on SCW conversion of HCFs was obtained in the autoclaves [11–13,15,17–21]. The disadvantage of the autoclave conversion without stirrers is a slow diffusive dissolution of the HCF high molecular components in SCW. As a result, the high molecular radicals generated during thermolysis recombine in the bulk followed by the formation of insoluble carbonaceous residue. Apparently, the role of the recombination reactions is insignificant for the flow mode of conversion because these radicals are removed from the bulk by means of the SCW flow, resulting in the residue yield decrease and the liquid hydrocarbons yield increase. A longer residence time of the reactants at the high temperature in the case of using the autoclaves is of great importance as well. This leads to extra gasification of conversion products,

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* Corresponding author. Tel.: +7 383 330 80 94; fax: +7 383 330 80 94.
E-mail address: vostrikov@itp.nsc.ru (A.A. Vostrikov).

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whose degree in the flow mode is regulated by the SCW flow rate through the reactor. Besides, since solubility of the HCF high molecular polyaromatic components (asphaltenes) in SCW depends on their molecular weight, fractionation of these components occurs in the SCW flow, i.e. the products of SCW conversion are enriched with oils and resins [7–9,14,16,22]. It provides for increase in the H/C atomic ratio as compared with that of raw HCF, in particular.

In this paper we present the detailed studies of the products yield and composition of bitumen conversion in a counter-current SCW flow at 400 °C, 30 MPa and at pumping the SCW through a layer of residual bitumen in the mode of uniform temperature increase up to 700 °C.

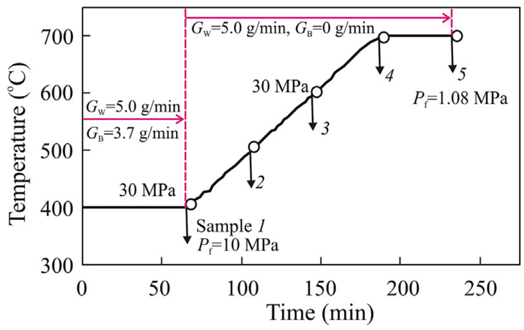

Fig. 2. Time dependence of experimental parameters during bitumen conversion in SCW. Figs. 1–5 indicate the sampler's number, and points indicate time and temperature of samplers replacing.

2. Experimental

2.1. Reagents and experimental procedure

The object of our investigation was bitumen of Omsk Oil Refinery (Russia). Elemental and group compositions of bitumen are given in Table 1. As can be seen, bitumen contains heteroatoms of sulfur and nitrogen and does not contain oxygen ones.

Fig. 1 presents the scheme of the experimental setup. The main parts of the setup are a tubular reactor (internal diameter 24 mm; length 700 mm) made of stainless steel 12Cr18Ni10Ti; a high-pressure plunger pump for pumping the compressed water through the reactor; a heat-exchanger for water heating; demountable samplers for collecting the liquid and volatile products with the volumes of 3.2 dm^3 (Sampler 1) and 0.95 ± 0.05 dm^3 (Samplers 2–5); a mass spectrometer vacuum unit. The experimental setup is equipped with the system measuring the water flow rate and the device for computer registration of pressure and temperature. Heating of the reactor and the heat-exchanger was carried out synchronously by outer resistance heaters and controlled by a temperature programmer. Temperature was measured by chromel–alumel thermocouples with the accuracy of 1 °C. Pressure was measured by membrane strain sensors, with an accuracy of 0.25%.

The experimental procedure was as follows. After the reactor was sealed, all the volumes with air were evacuated by a first-stage vacuum pump. Then, the reactor and the heat-exchanger were synchronously heated up to 400 °C. The rate of heating up to 350 °C was 10 °C/min, within the range of 350–380 °C heating rate was 5 °C/min, and up to 400 °C it was 2 °C/min. Then, SCW was supplied at the flow rate G_W = 5.0 g/min into the reactor through its bottom (Fig. 1). When the operating pressure (30 MPa) was attained, bitumen heated up to 100 °C was supplied into the reactor through its top, and the valve for discharging reactants into the product collecting sampler was opened to such an extent that the pressure in the reactor was 30.0 ± 0.5 MPa. The bitumen was supplied continuously at the average flow rate G_B = 3.7 g/min under the pressure of water pumped by a plunger pump through a damping vessel into the bitumen bin (Fig. 1). Bitumen was supplied into the reactor for 60 min (Fig. 2). Then, the flow rate of discharging reactants was increased to such an extent that within 3 min the pressure in the reactor decreased up to P_f = 10 MPa. This provided for removal of the

Table 1
The characteristics of bitumen: gross-formula, content (C) of oils, resins, asphaltenes and their gross-formulae.

Bitumen	Oils		Resins		Asphaltenes	
Gross-formula	C (wt.%)	Gross-formula	C (wt.%)	Gross-formula	C (wt.%)	Gross-formula
$CH_{1.47}N_{0.01}S_{0.007}$	54.4	$CH_{1.60}N_{0.01}S_{0.007}$	32.7	$CH_{1.35}N_{0.01}S_{0.007}$	12.9	$CH_{1.02}N_{0.01}S_{0.007}$

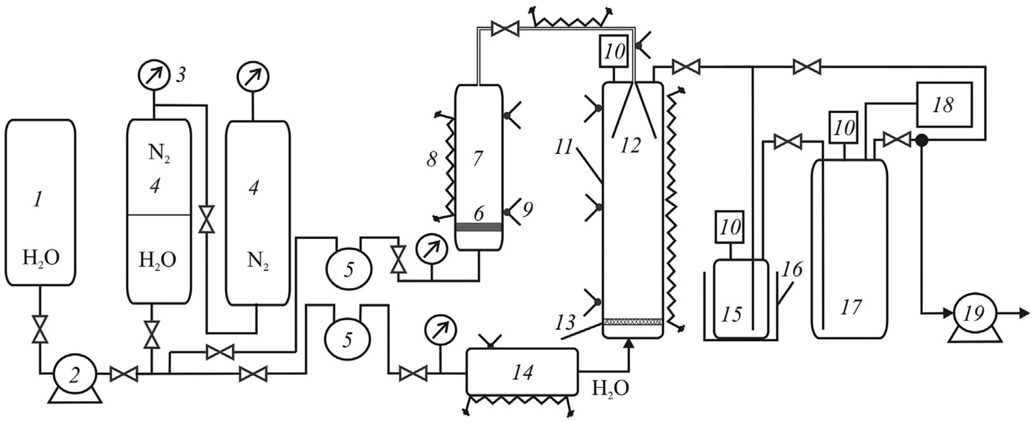

Fig. 1. Schematic diagram of the experimental setup: (1) vessel with distilled water; (2) high-pressure plunger pump; (3) strain gauge; (4) damping vessels; (5) flow meter; (6) piston; (7) bin for bitumen; (8) resistance heaters; (9) thermocouples; (10) membrane pressure gages; (11) reactor; (12) conical channel; (13) plate made from porous stainless steel; (14) heat exchanger; (15) sampler for collecting products; (16) vessel with ice; (17) prechamber; (18) mass spectrometer vacuum unit; (19) first-stage vacuum pump.

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