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Super-viscous oil conversion in supercritical water fluid

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Abstract. In this article, experimental research results of super-viscous oil conversion in supercritical water are shown. Reaction mixtures consisting of super-viscous oil, carbon substances and complex catalytic additive were influenced by the conversion. A catalytic additive is a mixture of dispersed nickel and copper salts of carbonic acid, aluminum oxide and coal. A content increase of paraffinonaphthenic hydrocarbon up to 76.2 wt % against 40.8 wt % of an initial oil is a main characteristic of supercritical conversion products. Light hydrocarbons formation is implemented by aromatic, resinous and asphaltene components destruction. Based on experimental methods of super-viscous oil conversion in a supercritical water, a principal technological conversion scheme is proposed.

1. Introduction

Today, the balance of extracted oil is described by a content increase of heavy super-viscous oil. Super-viscous oils are characterized by vast reserves and potential for use as raw materials for the petrochemical complex [1]. In this regard, an urgent problem is a providing of the rational processing of super-viscous oils for satisfying the increasing energy consumption [2]. In the scientific and technical community, the study of heavy hydrocarbon raw materials for the creation of new and the adaption of existing technologies for the preparation and processing of super-viscous oils is especially interest.

Today, super-viscous oils, as a rule, are initially converted to “synthetic” oils, which are then used according to classical schemes: for the production of light oil products, valuable industrial chemicals. A factor complicating the processing of super-viscous oils into light oil products is a high content of high-molecular weight and heteroatomic compounds such as resins and asphaltenes, addicted to coke formation and catalyst poisoning [3–4].

In recent years, the interest to supercritical water has increased in the scientific community. The interest is explained by an abnormal change in the water properties when it reaches a critical point ($T_c = 375^\circ\text{C}$, $P_c = 22.1 \text{ MPa}$). With regard to oil refining, the prospect of studying supercritical water fluids is determined by the following factors: proton donor activity, extremely low viscosity and high diffusion ability of supercritical water, unique properties of the SCW / oil system. SCW is not only a universal solvent, but also a catalyst, and it participates in redox reactions [5–11].

To create effective technologies for the processing of super-viscous oils, there is a need of knowledge of the chemistry and mechanism of transformations, the regularity of the conversion of hydrocarbon



feedstocks under the influence of factors complex: hydrothermal effects, the nature of catalytic agents and their influence on the stability of functional heteroatomic groups of tar and asphaltene molecules in natural and technogenic processes.

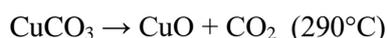
2. Methodology

The experimental setup is a reactor block, which directly includes the R-101 reactor itself (autoclave), three thermocouples, a manometer with a valve for gas extraction (Fig. 1). The reactor is a cylindrical vertical hollow apparatus ($V=200$ ml) of periodic action and made of stainless steel. The maximum acceptable pressure is 28.4 MPa, and the temperature is 600°C.

The experiments were carried out under conditions of high pressure and temperature, with parameters ensuring the transition of the aqueous phase to a supercritical state. The reaction mixtures, including heavy oil, water and additives were mixed, homogenized until the mixture was homogeneous, and loaded into the reactor. Achieving the required regime and the thermobaric conditions of the experiment, namely, the completion of a second-order phase transition for water (above $T_c = 375^\circ\text{C}$, $P_c = 22.1$ MPa), was 40 min. The thermobaric conditions of the experiment were occurred for 20-40 min. After the experiment, the reactor was naturally cooled to room temperature, the residual pressure in the autoclave was observed in the range of 0.7-1.8 MPa.

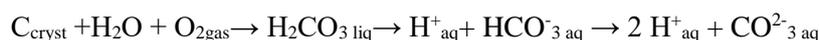
Aluminium oxide Al_2O_3 is a component that exhibits catalytic activity and is widespread in collector rocks in the clay mineral kaolinite. The catalytic activity of aluminium oxide is manifested in the acceleration of reactions of thermal degradation of bonds C-C hydrocarbons.

Catalytic systems based on nickel and copper are noticeably observed in hydrothermal processes for the refinement of heavy oil [12-24]. Nickel and copper salts of carbonic acid are selected as precursors of catalytically active compounds - nickel and copper oxides. In the reaction system, salts decompose with the formation of oxides at heating:

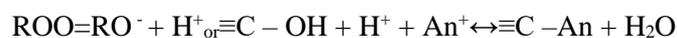


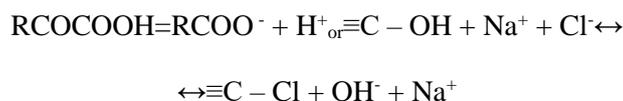
The high activity of the metal catalyst with rock-forming minerals is explained as follows: clay minerals are negatively charged, metals are positively charged. When a metal is added to a mineral rock reactor, for example, Ni^{2+} cations are adsorbed on the surface of the clay, and the clay mineral can serve as a support for metal cations, like highly active traditional catalysts.

Coal in water is practically insoluble, but when it contacts with oxygen soluble in water, its slow oxidation occurs [14]:



Which leads to the formation of various organic and inorganic compounds. The Gibbs free energy for this reaction is $\Delta G = -382.7$ kJ/mol. When interacting with water, hydroxyl or carboxyl groups are formed on the surface of the coal that are associated with the coal base. If we arbitrarily denote this unchanged structure by the letter R, then the structure of such a substance can be denoted by the formula ROH or RCOOH, depending on which oxidized group has formed. These groups are capable of dissociation, that is, the following processes occur in the water medium [14]:





In accordance with the foregoing, it is assumed that these transformations occur in the process of conversion of carbonaceous substance. In this work, natural caustobiolite (coal) and charcoal (alternative carbon substance of a fundamentally different origin) were selected as a prototype of the carbonaceous substance of the rocks.

Coal - anthracite, sapropelic origin, characterized by the following elemental composition: carbon content 90.5 - 91.5 wt %, oxygen 2.8 - 3.5 wt %, hydrogen 3.75 - 4.0 wt %, sulfur - less than 1 wt %. It is known that organic substance of sapropelic nature is the main supplier of hydrocarbon fluids. For the experiment, charcoal activated under the influence of water vapor at 800 - 950°C was used. Charcoal has an exceptionally developed surface; according to its structural characteristics, it is amorphous carbon in an amount of up to two-thirds and graphite crystallites, consisting of bundles of hexagonal rings that form planes with a length of 2-3 nm. Carbon substances are also capable of absorbing polar compounds and metals.

3. Results and Discussions

All products of the conversion of SVO in supercritical water are characterized by an increase in the content of paraffin-naphthenic hydrocarbons (Table 1). At the same time, a decrease in the content of aromatic and resinous substances is observed in the conversion product. The content of asphaltenes in the products of the conversion of SVO varies in different directions: for experiments involving coal (exp. 1) it increases to 9.9 wt %, which exceeds the value for the initial SVO (7.7 wt %). This can be caused by sorption reactions of polar compounds on the surface of coal, which means that surface compounds formed during the oxidation of coal — radicals with the -ROH or -RCOOH structure — interact with asphaltenes, increasing their mass content.

Table 1. The Component composition of the source oil and the products of the conversion of the SVO.

Sample	Experiment Conditions		Fractional yield, boiling point – 200°C, wt %	Component composition, wt %			
	T, °C	P, MPa		saturated	aromatic	resins	asphaltenes
Initial	-	-	9.8	40.8	13.7	37.8	7.7
1	375	22,5	11.7	53.5	11.1	25.5	9.9
2	375	22,5	19.1	76.2	4.1	13.1	6.6
3	385	23,0	19.3	68.2	5.5	20.8	5.5

Under subcritical thermobaric conditions (in the liquid-phase state and in the form of superheated steam), water molecules are polar and its polarity is higher than the polarity of petroleum hydrocarbons, which means that water displaces asphaltenes and other polar petroleum hydrocarbons from the surface of coal, thereby ensuring the availability of high molecular weight compounds for catalytic agents - metal oxides. Thus, the destruction of the high molecular weight part of the raw materials proceeds more efficiently, increasing the yield of light fractions in the product of the experiment. The increase in the content of asphaltenes is not a consequence of compaction processes, but a consequence of adsorption processes. Moreover, as a result of the conversion of SVO, the resin content is significantly reduced.

This can be explained by the fact that the resins not only collapsed with the formation of paraffin-naphthenic and aromatic structures, but also entered into interaction with asphaltenes, forming a solvate shell and forming a new structure of the oil disperse system.

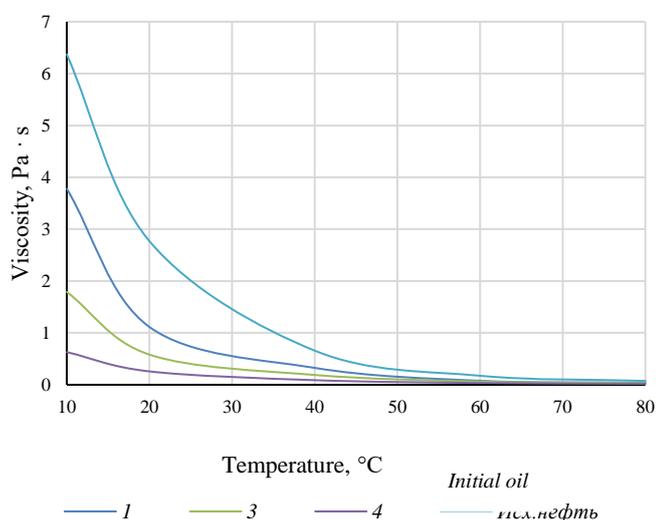


Figure 1. Viscosity-temperature dependences of the initial oil and experimental products.

The viscosity of all the products of the conversion of SVO in supercritical water decreases sharply, a further increase in temperature leads to a more gradual decrease in viscosity. The viscosity of the conversion product in experiment 3, compared with the initial SVO at 20°C, decreases by 96 % (0.08 Pa·s versus 2.7 Pa·s for the initial SVO). Similarly, a strong decrease in viscosity is explained by the transformation of the oil disperse system of the sample during the conversion of SVO, primarily an increase in the content of distillate fractions, as well as a decrease in the dispersed phase - a decrease in the content of asphaltenes.

Structural viscosity characterizes the additional resistance to the flow of fluid from the side of mesh-like structures. An extreme deviation in the dependence of ΔE_a on temperature is observed for the structural viscosity of product 3, this indicates a restructuring of the structure of associates, a change in their size, separation of several components from them, followed by a change in their structure, which leads to a strong decrease in viscosity.

On the basis of scientific data obtained in the experimental studies on the conversion of super heavy waves, a basic technological scheme of supercritical fluid technology is proposed for solving a practical problem (Fig. 2).

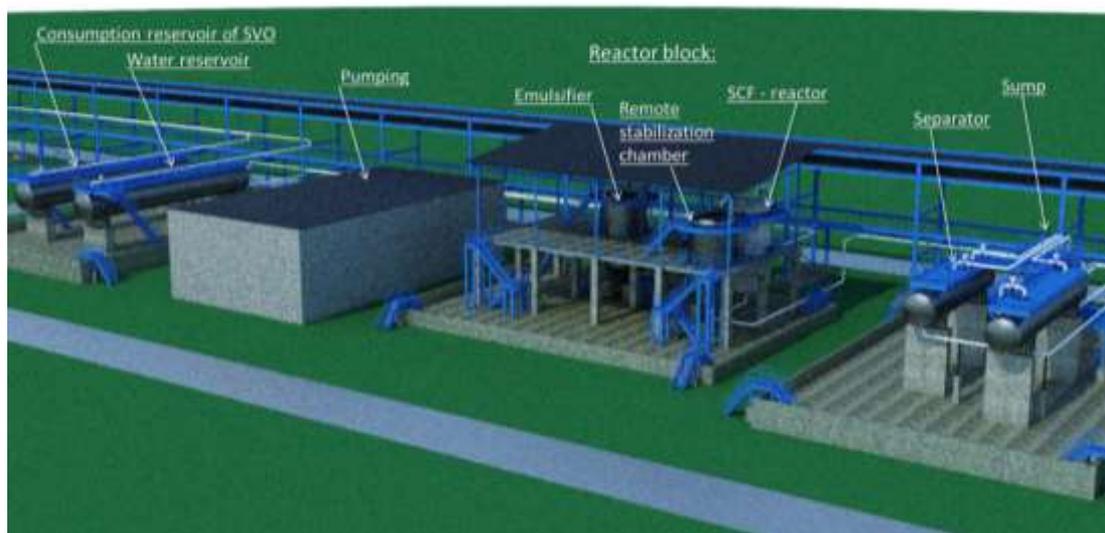


Figure 2. Schematic diagram of the installation of supercritical upgrading of SVO.

The raw materials may be well products - SVO prepared at SVOPU up to the 3rd quality group. The design capacity of this installation is up to 50 thousand tons / year. Well production with a water cut of 80-90% is supplied to the treatment unit, from where the output of high-viscosity marketable oil of the 3rd quality group is obtained according to State Standard R 51858-2002.

Consider the technological scheme of ennobled enrichment itself. Raw materials - SVO and technological water from the reservoirs in the storage park are heated and transferred to the emulsifier, where at 90°C a water-oil emulsion is created by mixing. The emulsifier input is not required due to the presence of natural emulsifiers - naphthenic acids in the SVO. The hot water-oil emulsion then enters the supercritical fluid reactor by injection through a nozzle in the reactor. Then the raw materials flow stops, the reactor starts to operate in the regime of creating supercritical water fluid (> 375°C and > 22.1 MPa) with parameters selected taking into account the composition of the raw materials to obtain the desired light fractions. The material of the reactor is hastelloy.

To further increase the yield of distillate fractions and reduce coke formation, the process can be carried out on the surface of powdered suspended coal. In this case, the reaction mass during gradual heating to a supercritical fluid will pass through the phase region of superheated steam and the reaction stage in a boiling layer of dispersed caustobiolite. For this purpose, a powdery carbon additive with a dispersion of 0.3 mm is added to the refining raw materials in the emulsifier together with a complex catalytic additive (a mixture of aluminum oxide with copper-nickel salts of carbonic acid). Vapors and gases are discharged from the top of the reactor.

At the end of the supercritical refinement cycle, the reactor cools down, due to the residual pressure in the reactor, the reaction mass flows by gravity into a four-phase separator, from which synthetic oil, water, gas and some part of the pitch with solid residues of the catalytic additive are removed. In the future, pitch can be used as a component of heating oil, in the production of road bitumen, as a raw material for gasification. The water released from the bottom of the separator is pumped to the sump park, where after cleaning and preparation it can again be used in the process and mixed with the raw material.

One of the advantages of the technology is the uniform mass and heat transfer provided by the supercritical fluid, as a result of which the formed coke is not deposited in significant quantities on the walls of the reactor, there are no frequent burnouts, and a high degree of quality control and composition of the product, synthetic oil, is maintained. Another advantage is the lack of need for operations with solid products (unloading of coke is not necessary). The low-tonnage technological design and mobility allows the processing of oil-and-gas production directly from the well product after initial preparation, then directing synthetic oil with high potential in light fractions to the pipeline to the ORF. Among the shortcomings can be noted the frequency of the process and the need to separate the pitch from the oil.

The technical and technological capabilities of today allow the use of supercritical fluid technologies in a wide variety of areas of chemical technology. There are flowing water-based SCF-technologies. However, other thermodynamic conditions of the process are supported in the flow system: the equilibrium shifts due to the constant removal of transformation products. The supercritical conversion of SVO in periodic design has fundamental differences in the chemistry of reactions in comparison with flowing analogs.

4. Conclusions

In this work, an experiment range of the super-viscous oil conversion in a supercritical water was carried out. Reaction system consisting of a heavy oil, carbon substances and complex catalytic additive was influenced by this process.

Based on complex analysis of initial super-viscous oil and conversion products compositions, the regularity and the depth of high molecular hydrocarbons conversion were determined. Structural group and component compositions change forming light fraction due to aromatic, resinous and asphaltene hydrocarbons destruction were shown.

It was demonstrated that in conversion processes there is high molecular components destruction forming normal and branched structured alkanes practically absented in an initial oil, and it lets us propose a principal technological conversion scheme of super-viscous oil on the base of experimental data.

Acknowledgements

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