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STRUCTURAL CHANGES OF HEAVY OIL IN THE COMPOSITION OF THE SANDSTONE IN A CATALYTIC AND NON-CATALYTIC AQUATHERMOLYSIS

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Abstract:

Currently in connection with exhaustion of actively developed resources of light crude and the increasing consumption of energy carriers the development task solution of scavenger oil which will soon become the most important resource of stabilization and increase of oil production is relevant. The share of scavenger oil which, in particular, treatsuperviscous heavy oil steadily grows in overall balance therefore in the next years the gain of oil extraction will be provided at the expense of such naptha. It is accepted to call these resources of hydrocarbons non-conventional as their extraction requires application of the technologies and methods different from traditional methods of light oil production. One of such methods is steam impact on the layer which is characterized by downloading settlement volume of the heat carrier through delivery wells, creation of a thermal fringe and its subsequent advance by not heated water on layer towards production wells. At the same time use of various additional receptions, in particular, forcing of catalytic systems will allow to increase energy efficiency and to intensify process of heavy oil extraction. Relevance of such researches does not raise doubts. In this work the heavy native oil structural changes are studied; they lie in a sample of petrosaturated sandstone of the Volga-Ural province, being impacted by process of catalytic and not catalytic aquathermolysis.

Keywords: Heavy crude oil, Bitumoid, Aquathermolysis, Catalyst precursor, Steam injection.

1. Introduction

In recent years in the world under the conditions of deterioration in structure of hydrocarbonic raw materials stocks the energy companies and the governments of the countries pay the increasing attention to non-conventional types of liquid hydrocarbons which potential considerably exceeds resources of usual oil [1]. It is accepted to call these resources of hydrocarbons non-conventional as their extraction from subsoil and obtaining energy from them requires application of technologies and methods which differ from those used in traditional resources of oil and hydro-carbonic gases development [2-8]. Similar production approaches of non-conventional resources are accompanied by a number of the problems connected with the high cost of equipment, complexity of forecasting course of processes at downloading the heat carrier in combination with the additives increasing energy production efficiency, influence of the last on technology and materials when mining in general. A serious problem is also that for pumping of both light and heavy oil one system of pipelines is used that leads to deterioration of all pumped-over oil. Due to stated development of new production technologies heavy and super-heavy naptha is the priority direction of entire oil branch development [9]. For Russia importance of the researches directed to deep studying of the processes proceeding in the productive layers leading to various transformations of heavy oil fluid components is caused by the importance of mineral resources reproduction as, on condition of input in development of fields heavy oil, the general oil extraction can be increased and the main task of fuel and energy complex development solved - maintenance of the reached level of oil production and reproduction of hydrocarbonic raw materials stocks. The reconnoitered geological reserves of heavy oil in Russia make 116.0 billion tons that makes 17.8% of the general world reserves share, and this is third place after Canada and Venezuela [1]. In Russia rather large number of heavy and super-heavy oil deposit fields which are concentrated generally in Western Siberia is at the moment opened, in the Komi Republic and the Arkhangelsk region, as well as in the territory of the Sakhalin island, the Udmurt Republic and Krasnodar Krai [10] and increase of production indicators takes place due to increase in a well stock and application of new technologies. One of such methods is steam impact on the layer which is characterized by downloading settlement volume of the heat carrier through delivery wells, creation of a thermal fringe and the subsequent its advance by non-heated water on layer towards production wells. At the same time use of various additional receptions, in particular, forcing catalytic systems will allow to increase energy efficiency and to intensify process of heavy oil extraction.

2. Research Methodology

Bitumoid from petrosaturated sandstone of the Mushaksky field selected from a well No. 485 in the range of selection of 1168-1168.5 m served as research object, as well as the last after catalytic and not catalytic hydrothermal influence.

As a molecular precursor the iron carboxylat synthesized with use of ligand-bound distilled arctic oil (DAO)- a product of vacuum rectification of crude arctic oil was chosen. DAO contains no more than 30% of resin acids, up to 6% of non-saponified substances, the rest fatty acids (olein, linoleic, linolenic). Acid number within 170–190 mg/g.The carboxylate of iron was received by exchange reactions of inorganic iron salt with the DAO sodium salt.

Process of fatty acid saponification is described by the equation (on the example of oleic acid):

$C_{17}H_{33}COOH + NaOH \rightarrow C_{17}H_{33}COONa + H_2O$.

The sodium carboxylate when heating interacts with iron salt:

$2C_{17}H_{33}COONa + FeSO_4 \rightarrow (C_{17}H_{33}COO)_2Fe + Na_2SO_4$

Process of aquathermolysis was carried out with use of the high pressure reactor (Parr Instrument, USA), of 300 cm^3 into which necessary amounts of petrosaturated solid and the distilled water under following conditions was loaded: initial pressure of 3 bars, working temperature of 150 and 200 °C. Duration of process was recorded at the level of 6 hours. Concentration of precursor of the catalyst made 0.5% for a hinge plate of solid sample. Made "averaging" of an initial core sample by its crushing in a porcelain mortar for receiving adequate results. After carrying out aquathermolysis the samples were quantitatively taken from reactors, the remains of water are removed with drying in a drying cabinet at a temperature of 40-50 °C. Extraction of bitumoid from the volume of solid both initial, and subjected to influence, was carried out with use of the Sokslet device, as the extracting solvent served mix of benzene, chloroform and isopropyl alcohol in the volume relation 1:1:1 for the purpose of the deepest process of sandstone lump oil fluid extraction. As criteria for evaluation of application efficiency of steam influence in combination with the synthesized catalytic agent research results of bitumoid components redistribution (group structure by the SARA method) [11] - saturated hydrocarbons, aromatic connections, pitches and asphaltens which was defined by the liquid and adsorptive chromatography on aluminum oxide taking into account methodical recommendations of the ASTM D4124-09 standard and GOST 32269-2013 were chosen. The maintenance of asphalten in a sample was determined by a "cold" method of Gold. Changes in structure of the most high-molecular connections allocated thus, in particular, of asphalten, investigated IK-spectroscopy. Before the SARA analysis determination of flying organic substances content (FISHING (volatile organic compounds-VOCs)) by the technique described in [12] was carried out. As solvent toluene which mixed up with the studied oil in a mass ratio toluene:oil 1:3 was applied.

IK removed curves with IK-Fourier's use of VERTEX 70 (BRUKER) spectrometer in the range 400 - 2000 $см^{-1}$.

3. Research Results and Discussion

In view of traditional methods application impossibility at production heavy oil now the considerable part of extraction efficiency increase researches is connected with application of non-conventional approaches which could provide lighter, so-called synthetic crude. Such oil can be delivered and be processed further at oil refineries without essential changes of the engineering procedures existing algorithms. Perspective way of receiving synthetic oil is hydrothermal transformation of non-conventional hydrocarbonic raw materials in the environment of water vapor (in emergency or super-emergency conditions) in the presence of catalytic agents directly in productive layer [13, 14]. Such transformation is caused by course of destruction processes of oil components at interaction got into condition by catalyst and vapors of water which in super-emergency conditions possesses properties of non-polar proton-donor solvent [15-17]. The formed hydrogen participates in reactions of hydrogenation and hydro-cracking, interfering thereby a recombination of free radicals that allows to increase efficiency of thermal processes of destruction significantly and, as a result, to intensify process of heavy oil extraction.

Studying of an oil fluid structure change as a part of solid in the conditions of aquathermolysis without, or in the presence of petrosoluble molecular precursor which is the main type of catalytic agents for efficiency increase of an intra layer up-classing heavy oil is of interest.

In this regard, obtaining new data on structural changes of a heavy oil fluid at catalytic and non-catalytic steam processing of solid samples of Mushaksky m / p, undergone process of aquathermolysis in the conditions modeling layer was the purpose of this work.

The Mushaksky field belongs to OJSC *RITEK* which was opened in 1993 by the search well 495 which discovered petrosaturated sandstones in the lower carbon fabrics. At test of the last in an operational column inflows of waterless high-viscosity oil with an output about 5 m^3/d were received. from C1-IV layer of the Tula horizon and from C1-V+VI layers of the Bobrikovsky horizon.

Results of the redistribution analysis of light and high-molecular components of the bitumoid extracted from initial solid after hydrothermal influence on the basis of carrying out the SARA analysis and determination of VOCs content are presented in the table.

Table 1. Component structure of the bitumoid extracted from initial solid and layers after catalytic and non-catalytic aquathermolysis

SARA-composition	Oil initial, extracted from solid	Oil after not catalytic aquathermolysis at 150 °C	Oil after not catalytic aquathermolysis at 200 °C	Oil after a catalytic aquathermolysis at 150 °C	Oil after a catalytic aquathermolysis at 200 °C
VOCs	5.89	6.66	6.34	6.20	5.52
Saturate	27.36	24.36	21.54	27.49	22.21
Aromatics	31.57	28.70	33.50	27.10	33.50
Resins	28.75	34.90	33.13	35.55	35.47

Asphaltenes	6.42	5.38	5.50	3.65	3.29
Sum	100.00	100.00	100.00	100.00	100.00

As we can see from the table, at processes implementation of catalytic and non-catalytic aquathermolysis sharp change in values of flying organic substances content is not observed, all of them remain approximately at one level. The greatest effect in aspect of reduction (almost twice) of a share of high-molecular asphalten is observed when using the catalyst and the largest temperature of experiment, influence of non-catalytic aquathermolysis is insignificant. In comparison with initial oil, the content of resinous connections increased forproducts of catalytic aquathermolysis as well, it is higher which is connected, apparently, with reduction of molecular weight at destruction of asphalten molecules. Up to the end redistribution of aromatic and saturated hydrocarbons of aquathermolysis products is not clear, however influence of temperature where it is visible that at a temperature of 200 °C both when using the catalyst, and in its absence, percentage of saturated components decreases and increases the share of aromatic hydrocarbons in comparison with influence of temperature of 150 °C is traced. It can be connected with the fact that at 200 °C there is deeper transformation to light fractions which then irrevocably are removed from the reactor in the atmosphere on completion of aquathermolysis process that naturally exerts impact on redistribution of oil components towards increase in less flying fractions.

On IR spectrums of asphalten of the bitumoid extracted from initial solid and solid after steam processing positive influence of the chosen conditions of aquathermolysis is traced, in particular when using the catalyst as a result of the reaction course of a hydrogenolysis promoting fuller thermal destruction of asphalten.

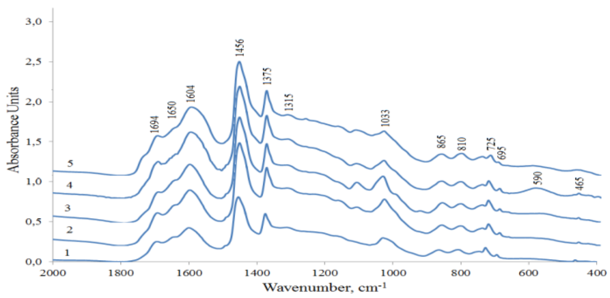

Figure – IR spectrums of initial bitumoid (1) and test products: 2 - product of non-catalytic aquathermolysis (150 °C); 3 - product of non-catalytic aquathermolysis (200 °C); 4 - product of catalytic aquathermolysis (150 °C); 5 – product of catalytic aquathermolysis (200 °C).

Summary

With use of the distilled arctic oil and watersoluble salt of iron the petrosoluble precursor catalyst the heavy oil destruction processes is synthesized.

Model experiments of steam impact on a petrosaturated sandstone sample with use of the synthesized catalyst are made.

On the basis of the research results received with application of physical and chemical methods it is established that unlike non-catalytic process the catalytic aquathermolysis even at the minimum temperature promotes fuller course of cracking reaction of the most high-molecular oil components and, as a result, decrease in heavy oil viscosity.

Conclusion

Thus, the received results demonstrate that the undertaken methods of steam processing including with use of the catalyst, allow to achieve to course of high-molecular asphalten destruction processes and, as a result, decrease in heavy oil viscosity.

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