In situ formed carboxylic acids effect on light hydrocarbons oxidation in a carbonate reservoir

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Abstract. Enhancing heavy oil recovery is attracting a considerable interest due to the depletion of conventional oil resources. In fact, thermal enhanced oil recovery methods are presenting a potential impact on improving heavy oil recovery especially for terrigenous reservoirs, where they are able to increase oil mobility due to heating (steam and thermal exposure) or due to its in-situ conversion to light fractions during ignition of the reservoir. At the same time, it is worthy to note that steam-thermal methods are accompanied by a significant heat loss when injecting steam into great depths heat. Moreover, oil deposits in heterogeneous low-permeability reservoirs (for example, carbonate) are among the potential unconventional oil resources. Along with geological heterogeneity, low porosity and permeability, fracturing, these reservoirs contain, in most cases, heavy oils with a high content of resins, asphaltenes and hard paraffins, characterized by a non-Newtonian fluid property. All this taken together makes the extraction of oil from such reservoirs a hard task to implement.

1. Introduction

For the development of heavy oil with high paraffin content, acid treatment treatments with surfactants, water repellents, retarders, and others have proven themselves well [1-5]. For a complex effect on the bottom-hole zone of a producing well, preliminary hot treatment with a solvent is carried out. Deposits of asphaltenes and paraffins and a film of oil from the rock are removed [6-8]. Then it is treated with an acid composition based on hydrochloric acid. The use of the oxidation product of a wide fraction of light hydrocarbons (oxidate) for treating the bottom-hole zone of the formation gives a similar complex effect, since in most cases the composition of the oxidate includes a wide range of solvents, including organic acids. A wide fraction of light hydrocarbons (WFLH) is a mixture of liquefied hydrocarbon gases (propane and butane) and heavier hydrocarbons (C5 and higher). The ratio of iso- and normal hydrocarbons in WFLH corresponds to the composition of the feedstock [9-13].

The problem in obtaining oxidate in reservoir conditions is the impossibility of an objective assessment of the fraction of a wide fraction of light hydrocarbons (WFLH) converted to oxidate. This is because there is a gravitational separation of components with different densities. The preparation of
oxidate on the surface, followed by its injection into the formation, also entails a number of technical problems.

2. Materials and Methods

The team of authors has set itself the task of developing a technology for downhole production of oxidized broad fractions of light hydrocarbons (BFLH). Its essence is to initiate the synthesis of oxidate in a special device, launched at the bottom of the well and installed in the required processing interval.

![Laboratory bench layout and appearance](image)

**Figure 1.** Laboratory bench layout and appearance

In order to optimize the technological parameters of the process of oxidation of light hydrocarbons under conditions close to reservoir, on the basis of the Institute of Organic and Physical Chemistry named after A.E. Arbuzov KazSC RAS was designed and manufactured a high-pressure model stand, consisting of an air cylinder with a reducer, a metering pump, a tank with a supplied reagent, a mixing reactor with electric heating, a shell-and-tube heat exchanger, a nitrogen trap, a sampling tank, and a gas meter.

The design features of the test bench allow simulation of oil displacement on a bulk sample and core in various modes (flow and closed) at various temperatures (up to 400°C) and pressures (up to 16 MPa) with the possibility of varying the composition of the coolant.
Table 1. Composition of a wide fraction of light hydrocarbons (WFLH)

| Components                                      | Content, wt % |
|------------------------------------------------|---------------|
| Carboxylic acids C2-C4                          | 30-45         |
| Ketones (acetone and methyl ethyl ketone)       | 10-20         |
| Alcohols C2-C4                                  | 5-8           |
| Esters                                         | 4-8           |
| Aldehydes                                      | 2-4           |
| Water                                          | 20-30         |
| High boiling hydrocarbons >200°C                | 3-6           |

Table 2. Properties of oxidate and HCl solution

|                        | Oxidate  | 15 wt % HCl |
|------------------------|----------|-------------|
| Density, g/sm³         |          |             |
| Viscosity at 20°C, cP  | 3.22     | 1.70        |
| at 20°C, cP            | 1.30     | 0.72        |
| Surface tension, dyn/sm| 2-3      | 0.6         |
| pH                     |          |             |
| Limestone Dissolving Capacity, kg/m²           | 350-415   | 220         |
| Limestone Dissolution Rate, kg/(m²·h)         |          |             |
| at 100°C               | 0.75     | 2.5         |
| at 150°C               | 0.90     | 6.0         |
| at 200°C               | 1.40     | 10.0        |

At the stand, optimization of the technological parameters of oxidation (air flow, pressure, temperature, catalyst) was carried out, as well as the production of laboratory lots of “oxidate”.

3. Results and Discussions

The composition of the oxidate, which is a mixture of carboxylic acids, ketones, alcohols, aldehydes, etc., was studied.

The obtained laboratory sample of “oxidate” was tested on linear models of the carbonate formation by repeatedly pumping the reagent through a water-saturated model to determine its effectiveness. The experiments carried out confirmed the possibility of increasing oil recovery through the use of the proposed technology. Under the influence of the “oxidate” on the oil-saturated carbonate formation, both the dilution and displacement of the BBH and the permeability of the formation occur due to the interaction of the “oxidate” carboxylic acids with the carbonate reservoir. The oil recovery factor increased by 20%.
Based on the results of field tests, it has been established that it is possible to obtain a complex coolant directly at the bottom of the well. A fraction of light hydrocarbons containing special selective catalysts and an air mixture are simultaneously and separately fed from the surface to the device. Then, in this device, the processes of oxidation of light hydrocarbons are initiated with the production of oxidate and a significant amount of heat. The temperature, the rate of formation of the oxidate and its composition are regulated by the selection of raw materials supplied from the surface and the technological parameters of the device. The design of the reactor eliminates the formation of an explosive mixture of WFLH with an oxidizing agent. Due to the intense electric heating at the initial stage of the reactor operation, the product yield is close to the maximum possible.
The impact of hot coolant on the bottomhole zone will provide a comprehensive thermochemical effect on the oil-containing reservoir:

- a wide range of solvents that are part of the oxidate will dissolve paraffin deposits when they are present in the bottomhole formation zone, destroy the boundary layer of oil in contact with rock-forming minerals, thin the oil and increase its mobility;

- due to the liberation of the pore space of rocks from high molecular weight hydrocarbon compounds, the conditions for access of carboxylic acids to the rock, chemical interaction with the carbonate reservoir, improve the hydrodynamic characteristics of the reservoir, increase the permeability and porosity of the reservoir and allow deeper treatment of the bottom hole zone;

- the formation and neutralization of acids will occur directly in the reservoir, without contact with the equipment of the well.

- an aqueous solution of an oxidized acid with a neutralized acid group is a heavy oil with surface-active properties, which will contribute not only to a better displacement of oil from the porous medium, but also a significant increase in exposure coverage.

- a combination of hot coolant and the catalytic properties of rock-forming minerals will allow for in-situ catalytic refinement of oil.

The technical solutions embedded in the device allow using it in vertical, deviated and horizontal wells, combining it with well-known and promising technologies, including thermo-alkaline or thermopolymer flooding, as well as combined heat exposure technologies:

- steam-air- WFLH;
- steam acid;
- steam surfactant;
- steam solvent;
- with the injection of gelling compositions;
- binary compositions and other multicomponent technologies.

Additional devices such as can be attached to the output:

- tubing with filler for the complete oxidation of BFLH and thereby receive the maximum possible heat that is transferred from the surface of the tubing in the well;
- tubing with perforation for the distribution of gases or vapors obtained during the reaction along the entire length of the pipe.

4. Conclusion

In sum, we have studied oxidate composition which has been set as a mixture of carboxylic acids, ketones, alcohols, aldehydes, etc. The obtained laboratory sample of "oxidate" was tested on linear models of carbonate formation by repeatedly pumping the reagent through a water-saturated model to determine its effectiveness. Interestingly, the provided experiments confirmed the possibility of
enhancing oil recovery through the use of the proposed technology. In addition, the influence of the “oxidate” on the oil-saturated carbonate formation lead to both the dilution and displacement of the BBH as well as the formation permeability due to the interaction between “oxidate” carboxylic acids and the carbonate reservoir. As a result, the oil recovery factor has increased by 20%.

It is noteworthy to suggest that injecting oxidate to create an integrated steam and thermal processing technologies for the bottom-hole formation zone will solve the problem of involving heavy oils located at depths of more than 700-800 m in the rational development. Moreover, a targeted choice of reagents is possible by taking into account specific conditions of the operation object to realize the possibility of a full EOR.

Acknowledgments

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

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