Supercritical fluid mediums for the extraction of oil products from tar sands

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Abstract. The prospects of using supercritical fluid medium for the extraction of oil products from tar sands are discussed. The results of an experimental study of the extraction process using propane-butane extractant (75% wt. propane + 25% wt. butane) in liquid (t = 80 °C, 100 °C, P = 5-10 MPa) and supercritical fluid (t = 140 °C, P = 5-10 MPa) states are presented. The results of quantum chemical simulation are presented in relation to the above process.

1. Introduction

The current level of technology is only approaching the possibilities of large-scale development of most of the unconventional sources of hydrocarbons. According to the US Geological Survey, the world reserves of oil shale and tar sands are estimated at 700-800 billion tons, which is 7-8 times more than the oil reserves discovered in the world [1]. Namely, tar sandstones and oil shales make up the largest part of natural organic minerals dispersed throughout the world. For many countries, they constitute an alternative to oil.

About 63% of superheavy oil is produced by the open pit method, the rest is accounted for by in-situ underground production methods [2].

Intra-layer production methods are divided into the so-called “steam-assisted gravity”, “cold” and “thermal” methods. The method of steam-assisted gravity drainage (SAGD) involves the drilling of paired horizontal wells with steam injection into a well located in the reservoir 5 meters above the product well. The modern “cold” CHOPS heavy oil production method involves oil production together with sand due to the conscious destruction of a weakly cemented reservoir and the creation of appropriate conditions for the flow of a mixture of oil and sand in the reservoir. The VAPEX (vapor extraction) method consists in injecting the solvent into the formation in the gravity drainage mode (steam injection in SAGD is replaced by solvent injection in VAPEX) [3].

In development of the VAPEX method, the so-called N-Solv method has been developed, which allows to increase the production of oil products from tar sandstone, allows to reduce the cost of oil and the harmful effects on the environment. N-Solv technology uses propane as a natural gas, which requires significantly lower energy consumption compared with the case of using water vapor. The solvent (propane) is heated to a low temperature (~ 50 °C) and pumped into tar sandstone. Propane decomposes bitumen, the heaviest components of bituminous oil remain underground, and the lighter oil product and reusable solvent rise up. As a result, bituminous oil is less viscous than in the traditional version of the underground method of development, and it can be transported immediately through the pipeline [3].
Thermal methods for developing oil fields in their various modifications are traditionally divided into three main groups: in-situ combustion, steam and thermal treatment of bottom-hole zones of wells, and, finally, injection of a heat carrier in the form of steam or hot water. Thermal methods have two significant drawbacks: a rather high cost of the resulting oil product and a fairly significant damage to the environment during production [4].

But in the end, we can conclude that in a number of the above methods and, in particular, in the N-Solv method, some key elements of the previously discussed mechanism for the displacement of conventional oil by carbon dioxide are also presented. However, if by the temperature of the same propane we can quite simply (experience of water vapor injection exists) reach supercritical values (tcr = 96.67 °C), then by pressure (Pcr = 4.247 MPa) this can be done only for cases of deep-lying seams of tar sandstone (over 450 m.). For, the average strength characteristics of the earth's thickness determine the possibilities without the destructive realization of excess pressure, for example, at 50 bar only at a depth of 500 meters or more; 100 bar only at a depth of 1000 meters or more. And such an opportunity exists, in principle! For example: Canada - according to various estimates, the depth of tar sandstone reaches 330-500 meters; The Republic of Tatarstan - if, according to early sources [5, 6], the maximum depth for various territories ranges from 100 to 360 meters, then in work [7] dated 2012, it is already noted that the largest deposits of super-viscous oil in the Republic of Tatarstan are confined to terrigenous and carbonate deposits of the Lower and Middle Carboniferous and Upper Devonian carbonates, and that most of the deposits are concentrated at depths of 700-1500 m, and in some cases productive formations occur even at depths of 2-2.5 km.

2. Experimental part
As an extractant in the extraction process described in detail in [8], a propane-butane mixture containing ~ 75% wt. propane and ~ 25% wt. butane are used. Figure 1 shows the yield of heavy oil from the oil sand of the Spiridonovskoye field of the Republic of Tatarstan during the extraction with propane - butane extractant in the liquid and supercritical fluid (SCF) states. The yield on isotherms with relatively close temperatures corresponding to the liquid state of the extractant (t = 80 °C and 100 °C) is close in magnitude. At the same time, with increasing pressure there is a slight drop in the yield of hydrocarbons.

![Figure 1](image.png)

Figure 1. The yield of heavy oil from oil sand in the processes of liquid and SCF extraction using propane-butane extractant: 1–80 °C, 2–100 °C, 3–140 °C; M2:M1 = 1.5:1 (mass ratio of extractant and oil sand).

With increasing pressure at the same temperature, the density of the extractant increases, as a result, the viscosity increases and the processing capabilities of oil sand are complicated, which in turn leads to a slight decrease in the yield of heavy oil from sandstone. The yield on the SCF isotherm (140 °C) is traditionally characteristic of processes with solvents in the SCF state. At high pressures, the absolute value of the yield of hydrocarbons with the extractant in the SCF state exceeds the yield of liquid extraction. And this is explained, apparently, by the fact that the SCF solvent has a significantly higher penetrating power and processes a large surface area of the original oil sand. The process under discussion allows extracting up to 96.34% wt. oil products from oil sandstone, which was originally estimated at 7.23% wt.
Quantum-chemical studies were carried out in the Linux operating system using the Gaussian 09 and Gaussian 16 software packages implementing the DFT method with the density functional B3LYP with the basic set 6-311++G(df, p) [9].

Oil sands contain atmospheric oxygen, for which the triplet state is its main form. Oxygen acts as an oxidizing agent in the studied reactions. Oxygen is responsible for the generation of other reactive radical oxygen species and, accordingly, alkyl, phenyl, aryl, phenoxy, alkoxy and other radicals. Typically, the interaction of hydrocarbons with oxygen is written by the following basic reaction equations [10]:

\[
\begin{align*}
\text{RH} + \text{O}_2 & \rightarrow \text{R}^\circ + \text{HOO}^\circ + \text{Q} \quad (1) \\
\text{ROO}^\circ + \text{RH} & \rightarrow \text{ROO}^\circ + \text{R}^\circ \quad (3) \\
\text{R}^\circ + \text{O}_2 & \rightarrow \text{ROO}^\circ \quad (2) \\
\text{HOO}^\circ + \text{RH} & \rightarrow \text{R}^\circ + \text{H}_2\text{O}_2 \quad (4)
\end{align*}
\]

We performed a quantum chemical study of reaction (1) in [11] using the direct oxidation of 2,3-dihydronaphthalene as an example using the DFT method with the density functional B3LYP with the basis 6-311++G(df,p) in the implementation of the Gaussian09 program. Also in [12], using the DFT method with the density functional B3LYP with the basis of 6-311+G(d,p), the elementary act of oxidation of n-hexane via the secondary C–H bond was described.

In this work, we give a quantum chemical description of the equations of reaction (1) using oxygen (3O2) oxidation of the series of alkanes, olefins, substituted arenes, and molecular structures with signs of asphaltenes and further interaction with the hydroperoxyl radical (4) (Figures 2-4, Table 1).

**Figure 2.** Interaction of O2 with non-cyclic hydrocarbons.

**Figure 3.** Interaction of O2 with cyclic olefins.

**Figure 4.** Interaction of a hydroperoxyl radical and molecules structurally similar to asphaltene (equation (4)).
Table 1. The calculated energy and thermodynamic parameters (in kcal•mol⁻¹) of the reaction systems corresponding to schemes 1-3, under conditions (P = 1 atm, T = 298 K) in the approximation of the DFT method with the density functional B3LYP/6-311++G(df, p).

| Chemical name (TS), substituents or structure | The forward direction of the reaction | The reverse direction of the reaction | Thermal effect and reaction enthalpy |
|-----------------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| R₁ R₂ R₃ E° ΔH° ΔG° E° ΔH° ΔG° Q Delta H Delta G |
| n-propane (TS1) H H Et 45.38 44.76 49.05 2.97 2.35 4.61 -42.41 42.41 44.44 |
| iso-propane (TS2) Me H Me 39.70 39.08 43.75 2.36 1.74 4.25 -37.34 37.34 39.50 |
| butane (TS3) Me H Et 39.51 38.89 43.52 2.45 1.83 4.34 -37.06 37.06 39.18 |
| hexane (TS4) Me H Bu 39.70 39.08 43.88 2.34 1.72 2.02 -37.36 37.36 41.86 |
| anthracene (TS5) 25.66 25.04 29.97 3.49 2.87 5.09 -22.18 22.18 24.88 |
| (TS6) 22.21 21.59 30.38 6.68 6.06 9.64 -15.53 15.53 20.74 |
| (TS7) 12.63 12.01 14.95 14.82 14.2 17.69 2.19 -2.19 -2.74 |

3. Conclusion
Due to the presence of methane in the composition of the propane-butane extractant, its interaction with oxygen to form a methyl radical, and further recombination of the methyl and propyl radicals, part of the propane goes into butane, as evidenced by the analysis of the extractant after the extraction process [13].

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