

# Low Temperature Oxidation of Highly Viscous Oil Under Reservoir Conditions

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## Summary

The study is focused on the low temperature oxidation of highly viscous oil by air oxygen and catalysts under reservoir conditions. The process leads to a decrease in oil density and changes in oil viscosity as well as to the formation of carbonyl, carboxyl, ketone, aldehyde and other oxygen bearing compounds in oil. Analysis of the composition of oil components and the molecular and mass distribution of n-alkanes shows partial oil upgrading.

## Introduction

Non-traditional methods are required to develop heavy oil reservoirs because of oil characteristics (high viscosity and density, high resin and asphaltene content, presence of sulphur and metals) and reservoir properties of unconventional deposits<sup>1,2</sup>. In situ upgrading of heavy oil<sup>3,4</sup> and thermal gas injection technology based on injection of oxygen from air in a reservoir look very promising. Low temperature oxidation of the liquid phase is an EOR technology for heavy oil reservoirs, in particular carbonates saturated with highly viscous oil. The technology is based on injection of air or air-oxygen blend and a catalyst in the reservoir that was previously heated in a particular location of the formation. Oxygen reacts with oil. That leads to the formation of oxygen bearing oil components (carbonyl acids, ketones, aldehydes, ethers and alcohols) and to a release of the large amount of heat. Partial oil upgrading taking place in situ because of the formation of light oil fractions due to oxidation reactions, released heat and surfactants lowering the surface tension at the oil-rock interface enhance oil recovery<sup>5</sup>.

## Theory and/or Method

Oil samples from the Permian formation located in the Ashalchi area (A) and from the Carboniferous formation (Bashkir deposit) located in the Arkhangelsk area (B) were used in the study. Experiments were conducted in a stainless steel autoclave manufactured by Parr.

Test parameters were close to the in situ conditions: 1 – 6 MPa pressure and 160-280°C temperature for oil B and 4 MPa pressure and 160°C temperature for oil A. Cobalt bearing compounds at a ratio of 0.2 wt% of oil were used as catalysts in the study. Test parameters are shown in Table 1.

Oil viscosity was measured by a needle-plate viscometer at 40°C, with a shear varying from 3 to 1,312 sec<sup>-1</sup>. Dynamic viscosity (mPa·s) was calculated based on the shear.

Table 1: Test Parameters

#	Oil, Catalyst	Temperature, °C	Pressure, MPa	Time, hrs
1	B	-	-	-
2	B	160	4.0	4.5
3	B, catalyst	160	4.0	4.5
4	A	-	-	-
5	A	160	1.4	4.5
6	A, catalyst	160	1.2	4.5
7	A, catalyst	211	1.0	4.5
8	A	280	6.0	4.5

## Examples

Test results show that post test oil A has lower viscosity and density than pre test oil. Samples 7 and 8 show the highest decrease in viscosity at 40°C. The decrease in oil density and viscosity might be attributed to the formation of a more compact disperse oil system compared to the original oil due to oxidation. That provides less resistance during viscosity measurements. However, oxidation of oil B leads to different results. Both samples of oil B (2 and 3) are more viscous but have lower density. That can be due to an increase in molecular aggregates and formation of larger molecules compared to the pre test oil.

Low temperature oxidation of oil in the autoclave leads to such typical results as a decrease in the light fraction with boiling point below 200°C, an increase in the fraction of hydrocarbon oils and an increase in the resin fraction. The increase in the fraction of hydrocarbon oils is associated with the fraction of paraffin-naphtene structures in oil. At the meantime, the fraction of aromatic hydrocarbons in oxidized oil A stays practically unchanged while the fraction of aromatic hydrocarbons in oxidized oil B increases by 2.7 per cent compared to the pre test oil. Pre test oil composition is the reason for such a difference between the fraction of aromatic hydrocarbons in two post test oils. Fraction of asphaltenes in oil A after oxidation decreases by 0.9 % while it increases in oil B by 1.7 %. Changes in the resin fraction of oil are also noticeable. Oxidation is likely associated with an increase in the size of the molecules followed by a decrease in API gravity of oil as well as with destruction of either original components of oil or the new components of oil related to the formation of paraffin-naphtene and aromatic compounds. A comparison of the oxidation products of oil gives an evidence about predominant transformation of the light fraction with boiling point below 200°C and hydrocarbon oils in two opposite directions: formation of asphaltenes in oil B and formation of lighter components (paraffin-naphtene and aromatic hydrocarbons) in oil A.

Molecular-mass distribution of n-alkanes shows an increase in the fraction of low molecular components in the post test oil compared to the pre test oil. Temperature of oil oxidation and the original oil composition are two main factors. Among all tests, the test with oil A at the 280°C temperature and the 6 MPa pressure and for 2.5 hours shows the most significant changes in oil characteristics.

Presence of catalysis leads to the more significant effects mentioned above, an increase in the amount of aromatic hydrocarbons and oils with a higher fraction or resins in the samples. It is likely that alcohol-benzene resins breaking into fragments during oxidation get trapped in a chromatographic column as a fraction of paraffin-naphtene and light hydrocarbons. When the catalyst is used, an increase in the oxidation temperature of oil A from 160°C to 280°C leads to a sharp increase in the asphaltene content and the amount of light fraction with the boiling point below 200°C, a significant decrease of the content of resins from 35.8 % to 24.3 % and an increase in the content of paraffin-naphtene hydrocarbons in oil by 14.4 %. Such changes in the chemical composition of the products of oil oxidation with or without the catalyst show the effect of catalyst on the directions of the oxidation of hydrocarbons.

Chromatography and mass spectrometry show that the light fraction (boiling point below 200°C) of oil A becomes a complex mix of oxygen bearing components with the prevailing fraction of ketones. Test results also show ethers of organic acids, acids and aldehydes. Reactions of air oxygen with oil in the presence of the catalyst lead to the formation of a larger variety of oxygen bearing compounds.

## Conclusions

The study shows that low temperature oxidation of highly viscous oil by air oxygen with in the presence of a catalyst under in situ conditions leads to a decrease in oil density, changes in oil viscosity depending on the oil composition, an increase in the resin and asphaltene content and a decrease in heavy fraction in the oil. Composition of n-alkanes changes towards a higher content of light molecular species. A complex mix of oxygen bearing compounds with the prevailing fraction of ketones forms due to oxidation.

Changes in the oil are associated with two main processes: condensation and thermal oxidation destruction. Further research is needed to better understand and tune low temperature oxidation of highly viscous heavy oil and bitumen that should include a search for efficient oxidation catalysts and inhibitors that would prevent asphaltene formation. Large scale physical modeling that would allow testing under in situ conditions, is required to decide on a technology of oil production for a particular reservoir.

## References

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