**The model of crude oil oxidation for in-situ combustion technology.**

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The models of crude oil oxidation in terms of chain reaction approach have been developed in the recent years. The set of chemical reactions suggested in our work was simplified and solved under certain conditions.

The formation and accumulation of hydroperoxides is a key stage of the oxidation process. First oxygen molecules penetrate into the oil chains and forms free radicals. Radicals are passed from one molecule to another (chain growth), until they form hydroperoxides. Also some products of the reactions are gases CO and CO2 water, oxidized components, aldehydes, ketones, acids. This stage is widely investigated in experiments and called low temperature oxidation (LTO). The hydroperoxides can decompose into a pair of radicals - this is a branching chain reaction. New radicals initiate the new chains and start the new processes of oxidation. The figure 1 shows the cyclic character of the oxidation through radical appearance and hydroperoxides accumulation. The more hydroperoxides are accumulated the higher is oxidation rate. This process self-accelerates and causes the ignition in crude oil with oxygen. With the temperature growth above 250 °C one can observe non-radical high temperature oxidation where chain mechanism takes place, but it is not the main one.



Figure 1. The scheme of chain reaction mechanism of oil oxidation

In the present oxidation scheme we consider active and inactive oil components at the initial oxidation stages. Both of these compounds oxidize simultaneously but they lead to different products. Crude oil separates into the main oxidizing components – alkanes (denoted Sat) and their oxidation inhibitors - aromatic compounds, which then form the fuel (denoted *Inh*). The other components - Resins and Asphaltenes become solid at the early oxidation stages and are out of the investigation here, they just make a gift into the heavy residuals for high temperature combustion.

The time dependence of hydroperoxides concentration strongly depends on the initial reactions rates. We drove out the dependencies for cases of exponential growth of free radical concentration – which lead to self ignition, limited growth – which leads to oxidized compound formation only and intermediate cases which have not been examined before but also exist in experiments of oil oxidation (figure 2).

Figure 2. Time dependence of hydroperoxides concentration in oxidation process.

Here we also consider the probability of inhibition on any stage of the reaction scheme – in the chain growth stage, hydroperoxide formation and decomposition stage. In fact different types of inhibitors act at different stages. Here we attempt to solve such system of equation and obtain how the inhibition of different stages governs the whole process. It is needed to mention that oil components are very different and various types of inhibitors exist in crude oils.

 We also suppose that catalytic effects of different additives which are explored in many papers cannot be we explained without inhibition scheme consideration. Because lots of catalysts prevent the inhibition reactions, act as inhibitors adsorbents or shift the balance towards slowing down the inhibition processes. All this shows that inhibition consideration is the step preceding any theoretical investigation of catalysts application.