

The free radical chain mechanism of the initial stages of crude oil oxidation in term of SARA fractions

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Abstract.

The formation and decomposition of hydro-peroxides are the key stages of combustion. These stages strongly depend on the several factors accelerating or slowing this process. The aim of this work is to estimate experimentally which oil components act as inhibitors of initial stages of oxidation and which accelerate the process. The next aim is to explore the process of adsorption of oil components on the grain of rock, which turned to be also a key process in the low temperature oxidation.

The work includes experimental part where differential scanning calorimeter (PDSC) experiments with pure saturates, mixtures of saturates and aromatic oil fractions and mixtures of saturates, aromatic fractions and rock samples are considered. Effects of inhibition and acceleration of the initial oxidation stages are explored.

1. Introduction

It is known that predicting the performance of enhanced oil recovery by air injection has remained a challenge. It occurs mainly because of the lack of accurate models of crude oil oxidation.

In the recent works crude oil oxidation for the application of in-situ combustion was considered from the positions of the free-radical reactions, including radicals and short living hydroperoxides [1, 2]. Such consideration enables us to drive out some parameters like induction time that experience a huge impact from inhibition and acceleration effects [2].

The chemical structure of hydrocarbons effects dramatically on the hydroperoxides' activity and free radicals formation. Chain mechanism of oxidation is impossible to consider without dividing oil components into some groups according to their structure. Because of the complexity of crude oil oxidation a great number of chemical models were introduced. In recent years the investigators focused on SARA fraction model for oil oxidation [3-5]. The differences in the oxidation behavior of each SARA fraction for the particular oil and its impact on the overall oxidation of the oil have been studied in the work [3]. In the work [4] it was suggested to use RTO experimental results for each SARA description and reaction constructing. The attempt to introduce hydroperoxides into the oxidation model of SARA fractions was done in the work [5]. But the main drawback of such complicated model was



the impossibility of identifying kinetic parameters for such reactions using combustion tube or RTO experiments.

As it was shown experimentally [6] the main fuel for low temperature oxidation is pure saturates. Other components has much higher temperature of combustion and slow the oxidation reaction of saturates. The similar results were obtained in [7] using PDSC. This work also has shown the different effect of rock sample upon the SARA fractions' oxidation. In the previous work [2] we have considered factors which are significant for self ignition process using model of SARA fractions. The initial stages of oxidation were considered from a position of radical chain process. We estimated the most valuable reactions by making a correlation among the oxidation stages and heat release obtained from experiment of oxidation with differential scanning calorimeter. The sequence of chemical reactions including free radicals, hydro-peroxides and inhibitors influence were considered.

The aim of this article is to clarify what kind of inhibitors act upon hydrocarbon oxidation process, which contain in the crude oil. We also considered the influence of crashed core samples on the oxidation in order to clarify if there are some kinds of oxidation catalysts in core material, or the core surface act upon the oxidation.

The differential scanning calorimetric technique was used for the oxidation experiments with oil saturates, oil aromatic components, their mixture and crashed core samples.

2. The main idea of the laboratory experiments.

It is well known that crude oil is multicomponent system, and oxidation of different oil fractions happens with different reaction rates and initial temperatures. There are two distinct areas for oxidation of any crude oil. The heat output increase in two temperature ranges 150-300 °C (low temperature oxidation LTO) and 350-500 °C (high temperature oxidation HTO). These areas one can easily observe using PDSC.

The catalytic or inhibitor effects come out mainly in the initial stages of oxidation. The inhibitors dramatically effect on the dependence of the initial heat appearance on the temperature. And this ability will be explored in the paper.

The papers mentioned above [2, 6] have shown that in the LTO region the saturate oil components exhibit oxidation. For light oils saturates make the main contribution into the heat release, the oxidation process for light oils is similar to saturates behavior. That is why the inhibition and catalytic effects were explored using pure saturates (paraffinic compounds) with different additives.

The experiments were designed in order to determine the influence of crashed rock on the oxidation of hydrocarbons as a catalyst or as an adsorbent of oxidized compounds. The possible catalytic effect of the rock on the oxidation and the inhibitory effect of some oil components suppressed by the rock were investigated separately.

The experiments were held with PDSC technique under 2,5 – 7 MPa pressure. The PDSC method allows making accurate measurements of heat release in constant flow of air with constant heating rate. The sample of 0,3 – 0,6 mg was hydrocarbone liquid or liquid with crashed rock, mixed in the ratio 1/15. The rock was taken from the core sample of the oilfield, which oil components were examined.

The oxidation of pure synthetic saturates C_{24} - C_{54} with linear structure was explored. Then tetracosane $C_{24}H_{50}$ oxidation curve was taken as a reference one, then C_{24} was mixed with oil aromatic components in concentrations 1/9 and 3/7 in order to observe inhibition process. Then mixtures of $C_{24}H_{50}$ with crashed core and mixtures of $C_{24}H_{50}$ with aromatics and with crashed core were explored.

The influence of different additives on the kinetic parameters was explored and the influence on the initial stages of oxidation was explored as well. The induction period – time period from the beginning of oxidation till the first measured heat release. Its value depends on the oxidation conditions and strongly depends on the temperature of the first heat release according to the work [7] in the following way:

$$\tau_{\text{ind}} \sim \exp\left(-\frac{1}{T}\right). \quad (1)$$

In coordinates $\ln(\tau_{\text{ind}})$ vs $1/T$ it is a straight line. This dependence can be used for estimation the inhibition and catalytic effects in the initial stages.

The other valuable feature of oxidation process is the curvature of the kinetic curve in the area close to zero. The development of oxidation process in time after completion of the induction period shows an exponential dependence:

$$dq/dt \sim \exp(\varphi t), \quad (2)$$

where coefficient φ is proportional to the quantity of active free radicals in the oxidizing system [8] at the given temperature. This coefficient as well as induction period is a significant characteristic of the activity of initial oxidation stages. Both these factors are strongly affected by inhibitors. The induction period increases with a decrease in the number of active radicals, the rate of the exponential time-dependence decreases if the activity of the radicals becomes insufficient. These two criteria are applied in this work.

3. The experiments of synthetic saturates oxidation

The oxidation of saturates was carried out by PDSC. The pressure effect and molecular weight effect on the oxidation process and the kinetic parameters determined using PDSC. Heat output of saturates' oxidation process starts at similar temperatures for C_{24} , C_{20} , C_{30} , C_{40} , C_{50} . Its value depends on the heating rate, but roughly lays in the range 195-219 °C. A slight difference has C_{40} , C_{50} in the direction of decreasing the initial temperature. Values of initial temperature at different heating rates are given in table 1.

Table 1. Onset temperature of combustion curves under different heating rates (5, 10, 15 20 °C/min) DSC of high-pressure analysis data for different alkanes.

heating rate (C°/ min)	$C_{20}H_{42}$	$C_{24}H_{50}$	$C_{30}H_{62}$	$C_{40}H_{82}$	$C_{54}H_{110}$
5	200,40	200,46	200,95	195,43	196,60
10	209,68	209,07	209,80	205,15	205,49
15	215,47	214,80	214,97	211,29	209,77
20	219,22	218,91	218,93	214,71	214,72

There also were determined integral heat release and activation energies, pre-exponents and all the kinetic parameter as well for each saturate oxidation. These values characterize the kinetic of the whole process. But the values are not decisive and do not reflect the kinetics of the initial stages of oxidation. That's why then we use only characteristics for initial stages and not the kinetic parameters for the whole process.

The induction period depending on temperature was determined for a set of kinetic curves at different heating rates. The coefficient φ in the exponential dependence of the kinetic curve on

time was also identified ($\varphi_{C_{24}} = 0,041 \pm 0,014$). These parameters are used later for comparison.

Different alkanes have similar kinetic curves of oxidation, quite close values of initial and peak temperature, activation energies. Their characteristics are also similar to the kinetic curves for saturates extracted from crude oils [6]. Therefore, to further study the inhibitory and catalytic effects on used tetracosane $C_{24}H_{50}$

4. The oxidation experiments of tetracosane mixed with aromatic compounds

Aromatic compounds were separated from the studied oil using SARA analysis. Tetracosane is a solid at room temperature, therefore, for the preparation of mixtures of aromatics with tetracosane they were both previously heated. Were investigated the oxidation curves for a mixture of tetracosane/aromatics 9/1 and 7/3 at three pressures of 2,5, 5 and 7,5 MPa (figure 1) and at different heating rates 5, 10, 15, 20 $^{\circ}\text{C}/\text{min}$.

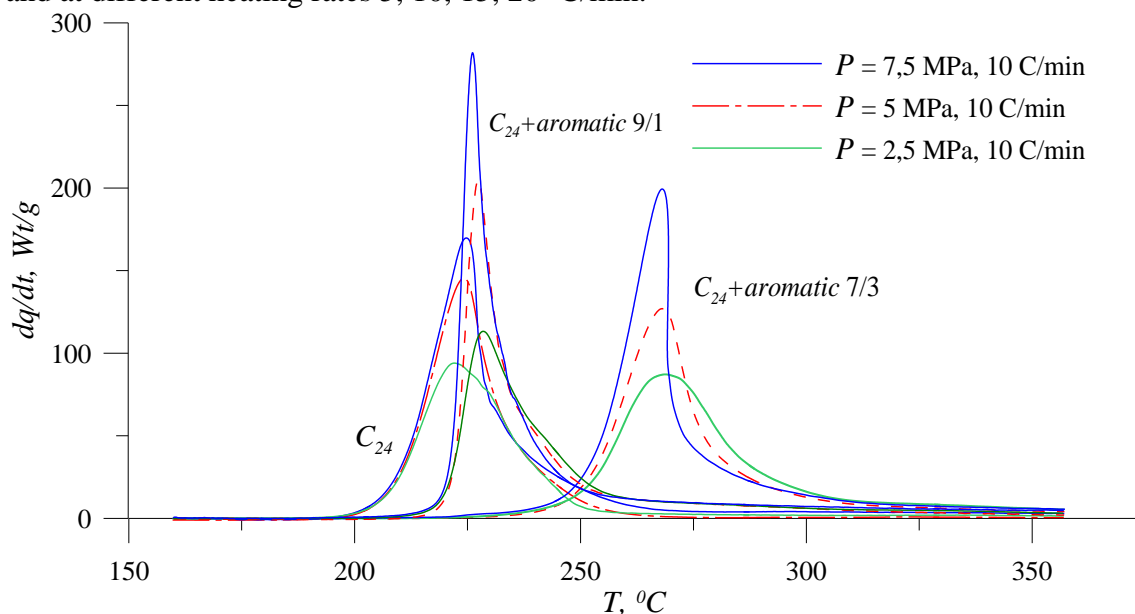


Figure 1. $C_{24}H_{50}$ and mixtures with Aromatics in 9 to 1 and 7 to 3 ratio combustion curves under 2.5, 5, 7.5 MPa.

It is well seen that the addition of aromatics inhibit the initial stages of tetracosane oxidation. The beginning of the oxidation is shifted to higher temperature. Oxidation temperature shifts increases from 200 to 230 $^{\circ}\text{C}$ for a ratio of 9/1 and up to 240 $^{\circ}\text{C}$ for a ratio of 7/3. Values of initial temperature at different heating rates for the mixtures are given in table 2. The initial stages of oxidation go slower. The first heat rise is smaller for mixtures the φ factor reduces from $\varphi_{C_{24}} = 0,041 \pm 0,014$ to $\varphi_{C_{24}+Arom} = 0,026 \pm 0,011$ (figure 4).

The effect of pressure is to increase the oxygen concentration and, accordingly, to increase the thermal effect of the reaction that has almost no effect on the beginning of the oxidation process and the heat rise of the initial stages (φ factor does not depend on the pressure). From this we can conclude that for saturates and saturates mixed with aromatics the appearance of hydroperoxides and free radicals occurs in the liquid phase during the initial stages of oxidation. The gas phase, entrained by the air steam in the flow mode does not affect the oxidation process.

5. The oxidation experiments of tetracosane mixed with crushed rock and tetracosane mixed with aromatics and crushed rock.

Further the oxidation of tetracosane and mixtures of tetracosane with the aromatics on crushed core material were investigated. We have taken the carbonate rock with the hydrocarbons in a ratio of 15/1, which corresponds to the average saturation of the considered oilfield.

To determine the effect of the rock were conducted experiments of C_{24} oxidation mixed with the crushed rock. Tetracosane was mixed at temperature 50-70 °C. The initial temperature of oxidation has not changed, but the pattern of the kinetic curve was changed to a more significant thermal effect at the initial stages of oxidation.

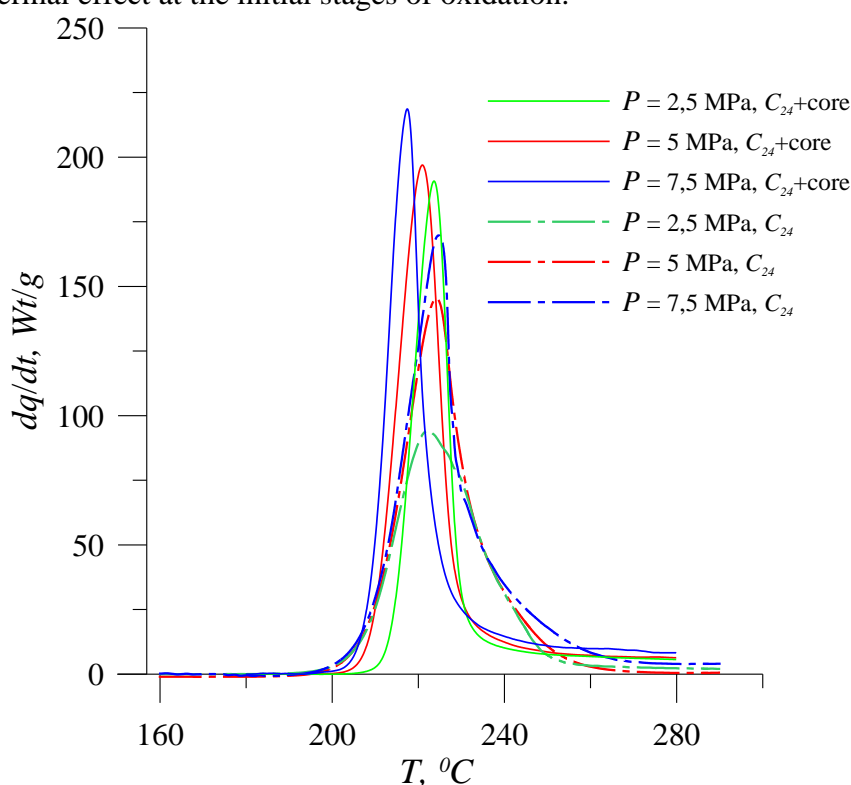


Figure 2 $C_{24}H_{50}$ and $C_{24}H_{50}$ mixed with crushed core combustion curves under 2.5, 5, 7.5 MPa.

One can observe the acceleration of oxidation at the initial stage with core material in comparison with pure tetracosane (figure 2) $\varphi_{C_{24}} = 0,041 \pm 0,014$, and $\varphi_{C_{24}+core} = 0,158 \pm 0,009$. The initial temperature of the heat output and accordingly, the induction time has not changed. But one can see a dependence of the induction period of the pressure for tetracosane mixed with core. The higher the pressure, the smaller induction time we observe (table 2).

The next step was to examine mixture of aromatic compounds and tetracosane with rock material. In the presence of crushed rock the aromatic compounds with tetracosane have a much lower initial temperature of heat release, it reduces by twenty degrees from 250 °C to 230 °C (table 2, figure 3).

Table 2. Onset temperature of combustion curves under different pressures (2.5, 5, 7.5 MPa) DSC of high-pressure analysis data for tetrakozane, tetrakozane with aromatics and with crushed core.

heating rate (C0/ min)	$C_{20}H_{42}$	$C_{20}H_{42}$ + core	$C_{24}H_{50}$ + aromatic 7/3	$C_{24}H_{50}$ + aromatic 7/3 +core
25	207,12	215,28	249,91	230,68
50	209,07	210,22	244,94	228,43
75	208,77	208,02	252,52	226,68

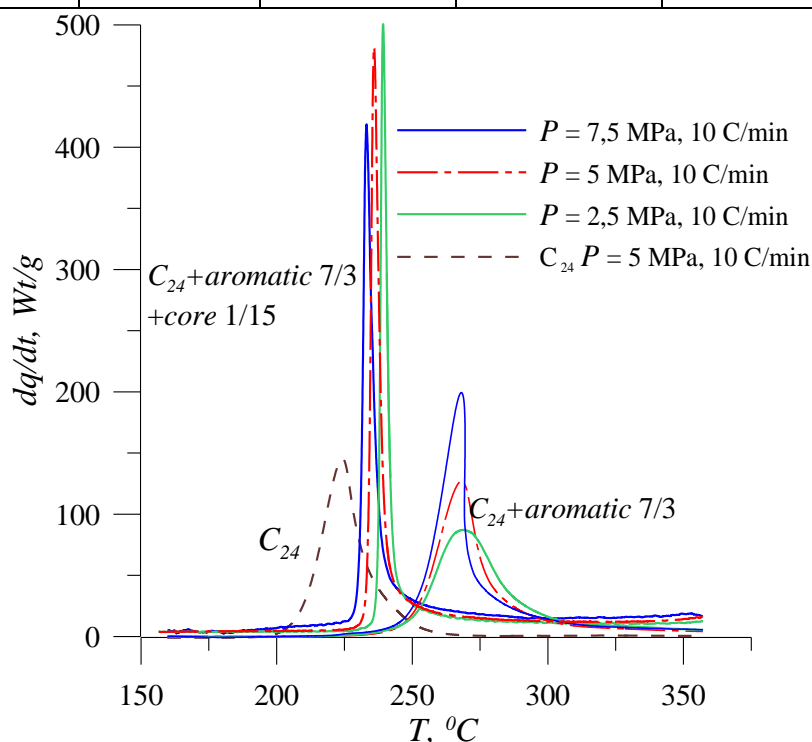


Figure 3. Pure $C_{24}H_{50}$ and $C_{24}H_{50}$ mixed with aromatics, $C_{24}H_{50}$ mixed with aromatics and crushed core, combustion curves under 2.5, 5, 7.5 MPa.

The induction time for mixtures on the rock also decreases. Such effect was not observed in earlier experiments with pure tetracosane (figure 2). Thus the effect is not associated with the catalytic effect of the crushed rock, but with the adsorption of aromatic compounds on the grains of the rock. Aromatic compounds are more prone to adsorption than the saturates. Mainly because of the linear structure of saturates and aromatic rings in aromatics. This effect is possible in the oil reservoir during in-situ combustion too.

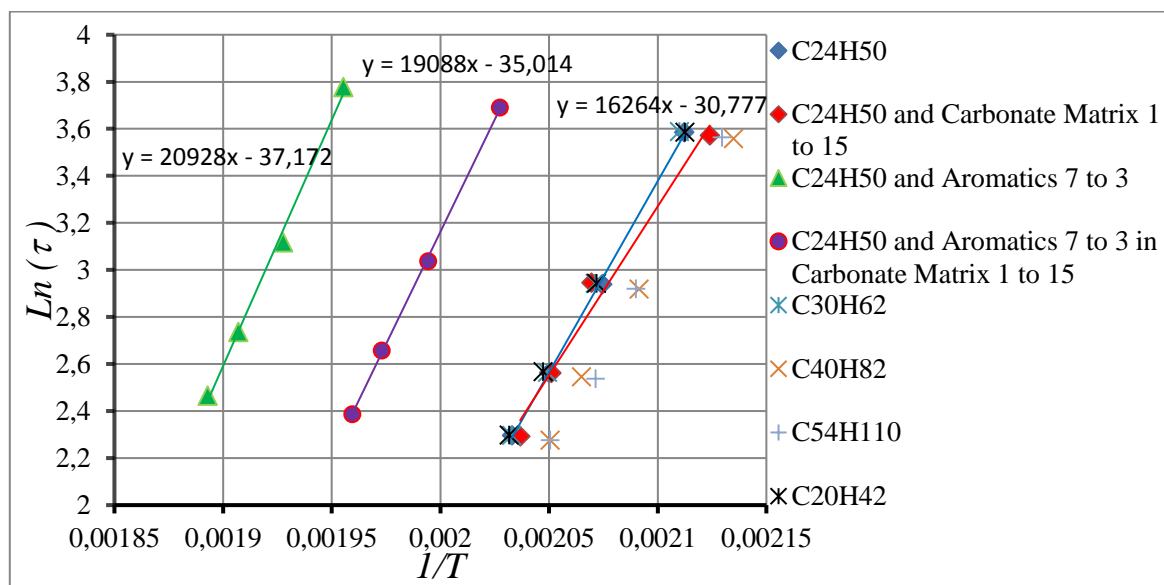


Figure 4 Induction time vs the inverse initial temperature for different saturates, C_{24} with crushed core, C_{24} with aromatic compounds, C_{24} with aromatic compounds and crashed core.

Figure 4 shows the dependence of induction time (period) for all studied compounds and mixtures. Saturates with linear structure, as mentioned earlier, did not significantly differ from each other in oxidation process, the induction period has the same dependence on initial temperature. The crushed rock does not affect the induction period as well (red rhombs), although the presence of rock significantly changes the form of kinetic curves.

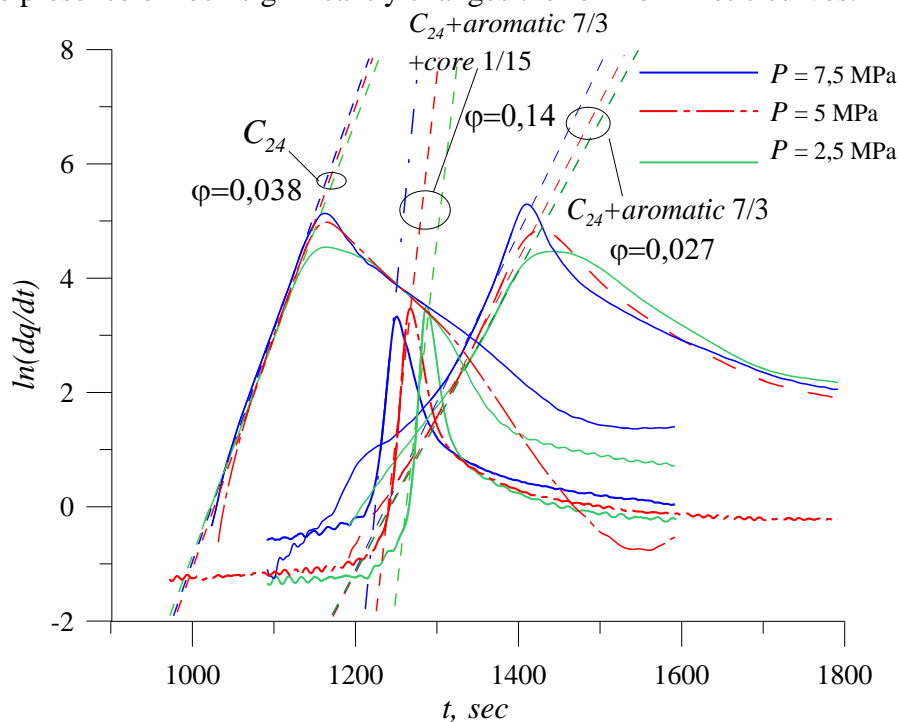


Figure 5 Natural logarithm of kinetic curve opposite time for pure C_{24} , C_{24} with aromatic compounds, C_{24} with aromatic compounds and crashed core under 2.5, 5, 7.5 MPa.

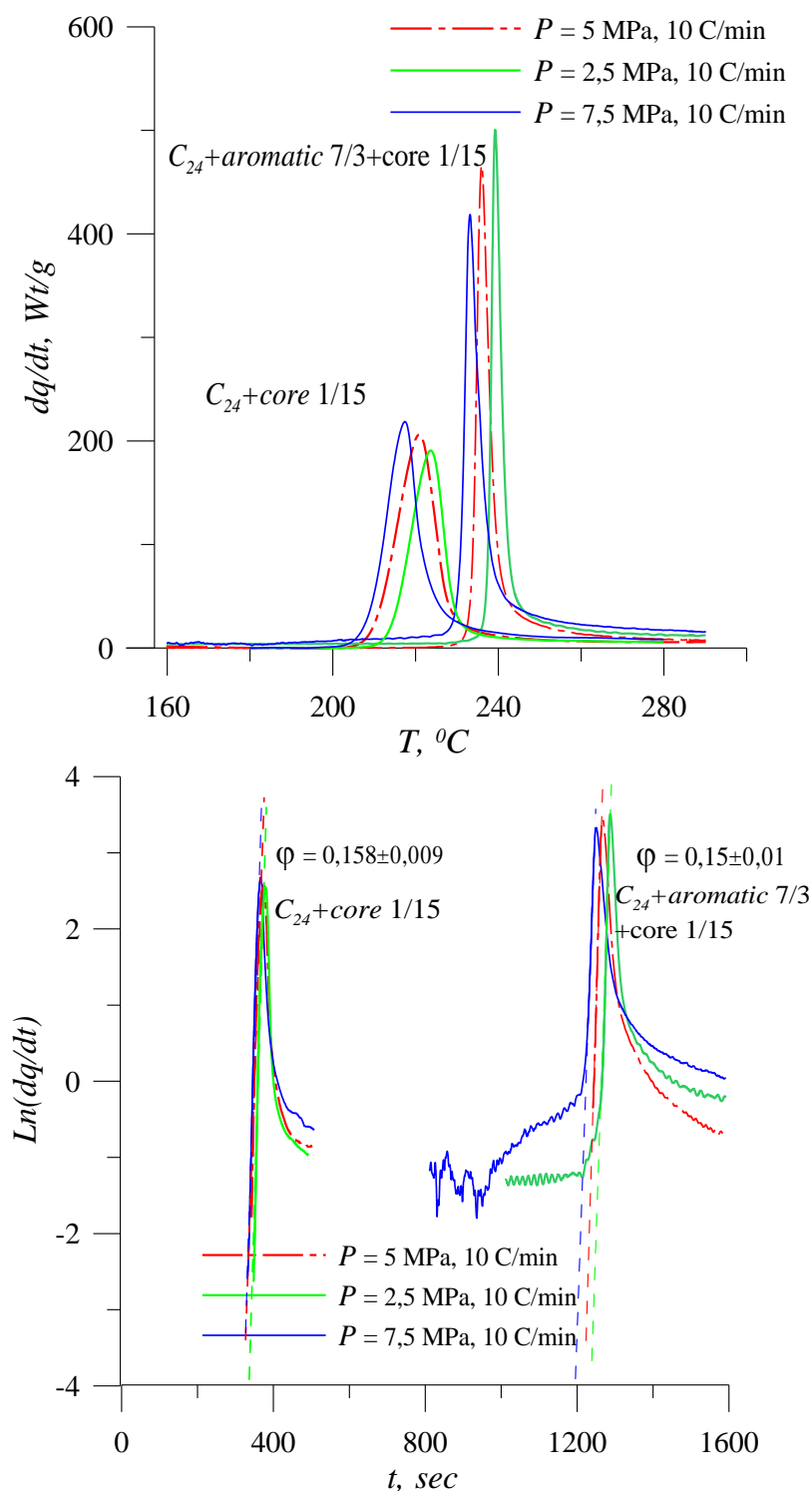


Figure 6 $C_{24}H_{50}$ mixed with aromatics, $C_{24}H_{50}$ mixed with aromatics and crushed core, combustion curves under 2.5, 5, 7.5 MPa (a) and natural logarithm of the same curves opposite time (b).

For tetracosane with aromatics 7/3 (green triangles) one observes the increase in initial temperature and in the slope of the straight line that characterizes the activation energy of the initial stages of oxidation. That is the effect of inhibition. Adding rock material shifts the line to the right (purple circles) and reduces its slope (the activation energy of the process).

Further we examined the influence of crushed rock on the initial stages. The exponential time dependence of initial heat release is expressed as straight lines at the figure 5. The ϕ factor for mixtures of C₂₄ with aromatics on the core, as well as for pure C₂₄ on the core within the experimental error reaches the same value regardless of whether there are aromatic compounds in the mixture applied to the crushed rock or not $\phi_{C_{24}+core} = 0,158 \pm 0,009$ and $\phi_{C_{24}+Arom+core} = 0,15 \pm 0,01$. This unexpected result suggests much larger influence of the geometry of the surface, than the inhibition effect of aromatics (figure 5 and 6b). This result also suggests that aromatic compounds are strongly adsorbed on the rock grains and does not take part in the initial stages of oxidation.

This effect requires more detailed study. PDSC experiments let one to determine the limit of adsorption i.e., the minimum concentration of aromatics in the saturates, which support the maximum amount of the adsorbed inhibitors (all the grains covered with adsorbed aromatics). After we reach this concentration of aromatics the effect of acceleration of the initial stages needs to disappear. Additionally, the effect of the surface should depend on the adsorbing properties of rocks, the properties of crushed rock, etc.

Such effect obviously plays a role for application of in-situ combustion in the oilfield. Therefore, to determine the effect of rock the experiments should be performed with the rock, which structure is as close as possible to reservoir internal structure.

6. Pressure effects on the oxidation

Another interesting effect was the influence of pressure on the peak of the oxidation kinetic curves for tetracosane and for tetracosane on the rock (figure 6a). As mentioned above in the case of oxidation in presents of rock the initial heat release and the induction period depend on pressure (table 2). The higher the pressure, the lower the induction period is. Most likely this indicates the presence of free radicals not only in liquid but in gas phase too at the initial stages of oxidation.

For tetracosane the higher the pressure, the more pronounced the peak of heat output is. This is common pressure effect which is in increasing the oxygen concentration.

The presence of aromatics leads to an inverse relationship – the lower the pressure the higher heat peak is (figure 6a). Most likely the low pressure leads to better evaporation of the inactive radicals formed by aromatic compounds. This also causes the decrease of the induction period, the more rapid spending of the inactive radicals. But this effect also requires further researches.

7. Conclusions

The oxidation experiments performed by PDSC with saturates, aromatics and crushed core has shown several effects which should be taken into account when in-situ combustion is considered.

- Saturates are the components which oxidize in low temperature mode. Thus high saturates concentration in crude oil lead to the oxidation mostly in LTO region with

small amount of fuel formed. And this is lucky for high pressure air injection application

- The aromatic compounds act as inhibitors of initial oxidation stages. Aromatic additives act in decreasing the initial temperature of oxidation, and result in a longer induction period before combustion. This means that high aromatic concentration in crude oil causes low activity and long period of self ignition for in situ combustion application.
- The pores media always act as the adsorption material for aromatic and oxidized components and accelerate the initial stages of oxidation regardless are there any chemical catalysts in mineral composition or not.
- The pressure dependence of saturates oxidation indicates mainly liquid phase oxidation. In presents of aromatics and crushed core the pressure dependence indicates the gas phase oxidation.

All this results can propagate to the reservoir conditions, but more precise estimation of rock influence it is better to perform experiments with real, not crushed core samples and high pressure.

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