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A comparative study of heavy oil oxidation thermal behavior in the presence of Cu-Mn tallates

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Abstract. Heavy oil in-situ combustion process has many benefits among other thermal enhancing oil recovery methods. However, its application is still a complex task due to the irregular propagation of combustion front in the reservoir and its early breaking down. Recent finding regarding in-situ combustion development have led to use catalysts based on transition metals in order to stabilize and enhance combustion front flow. Transition metals was chosen rather than other types of catalysts because of their practical, feasible and economic impact in a wide range of industrial processes.
Current solutions to catalytic in-situ combustion are inconsistent with their application in real fields due the problems associated to the injection of catalysts in the reservoir from one side and to the high cost that can be generated from the use of certain type of catalysts. In this context, we studied the effect of copper and manganese tallates in different metal ratios on the oxidation of heavy oil by applying various physical and physical-chemical methods. As a result, we have obtained accurate results demonstrating the potential effect of Cu-Mn tallates in stabilizing combustion front during high temperature oxidation reactions.

1. Introduction

Unconventional oil especially heavy and extra-heavy oils resources are generating considerable interest in terms of being an alternative way to replace conventional oils for at least the end of the current century. However, one of the major drawbacks in their exploitation is their high viscosity, which complicate their extraction. Thus, various methods, known as enhanced oil recovery methods have been proposed to solve the problem of high viscosity [1]. Thermal methods are among the most widely used techniques in the field and which are commonly investigated in the lab scale [2].

Among enhanced oil recovery methods, in-situ combustion process is believed to be an effective, economic and environmentally friendly way to increase heavy oil recovery factor [3]. It is based on injecting air in the reservoir to initiate heavy oil oxidation reactions and

hence to generate heat in-situ which propagates further and leads to increase reservoir temperature and thus decreasing viscosity. However, regardless the simplicity of the process in the theory as it seems, it is considered as one of the most complexes processes [4] and its application has witnessed few successful examples, which could be counted on the fingers of one hand like the Bellevue (Louisiana) and Rumania fields [5,6]. Researchers have always associated the process failing to front combustion earlier breakdown. Therefore, combustion front propagation was set to become an important component in a successful application of in-situ combustion process [7]. Various approached has been suggested to enhance combustion front propagation using catalysts based on transition metals due the important role played by them in industrial world [8]. In the literature of catalytic oil oxidation process, different catalysts in non-organic or organic salts form [9] have been used while other studies [10,11] applied micro and nanoparticle catalysts based on transition metals.

Several studies for example [9,12,13] have been performed on oil oxidation in the presence of non-organic catalysts based on various types of transition metals. It has been found that catalysts based on manganese and copper could be promising metals for in-situ combustion due to their low cost, positive impact on the environment and their availability [14,15]. The same idea has been obtained when applying oil soluble catalysts based also on transition metals on heavy oil oxidation. In addition to this, even when applying microparticles or nanoparticles based on transition metals, enhancing high temperature oxidation were obvious in the presence of manganese and copper [15,16].

Many experts now believe that rather than using catalysts in ionic or particle forms it might be useful to apply oil soluble catalysts since they can highly disperse in oil phase. The only problem limiting their use is cost of some organic salts. For this reason, some researchers have suggested the use of metal tallates as an economic alternative for use [17]. It is commonly known that tall oil is an environment friendly precursor with low cost and broad availability.

Our first studies on heavy oil oxidation in the presence of metal tallates [18] found that they are able to enhance metal dispersion in the oil phase which lead to a better combustion front stabilization. In addition, we have observed that during high temperature oxidation, copper and manganese effect the reactions in different temperature ranges. At the beginning of high temperature region, the effect resulted from copper was more than manganese's one. But at a certain temperature (about 745 K) the situation gets reversed and the effect of manganese becomes better that copper's one.

In order to understand the dual effect that could be generated from the application of copper tallates and manganese tallates we applied a complexe of physical and physic-chemical methods, which provided interesting information about oxidation kinetic behavior and its relation to copper and manganese oxide nanoparticles obtained during the process.

2. Materials and Methods

The crude oil (13.8 API°) was obtained from Ashalcha oilfield (Volga-Ural basin, Republic of Tatarstan, Russia). Organic solvent (dichloromethane - 99.5 % pure), was supplied from

Component-Reactiv and used without additional purification. Inorganic salts and pure quartz sand fraction of 43-64 µm were purchased from Sigma-Aldrich.

  Copper and manganese tallates were prepared according to a well-known method with some modifications. The experimental set up is detailed in [17]. Samples for DSC analysis were prepared by mixing heavy oil (10.0 wt %) with pure quartz sand fraction of 43-64 µm, ([90.0-ω] wt %) and symbolized as S(0). In the case of catalytic experiments, initial oil sample contained 2 wt % of Cu-Mn tallates in different Cu tallates:Mn tallates ratios and symbolized as follow: S(1) = (0:1), S(2) = (1:3), S(3) = (1:1), S(4) = (3:1), S(5) = (1:0).

  STA 449 F1 Jupiter thermal analyzer supplied by Netzsch company have been used at a temperature range of 30-600 °C to provide differential scanning calorimetric data about the process of heavy oil oxidation. A linear heating rate of 5, 10, 15, 20 K×min^{-1} was maintained during experiments, under an airflow of 50 ml×min^{-1}. The software package used to analyze the data was Proteus Analysis v5.2.1, NETZSCH Peak Separation (version 2010.09), and NETZSCH Thermokinetics 3.1 (version 06.08.2014).

3. Results and Discussions

Differential scanning calorimetry is a less time consuming, less costly approach to describe the kinetic behavior of heavy oil oxidation process. Its application in our current research allowed to shed light on the effect generated from Cu-Mn tallates on the general kinetic behavior of heavy oils. Figure 1 compares the heavy oil oxidation in the presence of catalysts at different Cu-Mn tallates ratios at 5 °C/min. It is apparent from figure 1 that the oxidation process includes two separated regions referred as low temperature oxidation (LTO) and high temperature oxidation (HTO) respectively. It is generally accepted that LTO region results in oxygenated compounds with minimal amount of carbon oxide and carbon dioxide. On the other hand, HTO regions includes coke oxidation and the formation of carbon oxides and water [19]. Peak temperature shifting is presented in figure 2.
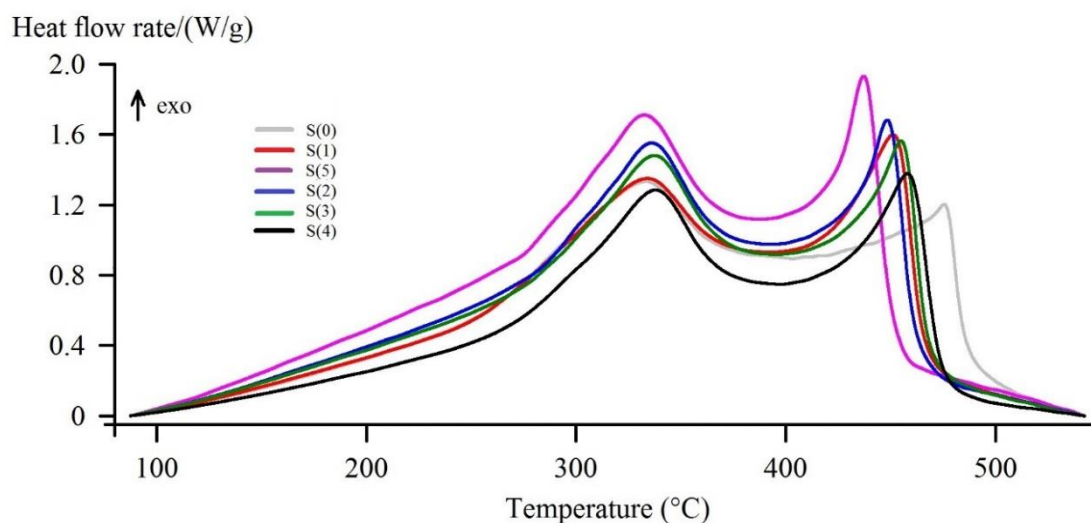
Figure 1. DSC curves for non-catalytic S (0) and catalytic heavy oil oxidation S (1-5).
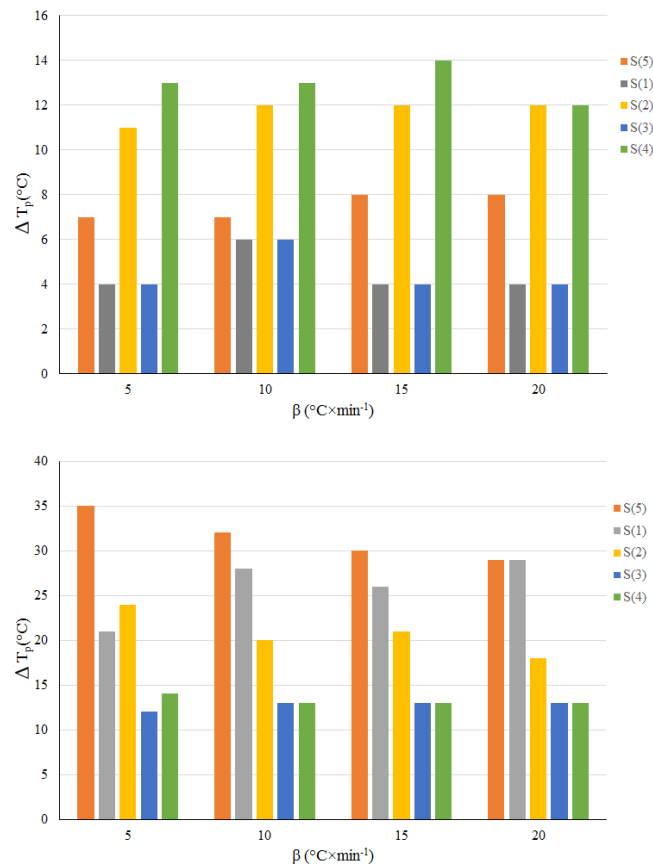
Figure 2. Differences between peak temperatures (ΔT_p) of non-catalytic s(0) and catalytic heavy oil oxidation S(1-5) in porous media for low (top) and high (bottom) temperature oxidations at different heating rates.

The correlation between figure1 and figure 2 is noteworthy because it demonstrates the efficiency resulted from applying Cu-Mn tallates in the process of heavy oil oxidation at different Cu tallates-Mn tallates ratios. As can be seen from this correlation, HTO peak has shifted significantly comparing to LTO peak shifting in the catalytic oxidation respectively especially in the case of S(1) and S(5) which were higher than the other catalysts S(2), S(3) and S(4). Further calculations have been performed on activation energy and pre-exponential factors of catalytic and non-catalytic oxidation in both LTO and HTO regions to confirm our observations.

It is common knowledge that the multiphasic nature of heavy oil oxidation process and its complexity make its kinetic study quite difficult comparing to traditional kinetics in homogeneous mediums. Therefore, several studies, for example [19] have been suggested that oil combustion rate is dependent on two essential parameters: conversion degree α which can be obtained from DSC data and oxygen partial pressure (Equation 1).

$$\frac{d\alpha}{dt} = k(T)P_{O_2}^a(1-\alpha)^b \quad (1)$$

Where *k(T)* is the rate constant which can be expressed by Arrhenius law (Equation 2):

$$k(T) = Ae^{-E/RT} \quad (2)$$

P_{O_2} is the oxygen partial pressure

$(1-\alpha)^b$ is the reaction model function

In order to simplify equation (1), we can consider the oxygen partial pressure constant during experiments because of the small sample size (less than 1 mg in each run), the high flow rate (50 ml/min) and the large furnace volume (approx. 250 ml). Beside this, many studies [20,21] have demonstrated the first order *(b=1)* in the model function $f(\alpha) = (1-\alpha)^b$. Thus, equation 1 becomes:

$$\frac{d\alpha}{dt} = k_{eff}(1-\alpha) \qquad (3), \text{ where } k_{eff} = kP_{O_2}$$

In our research we made call to Kissinger's method [22]. This method was chosen rather than other methods because it is one of the most rapid ways to estimate the kinetic behavior of oil oxidation process. In addition, it is independent on baseline choice and peak profile influence, simply because it connects kinetic parameters to peaks temperatures. Its logarithmic form is presented by equation 4 as follows:

$$ln(\frac{\beta}{T_p^2}) = -\frac{E}{R} \times \frac{1}{T_p} + ln(Af'(\alpha)) \ (4)$$

It is consistent with the chosen kinetic model (Equation 3) since it assumes first-order dependency of reaction rate on (1-α).

Figure 3 indicates the related Kissinger's plots and table 1 presents kinetic parameters for non-catalytic S(0) and catalytic heavy oil oxidation S(1-5). The interpretation of obtained results suggests the evident effect performed by the presence of Cu-Mn talltes on oxidation kinetic behavior where we almost note a significant decrease in energy of activation of both processes in the presence of catalyst comparing to energies of activation in its absence. However, in the presence of S(1) activation energy oppositely increases. On the other hand, the pre-exponential factor in both regions changed differently depending on the ratio of copper tallates to manganese tallates in the catalyst comparing to its absence where it increased in the presence of S(1) and S(4) while in the presence of S(2), S(3) and S(5) it decreases in both regions.
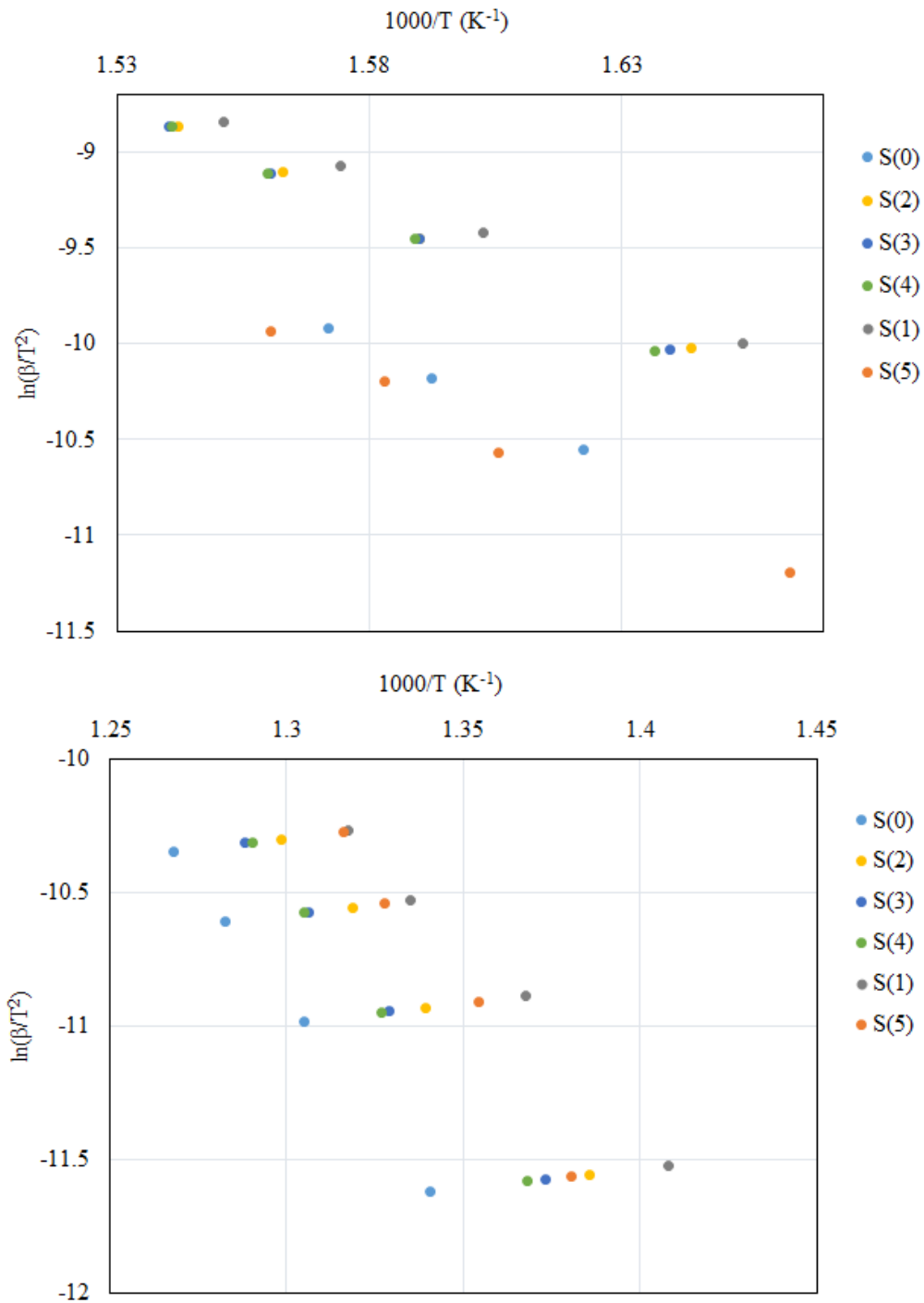
Figure 3. Kissinger's plots for catalytic and non-catalytic high temperature oxidation (top is for LTO, bottom is for HTO).

Table1. Kinetic parameters of the oxidation processes.

Kinetic parameters	Sample	LTO	HTO
E_a, kJ/mol	S(0)	104.6±1.6	145.8±8.5
	S(1)	103.4±1.3	163.3±8.1
	S(2)	95.17±2.4	120.6±7.4
	S(3)	97.48±1.4	123.57±5.3
	S(4)	101.4±2.6	135.1±6.6
	S(5)	94.3±2.7	112.4±4.8
$\log_{10}A$, A in min^{-1}	S(0)	9.4	11.8
	S(1)	9.8	15.1
	S(2)	8.7	8.5
	S(3)	9.1	8.8
	S(4)	9.9	10.6
	S(5)	8.7	7.5

Despite the fact that energy of activation decrease is a strong indicator of catalyst effect, we decided to calculate reaction effective rate constant in all cases (from S(0) to S(5)) to remove any doubt related to pre-exponential decrease in some catalytic oxidation processes.

Figure 4 presents the variation of effective rate constants with temperature for catalytic S(1-5) and non-catalytic S(0) oxidation (top is for LTO, bottom is for HTO) in the presence of copper and manganese tallates in different ratios.
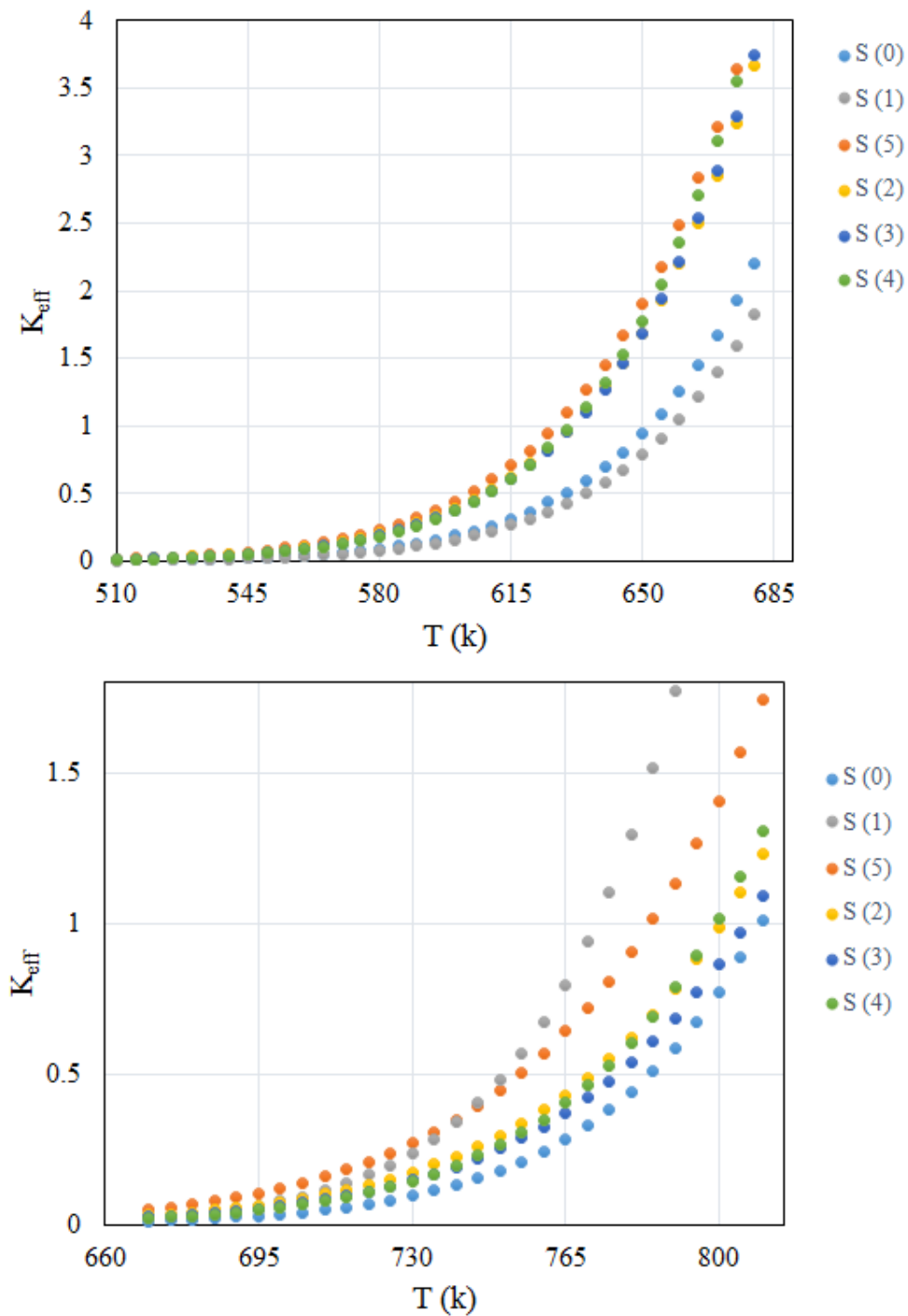
Figure 4. Variation of effective rate constants with temperature for catalytic and non-catalytic oxidation (top is for LTO, bottom is for HTO).

As expected, especially in HTO region, the effective rate constant was higher in the catalytic oxidation (S(1)≥ S(1)≥ S(5)≥ S(4)≥ S(2)≥ S(3)) comparing to non-catalytic oxidation S(0)

which indicates the stabilization of combustion front in the presence of Cu-Mn tallates rather than in their absence.

4. Conclusions

To sum up our work has led us to propose a new effective, less costly and eco-friendly catalyst to enhance heavy oil oxidation process. The evidence from this study points towards the idea of using catalysts based on tallates because they provide a high solubility in oil with less cost, which can be a powerful solution for catalyst injection problem into reservoirs during field-testing. We have obtained comprehensive results proving the potential effect of Cu-Mn tallates by applying thermal analysis methods especially in the case of using manganese tallates or copper tallates separately. The current research has also revealed the negative effect on hight temperature oxidation reactions rate generated from using copper and manganese tallates together. However, the present study has only compared the effect of copper-manganese tallates on the process of heavy oil combustion using thermal analysis which takes into account the thermal aspect of the process. Consequently, further investigation in medium and larger scales should be performed to study other aspects related to its application in the field.

Acknowledgments

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