Enhancement of the efficiency of in situ combustion technique for heavy-oil recovery by application of nickel ions

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HIGHLIGHTS

- Nano nickel particles were tested as catalyst in high and low temperature oxidation.
- The effect of nickel ions on combustion increases by increasing temperature.
- A significant catalytic effect on low temperature reactions was observed.
- Findings are of significant importance for improvement of in situ combustion oil recovery.
- Low temperature oxidation increases oil viscosity. Nickel reduce this effect considerably.

ABSTRACT

Thermogravimetry coupled to Fourier Transform Infrared Spectroscopy (TGA–FTIR) was used to study the effect of nickel ions on heavy oil combustion. Mainly, the low temperature oxidation (LTO) process was studied by conducting isothermal α0 experiments at three different temperatures: 200, 250 and 300 °C. The kinetics of the reactions was analyzed using the TG results. Nickel ions decreased the activation energy of the process from 16.9 kJ/mol to 10.9 kJ/mol. The FTIR spectra of the evolved gases were helpful in understanding the effect of nickel ions on the quality of LTO products. TGA–FTIR analysis revealed a production of different oxygenated compounds, such as phenols, carboxylic acids, sulfones and side products such as sulfur dioxide, during LTO. According to this analysis, using nickel ions decreased the concentration of oxygenated compounds in the evolved gases, and increased the concentration of carbon dioxide and water. It also decreased the concentration of sulfur dioxide. This effect was more promising at higher temperatures. This effect of nickel ions on LTO reactions can be of great interest in improving the efficiency of the in situ combustion technique used for heavy-oil recovery.

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1. Introduction

Heating is essential in in situ production of heavy-oil or bitumen. Steam-based thermal recovery techniques, such as steam assisted gravity drainage (SAGD), cyclic steam stimulation (CSS) and their modifications, are the most common ones. Despite its technical success, it is an energy intensive process due to the cost of steam generation. The in situ combustion technique is an alternative to heat generation at surface. This method is economically more viable compared to steam based techniques but it has its own technical challenges.

The main mechanism of the in situ combustion technique is the generation of heat via exothermic oxidation reactions which produce coke as the combustion fuel. Therefore, efficient oxidation of the oil is required for successful combustion. Since there are different zones in the reservoir with different temperatures, different types of oxidation are expected. Dabbous and Fulton [1] classified the hydrocarbon oxidation reactions as: (1) high temperature oxidation (HTO) which occurs at temperatures above 300 °C and (2) low temperature oxidation (LTO) which corresponds to temperatures lower than 300 °C. HTO reactions mostly consist of carbon–hydrogen bond breakage and the production of water and carbon dioxide [2]. These exothermic reactions provide the energy required for continuous combustion. These reactions result in the partial upgrading of oil. On the other hand, LTO reactions produce oxygenated hydrocarbons such as carboxylic acids and sulfones [3]. Therefore, they adversely increase the viscosity of oil which can affect the displacement efficiency and recovery factor.

The catalytic effect of transition metal compounds on steam stimulation and in situ combustion processes have been investigated by several authors. In the case of steam stimulation, it is...
shown experimentally that metal species catalyze the breakage of carbon–sulfur bonds existing in the organosulfur compounds. In other words, metal species catalyze the hydrodesulfurization and aquathermolysis reactions [4–7], which increase the upgrading effect of the steam-based techniques. He et al. [2] studied the catalytic effect of metallic salt additives on the efficiency of in situ combustion at the temperature range of HTO reactions. They observed that metallic salt additives (Fe3+) enhanced fuel deposition, reduced the activation energy and produced more complete combustion. However, the exact mechanism of the catalytic reactions is still unknown. Also, the effect of metallic additives on LTO reactions was not studied. Later, Ramirez-Garnica et al. [8] investigated the effect of a nickel ionic solution on the recovery factor of the in situ recovery technique through combustion tube experiments. Again, the experiments were run at the temperature range of the HTO reactions. Ramirez-Garnica et al. observed that the nickel catalyst improved oil upgrading during in situ combustion and increased the recovery factor [8]. The catalytic effect of metal species on heavy oil upgrading was also studied by other researchers in different processes [9–12].

In this paper, the effect of a nickel ionic solution on the LTO reactions is studied using the TGA–FTIR system. LTO reactions can create low mobility zones which reduce the displacement efficiency and recovery. It was observed that metal species catalyze HTO reactions [2,8,13], but their effect on LTO reactions is unknown. The production of oxidized compounds in heavy oil can drastically influence the oil viscosity and reduce the process efficiency. Metals may also coordinate to some basic asphaltene molecules and produce more complex structures, which adversely affect the oil viscosity. Therefore, the effect of metal species on oil properties at a low temperature needs to be investigated. Metals accelerate the HTO reactions by destroying the antioxidants which exist in oil [14,15] and we expect the same kind of catalytic reactions to occur in the temperature range of LTO reactions.

Thermogravimetric analysis (TGA) is a useful tool to study the kinetics of in situ combustion. The TGA was applied to study the kinetics of HTO reactions earlier [13,16,17]. Kok and Bagci [13] used simultaneous TG–DTA and reaction cell experiments to study the combustion of light crude oil in the presence of metallic additives. They observed that magnesium chloride and copper chloride lowered the reaction interval and peak temperature of the HTO reactions. The additives also decreased the activation energy of the crude oil. Ambalae et al. [17] applied TG experiments to study the pyrolysis and combustion behavior of heavy oil and its asphaltenes. Kok [16] investigated the effect of reservoir rock composition on combustion kinetics using TG/DTA. From the TGA data, they calculated the activation energy of the LTO and HTO reactions. In the case of a limestone matrix, the activation energy of LTO (between 10–20 kJ mol−1) reactions was about ten times smaller than the activation energy of HTO reactions (between 90–120 kJ mol−1). In the case of the sandstone matrix, the activation energy of HTO reactions decreased to values between 50–70 kJ mol−1 while the activation energy of LTO reactions did not change significantly [16]. These observations confirm the importance of the catalyst type on combustion kinetics.

In the present paper, a simultaneous TGA–FTIR (Fourier Transform Infrared Spectroscopy) system was used to study the kinetics of heavy oil combustion at low temperatures (LTO region), as well as the effect of a nickel ionic solution on this process. FTIR was used to analyze the evolved gases. The amount and type of the evolved gases detected by the FTIR system are the important parameters, which were used as the analysis parameters for studying the mechanisms of the catalytic reactions.

2. Experimental

The equipment utilized for this study consisted of a Cahn TGA interface to a Nicolet 6700 Fourier Transform Infrared Spectrometer (Thermo Scientific). The evolved gases from thermogravimetric measurements were transported by a vacuum pump at constant flow rate, to a gas cell installed in the FTIR spectrometer through a transfer line. The transfer line was kept at 200 °C using a heating tape to prevent condensation of the released gases. The results obtained from the TGA–FTIR are presented as follows: (1) a Gram–Schmidt plot, which shows related information with the total IR absorbance of the evolved components in the whole spectral range; (2) a three-dimensional spectra (as a stack plot) of the evolved gases; and (3) the IR spectra obtained at the maximum evolution rate for each decomposition stage.

Heavy oil with 14.7°API was used in all of the experiments. The physical and chemical properties of the oil sample are presented in Table 1. 0.1 M of nickel chloride solution was prepared and mixed with heavy oil with a 50–50 wt.% ratio. The suspension was mixed for 15 min at 6000 rpm using a Polytron PT6100 mixer. Around 20 mg of sample was put into a TG pan. The experiment started by heating the system at a 50 °C/min heating rate to reach the desired isothermal temperature. Then, the temperature was kept constant for a specific period of time. Air was used as the purge gas. Its flow rate was 40 cc/min in all of the experiments. The experiments were run at three different temperatures: 200, 250 and 300 °C.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Properties of the oil sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gr/cc)</td>
<td>Viscosity, cp</td>
</tr>
<tr>
<td>0.965 (gr/cc)</td>
<td>8500 cp</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Kinetic analysis

Fig. 1 shows the results of the TG experiments at 200 °C. The effect of water evaporation is seen as a sharp mass loss at the beginning of the test. Although the utmost effort was made to prepare the emulsion samples with an equal water fraction, according to the TG results, the percentages of water in the emulsions with and without additives are slightly different, as can be seen from Fig. 1. This can be seen by looking at the rapid slope change of the TG plots. To study the oil combustion, the water effect has to be removed from the TG plots. Boiling points of heavy oil components being higher than water, the rapid change of TG plot at earlier time zone belongs to the evaporation of water. Therefore, the extent of mass loss at the time of slope change corresponds to the water percentage in the initial emulsion samples. The TG plot part before this slope change is cut to remove the water effect, and the remaining section is normalized to the oil fraction. Another correction is made to consider the effect of the weight of the additives (1.3 wt.%) in the experiments conducted on the samples with nickel ions. Since the mass of nickel chloride in the pan remained constant during the test, this value was subtracted from the TG data. After these corrections, Figs. 2–4 were obtained. Comparing these three figures, we realize that the effect of metal additives becomes significant at higher temperatures. At 200 °C, no significant change on the TG plots is seen. However, there are considerable changes observed at 250 °C and 300 °C.

Figs. 2–4 demonstrate that the effect of nickel ions is to increase the amount of oil mass loss during LTO combustion. This effect is more significant at higher temperatures. At 300 °C, an increase in mass loss of about 10% can be seen. However at 200 °C, this effect is not observed. Therefore, the catalytic activity of nickel ions increases by increasing the temperature.

Increasing the mass loss during combustion is indicative of increasing the amount of light components production during the reactions. To understand this effect, the FTIR results have to be analyzed. However, more information can be obtained from TGA results about the kinetics of combustion and the effect of catalysts on kinetic parameters of LTO reactions. The kinetics of high temperature oxidation of oil were studied earlier using TG results [16,17]. According to Vyazovkin et al. [18], the rate of reaction can be calculated using the following equation:

$$\frac{dx}{dt} = -k(T)f(x)h(P)$$

In this equation, $k$ is the reaction rate, $h(P)$ is the pressure function and $f(x)$ is a function of the component fraction, $x$. The $h(P)$ is neglected in this work, because the experiments were conducted at constant atmospheric pressure. Based on the definition provided...
by Vyazovkin et al. [18] for the reaction models, the TG profiles (Figs. 2–4) show that the combustion reactions are of the decelerating type. Therefore, the reaction-order model can be applied to model the reaction [18] as follows:

\[ f(x) = x^n \]  

(2)

In this equation, \( n \) is the reaction order. The combustion reactions were assumed to be first-order. Validity of this assumption is investigated in the next section. The Arrhenius model was applied to model the TG results in order to determine the kinetic parameters. The Arrhenius equation describes the temperature dependence of the reaction rate as follows:

\[ k(T) = A \exp \left( -\frac{E}{RT} \right) \]  

(3)

where \( A \) is the exponential factor and \( E \) is the activation energy. With the assumption of the first-order reaction, Eq. (1) becomes:

\[ \frac{dx}{dt} = -k(T) \cdot x \]  

(4)

By integrating from Eq. (4), the following equation is obtained:

\[ \ln \left( \frac{x}{x_0} \right) = -k(T) \cdot (t - t_0) \]  

(5)

Therefore, a linear regression of the above equation can be used to obtain the reaction rate at a specific temperature. The TG data pointing to the time where the major mass loss happens were used for this analysis (e.g., data points to \( t = 1000 \) min for the experiments conducted at 300 °C according to Fig. 4). Table 2 reports the reaction rate values calculated at each temperature with the corresponding regression coefficient. The kinetic parameters can be calculated using the Arrhenius plot. This process is shown in Figs. 5 and 6. Based on these plots, the activation energy of the original oil sample was 16.9 kJ/mol; however, the activation energy of the reaction was reduced to 10.9 kJ/mol when nickel ions were used. The calculated activation energies and pre-exponential factors are tabulated in Table 2 along with the regression coefficient of the corresponding Arrhenius plot. The values of the regression coefficient indicate that Arrhenius equation provides a good description of the kinetics of the LTO in the experimental sample. About 35% reduction in activation energy confirms the catalytic effect of nickel chloride additive on LTO reactions.

The reactions were assumed to be of first order for performed kinetic calculations. Thus, an analysis of the reaction order is required to verify the kinetic calculations. If the reaction is of order \( n \), then by introduction of the reaction-order model (Eq. (2)) into Eq. (1), we obtain:

\[ \frac{dx}{dt} = -k(T) \cdot x^n \]  

(6)

Integration from both sides of Eq. (6) results in the following equation:

\[ \frac{1}{(n - 1)k_n x_0^{n-1}} \left[ \left( \frac{x}{x_0} \right)^{1-n} - 1 \right] = t \text{ for } n \neq 1 \]  

(7)
In Eq. (7), \( k_n \) is the reaction rate constant, \( a_0 \) is the initial concentration of the component (oil phase fraction here) and \( t \) is time. The oil phase is considered to be the only component. The calculated values of the reaction rates at different temperatures and the concentration changes at a specific time interval, from the TG results, were used to analyze the effect of the reaction order. According to Eq. (6), the plot of \( [(a/a_0)^{1-n} - 1] \) versus the time at different values of the reaction order (except \( n = 1 \)) should be linear. For \( n = 1 \), Eq. (5) was applied. Fig. 7 shows this curve fitting process for the experiment conducted on a sample with additives at 300 °C. Different reaction orders, in the range 0.3–2, were assumed. According to Fig. 7, although the regression coefficients \( R^2 \) corresponding to reaction orders \( n = 0.3, 0.6, 0.7 \) and 0.8 are very close to one, the value of the regression coefficient at \( n = 1 \) is the closest to one. Similar plots are obtained for other experiments with the result of the best regression coefficient for \( n = 1 \). These graphs confirm that the assumption of the first order reaction is valid. According to Fig. 7, any deviation of the reaction order from one results in decreasing the regression coefficient. (See Table 3).

3.2 TGA–FTIR analysis

The sample was scanned 12 times by the FTIR with the sampling interval of 12 s. The resolution is 4. 12 background scans were performed before the test. The results of TGA–FTIR are presented in three forms: (1) Total absorption (Gram-Schmidt) plot, which is used to detect the time at which the maximum amount of gas evolution/discharge occurs, (2) Three-dimensional (3-D) FTIR result, which shows the absorbance of the IR frequencies in the range of 500–4000 cm\(^{-1}\), and (3) absorbance spectrum at the time of maximum discharge. Interpretation of infrared spectroscopy is based on the detection of functional groups in the spectrum. Every chemical bond is absorbed at a certain wavelength which is characteristic of that bond. The magnitude of this wavelength depends on the strength of the chemical bond.

Fig. 8 demonstrates the Gram-Schmidt plots of the experiments conducted at 200 °C. According to this graph, there are three maximum discharge times (20, 52 and 113 min) observed in the experiment without nickel ion additives. However, a monotonic increase in the intensity is observed when additives are used. Figs. 9 and 10 present the 3-D FTIR spectra plots of the gases evolved during the experiments. Fig. 11 shows the IR spectra detected at the times of maximum discharge in the experiment without additives. For qualitative analysis of the effect of nickel ions on the combustion process, the FTIR spectra obtained at the first maximum discharge time, for both experiments, is presented in Fig. 12.

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Reaction rate ( \times 10^{-4} \text{ (s}^{-1}) )</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion without additives</td>
<td>200</td>
<td>1.92</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>2.50</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.11</td>
<td>0.992</td>
</tr>
<tr>
<td>Emulsion with additives</td>
<td>200</td>
<td>2.29</td>
<td>0.988</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>2.87</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>3.73</td>
<td>0.981</td>
</tr>
</tbody>
</table>

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During low temperature oxidation, a very small amount of carbon monoxide and carbon dioxide is produced since most of the available oxygen is consumed to produce oxygenated compounds such as carboxylic acids, ketones and phenols. These compounds are detected on FTIR spectra plots. Looking at the FTIR spectra at time $t = 20$ min in Fig. 11, a broad range of spectrums is observed at the wavenumber interval 3400–4000 cm$^{-1}$. These spectrums correspond to O–H stretching vibrations. They can be indicative of water, phenols or both compounds. Looking at the fingerprint spectrum region, the bending vibrations of the hydroxyl group corresponding to both water (1518 and 1701 cm$^{-1}$) and phenols (650–770 cm$^{-1}$ and 1330–1430 cm$^{-1}$ range) are observed, meaning that there is the presence of both compounds at the evolved gas mixture at early times. The intensity of these bands decreased at $t = 52$ min and almost vanished at $t = 113$ min. At later times, all the water content of the emulsion was most likely evaporated and the detected water must be the product of oxygenation reactions. Asymmetrical stretching and bending vibrations of CO$_2$ occur at 2360 cm$^{-1}$ and 670 cm$^{-1}$, respectively [19]. These spectra are observed in the FTIR results (Fig. 11). Some fraction of carbon dioxide gas is produced during oxidation of aromatic hydrocarbons to produce phenols, according to the following equation, as proposed by Kaeding [20]:

$$C_6H_5CH_3 + 2O_2 \rightarrow C_6H_5OH + CO_2 + H_2O$$ (8)

The other source of carbon dioxide is related to the production of carboxylic acids. According to Fig. 11, a small amount of carboxylic acids was detected at times $t = 20$ and $t = 52$ min (2900 cm$^{-1}$), which was confirmed by the presence of a carbonyl band at around 1700 cm$^{-1}$. The reason for the low concentration of carboxylic acids is that most of the produced carboxylic acids were involved in decarboxylation reactions to produce carbon dioxide. Therefore, a great amount of carbon dioxide is detected by FTIR.

### Table 3
Calculated kinetic parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy (kJ/mol)</th>
<th>Pre-exponential factor (1/min)</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion without additives</td>
<td>16.94</td>
<td>0.816</td>
<td>0.95</td>
</tr>
<tr>
<td>Emulsion with additives</td>
<td>10.94</td>
<td>0.219</td>
<td>0.99</td>
</tr>
</tbody>
</table>

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Fig. 8. Gram Schmidt plots of tests conducted at 200 °C.

Fig. 9. Three dimensional FTIR spectra plot of the gases evolved from the sample without additives, $T = 200$ °C wavenumber (cm$^{-1}$).
Table 1 indicates that the oil sample contains about 4% sulfur. The dissociation energy of the carbon–sulfur bond is the lowest amongst the existing chemical bonds in heavy oil. Therefore, they are the first bonds to break, producing hydrogen sulfide. However, the hydrogen-sulfide spectrum is not detected by IR. Thus, as stated by [3], the organosulfur compounds must have been oxygenated into sulfones. The produced sulfones can be converted to hydrocarbons and sulfur dioxide through an endothermic reaction.

Fig. 10. Three dimensional FTIR spectra plot of the gases evolved from the sample with additives, T = 200 °C.

Fig. 11. FTIR spectra of the sample without additives at the maximum discharge times at 200 °C.

Fig. 12. FTIR spectra of the gases evolved at time t = 20 min, T = 200 °C.
The following reactions, proposed by [3] describe the mentioned mechanism:

\[ R - S - R + O_2 \rightarrow R - SO_2 - R \]  
\[ R - SO_2 - R \rightarrow R - R + SO_2 \]  

The existence of sulfur dioxide in the products is confirmed by detection of the corresponding spectrum in the FTIR result. The asymmetric stretch, symmetrical stretch and bending vibrations of sulfur dioxide occurred at 1360 cm\(^{-1}\), 1150 cm\(^{-1}\), and 540 cm\(^{-1}\), respectively [19]. These spectrums were observed at times \( t = 20 \) and \( t = 52 \) min and entirely vanished at \( t = 113 \) min (Fig. 11).

As mentioned, the concentration of carboxylic acids, which is high initially (Fig. 11) is decreased at \( t = 113 \) min. Also concentration of sulfur dioxide is high initially, but decreases at later time. Therefore, the first peak in Fig. 8 corresponds to water, phenols, carboxylic acids, sulfur dioxide and little amount of carbon dioxide. The later peaks, especially the one at \( t = 113 \) correspond mainly to carbon dioxide. This means that at later times, the reactions producing CO2 prevails the oxygenation reactions.

In presence of nickel ions, the reactions generating carbon dioxide are catalyzed. This catalysis results in conversion of most of the hydrocarbons to carbon dioxide and water vapor without giving them the time to be oxidized. Therefore less amount of oxygenated hydrocarbons are generated. Comparison of the amount of gases released in two cases, with and without additives, is indicative of this mechanism. In presence of nickel ions, higher amount of gases are released, because there is fewer amounts of oxygenated compounds generated. The oxygenated compounds are complex molecules with high boiling point. Therefore in the experiment without additives, due to the oxygenation, less amount of gas is produced.

The effect of nickel ions on the evolved gas composition is presented in Fig. 12. Based on this result, nickel ions reduced the amount of evolved phenols, carboxylic acids and sulfur dioxide. In other words, nickel ions decreased the concentration of the products of oxygenation reactions. The other effect of nickel ions was to increase the concentration of carbon dioxide in the evolved gases, as can be seen in Fig. 12. Therefore, nickel ions acted as a catalyst for decarboxylation reactions.

Figs. 13–15 present the results of the experiments conducted at 250 °C. The Gram-Schmidt plot of the experiments conducted at 250 °C (Fig. 13) exhibits two and three maximum discharge times in the experiments with and without nickel ions, respectively. The earlier maximum discharge time, when additives are used, is due to the catalytic activity of nickel ions. According to Fig. 13, in the absence of catalysts, a delay of about 25 and 41 min are observed in the occurrence of the first and the second maximum discharge times, respectively. More proof for the catalytic activity of nickel ions can be seen from Figs. 14 and 15. A decrease in the concentration of phenols and carboxylic acids, as the main products of oxygenation, is observed in Fig. 14. Also, the concentration of sulfur dioxide declined. Furthermore, the concentration of carbon dioxide in the evolved gases increased. Fig. 15 shows very similar FTIR spectra at later times. At these times, carbon dioxide constitutes most of the evolved gases regardless of the application of nickel ions.

The results of the experiments conducted at 300 °C are illustrated in Figs. 16–18. According to the Gram-Schmidt plot (Fig. 16), two points of maximum gas discharge are observed when additives are used. However, the intensity of the discharged gases is monotonically increased in the absence of nickel ions. The absorption spectra of the experiment with nickel ions, at a very early time (Fig. 17), shows that more carbon dioxide evolved compared to the experiment on the sample without additives.

Another observation from Fig. 17, based on the spectra at a wavenumber range of 2800–3000 cm\(^{-1}\), is that almost the same level of carboxylic acids were generated in both experiments. Comparing Fig. 17 with Fig. 12, it can be seen that at 300 °C, a higher concentration of carboxylic acids was produced (look at the band around 2900 cm\(^{-1}\)). This is in contrast with the fact that by increasing the temperature, the intensity of the LTO reactions decreased. Therefore, we must doubt if the observed spectra at 2800–3000 cm\(^{-1}\) corresponds only to carboxylic acids. This range of spectra can also be representative of aliphatic compounds.

According to Figs. 17 and 18, there is a strong band around 1470 cm\(^{-1}\) which is indicative of methylene/methyl functional groups. Also, a weak methyl band around 1380 cm\(^{-1}\), and a weak band around 700 cm\(^{-1}\), which corresponds to methylene rocking vibration, are seen. Finally, the C–H stretching vibration is observed at 2800–3000 cm\(^{-1}\). From this information, it can be concluded that there are some linear aliphatic molecules in the evolved gases. The hydrocarbons with low boiling points must be evaporated at 300 °C. These hydrocarbons could be produced by the breakage of big molecules. At the later time of 44 min (Fig. 18), the concentration of hydrocarbons and carboxylic acids in the experiment with nickel ions was less compared to the other experiment. In addition, nickel ions caused an increase in the intensity of the carbon dioxide band and the band corresponding to the hydroxyl group. The hydroxyl group (3400–4000 cm\(^{-1}\)) must be representative of a water compound, since producing carbon dioxide is associated with water production.
According to the FTIR analysis, the following paragraphs summarize the main effects of nickel ions on LTO reactions.

1. Nickel ions reduce the concentration of carboxylic acids in the evolved gases at temperature range of the LTO reactions. Carboxylic acids can be generated by oxidation of aldehydes or benzylic hydrocarbons. These compounds are either present in the heavy oil sample or can be generated during the thermolysis of oil [21]. Nickel ions can produce very stable complexes with hydrocarbons [22]. Generation of these complexes will decrease the possibility of oxygenation of the hydrocarbons. However, some level of oxygenation of hydrocarbons will be inevitable, because not all the hydrocarbons will be protected by nickel ions.

Fig. 14. FTIR spectra of the gases evolved at the first maximum discharge times, $T = 250^\circ C$.

Fig. 15. FTIR spectra of the gases evolved at the second (and third for experiment without additives) maximum discharge times, $T = 250^\circ C$.

Fig. 16. Gram-Schmidt plots of tests conducted at 300 $^\circ C$. 
The generation of organic complexes with the catalyst can negatively affect the oil properties if the catalyst concentration is too high. Therefore, before any field application of the process, a careful study on the concentration of the catalysts should be performed. Since these kind of catalysts provide two opposite effects (the catalysis and generation of complex compounds), there must be an optimum concentration which would yield the maximum positive effect.

2. Nickel ions increase the concentration of carbon dioxide in the evolved gases. Carbon dioxide is generated either by combustion of the hydrocarbons or by decarboxylation of the generated carboxylic acids. It is been proved that hydrocarbon combustion reactions can be catalyzed by transition metals [23]. Catalysis effect of nickel ions causes the combustion of oil to happen at lower temperatures. Therefore, compared to the experiments conducted without the catalyst, during the experiments with catalysts more hydrocarbon molecules will be combusted (rather than being oxidized) and generate carbon dioxide and water. However, according to the FTIR spectra, even in presence of the catalyst, some traces of carboxylic acids are detectable. Some part of these carboxylic acids is converted to carbon dioxide and hydrocarbons. These decarboxylation reactions can also be catalyzed by transition metals [24].

3. The concentration of sulfur dioxide in the evolved gas mixture is decreased by nickel ions. As mentioned, the source of sulfur dioxide is by removal of sulfonyl group from the sulfone hydrocarbons generated by oxygenation of organosulfur compounds (Eq. (10)). The elimination of sulfonyl group from sulfones can also be catalyzed by nickel [25]. In presence of nickel ions, due to occurrence of combustion, oxygenation of organosulfur compounds is be reduced, and the generated sulfones are mostly converted to sulfur dioxide.

4. Conclusions

In this paper, the effect of nickel ions on low temperature oxidation (LTO) reactions was studied using TGA–FTIR. The kinetics of the process, as well as qualitative analysis of the evolved gases during the reactions was investigated. The followings are the main conclusions from this study:

1. The TG results showed that the effect of nickel ions on combustion increases by increasing temperature. This is in accordance with reports of other researchers at higher temperatures concerning the catalytic effect of metal species on the HTO process. However, a significant catalytic effect on LTO reactions was observed by studying the FTIR spectra of the evolved gases.
2. According to the kinetic analysis performed by using the TG results, nickel ions decreased the activation energy of the process. The activation energy of LTO reactions decreased from 16.9 kJ/mol to 10.9 kJ/mol.

3. Based on the obtained FTIR spectra, the amount of oxygenated compounds, such as phenols and carboxylic acids, is decreased by increasing the temperature.

4. At each temperature, nickel ions caused a significant decrease in the concentration of the oxygenated compounds and sulfur dioxide, and increased the concentration of carbon dioxide and water. Hence, nickel ions tend to shift the oxidation reactions from LTO to HTO. This effect is more promising at higher temperatures.

5. This finding can be of significant importance for improvement of in situ combustion. During this process, LTO reactions at low temperature regions tend to increase the oil viscosity. The application of metal species such as nickel ions would decrease this effect considerably.

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