Discussion of Thermal Experiments' Capability to Screen the Feasibility of Air Injection

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Abstract

Thermal experiments such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), accelerating rate calorimetry (ARC), and small batch reactor (SBR) are typically used to screen the feasibility of air injection in a reservoir. In this paper, the capability of these tools were studied. The screening criteria for air injection process (AIP) based on the thermal experiments were summarized. A practical workflow to use the thermal experiments to build a base simulation model for AIP it was proposed. In an AIP simulation model, there are about 12 variables to govern the process. Generally, researchers consider kinetic data as adjustable variables to match experimental or field data. How to properly adjust the kinetic data and understand the effect of the kinetic data on the production performance of a reservoir are not well established. In this paper, the reaction temperature ranges and the exothermic peak temperatures for the low temperature oxidation (LTO) stage and high temperature oxidation (HTO) stage were summarized from the experiments using 19 crude oils. The measured kinetic data of 22 different crude oils, and the kinetic data of 25 sets of crude oils with the presence of additives were also summarized. From these data, the ranges of activation energy and frequency factor were defined as the reference for future studies, if such data are readily available. A simulation study has been conducted to study the significance of the kinetic data on production performance. It is observed that the variation of the activation energy significantly influence the recovery performance while the variation of the frequency factor does not.

1. Introduction

AIP (air injection process) is one of EOR methods. For a heavy oil reservoir, the ISC (in-situ combustion) is usually considered, and for a light oil reservoir, the HPAI (high pressure air injection) is usually considered. The differences between conventional reservoir engineering and

combustion reservoir engineering has been discussed by Gutierrez et al. [1]. One reason for the differences is the complicated reaction mechanisms among crude oil, rock, and air.

Similar to other EOR techniques, feasibility tests including both numerical simulation studies and laboratory studies have to be considered before conducting a field test. In order to reliably predict the field performance through the numerical simulation, both a well understood kinetic model and a fluid model are required. A well-established kinetic model contains a series of relevant reactions of the oil, rock, and air, and this is also why the chemical reactions between air and oil-rock system are so important for an AIP project. In order to create a kinetic model for the AIP, the thermal-oxidative feature of the oil and rock system of a specific reservoir need to be understood. To do that, different experimental techniques have been utilized during the last few decades. There are two categories of experimental studies for the AIP: qualitative studies and quantitative studies. The quantitative study is known as the combustion tube test, which is not the focus of this paper. This study mainly talks about the role of the qualitative study, which is also called the “Screening” or “Fingerprinting” study. Thermal experiments such as TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), DTA (differential thermal analyzer), ARC (accelerating rate calorimetry), SBR (small batch reactor) etc., belong to qualitative studies.

The intention of these screening studies was to evaluate the potential of the reservoir for AIP implementation. However, it has been found that the established screening criteria may have to use the reservoir properties and production history to evaluate the reservoir [2, 3]. Questions such as “How do we use the thermal experiments to guide the selection of candidate reservoir for the AIP” and “What is the role of the thermal experiments in an AIP” are not well answered. Therefore, it is necessary to study the role of those screening techniques to guide the design of an AIP project.

This paper first reviews the attempts using screening tools for a feasibility study and summarize the screening criteria for the AIP based on the implementation of the thermal experiments. Then a practical workflow which uses the thermal experiments to build the base model for the further AIP simulation study was proposed. After that, the kinetic data of 22 crude oils and 25 crude oils with the presence of additives were summarized, and a general range of the kinetic data for researchers to tune their model or to set up their model were provided. Finally, a simulation

study was conducted, and the effect of the kinetic data on reservoir recovery performance is analyzed.

2. Overview of thermal experiments' functions

Over the last decades, thermal experiments have been applied to investigate the combustion reactions during the AIP. As mentioned previously, despite of the convention combustion tube tests, various thermal experiments were conducted to study the air injection process. This section briefly introduces the functions of the thermal experiments in the air injection study.

DTA and DSC are used to measure the thermal behavior of the crude oil through the experiment. During the experiment, the crude oil is heated at a constant heating rate with the presence of the continuous air flow. From the thermograms, information such as temperature intervals of different oxidation reaction stages and exothermic peaks are extracted and interpreted. Generally, there will be two exothermic peaks shown in the thermograms, which are signaled by the onset of LTO (low temperature oxidation) and HTO (high temperature oxidation), respectively. Identifying the exothermic peaks actually tells us at what temperature the oxidation reactions can be triggered, which helps determine the ignition condition. On the other hand, the relevant kinetic data such as frequency factor and activation energy can be obtained through analyzing the thermograms. TGA is used to measure the mass change of the crude oil through the experiment. Similar to the DTA and the DSC, during the TGA experiment, a sample is heated at a constant heating rate with the presence of the continuous air flow. In most of the cases, there will be two sudden mass losses of the crude oil present in the TGA thermograms. These losses indicate the LTO and the HTO. Between the LTO and HTO, there is a stage where the mass loss rate stays relatively unchanged, which indicates the FD (fuel deposition) stage. The relevant kinetic data such as activation energy and frequency factor can also be estimated through analyzing the thermograms of the TGA. ARC is used to detect the self-heat rate of the crude oil, and it can maintain nearly perfect adiabatic conditions through the test. During the test, once the self-heat rate is detected, the time, temperature, and pressure data are recorded. Then, the thermal data and kinetic data can be derived. The advantage of the ARC is that it can be applied at a very high pressure condition (till 6000 psi). A SBR has two sample holders, one is the reactor and the other is served as the reference cell. The reactor is subjected to a heating schedule while air is flown through. The heating is continued at the desired rate until the termination is reached and then

held at that temperature during the test of the test. During the test, the temperature profiles of both reactor and reference cell are measured. By comparing these two profiles, the temperature intervals of the exothermic and the endothermic process can be identified. Relevant kinetic data can also be estimated through analyzing SBR data.

3. Attempts to use thermal experiments in the feasibility study

Constant attempts were made by researchers to conduct an AIP feasibility study using thermal experiments. The objective of these attempts was to screen better reservoir candidates for field AIP implementation. The traditional experiment used for this purpose is known as the combustion tube test; however, this test cannot provide any kinetic data for the combustion reactions. Also, when compared to screening tools, the cost and time spent in conducting a combustion tube test is much higher. Tadema [4] first proposed that instead of using conventional combustion tube tests to evaluate the combustion reactions, we might use quicker and more cost-effective DTA and TGA (thermogravimetric analysis) tools. Later, Bae [5] used the DTA to study various crude oils, with gravity ranging from 6° to 38° API. The result shows that the API gravity of the oils have no obvious relation to their thermo-oxidative behaviors. Bae mentioned that when the pressure was at 1000 psig, the oil which could generate more heat in the LTO than the HTO stage from the DTA experiments could be considered as a good candidate for AIP. This is because when the crude oil shows highly reactive behavior in the LTO stage, more heat could be used to sustain the combustion front. Although he did not systematically discuss how to use the thermal experiments to screen the crude oils for AIP, he has mentioned about the screening function of the thermograms.

Attempts to use thermal experiments for AIP screening were made by Vossoughi et al. [6]. A kinetic model of the combustion reaction was built from TGA/DSC. They used TGA/DSC experiments to provide these parameters: minimum front temperature, minimum crude oil saturation, average H/C atomic ratio, minimum amount of fuel lay-down, minimum heat requirement, combustion zone thickness, average carbon combustion rate, combustion front velocity, average fuel heat value, heat available to sand, average combustion peak temperature which used to be provided by combustion tube tests. The estimated results have been compared with results from the combustion tube, and the results agreed except for those parameters associated with the heat of reaction. The heat value estimated from the TGA/DSC is significantly

lower than the value from the combustion tube test, and the reason is due to lack of the fluid flow and displacement behavior associated with DSC. This attempt also indicates that the combustion tube test cannot be replaced by those thermal experiments due to the lack of fluid flow and displacement behavior. After realizing the limitation of TGA/DSC, Kharrat et al. [7] built a new ISC feasibility study workflow by using the TGA/DSC. In this study, minimum crude oil content $W_{\min}$ is compared with the reservoir crude oil content W_R , and if $W_{\min}$ is higher than the W_R , then this reservoir is considered to be the candidate reservoir for ISC. The $W_{\min}$ is calculated by using the required minimum front temperature (which is obtained from the TGA) minus the room temperature, and the heat value of crude (which is obtained from the DSC). Corresponding combustion tube tests have also been conducted, which show consistent results with this predicted workflow. From this study, it is seen that the purpose of the TGA/DSC is actually to screen the prospective crude oil/cutting system for the combustion tube tests. In other words, this study transforms the role of TGA/DSC into screening tests which are conducted prior to the combustion tube tests. As mentioned before, the cost of a combustion tube test compared to a TGA/DSC test is enormous. In addition, the combustion tube cannot provide kinetic data. This workflow can serve as a precursory experimental work prior to combustion tube tests.

Another ISC feasibility study was proposed by Yannimaras et al. [8] which is similar to the feasibility study proposed by Kharrat et al. In their work, instead of using TGA/DSC, Yannimaras et al. used the ARC to conduct the feasibility test. They claimed it was inadequate to only be given a minimum oil content to screen the candidate crude oil for AIP, and stated that the ARC is a better technique for the screening process. They compared two ARC cases, the one which is classified as an unsuitable oil for ISC shows an exothermic temperature range ending at around 250 °C; the other, which is considered to be an ISC suited oil, presented continuous exothermic activity until 380 °C. This temperature is believed to be high enough to sustain the combustion front. After the ARC tests, they also conducted corresponding combustion tube tests to prove their prediction, and the results agree with their hypothesis. This study pointed out that besides only considering the minimum oil content, it is also important to analyze the continuous exothermic activity between ignition temperature and the combustion front temperature of the crude oil. However, this method is still a precursory screening step to the combustion tube test, instead of replacing it. Similar tests have been done by Fraim et al. [9]. Six ARC tests and five combustion tube tests were made in order to screen the air injection project in a waterflooded

North Sea oil reservoir. In their test, the role of ARC tests was also to determine whether the exothermic behavior is continuous or not. However, the difference between the study by Fraim et al. and that by Yannimaras et al. is that their expected exothermic temperature ranges were different. Instead of requiring the exothermic activity to continue from the reservoir temperature to 380 °C, they claimed the exothermic behavior should last to 500 °C. They stated that if the exothermic activity reaches 500 °C, the HTO mode will occur, which produces the highest carbon dioxide percentage. However, they did not discuss how to define the required exothermic temperature interval, and whether the maximum exothermic temperature should be used to sustain the combustion front or to trigger the HTO mode.

Sarma et al. [10] conducted both ARC and TGA/PDSC (pressurized DSC) experiments to rank three oils for combustion tube tests. Oils A, B, and C were analyzed through ARC and TGA/PDSC tests. In their study, the primary screening tool is ARC which provides information such as ignition temperature, exothermic temperature range, and activation energy. The TGA/PDSC were used as supplemental tools, which helps identify the reaction mechanism of crude oils. They recognized that the purpose of ARC and TGA/PDSC tests is to rank the crude oil for subsequent combustion tube tests rather than directly provide an answer to the feasibility test. Their method ranked the oil mainly based upon the results from ARC tests. Based on their results, the oil which has a lower activation energy is a better candidate for ISC; the oil which has a lower ignition temperature is more promising for ISC; the oil which has a longer and more stable exothermic activity zone is a better candidate for ISC; the oil which can quickly achieve the ignition temperature is a better candidate for ISC.

Other than what have been summarized above, many attempts have been made to study the feasibility of AIP by various thermal experiments other than combustion tube tests. However, most of these studies only qualitatively evaluated the possible potential of an oil and rock system for conducting an AIP. TGA and DSC have been employed by many researchers to identify the oxidation reaction scheme and examine the thermal-oxidative behavior of different crude oils and oil-rock mixture samples [11-19]. Although, these studies do not provide quantitative results, the information could still be interpreted in order to help predict the candidate oil samples for further combustion tube tests. Al-Saffar et al. [20] used a high pressure oxidation cell to study the oxidation behavior of a North Sea light oil. High oxygen utilization and corresponding flue

gas generation were observed at low temperature stages. This phenomenon has been viewed as a desirable characteristic for AIP, because a high level of flue production at low temperatures can increase oil displacement and has no negative effect on the oil properties. Hou et al. [21] used the SBR to study the oxidative feature of Xinjiang crude oils. The thermograms of the SBR show that the initial reaction rate at the reservoir temperature is relatively high, which indicates that thermal effects produced from the LTO stage can be more easily achieved in this reservoir. Juan et al. [22] used ARC and combustion tube tests to screen potential candidate reservoirs in two waterflooded light oil reservoirs. ARC tests were employed to provide kinetic data and detect the reactive and non-reactive temperature intervals. Abrupt temperature increases were detected around 230 °C – 240 °C for both oils, and this strong reaction in the low temperature range shows a favorable indication for subsequent combustion tube tests.

Based on the review above, the screening criteria can be built from the thermal experiments which is summarized below.

- 1) The minimum crude oil content $W_{\min}$ must be higher than the reservoir crude oil content W_R . [7]
- 2) The crude oil should exhibit a continuous exothermic activity between ignition temperature and the combustion front temperature. [8]
- 3) If the previous two criteria are satisfied, below are some methods to rank the oil.
 - The oil which has a lower activation energy is better for AIP; [10]
 - The oil which has a lower ignition temperature is more promising for AIP; [10]
 - The oil which has a longer and more stable exothermic activity zone is better for AIP; [10]
 - The oil which has a higher oxygen utilization and a stronger flue gas generation at the LTO is better for AIP; [20-22]

4. Role of the thermal experiments in the workflow for air injection modeling

It is acknowledged that a field scale simulation model can provide useful forecast to the field project. Although the field scale AIP simulation modeling has not been well established, the ultimate goal when building the AIP simulation model is to have a good predictability. A detailed work flow to build an AIP simulation model has been introduced by Gutierrez et al. [23].

In this paper, a practical workflow was proposed which focuses on the utilization of the thermal experiments in the air injection modeling. Similar to the previous section that the thermal experiment is served as the precursory experimental work prior to combustion tube tests. This workflow described how to use the thermal experiments to build a base simulation model before using the combustion tube tests to tune it. The workflow presented here is based on the method of Guitirrez et al. [23]. The workflow is an iterative process which generally starts with defining the pseudo components to represent the oil composition. It is important that the pseudo components should represent the oil in both physical and chemical aspects. The physical aspect includes the physical properties of the crude oil such as molecular weight, critical pressure, and critical temperature. The chemical aspect includes the thermo-oxidative behavior of the crude oil during an AIP. The thermo-oxidative behavior of crude oil is mainly controlled by the kinetic model which includes reaction scheme, enthalpy from the reactions, activation energy, and frequency factor etc.

After defined the pseudo components, build the fluid model and the kinetic model are the next step. Since most of the thermal experiments are lack of the fluid flow process. The fluid model can be simply built by applying the thermal simulators to estimate the phase behavior of the crude oil during the AIP process. For example, use the CMG-Winprop to calculate the K-Value tables to estimate the phase behavior of the crude oil during the simulation.

To build the kinetic model, it is necessary to first interpret the thermograms of the thermal experiments. Based on the interpretation of the thermograms, the dominant reaction in each specific temperature region can be defined. The reaction scheme can then be proposed based on the most relevant reaction mechanisms [1] and the pseudo components defined from the previous stage. In order to validate the kinetic model, the reaction scheme and other relevant kinetic data in the simulation model are adjusted within a reasonable range to match the thermo-oxidative behavior of the crude oil. The kinetic data estimated from the thermal experiments are matched with the kinetic data derived from the simulation model. If the match is not successful, the above processes to define pseudo components, to build fluid model and to define kinetic model need to be repeated. After the kinetic model and the fluid model been calibrated with the thermal experimental data, the base model is built and can be used in a further combustion tube tuning process.

Some of the practices which have used the thermal experiments to build the base simulation model are listed in this paragraph. Battarcharya et al. [24] developed the numerical model based on the ARC experiments. Khansari et al. [25] proposed the reaction scheme based on the analysis of the TGA experiments. Dechelette et al. [26] matched the ramped temperature experiments with CMG and proposed the improved reaction scheme.

In summary, the role of the thermal experiments in the air injection modeling is to build the base model for the further simulation study. Some of the examples are to determine the temperature ranges for LTO and HTO; to estimate the kinetic data from the thermal experiments and the sensitivity test of the experimental parameters are further reviewed in the next sections.

5. Define temperature regions for LTO and HTO by using thermal experiments

Generally, there are three reactions during the air injection process as: LTO, FD, and HTO. Based on the interpretation of the thermograms, temperature regions of each reaction stage can be determined. Since the kinetic data is estimated for different reaction stages, respectively. Defining the reaction temperature regions need to be done prior than estimation of the kinetic data. Also, based on the reaction temperature regions, researchers are able to predict what type of reactions could occur during the AIP and whether they are achievable. In this section, 19 crude oils' reaction temperature regions were summarized as shown in Fig. 1 [6, 10-12, 16, 17, 27-31]. It is observed that the API gravity of the oil does not show a direct relation to the reaction temperature regions. Based on the data in Fig. 1, the "average reaction temperature regions" for LTO and HTO were estimated as: 149 ~ 364 °C for the LTO and 415 ~ 542 °C for the HTO.

Thermal experiments as DTA, DSC and ARC can present the exothermic and endothermic behavior of the crude oil during the experiments. The sharpest and highest exothermic region in the exothermic region are named as exothermic peaks, which indicate the potential combustion of the crude oil. Generally, there are two exothermic peaks. One locates in the low temperature region which corresponds to the LTO. The other exothermic peak locates at the high temperature region which indicates corresponds to the HTO. The first peak was considered as liquid hydrocarbons combustion and the second peak was considered as coke combustion [27]. Generally, the second exothermic peak has a much stronger heat generation than the first peak, which is also the main source for the spontaneous ignition. Fig. 2 shows 12 crude oils'

exothermic peaks temperature in low temperature region and high temperature region, respectively [10-12, 16, 17, 27-30]. The exothermic peaks can help researchers to understand the spontaneous ignition potential of the crude oil. The lower temperature of the exothermic peak indicates it is easier to ignite the oil. Therefore, exothermic peaks can be considered as one aspect to screen the candidate oil for the AIP. Based on the data summarized in Fig. 2, the average combustion peak temperature are 320 °C in the LTO stage and 469 °C in the HTO stage.

Figure 1, LTO, FD and HTO temperature regions for 19 crude oils

Figure 2, LTO and HTO combustion peaks of 13 crude oils

6. Kinetic study of crude oil by using thermal experiments

As mentioned before, in order to build the numerical simulation model for the AIP, kinetic model which consists of the relevant kinetic data is required. Thermal experiments as TGA, DSC, ARC, and SBR are often utilized to establish kinetic data as E_a (activation energy), A_r (frequency factor) and order of the reaction for kinetic model. In most of the studies, the Arrhenius method is employed to derive the kinetic data. According to the Arrhenius model [32], the temperature-dependent rate constant $k(T)$ can be specified as:

$$k(T) = A_r \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where A_r is the frequency factor (s^{-1}), E_a is the activation energy ($KJ\ mol^{-1}$), T is the temperature (K), and R is the universal gas constant. After obtained the thermograms from the thermal experiments and defined the reaction temperature regions, kinetic data in each reaction stage can be estimated by analyzing the thermograms with different kinetic analysis methods.

Activation energy is the most frequently reported kinetic data which is often used for characterizing the reactivity of the crude oil, to qualitatively determine the conditions required to achieve ignition, and to determine if self-ignition will take place in the reservoir upon air injection. If the activation energy of a reaction scheme is lower, the reaction can be triggered more easily, or the reaction can be more readily sustained. In this paper, the kinetic data as activation energy in LTO and HTO are summarized separately, from 22 different crude oils, and with API gravity ranges from 11 to 44.3 [9, 14, 17, 20, 28, 30, 33, 35-43]. No relation between the API gravity and the activation energies were found based upon the data, which implies that the API gravity of the crude oil cannot be used as an all-descriptive measure of the thermal behavior of crude oil [5]. Fig. 3 shows the distribution of the kinetic data of these crude oils. It is observed that in the medium range, 20 ~ 80% of oils have activation energies in the LTO stage from 20 ~ 70 KJ/mol , and 50% of the oil has 33 KJ/mol E_a in the LTO stage. It is also observed that 20 ~ 80% of oils in the medium range have activation energies in the HTO stage from 70 ~ 180 KJ/mol , and 50% of the oil has 107 KJ/mol E_a in the HTO stage.

The frequency factor data from 11 different crude oils were also summarized as shown in Fig 4 [10, 17, 28, 30, 34, 39-41]. It is observed that the API gravity of the crude oil does not have a relation to the frequency factor values. Also, it is observed that the value of the frequency factor

in the LTO ($0.1 \sim 10^5 \text{ s}^{-1}$) are generally lower than the frequency factor in the HTO ($10^4 \sim 10^9 \text{ s}^{-1}$). The huge difference among the frequency factor values might be caused by the fact that A_r is obtained as the intercept on the log axis which is very sensitive to the slope selected by the researchers. In other words, a very small change in the slope could cause a large difference in A_r .

With the above E_a and A_r values, the rate constants can be calculated by using Equation 1. The rate constant curves in the LTO stage and the HTO stage for different crude oils are displaced in Fig 5 and Fig 6, respectively. The temperature ranges are selected as 25-350 °C for the LTO and 350-600 °C for the HTO [28]. Two "average reaction rate curves" were drawn in Fig 5 and Fig 6, which can be served as reference curves for researchers to compare their data. It is observed that the rate constant increases with temperature, and the value of the rate constant for different crude oils vary from $10^{-13} \sim 10^2 \text{ s}^{-1}$ in the LTO stage, and $10^{-9} \sim 10^2 \text{ s}^{-1}$ in the HTO stage. Fig 5 and Fig 6 again indicate that the value of the kinetic data has no direct relation to the API gravity of the crude oil.

Based on this section, a general range of kinetic data was provided for researchers to tune their model or as the starting point to set up their model. The activation energy in HTO (107 KJ/mol) should be higher than the activation energy in the LTO (33 KJ/mol). And a general range of activation energy is more likely to fall in 20 ~ 70 KJ/mol in the LTO and 70 ~ 180 KJ/mol in the HTO. The frequency factor range of the crude oil in LTO is 0.1 s^{-1} to 10^5 s^{-1} , and 10^4 s^{-1} to 10^9 s^{-1} in the HTO.

Since many variables in a numerical model need to be estimated from both thermal experiments and combustion tube experiments, most of the time, the E_a and the A_r values are adjusted [1]. More importantly, in a practical simulation model, researchers define a reaction scheme of several reactions for a single reaction state (e.g., HTO), then several sets of kinetic data are needed to define HTO reactions. Thus a single set of kinetic data for HTO may not serve the need in simulation, although thermal experiments are conducted to measure these data. This discussion reveals that the conventional analysis of thermal experimental data to obtain a single set of kinetic data based on Equation 1 may not be practically very useful. Khansari et al. [44] have provided a series of kinetic data based on the reaction products for the LTO stage, which makes the kinetic model more adequate for modeling the LTO process.

Figure 3, Activation energy (Ea) of 22 crude oil samples in LTO and HTO, respectively

Figure 4, Frequency factor (Ar) of 11 crude oil samples in LTO and HTO respectively

Figure 5, Reaction rate for different oils in LTO stage

Figure 6, Reaction rate for different oils in HTO stage

7. Sensitivity study on experimental parameters

The original objective of thermal studies was to develop an inexpensive and rapid screening test workflow to evaluate the feasibility of AIP. However, because the experiments are not able to simulate the combustion tube condition or a field combustion environment, most of the objectives of those "screening tests" became instead to test the sensitivity of the experimental parameters. The most commonly measured experimental parameters are pressure and the presence of additives. Additionally, the reservoir pressure condition and the rock type of the reservoir are the most relevant parameters to a field practice and a simulation test. Therefore, understanding the effect of pressure and the presence of additives on thermal behavior as well as the kinetic data can bring more effective conclusions for the operators.

7.1. Pressure effect

It is acknowledged that an increase of pressure results in an increase in reaction rate and heat released from reactions [5, 43]. Also, as the pressure increases, the oxidation reactions will shift to lower temperature ranges. This phenomenon occurs because decreasing of pressure will slow the oxidation reactions by decreasing the frequency factors [42, 45]. According to Bae et al. [5], as the pressure increased from 50 psig to 1000 psig, the peak exothermic temperature decreased from 315 °C to around 248 °C. Also, the research showed when the pressure is 1000 psig, LTO

could generate more heat than the HTO stage. Similar observations has also been described by Li et al. [43]. In their experiments, they also observed the increase of pressure can significantly enhance heat generation in the LTO stage for a light and a medium oil. The reason for this is believed to be that the increase of pressure extends the flammable limits for distilled hydrocarbon vapor. They also studied the pressure effect for the bitumen. For bitumen, the increase of pressure is more pronounced in its HTO stage. Therefore, it indicates that the pressure effect will be dependent upon the compositions of the crude oils. Both Bae et al. and Li et al. reported that a light crude oil presents a strong reactive behavior in the LTO stage once the pressure increases. The strong reactive behavior in LTO actually is an indication that more available heat could be used to sustain the combustion front if combustion is initiated. Thus, this behavior is a good sign for the HPAI process in a light oil reservoir.

Yoshiki et al. [42] stated variation of pressure will not affect activation energy data in LTO. A similar observation was also made by Kok [32]. He conducted a series of experiments and provided the pressure effect on kinetic data. The results show that as the pressure increased from 0.1 Mpa to 2 Mpa, the activation energy in the HTO generally decreased around 39% ~ 85%. However, the variations of activation energy in LTO are very small, which can be ignored when comparing the variations in the HTO stage.

To summarize, pressure does not show strong effects on activation energies in the LTO stage, but as the pressure increased, it significantly decreased the activation energies in the HTO stage to around 39% ~ 85%. Also, the increase of pressure can lead more heat generated in the LTO stage for a light oil, which is a promising sign for applying the HPAI in a light oil reservoir.

7.2. Presence of additives effect

Researchers have tested adding different additives into the oil to see their effects on the crude oil combustion process. Results indicate that additives such as pure quartz, sandstone, etc. only have a surface area effect on the combustion process. However, other additives such as clay minerals, metallic additives, etc. have been proven to have strong catalytic effect on the crude oil oxidation reactions. A typical examination method for the catalytic effect is to measure the activation energies with and without the presence of additives to the crude oil. If the activation energies

decrease with addition of additives, it means the additive has catalytic effect upon the crude oil combustion process.

Vossoughi et al. [46] presented that kaolinite has catalytic effect on crude oil combustion, but sand has no effect. A similar finding was obtained by Sarma et al. [10], who reported the presence of rock can significantly raise the self-heating rate and increase the exothermic termination temperature. The kinetic data estimated from the ARC shows the presence of cutting B and C won't decrease the activation energy. While with the presence of cutting A, the activation energy decreased around 48%, from 50 KJ/mol to 26 KJ/mol, which was due to the presence of clay content in cutting A. Huang et al. [18] compared the shale cuttings and sand cuttings effect on the oxidation reactions of the crude oil. The results show that after adding shale cuttings which contain clay minerals, the activation energies in the LTO stage decreased around 48%, from 16.96 KJ/mol to 8.82 KJ/mol, and decreased around 34%, from 145 KJ/mol to 93 KJ/mol in the HTO stage. However, the sand does not show significant effect on the crude oil combustion process. Similar findings have also obtained by Kok [47, 48]. He conducted a series of thermal experiments to investigate the effect of clay on crude oil combustion, and the results showed a uniform trend of decreasing activation energies with the addition of clay. In the HTO stage, activation energies generally decreased around 3% ~ 51%, from 98.6 KJ/mol ~ 101.8 KJ/mol to 48.5 KJ/mol ~ 97.7 KJ/mol. Jia et al. [49] studied the effect of cuttings on the crude oil combustion process, and the results indicate that after adding cuttings, the activation energies in LTO increased 12% ~ 45%, from 26.68 KJ/mol to 31.42 KJ/mol ~ 47.02 KJ/mol, and decreased 45% ~ 55%, from 153.05 KJ/mol to around 69.84 KJ/mol ~ 84.22 KJ/mol in the HTO region. The effects of different clays, including kaolinite, smectite, illite, and chlorite on the oxidation kinetics of the crude oil were also studied. The results show that after adding clay into the crude oil, the activation energies generally decrease around 37% ~ 86%, from 153 KJ/mol to 22.18 KJ/mol ~ 96.15 KJ/mol in the HTO stage, while the activation energies slightly increased or were unchanged in the LTO stage. Smectite was also observed to have the strongest catalytic effect on crude oil combustion among other clay minerals [15]. Pu et al. [50] studied the effect of metallic additives on kinetic data for combustion reactions. Their results indicate that CuCl_2 has an excellent catalytic effect on crude oil combustion. Activation energies in both the LTO and HTO regions have been reduced after adding metallic additives. Activation energies in the LTO

stage decreased around 9% ~ 30%, from 19 KJ/mol to 13.78 KJ/mol ~ 17.76 KJ/mol and around 9% ~ 65%, from 116.03 KJ/mol to 40.65 KJ/mol ~ 105.58 KJ/mol in the HTO stage.

To summarize, with the presence of sands or quartz, the activation energies stays almost unchanged or increases slightly. On the other hand, after adding additives such as clay minerals or metallic additives which have a catalytic effect on crude oil combustion reactions, the activation energies will generally decrease around 30%~70% in the HTO stage, while no obvious effects on the LTO stage were observed. Fig 7 below shows the activation energy distribution of crude oil with the presence of additives which includes 25 cases [6, 10, 15, 18, 33, 34, 35, 48-54]. It is observed that the activation energy in the HTO (73 KJ/mol) stage is higher than the LTO (26 KJ/mol) stage. A general range of activation energy for oil with presence of additives are 18 ~ 43 KJ/mol for the LTO stage and 60 ~ 100 KJ/mol for the HTO stage.

Figure 7, Activation energy of 25 crude oil samples with the presence of additives

8. Numerical simulation study

In this section, simulation approach is utilized to study the effects of the parameters from the screening experiments on thermal behavior and EOR performance.

8.1. Base reservoir simulation model

A base reservoir simulation model was built in CMG STARS based upon the Tingas's model which was described in his thesis [55]. The base model is justified by the fact that the model can predict a field oil recovery of 52.5% after 10 years of air injection. The field oil recovery was reported by Tingas in Table 5.6 of his thesis [55]. The grid size effect has been investigated through the simulation process, which does not show a strong effect on the recovery performance. The initial reservoir pressure is 6440 psia and the initial temperature is 99 °C. The initial oil and water saturations are 0.55 and 0.45, respectively. The total grid block size of the model is 2742 ft * 865 ft * 175 ft with a 3-D Cartesian grid of 22*9*5 with 990 active blocks in the model. The reservoir has a 15 degree dip angle, and the top depths of each grid column varies from 8620 ft to 8200 ft. Two horizontal wells are set in the reservoir. The injection well is located in the updip region of the reservoir, and the production well is located in the downdip region of the reservoir as shown in Fig 8. The injection rate for the injector is 4.8×10^6 ft³/day. The oil properties used in this model are from the North Sea light crude oil, which has 0.55 cP viscosity and 40.2°API gravity. There are 5 oil components which are C₂₁₊, C₁₁₋₂₀, C₆₋₁₀, C₂₋₅, CH₄, and six other components which are H₂O, CO₂, CO, N₂, O₂, Coke set in the model [55]. The components properties are shown in Table 1 below. The phase behavior of the pseudo components was estimated from CMG-Winprop by K-value tables. The reaction scheme is shown in Table 2, which contains three cracking reactions and seven combustion reactions.

Table 1, Component properties of the simulation model

Component	Reference Phase	Pcrit, psi	Tcrit, F	MW, lb/lbmol
WATER	Water Phase	0	0	0
C21+	Oleic Phase	171	1051.17	447.53
C11-20	Oleic Phase	266.56	837.64	218.38
C6-10	Oleic Phase	424.71	563.38	110.29
C2-5	Oleic Phase	579.02	249.13	72.15
CH4	Oleic Phase	667.2	-116.59	16.043
CO2	Oleic Phase	1069.87	87.89	44.01
N2	Oleic Phase	492.31	-232.51	28.013
O2	Gaseous Phase	731.86	-181.39	31.999
CO	Gaseous Phase	507.052	-220.45	28.01
COKE	Solid Phase			13.6

Figure 8. Reservoir simulation model

Table 2, Reaction scheme of the simulation study

Number	Reactions	Reaction Formula	Enthalpy, Btu/lbmol	Ea, KJ/mol	Ar, s-1
1	C21+ Cracking (with CH ₄ generation)	C21+ ==> 6.18 CH ₄ + 24.98 COKE	0	88	1.27E+05
2	C21+ Cracking (without CH ₄ generation)	C21+ ==> 3.47 C2-5 + 14.449 COKE	0	91	8.91E+04
3	C11-20 Cracking	C11-20 ==> 3.494 CH ₄ + 11.953 COKE	0	105	5.00E+04
4	C21+ Combustion	C21+ + 41.85 O ₂ ==> 39.287 WATER + 38.51 CO	10293.9	29	3.85E+10
5	C11-20 Combustion	C11-20 + 15.02 ==> 15.888 WATER + 14.829 CO	4920.3	33	3.85E+10
6	C6-10 Combustion	C6-10 + 7.39 O ₂ ==> 8.115 WATER + 7.152 CO	2420.2	33	3.85E+10
7	C2-5 Combustion	C2-5 + 3.734 O ₂ ==> 4.41 WATER + 4.015 CO	1463.4	33	3.85E+10
8	COKE Combustion	COKE + 1.4 O ₂ ==> 0.8 H ₂ O + CO ₂	461.3	13	3.00E+05
9	CH ₄ Combustion	CH ₄ + 1.5 O ₂ ==> 2 H ₂ O + 1 CO	1463.4	35	3.85E+10
10	CO Combustion	CO + 0.5 O ₂ ==> CO ₂	2.84E+05	8	1.91E+05

Fig 9 shows the recovery performance of the simulation model when displaced by air, CO₂ and N₂. It is observed that the recovery performance of air and CO₂ is much higher than the recovery efficiency of N₂. Air also shows a little higher recovery efficiency than CO₂. This little better

performance may be caused by the “bulldozing effect” of air injection process. This “bulldozing” effect has been discussed by Gutierrez et al. [1]. The bulldozing effect refers to that mechanism that a combustion front acts as a bulldozer to mobilize most of the oil immediately ahead of it, and the air fingering is reduced by the oil ahead of it. The oil could not be displaced earlier by other driving mechanisms like flue gas sweeping hot water or steam displacement. The track of the combustion front in one layer of grids from the injection well to the production well during the air injection process is shown in Fig 10. The combustion front was identified as the temperature peak which was initiated and sustained at around 193 °C. The combustion front temperature is lower than that generally sustained in a heavy oil reservoir, and this behavior is caused by the different oxidation reaction mechanisms between light oil and heavy oil to the air injection. Figure 11 shows the oil saturation profile of the same layer of grids shown in Fig 10. It is observed that after initiating the combustion front, the oil saturation suddenly decreased, and the oil inside the grid block was totally displaced afterwards.

Figure 9, Recovery performance by using air shown as base case, CO₂ and N₂

Figure 10. Combustion Front from injector to producer

Figure 11. Oil saturation from injector to producer

8.2. Sensitivity study of kinetic data on recovery performance

The focus of this simulation work is to investigate the effect of kinetic data on the air injection process. By using the activation energy and frequency factor values collected from the review section, several cases were run with different activation energy and frequency factor to observe the recovery performance and the reaction difference during the air injection process. Based on the reaction scheme shown in Table 2, reaction 1, 2, 3 are grouped into cracking reaction group and reaction 4, 5, 6, 7 are grouped into combustion reaction group. In order to investigate the effect of the crude oil's kinetic data on the production performance in the combustion reactions, only combustion reaction group is tested by changing their kinetic data. The kinetic data values for these reactions are assumed to be the same. These reactions are for pseudo components and have uncertainties. The other reactions are kept unchanged. Also, in order to investigate the effect of the crude oil's kinetic data on the production performance in the cracking reactions, only cracking reaction group is tested and the kinetic data in this group of reactions are assumed to be the same. For the cracking reaction group, the activation energy was tested from 70 KJ/mol to 130 KJ/mol and the frequency factor was tested from 10^1 s^{-1} to 10^9 s^{-1} . For combustion reaction group, the test range of the activation energy is set from 35 KJ/mol to 130 KJ/mol and 10^1 s^{-1} to 10^9 s^{-1} of the frequency factor.

Fig 12 shows the temperature profile of the observation grid block and the recovery performance of the air injection process under different frequency factor values. It is observed that different frequency factor values did not show a significant effect on neither recovery performance nor the ignition behavior of the air injection process.

Figure 12, Temperature profile of the observation grid block and the recovery performance of the air injection process under different frequency factor values

Table 3 displaces the effect of activation energy on the recovery performance of the reservoir. It is observed that the variation of the activation energy values in both combustion reactions and cracking reactions are sensitive to the recovery performance, and the effects of the variation of the activation energy on the low temperature reactions and the high temperature reactions on the recovery performance are the same. As shown in Table 3 that the recovery factors increase with the decrease of the activation energy in the combustion reaction tests. By changing the activation energy from 130 KJ/mol to 50 KJ/mol, the recovery factor increased around 10 %. The temperature profile of an observation grid block under different activation energy values is displaced in Fig 13. This grid block is located around the middle of the injection well and the production well. It is observed in Fig 13, that a higher activation energy of the combustion reaction will delay the initiation of the spontaneous ignition. This is because with a higher activation energy, it is more difficult to initiate the combustion reactions, which will delay the spontaneous ignition. As stated previously, in this simulation, the main AIP recovery mechanism is caused by the combustion front displacement. If the initiation of the combustion front is

delayed or the spontaneous ignition cannot be achieved, the recovery performance will be damaged significantly. Fig 13 shows when the activation energy is higher than 100 KJ/mol, the combustion front is never achieved during the whole AIP, which caused the recovery factor decreased significantly.

For cracking reactions, a lower activation energy also results in a higher recovery performance. It is observed in Table 3 that as the activation energy decreases from 180 KJ/mol to 80 KJ/mol, the recovery factor increases from 52.2% to 52.6%. It is seen that the effect of the cracking reaction's activation energy to the recovery performance is less sensitive than the effect of the combustion reaction's activation energy to the recovery performance. The reason is when changing the activation energy in the cracking reactions, it will not significantly affect the initiation of the combustion front as shown in Fig 14. In fact, the increase of the recovery factor with a lower activation energy is due to the increase of the CO₂ concentration. Since cracking reactions generate CH₄, C₂₋₅, and Coke. Therefore, as the activation energy lowers, the concentrations of these products increase due to the stronger reactivity of the cracking reactions, then the CO₂ concentration increases. The CO₂ concentration profile with different activation energy values is shown in Fig 14. It is seen that with a lower activation energy, CO₂ concentration is higher. A higher CO₂ concentration will increase the potential miscibility flooding by the CO₂, thus increasing the oil recovery. Therefore, the variation of the activation energy in the high temperature cracking reactions will affect the EOR by influence the CO₂ generation.

To summarize, the variation of the frequency factor does not show a significant effect on the recovery performance. And the observation of the effect of the activation energy is in accordance to the screening criteria which was summarized in the third section, that a lower activation energy will be more favorable for the recovery performance. The effect of the combustion reactions' activation energy to the recovery performance is more significant than the effect of the cracking reactions' activation energy to the recovery performance. The reason is the combustion reactions can significantly affect the initiation of the combustion front while the cracking reactions cannot.

Table 3, Effect of activation energy on reservoir recovery performance

Reaction	Ea KJ/mol	RF in 10 years %
Cracking Reaction 1, 2, 3	80	52.6
	90	52.4
	130	52.2
	180	52.2
Combustion Reaction 4, 5, 6, 7	50	57.6
	70	56.9
	90	56
	100	55
	130	47.5

Figure 13, Temperature profile of the observation grid block under different activation energy in combustion reactions

Figure 14, Reservoir CO₂ concentration and observation block temperature profile with different activation energy of cracking reactions

9. Conclusions

The following conclusions may be drawn from this study.

- Thermal experiments have two main roles.
 - 1) To work as a low-cost method to pre-screen the candidate oils before conducting combustion tube tests;
 - 2) To estimate the relevant kinetic data and study the thermo-oxidative behavior, and develop the base model before conducting combustion tube tests.
- The API gravity of the crude oil has no relation to the reaction temperature regions and the kinetic data of the crude oil.
- The reaction temperature ranges for LTO and HTO were estimated to be 149 ~ 364 °C for the LTO and 415 ~ 542 °C for the HTO. And the average combustion peak temperature are 320 °C in the LTO stage and 469 °C in the HTO stage.
- The activation energy in HTO (107 KJ/mol) is generally higher than that in the LTO (33 KJ/mol). The general activation energy ranges for a crude oil are 20 ~ 70 KJ/mol in the LTO

stage and 70 ~ 180 KJ/mol in the HTO stage. Also, the frequency factor in the LTO ($0.1 \sim 10^5 \text{ s}^{-1}$) are generally lower than that in the HTO ($10^4 \sim 10^9 \text{ s}^{-1}$).

- With the presence of the additives such as cuttings and metallic additives, the general activation energy ranges for a crude oil are 18 ~43 KJ/mol in the LTO stage and 60 ~ 100 KJ/mol in the HTO stage. High pressure environments could decrease the activation energy in the HTO stage to around 39 ~ 85 %, while they do not show a significant effect on the LTO stage's activation energy.
- A lower activation energy is more favorable for oil recovery, but the frequency factor may not.

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Nomenclature

AIP – air injection process

EOR – enhanced oil recovery

LTO – low temperature oxidation

HTO – high temperature oxidation

TGA – thermogravimetric analysis

DSC – differential scanning calorimetry

ARC – accelerating rate calorimetry

SBR – small batch reactor

ISC – in-situ combustion

DTA – differential thermal analyzer

FD – fuel deposition

PDSC – pressurized differential scanning calorimetry

Ea – activation energy, KJ mol^{-1}

Ar – frequency factor, s^{-1}

R – universal gas constant, $\text{J mol}^{-1} \text{ K}^{-1}$

K(T) – reaction rate, s^{-1}

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