Journal of Petroleum Science and Engineering 133 (2015) 29–39

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Recovery of light oil by air injection at medium temperature: Experiments

Negar Khoshnevis Gargar [a],*, Alexei A. Mailybaev [b], Dan Marchesin [b], Hans Bruining [a]

[a] Delft University of Technology, Civil Engineering and Geosciences, Stevinweg 1, 2628 CE Delft, The Netherlands
[b] Instituto Nacional de Matemática Pura e Aplicada (IMPA), Estrada Dona Castorina 110, Rio de Janeiro 22460-320, Brazil

A R T I C L E I N F O

Article history:
Received 12 April 2014
Received in revised form
24 February 2015
Accepted 21 May 2015
Available online 23 May 2015

Keywords:
Air injection
Medium temperature oxidation
Light oil recovery
Combustion

A B S T R A C T

Volatile oil recovery through air injection is a promising method for highly heterogeneous low permeability reservoirs. Thermal effects due to oxidation reaction, vaporization/condensation and flue gas drive are the most important mechanisms for light oil recovery by medium pressure air injection. To gather evidence for this claim, we performed ramped temperature experiments with consolidated cores filled with hexadecane injecting either air or nitrogen at different injection rates at medium pressures. The experiments show that oxygen is removed from the injected air through physical and chemical sorption by the hydrocarbon at low temperatures. Most of the bonded oxygen is released later at higher temperatures and reacts to form carbon oxides. The amount of oil burned in the air injection process relative to the amount of oil recovered increased from 2% at 10 bar to 18% at 30 bar, and again decreased to 5% at 45 bar and 3% at 70 bar. This trend was predicted theoretically in an earlier study of the medium temperature oxidation process.

1. Introduction

Recovery percentages from oil reservoirs range from 5% for difficult oil to 50% for light oil in highly permeable sandstone reservoirs. Due to the current difficulties encountered in the production of oil, in situ combustion (ISC) and high pressure air injection (HPAI) are considered as effective ways to enhance the recovery of oil. When high pressures are impractical, an air injection method can be proposed that is effective at medium temperatures and pressures for light oil reservoirs (Mailybaev et al., 2013). The experiments described in this work explain the reasons for its effectiveness.

The air injection process is often referred to as HPAI when it is applied to deep light oil reservoirs, where other recovery methods are uneconomic or ineffective, whereas the term in situ combustion traditionally has been used for heavy oil reservoirs. The effectiveness of HPAI depends on many oil recovery mechanisms (Clara et al., 2000) including sweeping by flue gases, field repressurization by the injected gas, oil swelling, oil viscosity reduction, stripping off light components from the oil by flue gas, and thermal effects generated by the oxidation reactions. The maximum amount of oil recovery in combustion processes is the initial oil-in-place exclusive the amount of fuel consumed in the combustion reactions (Mamora, 1995), i.e., even residual oil may be produced.

The mechanism responsible for oil displacement by air injection varies with the type of oil. For light oil, vaporization and condensation are just as important as the oxidation reaction (Mailybaev et al., 2013). Air injection is very effective in heterogeneous permeability reservoirs as the oil evaporates away from the lower permeability parts to be collected at the higher mobility streaks. There is a large body of literature describing the use of HPAI to recover oil (Abou-Kassem et al., 1986; Akin et al., 2000; Castanier and Brigham, 1997, 2003; Kok and Karacan, 2000; Lin et al., 1987, 1984; Mailybaev et al., 2011), which is appropriate at high pressures (>100 bar) in reservoirs at large depths. However, at shallower depths (300–1000 m), an alternative is to inject at medium pressures (10–90 bar) for light and medium oil in heterogenous low permeability reservoirs. High temperatures and high heat generation are not necessary for the displacement of light oil by air injection (Greaves et al., 2000a). However some form of oxidation is required in order to remove the oxygen from the injected air (Greaves et al., 2000a) to prevent it from reaching the production wells, which is considered a safety hazard.

In most of the experiments and simulation studies in the literature considered, scission reactions improve oil recovery, in which case oxygen is removed from the injected stream. However, it is suggested (Yannimaras and Tiffin, 1995) that only about 20% of the light oils are good candidates for undergoing full oxidation at

---

* Corresponding author.
E-mail addresses: n.khoshnevisgargar@tudelft.nl (N. Khoshnevis Gargar), alexei@impa.br (A.A. Mailybaev), marchesi@impa.br (D. Marchesin), J.Bruining@tudelft.nl (H. Bruining).

http://dx.doi.org/10.1016/j.petrol.2015.05.017
0920-4105/© 2015 Elsevier B.V. All rights reserved.

temperatures greater than 400 °C, and that the other 80% only incorporates the oxygen in the oil by low temperature oxidation (LTO) at lower temperatures. The mechanism for combustion of light or medium oils is fundamentally different from that for the combustion of heavy oils (Abou-Kassem et al., 1986; Akin et al., 2000; Bruining et al., 2009; Castanier and Brigham, 1997, 2003; Kok and Karacan, 2000; Lin et al., 1987, 1984; Xu et al., 2004; Khoshnevis Gargar et al., 2010), in which high temperatures are achieved. In the high temperature oxidation (HTO), the heat conducted out of the reaction zone converts the oil to coke before it is combusted. In the medium temperature oxidation (MTO) (Greaves et al., 2000b; Gutierrez et al., 2009; Germain and Geyelin, 1997) the oxidation reaction leads to scission of the molecules and formation of small reaction products such as water, CO or CO_2. In LTO, the oxygen is incorporated in the hydrocarbon molecules to form alcohols, aldehydes, acids or other oxygenated hydrocarbons. LTO is characterized by the production of little or no carbon oxides (Greaves et al., 2000b, 2000a; Hardy et al., 1972). Dabbous and Fulton (1974) also suggest that light crude oils appear to be more susceptible to partial oxidation at low temperatures because of their high hydrogen content. An increase in the viscosity of the oil subjected to LTO reactions was observed (Alexander et al., 1962), while a decrease in the API gravity of the oil was reported (Mamora, 1995). Freitag (2010) mentioned that the success of an ignition is strongly affected by LTO reactions.

Oxidation reaction mechanisms at reservoir conditions are complex. A number of conceptual combustion models describing ISC have been formulated in the past (Alexander et al., 1962; Belgrave and Moore, 1992; Fassihi et al., 1984). Most of the models assume liquid phase or coke combustion as the source of energy to sustain ISC. Some references indicate that gas-phase reactions in HPAI are relevant (Barzin et al., 2010). However, in view of the role played in these reactions (Schott, 1960) by free radicals (Helfferich, 2004; Levenspiel, 1999), which are easily annihilated at pore walls, it is still a matter of debate whether gas phase reactions are significant. Alexander et al. (1962) found that LTO reactions have a pronounced effect on fuel deposition and composition. In the experiment (Alexander et al., 1962) with crude oil 21.8° API and temperatures between 121 °C and 345 °C, large values of apparent atomic hydrogen-carbon ratio were indicative for oxygen consumption in LTO reactions, which do not produce carbon oxides. Another important fact is that oxygen diffusion rate into the oil phase is greater than the oxidation reaction rate, so that oxygen is dissolved throughout the oil phase during LTO (Dabbous and Fulton, 1974). In reactor experiments, oxidation inhibitors (Fodor et al., 1988; Freitag, 2010, 2014) naturally existing in oil lead to an induction period (a time delay between the initial exposure to oxygen of an oil or oil fraction and the start of rapid oxidation) for saturates component oxidation at low temperatures. These inhibitors are aromatic molecules with functional groups with easily abstractable hydrogen atoms (Matsuura and Ohkatsu, 1999). LTO reaction would occur, if all the inhibitors were consumed (Freitag, 2010). Normally the rapid oxidation of saturates is repressed and decreased when they mix with other aromatic-based fractions (Freitag and Verkoczy, 2005) in the heavy oil mixture. However, volatile saturates can be vaporized, moved away downstream and be separated from the aromatic compounds in a light oil mixture containing light alkanes. As we used one-component oil (pure hexadecane), the occurrence of free-radical intermediates scavengers cannot be investigated in this paper and will be studied in the future.

In the case of experiments in a combustion tube, the latter contains a mixture of oil and sand that is heated up, using nitrogen as a carrier gas. At initiation of the experiment the nitrogen is replaced by air and the combustion process starts (Abou-Kassem et al., 1986; Akin et al., 2000; Bruining et al., 2009; Castanier and Brigham, 1997, 2003; Kok and Karacan, 2000; Lin et al., 1987, 1984; Xu et al., 2004). For ramp temperature oxidation tests, such as the one we performed, the reactor is heated over the whole length of the tube. One set of experiments was carried out at high pressures (120 bar) and high injection rates with light oil (37° API) (Barzin et al., 2010), in which combustion occurred at 220 °C. In another set of tests, combustion tube experiments were also performed at a low air flux rate (Lin et al., 1984), so that oxygen consumption was close to 100% (the oxygen contents in the produced gas phase were only 1% or less). Under these conditions, the combustion rate is controlled by oxygen mass transfer, and the kinetics of the oxidation reactions are not important except during the ignition period. Greaves et al. (2000b) carried out two tests on a light Australian oil (38.8° API) starting at initial oil saturations of $S_o = 0.41$ and 0.45, at an operating pressure of 70 bar and an initial bed temperature of 63 °C. The combustion temperature was about 250 °C in both tests. High combustion velocities were achieved in all tests, varying from 0.15 to 0.31 m/h.

Medium pressure air injection is described directly or indirectly in the literature. Gillham et al. (1998) show that air injection can increase the light oil recovery to economical significance in the deep Hackberry reservoir. They distinguish between application of high and low pressures in the field trials. The low pressure experiment is conducted between 20 and 40 bar. Unfortunately, supporting tube tests were only reported at high pressures (230 bar) incidentally. The paper reports two incidents of fire, one in the high pressure test and one in the low pressure test, both occurring in the injection well. Gutierrez et al. (2008) describe a laboratory experiment at low pressure (14 bar) with light oil, which gave rise to relatively high temperatures (478 °C). The combustion is characterized initially by oxygen addition reaction followed by scission reactions. The authors conclude that high oxygen injection rates are required to stimulate the scission reactions. Germain and Geyelin (1997) describe combustion tube tests with light oil in heterogenous low permeability (1–100 mD) reservoirs using pressures of 40–45 bar and leading to combustion temperatures between 260 °C and 370 °C. Low pressure thermal gravity and differential scanning calorimetry test results (Li et al., 2004) show that distillation is a dominant process for the recovery of light and medium oils at elevated temperatures. This may indicate that pressure effects need to be taken into account. They also found that pressure enhances exothermic reaction rates in a pressurized differential scanning calorimeter test with a sample weight of 10 mg.

In a previous theoretical study based on two-component oil model, we found that the ratio between vaporization and reaction determines the effectiveness of the air injection process (Khoshnevis Gargar et al., 2014). If a large amount of heavy components is present in oil, the vaporization is weak and most oil is left behind for combustion. On the contrary, for a large amount of light component in the oil, most of the oil vaporizes and less oil is left behind for combustion. As a result, recovery of light oil is more efficient and requires less oxygen per amount of oil recovered. It is asserted that the oxidation mechanism also plays an important role in the effectiveness of the oil production, as partial oxidation of the light hydrocarbons forms oxygenated hydrocarbons with a higher boiling point (Greaves et al., 2000b, 2000a; Hardy et al., 1972) than the original hydrocarbons. In such a case vaporization will be hampered and the process may become less effective.

One of the purposes of our research is to investigate whether we can find experimental evidence for the medium temperature combustion mechanism described theoretically in Mailybaev et al. (2013) and Khoshnevis Gargar et al. (2014). We perform and interpret experiments involving air injection in sandstone rock filled with n-hexadecane (modeling light oil) at medium pressures and conditions that are typically away from the injection well. The air