

Review

A review of pyrolysis, aquathermolysis, and oxidation of Athabasca bitumen

Punitkumar R. Kapadia¹, Michael S. Kallos, Ian D. Gates^{*}*Department of Chemical and Petroleum Engineering, Schulich School of Engineering, University of Calgary, Canada*

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ABSTRACT

The recovery of heavy oil and oil sand deposits of western Canada by using in situ combustion or gasification recovery processes has always been a great technological and economical challenge. During in situ combustion bitumen recovery processes, pyrolysis, aquathermolysis and oxidation mechanisms coexist because of co-existence of bitumen, water and oxygen in the presence of high temperature and high pressure. The modeling of such processes requires comprehensive reaction schemes along with kinetic parameters to describe each of these mechanisms. The determination of such kinetic parameters requires extensive lab and/or pilot studies due to the complex chemical nature of bitumen. During these studies, it is customary to represent bitumen and products of bitumen combustion by pseudo-components to describe the bitumen combustion reaction scheme in a way which not only describes the process reasonably well but also is easy to understand. Although there have been numerous bitumen combustion experiments conducted over the past 80+ years, all of the data and experience have not been analyzed comprehensively with a focus towards integrating all of the evidence into a single vision of the process. Here, we review all previously published lab scale and pilot experimental data, various reaction schemes and field observations published for pyrolysis, aquathermolysis, oxidation, and/or gasification of Athabasca bitumen. These studies were conducted either to understand the chemical structure of bitumen or to develop reaction schemes for use in numerical simulators. This review reveals a new overall vision for combustion processes for in situ bitumen recovery and also shows that there are key data sets not currently available that would greatly enhance modeling and simulation work needed for the full recovery of Athabasca bitumen resources.

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^{*} Corresponding author. Tel.: +1 403 220 5751; fax: +1 403 284 4852.

E-mail address: ian.gates@ucalgary.ca (I.D. Gates).

¹ Now at Computer Modelling Group, Calgary, AB, Canada.

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1. Introduction

Heavy crude oil is oil that has viscosity typically greater than about 100 cP and density greater than 930 kg/m³. Bitumen, also referred to as extra heavy crude oil, is defined as being more viscous and denser than heavy oil with viscosity and density being higher than 10,000 cP and 1000 kg/m³ respectively [1]. In many oil sand reservoirs, the viscosity of bitumen exceeds 100,000 cP with average values typically just over 1 million cP [2]. There exists more than 6 trillion barrels of heavy oil and extra heavy oil on Earth. Due to declining rates of production of conventional oil, these oils are becoming more sought after by oil production companies. This is especially the case in Western Canada where roughly 1.7 trillion barrels of heavy oil and bitumen are hosted in the Western Canada Sedimentary Basin – this is the single largest resource of heavy oil and bitumen on Earth with the largest being the Athabasca oil sand deposit. With the current technology, only about 10% of it is considered to be recoverable with existing technology [3–5].

The key challenge for recovering bitumen is its viscosity – with viscosities often in the hundreds of thousands and millions of cP, it does not readily flow from the reservoir to the surface. However, when bitumen temperature is raised to above about 200 °C, its viscosity drops to less than 10 cP and under gravity drainage, solution-gas drive, thermally-induced geomechanical forces, or steam drive, the bitumen can be moved to production wells and extracted to the surface. In typical practice, bitumen is heated to greater than 200 °C by injecting high pressure and high temperature steam into the reservoir [6]. The key concern of steam-based recovery processes is that they consume large amounts of fuel and water and emit substantial volumes of greenhouse gases to generate steam [7]. An alternative is to generate heat and steam within the formation by in situ combustion – that is, inject oxygen underground into the bitumen formation and combust some fraction of it to generate heat (or steam) which lowers the viscosity of the oil enabling its movement to production wells [8–11].

The potential to recover or exploit heavy oil and/or oil sand deposits in Western Canada by in situ combustion and/or gasification has been extensively studied, mostly in laboratory studies and in a few field trials, over the past 50 years. However, no in situ combustion or gasification technologies to recover bitumen from oil sand reservoirs have been both technically and commercially successful despite all of the research. One major uncertainty that has hindered progress on designing robust in situ combustion and gasification recovery processes is that

associated with reaction schemes and attendant kinetic models and parameters. In a potentially productive Athabasca oil sand reservoir, the physical situation, illustrated in Fig. 1, is generally as follows.

1. The bitumen occupies roughly between 85 and 95% of the pore space, the remainder is filled with water. The sand grains are typically between 50 and 120 μm in size with pore sizes between sand grains typically equal to about 10 to 30 μm. The sand is typically composed largely of quartz and thus, the reservoir rock is water-wet.
2. The porosity of the reservoir ranges from 20 to 35% depending on the facies (whether clean sand or sand with embedded shale and/or clay, etc.). The absolute permeability of the reservoir rock ranges from 1 to 8 darcy depending on the porosity, shape of sand grains, and depth of the reservoir (deeper implies greater overburden stress which means lower porosity).
3. The initial temperature of the reservoir is typically between 8 and 20 °C which means the viscosity of the bitumen is in the low millions of cP. The viscosity does not depend strongly on pressure [12], but for Athabasca reservoirs targeted for in situ recovery processes, the initial reservoir pressure typically ranges from 800 kPa up to about 3500 kPa depending on the depth of the reservoir.
4. The solution-gas content is typically relatively low compared to conventional oil reservoirs with gas-to-oil ratios generally lower than 3 to 4 m³ gas per m³ of bitumen at reservoir conditions.

In processes that combust or gasify bitumen, thermal cracking, aquathermolysis, oxidation and other complex mechanisms coexist and potentially compete and operate in series or in parallel [13]. The modeling of such processes requires a comprehensive reaction scheme along with kinetic parameters to account for all the possible interactions the oil sands can have with water and oxygen in the presence of heat. There is also the possibility of chemical interactions among the products of pyrolysis (thermal cracking), aquathermolysis (hydrous pyrolysis), and oxidation reactions during combustion or gasification of Athabasca bitumen. For instance, coke gasification (coke is the product of pyrolysis) and water–gas shift (carbon monoxide and water chemical interaction) reactions could also occur during bitumen gasification. Chemical interactions of bitumen, water and oxygen constitute a system of multiple interacting reactions which involve pyrolysis, aquathermolysis, low temperature oxidation (LTO), high temperature oxidation (HTO), coke gasification, water gas shift, methanation, and methane, hydrogen, and other gas combustion reactions.

In situ gasification (ISG) of bitumen can be accomplished by in situ combustion (ISC) of a fraction of the bitumen in the reservoir. ISC generates heat which enables hydrogen generation reactions. During this process, since bitumen, water and oxygen are all present in situ, there are multiple reactions responsible for both production and consumption of hydrogen. Aquathermolysis [14], thermal cracking [15], water–gas shift [16] and coke gasification reactions have been reported to generate hydrogen gas during in situ combustion of heavy oil. For example, the in situ combustion pilot at Marguerite Lake, Alberta, Canada continuously generated up to 20 mol% hydrogen in the produced gases [17]. This pilot was operated in a 12°API (density 986 kg/m³) bitumen oil sand reservoir with oil viscosity, at original reservoir temperature and pressure, equal to about 100,000 cP. The capability to produce hydrogen from heavy oil as an alternate energy vector from the reservoir (instead of heavy oil) has obvious environmental benefits in the context of heavy oil upgrading to synthetic

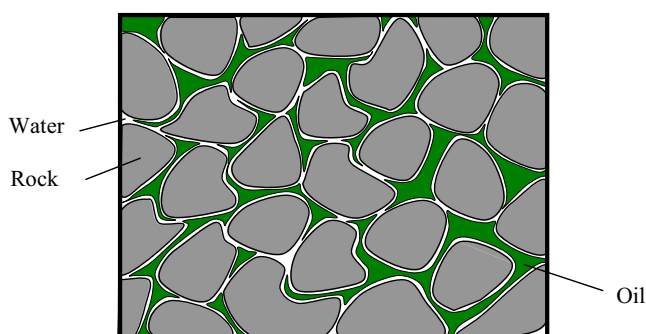


Fig. 1. Physical situation in typical water-wet oil sand reservoirs with bitumen, water and sand grain (rock matrix) present. Rock grain size varies from about 1 μm to 250 μm. Typical porosity is about 20 to 35% with oil saturations up to 95% of pore volume [92].

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