



## Review

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

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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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## 1. Introduction

Heavy crude oil is oil that has viscosity typically greater than about 100 cP and density greater than 930 kg/m<sup>3</sup>. 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/m<sup>3</sup> 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].

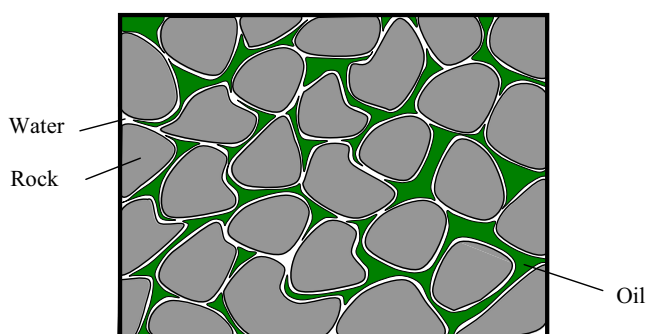
The potential to recover or exploit heavy oil and/or oil sand deposits in Western Canada by in situ combustion and/or gasification has been extensively studied, mostly in laboratory studies and in a few field trials, over the past 50 years. However, no in situ combustion or gasification technologies 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 m<sup>3</sup> gas per m<sup>3</sup> 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/m<sup>3</sup>) 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].

crude oil (SCO) and refining of SCO to transportation fuels and its eventual use in vehicles [11].

There are numerous experimental and pilot scale studies that have been conducted to understand bitumen pyrolysis, aquathermolysis, and oxidation mechanisms. Most of these studies were aimed to understand either bitumen structural changes during these reactions, or the quality of bitumen in terms of producing final refined products upon upgrading and refining, or the reaction scheme which can be practically incorporated into a numerical simulator. Other studies describe comprehensive reaction schemes during which pyrolysis, aquathermolysis, and oxidation mechanisms co-exist. Here, we review past studies on the pyrolysis, aquathermolysis, and oxidation of Athabasca bitumen along with those works which deal with bitumen combustion and gasification. We seek to understand consistencies and inconsistencies among the data and mechanisms to identify their usability and make recommendations for future experimental design.

## 2. Methods

The papers reviewed here were taken from conference proceedings and journal paper publications in the public domain. The search terms were narrowed to Athabasca whole bitumen and associated pyrolysis, aquathermolysis, oxidation, combustion, and gasification experimental, simulation, pilot, and field studies.

## 3. Primary reaction mechanisms – experimental and field data

### 3.1. Pyrolysis

#### 3.1.1. Overview

Pyrolysis (also referred to as thermolysis or thermal cracking) is thermochemical decomposition of oil sands at elevated temperatures in the absence of oxygen. Over the past ~80 years, there have been many thermal cracking experimental studies on Athabasca oil sands, as listed in Table 1. With the exception of a few studies which were done to characterize bitumen and observe changes in its physical properties and chemical structure during pyrolysis, most studies were aimed at obtaining reaction schemes with associated kinetics to describe thermal cracking quantitatively. Furthermore, despite many studies having determined reaction kinetics for pyrolysis of Athabasca bitumen, it is not clear how consistent were the reaction kinetics nor how the results were used to engineer a process or design a reactor. It appears that many experimental studies have been done with the end goal of simply proposing a reaction scheme with fitted reaction parameters with no end use for the data.

#### 3.1.2. Early years: 1920 to 1969

In the early years, there were no studies which focused comprehensively on combustion of bitumen as an in situ recovery process rather most of the focus was on the potential to upgrade bitumen to higher API fuels and products by thermal cracking.

Egloff and Morrell [18] obtained gasoline by thermal cracking of Athabasca bitumen. The products of thermal cracking were distillate, noncondensable gas and coke. The distillate obtained from thermal cracking of bitumen was further processed to obtain gasoline. The results of their experiments showed that more than one third of the Athabasca bitumen, after thermal cracking and further refinement, was converted into good quality gasoline. They demonstrated that bitumen has the capability to upgrade upon pyrolysis. The objective of subjecting bitumen to thermal cracking was to produce a motor fuel.

Ball [19] quoted results obtained by Universal Oil Products on thermal cracking of Athabasca bitumen which also demonstrated that about one third of the bitumen cracked produced clear, sweet, and non-corrosive gasoline. They also showed that a product of thermal cracking, referred to by them as a pressure distillate, when subjected to distillation, yielded gasoline as a main product and a gas oil as a byproduct. From the experiments, gasoline and gas oil yields were 36.3% and 17.6% of the original bitumen

volume, respectively. Similarly, coke and gas yields were 139 lb/bbl of bitumen (396.6 kg/m<sup>3</sup> of bitumen) and 1000 ft<sup>3</sup>/bbl of bitumen (178.1 m<sup>3</sup>/m<sup>3</sup> of bitumen), respectively.

McNab et al. [20] investigated thermal cracking of Athabasca tar sand in a series of experiments to evaluate conversion of heavy oils to the lower boiling, gasoline-containing crudes under low temperature cracking. They showed that the presence of reservoir sand and high pressure conditions during thermal cracking had little impact on the thermal cracking reaction rate of Athabasca bitumen. They also predicted that Athabasca bitumen would not significantly thermolyze at 150 °F (65.5 °C) over geologic time scales by using their calculated activation energy of Athabasca bitumen thermal cracking reaction they had found equal to about 49,000 cal/mol (205,016 J/mol). Also, the analysis of gas produced during thermal cracking showed high content of methane. Other gases present were carbon dioxide, hydrogen sulfide and hydrogen. Since the thermal cracking experiments were carried out at lower temperatures and in the presence of brine water there is a likelihood of aquathermolysis and thermal cracking reactions occurring together resulting into the generation of above-mentioned gases.

Henderson and Weber [21] estimated a time–temperature dependent viscosity relationship to predict the degree of viscosity reduction when crude oils were subjected to high temperature. They proposed that if pyrolysis is allowed to continue for a sufficient period of time or if the temperature is sufficiently high, the original material is almost entirely converted into a mixture of light gases, composed largely of methane and hydrogen, and a solid carbonaceous residue, coke. They proposed overall reaction for conversion of bitumen to gas and coke components due to thermal cracking. A reference distillation procedure, as described by McNab et al. [20], was used to calculate conversion of bitumen to gas and coke components. Results of experiments conducted on Athabasca bitumen demonstrated a linear relationship between the logarithm of the overall bitumen pyrolysis reaction rate constant and the reciprocal of the absolute temperature. This result implies that under their experimental conditions, thermal cracking reactions can be adequately described by first order reaction kinetics. Their calculations, based on first order reaction kinetics, yielded values of activation energy and the logarithm of the pre-exponential factor to be equal to 49.0 kcal/mol (205 kJ/mol) and 11.53, respectively. These values are very similar to that of McNab et al. [20]. Also, according to their calculations by using their reaction model, Athabasca bitumen required about 450 years, 1.9 years, 8.8 days and 0.26 days at 400, 500, 600 and 700 °F (204.4, 260, 315.6 and 371.1 °C), respectively, for 15% of its mass to be upgraded. The scale of upgrading was based on the weight percent reduction in the residuums from prescribed distillation. The experiments conducted in the presence and absence of sand, water and pressure, as also observed by McNab et al. [20], did not show any noticeable difference in results obtained. Thus, the results implied that the sand did not exhibit catalytic properties on thermal cracking of Athabasca bitumen.

Speight [22] described complex structural changes in Athabasca bitumen, Athabasca asphaltenes, and Athabasca de-asphalted heavy oil during thermal cracking experiments. The destructive distillation of Athabasca bitumen yielded 55.3 wt.% of light oil, 2.3 wt.% of resins, 25.4 wt.% of coke, and 17 wt.% of gases. Elemental analysis of light oil, resins and coke indicated that H/C (H = Hydrogen; C = Carbon) ratio of light oil improved (indicates reduced aromaticity) considerably whereas S/C (S = sulfur) ratio of light oil deteriorated (indicates sulfur removal from bitumen) considerably when these ratios were compared to those obtained for original bitumen. Also, 89.1 wt.% of carbon, 78.5 wt.% of hydrogen, 12.9 wt.% of oxygen, 51 wt.% of nitrogen, and 43.3 wt.% of sulfur originally present in Athabasca bitumen transferred to non-gaseous products of destructive distillation. The results of this study indicated that, upon thermal cracking of bitumen, there are significant chemical changes in bitumen and the products of thermal cracking as a result of distribution of carbon, hydrogen, nitrogen, oxygen and

**Table 1**  
Summary of thermal cracking studies on Athabasca bitumen.

Reference	Purpose of study	Experimental conditions	Components or pseudo-components	Proposed reaction scheme
Egloff and Morrell [18]	Upgrade bitumen by thermal cracking	Bitumen was subjected to temperature of 750 °F (399 °C) and pressure of 90 lbs (620.5 kPa).	<ul style="list-style-type: none"> <li>• Distillate</li> <li>• Noncondensable gas</li> <li>• Coke</li> </ul>	–
Ball [19]	Characterize Athabasca bitumen	Bitumen was cracked in a non-residual-type operation at 90 psi (620.5 kPa) pressure and temperature of 399 °C.	<ul style="list-style-type: none"> <li>• Distillate (38.8°API)</li> <li>• Coke</li> <li>• Gas</li> <li>• 80% feed residuum upon distillation</li> <li>• Gas</li> </ul>	–
McNab et al. [20]	Examine thermal cracking rates under reservoir conditions (in the presence of brine and mixture of sandstone, limestone and shale core)	Cracking experiments were carried out in stainless steel autoclave pressures of 1000 to 3000 psi (6895 to 20,684 kPa) and temperatures between 50 and 300 °F (10 to 149 °C).	<ul style="list-style-type: none"> <li>• 80% feed residuum upon distillation</li> <li>• Gas</li> <li>• Coke</li> </ul>	–
Henderson and Weber [21]	Study effect of mild thermal cracking on viscosity and specific gravity	Cracking experiments were done in Pyrex lined stainless steel reactor for sand and water free bitumen and rotating stainless steel reactor for mixture of sand, clay, bitumen and water.	<ul style="list-style-type: none"> <li>• Light oil</li> <li>• Resins</li> <li>• Coke</li> <li>• Gas</li> </ul>	–
Speight [22]	Examine structural changes in Athabasca bitumen during thermal cracking	Round-bottomed flask containing samples (50 ± 0.2 g) were heated by an alloy bath (bath temperature was raised to 450–455 °C over a period of 20 min) to start the distillation (the thermal cracking experiment). The alloy bath temperature was then maintained at 460–470 °C for 2 h, by which time all of the distillate had been collected.	<ul style="list-style-type: none"> <li>• Gases (C<sub>5</sub> and lighter)</li> <li>• Liquid condensate (C<sub>6</sub> to 535 °C boiling fraction)</li> <li>• Coke</li> </ul>	–
Bunger et al. [24]	Characterize products of ramped temperature thermolysis	10 g of bitumen was pyrolyzed in a distillation flask at a heating rate of about 5 °C/min to an end point of 625 °C.	<ul style="list-style-type: none"> <li>• Bitumen (organic portion of tar sand soluble in boiling benzene/ethanol)</li> <li>• Oil (sum of all liquid products, condensable at 0 °C, that volatilized from the heated tar sand material)</li> <li>• Gas (total volatile product, not condensable at 0 °C)</li> <li>• Coke (benzene/ethanol insoluble, nonvolatile carbonaceous material)</li> <li>• Gas evolved during pyrolysis contained neopentane, methane, acetaldehyde, propane, and propylene with trace quantities of C<sub>2</sub>–C<sub>5</sub> hydrocarbon, CO, H<sub>2</sub>S, COS, CS<sub>2</sub>, and SO<sub>2</sub></li> </ul>	–
Barbour et al. [25]	Study thermal cracking behavior in the presence of sand matrix	Tar sand samples were pyrolyzed in a horizontal tube furnace at temperatures of 500, 750 and 1000 °F (260, 399 and 538 °C) in stream of nitrogen gas.	<ul style="list-style-type: none"> <li>• Coke</li> <li>• Asphaltenes</li> <li>• Heavy oils (boiling point 400 °C+)</li> <li>• Middle oils (boiling point 200–400 °C)</li> <li>• Light oils (boiling point 20–200 °C)</li> <li>• Gas</li> </ul>	Bitumen → oil + gas + coke
Strausz et al. [26]	Analyze composition of produced gases during low temperature thermolysis of oil sands	Oil sand, about 900 g, in Pyrex vessel was subject to mild thermal cracking at the pressure of 0.1 Pa and temperatures of 5, 70, 95, 130, 170 and 210 °C.	<ul style="list-style-type: none"> <li>• Coke</li> <li>• Asphaltenes</li> <li>• Heavy oils (boiling point 400 °C+)</li> <li>• Middle oils (boiling point 200–400 °C)</li> <li>• Light oils (boiling point 20–200 °C)</li> <li>• Gas</li> </ul>	–
Hayashitani et al. [15,27]	Develop pseudo-component reaction model for thermal cracking of Athabasca bitumen	Bitumen (about 4 g) was thermally cracked in quartz glass tube over the temperature range of 303 °C to 452 °C.	<ul style="list-style-type: none"> <li>• Coke</li> <li>• Asphaltenes</li> <li>• Heavy oils (boiling point 400 °C+)</li> <li>• Middle oils (boiling point 200–400 °C)</li> <li>• Light oils (boiling point 20–200 °C)</li> <li>• Gas</li> </ul>	<p><i>Model A-1</i> Asphaltenes → coke Asphaltenes → heavy oils Heavy oils → asphaltenes Heavy oils → distillables Distillables → heavy oils Asphaltenes → distillables where distillables = gas + light oils + middle oils</p> <p><i>Model A-2</i> Asphaltenes → coke</p>

(continued on next page)

Table 1 (continued)

Reference	Purpose of study	Experimental conditions	Components or pseudo-components	Proposed reaction scheme
				Asphaltenes → heavy oils Heavy oils → asphaltenes Heavy oils → distillable oils Distillable oils → heavy oils Asphaltenes → gas where distillable oils = light oils + middle oils <i>Model B-1</i> Asphaltene-2 → coke Asphaltene-2 → heavy oils Heavy oils → asphaltene-2 Heavy oils → distillables Distillables → heavy oils Asphaltene-1 → heavy oils <i>Model B-2</i> Asphaltene-2 → coke Asphaltene-2 → heavy oils Heavy oils → asphaltene-2 Heavy oils → distillable oils Distillable oils → heavy oils Asphaltene-1 → heavy oils Asphaltene-2 → gas
Lin et al. [28]	Examine extent-of-reaction effects, i.e. how pseudo-component composition changes during the reaction process and determined reaction models with associated kinetic parameters	–	<ul style="list-style-type: none"> <li>• Heavy-oil</li> <li>• Medium-oil</li> <li>• Light-oil</li> <li>• Coke</li> </ul>	<i>Model A</i> Heavy-oil → coke + light-oil Light-oil → coke <i>Model B</i> Heavy-oil → coke + medium-oil + light-oil Medium-oil → light-oil + coke
Phillips et al. [29]	Study thermal cracking of Athabasca bitumen in the presence of a sand matrix to determine its catalytic effect on pyrolysis reactions	Mixture of ~20 g of bitumen and 100 g of sand was thermally cracked into glass-lined reaction vessel at temperatures of 633, 673 and 693 K (360, 400 and 420 °C).	<ul style="list-style-type: none"> <li>• Coke</li> <li>• Asphaltenes</li> <li>• Heavy oils (boiling point 400 °C+)</li> <li>• Middle oils (boiling point 200–400 °C)</li> <li>• Light oils (boiling point 20–200 °C)</li> <li>• Gas</li> </ul>	<i>Model A</i> Asphaltenes → coke Asphaltenes → heavy oils Heavy oils → asphaltenes Heavy oils → distillables Distillables → heavy oils where distillables = gas + light oils + middle oils <i>Model B</i> Asphaltenes → coke Asphaltenes → heavy oils Asphaltenes → gas Heavy oils → asphaltenes Middle oils → heavy oils Light oils → middle oils Heavy oils → middle oils Middle oils → light oils
Millour et al. [30]	Develop implicit correlation method using Hayashitani et al.'s experimental data to develop thermal cracking kinetic model and test this model against additional thermal cracking experimental data	Several experiments were performed in the presence of water and core at 360, 397 and 420 °C temperatures.	<ul style="list-style-type: none"> <li>• Coke</li> <li>• Asphaltenes</li> <li>• Maltenes</li> <li>• Gas</li> </ul>	$\text{Coke} = \left( k(T) \cdot \ln \left( \frac{t}{t_0} \right) \right)^2$ <p>where <math>k(T)</math> at 360, 397 and 422 °C equals 1.04, 1.22 and 1.59 respectively For <math>0 &lt; \text{coke} &lt; 6.48\%</math> Maltenes = <math>-0.0963 \cdot \text{Coke}^2 + 0.1610 \cdot \text{Coke} + 84</math> For <math>\text{coke} &gt; 6.48\%</math> Maltenes = <math>-1.08696 \cdot \text{Coke}^2 + 88.0436</math> Maltenes · Asphaltenes = <math>-201.49 \cdot \sqrt{\text{Coke}} + 1350</math> Gas = <math>100 - \text{Coke} - \text{Maltenes} - \text{Asphaltenes}</math></p>
Mazza and Cormack [31,32]	Subject SARA-separated fractions of Athabasca bitumen to liquid phase thermal cracking and developed kinetic	Thermal cracking experiments were carried out by introducing about 1.38 g of sample into the Vycor-lined reaction vessel at 365,	<ul style="list-style-type: none"> <li>• Saturate</li> <li>• Aromatic</li> <li>• Resin</li> </ul>	Saturate → volatiles Saturate → aromatic Aromatic → volatiles



model for pyrolysis of whole bitumen	382, 399, 417 and 441 °C temperatures.	<ul style="list-style-type: none"> <li>• Asphaltene</li> <li>• Volatiles (boiling points less than 105 °C)</li> <li>• Coke</li> </ul>	<p>Aromatic → resin Resin → volatiles Resin → aromatic Resin → asphaltene Asphaltene → volatiles Asphaltene → resin Asphaltene → coke</p>
Murugan et al. [33]	20 mg of Athabasca oil sands was subject to thermogravimetric analysis at heating rates of 5, 10 and 20 °C/min up to maximum temperature of 800 °C.	<ul style="list-style-type: none"> <li>• Maltenes</li> <li>• Asphaltenes</li> <li>• Coke</li> <li>• Methane</li> <li>• Hydrogen</li> <li>• Carbon monoxide</li> <li>• Carbon dioxide</li> <li>• Hydrogen sulfide</li> <li>• Heavy molecular weight gas</li> </ul>	
Kapadia et al. [34]	Develop new kinetic model for thermal cracking of Athabasca bitumen which has the ability to not only predict coke deposition but also gas composition		

sulfur atoms along with change in aromaticity among bitumen and thermal cracking products.

### 3.1.3. 1971 to 1979

From about 1971 onwards, thermal cracking studies of Athabasca bitumen were still focused largely on the use of pyrolysis to upgrade Athabasca bitumen to a value-added product such as a transportation fuel. However, in the later 1970s, there was a shift towards the design of in situ combustion processes for recovery bitumen from oil sand reservoirs. This shift was marked with greater efforts spent on developing reaction schemes and associated kinetic parameters that included use of pseudo-components. The characterization of bitumen by pseudo-components eased the depiction of reaction schemes by using fewer components and reactions in spite of the fact that during bitumen pyrolysis hundreds of reactions may occur simultaneously. This characterization scheme is similar to kinetic modeling of hydrocarbons [23].

Bunger et al. [24] subjected three Utah, one Athabasca bitumen, and a Wilmington, California petroleum residue to batch-type destructive distillation at atmospheric pressure under an inert atmosphere. Athabasca bitumen (extracted from oil sands) yielded 7.52 wt.% gases, 76.52 wt.% liquid condensate, and 15.96 wt.% coke. The majority of gas was produced above 500 °C when condensate production was tapering off. The gas products contained hydrogen, hydrogen sulfide, carbon oxides, methane and other heavy molecular weight organic gases. Unlike batch mode of pyrolysis experiments, this study was conducted by subjecting bitumen to temperature ramp as shown in Table 1. Hence, there is no possibility of extracting individual product evolution rate from bitumen thermal cracking as a function of temperature. Overall, the main conclusion of the ramped-temperature pyrolysis was that bitumen did not show appreciable thermal cracking below 300 °C whereas maximum cracking was observed to occur at around 450 °C.

Barbour et al. [25] studied thermal cracking behavior of four Utah tar sands and a Canadian tar sand in which no prior separation of bitumen from the mineral material was done to determine the combined behavior of bitumen and sand matrix during thermal cracking experiments. The tar sand samples were pyrolyzed in a horizontal tube furnace at temperatures of 500, 750 and 1000 °F (260 °C, 399 °C, and 538 °C) in a stream of nitrogen gas. Bitumen was considered to be the total native organic portion of tar sand that was soluble in boiling benzene/ethanol. The products of pyrolysis were defined as oil (sum of all liquid products, condensable at 0 °C, that volatilized from the heated tar sand material), gas (total volatile product, not condensable at 0 °C), and coke (benzene/ethanol insoluble, nonvolatile carbonaceous material). The thermal cracking experimental results revealed that oil recovery improved with increasing pyrolysis temperature. Elemental analysis of produced oil indicated that pyrolysis caused little change in the C/H ratio with reduced nitrogen and sulfur content as also observed by Bunger et al. [24]. As compared to the original bitumen, specific gravities of produced oils decreased throughout the pyrolysis temperature range. The produced oil contained substantially higher saturates and essentially no asphaltenes when compared to the original bitumen. The produced gas contained mainly hydrogen, methane, ethane, and hydrogen sulfide. Barbour et al. suggested that the overall (stoichiometrically unbalanced) thermal cracking reaction for bitumen was represented conceptually by:



Activation energy and frequency factor obtained for Athabasca bitumen overall thermal cracking reaction, which is conversion of bitumen to oil, gas and coke as described by Eq. (1), were 33 kcal/mol (138 kJ/mol) and  $16.4 \text{ s}^{-1}$  respectively, with order of reaction being one. This study revealed that the bitumen samples examined in the pyrolysis study had activation energies in range from 33 to 35 kcal/mol (138 to 146 kJ/mol) for the reaction proposed by Eq. (1) which suggests similarities of the chemical structures of these samples.

To determine the composition of produced gas during pyrolysis, Strausz et al. [26] carried out low temperature thermolysis of oil sand, asphaltenes, and maltenes. This first experimental attempt, available in the literature, determined in great detail the composition of gas that evolved during thermal cracking of bitumen. They found that the activation energies of thermal cracking products, as obtained from Arrhenius plots, had unusually low values (activation energy for the evolution of methane from bitumen in the presence of mineral matter was calculated to be 56.9 kJ/mol as compared to that from the asphaltene and maltene fractions in the absence of mineral matter were calculated to be 117 and 130 kJ/mol, respectively) suggesting that there were catalytic effects of the mineral matter present. Their study demonstrated that the major gaseous and volatile materials present in Athabasca oil sand (at temperature of about 5 °C) in decreasing order of importance (higher amount of gas carried higher importance) were neopentane, methane, acetaldehyde, propane and propylene. There also found trace quantities of other C<sub>2</sub> to C<sub>5</sub> hydrocarbons as well as CO, H<sub>2</sub>S, COS, CS<sub>2</sub>, SO<sub>2</sub>, etc. The volatile materials obtained during degassing experiments at 5 °C (nearly formation temperature) were considered to be the most important constituents present in the formation while the other constituents, as can be seen increasing with thermal cracking temperature, were considered to be evolving as a result of Athabasca oil–sand bitumen pyrolysis. Carbon oxides were the largest among all constituents, assuming that there is no air influx and all the carbon oxides were generated through thermal cracking. During thermal cracking experiments carried out at constant temperature with varying reaction times, yields of individual gas constituents increased initially and then reached plateau values upon prolonged heating. If Strausz et al. had determined the SARA analysis of bitumen undergoing thermal cracking, then their work would have helped to provide complete reaction model to describe consumption of reactants as well as generation of products. However, experimental data generated in the study provide a good basis for a kinetic model of the evolution of all the products.

Hayashitani et al. [15,27] conducted an experimental study of pyrolysis of Athabasca bitumen, free from water and mineral, to develop a reaction model that used components and pseudo-components. The objective of the research was to develop thermal cracking reaction models for Athabasca bitumen which could be incorporated into numerical simulators of thermal recovery processes. The gaseous products that evolved during most of the experimental runs were 40–50% methane, 20–25% ethane, 10–15% propane, 5–10% butane, 3–5% pentane, and the balance consisting of various constituents like CO, CO<sub>2</sub>, H<sub>2</sub>S, COS, etc. Hayashitani et al. proposed several pseudo-reaction mechanisms to simulate the experimental results. Their thermal cracking reaction schemes could predict bitumen composition changes measured in terms of pseudo-components and production of coke and gas (treated as pseudo-components) during thermal cracking of bitumen. Though several pseudo-reaction mechanisms were proposed to simulate the experimental results, none of the proposed reaction models could predict the measured time–temperature composition of gas evolved during bitumen thermal cracking. Instead, gas was considered as a pseudo-component in their reaction model.

### 3.1.4. 1980 to 1989

In the 1980s, efforts to determine pseudo-component based reaction models continued with a greater focus on in situ combustion based recovery processes for oil sand reservoirs. The reaction schemes developed previously were improved by introducing extent of reaction effects and by exploring effect of sand matrix on reaction rates which enabled modeling of physics of bitumen combustion more precisely.

Lin et al. [28] examined extent-of-reaction effects, that is, how pseudo-component compositions change during the reaction process and determined reaction models with associated kinetic parameters for the thermal cracking of bitumen. Two kinetic models, first having two pseudo-components (heavy-oil and light-oil) and second having

three pseudo-components (heavy-oil, medium-oil and light-oil), were proposed to describe the thermal cracking of crude oil. In addition to kinetic parameters, these new kinetic models included stoichiometric coefficients and correction factor accounting for bitumen composition change during the course of the thermal cracking reaction. Unlike previous kinetic models, Lin et al. found that apparent order of reaction for bitumen thermal cracking is not first order. These kinetic models were used to correlate experimental data available in the literature. The predictions for Hayashitani et al.'s Athabasca bitumen thermal cracking experimental data from Lin et al.'s kinetic model were better than those from Hayashitani et al.'s kinetic model. However, Lin et al.'s kinetic model did not consider gas as a part of its reaction scheme.

Phillips et al. [29] used the pseudo-component approach developed by Hayashitani et al. and developed a reaction scheme for thermal cracking of Athabasca bitumen in the presence of a sand matrix to determine the catalytic effect of the sand on thermal cracking reactions. The key observations regarding the evolution of components (and pseudo-components) during thermal cracking were very similar to those obtained by Hayashitani et al. The presence of sand matrix did not have the same effect on all the pseudo-components. In their study, the yields of coke and gas from cracking bitumen–sand mixture were higher than those from cracking bitumen alone for a given temperature and reaction time. The yield of heavy oils was lower at 633 and 673 K (360 °C and 400 °C) whereas it was higher at 693 K (420 °C). The yield of asphaltenes was higher at 633 (360 °C) and 673 K (400 °C) whereas it was lower at 693 K (420 °C). The yields of light oils and middle oils were higher at 633 K (360 °C) whereas they were lower at 673 (400 °C) and 693 K (420 °C). The produced gases contained 45–53% methane, 12–20% ethane, 10–15% propane, 1–10% butanes, 0.4–2.5% pentanes, 3–7.5% unsaturated hydrocarbons, 0.7–4% hydrogen, 2.5–6.5% carbon dioxide, 1–6% carbon monoxide, and 0.8–5.6% hydrogen sulfide. The activation energies reported by Phillips et al.'s experimental studies involving bitumen–sand mixtures were lower than those obtained by Hayashitani et al.'s experimental studies involving only bitumen which suggests that the sand matrix exhibits catalytic effects. Phillips et al.'s kinetic study, similar to Hayashitani et al., treated gas as a pseudo-component despite the fact that gas composition measurements were carried out. Hence, the reaction model proposed by this study cannot predict gas composition evolved during thermal cracking experiments.

Millour et al. [30] used Hayashitani et al.'s experimental data to develop a thermal cracking kinetic model for Athabasca bitumen which incorporated coke, asphaltenes, maltenes and gas as pseudo-components. They attempted to overcome the shortcomings of thermal cracking models by Hayashitani et al. and Lin et al. Also, thermal cracking experiments were carried out on seven other oils in the presence of water and oil sand core at 360, 397, and 420 °C. The thermal cracking model developed from Hayashitani et al.'s experimental data was then used to fit the experimental data gathered on these oils. The seven oils considered were: Athabasca original bitumen (Drum 433 which is the same oil used by Hayashitani et al.), Athabasca original bitumen (Drum 20, similar to Drum 433 bitumen, except Drum 20 core contained 4.4 wt.% clays as compared to 2.6 wt.% for Drum 433 core), Athabasca bitumen collected after an oxidation test conducted in the combustion tube using normal air for 5.5 h at a temperature of 150 °C (original bitumen was from Drum 299), 13° API oil, 13° API oil following oxidation in the combustion tube with air at 125 °C for 8 h, 24° API oil and 24° API oil following oxidation in the combustion tube with air at 125 °C for 8 h. The model predictions showed excellent agreement with Hayashitani et al.'s experimental data. Thermal cracking tests at 360, 397 and 420 °C were conducted on bitumen from Drums 433 and 20. The experimental study was conducted in the presence of oil sand core and water unlike the experimental study of Hayashitani et al. which was conducted on bitumen only. Millour et al.'s model was shown to describe the special features of thermal cracking reactions like the formation of an initial coke concentration during initial heating of the oil, the existence of initial delay time prior to the continuous formation of coke, and the existence

of an equilibrium coke concentration. Even though Millour et al. introduced new insights into the mechanism of bitumen thermal cracking, the implicit nature of kinetic model, developed in this paper, prohibits its use in present day numerical simulator.

Mazza and Cormack [31,32] subjected SARA-separated fractions of Athabasca bitumen to liquid phase thermal cracking and developed first-order kinetic models to describe the behavior of these fractions during pyrolysis experiments. In their experiments, volatiles were defined as reaction products with boiling points less than 105 °C. The products of direct thermolysis of the saturate fraction were postulated to be aromatics and volatiles formed by dealkylation and aromatization of the polycyclic structures. The experimental results and model predictions obtained for the saturate fraction showed that the thermal cracking behavior of the saturate fraction followed first order decay. Thermal cracking of the aromatic fraction produced volatiles and resin as direct cracking products. Thermal cracking of the aromatic fraction involved dealkylation and aromatization, followed by condensation of highly aromatic species produced. Hence, a reversible first order model was adopted in which the aromatic fraction produced resin and volatiles. These products were in turn assumed to recombine to form a different aromatic fraction. Resin decomposition involved dealkylation and aromatization with subsequent condensation of some of the polycyclic structures and fragmentation of others present in this fraction. Volatiles evolved during thermal cracking of the resin fraction showed saturated and unsaturated hydrocarbon gases from C<sub>2</sub> to C<sub>4</sub> together with small amounts of methane and C<sub>5</sub> and C<sub>6</sub> hydrocarbons. Also, significant amounts of CO, CO<sub>2</sub> and a trace of H<sub>2</sub>S were present. The major products of thermal cracking of the resin fraction were observed to be volatiles, aromatics, and asphaltenes. Hence, the saturate fraction was lumped with the aromatic fraction to model resin decomposition. The coke determined in the reaction products was assumed to be the product of asphaltene decomposition. A reversible first order model, similar to that used to represent the aromatic decomposition data, was fitted to the resin decomposition data. The asphaltene fraction was observed to undergo dealkylation and aromatization of their polycyclic structures. Volatiles produced during thermal cracking of the asphaltene fraction were similar to those evolved from thermal cracking of the resin fraction. The resin and a small quantity of the aromatic fraction in the product were assumed to be formed by fragmentation of asphaltenic structures. Thermal cracking of the asphaltene fraction resulted in production of coke, volatiles, resins, and aromatics. The aromatic fraction produced was less than 3.9 wt.%, which could have been formed from resin cracking and not directly from asphaltene. The production of volatiles was proportional to the production of coke suggesting that these were directly produced from the cracking of the asphaltene fraction. Based on the observations made for individual SARA-separated fractions, a conceptual reaction scheme was proposed for the thermal cracking of whole bitumen which was then combined with the extent of reaction effect correction, as described by Lin et al. [28], to predict bitumen composition during thermal cracking. Bitumen thermal cracking experiments conducted by Mazza and Cormack were quite extensive and, like previous investigators, they observed an extent of reaction effect. The only drawback of this reaction scheme is that it cannot be used to predict amount and composition of gas produced during thermal cracking.

### 3.1.5. 1990 to present (2013)

Since 1990s, the focus has remained on experimental methods with a shift to incorporation of reaction models into detailed and complex reactive thermal reservoir simulation models to enable recovery process design. During this time, a comprehensive approach to model in situ combustion of bitumen was developed by integrating various reaction mechanisms present during bitumen combustion. This necessitated development of detailed pyrolysis reaction scheme which can reasonably estimate coke deposition as well as composition of evolved gas.

Murugan et al. [33] studied thermal cracking behavior of Athabasca bitumen with and without sand by using thermogravimetric analysis (TGA) during multiple heating rates. The results of their study indicated two distinct stages (both having different Arrhenius parameters) with bitumen thermal cracking. Thermal cracking experiments conducted in the presence of different reservoir sands did not show significant effect on pyrolysis characteristics as compared to those performed on bitumen alone. They also found that the order of thermal cracking reaction was not unity during either stage of bitumen thermal cracking. TGA analysis conducted by Murugan et al. provided good qualitative insight into the behavior of bitumen when subjected to heat treatment but, in the absence of batch experiments, the research work conducted here only provided the reaction rate for overall consumption of bitumen and not that for product evolution.

Kapadia et al. [34] developed a detailed reaction scheme for the Athabasca bitumen thermal cracking which included breakdown of gas pseudo-component into the most abundant gas components along with capability to predict coke deposition. This new reaction scheme was then calibrated against available experimental data in the literature over the temperature range of 130 to 422 °C. This model was simple enough to be used in detailed thermal-reactive simulation models for the prediction of coke deposition and gas composition during in situ combustion process. The kinetic parameters of the reaction scheme were determined by fitting the final composition of the produced species of multiple experiments versus temperature. Additionally, the proposed reaction scheme demonstrated both examples of excellent matches and examples of poorer matches when global match between experimental results and model predictions were carried out (poorer matches may have been caused by some experiments having sand and others without sand). This suggests that this model must include the effect of factors like distribution of activation energies and bitumen composition to predict the entire spectrum of available bitumen pyrolysis experimental data.

## 3.2. Aquathermolysis

### 3.2.1. Overview

Aquathermolysis (also referred to as hydrous pyrolysis) is a chemical interaction of oil sands with water in the presence of heat and absence of oxygen. Hyne et al. [35] introduced the term aquathermolysis (aqua = water; thermos = hot; lysis = loosening, dissolution) to represent the breakdown of components of oil sands and/or heavy oils through chemical reactions in the presence of steam/hot water.

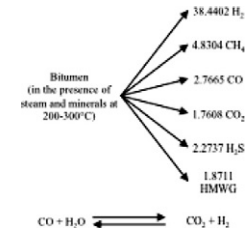
Aquathermolysis reactions are relatively non-destructive, as compared to the higher temperature thermal cracking process. There are very few detailed experimental studies on chemical interaction of Athabasca oil sands with water. Table 2 summarizes previous works on aquathermolysis of Athabasca bitumen. Most of the literature deals with qualitative understanding of chemical interaction of bitumen with steam condensate (or steam). To the authors' knowledge, there are not many attempts so far to develop comprehensive aquathermolysis reaction scheme to describe chemical interaction of bitumen and steam which can be used to design in situ gasification processes or to understand hydrogen sulfide generation in Steam Assisted Gravity Drainage (SAGD) operations for which steam injection temperature typically varies from 200 to 300 °C. Generally, aquathermolysis consists of relatively slow reactions in nature unless catalyzed by heavy metals. Hence, the total volume of gas generated on laboratory scale, as a product of aquathermolysis, is very small [35] as compared to total volume of bitumen that is stimulated by steam. Since, as compared to laboratory scale (of the order of centimeters), reservoir scale (of the order of tens to hundreds of meters) is considerably larger, the total volume of gas generated during field scale aquathermolysis is substantially higher. In addition, during steam injection into oil sand reservoirs, mineral matter present underground can potentially act as a catalyst to promote



**Table 2**  
Summary of aquathermolysis studies on Athabasca bitumen.

Reference	Purpose of study	Experimental conditions	Components or pseudo-components	Proposed reaction scheme
Hyne et al. [35]	Study chemical reaction between steam and bitumen components	Aquathermolysis experiments were carried out at 200, 240 and 300 °C in both Hastelloy autoclave and quartz tube placed inside autoclave. Amount of water at the starting of each experiment was chosen to ensure saturated steam condition at all the time during experiment.	<ul style="list-style-type: none"> <li>• CH<sub>4</sub></li> <li>• CO<sub>2</sub></li> <li>• H<sub>2</sub></li> <li>• H<sub>2</sub>S</li> <li>• C<sub>2+</sub></li> </ul>	–
Clark and Hyne [36]	Examine mechanisms for aquathermolysis of heavy oils and pathways for the formation of H <sub>2</sub> S, CO and CO <sub>2</sub> .	Steam stimulation of core samples was carried out in an autoclave (core sample = 150 g and water = 75 ml) and quartz tube (bitumen/water ratio = 0.2) at 240 °C temperature.	<ul style="list-style-type: none"> <li>• CH<sub>4</sub></li> <li>• CO<sub>2</sub></li> <li>• CO</li> <li>• H<sub>2</sub></li> <li>• H<sub>2</sub>S</li> <li>• C<sub>2+</sub></li> <li>• CH<sub>4</sub></li> <li>• CO<sub>2</sub></li> <li>• CO</li> <li>• H<sub>2</sub></li> <li>• H<sub>2</sub>S</li> </ul>	$\text{Bitumen} \xrightarrow[\text{Minerals}]{\text{Steam } 200\text{--}300^\circ\text{C}} \text{CH}_4 + \text{Hydrocarbons} + \text{H}_2\text{S} + \text{CO}_2 + \text{CO} + \text{H}_2$ $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
Hyne [37]	Summarize work on chemical reaction between water (steam) and heavy oil sands during steam stimulation	–	<ul style="list-style-type: none"> <li>• C<sub>2+</sub></li> <li>• CH<sub>4</sub></li> <li>• CO<sub>2</sub></li> <li>• CO</li> <li>• H<sub>2</sub></li> <li>• H<sub>2</sub>S</li> <li>• C<sub>2+</sub></li> <li>• Gas phase</li> <li>• Oil phase</li> <li>• Solid phase called pyrobitumen</li> </ul>	$\text{Bitumen} \xrightarrow[\text{Minerals}]{\text{Steam } 200\text{--}300^\circ\text{C}} \text{CH}_4 + \text{Hydrocarbons} + \text{H}_2\text{S} + \text{CO}_2 + \text{CO} + \text{H}_2$ $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$
Monin and Audibert [38]	Study thermal alteration of crude oils in the presence of water and different minerals representative of reservoir rocks	Experiments were carried out in an autoclave with an internal volume of 300 cm <sup>3</sup> made of Hastelloy at temperature of 350 °C for 200 h.	<ul style="list-style-type: none"> <li>• Saturate</li> <li>• Aromatic</li> <li>• Resin</li> <li>• Asphaltene</li> <li>• Gas</li> </ul>	–
Clark et al. [39]	Compare behaviors of samples of different oil sand deposits under steam stimulation conditions	100 g of homogenized oil sand and water (1:5 oil–water weight ratio) was aquathermolized in cap enclosure autoclave and quartz ampoules in an inert atmosphere of nitrogen at temperature of 240 °C for 28 days.	<ul style="list-style-type: none"> <li>• Bitumen</li> <li>• Light oil</li> <li>• Gas</li> </ul>	–
Chen et al. [40]	Investigate low temperature thermal decomposition of Alberta oil sand bitumens under conditions approximating in situ steam displacement processes	Oil sands (25 g) were pyrolyzed with varying amounts of water (0 to 20 wt.%) at 250 and 300 °C for 3, 7 and 14 days in sealed, evacuated quartz tubes.	<ul style="list-style-type: none"> <li>• Gas</li> <li>• Light oil (fraction boiling below 300 °C)</li> <li>• Heavy oil (300 °C plus fraction)</li> <li>• Asphaltene</li> </ul>	–
Belgrave et al. [41,42]	Study gas evolution from aquathermolysis of heavy oils and develop comprehensive kinetic models for aquathermolysis of heavy oils	200 g sample of premixed core into quartz glass tube (placed in stainless steel reaction vessel) was subject to aquathermolysis over the temperature range of 360 to 420 °C.	<ul style="list-style-type: none"> <li>• Coke</li> <li>• H<sub>2</sub>S</li> <li>• H<sub>2</sub></li> <li>• C<sub>1</sub></li> <li>• C<sub>2</sub>–C<sub>4</sub></li> </ul>	$\text{ASPH} \rightarrow a_{11}\text{Coke} + a_{12}\text{HO} + a_{13}\text{LO} + a_{14}\text{H}_2 + a_{15}\text{CH}_4 + a_{16}\text{CO} + a_{17}\text{CO}_2 + a_{18}\text{C}_2\text{H}_6 + a_{19}\text{C}_3 + a_{110}\text{H}_2\text{S}$ $\text{HO} \rightarrow a_{21}\text{Coke} + a_{22}\text{LO} + a_{23}\text{CH}_4 + a_{24}\text{C}_2\text{H}_6 + a_{25}\text{C}_3 +$ $\text{LO} \rightarrow a_{31}\text{Coke} + a_{32}\text{CH}_4 + a_{33}\text{C}_2\text{H}_6 + a_{34}\text{C}_3 +$ <p>where a<sub>ij</sub> represents stoichiometric coefficient</p>
Lamoureux-Var and Lorant [43]	To verify the reactions between organic sulfur compounds and water (aquathermolysis), organic and mineral interactions (sulfate reduction and/or pyrite oxidation) for Athabasca core samples	Core samples were subjected to 240 to 320 °C under 10 MPa pressure for time up to 203 h in gold tubes with and without steam/water and sand matrix in the atmosphere of nitrogen.	<ul style="list-style-type: none"> <li>• Saturates</li> <li>• Aromatics</li> <li>• Resins</li> <li>• Asphaltenes</li> <li>• Insoluble</li> <li>• CH<sub>4</sub></li> <li>• C<sub>2</sub>H<sub>6</sub></li> <li>• C<sub>3</sub>H<sub>8</sub></li> <li>• C<sub>4</sub>H<sub>10</sub></li> <li>• CO<sub>2</sub></li> <li>• H<sub>2</sub>S</li> <li>• H<sub>2</sub></li> </ul>	$\text{S(ASP)} \rightarrow \alpha_1\text{S(H}_2\text{S)} + \alpha_2\text{S(INS)} + \alpha_3\text{S(ARO)} + \alpha_4\text{S(RES)}$ $\text{S(RES)} \rightarrow \beta_1\text{S(H}_2\text{S)} + \beta_2\text{S(INS)} + \beta_3\text{S(ARO)}$ <p>where</p> $\text{S(ASP)} = \text{part of the sulfur contained in asphaltenes}$ $\text{S(RES)} = \text{part of the sulfur contained in resins}$ $\text{S(H}_2\text{S)} = \text{part of the sulfur contained in hydrogen sulfide}$ $\text{S(INS)} = \text{part of the sulfur contained in insoluble fraction}$ $\text{S(ARO)} = \text{part of the sulfur contained in aromatics}$ $\text{S(ASP)} + \text{S(RES)} + \text{S(H}_2\text{S)} + \text{S(INS)} + \text{S(ARO)} = 1$
Lamoureux-Var and Lorant [44]	Simulate in situ aquathermolysis in the laboratory in order to derive compositional kinetic model for H <sub>2</sub> S formation	Few grams of oil sand and demineralized water (to make oil and water saturations equal) were aquathermolized in gold tubes at 240, 260, 280, 300, and 320 °C under 10 MPa ± 0.5 MPa of isotropic pressure at two different times, 24 h and 203 h.	<ul style="list-style-type: none"> <li>• Saturates</li> <li>• Aromatics</li> <li>• Resins</li> <li>• Asphaltenes</li> <li>• Insoluble</li> <li>• CH<sub>4</sub></li> <li>• C<sub>2</sub>H<sub>6</sub></li> <li>• C<sub>3</sub>H<sub>8</sub></li> <li>• C<sub>4</sub>H<sub>10</sub></li> <li>• CO<sub>2</sub></li> <li>• H<sub>2</sub>S</li> <li>• H<sub>2</sub></li> </ul>	$\text{S(ASP)} \rightarrow \alpha_1\text{S(H}_2\text{S)} + \alpha_2\text{S(INS)} + \alpha_3\text{S(ARO)} + \alpha_4\text{S(RES)}$ $\text{S(RES)} \rightarrow \beta_1\text{S(H}_2\text{S)} + \beta_2\text{S(INS)} + \beta_3\text{S(ARO)}$ <p>where</p> $\text{S(ASP)} = \text{part of the sulfur contained in asphaltenes}$ $\text{S(RES)} = \text{part of the sulfur contained in resins}$ $\text{S(H}_2\text{S)} = \text{part of the sulfur contained in hydrogen sulfide}$ $\text{S(INS)} = \text{part of the sulfur contained in insoluble fraction}$ $\text{S(ARO)} = \text{part of the sulfur contained in aromatics}$ $\text{S(ASP)} + \text{S(RES)} + \text{S(H}_2\text{S)} + \text{S(INS)} + \text{S(ARO)} = 1$

Thimm [45,46]	Predict production of CO <sub>2</sub> and H <sub>2</sub> S during SAGD operations	-			
ConocoPhillips [47]	Understand aquathermolysis effects during SAGD pilot and commercial operation	Composition of produced gas evolved during SAGD operation is being monitored.			
Perez-Perez et al. [48]	Develop, using experimental data from literature, a kinetic model for H <sub>2</sub> S and CO <sub>2</sub> generation by aquathermolysis, and to integrate this model in reservoir simulation	-	<ul style="list-style-type: none"> <li>• H<sub>2</sub>S</li> <li>• CO<sub>2</sub></li> <li>• CH<sub>4</sub></li> <li>• CO<sub>2</sub></li> <li>• N<sub>2</sub></li> <li>• He</li> <li>• H<sub>2</sub></li> <li>• H<sub>2</sub>S</li> <li>• C<sub>2</sub>H<sub>6</sub></li> <li>• C<sub>3</sub>H<sub>8</sub></li> <li>• C<sub>4+</sub></li> <li>• HCS<sub>r</sub> (reactive sulfur specie)</li> <li>• HO (original bitumen)</li> <li>• H<sub>2</sub>S</li> <li>• Sand<sub>r</sub> (reactive sand)</li> <li>• CO<sub>2</sub></li> <li>• CH<sub>4</sub></li> <li>• H<sub>2</sub>O</li> </ul>	<p>170 to 190 °C: HCS<sub>r(1)</sub> → bH<sub>2</sub>S + cHO</p> <p>190 to 210 °C: HCS<sub>r(1)</sub> → bH<sub>2</sub>S + cHO HCS<sub>r(2)</sub> → bH<sub>2</sub>S + cHO</p> <p>210 to 230 °C: HCS<sub>r(1)</sub> → bH<sub>2</sub>S + cHO HCS<sub>r(2)</sub> → bH<sub>2</sub>S + cHO HCS<sub>r(3)</sub> → bH<sub>2</sub>S + cHO</p> <p>230 to 250 °C: HCS<sub>r(1)</sub> → bH<sub>2</sub>S + cHO HCS<sub>r(2)</sub> → bH<sub>2</sub>S + cHO HCS<sub>r(3)</sub> → bH<sub>2</sub>S + cHO HCS<sub>r(4)</sub> → bH<sub>2</sub>S + cHO</p> <p>170 to 190 °C: Sand<sub>r(1)</sub> → CO<sub>2</sub></p> <p>190 to 210 °C: Sand<sub>r(1)</sub> → CO<sub>2</sub> Sand<sub>r(2)</sub> → CO<sub>2</sub></p> <p>210 to 230 °C: Sand<sub>r(1)</sub> → CO<sub>2</sub> Sand<sub>r(2)</sub> → CO<sub>2</sub> Sand<sub>r(3)</sub> → CO<sub>2</sub></p> <p>230 to 250 °C: Sand<sub>r(1)</sub> → CO<sub>2</sub> Sand<sub>r(2)</sub> → CO<sub>2</sub> Sand<sub>r(3)</sub> → CO<sub>2</sub> Sand<sub>r(4)</sub> → CO<sub>2</sub></p> <p>Rate(H<sub>2</sub>S) = k<sub>1</sub>(T)[COMP1][H<sub>2</sub>O] Rate(CO<sub>2</sub>) = k<sub>1</sub>(T)[COMP2][H<sub>2</sub>O]</p> <p>where COMP1 = pseudo-component in bitumen that produces H<sub>2</sub>S COMP2 = pseudo-component in bitumen that produces CO<sub>2</sub></p>	
Ibatullin et al. [49]	Develop practical approach to simulate and forecast H <sub>2</sub> S and CO <sub>2</sub> production during thermal recovery using common reservoir simulation tools	-	<ul style="list-style-type: none"> <li>• COMP1</li> <li>• COMP2</li> <li>• H<sub>2</sub>S</li> <li>• CO<sub>2</sub></li> <li>• H<sub>2</sub>O</li> </ul>		
Kapadia et al. [50,51]	Develop new kinetic model for aquathermolysis of Athabasca bitumen which has the ability to predict acid gases such as hydrogen sulfide and carbon oxides and fuel gases such as methane and hydrogen	-	<ul style="list-style-type: none"> <li>• CH<sub>4</sub></li> <li>• Bitumen</li> <li>• Methane</li> <li>• Hydrogen</li> <li>• Carbon monoxide</li> <li>• Carbon dioxide</li> <li>• Hydrogen Sulfide</li> <li>• Heavy Molecular Weight Gas</li> </ul>		



aquathermolysis. Hence, at the reservoir scale, the generated gas has huge impact on steam partial pressure which is key element for heat delivery to the native reservoir and hence bitumen mobilization. To study this effect, one needs detailed and accurate estimation of total gas produced, along with its composition, during in situ steam stimulation of bitumen reservoirs. The main by-product of aquathermolysis of concern with respect to safety is hydrogen sulfide which is a toxic gas and thus it must be contained and handled on surface after it is produced to surface from the reservoir. In most cases, the hydrogen sulfide is combusted to form sulfur dioxide or recovered as elemental sulfur by using the Claus process.

### 3.2.2. 1980 to 1989

The focus of research on aquathermolysis in the 1980s was on batch-style experimental tests to determine reaction products and reaction models and the origin of hydrogen sulfide from aquathermolysis. Many of the experimental studies were foundational ones laying the groundwork for bitumen aquathermolysis research. Over this period of time, none of the research was targeting in situ aquathermolysis reactions for steam-based recovery processes.

Hyne et al. [35] conducted aquathermolysis experiments of bitumen in Hastelloy autoclaves and quartz tubes. The comparison of the gas produced from aquathermolysis experiments carried out in Hastelloy autoclave to that in quartz tube showed that the rate of gas production was catalyzed by the wall of the Hastelloy autoclave whereas the equilibrium values of produced gas concentrations were roughly the same. They demonstrated the similarity of gaseous products evolved during aquathermolysis of Athabasca bitumen with that of model organosulfur compounds such as thiolane and thiophene and showed that organosulfur species in bitumen were the principal initiators of the aquathermolysis sequence.

Clark and Hyne [36] found that carbon dioxide was the major gas product during aquathermolysis which they assumed to arise from decomposition of mineral carbonates, decarboxylation of humic acids in the oil sand, and aquathermolysis of organosulfur compounds. They proposed stoichiometrically unbalanced reactions for the aquathermolysis of Athabasca bitumen without kinetic parameters (i.e., Arrhenius constants). Their proposed reaction scheme involved the presence of minerals to include the catalytic effect of sand matrix. Comparison of hydrogen sulfide production from oil sand to that from bitumen showed that the oil component produced considerable hydrogen sulfide. Also, comparison of in-quartz and in-vessel whole core experimental results with separated oil experimental results showed that water–gas shift reaction was promoted by the mineral component of the oil sand.

Hyne [37] proposed the concept of the aquathermolysis “window” (<350 °C) wherein aquathermolysis appears to be the predominant form of chemical reaction for heavy oil and bitumen. In the aquathermolysis window there is little or no conversion of liquid to a solid deposit (coke) and gas production is smaller compared to the behavior above 300 °C (beyond 300 °C, thermal cracking reactions dominate with breakage of heavier molecules reflecting into the increasing amount of production of solid material “coke” and gas, even in the presence of water). Aquathermolysis reactions were considered to be happening upon production of reaction species from organosulfur compounds which then polymerized or reacted with water to yield smaller fragments. This work described various mechanisms and sources for the production of acid gases such as carbon dioxides and hydrogen sulfide during aquathermolysis. The effect of water gas shift reaction was also studied by modulating the carbon monoxide concentration in the mixture of gases produced during aquathermolysis.

Monin and Audibert [38] studied the thermal alteration of four crude oils with different geochemical compositions in the presence of water and mineral matrix representative of reservoir rocks. The products of thermal treatments were categorized into gas, oil, and solid they referred to as pyrobitumen. All the experiments were carried out in an autoclave with an internal volume of 300 cm<sup>3</sup> made of Hastelloy at

temperature equal to 350 °C for 200 h. Analysis of the evolved gas showed the presence of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub>, and H<sub>2</sub>S. The results of the experiments indicated that thermal cracking reactions were occurring along with aquathermolysis reactions. The emphasis of the research was to distinguish catalytic effects of different minerals (e.g. sand, calcite, kaolinite) during aquathermolysis. The results revealed that different minerals gave different catalytic effects with common observation in all of them that all of the minerals enhanced the rate of reaction. Experimental results obtained by Monin and Audibert cannot be used to develop aquathermolysis reaction scheme since all experiments were carried out only at 350 °C and also at this temperature pyrolysis co-exists with aquathermolysis [37].

### 3.2.3. 1990 to 1999

On aquathermolysis, in the 1990s, focus shifted to reaction mechanisms with reaction schemes and kinetic parameters. However, consistency between published results was an issue and much of the documented research is still focused on batch experiments with little or no focus on in situ aquathermolysis reactions and their impact on recovery processes.

Clark et al. [39] studied the behavior of Cold Lake, Peace River, Ethel Lake and Athabasca oil sand samples in the presence of high temperature steam. Homogenized oil sand and water (1:5 oil–water weight ratio) were aquathermolized in a cap enclosure autoclave and quartz ampoules in an inert atmosphere of nitrogen. The results showed that under similar steam stimulation conditions, different oils produced different amounts of gas products. In accordance with previous experimental work, the main gas products were H<sub>2</sub>S, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and gases having two or more carbon molecules. All bitumen samples showed different reactivity when measured in terms of SARA (Saturates, Aromatics, Resins, Asphaltenes) fractions before and after high temperature steam treatment. They also concluded that the combined behaviors of the separated oil sand components, that is, bitumen and sand minerals, did not equal to the whole oil sand matrix behavior when they were subject to the same steam treatment suggesting interaction between oil sand components. This implies that to understand in situ gas generation due to aquathermolysis during steam stimulation, the kinetic study must also include steam and oil sand interaction rather than only steam and bitumen interaction.

Chen et al. [40] pyrolyzed Athabasca, Peace River, Cold Lake and Wabasca oil sand samples in the presence of varying amounts of water (0 to 20 wt.%) at 250 and 300 °C for 3, 7 and 14 days in sealed, evacuated quartz tubes. The main products obtained from the experiments were bitumen, light oil (C<sub>8</sub> to C<sub>14</sub> hydrocarbons), and gas products (CO<sub>2</sub>, C<sub>1</sub>–C<sub>7</sub> hydrocarbons, H<sub>2</sub>S, H<sub>2</sub> and CO). The oil phase that resulted from their experiments had lower viscosity and asphaltene content and increased maltene content than that of the original oil. These changes were strong functions of temperature and weak functions of water content in the experiments. On the contrary, the CO<sub>2</sub> evolution demonstrated strong dependence on amount of water present during the aquathermolysis experiments, which is consistent with observation made by Clark et al. [39]. Chen et al. evaluated kinetic parameters for gas component evolution but did not propose a suitable reaction scheme for aquathermolysis.

Belgrave et al. [41] carried out an aquathermolysis (as suggested by the title of the paper) gas evolution study on Athabasca bitumen, North Bodo oil and Frisco Countess oil. Experiments conducted on Athabasca bitumen included runs with an initially pre-oxidized oil sample and two samples of bitumen mixed with different minerals. A 200 g sample of premixed core was placed into a quartz glass tube (placed in stainless steel reaction vessel) and subjected to high temperatures in the presence of steam. The products of aquathermolysis were gas, light oil (fraction boiling below 300 °C), heavy oil (300 °C plus fraction), asphaltenes, and coke. The experiments were conducted at 360, 397 and 420 °C. The gas evolved during the experiments contained H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>3+</sub> (group of hydrocarbons ranging from C<sub>3</sub>H<sub>8</sub> to C<sub>6</sub>H<sub>14</sub>).

The presence of coke and higher temperatures (>350 °C) are indicative of pyrolysis reactions and thus, the experiments and results do not pertain strictly to aquathermolysis alone. By using these experimental data, Belgrave et al. [42] developed a thermal cracking reaction model to describe the liquid and gas phase compositional changes. The results of the model demonstrated some scatter but followed the trend for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3+</sub> experimental data. The model showed poor matches for carbon oxides but reasonable matches for H<sub>2</sub>S and H<sub>2</sub> production. Also, the model did not allow for reactions among the products such as water gas shift and coke gasification reactions.

#### 3.2.4. Latest developments: 2000 to 2012

Over the past decade, aquathermolysis research has focused more on the development of detailed reaction schemes and associated kinetic parameters with increasing focus on in situ generation of hydrogen sulfide and its impact on the recovery process with respect to oil production rates and handling of hydrogen sulfide. In particular, this has been greatly enabled by measurements of hydrogen and hydrogen sulfide generation rates from in situ oil sand operations.

Lamoureux-Var and Lorant [43] studied the evolution of H<sub>2</sub>S with and without the presence of steam and oil sand matrix during aquathermolysis experiments conducted over a temperature range of 240 to 320 °C for 203 h. H<sub>2</sub>S generation drastically increased when the temperature exceeded about 240 °C whereas other gas components, H<sub>2</sub>, C<sub>1</sub>, and C<sub>2</sub>–C<sub>4</sub>, showed marked increase beyond about 280 °C indicating onset of thermal cracking reactions. The presence of steam contributed hydrogen to fuel gas generated during aquathermolysis. Experimental results indicated strong correlation between the amount of H<sub>2</sub>S generated and the labile organic sulfur content of the Athabasca oil sands. Although the experiments conducted in this research work provided a detailed account of various mechanisms during steam bitumen chemical interaction, a kinetic model to predict gas production during steam stimulation of bitumen on reservoir scale was not developed.

Lamoureux-Var and Lorant [44] experimentally studied and subsequently proposed a compositional kinetic model for distribution of sulfur in saturates, aromatics, resins, asphaltenes, insolubles (solid phase in oil sands), and gas phase before and after aquathermolysis of Athabasca bitumen at temperatures ranging from 240 to 320 °C. They quantitatively showed that, before aquathermolysis, sulfur in oil sands was mainly present in resins, asphaltenes and aromatics whereas, as aquathermolysis progressed, sulfur in asphaltenes and resins converted to accumulate mainly in insolubles and to a lower extent in the gas phase, as H<sub>2</sub>S, and aromatics. From the experimental observations, H<sub>2</sub>S generation was correlated as a function of time, temperature, oil sand sulfur properties, and kinetic parameters (conversion of sulfur in asphaltenes, resins, aromatics, and insolubles). Lamoureux-Var and Lorant proposed that the kinetic parameters (~10 of them) of the kinetic model can be estimated from experimental data to quantify H<sub>2</sub>S evolution during aquathermolysis. Although the model proposed by Lamoureux-Var and Lorant is thorough, it does not include the effect of water saturation on reaction rates. Also, predictions from this model require to be verified against field observations.

Thimm [45,46] derived simple solubility-based models to predict hydrogen sulfide content in the produced gas for Athabasca bitumen. Thimm used a zero-order reaction rate equation to determine hydrogen sulfide concentration and estimated Arrhenius parameters from Chen et al.'s [40] and Hyne's [37] experimental data. Although the prediction of hydrogen sulfide concentration was in good agreement with field data, the model does not allow for understanding the reactive zones in the reservoir as the process evolves. Thimm also carried out the measurements of H<sub>2</sub>S and CO<sub>2</sub> in field and found that the amount of carbon dioxide measured appears to show a minimum near 195 °C, indicating that aquathermolysis is not the only mechanism for CO<sub>2</sub> generation,

whereas the amount of H<sub>2</sub>S detected grows larger as the temperature rises.

Analysis of the gas evolved during SAGD operation of ConocoPhillips [47] Surmont Project Pilot and Phase 1 commercial operation revealed the presence of CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, N<sub>2</sub>, He, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4+</sub> components. During their study of aquathermolysis, during SAGD operation, ConocoPhillips found that below about 235 °C of steam injection temperature, hydrogen sulfide generation per unit mass of bitumen produced increased almost linearly with respect to steam injection temperature whereas above about 235 °C of steam injection temperature hydrogen sulfide generation increased almost exponentially.

Perez-Perez et al. [48] proposed a kinetic model for the evolution of H<sub>2</sub>S from organosulfur compounds contained in resins and asphaltenes of bitumen. Similarly, a kinetic model was proposed for the evolution of CO<sub>2</sub> from rocks accompanying bitumen. They assumed that aquathermolysis reactions reached equilibrium after 90 days and kinetic models were constructed to predict gas generation plateaus as a function of temperature as observed in the laboratory. These kinetic models were integrated in homogeneous SAGD simulation models to evaluate H<sub>2</sub>S and CO<sub>2</sub> generation due to aquathermolysis. In total, 13 components were included in their model. CH<sub>4</sub> and H<sub>2</sub>S were sourced in bitumen whereas CO<sub>2</sub> was sourced in the water. H<sub>2</sub>S and CO<sub>2</sub> were both soluble in water and oil phase. To achieve matches versus temperature, Perez-Perez et al. altered the reaction scheme versus temperature. Although the proposed kinetic model is complex in nature and omits the generation of other gases like H<sub>2</sub>, CH<sub>4</sub>, CO and C<sub>2+</sub> gas compounds, also observed during bitumen steam stimulation, the predictions from the model showed a good match with the experimental and field data, both from literature.

Ibatullin et al. [49] simulated the evolution of H<sub>2</sub>S and CO<sub>2</sub>, by using two second order reactions during SAGD operation in bitumen reservoirs. In their kinetic modeling, bitumen was split into reacting and non-reacting pseudo-components called COMP1 and COMP2, respectively. The rate of evolution of H<sub>2</sub>S was considered to be proportional to the concentrations of COMP1 and H<sub>2</sub>O whereas that of CO<sub>2</sub> was considered to be proportional to the concentrations of COMP2 and H<sub>2</sub>O. Kinetic parameters for the model were taken from the published literature. The model does not predict hydrogen, methane, carbon monoxide or fuel gas generation. Simulation model included solubility of H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub> into both oil and water phases. The results of their simulation indicated that the amount of sour gases produced per unit amount of bitumen increased with the growth of steam chamber with increasing accumulation at the top of reservoir.

Kapadia et al. [50,51] proposed new kinetic model for the aquathermolysis of Athabasca bitumen. This kinetic model was developed from the experimental observations of Hyne et al. [35], Clark and Hyne [36], Hyne [37], Clark et al. [39], and Chen et al. [40]. As observed in the laboratory, the proposed reaction scheme took into account the distribution of activation energy along with the possibility of chemical interaction among the products of aquathermolysis. The reaction scheme predicted composition of gas evolved during independently conducted aquathermolysis experiments. It was also observed that the kinetic parameters obtained from laboratory scale experiments required further tuning in order to predict gas evolution during steam stimulation of bitumen. Reaction scheme was also validated against wide range of laboratory and field data. To be complete, the model should be augmented to allow for the effect of bitumen composition on the steam–bitumen interaction.

### 3.3. Oxidation

#### 3.3.1. Overview

Oxidation of bitumen is complex and for Athabasca bitumen it is broadly classified into LTO and HTO. LTO reactions are dominant in



temperature range from 150 to 300 °C and products formed during LTO reactions are water, carbon oxides and oxygen-containing compounds such as carboxylic acids, aldehydes, ketones, alcohols, hydroperoxides [52]. When temperature is higher than 300 °C, bitumen starts to pyrolyze rapidly forming solid constituents called coke which gets combusted at higher temperature if sufficient oxygen is present and principle products are carbon oxides and H<sub>2</sub>O. Additionally, smaller molecules formed during pyrolysis are oxidized. HTO reactions basically supply most of the heat to sustain system of multiple reactions during in situ combustion of bitumen. During bitumen oxidation experiments conducted in the laboratory, in addition to the physical properties of the bitumen, the measurements are usually performed for oxygen uptake rates and the effect of temperature and partial pressure of oxygen on bitumen composition. There have been few attempts to understand the underlying mechanisms of bitumen oxidation in terms of change in species constitution with the generation or disappearance of certain species. As for pyrolysis studies, the main objectives of Athabasca bitumen oxidation studies have been to determine gas and solid products and to fit the experimental data to a reaction scheme. Table 3 summarizes the previous works on low temperature oxidation of Athabasca bitumen.

### 3.3.2. 1970 to 1989

Over this period of time, the main focus of the research documented in publications was to determine oxygen uptake rates, the temperature ranges of different sets of oxidation reactions and the changes in bitumen composition and to formulate pseudo-mechanistic systems of reaction equations.

Moschopedis and Speight [53] showed that the asphaltene content of the bitumen increased with temperature and duration of the air injection. Air injection also led to the formation of new resins from the bitumen simultaneously with its conversion to asphaltenes. Compositional analysis of the original bitumen and products indicated that condensation of saturates and/or aromatics to higher molecular weight material, like asphaltenes, was one of the transformations that occurred during the oxidation of bitumen at elevated temperatures.

Babu and Cormack [54] quantitatively revealed that low temperature oxidation of bitumen significantly increased fuel availability consequent on LTO. Also, they found that as the extent of oxidation increased, so too did the coke yield on subsequent rapid pyrolysis. The yield of coke residue decreased with increasing amount of sand during the oxidation. Babu and Cormack [55] indicated three different regimes of oxidations:

1. High rate first order regime (low extents or at the beginning of the oxidation experiments below 423 K),
2. Second order regime (low extents or at the beginning of the oxidation experiments above 423 K), and
3. Low rate first order regime (high extents or during the end of the oxidation experiments over the entire temperature range investigated).

An explanation of the transition from Regimes 1 to 3 is described in Burger and Sahuquet [52]. The experimental results also indicated that the mineral sand accompanying bitumen had no strong catalytic effect on the oxidation kinetics.

Results of low temperature oxidation (LTO) experiments conducted by Babu and Cormack [56] showed similarity with those obtained by Moschopedis and Speight with respect to bitumen composition. The saturate fraction of the bitumen did not change considerably during LTO. The aromatic fraction showed a steady decrease whereas the asphaltene fraction showed an increase with the extent of oxidation. The resin fraction decreased with the onset of oxidation then increased to maximum value and then again started decreasing with the extent of oxidation. The results suggested that the aromatic fraction is converted to resins which in turn were converted to asphaltenes.

Phillips and Hsieh [57] proposed two kinetic models for the oxidation of bitumen as listed in Table 3. They found that the oxidation reaction of bitumen is first order with respect to oxygen and volumes of CO and CO<sub>2</sub> produced were strong function of temperature. These kinetic models can predict gas composition but no stoichiometric coefficients were reported. Also, even if oxygenated hydrocarbons are treated as a pseudo-component, one needs its physical properties to use kinetic model in numerical simulator and none are provided in the paper. Predictions from Model 2 had better agreement with the experimental data than that of Model 1.

Yoshiki and Phillips [58] examined the effects of air, pressure, heating rate and support material (alundum and sand accompanying bitumen) on low temperature oxidation (LTO), high temperature oxidation (HTO), and thermal cracking reactions by differential thermal analysis cell. Results showed that higher oxygen content favored both LTO and HTO. On the contrary, when the oxygen content is too low, LTO reactions are followed by thermal cracking reactions for a given heating rate. The rate of LTO reaction was found to be first order with respect to oxygen concentration. It was also shown that linear heating rates can be varied to control the extent of different reaction regimes (LTO, HTO, and thermal cracking) and hence fuel availability during combustion. The proposed reaction scheme in Yoshiki and Phillips' study is stoichiometrically unbalanced and does not predict product distribution with respect to time and temperature during LTO or HTO.

Adegbesan et al. [59,60] studied the effect of LTO on bitumen composition (measured in terms of SARA fractions), viscosity, and density. During LTO of bitumen, their results showed that the SARA fractions of bitumen varied with time and temperature. Production of gas only occurred at 418 and 423 K (145 and 150 °C) and contained only carbon oxides whereas there was no gas production at 333, 378, 393 and 408 K (60, 105, 120, and 135 °C) temperatures. Results of the experiments indicated that oxidation of maltenes and asphaltenes resulted in the formation of more asphaltenes and coke components. This observation is in agreement with findings of Moschopedis [53] and Speight and Baba and Cormack [54–56]. The results also showed that the density and viscosity of the oil phase increased with the extent of oxidation. The predictions of pseudo-mechanistic model proposed by Adegbesan et al. showed good matches with experimental data.

Millour et al. [61] showed that oxygen uptake rates during Athabasca bitumen oxidation exhibited a distribution of activation energies within the experimental temperature range considered. The experiments conducted at different temperatures showed that the oxygen uptake rate did not follow typical Arrhenius behavior. Also, three regions of oxidation of bitumen were defined based on experimental data.

- Region I (oxygen uptake < 0.04 g of O<sub>2</sub>/g of bitumen): dominant reaction is conversion of maltenes to asphaltenes with very low coke formation.
- Region II (0.04 < oxygen uptake < 0.2 g of O<sub>2</sub>/g of bitumen): dominant reaction is conversion of asphaltenes to coke.
- Region III (oxygen uptake > 0.2 g of O<sub>2</sub>/g of bitumen): dominant reactions are coke oxidation and conversion of maltenes to coke.

Adegbesan et al.'s model was demonstrated to reasonably represent Region I experimental data for bitumen composition. Millour et al. proposed an implicit kinetic model to describe maltenes, asphaltenes, and coke concentrations in Region II. The implicit nature of kinetics requires further investigation to find out if the extent of reaction effect can be incorporated into the Arrhenius equation to represent the entire range of oxygen uptake data.

Barta and Hepler [62] also indicated two regimes of oxidation reactions for Athabasca bitumen. For temperatures less than about 285 °C, the predominant reaction of bitumen with oxygen led to deposition of

coke whereas for temperatures greater than about 285 °C, the heavy residue left on porous medium by distillation of light fractions converted completely to carbon oxides and water indicating complete combustion. Barta and Hepler also carried out energetics of bitumen oxidation in that they correlated heat of oxidation reaction to the temperature and partial pressure of oxygen by using factorial design. They also found that oxidation reaction order depended on temperature demonstrating the extent of reaction effect as described earlier by Lin et al. [28] for thermal cracking reactions.

Goulet [63] performed isothermal LTO experiments on Athabasca bitumen to study the effect of air flux on bitumen composition. These experiments were carried out in plug flow reactor at a temperature of 150 °C, gauge pressure of 4137 kPa and for oxidation periods of 12 and 24 h. Air flux was varied from 8 to 126 m<sup>3</sup> (STD)/(m<sup>2</sup> h). During these experiments coke deposition, evolved gas composition, concentration of asphaltenes and oil saturations were measured with respect to air flux. During all the experiments, the oxygen uptake rates remained constant up to about 7 h and decreased considerably towards the end of the experiment and the rate of coke formation accelerated when air flux was increased. Similarly, the rate of asphaltenes consumption increased (as compared to its rate of formation due to LTO) considerably when air flux was increased. Goulet observed that the implicit model proposed by Millour [61] failed to predict the amount of coke formed during LTO whereas, the model reasonably predicted the yields of maltenes and asphaltenes.

### 3.3.3. 1990 to 1999

In the 1990s, research shifted to evaluating burning characteristic of bitumen and fuel (coke) generated in the laboratory combustion tube test experiments. Combustion tube experiments provided good basis for validation of reaction schemes developed earlier.

Moore et al. [64] performed combustion-tube tests to evaluate the effect of enriched air (95% oxygen) injection on combustion behavior of Athabasca bitumen. The results of their study show that by increasing the total pressure of the combustion-tube tests resulted in increased low temperature reactions. This resulted in higher fuel formation leading to higher burn instability. An increase of the total pressure also resulted in higher oxygen requirements. They also examined the effect of water injection on fuel availability during combustion-tube tests.

Moore et al. [65] showed the presence of the so-called negative temperature gradient region (NTGR) between 370 and 500 °C for Athabasca bitumen by using ramped-temperature oxidation (RTO) tests. In this temperature range, even though bitumen is in the presence of excess oxygen, the oxygen uptake rates and hence energy formation rates from oxidation reactions decrease with an increase of temperature. Oxidation of bitumen below the NTGR was found to be mass transfer controlled whereas that above NTGR was controlled by oxygen availability. The results of RTO experiments also suggested that significant oxygen uptake and hence energy generating reactions started above about 170 °C for Athabasca bitumen. In later research, Moore et al. [66,67] described the oxidation characteristic of Athabasca bitumen by RTO experiments. Among feed oxygen concentration, total gas injection flux, and operating pressure, gas injection flux was found to be the key parameter to transition from a low temperature oxidation regime to a high temperature combustion regime. Lower gas injection flux was shown to be insufficient to overcome NTGR for achieving high temperature combustion. RTO tests that exhibited a high temperature combustion zone also had improved oil recovery. Moore et al. also observed coke formation as dominant process during low temperature oxidation of bitumen. Although, a series of combustion tube tests performed by Moore et al. described the effects of temperature, oxygen partial pressure, and water injection on fuel availability and fire-front stability and characteristics, there was no attempt to model combustion-tube experiments by using intrinsic kinetics and transport phenomena.

Stipanov [68] proposed a kinetic model describing LTO and HTO of Athabasca bitumen. The stoichiometric coefficients and kinetic parameter for the proposed reaction scheme were then estimated by history matching several RTO and LTO experiments. A simulation model was constructed for non-isothermal, integral, plug-flow reactor with Arrhenius-type rate equation incorporated into the model. The reaction rate equations were assumed to be first order with respect to oxygen partial pressure and heavy oil concentration. The LTO simulation model consisted of three simultaneous irreversible reactions whereas the HTO model used single, irreversible reaction involving combustion of coke to carbon oxides, methane and water. An examination of Stipanov's proposed LTO reaction scheme reveals that it has two oxidation reactions with one low temperature thermal cracking reaction.

### 3.3.4. Latest developments: 2000 to present (2013)

Over the past decade, there is no significant development as far as oxidation reaction scheme is concerned. Instead, focus shifted more towards the technology which can enable in situ upgrading of bitumen.

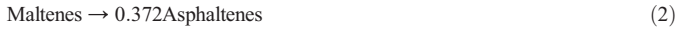
Xu et al. [69] experimentally studied the effect of oxygen partial pressure, temperature, reaction time, agitation, and the presence of rock and brine on upgrading (measured in terms of viscosity) of Athabasca bitumen during two-stage LTO process. During the first stage (low temperature soak, LTS) of the process, the bitumen sample was exposed to oxygen at varying temperatures. In the second stage, referred to as the extended temperature soak stage (ETS), the reacting mixture from the first stage was exposed to higher temperature (as per Table 3). The results of their experiments indicated that shorter LTS oxidation periods (six days), longer ETS periods (nine days), lower LTS temperatures (80 °C), higher ETS temperatures (220 °C), agitation, and presence of distilled water (rather than brine) promoted oil viscosity reduction. Jia et al. [70] extended Xu et al.'s experimental work to include additionally the effect of air and nitrogen on composition of Athabasca bitumen during LTS and ETS. The results, under the same experimental conditions, indicated that the presence of nitrogen during LTS and ETS enhanced bitumen upgrading (measured in terms of viscosity), increased the coke content and decreased the asphaltene content as compared to the case when air was present during LTS and ETS. The results also indicated a low extent of thermal cracking reactions below 220 °C.

Khansari et al. [71] conducted low temperature oxidation (LTO) of Alaskan heavy oil samples between 100 and 350 °C by using a TGA. Their experimental results suggested that there are four temperature intervals over which different modes dominate the LTO process. The data shows that over the first temperature interval, ranging from 100 to 150 °C, and the third interval, ranging from 200 to 250 °C, the reactions are endothermic. In the second zone, from 150 to 200 °C, and the fourth sub-zone, from 250 to 350 °C, the reactions are exothermic. They observed that the peak LTO rate occurs in the fourth interval, between 250 and 350 °C, and that a NTGR occurs where the greater the temperature, the lower is the reaction rate. Khansari et al. [72] extended their previous study by developing a numerical model where pseudo-components of the LTO subintervals were identified from comparisons to elemental analysis. However, they did not have gas and liquid component data and thus their proposed reaction scheme still requires validation for gas and liquid products.

## 4. Comprehensive reaction scheme for in situ combustion

The literature review done so far has focused individually on pyrolysis, aquathermolysis, and oxidation of Athabasca bitumen. There are few studies in literature which deal with comprehensive approach to model kinetics of in situ combustion process. Among these studies, Belgrave et al. [73] for the first time introduced comprehensive

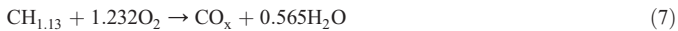
pseudo-mechanistic kinetic model for in situ combustion modeling. This kinetic model consolidated experimental kinetic studies on thermal cracking, low temperature oxidation of Athabasca bitumen along with high temperature oxidation of coke. The model used maltenes, asphaltenes, coke and gas as pseudo-components. Based on Hayashitani et al.'s experimental data, the proposed thermal cracking reaction scheme was as follows:



Similarly, based on Adegbesan et al.'s experimental data, the proposed LTO reaction scheme was given by:



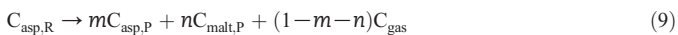
The coke high temperature reaction scheme was expressed by [74]:



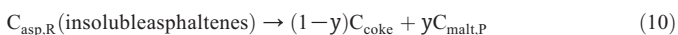
where  $\text{CO}_x$  is a lumped pseudo-component for carbon oxides. Six reactions were proposed to model in situ combustion reactions for use in a thermal numerical simulator. However, the proposed kinetic model did not include the possibilities of aquathermolysis reactions and reactions among the products which can occur during in situ combustion process.

Coates et al. [75] simulated top down in situ combustion process on laboratory scale by using Belgrave et al.'s kinetic model (Eqs. (2) to (7)). The kinetic parameters were obtained from Belgrave et al.'s paper whereas stoichiometric coefficients were recalculated by using molecular weight of components and pseudo-components. This modified kinetic model was then used by Coates and Zhao [76] to simulate, for the first time, Toe-to-Heal Air Injection (THAI) process for combustion of Athabasca bitumen. THAI process consists of two horizontal wells. The injector is placed normal to horizontal producer [77]. Coates and Zhao history-matched THAI laboratory experiments and predicted field scale performance of THAI process.

Jia et al. [78] used kinetic model originally proposed by Wiehe [79] for coke formation during thermal cracking of Cold Lake bitumen vacuum residue, to model thermal cracking and LTO of Athabasca bitumen. Jia et al. proposed that during the coke-induction period, the reactant asphaltenes form only lower molecular weight products like gas and maltenes. Additionally, if the formation of asphaltenes from maltenes is beyond its solubility limit in maltenes, then excess asphaltenes will react to form coke. The coke-induction period was modeled by two first-order reactions:



where,  $a$ ,  $m$ , and  $n$  are stoichiometric coefficients. After the production of asphaltenes causes it to exceed its solubility limit, then excess asphaltenes will react to form coke as per the following reaction:



where,  $y$  is a stoichiometric coefficient. Jia et al. proposed four first-order reactions for thermal cracking and LTO of Athabasca bitumen,

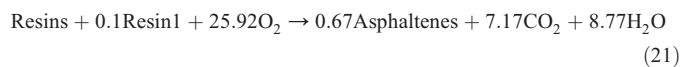
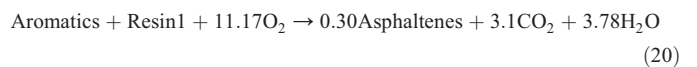
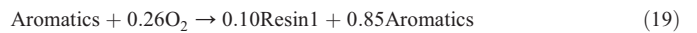


In the above reactions, the subscripts asp, malt, gas, and coke represent asphaltenes, maltenes, product gas and product coke, respectively whereas, subscripts P, R, and SR represent product, reactive, and slow-reactive component, respectively. The proposed reaction scheme was then used to predict thermal cracking and LTO experimental data of Hayashitani et al. [15,27], Adegbesan et al. [59,60], Millour et al. [30,61], and Xu et al. [69]. The model predictions are in good agreement with published experimental data but it has many pseudo-components to be characterized. Although Jia et al.'s kinetic model can effectively model coke delay; this model fails to predict gas composition during in situ combustion. Additionally, there is no information provided on the properties of pseudo-components which limits its applicability to numerical simulation models.

Sequera et al. [80–82] reinterpreted the model proposed by Jia et al. [78] and replaced slow reactive maltenes, reactive maltenes, product maltenes by aromatics, resins, and saturates, respectively. Sequera Marin et al. proposed the following LTO reaction scheme (Model LTO 1):



Model LTO 1 was used to match Adegbesan et al.'s [59,60] isothermal and Moore et al.'s [83] RTO experiments. Model LTO 1 could not match all of the Adegbesan et al.'s experimental data by using single set of kinetic parameters. Coke delay was modeled by using partial equilibrium feature available in the commercial thermal reservoir simulator used in the research, in which coke formation was related to the asphaltenes solubility limit in maltenes. Since, Model LTO 1 could not satisfactorily model RTO experiment, an improvement to Model LTO 1 was proposed by introducing new intermediate component called Resin1. This new model was labeled as Model LTO 2 and is described by:



Model LTO 2 excluded the saturate oxidation reaction (Eq. (18)) in the LTO 1 model. The saturate oxidation reaction generated a large

**Table 3**  
Summary of low temperature oxidation studies on Athabasca bitumen.

Reference	Purpose of study	Experimental conditions	Components or pseudo-components	Proposed reaction scheme
Moschopedis and Speight [53]	Study the effect of air blowing on the properties and constitution of bitumen	Known weight of bitumen was bubbled with air at a rate of 2 to 3 cm <sup>3</sup> /(min g of bitumen) in a two-necked round-bottom flask at the temperatures of 260, 290 and 320 °C.	<ul style="list-style-type: none"> <li>• Asphaltenes</li> <li>• Resins I</li> <li>• Resins II</li> <li>• Saturates</li> <li>• Aromatics</li> <li>• Coke</li> </ul>	–
Babu and Cormack [54]	Examine quantitatively the effect of low temperature oxidation on ultimate coke residue from Athabasca bitumen	Around 200 g of bitumen (with or without sand) was oxidized with mixture of nitrogen and oxygen (10 wt.%) at pressure and temperature of 3.5 MPa and 125 °C respectively in stainless steel, stirred autoclave.	–	–
Babu and Cormack [55]	Investigate kinetics of low temperature oxidation in Athabasca oil sands	0.2 kg of bitumen was oxidized in stainless steel reaction vessel placed inside autoclave over temperature range of 373 to 459 K (100 to 186 °C)	–	–
Babu and Cormack [56]	Examine effect of low temperature oxidation on the composition of Athabasca bitumen	200 g of bitumen (with or without sand) was oxidized with the mixture of nitrogen and oxygen (10 wt.%) at pressure of 3.5 MPa and over temperature range of 125 to 135 °C.	<ul style="list-style-type: none"> <li>• Asphaltene</li> <li>• Resin</li> <li>• Saturates</li> <li>• Aromatic</li> <li>• Bitumen</li> <li>• CO</li> <li>• CO<sub>2</sub></li> <li>• H<sub>2</sub>O</li> <li>• Oxygenated hydrocarbons</li> <li>• Bitumen</li> <li>• H<sub>2</sub>O</li> <li>• Oxygenated hydrocarbons</li> <li>• Saturates</li> <li>• Aromatics</li> <li>• Oils</li> <li>• Resins I</li> <li>• Resins II</li> <li>• Asphaltenes</li> <li>• Coke</li> </ul>	Oils → resins → asphaltenes
Phillips and Hsieh [57]	Investigate oxidation reaction kinetics of bitumen from Athabasca oil sands	100 g sample of oil sands was oxidized in fixed bed reactor at pressure of 400 kPa and temperatures from 175 to 300 °C	–	<p><i>Model 1</i> Bitumen + O<sub>2</sub> → CO + CO<sub>2</sub> + H<sub>2</sub>O + oxygenated hydrocarbons</p> <p><i>Model 2</i> Bitumen + O<sub>2</sub> → H<sub>2</sub>O, oxygenated hydrocarbons Bitumen + O<sub>2</sub> → CO + CO<sub>2</sub> Bitumen + O<sub>2</sub> → H<sub>2</sub>O, oxygenated hydrocarbons</p>
Yoshiki and Phillips [58]	Examine qualitatively and quantitatively the thermo-oxidative and thermal cracking reactions of Athabasca bitumen using differential thermal analysis (DTA)	1.0 g sample of 30 wt.% bitumen in 250 μm Norton alundum was treated in cell for 2.8 to 24.0 °C/min heating rate (up to 900 °C)	–	–
Adegbesan et al. [59,60]	Develop low temperature oxidation reaction model for Athabasca bitumen that can be used in numerical simulators of in situ combustion	Feed gas having oxygen was bubbled through liquid bitumen in semi-batch stirred reactor at temperature from 333 to 423 K (60 to 150 °C). The total pressure applied during low temperature oxidation of bitumen ranged from 2190 to 4415 kPa.	–	<p><i>Model C-1</i> Bitumen + O<sub>2</sub> → products</p> <p><i>Model C-2</i> Maltenes → asphaltenes–coke</p> <p><i>Model C-3</i> Oils → resins → asphaltenes–coke</p> <p><i>Model C-4A</i> Oils → resins I → asphaltenes–coke Oils → resins II → asphaltenes–coke</p> <p><i>Model C-4B</i> Oils → resins I → resins II → asphaltenes–coke where, maltenes = saturates + aromatics + oils + resins (Coke)<sup>0.5</sup> = –0.00256 (maltenes) (Asphaltenes) + 7.76; for Region II (Coke)<sup>2</sup> = k ln(t/t<sub>0</sub>); for Region II and III Maltenes → asphaltenes–coke; for Region I</p>
Millour et al. [61]	Develop implicit compositional model for low temperature oxidation of Athabasca bitumen	Low temperature oxidation experiments were conducted in plug flow reactor at total pressure of 4190 kPa. The experiments included wider temperature range (22 to 275 °C)	<ul style="list-style-type: none"> <li>• Asphaltenes</li> <li>• Maltenes</li> <li>• Coke</li> </ul>	–

(continued on next page)



Table 3 (continued)

Reference	Purpose of study	Experimental conditions	Components or pseudo-components	Proposed reaction scheme
Barta and Hepler [62]	Apply factorial experimental design to measurements of Athabasca bitumen oxidation rates	Experiments were conducted in porous medium under nearly isothermal conditions in temperature range of 155 to 320 °C and in flowing gas atmosphere of pure oxygen at 400 kPa absolute pressure.	<ul style="list-style-type: none"> <li>• Bitumen</li> <li>• Coke</li> <li>• Chemical products</li> </ul>	Coke + asphaltenes + maltenes = 100 Bitumen + O <sub>2</sub> → coke + chemical products + heat Bitumen + coke + O <sub>2</sub> → chemical products + heat
Goulet [63]	Study the effects of air flux on the LTO of Athabasca bitumen using isothermal plug flow experiments	Athabasca sand, bitumen and distilled water were premixed in the proportion of 82.9, 13.2, and 3.9 wt.% respectively. Oil sand samples were subjected to isothermal LTO experiments conducted at temperature of 150 °C and gauge pressure of 4137 kPa. The air flux was varied from 8 to 126 m <sup>3</sup> (ST)/(m <sup>2</sup> h) for oxidation periods of 12 to 24 h.	<ul style="list-style-type: none"> <li>• Maltenes</li> <li>• Asphaltenes</li> <li>• Coke</li> <li>• CO<sub>2</sub></li> <li>• CO</li> <li>• O<sub>2</sub></li> </ul>	–
Moore et al. [64]	Study enriched-air in situ combustion through combustion tube tests	10 combustion tube tests were conducted on Athabasca bitumen with 95% oxygen into feed gas with total pressure ranging from 2760 to 10,300 kPa.	–	Oxygen uptake (Sm <sup>3</sup> /m <sup>3</sup> ) = 1.518 (oxygen partial pressure) <sup>0.45</sup>
Moore et al. [65]	Study low and high temperature oxidation mechanisms using ramped-temperature oxidation tests	Experiments consisted of subjecting Athabasca oil sands in air flowing atmosphere in tubular reactor to linear heating rate of 20 °C/h or 40 °C/h at 4100 kPa gauge pressure.	–	–
Moore et al. [66,67]	Study oxidation and combustion characteristic of Athabasca bitumen	Experiments consisted of subjecting Athabasca oil sands in tubular reactor to linear heating rate of 40 °C/h at 867, 2525, 4190 and 7090 kPa pressures with 7, 21, and 65 mol% of oxygen in feed gas.	–	–
Stipanov [68]	Develop LTO and HTO reaction schemes by simulating and history matching Ramped Temperature Oxidation (RTO) experimental data	The active reactor in each RTO experiment was pre-mixed with approximately 200 g of core which contained 13.2 wt.% bitumen and 3.9 wt.% distilled water with two temperature set points of 260 and 350 °C in which pressure was varied from 870 to 7090 kPa. Oxygen concentration was varied from 7 to 63 vol.% whereas gas flux was varied from 14 to 105 m <sup>3</sup> (ST)/(m <sup>2</sup> h)	<ul style="list-style-type: none"> <li>• Maltenes</li> <li>• Asphaltenes</li> <li>• Coke</li> <li>• CO<sub>2</sub></li> <li>• CO</li> <li>• O<sub>2</sub></li> <li>• CH<sub>4</sub></li> <li>• H<sub>2</sub>O</li> </ul>	LTO reactions $\text{Maltenes}_{(s)} + d_1\text{O}_{2(g)} \rightarrow e_1\text{CO}_{(g)} + f_1\text{CO}_{2(g)} + g_1\text{H}_2\text{O}_{(g)}$ $\text{Maltenes}_{(s)} + d_2\text{O}_{2(g)} \rightarrow b_2\text{Asphaltenes}_{(s)} + g_2\text{H}_2\text{O}_{(g)}$ $\text{Asphaltenes}_{(s)} \rightarrow a_3\text{Maltenes}_{(s)} + c_3\text{Coke}_{(s)} + f_3\text{CO}_{2(g)} + h_3\text{CH}_4$ HTO Reaction $\text{Coke}_{(s)} + d_3\text{O}_{2(g)} \rightarrow e_4\text{CO}_{(g)} + f_4\text{CO}_{2(g)} + g_4\text{H}_2\text{O}_{(g)} + h_4\text{CH}_4$
Xu et al. [69]	Estimate optimum conditions for viscosity reduction of Athabasca bitumen using two stage low temperature oxidation process (low temperature soak followed by extended temperature soak)	100 g of samples (without core samples: 50 g bitumen + 50 g distilled water or brine, with core samples: 71 g core + 20 g bitumen + 9 g brine) in quartz lined high pressure batch reactor was subject to low temperature soak (80, 100 and 120 °C) and extended temperature soak (150, 175, 200 and 220 °C) for 4 to 18 days.	<ul style="list-style-type: none"> <li>• Asphaltenes</li> <li>• Maltenes</li> <li>• Coke</li> <li>• Gas</li> </ul>	–
Jia et al. [70]	Study bitumen compositional changes during low temperature soak and extended temperature soak in the presence of air and nitrogen	100 g of samples (50 g bitumen + 50 g water or brine) without core or 190 g of samples (71 wt.% sand + 20.4 wt.% bitumen + 8.6 wt.% brine) with core was subject to low temperature soak (80 to 120 °C) and extended temperature soak (200 to 220 °C) for 4 to 24 days.,	<ul style="list-style-type: none"> <li>• Asphaltenes</li> <li>• Maltenes</li> <li>• Coke</li> <li>• Gas</li> </ul>	–

amount of heat as compared to that of other reactions in Model LTO 1 which caused an over prediction of the RTO experiment temperature profiles. Also, Strausz and Lown [84] elaborated the affinity of SARA fractions to react with oxygen at low temperatures. In their study, saturates, among the four SARA fractions, showed the least affinity towards oxidation at low temperatures. Hence, Sequera et al. considered the saturate oxidation reaction to be occurring at high temperatures. Model LTO 2 captured bitumen phase compositional changes effectively but has five pseudo-components to represent the oil phase. Also, Model LTO 2 can predict effectively gas composition during LTO reactions.

Later, Yang and Gates [8,9] improved Belgrave et al.'s kinetic model by adding two additional reactions to account for combustion of methane and combustible gas, pseudo-component gas, resulting from the thermal cracking reactions. These additional reactions were given by:



The kinetic parameters of these reactions were obtained by history matching combustion tube runs on Athabasca bitumen. One key limitation of these models is the use of the "Gas" pseudo-component. It is known that gas components generated include hydrogen, methane, and hydrogen sulfide. However, all models devised to date cannot model the production of these gas components evolved during either in situ combustion or steam stimulation of bitumen. Yang and Gates [9] also used these kinetics to model a hybrid steam-oxygen recovery processes for bitumen reservoirs.

Rahnema and Mamora [85] compared performance of Combustion Assisted Gravity Drainage (CAGD), SAGD and THAI processes by using Belgrave et al.'s kinetic model for bitumen combustion. Field scale numerical simulation study conducted in this paper primarily focused on process performance and not the comprehensiveness of reaction scheme. Similarly, Greaves et al. [86] used Model A of Phillips et al. [29] (Table 1) to construct reaction scheme for THAI process laboratory and field scale simulation. This reaction scheme is given by



where, asphaltenes and heavy oil pseudo-components of Phillips et al.'s model were grouped to form another pseudo-component, Heavy Oil in Eq. (25) whereas Light Oil pseudo-component includes medium oil, light oil and gases. This kinetic model proposed here omitted LTO and aquathermolysis reactions assuming that HTO prevails in THAI process. Later, Greaves et al. [87,88] added additional two reactions to account for Light Oil and Heavy Oil pseudo-components combustion.



Stoichiometric coefficients of reactions in Eqs. (25) and (26) were obtained by tuning the reaction model to produce sufficient coke for sustained combustion and fire-front propagation and to match oil production data.

Kapadia et al. [10,11] extended Yang and Gates' kinetic model by replacing the "Gas" pseudo-component with hydrogen, methane, carbon oxides, hydrogen sulfide and higher molecular weight gas (HMWG) components. Furthermore, aquathermolysis reactions together with coke gasification, water-gas shift, methanation [89], hydrogen combustion, and carbon monoxide combustion [90] were also added into the overall reaction scheme. This reaction scheme was further tested to delineate different reaction regimes observed during in situ bitumen combustion. Amount of hydrogen generated during bitumen

gasification, as predicted by this reaction scheme, shown good match with published literature data. Reaction scheme was further tuned on field scale to history match Marguerite Lake combustion pilot plant and for design of in situ bitumen gasification recovery processes.

## 5. Limitations and recommendations for future studies

The review documented here discusses independently conducted experiments and pilot study on thermal cracking, aquathermolysis and oxidation of Athabasca bitumen. Additionally, it was also discussed how comprehensive reaction scheme for bitumen combustion was constructed, in literature by various authors, by integrating various co-existing mechanisms. Chemical interaction of bitumen with water and/or oxygen in the presence of heat constitutes complex multiphase reaction scheme. There could be as many as four different phases (oil, water, gas and solid) chemically interacting depending upon if anyone or all of pyrolysis, aquathermolysis, and oxidation occur. Developing a reaction scheme for each of these reaction types from laboratory experiments is the key to successful modeling and simulation of bitumen combustion or gasification processes. Although there are many studies in literature which employ thermogravimetric, RTO, combustion tube test, and three-dimensional physical model apparatus combustion analysis to develop reaction schemes with associated kinetic parameters, to separate mass transfer limitations from reactions, we believe that batch mode experiments conducted isothermally over various periods of time at different temperatures provide the best way to obtain a complete kinetic model [91]. Additionally, the concentration measurements of each component or pseudo-component in each phase with respect to time for a given temperature can provide detailed chemical interaction which would help develop reaction scheme, estimate stoichiometry and kinetic parameters. The large number of such measurements would directly facilitate construction of a more detailed reaction scheme. Qualitative analysis of such measurements can also help determine the existence of distribution of activation energy or extent of reaction effect [50]. Upscaling of kinetic parameters, as obtained from laboratory experiments, to field scale poses challenging task which involves considerable amount of uncertainty [51]. Upscaling of kinetic parameters is required to take into account the convective fluxes such as mass and heat fluxes and convective flow assisted diffusion (dispersion), which are absent in batch mode of laboratory experiments but present in field scale reservoir studies. Based on the review work done here, the following recommendations are suggested for future studies:

- It remains unclear as to what the exact products of LTO and HTO of bitumen are despite many decades of study. As combustion occurs in batch experiments, liquid and gas samples must be taken and analyzed to determine the products versus time and temperature.
- The effect of sulfur chemistry on thermal cracking and oxidation remains unclear. Future studies should also focus on the interrelationships between sulfur chemistry and thermal cracking and oxidation.
- Nearly all studies separate aquathermolysis and LTO and HTO and thermal cracking. Most likely, these reaction classes do not occur in isolation with each other and thus future studies should attempt to understand the linkages between the reaction classes with respect to reactants, products, kinetics, and compositional variations.
- Given the complexity of the reactions, components, and competing reactions, the Athabasca bitumen thermal cracking, oxidation, and aquathermolysis reaction scheme may potentially require the use of distribution of activation energies to represent the entire spectrum of available experimental data.
- Pyrolysis and aquathermolysis studies conducted so far do not incorporate the effect of bitumen composition on kinetic parameters. It is well known that the properties and composition of bitumen vary within oil sand reservoirs and thus, so too must the kinetics of the reactions that occur with the oil. Hence, it is recommended that future pyrolysis and aquathermolysis experimental data are collected

together with bitumen composition data so that the influence of composition can be fully understood.

It is also observed that not all of the experiments or pilot studies conducted so far follow a common procedure during experimental design and analysis of data for a given objective. Ramped-temperature experiments provide qualitative insights into the nature of reaction like parallel competing or cascading or series reactions. Kinetic parameters obtained from isothermal batch mode of experiments can always be validated by results of ramped-temperature experiments. The issues of mass transfer limitations in combustion tube experiments and physical model apparatus tests are not always addressed in the published literature.

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