

An overview of the origin, pathways and controls of H₂S production during thermal recovery operations of heavy and extra-heavy oil

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Summary

In this work we review the origin, chemical pathways and factors that control the generation of H₂S during steam assisted thermal recovery of heavy oil and bitumen.

Introduction

Steam-assisted thermal recovery methods are commonly applied for the production of heavy (10-20° API) and extra heavy (<10° API, >10,000 cP) oil. Steam-assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS) are two of the procedures most frequently used, with operating temperatures generally up to 250 °C and 330 °C, respectively. Under these conditions, chemical transformations involving thermolysis and aquathermolysis impact the oil properties and also lead to the generation of acid gases, such as hydrogen sulfide (H₂S) and carbon dioxide (CO₂). Since H₂S is a highly poisonous and corrosive gas, understanding and predicting the generation of H₂S during thermal recovery operations of heavy and extra heavy oil is instrumental to provide sustainable recovery of the giant fossil fuel reserves of Alberta. Here we review laboratory and field data regarding the production of H₂S from heavy and extra heavy oil under thermal recovery conditions; and present some results of the production of sulfur containing compounds and transformations of sulfur compound classes in the polar fraction of oil pyrolyzates analyzed by FT-ICR-MS.

Theory

Sulfur in crude oil is mostly organically bound and is mainly incorporated into organic matter via diagenetic reactions (Mossmann et al., 1990, Putschew et al., 1996). Regardless of the bulk sulfur content of oil, the relative abundance of different sulfur species can be highly variable. Sulfur speciation in petroleum and sulfur reactivity during thermal recovery of heavy oil are topics of great interest due to the negative impact of petroleum and inorganic sulfur compounds (e.g. H₂S, SO₂) on the environment (Brimblecombe et al., 1989; Ivanov, 1981) and on the production and upgrading infrastructure.

The complex nature associated with determining the oil sulfur composition makes it challenging to identify the reaction pathways contributing to H₂S production during oil heating (possibility of multiple precursor moieties). Typical sulfur species in bitumen include thiols (R-SH), sulfide (R-S-R), disulfides (R-S-S-R), polysulfides (R-S_x-), thiophenes (C₄H₃S-), benzothiophenes (C₈H₅S-) and dibenzothiophenes (C₁₂H₇S-), among others. Generally, the production of H₂S by thermal decomposition of oil appears to be proportional to the sulfur content of the oil (Ritchie, 1985). However, the different forms of organic sulfur play an important role in the kinetics of H₂S generation. In this regard, disulfides and thiols have been identified as being the most reactive sulfur species under thermal stress conditions, followed by aliphatic sulfides, thiophenic compounds, while benzothiophenic compounds appear to be the most stable organically bound sulfur species during oil thermal decomposition (Hyne et al., 1982, Clark et al., 1984; Ritchie et al., 1985; Katritzky et al., 1991; Kelemen et al., 1991). Experimental evidence suggests that many of the individual reactions of organosulfur

compounds are consistent with unimolecular decompositions and thus follow first order Arrhenius kinetics (Ritchie, 1985).

Examples

The production of H₂S by thermolysis and aquathermolysis of heavy oil has been verified in laboratory experiments (Hyne et al., 1982; Ritchie et al., 1985; Belgrave et al., 1997, Lamoureux-Var et.al., 2010) and in field data from steam assisted heavy oil and oil sand thermal recovery operations (Hyne et al., 1982; Thimm, 2008; Kapadia et. al., 2012). Laboratory experiments suggest that the H₂S generation reaction can be modeled as a first order reaction with the rate of generation at high temperatures (300 °C) being proportional to the sulfur content of the bitumen (Ritchie et al., 1985), although Thimm (2008) assumes a zero order reaction, i.e. reaction rate independent of the concentration of the reactants, to model the production of H₂S from steamed oil under SAGD conditions.

Hyne et al. (1982) have suggested that at temperatures below 240 °C aquathermolysis reactions between oil and saturated steam are dominant, while above this temperature thermolysis (thermal cracking), through free radical pathways, may become increasingly important in the generation of H₂S and other gas products. The kinetic behavior of the thermal decomposition of oil suggests that chemical reactions can take place at lower temperatures, i.e. below 200 °C, over longer periods of time. Figure 1 shows typical behaviours reported for the production of H₂S in laboratory and field studies.

More recently, Kapadia et. al. (2012) achieved the simulation of the generation of H₂S during thermal recovery operations of Athabasca bitumen, by incorporating aquathermolysis reactions in a reservoir simulator. Chemical interactions between bitumen and steam condensate were modeled by defining a group of pseudo-components and seven parallel aquathermolysis reactions with independent kinetic parameters. The results revealed that the production of H₂S during SAGD operations is a direct function of temperature and it rises significantly above 235 °C.

Our simulated thermal recovery experiments using core samples from the Alberta oil sands, carried out under isothermal hydrous pyrolysis conditions in the temperature range between 250 °C and 350 °C, for up to 7 days of heating reveals significant transformation in sulfur compounds (Marcano N., 2011). The production of H₂S was not quantitatively investigated in this study, but it is inferred that it partially accounts for the net decrease in whole oil sulfur content by 1 wt% after 7 days of hydrous pyrolysis at 350 °C. Figure 2a shows that under these same conditions over 5000 ppm of C₀-C₂ alkylbenzothiophenes and over 2500 ppm of C₀-C₂ alkyldibenzothiophenes are generated. Figure 2b shows the general distribution of sulfur compound classes determined by APPI FT-ICR-MS in the polar fractions of the unheated oil and the processed oil. A general removal of sulfur with heating is inferred from the decrease in relative concentration of S1, S2 and S3 species from the unheated to the processed oil. This suggests that the polar fractions of the oil are the main source of the sulfur aromatic compounds generated in the hydrocarbon fraction (Fig. 2a) and partially accounts for the generation of H₂S gas, commonly observed during aquathermolysis reactions (Hyne et al., 1982).

Another chemical reaction to be considered that may take place in petroleum accumulations during thermal recovery operations is thermochemical sulfate reduction (TSR). This reaction consists of the oxidation of petroleum and reduction of sulfate to form CO₂ and H₂S, at temperatures generally above 120 °C, in the presence of sulfur and water sulfate. Cross et al. (2004) reported that up to 95% of the original sulfate in water can be converted within about 25 days of TSR reaction when the temperature is 300 °C (independent of oil sulfur content). Thus not only temperature and oil composition, but also other parameters such as formation water chemistry and rock mineralogy are important factors to be considered in the selection of steam assisted heavy oil recovery operating parameters.

Summary

Hydrogen sulfide (H₂S) is generated by aquathermolysis and thermolysis of heavy oil under thermal recovery conditions. The main factors controlling this production are temperature and time of heating, sulfur content and the distribution of different organosulfur species in the oil. The results of heating

experiments of oil sands samples suggest that the oil polar fractions are the main source of the newly formed thioaromatic compounds. Moreover, the analysis of the polar fractions by FT-ICR-MS reveals that removal of sulfur is one of the main transformations taking place in the oil heavy ends under simulated thermal recovery conditions. It is suggested that the oil polar components are the main source of the sulfur aromatic compounds generated in the hydrocarbon fraction and partially accounts for the generation of H₂S gas causing a net decrease in whole oil sulfur content. Further transformation of the thioaromatic compounds may also lead to generation of H₂S.

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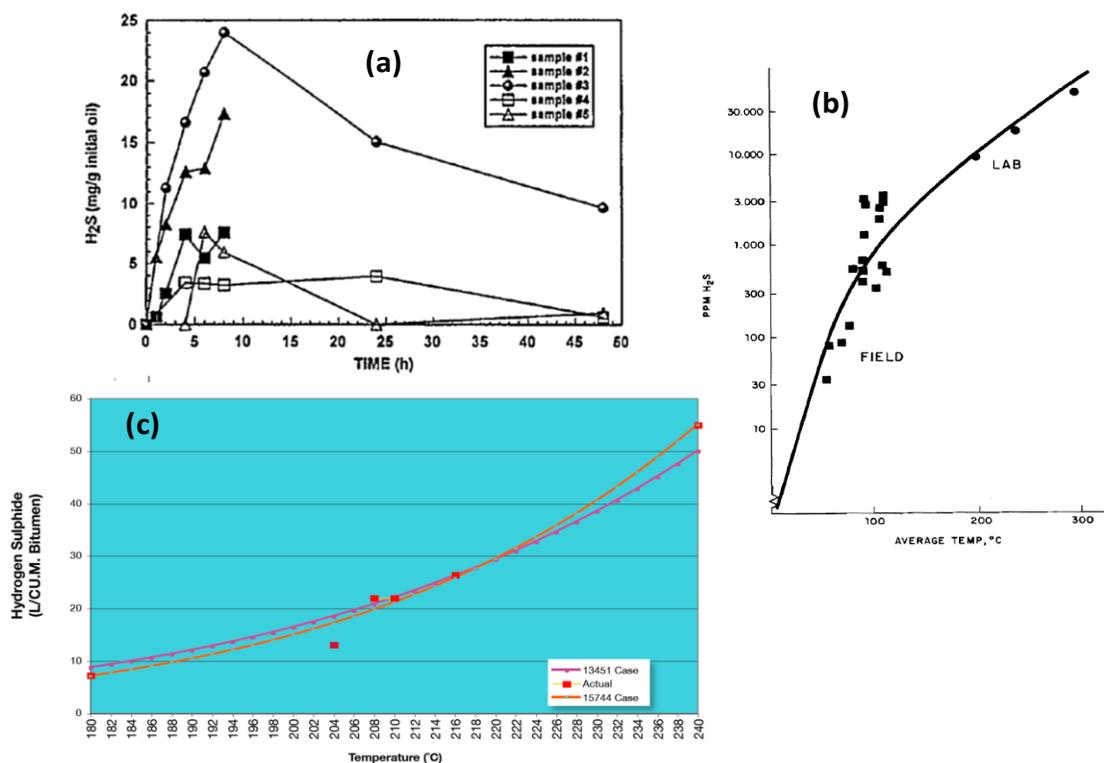


Figure 1: Typical behaviours reported for the generation of H₂S with increasing time (a) and temperature (b and c) of heating in laboratory (and theoretical) and field studies. (a) H₂S generation during aquathermolysis of bitumen/oil samples at 397°C. Samples 1-3 correspond to Athabasca bitumen cores. Samples 4-5 correspond to oils with lower sulfur content than Athabasca bitumen (after Belgrave et al., 1997), (b) Comparison of field data and laboratory data of the H₂S production from heavy oil with increasing steam temperature (after Hyne et al., 1982), (c) Comparison of field data of H₂S generation during SAGD operations and theoretical lines predicting the H₂S generation as a function of steam temperature (after Thimm, 2008).

