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Forecasting H₂S Generated from Steamed Oil Sands
Insights into H₂S Generation through Experimental Investigation

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Steam injection process is used in oil sands reservoirs for enhancing oil recovery whereby oil viscosity is reduced by heat transfer and consequently oil flows more readily. Chemical reactions called «aquathermolysis» are also induced by steam injection within the reservoir (Hyne *et al.*, 1984). Depending on oil sand composition and steam injection conditions, aquathermolysis can lead to the production of high amounts of H₂S at the well-head (Thimm, 2001). Hence H₂S forecasting is critical in development plans of an oil field in terms of surface facilities design and safety.

To forecast H₂S generation within the reservoir, we developed an experimental approach simulating aquathermolysis in the laboratory. In order to propose a kinetic model based on sulfur evolution, we addressed several preliminary questions: How much H₂S is produced upon aquathermolysis as a function of time and temperature? What are the parameters significantly impacting H₂S generation? What are the sources of H₂S? How is sulfur evolving relatively to H₂S generation?

For that, four oil sands samples originating from four fields in Canada were investigated: Fisher Field, Leismer Field, Resdeln Field (Athabasca), and Ethel Lake Field (Lloydminster).

Their mineral and organic sulfur contents were determined by Rock-Eval including a new capability for sulfur characterization and quantification. The organic sulfur content was split into pyrolyzable sulfur content (reactive to temperature) and non-pyrolyzable sulfur content.

Aquathermolysis experiments consisted of heating each oil sand sample with water, in a closed, static and inert system, at constant temperature from 240°C to 320°C, under 100 bar, for 203 hours. After each aquathermolysis experiment, the produced H₂S was recovered via a vacuum line and then quantified in absolute amounts by the combination of manometric measurements and gas chromatography (GC/TCD).

To follow the evolution of sulfur with aquathermolysis, the oil from Fisher Field was characterized after each aquathermolysis experiment. The effluent was extracted with solvent and then fractionated by liquid chromatography into saturates (S), aromatics (A), resins (R) and asphaltenes (A). The atomic sulfur content was then quantified in each SARA fraction and in the insoluble residue (mineral + organic). Finally, the sulfur distribution was deduced.

To address the effect of water state on H₂S generation, aquathermolysis experiments were performed on an heavy crude oil (Boscan, Venezuela) utilizing two states of water: water in liquid state (280°C, 100bar) and water in the liquid/vapor equilibrium state (280°C, 62bar).

Results

Sensitivity to temperature

Temperature is one of the main factors significantly influencing H₂S generation. The aquathermolysis experimental results indicate that whatever the oil sands composition and their sulfur content, H₂S generation increases with temperature in our experimental conditions from 240°C to 320°C (duration=203 hours, P=100bar, Voil~Vwater).

Sensitivity to sulfur content

The amount of H₂S varies significantly among oil sands despite a small difference in organic sulfur content - from 4.9wt% (Ethel Lake extract) to 5.5wt% (Resdeln extract). Resdeln produced 2.7 mg H₂S / g oil after 203hours upon aquathermolysis at 280°C, whereas Ethel Lake produced no H₂S. This variability can be explained by addressing the origin of H₂S.

Origin of H₂S

Mineral sulfur

The initial oil sands do not contain any mineral sulfur (sulfates, pyrite) or organic insoluble sulfur, as shown by X-Ray Diffraction Spectrometry identification, Rock-Eval characterization and sulfur elemental analysis. The absence of sulfates indicates that Thermochemical Sulfate Reduction (TSR), which is known to yield high amounts of H₂S (Worden et Smalley, 1996), does not occur during aquathermolysis.

Organic sulfur

The initial extracted oils were characterized by Rock-Eval. Their "pyrolyzable sulfur content" varies between 3.8wt% for Ethel Lake Field to 4.7wt% for Resdeln Field. Figure 1 shows a good correlation between pyrolyzable sulfur content and H₂S produced upon laboratory aquathermolysis. This suggests that H₂S may be derived from pyrolyzable sulfur. This would be validated if H₂S generation at steady state corresponds to the pyrolyzable sulfur content.

Evolution of organic sulfur

In order to decipher the evolution of organic sulfur related to H₂S generation, sulfur distribution within the oil sand was addressed, before and after aquathermolysis. The results on Fisher Field oil sand show that, with increasing aquathermolysis temperature:

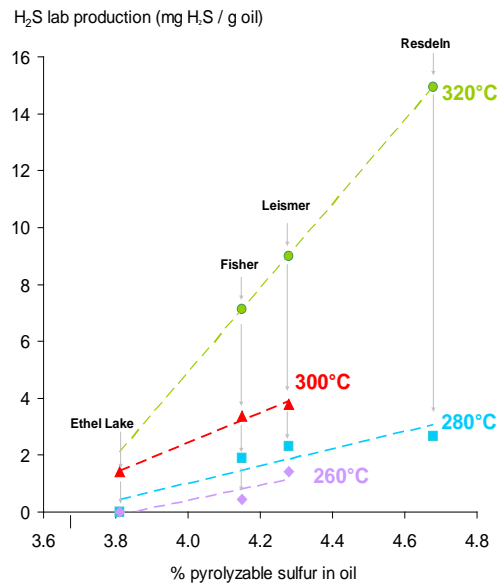


Figure 1: H₂S production (in mg H₂S/g oil) from experimental aquathermolysis (duration=203 hours, P=100bar, Voil~Vwater) versus pyrolyzable sulfur content (Rock-Eval analysis) of the initial extracted oils.

1. Resins and asphaltenes are depleted and get poorer in sulfur.
2. Both aromatics and saturates are generated with the aromatics enriched in sulfur. This is consistent with the experimental results obtained by Chen and coworkers (Chen *et al.*, 1991).
3. Resins, asphaltenes and aromatics are aromatized as indicated by an increase in the molar H/C ratio.
4. Above 280°C H₂S production increases drastically with a simultaneous generation of organic sulfur residue.
5. The mass balance on sulfur indicates that aquathermolysis redistributes sulfur from resins and asphaltenes to H₂S, aromatics and organic insoluble residue (Fig 2).

These observations suggest that resins and asphaltenes would: 1. crack into aromatics, H₂S and saturates, and 2. polymerize into heavy sulfured residue. The increase in residue is very interesting from the point of view of the producer, because it seems to “trap” part of the organic sulfur initially present in the oil in compounds, which are too heavy to be produced. The related question of an infill of porosity by the residue is also an issue.

Water effect

Effect of oil/water ratio

We compared H₂S produced by experimental aquathermolysis with two different oil/water ratios: Voil/Vwater ca.1 (added water in laboratory) and Voil/Vwater ca. 3 (formation water). Our results obtained on Fisher and Leismer oil sands showed that an excess of water did not lead to a significant increase of H₂S production, while water vapor resulted in an increase in H₂S production.

Effect of water state

In “steam assisted gravity drainage” (SAGD) process, water is encountered under different states according to its position in the reservoir. Our experimental results, obtained on the heavy crude from Boscan, showed that, after 27 days of aquathermolysis at 280°C, H₂S production is two times higher when water is in liquid/vapor equilibrium state than when water is in a liquid state.

Conclusion

- Experimental aquathermolysis carried out on four oil sands from Canada showed that H₂S production depends strongly on temperature and

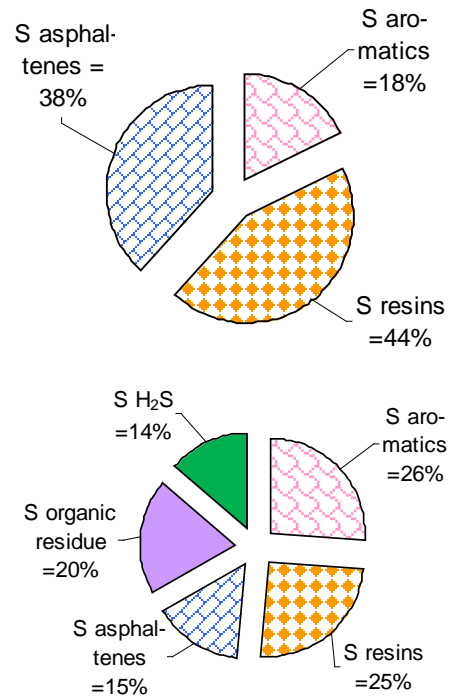


Figure 2: Comparison of atomic sulfur distribution over oil SARA fractions, organic residue, and H₂S, before and after aquathermolysis. Upper chart: sulfur in initial oil sand, before aquathermolysis. Lower chart: sulfur in oil sand and H₂S after aquathermolysis at 320°C for 203 hr at 100bars (water was in a liquid/vapor equilibrium state). Saromatics = mass of sulfur in the aromatics, normalized by the mass of total sulfur (wt%); Sresins = mass of sulfur in the resins, normalized by the mass of total sulfur (wt%); Sasphaltenes = mass of sulfur in the asphaltenes, normalized by the mass of total sulfur (wt%); Saromatics + Sresins + Sasphal

- sulfur content, and that water state has a significant impact on H₂S generation.
- H₂S production could be related to the “pyrolyzable sulfur content” of the initial oils, defined with Rock-Eval, suggesting that H₂S may be derived from pyrolyzable sulfur.
 - We showed that the resins and maybe even more the asphaltenes are the sources of H₂S upon aquathermolysis. Their sulfur is redistributed into aromatics, insoluble organic residue, and as H₂S. The insoluble residue acts as a trap for the sulfur initially present in the oil.
 - Our work aims at developing a kinetic model for H₂S generation, based on sulfur redistribution in oil fractions, organic residue and H₂S. A first model was already proposed (Lamoureux-Var and Lorant, 2005), which now needs to be advanced from our insights. The effect of water state should be taken into account. Moreover, it should be constrained with additional H₂S production data, gathered at higher H₂S production levels.
 - Finally, forecasting H₂S production at the well-head requires coupling such a kinetic model: (1) to a thermodynamic model describing H₂S distribution over the fluid phases within the reservoir, and (2) to a reservoir model describing fluid flows.

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