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Oil sand pyrolysis: Evolution of volatiles and contributions from mineral, bitumen, maltene, and SARA fractions



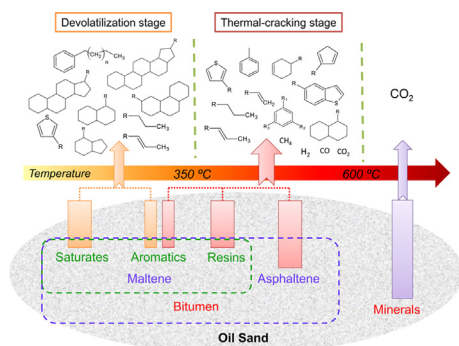
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GRAPHICAL ABSTRACT



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ABSTRACT

In order to investigate the pyrolysis behavior through the volatile evolution, pyrolyzer-evolved gas analysis-mass spectrometry and thermogravimetric analysis-mass spectrometry were adopted for in situ analysis and comparison the pyrolytic volatiles derived from two different oil sands as well as their mineral, bitumen and SARA fractions. For both oil sands, the weight loss and volatile release during the oil-producing process exhibited two stages: a devolatilization stage ($< 350\text{ }^{\circ}\text{C}$) and a thermal-cracking stage ($350\text{--}600\text{ }^{\circ}\text{C}$). These two stages afforded different volatile yields and displayed distinct activation energy distributions. Additionally, heart-cut analysis indicated that the volatiles were in disparate compositions at each stage. The volatile evolution of the oil sand bitumen, maltene, and SARA fractions revealed individual contributions on volatile release with increasing pyrolysis temperature. Specifically, volatiles in the devolatilization stage predominantly originated from the saturates in maltene. These resulted in a significant amount of polycyclic biomarkers and contributed toward the release of higher-molecular-weight substances over a temperature range of $200\text{--}350\text{ }^{\circ}\text{C}$. The thermal-cracking stage was the main stage in which most of the gaseous and light pyrolytic products, including amounts of alkanes and olefins, were generated. These compounds mostly originated from cracking of resin and asphaltenes. The aromatic fraction was observed that released volatiles in both stages. Thus, due to the disparity in temperature region for volatile release, the volatile yields during the different stages of the process were mainly determined from the organic constituents of the oil sand. Notably, the volatile compositions predominantly correlated to the original organic structures. Moreover, the minerals exhibited little influence during

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the oil-producing stage of the two oil sand samples under the tested heating conditions. However, the presence of interactions between these organic sub-fractions during oil sand pyrolysis is suggested.

1. Introduction

In 2016, the world's primary energy consumption was equivalent to 13276.3 million tons of oil. Moreover, due to the projected economic development and increase in productivity, mostly related to Africa and South and East Asia, energy consumption is predicted to increase over the next decades. In fact, according to world's energy outlook, fossil fuels will remain the dominant sources of energy powering the world economy, accounting for more than three-quarters of the total energy supply by 2035 [1,2]. Consequently, to mitigate the resultant environmental and energy security issues, there is an ever-growing demand for the production of clean diversified fuel supplies and the technological development of and research on the conversion process of fossil resources.

Oil sand is an unconventional petroleum resource with abundant reserves that is attracting much attention as an alternative energy supplement. Generally, oil sand is a natural mixture of clays (minerals), bitumen (organics), and a small amount of water. The critical step during its utilization is bitumen recovery, with related methods including pyrolysis, hot water extraction, organic solvent extraction, and some in situ methods. Among these techniques, pyrolysis is considered as a promising method, especially for oil-wet types in which bitumen is less efficiently recovered by hot-water extraction [3]. Moreover, pyrolysis is also an important method for the production of high value-added light oils from oil sand [4].

Pyrolysis of oil sand is a thermal chemical process during which oil sand particles generate volatiles through desorption of the dissociative and thermal-cracking of chemical bonds. The separation of organics and minerals is finally accomplished by exportation and condensation of these volatiles. Therefore, the temperature greatly influences the degree of devolatilization, yield and quality of the pyrolytic products. Recently, several studies have been reported on the evolved volatiles during oil sand pyrolysis through indirect or direct methods [5]. Studies through thermogravimetric analysis revealed the presence of two relatively distinct weight-loss stages during the process [6,7]: devolatilization of light organics at temperatures < 350 °C and carbonaceous decomposition of heavy organic macromolecules at temperatures ranging between 350 and 600 °C. Simultaneously, the distinct Arrhenius parameters of both stages were also determined according to the first-order kinetic model [8]. Other studies involved in situ analysis,

especially aimed at gaseous products. Zhao et al. [9] investigated the behavior of evolved volatiles during pyrolysis of an Alberta oil sand by thermogravimetric mass spectrometry (TG-MS). Through the evolution curves of specific mass fragments, they discovered that the release of organic compounds such as fragments of aliphatic hydrocarbons appeared as two peaks at 130 °C and 480 °C, respectively. On the other hand, inorganic compounds such as H₂, H₂S, COS, and SO₂ were observed from ~380 °C. Similar results were reported by Hao et al. [10] who studied the evolving tendency of several typical gaseous products with varying temperature by thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG-FTIR). However, the gaseous products were only a component of the released volatiles and most gaseous products originated from intense decomposition reactions, especially during the thermal-cracking stage. Thus, simply tracing these gaseous products probably leads to a loss of information during the devolatilization stage.

Volatile generation during pyrolysis is rather complicated due to the complex and varied compositions and structures of the organics present in oil sand. However, the pre-separation of the comprehensive organic mixture and the subsequent study of the individual species is beneficial toward understanding the whole mixture. According to the differences in polarity and aromaticity, oil sand bitumen can be separated into saturate, aromatic, resin, and asphaltene fractions (SARA fractions) [11]. To investigate the thermal cracking behavior of each fraction and their contributions toward volatile generation during oil sand pyrolysis, Hao et al. [12] utilized a TG-FTIR technique for the gas-releasing on-line-analysis of the SARA fractions. They reported that the release behavior of CO₂, CO, methane, ethylene, and light aromatics was different due to the structural differences of these species. The activation energy of each SARA fraction, representing the degree of difficulty of each pyrolytic reaction, was also variant [13,14]. However, weight-loss analysis has revealed that the SARA fractions displayed fewer interactions during co-pyrolysis than in their independent pyrolysis [15].

To date, several coupling techniques have been widely used for in situ evolved gas analysis (EGA). Among them, TG-coupled methods are the most popular as they require a short analysis time and offer quantitative information on weight loss. Although ~10 mg of sample is usually required for TG measurements because of the sensitivity of the balance, a smaller sample mass is preferable to avoid volatile condensation in the transfer system between the TG analyzer and the

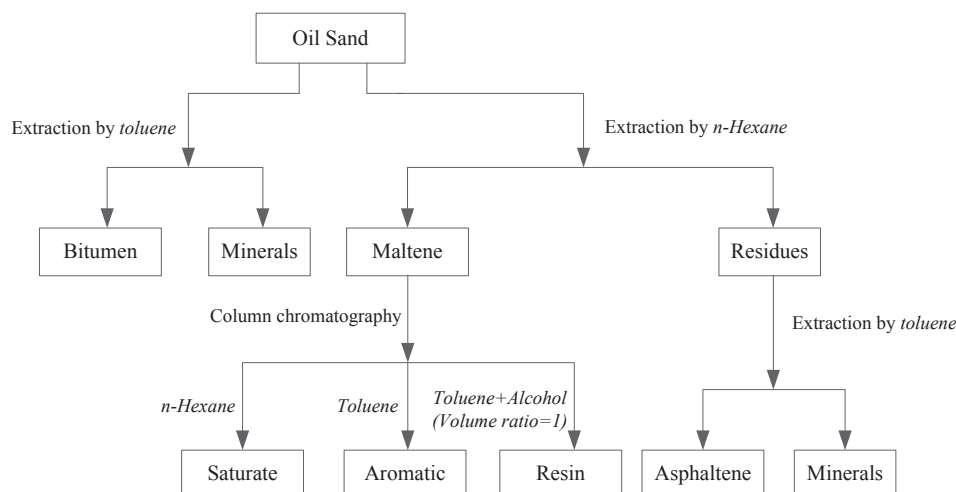


Fig. 1. Separation flow diagram of each fraction of oil sand.

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