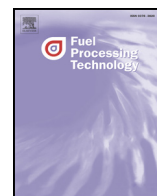




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## The influence of abundant calcium oxide addition on oil sand pyrolysis

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## ABSTRACT

The influence of abundant calcium oxide (CaO) addition on oil sand pyrolysis was firstly studied by thermogravimetric analysis (TGA) and in a fixed bed reactor. CaO additives calcined from analytically pure CaCO<sub>3</sub> (named A) and oil sand minerals (named B) were compared with the addition ratio at 1:1 (oil sand:CaO, mass ratio). Observed by TGA, abundant addition of CaO would inhibit the devolatilizing during oil-producing stage (150–600 °C). However, higher temperature appeared to weaken the inhibition effects. Comparison of pyrolysis in the fixed bed reactor was at 480 °C, 140 mL/min pure N<sub>2</sub> carrier gas, 0.1 MPa for 40 min. When pyrolyzed with abundant CaO, the gas yields (including H<sub>2</sub>S and COS) decreased which met the result of TG/MS analysis. Tiny differences were found on tar yields which achieved around 88% of raw bitumen. But through column chromatography and gas chromatography/mass spectrometry (GC/MS) analysis, the proportion of aliphatic fraction increased, interestingly observing more alkanes with long carbon chain and less olefins. The proportion of aromatic fraction decreased by about 10 wt%, but the relative amount of polycyclic aromatic hydrocarbon (PAHs) got an obvious increase when pyrolyzed oil sand with abundant CaO. As expected, acidic compounds in resin (e.g. phenols and carboxylic acids) were significantly reduced. In general, it was both physically and catalytically that abundant addition of CaO influence on oil sand pyrolysis. But no evident differences between additive A and additive B were found on yields and product compositions.

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## 1. Introduction

Oil sand, as an unconventional oil resource, is thought to be a considerable complement for today's increasing energy consumption. And thermal method is one of promising methods for the recovery and upgrading bitumen of oil sand, especially for oil-wet types [1]. Generally, a major component of the bitumen is asphaltene which is a high-molecular-weight, solid, random organic geomacromolecule, which is colloiddally suspended, forming micellar aggregates in the oily portion of the bitumen [2]. It is shown that the predominant feature of asphaltenes from the Athabasca oil sand is the presence of sulfide linkages holding together an average of four core segments. The core segments comprise aromatic and aliphatic units bound together by polymethylene bridges. And it is these sulfide-bound core segments of

asphaltenes result in upgradability of bitumens without formation of excessive amount of coke [3].

Over past years, a plenty of pyrolysis experimental studies on oil sand have been carried out. Most studies were aimed at obtaining reaction schemes with associated kinetics to describe thermal cracking quantitatively [4]. Hayashitani et al. [5] placed Athabasca bitumen (about 4 g, free from water and minerals) in quartz glass tube thermally cracked over the temperature range of 303 °C to 452 °C and developed pseudo-component reaction models for thermal cracking. Barbour et al. [6], Pulikesi Murugan et al. [7] and Phillips et al. [8] studied thermal cracking behavior in the presence of mineral matrix to determine the effect on thermal cracking reactions which found that the yields of coke and gas from cracking bitumen–sand mixture were higher than those from pyrolyzed bitumen alone under a given temperature and reaction time. With the help of thermogravimetric analyzer, two distinct stages (both having different Arrhenius parameters) were showed during bitumen thermal cracking [7,9]: a relatively light organic substance volatilizing and desorbing from 150 °C to 350 °C; a relatively heavy organic substance cracking between 350 °C and 600 °C. Moreover, models such as Coats-Redfern [10], distributed activation energy model (DAEM) [1,

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[11], Friedman procedure [12], integral iso-conversional non-linear (NL-INT) method [9], Flynn-Wall-Ozawa method (F-W-O) [13] etc., were applied to obtaining kinetics during pyrolysis.

Another major issue in oil sand processing is the disposal of the large volume of tailings, which are a mixture of sand and fine clay, with a hydrocarbon content of less than 1% [14]. Especially, when pyrolysis is applied to bitumen recovery and upgrading of oil sand, little fixed carbon and calorific value remain in the tailings which is quite different from coal char. Considering potentially environmental problems and land shortage, high inorganics ratio of pyrolytic residues may make against to the development of oil sand. But carbonates, dominated minerals in oil sand, can be calcined into oxidate which may serve as heat-carrier for pyrolysis. Meanwhile, oxidate, such as calcium oxide (CaO), are also widely used for fundamental building material, flue gas desulfurization adsorbent [15] or tar cracking catalyst for gasification and chemical looping [16]. Gadallah et al. [17] once attempted to utilize synthesis gas and tiny calcium oxide addition (5% by wt of bitumen) to upgrade bitumen by pyrolysis which improved the liquid yield and its quality. However, when pyrolyzed oil sand with abundant CaO, the pyrolytic or devolatilizing process may be different from the situation of tiny addition. Whether and how the abundant addition of CaO would change the yield or composition of pyrolytic products is deserving of studying.

In our present work, the influence of abundant calcium oxide (CaO) addition on oil sand pyrolysis was firstly studied by thermogravimetric analysis (TGA) and in a fixed bed reactor. Devolatilizing process, pyrolysis kinetics, yield and product distribution were as factors to estimate the influence between oil sand pyrolysis with and without abundant CaO addition.

## 2. Experimental and equipment

### 2.1. Sample and additives

The oil sand was collected from Indonesia. Considering the possibility of devolatilization when oil sand bitumen was dried in the oven, the proximate except moisture content was performed according to Chinese standard GB/T 212-2008. Furthermore, we conducted the content of carbonates by the release of CO<sub>2</sub> (Chinese standard GB/T 218-1996) which could clarify the inorganic matters in content of volatiles. The moisture and bitumen content were given by Soxhlet extraction in toluene, while maltenes was extracted in *n*-heptane. Ultimate analysis was

**Table 1**  
Basic properties of oil sand sample.

Properties	
Proximate analysis (wt%, dry basis)	
Ash	52.78
Volatiles	13.49
CO <sub>2</sub> (for carbonates)	25.69
Fixed carbon <sup>a</sup>	8.04
Ultimate analysis (wt%, dry ash free basis)	
C	75.13
H	7.09
N	0.66
S	6.12
O <sup>a</sup>	11.03
Oil sand component (wt%, as received)	
Bitumen <sup>b</sup>	19.33
Maltenes <sup>c</sup>	13.72
Asphaltenes <sup>d</sup>	5.61
Moisture	2.38
Solid dreg	78.29

<sup>a</sup> By difference.

<sup>b</sup> Toluene soluble.

<sup>c</sup> *n*-heptane soluble.

<sup>d</sup> *n*-heptane insoluble.

**Table 2**  
Mineral analysis by X-ray fluorescence (%).

Element	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	MgO
Content	76.3	11.5	3.97	2.93	1.96	1.80
Element	K <sub>2</sub> O	Na <sub>2</sub> O	SrO	TiO <sub>2</sub>	BaO	P <sub>2</sub> O <sub>5</sub>
Content	0.483	0.380	0.271	0.241	0.141	0.102

conducted by element analyzer vario EL III (Elementar, Germany). All the results were listed in Table 1.

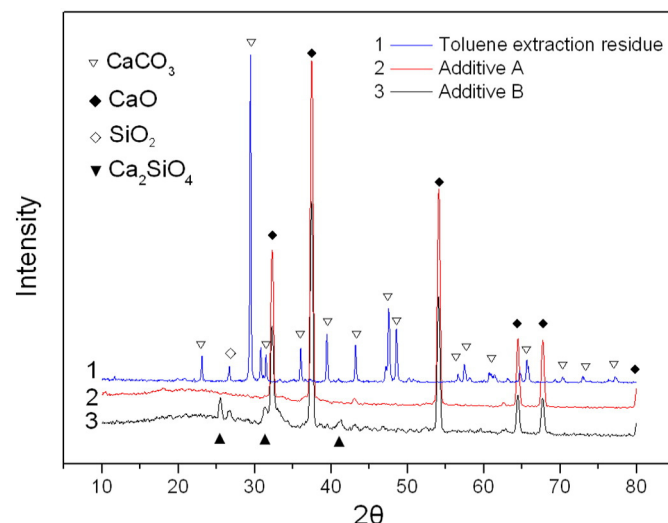
According to both Table 1 and Table 2, mineral in the sample is full of calcium carbonates. And the XRD pattern of toluene extraction residue in Fig. 1 also verified its dominated content. Thus, we took advantage of calcined oil sand char named additive B as a source of CaO, while additive calcined analytical pure calcium carbonate named additive A was as a comparison. The both kinds of additives were prepared in muffle furnace for 3 h at 900 °C. The surface area of additive A and B respectively were 4.40 m<sup>2</sup>/g and 3.61 m<sup>2</sup>/g. As shown in Fig. 1, additive A has better crystal form of CaO for its sharper and higher intensity of X-ray diffraction peaks. Due to the existence of SiO<sub>2</sub>, peaks of Ca<sub>2</sub>SiO<sub>4</sub> were also detected in additive B. The addition ratio was chosen 1:1 (oil sand:CaO, mass ratio) in this study.

### 2.2. TG/MS analysis

TG analysis was performed using a Mettler Toledo TGA/SDTA851e thermogravimetry analyzer. During the experiment, about 15.00 mg sample (grind below 160 mesh) was placed in a ceramic crucible and heated from room temperature to 850 °C with a constant heating rate using argon as carrier gas at a constant flow rate of 60 mL/min. In order to compare typical products' evolutions varying temperature, a quadrupole mass spectrometer (GSD-301 T3, MS) was linked to the thermogravimetric apparatus to measure the evolved gas including hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), carbon oxide (CO) and carbon dioxide (CO<sub>2</sub>) in this work. All TG/MS analysis was carried out at 10 °C/min.

### 2.3. Fixed bed pyrolysis

Schematic diagram of the fixed bed pyrolysis experimental setup is shown in Fig. 2. Oil sand pyrolysis with and without CaO addition was carried out in a vertical fixed bed reactor. Before the experiment, samples have been crushed below 3 mm. When oil sand pyrolyzed with CaO additives, they were firstly premixed. The operating condition was same as the one that highest tar yield was achieved when pyrolyzed



**Fig. 1.** XRD of toluene extraction solid dreg and each additive.

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