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Understanding the pyrolysis progress physical characteristics of Indonesian oil sands by visual experimental investigation

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ABSTRACT

The oil sand pyrolysis progress in this study was captured by a digital camera. The pyrolysis experiments were carried out in a fixed bed batch reactor at a heating rate of 10 °C/min. The solid products of different final temperature were identified by way of scanning electron microscopy (SEM), and the specific surface area and pore volume were determined by way of isothermal adsorption. Thermogravimetric analysis (TGA) was conducted to obtain a weight loss acceleration curve to study the accumulated liquid amount in the channels of the solid particles. It was found that the first light and second heavy organic film appeared in the low and high temperature region respectively. The specific surface area and pore volume of the solid products was not increasing throughout the process. The accumulated liquid amount peaked at 230 °C and 460 °C respectively. On the basis of the experimental results and findings, an oil sand pyrolysis progress physical model (PPP model) was proposed.

1. Introduction

With the continuous decrease of oil resources, unconventional crude oil is increasingly becoming a topic of research interest. Oil sand is one such unconventional fossil energy resource that is becoming an important supplement of current oil reserves. At present there are three main types of separation processes that are employed to isolate bitumen from sand grains. Hot water extraction has been commercially used as a process for bitumen recovery for decades [1,2]. However, since the process produces significant amounts of waste water that must be consolidated into oil sands tailing ponds. The storage of large volumes of such tailings has become an issue for the Canadian oil sands industry [3,4]. Solvent extraction process has been studied by a considerable number of researchers [5–8], yet the removal of the organic solvent from the bitumen requires an additional distillation process, which is problematic due to increased energy costs and the need for an inert volatile solvent [9]. Pyrolysis is an easier process to realize in industrial production as it does not produces tailings and requires no solvent or water consumption, and can simultaneously perform bitumen upgrading during the separation [10,11].

Many studies concerning oil sand pyrolysis primarily focus on the reaction yield, the compositional analysis of gaseous or liquid products, as well as the thermogravimetric analysis (TGA) of solid oil sands [12–16]. Pyrolysis kinetics models have been widely studied, and are generally described to by a first-order reaction [17,18]. This includes the Coats-Redfern, Flynn-Wall-Ozawa and distributed activation energy model methods that have also been applied for kinetic analysis [19]. Much of the research has been devoted to modeling the occurring mass transfer in the reaction, as well as describing coking reactions of thin films of bitumen derived from oil sands, the objective of which is to investigate the coking or fluid coking of bitumen rather than the direct pyrolysis of oil sands [20–24].

As such, current studies concerning oil sand pyrolysis models are limited to mostly kinetics models. To the best of our knowledge, there are few studies on oil sand pyrolysis progress physical characteristics, especially those that describe the diffusion of cracking products from oil sand particle pores and pore structure variations that occur with increasing temperature. Nonetheless, a pyrolysis progress physical model is needed to be formulated to acquire a better understanding of the pyrolysis process and the optimization of the pyrolysis process.

In the present study, a visualization setup was designed to study the pyrolysis progress, in which the specific surface area and pore volume were characterized to investigate the occurring mass transfer conditions. The oil sand particle cluster was proposed as a new basic unit for the analysis of the pyrolysis progress. The acceleration curve of weight loss was applied to analyze the accumulated liquid in the channels. By

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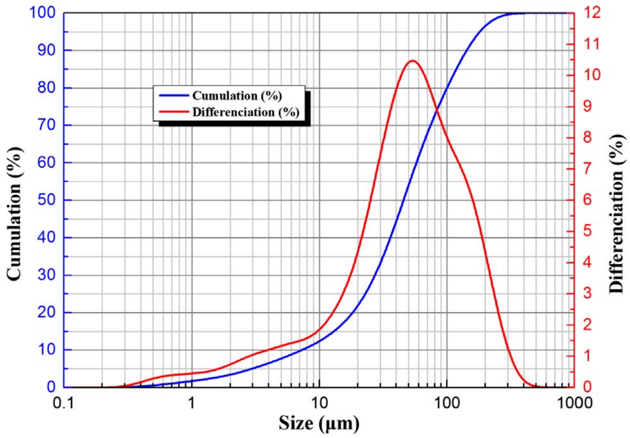

Fig. 1. Particle size distribution of sand grains after solvent extraction (toluene).

way of this analysis, a physical progress model was proposed to describe the oil sand pyrolysis characteristics, which can be used to determine the energy supply needed for different pyrolysis stages, data from which can be used to realize energy saving.

2. Experimental

2.1. Materials

Oil sands are mixtures of sand grains, bitumen and a small fraction of water. The sand grains are impregnated with bitumen, thus each sand grain is surrounded and coated by a bituminous layer [25,26]. Since the oil sand grains vary in size from 1 millimeter to sub-micrometer level [25]. The particle size distribution of sand grains in this study was performed by Bettersize 2000 laser particle size analyzer and the result is shown in Fig. 1. The particle size mainly distributes in the range of 1–500 μm. In an actual production pyrolysis process, the smallest unit is not a single oil sand grain but an oil sand particle cluster made of countless oil sand grains, therefore the oil sand particle cluster will be herein treated as the research unit.

The oil sand was obtained from Indonesia. By way of Soxhlet extraction, analysis showed that the oil sand contained 27.27 wt% bitumen, 1.18 wt% water and 71.55 wt% solids. The composition of the extracted bitumen was analyzed using the ASTM D4124-01 standard method [27]. The analysis data was shown in Table 1. More chemical characteristics and analysis can be found in our previous work [28].

2.2. Visualization of oil sand pyrolysis

To observe the oil sands pyrolysis progress, an oil sand particle cluster with a diameter of 3.2 cm was placed in a temperature programmed electric heating furnace as shown in Fig. 2. The furnace was sealed leaving a small window for digital camera lens, which can capture dynamic moments during pyrolysis. An LED lamp with constant luminance was used to illuminate the oil sand particle cluster through the window. Preheated high-purity nitrogen was introduced into the furnace during the course of heating in order to prevent combustion and sweep the organic vapors out.

The oil sand particle cluster was heated from room temperature to 550 °C at a heating rate of 10 °C/min, and was kept at 550 °C for 55 min. Nitrogen that was also preheated to 550 °C was fed into the furnace at a flow rate of 0.04 m^3/h (25 °C and 0.101 MPa) and exited along with the pyrolysis gaseous products through the gas vent. The first photograph was taken at room temperature and subsequent photographs were taken in intervals of 25 °C from 100 °C to 550 °C.

Table 1
Analysis of the Indonesian oil sands.

Analysis Item	Content (wt%)
Ultimate Analysis (daf)	
C	81.75
H	8.68
N	0.55
S	6.59
O[a]	2.43
Fraction Analysis of Oil Sand Bitumen	
Saturates	18.42
Aromatics	30.42
Resin	28.74
Asphaltenes	22.42

[a] By difference.

2.3. Pyrolysis in a fixed bed batch reactor

The schematic diagram of the fixed bed pyrolysis apparatus can be found in our previous work [28]. A mass of 100 g of oil sand particles less than 5 mm in diameter was inserted into the horizontal fixed bed reactor furnace tube. To prevent combustion, preheated high-purity nitrogen at the final reaction temperature was introduced into the reactor at 0.04 m^3/h (25 °C and 0.101 MPa). The pyrolysis reaction was performed at atmospheric pressure. The furnace was heated electrically at 10 °C/min from room temperature. The final temperature started from 100 °C and was increased in intervals of 50 °C up to 550 °C. The final sample was heated to 550 °C and kept for 1 h. A total of 12 solid samples were collected, including the raw sample, for analysis. To obtain the surface morphology of the oil sand particles nearest to the final temperature, when the thermocouple inside reached the final reaction temperature, the reactor tube was immediately removed from the furnace and placed in a water cooling system while the tube remained closed, as shown in Fig. 3. The cooling water was injected to the cotton cloth packing to cool the tube, which should be wetted before placing the tube. The cooling water injection temperature was 20 °C and the outlet temperature was from about 50 °C down to 20 °C. When the reactor tube had cooled to room temperature, the oil sand particles were removed from the tube.

2.4. Thermogravimetric analysis

A TA Instruments Q50 thermogravimetric analyzer was used to study the oil sand pyrolysis behavior. The experiment was carried out using an approximate 20 mg oil sand sample with a diameter of less than 2 mm, heated from 30 °C to 650 °C at a rate of 10 °C/min, in the presence of 50 mL/min of nitrogen flow.

2.5. Solid samples characterization

The surface morphology of the fixed bed pyrolysis solid products was analyzed through a Hitachi S-4800 scanning electron microscope (SEM). The test was carried out at room temperature (5 kV, 500 ×) without coating. The specific surface area and pore volume of the solid products were determined by way of isothermal adsorption of N_2 at 77.4 K in a Quantachrome Instruments NOVA2000 system. Prior to recording the adsorption measurements, the samples were degassed under vacuum at 100 °C for 12 h.

3. Results and discussion

3.1. Visualization of oil sand pyrolysis

In this section, we are going to study the pyrolysis progress from macroscopic perspective. The following chain of events can describe the pyrolysis progress phenomenon observed. As shown in Fig. 4, the appearance of the particle cluster remained constant at temperatures lower than 150 °C. A partial wetting phenomenon appeared at 150 °C,