



## Research article

# Upgrading of oil sand bitumen over an iron oxide catalyst using sub- and super-critical water



Hisaki Kondoh<sup>a</sup>, Yuta Nakasaka<sup>a,\*</sup>, Tatsuya Kitaguchi<sup>a</sup>, Takuya Yoshikawa<sup>a</sup>, Teruoki Tago<sup>b</sup>, Takao Masuda<sup>a</sup>

<sup>a</sup> Research Group of Chemical Engineering, Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

<sup>b</sup> Department of Chemical Engineering, Graduate School of Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8852, Japan

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## ABSTRACT

Upgrading of oil sand bitumen was examined using a catalyst consisting of  $\text{CeO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$  and sub- and super-critical water in two reactor types: batch-type and fixed-bed flow-type. Bitumen diluted with benzene was used as a feedstock, and the effects of reaction pressure and temperature on product yield were investigated. Under conditions of high pressure (approximately 19 MPa), catalytic decomposition of bitumen proceeded effectively over the  $\text{FeO}_x$ -based catalyst, with the yield of lighter components such as gas oil and vacuum gas oil (VGO) reaching 70 mol%-C at a reaction temperature of 693 K. Moreover, because coke formation on the catalyst was suppressed (less than 10 mol%-C under optimized reaction pressure and temperature), the  $\text{FeO}_x$ -based catalyst showed excellent durability and reusability for catalytic decomposition of bitumen.

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## 1. Introduction

In recent years, the demand for useful fuels such as gasoline and kerosene has grown constantly. According to the BP Statistical Review of World Energy, approximately half of the Earth's primitive petroleum deposits have already been consumed [1]. Therefore, new techniques to produce fuels from unused heavy oil, such as atmospheric-distilled or vacuum-distilled residual oil, oil sands, and Orinoco tar, are required. Oil sand bitumen, in particular, is an important energy resource because large deposits are known to exist. The proven reserve in Canada is estimated to be about 170 billion barrels [1]. Because about 80% of oil sand bitumen is found in deep layers, it is recovered by the steam-assisted gravity drainage (SAGD) method, in which high-pressure, high-temperature steam is injected into the deep layer. The viscosity of bitumen mined by the SAGD method is too high to allow transportation by pipeline, so post-mining treatment is required to decrease the viscosity. Recently, the decomposition and upgrading of bitumen using sub- and super-critical water, using the high-temperature, high-pressure water used for recovery of bitumen, has attracted the attention of many researchers [2–5].

Previously reported methods of upgrading heavy oil include thermal cracking [6], hydrocracking, and catalytic cracking [7,8]. Moreover, researchers have subjected several types of heavy crude oil, including oil sand bitumen [9], vacuum residue [10,11], and asphalt [12], to super-critical water treatment. They reported that super-critical water

treatment resulted in greater yields of the lighter components and smaller amounts of coke compared to thermal decomposition.

After developing catalysts composed of iron oxide (abbreviated  $\text{FeO}_x$ ) supported on zirconia ( $\text{ZrO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and ceria ( $\text{CeO}_2$ ) ( $\text{CeO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ , abbreviated as “ $\text{FeO}_x$ -based catalyst”), we succeeded in producing lighter components from atmospheric residual oil (AR) by catalytic cracking in a steam atmosphere [13–19]. Iron oxide has the advantage of being relatively inexpensive. Moreover, metal oxides have been utilized in the decomposition of glycerol [20,21], cacao pod husks [22], lignin [23], pyrolygneous acid [24], and ethanol fermentation stillage [25] to give useful materials. Compared with AR, the concentration of heavy components such as VR (vacuum residue) and asphaltene is much higher in bitumen, which means that carbonaceous residues and coke are easily formed during its decomposition. The deposition of carbonaceous residue on catalysts and in reactors is a serious problem [26,27]. Several methods have been proposed to overcome this problem. Cho et al. reported a catalyst that resisted the deposition of heavy metals, and a regeneration method for deactivated catalysts was developed [28]. Matsumura et al. reported that the formation of carbon residues was inhibited under hydrogen at high pressure [29]. However, hydrogen, which is produced by reforming petroleum, is expensive. Other researchers developed an aquaconversion process for degrading heavy oil by catalytic cracking with steam [30–32]. They reported that a catalytic steam conversion process allowed for the transfer of hydrogen from water vapor to the unconverted crude oil bottoms. The process starts with the well-known thermal cracking reaction to produce hydrocarbon-free radicals, followed by catalytic formation of hydrogen-free radicals, as well as hydrogen addition

\* Corresponding author.

E-mail address: [nakasaka@eng.hokudai.ac.jp](mailto:nakasaka@eng.hokudai.ac.jp) (Y. Nakasaka).

to the hydrocarbon-free radicals to prevent the formation of polycondensate compounds or polymerization reactions. However, the use of water-soluble alkali-metal-based catalysts is costly [33]. Because the use of pressurized water, including sub-critical and super-critical water, was expected to suppress the formation of coke and other residues, we examined the catalytic decomposition of bitumen under high pressure with the aim of efficiently producing lighter fuels.

The main objective of the study was continuous decomposition of bitumen over an  $\text{FeO}_x$ -based catalyst under conditions of high-pressure water. In order to decrease the amount of coke deposited on the catalyst during the reaction, the effects of reaction pressure and temperature on the product yield and the yield of coke were investigated. Under high-pressure conditions (approximately 19 MPa), the amount of coke deposited on the catalyst decreased significantly. This decrease in the coke deposition was one of the most important factors in the effective decomposition of bitumen and the durability and reusability of the catalyst.

## 2. Experimental

### 2.1. Preparation and characterization of $\text{CeO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ catalyst

The  $\text{CeO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$  catalyst ( $\text{FeO}_x$ -based catalyst) was prepared by a co-precipitation method using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  aqueous as catalyst sources. The pH of the solution was adjusted to 9.0 by addition of ammonia. All reagents were purchased from Wako Pure Chemical Industries (Japan). The resulting precipitate was dried at 373 K and calcined at 773 K for 2 h in air. The composition of the catalyst with respect to  $\text{CeO}_2$ ,  $\text{ZrO}_2$ , and  $\text{Al}_2\text{O}_3$  was 2.5, 7.5, and 7.0 wt.%, respectively. The crystallinity of the catalyst prior to and after the reaction was analyzed using an X-ray diffractometer (JDX-8020; JEOL).

### 2.2. Experimental procedure

Canadian oil sand bitumen (10 wt.%) diluted with benzene to reduce the viscosity, was used as a feedstock. The  $\text{FeO}_x$ -based catalysts were confirmed in advance to be inactive toward benzene. There was no

change with benzene under each condition of the reaction. Catalytic decomposition of bitumen using  $\text{FeO}_x$ -based catalysts was carried out in batch and fixed-bed reactors, as illustrated in Fig. 1(a) and (b), respectively.

The process in the batch reactor was as follows. The feedstock of diluted bitumen was placed in the reactor along with water and the catalyst. The weight ratio of catalyst to bitumen ( $W_{\text{cat}}/W_{\text{b}}$ ,  $W_{\text{cat}}$ : catalyst amount [g];  $W_{\text{b}}$ : weight of bitumen [g]) and water to bitumen ( $W_{\text{H}_2\text{O}}/W_{\text{b}}$ ,  $W_{\text{H}_2\text{O}}$ : weight of water [g];  $W_{\text{b}}$ : weight of bitumen [g]) were 4 and 20, respectively. Prior to catalytic decomposition, nitrogen gas was substituted for air inside the reactor, followed by adjustment of the initial pressure to 0.1 MPa, and the valve was closed. The reactor was heated to the reaction temperature of 693 K. The heating time and reaction time were set at 40 and 60 min, respectively. During the heating process, the pressure inside the reactor increased, so the pressure was measured and adjusted by changing the total amount of feedstock (bitumen) and water inside the reactor.

The phase of the water depended on the pressure in the system at high temperature and high pressure, which affected the catalytic decomposition of bitumen. Accordingly, in order to optimize the pressure, its effect on the decomposition efficiency of bitumen was examined using the batch reactor, with pressure adjusted in the range 2.9–28.3 MPa.

The process for the fixed-bed reactor was as follows. Prior to the reaction, the catalyst was preheated under steam flow to the reaction temperature under high pressure. The feedstock of diluted bitumen, along with water, was fed into the reactor using a high-pressure pump. High-pressure water was fed from the pump into the cylinder of a syringe and the cylinder was gradually pushed to feed the contents into the reactor. The reaction temperature was fixed at 623–673 K, and reaction time was set to 2 h. After termination of the reaction, the liquid and gaseous products were collected with an ice trap and a gas pack, respectively. The time factor, which is defined as the ratio of the catalyst mass to the feed rate  $W_{\text{cat}}/F_{\text{b}}$  ( $W_{\text{cat}}$ : catalyst amount [g],  $F_{\text{b}}$ : bitumen rate [ $\text{g h}^{-1}$ ]), and  $F_{\text{H}_2\text{O}}/F_{\text{b}}$  ( $F_{\text{H}_2\text{O}}$ : water rate,  $\text{g h}^{-1}$ ,  $F_{\text{b}}$ : bitumen rate,  $\text{g h}^{-1}$ ) were 4 and 20, respectively. The effects of reaction temperature on product yield, the decomposition efficiency of bitumen, and the durability of the catalyst were examined.

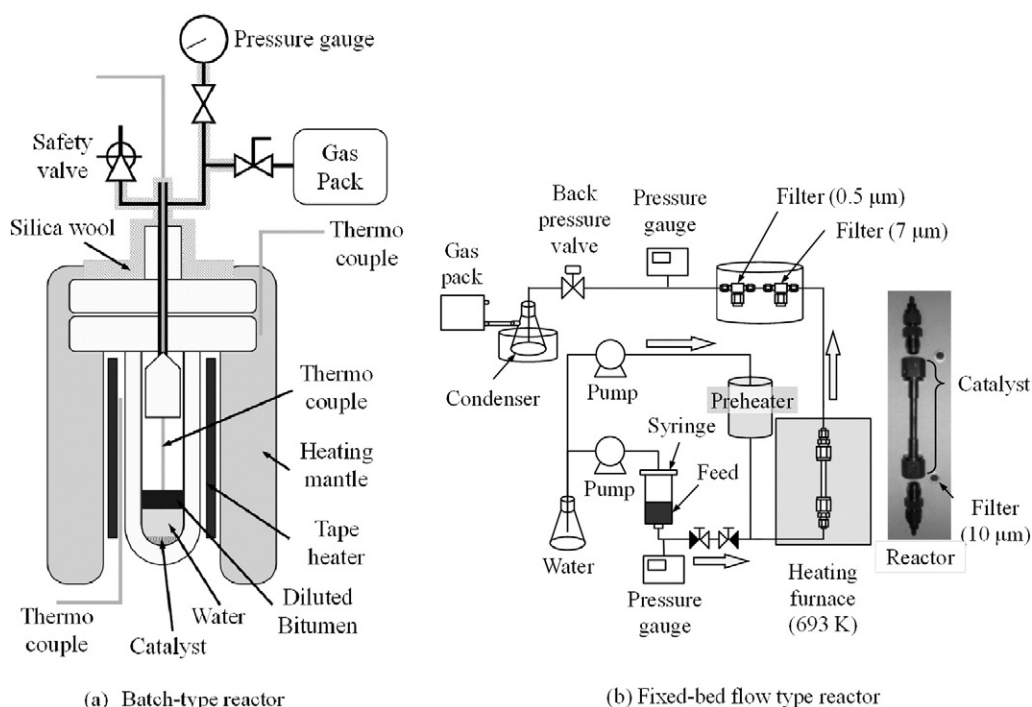


Fig. 1. Experimental apparatus for catalytic decomposition of bitumen. (a) High-pressure batch reactor; (b) high-pressure fixed-bed flow reactor.

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