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

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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

5 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

10 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.

## **Keywords**

15 Oil sand bitumen, Heavy oil, Iron oxide catalyst, Catalytic decomposition, Lighter fuel

## 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, 5 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 10 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, 15 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.

5 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  
10 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 asphaltenes is much higher in bitumen, which means that carbonaceous residues and coke are easily formed during its decomposition. The  
15 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 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 FeO<sub>x</sub>-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.

## 5 **2. Experimental**

### *2.1. Preparation and characterization of CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> catalyst*

The CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>x</sub> catalyst (FeO<sub>x</sub>-based catalyst) was prepared by a co-precipitation method using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>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 CeO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> 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).

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### *2.2. Experimental procedure*

Canadian oil sand bitumen (10 wt%) diluted with benzene to reduce the viscosity, was used as a feedstock. The FeO<sub>x</sub>-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 FeO<sub>x</sub>-based catalysts was carried out in batch and fixed-bed reactors, as illustrated in Figs. 1(a) and 1(b), respectively.

[Figs. 1(a) and 1(b)]

5        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  
10    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 minutes, 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  
15    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.

15

### 2.3. Analysis

The procedure for gaseous, liquid, and solid products after experimental runs using the batch reactor is shown in Fig. 2. Gaseous and liquid products were collected and

analyzed by gas chromatography (GC) and high-performance liquid chromatography (HPLC), respectively. The gaseous products were analyzed by GC with thermal conductivity and flame ionization detectors (GC-8A; Shimadzu Co. Ltd.) with activated charcoal and Porapak Q columns, respectively. Liquid products were centrifuged to  
5 separate the oil phase from the water phase. The resulting oil phase was analyzed by HPLC using a PL-gel Mixed-D column with a refractive index (RI) detector to calculate the molecular weight distribution. By assuming the unit structure of heavy oil to be -CH<sub>2</sub>-, the carbon number distributions of bitumen and the resulting lighter components were calculated from the molecular weight distribution. Because benzene was used as a  
10 cutter stock for HPLC analysis, liquid products with a carbon number below 13 were ignored in the calculation of the production yield. The carbonaceous residue remaining on the reactor wall was almost entirely rinsed away using 40 grams of CH<sub>2</sub>Cl<sub>2</sub>. The resulting hydrocarbon fraction in CH<sub>2</sub>Cl<sub>2</sub> was analyzed by HPLC. The solid mixture of catalyst and carbon was dried under vacuum conditions at 343 K and the amount of  
15 carbon deposited on the catalyst during the reaction was analyzed using an elemental analyzer (ECS 4010; Costech Analytical Technologies Inc.).

[Fig. 2]

The analytical procedure for the gaseous and liquid products obtained from the

high-pressure fixed-bed reactor was almost the same as for the products obtained in the batch reactor. The liquid and gaseous products were collected with an ice trap and a gas pack, respectively.

## 5 **3. Results and Discussion**

### *3.1 Effect of reaction pressure on product yield in the batch-type reactor*

In the batch reaction system, catalytic decomposition of bitumen occurred during the heating and cooling processes between the ambient and reaction temperatures. In order to evaluate the decomposition activity of the catalyst, it is necessary to minimize undesirable reactions. Accordingly, the effect of reaction time on product yield during the catalytic decomposition of bitumen was examined. The reaction temperature and pressure were 693 K and 20 MPa, respectively. The changes in product yield with time are listed in Table 1. The products were classified into four categories: gas oil (carbon number 14–20), VGO (21–40), VR (> 41), and coke + residue. Although CO<sub>2</sub>, methane, and light hydrocarbons were generated as gaseous products, their total yield was less than 0.1 mol%-C, so the gaseous yield was ignored.

[Table 1]

In the batch reaction system, the reactor was heated from room temperature to the

reaction temperature. Since cracking reactions as well as coke formation proceeded during the heating process, the decomposition of bitumen and the formation of carbonaceous residue took place only to a limited extent. After 0 min, the yield of carbonaceous residue (coke + residue) was approximately 11.1 mol%-C; this residue  
5 was formed during the heating process as the mixture was heated from ambient temperature. The yield of lighter fuels (gas oil and VGO) increased rapidly with reaction time up to 30 min, and increased gradually from 30 to 60 min reaction time. In contrast, the yield of carbonaceous residue increased slightly, from 11.1 to 17.9 mol%-C, with reaction time. Accordingly, a reaction time of 60 min was decided on for the batch  
10 reaction.

Next, the effect of reaction pressure on the product yield was investigated (Fig. 3). Although the major gaseous product was CO<sub>2</sub>, the yield was less than 0.1 mol%-C, so the gaseous yield was ignored. As shown in the figure, the reaction pressure had a dramatic influence on the catalytic decomposition of bitumen. The total yield of lighter  
15 components (gas oil and VGO) reached approximately 70 mol%-C, and the formation of carbonaceous residue was suppressed as the reaction pressure increased to approximately 22 MPa. In contrast, at reaction pressures above 25.8 MPa and under super-critical water conditions, the yield of lighter components decreased to about 45

mol%-C. Morimoto *et al.* reported that the polymerization of heavy oil components was suppressed in super-critical water due to the cage effect [34]. In that experiment, heavy components with high molecular weights were dispersed in super-critical water. Since heavy components as well as lighter components produced in the reaction were highly dispersed in super-critical water due to the cage effect, adsorption of these components on the catalyst surface was enhanced, leading to recombination of the lighter components and/or reaction of heavy components with the lighter components on the catalyst surface.

[Fig. 3]

From the viewpoint of the yield of lighter components and the production of carbonaceous residue, it was concluded that a reaction pressure of approximately 19 MPa was suitable for upgrading of bitumen using the FeO<sub>x</sub>-based catalyst. Next, the effects of reaction temperature and reaction time on product yield and the stability of the catalyst were examined using a fixed-bed reactor (19 MPa) for continuous upgrading of bitumen over an FeO<sub>x</sub>-based catalyst.

### 3.2. Effect of reaction temperature using a fixed-bed flow-type reactor

The effect of reaction temperature on the catalytic decomposition of bitumen was

examined over an FeO<sub>x</sub>-based catalyst using a fixed-bed reactor. The reaction temperature was varied in the range from 623 K to 693 K, and, based on the above results, the reaction pressure was fixed at approximately 19 MPa.

Figure 4 shows the molecular weight distributions of bitumen and the liquid products.

5 Based on the assumption that the unit structure of heavy oil was -CH<sub>2</sub>-, the molecular weight distributions (Fig. 4) were converted to the carbon number distributions for bitumen and liquid products (Fig. 5), and these were divided into three groups (gas oil, VGO, and VR). “Residue” and “Coke” represent the carbonaceous residue deposited on the reactor wall and that deposited on the catalyst surface, respectively. The gaseous  
10 products generated during the reaction, and liquid products, are also shown in Fig. 5.

[Fig. 4 and Fig. 5]

As shown in Figs. 4 and 5, VR (with a molecular weight above 500 g/mol) made up approximately 65 mol%-C of the bitumen used in the reaction. Moreover, it was found that the bitumen contained heavy components with molecular weights above 2000  
15 g/mol. After catalytic decomposition of bitumen, the fraction of heavy components with molecular weights above 2000 g/mol disappeared. Moreover, the distribution shifted toward the lower molecular weight region, and the fractions of gas oil and VGO (molecular weight of approximately 300 g/mol) increased significantly as the reaction

temperature increased.

As shown in Fig. 5, although the yield of residue, i.e., carbonaceous residue deposited on the reactor wall, was approximately 20 mol%-C at reaction temperatures of 623 and 653 K, it decreased to less than 10 mol%-C at reaction temperatures above 673 K. The  
5 decrease in the yield of residue was ascribed to the change in the viscosity of bitumen with reaction temperature. The viscosity of bitumen decreased and its fluidity was improved at temperatures above 673 K, which contributed to an increase in access to the active site of catalyst. Under the conditions used, the heavy bitumen molecule dissolves easily in the solvent, and the lower viscosity of the solvent improves contact between  
10 the oil and the catalyst, resulting in a decrease in a coke formation. As shown in Figs. 5(a) and 5(b), the amount of CO<sub>2</sub> generated during the reaction and the yields of lighter components such as gas oil and VGO increased with reaction temperature. The increase in the CO<sub>2</sub> generation was ascribed to oxidative cracking of bitumen by the lattice oxygen of the FeO<sub>x</sub> catalyst. Accordingly, the catalytic decomposition of bitumen  
15 proceeded effectively over the FeO<sub>x</sub>-based catalyst at reaction temperatures above 673 K due to the greater fluidity of bitumen and high catalytic activity. The yields of lighter components reached approximately 70 mol%-C at a reaction temperature of 693 K.

### 3.3. Catalyst durability

As discussed above, since the generation of CO<sub>2</sub> increased at reaction temperatures above 673 K, it was considered that the active site for the conversion of bitumen to lighter components was the lattice oxygen of FeO<sub>x</sub>, on which the adsorbed hydrocarbon molecules of bitumen were oxidatively decomposed into lighter components. We reported previously that the lattice oxygen consumed in the reaction (defect of lattice oxygen) can be regenerated by active oxygen species produced on ZrO<sub>2</sub> from H<sub>2</sub>O [17, 35], and that the consumption/regeneration cycle of the lattice oxygen in FeO<sub>x</sub> contributes to continuous activity in bitumen decomposition. Because the durability of the catalyst is indispensable for continuous decomposition of bitumen over the FeO<sub>x</sub>-based catalyst using the fixed-bed reactor, the durability of the catalyst was examined during catalytic decomposition of bitumen. The reaction temperature and pressure were 693 K and 19 MPa, respectively. Figures 6 and 7 show the changes in product yield and the XRD pattern of the catalyst, respectively, with reaction time. The product yield and the XRD pattern after the reaction under atmospheric pressure (0.1 MPa) are also shown in these figures for comparison.

[Fig. 6 and Fig. 7]

During the initial reaction time of 0–2 h, carbonaceous residue was deposited on the

reactor wall under both low- (0.1 MPa) and high-pressure (19 MPa) conditions. While decomposition of bitumen occurred under low-pressure conditions, the yield of lighter components was much lower and the coke yield was much higher than under high-pressure conditions. Under low-pressure conditions, coke on the catalyst surface  
5 inhibited the adsorption and reaction of the hydrocarbon molecules of bitumen on the active sites, leading to a lower yield of lighter components. In contrast, suppression of coke formation under high-pressure conditions enhanced the catalytic decomposition of bitumen. Moreover, the total yields of gas oil and VGO were as high as 65 mol%-C after 6 h under high-pressure conditions, indicating stable activity in the catalyst.

10 As shown in Fig. 7, the XRD pattern of catalyst before the reaction showed peaks corresponding to hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ); almost no peaks corresponding to other metal oxides were observed. The pattern after the reaction at low pressure showed peaks corresponding to magnetite ( $\text{Fe}_3\text{O}_4$ ), indicating that the  $\text{FeO}_x$  in the catalyst was reduced from hematite to magnetite during the reaction. In contrast, under high-pressure  
15 conditions, the catalyst maintained its hematite structure for 6 h. In the catalytic decomposition of bitumen, oxidative cracking of bitumen proceeded using the lattice oxygen of  $\text{FeO}_x$ . Lattice oxygen consumed during the reaction was regenerated by active oxygen species produced by the decomposition of  $\text{H}_2\text{O}$  on  $\text{ZrO}_2$  [35]. As shown

in Fig. 6, the deposition of large amounts of coke on the catalyst surface suppresses the regeneration of the consumed lattice oxygen, leading to excessive consumption of lattice oxygen as well as reduction of  $\text{FeO}_x$  from hematite to magnetite (Fig. 7). Under high-pressure conditions, since the consumption/regeneration reactions cycled  
5 effectively, the catalyst maintained the hematite structure, as shown in Fig. 7.

After the decomposition of bitumen for 6 h, the yield of coke was approximately 10 mol%-C. This was removed from the catalyst by air calcination at 773 K for 2 h, and the calcined catalyst was reused for catalytic decomposition of bitumen for 2 h. The product yield and XRD pattern of the catalyst after the reaction are also shown in Figs. 6 and 7,  
10 respectively. After air calcination, the catalyst gave almost the same product yield and exhibited almost the same XRD pattern as before air calcination. Accordingly, the  $\text{FeO}_x$ -based catalyst showed excellent durability during the catalytic decomposition of bitumen.

#### 15 **4. Conclusion**

Upgrading of Canadian oil sand bitumen over an  $\text{FeO}_x$ -based catalyst was examined with the aim of producing lighter fuels. It was revealed that the catalytic decomposition of bitumen proceeded effectively under high-pressure conditions (around 19 MPa) with

low coke deposition on the catalyst. Moreover, the yield of lighter components (gas oil and VGO) reached approximately 70 mol%-C, and continuous decomposition of bitumen with high yields was achieved using a fixed-bed reactor. Since the amount of coke deposited on the catalyst was as low as 10 mol%-C under optimized conditions  
5 (reaction temperature and pressure of 693 K and 19 MPa, respectively), the FeO<sub>x</sub>-based catalyst showed excellent durability and reusability for catalytic decomposition of bitumen.

## **5. Acknowledgements**

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Fig. 1 Experimental apparatus for catalytic decomposition of bitumen.

(a) High-pressure batch reactor; (b) high-pressure fixed-bed flow reactor.

Fig. 2 Analytical procedure for products after decomposition of bitumen using batch

5 reactor.

Fig. 3 Effect of reaction pressure on product yield for catalytic decomposition of

bitumen over  $\text{FeO}_x$ -based catalyst using a batch reactor. Reaction conditions: 10 wt%

bitumen solution,  $W_{\text{cat}}/W_{\text{b}} = 4$ ,  $W_{\text{H}_2\text{O}}/W_{\text{b}} = 20$ ,  $P$  (reaction pressure) = 2.9–28.3 MPa,  $T$

10 (reaction temperature) = 693 K, and  $t$  (reaction time) = 60 min.

Fig. 4 Changes in the molecular weight distribution of bitumen and liquid products

with reaction temperature during catalytic decomposition of bitumen using a fixed-bed

flow reactor. Reaction conditions: 10 wt% bitumen solution,  $W_{\text{cat}}/F_{\text{b}} = 4$ ,  $F_{\text{H}_2\text{O}}/F_{\text{b}} = 20$ ,

15 reaction pressure ~19 MPa.

Fig. 5 Changes in (a) amount of gaseous products generated, and (b) yield of liquid

product with reaction temperature during catalytic decomposition of bitumen using a

fixed-bed flow reactor. Reaction conditions: 10 wt% bitumen solution,  $W_{\text{cat}}/F_{\text{b}} = 4$ ,  $F_{\text{H}_2\text{O}}/F_{\text{b}} = 20$ ,  $P$  (reaction pressure) = 19 MPa,  $T$  (reaction temperature) = 623–693 K, and  $t$  (reaction time) = 2 h.

5 Fig. 6 Changes in product yields with time on stream during catalytic decomposition of bitumen using a fixed-bed flow reactor. Reaction conditions: 10 wt% bitumen solution,  $W_{\text{cat}}/F_{\text{b}} = 4$ ,  $F_{\text{H}_2\text{O}}/F_{\text{b}} = 20$ , reaction pressure ~19 MPa.

Fig. 7 XRD patterns of catalysts prior to and after the reaction with different reaction  
10 times. Reaction conditions: 10 wt% bitumen solution,  $W_{\text{cat}}/F_{\text{b}} = 4$ ,  $F_{\text{H}_2\text{O}}/F_{\text{b}} = 20$ , reaction pressure ~19 MPa.

Table 1 Changes in product yield with reaction time during catalytic decomposition of bitumen over an  $\text{FeO}_x$ -based catalyst using a batch reactor. Reaction conditions: 10  
15 wt% bitumen solution,  $W_{\text{cat}}/W_{\text{b}} = 4$ ,  $W_{\text{H}_2\text{O}}/W_{\text{b}} = 20$ ,  $P$  (reaction pressure) = 20 MPa,  $T$  (reaction temperature) = 693 K, and  $t$  (reaction time) = 0–60 min.

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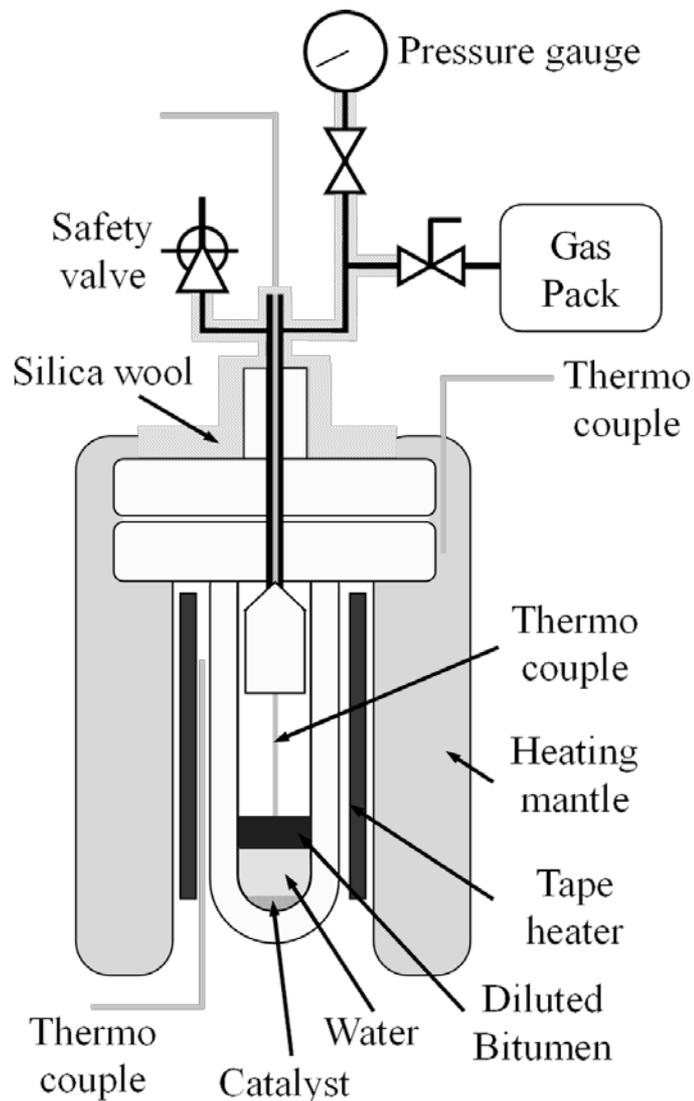
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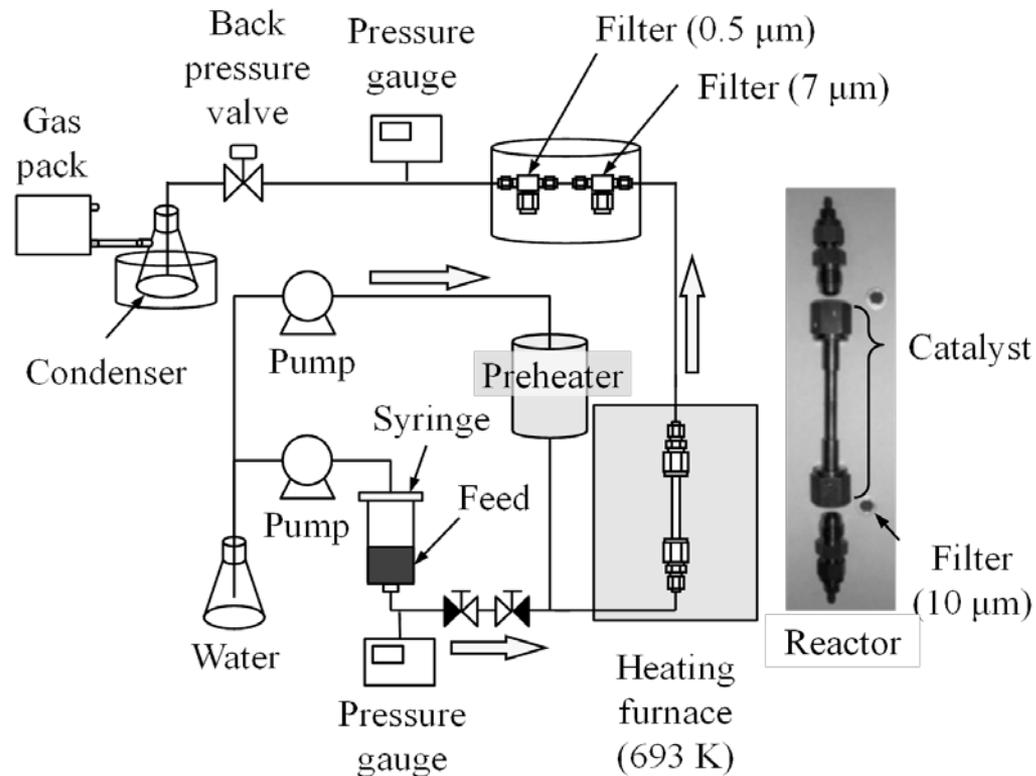
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**Upgrading of oil sand bitumen  
over iron oxide catalyst  
using sub- and super-critical water**

Fig.



(a) Batch-type reactor



(b) Fixed-bed flow type reactor

Fig. 1 Experimental apparatus for catalytic decomposition of bitumen.

(a) High-pressure batch reactor; (b) high-pressure fixed-bed flow reactor.

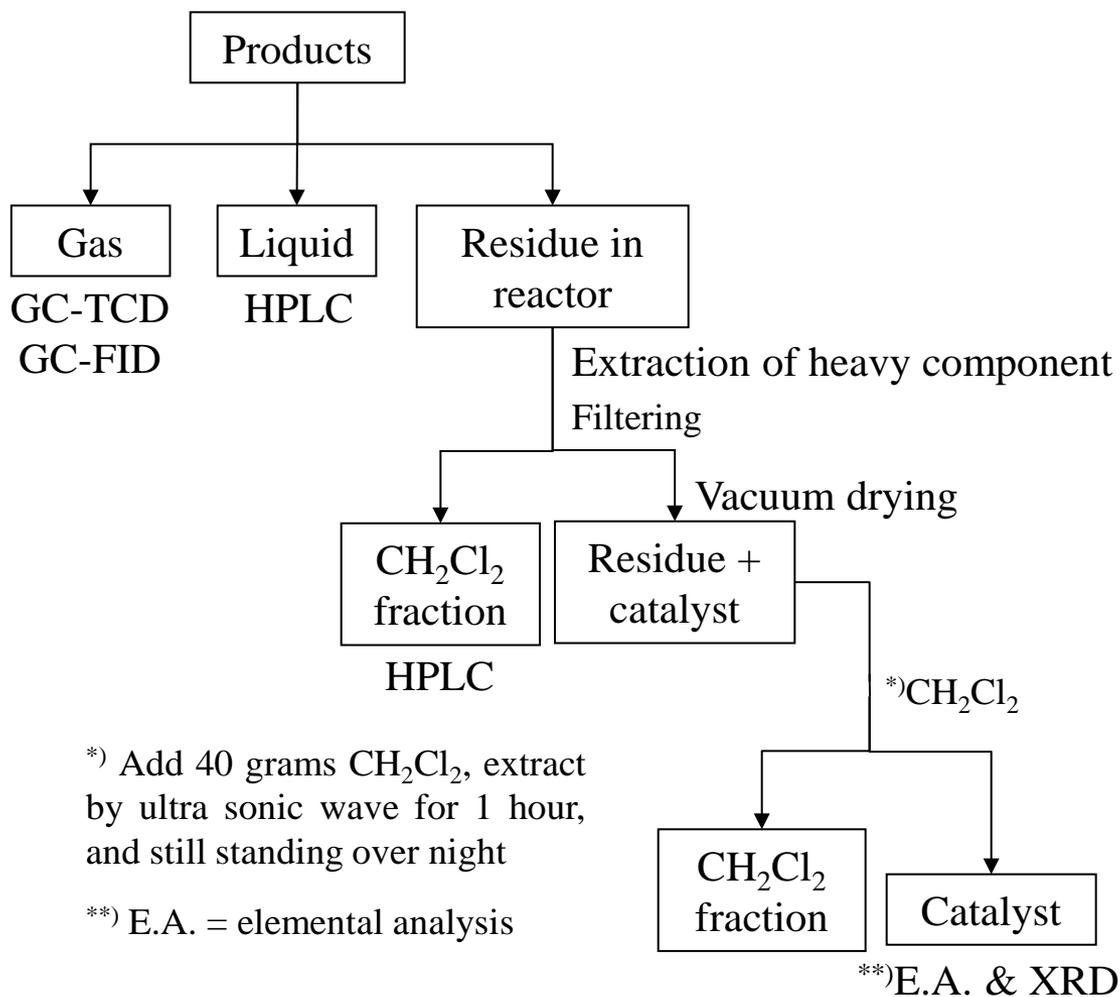


Fig. 2 Analytical procedure for products after decomposition of bitumen using batch reactor.

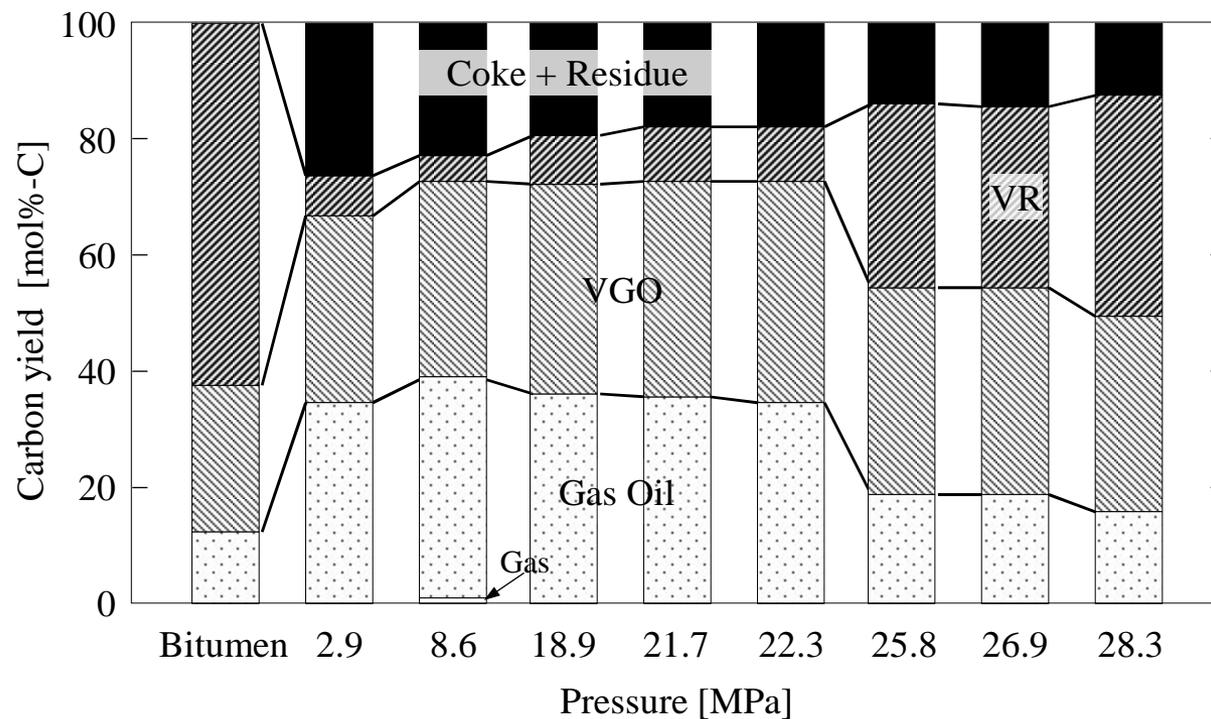


Fig. 3 Effect of reaction pressure on product yield for catalytic decomposition of bitumen over  $\text{FeO}_x$ -based catalyst using a batch reactor. Reaction condition: 10 wt% bitumen solution,  $W_{\text{cat}}/W_{\text{b}} = 4$ ,  $W_{\text{H}_2\text{O}}/W_{\text{b}} = 20$ ,  $P$  (Reaction pressure) = 2.9–28.3 MPa,  $T$  (Reaction temperature) = 693 K, and  $t$  (Reaction time) = 60 min.

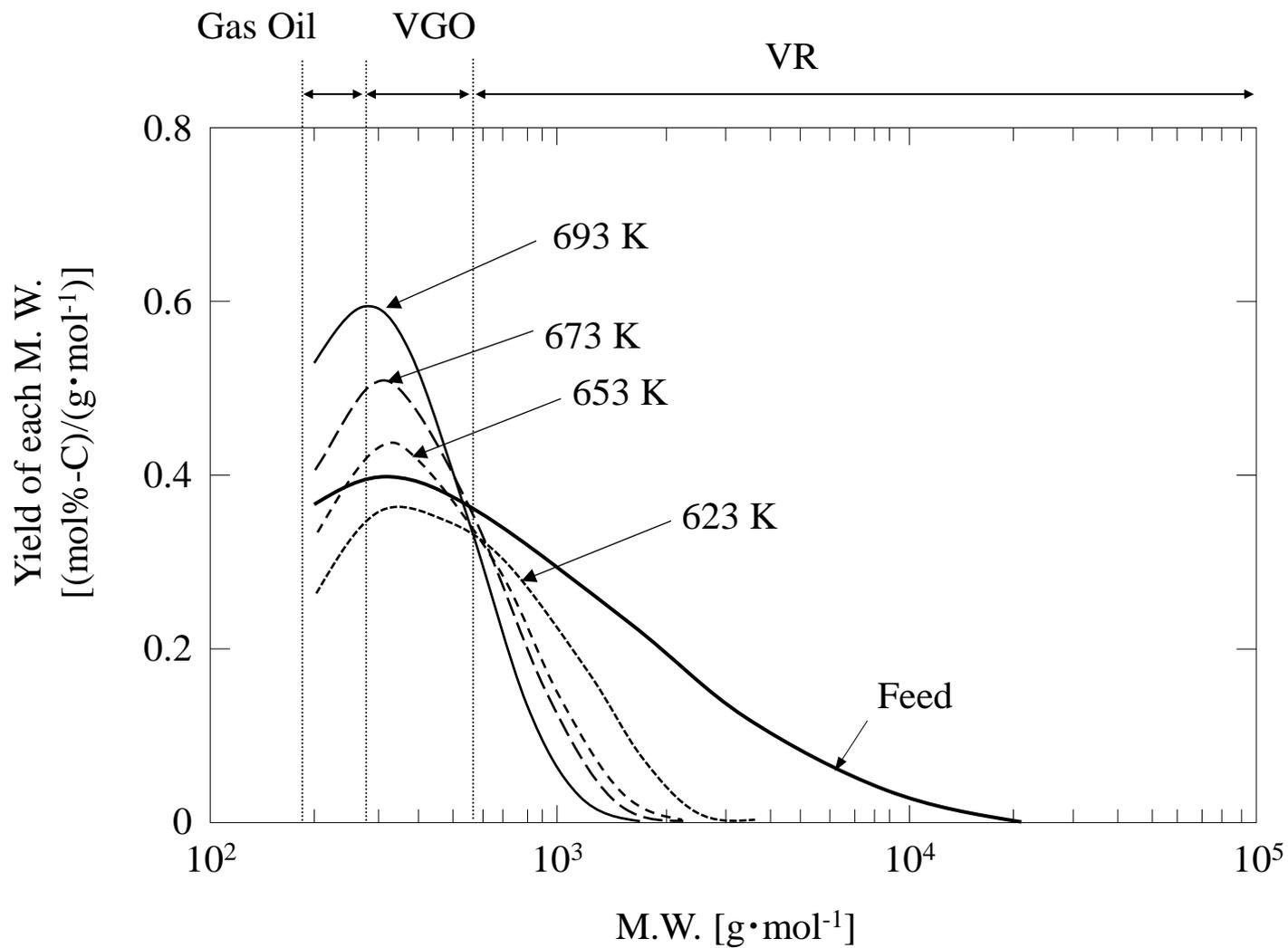


Fig. 4 Changes in the molecular weight distribution of bitumen and liquid products with reaction temperature during catalytic decomposition of bitumen using a fixed-bed flow reactor. Reaction condition: 10 wt% bitumen solution,  $W_{\text{cat}}/F_{\text{b}} = 4$ ,  $F_{\text{H}_2\text{O}}/F_{\text{b}} = 20$ , Reaction pressure was  $\sim 19$  MPa.

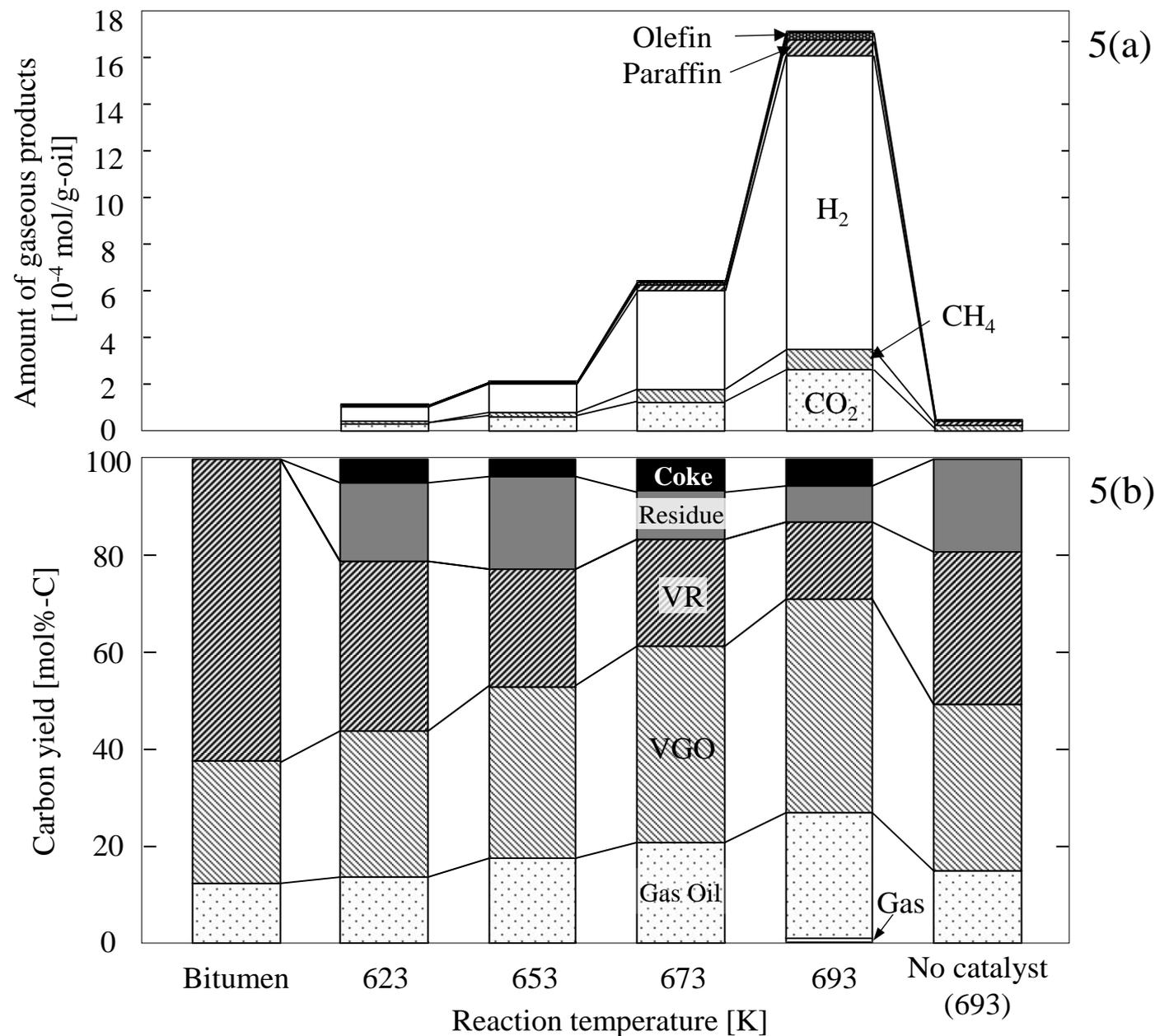


Fig. 5 Changes in (a) amount of gaseous products generated, and (b) yield of liquid product with reaction temperature during catalytic decomposition of bitumen using a fixed-bed reactor. Reaction condition: 10 wt% bitumen solution,  $W_{\text{cat}}/F_b = 4$ ,  $F_{\text{H}_2\text{O}}/F_b = 20$ ,  $P$  (Reaction pressure) = 19 MPa,  $T$  (Reaction temperature) = 623-693 K, and  $t$  (Reaction time) = 2 h.

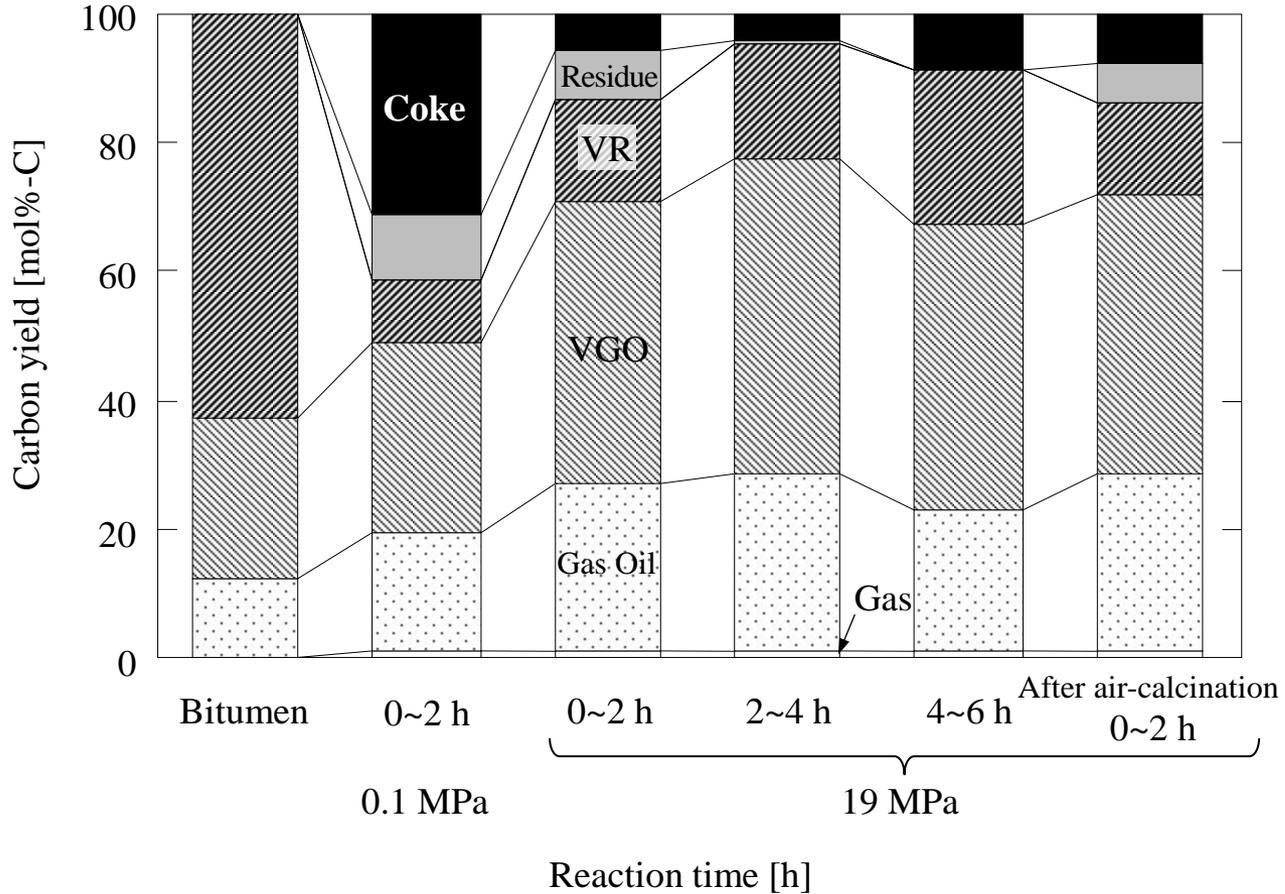


Fig. 6 Changes in product yields with time on stream during catalytic decomposition of bitumen using a fixed-bed flow reactor. Reaction condition: 10 wt% bitumen solution,  $W_{\text{cat}}/F_b = 4$ ,  $F_{\text{H}_2\text{O}}/F_b = 20$ , Reaction pressure was  $\sim 19$  MPa.

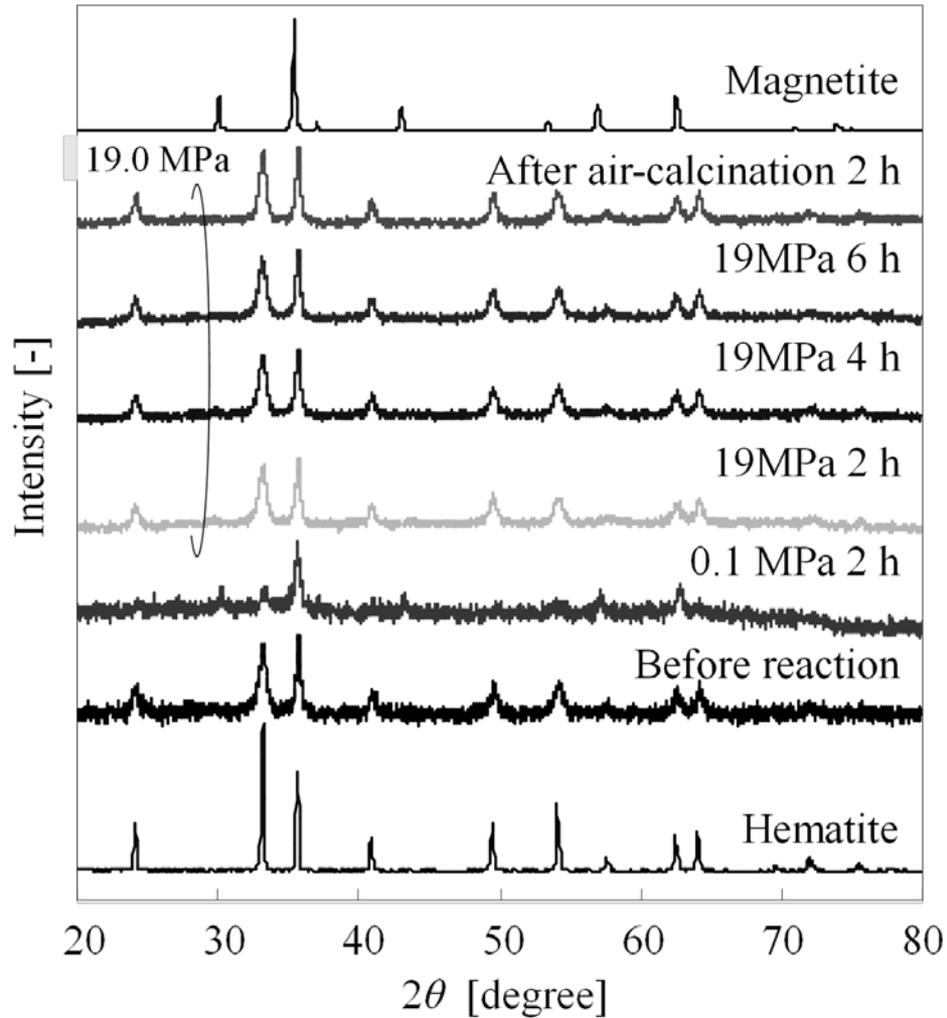


Fig. 7 XRD patterns of catalysts prior to and after the reaction with different reaction times. Reaction condition: 10 wt% bitumen solution,  $W_{\text{cat}}/F_{\text{b}} = 4$ ,  $F_{\text{H}_2\text{O}}/F_{\text{b}} = 20$ , Reaction pressure was  $\sim 19$  MPa.

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Table

Table 1 Changes in product yield with reaction time during the catalytic decomposition of bitumen over FeOx-based catalyst with a batch reactor. Reaction condition: 10 wt% bitumen solution,  $W_{\text{cat}}/W_{\text{b}} = 4$ ,  $W_{\text{H}_2\text{O}}/W_{\text{b}} = 20$ ,  $P$  (Reaction pressure) = 20 MPa,  $T$  (Reaction temperature) = 693 K, and  $t$  (Reaction time) = 0–60 min.

Reaction time [min.]	Carbon yield [mol%-C]			
	Gas Oil	VGO	VR	Coke + Residue
0	17.5	34.6	36.8	11.1
15	27.1	40.6	19.6	12.7
30	31.4	38.1	15.2	15.3
60	35.3	37.2	9.3	17.9
60 (Without catalyst)	22.0	41.5	32.6	3.9