



## Research article

## Bifunctional base catalyst for vacuum residue cracking gasification

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## ABSTRACT

The residues cracking gasification was performed in a dual fluidized bed reactor by using calcium aluminate as the bifunctional catalyst, which was prepared by the solid phase method. Besides, carbon black assisted could contribute to improve the specific surface area of the catalyst. The performances of the reaction temperature and hydrothermal treatment catalysts on the products distribution for vacuum residue cracking were studied. It was found that solid base catalyst could promote to produce the products of light oils and light olefins, and co-producing the H<sub>2</sub>-rich syngas. The results showed that the C<sub>2</sub> + C<sub>3</sub> olefinicity of higher than 58.0%, heavy oil conversion of above 92.0%, and carbon deposited of ca. 4.2 wt% were achieved by cracking over two self-made solid base catalysts at 650 °C with a catalyst-to-oil ratio 7.0. Moreover, the catalyst with higher specific surface area displayed a better cracking performance than the one with lower specific surface area. Hydrothermal treatment base catalysts indeed decreased its activity, and thus led to higher liquid yield and lower gas yield. The carbon deposited on the catalyst was well gasified at 800 °C in steam-5.0 vol% oxygen. The H<sub>2</sub> content and the H<sub>2</sub>/CO ratio were reached about 58.0 vol% and 4.5, respectively, with the CH<sub>4</sub> content <0.5 vol%. Besides, in comparison with an industry solid base catalyst, the coke gasification rate was obviously accelerated over two self-made solid base catalysts. Furthermore, the cracking performance of the solid base catalysts could reach basically stable via a few cracking gasification cycles.

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## 1. Introduction

The proportion of unconventional oil resources reached about 14% of the world's oil supply. Extra-heavy oil and tar sand occupied about two thirds of unconventional oil resources. Therefore, processing these above-mentioned oils feedstock would have to produce a great amount of vacuum residue and atmospheric residue. At present, these residues are usually processed by the technologies of residue fluid catalytic cracking (RFCC) [1,2], coking [3–5], hydro-cracking [6] and visbreaking [7]. In some situations, several technologies could be integration used. RFCC technology is hard to directly processing the inferior feedstock due to the catalyst deactivation. Visbreaking technology is always used as a non-catalytic thermal pre-treatment process to reduce the viscosity of residual oils [8]. But it is difficult to treat high asphaltenes content of oil feedstock. Coking technology is widely used to treat the low-grade residues due to wide feedstock adaptability and high operation reliability. However, it would have to produce plenty of the petroleum coke might containing high content of contaminants. In addition, hydrogen was the important material for pre-treatment the low-grade oil

feedstock and converting the cracking liquids of the residues into clean vehicle fuel and petrochemical material [9,10]. Now, in petroleum industry, hydrogen was mainly produced via catalytic reforming of naphtha or separation from the dry gas and LPG. The residues cracking gasification process would provide a novel route to convert the above-mentioned residues into light products, and meanwhile co-producing hydrogen.

And the truth, petroleum residue consists of large molecules and has high content of contaminants and low hydrogen content [11]. The desired products of cracking oil and gas, which are mainly the gasoline and diesel fraction, have high light olefins and H<sub>2</sub>-rich syngas. Thus, it has to contain two types of reactions. Namely, the residues are first converted into light products and also conducive to remove the contaminants via catalytic cracking. Then the H<sub>2</sub>-rich syngas and regenerated catalyst was produced via gasifying the cracking-generated coke. For integration of these two reactions, a dual fluidized bed reaction system was thus used and the catalyst particles could circulate between cracking and gasification reactions. Thus, the catalyst could provide not only the proper activity and stability for the residue cracking and coke gasification, but also the exothermic heat for the cracking reaction.

The catalyst used in the cracking gasification cycle process was crucial. It should have not only proper activity for the residue cracking, but also high resistance to the contaminants. Both of these could ensure the stability of the catalysts, and produce the expected products at the

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possibly maximum degree. In regeneration, the used catalyst should have high the hydrothermal stability to the coke gasification in steam-oxygen. There are many literatures studies on increasing light products yields and inhibiting the coke formation via optimizing or developing the residues cracking catalyst. The distribution of the cracking products was decided by the base strength of the catalyst. It was found that the addition of alkaline oxides could obtain the desired base strength and reactivity of the catalysts to reduce the coke and enhance the light products yields. Kolombos [12] found the yield of ethylene could reach 17–23 wt% and no carbon deposited on the catalyst in 2 h by using  $\text{MnO}_2$  as the assistant. Basu [13] and Mukhopadhyay [14] found the reaction activation energy and the reaction temperature could efficiently reduce by using potassium impregnated calcium aluminate catalyst. Besides, solid base catalyst has been applied in the reactions of producing biodiesel [15–17] and coke gasification due to its good stability, high reactivity and production selectivity [18,19]. Wu [20] and Li [21] found the base catalysts were beneficial to convert petroleum coke into syngas and enhance the coke gasification rate. But it was rarely used solid base as bifunctional catalyst for the residues cracking gasification.

The aim of this research is to study the performance of bifunctional solid base catalyst (calcium aluminate with different the base density) for both catalyzing the residues cracking and enhancing the coke gasification effects in a dual fluidized bed reactor. Three catalysts including an industry solid base catalyst and two self-made solid base catalysts with different base density were used to study the proper activity for vacuum residue conversion. An industry solid base catalyst with the lower base density was used as a reference to study the thermal cracking performance of vacuum residue. Silica sand is used as a reference to study the thermal cracking performance of vacuum residue. Two self-made solid base catalysts with higher base density were prepared on the basis of the industry solid base catalyst with the same crystal structure for vacuum residue conversion. The desired catalyst for the residues cracking and carbon deposited gasification has to maintain the catalyst properties steadily for the residues cracking. Hydrothermal treatment was performed for the fresh catalysts to adjust their cracking activity. Coke gasification process was conducted to remove carbon deposited on the catalysts, and the stability of the catalysts was also tested.

## 2. Experimental

### 2.1. Materials and reagents

$\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$  were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd, China, and calcined at 200 °C for 1 h. Hammett indicators and benzoic acid was purchased from Qingdao Jingke Chemical Reagent Co., Ltd, China. Carbon black (CB) purchased from Alfa Aesar and dried at 120 °C overnight, and used without further purification. Vacuum residue (VR) purchased from wintek refinery, China, and their properties were listed in Table 1. An industry solid base catalyst (calcium aluminate denoted as CA-0) was supplied by Zibo catalyst Factory, China, and their properties were exhibited in Table 2.

**Table 1**  
Properties of wintek VR.

Properties	VR		
Density 20 °C/g·cm <sup>-3</sup>	0.98		
Viscosity 100 °C/mm <sup>2</sup> ·s <sup>-1</sup>	900		
H/C ratio	1.67		
Carbon residue/wt%	6.7		
Elemental analysis/wt%	Group composition/wt%		
C	87.0	Saturates	38.6
H	12.0	Aromatics	33.5
S	0.30	Resins	26.8
N	0.50	Asphaltenes	1.10
O (by difference)	0.20		

**Table 2**  
Textural properties of solid base catalysts and  $\text{Al}_2\text{O}_3$ .

Catalysts	Specific surface area/m <sup>2</sup> ·g <sup>-1</sup>	Total pore volume/cm <sup>3</sup> ·g <sup>-1</sup>	Bulk density/g·cm <sup>-3</sup>	Average pore diameter/Å
$\text{Al}_2\text{O}_3$	112.5	0.25	0.78	95.4
CA-0	3.2	0.01	1.50	92.8
CA-1	9.6	0.02	1.45	91.6
CA-1-800	8.3	0.02	1.40	105.5
CA-2	25.9	0.05	1.30	70.9
CA-2-800	23.6	0.04	1.31	95.3

### 2.2. Solid base catalyst preparation

Bifunctional calcium aluminate catalyst was prepared by the solid phase method. The schematic diagram of the formation process of calcium aluminate catalyst with (a) and without (b) the addition of CB was shown in Fig. 1.  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$  were firstly mixed with a  $\text{CaCO}_3/\text{Al}_2\text{O}_3$  molar ratio of 12:7, and they were evenly divided into two portions. In addition, 6.0 wt% CB was added in one of them. Then both of them were triturated respectively in the grinder for 3 min (3000 r·min<sup>-1</sup>) and calcinated at 1350 °C in argon for 2 h. And the carbon removal was performed at 600 °C for 2 h in air. These catalysts were denoted as CA-1 (without CB) and CA-2 (with CB), respectively. In addition, the fresh CA-1 and CA-2 catalysts were deactivated by hydrothermal treatment in steam to adjust its catalytic activity for VR cracking. The hydrothermal treatment temperature of 800 °C was adopted and maintained for 7 h. Thus, CA-1-800 and CA-2-800 was used to denote the hydrothermally treated CA-1 and CA-2 catalyst at 800 °C, respectively.

### 2.3. Cracking gasification experiment

The residues cracking gasification was performed in a fluidized bed reactor. The schematic diagram of the test device was shown in Fig. 2. The test device consists of the oil feeding system, the temperature controlling system, the reaction system, as well as the separation and analysis system. The reactor was the core of the test device, which was made up of stainless steel with the total length of 800 mm and the inner diameter of 25 mm. The expanded section at top with the dimensions of L = 200 mm and D = 90 mm, and the reaction section of 60 mm in diameter. And a self-designed porous stainless steel distributor was used to fluidize the catalyst particles. VR and steam were preheated and was continuously into the reactor by a plunger oil pump. Of steam was used to atomize VR and purge the whole reaction systems, which was also part of the reagent gas for coke gasification. In addition, oxygen was used to form the reagent gas for the coke gasification and combusted the remaining coke. Nitrogen was used as the purging gas for each cycle process.

For cracking, the fluidized bed reactor was first heated up to the needed reaction temperature under the atmosphere of nitrogen. Then VR and water was preheated to about 100 °C and 200 °C, respectively. Steam was first fed into reactor via an upward nozzle to fluidize the catalyst particles. When the temperature is stable, VR was fed into this reactor via another upward nozzle. And then vacuum residue and steam are mixed in the preheated section at the bottom of this reactor. Then the oil-steam mixtures pass through the upward nozzle at high speed and atomized into the tiny oil droplets, which was transported into the middle of the catalysts bed (such as silica sand and solid base catalysts) via a porous distributor, where are in turn vaporized and cracked through interacting with the catalyst particles. The cracking gas products were separated by an oil-gas separation system. The liquid products were cooled by a water-cooled tube. The heavier oil was collected in the first collector, and then the lighter oil in the second collector was collected with the cooling water of 1 °C. The non-condensable gas contents were measured by the wet gas meter and analysis by GC.

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