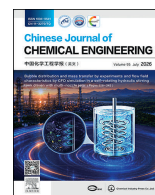




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Full Length Article

Oil hydrogenation in a HiGee-aided fixed bed reactor: Process intensification and macro-kinetic model

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ABSTRACT

Vacuum gas oil (VGO), an important raw material for catalytic cracking and hydrocracking units, undergoes hydrogenation process to remove sulfur and nitrogen compounds. However, the VGO hydrogenation process is limited by the gas-liquid mass transfer, resulting in a low reaction rate and high energy consumption. In this work, a HiGee-aided fixed bed reactor (HFBR) with excellent mass transfer performance has been developed and applied for VGO hydrogenation. The bed structure of HFBR was optimized and the effects of operating conditions on VGO hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) efficiency were investigated. Compared with fixed bed reactor at equivalent removal efficiency, pressure in HFBR was reduced by 5% to 15% and H/O ratio was lowered by 35% to 60%. The macro-kinetic models for HDS and HDN of VGO were established and the deviations between the calculated and experimental values were within $\pm 20\%$. This study provides guidance for the reactor design and process optimization of VGO hydrogenation.

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1. Introduction

Vacuum gas oil (VGO) is a condensate distillate from crude oil vacuum distillation unit, accounting for 20% to 30% of vacuum distillation products. It is often used as a vital feedstock for catalytic cracking and hydrocracking units [1–3]. As global environmental regulations become increasingly stringent, the efficient and clean processing of VGO has emerged as a core factor for refineries, aiming to upgrade their product and achieve green transformation [4]. The residual sulfur and nitrogen compounds in VGO not only cause catalyst poisoning and deactivation during subsequent processing, but also corrode high-pressure equipment and pipelines. It is necessary to reduce the sulfur and nitrogen content in VGO through hydrotreating [5–7].

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Studies of hydrotreating process and its kinetics were carried out as an important basis to guide reactor scale-up and process optimization. Karim *et al.* [8] studied the hydrodesulfurization (HDS) process of VGO using Co-Mo/Al₂O₃ commercial catalysts and investigated the effect of temperature and liquid hourly space velocity (LHSV) on the desulfurization efficiency. They found that the desulfurization efficiency increased as the temperature increased and LHSV decreased. Maximov *et al.* [9] conducted HDS experiments on mixed feedstocks, containing VGO and heavy coking gas oil, at a hydrogen partial pressure of 5 MPa. The effects of temperature and LHSV on the HDS were studied and a kinetic model was developed. Rodríguez *et al.* [10] simulated the behavior of HDS of VGO in a pilot trickle bed reactor through five combinations of kinetic models and then evaluated their accuracy. Becker *et al.* [11] developed a reaction network including HDS, hydrodenitrogenation (HDN), and hydrocracking. Then they proposed a kinetic model of VGO hydrogenation based on a continuum approach to optimize the operating conditions (e.g., temperature, pressure, and LHSV) of the hydrotreating process. Based on the above kinetic studies, it is found that VGO hydrotreating

processes in traditional reactors were often limited by gas-liquid mass transfer rate, resulting in low reaction efficiency, high energy consumption, and large equipment size. There is an urgent need to find suitable process intensification technology to increase the gas-liquid mass transfer rate [12].

Microbubbles usually refer to bubbles with diameters of 1 μm –1 mm, which have the advantages of long residence time [13], large gas-liquid interfacial area [14], and large pressure difference between the bubble gas-liquid sides [15]. They have been widely used in the process intensification for the gas-liquid mass transfer in the hydrogenation [16–18], oxidation [19,20], and other processes. The HiGee microbubble generator (HMG) can break millimeter-sized bubbles into microbubbles through the shearing action of internal packing and the strong disturbance of turbulent eddies, to intensify gas-liquid mass transfer [21,22]. HMG has the advantages of a wide range of gas-liquid ratios and controllable preparation of microbubbles by varying the rotational speed, which has great potential for application in VGO hydrotreating. However, before being towards industrial applications, there is a great lack of basic researches on internal optimization, hydrogenation performance, kinetics, etc.

In this work, experimental set-up, including a HiGee-aided fixed bed reactor (HFBR) composed of a HMG for generating microbubbles and a catalyst bed for hydrogenation, for VGO hydrotreating was innovatively designed and constructed. Firstly, the structure of the catalyst bed was optimized from the perspectives of filling volume of top quartz sand and catalyst shape. Based on the optimized catalyst bed, the effects of the operating conditions such as rotational speed (N) of HMG, reaction temperature (T), pressure (P), H_2 -oil volumetric flow rate ratio (H/O), and LHSV on the effect of VGO hydrotreating were then investigated from the perspectives of HDS and HDN. Finally, a macro-kinetic model for HDS and HDN was developed to guide the design of HFBR.

2. Experimental and Analysis Method

2.1. Materials

The nitrogen (N_2) used in this experiment was provided by Sichuan Qiaoyuan Gas Co., Ltd, and the hydrogen (H_2) was provided by Jiangsu Huazhong Gas Co., Ltd. The physical properties of the gases are shown in Table 1. The two feedstocks used in this experiment, VGO (I) and VGO (II), were produced by the crude oil vacuum distillation unit. Its physical properties are shown in Table 2. The four catalysts used in this experiment were all

independently developed by SINOPEC (Dalian) Research Institution of Petrochemicals Co., Ltd. This catalyst uses Mo-Ni as the active components. By optimizing the catalyst impregnation technology, it enhances HDS and HDN activity and metal removal capacity, making it particularly suitable for meeting the current demand of high activity and long-term stable operation in VGO hydrotreating units [23].

2.2. Apparatus and process

Fig. 1(a) shows a schematic diagram of the experimental set-up, which was jointly constructed by SINOPEC (Dalian) Research Institution of Petrochemicals Co., Ltd. and Beijing University of Chemical Technology. Before starting the experiment, first use nitrogen to purge the entire experimental set-up. Then switch from nitrogen to hydrogen for the experiment. Finally, after the experiment is finished, nitrogen is used again to purge the system to ensure no hydrogen residue remains [24]. The gas in the hydrogen cylinder is measured by a mass flow-meter and introduced into the inlet of the HMG. The hydrogen is pre-mixed with VGO and then fed into the HMG together. Millimeter-sized bubbles are cut by the high-speed rotating packing and further broken into microbubbles under the influence of turbulence. The VGO containing H_2 microbubbles enters the catalyst bed from top to bottom for HDS and HDN. The products at the bottom of the catalyst bed go into the high-pressure gas-liquid separator. Simultaneously, VGO flows out from the bottom of the high pressure gas-liquid separator, undergoes further pressure reduction, and enters the low pressure gas-liquid separator for deep impurity removal. Samples are taken at the bottom of the low-pressure gas-liquid separator for subsequent testing of sulfur and nitrogen content. In this experimental set-up, all pipelines through which VGO flows are wrapped with heating cables, while the feed tank and HMG are insulated and pre-heated using industrial electric heating blankets. Within the catalyst bed, three axial thermocouples are installed, enabling real-time control of the tube furnace's heating power via a PID (proportional-integral-derivative) control system, thereby controlling the temperature of the catalyst bed.

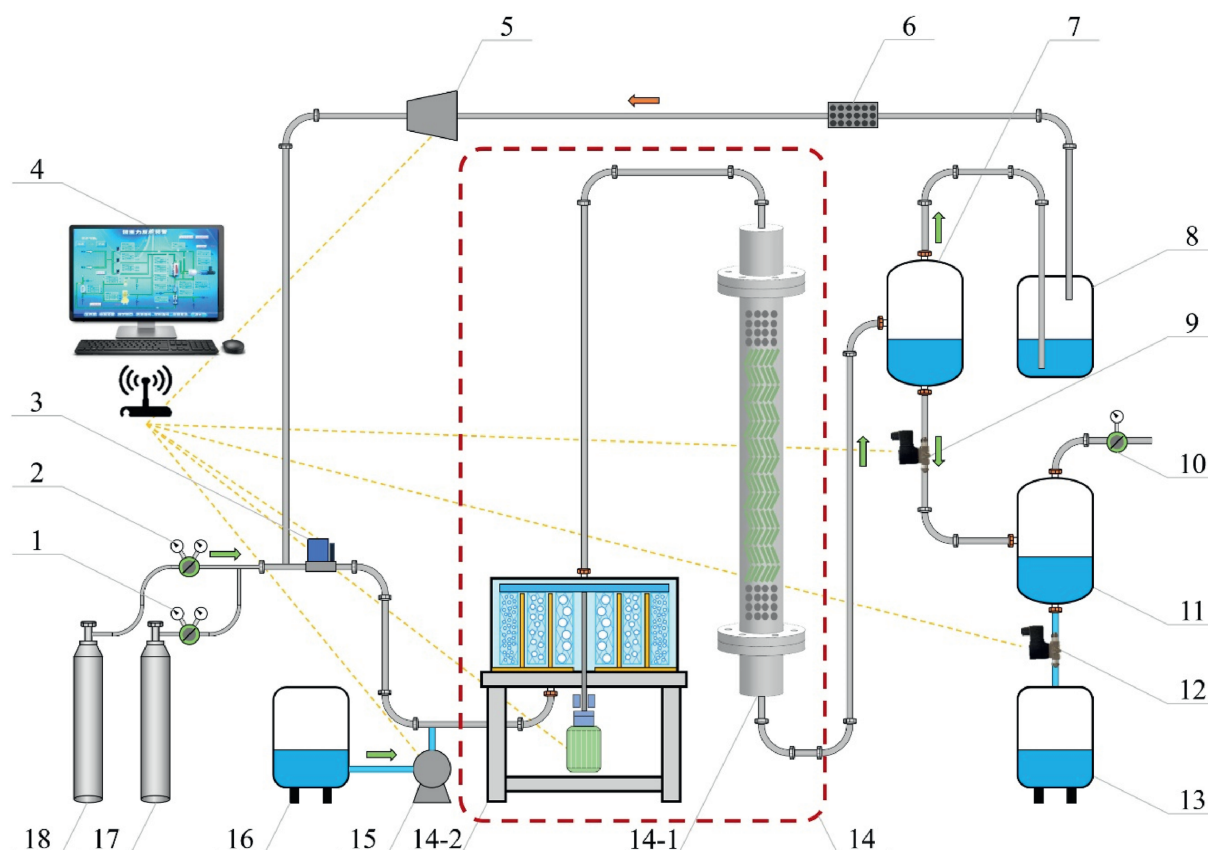
Fig. 1(b) shows a schematic diagram of the structure of catalyst bed for VGO hydrogenation. The bottom layer of the catalyst bed was firstly covered with a 300 mm thick layer of quartz sand to prevent catalyst loss [25,26]; then, the catalyst particles were filled with 600 mm thick in the middles; finally, a certain amount of quartz sand was added to the top. The filling volume of top quartz sand will affect the Sauter mean diameter (d_{32}) of the bubble swarm entering the catalyst bed and the size and shape of the catalyst particles affect the structure and porosity of the flow channel, which together affect the gas-liquid mass transfer and reaction performance [27–30]. The filling volume of top quartz sand (2 ml, 5 ml, 10 ml, and 20 ml) and 4 shapes of catalysts (cylinder, trilobe, quadrilobe, and toothed sphere) as shown in Fig. 1(c) were investigated in this study.

Table 1
Physical parameters of gas.

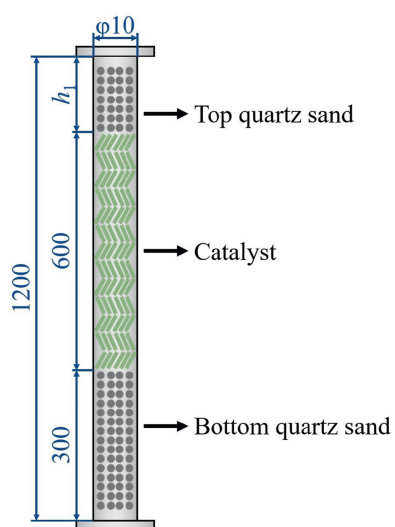
Items	Nitrogen	Hydrogen
Density (20 °C)/ $\text{kg}\cdot\text{m}^{-3}$	1.1650	0.0838
Viscosity (20 °C)/ $\text{mPa}\cdot\text{s}$	0.0088	0.0175
Content/(%) (vol)	99.95	99.95

Table 2
Physical parameters of VGO.

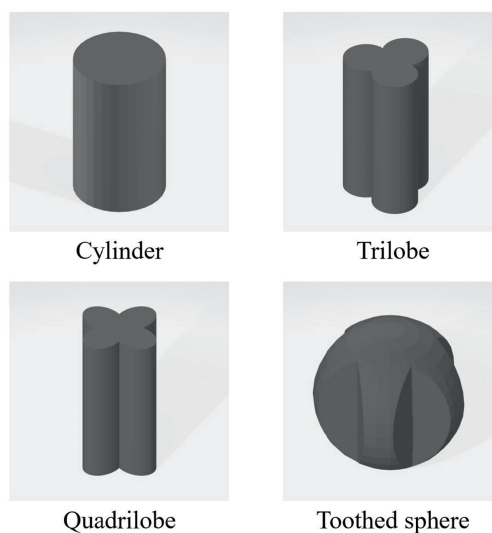
Items	VGO (I)	VGO (II)
Density (20 °C)/ $\text{kg}\cdot\text{m}^{-3}$	898.6	914.7
Sulfur content/(%) (mass)	2.56	2.49
Nitrogen content/ $\mu\text{g}\cdot\text{g}^{-1}$	998	3280
Mass spectrometry		
Components/(%) (mass)		
Chain alkanes	24.6	20.2
Naphthenic hydrocarbon	30.0	29.5
Aromatics	43.9	49.9
Gelatin	1.5	0.4



(a)



(b)



(c)

Fig. 1. Schematic diagram of (a) experimental set-up (1, nitrogen pressure relief valve; 2, hydrogen pressure relief valve; 3, gas mass flow meter; 4, DCS remote intelligent control system; 5, hydrogen compressor; 6, gas dryer; 7, high pressure gas-liquid separation; 8, absorption tower; 9, solenoid valve; 10, back pressure valve; 11, low pressure gas-liquid separation; 12, solenoid valve; 13, product tank; 14, HFBR (14-1, catalyst bed; 14-2, HMG); 15, oil pump; 16, feed tank; 17, nitrogen cylinder; 18, hydrogen cylinder), (b) the structure of catalyst bed, and (c) different shapes of catalyst particles.

2.3. Analysis method of samples

Samples were taken from the product tank, shown in Fig. 1(a), for the measurement of sulfur and nitrogen content. The sulfur and nitrogen content of the samples was determined using the ultraviolet fluorescence total sulfur analyzer and the chemiluminescence total nitrogen analyzer, both manufactured by PHOTONLAB. Before the analysis, argon and oxygen are first fed into the total sulfur analyzer and total nitrogen analyzer. After heating to the specified temperature, standard samples are used to calibrate the instruments. Next, the sulfur and nitrogen content of the experimental samples is tested, with each sample undergoing three replicate analyses.

3. Results and Discussion

3.1. Structure optimization

3.1.1. Effect of filling volume of top quartz sand

Fig. 2 shows the effect of filling volume of top quartz sand on the HDS and HDN performances of VGO in HFBR at different temperatures, respectively. When the operating conditions was $P = 8 \text{ MPa}$, $H/O = 500$, $LHSV = 1 \text{ h}^{-1}$, and $N = 1250 \text{ r} \cdot \text{min}^{-1}$, sulfur

and nitrogen content showed an increase with a greater filling volume of top quartz sand at different temperatures, indicating that the effectiveness of VGO hydrotreating decreased. A thicker layer of quartz sand accelerated bubble coalescence, resulting in an increase in the d_{32} of bubbles and a decrease in gas-liquid mass transfer rates [27]. However, if the HFBR has no quartz sand layer, it will lose its function of gas and liquid distribution, which further weakens the hydrotreating effect of VGO. Therefore, the optimal V_{qs} was selected as 2 ml.

3.1.2. Effect of catalyst particle shape

Fig. 3 illustrates the influence of catalyst particle shape on the HDS and HDN performances of VGO in HFBR at different temperatures, respectively. When the operating conditions was $P = 8 \text{ MPa}$, $H/O = 500$, $LHSV = 1 \text{ h}^{-1}$, and $N = 1250 \text{ r} \cdot \text{min}^{-1}$, the order of hydrotreating effectiveness was as follows: toothed sphere > quadrilobe > trilobe $\approx$ cylinder. The key catalyst parameters (including surface area, pore volume, and metal loading) were maintained nearly identical to eliminate the influence of geometric changes on the intrinsic catalytic performance [31]. Additionally, among the four shapes of catalyst particles with an equivalent diameter of 1.6 mm, the toothed spherical catalyst has the highest void fraction, which not only reduces the pressure drop

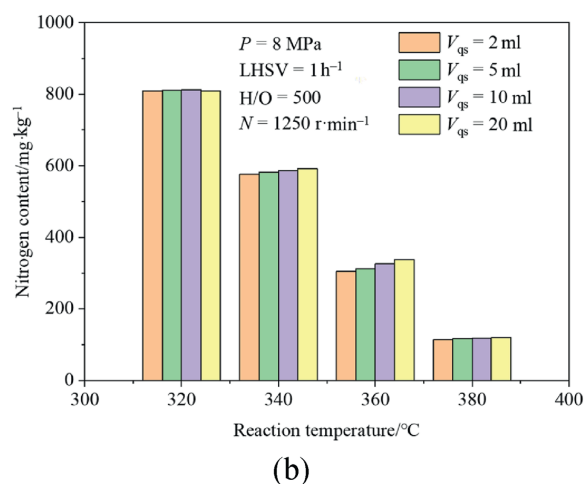
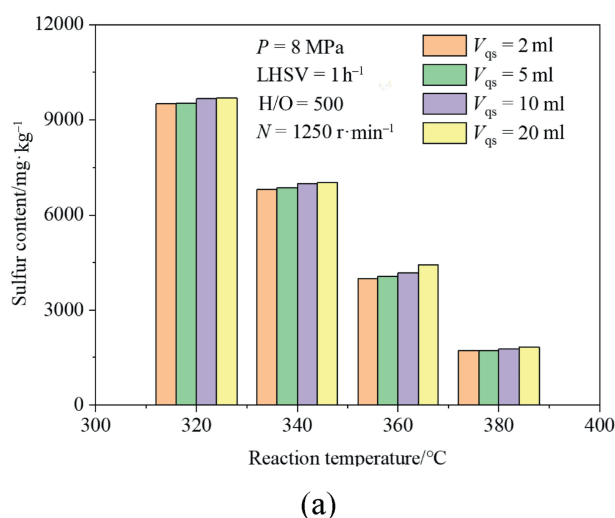


Fig. 2. Effect of filling volume of top quartz sand on (a) sulfur content and (b) nitrogen content.

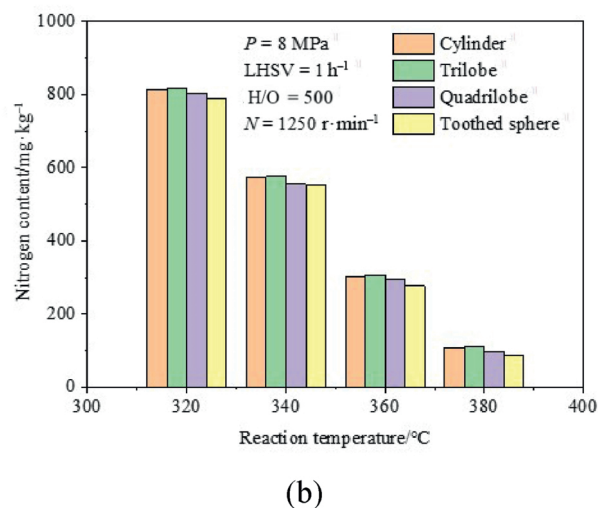
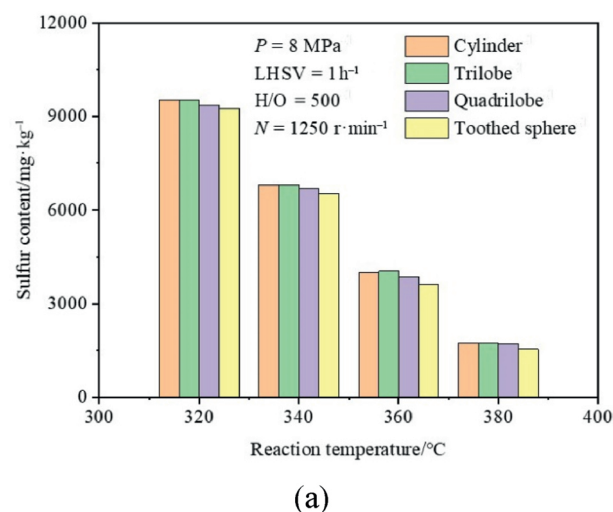


Fig. 3. Effect of catalyst particle shape on (a) sulfur content and (b) nitrogen content.

in the bed but also prevents excessive coalescence of microbubbles within the bed. Therefore, the optimal catalyst particle shape for this system is toothed sphere, which is used for the subsequent evaluation of hydrogenation performance under different operating conditions.

3.2. Hydrogenation performance

3.2.1. Effect of rotational speed of HMG

Fig. 4 illustrates the effect of rotational speed on the sulfur and nitrogen content in the VGO product. When the operating conditions was $P = 8$ MPa, $H/O = 500$, $T = 380$ °C, and $LHSV = 1$ h⁻¹, both sulfur and nitrogen content in the VGO product decreased with the increment of HMG's rotational speed. As N was increased from 200 r·min⁻¹ to 1500 r·min⁻¹, the sulfur content decreased from 1801 mg·kg⁻¹ to 1556 mg·kg⁻¹, and the nitrogen content decreased from 1069 mg·kg⁻¹ to 952 mg·kg⁻¹. The enhancement of HDS and HDN by increasing rotational speed demonstrates stronger dependence at low rotational speeds ($N < 800$ r·min⁻¹), which can be attributed to the ability of HMG to disperse the gas into microbubbles. By adjusting the rotational speed, the increment of rotational speed reduced the characteristic size of these microbubbles, thereby enhanced the gas-liquid interfacial area and

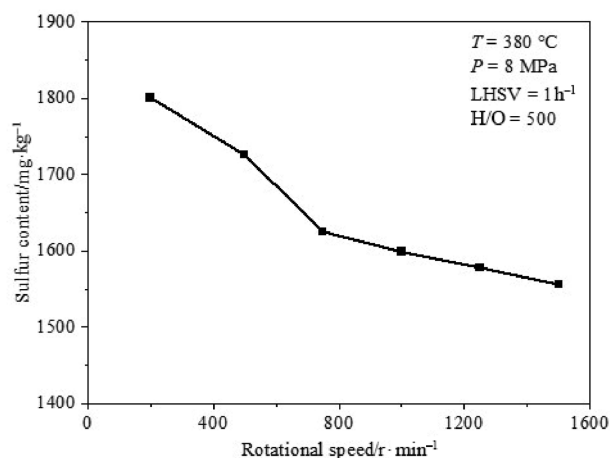
intensified the mass transfer of hydrogen within the VGO, which ultimately improved the reaction efficiency.

3.2.2. Effect of reaction temperature

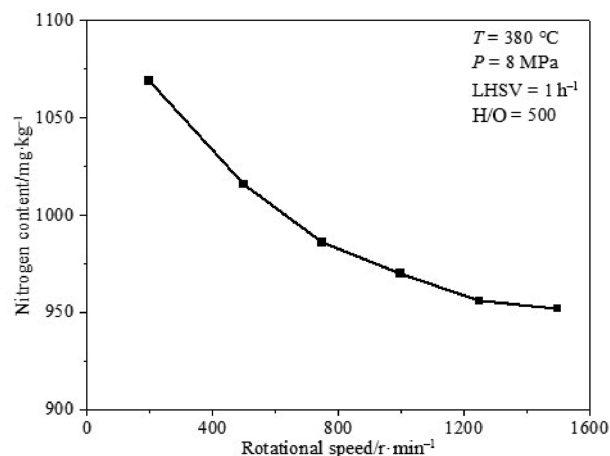
Fig. 5 illustrates the effect of reaction temperature on the sulfur and nitrogen content in the VGO products. When the operating conditions was $P = 8$ MPa, $H/O = 500$, $LHSV = 1$ h⁻¹, $N = 0$ r·min⁻¹ and 1250 r·min⁻¹, both sulfur and nitrogen content in the VGO product showed a decreasing trend as the temperature increased. When the reaction temperature was increased from 320 °C to 400 °C in the experiment, the sulfur content decreased from 9215 mg·kg⁻¹ to 246 mg·kg⁻¹, and the nitrogen content dropped from 2869 mg·kg⁻¹ to 193 mg·kg⁻¹. Due to the acceleration of the HDS and HDN at higher temperatures, it enhanced the overall reaction performance. The effect could be further strengthened under the influence of a rotational speed of 1250 r·min⁻¹, ultimately achieving the removal efficiency of 99.3% sulfur and 95.8% nitrogen from the feedstock.

3.2.3. Effect of pressure

Fig. 6 demonstrates the impact of pressure on the sulfur and nitrogen content in the VGO products. When the operating conditions was $H/O = 500$, $T = 380$ °C, $LHSV = 1$ h⁻¹, $N = 0$ r·min⁻¹ and

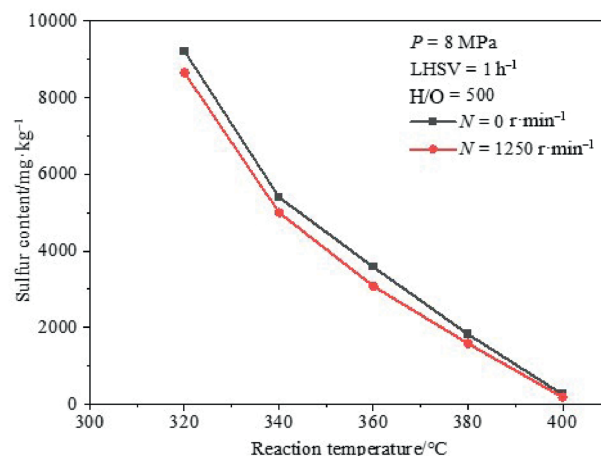


(a)

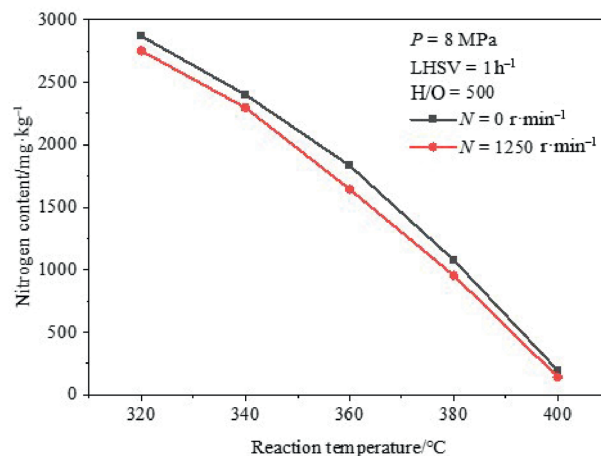


(b)

Fig. 4. Effect of rotational speed of HMG on (a) sulfur content and (b) nitrogen content.

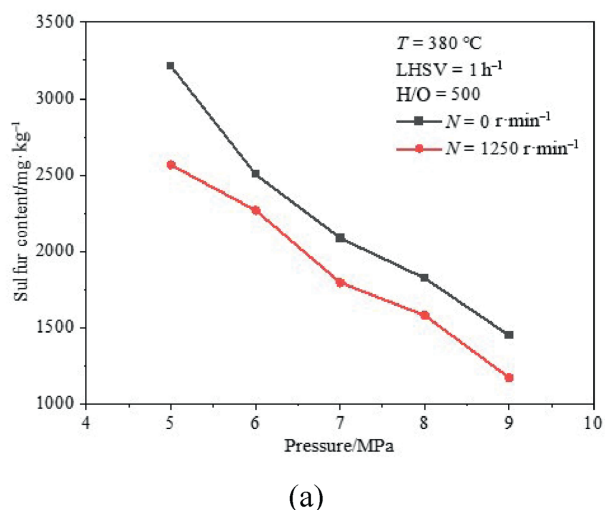


(a)

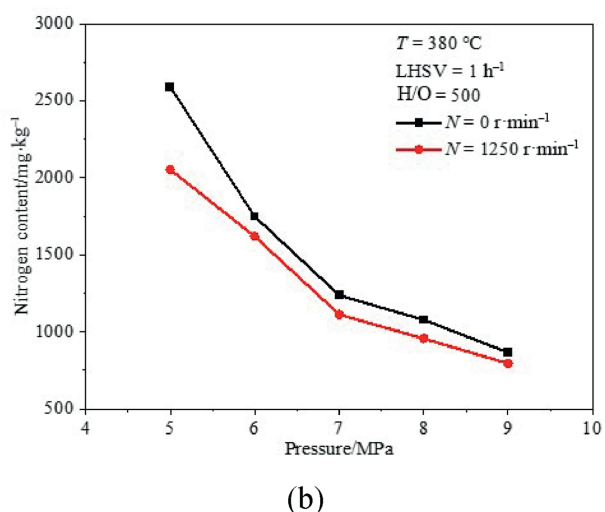


(b)

Fig. 5. Effect of reaction temperature on (a) sulfur content and (b) nitrogen content.



(a)



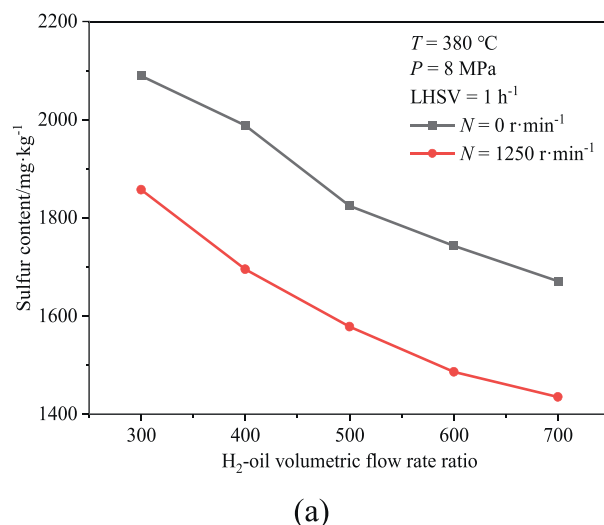
(b)

Fig. 6. Effect of pressure on (a) sulfur content and (b) nitrogen content.

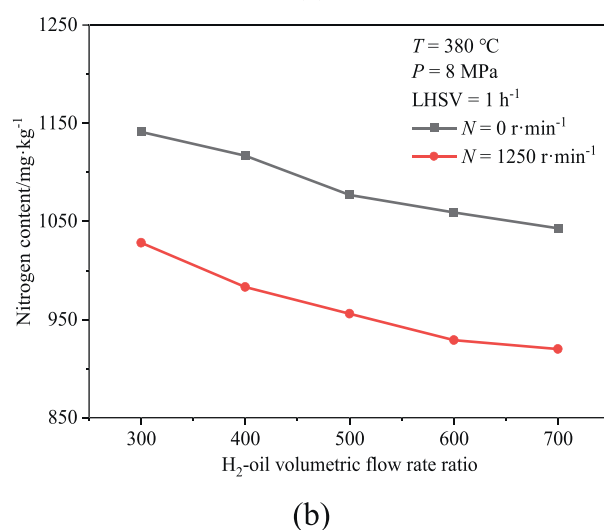
1250 r·min⁻¹, both sulfur and nitrogen content in the VGO product continuously decreased with the increment of pressure. With the pressure increased from 5 MPa to 9 MPa, at $N = 0$ r·min⁻¹, the sulfur and nitrogen content decreased from 3213 mg·kg⁻¹ and 2590 mg·kg⁻¹ to 1446 mg·kg⁻¹ and 866 mg·kg⁻¹, respectively. At $N = 1250$ r·min⁻¹, the final sulfur and nitrogen content reached 1169 and 793 mg·kg⁻¹, respectively, showing a further decrease compared to $N = 0$ r·min⁻¹. It can be attributed to the increased driving force for hydrogen diffusion through the liquid film to the active sites on the catalyst surface, which enhanced the diffusion rate and further accelerated the reaction rate. Compared to the operations at $N = 0$ r·min⁻¹, HDS and HDN efficiencies at $N = 1250$ r·min⁻¹ significantly improved, reducing the required pressure by 5% to 15% with the same sulfur and nitrogen removal rates. These results indicate that the HiGee-enhanced VGO hydrogenation technology could effectively reduce the pressure, positively contributing to lower the operating costs and energy consumption.

3.2.4. Effect of H₂-oil volumetric flow rate ratio

Fig. 7 shows the influence of the H/O on the sulfur and nitrogen content in the VGO products. When the operating condition was $P = 8$ MPa, $T = 380$ °C, $LHSV = 1$ h⁻¹, $N = 0$ r·min⁻¹ and 1250 r·min⁻¹, the sulfur and nitrogen content of the VGO product decreased monotonically as the H/O increased. When the H/O ratio increased



(a)



(b)

Fig. 7. Effect of H₂-oil volumetric flow rate ratio on (a) sulfur content and (b) nitrogen content.

from 300 to 700, the sulfur and nitrogen contents decreased by approximately 20.0% and 8.6% at $N = 0$ r·min⁻¹, and by 21.6% and 10.5% at $N = 1250$ r·min⁻¹, respectively. The higher H/O could maintain a relatively high partial pressure of hydrogen and increase the density of microbubble swarm in the liquid phase [32], thereby enhanced the mass transfer efficiency of hydrogen to accelerate the hydrogenation rate. Furthermore, increasing the rotational speed to 1250 r·min⁻¹ enabled a 35% to 40% reduction in the required H/O for HDS and an approximately 60% reduction for HDN, while maintaining constant removal rates. Especially for reactions with a high hydrogen consumption like VGO, HFBR improved hydrogen utilization efficiency and significantly reduced energy consumption.

3.2.5. Effect of liquid hourly space velocity (LHSV)

Fig. 8 demonstrates the effect of liquid hourly space velocity on the sulfur and nitrogen content in the VGO products. When the operating condition was $P = 8$ MPa, $T = 380$ °C, $H/O = 500$, $N = 0$ r·min⁻¹ and 1250 r·min⁻¹, the sulfur and nitrogen content in the VGO product increased with the increment of LHSV. Because increasing the LHSV shortened the residence time of VGO in the catalyst bed and would lead to insufficient reaction degree of HDS and HDN, it resulted in higher sulfur and nitrogen content. When $N = 1250$ r·min⁻¹, the sulfur and nitrogen content decreased at

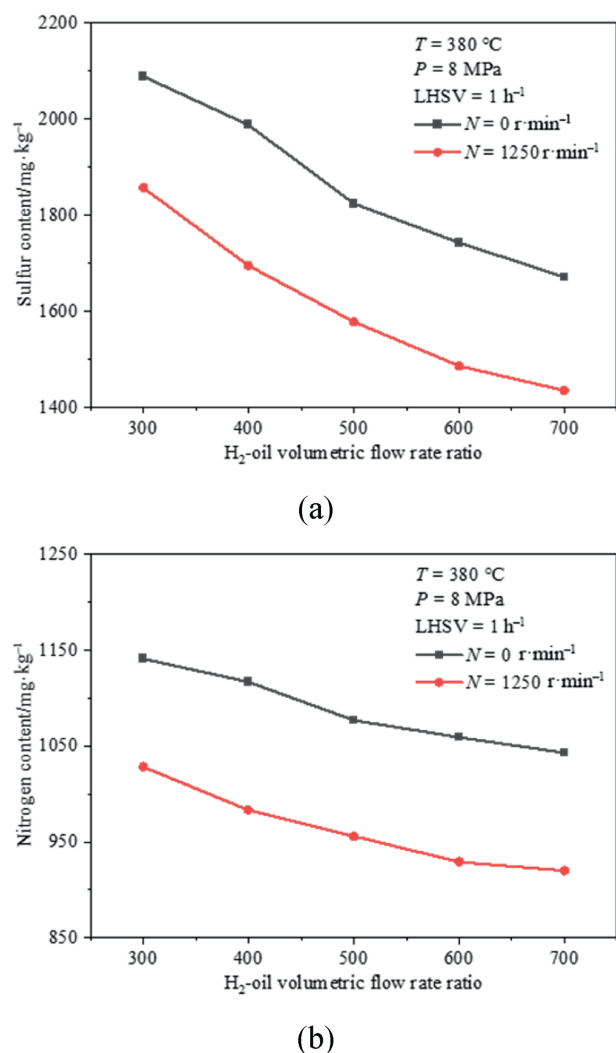


Fig. 8. Effect of liquid hourly space velocity on (a) sulfur content and (b) nitrogen content.

various LHSV. It was indicated that HFBR for hydrogenation was advantageous to increase the reactor processing capacity or reduce catalyst loading.

3.3. Macro-kinetic model

3.3.1. VGO hydrodesulfurization

Establishment of macro-kinetic model usually starts from basic Eq. (1), coupling the relevant process parameters into the reaction rate constant (K). The following are the steps to establish macro-kinetic model for VGO hydrodesulfurization.

(i) Determine the structure of the macro-kinetic equation: firstly, assuming that the reaction order of VGO hydrodesulfurization process is n , the reaction rate can be expressed as Eq. (1).

$$\frac{dC_A}{dt} = -KC_A^n \quad (1)$$

where C_A is the total sulfur content; t is the reaction time; n is the total sulfur reaction order; K is the reaction rate constant of VGO hydrodesulfurization. The hydrogen partial pressure (P), H/O, and

HiGee level (β) are included in the reaction rate constant K , which is expressed as Eq. (2).

$$K = K' P^a \left(\frac{H}{O}\right)^b \beta^c \quad (2)$$

where K' is the reaction rate constant of VGO hydrodesulfurization; a is the hydrogen partial pressure index; b is the H/O index; c is the HiGee level index. The K' is calculated by Arrhenius Eq. (3).

$$K' = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where A refers to the pre-exponential factor; E_a is the apparent activation energy of hydrodesulfurization reaction; R is the gas constant; T is the reaction temperature. By combining Eqs. (1)–(3), Eq. (4) can be obtained.

$$-\frac{dC_A}{dt} = A \exp\left(-\frac{E_a}{RT}\right) P^a \left(\frac{H}{O}\right)^b \beta^c C_A^n \quad (4)$$

(ii) Determine the order of the reaction: Table 3 shows the sulfur content of VGO hydrodesulfurization products in HFBR at different LHSV. The relationship between C_A and t is obtained to get $-\frac{dC_A}{dt}$, and then take the logarithm of both sides of Eq. (4) to obtain Eq. (5). After that, the relationship between $\ln\left(-\frac{dC_A}{dt}\right)$ and $\ln C_A$ is drawn, as shown in Fig. 9(a). Its slope is n . It can be seen from Fig. 9(a) that $n = 0.8$ and $R^2 = 0.9971$. Substituting the calculated reaction order into Eq. (4), Eq. (6) is obtained.

$$\ln\left(-\frac{dC_A}{dt}\right) = \left(-\frac{E_a}{RT}\right) + \ln A + a \ln P + b \ln\left(\frac{H}{O}\right) + c \ln \beta + n \ln C_A \quad (5)$$

$$-\frac{dC_A}{dt} = A \exp\left(-\frac{E_a}{RT}\right) P^a \left(\frac{H}{O}\right)^b \beta^c C_A^{0.8} \quad (6)$$

Reaction conditions: $T = 380^\circ\text{C}$, $P = 8\text{ MPa}$, $H/O = 500$, $N = 400\text{ r}\cdot\text{min}^{-1}$, and the sulfur content in VGO crude products is $24900\text{ mg}\cdot\text{kg}^{-1}$.

(iii) Determine the activation energy of the reaction: the sulfur content of VGO hydrodesulfurization products obtained in HFBR at different temperatures is shown in Table 4. It can be seen that when the temperature rose from 320°C to 400°C , the sulfur content of VGO products changed significantly. Therefore, the data of $320\text{--}400^\circ\text{C}$ were selected to analyze the activation energy of the reaction. Take the integral of both sides of Eq. (6), the specific process is as Eqs. (7)–(9). Fig. 9(b) illustrates the relationship between $\ln\left(\frac{C_{A0}^{0.2} - C_A^{0.2}}{C_{A0}^{0.2}}\right)$ and $\frac{1}{T}$, where $-\frac{E_a}{R}$ is the slope. It can be obtained from Fig. 9(b) that $E_a = 48150\text{ J}\cdot\text{mol}^{-1}$ and $R^2 = 0.9888$.

$$-\frac{dC_A}{C_A^{0.8}} = A \exp\left(-\frac{E_a}{RT}\right) P^a \left(\frac{H}{O}\right)^b \beta^c dt \quad (7)$$

Table 3
Sulfur content of VGO hydrodesulfurization products at different LHSV.

Items	Values		
Liquid hourly space velocity/h ⁻¹	0.5	1.0	1.5
Sulfur content/mg·kg ⁻¹	179	1765	2819

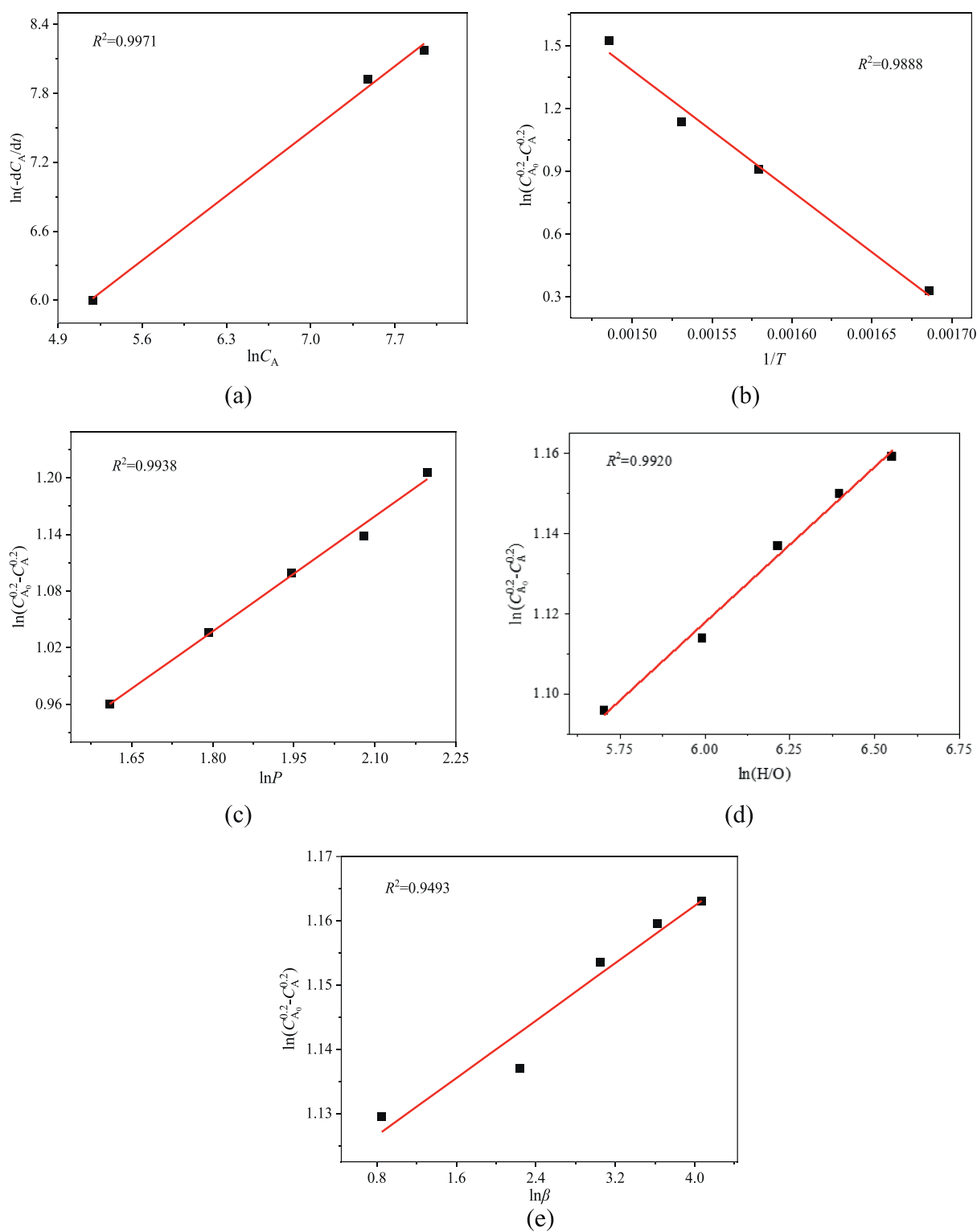


Fig. 9. Calculation of (a) order of reaction, (b) apparent activation energy, (c) hydrogen partial pressure index, (d) H_2 -oil volumetric flow rate ratio index, and (e) HiGee level index.

Table 4

Sulfur content of VGO hydrodesulfurization products at different T .

Items	Values			
Reaction temperature/ $^{\circ}\text{C}$	320	360	380	400
Sulfur content/ $\text{mg} \cdot \text{kg}^{-1}$	9036	3419	1746	232

Reaction conditions: $P = 8 \text{ MPa}$, $H/O = 500$, $N = 400 \text{ r} \cdot \text{min}^{-1}$, and $LHSV = 1.0 \text{ h}^{-1}$.

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^{0.8}} = \int_0^{\tau} A \exp\left(-\frac{E_a}{RT}\right) P^a \left(\frac{H}{O}\right)^b \beta^c dt \quad (8)$$

$$-\frac{dC_A}{dt} = A \exp\left(-\frac{48150}{RT}\right) P^a \left(\frac{H}{O}\right)^b \beta^c C_A^{0.8} \quad (9)$$

(iv) Determine the index of the hydrogen partial pressure: the sulfur content of VGO hydrosulfurization products in HFBR at different P is listed in Table 5. Fig. 9(c) presents the relationship between $\ln(C_{A0}^{0.2} - C_A^{0.2})$ and $\ln P$, and its slope is a . Fig. 9(c) shows that $a = 0.4$ and $R^2 = 0.9938$. Substituting the calculated hydrogen partial pressure index into Eq. (9), and the following equation is obtained:

$$-\frac{dC_A}{dt} = A \exp\left(-\frac{48150}{RT}\right) P^{0.4} \left(\frac{H}{O}\right)^b \beta^c C_A^{0.8} \quad (10)$$

(v) Determine the index of the H/O: the sulfur content of VGO hydrosulfurization products from the HFBR at different H/O is presented in Table 6. The relationship between $\ln(C_{A0}^{0.2} - C_A^{0.2})$ and $\ln\left(\frac{H}{O}\right)$ is shown in Fig. 9(d), and its slope is b . It can be calculated that $b = 0.078$ and $R^2 = 0.9920$. Substituting the calculated H/O index into Eq. (10) to obtain the following equation:

$$-\frac{dC_A}{dt} = A \exp\left(-\frac{48150}{RT}\right) P^{0.4} \left(\frac{H}{O}\right)^{0.078} \beta^c C_A^{0.8} \quad (11)$$

(vi) Determine the index of the HiGee level and the pre-exponential factor: the sulfur content of VGO hydrosulfurization products in HFBR at different N is listed in Table 7. β is expressed as Eq. (12a). Fig. 9(e) illustrates the relationship

between $\ln(C_{A0}^{0.2} - C_A^{0.2})$ and $\ln(\beta)$, and its slope is c . It can be calculated that $c = 0.011$ and $R^2 = 0.9493$.

$$\beta = \frac{\omega^2 r}{g} \quad (12a)$$

$$\omega = \frac{2\pi N}{60} \quad (12b)$$

$$r = \sqrt{\frac{r_o^2 + r_i^2}{2}} \quad (12c)$$

where ω is the angular velocity of the HMG, which can be calculated by Eq. (12b); r is the characteristic size of the rotor of the HMG; g is the acceleration of gravity; N is the rotational speed of the HMG; r_o is the outer radius of the rotor of the HMG; r_i is the inner radius of the rotor of the HMG. Substituting the calculated HiGee level index into Eq. (11), Eq. (13) is got.

$$-\frac{dC_A}{dt} = A \exp\left(-\frac{48150}{RT}\right) P^{0.4} \left(\frac{H}{O}\right)^{0.078} \beta^{0.011} C_A^{0.8} \quad (13)$$

All experimental data are substituted into Eq. (13) and the pre-exponential factor $A = 30925$ is obtained finally. As a result, the macro-kinetic equation of HiGee microbubble VGO hydrosulfurization in HFBR is expressed as Eq. (14).

$$-\frac{dC_A}{dt} = 30925 \exp\left(-\frac{48150}{RT}\right) P^{0.4} \left(\frac{H}{O}\right)^{0.078} \beta^{0.011} C_A^{0.8} \quad (14)$$

(vii) Validation of the model: Fig. 10 shows the comparison of calculated and experimental sulfur content. As can be seen, the errors of the experimental values to the calculated values are almost between $\pm 20\%$, indicating that the model can well predict the VGO hydrosulfurization process in HFBR.

3.3.2. VGO hydrodenitrogenation

Fig. 11(a)–(e) show the similar method and process referring to Section 3.3.1 and the macro-kinetic model of VGO hydrodenitrogenation in HFBR is obtained:

Table 5
Sulfur content of VGO hydrosulfurization products at different P .

Items	Values				
Pressure/MPa	5	6	7	8	9
Sulfur content/mg·kg ⁻¹	3006	2428	1992	1746	1358

Reaction conditions: $T = 380^\circ\text{C}$, $H/O = 500$, $N = 400 \text{ r} \cdot \text{min}^{-1}$, and $LHSV = 1.0 \text{ h}^{-1}$.

Table 6
Sulfur content of VGO hydrosulfurization products at different H/O.

Items	Values				
H ₂ -oil volumetric flow rate ratio	300	400	500	600	700
Sulfur content/mg·kg ⁻¹	2017	1900	1755	1676	1621

Reaction conditions: $T = 380^\circ\text{C}$, $P = 8 \text{ MPa}$, $N = 400 \text{ r} \cdot \text{min}^{-1}$, and $LHSV = 1.0 \text{ h}^{-1}$.

Table 7
Sulfur content of VGO hydrosulfurization products at different N .

Items	Values				
Rotational speed/r·min ⁻¹	200	400	600	800	1000
Sulfur content/mg·kg ⁻¹	1801	1755	1655	1619	1599

Reaction conditions: $T = 380^\circ\text{C}$, $P = 8 \text{ MPa}$, $H/O = 500$, and $LHSV = 1.0 \text{ h}^{-1}$.

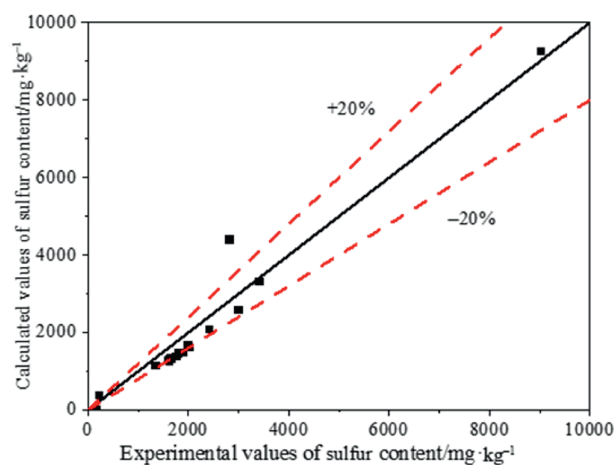


Fig. 10. Comparison of calculated and experimental values of sulfur content.

$$-\frac{dC_B}{dt} = 7688905 \exp\left(-\frac{95245}{RT}\right) p^{2.12} \left(\frac{H}{O}\right)^{0.078} \beta^{0.022} C_B^{0.575} \quad (15)$$

A comparison between the calculated and experimental nitrogen content is presented in Fig. 12. The deviations are well within $\pm 20\%$, validating the model's capability to accurately predict the VGO hydrodenitrogenation process in HFBR.

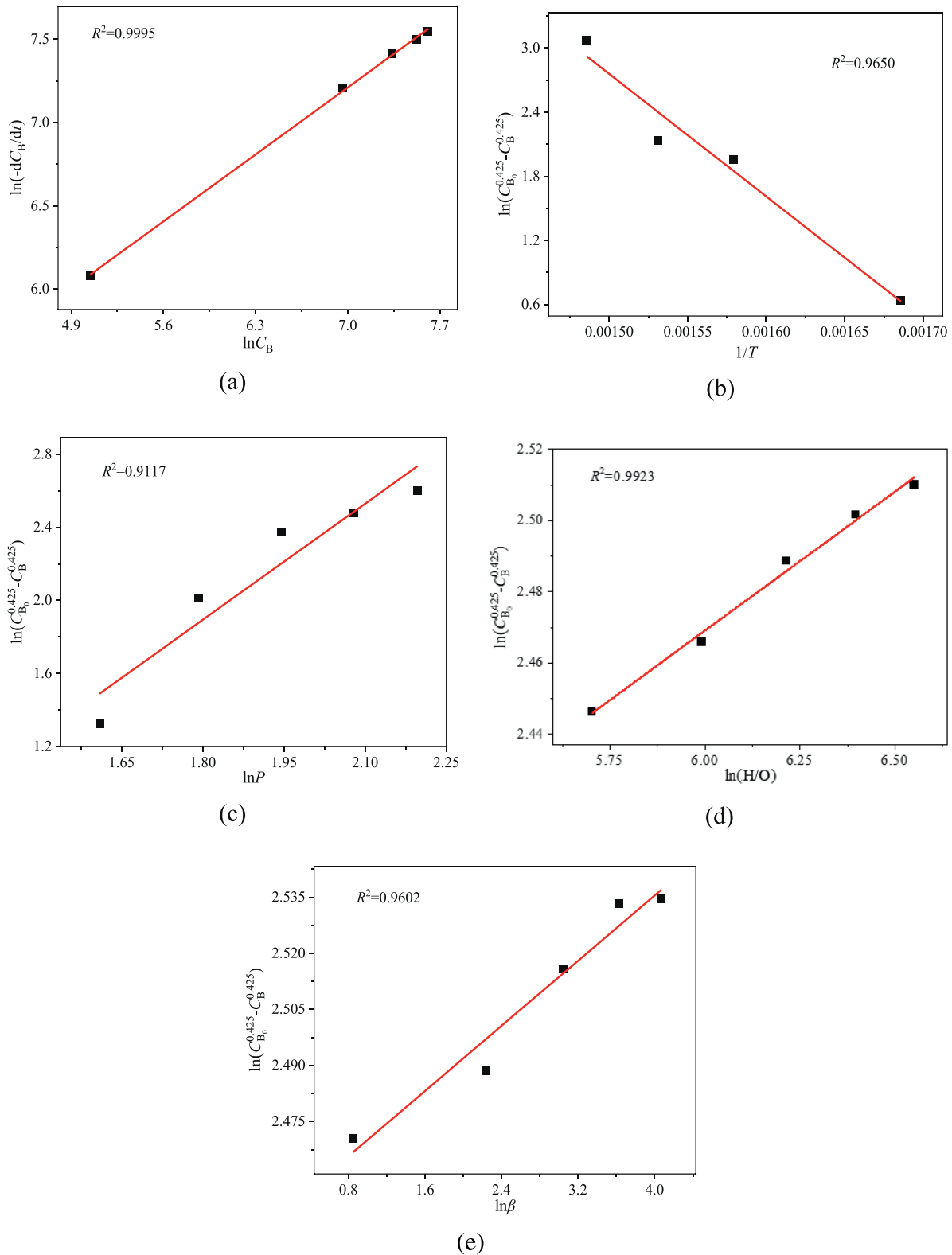


Fig. 11. Calculation of (a) order of reaction, (b) apparent activation energy, (c) hydrogen partial pressure index, (d) H_2 -oil volumetric flow rate ratio index, and (e) HiGee level index.

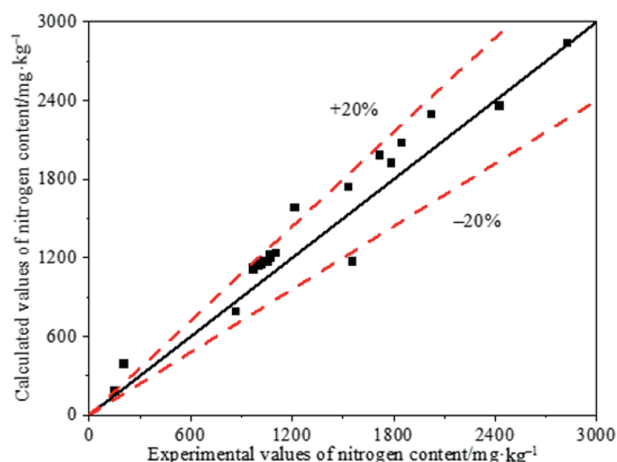


Fig. 12. Comparison of calculated and experimental values of nitrogen content.

4. Conclusions

In this work, the HiGee technology was innovatively applied to the process intensification of VGO hydrogenation, and a HFBR for VGO hydrogenation reactor was designed and built. The optimal bed structure of the 2 ml top quartz sand filling volume and the toothed sphere catalyst was obtained. The results of the influence of process conditions on the VGO hydrogenation showed that the removal effect is better under high reaction temperature and pressure, high H₂-oil volumetric flow rate ratio, and low liquid hourly space velocity. Compared with fixed bed reactor, the HDS and HDN efficiency in the HFBR were significantly improved. The pressure in HFBR could be reduced by 5% to 15% and the H/O could be reduced by 35% to 60% at the equivalent removal efficiency. The macro-kinetic models for HDS and HDN of VGO were established and the deviation between the calculated and experimental values was within $\pm 20\%$. This study provides guidance for the reactor design and process optimization of VGO hydrogenation.

CRediT Authorship Contribution Statement

Si-Qiang Fan: Writing – original draft, Investigation, Formal analysis, Conceptualization. Yong-Rui Xu: Writing – review & editing, Formal analysis, Data curation. Jun-Kai Zhang: Visualization, Formal analysis. Hua Li: Software, Formal analysis. Yuan-Bing Xi: Validation, Supervision. Chen Zhang: Supervision, Methodology. Lan Jiang: Writing – review & editing, Validation, Supervision. Yong Luo: Writing – review & editing, Project administration, Methodology, Funding acquisition. Jian-Feng Chen: Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclatures

C_A	sulfur content, $\text{mg} \cdot \text{kg}^{-1}$
C_B	nitrogen content, $\text{mg} \cdot \text{kg}^{-1}$
E_a	apparent activation energy, $\text{kJ} \cdot \text{mol}^{-1}$
H/O	H ₂ -oil volumetric flow rate ratio
N	rotational speed of HMG, $\text{r} \cdot \text{min}^{-1}$
P	pressure, MPa
R^2	coefficient of determination
r	characteristic size of the rotor of the HMG, m
r_i	outer radius of the rotor of the HMG, m
r_o	inner radius of the rotor of the HMG, m
T	reaction temperature, $^{\circ}\text{C}$
t	reaction time, s
V_{qs}	filling volume of top quartz sand, ml
β	HiGee level
τ	residence time, s
ω	angular velocity of the HMG, $\text{rad} \cdot \text{s}^{-1}$

References

- [1] I. Elizalde, F.S. Mederos, V.Y. Mena-Cervantes, R. Hernández-Altamirano, J.A. D. Muñoz, Dynamic modeling of adiabatic reactor for hydrocracking of VGO by using of the continuous lumping approach, *Fuel Process. Technol.* 152 (2016) 200–206.
- [2] H. Wang, W. Mao, K. Wang, Y.C. Qin, Q. Li, C. Peng, J.F. Wang, Z.L. Sun, L.J. Song, Insight into the effects of mass transfer performance of Y zeolite on the product selectivity of VGO hydrocracking, *Ind. Eng. Chem. Res.* 61 (50) (2022) 18270–18281.
- [3] I.M. Dahl, E. Tangstad, H.B. Mostad, K. Andersen, Effect of hydrotreating on catalytic cracking of a VGO, *Energy Fuels* 10 (1) (1996) 85–90.
- [4] Y. Zhang, E.H. Xing, W. Han, P.F. Yang, S. Zhang, S. Liu, D.X. Cao, M.F. Li, Petrochemical industry for the future, *Engineering* 43 (2024) 99–114.
- [5] A. Tanimu, K. Alhooshani, Advanced hydrodesulfurization catalysts: a review of design and synthesis, *Energy Fuels* 33 (4) (2019) 2810–2838.
- [6] Z.L. Wang, S.Q. Wang, L.X. Ling, C.P. Ma, R.G. Zhang, B.J. Wang, Revealing the regularity of hydrogenation and ring-opening via hydrodenitrogenation on the CaO surface of pyrolysis conditions—taking pyrrole and pyridine as examples, *J. Anal. Appl. Pyrolysis* 187 (2025) 107000.
- [7] H.F. Lu, Y. Frank Cheng, Artificial intelligence in energy pipelines: opportunities and risks, *Engineering* (2025) <https://doi.org/10.1016/j.eng.2025.08.032>.
- [8] A.M.A. Karim, Effect of operating conditions on hydrodesulfurization of vacuum gas oil, *Diyala J. Eng. Sci.* 1 (1) (2008) 19–31.
- [9] N.M. Maximov, A.V. Moiseev, P.S. Solmanov, N.N. Tomina, I.I. Zanozina, A.A. Pimerzin, Hydrodesulfurization reactions group kinetics of “vacuum gas oil—deasphalted vacuum residues—heavy coker gasoil” feedstock in the presence of a Ni6–PMonW12–n/γ–Al₂O₃ catalysts, *React. Kinet. Mech. Catal.* 132 (2) (2021) 877–892.
- [10] M.A. Rodríguez, I. Elizalde, J. Ancheyta, Comparison of kinetic and reactor models to simulate a trickle-bed bench-scale reactor for hydrodesulfurization of VGO, *Fuel* 100 (2012) 91–99.
- [11] P.J. Becker, B. Celse, D. Guillaume, H. Dulot, V. Costa, Hydrotreatment modeling for a variety of VGO feedstocks: a continuous lumping approach, *Fuel* 139 (2015) 133–143.
- [12] A.K. Sinha, M.G. Sibi, N. Naidu, S.A. Farooqui, M. Anand, R. Kumar, Process intensification for hydroprocessing of vegetable oils: experimental study, *Ind. Eng. Chem. Res.* 53 (49) (2014) 19062–19070.
- [13] R. Parmar, S.K. Majumder, Terminal rise velocity, size distribution and stability of microbubble suspension, *Asia Pac. J. Chem. Eng.* 10 (3) (2015) 450–465.
- [14] L.S. Metcalfe, Chemical Reaction Engineering, Oxford University Press, Oxford, 2022.
- [15] R. Parmar, S.K. Majumder, Microbubble generation and microbubble-aided transport process intensification: a state-of-the-art report, *Chem. Eng. Process. Process Intensif.* 64 (2013) 79–97.
- [16] L. Zhao, Q. Sun, Z.Y. Tang, Multi-phase CFD modelling for hydroformylation of 1-hexene with microbubbles, *Chem. Eng. Process. Process Intensif.* 181 (2022) 109163.
- [17] W.L. Wang, X.T. Guo, Z.K. Liu, S. Dong, H.J. Liu, Y.D. Wu, Z.G. Cao, Micro-nano H₂ bubbles enhanced hydrodehalogenation of 3-chloro-4-fluoroaniline: mass transfer and action mechanism, *Chemosphere* 363 (2024) 142816.
- [18] J. Tan, Y. Zhou, Z.K. Li, Y.N. Ji, Catalytic hydrogenation of acetophenone via an intensified trickle bed reactor for efficient hydrogen storage, *Int. J. Hydrog. Energy* 86 (2024) 800–807.
- [19] R. Zhang, H.Q. Wang, E.M. Hu, Z.W. Lei, F. Hu, W. Hou, Q.L. Wang, Oxidation of pyrite using ozone micro-nano bubbles, *Min. Metall. Explor.* 39 (2) (2022) 709–719.

- [20] X.L. Yang, L. Chen, S. Oshita, W.H. Fan, S. Liu, Mechanism for enhancing the ozonation process of micro- and nanobubbles: bubble behavior and interface reaction, *ACS ES&T Water* 3 (12) (2023) 3835–3847.
- [21] L.H. Wang, L. Jiang, H.L. Liao, S.H. Cai, Y. Luo, J.F. Chen, A pilot-scale HiGee-aided fixed bed reactor: size characteristics of microbubbles in diesel, *Ind. Eng. Chem. Res.* 62 (45) (2023) 18867–18878.
- [22] C. Yang, G.W. Chu, X. Feng, Y.B. Li, J. Chen, D. Wang, X.X. Duan, J.F. Chen, Mixing intensification for advanced materials manufacturing, *Engineering* 44 (2025) 135–144.
- [23] Z.L. Yang, S.J. Ding, Y. Liu, S.Z. Peng, H.G. Wang, H. Jiang, J.F. Wang, F.Z. Wang, P. Wang, Grading system of hydrogenation catalyst and application thereof and grading method of hydrogenation catalyst, US Pat., 18704623 (2024).
- [24] H. Zhang, B.S. Nie, X.F. Liu, F.F. Hu, H.Y. He, P.J. Liu, L.T. Zhang, The availability of industrial purge gas: experimental and kinetic study of explosion characteristics of low-concentration H_2/CH_4 mixtures, *Energy* 313 (2024) 133910.
- [25] S. Ramírez, M.C. Cabrera, P. Vega, H. Vaca, O. Bermúdez, C. Aguilar, A. García, R. Agueda, R. Santiago, P. Schacht, Integral evaluation for hydrotreating catalyst activity, *Petrol. Sci. Technol.* 22 (1–2) (2004) 189–199.
- [26] S.K. Bej, Performance evaluation of hydroprocessing Catalysts A review of experimental techniques, *Energy Fuels* 16 (3) (2002) 774–784.
- [27] Q. Luo, L.H. Wang, W.T. Jiang, C.H. Li, Y. Luo, H.K. Zou, J.F. Chen, Flow behavior and size characteristics of microbubble swarm in a HiGee-aided fixed bed reactor with different packed structures, *Chem. Eng. Sci.* 291 (2024) 119960.
- [28] A. Srivastava, K.D.P. Nigam, S. Roy, Bed structure and its impact on liquid distribution in a trickle bed reactor, *AIChE J.* 69 (1) (2023) e17649.
- [29] Z.L. Gao, J. Wei, H.Y. Wang, C.Y. Zhou, Research on the influence of the scaling-up process on the flow structure and two-phase distribution of gas–solid fluidized beds, *Separations* 11 (7) (2024) 202.
- [30] G.C. Gardner, The effect of fine material on the structure and resultant pressure drop of a bed charged against an uprising gas stream, *Chem. Eng. Sci.* 7 (1–2) (1957) 73–82.
- [31] N.H. Fu, X. Liang, Z. Li, Y.D. Li, Single-atom site catalysts based on high specific surface area supports, *Phys. Chem. Chem. Phys.* 24 (29) (2022) 17417–17438.
- [32] H.L. Liao, L. Jiang, L.H. Wang, Y. Luo, Q.F. Tan, S.T. Ma, J.F. Chen, Hydrodynamics, mass transfer, and hydrogenation performance of a HiGee-aided fixed bed reactor, *AIChE J.* 70 (5) (2024) e18384.