Optimization of adsorptive desulfurization process conditions for FCC gasoline

Xiong Nan-ni¹, Li Zheng¹*, Wang Peng 2

¹College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun, Liaoning Province, 113001, China
²Geno biological enzyme co. LTD, Zaozhuang, Shandong Province,277100, China
*Corresponding author’s e-mail: lizheng.zz@163.com

Abstract: In order to study the desulfurization of FCC gasoline, Zn/NaY zeolite FCC gasoline adsorbent was synthesized by impregnation method. The effects of space velocity, adsorbent bed temperature, adsorbent roasting temperature and roasting time on the desulfurization rate of FCC gasoline were investigated by adsorbent and fixed bed process. The results showed that the desulfurization rate of FCC gasoline reached about 85% under the conditions of 0.5 h⁻¹ air velocity, 35°C adsorbent bed temperature, 700°C adsorbent roasting temperature and 4 h roasting time. Adsorption desulfurization as a technology with many advantages, such as low investment, low operation cost, complete desulfurization, had good application prospects and popularization value. To develop a fixed bed adsorption desulfurization technology for FCC gasoline which meets the requirements of V gasoline quality standards of producing countries.

1.Introduction
With the rapid economic development and the explosive growth of the world's population, people not only have a growing demand for oil, but also become more and more aware of the importance of environmental protection, so there are higher requirements for the oil industry[1]. The quality requirements for vehicle fuel oil in China are becoming more and more stringent, and the sulfur content of gasoline from the National IV to the National V has been reduced from 50μg/g to 10μg/g[2-3], and it is expected that the National VI standard will be introduced after 2020, which puts forward higher requirements for automobile gasoline[4]. Therefore, the production of sulfur-free gasoline has been the general trend, how to produce low-sulfur gasoline with the ideal operating cost has become an urgent task of China's oil refining industry[5].

Adsorption desulfurization technology has the advantages of mild operating conditions, low investment and operating costs, good desulfurization effect and no reduction of gasoline octane number[6], and has many kinds of optional adsorbent, renewable, small environmental pollution and become a promising desulfurization method[7].

In this paper, the removal of sulfur from fluid-bed catalytic cracking (FCC) gasoline was studied by adsorbent and fixed bed process, and the effects of airspeed, adsorption bed temperature, adsorbent roasting temperature and roasting time on the desulfurization rate of FCC gasoline were investigated. In order to develop a high standard FCC gasoline fixed bed adsorption desulfurization technology.
2. Materials and methods

2.1. Experimental materials
Main reagents: NaY molecular sieve, Liaoning Haitai Technology Development Co., Ltd.; zinc nitrate (analysis Pure), Sinopharm Group Chemical Reagents Co., Ltd.
Main instruments: LC-2.6 microcomputer Universal Coulomb Instrument, Jiangsu Instrument General factory; ZNHW-SX constant temperature Heating sleeve, Yuncheng Yongxing instrument factory in Shandong Province; adsorption reaction device, laboratory homemade; SRJX high temperature Furnace, Shanghai Guizhou Company; 76-1A Super Thermostatic water bath, Hangzhou Instrument Motor Co., Ltd. FCC gasoline is taken from a refinery in PetroChina.

2.2. Preparation of FCC Gasoline Adsorptive Desulfurizer
FCC gasoline adsorption desulfurizer the NaY Molecular sieve press plate (pressure 20.0MPA) was pressed into pieces, and then shredded with a mortar, the powder would be studied over 40-60 target sieve. Accurately called 20g NaY powder, added 10% mass fraction of zinc nitrate 10 mL, more than 10mL deionized water, Invasion 8 h. Heat and stir 1 h in a flask with a temperature of 65 ℃, then vacuum filter, placed in 120 ℃ oven to dry 8 h, and finally baked 4 h in a temperature of 700 ℃ high temperature furnace to make FCC gasoline adsorption desulfurizer Zn/NaY molecular sieve.

2.3. Adsorption desulfurization reaction device
First put the prepared adsorbent into the reactor (the upper and lower ends of the reactor were stuffed into the porcelain ring, quartz sand, to prevent the loss of adsorbent), and then connected the reaction device, the raw oil into the reactor so that the adsorbent immersed in raw oil. After a period of full immersion, different airspeed, adsorption temperature, adsorbent roasting temperature and roasting time were set, and different products were obtained to determine the sulfur content. The adsorption desulfurization reaction process is shown in Figure 1.

2.4. Desulphurization rate
The sulfur content in FCC gasoline was measured by LC-2.6.

\[
\text{Desulphurization rate} = \frac{C_1 - C_2}{C_1} \times 100\%
\]

\(C_1\) —— sulfur content in a raw gasoline.
\(C_2\) —— Sulfur content in gasoline after desulfurization

3. Results and discussions

3.1. Effect of airspeed on desulfurization rate
Under temperature 35 ℃, the effect of Zn/NaY molecular sieve adsorbent on the desulfurization
effect of FCC gasoline was investigated under different airspeed conditions, and the results were shown in Figure 2.

![Figure 2. Effect of space velocity on the desulfurization rate](image)

It could be known from Figure 2, as the airspeed increases, FCC gasoline desulfurization was the first to increase and then decrease. Low airspeed also affected production capacity and was not conducive to large-scale industrial production, while high airspeed meant less time contact between adsorbent and gasoline, resulting in inadequate response. Therefore, for Zn/NaY molecular sieve adsorbent, the best airspeed was 0.5 h⁻¹, and its desulfurization rate could reach 85%.

3.2. Effect of adsorption temperature on desulfurization rate

Under the condition that the airspeed was 0.5 h⁻¹, the influence of Zn/NaY molecular sieve adsorbent on the desulfurization effect of FCC gasoline under different adsorption temperature was investigated, and the results are shown in Figure 3.

![Figure 3. Effect of adsorption temperature on desulfurization Rate](image)

It could be seen from figure 3, low temperature was conducive to desulfurization, while energy saving, but too low adsorption temperature (lower than the dry point of raw gas) led to a small amount of raw oil liquefaction, affecting the effect of desulfurization. For the raw oil used in this experiment, when the temperature of the adsorption bed was 35 °C, the desulfurization effect was the best, and the desulfurization rate was 85%.

3.3. Effect of adsorbent roasting temperature on desulfurization rate

The effect of different roasting temperatures of Zn/NaY molecular sieve adsorbent on the desulfurization effect of FCC gasoline was investigated under the conditions of temperature 35 °C, airspeed 0.5h⁻¹ and adsorbent roasting time of 4 h. The results were shown in Figure 4.
Figure 4. Effect of calcination temperature on the desulfurization rate

From Figure 4, with the increase of roasting temperature, the desulfurization rate increased gradually, and when the roasting temperature was 700 °C, the desulfurization effect of FCC gasoline was the best, the desulfurization rate was 87%, and with the further increase of temperature, the structure of adsorbent was destroyed, which led to the decrease of activity and the decrease of desulfurization rate. Thus, the optimum roasting temperature of Zn/NaY molecular sieve adsorbent was 700 °C.

3.4. Effect of adsorbent roasting time on desulfurization rate

Under the conditions of temperature 35 °C, airspeed 0.5h⁻¹ and roasting temperature of 700 °C, the influence of different roasting time on the desulfurization effect of Zn/NaY molecular sieve adsorbent on FCC gasoline was shown in Figure 5.

Figure 5. Effect of roasting time on desulfurization rate

As the Figure 5 showed, in the case of other conditions unchanged, with the increase of roasting time, desulfurization took the lead to increase gradually, when the roasting time was 4h, the desulfurization rate reached the maximum value of 85%, and with the continuous extension of roasting time, the activity of adsorbent decreased and the desulfurization rate decreased. This showed that the roasting temperature of Zn/NaY molecular sieve adsorbent was best of 4h.

4. Conclusion

The desulfurization rate of FCC gasoline was about 85% under the condition that the Zn/NaY molecular sieve FCC gasoline adsorption desulfurizer was synthesized by impregnation, 0.5 h⁻¹, adsorption bed temperature was 35 °C, adsorbent roasting temperature was 700 °C and roasting time
was 4 h. Adsorption desulfurization, as a technology with few advantages, such as less investment, low operating cost and thorough desulfurization, has good application prospect and popularization value.

Acknowledgements
This work was financially supported by the National Natural Science Foundation of China (41701364), Liaoning Province PhD Startup Fund (20170520109) and Liaoning Provincial Department of Education Services Local Projects (L2017LFW010).

References
[1] Jia, C.Z. (2017) Breakthrough and significance of unconventional oil and gas to classical etroleum geology theory. Petroleum Exploration & Development, 1:1-10.
[2] Chen, Q., Lei, R., Wang, W.J. (2014) Discussion on tier 5 gasoline standard for vehicles from TBT view. China Standardization, 8: 98-101.
[3] Zuo, Q.W. (2016) Study on clean gasoline production scheme of Jingmen Branch. Hubei: Wuhan Institute of Technology, 2016.
[4] Chen, W.C. (2018) The study on preparation, characterization, kinetics and regeneration ability of S Zorb reactive adsorption desulfurization adsorbent, Shanghai: East China University of Science and Technology.
[5] Cao, Y., Zhang, J.K. (2016) The Research in Adsorbents of Adsorptive Desulfurization of FCC Gasoline. SHANDONG CHEMICAL INDUSTRY, 45: 34-36.
[6] Song, C., Ma, X. (2003) New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. Applied Catalysis B: Environmental, 41: 207-238.
[7] Tang, X.D., Jiang, T., Li, J.J., et al. (2013) Research advances in solid adsorbents for the adsorptive desulfurization of vehicle fuel oil. CHEMICAL INDUSTRY AND ENGINEERING PROGRESS, 32: 1253-1260.