Exploration on Spent FCC Catalyst for Decolorization of Vegetable Oil

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Abstract. In the present work, an FCC equilibrium catalyst (E-cat) was used as a decolorizer in decolorization of vegetable oil. E-cat is an excellent and stable decolorizer, which can even be directly applied to the decolorization of vegetable oil after being discharged. The process conditions were investigated and optimized, mainly the bleaching temperature, time, and E-cat amounts. The spectrophotometric method was used to calculate the decolorization rate after detecting the absorbance of vegetable oil. As the bleaching time, temperature and E-cat amounts increase, the effects on the decolorization of rapeseed oil by E-cat were all improved to varying degrees. The best decolorization utility of E-cat was performed at 115°C and an E-cat ratio of 5wt% for 40min, the decolorization rate of the rapeseed oil was 93.3%. Compared with the fresh FCC catalyst with high catalytic activity, the decolorization capability of E-cat was not much reduced. It indicates that the structural characteristics of E-cat are more desirable in the decolorization of vegetable oil, as evidenced by the alkali treatment test.

1. Introduction
Globally, vegetable oil has become an indispensable part of daily life, such as palm oil[1], rapeseed oil[2], peanut oil, olive oil[3] and so on. In China, rapeseed oil is the main edible vegetable oil, which has been shown to contribute to high absorptivity in the human body and certain functions of softening blood vessels and delaying aging. The annual production of rapeseed has reached 14 million tons in recent years in China. Production has been steadily rising since the crop entered the food market in the 1970s and is predicted to continue in this upward trend as global oil consumption increases[4]. The crude rapeseed oil derived from pressing or leaching is disadvantageous for storage and hydrogenation to prepare downstream products such as margarine and shortening because of colloids, free carboxylic acid and colorants[5]. In the refining of rapeseed oil, the processes of degumming, deacidification, deodorization and decolorization are generally carried out, and the decolorization process is an important operation[6]. By removing the colorants from the crude rapeseed oil, it not only gives the consumer a sense of comfort, but also enriches the way the product is used and extends the shelf life of the product[7].

At present, the main process for decolorization of oil is adsorption. Commonly used decolorizer include activated kaolin[8, 9], activated bentonite[10] and activated clay based on aluminosilicate mineral processing. Activated carbon[11] and synthetic porous silica-based products[12] are also being studied as decolorizer. These decolorization materials require a large amount of resources to be
consumed. The catalyst used in the fluid refining cracking of the petroleum refining industry is commonly referred to as FCC catalyst, with an annual global supply of approximately 840,000 tons\[13\]. The catalyst is mainly made up of natural and synthetic aluminosilicates such as kaolin, faujasite and aluminum sol[14]. In the process of use, the FCC catalyst is deactivated due to the refinement of particle size as a result of catalyst attrition, sintering during calcination regeneration at around 700 °C and amorphization[15]. It is therefore necessary to continuously add fresh FCC catalyst and continuously discharge the deactivated catalyst (commonly referred to as FCC equilibrium catalyst, E-cat) in such process. The progress in the resource utilization of such the largest tonnage of spent catalysts in the world is often reviewed, and its application potential is expected to be explored. Obviously, E-cat is a stable porous aluminosilicate material with acidic active sites on the surface, exhibiting adsorption and catalysis, but so far there has been relatively little research attention on adsorption properties. In this work, the influencing factors on the decolorization performance of the E-cat for rapeseed oil were investigated.

2. Experimental

2.1. Materials

All reagents are analytically pure by purchase. The alkali-refined rapeseed oil was taken from the rapeseed oil alkali refining device of Daodaoquan Grain and Oil Yueyang Co., Ltd. The E-cat was discharged from the catalytic cracking unit of Sinopec Changling Branch, of which the BET surface area and pore volume are 94.7 m²/g and 0.13 cm³/g respectively from as measured using NH₃-TPD.

2.2. Decolorization experiment

The experiment was carried out in a round bottom flask with a stirring speed of 200 r/min during the decolorization. First, we put 50ml of alkali-refined rapeseed oil into the flask. Secondly, E-cat was added after reaching the bleaching temperature. The decolorization was allowed to progress for a period of time, during which oil samples were taken at regular intervals and tested after E-cat was removed from the oil by centrifugation, the process had been carried out at a bleaching temperature of 105°C and an E-cat amount of 4wt% for 40min.

3. Calculation of decolorization rate

In previous studies, the spectrophotometric method has been used to detect the absorbance of vegetable oil and calculate the decolorization rate (R) of the alkali-refined rapeseed oil[16, 17]. In this various solution system, a spectrum was obtained by detection, and a wavelength of 670 nm was selected as an object of investigation. The absorbance of vegetable oil was detected by a TechcompUV-1102 II spectrophotometer (Techcomp Corporation, Shanghai, China). The standard curve was plotted at the wavelength of 670 nm and the correlation coefficients were 0.999. In the appropriate range, it can be used to conveniently calculate the decolorization rate (R) of the alkali-refined rapeseed oil.

\[ R(\%) = \frac{(A_0 - A_t)}{A_0} \times 100\% \]  

where R is the decolorization rate (%) of the oil, A₀ is the absorbance of the original oil, and Aₜ is the absorbance of the decolorized oil.

4. Results and Discussion

Due to the dealumination of the zeolite catalyst component, new discharged E-cat has different particle sizes and external surface areas, which will affect its decolorization performance. During the use of the FCC catalyst, the process temperature is generally above 700 °C. The discharged E-cat might absorb water in a natural air atmosphere during the storage period. The effects of these factors were investigated on the decolorization of vegetable oil by E-cat. It can be seen from Table 1 that the decolorization abilities of E-cat having particle sizes in the range of 60-300 mesh did not show much variation, for the decolorization of the alkali refining rapeseed oil. This suggested that the application
of E-cat to the decolorization process was not limited by the need for screening. The decolorization performance of E-cat was slightly increased after calcination (Table 1). It was found that the correlation between the water content in E-cat and the decolorization effect was not very significant. It also suggested that the water molecules physically block or produce a surface-interface effect on E-cat, thereby inhibiting the decolorization of E-cat on the alkali-refined rapeseed oil. The calcined E-cat absorbed water and reached saturation, then its decolorization performance decreased less. It was therefore theoretically possible to apply the just discharged E-cat directly to the decolorization process of the vegetable oil refining process, which will reduce the number of required operations and energy consumption.

| E-cat | Origin | Screened (mesh) | Calcined | Reabsorb |
|-------|--------|-----------------|----------|----------|
|       |        | 60-100 | 100-150 | 150-200 | 200-300 |
| R (%) |        | 57.7   | 52.5    | 45.8    | 47.8    | 54.8    | 61.3    | 58.9    |

Table 1. Effect of physical treatment of E-cat on decolorization

In the decolorization process of rapeseed oil refining, the bleaching temperature is generally 105 °C[7]. If the temperature is too high, some oxidation reactions will occur in the oil[18, 19]. The decolorization ability of E-cat was investigated at a suitable temperature range: as the bleaching temperature increases, the colour of oil was significantly lighter. The results showed that the increase in temperature greatly enhanced the decolorization effect of E-cat on rapeseed oil (Figure. 1. a). Within the appropriate range, the maximum temperature was therefore the optimum temperature for decolorization of vegetable oil. Increasing the temperature will improve the application effect of E-cat, so it was obvious that the influence of bleaching time should also be investigated: this was carried out at the low temperature of 75 °C. As was evident from Figure. 1. b, as the bleaching time increased, colorants in the alkali-refined rapeseed oil were continuously adsorbed. During the whole decolorization process, the decolorization rate of rapeseed oil by E-cat slowly eased. Bleaching vegetable oil more than forty minutes, E-cat can fully exert its adsorption performance. Not only the decolorization temperature and time should be considered, but the amount of decolorizer was also a key operating parameter in the decolorization process of the rapeseed oil refining. The effect of E-cat amounts on decolorization of the oil was investigated under the more favourable conditions (115°C, 40min). As the amount of E-cat increases, the colour of the alkali-refined rapeseed oil became lighter.

Figure 1. Effect of reaction conditions: a (temperature); b (bleaching time) and c (E-cat amount) on decolorization, respectively.
(Figure. 1. c). When the amount of E-cat reached 5wt%, the decolorization rate of rapeseed oil was 93.7%. A further increase in the amount of E-cat did not significantly enhance the decolorization effect.

| FCC catalysts | F-cat untreated | E-cat Base-treatment |
|---------------|----------------|---------------------|
| R (%)         | 94.7           | 93.7                | 16.8                |

As seen from Table 2, compared with E-cat, the fresh FCC catalyst (F-cat) did not have much higher decolorization performance on rapeseed oil. This suggested that higher catalytic activity was not required for rapeseed oil bleaching. E-cat was treated by impregnation with NaOH solution. By alkali treatment, the adsorption ability of E-cat declined greatly. It indicated that the acid sites on E-cat were neutralized by alkali, and the lye also destroyed the silica-alumina structure of the molecular sieve. In summary, E-cat and F-cat are molecular sieve catalysts with excellent structure, which was the suitable decolorizer for the decolorization of rapeseed oil.

5. Conclusions
E-cat was applied for the decolorization process of vegetable oil refining, which was a supplement and optimization of the structure of resource use to make full use of the FCC catalyst. Its decolorization performance was investigated for the decolorization process of the oil. The results showed that E-cat was an excelled decolorizer for the decolorization of vegetable oil. The increase in bleaching temperature, time, and E-cat amounts promoted the decolorization of rapeseed oil. The decolorization rate of the alkali refined rapeseed oil by E-cat was 93.7% under optimized decolorization conditions (bleaching temperature, 115°C; bleaching time, 40min; E-cat amounts, 5wt%). Although these process conditions were important, the structural characteristics of E-cat were more important for decolorization of vegetable oil.

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