Purification of fluid catalytic cracking slurry oil at room temperature using ceramic membrane

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Keywords: FCC slurry oil, viscosity, purification, ceramic membrane

Abstract

The catalyst particles were removed from fluid catalytic cracking (FCC) slurry oil by two-step separation processing. FCC slurry oil was mixed with water and surfactant to make the lower viscosity emulsion. The catalyst particles were removed from the emulsion using the modified hydrophobic ceramic membrane (0.1 $\mu$m) and then the water was filtered out from oil/water emulsion using an unmodified hydrophilic ceramic membrane (0.05 $\mu$m) at room temperature. The separation efficiency of catalyst particles and emulsion reached 99.9% and the oil/water separation efficiency also reached 99.9%. FCC slurry oil was effectively purified at room temperature by a two-step treatment.

1. Introduction

In the FCC process of heavy oil, a large number of by-products, such as catalytic slurry oil, are produced. The slurry oil with particles possesses the characters of high viscosity, high molecular weight and high asphaltene content [1–4]. Usually, catalytic slurry oil is sold as waste oil or burned directly by corporate refineries. Due to the rapid rise in fuel prices and the increasingly stringent environmental regulations, these two disposal methods result in a waste of resources and irreversible pollution to the ecological environment [5–7].

Cyclic aromatic hydrocarbon as the main component in FCC slurry oil can be used to produce needle coke, carbon fiber, carbon black, rubber softener and filler oil, plastic plasticizer, asphalt, and other chemical products [8–11]. But the particulate matter in the slurry oil should be removed for recycling and reuse. The electrostatic separation and membrane separation technology are usually used for the removal of solid particles from FCC slurry oil. Guo et al [12] reported that the catalyst particles were removed from FCC slurry oil using electrostatic separation. The results showed that the particulate matter in the purified slurry was less than 10 ug/g. However, there are some problems with the electrostatic separation such as high investment and high operating cost. Compared with electrostatic separation, membrane separation technology is widely used in FCC slurry oil treatment due to the good purification effect and low operating cost [13–17]. However, membrane fouling in the separation of high-viscosity media is quite serious, which restricts the industrial applications of membrane. One of the most effective methods to solve this problem is to reduce the viscosity of liquid for separation. The viscosity of FCC slurry oil is considerably high at room temperature and usually decreased with the increase of temperature. Thus, the operation temperature for membrane separation is commonly controlled at a relatively high temperature to enhance the fluidity of slurry oil and reduce the frictional resistance between the slurry oil and the membrane. Zhang et al [18] achieved effective separation of particulate matter from slurry oil by thermal treatment method. The separation efficiency of catalyst particles reached 99.96% at 210 °C. But the thermal treatment increases energy consumption and poses a great potential safety hazard. In addition, the viscosity of slurry oil will return to the previous viscous state after the device stops running. The viscous slurry oil will pollute the surface of membrane and the flux is hard to recover to original value after the removal of the pollutant from the membrane surface. For keeping the equipment in a good work order, the surface of ceramic membrane need to be cleaned repeatedly or the membrane component is replaced, which significantly increases the cost [19–24]. Adding water and surfactant into the slurry oil to make the lower viscosity emulsion is another way to increase
the fluidity of slurry oil. It is reported that the viscosity of heavy oil reduced from 6685.17 mPa·s to 601.7 mPa·s by adding 0.2% FC-01 fluorocarbon surfactant + 1% YN hydrocarbon surfactant to heavy oil \(^\text{[25]}\). Compared with the previous studies, the method for reducing the viscosity greatly improves the safety and provides a prerequisite for the purification of slurry oil at room temperature.

The aim of the present study was to remove catalyst particles from FCC slurry oil at room temperature using ceramic membrane. Firstly, the viscosity of FCC slurry oil was reduced by adding surfactant and water. Then, the surface modification of ceramic membrane was performed by introducing hexadecyltrimethoxysilane (HDTMS) to change the surface polarity from hydrophilicity to hydrophobicity. The impurity particles in the slurry oil/water emulsion were removed using the hydrophobic ceramic membrane (0.1 \(\mu\)m) at room temperature. Secondly, oil/water emulsion was separated using an unmodified ceramic membrane with a pore size of 0.05 \(\mu\)m. The influence of water/oil ratio on the viscosity of the emulsion and the filtration performance was studied. The modified surface of ceramic membrane was characterized and the effect of particle removal using the two-step separation process was presented.

2. Experimental

2.1. Surface modification of ceramic membrane

The tubular ceramic membranes with a mean pore size of 0.1 \(\mu\)m or 0.05 \(\mu\)m (Anhui Tianling Technology Co., Ltd) were used to process the slurry oil. The surface modification of ceramic membranes was described as following steps: the ceramic membrane with a pore size of 0.1 \(\mu\)m was immersed in distilled water at least 2 h for attaching more hydroxyl groups. Then, the pretreated ceramic membrane was immersed in 0.01M HDTMS (Hexadecyltrimethoxysilane, Shanghai Aladdin Biochemical Technology Co., Ltd) solution using ethanol as a solvent for 12 h. The modified ceramic membrane was washed with ethanol and rinsed with distilled water, followed by drying at 120 °C for 2 h.

2.2. Preparation of slurry oil/water emulsion

The alumina powder (1 ~ 80 \(\mu\)m) and shearing fluid with surfactant (260 mPa·s at RT, Jiangsu Kuorun Chemical Co., Ltd) was mixed in a mass ratio of 1:20 to simulate the FCC slurry oil for the experiments.

Water was added to the shearing fluid in a mass ratio of 10:1, 20:1, 30:1, 40:1, 50:1 and 60:1 and the mixture was stirred at room temperature for 30 min to obtain a stable model slurry oil/water emulsion.
2.3. Purification of model FCC slurry oil

The catalyst particles were removed from model slurry oil/water emulsion using the modified ceramic membrane (0.1 μm) at 0.34 MPa and the separation of oil/water emulsion was carried out using a ceramic membrane (0.05 μm) at 0.1 MPa.

The flux ($J_R$) was calculated using the following equation:

$$ J_R = \frac{V}{At} $$

where $J$ is the flux (L·m$^{-2}$·h$^{-1}$), $V$ is the filtrate volume (L), $A$ is the effective filtration area (m$^2$), $t$ is the separation time (h). Each data point was taken at least the average of three parallel experiments.

The filtration apparatus is shown in figure 1.

In the continuous experiment, the separation efficiency and flux were measured at the beginning and the end of 150 min.

The separation efficiency was calculated using the following equation:

$$ E = \left(1 - \frac{m_1}{m_0}\right) \times 100\% $$

where $E$ is the separation efficiency, $m_0$ is the particle (or oil) content in the model slurry oil (or oil/water emulsion) before separation, and $m_1$ is the particle (or oil) content remaining in the filtrate after separation.

2.4. Characterization

The surface chemical groups of the ceramic membrane were analyzed by Fourier transform infrared spectroscopy (FTIR, Bruker Vector 22 FTIR spectrometer, USA). The morphology of the membrane was observed by scanning electron microscopy (SEM, JSM-IT 300 JEOL, Japan). The chemical composition of the membrane surface was examined by x-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, USA). The water contact angle (WCA) on the membrane surface was measured with a contact angle goniometer (KRUSS DSA-100, Germany). The surface roughness of the ceramic membrane was tested using a roughness meter (TR-100, China). The oil content in water was measured by an Infrared spectrophotometer (JLBG-121U, China). The filtrate was observed by an optical microscope (OLYMPUS OLS40-SU, Japan).

| Water/oil ratio | 10:1 | 20:1 | 30:1 | 40:1 | 50:1 | 60:1 |
|-----------------|------|------|------|------|------|------|
| Viscosity/ mPa·s | 4.9  | 4.3  | 4    | 3.8  | 3.5  | 3.5  |
3. Results and discussion

3.1. The viscosity of model slurry oil/water emulsion

The viscosity of the model slurry oil was reduced by adding water for particle removal at room temperature. The viscosity of the model slurry oil/water emulsion with different water/oil ratio at room temperature are listed in Table 1. The viscosity of the emulsion gradually decreased as the proportion of water increased and the viscosity was no longer increasing after the water/oil ratio exceeded 50:1.

The flux for the separation of particulate matter from model slurry oil emulsion was measured to determine the optimum water/oil ratio and the results are shown in Figure 2. The filtration flux was 52.1 m$^{-2} \cdot$h$^{-1}$ for the emulsion with the water/oil ratio of 10:1. When water/oil ratio reached to 50:1, the filtration flux increased to 180 l$^{-2} \cdot$h$^{-1}$ and it was almost unchanged after the ratio of water/oil was more than 50:1. This experimental data of filtration flux provides the feasibility of purifying model slurry oil at room temperature.

In consideration of economic benefits, the water/oil ratio of 50:1 was selected for the particulate separation from model slurry oil/water emulsion.

3.2. Analysis of the surface-modified ceramic membrane

3.2.1. The effect of ceramic membrane modification on separation

The particles in the model slurry oil were removed effectively using the modified hydrophobic ceramic membrane. Figure 3 shows the appearance of model slurry oil/water emulsion permeated through the unmodified ceramic membrane and modified ceramic membrane.

The model slurry oil/water emulsion passed through the unmodified membrane was demulsified and the filtrate was no longer milky white. It can be confirmed by polarized light microscopy. The polarized microscope photo shows that the filtrate permeated through the unmodified membrane appeared clear, which means that only water passed through the unmodified membrane. This phenomenon indicated that the model slurry oil and the particles could not be separated effectively using unmodified ceramic membrane.

When slurry oil/water emulsion was treated with the modified membrane, the filtrate remained as a milky white oil-water emulsion and the particles could be removed from emulsion. It can be seen obviously from the polarized microscope photo that there are small oil droplets for the emulsion permeated through the modified membrane. Therefore, the hydrophobic modification of ceramic membranes was a critical step to remove the particles from model slurry oil.

3.2.2. Characterization of the surface-modified ceramic membrane

For modified ceramic membrane, the surface polarity was changed from hydrophilic to hydrophobic by introducing HTDMS on the surface. The principle of surface modification is described in figure 4(a). The R–Si–(OH)$_3$ formed by the hydrolysis of HDTMS would undergo polycondensation reaction with –OH on the surface of the membrane. The hydrophobicity of the ceramic membrane was highly dependent on the number of R–Si–O$_3$– groups on the membrane surface. And the number of R–Si–O$_3$– groups grafted on the membrane surface was closely related to the number of hydroxyl groups on the membrane surface. Thus, it is benefit to graft more R–Si–O$_3$ groups by increasing the number of –OH group on the surface of ceramic membrane. A pretreatment of immersing the ceramic membrane in water was applied to increase the number of hydroxyl groups on the membrane surface. Figure 4(b) shows the effect of pretreatment time on the hydrophobicity of the ceramic membrane surface. The surface hydrophobicity of the ceramic membrane increased with the increase of
the pretreatment time and the surface contact angle increased accordingly. In addition, the transmittance of hydroxyl stretching vibration also increased with the increase of immersion time according to infrared characterization. When the pretreatment time was more than 120 min, the water contact angle on the membrane surface reached 148°. The transmittance of hydroxyl stretching vibration and the contact angle no longer changed with the time of preprocessing. Figure 4(c) shows FTIR spectra of ceramic membrane, pretreatment membrane, modified membrane and hexadecyltrimethoxysilane. (d) XPS spectra of ceramic membrane (A) and modified ceramic membrane (B).

The surface composition of the ceramic membrane before and after modification is characterized by XPS (figure 4(d)). The characteristic peak of Si appeared at 100–105 eV for the modified ceramic membrane. The existence of Si element demonstrated that HDTMS was successfully grafted onto the ceramic membrane through a chemical bond, which was consistent with the result of FTIR spectra analysis.
Figure 5 shows water droplet on the ceramic membrane surface before and after modification. The surface of unmodified ceramic membrane showed hydrophilic property with the water contact angle of 0°. The water penetrated into the membrane pores quickly. While the water droplets on the surface of modified ceramic membrane existed stably in an ellipsoidal form due to the existence of an organic hydrophobic layer on the membrane surface. The water contact angle on the membrane surface increased from 0° to 148°. The surface polarity of ceramic membrane changed from hydrophilicity to hydrophobicity.

Figure 6. SEM images of ceramic membrane surface: (a) unmodified (0.1 μm) (b) modified (0.1 μm).

Figure 5 shows water droplet on the ceramic membrane surface before and after modification. The surface of unmodified ceramic membrane showed hydrophilic property with the water contact angle of 0°. The water penetrated into the membrane pores quickly. While the water droplets on the surface of modified ceramic membrane existed stably in an ellipsoidal form due to the existence of an organic hydrophobic layer on the membrane surface. The water contact angle on the membrane surface increased from 0° to 148°. The surface polarity of ceramic membrane changed from hydrophilicity to hydrophobicity.

The surface roughness was also critical to the hydrophobicity of the ceramic membrane. According to the Wenzel model \( \cos \theta \omega = \gamma \cos \theta \), \( \theta \omega \) is the apparent contact angle, \( \gamma \) is the roughness factor, \( \theta \) is Young’s contact angle), the contact angle increases with the increase of surface roughness when \( \theta > 90° \). Thus, the membrane surface became more hydrophobic. The surface roughness (Ra) of the ceramic membrane was
Figure 7. The flux of water using unmodified membrane and modified membrane at 0.34 MPa.

Figure 8. (a) Separation principle (b) filtration flux for particles separation at 0.34 MPa (c) filtration flux for oil/water separation at 0.1 MPa.
measured and the value increased from \( Ra = 2.03 \ \mu \text{m} \) to \( Ra = 2.47 \ \mu \text{m} \) after surface modification, which increased the hydrophobic properties of the ceramic membrane surface.

The surface morphology of the ceramic membrane is shown in figure 6. It can be observed that materials adhere to the ceramic particles and occupy partial pore space in the electron microscope image. But the results of filtration experiments using the modified and unmodified membranes shows that both fluxes stabilized at around 185 l·m⁻²·h⁻¹, which can be observed from figure 7. This confirmed that the pores in the membrane were still connected.

### 3.3. Separation performance for model FCC slurry oil by two-step treatment

The separation efficiency and flux were measured to verify the removal effect of particles. The two step separation process included particle removal and oil-water separation is indicated in figure 8(a). In the first step, the particles were filtered out using hydrophobic ceramic membrane (0.1 \( \mu \text{m} \)) and an oil/water emulsion without particles was remained. In the second step, the water was separated from the oil/water emulsion using ceramic membrane (0.05 \( \mu \text{m} \)) to obtain the recycling oil.

The flux for particle separation using hydrophobic membrane (0.1 \( \mu \text{m} \)) is exhibited in figure 8(b). The flux reached 2481 l·m⁻²·h⁻¹ initially and stabilized at 180 l·m⁻²·h⁻¹ finally. In this step, the particles were almost removed and the purification of model slurry oil at room temperature was achieved. Then, the oil/water emulsion was separated using ceramic membrane (0.05 \( \mu \text{m} \)) and the flux versus filtration time is shown in figure 8(c). The initial flux was 60 l·m⁻²·h⁻¹ and the separation efficiency was 99.9%. After multiple cycles, the flux maintained 73.3% of the initial flux and the separation efficiency was still 99.9%. The content of particles in the recycling oil was less than 5 \( \mu \text{g g}^{-1} \), and the removal efficiency of particles reached 99.9%. Compared with conventional purification, the purification of slurry oil using ceramic membrane at room temperature offers a great safety by reducing the viscosity of the slurry. In addition, this method reduces energy losses and offers a new direction for the purification of slurry oil.

The filtrate obtained in the first and second steps was investigated by the optical microscope to prove the effectiveness of separation. Figure 9 presents the macro digital photo and polarized microscope photo of the emulsions. From the digital photos, the model slurry oil/water emulsion was considerably muddy and exhibited a milky white state. There were no obvious differences in appearance between the model slurry oil/water emulsion and the oil/water emulsion. Whereas numerous small particles were observed in the model slurry oil/water emulsion, and no particles were observed in the oil/water emulsion from the polarized microscope photos. This phenomenon indicated that the particles in model slurry oil/water emulsion were completely removed. After the second step separation, the milky white emulsion became clear and no small oil droplets were observed from the polarized microscope photos. The results showed that the model slurry oil was effectively purified.

![Figure 9](https://example.com/figure9.png)

**Figure 9.** Optical micrographs of model slurry oil/water emulsion, oil/water emulsion after particle removal, and filtrate after oil/water separation.
4. Conclusion

The viscosity of the model slurry oil was reduced by adding surfactant and water. The model slurry oil can be efficiently purified at room temperature by a two-step separation process. At the first step, the particles in the model slurry oil were almost completely removed using modified ceramic membrane (0.1 μm). Subsequently, the oil/water emulsion was separated using hydrophilic ceramic membrane to obtain the recycling model slurry oil. The flux of particle removal and oil/water separation were 180 l·m⁻²·h⁻¹ and 44 l·m⁻²·h⁻¹, respectively. The separation efficiency reached 99.9% for both separation step. After multiple cycles, there was no significant decrease of flux and the separation efficiency. The slurry oil purification with the combination of reducing the viscosity and membrane separation at room temperature not only reduces the risks in the purification process, but also reduces energy losses and saves significantly on purification costs.

Acknowledgments

This work was financially supported by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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