Study on deacidification process of waste internal combustion engine oil under the action of ultrasound

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Abstract. Internal combustion engine oil must be replaced periodically because it deteriorates during use, owing to the formation of oxidized species, particularly organic acids. The oil can be regenerated by removing the acids through alkali washing and neutralization. However the neutralization forms soaps that can cause significant emulsification that decrease the rate of acid removal. We have found that the washing process can be enhanced by using ultrasound, which produces strong shock waves and cavitation that increase the rates of diffusion and mass transfer, leading to an increased rate of deacidification. Our experiments show that a binary base composed of 58 wt% alum and 1.8 wt% diethylamine works well at a deacidification temperature of 50 °C, ultrasonic power of 800W, deacidification reaction time of 18 min. The extent of deacidification can be as high as 88% at 1.5 h.

1. Introduction

With the development of automobile industry, the demand of internal combustion engine oil keeps increasing. According to the statistics of Shuimu Tsinghua Research Center, in recent years, China's internal combustion engine oil output grew at an average annual rate of 8.4%, far higher than the world's 1.4% [1-2]. The working conditions of internal combustion engine oil are relatively harsh. The sulfide in the fuel and the decomposition of lead containing antiknock agent, as well as the acid substances (mainly SO2 and SO3) produced during combustion, will leak into the crankcase along with the gas, and then dissolve in the water contained in the oil pan engine oil to generate sulfuric acid and sulfite. In the inner wall of piston top and piston ring area, the internal combustion engine oil flows in these parts within a thin layer, which is oxidized by temperatures lower than 130°C, and will generate organic acids, peroxides and other substances. At the same time, zinc hydroxythiophosphate, as an antioxidant and corrosion inhibitor, decomposes and produces free acid and other substances in the process of reaction with peroxide [2]. Therefore, the internal combustion engine oil will deteriorate after being used for a certain period of time and must be replaced. From the perspective of environmental protection and resource utilization, it is an appropriate choice to treat the waste internal combustion engine oil properly, remove the deteriorated components and impurities, and regenerate the oil. The waste internal combustion engine oil must be deacidified before regeneration, to avoid corrosion in downstream processes, and also to extend the service performance of the regenerated oil [3-4]. At present, the oils can be deacidified through alkali washing and neutralization, but the steps generate emulsions that increase the volume of the waste stream, and decrease the extent of the deacidification to less than 40% [5-6]. So far deacidification via simple washing has not been industrialized. Ultrasound has unique properties: when it propagates in the medium, it causes physical and chemical changes in the medium, resulting in a series of mechanical, thermal, electromagnetic and
chemical effects. In order to improve the deacidification rate, this study explored the application of ultrasound in the deacidification process of waste internal combustion engine oil, choosing diethylamine which can react with inorganic acids to form salt, and with carboxylic acid and acid anhydride to form corresponding amide as the neutralizer. Commercial alum, KAl(SO₄)₂·12H₂O plus trace quantities of Cu²⁺ and Pb²⁺ was selected as the demulsifier [7]. Suitable conditions for the deacidification of waste internal combustion engine oil were determined.

2. Experimental raw materials
Fujian Century Toyota Automobile Service Co., Ltd. Supplied the waste internal combustion engine oil (acid value 1.23 mg KOH/g, Kinematic viscosity at 100 °C 9.6 mm²/s, dark brown). Alum was purchases from Zibo yiqiang Alum Co., Ltd. The diethylamine and other reagents were analytical pure.

2.1. Analytical methods
(1) Determination of acid value of waste internal combustion engine oil: According to GB/T 28552-2012 standard.
(2) Calculation of the extent of deacidification:

\[ D = \frac{L_0 - L_1}{L_0} \times 100\% \]

Formula: \( D \) The extent of deacidification of waste internal combustion engine oil; \( L_0 \) The original acid value of waste internal combustion engine oil; \( L_1 \) The acid value of waste internal combustion engine oil after deacidification.

2.2. Experimental methods
Alum was dissolved in distilled water to prepare solutions with mass concentrations of 20%-60%. Diethylamine was mixed into the solutions to achieve mass concentrations of 0.2%-2%. 80 g waste internal combustion engine oil was added to the ultrasonic reactor, and different composite deacidifiers were added to investigate the deacidification effect of ultrasound on waste internal combustion engine oil at different temperatures and ultrasonic power.

3. Results and analysis
3.1. Determination of optimum composition of compound deacidifier
The deacidification of waste internal combustion engine oil by ultrasonic wave was investigated at 30 °C and 900W. After 15 minutes of reaction, the decolorizer was allowed to separated into layers over 1.5 h. The acid value was measured and the deacidification rate was calculated. The results are shown in Table 1.

Table 1 shows that the phenomena and deacidification rate of the deacidification process are different when the composition of the composite deacidifier is different. When the dosage of neutralizer and demulsifier is too small, the phenomenon of non-stratification of emulsification occurs. This may be due to the formation of sulfonate and other substances in alkali neutralization. The emulsification performance is better, and the amount of demulsifier added is too small, which makes it impossible to stratify after standing. Two test tubes were added with gasoline and water respectively. One drop of emulsified oil was dropped in gasoline and the other drop in water. The bottom of the oil was found in gasoline and dispersed in water, which indicated that the emulsification was hydrophilic. The addition of alum can neutralize the electric properties of oil droplets by compressing the double electric layer and neutralizing the electric properties of oil droplets with the hydrolysates of K⁺, Al³⁺, Cu²⁺, and Pb²⁺. Therefore, the emulsion has demulsification effect [7-8]. With the increase of demulsifier and alkali dosage, stratification occurs, but there are still some emulsification, indicating that the demulsification effect increases with the use concentration of demulsifier. When the mass concentration of demulsifier reaches 58% and diethylamine reaches 1.8%, the deacidification rate
reaches 70.09%. With the increase of the dosage of demulsifier and alkali, the deacidification rate no longer increases, which indicates that there is no acid substance in waste internal combustion engine oil that can react with alkali. Therefore, considering the cost savings, the optimum compound deacidifier is composed of alum 1.5g with 58% mass concentration and diethylamine 40g with 1.8% mass concentration.

Table 1. Deacidification rate of different composite deacidifiers.

| Compound deacidifier | Composition | Phenomenon | Deacidification rate /% |
|----------------------|-------------|------------|-------------------------|
| 1                    | The mass concentration of alum 20% is 1.5g and diethylamine is 0.2% 40g. | Emulsification without stratification | - |
| 2                    | The mass concentration of alum is 30% 1.5g and diethylamine is 0.5% 40g | Emulsification without stratification | - |
| 3                    | The mass concentration of 40% alum is 1.5g, and diethylamine is 0.8% 40g. | Emulsification without stratification | - |
| 4                    | The mass concentration of alum is 45% 1.5g and diethylamine is 1.0% 40g. | Emulsification without stratification | - |
| 5                    | The mass concentration of alum is 50% 1.5g and diethylamine is 1.2% 40g. | Layered with emulsification | 55 |
| 6                    | The mass concentration of alum is 52% 1.5g and diethylamine is 1.4% 40g. | Layered with emulsification | 62 |
| 7                    | The mass concentration of alum is 55% 1.5g and diethylamine is 1.6% 40g. | The stratification is obvious | 68 |
| 8                    | The mass concentration of alum is 58% 1.5g and diethylamine is 1.8% 40g. | The stratification is obvious | 70 |
| 9                    | The mass concentration of alum is 60% 1.5g and diethylamine is 2% 40g. | The stratification is obvious | 70 |

3.2. Effect of deacidification temperature on Deacidification rate

80 g waste internal combustion engine oil was added into the ultrasonic reactor. After pouring into the optimum compound deacidifier, the temperature rises to 30, 35, 40, 45, 50, 55 and 60 °C respectively. The ultrasonic power is 900W. After 15 minutes of reaction, the static stratification is 1.5 h. The acid value is measured and the deacidification rate is calculated. The results are shown in Figure 1.

Figure 1. Effect of deacidification temperature on extent of deacidification.
The temperature of deacidification will affect the viscosity and density of liquid phase, thus affecting the speed of deacidification. Observing the effect of deacidification temperature on Deacidification rate, we can see that the increase of deacidification temperature, the decrease of liquid viscosity, the increase of molecular movement rate and collision probability, and the increase of deacidification rate. However, acid-base neutralization reaction is generally exothermic reaction. According to Lechatelier's principle, with the increase of deacidification temperature, the chemical equilibrium will go in the direction of weakening this change, that is, the chemical equilibrium will go in the direction of decreasing the decolorization rate, so the decolorization rate will increase with the increase of temperature below 50℃, and the deacidification rate will begin to decrease when the temperature is higher than 50℃. It is also found that when the temperature is higher than 50℃, the color of waste internal combustion engine oil gradually becomes deeper with the increase of temperature. This is due to the oxidation of chromoplasts in waste internal combustion engine oil into new pigments, which results in the deepening of oil color[9]. Therefore, 50℃ is an appropriate deacidification temperature.

3.3. Effect of deacidification time on Deacidification rate

80 g waste internal combustion engine oil was added into the ultrasonic reactor. After pouring the optimum compound deacidifier into the reactor, the temperature was raised to 50℃. The ultrasonic power was 900W. The deacidification time was 9, 12, 15, 18 and 21 minutes, and then the deacidification time was 1.5 hours. The acid value was measured and the deacidification rate was calculated. The results were shown in Figure 2.

![Figure 2. Effect of deacidification time on extent of deacidification.](image)

Observing the effect of deacidification time on Deacidification rate, we can see that the deacidification rate is very fast in the initial stage, the extent of deacidification reaches 74.8% in 9 minutes, peaks at 18 minutes, and then the deacidification rate decreases with the prolongation of deacidification time. This may be due to the oxidation of some substances in waste internal combustion engine oil to produce new acidic oxides with the prolongation of reaction time, resulting in the decrease of deacidification rate. Therefore, 18 minutes is suitable for deacidification.

3.4. Effect of ultrasonic power on Deacidification rate

80 g waste internal combustion engine oil was added into the ultrasonic reactor, and the optimum compound deacidifier was poured into the reactor, then the temperature was raised to 50℃. Under the conditions of 500 W, 600 W, 700 W, 800W, 900W and 1000W of ultrasonic power, respectively, the deacidification reaction was carried out for 18 minutes, then the acid value was measured and the deacidification rate was calculated. The results are shown in Figure 3.
Sound wave is the transmission form of mechanical vibration of an object, and it is the reciprocating motion of a particle near its equilibrium position. From the experimental results of Figure 3, it can be seen that the deacidification rate increases with the increase of ultrasonic power. This is due to the fact that the deacidification rate is related to the diffusion of reactants. When ultrasound propagates in liquid medium, it can produce strong shock and cavitation phenomena at the interface, which is conducive to increasing diffusion and mass transfer and promoting the deacidification reaction to proceed in a positive direction. When the ultrasonic power exceeds 800 W, the deacidification rate does not change. This is because the deacidification reaction takes place at the phase interface of the whole system. When the ultrasonic power reaches a certain value, the renewal rate of the phase interface of the whole system will not increase, and the deacidification rate will not increase. Therefore, 800 W ultrasonic power is suitable.

3.5. Single factor experimental results and verification of deacidification
According to the above single factor experimental results, 80 g waste internal combustion engine oil was added into the ultrasonic reactor, and the optimal compound deacidifier was poured into the reactor, then the temperature was raised to 50 °C, the ultrasonic power was 800 W, and the deacidification reaction lasted for 18 minutes. The acid value was measured and the deacidification rate was calculated. Under this condition, the deacidification rate of the waste internal combustion engine oil was 88.20%, 88.18%, 88.22%, respectively. The results of single factor experiment are similar, which indicates that the results of single factor experiment are reliable, and the error may come from the limitation of operation accuracy and experimental conditions.

3.6. Comparison of results between new deacidification process and traditional deacidification process
According to the traditional method of acid removal, 10% NaOH solution was added to the waste internal combustion engine oil, stirred at 50 °C for 20 minutes, and then washed to PH equal to 7. The acid removal rate was 41.12% by removing the water phase after static stratification. Compared with the deacidification rate of the new deacidification process, it is obvious that the effect of the new deacidification process is better than that of the traditional deacidification process, so it is better to choose a new deacidification process to deacidify the waste internal combustion engine oil.

Due to the limitation of the source of waste internal combustion engine oil, this method has not been used to study the deacidification of other types of waste internal combustion engine oil. We will discuss it in the future research.
4. Concluding remarks

(1) The results show that the best compound deacidifier is composed of alum 1.5g with 58% mass concentration and diethylamine 40g with 1.8% mass concentration, which has good deacidification effect. The single factor experimental results of deacidification show that the optimum process conditions are: deacidification temperature 50°C, ultrasonic power 800W, deacidification reaction 18 min and static stratification 1.5h. Under this condition, the deacidification rate of waste internal combustion engine oil can reach 88.20%.

(2) The deacidification process is simple, easy to operate, and has the characteristics of low alkali consumption, non-emulsification and low sewage discharge. It provides a new idea for the industrial application of the deacidification of waste internal combustion engine oil.

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