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Used lubricating oil recycling using a membrane filtration: Analysis of efficiency, structural and composing

Yuhe Cao, Feng Yan, Jianxin Li*, Xiaoping Liang, Benqiao He

The Key Lab of Hollow Fiber Membrane Materials and Processes of Ministry of Education,
School of Material Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, China
Tel. +86-22-2452 8072; Fax. +86-22-2452 8001; email: jxli@tjpu.edu.cn (J.X. Li) or jxli0288@yahoo.com.cn

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ABSTRACT

Three kinds of polymer hollow fiber membranes—polyethersulphone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN)—were used for recycling of used lubricating oil. The efficiency of membrane separation was characterized by means of the membrane rejection and the physical and chemical properties of the oils. The separation and analytical methods, for example, Fourier Transform Infrared (FTIR), UV-visible absorption spectra, column chromatography, etc. were employed to illustrate the separation mechanism and the potential structures of used lubricant oil so as to assess the differences between the used lubricating oil and the permeate. Results show that the membrane process can not only remove metal particles and dusts from waste lubricant oil, but also improve its liquidity and flash point. Further, the ultrafiltration membrane (PAN) has higher rejection than microfiltration membranes (PES and PVDF). The results of FT-IR and UV absorption spectra show that waste lubricant oil has almost 90% long chain saturated hydrocarbons, which are originally from the base oil. The middle polarity compositions may be lactones, esters, aldehydes, ketones, carboxylic acids, which may come from the oxidation of base oil and additives during the use of lubricating oil. Moreover, the molecules of the retentate contain aromatic rings as the basic unit in structure. The conjugated aromatic rings in the unit are mainly composed of two rings and three rings, whose connections are "linear order", namely cata-condensed. Overall, it will provide much more reference data for optimizing the regeneration processes of used lubricant oil.

Keywords: Hollow fiber membrane; Used lubricating oil; Column chromatography; UV–Vis spectrum; IR spectrum

1. Introduction

Lubricating oils are used to reduce friction and wear by interposing a film of material between rubbing surfaces. Lubricating oils mainly consist of two materials namely the base oil and the chemical additives. Various kinds of additives are blended with the base oil according to its grade and specific duty. These additives can be metallic detergents, zinc dialkyl dithiophosphates, ashless dispersants, anti-oxidant, anti-water, friction modifier, antifoam and pour point depressants [1].

Lubricating oils are the most valuable constituents in crude oil. Waste or used lubricating oils are by-products of oil used in vehicles and machinery. They must be replaced on a regular basis in all operating equipment due to the contamination from dirt, metal scrapings, water, incomplete products of combustion or other materials. In principle, the composition of a typical used lubricating oil is a stable dispersion of undegraded base oil and additives with high concentration of metals, varnish, gums and other asphaltic compounds coming from overlay of bearing surfaces and degradation of the fresh lubricant components. The polycyclic aromatic hydrocarbons (PAHs) will be formed during combustion

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*Corresponding author.

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in petrol engines and accumulate in lubricants over time. PAHs are of particular concern due to their known carcinogenicity [2]. Therefore, recycling and refining of waste into virgin lubricating oil may be a suitable option for protecting the environment from hazardous waste [3]. Another benefit associated with used lubricating oils recycling could be the economic gain due to the high price of mineral oils.

A number of processes such as coagulation, oxidization of sulfuric acid, vacuum distillation [4], extraction [5–7], hydro-treating [8] and adsorption [9–10] has been used for purification and reprocessing of the lubricating oils. In addition to the low yield of oil, these traditional treatment and regeneration technologies have important disadvantages—second pollution and/or high cost of energy. For this reason, improvement of processes for regeneration of used lubricating oils is a pressing problem and the use of membrane technology is a promising alternative for solving it.

Membrane technology for separation is a rapidly emerging technology due to its continuous operation, low energy consumption, easy adaptability, versatility and the requirement for only relatively mild operating conditions in comparison with conventional separation processes such as distillation, evaporation and crystallization. Membrane based separations are well-established technologies in water purification, protein separation and gas separation. To date, commercial applications of membrane technologies are limited to separations involving aqueous solution and relative inert gases. The use of membranes to treat non-aqueous fluids is an emerging area in membrane technologies [11]. Membrane technology is now being used for regeneration of used lubricating oils. Mynin et al. [12] reported the treatment of used lubricant oils with inorganic membranes made in laboratory condition. Results showed that the rejection was 98–100% for particulate contaminants, 25–40% for resins and asphaltenes, 72–94% for ash content. The recovery of regenerated oil was 85–90% with inorganic membranes. The permeate was 6 L/(m^2 h^{-1}) at 0.6 MPa. In order to remove the impurities from a waste oil in high efficiency, and to facilitate the separation of diluent and the cleaned oil after permeation treatment, the waste oil was often diluted with some diluents such as hexane, petroleum ether, etc. before membrane separation process [13–15]. Using membrane separation, the ash content of permeate was found to decrease by 55–75% compared to the conventional method [16]. However, the diluents were recycled from the permeate mixture by distillation which was energy-consuming.

With the development of membrane technology, hollow fiber membrane has shown many advantages such as high packing density, small footprint, etc. In the present work, three kinds of hollow fiber membranes were fabricated and used for purification and reprocessing of used lubricating oils. The aim of this work is to investigate the efficiency of membrane separation. Some separation and analytical methods, for example, Fourier Transform Infrared (FTIR), UV-visible absorption spectra, column chromatography, etc. were employed to illustrate the separation mechanism and the compositions and structures of waste lubricant oil purified by hollow fiber membrane process so as to assess the differences occurring between the used lubricating oil and the permeate. It will provide much more reference data for optimizing waste lubricant oil regeneration process.

2. Experimental details

2.1. Materials

Waste lubricant oil used in this study was collected from a vehicle garage. Three kinds of hollow fiber membranes—polyethersulphone (PES) with a pore size of 0.1 μm, polyvinylidene fluoride (PVDF) with a pore size of 0.1 μm and polyacrylonitrile (PAN) (MWCO 50 kDa) made by our laboratory—were used to separate waste lubricant oil. Column chromatography filled with silica gel (G60, Qingdao Haiyang Chemical Co., Ltd, China) were employed to separate different polarity components from waste lubricant oil and permeate with petroleum ether, ethyl acetate and ethanol as eluents, which were all analytical reagent grade.

2.2. Methods

2.2.1. Membrane separation processes and experimental design

A flow chart of regeneration of waste lubricant oil with membrane technology is shown in Fig. 1. It can be seen in Fig. 1 that the wasted lubricant oil was pretreated by centrifugation for 30 min at the speed of 2000 r min^{-1} [12], and the pretreated waste lubricant oil was separated by hollow fiber membrane. The pretreatment could protect the membranes from the damage and fouling caused by large particles came from waste lubricant oil. At the end of each separation batch, the permeate was sampled. The recovery was kept at 65% during all the experiments. The PES, PVDF and PAN membranes were carried out at 40°C and pressure 0.1 MPa.

The particle size distribution of the waste lubricant oil and permeate was measured by Laser Particle Size Analyzer (BT-9300H, Dandong Bettersize Instruments Ltd, China). The transparency of oils will present the purity in a sense [17]. UV-visible absorption spectra (UV-240, Shimadzu, Japan) were employed to measure the absorbencies of the waste lubricant oil and permeate so as to estimate (quantify) the membrane separation

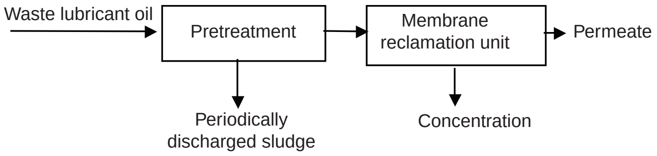

Fig. 1. Flow chart of the unit for regeneration of waste lubricant oil using hollow fiber membrane.

efficiency. The normalized membrane rejection, R, can be determined from the following equation:

$$R = \frac{A_0 - A}{A_0} \qquad (1)$$

where A_0 is the absorbance of the waste lubricant oil, A is the absorbance of permeate. Since the waste lubricant oil's absorbance is beyond the scale of the UV-visible absorption spectra, the waste lubricant oil and permeate were diluted by cyclohexane during the test. The volume ratio of sample to cyclohexane was 1:4. The absorbance was measured at 600 nm [17].

2.2.2. Composition and structure analysis

In order to illustrate the compositions of waste lubricant oil and permeate, column chromatography was used to separate them into different polarity fractions. The process was as follows: the column chromatography was filled with silica gel 60 and the sample (waste lubricant oil or permeate) was placed to the top layer of the column. Three types of eluents such as petroleum ether, ethyl acetate or ethanol were employed to elute the samples one by one with an increase with their polarity. After the samples were eluted, the eluent was eliminated by vacuum distillation. Finally, Elution I, Elution II, Elution III were obtained and characterized by FTIR (TENSOR37 BRUKER Co.) and UV absorption spectrum.

The viscosity, flash point (open cup) and ash content of both waste lubricant oil and permeate were measured according to Chinese Standard procedures GB/T 265-88, GB/T 267-88, GB/T 508-85, respectively. The samples of waste lubricant oil and permeate were first mineralized and then analyzed for the amount of the cations such as Na, Zn, Ca, and Mg by atomic emission spectrophotometry analysis (MPT1020, ChangChun Jilin University Little Swan Instruments Co., Ltd, China).

3. Results and discussion

3.1. Membrane separation

Fig. 2 shows the relationship between the fluxes and operation time. The flux obtained by PES was 1.2 L/($m^2 h^{-1}$), which was more than that obtained by PVDF and PAN. All the fluxes were quite steady during the operation time. The flux was low, compared with distillation, the energy consumed by membrane was much lower and this process will protect the environment from second pollution.

The rejection obtained by PES, PVDF and PAN was 88.6%, 91.3% and 99.6%. The rejection obtained by PAN is higher than that by PES and PVDF, that is to say, the ultrafiltration membrane (PAN) has higher rejection than microfiltration membranes (PES and PVDF). In order to further illustrate the efficiency of membrane separation, the chemical and physical properties of the used lubricating oil and permeate (sampled by PAN) were further characterized in the following section.

3.2. Chemical and physical properties

Fig. 3 shows the particle size distribution of waste lubricant oil. The particle size of waste lubricant oil ranges from 0.1 μm to 10 μm, and most of the particles are approximately 1 μm. The particle size over 0.1 μm in permeate was not detected by the Laser particle size analyzer as the limit of its sensitivity. It means that

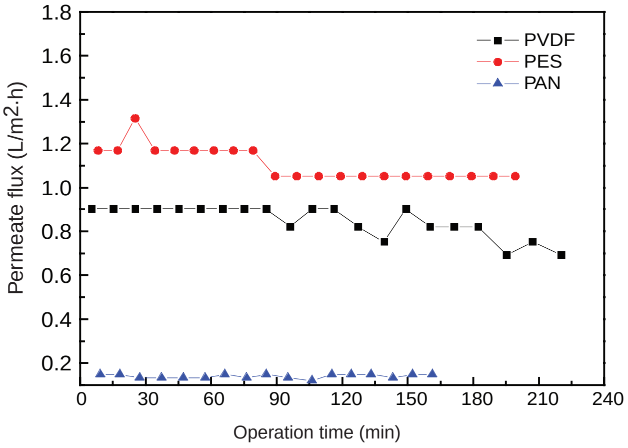

Fig. 2. Permeate fluxes versus operation time carried out with different membranes at 40°C and pressure 0.1 MPa.

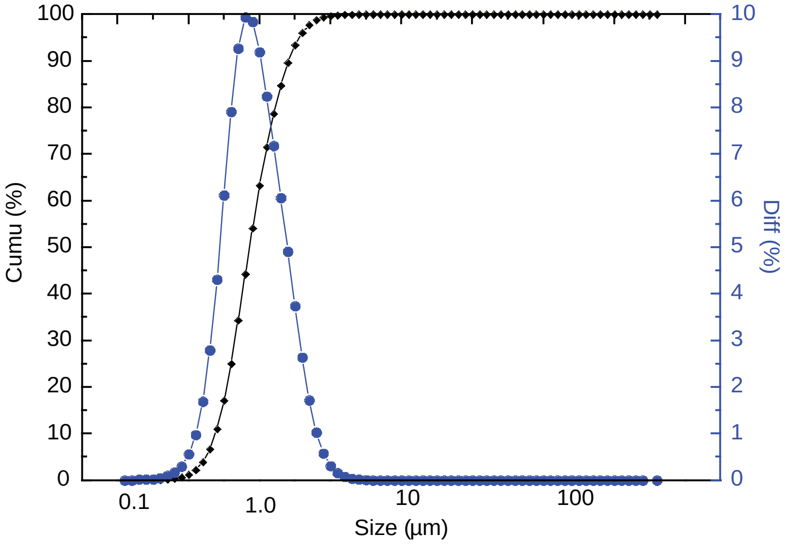

Fig. 3. Particle size distribution of the waste lubricant oil.

the particles which sizes were larger than 0.1 μm were removed by the hollow fiber membranes.

In general, there are many impurities in the waste lubricant oil, such as sludge, carbonaceous particles, unburned fuel, metal particles, tars, polymerized material and the like [12,18]. These impurities are present either in suspension or in solution. Fig. 4 shows the photos of the samples of waste lubricant oil and permeate obtained. It can be seen from Fig. 4 that the color of permeate is red and transparent, while that of used lubricating oil is black and non-transparent. This suggests that the hollow fiber membranes used in this study can efficiently remove most of the impurities.

In order to explore the efficiency of the membrane process, the chemical and physical properties of the waste lubricant oil and permeate obtained by PAN were summarized in Table 1. As shown in Table 1, the viscosity of waste lubricant oil was 63.0 mm^2 s^{-1} and 10.1 mm^2 s^{-1} at 40°C and 100°C, while that of permeate was 29.8 mm^2 s^{-1} and 5.3 mm^2 s^{-1} at 40°C and 100°C. The viscosity of permeate became lower after membrane separation due to elimination of sludge, carbonaceous particles, etc. which were generated from all sorts of additives in lubricant oil product. Moreover, the flash point of permeate increased from 214°C to 220°C (Table 1). Furthermore, the removal rate of the cations in the waste lubricant oil was over 70%. The ash content decreased from 0.82 wt % to 0.17 wt % after membrane separation. As various additives such as antioxidants, pour point depressants, viscosity index improvers, detergents, dispersants, and other additives are added in the lubricant production in order to meet the demands of modern engines, particularly for those of internal combustion engines [19], the high ash content in the waste lubricant oil is typically associated with metals (mainly Zn and Ca) which as ingredients of additives were added to the base oil [20].

Thus, the membrane process could not only remove metal particles and dusts from waste lubricant oil, but also improve its liquidity and flash point.

Fig. 4. Photos of the permeate and waste lubricant oil samples.

3.3. Composition analysis

Column chromatography was employed to separate waste lubricant oil and permeate into different polarity fractions so as to illustrate the difference between the used lubricating oil and permeate in their composition. Three different elutions—Elution I (eluted by petroleum ether), Elution II (eluted by ethyl acetate), and Elution III (eluted by ethanol)—were obtained for permeate by PAN separation. The elution results are illustrated in Fig. 5.

The waste lubricant oil was separated into four kinds of compositions which contents were 90.6 wt% in Elution I, 3.8 wt % in Elution II, 3.9 wt % in Elution III,

Table 1
The chemical and physical properties of the used oil and permeate.

Index		Waste oil feed	Permeate	Method of evaluation
Viscosity at 40°C $mm^2 s^{-1}$		63.0	29.8	GB/T 265–88
Viscosity at 100°C $mm^2 s^{-1}$		10.2	5.3	GB/T 265–88
Flash point (open cup)°C		214	220	GB/T 267–88
Ash content (%wt)		0.82	0.17	GB/T 508–85
Metal content (ppm weight)	Na	54.9	14.1	SH/T 0582–94
	Zn	1100	310	SH/T 0309–92
	Ca	1860	286	SH/T 0309–92
	Mg	60	10.8	SH/T 0061–91

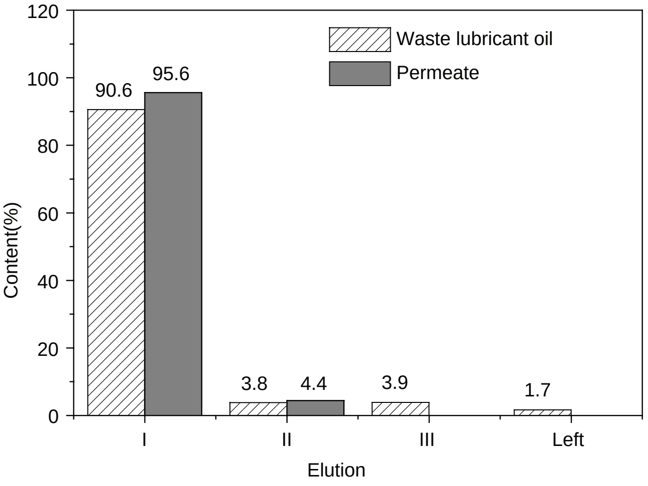

Fig. 5. The elution results of waste lubricant oil and permeate.

1.7 wt % residual (Fig. 5). However, the permeate was separated into only two fractions. Their contents were 95.6 wt % in Elution I and 4.4 wt % in Elution II. It implies that the membrane process was able to eliminate some elutes in Elution III and the left (metal particles, carbon dust, etc.).

3.4. Structure analysis

Waste/used engine oils differ in chemical and physical composition from virgin oil as a result of the changes occurring during their use. Since membrane separation in this study was merely a physical process, there was no chemical change for the compositions of waste lubricant oil. We chose the fractions (Elution I, Elution II, Elution III) obtained from waste lubricant oil to investigate their basic structures by FTIR and UV absorption spectrum so as to analyze the differences occurring between the used lubricating oil and the permeate.

Fig. 6a shows the IR spectrum of Elution I. The band at 1460 cm^{-1} is the scissoring frequency of CH_2 groups and that at 1379 cm^{-1} is from the symmetrical bending model of a CH_3 group as shown in Fig. 6a. The potential function groups can be seen in Table 2. The absence of bands between 1300 and 750 cm^{-1} suggests a straight chain structure, while the band at 722 cm^{-1} indicates that there are four or more CH_2 groups in the chain. The C═H stretching bands confirm that no unsaturated bond is present, since there are no bands above 3000 cm^{-1} [21]. From the above observation, we can infer that the Elution I only has saturated hydrocarbon chain, and this part is mainly the base oil of lubricant oil.

Elution II was characterized by FT-IR. The band at 1728 cm^{-1} is assigned to the carbonyl stretching vibration (Fig. 6b). The band at 981 cm^{-1} is inferred to be stretching vibration of P-O-R, which maybe come from the additive such as zinc dialkyldithiophosphate. In addition, other FT-IR bands of Elution II are summarized in Table 3. It can be found that there are possibly unsaturated hydrocarbon chains (at 1598 cm^{-1}) and azo groups (at 1259 and 1512 cm^{-1}) in the fraction. Furthermore, it also can be seen that the band at 1728 cm^{-1} is related to the carbonyl stretching vibration of the oxidation products (ASTM E-2412-0) [22]. These have been identified as lactones, esters, aldehydes, ketones, carboxylic acids and salts, which could come from the oxidations of the base oil and additives [23].

The Elution III from waste lubricant oil was rejected by the PAN hollow fiber membrane. The FTIR spectra of Elution III are shown in Fig. 6c and also summarized in Table 4. It can be seen in Fig. 6c that the absorption band at 1541 and 1631 cm^{-1} responds to the stretching vibration of C═C. Their potential function groups are aromatic rings. These aromatic rings maybe come from the oxidations of the aromatic compounds of lubricant oil. The absorption bands at 1045, 1130 and 1209 cm^{-1} respond to amidocyanogens group of the compositions' molecular. The amidocyanogens group may come from aromatic amine. The absorption band at 1735 cm^{-1} corresponds to carbonyls stretching vibration, which maybe come from the oxidations of alkyl. The band between 3800 and 3000 cm^{-1} is related to hydroxyl groups or amidocyanogens associated, since the Elution III has strong polarity.

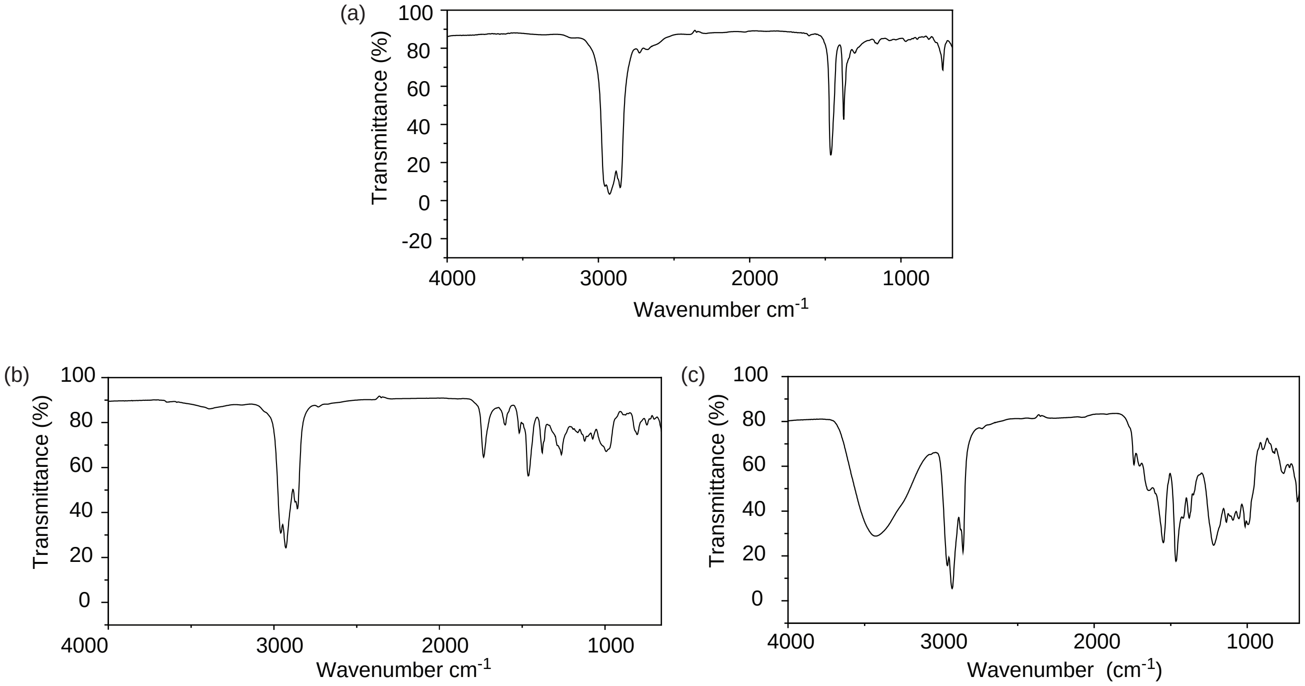

Fig. 6. FTIR spectrum of (a) elution I, (b) elution II and (c) elution III.

Table 2
FTIR bands of the elution I.

Elution I	Adscription	Potential function groups
722 (m)	ν CH	$—(CH_2)_n$ $—n > 4$
1379 (s)	δ CH_3	$—CH_3$
1460 (s)	δ CH_2	$—CH_2—$
2713 (w)	ν CH	$—CH_2—$ $—CH_3$
2853 (s)	ν CH	$—CH_2—$
2918 (s)	ν CH	$—CH_2—$

Note: w, weak intensity; m, middle intensity; s, strong intensity; ν, stretching vibration; δ, deformation vibration.

Table 3
FTIR bands of the elution II.

Elution II	Adscription	Potential function groups
981 (m)	ν P—O	—P—O—R
1259 (m)	ν C—O ν C—N	—COOH Ar—NH ArOH
1375 (m)	δ CH_3	$—CH_3$
1458 (m)	δ CH_2	$—CH_2—$
1512 (w)	ν N═N	—N═N—
1598 (m)	ν C═C	Ar—H—C═C—
1728 (m)	ν C═O	—COOH —COOR
2852 (s)	ν CH	$—CH_2—$
2922 (s)	ν CH	$—CH_2—$
2952 (s)	ν CH	$—CH_2—$

Note: w, weak intensity; m, middle intensity; s, strong intensity; ν, stretching vibration; δ, deformation vibration.

Table 4
FTIR bands of the elution III.

Elution III	Adscription	Potential function groups
1045 (w)	ν C—O ν C—N	R—OH Ar—O—R Ar—H
1130 (w)	ν C—O ν C—N	—COOH Ar—NH ArOH
1209 (m)	ν C—O ν C—N	—COOH Ar—NH ArOH
1373 (w)	δ CH_3	—CH_3
1460 (s)	δ CH_2	—CH_2—
1541 (s)	ν C═C ν NH	Ar—H Ar—NH NHR
1631 (w)	ν C═C	Ar—H Ar—NH NHR
1735 (w)	ν C═O	—COOH —COOR
2852 (s)	ν CH	—CH_2—
2922 (s)	ν CH	—CH_2—
2952 (s)	ν CH	—CH_2—
3425 (s)	ν OH ν NH	—OH —COOH NH_2

Note: w, weak intensity; m, middle intensity; s, strong intensity; N, stretching vibration; δ, deformation vibration.

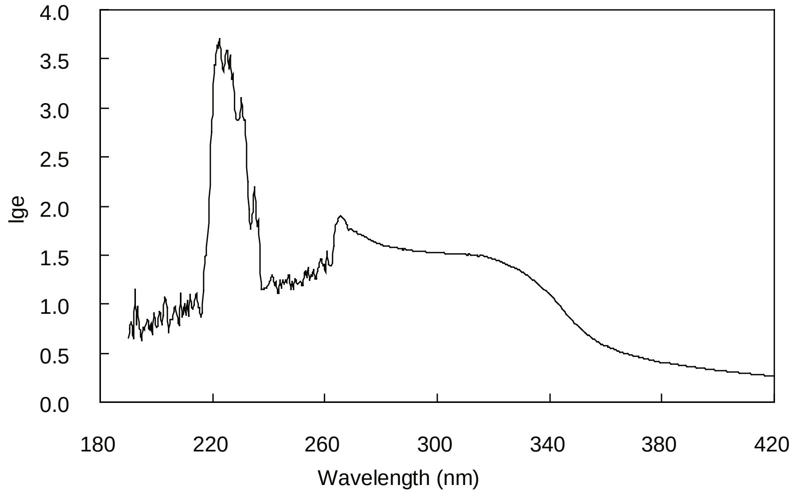

Fig. 7. UV spectra of elution III.

UV absorption spectrum was employed further to investigate the structures of fraction part from the used lubricating oil. Fig. 7 shows the UV absorption spectra of elution III. There are maximum absorption peaks near the wavelengths of 222, 280 and 330 nm. The ultraviolet absorption strength becomes weaker and weaker with the increase in the wavelength. By using the second derivative spectroscopy analysis of the absorption data, the results display that Elution III has maximum absorption peaks near the wavelengths of 222, 250, 258, 269, 294, 308 and 315 nm. Further, the ultraviolet absorption strength between 265 nm and 340 nm is very strong, which indicates that the compounds with mainly two or three aromatic sheets exist in the retentate fraction. This is consistent with the results obtained by Loeber et al. [23]. They employed model compounds. Compared with the model compounds' absorption wavelength, it is mainly naphthalene causing absorption at 220 nm. The absorption near the wavelengths of 258, 269, 294, 308 and 315 nm is connected with three to four aromatic rings in mainly "linear order", namely cata-condensed. Since there is also absorptions near 340 nm, it indicates there are a few five aromatic rings and their aromatic rings are plane order, namely peri-condensed [23,24].

Overall, the results of FT-IR and UV absorption spectra indicate that the molecules of Elution III contain aromatic rings as the basic unit in structure, and have very strong hydrogen-bond action with each other.

4. Conclusion

Hollow fiber membrane filtration is a promising membrane technology for used lubricating oil recycling. The membrane process can not only remove metal particles and dusts from waste lubricant oil, but also improve its liquidity and flash point. Further, the ultrafiltration membrane (PAN) used has higher rejection than microfiltration membranes (PES and PVDF). Furthermore, FT-IR and UV absorption spectra show that waste lubricant oil has almost 90% long chain saturated hydrocarbons, which are from the base oil. The middle polarity compositions may be lactones, esters, aldehydes, ketones, carboxylic acids, which may come from the oxidation of base oil and additives during the use of lubricating oil. Moreover, the molecules of the retentate contain aromatic rings as the basic unit in structure. The conjugated aromatic rings in the unit are mainly composed of two rings and three rings, whose connections are "linear order", namely cata-condensed.

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