Separation of radioactive waste oil by membrane with scCO₂

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1. Introduction

The radioactive waste oil from the nuclear industry is potentially hazardous due to the possible contamination of soils, waterways. Pollutants in waste oil are generally heavy and radioactive metals or metal oxides. These radioactive oils are highly viscous fluids that are similar to used motor oils. Several processes are developed for the regeneration of used motor oils, such as clay treatment, chemical addition, vacuum distillation and hydrofinishing. However these technologies are difficult to apply for separation of nuclides from radioactive waste oils. In recent years, a few laboratories tried to use membrane for the regeneration of used motor oils. But, the membrane filtration of viscous fluids demands high temperature to increase the permeate-flow rate. Generally, increasing the process temperature(up to 350℃), leads to decrease the fluid viscosity [1]. Consequently, the membrane filtration of viscous fluids is difficult for commercial operation because of high energy consumption. Hence, a new method of separation of used oils which overcomes these disadvantages are urgently needed. Also we need environmentally-friendly and efficient processes for separation of used oils. This work have used supercritical CO_2 ($scCO_2$) as a viscosity-reducing agent at lower process temperature in order to improve the membrane permeability and thus the energy consumption in the process [2, 3]. $scCO_2$ is considered as an alternative process medium. Since, it is non-toxic, non-flammable, inexpensive and easy to handle [4]. Additionally, the tunable properties of carbon dioxide through pressure and temperature control are versatile for use in extracting many organic materials [5].

The membrane can be classified as microfiltration (MF: 0.01 ~ 10 ㎛), ultrafiltration (UF: 1 nm ~ 5 ㎛) and reverse osmosis (RO: ~ 1nm). We have used the membrane of 0.1 ㎛ and 7 ㎛ pore size. Most of metals or metal ions have the size of ~1 ㎛. Specially, ceramic membranes are favorable, because it can be reusable by various washing methods, such as back pressure washing [7]. In this paper, we examine the filtering efficiency of ceramic membranes under $scCO_2$ and discuss about possible usages in the separation of used oils.

2. Methods and results

2.1 Apparatus

The experimental apparatus contains a pressurized cross-flow filtration loop to separate the filtrate and the retentate. The working pressure and temperature are to 200bar and 200℃ (Fig 1). The ceramic membrane is a single tube (inner area = 55 ㎠) of Al_2O_3. The membrane pore size is 0.1 ㎛ and 7 ㎛. These membranes are manufactured by CERACOMB CO.. LTD. The high pressure filter housing fabricated by HANWOOL ENGINEERING CO. The operating temperature was controlled by a PID controller. A high pressure preheating/mixing cell was used in order to ensure constant operating temperature and increasing $scCO_2$ solubility to the oils. The radioactive waste oils were obtained from the nuclear power plant (Wolsong Nuclear Power Division).

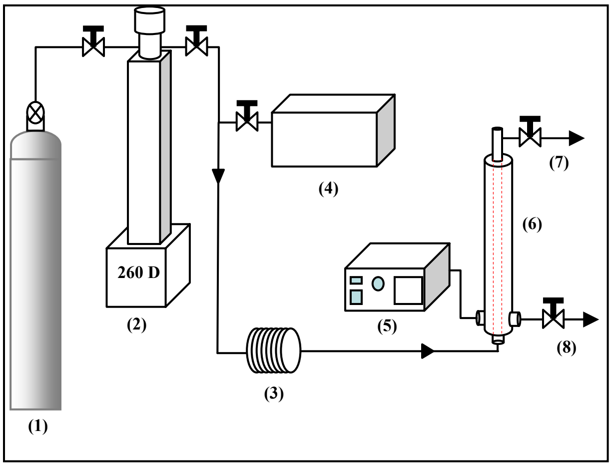

Figure 1. (1) CO_2 Tank (2) Syringe pump
(3) Preheater / Mixer (4) Liquid pump
(5) Thermo-controller (6) Membrane
(7) Retentate (8) Filter out

2.2 Experimental conditions

The radioactive waste oil is supplied to the membrane cell (5ml/min) by HPLC liquid pump and the CO_2 is supplied by a syringe pump at constant operating pressure. Radioactive waste oil and $scCO_2$ are mixed in the preheating/mixing cell. The temperatures of membrane housing and preheating/mixing cell are controlled by PID temperature with a thermocouple inserted to the filter housing body. During the operation, the transmembrane pressure is maintained ($\Delta P = P_{CO2} - P_{Filtered}$) less than 5bar, because the ceramic membrane is brittle. Pressure over 10bar can break the ceramic membrane.

Table 1. γ-ray activities in the waste oil before and after membrane filteration. The value in % indicates the % reduction

	Before [μCi/mℓ]	40℃, 90 bar, , 7 ㎛ [μCi/mℓ]	40℃, 150 bar, 7 ㎛ [μCi/mℓ]	40℃, 90 bar, 0.1 ㎛ [μCi/mℓ]	80℃, 90 bar, 7 ㎛ [μCi/mℓ]
K-40	2.01E-06	1.85E-06	1.98E-06	2.01E-06	1.74E-06
		8 %	2 %	0.1 %	13 %
Co-60	2.37E-07	1.14E-07	9.34E-08	9.64E-08	1.37E-07
		52 %	61 %	59 %	42 %
Cs-137	3.60E-07	1.47E-07	1.60E-07	1.68E-07	1.53E-07
		60 %	55 %	53 %	57 %

2.3 Results and discussion

The viscosity of mixture became lower than oil, as $scCO_2$ dissolved into the used oil. The extent of viscosity reduction by the addition of $scCO_2$ to the oil is a function of pressure and temperature [6]. In addition, the following facts are known.

- The higher the CO_2 pressure, the lower the viscosity
- The lower the temperature, the higher the viscosity reduction effect
- The higher the molecular mass, the higher the viscosity reduction effect [7].

The operating temperatures and pressures were 40 to 80℃ and 90 to 150bar. Two types of membrane (pore size: 7 ㎛ and 0.1 ㎛) were used. The gamma ray activities of the waste oil were measured by a germanium detector (CANBERRA) before and after the filtration, respectively. The results of the membrane filtration are shown in table 1. Contaminants containing K-40 seem to penetrate the membrane easily, while those of Co-60 and Cs-137 were filtered about 50%. Pressure increases in the membrane system slightly increase the filtering efficiency. The water containing the radioactive nuclei may exist in the waste oil, which explains the higher penetration tendency of contaminants. We checked the water content in the oil and found to be about 0.2% water in the waste oil.

3. Conclusion

The membrane filtration of waste oil from nuclear power plants was tested. Membrane worked as a filter for the separation of radioactive contaminants from the oil. However, the filtering efficiency turned out to be lower then expected. We suspect some radioactive nuclei exist in the water in the oil.

Acknowledgment

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