Regeneration of used motor oil by supercritical carbon dioxide

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ABSTRACT

This study was aiming at regeneration of used motor oil (UMO) by separation of engine wear residues (lees) using supercritical carbon dioxide. The experiments were carried out at 35-65 MPa of pressure and 70-80 ^{o}C of temperature. The UMO purification from lees was achieved by the use of sand as porous media filter at lower temperature. The samples extracted at 70 ^{o}C were clean, transparent and reddish-brown. Similar clean samples were obtained at 80 ^{o}C at 45 MPa only.

The temperature effect was mainly revealed in its impact on the purification of the extracted used motor oil samples, while the cumulative recovery after three runs varied from 50 % to 60 % in the pressure range of 45-65 MPa at both temperatures after three runs.

The complex interplay between the solubility and the kinetics of the process requires further study. The proposed method can be an alternative to the existing methods of cleaning used motor oil.

Keywords: used motor oil, carbon dioxide, extraction

1 INTRODUCTION

Motor oil is used for lubrication of engines in all kinds of vehicles, which leads to large quantities of used motor oil worldwide. Motor oil degradation occurs under working conditions at high temperatures, resulting in the changes of its original composition and generation of suspended particles (lees) [1]. 570 million litres of used motor oil (UMO) are produced every year in the United States of America (USA) alone, and just over 50 % of it is recycled [2].

The UMO contains various hazardous contaminants including engine wear residues, hydrocarbons, chemical elements, detergents, dispersants, inhibitors, dirt, ash, soot, and other. The pollution from improper disposal of motor oil comprises over 40 % of the total pollution in the USA alone. In many countries the UMO is disposed straight onto the ground.

On the other side, the base oil of the UMO is a valuable product. The production of motor oil requires large consumption of crude oil. 67 litres of raw crude oil are used to produce one litre of motor oil [3].

The base oil of the UMO is non-oxidized and can be re-cycled back to a lubricating oil or used as a base stock for transformer and hydraulic oil after purification.

Several techniques are used for the regeneration of used motor oil. The acid-clay method is still prevailing in many countries. Newer technologies include steps of propane de-asphalting, atmospheric or vacuum distillation, and hydrofinishing.

The treatment of UMO begins from dewatering, that is removal of water by gravitational separation in the large settling tanks. Solid particles are removed by filtering. Inorganic materials, bituminous fractions and some other compounds are removed in the steps of demineralization, propane de-asphalting and solvent extraction, respectively. The purified UMO is distilled to separate hydrocarbons by boiling range and regenerated by a hydrofinishing.

In the process of propane de-asphalting, some pollutants and metals are not removed because they are soluble in propane and, therefore, co-extracted with the base oil. Ethane was also tested because it is lighter than propane and dissolves preferentially the base oil fraction of the UMO. The use of ethane facilitated better precipitation and separation of the solid particles and other undissolved components compared to propane [4].

The choice of treatment technique also depends on the availability of solvents and cost of equipment. The selection of most appropriate fluid and extraction conditions such as pressure, temperature, flow rate, and type of carrying matrix may improve the results of the UMO filtration and separation of lees.

Carbon dioxide has been chosen for many extraction processes because it provides excellent efficiency and speed at supercritical conditions. Supercritical carbon dioxide

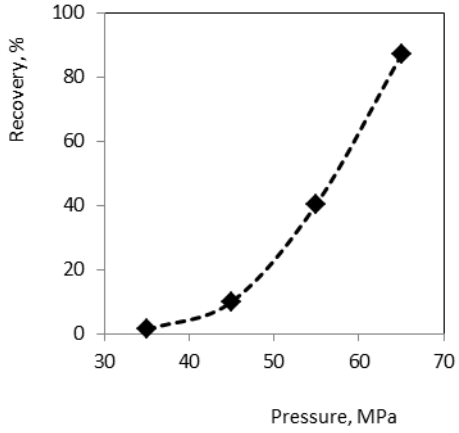

Figure 1: Recovery of used motor oil from the towel.

(SC-CO_2) was used for the extraction of various contaminants from soils, and it was also proposed for extraction of used lubricating oils as an environmentally friendly process (Krukonis et al., 1994) [5]. Its gas-like mass-transfer properties and liquid-like solvation characteristics allows it to penetrate low-porosity solid matrices. Carbon dioxide can be available in large quantaties from natural deposits or CO_2 storages.

Several authors reported separation of various substances by precipitating particles in the process of SC-CO_2 extraction. In our previous experiments the grease used for lubricating of bearings of wind turbines was separated from dust accumulated during many years of exposure to air [6]. In a similar extraction process we have obtained oil fractions free from asphaltene and cokes from bituminous oil of tar sand [7].

The potential of SC-CO_2 extraction process for the separation of base oil from solid particles of engine wear residues contained in the UMO was tested in this study.

2 EXPERIMENTAL

2.1 Materials

Used motor oil was collected from a car service centre. The UMO was of intense black color. Experiments were carried out in two series of tests.

For the first series, the sample was prepared by soaking towels weighing 5.5 g with 50 g of used motor oil each for about 48 hours.

For the second series, the samples were prepared by saturating sand with the UMO. Preliminary the sand was washed, passed through a sieve with 2 mm openings, and dried in the oven at 90 ^oC. The 98 g sample consisted of 84.8 g of the sand and 13.2 g of the UMO.

2.2 Methods

The experiments were performed using supercritical extractor Spe-ed SFE. The sample was put in a 100 mL extraction cell placed into the oven vertically. The extraction cell is a steel tube closed tightly on both ends by cap-ends. After the system achieved the required temperature by heating, inlet valve of the system was opened, and CO_2 was fed into the system from storage tank until the required pressure was achieved. The system was left for 30 min to equilibrate in a static mode. The extracts were collected in a dynamic mode during approximately 15 min. In the experiment with the UMO saturated sand, the procedure was repeated for each sample in three consecutive runs.

The samples and collected extracts were weighed before and after the experiment to measure the UMO recovery. The UMO recovery was calculated as a ratio of the weight of the extract after each run to the initial weight of the UMO contained in the sample before the experiment (13.2g). The sum of recoveries of all three runs at specific pressure is cumulative recovery. The total recovery was calculated as the difference between weights of samples before and after experiments. The outgassing losses were calculated as the difference between total recovery and cumulative recovery.

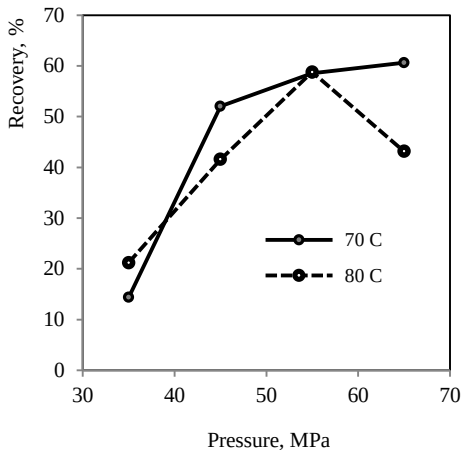

Figure 2: Cumulative recovery of used motor oil at 70 ^oC and 80 ^oC.

3 DISCUSSION

3.1 Extraction from towels

Extraction from the towels was carried out at 70 ^oC and 35-65 MPa in one run. It was evaluated that the towel occupied about 60 % of the space in the extraction cell. The recovery increased hyperbolically from 1.4 % at 35 MPa to 86.9 % at 65 MPa as a response to the increase of carbon dioxide density (Fig.1). Considering that the outgassing losses were estimated as 7 % on the average, almost all UMO was extracted at 65 MPa.

Visual inspection of the towel after experiment at 65 MPa revealed that the towel was not completely clean because remains of used motor oil accumulated in the bottom part of the towel, which was placed in the vertical position in the extraction cell. All samples extracted from towels by SC-CO_2 were an intense black and contained engine wear residues, even at the lowest pressure.

It can be deduced that the extraction efficiency at the pressure of 65 MPa can be very high but the use of such simple carrying matrix as a towel leads to unavoidable co-extraction of lees together with the base oil.

3.2 Extraction from sand

In order to investigate whether the separation of base oil from lees can be obtained if the UMO is contained in a different type of carrying matrix, the second series of tests

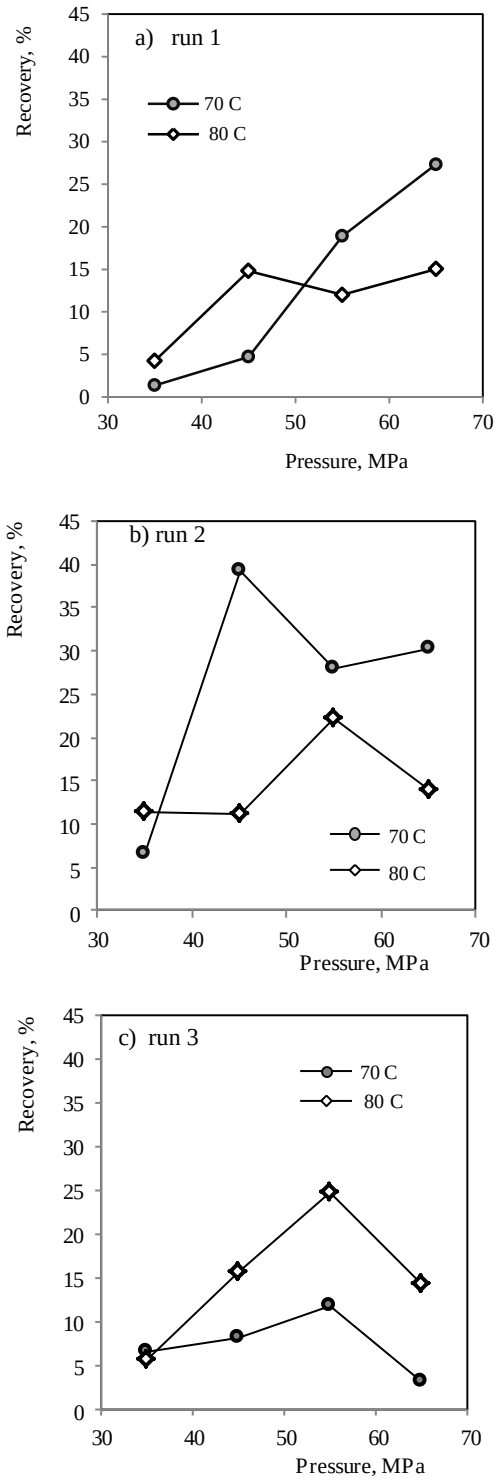

Figure 3: Recovery of used motor oil after run 1, 2 and 3.

were performed using sand at the same experimental conditions. The SC-CO_2 easily penetrates low-porosity materials due to its high diffusivity and dissolves liquids contained in a solid matrix.

When the suspension flows through the porous medium, liquid-solid separation by filtration can be accomplished by retention of the suspended particles inside a porous bed [8]. The filtration process is controlled by the properties of carrier fluid, suspension and porous media filter. The porous media is characterised by porosity, diameter of pores, size and shape of grains, and volume fraction already clogged by flowing particles.

Dependent on flowrate, viscosity, and density of the carrier fluid, and concentration, size, and shape of particles, the particles will be stopped or carried away by the flow.

The solute/solvent ratio can also play a role. In the described experiment, the extraction cell was fully packed with the sand saturated with the UMO. This implies that access of carbon dioxide is limited to the solute, especially in a first run. The gas injection was repeated in two more runs expecting that more space would be available after some part of the UMO is extracted in run 1.

The sand consisted mainly of two phases: sand grains of 2-3 mm of size and fine particles of less than 2 mm. Rincon et al., 2007 used glass beads of 3 mm diameter to clean used motor oil by propane or ethane [4].

Particle size can play a determining role in extraction processes. A smaller mean particle size reduces the length of diffusion of the solvent. As demonstrated by various studies, the decrease of particle size increased the extraction efficiency due to an increase in exposed sample surface area [9].

In order to eliminate the effect of fine particles and avoid the overlap of various counteracting factors, the sand was sieved to remove fine sand. The experiments were carried out at the same pressure range of 35-65 MPa at 70 ^{o}C and 80 ^{o}C. The cumulative recoveries after all three runs at 70 ^{o}C and 80 ^{o}C are shown in Figure 1.

Compared to the hyperbolic trend of the recovery increase in the experiment with the towel, the recovery curve obtained from the experiment with sand at 70 ^{o}C demonstrates a clear breakover point at 45 MPa. The breakover points at this pressure were also obtained in our experiments with the crude oil.

The outgassing losses were maximal of 18 % at 35 MPa on the average at both temperatures further decreasing at 65 MPa to 7 % at 70 ^{o}C and 9 % at 80 ^{o}C. Hence, the vaporization decreased at rising pressure.

At 80 ^{o}C, the cumulative recovery linearly increases up to 55 MPa further decreasing at 65 MPa. The outgassing losses at 80 ^{o}C is 2-3 % higher than at 70 ^{o}C. At increasing temperature, the increased fraction of vapor phase can worsen the solubility of carbon dioxide. As the result, the shape of recovery curve also changes.

The recovery at 70 ^{o}C is higher than at 80 ^{o}C by 7 % on the average mainly because it is higher at 45 and 65 MPa.

The distribution of the recoveries between runs at specifics temperatures is shown in Figure 2. After run 1, recovery at 70 ^{o}C exhibited typical for SC-CO_2 extraction features of crude oil recovery changes, gradually increasing at rising pressure. At 80 ^{o}C, the recovery increased to 15 % at 45 MPa and remained similar at higher pressures up to 65 MPa. The cross-over pressure can be

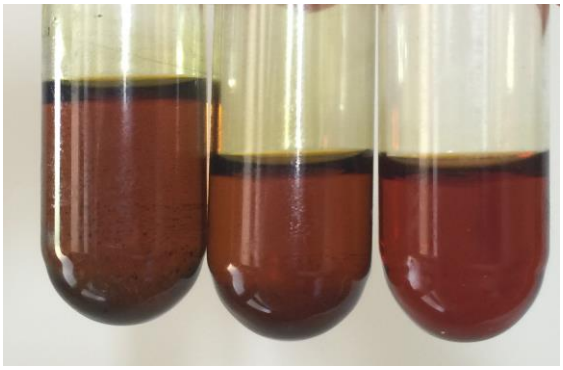

Figure 4: Samples of used motor oil extracted at 45 MPa and 70 °C after run 1, 2 and 3 (from left to rigth).

determined at 50 MPa, which separates two intervals. At the pressures below 50 MPa the recovery at 70 °C is lower than at 80 °C, while it is the opposite at the pressures above it. The recovery at 70 °C was higher than at 80 °C over pressure range of 45-65 MPa by average 16 %. After run 2, the recovery curves changed in a reciprocal manner, that is while recovery increased at 70 °C, it decreased at 80 °C. On the contrary, the recoveries after run 3 followed each other over entire pressure range. The recovery was higher by average 12 % at 80 °C over entire pressure range after run 3. After all runs at 35 MPa the recovery at 70 °C was similar or lower than at 80 °C. At 45-65 MPa, recovery was higher after run 2 and lower after run 3 at 70 °C compared to 80 °C.

In summary, the recovery substantially increased as a result of a mulitple extraction.

3.3 Visual inspection of extracts

All of the samples extracted at 70 °C were brownish with the exception of the sample extracted after the first run at 65 MPa, which contained some of the black residues. The examples of the UMO extracted at 70 °C are shown in Figure 4. With extraction at 80 °C, clean UMO samples were only obtained at 45 MPa and after a third run at 35 MPa. Most of the clean samples were transparent. However, some of them contained undetermined particles. Such particles can be seen in a test tube with the sample after run 1. The sample after run 3 has different color and does not contain visible particles.

3.4 Effects of temperature and porous media on separation of lees

Several effects contributed in the separation of base oil of the UMO from the engine wear residues. The presence of sand is decisive in the described process as follows from the comparison with the extraction results from the towels, where the lees have been co-extracted with the base oil. Second decisive factor was temperature. At higher flow velocity or pressure drop the particles are being torn from the retention sites and move with the carrier fluid. In the described experiment the stabilization of particles were disturbed by the increased temperature which also led to the increased pressure drop because of the increased vapor fraction. The complex interplay between solubility and kinetics requires further investigation.

CONCLUSIONS

Lower temperature of 70 °C facilitate the preferential extraction of the base oil of used motor oil. The engine wear residues precipitated in the sand, which suggests that this method could be employed for the regeneration of used motor oil using SC-CO_2.

Although the cost of the process has to be yet estimated, the method we describe seems to be fast, easy to manage, and is capable of treating small volumes of used motor oil. It also can replace some or several steps in the traditional procedure of the UMO re-refining.

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