Clean up Process for Oil-polluted Materials by Using Liquefied DME*

Hideki KANDA** and Hisao MAKINO**

**Energy Engineering Research Laboratory, Central Research Institute of Electric Power Industry,
2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, JAPAN
E-mail: kanda@criepi.denken.or.jp

Abstract
The proposed technology is a new concept that aims at energy-efficient drying and cleanup for general purposes by the use of liquefied DME (dimethyl ether) gas. Large amounts of energy are required for the cleanup of the ground since the water contained in the soil hinders the extraction processes that use hydrophobic organic solvents. Therefore, we focus on the use of liquefied DME, which is eco-friendly, as an extractant. The saturated pressure of DME is moderate—0.51 MPa at 20°C and 0.68 MPa at 30°C. Liquefied DME resolves high volume organic contaminants and water. Moreover, water can be easily separated from DME by flash distillation. This technology reduces the energy required for water-removal to half the latent heat of water. We almost completely removed water and other oily materials by using DME. DME was completely recycled and none of it remained in these materials. The world’s first prototype of a DME deoiling/dewatering process is shown. The capacity of this system is 10 L. Because of the low normal boiling point (−25°C) of DME, it does not remain in the soil and it can thus be reused as an extractant. In this presentation, we show the general purpose deoiling and dewatering processes for several materials.

Key words: Dimethyl Ether, Deoiling, Dewatering, Oil Pollution, Prototype

1. Introduction
We have developed a new method for dewatering coal and lignite using liquefied dimethyl ether (DME). This method can be used for the efficient extraction of water (dewatering) from high-moisture coal at ordinary temperatures; thus, it can be used to increase the calorific value per weight of coal and make such fuels easy to use. Sub-bituminous coal and lignite, which are “porous fuels with a high specific surface area,” can be easily dewatered using the DME dewatering process developed by the authors (1)–(3), a part of the combustible component of the coal erodes and dissolves in liquefied DME. Therefore, lipophilic substances are believed to dissolve in liquefied DME. Therefore, by focusing on this property, we explored the possibility of developing principles, methods, and devices for deoiling by using liquefied DME at ambient temperatures without heating.

Ground pollution is a significant environmental concern. When an oil spill occurs on water or on land that threatens the environment, the oil needs to be quickly recovered. In this situation, typical recovery methods are rinsing with water and detergent; using bacteria and flocculation; using combinations of heating, pressure filtration, pH adjustment, centrifugal separation, electrical treatment, and other processes; absorption using sand, earth, or oil sorbents; manual recovery of the oil in containers; and suction recovery using vacuum devices.

However, the methods involving bacteria or flocculation and those involving heating...
and pressure filtration are difficult to implement; this is because of the difficulty in establishing the treatment conditions, complicated processing systems, and the requirement of expensive treatment equipments.

Furthermore, although the methods that use water, detergent, and oil sorbents are able to separate the oil from the target material, the recovered oil includes water and detergent. Therefore, these methods are not efficient in terms of resource utilization as the separation of oil in its pure form ultimately produces effluent and waste materials.

Oil is used as a key ingredient in various industrial and domestic products such as heavy fuel oils, insulating oils, paints, solvents, lubricants, fuels, soaps, and food, which utilize various properties originating from its chemical structure. Therefore, a means of efficiently extracting, separating, and recovering only the oil when these products are discarded is sought from the perspective of recycling to preserve the environment.

Another environmental issue is the removal of PCBs (polychlorinated biphenyls) from the mud that collects in seabeds and riverbeds (4)-(8). Although PCBs can be extracted from mud using acetone and other chemicals using existing techniques, there have been problems with the acetone residue in the environment (9)-(11). The extraction also involves a cleaning cost because heating is required to vaporize the acetone residue. Furthermore, because of the need to reduce the treatment duration and the large number of the quantities requiring treatment, the required processing is currently not proceeding as planned by the public administrators. Solvent extraction with an organic extractant (80% ethanol and 20% water at 78 °C) is a physico-chemical method employed for the removal of organic contaminants such as polychlorinated dibenzodioxins, dibenzofurans, PCBs, and polycyclic aromatic hydrocarbons (12)-(13). However, in this method, a mixture of ethanol, water, and organic contaminants is formed as the waste liquid. Soil has a high water content, and soil particles have a high specific-surface-area with diameters ranging from a few sub-micrometers to a few millimeters. Owing to capillary effect, water adsorbed on the surface of the soil particles condenses in the space between them, thereby making deoiling a difficult task.

Therefore, this research aims to resolve the problems involved in conventional oil removal methods by applying the DME dewatering technology developed in our laboratory for oil removal. More specifically, a method and system for deoiling that separate oil in a short period of time at ambient temperatures without heating and with a high recovery rate are proposed. The proposed method and system can be used for a variety of oil-bearing materials, regardless of the types of oil molecules or the amount of oil contained.

2. Outline of the deoiling/dewatering process by using liquefied DME

Even in existing oil removal technologies, the situation under which deoiling alone is performed is different from that under which both dewatering and deoiling of moisture-containing materials such as sludge and soil are simultaneously performed.

Firstly, in the case of oil removal from a transformer or other devices, there are a few impurities such as moisture, and the process of oil removal is relatively simple even when using existing solvent extraction methods.

In cases in which the target materials contain moisture, such as the removal of PCBs from the mud found in seabeds or riverbeds and the removal of volatile organic compounds (VOC) such as benzene from soil, the solvents used to remove PCBs, benzene, and other VOC compounds are lipophilic and are immiscible with water. Therefore, the water particles in the target material prevent contact between the solvent and the target material, thereby drastically reducing the efficiency.

However, the DME dewatering technology utilizes the property that DME liquefies under pressures of 0.5 to 0.7 MPa at ambient temperatures and dissolves both oil and water, making it possible to simultaneously perform in both dewatering and deoiling.
For example, when removing PCBs and other lipophilic substances from materials with high-moisture content, such as sludge, the moisture is removed simultaneously, as shown in Figure 1.

![Diagram of DME deoiling/dewatering process](image)

The sludge and liquefied DME are first mixed in an extraction tank, and solid-liquid separation is then performed on the sludge and liquefied DME using sedimentation, centrifugal separation, or other methods. A large amount of moisture and lipophilic substances can be dissolved in liquefied DME, which is in contact with the sludge.

If DME in which the water and lipophilic substances are dissolved is evaporated to separate out the water, the concentration of water within the liquefied DME becomes supersaturated, forming a state where the water is unable to dissolve completely in liquefied DME. In this state, phase separation occurs, resulting in a water phase and a liquefied DME phase (in the DME/water separator in Figure 1). Because lipophilic substances can dissolve more easily in DME than in water, the noxious lipophilic substances can be efficiently separated from water by separating the water and DME phases.

As DME is repeatedly liquefied and vaporized in this process, it is essential that the energy required for the liquefaction and vaporization be reduced. Furthermore, because the system is operated at the ambient temperature, heat exchange in a moderately warm environment close to the ambient temperature is sufficient.

3. The world’s first prototype of deoiling/dewatering process

The usability of a DME deoiling/dewatering process was demonstrated by conducting deoiling experiments for a variety of substances by using liquefied DME as the oil extraction agent in the DME dewatering system that consists of a compressor and a flash distillation tower, as shown in Figure 2.

The deoiling experiments were first conducted for an artificial oil absorption agent, oil sorbent that is believed to be the most difficult substance to deoil. Because oil sorbents were
developed for absorbing oil spilled by grounded tankers and other sources, they cannot be used to absorb oil by using simple techniques such as merely soaking up the oil or adsorbing the oil; however, at the molecular level, they possess extremely high oil absorption capabilities.

Two sets of experiments were conducted. First, the flow rate of DME and the duration of the liquefied DME treatment were varied without altering the total quantity of DME used (100 L) for determining the deoiling performance with respect to the flow rate of liquefied DME. Experiments were then conducted at the liquefied DME flow rate at which the deoiling performance was found to be optimum, and the duration of deoiling was reduced to determine the total quantity of DME required for deoiling.

After the deoiling treatment, the reduction in weight was measured from the mass of the oil sorbent before deoiling and the mass after deoiling, and the mass of the expelled oil was measured. Table 1 shows the experimental conditions and results.

Table 1 shows that the mass of the oil sorbent after treatment was significantly reduced when compared with that before treatment under all experimental conditions, and it is clear from the mass of the expelled oil that the majority of the absorbed vacuum pump oil was extracted. Although there are some cases where the mass of the expelled oil exceeds the reduction in mass, this is believed to be due to some amount of DME being present in the oil sorbent and expelled oil after treatment.

Table 1  Deoiling test for oil sorbent.

<table>
<thead>
<tr>
<th>Measurement items</th>
<th>Unit</th>
<th>Change in flow rate and time (Total DME amount is constant.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of DME.</td>
<td>L./h.</td>
<td>100 200 300 400</td>
</tr>
<tr>
<td>Deoiling time.</td>
<td>Min.</td>
<td>60 30 20 15</td>
</tr>
<tr>
<td>Weight of the deoiled oil sorbent.</td>
<td>g</td>
<td>360 375 350 475</td>
</tr>
<tr>
<td>Reduced weight of the oil sorbent.</td>
<td>g</td>
<td>2570 2555 2555 2120</td>
</tr>
<tr>
<td>Weight of the removed oil.</td>
<td>g</td>
<td>2775 2725 2740 2120</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurement items</th>
<th>Unit</th>
<th>Change in Total DME amount (Flow rate is constant.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of DME.</td>
<td>L./h.</td>
<td>200 200 200 200</td>
</tr>
<tr>
<td>Deoiling time.</td>
<td>Min.</td>
<td>30 15 10 5</td>
</tr>
<tr>
<td>Weight of the deoiled oil sorbent.</td>
<td>g</td>
<td>375 555 400 600</td>
</tr>
<tr>
<td>Reduced weight of the oil sorbent.</td>
<td>g</td>
<td>2555 2375 2530 2330</td>
</tr>
<tr>
<td>Weight of the removed oil.</td>
<td>g</td>
<td>2725 2355 2490 2295</td>
</tr>
</tbody>
</table>
First, under experimental conditions where the flow rate and duration were varied without changing the total amount of DME (100 L), it was found that the maximum flow rate of liquefied DME that was able to properly extract oil was 300 L/h, and the duration at this rate was 20 min. The results of reducing the total amount of liquefied DME under conditions where the flow rate of liquefied DME was 200 L/h showed that extraction was possible with a deoiling duration of 10 min, i.e., with a total quantity of 33 L of liquefied DME. Furthermore, when the oil sorbent after deoiling was again allowed to soak up 650 g of oil per sheet, it was verified that the oil sorbent retained its oil retention capability. Therefore, it is clarified that this process is applicable for reusing an oil sorbent that contains oil. In order to verify that the process of oil removal using the DME dewatering technology is applicable to a variety of substances, similar experiments were conducted for stainless steel, glass, paper, and wood chips. For the experiments, the liquefied DME flow rate was set to 100 L/h, and the deoiling duration was 60 min. These study results show that this process is widely applicable to the deoiling treatment for a variety of substances.

4. Simultaneously Remove Oil and Water from Oil-contaminated Moist Soil

Similar experiments were conducted for moist soil. The experiments were conducted on soil (3630 g) that had soaked up 1150 g of heavy fuel oil. The soil was not dried or subject to any other pretreatment and contained moisture. However, the soil is believed to have undergone some chemical changes when dried at over 100°C because it produced a strange burning smell; therefore, the initial moisture content could not be measured correctly. For the experiment, the liquefied DME flow rate was set to 100 L/h and the deoiling duration was 60 min. The results of this experiment showed that a reduction of 1900 g was achieved in the weight of the soil. The reason for the reduction in the weight of the soil being larger than the weight of soaked up heavy oil is that the moisture was removed from the soil in addition to the removal of fuel oil. This was demonstrated by the results of the skimming of the black supernate from the expelled liquid, which showed that the supernate was fuel oil weighing 1150 g. Furthermore, the liquid remaining beneath the supernate primarily comprised relatively clear water, demonstrating that dewatering could be performed simultaneously with deoiling (Figure 3).
5. Conclusions

In this study, it was shown that DME can also be used for deoiling. In addition to the experimental examples, the proposed process is suitable for cleaning oil mist filters in air conditioners, cutlery, heavy fuel oil tanks, this process can also be used for adjusting the fat content in low-fat food. Furthermore, oil sorbents, glass, paper, wood chips, etc. that have been contaminated by oil can be cleaned and reused by applying the proposed process. This process is also successful in simultaneously removing both moisture and oil from soil powder. One application of this technology is expected to be the recovery of PCBs that leak into the urban rivers and other parts of the environment and from transformers that have been contaminated by oil containing PCBs. We would like to investigate the properties of PCBs in liquefied DME extracted from the sludge obtained from urban rivers etc. that contains PCBs and expand the range of materials to which the DME dewatering and deoiling technologies are applicable.

Acknowledgement

This research was supported in part by the Hosokawa Powder Technology Foundation.

References