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New Energy and Industrial Technology Development Organization (NEDO)

Central Research Institute of Electric Power Industry (CRIEPI)

Successful Extraction of "Green Crude Oil" from Blue-Green Algae
High Yield Extraction at Room Temperature without Drying nor Pulverizing
Process-

As a project funded under NEDO's "Grant for Industrial Technology Research Program", NEDO, CRIEPI and Hideki Kanda, Chief Scientist of CRIEPI successfully developed a method to extract "Green Crude Oil" Note3 from algae (blue-green algae) Note2 using liquefied dimethyl ether (DME)Note1 at room temperature in high yield.

Because this method utilizes the unique nature of liquefied DME, namely its ability to mix easily with water and oil, and can dewater and extract oils from blue-algae at room temperature concurrently, it can not only reduce the amount of energy required for dewatering and drying to a significant extent compared to conventional methods but also eliminate the organic solvents required for oil extraction, thereby representing a good opportunity to develop an environmentally friendly and economical oil extraction process.

The achievement mentioned herein is scheduled for presentation during the 90th Springtime Annual Meeting of The Chemical Society of Japan (CSJ) (Main campus, Kinki University) from 26-29 March, 2010.



Photo of Hirosawa Pond in Kyoto City from which blue-green algae were collected (Collected on 16 July, 2009)

(Note 1) Liquefied dimethyl ether (DME: chemical formula: CH₃OCH₃) is the simplest form of ether. Unlike other ethers, DME does not form peroxides, is non-toxic, has no effect on global warming nor ozone depletion and can be considered an environmentally friendly solvent. Both synthesized gas and liquid from coal are being utilized more frequently as inexpensive fuels in the People's Republic of China. Likewise in Japan, DME is used as a propellant for aerosol spray cans and its safety has been confirmed. The standard boiling point of DME is minus 25 °C and we used liquefied DME under 20 °C •0.5MPa in this study.

(Note 2) Algae show a high capacity to fix carbon dioxide, and therefore have the advantage of not competing with other edible resources and represent a good biofuel candidate. Conversely, because blue-green algae proliferation occurs in eutrophied lakes and ponds but has a negative impact on fisheries, this means such lakes and ponds cannot be considered for use as drinking water and often disrupts ecosystems, promoting the beneficial utilization of blue-green algae is sought-after and highly anticipated.

(Note 3) "Green Crude Oil" is a collective designation for an oily substance in the cells of microalgae and its trial utilization as a substitute fuel for petroleum is spreading.

■ Summary ■

As a project funded under NEDO's "Grant for Industrial Technology Research Program", Hideki Kanda, Chief Scientist of the Energy Engineering Research Laboratory (Toshio Mimaki, Director), Central Research Institute of Electric Power Industry (Kakumu Masahiro, President) successfully developed a method to extract "Green Crude Oil" from algae (blue-green algae) using liquefied dimethyl ether at room temperature in high yield.

To date, CRIEPI has been involved in developing dewatering extraction technology using DME to enhance our national energy security and facilitating the use of high—water content coal (brown and sub-bituminous coals) by dewatering and increasing calorific value*. This method is a kind of dewatering technology operated at room temperature and exploiting the high water absorption rate of DME, which will open up huge potential to significantly reduce the energy required for the dewatering and drying process.

(* Please refer to CRIEPI-NEWS No. 445 "Dewatering technology using liquefied dimethyl ether (DME) was developed" for details

URL: http://criepi.denken.or.jp/en/e publication/pdf/den445.pdf)

This time we demonstrated substantial energy saving by simplifying the complex process of existing technologies and applying DME dewatering technology to extract the organic compounds (oily component) from high water-content microalgae.

1. Background

Phytoplankton in µm long is known as microalgae. It has a high photosynthetic capacity (the absorption capacity of carbon dioxide) and its capacity per unit area can be rated at more than 100 times that of corn. Certain microalgae, which can synthesize "Green Crude Oil" such as heavy and light oils, have attracted the public's attention recently as non-competitive biofuels with edible foods, together with the high absorption rate of greenhouse gases.

Microalgae, however, contain significant volumes of water because the photosynthetic reaction takes place in water and the water contained inside has become a major obstacle to extracting "Green Oil" from them.

2. Summary of research achievement and its significance

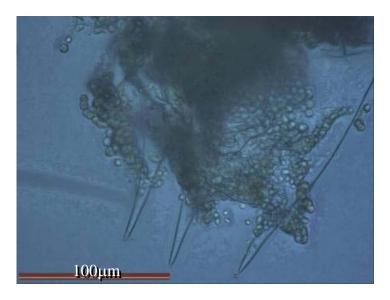
Traditional methods dewater microalgae until they become slurry by compression or mechanical

treatment such as centrifuging. Slurry-state yet contains 90% of water. Moreover, the remaining cell walls in the 10% water cannot be utilized as "Green Crude Oil". Slurry-state microalgae are subsequently sun-dried or dried by heating to make a powder. During this stage, powdery microalgae are covered with cell walls, which should be broken down with acid or by pulverizing to extract oil, then organic solvents such as hexane, acetone or chloroform shall be used. Further in the final stage, large volume of organic solvent must be evaporated from the extracted liquid phase.

In other words there were many complex steps involved, such as drying, breaking cell walls, and using & removing toxic solvents together with the problem of the considerable energy required to extract the "Green Crude Oil" (= source of energy) produced by photosynthesis. In this context, traditional research work involving microalgae has been focused on the production of a special kind of algae by manipulating genes or selective breeding assuming the aforementioned extraction process as a precondition.



Fig. 2 Harvesting blue-green algae (picture to show screening dirt)



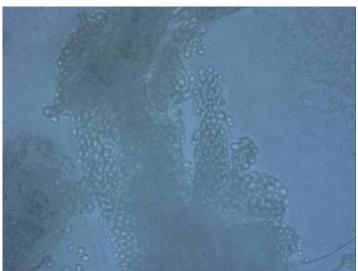


Fig. 3 Image of experimented microalgae under the optical microscope

CRIEPI has therefore been conducting basic research to develop an energy-saving and environmental friendly method to extract "Green Crude Oil" using liquefied dimethyl ether (DME) from algae harvested in nature and by simplifying the post-drying process.

Although a kind of ether, DME does not form peroxides, is non-toxic, and has no effect on global warming or ozone depletion, thus making it an environmentally friendly solvent. Its standard boiling point is minus 25 °C but liquefied DME under 20 °C, 0.5MPa shows a good affinity with oil and the capacity to partially mix with water. Thus if liquefied DME is used as a solvent, its molecules-disperse inside cells through cell walls and bind strongly to the oily components, whereupon DME molecule bound by oily components eventually comes out of the microalgae. With this in mind, we assumed "Green Crude Oil" could be extracted efficiently, even if the



Fig. 4 Column filled with Green Algae



Fig. 5 Picture of the inside column where DME was circulated upward from the bottom. (The dark-colored lower half portion is blue-green algae and the light green liquid in the upper half is DME, including extracted "Green Crude Oil")

microalgae have a high water content.

To verify this assumption, we experimented using naturally grown blue-green algae (a mixture of many microalgae, including mainly genus Microcystis) collected from Hirosawa Pond in Kyoto City. Consequently, we were successful in extracting 4.12g of water and 0.24g of "Green Crude Oil" (corresponding to 40.1% of dry weight) by adding liquefied DME under $20\,^{\circ}\text{C} \cdot 0.5\text{MPa}$ at the rate of $10\,\text{cm}^3$ /min to the sample of 6.65g containing 91.0% water, which was prepared beforehand following rough dehydration by centrifugal separation. Analysis of

the extracted "Green Crude Oil" showed a molecular weight of 200~400 and calorific value of 10,950cal/g. In contrast, we extracted only 0.60% of the dry blue-green algae weight using a traditional method. In other words, the method using DME was capable of extracting more than 60 times the "Green Crude Oil" compared to traditional methods and demonstrated a far superior extraction performance as an extracting agent.

Further in this process, we must separate liquefied DME from "Green Crude Oil" in the final stage of the process and liquefied DME can be easily recovered as vapor only through a depressurization step, because the liquefied DME evaporates at room temperature under the condition of 0.5MPa or less. Once recovered, DME can be re-liquefied and reused as an extracting agent.

Also, if there is a heat source in the range of $50\,^{\circ}$ C, this can allow DME to absorb it for the heat of evaporation and vaporize efficiently under atmospheric pressure. Therefore, if the extraction of "Green Crude Oil" is materialized utilizing around $50\,^{\circ}$ C of wasted heat currently released from plants, we can see significant potential to establish a system far superior to



Fig. 6 Extracted "Green Cude Oil" at room temperature

those existing in order to save energy during solvent recovery.

3. Vision of the Future

To commercialize this liquefied DME extraction process, we must conduct basic experiments using varieties of algae and develop the "Green Crude Oil" concentration technology in DME. In an effort to implement early commercialization, we plan to continue experiments and continue improving this process.

Again in future, we will consider scaling-up the whole process, from the basic experimental level apparatus in cooperation with business enterprises.

4. Contact Information

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