PAPER

Application of green solvent extraction for citrus residues

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■Abstract

Currently, various sour citrus fruits are cultivated in Japan. In particular, citrus peculiar to Japan such as *Yuzu* (*citrus jinos*) and *Shekwasha* (*citrus depressa*) has been treated as a raw material for juice processing. At that time, it is a problem that a large amount of citrus residue is generated. Citrus residues are disposed of as industrial waste despite containing high value added compounds. Moreover, the citrus processing residue accounts for about 50% of the fruit. From our earlier research [1], it is known that citrus processed residues contain good hydrocarbons such as water soluble dietary fiber such as essential oils and pectin.

In this study, two kinds of extraction experiments were conducted in order to investigate Yuzu and Shekwasha as experimental subjects and components with high added value contained in their processing residues. The first is the recovery experiment of valuable materials using supercritical carbon dioxide. The second one is a recovery experiment of that using liquefied DME.

As a result, in the recovery experiment in the liquefied DME, a yield exceeding the experimental result by the supercritical carbon dioxide was obtained.

現在、我が国では様々な香酸柑橘が栽培されている。特に、柚子（*Citrus junos*）やシークワーサー（*Citrus depressa*）などの日本特有の柑橘類の果汁は、ジュースの原料として広く扱われている。一方で、果汁の搾汁後には多量の搾汁残渣が発生するという問題がある。柑橘の搾汁残渣には付加価値の高い化合物が含有されているにもかかわらず、そのほとんどが産業廃棄物として処分されている。しかも、搾汁残渣が元の果実のうちで占める割合は、重量換算して約50％であり決して少なくない。

我々は既往研究として、柑橘の搾汁残渣には、精油およびペクチンのような水溶性食物繊維のような良好な炭化水素を含むことを明らかにした。そこで本研究では、実験対象柑橘にユズおよびシークワーサーの搾汁残渣を用いて、より付加価値の高い成分を調査することを目的とし、2種類の抽出実験を行った。第１に、超臨界二酸化炭素を用いた有価成分の回収実験である。第2に、液化DMEを用いた有価成分の回収実験である。その結果、液化DMEにおける回収実験では、超臨界二酸化炭素による実験結果を上回る収率が得られた。

Key Words: *Citrus junos*, *Citrus depressa*, essential oil, pectin, Supercritical carbon dioxide, Liquefied DME

キーワード：ユズ、シークワーサー、精油、ペクチン、SC-CO_2、液化DME

Introduction

In recent years, due to the health promotion boom, many citrus foods are handled. ASCII Co., Ltd. (Kawasaki Town, Tagawa-gun, Fukuoka) is squeezing Japanese citrus and manufacturing and selling fruit juice, which is responsible for a majority of the domestic citrus fruit juice sales volume. However, at present, there is a problem of fruit juice residue that is discharged in large quantities, and it is

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urgent to establish an effective method for recovering valuables from citrus residue. The squeezing rate of fruit juice products varies depending on varieties, but about 30% of fruit juice fruits are most, and the amount of citrus processing residues generated reaches 3000 tons annually. However, these are currently being disposed of at high cost as industrial waste without utilization. In previous studies, focusing on peel essential oil or seed oil, which is used as a perfume high added value among the valuable materials contained in citrus, has conducted experiments about the establishment of a more efficient extraction method [2][3]. In addition, attention is focused on industrial technologies that contribute to reducing environmental burden due to recent changes in the global environment. Among them, with regard to the extraction technique, development of an extraction method utilizing a solvent that is less burdensome to the environment called green solvent has been made.

Therefore, in this research, we will conduct efficient recovery of citrus valuable materials from processed residues of citrus, using supercritical carbon dioxide and liquefied DME, which are green solvents, for residues of Yuzu and Shekwasha among citrus residue. Then investigate novel valuable components. This can be a basic research for establishing how to utilize citrus residue, and when this is achieved, economic effects such as new market expansion for the citrus processing industry and the resulting creation of employment are expected, and it has the potential to have a positive influence on society.

2. Experiment

2.1 Materials

Among various citrus fruits, Yuzu and two types of Shekwasha were used in this experiment. The first is a Taiwanese Shekwasha and the second is Okinawan Shekwasha. The state of the sample was used in a raw state without special handling such as drying treatment in particular.

2.2 Chemicals

2.2.1 Characteristic of Supercritical carbon dioxide

Supercritical carbon dioxide, which is heated and pressurized to carbon dioxide above its critical temperature (31.1 ℃) and critical pressure (7.38 MPa), is characterized by an increase in solubility of nonpolar or low polarity substances due to non-polarity *has features such as rapid increase of the diffusion rate*. Based on this, it is used for extraction of nonpolar or low polar substances present in natural products such as citrus processed residues (Fig. 1). The properties of supercritical carbon dioxide are summarized below.

● Control of density by operation of temperature and pressure is possible. Therefore, it is possible to precisely adjust the solvent characteristics.

●It has low viscosity and high diffusibility. Therefore, it has excellent permeability to solid sample and high mass transfer rate can be expected.

●Since kinematic viscosity is smaller than gas and liquid and natural convection tends to occur, it is more effective than liquid in terms of substance and heat transfer.

● Thermal conductivity in the vicinity of the critical point shows maximum and high heat transfer speed can be obtained. Removal of reaction heat and heat exchange can be effectively performed.

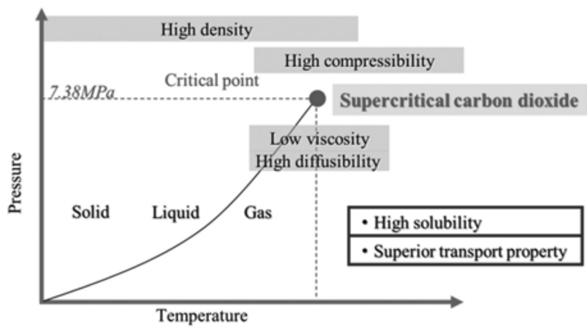

Fig. 1 Characteristics of supercritical carbon dioxide

2.2.2 Characteristic of liquefied DME

Dimethyl ether (DME) is a type of ether and has the simplest structure. Practical application is being promoted as a spray propellant or an inexpensive alternative fuel rather than LPG. It can be obtained from various raw materials such as coal, biomass, industrial waste such as refinery residual oil and so on. Sulfur oxides and smog are not generated by atomic composition, so they are drawing attention as clean fuel. Although DME is a gas at room temperature, it can be liquefied under relatively mild conditions of 20 ℃ to 5 atmospheres or −25 ℃. DME is amphiphilic and has the feature of being relatively safe without causing harm to the human body and the natural world. Fig. 2 shows the vapor pressure curve of DME, and Fig. 3 shows the relationship between the temperature and the density of liquefied DME [4].

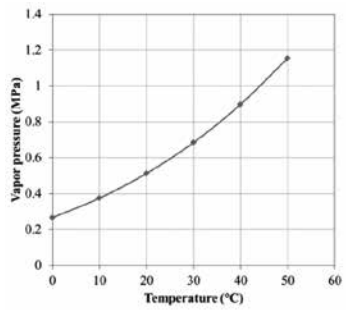

Fig. 2 Vapor pressure curve of DME

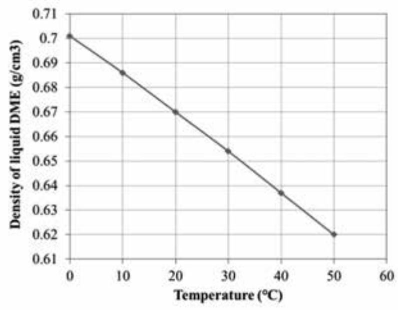

Fig. 3 Temperature vs density of liquefied

2.3 Experimental method

2.3.1 Supercritical carbon dioxide extraction method

50 g of each citrus processed residue was placed in an extraction tube, extraction pressure and temperature were set to 30 MPa and 80 ℃., respectively. Samples were collected every 30 minutes of extraction time. The number of experiments is five. Fig. 4 shows the schematic diagram of Supercritical carbon dioxide extraction method. Analysis of samples are achieved on HPLC LC-10AD gradient system, equipped with Diode Array Detector SDP-M10A. Inertsil ODS-3 column (4.6 mm × 250 mm, 5 μm) was used for separation at 35 ℃. The mobile phase consisted of 0.1% acetic acid (solvent A) and 75% acetonitrile dissolved in solventA (solventB). The flow rate was 1.0 mL/min and a stepwise solventB gradient (12-100%) was applied. Detection was accomplished by monitoring the absorbance signal at 285 nm.

2.3.2 Liquefied DME extraction method

50 g of each citrus processed residue was placed in an extraction tube, extraction pressure and temperature were set to 1.2 MPa and 50 ℃., respectively. The number of experiments is five. Fig. 5 shows the schematic diagram of liquefied DME extraction method. The obtained sample is analyzed by the same method as the supercritical carbon dioxide extraction method.

3. Result and discussion

As a result of extraction experiments on Yuzu and each Shekwasha, it was found that flavonoids such as *Hesperidin, Naringin*, and *Nobiletin* were contained. *Hesperidin* has an effect of improving adult diseases such as lowering blood pressure and decreasing cholesterol level as a physiological effect. *Naringin* is also a causative agent of bitterness contained in the peel of citrus. This physiological action includes antiallergic action and fatty acid decomposition function. And Nobiletin has anti dementia function. Both of these are a type of flavonoid peculiar to citrus and its added value is considered high.

Fig. 6 to Fig. 8 shows the recovery rates of *Hesperidin, Naringin, Nobiletin* in each experiment. This is the ratio of the extracted amount of this experiment to the calculated amount, assuming that the extraction amount by the organic solvent extraction method which is the traditional component extraction method used heretofore is 100%. The whole thing can be said that the recovery behavior of each component is similar. Although the weight of the sample used in the experiment is same, the recovery rate is higher as the size of the original fruit is larger and the thickness of the peel is larger. In addition, the recovery

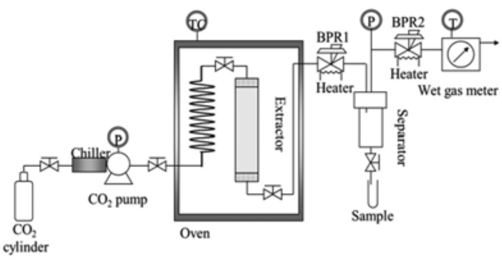

Fig. 4 Schematic diagram of Supercritical carbon dioxide extraction method

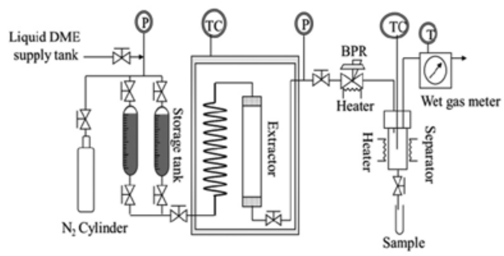

Fig. 5 Schematic diagram of liquefied DME extraction method

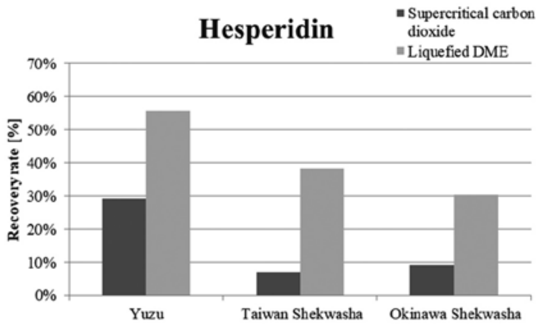

Fig. 6 Recovery rate of ***Hesperidin***

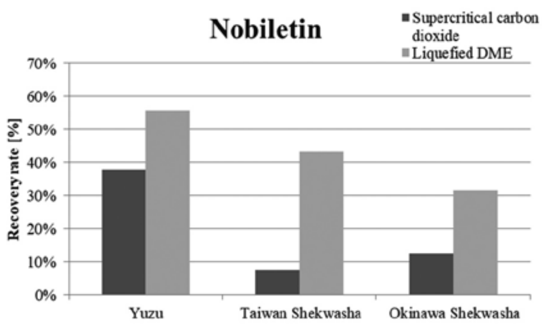

Fig. 7 Recovery rate of ***Naringin***

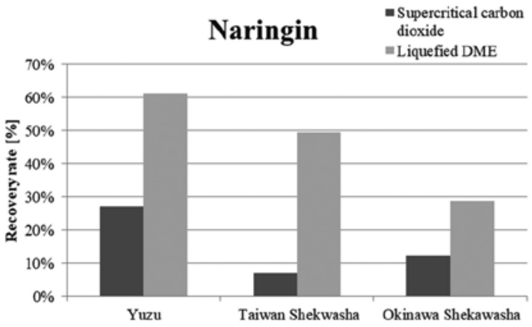

Fig. 8 Recovery rate of ***Nobiletin***

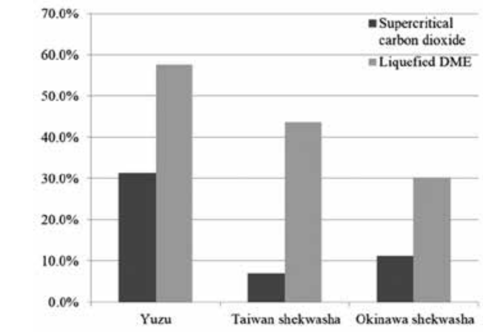

Fig. 9 The average yield of each experiment

rate by liquefied DME extraction method was generally higher than that by supercritical carbon dioxide. The reason for it is assumed that liquefied DME has better dehydrating ability than supercritical carbon dioxide. In *Yuzu*, the recovery rate of functional ingredient is about 60%. In each *Shekwasha*, the recovery rate is about 30% to 40%. In other words, it was not possible to recover more functional ingredients than organic solvent extraction method in this experiment. In addition, in the experiment by the supercritical carbon dioxide extraction method, it is thought that the recovery rate of *Taiwan Shekwasha* was lower than the recovery rate of *Okinawa Shekwasha* is due to separation of the extracts into oil phase and liquid phase. Figure 9 shows the average recovery rate for each sample in each experiment.

Conclusions

In extracting functional ingredients from natural products, attention is focused on green solvents that contribute to reducing environmental burden. In this research, valuable materials recovery experiments from citrus processed residues were conducted using supercritical carbon dioxide and liquefied DME, which are green solvents. The recovery rate is calculated from the experimental results in the organic solvent extraction method which is a classical component extraction method and the result in this experiment.

The results of the two experiments performed this time showed that the recovery rate was lower than the result by the organic solvent extraction method. In order to improve this, we think that it is necessary to adjust experimental conditions such as applying preliminary treatment such as drying treatment to experimental samples. However, in any of the experiments, since the extraction behaviour of valuable substances is stable, there is a great possibility that functional ingredients can be efficiently obtained as the recovery rate is improved.

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