SEPARATION OF FATTY ACID METHYL ESTERS AND TOCOPHEROLS WITH SUPERCRITICAL CO_2 – PHASE EQUILIBRIA AND FRACTIONATION EXPERIMENTS

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ABSTRACT

In order to study the possibility of using supercritical CO_2 to concentrate natural tocopherols from soybean oil de-odorizer distillate (DOD), the phase equilibria for the realistic system of CO_2 - ME-DOD (the methyl esterified DOD) was investigated. According to the measured data, the distribution coefficients and separation factor were calculated. The fundamental research indicated that for the system of methyl esterified DOD, supercritical CO_2 is a kind of feasible method for separating fatty acid methyl esters (FAMEs) from natural tocopherols in the experimental range investigated. Finally, based on this conclusion, the separation experiments were carried out with a fractionation column. The result indicated that supercritical CO_2 fractionation is effective to produce FAMEs at 16 MPa and then by increasing pressure, natural tocopherols (> 60 %) can be obtained with high recovery (> 80 %).

1. INTRODUCTION

Oil de-odorizer distillate (DOD) is a kind of byproduct of oil refining process and is rich in natural tocopherols (vitamin E) and sterols, which are widely used in food, feed and medical industries [1]. Although vacuum or molecular distillation, as the conventional methods, have been applied to commercial production of tocopherols from DOD, since there are some drawbacks such as high production cost, unstable quality of products and thermal degradation of tocopherols caused by high processing temperature [2], development of new alternative isolation techniques has been desired.

Supercritical extraction with carbon dioxide offers unusual possibilities for the selective extraction, fractionation and purification of many natural components. Although some researchers tried to concentrate tocopherols from DOD by supercritical CO_2 [1, 3 - 5], the operation parameters, especially pressure, are different from author to author. To find reasonable operating conditions, phase equilibria of DOD - CO_2 must be clarified.

To simplify the composition of DOD, methyl esterification is generally carried out and then sterols are removed from the esterified system. After such treatments, the methyl esterified DOD (ME-DOD) mainly contains fatty acid methyl esters (70-80 wt. %), tocopherols (10-15 wt. %) and other impurities (such as residual sterols, glycerides, squalene, pigments, long chain paraffins, all of these compounds hold about 10-15 wt. % in system), such complex system can be regarded as a pseudo ternary (CO_2 - tocopherols - FAMEs)

system. Up to now, there is no literature reporting the phase equilibrium data about the realistic system of ME-DOD - CO_2. This paper measured the phase behaviors of this system and then according to fundamental data, the separation operation was carried out for separating FAMEs and tocopherols from ME-DOD.

2. MATERIALS AND METHODS

2.1 Experimental materials

ME-DOD (10.19 % tocopherols) was supplied by Kaidi Fine Chemistry Co., Wuhan, China. CO_2 was supplied from Uchimura Sanso Co. Ltd. (Osaka, Japan) with purity of 99.97%.

Methyl oleate and Dl-*a*-tocopherol were obtained from Wako Pure Chemical Industries Inc. (Tokyo, Japan) with purities of = 98 %.

2.2 Apparatus and procedure

2.2.1 Apparatus for measuring phase equilibrium[6]

A gas-liquid alternating circulation system (170 mL, max. pressure 30 MPa) was established for measuring vapor – liquid – equilibrium and a view cell (30 mL, max. pressure 30 MPa) was employed for visually observing the equilibrium systems.

2.2.2 Supercritical CO_2 fractionation systems

An apparatus for supercritical CO_2 fractionation was described in our previous paper [7]. The experimental setup consisted of a countercurrent contact column (750 mL, 2.4 m × 20 mm i.d.) and a separator (600 mL) for the top product. The column was packed with stainless steel 3 mm Dixon Packing (Naniwa Special Wire Netting Co., Ltd., Tokyo) over a length of 1.8 m and the column temperature was separately controlled by eight PID controllers.

2.3 Analysis methods [6]

GC and HPLC were employed for analyzing FAMEs and tocopherols, respectively. Methyl oleate and Dl-*a*-tocopherol were applied as the external standards for analyzing FAMEs and tocopherols, respectivlely.

3. RESULTS AND DISCUSS

3.1 Phase equilibrium properties

3.1.1 Phase equilibrium properties

The phase equilibrium data of CO_2 - ME-DOD were measured in the range of 10 - 23MPa at 313.15 K, 333.15K. The results are shown in **Fig. 1**.

The equilibrium data illustrate that the mass fraction of CO_2 in liquid rises with pressure increase, while the CO_2 fraction in gas tends to decrease, it means that more ME-DOD solve in the gas phase with pressure increase, and the compositions in both gas and liquid close to each other. Meanwhile the influence of temperature on equilibrium data is contrary to that of pressure, a higher temperature weakens the tendency of mutual solution between ME-DOD and supercritical CO_2.

3.1.2 Solubility:

The solubilities of ME-DOD and tocopherols in supercritical CO_2 were calculated from the gas phase data. The solubility data are shown in **Fig. 2**, as a function of CO_2 density.

The solubility of ME-DOD in CO_2 and the tocopherols' content in ME-DOD increase with CO_2 density, at a constant density, a higher temperature increases the solubilities of ME-DOD and tocopherols in supercritical CO_2, because an increase in temperature leads to an higher vapor pressure of the solutes. Moreover the solubility of tocopherols in supercritical CO_2 is lower compared with that of ME-DOD, for example at 21.9 MPa and 313.15 K, the solubility of tocopherols is less than 1.3 g/100g CO_2.

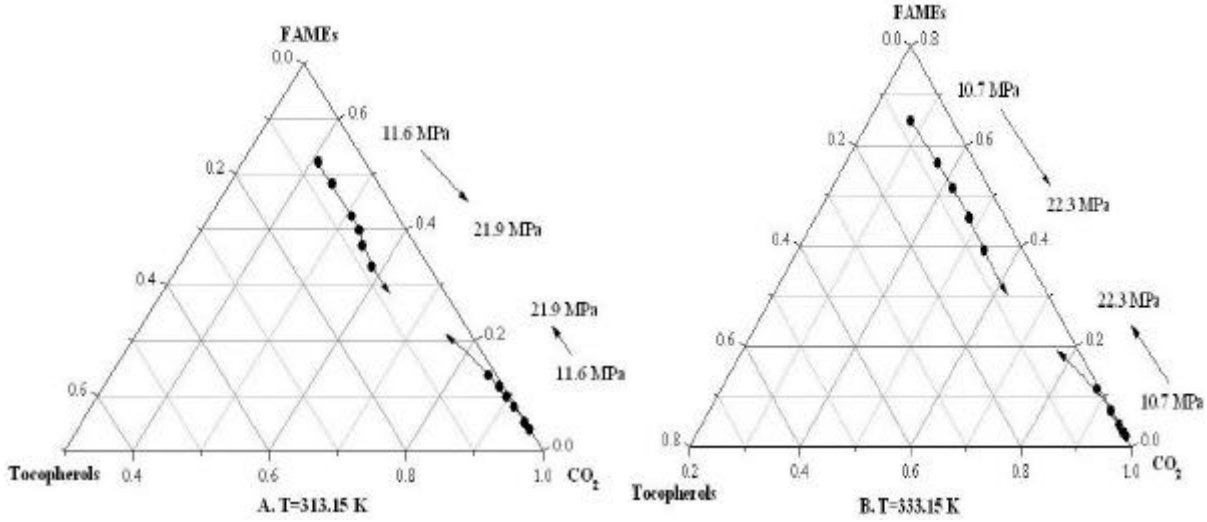

Fig 1. The phase behaviors of ME-DOD in supercritical CO_2

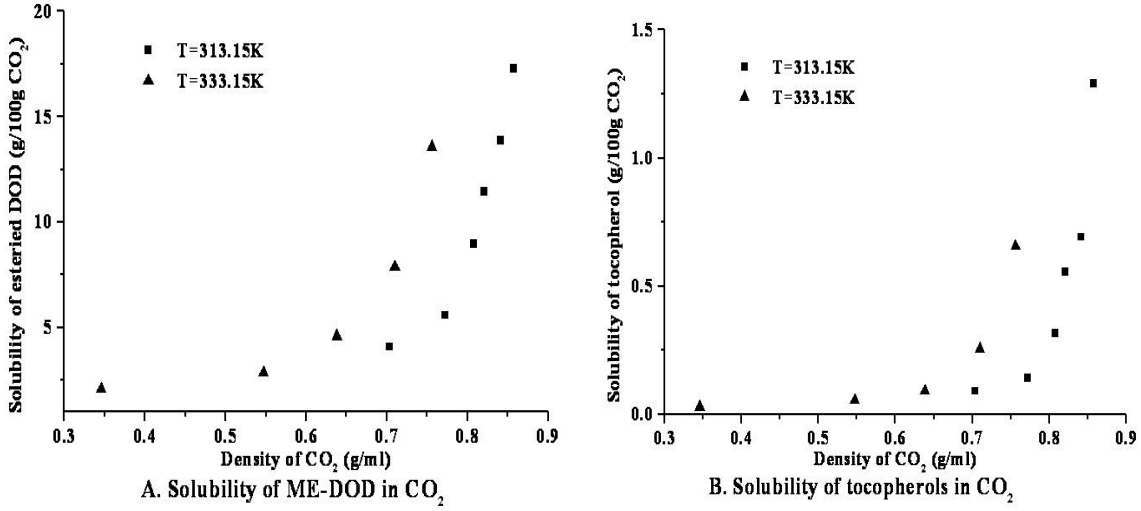

Fig. 2 The solubilities of ME-DOD and tocopherols in supercritical CO_2

3.1.3 Distribution coefficient and separation factor

According to the measured VLE data, the distribution coefficient of tocopherols (CO_2 basis) was calculated by:

$$K_{TO}=Y_{TO}/X_{TO} \quad (1)$$

The separation factor between tocopherols and FAMEs was defined as:

$a = (Y_{TO}/X_{TO})/(Y_{FA}/X_{FA})$ (2)

Where *Y* stands for the mass fraction of tocopherols (TO) and FAMEs (FA) in the gas phase and *X* for the mass fractions of tocopherols (TO) and FAMEs (FA) in the liquid phase.

In **Fig 3.**, the distribution coefficient of tocopherols in the realistic systems is shown and compared with that in the binary system (DL- *a*-tocopherol – CO_2)[6].For either realistic or binary system, the distribution coefficient of tocopherols is positively affected by pressure, but negatively affected by temperature.

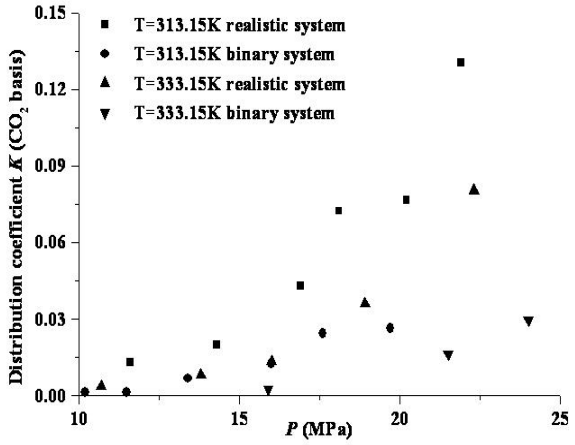

Fig.3 Distribution coeffecients of tocopherols in two systems

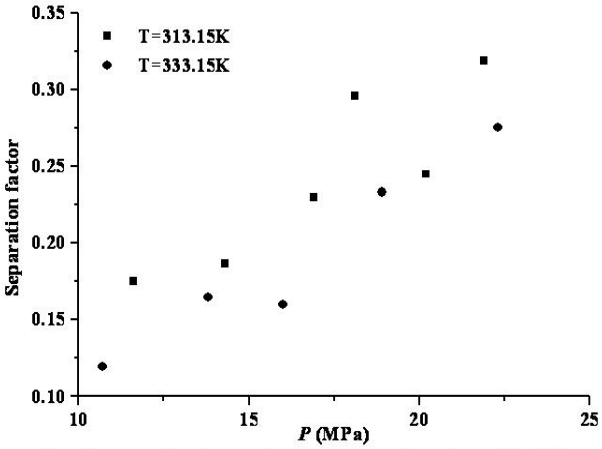

Fig.4 Separation factor between tocopherols and FAMEs

Additionally there is another interesting phenomenon. As to the realistic system of supercritical CO_2 - ME-DOD, the distribution coefficient of tocopherols, *K* (CO_2 basis) is dramatically larger than that in the binary system of supercritical CO_2 - DL-*a*-tocopherol. For example, when at 20 MPa and 313.15 K, the distribution coefficient for tocopherols in the realistic system is 2-3 times larger than that in binary system. This phenomenon is explained that because of the large existence of FAMEs, which is easier to solve in supercritical CO_2 and take an action of cosolvent, the distribution of tocopherols in supercritical CO_2 is remarkably increased. An alike phenomenon was also reported by Bamberger et al [8], as for the multicomponent system composed of trilaurin, palmitin and nutmeg butter, among which trilaurin is the easiest to solve in supercritical CO_2, the existence of trilaurin results in a dramatic increase in the distribution coefficients of palmitin and nutmeg butter.

Fig 4. shows the separation factor between tocopherols and FAMEs. The separation factore is always smaller than unity in the range investigated and this indicates that using supercritical CO_2 as the process media, compared with FAMEs, tocopherols tend to enrich in the liquid phase, and an increase in temperature strengthens this tendency and it means the selectivity of the process increases, while the influence of pressure on this tendency is contrary to that of temperature. Consequently, for separating FAMEs from tocopherols, low pressure and high temperature are advantageous to obtain high selectivity. In details, as shown in **Fig. 4**, when pressure is less than or equal to 16MPa, the separation factor of tocopherols and FAMEs is less than 0.2, indicating that tocopherols and FAMEs can be well separated by supercritical CO_2 at this condition.

3.2 Fractionation operation

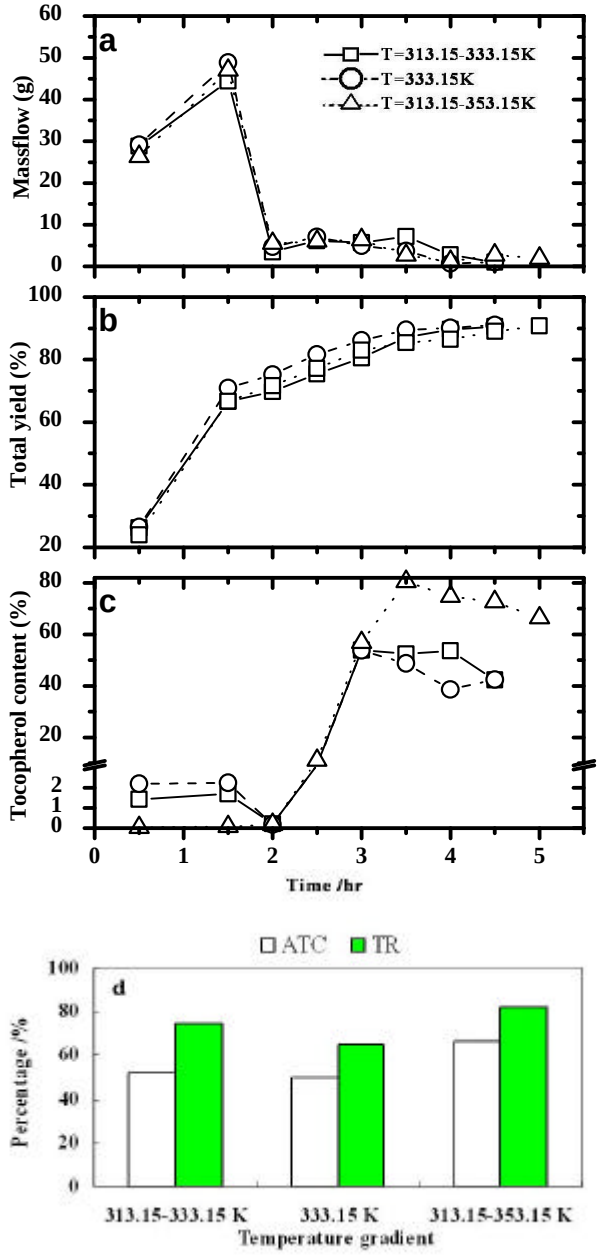

Fig. 5 Effect of temperature gradient on fractionation

Based on the fundamental information obtained from the realistic system of CO_2 – ME-DOD, the basic separation strategy was made certain: first of all, SC-CO_2 was employed to remove most of FAMEs from ME-DOD at 16 MPa and then the operation pressure was increased for extracting tocopherols.

In fractionation experiment, 110 g ME-DOD was initially charged into the column. The first step was to remove most of FAMEs (about 70 wt. % feed) at 16 MPa (initial pressure). The operation was in batch mode and CO_2 flowrate was fixed at 3 Kg/hr. When the total yield from the column top reached about 70 wt.% of the feed, the second step began for separating tocopoherols from other impurities by increasing the column pressure to 20 MPa (end pressure). The experiment was terminated when the total extract reached to about 90 % feed.

The total and tocopherol yields were calculated from the massflow and tocopherol content in the fractions. We mainly investigated the influence of the temperature gradient on the average tocopherol content (ATC) and tocopherol recovery (TR) in the 20 MPa fractions.

The results shown in **Figure 5** indicated that the temperature gradient of 313.15 - 353.15 K decreased the tocopherols' content in the FAMEs at 16 MPa (lower than 0.1 wt.%), enriching tocopherols in the fractions at 20 MPa (**Figure 5. c**).

Generally, the temperature increase along the column causes an internal reflux, where less soluble components condense and drop back when the supercritical fluid containing dissolved solutes at lower temperature flow into the higher temperature zone due to the solubility decrease of solutes with the increase in temperature. These internally refluxed drops countercurrently contact with the fluid flowing up in the column, resulting in the rectification. In our separation experiments, the temperature gradient of 313.15-353.15 K resulted in satisfactory ATC (66.22%) and TR (82.53 %). In addition, compared with the uniform

temperature of 333.15 K, 313.15 – 333.15 K didn't lead to an obvious difference in the tocopherol content of 20 MPa fractions. The possible reason was that the small difference of 20 K didn't cause enough internal reflux for improving the selectivity of the whole process. Moreover, at the two temperature modes, the tocophperol contents in FAMEs were in range of 1.4 – 2.2 % (**Figure 5. c**). As a result there were more than 20 % tocopherol yield coextracted with FAMEs at16 MPa, decreasing the tocopehrols' content and recovery of 20 MPa fractions.

4. CONCLUSION

The phase equilibrium data about the realistic system of supercritical CO_2 - ME-DOD indicated that it is feasible to separate tocopherols from ME-DOD by means of supercritical CO_2 at 10-23 MPa, a better separation result can be obtained at low process pressure. In addition, the large existence of FAMEs was proven to increase the distribution of tocopherols in gas, so FAMEs is regarded as a cosolvent in the system.

According to the fundamental information, the fractionation operation was conducted at 16 MPa with different temperature gradients. The results show at the temperature gradient of 313.15-353.15 K, FAMEs and tocopherols can be well separated from ME-DOD at 16 MPa and 20 MPa, respectively.

Finally, it should be noticed that only the fundamental data of ME-DOD in CO_2 are not enough for completing the process design, because the necessary length of fractionation column couldn't be calculated with the obtained data, the phase equilibria of different tocopherols – FAMEs ratio should be systematically investigated, and then combining with separation experiments, more valuable data can be provided for process designing and scale-up.

ACKNOLEDGEMENT

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