

SELECTIVE EXTRACTION OF A MIXTURE OF STEARIC, OLEIC, LINOLEIC, AND LINOLENIC ACID METHYL ESTERS WITH SUPERCRITICAL CARBON DIOXIDE USING A GAS-FLOW METHOD

YUTAKA IKUSHIMA, MASAHIKO ARAI, KIYOTAKA HATAKEDA,
SHOTA ITO, NORIO SAITO AND TOMIO GOTO
Government Industrial Research Institute, Tohoku, Sendai 983

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In recent years, highly unsaturated fatty acids such as linoleic and linolenic acids have been noted in terms of their pharmaceutical importance^{3,6)} and usefulness as precursors of prostaglandins.^{1,11)} However, it is difficult to effectively separate desired components from a mixture of fatty acid methyl esters that have the same number of C-atoms and differ only by the degree of unsaturation. This is because they are homologous in chemical and physical properties and are liable to be denatured by heat. Thus, a possible method of selective extraction from such a mixture is greatly anticipated.

A supercritical fluid (SCF) method can be used in extracting nonvolatile hydrophobic and thermolabile materials without denaturation because of its low operating temperature.⁷⁻⁹⁾ Furthermore, it does not need a post-treatment for purification such as the removal of used solvents.²⁾ We now present a supercritical CO₂ (SC-CO₂) extraction technique to isolate specific components, especially stearic and linolenic acid methyl esters, from a mixture of stearic (C₁₈₋₀), oleic (C₁₈₋₁), linoleic (C₁₈₋₂), and linolenic (C₁₈₋₃) acid methyl esters. The first and second figures in the parentheses refer to the number of carbons and the degree of unsaturation in the molecule, respectively. It is difficult to separate selectively the desired components from the mixture with SC-CO₂ alone.¹⁰⁾ In this work, therefore, we used an extraction system having a separation tube in which AgNO₃ supported on silica gel is packed to isolate unsaturated fatty acid methyl esters more effectively. In addition, ethyl acetate was used as an entrainer to enhance the separation efficiency of C₁₈₋₃ acid methyl ester.

1. Experimental

The SCF extraction apparatus used was a gas-flow

type and it is shown schematically in **Fig. 1**. A 0.1-l extractor was maintained at 313 K and CO₂ was delivered at a constant flow rate of 60 Nl/h (1 Nl = 1 l of gas at 293 K and 101.3 kPa). Liquid CO₂ and/or an entrainer were charged into each high-pressure pump, compressed to the desired pressure and then fed into the extractor. For the selective removal of the desired compounds from the extractor effluent, a chamber was installed between the extractor and a back-pressure regulator. The chamber was a stainless steel tube 80 cm long and 0.5 cm in inner diameter, and was packed with 7 wt% AgNO₃ supported on silica gel (65–100 mesh). The temperature of the tube was kept at 330 K by a temperature controller.

Each run of the present experiments was conducted first with SC-CO₂ alone until some degree of extraction occurred and then together with the entrainer. Fractions were taken every 30–100 Nl of CO₂. We sampled and analyzed more than 50 fractions for each run.

2. Results and Discussion

Figure 2 shows results of changes in the extraction of a mixture of C₁₈₋₀, C₁₈₋₁, C₁₈₋₂ and C₁₈₋₃ methyl esters with SC-CO₂ alone at 8.8 and then 10.8 MPa. The amount of CO₂ consumed in this extraction process is indicated in Fig. 2(b). The concentrations of

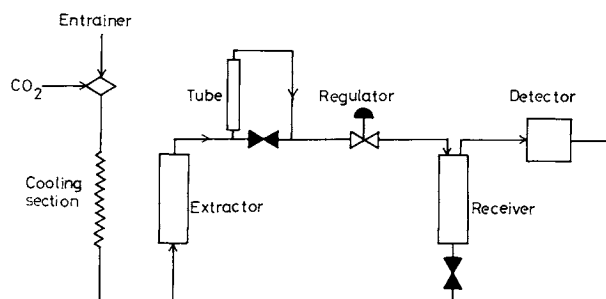


Fig. 1. Schematic diagram of supercritical extraction apparatus used

Received April 25, 1987. Correspondence concerning this article should be addressed to Y. Ikushima. M. Arai is at Chem. Res. Inst. of Non-Aqueous Sol., Tohoku Univ., Katahira, Sendai 980.

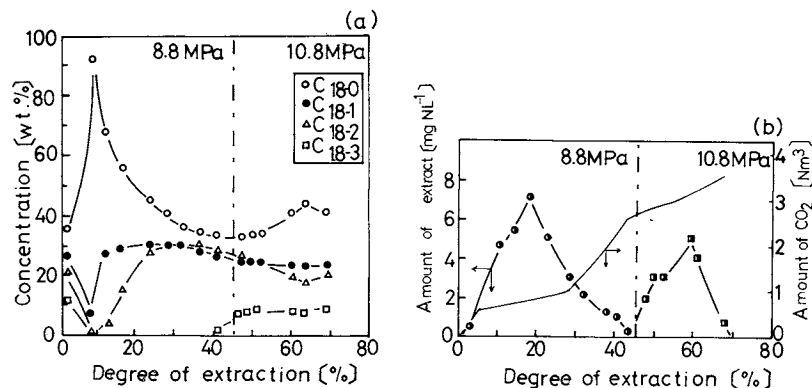


Fig. 2. Change of concentrations (a) and total amount (b) of C_{18-0} , C_{18-1} , C_{18-2} and C_{18-3} methyl esters during extraction with SC- CO_2 alone at 313 K. Operating pressure is changed from 8.8 to 10.8 MPa at a degree of extraction of about 45%. Initial concentrations of the esters are 28.95, 19.45, 28.19 and 23.41 wt% respectively.

feed materials C_{18-0} , C_{18-1} , C_{18-2} and C_{18-3} methyl esters are 28.95, 19.45, 28.19 and 23.41 wt%, respectively. It is found from Fig. 2(a) that C_{18-0} methyl ester can selectively be separated before the degree of extraction reaches about 15%. In particular, at a degree of extraction near 10% its concentration has a maximum above 90 wt%. However, C_{18-2} and C_{18-3} methyl esters can scarcely be extracted. In particular, C_{18-3} methyl ester cannot be obtained at all until the degree of extraction reaches ca. 40%. It is thought that when flowing out of the extractor and then passing through the $AgNO_3$ -supported silica gel tube, fatty acid methyl esters having a higher degree of unsaturation such as C_{18-2} and C_{18-3} methyl esters form some adducts with $AgNO_3$. This result indicates that it is possible to isolate C_{18-3} methyl ester in adequate purity from the mixture of esters by a subsequent treatment. Unless the $AgNO_3$ -supported silica gel tube is used, the composition of the mixture extracted is almost identical to that of the feed material.⁴⁾ Figure 2(b) shows the amount of the whole extract obtained. It has a maximum between 10 and 20% of degree of extraction and the average in this range is about 5.8 mg/Nl. This value is considerably lower than that without use of the tube packed with $AgNO_3$ supported on silica gel. The average value during the whole extraction at 8.8 MPa is 1.1 mg/Nl. When the pressure is increased to 10.8 MPa, the concentration of C_{18-3} methyl ester is gradually increased (Fig. 2(a)). Further, the average amount of the whole extract is enhanced from 1.1 to 2.2 mg/Nl (Fig. 2(b)). The pressure effect may be due to the increased solute holding power of SC- CO_2 .

When the above-mentioned experiment reached a degree of extraction of about 70% as shown in Fig. 2, SC- CO_2 was further fed with ethyl acetate as entrainer. The concentration of ethyl acetate in SCF was ca. 4 wt%. Figure 3 shows the effect of ethyl acetate on the separation of C_{18-3} methyl ester held in the

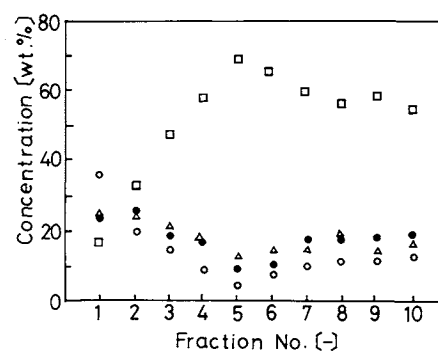


Fig. 3. Change of concentrations of C_{18-0} , C_{18-1} , C_{18-2} and C_{18-3} methyl esters during treatment with SC- CO_2 and ethyl acetate as entrainer at 10.8 MPa and 313 K following the extraction shown in Fig. 2. Keys are the same as in Fig. 2. Final degree of extraction (at fraction no. 10) is about 76%.

$AgNO_3$ tube during the SC- CO_2 extraction. The addition of ethyl acetate to the CO_2 was previously found to enhance the selectivity of higher fatty acid methyl esters and glycerides in the supercritical phase.⁵⁾ Evidently a fractionation takes place with the addition of ethyl acetate after fraction 3, and C_{18-3} methyl ester can be separated in a purity above 45 wt% for every fraction, with maximum of 70 wt% for fraction 5. The concentration of C_{18-3} methyl ester reaches about three times that in the feed. The amounts of the whole extract in fractions 5 and 6 are both about 4.3 mg/Nl and that of the extract in each of the fractions except Nos. 5 and 6 is about 0.5 mg/Nl. The amounts in fractions 5 and 6 are approximately four times that of the average amount of the whole extract through the extraction process shown in Fig. 3 (1.0 mg/Nl). The concentration of C_{18-3} methyl ester in fractions 5 and 6 is the highest, and its amount of the extract is also the largest.

The present method, using the flow system described above, may be suitable for both extraction and separation from a mixture of fatty acid methyl esters that differ only by the degree of unsaturation.

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TURBULENT DRAG REDUCTION IN A DILUTE POLYMERIC SOLUTION FLOWING THROUGH A FIBER-IMPLANTED CIRCULAR PIPE

HIROTSUGU HATTORI, TOMOO YAMAUCHI, SEIICHI TANABE
AND HIDEOMI MATSUDA

Department of Fine Material Engineering, Shinshu University, Ueda 386

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Introduction

It is well known that both dilute polymeric solutions and fiber suspensions show drag reduction under turbulent flow conditions.^{1,3-5)} Furthermore, it has been shown by Lee that polymeric and fiber additives used together produce much larger reductions in drag than the case of polymeric solution alone.²⁾

We have found that a similar effect is obtained by implanting fibers on the inside wall of the pipe instead of suspending the fibers in solution. The present work determined that the flow of polymeric solutions in such a pipe produces a much larger reduction in drag than that in a smooth pipe at high Reynolds numbers.

1. Experimental

The fibers used in the present investigation were nylon fibers. They were implanted on the inside wall of a 13 mm-i.d. polyvinyl chloride pipe, as follows. Small holes of 0.3 mm diameter were made through the wall of the pipe. Yarn staples of nylon were let through the holes and then secured with epoxy resin. The length of the yarn staple immersed in a liquid stream is 13 mm, which is the same as the pipe

diameter. Each yarn staple consists of 34 slender fibers of 0.015 mm diameter. Each yarn staple separates into fibers, which orient themselves to the flow direction in the stream near the pipe wall. At each of a number of points at 10 mm intervals along the pipe, eight yarn staples were implanted at equal distances round the circumference of the pipe, as shown in Fig. 1.

Polymeric solution was stored in a supply tank and was fed through the test pipe to another tank, by injecting compressed air into the supply tank.

The pressure drop along the test pipe was measured by using a manometer. Pressure taps were located at the positions shown in Fig. 1. The first two taps were for measurement of the pressure drop in the smooth pipe section, and the second and the third taps were for its measurement across the fiber-implanted pipe section. The second and the third pressure taps were a few centimeters away from the test section in which the fibers were implanted, to prevent their being clogged by the fibers. Therefore, the pressure drop measured by these pressure taps includes a small quantity of the pressure drop in the smooth pipe section. We abstracted this from the observed values. The first pressure tap was located only 26 pipe diameters away from the entrance of the pipe. However, the short entrance length does not seem to

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