Supercritical Carbon Dioxide Extraction of Lignan from Cold-Press By-product of Sesame Seed

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Abstract

Sesame lignan is the generic name of the soluble antioxidants in sesame oil. Lignans found in sesame consists of sesamin, sesamol and sesamolin. They are valuable compounds that reduces neutral fats and cholesterol in serum lipid by raising fatty acid metabolism of liver and decreasing synthesis of fatty acids. The conventional cold-press method for the extraction of sesame oil can recover only about half of the original oil content. Thus, a lot of oil containing high amount of lignans still remains in the by-products of extraction.

In this work, sesame oil was extracted from cold-press extraction by-products of sesame seeds using supercritical carbon dioxide (SC-CO_2). In order to concentrate the sesame lignans, sesame oil was also fractionated using SC-CO_2. Extraction and fractionation were carried out at various temperatures (40 – 80^{o}C) and pressures (20 – 40 MPa). Extracted oil and lignans were analyzed using HPLC at a UV detection wavelength of 290 nm. The highest yield of sesame oil was obtained at 60^{o}C and 40MPa. The composition of lignans (sesamol, sesamin and sesamolin) was found to be dependent on extraction conditions. Fractionation of sesame oil resulted in high concentration of sesamin and sesamolin at 60^{o}C and 20MPa.

INTRODUCTION

Sesame lignan is the generic name of the soluble antioxidants in sesame oil. Sesame lignan consists of sesamin, sesamol, and sesamolin. As antioxidative foods are generally water-soluble, they dissolve in blood and don't reach to liver. However, sesamin reaches to liver because it is fat-soluble. It raises fatty acid metabolism of liver and decreasing synthesis of fatty acids. Then, it reduces neutral fats and cholesterol in serum lipid. Sesame oil contains 11.5 mg/g lignans, with 9.43 mg sesamin, and 1.73 mg sesamolin, whereas the content of sesamol is under 3% [1]. Sesamol content was relatively higher in those with darker colour. The commercial method for the extraction of sesame oil from sesame seeds is cold-pressed extraction. In this method, about 50% of oil contained in the seed could be extracted, while 50% oil was remained in the sesame seed residue. Therefore, the sesame seed residue contains higher amount of lignan. Furthermore, it is necessary to extract sesame oil containing lignan from cold-pressed residue of sesame seeds.

Organic solvents are frequently used to extract oil. However, environmental safety regulations and increased public health risk are necessitating the industry to consider alternatives to the organic solvents for use in oil extraction [2]. Supercritical fluid extraction with carbon dioxide is getting popular as a cost effective and environmentally friendly method for extracting useful components. Supercritical fluids possess both gas-like and liquid-like qualities, and the dual role of such fluids provide ideal conditions for extracting compounds with a high degree of recovery in a short period of time [3, 4]. Supercritical carbon dioxide (SC-CO_2) is an odorless, chemically inert, non-toxic, non-flammable, non-corrosive, and low cost solvent with high purity, and leaves no residue or contamination in the extract. SC-CO_2 possesses moderately low critical temperature (31.1 °C) and pressure (7.38 MPa) and the solvent can be removed by simple depressurization [4-6]. SC-CO_2, with its particularly attractive properties, is the preferred solvent for many supercritical fluid extractions [6]. SC-CO_2 possesses superior mass transfer properties with a higher diffusion coefficient and lower viscosity than liquid solvents. The absence of surface tension allows the rapid penetration of SC-CO_2 into the pores of heterogeneous matrices and helps to enhance extraction efficiencies [5, 6]. By these reasons, SC-CO_2 extraction is suitable for extracting of sesame oil from sesame seeds by product. The purpose of this work was to extract sesame oil from cold-pressed residue of sesame seeds and to fractionate and concentrate sesame lignan from the oil using SC-CO_2.

EXPERIMENTAL

Materials and chemicals

Starting material of extraction was cold-pressed residue of sesame seed and lignan rich oil supplied by Kamaya Co., Japan. Standard sesamol and sesamin with purity of 98% were purchased from Sigma Aldrich Co., Japan. HPLC grade of methanol for analysis was supplied by Wako, Japan. CO_2 was obtained from Uchimura Co., Japan.

SC-CO_2 extraction

Figure 1 shows a schematic diagram of SC-CO_2 extraction apparatus. This apparatus was used for the extraction of cold-pressed residue of sesame seed. The apparatus included a chiller (Cooling nit CLU-33, Iwaki Asahi Techno Glass, Japan), a pump for CO_2 (Intelligent Prep. Pump. PU-2086 Plus, Jasco, Japan), a heating chamber (WFO-400W, Tokyo Rikakikai Co., Japan), an extractor (Thar Tech, Inc., USA, 25 mL in volume), back-pressure regulator (Automatic Back -Pressure Regulator, BP-2080 Plus, Jasco, Japan), collection vials, and a wet gas meter (Sinagawa Co., Japan).

Cold-pressed residue of sesame seed extraction was conducted under various pressures (20 – 40 MPa) and temperatures (40 – 80 °C) at constant CO_2 flow rate (3 mL/min (based on the flow rate of CO_2 pump)) using 0.556 mm of particles size. In each experiment, approximately 7.0 g of sesame seeds were loaded into a 25 mL extraction vessel and the remaining volume was filled with glass beads in the bottom and upper of the vessel. The vessel was placed in the heating chamber to maintain the operating temperature. The extract was collected in the vial at 15, 30, 60, 90, 120, 180, 240 min for 4 h, and weighted immediately after the collection.

Figure 2 shows a schematic diagram of SC-CO_2 extraction apparatus. This apparatus was used for the extraction of lignan rich oil. The extraction of lignan rich oil was carried out in a 50 mL extractor cell. CO_2 was flowed from the top of extractor by bubbling it into the oil.

Lignan oil extraction was conducted under various pressures (20 – 40 MPa) and temperatures (40 – 80 °C) at constant CO_2 flow rate (2 mL/min (based on the flow rate of CO_2

pump)). In each experiment, approximately 20.0 mL of lignan rich oil was loaded into a bublling extraction vessel. The vessel was placed in the heating chamber to maintain the operating temperature. The extract was collected in the vial at 15, 30, 60, 90, 120, 180, 240 min for 4 h.

Analysis

Extracted sesame oil was analyzed using HPLC equipped with an Inertsil®ODS-3 column (25 cm × 4.6 mm i.d., 5 μm film; GL Sciences Inc., Japan). The mobile phase was a mixture of methanol-deionized water (70:30, v/v) at a flow rate of 1.0 ml/min. Absorption at 290 nm was monitored. 40 μL aliquots of oils dissolved in chloroform (1.0 mg/ml), were used for analysis. The retention times for sesamol, sesamin, and sesamolin were 4.95, 22.0 and 30.0 min, respectively, based on the standards.

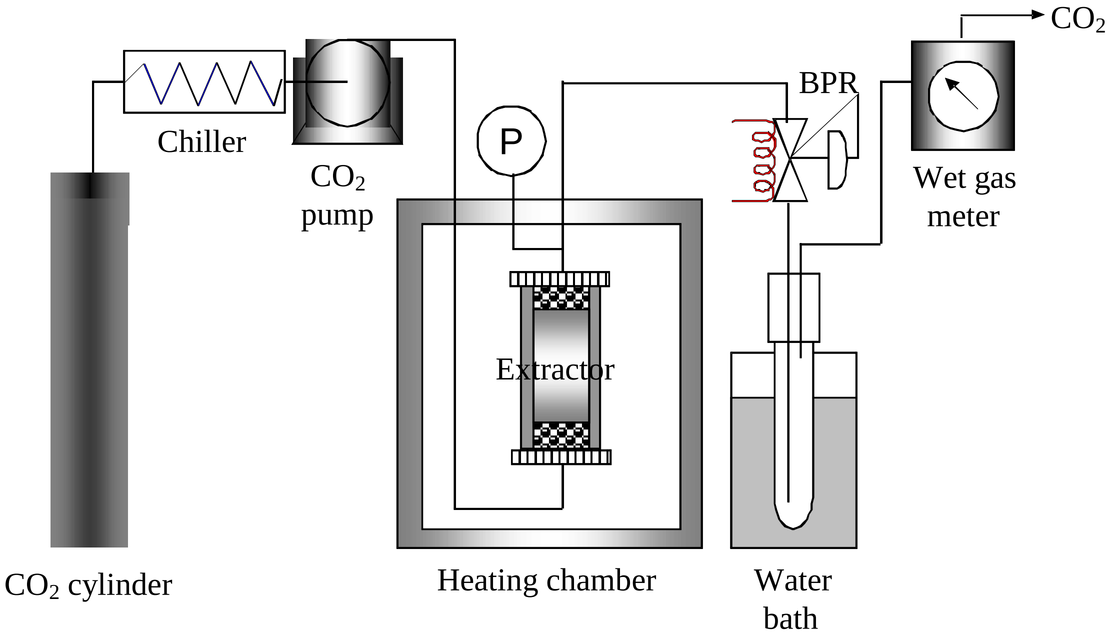


Figure 1: Schematic diagram of SC-CO_2 extraction apparatus for sesame seed

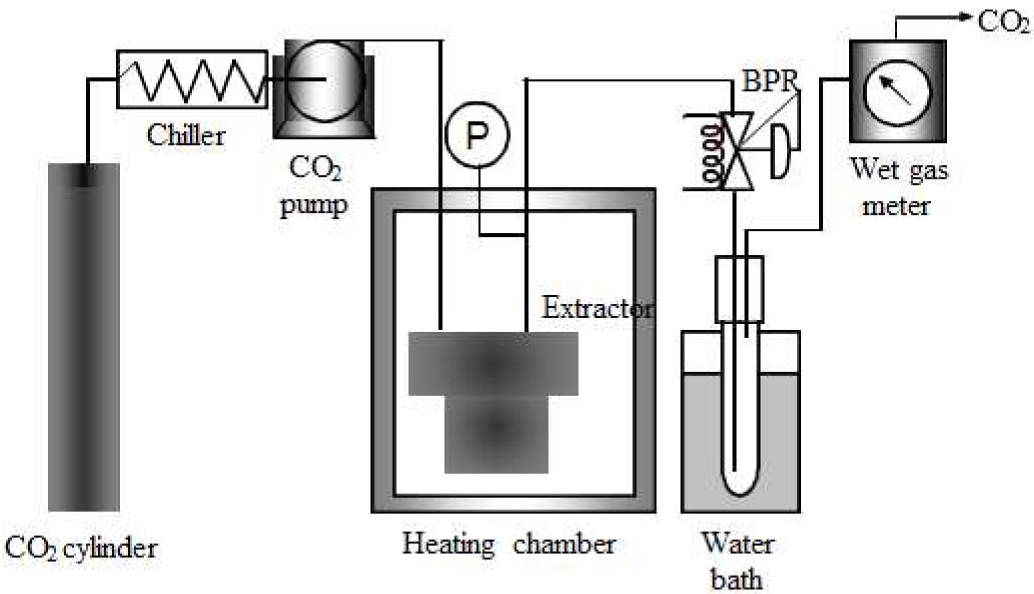


Figure 2: Schematic diagram of SC-CO_2 extraction apparatus for lignan rich oil

RESULTS AND DISCUSSION

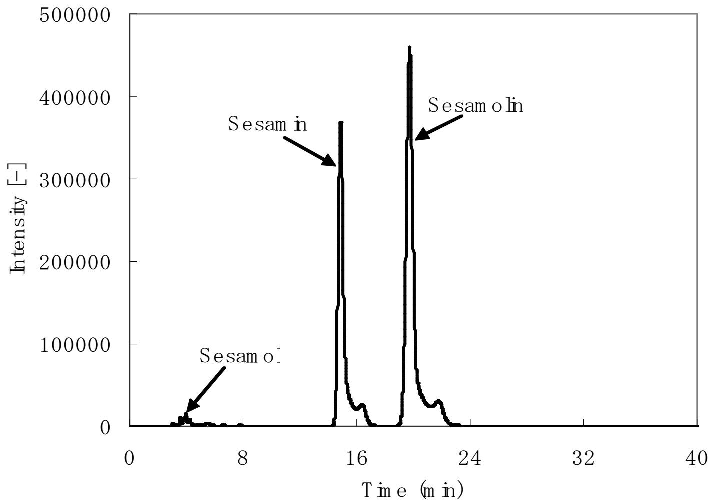


Figure 3: HPLC chromatogram of extracted sesame oil at 40 °C and 30 MPa

Figure 3 shows HPLC chromatogram of extracted sesame oil. Based on the HPLC analysis, extracted sesame oil mainly contained sesamolin followed by sesamin and small amount of sesamol. Sesame lignans (sesamolin, sesamin, sesamol) content in the extracted sesame oil varied with varying extraction condition.

Extraction of sesame seed residue

Effect of temperature

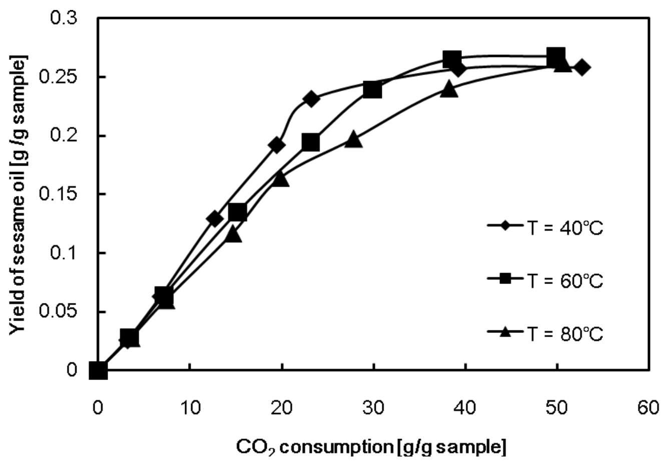


Figure 4: Effect of temperature on the yield of extracted sesame oil at 30 MPa, 3 mL/min for 240 min

Effect of temperature on the yield of extracted sesame oil and sesame lignans was studied at pressure of 30 MPa, 3 mL/min of CO_2 flow rate for 240 min of extraction time. Yield of extracted sesame oil and sesame lignans were defined as weight of extracted oil and sesame lignans, respectively, divided by weight of sesame seeds loaded in the extraction vessel.

Figure 4 shows the effect of temperature on the yield of extracted sesame oil. Increasing temperature caused decreasing solubility of sesame oil due to the decrease in CO_2 density. And as the result yield of sesame oil decreased. However, at all extraction temperature, the yield of sesame oil could reach more than 25 % of initial sesame seeds loaded in the extractor. Based on the Kamaya Co. data, in the cold-pressed process almost 50% oil contained in the sesame seeds has been extracted, and the other 50% was remained in the sesame seeds residue. In this work, all oil contained in the sesame seeds residue could be extracted by using SC-CO_2 extraction.

Effect of temperature on the yield of sesame lignans is shown in Figure 5 (a), (b) and (c) for temperature of 40, 60, and 80 ^oC, respectively. As mention above, the extracted sesame oil mainly contained sesamolin and sesamin, and small amount of sesamol. At certain condition, sesamol could not be extracted. At 40 ^oC, the highest lignan extracted was sesamolin, and small amount of sesamol was extracted. As increasing temperature, the selectivity of sesamolin decreased, and it resulted in increasing selectivity of sesamin without any sesamol extracted. Based on the result, the highest lignans contained in the extracted sesame oil was obtained at 60 ^oC. The total lignans contained was 24 mg/g oil.

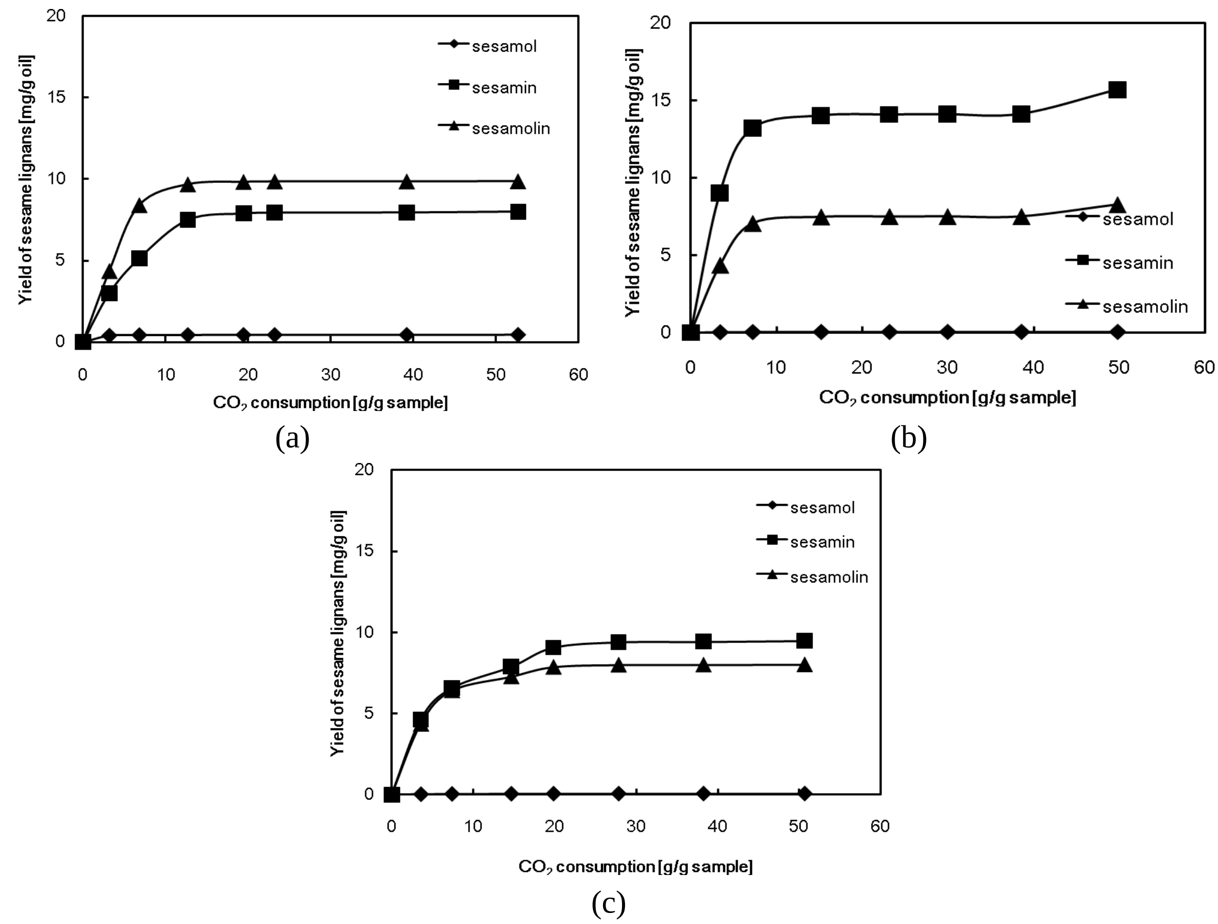


Figure 5: Effect of temperature on the yield of sesame lignans at 30 MPa, 3 mL/min for 240 min. (a) 40 ^oC; (b) 60 ^oC; (c) 80 ^oC

Effect of pressure

Effect of pressure on the yield of extracted sesame oil and sesame lignans was studied at pressure of 60 ^oC, 3 mL/min of CO_2 flow rate for 240 min of extraction time. Figure 6 shows the effect of pressure on the yield of extracted sesame oil. As expected, the solubility of sesame oil increased as increasing pressure due to the increasing CO_2 density [7]. And it resulted in dramatically increasing yield. At this condition, all oil remained in the sesame seeds residue could be extracted at 30 and 40 MPa.

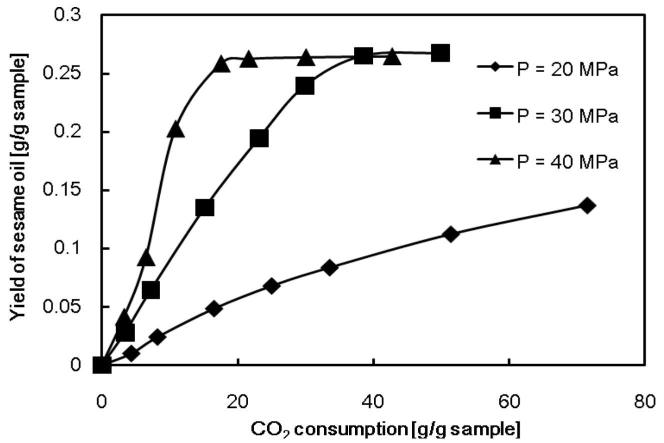
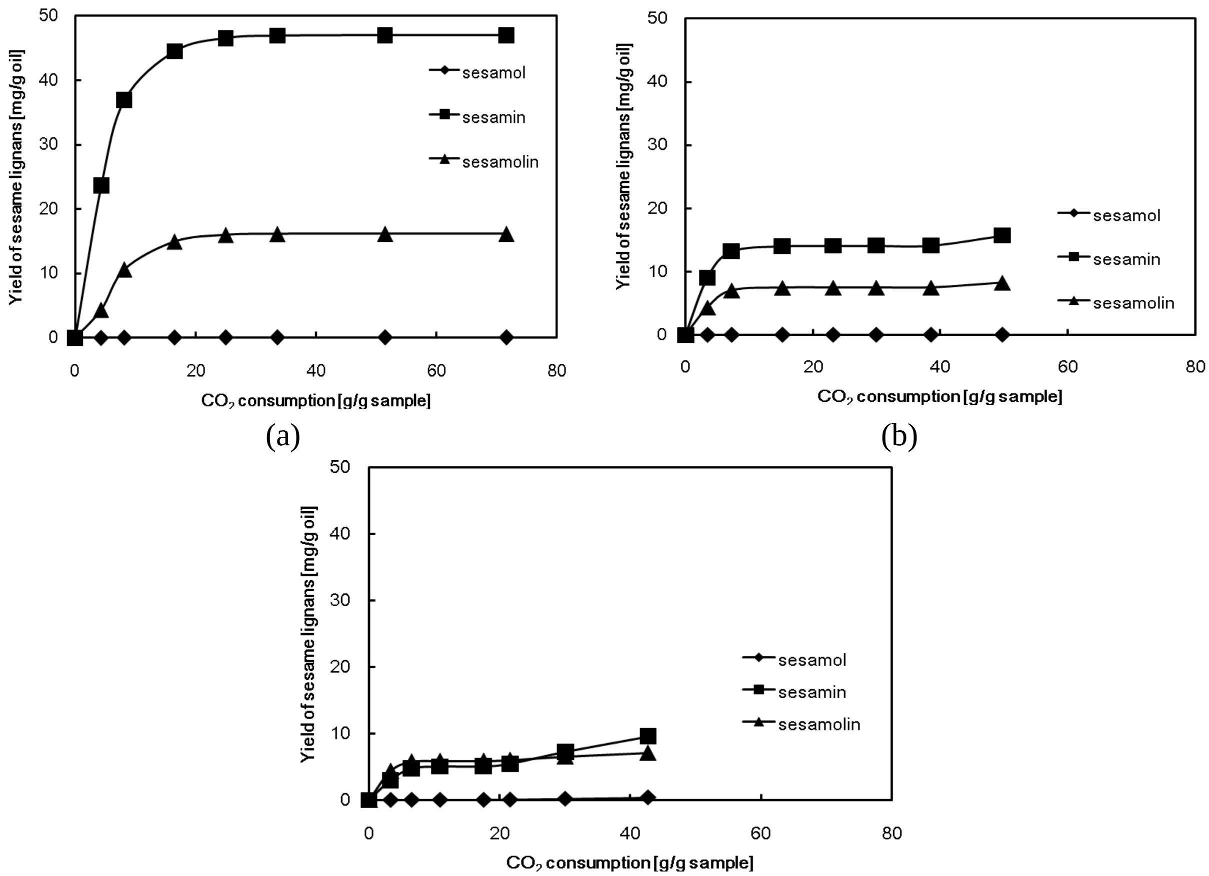


Figure 6: Effect of pressure on the yield of extracted sesame oil at 60 ^{o}C, 3 mL/min for 240 min



(c)

Figure 7: Effect of pressure on the yield of sesame lignans at 60 ^{o}C, 3 mL/min for 240 min. (a) 20 MPa; (b) 30 MPa; (c) 40 MPa

Figure 7 (a), (b) and (c) shows the effect of pressure on the yield of sesame lignans at 20, 30 and 40 MPa, respectively. At low pressure, very high amount of lignans could be extracted. At 20 MPa and 60 °C, sesamin and sesamolin contained in the oil reached 47 and 16.2 mg/g oil, respectively. The content of sesame lignans in the oil decreased as increasing pressure. It indicated that the extract mostly contains lipid from the seed.

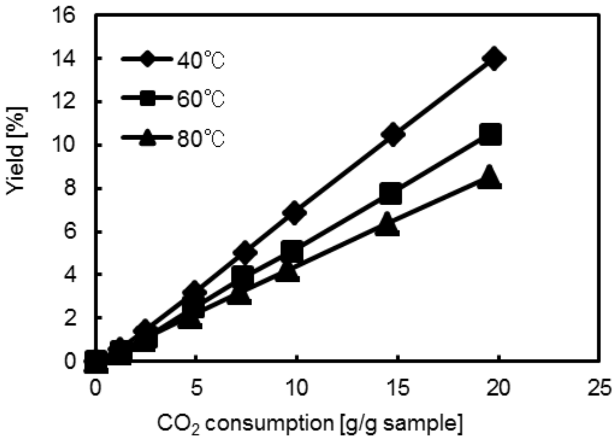
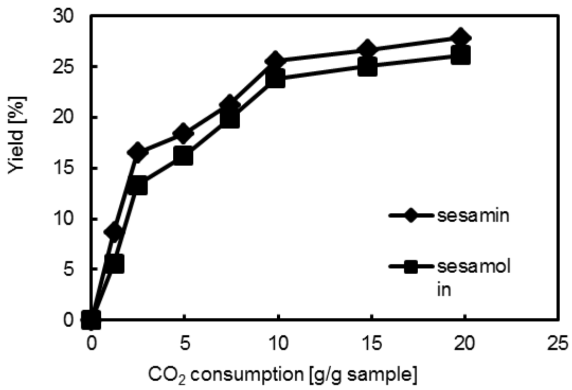
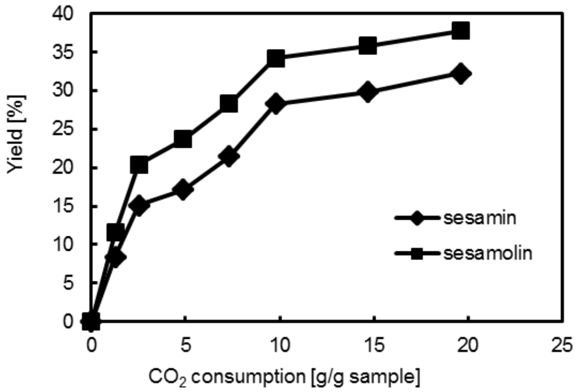


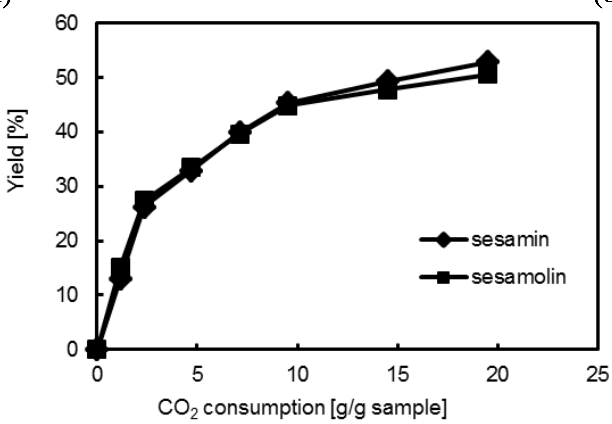
Figure 8: Effect of temperature on the yield of extracted sesame oil at 30 MPa, 2 mL/min for 240 min



(a)



(b)



(c)

Figure 9: Effect of temperature on the yield of sesame lignans at 30 MPa, 2 mL/min for 240 min. (a) 40 °C; (b) 60 °C; (c) 80 °C

Extraction of Lignan rich oil

Effect of temperature

Effect of temperature on the yield of extracted lignan rich oil and sesame lignans from sesame oil was studied at pressure of 30 MPa, 2 mL/min of CO_2 flow rate for 240 min of extraction time. Yield of extracted lignan rich oil and sesame lignans were defined as weight of extracted oil and sesame lignans, respectively, divided by weight of sesame lignan rich oil loaded in the extraction vessel.

Figure 8 shows the effect of temperature on the yield of extracted lignan rich oil. The highest yield was obtained at 40 ^{o}C with 14 % yield. Increasing temperature caused decreasing yield of oil due to decreasing CO_2 density. This behavior is similar with the extraction of oil from cold-pressed residue of sesame seed.

Effect of temperature on the yield of sesame lignans is shown in Figure 9 (a), (b) and (c) for temperature of 40, 60, and 80 ^{o}C, respectively. The amount of sesamin and sesamolin was almost similar at all conditions. The largest amount and the highest selectivity of lignan was obtained at 80 ^{o}C. In the extract, sesamol was not detected because sesame lignan rich oil mostly contained sesamin and sesamolin. The total lignans contained at 80^{o}C was 102 mg/g oil.

Effect of pressure

Effect of pressure on the yield of extracted lignan rich oil and sesame lignans was studied at pressure of 60 ^{o}C, 2 mL/min of CO_2 flow rate for 240 min of extraction time. Figure 10 shows the effect of pressure on the yield of extracted lignan rich oil. As expected, the solubility of sesame oil increased as increasing pressure due to the increasing CO_2 density. At high pressure, large amount of oil was extracted. The yield of extraction at 40 MPa was twice of the yield of extraction at 30 MPa.

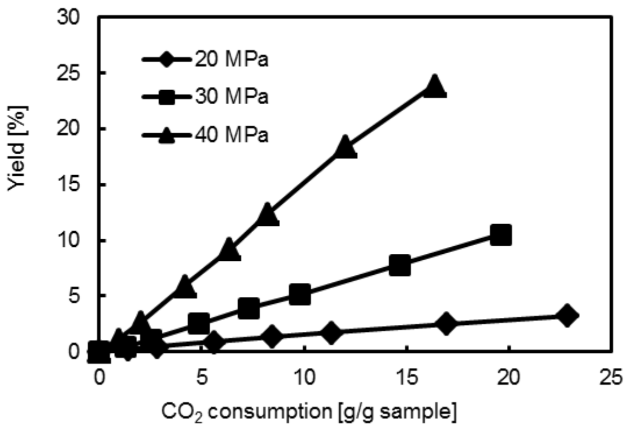


Figure 10: Effect of pressure on the yield of extracted sesame oil at 60 ^{o}C, 2 mL/min for 240 min

Figure 11 (a), (b) and (c) shows the effect of pressure on the yield of sesame lignans at 20, 30 and 40 MPa, respectively. At 20 MPa and 60 ^{o}C, sesamin and sesamolin contained in the oil reached 131 and 133 mg/g oil, respectively. The highest amount and selectivity of lignan was obtained at this condition. The amount of sesamin and sesamolin was almost similar at all conditions.

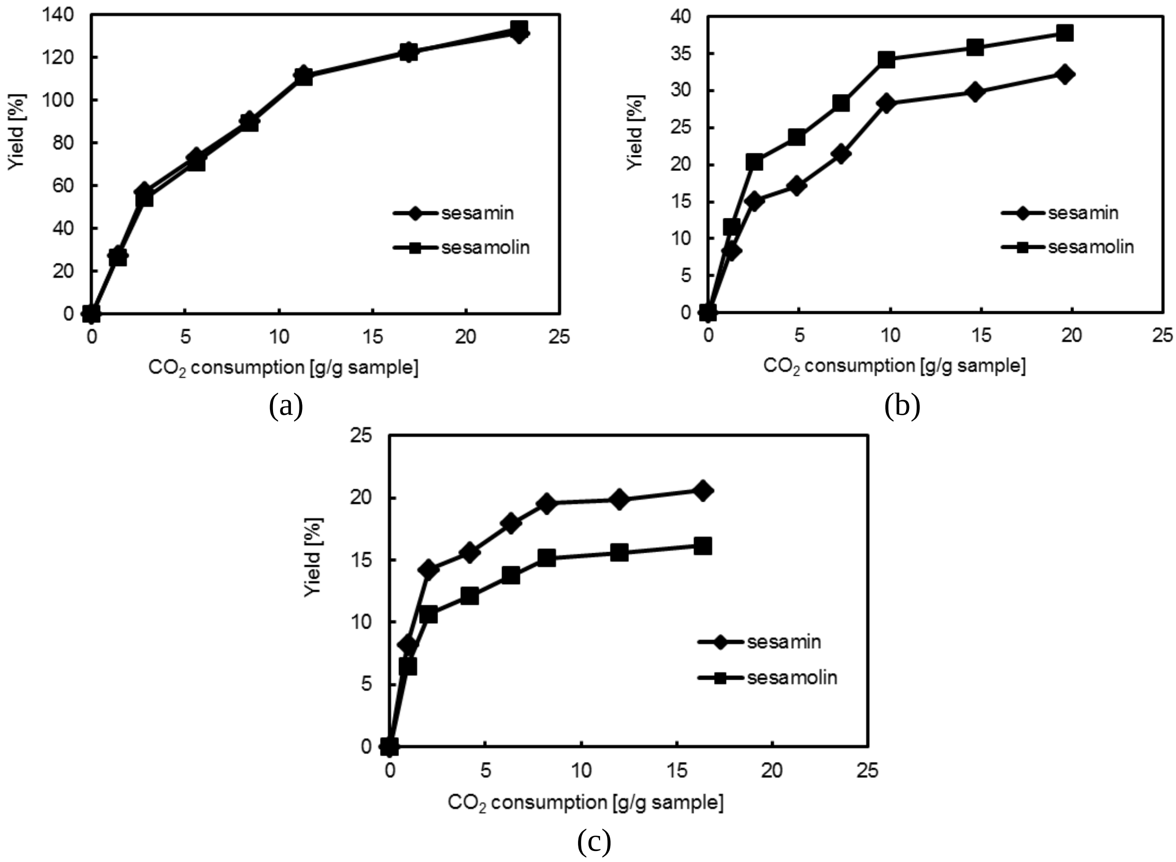


Figure 11: Effect of pressure on the yield of sesame lignans at 60 ^{o}C, 2 mL/min for 240 min. (a) 20 MPa; (b) 30 MPa; (c) 40 MPa

CONCLUSION

All sesame oil remained in the cold-pressed sesame seeds residue could be extracted by using SC-CO_2 extraction. The best condition of extraction was 60 ^{o}C and 40MPa. At the extraction of oil from cold-pressed residue of sesame seed, the highest yield of total lignans extracted was obtained at 60 ^{o}C and 20 MPa. At that condition, sesamin and sesamolin contained in the oil reached 47 and 16.2 mg/g oil, respectively.

At the extraction of lignan rich oil from sesame oil, the highest yield of total lignans extracted was obtained at 60 ^{o}C and 20 MPa. At this condition, sesamin and sesamolin contained in the oil reached 131 and 133 mg/g oil, respectively. By changing the temperature and pressure of extraction, sesame lignans could be concentrated.

Acknowledgement

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