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Purification of used frying oil by supercritical carbon dioxide extraction

Jungro Yoon [a], Byung-Seok Han [b], Yun-Chang Kang [b], Kong Hwan Kim [b], Mun Yhung Jung [c], Young An Kwon [c],*

[a]*Department of Food Science, Kangneung National University, Kangneung, 210-702 South Korea*
[b]*Division of Chemical Engineering & Biotechnology, Ajou University, Suwon, 442-749 South Korea*
[c]*Department of Food Science and Technology, Woosuk University, Hujung-Ri 490, Samrae-Up, Jeonbuk Province 565-701, South Korea*

Abstract

Supercritical fluid extraction (SFE) was used for the purification of used frying oil at different temperatures (40 and 60°C) and pressures (150, 225 and 300 bar). The calculated solubilities of the oil ranged from 0.3×10^{-3} to 7.4×10^{-3} g oil/g CO_2 depending on the extraction conditions. The solubility and the selectivity of triglycerides (TG) were between those of the low molecular weight compounds (LMWC) and the polymers. The calculated relative separation efficiency (R) of low molecular weight compounds (LMWC) from TG was highest under the low pressure and high temperature extraction conditions, but the extraction rate was minimal under this condition. However, the separation efficiency (R) of polymers from TG was not greatly dependent on the pressure and temperature. Based on the relative separation efficiency result, two-stage supercritical carbon dioxide extraction was performed for the effective purification of TG from used frying oil. LMWC were removed under the low pressure extraction conditions (150 bar, 60°C) of the first stage extraction, and then TG were concentrated under the high pressure extraction conditions of the second stage extraction (300 bar, 60°C). The extracts obtained from the second to the fifth fraction of the second stage included less than 1% polymer, more than 92% TG, and less than 8% LMWC. The conjugated diene contents of these extracts ranged from 0.202 to 0.231%, showing a similar conjugated diene content to the fresh frying oil. The present data clearly showed that two-stage supercritical CO_2 extraction was an efficient method for the purification of TG from used frying oil. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Supercritical fluid extraction; Purification; Triglycerides; Polymer; Used frying oil

1. Introduction

A large proportion of fats and oils in the world is used for the preparation of fried foods. Oils undergo a complex series of changes and reactions during frying. The principal reactions during deep-fat frying include formation of conjugated dienes, formation and decomposition of hydroperoxides, formation of low molecular carbonyl compounds, hydrolysis of triglycerides, and polymerization via complex free radical processes at elevated temperatures around 180°C. Used frying oils are generally discarded because oxidized lipid degrades the quality of fried foods. The discarded used-frying oil still has a large portion of triglycerides. Economic considerations and the need to produce fried foods of uniformly desirable quality have stimulated an interest in purification of frying oil.

Purification of used-frying oil could be achieved by removing the undesirable oxidized low molecular weight material and polymer. Several attempts have been previously made to purify the used frying oil by adsorbent treatments (Jung & Rhee, 1994; Lin, Akoh & Reynolds, 1999; Mancini-Filho, Smith, Creveling & Al-Shaikh, 1986; McNeil, Kakuda & Kamel, 1986; Yates & Caldwell, 1992, 1993).

Supercritical fluid extraction might be an another alternative for the purification of used frying oil. The supercritical fluid can separate various types of organic compounds based on their polarity and molecular weight (Rizvi, Daniels, Benado & Zollweg, 1988; Stahl, Quirin & Gerard, 1988). Major advantages of this purification process might be low temperature separation, low energy consumption, and good selectivity. Selectivity of the supercritical fluid requires only a change in the density of the fluid via manipulating pressure and temperature (McHugh & Paulaitis, 1980). This SFE technique has

* Corresponding author.

been successfully applied to extract and separate lipid components from various different food products (Arul, Boudreau, Makhlouf, Tardif & Sahasrabudhe, 1987; Chao, Mulvaney, Bailey & Fernando, 1991; Fattori, Bulley & Mersen, 1987; Kwon & Chao, 1995; Kwon & Yoon, 1996; List & Friedrich, 1985; Shishikura, Fujimoto, Kaneda, Arai & Saito, 1986). However, the purification of used frying oil by supercritical fluid extraction has never been previously reported.

The objectives of this paper were to determine (1) the solubility of used frying oil, (2) the relative separation efficiency (R), and (3) the optimum condition of supercritical fluid extraction for the efficient separation of triglycerides from used-frying oil.

2. Materials and methods

2.1. Materials

Fresh and used frying oil (hydrogenated soybean oil) were provided from a local fast-food restaurant. Carbon dioxide (purity, over 99.9%) was purchased from Hankuk Special Gas Co. (Chonju, Korea). Ethyl alcohol (purity, over 99.9%) was obtained by J.T. Baker (Phillipsburg, NJ, USA). Methylene chloride (HPLC grade) and 2,2,4-trimethylpentane (HPLC grade) were purchased from Sigma Co. (St. Louis, MO, USA).

2.2. SFE system and process

The apparatus (Fig. 1) using CO_2 as the solvent medium for the flow-through SFE system was assembled by high pressure manufactured parts such as extractor, connector, and micrometering valve.

Carbon dioxide was supplied through a microfilter (20-41LF4, High Pressure, USA) to a gas boosting pump (Nova Co., Swiss) and then pressurized to a desired pressure by a forward pressure regulator. The modifier was pressurized by a HPLC pump (LC1110, GBC Co., Australia). For each experimental trial, about 20 g of used frying oil was mixed with the same amount of glass bead (Ø 0.4 mm) and then charged to a sealed extractor (500 ml, High Pressure, USA) where lower and upper parts were filled with glass wool to prevent channelling accompanying the CO_2. The pressure of loaded supercritical CO_2 (SC-CO_2) stream leaving the extractor was reduced to atmospheric pressure. Sample was collected at a separator which temperature was maintained constant to prevent dry-ice making by a Joule-Thompson effect. The extracted lipids were fractionated in a separator. Carbon dioxide gas was released through a rotameter (RK-1050,
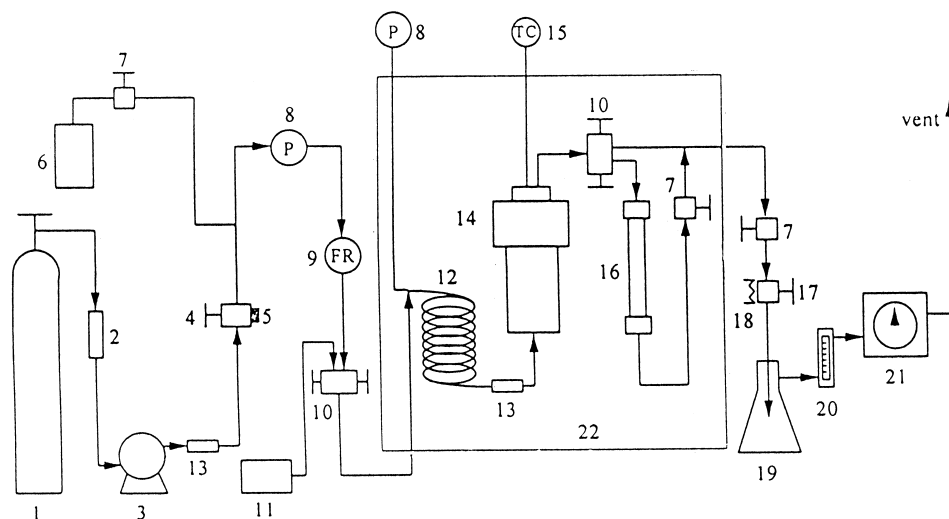
1. CO₂ Cylinder	8. Pressure gauge	15. Thermocouple
2. Line filter	9. Forward regulator	16. Adsorption column
3. Compressor	10. Two stem combination	17. Micrometering valve
4. Three way valve	valve	18. Heating tape
5. Rupture disk	11. Co-solvent pump	19. Collector
6. Surge tank	12. Pre-heating coil	20. Rotameter
7. Two way valve	13. Check valve	21. Wet gas meter
	14. Extractor	22. Oven

Fig. 1. Schematic diagram of supercritical fluid extraction system.

Kpfloc, Tokyo, Japan) and a wet gas meter (W-NK-1, Sinagawa Co., Japan) which measured the flow rate and volume of CO_2 gas, respectively. The volumetric flow rate of CO_2 was maintained at 7–8 l/min.

2.3. High performance size exclusion chromatography

For the analysis of polymer, triglycerides and lower molecular weight compounds, a high performance size exclusion liquid chromatograph (HPSEC, LC10AD, Shimazu, Japan) equipped with UV detector (UV-160A, Shimazu, Japan) was used. The sample oils (0.3500 g) were dissolved with 20 ml methylene chloride and then filtered (0.45 μm microfilter). 20 μl of the aliquot from the filtered sample was injected into the HPSEC. The flow rate of mobile phase (methylene chloride) was 0.8 ml/min. Shodex GPC K803 (Alltech Associates, IL, USA) and Shodex GPC K8025 (Alltech Associates, IL, USA) were connected in series and used for the analysis. The detection of polymer, TG and LMWC was made with a UV detector at 233 nm. The composition of the polymer, TG and LMWC in the samples was determined by calculating the relative peak areas of each peak.

2.4. Determination of conjugated diene content

The conjugated diene (CD) contents in the oils were determined by measuring the absorbencies of the samples prepared in spectral grade 2,2,4-trimethyl pentane at 233 nm according to the AOCS Official Method of Ti la-64 (Firestone, 1990).

3. Results and discussion

3.1. Solubility of used frying oil by supercritical carbon dioxide (SC-CO₂)

The cumulative yields of collected lipids during the supercritical fluid extraction of used frying oil (20 g) under various operating conditions are shown in Fig. 2. Results showed that the solubility of extracted lipids by CO_2 depended greatly upon the pressure and temperature. The higher the pressure, the higher the solubility of used frying oil. The lower the temperature, the higher the solubility. This result also showed that the extraction rate under low density conditions (low pressure and high temperature) was much lower than under high density conditions (high pressure and low temperature). These results were in good agreement with previously reported ones (Kwon & Chao, 1995; Shishikura et al., 1986; Yoon, 1993). The result also showed that extraction rate was constant at early stages of the extraction, and then decreased gradually as the extraction proceeded. This result seemed be due to the solubility difference between high molecular weight and low molecular weight compounds and the absolute lack of solute at later stages of the extraction.
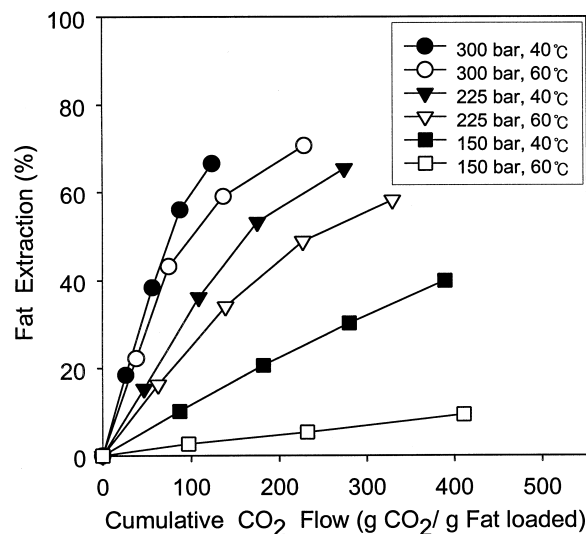

Fig. 2. Fat extraction from used frying oil by supercritical CO_2.

The solubility was calculated from the straight slope of each isotherm and the results are shown in Table 1. The solubilities of extracted lipids vary from 0.3×10^{-3} to 7.4×10^{-3} g lipid/g SC-CO₂ depending on the extraction conditions used. These solubilities were similar to the solubilities of saturated triglycerides in the binary system (Kwon, 1998), but were about 3 times lower than the previously reported solubility of butter fat under almost the same extraction conditions (Yoon, Hartel & Wang, 1993). This was due to the fatty acid composition of used-frying oil examined in this study. The tested frying oil was hydrogenated vegetable oil, which mainly consisted of long chain saturated fatty acids. However, butter fat included a large proportion of short chain-saturated or long-chain unsaturated fatty acids. The solubilities of short chain saturated triglycerides and long chain unsaturated triglycerides are reportedly several times larger than the solubility of long chain saturated triglycerides (Kalra, Chung & Chen, 1987; Shishikura et al., 1986).

3.2. Separation of LMWC, TG and polymers by single stage supercritical fluid extraction

The used frying oil was extracted and fractionated with SC-CO₂ under various extraction conditions. The

Table 1
Solubility of extracted lipids in SC-CO₂ under various conditions

Pressure (bar)	Temperature (°C)	Density (g/cm³)	Solubility (g lipids/g CO₂)
150	40	0.78	1.2
225	40	0.86	3.3
300	40	0.91	7.4
150	60	0.61	0.3
225	60	0.76	2.6
300	60	0.83	5.9

contents of low molecular compounds (LMWC), trigly-cerides (TG), and polymers in each fraction were analyzed by high performance size exclusion liquid chromatography and the results are shown in Table 2. The fresh frying oil did not contain LMWC and polymers. The used frying oil before SFC treatment contained 28.9% polymers, 53.4% TG and 17.3% LMWC. The results showed that low density condition (low pressure and high tempera-ture) were favorable for the extraction of LMWC, and that high density conditions (high pressure and low tem-perature) were favorable for the extraction of polymers.

3.3. Relative separation efficiency

For the optimization of SFE, it is important to con-sider the extraction rate as well as the efficient separation of each solute. Liang and Yeh (1991) introduced the rela-tive separation efficiency, R, for the exclusion of the effect of feed composition which affects the separation efficiency.

The R value was calculated from the following equation and indicated the degree of separation difficulty in SFE.

$$R = (X_i/X_{TG})_{extract}/(X_i/X_{TG})_{feed}$$

where X_i = content of polymer, TG or LMWC in feed or extract, X_{TG} = content of TG in feed or extract.

With this equation, the R value of triglyceride is always 1. As the R value of other compounds is far from 1, the separation of other compounds from triglyceride is easier. The R values of this study at various extraction conditions are shown in Fig. 3. The results clearly show that the R values of LMWC were greatly dependent on the pressure and temperature, and that R values of polymer were not very dependent on the pressure and temperature. This means that the separation efficiency between LMWC and TG with SC-CO_2 is greatly dependent on extraction conditions. That is, LMWC and TG could be effectively separated under the low density region (low pressure and high temperature). However, under this low density condition, the extrac-tion rate is very low. As shown in Fig. 3, the relative separation efficiency of polymer is not dependent on extraction conditions. Thus rapid separation of TG from polymer could be achieved under the high pressure condition without the sacrifice of separation efficiency. This result suggested that two-stage supercritical fluid extraction (low pressure at initial stage followed by high pressure at later stage) might be very effective for the separation of TG from LMWC and polymers.

3.4. Two stage supercritical fluid extraction

Two stage SFE was carried out at the low SC-CO_2 pressure of 150 bar and 60°C in the early stage and then increased pressure to 300 bar later. The contents of LMWC, TG, polymer and conjugated diene of each fraction obtained during the two-stage SFE are shown in Fig. 4. The first and second fractions of the first stage

Table 2
HPSEC analysis of fractions extracted from used frying oil under various SFE extracting conditions

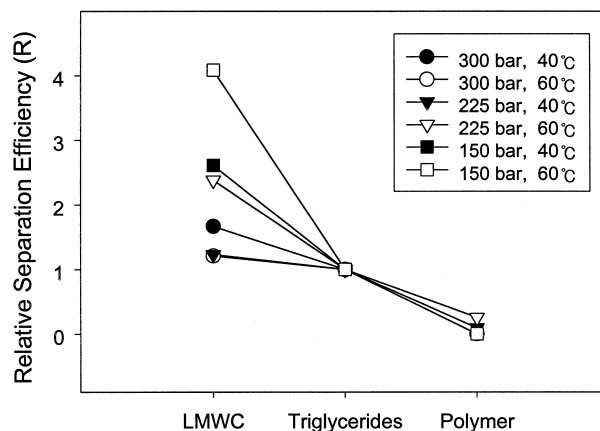| Experimental condition	Fraction	Polymer (%)	Triglyceride (%)	LMWC (%)	CD value (%)
Control (fresh frying oil)		0	100	0	0.217
Feed (used frying oil)		28.91	53.44	17.29	0.374
	1	0	70.3	29.7	0.250
300 bar, 40°C	2	4.1	66.5	29.4	0.222
	3	8.2	79.8	12.0	0.220
	4	23.7	68.2	8.1	0.329
	Residue	55.6	37.1	7.4	0.997
	1	0	72.2	27.6	0.232
300 bar, 60°C	2	5.6	63.4	31.0	0.233
	3	21.5	51.3	27.2	0.344
	4	29.3	47.6	23.1	0.399
	Residue	53.5	38.2	8.3	0.683
	1	3.7	61.7	34.6	0.256
225 bar, 40°C	2	0	81.2	18.8	0.232
	3	4.0	45.4	50.6	0.259
	4	16.6	34.9	48.5	0.358
	Residue	56.0	34.4	9.7	0.730
	1	7.4	50.9	41.7	0.244
225 bar, 60°C	2	10.3	60.1	29.6	0.208
	3	7.4	71.4	21.2	0.255
	4	20.2	68.2	11.6	0.343
	Residue	51.5	40.9	7.6	0.560
	1	0	60.1	39.9	0.299
150 bar, 40°C	2	0	67.4	32.6	0.274
	3	0	78.8	21.2	0.253
	4	8.2	68.2	23.5	0.230
	Residue	44.4	49.5	6.2	0.496
	1	0	28.0	71.2	0.456
150 bar, 60°C	2	0	34.1	65.9	0.428
	3	0	39.3	60.7	0.316
	Residue	33.3	51.3	15.3	0.382

Fig. 3. Relative separation efficiency of the LMWC, TG and polymer present in used frying oil under different extraction conditions.
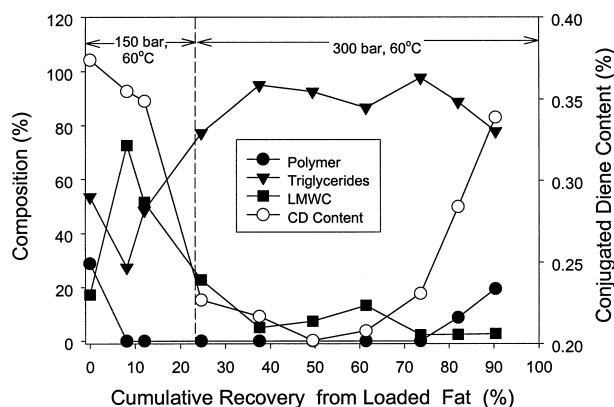
Fig. 4. The contents of LMWC, TG, Polymer, and conjugated diene in the fractions obtained during two-stage supercritical fluid extraction.

of 150 bar contained no polymer and more than 50% of LMWC, indicating the efficient separation of LMWC at the first extraction stage. After the second fraction of the first stage extraction was obtained, the extraction pressure increased and the second stage extraction started. The extracts obtained from the second to the fifth fractions of the second stage of extraction included less than 1% polymer, more than 92% TG, and less than 8% LMWC. The results indicate that supercritical fluid extraction is a very efficient method for the removal of polymers compared to adsorbent treatments. Yates and Caldwell (1992, 1993) studied the effects of various adsorbent treatments for the purification of used frying oil. The authors reported that the adsorptive capacity varied from 0 to 59.7 mg polymers per gram of adsorbent treated, indicating the low efficiency of the adsorbent treatment for the removal of polymers from the used frying oil. The conjugated diene contents of the extracts obtained from the second to the fifth fraction of the second stage of extraction ranged from 0.202 to 0.231%, showing a similar conjugated diene content to fresh frying oil. The conjugated diene content shows the degree of oxidation of the oil tested. The high TG and low conjugated diene content of these fractions indicate that the obtained extracts are mainly unoxidized triglyceride. The highest content of TG (97.0%) was obtained at the fifth fraction of the second stage. The residue obtained after the extraction included 67.2% polymer, 29.4% TG, and 3.4% LMWC (data not shown). This result clearly shows, for the first time, that two-stage supercritical fluid extraction can successfully separate unoxidized triglycerides from used frying oil.

Acknowledgements

References

Arul, J., Boudreau, A., Makhlouf, J., Tardif, R., & Sahasrabudhe, M. R. (1987). Fractionation of anhydrous milk fat by supercritical carbon dioxide. *Journal of Food Science, 52*, 1231–1236.

Chao, R. R., Mulvaney, S. J., Bailey, M. E., & Fernando, L. N. (1991). Supercritical CO_2 conditions affecting extraction of lipid and cholesterol from ground beef. *Journal of Food Science, 56*, 183–187.

Fattori, M., Bulley, N. R., & Meisen, A. (1987). Fatty acid and phosphorous contents of canola seed extracts obtained with supercritical carbon dioxide. *Journal of Agricultural Food Chemistry, 35*, 739–743.

Firestone, D. (1990). *Official methods and recommended practicies of the American Oil Chemists Society* (4th ed.). Champaign, IL: American Oil Chemists' Society.

Jung, M. Y., & Rhee, K. C. (1994). Quailty improvement of used frying cottonseed oil by adsorbent or chemical treatments. *Foods and Biotechnology, 3*, 65–70.

Kalra, H., Chung, S. Y. K., & Chen, C. J. (1987). Phase equilibrium data for supercritical extraction of lemon flavors and palm oils with carbon dioxide. *Fluid Phase Equil, 36*, 263–278.

Kwon, Y. A. (1998). Solubility interactions between saturated triglycerides and cholesterol in supercritical carbon dioxide. *Food Science and Biotechnology, 7*, 286–291.

Kwon, Y. A., & Chao, R. R. (1995). Fractionation and cholesterol reduction of beef tallow by supercritical CO_2 extraction. *Foods and Biotechnology, 4*, 238–243.

Kwon, Y. A., & Yoon, S. K. (1996). Concentration of medium chain fatty acids from coconut oil by supercritical CO_2 extraction. *Foods and Biotechnology, 5*, 229–233.

Liang, J. H., & Yeh, A. I. (1991). Process conditions for separating fatty acid esters by supercritical CO_2. *Journal of the American Oil Chemists' Society, 68*, 687–693.

Lin, S., Akoh, C. C., & Reynolds, A. E. (1999). Determination of optimal conditions for selective adsorbent combinations to recover used frying oils. *Journal of American Oil Chemists' Society, 76*, 739–744.

List, G. R., & Friedrich, J. P. (1985). Processing characteristics and oxidative stability of soybean oil extracted with supercritical carbon dioxide at 50°C and 8000 psi. *Journal of American Oil Chemists' Society, 62*, 82–84.

Mancini-Filho, J., Smith, L. M., Creveling, R. K., & Al-Shaikh, H. F. (1986). Effects of selected chemical treatments on quality of fats used for deep frying. *Journal of American Oil Chemists' Society, 63*, 1452–1456.

McHugh, M., & Paulaitis, M. E. (1980). Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide. *Journal of Chemical & Engineering Data, 25*, 326–330.

McNeill, J., Kakuda, Y., & Kamel, B. (1986). Improving the quality of used frying oils by treatment with activated carbon and silica. *Journal of the American Oil Chemists' Society, 63*, 1564–1567.

Rizvi, S. S. H., Daniels, J. A., Benado, A. L., & Zollweg, J. A. (1986). Supercritical fluid extraction: Operating principles and food applications. *Food Technology, 40*, 57–64.

Shishikura, A., Fujimoto, K., Kaneda, T., Arai, K., & Saito, S. (1986). Modification of butter oil by extraction with supercritical carbon dioxide. *Agricultual and Biological Chemistry, 50*, 1209–1215.

Stahl, E., Quirin, K. W., & Gerard, D. (1988). *Dense gases for extraction and refining*. Berlin: Springer-Verlag (pp. 1–29).

Yates, R. A., & Caldwell, J. D. (1992). Adsorptive capacity of active filter aids for used cooking oil. *Journal of American Oil Chemists Society, 69*, 894–897.

Yates, R. A., & Caldwell, J. D. (1993). Regeneration of oils used for deep frying: A comparison of active filter aids. *Journal of American Oil Chemists Society, 70*, 507–511.

Yoon, J. (1993). Extraction of EPA and DHA from tuna oil using supercritical carbon dioxide. *Korean Journal of Food Science and Technology, 25*, 288–294.

Yoon, J., Hartel, R. W., & Wang, Y. C. (1993). Analysis of butter fat extraction and fractionation using supercirtical carbon dioxide. *Journal of Food Processing and Preservation, 17*, 471–484.