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Modification of Beef Tallow by Supercritical Carbon Dioxide

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초임계이산화탄소에 의한 쇠고기 기름의 변형

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Summary

Edible beef tallow was processed using supercritical carbon dioxide at temperature of 48℃ and pressure of 276 bar. The extraction efficiency of the process was 11% per hour. The total cholesterol reduction was 75% with 86% fat yield. A simultaneous fractionation of beef tallow with different physico-chemical properties was also achieved. The concentration of medium (C44-C48) molecular weight triglycerides was high in the extracted fractions. The residue was enriched in high (C50-C54) molecular weight triglycerides. The extracts contained more fatty acids with shorter carbon chains. The residue had the highest melting points, mainly caused by having higher stearic acid content. The extracts showed lower solid fat index than the residue at several temperatures.

Introduction

During recent years, considerable interest has been shown in the application of supercritical fluids as solvents for extraction and separation of food constituents. A supercritical fluid is any fluid at a temperature and pressure above its critical value. It exhibits unique physico-chemical properties intermediate between those of liquids and gases, which enhance its role as a solvent. Its relatively high density gives good solvent power, while its relatively low viscosity and high diffusivity values provide appreciable penetrating power into the solute matrix (Rizvi et al., 1986a).

The chemical complexity of most food ingredients and their vulnerability to react and degrade at elevated temperatures emphasize the considerations that solvent is chosen upon its ability to

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solubilize the desired product from a mixture. However, there are othe factors to be considered in selecting a supercritical solvent. Some important characteristics of a solvent include (a) inertness with respect to the raw material, human body, and itself under the conditions of extraction, (b) a moderate critical pressure to minimize the compression costs, (c) a low boiling point for ease of removal after processing, and (d) low cost, nontoxicity, non-flammability, and availability in high purity. In view of these considerations, carbon dioxide has been recognized as the most acceptable solvent for supercritical fluid extraction (SFE) processing of food products (Rizvi et al., 1986b).

Consumption of edible beef tallow in the united states has been relatively low and constant as compared to inedible beef tallow consumption for several years. In fact, much edible beef tallow is diverted to inedible channels due to lack of market. Beef tallow is very hard at ambient temperature with poor plasticity range which makes it undesirable as an ingredient in many foods. Beef tallow contains about 50% saturated fatty acids, mainly myristic, palmitic, and stearic acids. Beef tallow is also reported to contain 0.14-0.20% cholesterol (Ryan and Gray, 1984; Ryan et al., 1981), which like other animal fats is implicated in promoting cardiovascular disorders such as atherosclerosis and athrothrombosis in humans.

Fractionation of beef tallow has been reported by many researchers employing various methods such as aqueous detergent fractionation (Ryan and Gray, 1984), dry fractionation by crystallization from the melt (Grompone, 1989), acetone crystallization (Luddy et al., 1973), and Tirtiaux fractionation using a continuous vacuum filter equipped with a perforated belt as filtration support (Tirtiaux, 1983). Although the reduction of cholesterol in beef tallow fraction has been pointed out in some reports (Krukonis, 1988), a through investigation was needed to introduce a practical, efficient, and clean process to achieve simultaneous fractionation and cholesterol reduction of beef tallow.

In the present study, the application of supercritical fluie processing of edible beef tallow is investigated. Physico-chemical properties of the fractions are characterized and compared to the original beef tallow.

Materials and Methods

A 20*kg* block of refined beef tallow was obtained from a commercial supplier. Two hundred gram portion were cut, transferred into freezer plastic bags and stored at -20℃. Whenever needed, a 200*g* sample was taken out, melted at 60℃ and filtered through Whatman No. 1 filter paper. Approximately 50*g* of the sample was used for processing with supercritical carbon dioxide ($SC-CO_2$). A conventional batch type SFE-system was employed during this study. A flow diagram of the process is shown in Fig. 1.

The SFE-process was carried out as shown in Table 1. Fifty grams of beef tallow was pumped into an extraction vessel attached to a packed reaction column where it was dissolved in $SC-CO_2$, then carried through an adsorption column packed with magnesium silicate for adsorption of cholesterol. The decholesterolized beef tallow fractions were collected in the separation vessel by pressure reduction. The fractionation of beef tallow was carried out in two steps. After collection of about 20*g* of extract, the process was interrupted, the adsorbents was stripped with ethyl alcohol and adsorption column was repacked with 20*g* of fresh adsorbent. Then the process was carried out as the second step

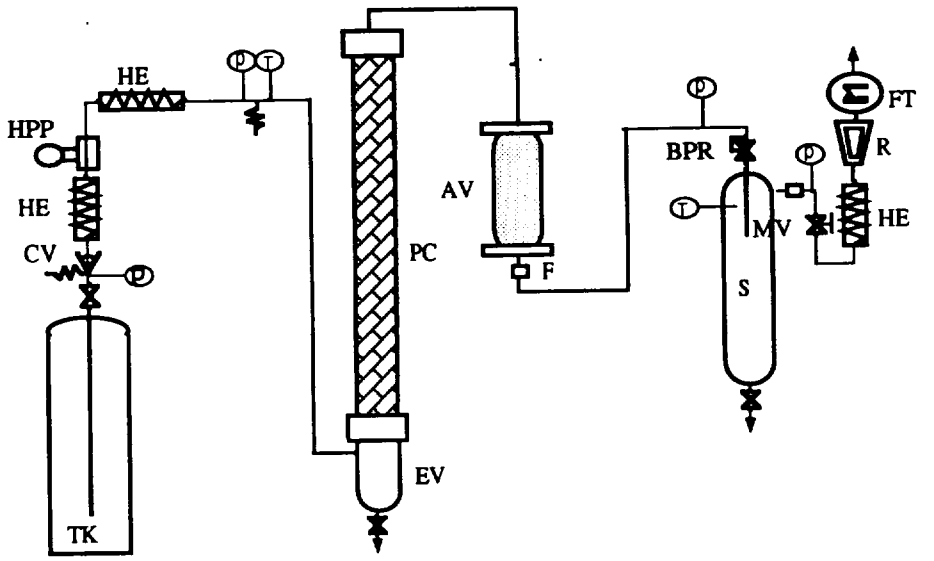


Fig. 1. Flow diagram of supercritical fluid extraction system.
(AV : adsorption vessel, BPR : back pressure regulator, CV : check valve, EV : extraction vessel, F : filter, FT : flow totalizer, HE : heat exchanger, HPP : high pressure pump, MV : metering valve, P : pressure gauge, PC : packed column, R : rotameter, S : separator, T : temperature indicator, TK : carbon dioxide tank)

extraction.

All the fractions collected during the first and second extraction steps as well as the adsorbates after stripping and desolventization, and the undissolved residue drained from the extraction vessel were quantified and analyzed. Flow totalizer is used to measure the quantity of carbon dioxide passed through the separator.

Table 1. Experimental condition for SC-CO_2 extraction of beef tallow

Material : 50g beef tallow
Solvent : Carbon dioxide, flow rate : 2.6kg/hr.

Extraction	First step	Second step
Temperature (℃)	48	48
Pressure (bar)	276	276
Separation		
Temperature (℃)	20	20
Pressure (bar)	atm.	atm
Magnesium silicate (g)	20	20

The cholesterol content was determined according to the AOAC method (AOAC, 1984). A Perkin-Elmer GC Model G3, equipped with a non-packed wide bore capillary glass coumn, 10m ×0.53㎜, coated with 1.2 micron of polydimethylsiloxane RSL-150 (Alltech Associated, Inc.) was used. The triglycerides and fatty acids were analyzed by the AOCS official methods (AOCS,

1984) using a Hewlett Packard GC Model 5890. A fused silica capillary column, 25m×0.25㎜, coated with 0.1 micron of TAP (Chrompack Co.) was employed for the analysis of triglycerides. The fatty acids were analyzed on a capillary glass column, 15m×0.25㎜, Durabond-225 (J & W Scientific Co.). Other physico-chemical analyses such as solid fat index (SFI), refractive index, saponification value, iodine value, and melting point were performed according to the AOCS official methods (AOCS, 1984).

Results and Discussions

Extract yield and efficiency

Fig. 2. is a plot of % extract yield vs. solvent-to-feed ratio. The percent extract yield, E, is defined as

$$E = (m_e/m_o) \times 100$$

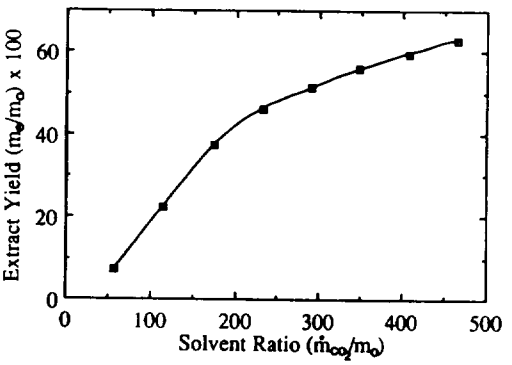
where, m_e=mass of extract, and m_o=mass of feed.

The yield was higher at the beginning of the process, then gradually decreased for the rest of the processing period. During the SFE process, the low molecular weight components of beef tallow being more readily soluble in SC-CO_2 were extracted in the beginning. The high molecular weight components were less soluble and harder to extract; therefore, a gradual decrease in extractability of beef tallow was observed with the processing time.

If the extraction efficiency η_{ex}, for the process is defined as :

$$\eta_{ex} = E/\tau_{ex} = (m_e/m_{co2})\ (\dot{m}_{co2}/m_o) \times 100$$

where, τ_{ex}=extraction time, m_{co2}=mass of CO_2 and $\dot{m}_{co2}$=mass flow rate of CO_2. Then the extraction efficiency of the process shown in Fig. 2 turns out to be about 11% per hour.



Fgi. 2. Extract yield vs. solvent-to-feed ratio for SC-CO_2 extraction of beef tallow.

Cholesterol reduction

The amount of cholesterol in the original beef tallow was 100㎎/100g. A typical reduction of cholesterol in beef tallow fractions, obtained by SC-CO_2 extraction is shown in Table 2. There were significant reduction of cholesterol in the extracted fractions. The overall cholesterol reduction in the two extracted fracions was 86.2% with 55.3% fat yield. The residue fraction, containing mostly higher molecular weight triglycerides, was also reduced in the cholesterol content by 53.8%.

By combining the extracts with the residue, the total reduction of cholesterol from SFE processing of beef tallow was 74.6% with 86.1% fat yield by weight. Although it should be possible to enhance the total cholesterol reduction and percent yield from SC-CO_2 extraction by extending the extraction time which would leave less amount of the residue, the processing cost is expected to rise sharply due to a decrease in the solubility of beef tallow with the processing time. As expected, most of the cholesterol which was removed using SC-CO_2 extraction of beef tallow was concentrated in the adsorbates.

Table 2. Cholesterol reduction of beef tallow and its SC-CO_2 fractions

Fractions	Yield (wt%)	Cholesterol (mg/100g)	Cholesterol change (%)
Feed	100.0	100.0	-
Extract-1	26.2	15.6	-84.4
Extract-2	29.1	12.2	-87.8
Total Extract	55.3	13.8	-86.2
Residue	30.8	46.2	-53.8
Subtotal	86.1	25.4	-74.6
Adsorbate-1	7.5	605.4	+505.4
Adsorbate-2	6.4	264.0	+164.0
Subtotal	13.9	448.2	+348.2

Table 3. Triglyceride composition (wt%) of beef tallow and its SC-CO_2 fractions

Acyl carbon number	Beef tallow	Extract E1	Extract E2	Residue R	Adsorbate A1	Adsorbate A2
44	0.7	0.4	0.3	0.3	1.1	0.6
46	2.7	4.1	3.6	1.8	2.2	2.5
48	14.1	18.9	16.8	11.9	11.0	10.7
50	29.1	30.7	29.3	27.5	28.7	27.4
52	40.2	35.9	39.1	43.0	43.3	43.0
54	13.2	10.0	10.9	15.6	13.7	15.8
(a) 44-48	17.5	23.4	20.7	14.0	14.3	13.8
(b) 50-54	82.5	76.6	79.3	86.0	85.7	86.2
Ratio b/a	4.7	3.3	3.8	6.1	6.0	6.2

Physico-chemical properties

The triglyceride composition of beef tallow and various fractions obtained by SC-CO_2 extraction is presented in Table 3. Six groups of triglycerides corresponding to even acyl carbon numbers from C44 to C54 were identified for all of the samples.

The concentration of medium (C44-C48) molecular weight triglycerides was higher in both extracts than the original beef tallow. These triglycerides, which are more readily dissolved and carried out by SC-CO_2, were concentrated mostly in the extracts. On the other hand, the residue was gradually enriched in high (C50-C54) molecular weight triglycerides as the medium molecular weight triglycerides were carried out by solvent during the process. The triglyceride composition of the adsorbates was found to be similar to the residue.

The fatty acids composition of beef tallow and its fractions is presented in Table 4. The fatty acid analysis indicated that triglycerides containing shorter chain fatty acids were dissolved more readily in SC-CO_2 and were preferentially concentrated in the extracts. These results were in agreement with Shishikura et al. (1986) who demonstrated that short-chain triglycerides are preferentially extracted in the initial phases.

Table 4. Fatty acids composition (wt%) of beef tallow and its SC-CO_2 fractions

Fatty acids	Beef tallow	Extract E1	Extract E2	Residue R	Adsorbate A1	Adsorbate A2
C14 : 0	3.2	4.2	3.5	2.2	3.3	2.4
C16 : 0	25.5	26.8	26.6	23.2	25.0	24.4
C18 : 0	20.2	16.6	17.4	23.1	23.4	24.9
C18 : 1	42.4	43.0	43.2	43.3	39.9	41.5
C18 : 2	3.0	3.1	3.0	2.8	2.8	2.7
Unsaturated	49.2	50.3	50.4	49.2	46.2	46.1
Saturated	50.8	49.7	49.6	50.8	53.8	53.9
Unsat/Sat	0.97	1.0	1.0	0.97	0.86	0.86

Some physico-chemical properties of beef tallow and its fractions are shown in Table 5. As expected, the extracts had lower melting points as compared to the original beef tallow. The extracts contained more fatty acids with shorter carbon chains, and higher degree of unsaturation which attributed to their lower melting points. The residue had the higher melting points, mainly caused by having higher stearic acid content. Comparatively, among beef tallow fractions the extracts had higher iodine values, while the residue and the adsorbates had lower iodine values.

Table 5. Some physico-chemical properties of beef tallow and its fractions obtained by SC-CO_2 extraction

Sample	Weight (g)	Melting Point (℃)	Iodine value	Saponification value	Refractive Index (60℃)
Beef tallow	49.6	48.2	48	218	1.4511
Extract-1	13.0	44.8	48	220	1.4506
Extract-2	14.4	46.2	49	210	1.4509
Residue	15.3	52.0	36	215	1.4516
Adsorbate-1	3.7	47.1	43	216	1.4526
Adsorbate-2	3.2	48.9	42	-	1.4530

The refractive indices of the extracts found to be lower than the original beef tallow, while the residue and the adsorbates had higher refractive indices. Generally, the refractive index of the fat increased with increasing chain length of fatty acids in the triglycerides. Therefore, the refractive index measurements of all fractions were in agreement with their triglyceride compositions as shown in Table 3.

The solid fat index (SFI) profile of the original beef tallow and its SC-CO_2 fractions is shown in Fig. 3. The extracts showed lower SFI which

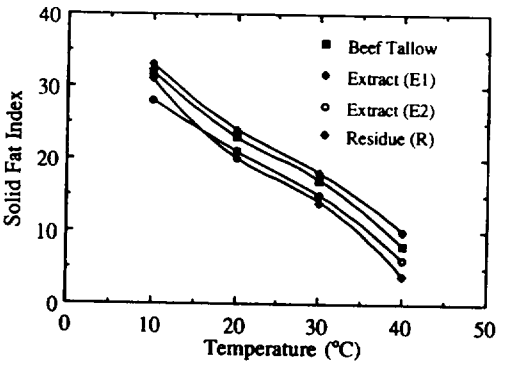


Fig. 3. Solid fat index of beef tallow and its SC-CO_2 fractions at various temperatures.

means less solid fat content at different temperatures, as compared to the original beef tallow. The residue had comparatively higher SFI than others. The SFI profile of these fractions corresponds to their melting measurements in Table 5.

Based on those results, supercritical fluid extraction is a practical and promising technique for fractionation and extraction of beef tallow. Using SC-CO_2, it is feasible to obtain beef tallow fractions with different physico-chemical characteristics along with significantly lower cholesterol contents. The lower melting fractions would be of interest to the food industry and can be used along with other fats in various food products. Further investigation is needed to establish the most economical conditions for SFE processing of beef tallow and other animal fats. Specialty fat products similar to cocoa-butter, confectionery fats, frying fats, etc. can be developed by controlling the process conditions and blending the proportions of various SFE-processed fractions.

References

AOAC, 1984, *Official Methods of Analysis*, 14th ed., Association of Official Analytical Chemists, Washington, DC

AOCS, 1984, *Official Methods and Recommended Practice of the American Oil Chemists' Society*, 4th ed., American Oil Chemists' Society, Champaign, Illinois.

Grompone, M.A., 1989, Physico-chemical Properties of Fractionated Beef Tallows, *JAOCS*, 66, 253.

Krukonis, V.J., 1988, Supercritical Fluid Processing : Current Research and Operations, *Proc. Int. Symp. on Supercritical Fluids*, Nice, France, p. 541.

Luddy, F.E., J.W. Hampson, S.E. Herb and H.C. Rothbart, 1973, Development of Edible Tallow Fractions for Specialty Fat Uses, *JAOCS*, 50, 240.

Rizvi, S.S.H., A.L. Benado, J.A. Zollweg and J.A. Daniels, 1986a, Supercritical Fluid Extraction : Fundamental Principles and Modeling Methods, *Food Technol.*, 40 (6), 55.

Rizvi, S.S.H., J.A. Daniels, A.L. Benado and J.A. Zollweg, 1986b, Supercritical Fluid Extraction : Operating Principles and Food Applications, *Food Technol.*, 40 (7), 57.

Ryan, T.C. and J.I. Gray, 1984, Distribution of Cholesterol in Fractionated Beef Tallow, *J. Food Sci.*, 49, 1390.

Ryan, T.C. J. I. Gray and I.D. Morton, 1981, Oxidation of Cholesterol in Heated Tallow, *J. Sci. Food Agric.*, 32, 308.

Shishikura, A., K. Fujimoto, T. Kaneda, K. Arai and S. Saito, 1986, Modification of Butter Oil by Extraction with Supercritical Carbon Dioxide, *Agric. Biol. Chem.*, 50 (5), 1209.

Tirtiaux, A., 1983, Tirtiaux Fractionation : Industrial Application, *JAOCS*, 60, 425A.

〈국문초록〉

초임계이산화탄소에 의한 쇠고기 기름의 변형

48℃, 276 bar의 초임계 이산화탄소를 이용하여 식용 쇠고기기름을 가공하였다. 쇠고기기름의 추출율은 시간당 11%였다. 총 콜레스테롤 제거율은 75%였으며 이 때 지방의 회수율은 86%였다. 쇠고기기름을 물리화학적 성질이 다른 분획으로 분별하였다. 중급트리글리세리드(C44-C48)의 농도는 추출된 분획들에서 높았으며, 잔류물에는 고급트리글리세리드(C50-C54)가 다량 함유되어 있었다. 추출물에는 저급지방산의 함유율이 높았다. 잔류물에는 스테아르산의 함량이 특히 높았으며, 이로 인하여 높은 녹는점을 보였다. 고형지방은 여러 온도에서 추출분획들 보다 잔류물에 많았다.