J. Korean Soc. Food Nutr.
23(3), 459 ~ 465(1994)

Continuous Cocurrent Extraction of Milk Fat by Supercritical Carbon Dioxide

Sang-Bin Lim† and Syed S. H. Rizvi*

Dept. of Food Science and Technology, Cheju National University, Cheju 690-756, Korea
**Dept. of Food Science, Cornell University, Ithaca, NY 14853, U. S. A.*

Abstract

Performance of a continuous cocurrent supercritical fluid extraction column for processing of anhydrous milk fat (AMF) was determined. The extract loading increased and the extraction yield decreased as the superficial velocity of AMF increased. The maximum solubility of AMF in CO_2 at 40°C/3,500 psig was 0.0195g/g. The increase of the carbon dioxide density enhanced the solubility of milk fat and decreased the cholesterol concentration in the extract. Three operation conditions, such as recycle, reflux, and temperature gradient of extraction column, were tested. More short-chain fatty acids were extracted by the reflux operation. Long-chain fatty acids and the highest ratio of long-chain unsaturated to saturated fatty acids were also obtained in the raffinate phase with reflux.

Key words : supercritical fluid extraction, milk fat

INTRODUCTION

Milk fat is a good source of essential fatty acids and contains many short chain fatty acids, such as C4, C6 and C8 compared to other animal fats. Milk fat has a characteristic flavor and aroma, and an antioxidant activity because of vitamin E[1]. For those reasons, milk fat is used in the food industry for recombined milk fat preparation and as an ingredient in ice cream, chocolate, etc. Although milk fat is highly desired in many food products, its unique physical property, especially crystallization and melting property, makes it unsuitable for a number of food applications. Thus, much interest has been focussed on fractionation of milk fat[2], offering the dairy industry new possibilities for milk fat utilization.

Supercritical fluid extraction (SFE) is a process which is designed to exploit the properties of a supercritical fluid to separate materials that are sensitive, or heat labile and could not be separated by conventional techniques. Subsequently, research focus was on those segments of the food industry where separations were difficult or where solvents were under FDA scrutiny. Potential advantages of SFE include low-temperature solvent/extract separation, favorable phase equilibria, and enhanced transport properties[3,4].

In order to design an extractor, there is a need for basic knowledge of phase equilibria, system properties, and the mass transfer and hydrodynamic performance of extraction devices. This type of data is required for industrial scale extraction system design[5].

The vast majority of the commercial packed columns for gas-liquid contacting is operated countercurrently. However, the gas throughput in this type of operations is limited. Above a critical gas velocity the gravity forces on the downflowing liquid are exceeded by the drag forces on the liquid by the upflowing gas. This unstable condition, flooding, is the characteristic of all countercurrent gas-liquid contacting operations. One means of overcoming this throughput limitation of a countercurrent operation is to operate the packed column cocurrently. There is no flooding limit for this type of operation, and the throughput of gas and liquid, upto choked flow, depends only on the available pressure to drive the fluids through the column. Cocurrent operation has advantages from the fluid mechanics standpoint, in that flooding can

† To whom all correspondence should be addressed

be eliminated[6].

The purpose of this work was to provide information on performance of a packed column in a cocurrent process for extraction of milk fat. Effect of supercritical velocity of AMF on extract loading and extraction yield of milk fat was investigated. Operation conditions, such as recycle, reflux, and temperature gradient of extraction column, were tested.

MATERIALS AND METHODS

Commercial grade butter was purchased from the Cornell Dairy Store and converted into AMF by melting at 60° C and filtering through Whatman No. 1 filter paper under vacuum. AMF was subsequently stored at −20° C for future use.

A continuous supercritical fluid extraction system was operated to investigate its performance for cocurrent extraction of AMF. The flow diagram of the system is shown in Fig. 1. The extraction column is a 61 cm contacting height and 1.75cm I.D. stainless steel tube rated to 20,000psig. The column was operated as a packed column. Knitted mesh packing consists of fine wire, knitted into a tubular form, which is flattened to form a strip, crimped, and rolled to form a cylindrical cartridge. The slightly compressed cartridges (four pieces of 14.6×5.7cm and one piece of 6.9×5.7cm) are inserted into the column and expanded to fully fill the column.

A graduated feed tank was used to hold 1 liter of AMF feed. The carbon dioxide solvent was supplied from cylinders. The pumps used to transport the AMF feed and supercritical carbon dioxide ($SC-CO_2$) solvent streams were positive displacement pumps. Immediately before passing to the column, the feed and solvent streams each flowed through a 3m length of coiled tubing in a controlled air temperature bath maintained at the desired operating temperature. To ensure that the system was operated at the desired temperature, the extraction column was wrapped with heating tape and insulated. Thermocouples were placed at bottom, middle and top of the column, and

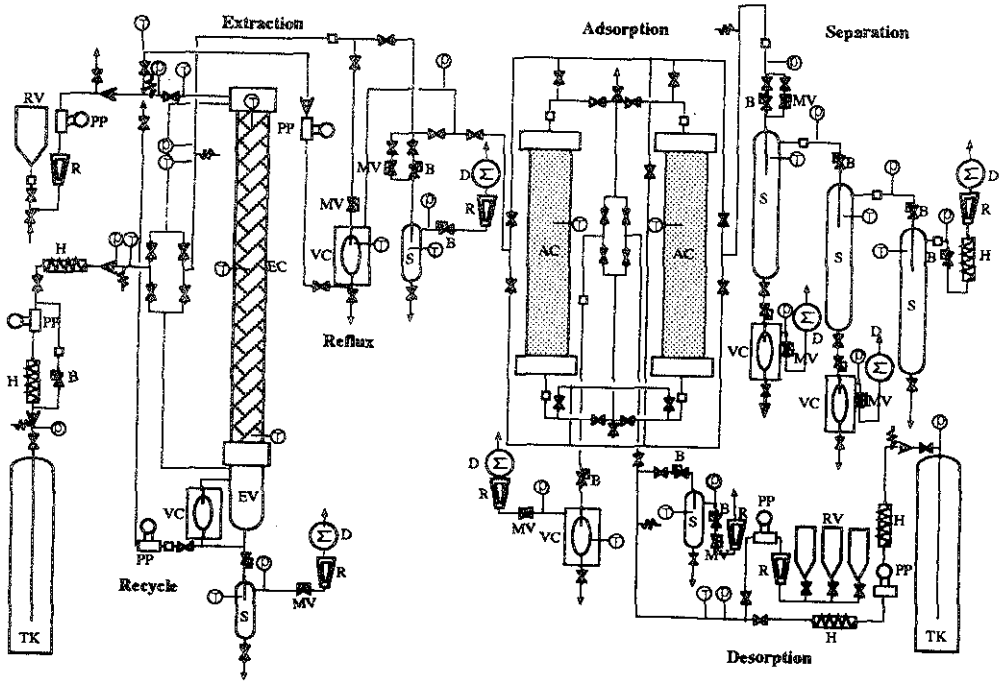

Fig. 1. Schematic diagram of continuous supercritical fluid fractionation system.
AC : adsorption column, B : back pressure regulator, D : dry test meter, EC : extraction column, EV : extraction vessel, H : heat exchanger, MV : metering valve, P : pressure reading, PP : high pressure pump, PR : pressure regulator, R : rotameter, RV : AMF reservoir, S : separator, T : temperature reading, TK : carbon dioxide cylinder, V : on/off valve, VC : view cell

the temperature of the column was monitored and controlled to maintain a constant temperature. The back pressure regulator was used to maintain a constant system pressure. A micrometering valve was used to control the flow rate of the solvent stream. The flow rate of the AMF feed stream was controlled by pump displacement and measured by reading the scale of a graduated feed tank. Quantified runs were performed after steady state has been achieved as determined by constant fatty acids and cholesterol compositions and steady flows of the exit stream. Steady flows of AMF feed and CO_2 was checked by the rotameters.

An extraction was performed for determination of the effect of superficial velocity of AMF on extract loading and extraction yield of AMF. The column packed was operated at 40° C/3,500 psig at a superficial velocity of AMF of 0.25 to 2.5cm/min with a constant superficial velocity of CO_2 of 23.9cm/min. The process was also performed at pressures of 2,000 to 3,500psig and at temperatures of 40 and 60° C for determination of the effect of the processing conditions on fat and cholesterol extraction.

In order to investigate the effect of operating conditions such as temperature gradient in a column, recycle of the raffinate, and reflux of the extract on fat and cholesterol extraction, the column was operated at 40° C/3,500 psig. When a temperature gradient was used in an extraction column, the extraction pressure was 3,500 psig, and the temperatures were 40° C at the top, 50° C in the middle and 60° C at the bottom. For the recycle operation, the extraction temperature and pressure were 40° C and 3,500psig, and the ratio of the recycle to the raffinate was 15.0. For the reflux operation, the extraction temperature and pressure were 40° C/3,500 psig, and the reflux ratio was 1.2 and the temperature and pressure of the reflux chamber were 40° C/2,000 psig.

To evaluate the effectiveness of continuous in-line adsorption of cholesterol on magnesium silicate from the SC-CO_2 phase, an extraction was performed at 40° C/3,500 psig. A SC-CO_2 phase containing the dissolved extract passed through an adsorption column loaded with 42.5g of magnesium silicate. The cholesterol and some triglycerides were adsorbed onto the adsorbed bed. The cholesterol reduced milk fat fraction was collected in the separator. Every 30 minutes, the sample was drawn off, weighed and analyzed for cholesterol.

Analysis of cholesterol

The cholesterol content was determined by the modified AOAC and AOCS methods[7,8]. First, the milk fat fractions were saponified and the unsaponifiable fraction containing cholesterol and other sterols was extracted with hexane. Sterols were derivatized to form trimethylsilyl (TMS) esters which were determined in a gas chromatograph (Hewlett Packard, HP 5890). A capillary column coated with SE-30 (Chrompack Co.) was used at 523K for 10 minutes using 5-α cholestane (Sigma Chemical Co.) as an internal standard. Temperatures of the injector and the flame ionization detector (FID) were 270 and 300° C, respectively. The carrier gas was helium at a rate of 1.5ml/min. Injection volume of the sample was 3.8μl.

Analysis of fatty acids

Fatty acids were determined after hydrolysis of the triglycerides into the fatty acids and conversion of the fatty acids into fatty acid methyl esters[8]. The fatty acid methyl esters were then analyzed in a gas chromatograph with a fused silica capillary column (3m × 0.25min I.D.) coated with OV-225 Durabond (0.25μm) (J & W Scientific Co., Folsom, CA). The oven temperature was held at 60° C for 2min and was increased at 4° C/min to 220° C, and was finally held for 10min at 220° C. The temperatures of the injector and detector (FID) were 200 and 240° C, respectively. The carrier gas was helium at a rate of 1.5ml/min. Samples were injected by split technique (1 : 100). Retention times and relative response factors were determined by standard mixtures of fatty acid methyl esters. Injection volume of the sample was 3μl.

RESULTS AND DISCUSSION

Effect of superficial velocity of AMF on extract loading and extraction yield of milk fat

To make any supercritical fluid extraction process viable as a commercial process for fractionation and

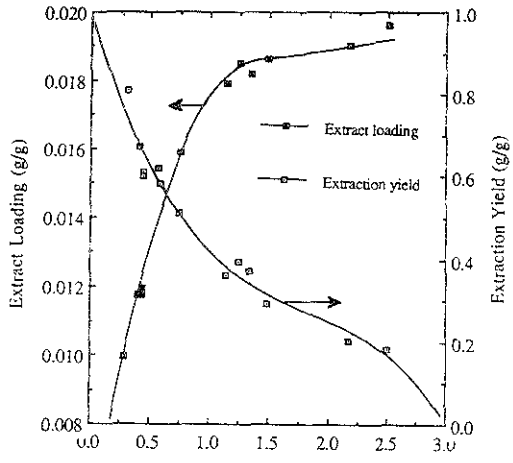

Fig. 2. Extract loading and extraction yield of AMF versus superficial velocity of AMF at 40°C/3,500 psig.

cholesterol reduction of milk fat, the amount of extract obtained per unit time should be maximized. One parameter for maximization of extraction rate is the flow rate. Thus it is necessary to investigate how the extract loading and the extraction yield depend on the flow rate. The extract loading is defined as the ratio of fat to carbon dioxide in the extract. The extraction yield is defined as the ratio of fat in the extract to fat in the AMF feed.

The extraction column was operated as a stripping column with SC-CO_2 as the continuous phase and AMF as the dispersed phase. Fig. 2 shows the extract loading and the extraction yield of AMF in a packed column as a function of the superficial velocity of AMF with a constant superficial velocity of CO_2 of 23.9cm/min at 40°C/3,500 psig. The extract loading increased and the extraction yield decreased as the superficial velocity of AMF increased. At a low superficial velocity of AMF, the dissolved milk fat was diluted by excess CO_2 and low loadings were observed. An increase in the superficial velocity of AMF resulted in an increase in the extract loading until the capacity of SC-CO_2 limited any further intake of milk fat due to phase equilibrium.

In the cocurrent operation, when the system was operated at a superficial velocity of AMF above 1.3 cm/min, a "pinch" point was developed at the bottom of the column where the exiting extract stream approached equilibrium and the extract loading was a maximum at 0.0195g/g at 40°C/3,500 psig. This differs by only 7% from the equilibrium solubilities reported by others[9,10].

Table 1. Effects of processing condition on fat and cholesterol extraction

Extraction (°C/psig)	60/2,000	60/2,500	40/3,500
CO_2 density (kg/m^3)	526	655	873
Extract			
Fat yield (wt%)	4	18	57
Cholesterol yield (wt%)	8	23	60
Cholesterol change (%)	+110	+28	+5
Raffinate			
Fat yield (wt%)	96	82	43
Cholesterol yield (wt%)	92	77	40
Cholesterol change (%)	−4	−6	−7

In order to verify the accuracy of the experimental procedure, the equilibrium solubility (extract loading) of AMF in carbon dioxide at 60°C/2,000 psig was evaluated at a superficial velocity of AMF of 1.5cm/min and a superficial velocity of CO_2 of 24cm/min. The extract loading was 0.00074g/g which was comparable to the literature value of 0.0007g/g at this condition[10].

The single pass method for the determination of equilibrium solubility with an extraction column by going to sufficiently high superficial velocity of the dispersed phase in order to achieve equilibrium has also been used by Lahiere and Fair[11] for extraction of 2-propanol from an aqueous mixture and de Haan[9] for extraction of fat and lactones from milk fat using SC-CO_2.

Effect of processing conditions on fat and cholesterol extraction

The capacity of a supercritical solvent is mainly controlled by the solvent density, the temperature, and the affinity of the solvent for the solutes[12]. Table 1 shows the measured effect of the carbon dioxide density on fat and cholesterol extraction in a packed column. Raising the pressure from 2,000 to 2,500 psig increases the carbon dioxide density[13] from 526 to 655kg/m^3. This increase of 1.24 times in the carbon dioxide density enhanced the solubility of milk fat in SC-CO_2 by 4.5 times due to the stronger sovent-solute interactions at high pressure[12]. As the pressure is

raised further to 3,500 psig the carbon dioxide density increases to 873kg/m^3 and the solubility of milk fat is enhanced 14 times compared to that at 60° C /2,000 psig.

Meanwhile, the cholesterol in the extract decreases as the extraction pressure increases. A large cholesterol change at low pressure indicates that cholesterol is selectively soluble in the SC-CO_2. This happens because cholesterol possesses a high affinity for short - and medium-chain triglycerides which have a relatively high solubility in SC-CO_2 at low pressures[2,14]. When the pressure increases, the decrease in cholesterol concentration illustrates that the high pressure that leads to a higher solubility of milk fat decreases the solvent selectivity for cholesterol. This indicates that the solubility of milk fat in SC-CO_2 rises more rapidly than that of cholesterol at high pressure. For practical applications, then, the affinity of SC-CO_2 for cholesterol is not high enough to be able to separate cholesterol from milk fat by simple extraction.

Effect of operation conditions on fat and cholesterol extraction

As the solubilities of solutes in SC-CO_2 vary widely with pressure and temperature, the separation of a multicomponent mixture can be carried out more efficiently at the top or bottom of the extraction column by taking advantage of the temperature profile therein, making it easy to separate a desired component.

Table 2 shows the effects of selected operation conditions on fat and cholesterol extraction in a packed column at 40° C/3,500 psig. Temperatures were maintained at 40, 50 and 60° C at the top, in the middle and at the bottom of the extraction column, respectively. By increasing temperature at the bottom of the column which results in a decrease of the density of carbon dioxide due to density changes associated with the imposed temperature gradient in the extraction column, fat yield decreased by 23% as compared to isothermal operation. However, the cholesterol concentration in the extract increased by 50% as compared to isothermal operation because the extract phase became enriched with short-, and medium-chain fatty acids which had high affinity for cholesterol on the way from the top to the bottom of the column.

Recycle is one of the operation method to increase the contact area by recycling the raffinate phase back to the extraction column, especially when the ratio of liquid flows is small, and the interfacial area, with minority liquid dispersed, may be small[15]. On recycling part of the raffinate, fat yield in the extract increased by 14% as compared to operation without recycle. This happens because by recycling part of the raffinate, the flow of the AMF feed increased and it allows more interfacial area between two phases. The

Table 2. Effects of operation conditions on fat and cholesterol extraction of AMF at 40° C/3,500psig

Operation	Original AMF	Isothermal operation	Temp. gradient (40~60° C)	Recycle (R=15.0)	Reflux (R=1.2)
Extracts					
Fat yield (wt%)		57	44	65	51
Cholesterol change (%)		+5.6	+8.4	−3.6	−3.9
Fatty acids (wt%)					
Short chain (C4~C8)	6.8	8.5	8.7	5.2	10.1
Medium chain (C10~C12)	5.3	5.8	6.4	5.5	7.9
Long chain (C14~C18)	87.9	85.7	84.8	89.3	82.0
Unsat/sat	0.49	0.45	0.41	0.45	0.35
Raffinates					
Fat yield (wt%)		43	56	35	49
Cholesterol change (%)		−7.5	−6.5	+6.8	+4.2
Fatty acids (wt%)					
Short chain (C4~C8)		4.5	5.3	9.8	3.3
Medium chain (C10~C12)		4.6	4.4	4.9	2.6
Long chain (C14~C18)		90.9	90.3	85.3	94.1
Unsat/sat*		0.54	0.55	0.57	0.64

*Unsat/sat ; ratio of unsaturated to saturated fatty acids

cholesterol concentration in the extract decreased by 3.6% compared to that of the original AMF.

Reflux is also one of the unit operation to increase product purity in chemical engineering operation[15]. With the reflux operation, fat yield decreased by 11% compared to operation without reflux. This happens because part of the extract is precipitated at the reflux condition, and pumped back and combined with the incoming AMF feed. The cholesterol concentration in the extract decreased by 3.9% compared to the original AMF.

More short- and medium-chain fatty acids were extracted by the reflux operation because the lighter glyceride-rich precipitate at the reflux condition was pumped back and combined with the incoming feed. Long-chain fatty acids and the highest ratio of long-chain unsaturated to saturated fatty acids were obtained in the raffinate phase with reflux because many short- and medium-chain fatty acids were stripped away from the raffinate phase.

From the results above, it was clear that none of the above strategies were likely to provide the desired cholesterol reduction in milk fat. In addition, simple extraction and separation of milk fat is not sufficient to obtain unique products in terms of fatty acid compositions.

Utilization of adsorbent for cholesterol reduction from AMF

Adsorption, as a complementary process to supercritical fluid extraction, confers an extra degree of flexibility in the separation and fractionation of solutes dissolved in the fluid phase[16].

Table 3 showed the cholesterol content of fractions obtained by continuous cocurrent SC-CO_2 extraction in conjunction with in-line adsorption of cholesterol by magnesium silicate at 40°C/3,500 psig. The cholesterol reduction was 70~92% by the run time of 100min. After that, the cholesterol reduction decreased because the adsorbent packed in the adsorption column became saturated with cholesterol.

Table 3. Fat yield and cholesterol content of milk fat fractions by SC-CO_2

Run time (min)	Fat yield (g)	Cholesterol conc. (mg/100g)	Cholesterol reduction (%)
0	-	240.4	-
40	6.9	72.1	70.0
70	13.0	18.3	92.4
100	18.2	19.8	91.8
130	16.8	45.1	81.2
160	17.6	74.9	68.8
195	19.5	-	-
230	23.3	152.8	36.4
260	14.3	183.4	23.7

Based upon the results, supercritical extraction in conjunction with in-line adsorption turns out to be a promising procedure which is lowering the cholesterol level in milk fat.

CONCLUSIONS

Experimental studies were conducted to investigate performance of a continuous cocurrent supercritical fluid extraction column for processing of milk fat. The data will provide a comparative evaluation concerning the effectiveness of the solubility enhancing and the cholesterol reducing techniques employed, and any interactions that may exist between them. Even if none of the procedures tested except in-line-adsorption process proved to be effective for reducing cholesterol from AMF, the data collected may suggest further modifications to the extraction system, or other techniques that may be evaluated.

REFERENCES

1. Walstra, P. and Jenness, R. : *Dairy chemistry and physics*. John Wiley & Sons, New York, p.58 (1984)
2. Rizvi, S. S. H., Lim, S., Nikoopour, H., Singh, M. and Yu, Z. : Supercritical fluid processing of milk fat. In "*Engineering and food*" Spiess, W. E. L. and Schubert, H. (eds.), Elsevier Applied Science, New York, Vol. 3, p.145 (1989)
3. Rizvi, S. S. H., Benado, A. L., Zollweg, J. A. and Daniels, J. A. : Supercritical fluid extraction : fundamental principles and modeling methods. *Food Technol.*, **40**, 55 (1986)
4. Rizvi, S. S. H., Daniels, J. A., Benado, A. L. and Zollweg, J. A. : Supercritical fluid extraction : operating principles and food applications. *Food Technol.*, **40**, 57 (1986)
5. Treybal, R. E. : *Mass transfer operations*. McGra-Hill Book Co., New York, p.187 (1980)
6. Reiss, L. P. : Cocurrent gas-liquid contacting in packed columns. *I & EC Process Design Development*, **6**, 486 (1967)
7. A.O.A.C. : *Official methods of analysis*. 14th ed.,

Association of official analytical chemists, Washington, D. C., p.883 (1984)
8. Lynch, J. and Barbano, D. M. : Private communication. Dept. of Food Science, Cornell University, Ithaca, New York (1991)
9. de Haan, A. B. : Supercritical fluid extraction of liquid hydrocarbon mixtures. Dissertation, Deft University of Technolgoy, Netherlands (1991)
10. Yu, Z. R., Rizvi, S. S. H. and Zollweg, J. A. : Phase equilibria of oleic acid, methyl oleate, and anhydrous milk fat in SC-CO_2. *J. Supercritical Fluids*, **5**, 114 (1992)
11. Lahiere, L. R. and Fair, J. R. : Novel technique to measure equilibria of supercritical solvents and liquid mixtures. *J. Chem. Eng. Data*, **34**, 275 (1989)
12. McHugh, M. A. and Krukonis, V. J. : *Supercritical fluid extraction : principle and practices*. Butterworths, Massachusetts, p.5 (1986)
13. Angus, S., Armstrong, B. and de Reuck, K. M. : *IUPAC international thermodynamics of the fluid state-carbon dioxide*. Pergamon Press, Oxford, England, p.160 (1979)
14. Shishikura, A., Fujimoto, K., Kaneda, T., Arai, K. and Saito, S. : Modification of butter oil by extraction with supercritical carbon dioxide. *Agric. Biol. Chem.*, **50**, 1209 (1986)
15. McCabe, W. H. and Smith, J. C. : *Unit operations of chemical engineering*. 3th ed., McGraw-Hill Book Co., New York, p.512 (1976)
16. King, J. W., Eissler, R. L. and Friedrich, J. P. : Supercritical fluid-adsorbate-adsorbent systems. In "*Supercritical fluid extraction and chromatography*" Charpentier, B. A. and Sevenants, M. R. (eds.), ACS symposium series 366, Chapter 4, American Chemical Society, Washington, D. C., p.63 (1988)

(Received April 8, 1994)

초임계이산화탄소에 의한 유지방의 연속 병류식 추출

임상빈† · 리즈비*
제주대학교 식품공학과
*미국 코넬대학교 식품공학과

요 약

초임계이산화탄소에 의한 유지방의 연속 병류식 추출특성에 대하여 연구를 수행하였다. 유지방의 유속이 증가함에 따라 유지방의 초임계이산화탄소에 대한 용해도는 증가하였지만, 가한 유지방 중 추출된 지방의 양은 감소하였다. 40°C/3,500 psig에서 무수유지방의 초임계이산화탄소에 대한 최고용해도는 0.0195g/g이었다. 이산화탄소의 밀도를 증가시킴에 따라 유지방의 용해도는 증가하였으나, 추출물 중의 콜레스테롤 농도는 감소하였다. 세가지 시스템 변수들 즉 순환, 환류, 추출칼럼의 온도구배 등도 검토하였다. 저급지방산들은 환류공정에 의해 보다 많이 추출되었으며, 그 결과 고급지방산들과 그 중 불포화 지방산들은 추잔물에 많이 분포되어 있었다.