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Purification of Waste Cooking Oils via Supercritical Carbon Dioxide Extraction

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Purification of waste cooking oils (palm oil and soybean oil) using supercritical carbon dioxide ($scCO_2$) extraction has been investigated. The purified oils were characterized by their acid value, conjugated diene value, total polar compound measurements, and high-performance size exclusion chromatography. Using optimal extractions conditions of 353.15 K, 20 MPa, and CO_2 flow rate of 40 g/min, 80% of the oil was recovered and the purified oil compositions and properties were very close to those of the fresh oils. At higher pressures or lower temperatures, the separation efficiency of the $scCO_2$ extraction was significantly reduced.

Keywords extraction; supercritical carbon dioxide; waste cooking oil

INTRODUCTION

Larger amounts of oils are used to prepare various kinds of fried foods. Typically the food frying process is carried out at high temperatures (~473.15 K) in the open air for an extended period of time. Under these conditions, the main components of the oils, triglycerides (TG), undergo many complex chemical changes, often leading to the formation of toxic and odorous chemicals. The chemical reactions during the frying process include hydrolysis, oxidation, and polymerization of the triglycerides. This leads to form low-molecular-weight polar compounds, free fatty acids (FFA), conjugated diene compounds, and polymerized high-molecular-weight compounds (H.M.W.C). Thus oils that are used in the food frying process are typically discarded, which causes serious environmental problems.

Currently only a small portion of the used cooking oils are recycled for use in areas of animal foods, paint materials, and preparation of soaps and machine oils. Several attempts have been made to purify the waste cooking oils using a number of physical or chemical methods. These include filtration (1), distillation (2), and adsorbent treatments (3–5). However, these methods often suffer from low separation efficiency, use of small quantity of toxic chemicals, and generation of waste chemicals and wastewater.

Supercritical carbon dioxide ($scCO_2$) extraction has been widely used as an environmentally benign alternative to the conventional purification methods. For example, high FFA containing olive oil (~30 wt% FFA) or black cumin seed oil (37.7 wt% FFA) was deacidified using the $scCO_2$ extraction method (6–8). Waste frying oil was purified by a batch-wise $scCO_2$ extraction technique (9). In this study, a two-stage $scCO_2$ extraction was used. The first extraction was carried out at a low pressure (15 MPa) to remove low-molecular-weight compounds such as FFA and other polar compounds. The second extraction was carried out at a high pressure (30 MPa) to recover triglycerides. However, the extracts still contained approximately 8% low-molecular-weight compounds. A pilot-scale, continuous countercurrent $scCO_2$ fractionation was used to deacidify crude rice bran oil (10). At a low pressure of 13.8 MPa and a high temperature of 353.15 K, the FFA content in the oil decreased from 5 to 2.5 wt%. Used peanut oil was purified using a continuous $scCO_2$ fractionation method with ethanol as a co-solvent (11,12). At an optimal operating condition of 35 MPa, 328.15 K, and a solvent-to-feed ratio of 53, the recovery of triglycerides was 97%. However, the acidity of the purified oil was higher

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(1.21%) than that of the used peanut oil (0.8%). Most of the previous studies focused on deacidification of the high FFA containing oils (10–30 wt% FFA in oils). There were still a considerable amount of FFA that remained after the $scCO_2$ extraction (1–5 wt%).

In this study, heat-treated palm oil and waste soybean oil were purified using $scCO_2$ extraction without using co-solvents. Based on the Korea Food and Drug Administration (KFDA) regulation, oils with FFA content larger than 0.02 wt% (or an acid value greater than 0.2) should not be used again in the frying process. The typical FFA content in the waste cooking oils is in the range of 0.04–0.05 wt%. Thus, in contrast to the previous studies, in this investigation, low FFA content oils (0.05 wt%) were used as the starting waste oils and various experimental parameters were explored to reduce the FFA content below 0.02 wt%, so that the purified oil can be reused in the food frying process.

EXPERIMENTAL AND METHODS

Materials

Pure palm oil was kindly provided by Lotte Samgang Co. (Chung Nam, Korea). The palm oil was acidified by heating at 523.15 K and stirring at 300 rpm for 3 h in open air. Pure soybean oil was purchased from a local market in Korea. Waste soybean oil was obtained from a cafeteria at the Korea Institute of Science and Technology (KIST). The oil has been used to fry the fork cutlet at 170°C for 2 hr. Oleic acid (purity of >95.0%) was purchased from Deajunghwagum Co. (Kyungkido, Korea). Carbon dioxide (purity of >99.0%) was purchased from Shinyang Sanso Co. (Seoul, Korea).

Supercritical Fluid Extraction (SFE) Apparatus and Procedure

All purification experiments were carried out using a custom-built, supercritical carbon dioxide extraction apparatus. A schematic of the apparatus is shown in Fig. 1. Details on the extraction apparatus are given in the previous paper (13). Previously one separator was used at the downstream of the extractor. In this study, three separators and four back-pressure regulators were used. The size of the separator is 3 cm in inside diameter and 24.7 cm in height, giving a volume of 60 cm^3. The pressures of the separators were controlled by four back-pressure regulators at 15, 10, and 7 MPa, respectively.

Prior to each extraction experiment, the temperature of the extractor was set at an experimentally-desired temperature. Sixty grams of the heat-treated palm oil or the waste soybean oil was placed in the metal basket and the metal basket containing the oil was introduced in the extractor. The pressures of the extractor and the three separators were set at experimentally-desired pressures using the back-pressure regulators. After a desired time of extraction, the CO_2 flow was stopped and the extracts in each separator were collected by opening valves at the bottom of the separator. The extractor was then carefully depressurized to atmospheric pressure and the oil in the extractor was collected. The oils from the extractor and the oils from the separators were then weighed and analyzed.

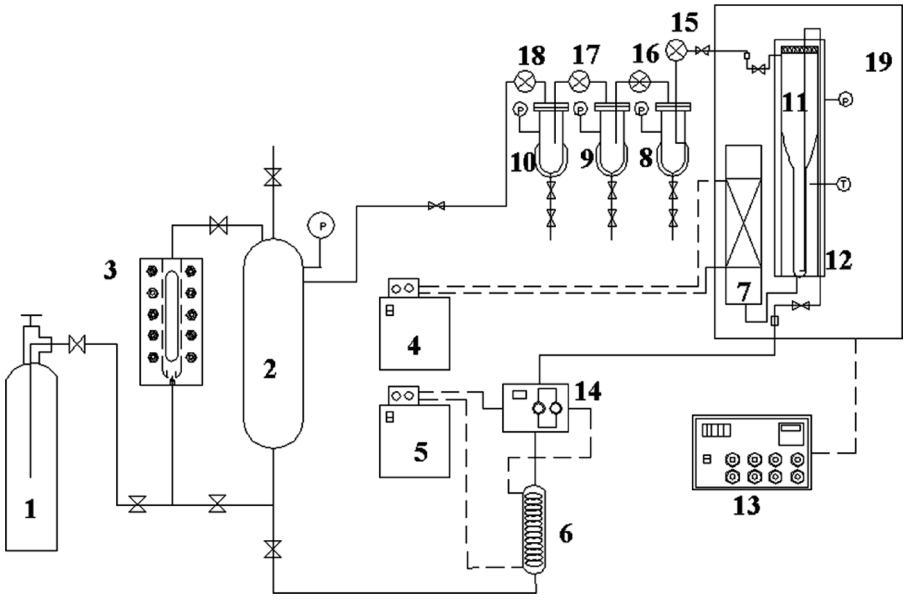

FIG. 1. A schematic diagram of the experimental apparatus for extraction system: (1) CO_2 cylinder; (2) CO_2 storage tank; (3) level gauge cell; (4), (5) circulators; (6) condenser; (7) preheater; (8) separator 1; (9) separator 2; (10) separator 3; (11) extractor; (12) metal basket; (13) control box; (14) CO_2 inlet pump; (15), (16), (17), (18) back pressure regulators; (19) air bath.

Analytical Methods

Acid values (AV), a value indicating FFA content in oils, were measured according to the American Oil Chemists Society (AOCS) Official Method (Cd 3a-63) (14). Conjugated diene (CD) values were measured according to the AOCS Official Method (Ti 1a-64) (14). The amount of total polar compounds (TPC) in oils was measured according to the AOCS Official Method (Cd 20–91) (14). In this method, polar and non-polar compounds in oils were separated using a silica gel column chromatography technique.

The composition of the oils was analyzed using a high-performance size exclusion chromatogram (HPSEC) with tetrahydrofuran (THF) as a mobile phase. The HPSEC system was equipped with an auto sampler (Model 717 PLUS, Waters Corporation, Milford, USA), a 20 μL sample injector loop, three THF Stragel® columns (Models HR4 HR2, HR0.5, Waters Corporation), a refractive index detector (Model 2414, Waters Corporation). The elution time of free fatty acid in the oils was determined by comparing elution times of standards (23.29 min for triolein, 25.42 min for oleic acid, and 25.54 min for palmitic acid). The elution times of diglyceride and monoglyceride were estimated based on their molecular weights. The amount of high-molecular-weight compounds, monoglyceride, diglyceride, triglyceride, and free-fatty acid in the oils was determined by deconvoluting the HPSEC peaks and calculating the relative area of each section of the deconvouted peak.

RESULTS AND DISCUSSION

Figure 2 shows the solubility of the palm oil and oleic acid in $scCO_2$ at temperatures ranging 333.15–373.15 K and pressures ranging 20–35 MPa. Details on the solubility measurement were given in the previous work (15). In the case of the oleic acid-$scCO_2$ system, the solubility difference between the data reported here and the previously reported data (16–19) is in the range of 0.1–30%. As Bharath et al. (18) pointed out, the relatively large deviation can be mainly due to purifying of the oleic acid. Brunetti et al. (6) used oleic acid with 68% purity. Bharath et al. reported the purity of oleic acid was >90%. The purity of oleic acid used herein was >95%. Due to the large solubility difference between the reported data, the solubility of oleic acid and palm oil in $scCO_2$ was measured in this study. It can be seen that the solubility of oleic acid in $scCO_2$ is higher than that of the palm oil at a given temperature and pressure. This solubility difference of the palm oil and oleic acid in $scCO_2$ makes it possible to extract FFA selectively from the heat-treated palm oil or the waste soybean oil. The solubility of the palm oil and oleic acid decreased with a decrease in pressure or with an increase in temperature. When the pressure increased from 20 to 35 MPa at 333.15 K, the solubility of oleic acid

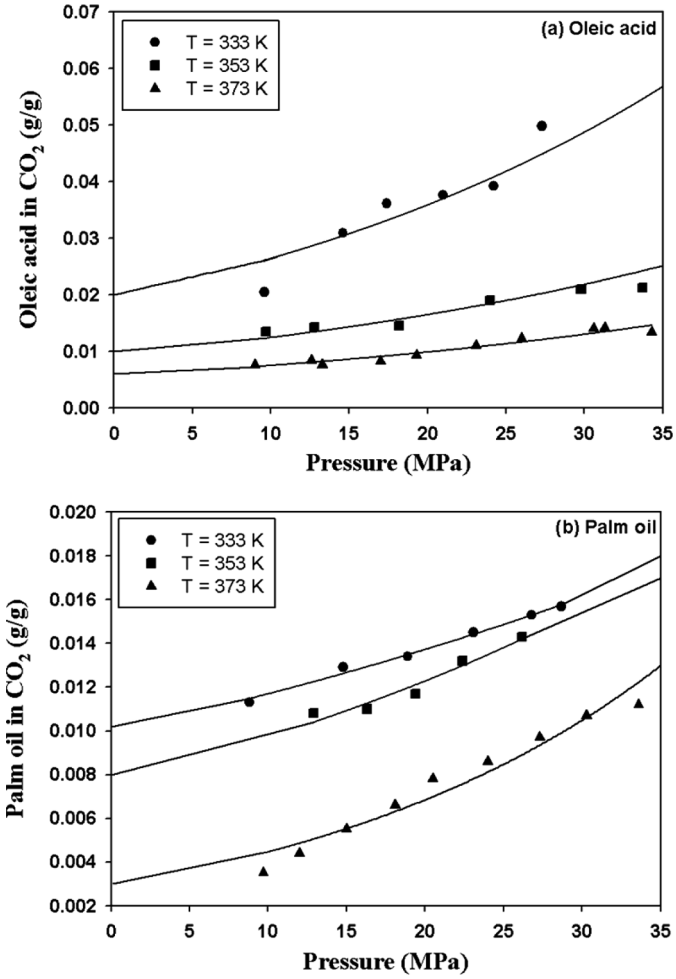

FIG. 2. The solubility of (a) oleic acid and (b) palm oil in $scCO_2$; (-●-) 333.15 K (-■-) 353.15 K (-▲-) 373.15 K.

increased from 0.0376 to 0.0578 g/g CO_2, and the solubility of palm oil increased from 0.0134 to 0.0165 g/g CO_2. A crossover point, above which the solubility increases with an increase in temperature, is not observed in the current ranges of pressure and temperature. It is noted that at a higher pressure of 37 MPa, a crossover point was seen in the solubility of palm kernel oil in $scCO_2$ (20). Thus the higher solubility at lower temperature or at higher pressure is because $scCO_2$ density increases as temperature decreases or as pressure increases.

The fresh palm oil, the heat-treated palm oil, the fresh soybean oil, and the waste soybean oil were characterized using HPSEC, determining the AV, CD value, TPC measurements, and these results are listed in Table 1.

Figure 3 shows representative HPSEC profiles of the fresh palm oil and the heat-treated palm oil. The peaks were deconvoluted to quantify the amount of TG, DG, MG, H.M.W.C., and FFA contents in the oils. Over 90% of TG (91.20%) and a small amount of DG (2.50%), MG

TABLE 1
Compositions and properties of fresh palm oil, heat-treated palm oil, fresh soybean oil, and waste soybean oil

Sample	H.M.W.C[a] (%)[i]	TG[b] (%)	DG[c] (%)	MG[d] (%)	FFA[e] (%)	AV[f]	CD[g]	TPC[h]
Fresh palm oil	0	91.2	2.5	5.6	0.7	0.22	0.077	9.19
Heat-treated palm oil	4.6	70.1	16.2	6.8	2.4	0.49	0.114	22.8
Fresh soybean oil	0.3	97.9	0.45	0.55	0.8	0.12	0.098	10.4
Waste soybean oil	4.4	77.7	9.88	6	2	0.52	0.193	26.1

[a]High molecular weigh compounds.
[b]Triglyceride.
[c]Diglyceride.
[d]Monoglyceride.
[e]Free fatty acids.
[f]Acid values.
[g]Conjugated diene values.
[h]Total polar compounds.
[i]The percent was estimated by the area of the HPSEC peaks.

(5.60%), and FFA (0.70%) were present in the fresh palm oil. After the palm oil was heat-treated at 523.15 K in open air, the amount of TG decreased to 70.10% while the amount of DG, MG, and FFA increased to 16.20%, 6.80%, and 2.40%, respectively. This indicates that triglycerides were degraded to the smaller molecular weight compounds during the heat treatment. In addition, 4.60% of H.M.W.C. was present in the heat-treated palm oil, suggesting that the polymerization reaction occurred during the heat treatment. As listed in Table 1, the AV, CD, and TPC values of the heat-treated palm oil were higher than those of the fresh palm oil. This indicates that acidified compounds, conjugated-diene compounds, and polar compounds were produced during the heat treatment. Similar trends were observed in the fresh soybean oil and the waste soybean oil.

Figure 4 shows the effects of the extraction time on palm oil recovery and the acid value at 25 MPa, 333.15 K, and CO_2 flow rate of 40 g/min. Oil recovery in this study was defined as the weight percent of the purified oil to the initial waste oil charged to the extractor. When the extraction

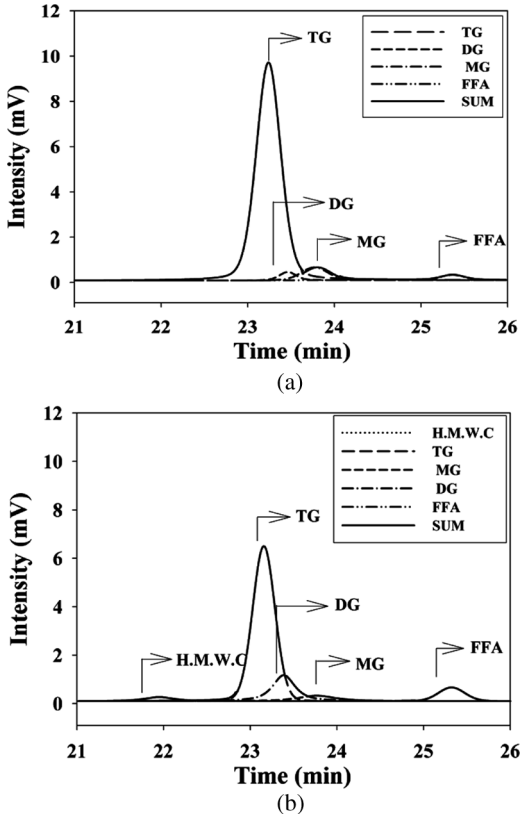

FIG. 3. High-performance size exclusion chromatograms (HPSEC) of (a) fresh palm oil and (b) heat-treated palm oil.

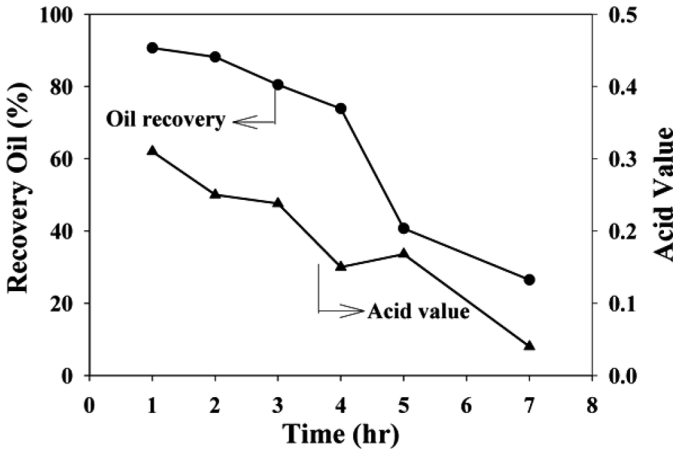

FIG. 4. Effect of the extraction time on the oil recovery and acid value at 25 MPa, 333.15 K, CO_2 flow rate of 40 g/min.

time increased from 1 to 7 h, the oil recovery decreased significantly from 90 to 26%. This indicates that a large amount of the oil was extracted and transferred to the separators at longer extraction time. The acid value of the purified oil decreased from 0.31 to 0.04 with an increase in extraction time from 1 to 7 h. As discussed previously, the solubility of FFA in $scCO_2$ is higher than that of the palm oil. Thus at longer extraction time, a larger amount of FFA relative to palm oil was extracted, resulting in the decrease in acid value.

Figure 5 shows the effect of the CO_2 flow rate on the palm oil recovery and the acid value at 3 h, 353.15 K, and 20 MPa. As the CO_2 flow rate increased from 10 to 40 g/min, the oil recovery decreased from 94 to 71%. The acid value decreased from 0.57 to 0.13 as the CO_2 flow rate increased from 10 to 40 g/min, indicating a larger amount of FFA than palm oil was extracted at a higher CO_2 flow rate.

Figure 6 shows the effect of the extraction temperature on the palm oil recovery and the acid value at 3 h, 25 MPa, and CO_2 flow rate of 44 g/min. As the extraction temperature increased from 313.15 to 373.15 K, the oil recovery did not change much (~80%) and the acid value decreased significantly from 0.54 to 0.14.

As discussed previously, the solubility of palm oil and oleic acid in $scCO_2$ decreased with an increase in temperature up to 373 K. If the solubility variation of the palm oil with temperature had been the dominant effect, the oil recovery would have increased with an increase in temperature because the palm oil is less soluble as the temperature increases from 333 to 373 K. Thus the constant oil recovery values are not explained by the solubility effect. It should be noted that the linear $scCO_2$ flow rate in the extractor at different temperatures is not the same because the flow rate was fixed to 44 g/min at room temperature. Our calculations showed that the linear velocity of CO_2 in the extractor increased from 3.28 to 4.91 cm/min with an increase in temperature from 313.15 to 373.15 K at 25 MPa. Thus the higher CO_2 flow rate in the extractor at elevated temperatures would extract a larger amount of palm oil and FFA. The decrease of acid value with an increase in temperature implies that the flow rate effect was dominant in the extraction of FFA. The constant oil recovery with an increase in temperature may be due to a balance between the solubility effect and the flow rate effect.

Figure 7 shows the effect of the extraction pressure on the palm oil recovery and the acid value at 3 h, 353.15 K, and CO_2 flow rate of 42 g/min. As the pressure increased from 20 to 35 MPa, the oil recovery decreased significantly from 80% to 19% and the acid value increased from 0.13 to 0.41. The extraction of the larger amount

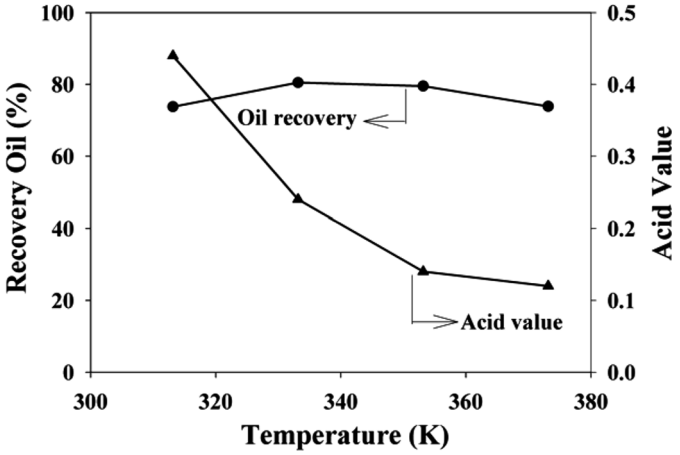

FIG. 6. Effect of the extraction temperature on the oil recovery and acid value at 25 MPa, CO_2 flow rate of 44 g/min, and 3 h.

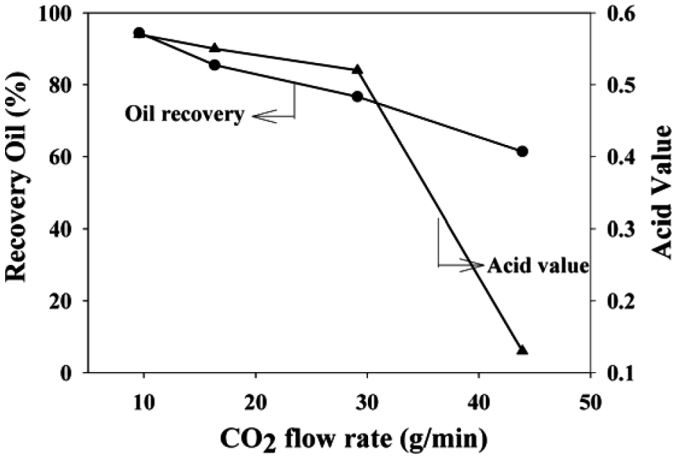

FIG. 5. Effect of the CO_2 flow rate on the oil recovery and acid value at 20 MPa, 353.15 K and 3 h.

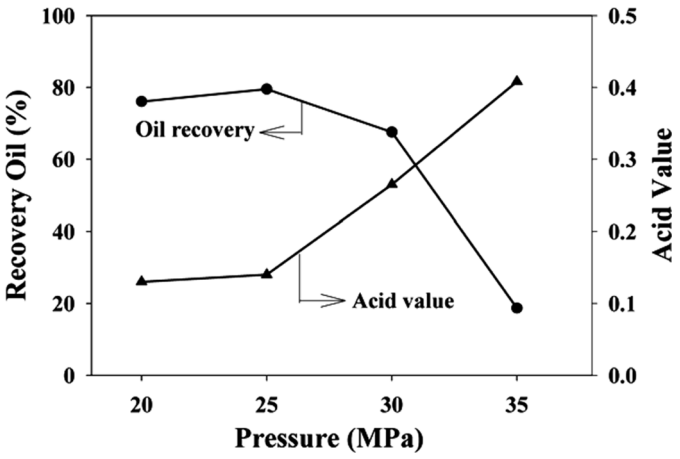

FIG. 7. Effect of the extraction pressure on the oil recovery and acid value at 353.15 K, CO_2 flow rate of 42 g/min, and 3 h.

of the oil at the elevated pressures is because the solubility of the oil increased with an increase in pressure up to 35 MPa, as discussed in the previous section. The acid value of the oil in the extractor approached the acid value of the heat-treated oil at high pressure, indicating a loss of separation efficiency. Thus extraction at low pressure is more effective to separate FFA from the heat-treated oil.

The purified palm oils in the extractor and the oils in the separators that were collected after the extraction at 353.15 K and 313.15 K with using pressures of 20 MPa and 35 MPa, a CO_2 flow rate of 44 g/min and an extraction time of 3 h were characterized in detail using HPSEC, CD, and TPC measurements and the results are listed in Table 2. At the extraction temperature of 353.15 K, the TG, MG, DG, and FFA contents of the purified oil were very similar to those of the fresh palm oil. In addition, AV, CD, and TPC values were very similar to those of the fresh palm oil. The oils in the separators retained higher DG, MG, and FFA contents, and AV, CD, and TPC values were higher compared to the purified oils in the extractor. Thus, $scCO_2$ extraction under the low density regime can effectively separate the polar, small-molecular-weight species in the heat-treated palm oil. Thus the purified oils can be reusable in the frying food process. This high separation efficiency can be because the $scCO_2$ density at 353.15 K and 20 MPa (0.594 g/cm^3) is high enough to have good solubility of the low-molecular-weight species while low enough not to have good solubility of the higher molecular weight triglyceride (9,21,22).

As listed in Table 2, at the extraction temperature of 313.15 K (high density regime, density of $scCO_2 =$ 0.840 g/cm^3), the TG, DG, MG, and FFA contents of the oil in the extractor were very similar to those of the oils in the separator. In addition, AV, CD, and TPC values of the oil in the extractor were very close to those of the oils in the separator. This indicates the separation efficiency of triglycerides from the low-molecular-weight compounds was low in the higher CO_2 density regime. In contrast to the extraction at 353.15 K, high-molecular-weight compounds (3.91–4.45%) were found in the oils in the separators when extracted at 313.15 K, indicating that the $scCO_2$ density at 313.15 K was high enough to have good solubility for the higher-molecular-weight compounds.

When pressure increased from 20 to 35 MPa at 353.15 K, thus the $scCO_2$ density increased from 0.594 to 0.789 g/cm^3, the oil recovery decreased significantly from 76.1% to 20.0%. The TG, DG, MG, FFA contents and AV, CD, TPC values of the oil in the extractor were similar to those of the oil in the separators. Again, this indicates that the separation efficiency of $scCO_2$ at higher pressure (or high density regime) was very low. Therefore, separation of the low-molecular-weight species from the oils with the $scCO_2$ extraction method should be carried out at the low density regime (high temperature and low pressure).

The waste soybean oil was purified at the optimal condition (353.15 K, 20 MPa, CO_2 flow rate of 41 g/min, 3 h), and the results are listed in Table 3. After the $scCO_2$ extraction, the FFA content, and AV, CD, TPC values

TABLE 2
Triglyceride (TG), diglyceride (DG), monoglyceride (MG), and free fatty acid (FFA) contents estimated by HPSEC and acid values (AV), conjugated diene values (CD), total polar compounds values (TPC) of the fresh palm oil, heat-treated palm oil, and the purified palm oil (in the extractor) and the oils in the separator

		Recovery (%)	H.M.W.C (%)	TG (%)	DG (%)	MG (%)	FFA (%)	AV	CD	TPC
Fresh palm oil		–	0.00	91.2	2.50	5.60	0.70	0.22	0.077	9.19
Heat treated palm oil		–	4.60	70.1	16.2	6.80	2.40	0.49	0.114	22.8
	Extractor	76.1	1.50	87.2	4.45	6.08	0.90	0.13	0.070	9.0
P = 20 Mpa	Separator 1	3.70	–	87.1	4.54	6.13	1.75	0.21	0.138	19.5
T = 353.15 K	Separator 2	4.90	–	87.1	4.55	6.13	1.76	0.24	0.165	20.6
ρ = 0.594 g/cm^3	Separator 3	3.20	–	87.1	4.45	5.99	1.78	0.24	0.215	21.3
	Extractor	62.4	4.50	81.40	6.70	5.60	1.80	0.5	0.165	25.4
P = 20 Mpa	Separator 1	0.27	4.45	81.39	6.69	5.59	1.77	0.52	0.158	N.A.
T = 313.15 K	Separator 2	1.41	3.93	81.17	6.60	5.60	2.70	0.60	0.166	N.A.
ρ = 0.840 g/cm^3	Separator 3	7.71	3.91	81.16	6.58	5.59	2.72	0.61	0.166	28.2
	Extractor	20.0	4.59	81.6	7.12	5.06	1.65	0.55	0.1605	22.1
P = 35 MPa	Separator 1	53.9	4.58	81.6	7.11.	5.01	1.68	0.50	0.1531	21.8
T = 353.15 K	Separator 2	9.55	3.97	81.5	7.03	4.98	1.69	0.54	0.1608	24.3
ρ = 0.789 g/cm^3	Separator 3	4.39	3.95	81.4	6.96	4.89	2.18	0.58	0.1650	26.6

TABLE 3
Triglyceride (TG), diglyceride (DG), monoglyceride (MG), and free fatty acid (FFA) contents estimated by HPSEC and acid values (AV), conjugated diene values (CD), total polar compounds values (TPC) of the fresh soybean oil, waste soybean oil, and the purified soybean oil (in the extractor) and the oils in the separator. The purification conditions were 353.15 K, 200 bar, 40 g/min CO_2, and 3 h

	Recovery (%)	H.M.W.C (%)	TG (%)	DG (%)	MG (%)	FFA (%)	AV	CD	TPC
Fresh soybean oil	–	0.30	97.9	0.45	0.55	0.80	0.12	0.0984	10.4
Waste soybean oil	–	4.41	77.7	9.88	6.00	2.00	0.52	0.1927	26.1
Purified oil (Extractor)	72.4	3.45	80.5	9.93	5.45	0.68	0.11	0.0901	9.48
Oil in separator 1	9.42	–	80.0	9.56	5.38	1.67	0.16	0.2246	24.6
Oil in Separator 2	7.70	–	80.0	9.25	5.08	2.3	0.20	0.2416	24.5
Oil in Separator 3	10.5	–	80.1	9.22	5.05	2.31	0.22	0.2703	26.7

of the oil in the extractor decreased and approached those of the fresh soybean oil. Thus, as in the case of the palm oil purification, $scCO_2$ extraction can selectively separate polar, small-molecular-weight species in the waste soybean oil. Therefore, simple, efficient, environmentally-friendly purification of waste cooking oils can be achieved using the $scCO_2$ extraction.

CONCLUSION

Purification of waste cooking oil (palm oil and soybean oil) was carried out using the $scCO_2$ extraction method. Various experimental conditions, temperatures ranging 313.15–373.15 K, pressures ranging 20–35 MPa, CO_2 flow rates ranging 10–40 g/min^{-1}, and extraction time ranging 1–7 h were explored to find high oil recovery and high separation efficiency conditions. At the high density regime (high pressure and low temperature) the separation efficiency and the oil recovery were very low while at the low density regime (low pressure and high temperature) the separation efficiency and the oil recovery were high. At 353.15 K, 20 MPa, 40 g/min^{-1} flow rate, and 3 h, the oil recovery was ~80% and the triglyceride (TG), diglyceride (DG), monoglyceride (MG), and free fatty acid (FFA) contents were very close to those of the fresh oil. In addition, acid values (AV), conjugated diene values (CD), and total polar compounds (TPC) were also very similar to those of the fresh oil. Thus the oils purified at the low density regime can be reusable in the food frying process.

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