SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF APRICOT KERNEL OIL

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Approval of the Graduate School of Natural and Applied Sciences.

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

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ABSTRACT

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF APRICOT KERNEL OIL

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The purpose of this research was to determine the solubility of apricot (*Prunus armeniaca* L.) oil in supercritical carbon dioxide (SC-CO_2), effects of parameters (particle size, solvent flow rate, pressure, temperature and co-solvent (ethanol) concentration) on extraction yield and to investigate the possibility of fractionation.

Solubility, increased with pressure and increased with temperature above the crossover pressure, which was found between 200 and 300 bar, and decreased with temperature below the crossover pressure. Appropriate models were fitted to data.

Extraction of apricot kernel oil occurred in two extraction periods as fast and slow extraction periods. Most of the oil was extracted in the fast extraction period and the oil recovered in the slow extraction period was negligible. Extraction yield increased with decrease in particle size and recovery of more than 99 % of the oil was possible if particle diameter decreased below 0.425 mm. Extraction rate increased with increase in flow rate, pressure, temperature and ethanol concentration. The volume mass transfer coefficient in the fluid phase changed between 0.6 and 3.7 /min, whereas the volume mass transfer coefficient in the solid phase changed between 0.00009 and 0.00048 /min.

Extraction yield at 15 min for particle diameter smaller than 0.85 mm was formulated as a function of solvent flow rate, pressure, temperature, and ethanol concentration by using Response Surface Methodology. According to the model yield was highest (0.26 g /g) at 4 g/min flow rate, 60 ^{o}C, 450 bar and 3 % ethanol concentration. Fractionation was not possible at significant levels.

Key Words: Apricot kernel oil, supercritical carbon dioxide, extraction, mass transfer, Response Surface Methodology.

ÖZ

KAYISI ÇEKİRDEĞİ YAĞININ SÜPERKRİTİK KARBONDİOKSİTLE EKSTRAKSİYONU

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Bu araştırmada kayısı (*Prunus armeniaca* L.) çekirdeği yağının süperkritik karbon dioksit (SC-CO_2) içerisindeki çözünürlüğü ve ekstraksiyon verimine şüreç parametrelerinin (parçacık boyutu, çözücü akış hızı, basınç, sıcaklık ve ek çözücü (etanol) konsantrasyonunun etkilerinin belirlenmesi ile yağın fraksiyonlarına ayrılması olanaklarının araştırılması amaçlanmıştır.

Kayısı çekirdeği yağının çözünürlüğün, basınçtaki yükselmeyle arttığı, sıcaklıktaki yükselmeyle ise 200 ile 300 bar arasında olduğu belirlenen kesişme basıncının üzerindeki basınçlarda arttığı bu basıncın altında ise azaldığı belirlenmiştir. Ayrıca, elde edilen sonuçlar için uygun modeller oluşturulmuştur.

Kayısı çekirdeği yağının ekstraksiyonu hızlı ve yavaş ekstraksiyon bölgeleri olarak iki ana bölgeye ayrılmıştır. Yağ miktarının çoğunluğunun hızlı ekstraksiyon bölgesinde ekstrakte edildiği ve yavaş ekstraksiyon bölgesinde elde edilen yağ miktarının ihmal edilebilecek düzeyde az olduğu saptanmıştır. Parçacık boyutu küçüldükçe ekstraksiyon veriminin arttığı ve parcacık çapının 0.425 mm'nin altına düşürülmesiyle çekirdekteki toplam yağ miktarının % 99'unun alınabileceği belirlenmiştir. Akış hızı, basınç, sıcaklık ve etanol ilavesindeki artışın ekstraksiyon hızını artırdığı saptanmıştır. Akışkan fazdaki kütle aktarım katsayısının 0,6 ile 3,7 /dakika arasında değiştiği belirlenirken, katı fazdaki kütle aktarım katsayısının 0,00009 ile 0,00048 /dakika arasında değiştiği saptanmıştır.

Parcacık çapı 0,85 mm'den küçük örneklerin 15 dakika ekstraksiyonu sonucu elde edilen verim değerleri Tepki Yüzey Metodu kullanılarak, çözücü akış hızı, basınç, sıcaklık ve ek çözücü konsantrasyonunun bir fonksiyonu olarak ifade edilmiştir. Elde edilen model denkleminden ekstraksiyon veriminin en yüksek değeri 4 g/dak akış hızı, 60 ^{o}C, 450 bar ve % 3 ethanol ilavesi şartlarında yaklaşık 0.26 g yağ/g çekirdek olarak saptanmıştır. Ayrıca, kayısı çekirdeği yağını önemli seviyelerde fraksiyonlarına ayrılmadığı belirlenmiştir.

Anahtar Kelimeler: Kayısı çekirdeği yağı, süperkritik karbon dioksit, ekstraksiyon, kütle aktarımı, Tepki Yüzey Metodu.

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a	Specific interfacial area (area/volume of fixed bed)
c	Solubility (mass/volume)
C	Ethanol concentration (weight %)
E	Mass of extract (mass)
G	Grinding efficiency ($0 \leq G \leq 1$)
h	Dimensionless axial coordinate ($0 \leq h \leq 1$)
J	Mass transfer rate per volume of fixed bed (mass/volume.time)
k	Mass transfer coefficient (length/time)
K	Mass of unreleased oil inside the intact cells of the particles (mass)
l	Axial coordinate (length)
m	Oil recovery (mass of oil extracted/ mass of initial oil in kernel feed)
N	Mass of the oil free solid phase (mass)
O	Mass of the oil contained initially in the solid phase (mass)
P	Pressure (bar)
Q	Mass flow rate of solvent (mass/time)
R	Mass of released oil (mass)
T	Temperature (K)
t	Time (time)
x	Solid phase concentration (mass/mass)
X	Parameter of the response function Eq. 2.5
w	Oil yield (mass of oil extracted/mass of kernel feed)

y	Solvent phase concentration (mass/mass)
y_r	Solubility (mass/mass of solvent)
Y	Parameter of the slow extraction period, Eq. 1.21
Z	Parameter of the fast extraction period, Eq. 1.20

Greek letters

ε	Void fraction (volume/volume of bed)
ρ	Density (mass/volume)
Ψ	Dimensionless time

Superscript

$+$	At interfacial boundary

Subscripts

f	Solvent phase
k	Boundary between the fast and slow extraction periods
s	Solid phase
0	Initial condition
90	Time is 90 min

CHAPTER 1

INTRODUCTION

1.1. Basics of Supercritical Fluid Extraction

Each gas has a temperature above which cannot be liquefied regardless of the applied pressure. This temperature is called the critical temperature and the pressure required to liquefy the gas at this temperature is called the critical pressure. The fluid above this critical temperature and pressure is called a supercritical fluid (SCF) (Mchugh and Krukonis, 1994). The SCF region on a phase diagram of a pure component is shown in the pressure temperature diagram in Figure 1.1.

In the traditional extraction process, generally liquid solvents are used because of their high solubilizing power (Zhang et al., 1995). Since, vapors and gases have low solubilizing power, the gas-phase extractions have been performed at elevated pressures and temperatures. SCFs are highly compressible in the vicinity of their critical points where large density changes can be caused by relatively small changes in either pressure or temperature. Higher densities of SCFs result in greater solvent power towards materials that normally have low solubility in gas or liquid state of the fluid (Teberikler, 2001). Besides improved solubilizing properties, SCFs have extremely high diffusion coefficients, resembling that of a natural gas. SCFs also have viscosities similar to that of gas phases (Starmans and Nijhius, 1996). Physical properties of different fluid states are given in Table 1.1.

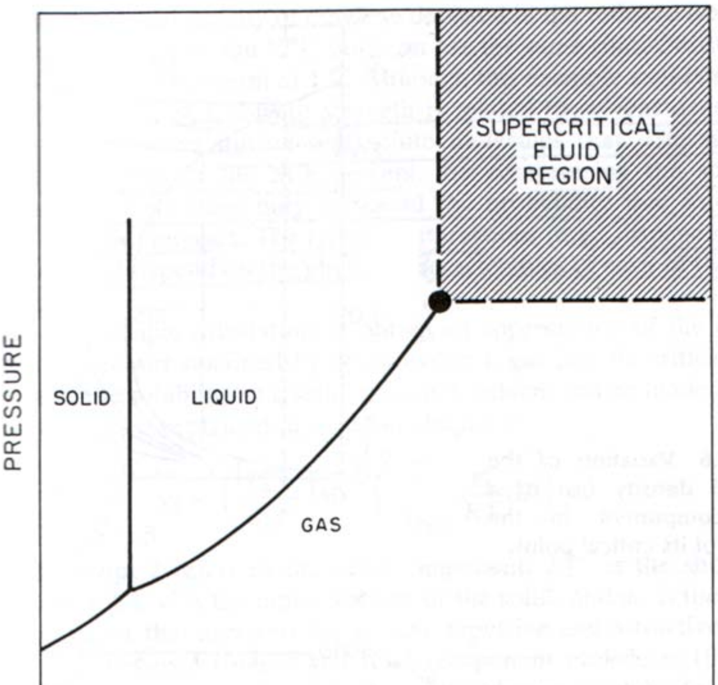


Figure 1.1. Pressure temperature diagram of a pure component (Mchugh and Krukonis, 1994).

Table 1.1. Physical properties of different fluid states (Rizvi et al., 1986)

State of Fluid	Density (kg/m^3)	Diffusivity (m^2/s)	Viscosity (kg/ms)
Gas	0.6-2	$1x10^{-5}$-$4x10^{-5}$	$1x10^{-5}$-$3x10^{-5}$
Liquid	600-1600	$0.2x10^{-9}$-$2x10^{-9}$	$0.2x10^{-3}$-$3x10^{-3}$
Supercritical			
$P=P_c$, $T= T_c$	200-500	$7x10^{-8}$	$1x10^{-5}$-$3x10^{-5}$
$P=4P_c$,$T=T_c$	400-900	$2x10^{-8}$	$3x10^{-5}$-$9x10^{-5}$

Conventional methods such as solvent extraction and soxhlet, although effective for extraction, can lead to degradation of heat sensitive compounds as well as leave traces of toxic solvents in the solute. This is a concern for food and medicinal extracts, because of the increasing regulation of solvents used. On the other hand, supercritical fluid extraction (SFE), with its advantages, attracts the interest of process engineers. With SFE higher yields and better quality products can be achieved. One particular application, where the process is proved to be useful, is the recovery of high-value and low-volume end products from dilute process streams that are typical of many specialty chemical, pharmaceutical, and biotechnology processes. In addition, SFE can be operated under a wide range of conditions to selectively extract specific end products or new products with improved functional or nutritional characteristics for use as building blocks in creating new formulated foods (Rizvi et al., 1986; Tonthubthimthong et al., 2001).

Although SFE is a viable alternative to solvent extraction, it has been slow to find commercial applications, due in part to the sophisticated and expensive high pressure equipment and technology required (Tonthubthimthong et al., 2001). Most of the researches have been carried out in SFE of oilseeds, however, commercial SFE applications involve decaffeination of coffee and tea, extraction of hops, flavors and spices where the products have high economical values (King and Bott, 1993). On the other hand, economical analysis of the processing of milk fat by supercritical carbon dioxide (SC-CO_2), shows that the operation is viable, if it is continuous with high capacity (Raj et al., 1993).

1.1.1. Selection of a SCF

Selection of a SCF for the extraction of natural materials is important for the selectivity and yield of the product. The critical temperature and pressure of a substance and its safety, availability and polarity generally considered. Critical properties of some common solvents are shown in Table 1.2. High pressure increases the cost of the equipment and high temperature may destroy heat sensitive materials. Ammonia is toxic and propane is explosive. Water has high

Table 1.2. Critical properties of various solvents (McHugh and Krukonis, 1994)

Solvents	T_c (^oC)	P_c (bar)
Ethylene	10	50
Carbon dioxide	31	74
Ethane	32	49
Propane	97	43
Ammonia	132	114
Methanol	240	81
Ethanol	241	61
Toluene	319	41
Water	374	221

critical temperature and it is polar in nature. Therefore, carbon dioxide (CO_2) is generally the most desirable solvent for SFE of natural products and the reasons of choosing CO_2 as the extraction medium (Zhang et al., 1995; Starmans and Nijhius, 1996; Teberikler, 2001; Tonthubthimthong et al., 2001) include;

1. The critical temperature of CO_2 is only 31^{o}C, which makes it attractive for the extraction of heat sensitive compounds, i.e. the temperature of the process is low enough and does not harm the physicochemical properties of the extract,
2. It is inert in nature; thus there is no risk of side reactions such as oxidation,
3. It is non-toxic and is generally accepted as GRAS ingredient in pharmaceuticals and food,
4. It has a low polarity; the polarity of CO_2 is close to that of pentane and hexane, which are solvents commonly used in liquid extraction. Thus, a similar range of compounds can be extracted using both techniques,
5. It is non-flammable, non-explosive, inexpensive, odorless, colorless, clean solvent that leaves no solvent residue in the product.

SC-CO_2 is used in food applications as a solvent for the extraction of non-polar solutes. However, for the extraction of polar solutes, addition of a polar co-solvent is needed and generally ethanol is preferred due to its non-toxic nature (Temelli, 1992). The addition of ethanol to SC-CO_2 increases the critical pressure and temperature of the mixture. As it is shown in Table 1.3 addition of ethanol up to 7.32 mole % increases Tc and Pc of the SC-CO_2 to 52 ^{o}C and 97 bar (Gurdial et al, 1993).

Table 1.3. Change in critical properties of CO_2 with ethanol addition (Gurdial et al, 1993)

Ethanol Concentration (Mole %)	T_c (^oC)	P_c (bar)
0.95	32.7	76.5
2.14	35.3	78.3
2.78	37.2	80.7
3.66	39.0	82.5
4.64	42.1	86.1
6.38	47.0	91.9
7.32	52.0	97.4

1.2. Solubility of Solutes in SCF

The conditions consistent with the highest throughput during SFE are often defined by the solubility maxima of solutes in a critical fluid (King, 2000). Therefore, knowledge of the solubility of solutes in SCFs is required for the design and development of supercritical extraction and fractionation (Began et al., 2000).

Solubility of a solute in a supercritical solvent depends on several factors. These include the solvent density and polarity, the solute volatility (vapor pressure), molecular weight and polarity. Increase in solvent density, which depends on both temperature and pressure, increases the solubility of solutes. Higher the solutes vapor pressure easier the removal of the solute so as the solute vapor pressure increases the solubility increases (King and Bott, 1993). Presence of polar groups in the structure of the solute decreases its solubility in non-polar solvents. As molecular weight of the solute increases the solubility decreases.

1.2.1. Solubility of Vegetable Oils in SC-CO_2

One of the important factors affecting the solubility of vegetable oils in SC-CO_2 is the process condition. Process temperature and pressure affects the physical properties of the oil and the density of the solvent, therefore, the solubility of the oil. As it is shown in Fig 1.2, solubility of soybean oil in SC-CO_2 is a function of pressure and temperature. At constant temperature, as the pressure of CO_2 increases the solubility of oil increases. However at very high pressures the solubility no longer increases and starts to decrease (e.g. at 40 ^oC around 1000 bar soybean oil solubility exhibits a maximum). Such a high pressure causes the solvent to become too compact and this produces unmixing effect (King and Bott, 1993).

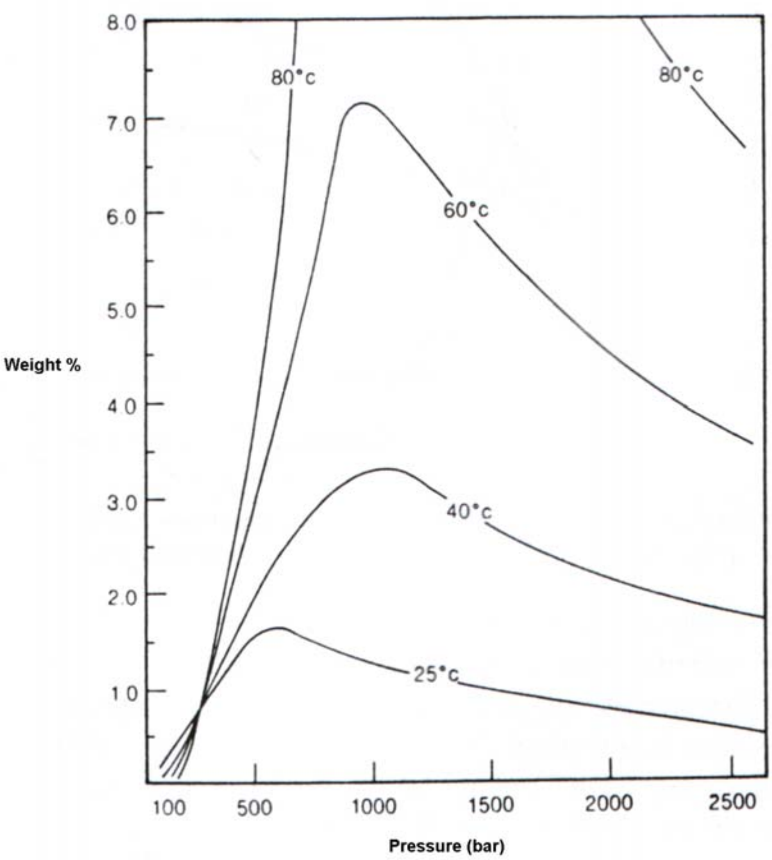


Figure 1.2. Solubility of soybean oil in SC-CO_2 (King and Bott, 1993).

However, effect of temperature at constant pressure doesn't show this trend; at low pressures the oi1 solubility decreases with temperature, whereas at higher pressures the solubility increases with temperature. The reason of this behavior is the competing effects of reduction in solvent density and the increase in solute volatility, which accompanies the temperature rise. A rise in temperature at constant pressure leads to a decrease in CO_2 density (Figure 1.3). Whereas, a rise in temperature leads to an exponential increase in the vapor pressure of the oil (King and Bott, 1993). Near the critical point of CO_2 (31°C, 73 bar) the density changes rapidly with temperature. A small temperature change in this region (increase of temperature from 32 to 50°C at 140 bar) may lead to a large change in CO_2 density (0.81 to 0.62 g/cm^3) and a resulting change in oil solubility (2.8 to 1.8 mg oil/g CO_2). At higher pressures (at 360 bar), however, the same temperature change has a smaller effect on CO_2 density (0.96 to 0.92 g/cm^3). In this case, the increase in the vapor pressure of the oil may more than offset the decreased solvent capacity of the fluid due to its decreased density. The net effect is an overall increase in solubility (9.7 to 11.1 mg oil/g CO_2) (Fattori et al., 1988; King and Bott, 1993). Therefore, generally, above the crossover pressure (250-350 bar) the solubility of oils in SC-CO_2 increase both with pressure and temperature. This behavior was observed in peanut oil (Goodrum and Kilgo, 1987), canola oil (Fattori et al., 1988; Temelli, 1992), pistachio nut oil (Palazoğlu and Balaban, 1998) and crude soylecithin lipid (Began et al., 2000).

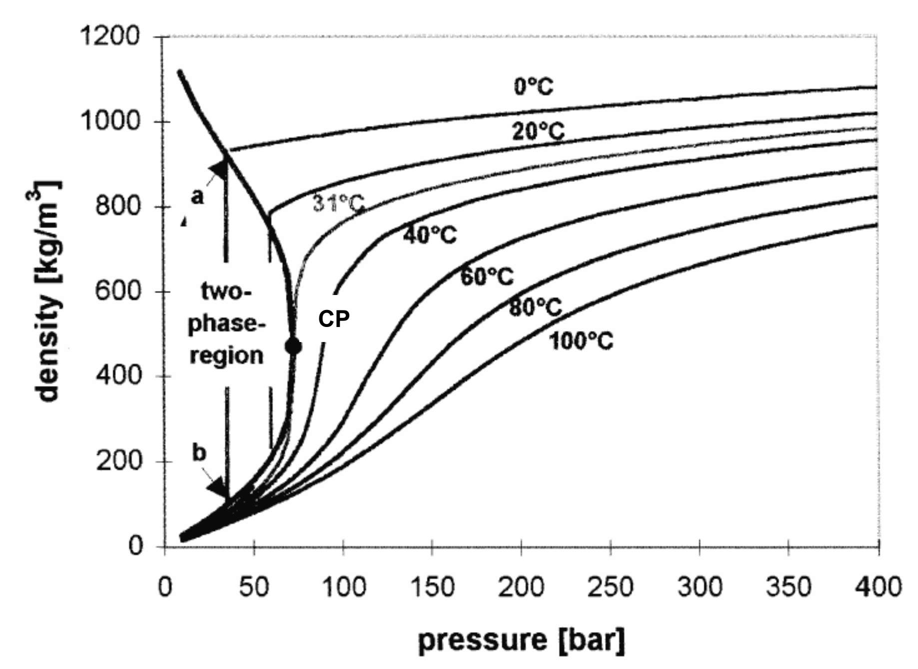


Figure 1.3. Density of CO_2 as a function of temperature and pressure (Marr and Gamse, 2000).

Besides the process conditions the properties of the oils such as molecular weight and polarity, also, affect their solubility. Polar lipids are less soluble in SC-CO_2. Esterification enhances the solubility of fatty acids in SC-CO_2 due to conversion of polar acid groups into less polar ester groups (Güclü-Üstündağ, and Temelli, 2000). Free fatty acids, mono- and diglycerides are more soluble in CO_2 than the triglycerides (Shen et al., 1997). Solubility of mono- and diglycerides are between that of free fatty acids and triglycerides (Sovová et al., 2001). Solubility of monolaurin is less than that of di- and trilaurin due to high polarity of monolaurin. However, the most soluble compounds in the mixture of mono-, di- and triglycerides composed of almost 97 % eighteen carbon fatty acids (about 59 % oleic acid) are monoglycerides (Sahle-Demisse, 1997). Triglycerides with short chain and low polarity fatty acids are more soluble in SC-CO_2 and can be easily removed from extracting materials (Hassan et al., 2000).

Solubility of polar lipids can be enhanced by addition of small amount of polar co-solvents (called entrainers or modifiers as well) which changes the polarity of SC-CO_2 at the same temperature and pressure (Temelli, 1992; Ooi et al., 1996). Co-solvent addition, such as ethanol is proved not only to increase the solubility of oils (Palazoğlu and Balaban, 1998), but improve their selectivity as well (Temelli, 1992).

Degree of unsaturation may affect solubility, however molecular weight is more important factor effecting solubility than the degree of unsaturation (Yu et al., 1994). Güclü-Üstündağ, and Temelli (2000), stated that oleic acid is more soluble than the stearic acid at 35 ^{o}C due to the decrease in the melting point as a result of the double bond present in the oleic acid. However, when both are liquid their solubility are fairly similar. They, also, indicated that large changes in solubility due to unsaturation in fatty acid esters could not be observed, where only slight changes are present, and increase or decrease in solubility of fatty acid esters with a higher degree of unsaturation are present. Therefore, effect of the unsaturation in the solubility is most probably due to the difference in the physical state of the solutes (Güclü-Üstündağ and Temelli, 2000).

These trends in solubility of oils in SC-CO_2 can be used as the basis not only for extracting the target solute, but also to affect separation from the critical fluid phase. By raising both the temperature and pressure, significant quantities of triglyceride can be solubilized in SC-CO_2 (King, 2000) and after extraction, fractional separation of the solutes could be achieved by adjusting the temperature and pressure (Starmans and Nijhius, 1996).

1.2.2. Measurement of Solubility

There are mainly three types of methods used to measure the solubility of solutes in SCFs: static, recirculation and continuous flow (dynamic) methods (King and Catchpole, 1993).

In static methods, fixed amount of solute and solvent is loaded into high-pressure cell, which may contain window, and allowed to reach equilibrium. Agitation is applied to reach equilibrium rapidly. Temperature and pressure in the cell is adjusted to dissolve all or a portion of the solute in SCF. If required, samples of the fluid phases can be taken, and analyzed. In the windowed cell sampling is not needed for binary system, conditions adjusted to reach the equilibrium by observing.

In recirculation methods, one or both phases are recirculated through the other to achieve equilibrium conditions faster. After equilibrium is reached, pressure is noted and representative samples of liquid and vapor samples are analyzed. If solid vapor equilibrium is investigated only vapor phase is recirculated.

Most of the data reported for CO_2 in literature obtained by dynamic methods where the data are obtained in flow-through apparatus. SC-CO_2 flows slowly through a bed of solids or large surface solid material wetted with liquid, becomes saturated and composition of the exit gas stream is determined after its expansion and separation of the solute from CO_2. Failure to reach equilibrium is one of the important sources of error using the dynamic method. To eliminate the error experiments must be conducted at different flow rates in descending order, to determine the one at which the solubility is no longer flow rate dependent, showing that equilibrium is reached.

1.2.3. Correlations for Solubility Prediction

There are two common approaches to correlate or predict solubility. Namely theoretical approaches using equation of state and empirical approaches. Prediction of solubility from equation of state requires tedious computational effort and physical property data that are often difficult to obtain. Furthermore, for higher molecular weight compounds like triglycerides, fats and oils, equation of state does not give good agreement with the experimental solubility results (Yu et al., 1994). Therefore, semi empirical or empirical equations are more commonly used for solubility prediction at limited temperature and pressure range.

Due to dependency of solubility on CO_2 density, which is highly sensitive to pressure changes near the critical point (Figure 1.3), the solubility of oils is correlated as a function of density of pure SC-CO_2 and temperature. One of the equations, which are commonly used for correlating the solubility behavior of oils (Güçlü-Üstündağ and Temelli, 2000; Sovová, et al., 2001), is proposed by Chrastil (1982). It is based on a hypothesis that one molecule of a solute A associates with k_1 molecules of a solvent B and forms solvato complex AB_{k_1} at equilibrium with the system. There is a linear relationship between the logarithmic solubility and logarithmic density of pure SC-CO_2, and the temperature dependency of solubility is included as,

$$c = \rho_f^{\,k_1} \exp\left(\frac{a_1}{T} + a_2\right) \qquad (1.1)$$

where c is the solubility (kg/m^3), ρ_f is density of CO_2 (kg/m^3) and T is temperature (K). The parameter k_1, slope of the solubility isotherm, is association number. It represents average number of CO_2 molecules in solvato-complex and reflects the density dependence of solubility. The constant a_1 depends on total heat of reaction (vaporization and solvation enthalpies of the solute) ($a_1 = \Delta H/R$) and shows the temperature dependence of solubility at constant density. The constant a_2 depends on molecular weights of solute and of SC-CO_2 and association constant. Güçlü-Üstündağ and Temelli (2000) estimated the constants of the Chrastil Equation for different oil classes by collecting the published data in literature. In Table 1.4 these constants and the experimental ranges of the data for monoolein, diolein and triolein are presented.

Table 1.4. Constants of Chrastil Equation for different oils (Güçlü-Üstündağ and Temelli, 2000)

Oil	Constants			Temperature Range (°C)	Pressure Range (bar)	R^2
	k_1	a_1	a_2			
Monoolein	10.68	-7925	-45.8	35-60	104-309	0.828
Diolein	10.48	-4601	-54.3	50-60	151-309	0.996
Triolein	10.28	-2057	-61.5	25-60	70-310	0.934

Second model, is improved form of the Chrastil Equation by adding one more term, is proposed by del Valle and Aguilera (1988), which is in the form,

$$c = {\rho_f}^{k_1} \exp\left(\frac{a_1}{T} + a_2 + \frac{a_3}{T^2}\right) \tag{1.2}$$

Estimated constants of this equation based on the solubility of soybean oil, sunflower oil, cottonseed oil and corn oil are,

$$c = {\rho_f}^{10.724} e^{(40.361 - \frac{18708}{T} + \frac{2186840}{T^2})} \tag{1.3}$$

In this equation solubility, *c*, is expressed in kg/m^3, temperature, *T*, is in K, while density of CO$_2$, ρ_f, is in kg/dm^3 and T is temperature in K. Eq. 1.3 was validated for the temperatures 20 to 80 ^{o}C, pressures between 150 and 880 atm and for the solubility less than 100 kg/m^3.

Another modification of the Chrastil Equation for solubility of triglycerides is given by Adachi and Lu (1983) is,

$$c = \rho_f^{\,k_1 + k_2\rho_f + k_3\rho_f^{\,2}} \exp\left(\frac{a_1}{T} + a_2\right) \tag{1.4}$$

where c is solubility (kg/m^3), ρ_f is density of CO_2 (kg/m^3) and T is temperature (K). The constants of Eq. 1.4 for combined data of refined black currant oil and rapeseed oil (Sovová et al., 2001) are,

$$c = \rho_f^{\,1.4 + 0.0048\rho_f - 0.000002\rho_f^{\,2}} e^{(-10.14 - \frac{5000}{T})} \tag{1.5}$$

Since the density of pure CO_2 is a function of temperature and pressure, non-empirical equations including pressure and temperature terms are used as well to correlate solubility in ranges studied (Yu et al., 1994, Gordillo et al., 1999, Began et al., 2000). In Equation 1.6 solubility of crude soy lecithin lipid in SC-CO_2 in the rages of 120 to 280 bar and 40 to 60 ^oC is represented as (Began et al., 2000),

$$y_r = -3.237 + 0.0431P - 7.3 \times 10^{-5} P^2 - 1.1 \times 10^{-4} PT \tag{1.6}$$

where y_r is total lipid solubility (g/kg CO_2), P is pressure (bar) and T is temperature (^oC).

1.3. Supercritical Fluid Extraction and Fractionation of Vegetable Oils

1.3.1. Process Configurations Used for SFE

An SFE system consists of four basic components: a solvent compressor or pump, an extractor, a temperature/pressure-control system, and a separator. Additionally, other equipment, including ancillary pumps, valves, back pressure regulators, flow meters, and heater/coolers for temperature control of the fluid are needed for proper operation of the process (Rizvi et al., 1986).

There are four common processing configurations used for SFE, based on the separation of the solute from solvent. After charging the extractor, extraction occurs at a temperature where the desired product's solubility is maximized, and then the solute is separated from the solvent. In the first configuration temperature is manipulated to remove the desired solute from the solvent. The solute-laden solvent is passed through a heat exchanger and the temperature is adjusted to minimize the solubility in the supercritical phase. After collecting the solute in the separator, the solute-lean solvent can be recompressed (or liquefied in the condenser by decreasing the temperature and re-pressurized to supercritical conditions with a pump (Starmans and Nijhius, 1996) and recycled to the extractor (Rizvi et al., 1986). In the second configuration pressure is manipulated to separate the desired solute from the solvent. The solute-laden solvent exiting the extractor is passed through a valve where the pressure is decreased and the solute separates out. The solvent may be recompressed and recycled, or simply vented from the system. The third configuration-the fixed-bed method-involves removal of solutes from the solvent stream by means of a suitable adsorbing material such as activated carbon at isothermal and isobaric conditions (Rizvi et al., 1986). The fourth configuration uses an absorber at isothermal and isobaric conditions for removal of solute (Eggers, 1995).

In fractionation applications usually two configurations are used. First one applies several separator vessels operated at different pressure temperature combinations after extraction (e.g. stepwise decrease of pressure) (Ooi et al., 1996). Second one applies thermal gradient separation in a packed column including separately heated zones, where the temperature increased from first to last, and therefore creating a density gradient along the column (King et al., 1997). Fractionation of natural materials by collection of extracts at different time intervals is also applied (Gomez et Al., 1996, Hassan et al., 2000). Combinations of these schemes can, and are, used in practice, depending on the objectives of the separation and the phase equilibria of the compounds involved.

1.3.2. Applications of SFE to Vegetable Oils

Various studies have shown that SC-CO_2 is very effective in removing oil from different seed matrices. These include extraction of oils from plant materials (seeds and nuts), fractionation and refining of crude vegetable oils (Table 1.5).

Parameters which effect the SFE of oil from plant materials are divided into two main groups: First group includes specific features of the material, as bulk density, oil content, specific surface, pore diameter, porosity, particle size and geometry and moisture content. Second group includes parameters of the process as extraction pressure and temperature, separation pressure, superficial solvent velocity, vessel geometry and residence time (Eggers, 1996).

High moisture content in the plant material before starting SFE is generally a disadvantage. The influence of moisture on oil mass transfer is negligible in the range between 3 and 12% by weight; but additional moisture in oilseeds leads to an increase in extraction time. For extraction pressures above 200 bar the solubility of triglycerides in CO_2 is much higher than that of water. Only at the end of the extraction the water content of the extract increases considerably (Eggers, 1996). Increasing the moisture content of peanuts increases the volatile loss as well (Goodrum and Kilgo, 1987). On the other hand, during the extraction of caffeine from raw coffee, water swells the beans and the enhanced solubility of caffeine in water influences the mass transfer (Eggers, 1996).

Table 1.5. Selected SFE applications to vegetable oils

Application	Reference
Extraction	
Rape seed oil	Eggers, 1985
Peanut oil	Goodrum and Kilgo, 1987 Santerre et al., 1994
Canola oil	Fattori et al., 1988 Temelli, 1992
Grape seed oil	Gomez et al., 1996
Almond oil	Marrone et al., 1998 Passey and Groslouis, 1993
Pecan oil	Zhang et al., 1995
Hazelnut oil	Ünal and Pala, 1996
Pistachio nut oil	Palazoğlu and Balaban, 1998
Fermented Çupuaçu seed oil	Azevedo et al., 2003
Rosa hip oil	Szentmihalyi et al., 2002
Sunflower seed oil	Kriamiti et al., 2002
Olive oil	Hurtado-Benavides et al., 2004
Fractionation and Refining	
Canola oil	Fattori et al., 1987
Olive oil	Brunetti et al., 1989
Soybean oil	List et al., 1993
Palm oil	Ooi et al., 1996
Rice bran oil	Shen et al.,1997
Palm kernel oil	Hassan et al., 2000 Norulaini et al., 2004
Crude palm oil	Markom et al., 2001

Mechanical pretreatment of plant material has a major effect on extraction of oils. Only the surface oil is directly contacted by SC-CO_2, so the amount of surface area presumably limits the kinetics as well as the oil recovery (Goodrom and Kilgo, 1987). Large particles lead to a distinct, diffusion-dominated extraction and long processing times, due to their small specific surface area (Eggers, 1996). Therefore, for rapid and complete oil recovery, oil seeds must be ground or flaked to rupture the cell walls and to maximize CO_2 contact with the oil (Goodrom and Kilgo, 1987). Extraction yield of rapeseed oil at 750 bar and 40^{o}C increased when different mechanical pretreatments including decorticating, flaking and pressing were applied. The best results were obtained with a flaked rapeseed press cake (Eggers, 1985). It was reported that, decreasing the particle size to 0.864 mm increased the overall yield of peanut oil (Goodrum and Kilgo, 1987). Gomez et al. (1996) stated that the desired milled grape seed size was 0.35 mm or smaller for high process efficiency.

Recovery of a solute from a natural material is highly dependent on the flux of the solute removed under specific conditions, and the flux is a complex function of both solubility and diffusion (i.e., mass transfer) in the critical fluid medium (King, 2000). The solubility behavior of the oils is directly related with temperature and pressure. Zhang et al. (1995) reported that, the amount of oil recovered from whole pecan increases with temperature and pressure, but temperature has more effect than pressure on the yield, in the ranges of 40 to 80 ^{o}C and 177 to 689 bar. The maximum extraction oil yield from roasted pistachio nuts was obtained at 345 bar and 60^{o}C with 10 % ethanol over the ranges of 50 to 70 ^{o}C, 207 to 345 bar and 0 to 10% ethanol (Palazoğlu and Balaban, 1998).

Besides temperature and pressure, flow rate is also an important parameter in SFE. The specific mass flow must be optimized per unit weight of the oilseed to be extracted. Increasing the solvent flow reduces the residence time but increases the solvent requirement. However, the residence time of the solvent in the extraction vessel should not be too long, resulting in a long extraction time (Eggers, 1996). Gomez et al. (1996) stated that, the yield of grape seed oil increases with flow rate up to 1.5 l/min within 3 h operation.

In fractionation applications, separation pressures and temperatures has great importance, due to their effects on solubility. Shen et al. (1997) studied fractionation of rice bran oil in two-stage process: After extraction at 40^{o}C and 241 bar, oil is passed through a fractionator column operated at various temperatures and pressures. Some of the solute (oil phase) precipitates in the fractionator to form raffinate at the bottom, while others carried out with SC-CO$_2$ and separated after depressurization in a separation vessel. By this way, fractionation removes almost all of the water and reduces the free fatty acid concentration in raffinate to 50 %, if fractionator kept at 40 ^{o}C and 112 bar.

Fractionation also could be done by sample collection at different time intervals. Gomez et al. (1996) fractionated grape seed oil at 40^{o}C and 200 bar and Hassan et al. (2000) fractionated the palm kernel oil at 70^{o}C and 345 bar. Earlier fractions of grape seed oil contained less linoleic acid (C18:2) than the later fractions. Earlier fractions of palm kernel oil were solid and white where the last fractions were liquid and yellowish. From initial to final fraction, concentration of lauric acid (C12:0) decreased and that of oleic acid (C18:1) increased. Hassan et al. (2000), also, indicated that, increasing pressure reduced the fractionation effect. Markom et al. (2001), fractionated crude palm oil at conditions 40, 50 and 60^{o}C and 110, 140 and 200 bar by collecting different fractions at various time intervals, also. They indicated that the system pressure was more significant than temperature in fractionation. While compositions of small fatty acids (C12:0, C14:0, C16:0) decreased, compositions of larger ones (C18:1, C18:2, C20:0) increased from first to last fractions of palm oil at 50 ^{o}C and 140 bar.

Thermal gradient separation of glyceride mixtures in a packed bed column including separately heated zones is also possible (King et al., 1997 and Sahle-Demissie, 1997). To obtain monoglyceride rich fractions, temperature in the column was increased from first (bottom) to last (top) zone to enable concentration of higher vapor pressure monoglyceride at the top of the column. Best result was obtained at 207 bar with linear temperature gradient varying from 65 to 95 ^oC (King et al., 1997).

1.4. Mathematical Modeling of SC-CO_2 Extraction of Plant Matrices

An extraction system involves a fluid phase, the supercritical solvent and dissolved extracts, and a solid phase retained in the extraction vessel. During extraction mass transfer occurs between two phases, extractable materials in solid phase dissolves in bulk fluid. The mechanism of dissolution could be relatively simple if material is free on the surface. However, it could be more complex when the extracted materials are located within pores or develop interaction with non-extractable part of the solid. The mass transfer proceeds by diffusion through the matrix structures or pores, up to the bulk fluid where the components are swept along to the extractor outlet. Experimental conditions and structure of the solid matrix led to different successive mass transfer mechanisms or transition between the mass transfer mechanisms during extraction. Different models have been used to account for these mass transfer mechanisms during SFE of natural products. These models can be classified as,

(1) Empirical models (Kandiah and Spiro, 1990; Subra et al., 1998; Papamichail et al. 2000)

(2) Models based on heat transfer analogy (Reverchon et al., 1993; Esquivel et al., 1999)

(3) Models based on differential mass balance (Sovová, 1994; Perrut et al., 1997; Marrone et al., 1998; Reverchon and Marrone, 2001)

(4) Shrinking core model (Catchpole et al., 1996; Roy et al., 1996; Akgün et al., 2000; Döker et al., 2004).

Empirical models are useful, if the information on the mass transfer mechanisms and on the equilibrium relations are not present. The empirical model considers the extractor as a “black box” and one adjustable parameter that is obtained by fitting the experimental kinetic curve describes the extraction (Subra et al., 1998).

Models based on heat transfer analogy assume SFE as a heat transfer phenomenon. Each single particle is considered as a hot ball cooling in a uniform medium. Components to be extracted are assumed to be uniformly distributed inside the particle and all particles are assumed to be at the same extraction conditions in the whole bed. The model overestimates the extraction yield since it considers the ideal extraction behavior for each single particle and neglects their interactions (Reverchon et al., 1993).

Most of the models based on differential mass balance equations include the resistances in both or one of the bulk phases. They take into account particle and bed characteristics via porosity and diameter. Although the models imply many assumptions and/or determination of several coefficients involved in the equations, they reflect the various mechanisms that contribute to overall behavior of an extraction process (Subra et al., 1998). Some authors modeled the extraction of oil from oilseeds taking into account only the mass transfer resistance in the fluid phase (Bulley et al., 1984; Lee et al., 1986; Fattori et al., 1988). On the other hand, mass transfer resistance in the solid phase was found to be important in the case of sage leaves essential oil (Reverchon, 1996). Sovová (1994) proposed a model for extraction of vegetable oils including the resistances both in the fluid and solid phases by introducing the physical description of the vegetable substrate. Štastová et al. (1996), used modified and improved form of the simplified solution by introducing new terms to simplify the solution. França and Meireles (2000), Povh et al. (2001) and Ferreire and Meireles (2002), also, used Sovová's (1994) simplified solution in their studies. Marrone et al. (1998) and Revechon and Marrone (2001) used similar approach for almond oil extraction and various seeds oil extraction, respectively.

Shrinking-core model has been also applied to the SFE of plant matrices (King and Catchpole, 1993; Catchpole et al., 1996; Goto et al. 1996; Akgün et al., 2000; Döker et al., 2004). This model is applicable for the porous solid particles that has no affinity for the liquid solute trapped in the pores. Model assumes a sharp boundary between the solute and solvent, as the solute extracted this boundary shrinks towards the center of the particle.

1.4.1. Broken and Intact Cells Model for SC-CO_2 Extraction of Vegetable Oil

The model, proposed for vegetable oil extraction by Sovová (1994) and improved by Štastová et al. (1996), is based on differential mass balance equations in a fixed bed extractor. Model assumes that, vegetable oil (solute) is deposited in the oil cells of the vegetable matrix and protected by cell walls. Some of the cells are broken up during grinding and a part of the oil is released from the cells and directly proposed to the solvent on the surface of the particles. The mass of the oil in the solid phase initially contained, O, consists of mass of released oil, R, and mass of unreleased oil inside the intact cells of the particles, K:

$$O = R + K \tag{1.7}$$

The mass of oil free solid phase, N, remains constant during the extraction. Amounts of the oils are related to this quantity so that the initial concentrations are

$$X\,(t = 0) = x_0 = O/N = x_R + x_K = R/N + K/N \tag{1.8}$$

Further assumptions used are:

- Plug flow of the solvent in the fixed bed,
- Axial dispersion is negligible,
- Initial oil content of the particles is x_0,
- Temperature, pressure and bed void fraction (ε) are constant during the extraction in the bed,
- The solid bed is homogenous with respect to both particle size and initial distribution of the solid,
- Solute accumulation in the solvent is negligible.

The material balance in a volume element of the cylindrical bed for the solid phase is;

$$-\rho_s(1-\varepsilon)\frac{\partial x}{\partial t} = J(x, y) \tag{1.9}$$

and for the fluid phase is

$$\rho_s(1-\varepsilon)\frac{\dot{Q}}{N}\frac{\partial y}{\partial h} = J(x,y) \tag{1.10}$$

where, *h*, is dimensionless height of the bed.

Boundary conditions are:

$$x(h, t = 0) = x_o \quad y(h = 0, t) = 0 \tag{1.11}$$

The mass of the extracted oil from the fixed bed is:

$$E = Q\int_0^t y(h=1,t)dt \tag{1.12}$$

Concentration of the released oil (g free oil/g solid) in the bed is Gx_0 at the beginning of the extraction. The grinding efficiency, *G*, shows the ratio of the released oil to total oil in the bed. Extraction occurs in two periods as fast and slow extraction periods. The released oil is extracted in the fast extraction period with a rate controlled by its diffusion and convection in the solvent,

$$J(x,y) = k_f a \rho_f (y_r - y) \quad \text{for } x > (1-G)\,x_0 \tag{1.13}$$

When the released oil is removed, the unreleased oil in the intact cells is extracted in the slow extraction period with a rate controlled by the diffusion of the oil from the interior of the particles to the surface. Instead of taking into account the complex nature of the vegetable matrix, the mass transfer is expressed with solid phase mass transfer coefficient, $k_s a$,

$$J(x,y) = k_s a \rho_s (x - x^+) \quad \text{for } x \leq (1\text{-}G)\, x_0 \tag{1.14}$$

If extraction rate in the solid side is too small compared to the fluid side, i.e. $k_s << k_f$, Eq. 1.14 can be re arranged as;

$$J(x,y) = k_s a \rho_s x(1 - y/y_r) \quad \text{for } x \leq (1\text{-}G)\, x_0 \tag{1.15}$$

Approximate solution for this condition gives the oil recovery as (g oil extracted/ g oil initially present in the bed);

$$\frac{E}{Nx_0} = \begin{cases} \psi[1 - \exp(-Z)] & for \quad \psi < \dfrac{G}{Z} \\ \psi - \dfrac{G}{Z}\exp[Z(h_k - 1] & for \quad \dfrac{G}{Z} \leq \psi \leq \psi_k \\ 1 - \dfrac{1}{Y}\ln\left\{1 + [\exp(Y) - 1]\exp\left[Y(\dfrac{G}{Z} - \psi)\right](1 - G)\right\} & for \quad \psi \geq \psi_k \end{cases} \tag{1.16}$$

where, Ψ is dimensionless time which is defined as,

$$\Psi = t\,\dot{Q}\,y_r / (N\,x_0) \tag{1.17}$$

The released oil is extracted inside the bed until the dimensionless time G/Z. Two regions exist inside the bed in the interval of dimensionless time Ψ from G/Z to Ψ_k;

$$\psi_k = \frac{G}{Z} + \frac{1}{Y}\ln(1 - G[1 - \exp(Y)]) \tag{1.18}$$

Ψ_k is the dimensionless time when the released oil in the bed is totally extracted. The dimensionless coordinate of the division between the two regions is h_k,

$$h_k = \frac{1}{Y}\ln\left[1 + \left\{\exp\left[Y\left(\psi - \frac{G}{Z}\right)\right] - 1\right\} \Big/ G\right] \qquad \text{for } \frac{G}{Z} \le \psi \le \psi_k\,. \tag{1.19}$$

It is a boundary between the parts of bed that the unreleased oil and the released oil are being extracted. As the free oil is extracted first from the top (entrance) of the bed it moves from top to bottom between G/Z to Ψ_k. After dimensionless time Ψ_k, only the unreleased oil is extracted in the bed.

Z and Y are the dimensionless parameters of the model and they are proportional to the mass transfer coefficients,

$$Z = \frac{Nk_f a \rho_f}{\dot{Q}(1-\varepsilon)\rho_s} \tag{1.20}$$

$$Y = \frac{Nk_s a x_0}{\dot{Q}(1-\varepsilon) y_r} \tag{1.21}$$

Therefore, the model has four adjustable parameters (*G*, Ψ_k, *Z* and *Y*) that are determined by minimizing the errors between experimental and calculated results.

1.5. Response Surface Methodology

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experimental designs to determine and simultaneously solve multivariate equations. These equations can be graphically represented as response surfaces which can be used in three ways: (1) to describe how the test variables affect the response; (2) to determine the interrelationships among the test variables; and (3) to describe the combined effect of all test variables on the response (Giovanni, 1983).

Due to the advantage of being easy to fit using multiple regressions, the following second order model is often preferred in RSM studies:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i \le j}^{k} \beta_{ij} x_i x_j \qquad (1.22)$$

where β_0, βi, β_{ij} are constant coefficients.

One of the common experimental designs used in engineering purposes is the Box Bhenken design that includes three levels of independent variables rather than 4 and 5 levels used in other designs, such as central composite design and San Cristobal design. Therefore, it requires relatively few amounts of experimental data (Thomson, 1982).

Estimation of the model parameters in RSM is done by linear least squares regression. Than the estimated model is tested for the adequacy and if it not satisfactory mathematical transformations could be done (Thomson, 1982).

Due to its efficiency and less data requirement compared to the classical methods, RSM is increasingly being used for optimization purposes (Giovanni, 1983; Began et al., 2000). Response surfaces of essential oil of Turkish lavender flowers (Adaşoğlu et al., 1994), onion oleoresin yield (Sass-Kiss et al., 1998), pistachio nut oil yield (Palazoğlu and Balaban, 1998), turmeric oil yield (Began et al., 2000) and *Thymbra spicata* essential oil (Sonsuzer et al., 2004) in SC-CO_2 are some selected studies reported in literature.

1.6. Aims and Scope of the Study

Table 1.6, shows the data taken from the website of the USDA (2001) and summarizes oil contents and fatty acid compositions of selected vegetable materials. It is obvious that nuts have high oil contents, which are rich in unsaturated fatty acids, especially linoleic (C18:2) and oleic (C18:1) acids. Linoleic acid is an essential fatty acid. Essential fatty acids and their longer chain-molecular products are necessary for maintenance of growth and reproduction, and they are one of the main stones of the biological membranes (Eastwood, 1997). Furthermore, it is

Table 1.6. Oil contents and fatty acid compositions of various plant materials (USDA, 2001)

Seed	Lipids (%)	Protein (%)	Water (%)	Unsaturated Total	Fatty Acid Compositions (%)*							
					C14:0	C16:0	C18:0	C16:1	C18:1	C18:2	C18:3	C20:1
Safflower Seed Kernels	38	16	5.6	86.0	0.1	8.0	2.5	0.1	14.0	73.0	0.3	
Sunflower	50	23	5.4	85.0	0.1	5.5	4.5	0.1	18.5	65.0	0.1	0.1
Canola				88.5		4.0	1.8	0.2	56.1	20.3	9.3	1.7
Soybean	20	36	8.5	85.0		10.0	2.4	1.0	24.0	51.0	7.0	
Sesame Seed Whole	50	18	4.7	85.0	0.2	8.9	4.8	0.2	39.3	41.3	0.3	0.2
Apricot Kernel	40	21		90.0		5.8	0.5	1.5	58.5	29.3		
Pistachio nut	44	21	4.0	83.6		11.0	1.0	1.0	51.0	30.0	0.5	0.2
Walnut	65	15	4.1	86.1		7.0	2.0	0.1	22.2	53.0	10.4	0.4
Hazelnut	61	14	5.6	88.0	0.1	5.2	2.0	0.2	77.8	10.1		
Peanuts	49	26	6.5	78.2	0.1	9.5	2.2	0.1	44.8	32.0		1.3
Almond	51	21	5.3	87.3		6.5	1.7	0.6	69.4	17.0		

* C14:0, myristic acid; C16:0, palmitic acid, C18:0, stearic acid, C16:1, palmitoleic acid; C18:1, oleic acid; C18:2, linoleic acid; C18:3, linolenic acid; C20:1, gadoleic acid.

known that oleic acid is an unsaturated fatty acid that increases the stability of vegetable oil and reduces cholesterol level in the enriched diets (Şimşek and Aslantaş, 1999). Besides the health benefits, these fatty acids improve the physical properties (e.g. spredibility) of margarine and butter formulations because of their lower viscosities compared to saturated fats. Therefore, extraction of oils from nuts and seeds using SC-CO_2 are studied in many researches (Table 1.5). However, researches including apricot kernel oil are scarce and it has not been processed by SFE.

Apricot kernels contain about 40 % oil, and this oil contains 60 % oleic acid and 30% linoleic acid (Table 1.6). The largest production of apricot in the World is in Turkey, which is about 500.000 tons/year (DİE, 1999). Most of the harvested apricots are processed in fruit juice industry or dried.

Design and optimization of the SFE process requires the knowledge of solubility and mass transfer behavior and related data. Vegetable matrices and their oils are complex structures leads to changes in solubility and mass transfer behavior for different vegetables. Therefore, aims of SFE of apricot kernel included are:

1. To determine the solubility of apricot kernel oil in SC-CO_2 and to represent the solubility behavior with an appropriate model,

2. To determine the effects of process parameters (particle diameter, solvent flow rate, pressure, temperature and ethanol concentration as a co-solvent) on the extraction of apricot kernel oil,
3. To represent the extraction data with suitable mass transfer model and to evaluate of the mass transfer coefficients in both fluid phase (k_fa) and solid phase (k_sa),
4. To obtain Response Surface Model for extraction yield including effects of flow rate, pressure, temperature and co-solvent (ethanol) concentration,
5. To investigate possible fractionation, to obtain linoleic acid rich fractions.

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

Unshelled and dried apricot kernel samples were obtained from local market and stored at +4^{o}C in sealed glass jars. The moisture and oil contents were 3.9 % and 48.1 %, respectively. Without any pretreatment samples were chopped into small size by using kitchen type chopper (Arçelik, Turkey), sieved and fractionated according to particle size by certified test sieves (Endecotts Ltd., London, England). Sieving (if possible) was performed by a shaker (Octagon 200, Endecotts Ltd., London, England). The fractions between two successive sieves were assigned a size number as shown in Table 2.1. A definite mean particle diameter could not be defined for small sized fractions due to difficulty in sieving smaller particles. High degree of grinding released the oil in the oil cells of the apricot kernel and this caused adhesion of particles and inhibition of further sieving by a shaker. CO_2 was purchased from Habaş (Turkey).

Table 2.1. Size specifications of the apricot kernel fractions

Particle Size	Sieve Openings (mm)	Dp_m (mm)
1	Pan-0.425	< 0.425
2	Pan-0.85	< 0.850
3	0.85-1.0	0.92
4	1.0-2.0	1.5

2.2. Methods

2.2.1. Analytical Methods

Moisture content of the samples was determined using AOAC Method 926.12 (AOAC, 1995).

Total fat determination and extraction of oil with hexane were done with soxhlet (Nas et al., 1992), where 5.0 g of samples were extracted using *n*-hexane with 8 hour extraction time.

Extracted oils were esterified using boron thrifluoride solution in methanol according to AOAC Method 969.33 (AOAC, 1995) and analyzed using gas chromatography (GC-14A, Shimadzu, Kyoto, Japan) equipped with FID and a 30 m fused capillary column with 0.25 mm inner diameter and 0.20 μm film thickness (SP2330, Supelco, Bellefonte, PA). Carrier gas was helium and working temperature of the injector, column and detector were 240, 190 and 250 ^{o}C, respectively. Samples were injected with split ratio of 1:50 and split flow rate was 2 ml/min.

2.2.2. Density Measurement

True density of oil free solid particles was determined from the formula, $\rho_p = m / V_p$. m is mass of solid particle and V_p is the particle volume, determined by gas displacement method (Karathanos and Saravacos, 1993), with a nitrogen stereopycnometer (Quantachrome, Boynton Beach, FL).

2.3. Supercritical Fluid Extraction System

The solubility measurements and SFE experiments were performed by using Supercritical Fluid Extraction System (SFX System 2120, Isco Inc., Lincoln, NE). Fluid flow diagram of the extraction system is presented in Figure E1. The system consists of an extractor (SFX 220) and two syringe pumps (Model 100DX). The pumps could pump up to 690 bar with flow rates ranging between 0.1 μL/min to 50 ml/min which is controlled and measured by the pumps. The temperature in the extractor chamber could be controlled up to 150 ^{o}C and the system enables addition of co-solvent if required. The extractor is a 10 ml steel cartridge. SC-CO_2 flows downward in the extractor. The extract was passed through a coaxially heated adjustable restrictor. The extracted oil was precipitated in test tubes containing glass wool. Amount of oil was measured gravimetrically.

2.4. Solubility Measurement and Modeling

The solubility of apricot kernel oil in SC-CO_2 was measured at 150, 300, 450, 525 and 600 bar and each at 40, 50 and 60^{o}C by using apricot kernel samples of particle size 2 (Table 2.1). Before the extraction starts 2 min stabilisation is allowed to provide saturation at the start. SC-CO_2 flow rate was kept lower than 0.5 g/min to assure saturation since the oil concentration was determined to be dependent on flow rate at higher values. Amount of collected oil was measured with time and the solubility was calculated as mg oil/g CO_2 from the slopes of the linear part of each extraction curve.

Solubility behavior was represented by the Chrastil (Eq. 1.1), del Valle and Aguilera (Eq. 1.2) and Adachi and Lu (Eq. 1.4) Equations by performing a multilinear regression to determine the model constants. Besides these models an empirical model equation representing the solubility of apricot kernel oil in SC-CO_2 within the experimental range as a function of pressure and temperature was proposed.

The accuracy of the models were quantified by analysis of variance and average absolute deviation (AAD) defined as,

$$\text{AAD (\%)} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{y_{\text{experimental}} - y_{\text{model}}}{y_{\text{experimental}}}\right|_i \times 100 \tag{2.1}$$

where n is the number of data, $y_{\text{experimantal}}$ and y_{model} are data obtained from experiment and model equations, respectively at the i^{th} condition.

2.5. Extraction

2.5.1. Experimental Design for Mass Transfer Model

Effects of particle size (sizes 1, 2, 3 and 4 (Table 2.1)), solvent flow rate (1, 2, 3, 4 and 5 g/min), pressure (300, 375, 450, 525 and 600 bar), temperature (40, 50, 60 and 70 ^{o}C) and co-solvent (ethanol) concentration (0, 0.5, 1.0, 1.5 and 3.0 % by weight) on extraction yield were investigated. The standard extraction conditions were selected as, particle size 2, 3 g/min solvent flow rate, 450 bar, 50 ^oC and 0 % ethanol addition. One parameter was changed at a time while the other parameters were kept constant at these standard conditions.

To perform extractions, about 5 g of the sample was placed into the 10 ml extractor. Solvent containing the extract was passed through a coaxially heated adjustable restrictor where temperature was set above 110^oC. During the extraction the extracted oil was precipitated in test tubes containing glass wool and its amount was measured gravimetrically. Extracted oils were collected at definite time intervals until no significant amount of oil was extracted.

Then, experimental data obtained were fitted to modified form of the broken and intact cells model (Eq. 1.16). Adjustable parameters of the model; G, Ψ_k, Z and Y were evaluated by minimizing AAD values (Eq. 2.1) between experimental and calculated yield values. These parameters were used to determine, the time for fast extraction period (t_k) (Eq. 1.17 and 1.18), yield value reached at this time (w_k) (Eq. 1.16), volume mass transfer coefficients in the fluid phase (k_fa) (Eq. 1.20) and solid phase (k_sa) (Eq. 1.21).

2.5.2. Experimental Design for RSM

Extraction yield was modelled as a function of pressure, temperature, solvent flow rate and co-solvent (ethanol) concentration by Response Surface Methodology. The three level Box-Behnken Design with four independent variables was applied for response function fitting. Particle size 2 (Table 2.1) was used in the extractions. Oil yields obtained after 15 min of extraction were used in the estimation complex response function.

The coded values of the independent variables were found from equations,

$$X_1 = \frac{flow\ \ rate - 3}{1} \qquad (2.2)$$

$$X_2 = \frac{pressure - 375}{75} \qquad (2.3)$$

$$X_3 = \frac{temperature - 50}{10} \qquad (2.4)$$

$$X_4 = \frac{ethanol\ \ \% - 1.5}{1.5} \qquad (2.5)$$

and are given in Table 2.2.

Table 2.2. Coded levels of the independent variables for Box-Behnken Design

Independent Variables	**Coded Levels**		
	-1	**0**	**+1**
X_1: Flow Rate (g/min)	2	3	4
X_2: Pressure (bar)	300	375	450
X_3: Temperature (^{o}C)	40	50	60
X_4: Ethanol Concentration (%)	0.0	1.5	3.0

The experimental design is presented in Table 2.3 and the expected form of the response surface model is in the form of,

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{44}X_4^2 + \\ a_{12}X_1X_2 + a_{13}X_1X_3 + a_{14}X_1X_4 + a_{23}X_2X_3 + a_{24}X_2X_4 + a_{34}X_3X_4 \qquad (2.5)$$

Y represents the total oil yield in SC-CO_2 as g oil / g kernel feed and a_{ij} values are coefficients of the function. The evaluation of the model was performed using Minitab software (Minitab Inc., Minitab release 12.1, 1998).

Table 2.3. Three level Box-Behnken Design with four independent variables

Standard Order	Experiment No.	X_1	X_2	X_3	X_4
1	12	-1	-1	0	0
2	5	+1	-1	0	0
3	17	-1	+1	0	0
4	16	+1	+1	0	0
5	19	0	0	-1	-1
6	1	0	0	+1	-1
7	8	0	0	-1	+1
8	18	0	0	+1	+1
9	21	-1	0	-1	0
10	27	+1	0	-1	0
11	13	-1	0	+1	0
12	20	+1	0	+1	0
13	10	0	-1	0	-1
14	7	0	+1	0	-1
15	26	0	-1	0	+1
16	15	0	+1	0	+1
17	11	-1	0	0	-1
18	2	+1	0	0	-1
19	14	-1	0	0	+1
20	3	+1	0	0	+1
21	9	0	-1	-1	0
22	23	0	+1	-1	0
23	22	0	-1	+1	0
24	6	0	+1	+1	0
25	24	0	0	0	0
26	4	0	0	0	0
27	25	0	0	0	0

2.6. Fractionation

For fractionation purposes, two set of extraction were performed. In the first set, extraction was performed at 300 bar and 50 ^{o}C, and fractions were collected between time intervals of 0-15, 30-60, 120-150 min. In the second set, extraction was performed at 50 ^{o}C in two successive periods of 30 min, the former at 150 bar and the later at 400 bar. The fractions were collected during periods. In order to be able to determine the fatty acid composition of the fractions, they were collected in tubes containing ethanol. After extraction, ethanol contents of tubes were evaporated at 50 ^{o}C under vacuum. Then remaining oil was used for methyl esterification. Also extraction with hexane was performed. Fatty acid compositions of the fractions and oil extracted with hexane were determined. Triplicate measurements were made. The means of each fatty acid composition of oils were compared using Duncan's Multiple Range test to estimate statistically significant differences ($p < 0.01$).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Solubility of Apricot Kernel Oil in SC-CO_2

Solubility of apricot kernel oil in SC-CO_2 at 40, 50 and 60 ^{o}C and 150, 300, 450, 525 and 600 bar are given in Table 3.1. The observed trend was the increase of solubility with temperature and pressure except at 150 bar where solubility decreased with temperature. This is consistent with the crossover phenomena generally observed for oils. Solubility of oils in SC-CO_2 increases both with density of SC-CO_2 and the volatility of fatty acids. The crossover phenomenon is due to the competing effects of reduction in density of SC-CO_2 and increase in the fatty acids volatility, which accompany the temperature rise (King and Bott, 1993). Figure 3.1 clearly shows that the crossover pressure of apricot kernel oil is between 200 and 300 bar. This pressure is low, compared to 350 bar for peanut oil (Goodrum and Kilgo, 1987), 300 bar for soybean oil (King and Bott, 1993) and 280-340 bar for pistachio nut oil (Palazoğlu and Balaban, 1998). This is most probably due to the difference in the composition of these oils, because oils are complex mixtures of different components, such as, free fatty acids, mono-, di-, triglycerides and etc. All these components and their compositions effect the volatility so the solubility of the oil. Generally solubility of oils in SC-CO_2 decreases, with increase in polarity and molecular weight and in the order of, fatty acid esters, fatty acids, and triglycerides (Shen et al., 1997; Güçlü-Üstündağ and Temelli, 2000).

Table 3.1. Effect of pressure and temperature on solubility of apricot kernel oil in SC-CO_2

Pressure (bar)	Temperature (^oC)	Density of CO_2* (kg/m^3)	Solubility y_r (mg/g)	Solubility c (kg/m^3)
150	40	787	1.1	0.87
	50	705	0.9	0.63
	60	603	0.2	0.12
300	40	922	6.7	6.18
	50	883	7.1	6.27
	60	841	7.6	6.39
450	40	985	12.9	12.71
	50	951	14.8	14.07
	60	921	18.1	16.67
525	40	1009	15.5	15.64
	50	979	19.7	19.29
	60	951	24.2	23.01
600	40	1032	17.1	17.65
	50	1007	23.8	23.97
	60	981	29.1	28.55

*Density data for CO_2 were obtained using the SF-Solver Program (Isco Inc., Lincoln, NE).

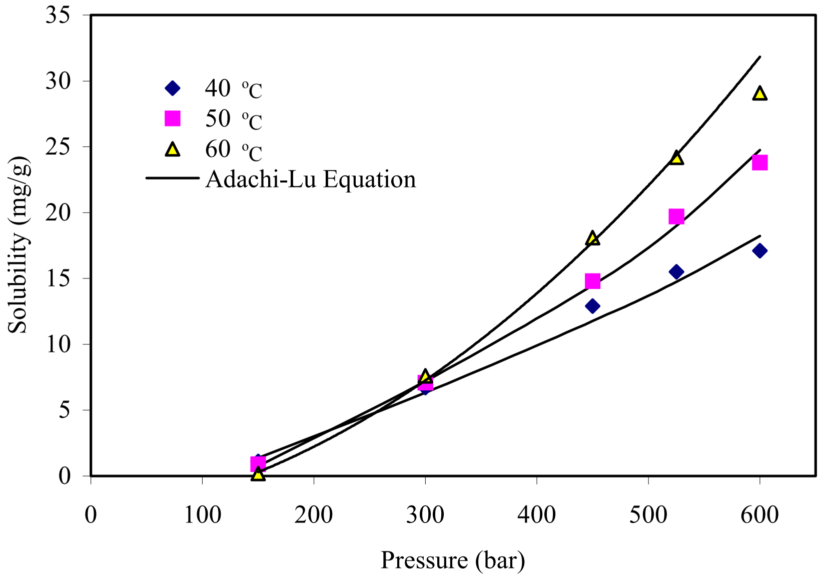


Figure 3.1. Solubility of apricot kernel oil in SC-CO_2.

Solubility behavior was modeled by the Charstil (Eq. 1.1), del Valle and Aguilera (Eq. 1.2) and Adachi and Lu (Eq. 1.4) Equations. Constants of the equations are given in Table 3.2. Parameters and their units used in the regressions were, solubility in kg/m^3 and temperature in K in all the equations, density of CO_2 in kg/m^3 in the Chrastil Equation and in kg/dm^3 in the others.

Comparison of the experimental and the predicted solubility values are presented in Figure 3.1. All of the models fitted the experimental data well (R^2>0.99) (Table 3.2). This was indicated by analysis of variance (p<0.001) (Tables B1, B2, B3) and small AAD values (Table 3.2), also. However, best fit of the experimental data was obtained by Adachi and Lu Equation (Eq. 1.4) with smallest AAD value of 6.48 % (Table 3.2).

Table 3.2. Constants for solubility equations

Equation	**Constants**						$\mathbf{R^2}$	**AAD**
	a_1	a_2	a_3	k_1	k_2	k_3		(%)
Charstil	-5369	- 56.8		11.1			0.995	8.45
del Valle- Aguilera	44541	-57.5	-8055332	11.1			0.996	8.68
Adachi-Lu	-5429.5	19.94		17.81	-15.85	8.4	0.997	6.48

Some similarities present between estimated models constants for apricot kernel oil and the literature data. The term a_1 representing the total heat of reaction ($\Delta H/R$) in Charstil's Equation (Eq. 1.1) are given for pure monoolein, diolein and triolein as –7925, -4601 and –2057, respectively (Table 1.4) (Güçlü-Üstündağ and Temelli, 2000). The value given in Table 3.2 for apricot kernel oil is close to them. Moreover, a_1 term of Adachi and Lu Equation (Eq. 1.4) for refined black currant oil and rapeseed oil is -5000 (Sovová et al., 2001) and it's very close to the value obtained for apricot kernel oil (-5429.5) (Table 3.2).

Solubility data at 300 bar and 40, 50 and 60 ^oC for different oils were calculated from the equations reported in the literature including; del Valle and Aguilera Equation for soybean, sunflower, cottonseed and corn oil (Eq. 1.3) and Adachi and Lu Equation for refined black currant oil and rapeseed oil (Eq. 1.5). The values obtained are in the order of 40, 50 and 60 ^oC for del Valle and Aguilera Equation 7.37, 7.56, 7.39 kg/m^3; and for Adachi and Lu Equation 7.75, 7.76, 6.91 kg/m^3. Although the data obtained from different equations were close to each other and to the solubility of apricot kernel oil determined at the same conditions (Table 3.1), some differences were present as expected due to compositional differences between the oils used for the estimation of model constants.

All of the models discussed above require the density data for SC-CO$_2$, which depends on temperature and pressure. Therefore it is more useful to estimate the solubility as a function of temperature and pressure without density data requirement. To construct the model for solubility of apricot kernel oil, change of solubility with pressure and temperature were analyzed in the range of experiments. Linear change of solubility isotherms with temperature was observed (Figure 3.2). Therefore, each isotherm was represented with a linear equation like $y_r = a + bT$. Changes in both constants a and b of the equations of the solubility isotherms were best represented with second-degree polynomial function of pressure as,

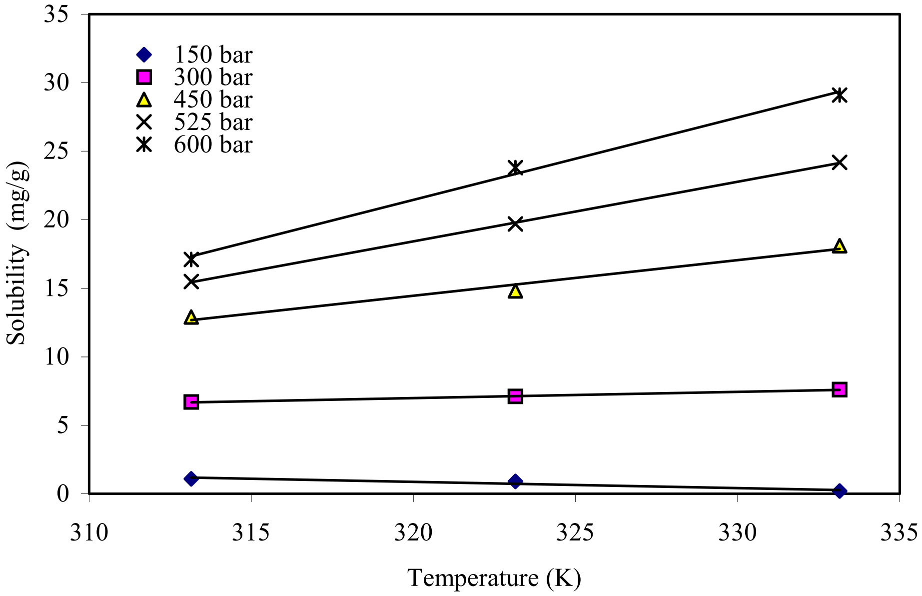


Figure 3.2. Solubility isotherms of apricot kernel oil at different pressures.

$$a = 0.2 + 0.233\,P - 0.000868\,P^2 \qquad (3.1)$$

$$b = -\,0.0179 - 0.000602\,P + 0.000003\,P^2 \qquad (3.2)$$

Therefore, final equation obtained was,

$$y_r = 0.2+0.233\,P - 0.000868\,P^2 - 0.0179\,T -0.000602\,PT+0.000003\,P^2T \qquad (3.3)$$

where y_r is solubility in mg/g, P is pressure in bar and T is temperature in K. This equation fitted the experimental results also well ($p < 0.001$, $R^2 = 0.998$ and AAD = 7.43 %) in the experimental conditions (Table B4).

3.2. Mass Transfer Model

Effects of particle size, SC-CO_2 flow rate, pressure, temperature and ethanol concentrations, as co-solvent, were studied. Experimental results were fitted to broken and intact cells model (Eq. 1.16). Adjustable parameters of the model were determined by minimizing difference between experimental and predicted data which are given in Appendix A, by estimation of AAD values (Eq. 2.1).

Density of oil free particles, ρ_s, was measured as 1.8 g/cm^3. Void fraction in the bed, ε, was about 0.85 cm^3/cm^3. Measured solubility of apricot kernel oil in SC-CO_2 and in SC-CO_2-ethanol mixture were used in model calculations.

3.2.1. Effect of Particle Size

Ground apricot kernel fractions with sizes 1, 2, 3 and 4 (Table 2.1) were used to determine the effect of particle size on the extraction of apricot kernel oil. Extractions were done at 450 bar and 50^{o}C. SC-CO_2 flow rate was set to 3 g/min.

Figure 3.3 shows the effect of particle size and amount of SC-CO_2 used on extraction yield of apricot kernel oil. The extraction curves for different particle sizes coincided at the beginning of the extraction showing that SC-CO_2 left the extractor saturated with apricot kernel oil and the slopes of the curves indicated the solubility of the oil in SC-CO_2.

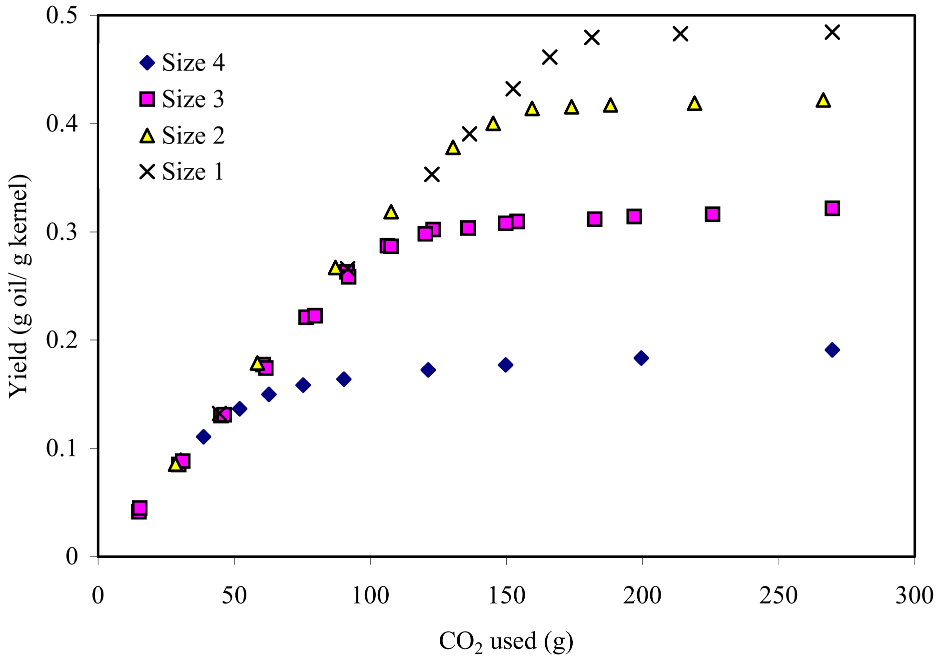


Figure 3.3. Effect of particle size and amount of CO_2 used on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, T = 50°C, Q = 3 g/min, ρ_f = 951 kg/m^3).

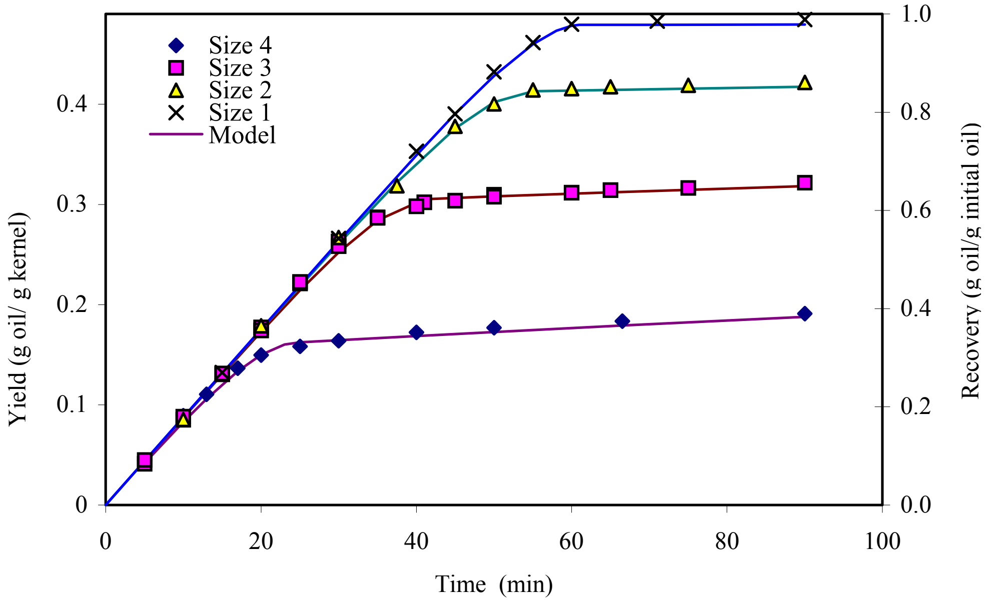


Figure 3.4. Effect of particle size on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, T = 50°C, Q = 3 g/min, $\rho_f = 951$ kg/m^3).

Table 3.3. Parameters of mass transfer model at different particle sizes (Extraction conditions: P = 450 bar, T = 50°C, Q = 3 g/min, ρ_f = 951 kg/m^3)

Particle Size	Dp$_m$ (mm)	y_r (g/g)	G	t_k (min)	w_k (g/g kernel)	m_{90} (g/g initial oil)	$k_f a$ (1/min)	$k_s a$ (1/min)	AAD (%)
1	< 0.425	0.0148	0.998	61.3	0.479	0.998	2.526	0.00030	0.9
2	< 0.850	0.0148	0.854	54.7	0.413	0.867	1.895	0.00028	1.1
3	0.92	0.0148	0.627	41.6	0.306	0.662	1.579	0.00023	1.7
4	1.5	0.0148	0.322	24.5	0.162	0.391	0.947	0.00019	2.4

Grinding of the apricot kernel before extraction not only increases the interfacial area but also releases oil from the broken cells (Šťastová et al, 1996; Marrone et al., 1998). As a result, two extraction periods as fast and slow extraction periods could be easily distinguished in Figure 3.4. This indicates two different mass transfer mechanisms. In the fast extraction period, released oil on the solid surface was extracted with a rate controlled by its diffusion and convection in the solvent. In the slow extraction period the unreleased oil inside the intact cells was extracted with a rate controlled by its diffusion inside the particles. Scanning electron microscope images of the surface of an apricot kernel particle (particle size 2) before and after extraction are given in Figures E2 and E3, respectively. Released oil on the surface of the particles before extraction and empty oil cells after extraction are evident from the figures.

The two mass transfer mechanisms were explained by the application of the broken and intact cells model (Šťastová et al, 1996). Table 3.3 shows the fraction of the total oil released upon grinding. Particle size 1 represents the sample with the smallest particle size ($Dp_m < 0.425$ mm) and particle size 4 represents the sample with the largest particle size ($Dp_m = 1.5$ mm) (Table 2.1). As the particle size decreased the grinding efficiency, *G*, increased. The extracted apricot kernel sample with particle size 1 contained mostly the released oil upon grinding. However, in the sample with particle size 4, about 32 % of the oil was released and the rest was unreleased oil. Consequently, the time for the fast extraction period, t_k, where the released oil was extracted, was shorter for the sample with particle size 4 (24.5 min) compared to t_k for the samples with particle size 1 (61.3 min). At the end of the fast extraction period the released oil in the extractor were completely removed and the unreleased oil remained in the particles was extracted during slow extraction period. Since the extraction is controlled by the diffusion of the oil inside the particles the extraction rate and therefore oil recovery were much smaller compared to those in the fast extraction period (Figure 3.4). Considering the oil recovered during 90 min extraction (m_{90}), the oil recovered in the slow extraction period was only 3-7 % for the large particles (particle size 3 and 4). However, insignificant amount of oil was recovered in the slow extraction period when the particles were small. Almost all the initial oil in the small sized apricot kernel samples (particle size 1) was recovered at the end of the fast extraction period. However, only 39 % of the oil in the samples was recovered during 90 min extraction for large particles (particle size 4) (Table 3.3).

These results were also reflected to the calculated mass transfer coefficients. The magnitudes of volume mass transfer coefficient in the fluid side, $k_f a$, were about four orders of magnitude larger than magnitudes of volume mass transfer coefficient in the solid phase, $k_s a$ (Table 3.3). This was due to the fact that $k_s a$ is related with the diffusion of the unreleased oil in the particles. This depends on the properties of the kernel, the permeability of cell walls, and the efficiency of the solvent to access the inner parts of the particles. The results revealed that the penetration of the solvent was low and the diffusion was slow due to the physical structure of the kernel. This is consistent with results presented for oil of sea bucthron berries (Šťastová et al., 1996), essential oil of black pepper (Sovová et al, 1995; Ferreire and Meireles, 2002) and essential oil and oleoresin from cahamomile (Povh et al., 2001), where several orders of magnitude difference between the mass transfer coefficients were reported.

Volume mass transfer coefficient in the fluid phase, $k_f a$, and volume mass transfer coefficient in the solid phase, $k_s a$, increased with the decrease in the particle size as expected, due to the increase in the surface area and the decrease in the diffusion path length (Table 3.3). Similar results were given for extraction of oil from sea buckthorn berries at 270 bar and 40 °C with 1 l/min CO_2 flow rate (measured at atmospheric conditions), where values of $k_f a$ and $k_s a$ are increased from 0.34 to 0.56 /min and 0.00037 to 0.00060 /min, respectively as grinding grade increased (or particle size decreased) (Šťastová et al., 1996).

Results indicated that extraction rate is high if the oil is released on the surface of particles, and it is comparably very slow if it is embedded in the kernel particles. The reduction of particle size of the kernel is required to decrease the extraction time; otherwise extraction in the slow extraction period may not be feasible. Similar results were indicated for peanut oil (Goodrum and Kilgo, 1987), rapeseed oil (Eggers and Sievers, 1989) and grape seed oil (Gomez et al., 1996). On the other hand, the production of very small particles can largely increase grinding cost and could produce bed caking with formation of channels along the bed in which SCF can preferentially flow, thus reducing the extraction efficiency (Reverchon and Marrone, 2001).

3.2.2. Effect of Solvent Flow Rate

To investigate the effect of SC-CO_2 flow rate on the extraction of apricot kernel oil, samples with particle size 2 ($Dp_m < 0.850$ mm) were extracted at 450 bar and 50 ^oC with flow rates of 1, 2, 3, 4 and 5 g/min. Extraction curves (Figure 3.5) indicate that, when the flow rate was between 1 and 5 g/min, almost the same amount of oil could be extracted with the same amount of CO_2. The slopes of initial parts of the curves gave the solubility of oil in SC-CO_2 at 450 bar and 50 ^oC. This trend in extraction curves was observed due to high solubility of the oil, y_r, at 450 bar and 50 ^oC, where the amount of oil extracted per g of SC-CO_2 used was independent of flow rate especially at the initial linear parts of the extraction curves.

Representation of the data as in Figure 3.6 clarifies the effect of flow rate on oil yield. Since the particle size was constant the fraction of the released oil, *G,* and the oil yield at the end of the fast extraction period, w_k, were constant as 0.854 g/g initial oil and 0.413 g/g kernel, respectively. However, the time for the fast extraction period, t_k, decreased with increase in SC-CO_2 flow rate. This decrease was as high as 4.5 folds when the flow rate increased from 1 to 5 g/min (Table 3.4).

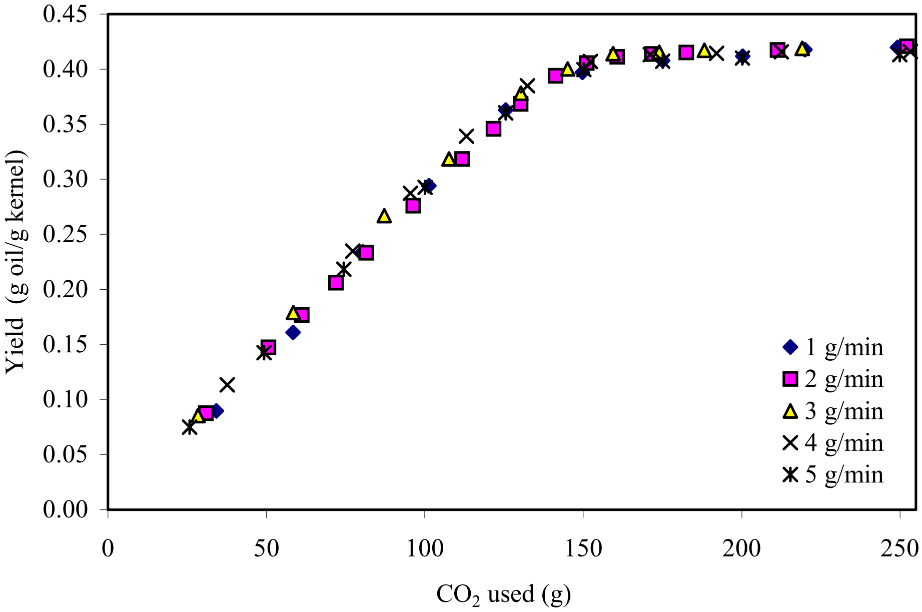


Figure 3.5. Effect of flow rate and amount of CO_2 used on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, T= 50^{o}C, particle size 2, ρ_f = 951 kg/m^3).

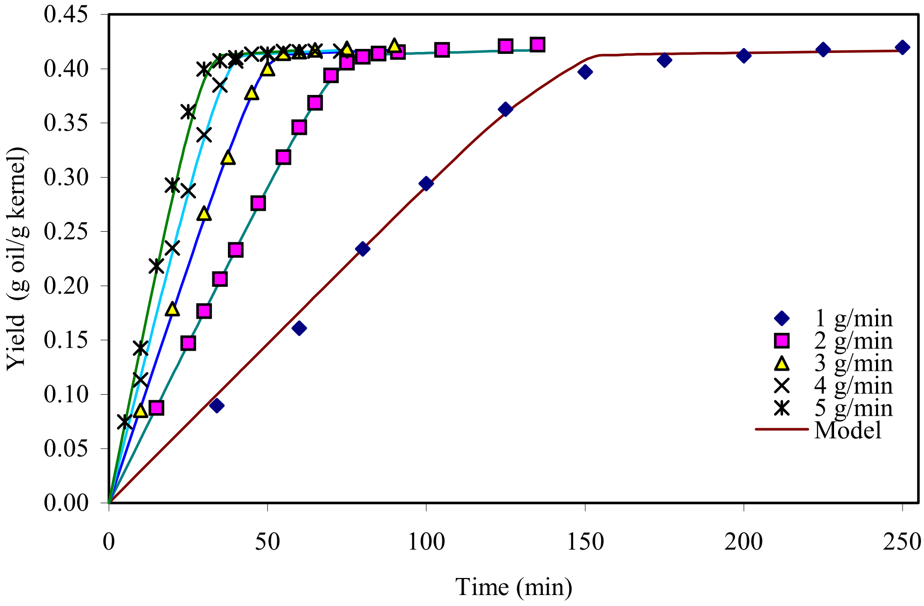


Figure 3.6. Effect of flow rate on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, T= 50°C, particle size 2, ρ_f = 951 kg/m^3).

Table 3.4. Parameters of mass transfer model at different flow rates (Extraction conditions: P = 450 bar, T= 50°C, particle size 2, ρ_f = 951 kg/m^3)

Q (g/min)	y_r (g/g)	G	t_k (min)	w_k (g/g kernel)	$k_f a$ (1/min)	$k_s a$ (1/min)	AAD (%)
1	0.0148	0.854	157.9	0.413	0.863	0.00009	2.9
2	0.0148	0.854	80.1	0.413	1.516	0.00018	0.5
3	0.0148	0.854	54.7	0.413	1.895	0.00028	1.1
4	0.0148	0.854	42.6	0.413	1.979	0.00033	0.7
5	0.0148	0.854	35.3	0.413	2.053	0.00040	2.2

Mass transfer coefficients, k_fa and k_sa increased with the increase in flow rate of the solvent (Table 3.4). Increase in k_fa with flow rate was also reported for grape seed oil (Sovová et al., 1994) and egg yolk oil (Wu and Hou, 2001). This was due to the decrease in mass transfer resistance, as a result of, increase in convection and decrease in film thickness. Increase in k_sa was most probably due to decrease in particle size observed after extraction with increase in flow rate and increase in convection outside the particle. However, since the oil recovery in the slow extraction period was insignificant compared to that in the fast extraction period the increase in k_sa did not affect the results and could be considered negligible.

In the fast extraction period, the rate of extraction increased with increase in flow rate. As an example, the oil yield after 30 min of extraction increased from 0.09 to 0.4 g/g kernel with the change of flow rate from 1 to 5 g/min. This increase in extraction rate shortens the extraction time. The time required to extract 0.4 g oil /g oil reduced from 70 min to 30 min as the flow rate increased from 2 g /min to 5 g /min, respectively (Figure 3.6).

3.2.3. Effect of Extraction Pressure

Effect of pressure on extraction of apricot kernel oil was investigated between 300 and 600 bar at 50°C. SC-CO_2 flow rate was kept constant at 3 g/min and particle size 2 (Dp_m < 0.850 mm) was used. The increased slopes of the initial parts of the extraction curves with increasing pressure indicated the increase in solubility of the oil in SC-CO_2 (Figure 3.7). The solubility of apricot kernel oil in SC-CO_2 increased from 7.1 mg/g to 23.8 mg/g as pressure increased from 300 to 600 bar (Table 3.5).

Figure 3.8 shows the effect of pressure and time on oil yield. Due to constant particle size, the fraction of released oil, *G,* and the oil yield at the end of the fast

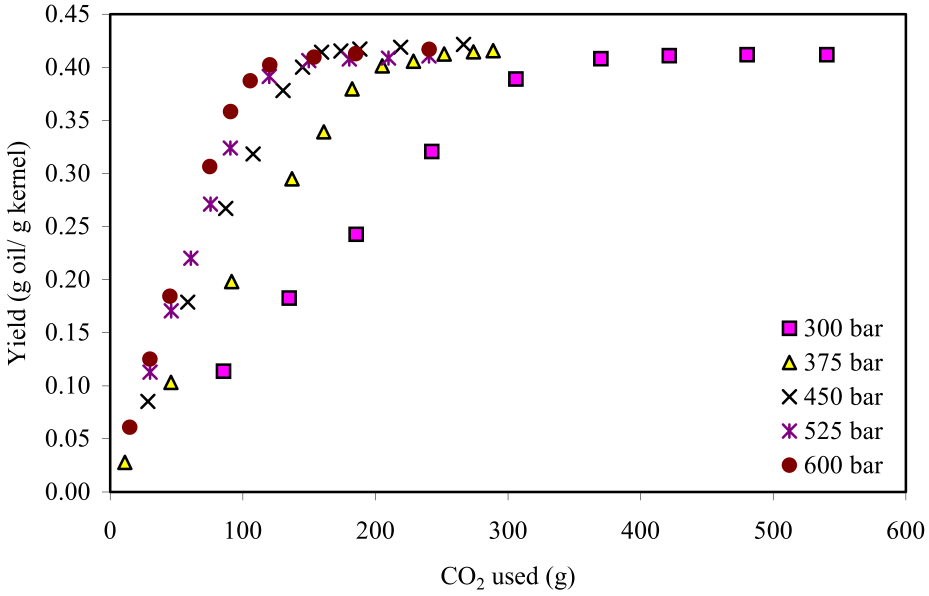


Figure 3.7. Effect of extraction pressure and amount of CO_2 used on extraction of apricot kernel oil (Extraction conditions: T = 50°C, Q = 3 g/min, particle size 2).

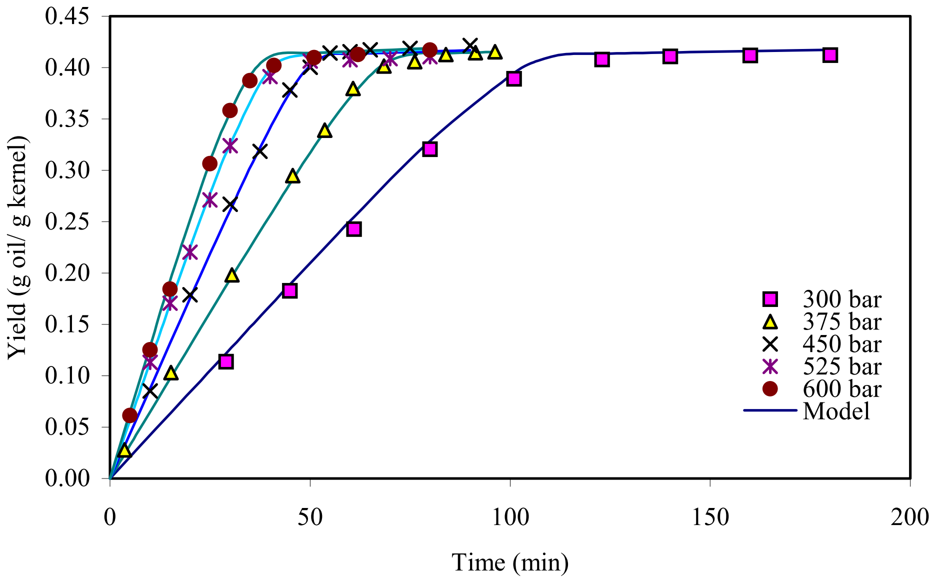


Figure 3.8. Effect of extraction pressure on extraction of apricot kernel oil (Extraction conditions: T = 50^{o}C, Q = 3 g/min, particle size 2).

Table 3.5. Parameters of mass transfer model at different pressures (Extraction conditions: T = 50^{o}C, Q = 3 g/min, particle size 2)

Pressure (bar)	y_r (g/g)	G	t_k (min)	w_k (g/g kernel)	$k_f a$ (1/min)	$k_s a$ (1/min)	AAD (%)
300	0.0071	0.854	114.4	0.413	2.005	0.00014	2.5
375	0.0109	0.854	74.3	0.413	1.957	0.00022	2.3
450	0.0148	0.854	54.7	0.413	1.895	0.00028	1.1
525	0.0197	0.854	45.3	0.413	1.081	0.00032	1.4
600	0.0238	0.854	41.3	0.413	0.673	0.00037	2.1

extraction period, w_k, were constant as 0.854 g/g initial oil and 0.413 g/g kernel, respectively. Time for the fast extraction period, t_k, decreased with increase in pressure. Increase in pressure from 300 to 600 bar caused 2.8 fold decrease in t_k (Table 3.5).

Volume mass transfer coefficient in the fluid phase, k_fa, decreased while, volume mass transfer coefficient in the solid phase, k_sa, showed a slight increase with increased pressure (Table 3.5). This decrease in k_fa was result of decrease in the diffusivity of oil in SC-CO_2, which increased the mass transfer resistance, due to the increase in pressure. On the other hand, the reason for the increase of k_sa with pressure could be the observed reduction in the particle size of the kernels and possible destruction of cell structure at high pressures. However, the oil recovered in the slow extraction period was negligible, indicating that the change in k_sa did not affect the extraction rate significantly. A decrease in mass transfer coefficient (k_f) with pressure rise in the extraction of β-carotene from apricot bagesse with SC-CO_2 was also reported in a recent study (Döker et al., 2004).

Increase in the solubility of the oil in SC-CO_2 increases the driving force and consequently increasing the mass transfer rate. On the other hand, decrease in k_fa increases mass transfer resistance, and consequently decreasing mass transfer rate.

Therefore, the former effect overcame the later resulting in shorter extraction time in the fast extraction period.

3.2.4. Effect of Extraction Temperature

The effect of temperature was studied at 450 bar, between 40 and 70^{o}C by performing extractions with SC-CO_2 flow rate of 3 g/min and using samples with particle size 2 (Dp_m < 0.850 mm). The increased slopes of the initial parts of extraction curves indicated the increase in solubility of the oil in SC-CO_2 as temperature increased (Figure 3.9). Therefore, solubility, y_r, increased from 12.9 mg/g to 20.1 mg/g with increase in temperature from 40 to 70 ^{o}C (Table 3.6), since the extraction pressure (450 bar) was greater than the crossover pressure which was between 200 and 300 bar (Section 3.1). This was expected, due to increasing trend of solubility above the crossover pressure with temperature increase at constant pressure as a result of competing effects of increasing solute volatility and decreasing solvent density (King and Bott, 1993). This increase in solubility increased driving force during extraction (Eq. 1.13).

The data presented in Figure 3.10 show the effect of temperature on oil yield. Yield at the end of the fast extraction period, w_k, did not change with temperature due to constant grinding efficiency, G. Time for the fast extraction period, t_k, decreased with increase in temperature. This decrease was about 2 fold when the temperature increased from 40 to 70 °C (Table 3.6).

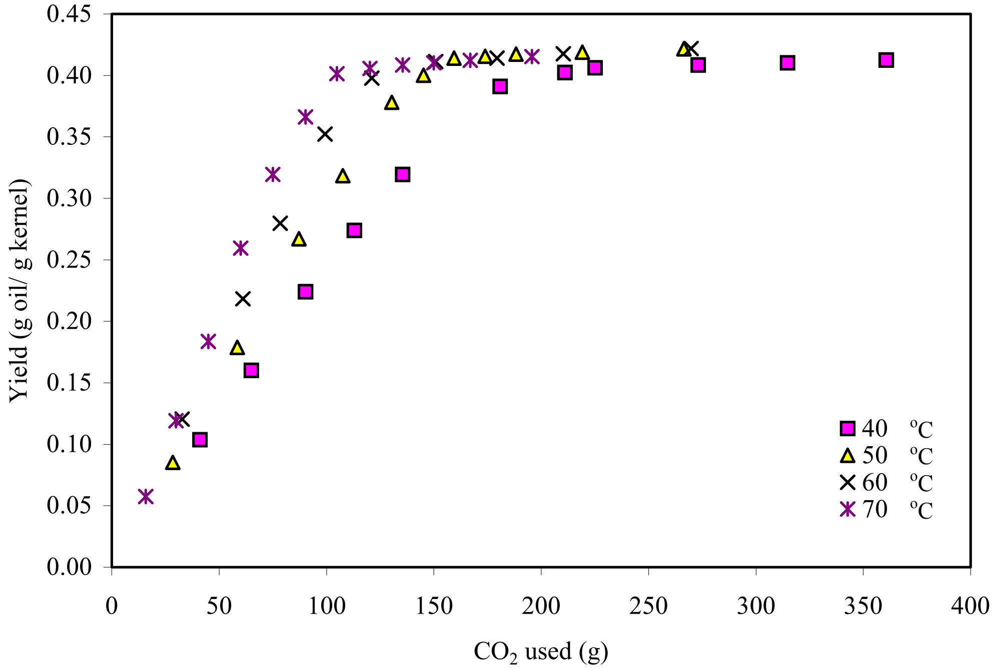


Figure 3.9. Effect of extraction temperature and amount of CO_2 used on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2).

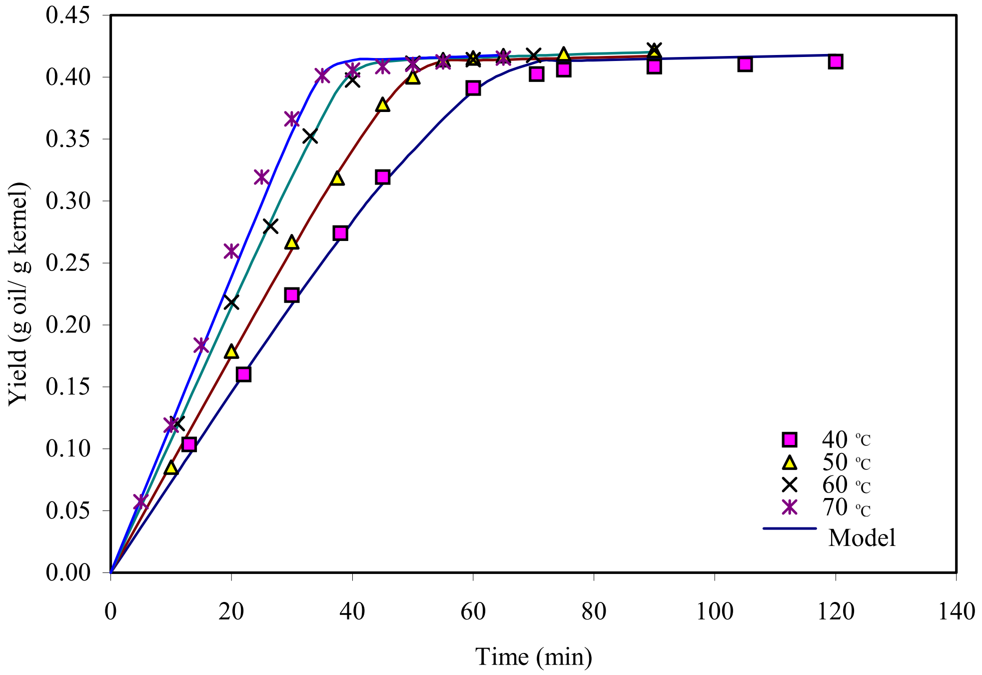


Figure 3.10. Effect of extraction temperature on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2).

Table 3.6. Parameters of mass transfer model at different temperatures (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2)

Temperature (^{o}C)	y_r (g/g)	G	t_k (min)	w_k (g/g kernel)	k_fa (1/min)	k_sa (1/min)	AAD (%)
40	0.0129	0.854	71.7	0.413	0.914	0.00023	2.2
50	0.0148	0.854	54.7	0.413	1.895	0.00028	1.1
60	0.0181	0.854	43.2	0.413	2.606	0.00036	0.9
70	0.0201	0.854	37.7	0.413	3.720	0.00040	2.6

Volume mass transfer coefficient in the fluid side, k_fa, increased with increase in temperature due to increase in diffusivity of oil in SC-CO_2. Volume mass transfer coefficient in the solid phase, k_sa, increased with increase in temperature due to increase in effective diffusivity of oil in the kernel particles. Increase in k_sa did not affect the oil yield significantly, because the oil recovery in the slow extraction period was negligible (Table 3.6).

As a result, increase in the temperature from 40 ^oC to 70 ^oC caused increase in the extraction rate therefore decrease in extraction time, due to increase in solubility and mass transfer coefficient, k_fa. Increase in the oil extraction rate of flaked rapeseed press at 750 bar (Eggers and Sievers, 1989), pecan at 413.4, 551.2 and 689. 0 bar (Zhang et al., 1995) and peanut meals at 552 bar (Chiou et al., 1996) with rise in extraction temperature were also reported.

3.2.5. Effect of Co-solvent Concentration

To determine the effect of co-solvent on extraction of apricot kernel oil, ethanol was used with concentrations of 0.0, 0.5, 1.0, 1.5 and 3.0 wt % in SC-CO_2. Extractions were done at 450 bar and 50^oC with flow rate of 3 g/min and particle size 2 ($Dp_m < 0.850$ mm). As ethanol concentration increased in the solvent, initial slopes of the extraction curves (Figure 3.11) increased, indicating that solubility, y_r, increased due to increase in polarity of solvent. Addition of 3 % ethanol to SC-CO_2 increased the solubility of apricot kernel oil 1.5 times compared to its solubility in pure SC-CO_2 (Table 3.7).

Data represented in Figures 3.12 show effects of 1.5 and 3.0 % ethanol concentration in SC-CO_2 on apricot kernel oil yield, while the data represented in Figure 3.13 show the effect of 0.5 and 1.0 % ethanol concentration. Time for fast extraction period, t_k, decreased with increasing ethanol concentration, where addition of 3.0 % ethanol to CO_2 decreased t_k from 54.7 min to 34.5 min (Table 3.7).

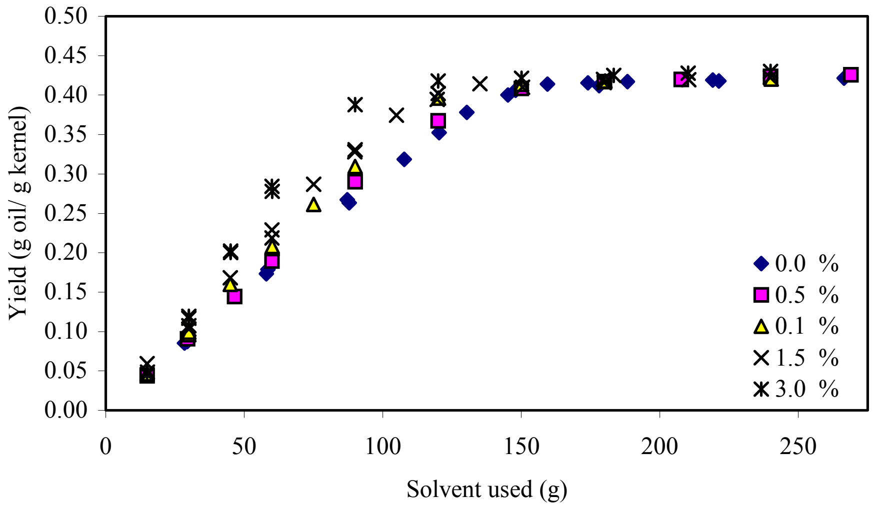


Figure 3.11. Effect of ethanol concentration (wt %) and amount of solvent used on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2).

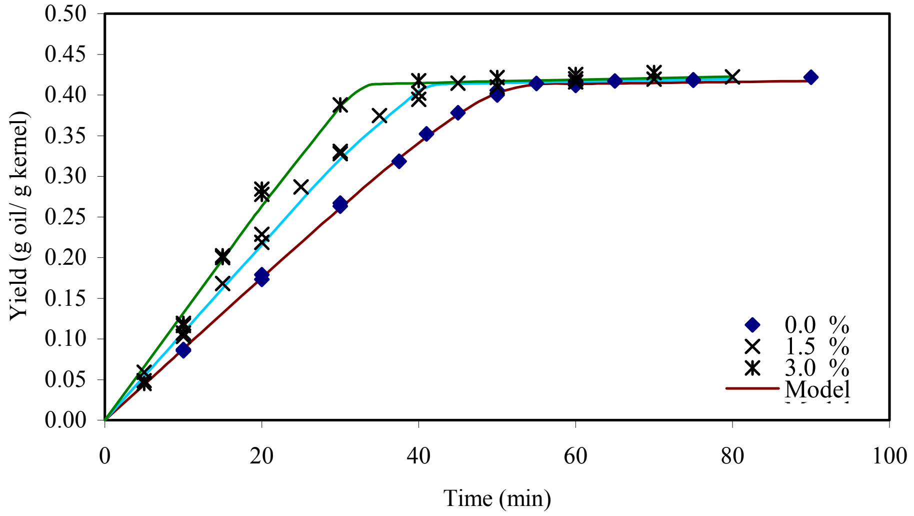


Figure 3.12. Effect of ethanol concentration (wt %) on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2).

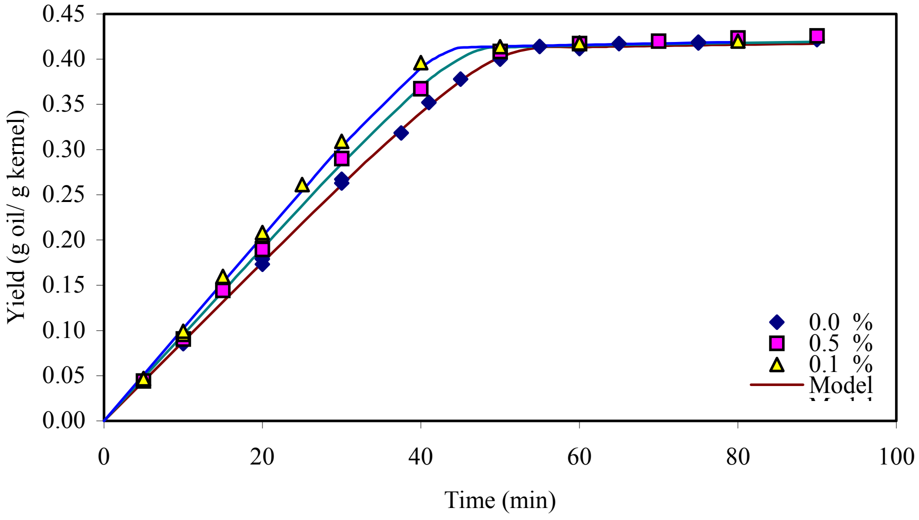


Figure 3.13. Effect of ethanol concentration (wt %) on extraction of apricot kernel oil (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2).

Table 3.7. Parameters of mass transfer model at different ethanol concentrations (Extraction conditions: P = 450 bar, Q = 3 g/min, particle size 2)

Ethanol (wt %)	y_r (g/g)	G	t_k (min)	w_k (g/g kernel)	k_fa (1/min)	k_sa (1/min)	AAD (%)
0.0	0.0148	0.854	54.7	0.413	1.895	0.00028	1.1
0.5	0.0161	0.854	49.3	0.413	2.211	0.00035	2.2
1.0	0.0172	0.854	45.8	0.413	2.368	0.00037	3.3
1.5	0.0182	0.854	43.0	0.413	2.526	0.00039	3.2
3.0	0.0222	0.854	34.5	0.413	3.158	0.00048	7.3

Volume mass transfer coefficients in the fluid side, k_fa, and in the solid side, k_sa, increased with ethanol addition, due to possible increases in the diffusivity of oil in SC-CO_2 and effective diffusivity in particle, respectively (Table 3.7).

Therefore, addition of ethanol up to 3 % into the SC-CO_2 caused increase in extraction rate in the fast extraction period so decrease in total extraction time, because the oil recovered in the slow extraction period was negligible. This was due to increase in both solubility of the oil in SC-CO_2 increased driving force and volume mass transfer coefficient, k_fa (Figure 3.12, 3.13 and Table 3.7). Similar effects of ethanol addition to SC-CO_2 were reported for pistachio nut oil (Palazoğlu and Balaban, 1998).

Decrease in extraction time caused by addition of 3 % ethanol is more than the value obtained from the extraction at 600 bar with pure SC-CO_2 at the same extraction conditions, where t_k was about 41 min (Table 3.5). This indicates that instead of operating at higher pressures small amount of ethanol may be added to reach the same extraction rate.

3.3. Response Surface Modeling of Apricot Kernel Oil Yield

Effects of flow rate, temperature, pressure and co-solvent (ethanol) concentration on apricot kernel oil extraction yield were studied by Response Surface Methodology. Solubility of apricot kernel oil in SC-CO_2 was very low below 300 bar (Table 3.1, Figure 3.1), and effect of pressure on extraction rate of apricot kernel oil was high at low pressures (below 450 bar) in the interval of 300 to 600 bar (Figure 3.8). Furthermore, higher pressures increase the operational cost of the process. Addition of co-solvent alters the critical conditions of CO_2. Addition of about 3.5 weight % ethanol to CO_2 increases the critical temperature to 40 ^{o}C (Table 1.3) (Gurdial et al., 1993). Therefore, levels of the parameters chosen include, pressure (300, 375 and 450 bar), temperature (40, 50 and 60 ^{o}C), SC-solvent (ethanol + CO_2) flow rate (2, 3 and 4 g/min), and co-solvent concentration (0, 1.5 and 3 weight % ethanol). Apricot kernel samples of particle size 2 (Dp_m < 0.850 mm) was used in this part of the research.

As indicated previously in Sec. 3.2.1 extraction rate is several orders of magnitude greater in the fast extraction period than the slow extraction period and extraction in the slow extraction period is not important. Thus, extraction in the fast extraction period, where the maximum yield is about 0.4 g/g kernel for the selected particle size (Figure 3.4 and Table 3.3) was considered in Response Surface Model estimation and yields after 15 min were used.

Experiments were performed according to the Box-Behnken design (Tables 2.2 and 2.3). Experimental conditions and experimental and predicted yield data are presented in Table 3.8. Second order polynomial model (Eq. 2.5) was used to represent response surfaces. The terms that were not significant ($p > 0.05$) were eliminated from the model equation (Table C1) and refitted (Table C2). Than, obtained model was in the form,

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{12}X_1X_2 + a_{23}X_2X_3 \tag{3.4}$$

Constants of the reduced model are given in Table 3.9. Obtained second-degree polynomial was found to represent the experimental data well ($R^2 = 0.946$ and AAD = 8.3 %). All the independent parameters (extraction conditions) ($p< 0.001$), and interactions between, flow rate and pressure ($p = 0.005$), and pressure and temperature ($p = 0.015$) affected the yield significantly (Table C2).

Table 3.8. Experimental conditions and results obtained for Response Surface Model estimation of apricot kernel oil yield

Stand. Order+	Flow Rate (g/min)	Pressure (bar)	Temperature (°C)	Ethanol Conc. (wt %)	Yield: Experimental (g /g kernel)	Yield: Predicted (g /g kernel)*
1	2	300	50	1.5	0.042	0.042
2	4	300	50	1.5	0.088	0.084
3	2	450	50	1.5	0.096	0.092
4	4	450	50	1.5	0.217	0.208
5	3	375	40	0	0.079	0.074
6	3	375	60	0	0.104	0.105
7	3	375	40	3	0.114	0.108
8	3	375	60	3	0.156	0.139
9	2	375	40	1.5	0.055	0.052
10	4	375	40	1.5	0.145	0.131
11	2	375	60	1.5	0.079	0.082
12	4	375	60	1.5	0.164	0.162
13	3	300	50	0	0.059	0.046
14	3	450	50	0	0.132	0.133
15	3	300	50	3	0.083	0.08
16	3	450	50	3	0.187	0.167
17	2	375	50	0	0.061	0.05
18	4	375	50	0	0.119	0.129
19	2	375	50	3	0.071	0.084
20	4	375	50	3	0.146	0.163
21	3	300	40	1.5	0.059	0.064
22	3	450	40	1.5	0.108	0.119
23	3	300	60	1.5	0.065	0.063
24	3	450	60	1.5	0.177	0.181
25	3	375	50	1.5	0.089	0.107
26	3	375	50	1.5	0.091	0.107
27	3	375	50	1.5	0.094	0.107

+ Experiments were performed in random order.

* AAD = 8.3 %

Table 3.9. Estimated coefficients of the second order regression model for the SFE of apricot kernel oil

Term	Coefficient	Value
Intercept	a_0	0.10662
X_1 (flow rate)	a_1	0.03958
X_2 (pressure)	a_2	0.04334
X_3 (temperature)	a_3	0.01542
X_4 (% ethanol)	a_4	0.01692
X_1 (flow rate) * X_2 (pressure)	a_{12}	0.01863
X_2 (pressure) * X_3 (temperature)	a_{23}	0.01587

Standard Error = 0.01192, R^2 = 94.6%, R^2(adj) = 93.0%, AAD = 8.3 %

$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{12} X_1X_2 + a_{23}X_2X_3$

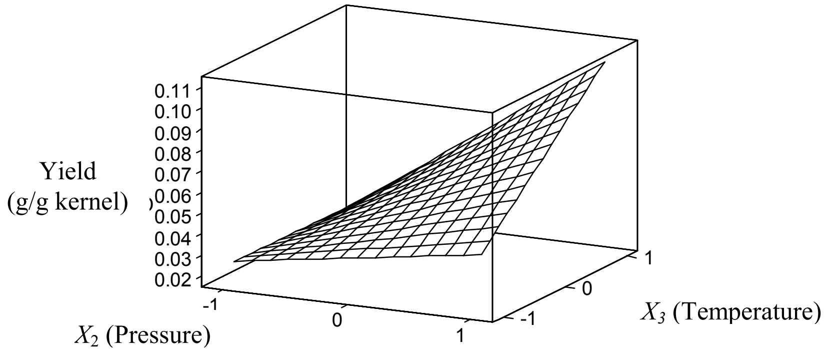
After inserting Eqs. 2.2 – 2.5 into Eq. 3.4 uncoded form of the model is

$$Y = 0.35366 - 0.05357\, Q - 0.00123\, P - 0.00639\, T + 0.01128\, C + 0.0002484\, QP + 0.0000212\, PT \qquad (3.5)$$

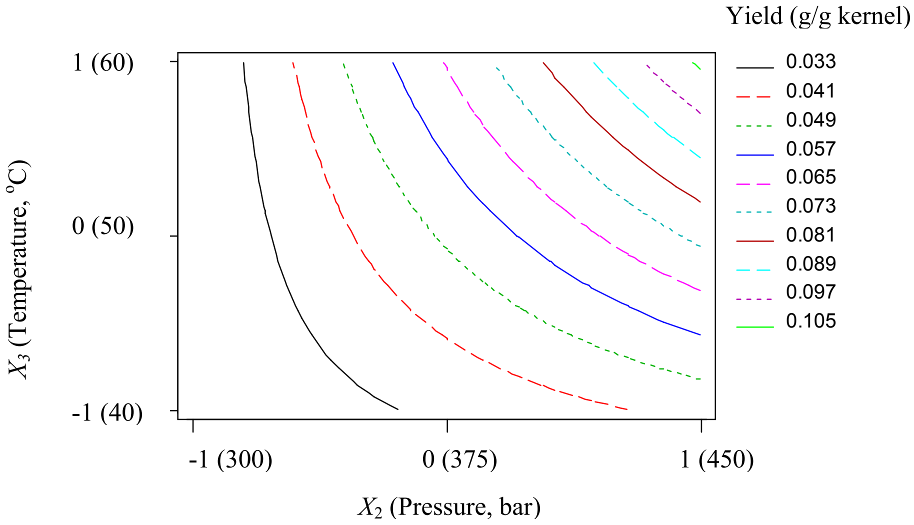
where Q is flow rate of solvent (g/min), P is pressure (bar), T is temperature (^{o}C) and C is concentration of ethanol in CO_2 (weight %).

Analysis of the variance of the model developed, also, indicated that the model fitted the experimental data with high significance. Small p values show this accuracy (Table C2).

The best way of expressing the effect of any parameter on yield within the experimental space under investigation from these responses was to generate response surface and contour plots of the model. Response surface and contour plot showing the effects of pressure and temperature on yield are presented in Figure 3.14, where flow rate was 2 g/min (X_1 = -1) and ethanol concentration was 0 % ethanol (X_4 = -1). Both factors affected the yield positively. However, it was noticed that as pressure decreased from 450 to 300 bar, effect of temperature decreased and nearly became zero at 300 bar. Although increasing temperature from 40 to 60 ^{o}C at 450 bar increased the yield from 0.045 to 0.1 g/g kernel, at 300 bar this temperature increase did not change the yield significantly from 0.033 g/g kernel. This was expected because; 300 bar is close to the crossover pressure of apricot kernel oil (determined between 200 and 300 bar, Figure 3.1). Above the crossover pressure the solubility of oils in SCF increases with temperature. As pressure decreases to the crossover value, this change in solubility diminishes and becomes zero at the crossover value, due to the competitive effects of the solute volatility and solvent density (King and Bott, 1993). Furthermore, effect of pressure at higher temperatures was more than that at lower temperatures. Increasing pressure from 300 to 450 bar at 40 ^{o}C increased the yield only from 0.030 to 0.045 g/g kernel but the same pressure change at 60 ^{o}C increased the yield from 0.030 to 0.1 g/ g kernel. This was due to the higher effect of pressure change at high temperatures compared to the low temperatures on solubility (Fig 3.1, Table 3.1).



(a)

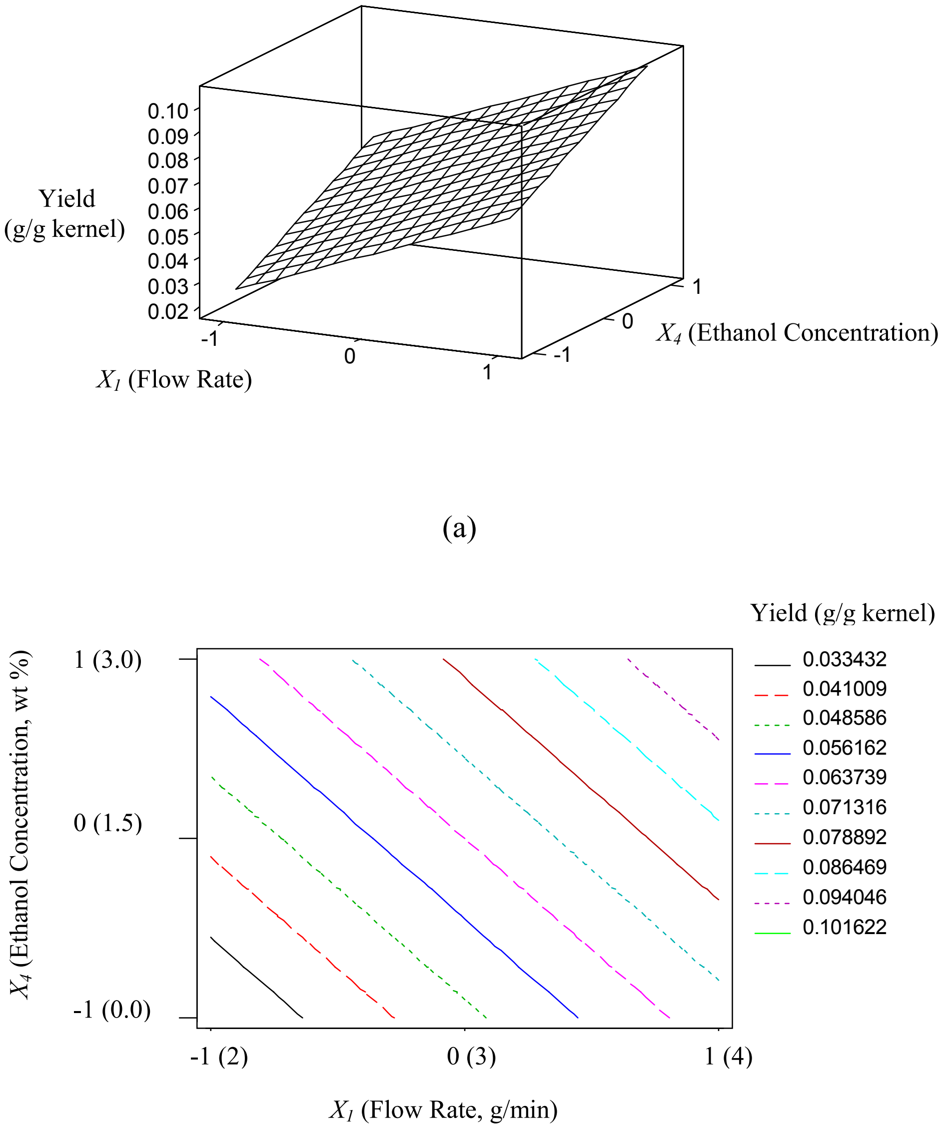


(b)

Figure 3.14. Effects of pressure and temperature on yield (g oil/g kernel) (X_1 = -1 (2 g/min), X_4 = -1 (0 % ethanol)); a- surface, b-contour plots.

Figure 3.15 represents the effects of flow rate and ethanol content to oil yield at constant conditions of 300 bar (X_2 = -1) and 40 °C (X_3 = -1). Both factors affected the yield positively in the ranges of 2 to 4 g/min and 0.0 to 3 % ethanol in CO_2 and caused gradual increase on the yield. Increase in the flow rate of the SCF decreases the thickness of the film layer around the solid so the mass transfer resistance surrounding the solid particle (Subra et al., 1998 and Döker et al., 2004) and addition of ethanol increases polarity of SC-CO_2, this causes increase in the solubility of the oil in SCF (Palazoğlu and Balaban, 1998). Therefore, increases in both flow rate and ethanol concentration increased extraction rate, therefore the yield obtained at constant time of 15 min.

Maximum yield value obtained, after 15 min extraction time, from the Response Surface Model is 0.26 g oil/ g kernel (54 % of the oil present in the kernel) and the extraction conditions were 4 g/min solvent flow rate, 60°C temperature, 450 bar pressure and 3 % ethanol concentration. Therefore, it can be concluded that 30 min extraction time at this conditions is enough to reach slow extraction period.



(a)

(b)

Figure 3.15. Effects of flow rate and ethanol content on yield (g oil/g kernel), (X_2 = -1 (300 bar), X_3 = -1 (40 ^{o}C)); a- surface, b-contour plots

To examine the validity of the Response Surface Model obtained, additional experiments were performed at flow rates of 3 g/min (X_1= 0) and 4 g/min (X_1= 1) at the maximum conditions of Response Surface Model (450 bar (X_2=1), 60 ^{o}C (X_3=1) and 3 % ethanol (X_4= 1)) with samples of particles size 2. Experimental yield values after 15 min for these extractions were determined as 0.22 and 0.29 g oil/g kernel, respectively (Tables A20 and A21). Results of the model for the same conditions were 0.20 and 0.26, respectively. Model and experimental data were very close to each other, therefore, obtained Response Surface Model represented the experimental data in an acceptable range.

In addition to 3 and 4 g/min, extraction with 5 g/min was done to see the effect of the higher flow rate at these conditions. Extraction curves are presented in Figure 3.16. Increase in the flow rate from 3 to 5 g/min increased extraction rate in the fast extraction period, so decreased extraction time. Time required to reach the slow extraction period for all the flow rates were found to be less than 30 min and the shortest value which was around 25 min was obtained at 5 g /min (Figure 3.16). This results indicated that at 60 ^{o}C and 450 bar with 5 g/min solvent flow rate and 3 % ethanol addition into CO_2, extraction of all the released oil content of 5 g apricot kernel samples of particle size 2 is possible in 25 to 30 min extraction period.

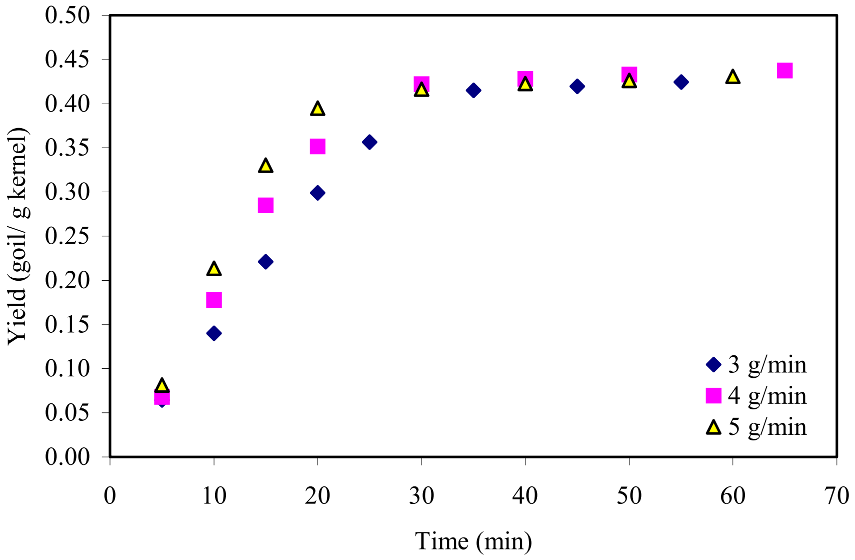


Figure 3.16. Comparison of different flow rates for extraction conditions of 450 bar (X_2=1), 60 ^{o}C (X_3=1), 3 % ethanol (X_4= 1) and particle size 2.

3.4. Fractionation and Comparison with Hexane Extraction

For fractionation purposes two set of extraction experiments were done. In the first set, fractionation by time intervals was aimed; extraction was done at 300 bar and 50 ^{o}C and fractions were collected between time intervals of 0-15, 30-60, 120-150 min. In the second set, fractionation by pressure increase was aimed; extraction was performed at 50 ^{o}C in two periods of 30 min. In the first period extraction was performed at 150 bar and in the second period at 400 bar. Also, to compare with the oil extracted with hexane, extraction with n-hexane was performed. Fatty acid compositions of the fractions were compared by Duncan's Multiple Range tests (Table D1-D10). Results are summarized in Tables 3.10 and 3.11.

Fatty acid compositions of all the fractions extracted in the first set (P=300 bar, T=50 ^oC) and oil extracted with hexane were similar, except the composition of palmitic acid (C16:0). Compositions of palmitic acid (C16:0) fractions extracted in the first two intervals were significantly higher than the oil extracted with hexane ($p < 0.01$) (Table 3.10).

Table 3.10. Fatty acid compositions of the apricot kernel oil fractions obtained at different time intervals during SC-CO_2 extraction and the oil extracted with hexane

Set No	P (bar)	T (^oC)	Time interval (min)	Fatty Acid Composition (%)*				
				C16:0	**C16:1**	**C18:0**	**C18:1**	**C18:2**
1	300	50	0-15	5.71^a	0.78^a	1.30^a	67.37^a	24.84^a
	300	50	30-60	5.73^a	0.69^a	0.91^a	67.50^a	25.18^a
	300	50	120-150	5.43^{ab}	0.83^a	0.99^a	67.53^a	25.22^a
Hexane				5.22^b	0.60^a	1.00^a	68.07^a	25.11^a

*Numbers with different letters in each column are significantly different at $p<0.01$ level.

In the second set, palmitic acid (C16:0) composition of the fraction obtained at 150 bar and 50 °C was significantly greater than that of the fraction obtained at 400 bar and than the oil extracted with hexane ($p<0.01$). Furthermore, stearic acid (C18:0) composition of the fraction obtained at 400 bar were significantly smaller than that of the fraction obtained at 150 bar and than the oil extracted with hexane ($p<0.01$) (Table 3.10).

Table 3.11. Fatty acid compositions of the apricot kernel oil fractions obtained at different pressures during SC-CO_2 extraction and the oil extracted with hexane

Set No	P (bar)	T (°C)	Time interval (min)	Fatty Acid Composition (%)* C16:0	C16:1	C18:0	C18:1	C18:2
2	150	50	0-30	6.21^a	0.74^a	0.97^a	66.88^a	25.20^a
	400	50	30-60	5.42^b	0.83^a	0.43^b	67.56^a	25.75^a
Hexane				5.22^b	0.60^a	1.00^a	68.07^a	25.11^a

*Numbers with different letters in each column are significantly different at $p<0.01$ level.

Therefore, significant differences were found only in palmitic (C16:0) and stearic (C18:0) acid compositions of the oil fractions. However, these fatty acids make only the 6 - 7 % of the total composition and main fatty acids in the oil are oleic

(C18:1) and linoleic (C18:2) acids with about 67 and 25 % compositions, respectively, for all the oils. This indicated that most of the glycerides in the apricot kernel oil contains these fatty acids (especially C18:1) in their structures, therefore solubility of these glycerides are nearly similar. Due to these properties of apricot kernel oil, fractionation of the oil according to fatty acid composition was not possible.

CHAPTER 4

CONCLUSIONS AND RECOMENDATIONS

Crossover pressure of apricot kernel oil was determined to be between 200 and 300 bars. Above the crossover pressure solubility increased with increasing pressure and temperature in the ranges of 150 to 600 bar and 40 to 60 ^{o}C. All the density-based models represented the solubility data well but the best one was found to be Adachi and Lu Equation. The empirical model proposed for solubility as a function of temperature and pressure was equally successful.

Extraction of apricot kernel oil occurred in two stages as fast and slow extraction periods. Rate of the fast extraction period was found several orders of magnitude greater than rate of the slow extraction period. In fast extraction period the released oil was extracted while in slow extraction period the unreleased oil was extracted. The oil recovered in the slow extraction period was negligible compared to the oil recovered in the fast extraction period. Therefore, continuation of extraction in the slow extraction period was unnecessary.

Grinding is necessary to release the oil from intact oil cells of kernel structure to increase the released oil percentage in the particle. Apricot kernel oil yield (or oil recovery) increased with the degree of grinding. More than 99 % apricot kernel oil recovery compared to hexane extraction was possible if particle diameter decreased below 0.425 mm.

Broken and intact cells model for vegetable oils represented the apricot kernel oil extraction well. Volume mass transfer coefficient in the fluid phase was several orders of magnitude greater than mass transfer coefficient in the solid phase and it represented the mass transfer in the fast extraction period. Its value increased with; decrease in particle size and pressure, and increase in flow rate, temperature and ethanol concentration. The value of mass transfer coefficient in the fluid phase was changed from 0.6 to 3.7 /min in the range of experiments. Changes in mass transfer coefficient in the solid phase were not important due to insignificant amount of oil recovery in the slow extraction period.

Addition of ethanol as co-solvent in SC-CO_2 increased the solubility of apricot kernel oil. This increase in solubility affected extraction rate positively which indicated that instead of higher pressures ethanol addition could be done in to SC-CO_2 to decrease extraction time.

Flow rate, pressure, temperature and ethanol concentration, as well as interactions between, flow rate and pressure, and, pressure and temperature affected apricot kernel oil yield significantly in the ranges of 2 to 4 g/min, 300 to 450 bar, 50 to 60 ^{o}C, 0.0 to 3.0 % ethanol. The yield increased with increase in flow rate, temperature, pressure and ethanol concentration, indicating the increase in extraction rate. Apricot kernel oil yield during 15 min extraction was represented by a Response Surface Model in this experimental range. Maximum value of oil yield was found to be around 0.26 g oil /g kernel at conditions of 4 g/min flow rate, 60 ^{o}C, 450 bar and 3 % ethanol concentration in the ranges of the study. At these conditions 30 min extraction time was found to be enough to extract all of the released oil in the bed. Additional increase in flow rate to 5 g/min further decreased this extraction time.

Apricot kernel oil contained mainly oleic (67 %) and linoleic (25 %) acids, and their concentrations in the oil were not significantly affected by experimental conditions. Therefore, fractionation of the oil according to fatty acid composition was not possible.

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APPENDIX A

SFE DATA

Table A1. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=3 g/min, particle size 1)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
15	44.6	0.133	0.132
30	91.7	0.267	0.263
40	122.7	0.354	0.349
45	136.4	0.391	0.390
50	152.5	0.433	0.428
55	165.9	0.462	0.460
60	181.3	0.481	0.478
71	213.9	0.484	0.479
90	269.7	0.485	0.479

AAD: 0.9 %

Table A2. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
10	28.4	0.085	0.088
20	58.5	0.179	0.175
30	87.2	0.267	0.261
38	107.7	0.318	0.322
45	130.4	0.378	0.376
50	145.1	0.400	0.402
55	159.4	0.414	0.413
60	174.0	0.415	0.413
65	188.3	0.417	0.414
75	219.1	0.419	0.415
90	266.4	0.422	0.417
10	29.4	0.087	0.088
20	58.0	0.173	0.175
30	87.9	0.263	0.261
41	120.3	0.352	0.349
50	148.0	0.406	0.402
60	178.1	0.412	0.413
75	221.3	0.418	0.415

AAD: 1.1 %

Table A3. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50^{o}C Q=3 g/min, particle size 3)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
5	15.0	0.041	0.044
10	29.6	0.085	0.087
15	45.1	0.130	0.131
20	60.6	0.177	0.173
25	76.4	0.221	0.214
30	91.4	0.263	0.252
35	106.2	0.287	0.284
41	123.1	0.302	0.306
50	153.9	0.310	0.309
65	197.0	0.314	0.314
90	269.7	0.322	0.321
5	15.3	0.045	0.044
10	31.0	0.088	0.087
15	46.2	0.131	0.131
20	61.6	0.174	0.173
25	79.6	0.222	0.214
30	92.0	0.258	0.252
35	107.6	0.286	0.284
40	120.2	0.298	0.304
45	135.8	0.303	0.308
50	149.7	0.307	0.309
60	182.4	0.312	0.312
75	225.7	0.316	0.317

AAD: 1.7 %

Table A4. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=3 g/min, particle size 4)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
5	15.0	0.044	0.042
10	30.4	0.089	0.083
13	38.8	0.111	0.106
17	52.0	0.137	0.133
20	62.8	0.150	0.149
25	75.3	0.158	0.160
30	90.3	0.164	0.163
40	121.2	0.172	0.169
50	149.7	0.177	0.174
67	199.5	0.183	0.183
90	269.7	0.191	0.195

AAD: 2.4 %

Table A5. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=1 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
34	34.2	0.090	0.100
60	58.4	0.161	0.176
80	80.4	0.234	0.234
100	101.3	0.294	0.291
125	125.5	0.363	0.359
150	149.7	0.397	0.408
175	175.1	0.408	0.414
200	200.4	0.412	0.415
225	220.0	0.418	0.416
250	249.2	0.420	0.416

AAD: 2.9 %

Table A6. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=2 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
15	30.8	0.088	0.088
25	50.6	0.147	0.146
30	61.1	0.177	0.175
35	72.0	0.206	0.205
40	81.5	0.233	0.234
47	96.3	0.276	0.274
55	111.8	0.319	0.318
60	121.7	0.346	0.344
65	130.2	0.369	0.369
70	141.3	0.394	0.390
75	151.1	0.406	0.406
80	160.7	0.411	0.413
85	171.6	0.414	0.413
91	182.5	0.415	0.414
105	211.4	0.417	0.415
125	252.1	0.421	0.416
135	269.7	0.422	0.417

AAD: 0.5 %

Table A7. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=4 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
10	37.7	0.114	0.116
20	77.3	0.235	0.230
25	95.5	0.287	0.285
30	113.2	0.339	0.335
35	132.4	0.385	0.379
40	152.3	0.407	0.408
45	171.2	0.413	0.413
50	192.1	0.414	0.414
55	212.5	0.416	0.415
65	253.2	0.416	0.416
73	286.3	0.416	0.418

AAD: 0.7 %

Table A8. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50^{o}C Q=5 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
5	25.8	0.075	0.072
10	49.2	0.143	0.143
15	74.4	0.218	0.213
20	100.1	0.293	0.280
25	125.5	0.360	0.341
30	150.2	0.400	0.389
35	175.1	0.407	0.413
40	200.3	0.410	0.414
50	249.9	0.413	0.416
60	302.8	0.416	0.418

AAD: 2.2 %

Table A9. Experimental and predicted yields (Extraction conditions: P=300 bar, T=50^{o}C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
29	85.4	0.114	0.122
45	135.0	0.183	0.189
61	185.5	0.243	0.254
80	242.5	0.321	0.329
101	305.9	0.389	0.395
123	369.9	0.408	0.413
140	421.6	0.411	0.414
160	480.2	0.412	0.415
180	540.5	0.412	0.417

AAD: 2.5 %

Table A10. Experimental and predicted yields (Extraction conditions: P=375 bar, T=50°C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
4	29.1	0.028	0.024
15	120.5	0.103	0.099
31	241.0	0.198	0.197
46	360.5	0.295	0.291
54	423.9	0.339	0.338
61	479.9	0.380	0.374
68	540.2	0.401	0.404
76	601.5	0.406	0.413
84	662.8	0.413	0.414
91	720.9	0.414	0.414
96	759.7	0.416	0.415

AAD: 2.3 %

Table A11. Experimental and predicted yields (Extraction conditions: P=525 bar, T=50°C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
10	30.0	0.113	0.113
15	46.0	0.171	0.170
20	60.8	0.220	0.224
25	75.6	0.271	0.277
30	90.7	0.324	0.325
40	119.9	0.391	0.399
50	149.9	0.406	0.414
60	180.3	0.408	0.415
70	209.9	0.409	0.417
80	240.5	0.411	0.418

AAD: 1.4 %

Table A12. Experimental and predicted yields (Extraction conditions: P=600 bar, T=50°C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
5	14.8	0.061	0.064
10	30.1	0.125	0.129
15	45.2	0.184	0.192
25	75.1	0.306	0.308
30	90.8	0.358	0.356
35	105.6	0.387	0.393
41	120.3	0.402	0.413
51	153.8	0.410	0.415
62	185.2	0.413	0.417
80	240.6	0.417	0.420

AAD: 2.1 %

Table A13. Experimental and predicted yields (Extraction conditions: P=450 bar, T=40°C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
13	41.1	0.104	0.095
22	65.0	0.160	0.160
30	90.2	0.224	0.216
38	113.0	0.274	0.270
45	135.5	0.319	0.314
60	180.9	0.391	0.388
71	211.0	0.402	0.412
75	225.2	0.406	0.413
90	273.1	0.408	0.415
105	314.8	0.410	0.416
120	360.7	0.413	0.418

AAD: 2.2 %

Table A14. Experimental and predicted yields (Extraction conditions: P=450 bar, T=60^{o}C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
11	32.8	0.120	0.118
20	61.1	0.218	0.215
27	78.4	0.280	0.283
33	99.3	0.352	0.349
40	121.1	0.398	0.403
50	150.8	0.411	0.414
60	179.5	0.414	0.415
70	210.3	0.418	0.417
90	269.7	0.422	0.419

AAD: 0.9 %

Table A15. Experimental and predicted yields (Extraction conditions: P=450 bar, T=70^{o}C Q=3 g/min, particle size 2)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
5	15.7	0.057	0.060
10	29.9	0.119	0.119
15	45.0	0.184	0.179
20	60.0	0.260	0.239
25	75.0	0.319	0.298
30	90.2	0.366	0.355
35	104.9	0.401	0.402
40	120.2	0.406	0.413
45	135.5	0.408	0.414
50	150.0	0.410	0.415
55	166.9	0.412	0.416
65	195.6	0.415	0.417

AAD: 2.6 %

Table A16. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50^{o}C Q=3 g/min, particle size 2, ethanol concentration = 0.5 %)

Time (min)	**CO_2 Used (g)**	**Yield (g oil/ g kernel)**	
		Experimental	**Predicted**
5	15.0	0.044	0.048
10	29.5	0.091	0.096
15	46.5	0.144	0.143
20	60.0	0.190	0.191
30	90.0	0.290	0.284
40	120.0	0.367	0.369
50	150.0	0.409	0.413
60	179.9	0.417	0.414
70	207.7	0.420	0.416
80	239.9	0.424	0.417
90	268.9	0.426	0.418

AAD: 2.2 %

Table A17. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50^{o}C Q=3 g/min, particle size 2, ethanol concentration = 1.0 %)

Time (min)	**CO_2 Used (g)**	**Yield (g oil/ g kernel)**	
		Experimental	**Predicted**
5	15.0	0.047	0.051
10	30.0	0.096	0.102
20	60.1	0.205	0.204
5	15.0	0.046	0.051
10	30.0	0.099	0.102
15	45.0	0.160	0.153
20	60.1	0.208	0.204
25	75.0	0.261	0.254
30	90.0	0.309	0.304
40	120.1	0.396	0.390
50	150.0	0.414	0.413
60	180.2	0.418	0.415
80	240.1	0.420	0.418

AAD: 3.3 %

Table A18. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50°C Q=3 g/min, particle size 2, ethanol concentration = 1.5 %)

Time (min)	CO_2 Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
5	14.9	0.059	0.054
10	30.0	0.103	0.108
20	60.0	0.219	0.216
30	89.9	0.328	0.321
40	120.0	0.402	0.405
50	150.4	0.410	0.414
60	179.9	0.416	0.415
70	210.4	0.419	0.417
80	239.8	0.422	0.418
5	15.0	0.049	0.054
10	30.0	0.107	0.108
15	45.0	0.168	0.162
20	60.0	0.229	0.216
25	75.0	0.287	0.269
30	90.0	0.331	0.321
35	105.0	0.375	0.369
40	119.7	0.395	0.405

AAD: 3.2 %

Table A19. Experimental and predicted yields (Extraction conditions: P=450 bar, T=50^{o}C Q=3 g/min, particle size 2, ethanol concentration = 3.0 %)

Time (min)	CO$_2$ Used (g)	Yield (g oil/ g kernel)	
		Experimental	Predicted
10	30.0	0.119	0.132
15	45.0	0.202	0.198
20	60.0	0.284	0.263
5	15.0	0.045	0.066
10	30.0	0.117	0.132
15	45.1	0.200	0.198
20	60.1	0.278	0.263
30	90.0	0.388	0.386
40	120.0	0.418	0.414
50	150.1	0.422	0.416
60	183.3	0.425	0.417
70	210.1	0.428	0.419
80	240.0	0.430	0.421

AAD: 7.3 %

Table A20. Experimental yields (Extraction conditions: P=450 bar, T=60^{o}C Q=3 g/min, particle size 2, ethanol concentration = 3.0 %)

Time (min)	Yield (g oil/ g kernel)
5	0.065
10	0.140
15	0.221
20	0.299
25	0.357
35	0.415
45	0.420
55	0.425

Table A21. Experimental yields (Extraction conditions: P=450 bar, T=60^{o}C Q=4 g/min, particle size 2, ethanol concentration = 3.0 %)

Time (min)	Yield (g oil/ g kernel)
5	0.068
10	0.178
15	0.285
20	0.352
30	0.422
40	0.428
50	0.433
65	0.438

Table A22. Experimental yields (Extraction conditions: P=450 bar, T=60^{o}C Q=5 g/min, particle size 2, ethanol concentration = 3.0 %)

Time (min)	Yield (g oil/ g kernel)
5	0.082
10	0.214
15	0.330
20	0.395
30	0.417
40	0.423
50	0.426
60	0.431

APPENDIX B

REGRESSION TABLES FOR SOLUBILITY MODELING

Table B1. Regression table for the Chrastil Equation

```
Regression Analysis

The regression equation is
ln c = - 56.8 + 11.1 ln d - 5369 1/T

Predictor          Coef        StDev           T          P
Constant        -56.833        1.655      -34.34      0.000
ln d            11.0926       0.2216       50.06      0.000
1/T             -5368.8        411.4      -13.05      0.000

S = 0.1190      R-Sq = 99.5%     R-Sq(adj) = 99.4%

Analysis of Variance

Source              DF           SS           MS          F          P
Regression           2       35.522       17.761    1255.01      0.000
Residual Error      12        0.170        0.014
Total               14       35.692

Source         DF       Seq SS
ln d            1       33.112
1/T             1        2.410
```

```
Obs     ln d      ln c        Fit  StDev Fit    Residual    St Resid
  1     6.67   -0.1442    -0.0101     0.0634     -0.1342       -1.33
  2     6.56   -0.4549    -0.6997     0.0609      0.2448        2.40
  3     6.40   -2.1153    -1.9348     0.0898     -0.1805       -2.31
  4     6.83    1.8209     1.7459     0.0492      0.0750        0.69
  5     6.78    1.8357     1.7973     0.0308      0.0384        0.33
  6     6.73    1.8550     1.7557     0.0483      0.0992        0.91
  7     6.89    2.5421     2.4791     0.0497      0.0630        0.58
  8     6.86    2.6444     2.6203     0.0336      0.0241        0.21
  9     6.83    2.8136     2.7641     0.0515      0.0496        0.46
 10     6.92    2.7498     2.7465     0.0510      0.0033        0.03
 11     6.89    2.9594     2.9420     0.0367      0.0174        0.15
 12     6.86    3.1361     3.1190     0.0544      0.0171        0.16
 13     6.94    2.8706     2.9972     0.0527     -0.1266       -1.19
 14     6.91    3.1767     3.2548     0.0405     -0.0782       -0.70
 15     6.89    3.3516     3.4640     0.0579     -0.1124       -1.08
```

Table B2. Regression table for the del Valle and Aguilera Equation

```
Regression Analysis

The regression equation is
ln c = - 57.5 + 11.1 ln d + 44541 1/T - 8055332 1/T2

Predictor        Coef       StDev          T        P
Constant       -57.47       67.49      -0.85    0.413
ln d          11.0872      0.2191      50.61    0.000
1/T             44541       43588       1.02    0.329
1/T2         -8055332     7034415      -1.15    0.276

S = 0.1176      R-Sq = 99.6%     R-Sq(adj) = 99.5%

Analysis of Variance

Source            DF          SS          MS         F        P
Regression         3      35.540      11.847    857.06    0.000
Residual Error    11       0.152       0.014
Total             14      35.692

Source       DF      Seq SS
ln d          1      33.110
1/T           1       2.412
1/T2          1       0.018

Obs   ln d       ln c         Fit  StDev Fit    Residual   St Resid
  1  -0.239    -0.1442    -0.0327     0.0658     -0.1115      -1.14
  2  -0.350    -0.4549    -0.6500     0.0747      0.1951       2.15
  3  -0.506    -2.1153    -1.9577     0.0911     -0.1576      -2.12
  4  -0.081     1.8209     1.7224     0.0528      0.0985       0.94
  5  -0.124     1.8357     1.8469     0.0527     -0.0112      -0.11
  6  -0.173     1.8550     1.7299     0.0526      0.1251       1.19
  7  -0.015     2.5421     2.4552     0.0535      0.0869       0.83
  8  -0.050     2.6444     2.6695     0.0541     -0.0251      -0.24
  9  -0.082     2.8136     2.7378     0.0557      0.0759       0.73
 10   0.009     2.7498     2.7224     0.0547      0.0274       0.26
 11  -0.021     2.9594     2.9911     0.0559     -0.0317      -0.31
 12  -0.050     3.1361     3.0937     0.0584      0.0425       0.42
 13   0.032     2.8706     2.9719     0.0562     -0.1013      -0.98
 14   0.007     3.1767     3.3037     0.0583     -0.1271      -1.24
 15  -0.019     3.3516     3.4374     0.0616     -0.0858      -0.86
```

Table B3. Regression table for the Adachi and Lu Equation

```
Regression Analysis

The regression equation is
ln c = 19.9 + 17.8 ln d - 15.8 d ln d + 8.4 d^2 ln d - 5430 1/T

Predictor          Coef        StDev           T         P
Constant         19.944        1.344       14.85     0.000
ln d             17.812        9.350        1.91     0.086
d ln d           -15.85        25.96       -0.61     0.555
d^2 ln d           8.40        17.79        0.47     0.647
1/T             -5429.5        429.5      -12.64     0.000

S = 0.1085      R-Sq = 99.7%     R-Sq(adj) = 99.5%

Analysis of Variance

Source            DF          SS          MS         F         P
Regression         4     35.5746      8.8936    755.86     0.000
Residual Error    10      0.1177      0.0118
Total             14     35.6922

Source       DF      Seq SS
ln d          1     33.1099
d ln d        1      0.0921
d^2 ln d      1      0.4919
1/T           1      1.8807

Obs    ln d     ln c        Fit     StDev Fit    Residual    St Resid
1    -0.239  -0.1442     0.0805        0.0721     -0.2247       -2.77
2    -0.350  -0.4549    -0.6393        0.0838      0.1844        2.68
3    -0.506  -2.1153    -2.0744        0.1071     -0.0408       -2.40
4    -0.081   1.8209     1.7659        0.0702      0.0549        0.66
5    -0.124   1.8357     1.8525        0.0474     -0.0168       -0.17
6    -0.173   1.8550     1.8403        0.0604      0.0147        0.16
7    -0.015   2.5421     2.4496        0.0515      0.0925        0.97
8    -0.050   2.6444     2.6236        0.0392      0.0208        0.21
9    -0.082   2.8136     2.7953        0.0512      0.0183        0.19
10    0.009   2.7498     2.6996        0.0525      0.0502        0.53
11   -0.021   2.9594     2.9231        0.0351      0.0363        0.35
12   -0.050   3.1361     3.1279        0.0501      0.0082        0.09
13    0.032   2.8706     2.9337        0.0739     -0.0632       -0.80
14    0.007   3.1767     3.2152        0.0496     -0.0386       -0.40
15   -0.019   3.3516     3.4478        0.0556     -0.0963       -1.03
```

Table B4. Regression table for Eq. 3.1

```
Regression Analysis

The regression equation is
S(mg/g) = 0.2 + 0.233 P -0.000868 P^2 - 0.0179 T (K) -0.000602 P*T
           +0.000003 P^2*T

Predictor         Coef        StDev          T        P
Constant          0.24        31.31       0.01    0.994
P               0.2329       0.1905       1.22    0.253
P^2         -0.0008678    0.0002522      -3.44    0.007
T (K)         -0.01792      0.09687      -0.18    0.857
P*T         -0.0006019    0.0005892      -1.02    0.334
P^2*T       0.00000274   0.00000078       3.51    0.007

S = 0.4991      R-Sq = 99.8%     R-Sq(adj) = 99.7%

Analysis of Variance

Source            DF          SS          MS          F        P
Regression         5     1150.82      230.16     923.92    0.000
Residual Error     9        2.24        0.25
Total             14     1153.06

Source         DF      Seq SS
P               1     1024.88
P2              1        1.82
T (K)           1       67.08
P*T             1       53.97
P2*T            1        3.07

Obs      P      S(mg/g)        Fit      StDev Fit      Residual   St Resid
  1    150      1.100        1.056       0.442          0.044        0.19
  2    150      0.900        0.590       0.280          0.310        0.75
  3    150      0.200        0.124       0.442          0.076        0.33
  4    300      6.700        7.024       0.328         -0.324       -0.86
  5    300      7.100        7.504       0.208         -0.404       -0.89
  6    300      7.600        7.984       0.328         -0.384       -1.02
  7    450     12.900       12.534       0.300          0.366        0.92
  8    450     14.800       15.192       0.190         -0.392       -0.85
  9    450     18.100       17.850       0.300          0.250        0.63
 10    525     15.500       15.117       0.257          0.383        0.89
 11    525     19.700       19.326       0.162          0.374        0.79
 12    525     24.200       23.536       0.257          0.664        1.55
 13    600     17.100       17.586       0.404         -0.486       -1.66
 14    600     23.800       23.654       0.256          0.146        0.34
 15    600     29.100       29.723       0.404         -0.623       -2.13
```

APPENDIX C

RESPONSE SURFACE REGRESSION TABLES

Table C1. Response Surface Regression table for yield

```
Response Surface Regression

The analysis was done using coded units.

Estimated Regression Coefficients for YIELD

Term                          Coef      StDev          T      P
------------------------------------------------------------------
Constant                  0.091367   0.006690     13.656  0.000
X1 (FLOW RATE)            0.039583   0.003345     11.833  0.000
X2 (PRESSURE)             0.043342   0.003345     12.956  0.000
X3 (TEMPERATURE)          0.015417   0.003345      4.609  0.001
X4 (% ETHANOL)            0.016925   0.003345      5.059  0.000
X1*X1                     0.006062   0.005018      1.208  0.250
X2*X2                     0.009900   0.005018      1.973  0.072
X3*X3                     0.008713   0.005018      1.736  0.108
X4*X4                     0.009650   0.005018      1.923  0.079
X1*X2                     0.018625   0.005794      3.214  0.007
X1*X3                    -0.001500   0.005794     -0.259  0.800
X1*X4                     0.004225   0.005794      0.729  0.480
X2*X3                     0.015875   0.005794      2.740  0.018
X2*X4                     0.007475   0.005794      1.290  0.221
X3*X4                     0.004125   0.005794      0.712  0.490
------------------------------------------------------------------

S = 0.01159     R-Sq = 97.0%     R-Sq(adj) = 93.4%
```

```
Analysis of Variance for YIELD

Source          DF     Seq SS      Adj SS      Adj MS      F      P
Regression      14   0.051261    0.051261    0.003661  27.27  0.000
  Linear         4   0.047634    0.047634    0.011908  88.68  0.000
  Square         4   0.000859    0.000859    0.000215   1.60  0.238
  Interaction    6   0.002768    0.002768    0.000461   3.43  0.033
Residual Error  12   0.001611    0.001611    0.000134
  Lack-of-Fit   10   0.001601    0.001601    0.000160  29.35  0.033
  Pure Error     2   0.000011    0.000011    0.000005
Total           26   0.052872


Observation    YIELD       Fit     StDev Fit   Residual    St Resid
          1    0.104     0.104         0.009     -0.000       -0.01
          2    0.119     0.126         0.009     -0.006       -0.83
          3    0.146     0.168         0.009     -0.022       -2.97
          4    0.091     0.091         0.007     -0.000       -0.05
          5    0.088     0.085         0.009      0.003        0.45
          6    0.177     0.185         0.009     -0.008       -1.00
          7    0.132     0.130         0.009      0.002        0.31
          8    0.114     0.107         0.009      0.007        0.95
          9    0.059     0.067         0.009     -0.008       -1.10
         10    0.059     0.058         0.009      0.000        0.05
         11    0.061     0.055         0.009      0.007        0.87
         12    0.042     0.043         0.009     -0.001       -0.08
         13    0.079     0.083         0.009     -0.005       -0.65
         14    0.071     0.080         0.009     -0.009       -1.27
         15    0.187     0.179         0.009      0.008        1.12
         16    0.217     0.209         0.009      0.008        1.02
         17    0.096     0.092         0.009      0.004        0.49
         18    0.156     0.146         0.009      0.010        1.32
         19    0.079     0.082         0.009     -0.003       -0.39
         20    0.163     0.160         0.009      0.004        0.52
         21    0.054     0.050         0.009      0.005        0.65
         22    0.065     0.066         0.009     -0.001       -0.17
         23    0.108     0.122         0.009     -0.014       -1.93
         24    0.089     0.091         0.007     -0.002       -0.22
         25    0.094     0.091         0.007      0.003        0.27
         26    0.083     0.077         0.009      0.006        0.85
         27    0.145     0.132         0.009      0.014        1.82
```

Table C2. Response Surface Regression table for yield (after removal of insignificant terms)

```
Response Surface Regression

The analysis was done using coded units.

Estimated Regression Coefficients for YIELD

Term                              Coef       StDev            T      P
Constant                          0.10662    0.002294    46.470  0.000
X1 (FLOW RATE)                    0.03958    0.003442    11.501  0.000
X2 (PRESSURE)                     0.04334    0.003442    12.593  0.000
X3 (TEMPERATURE)                  0.01542    0.003442     4.479  0.000
X4 (% ETHANOL)                    0.01692    0.003442     4.918  0.000
X1 (FLOW RATE)*X2 (PRESSURE)      0.01863    0.005961     3.124  0.005
X2 (PRESSURE)*X3 (TEMPERATURE)0.01587    0.005961     2.663  0.015

S = 0.01192     R-Sq = 94.6%     R-Sq(adj) = 93.0%

Analysis of Variance for YIELD

Source          DF    Seq SS      Adj SS      Adj MS       F      P
Regression       6  0.050029    0.050029    0.008338   58.66  0.000
  Linear         4  0.047634    0.047634    0.011908   83.78  0.000
  Interaction    2  0.002396    0.002396    0.001198    8.43  0.002
Residual Error  20  0.002843    0.002843    0.000142
  Lack-of-Fit   18  0.002832    0.002832    0.000157   28.85  0.034
  Pure Error     2  0.000011    0.000011    0.000005
Total           26  0.052872
```

Observation	YIELD	Fit	StDev Fit	Residual	St Resid
1	0.104	0.105	0.005	-0.001	-0.10
2	0.119	0.129	0.005	-0.010	-0.94
3	0.146	0.163	0.005	-0.018	-1.65
4	0.091	0.107	0.002	-0.016	-1.34
5	0.088	0.084	0.008	0.004	0.46
6	0.177	0.181	0.008	-0.004	-0.47
7	0.132	0.133	0.005	-0.001	-0.08
8	0.114	0.108	0.005	0.006	0.57
9	0.059	0.064	0.008	-0.005	-0.55
10	0.059	0.046	0.005	0.012	1.14
11	0.061	0.050	0.005	0.011	1.05
12	0.042	0.042	0.008	0.000	0.01
13	0.079	0.082	0.005	-0.004	-0.36
14	0.071	0.084	0.005	-0.013	-1.25
15	0.187	0.167	0.005	0.020	1.89
16	0.217	0.208	0.008	0.008	0.95
17	0.096	0.092	0.008	0.004	0.49
18	0.156	0.139	0.005	0.017	1.61
19	0.079	0.074	0.005	0.004	0.41
20	0.163	0.162	0.005	0.002	0.18
21	0.054	0.052	0.005	0.003	0.27
22	0.065	0.063	0.008	0.002	0.24
23	0.108	0.119	0.008	-0.011	-1.26
24	0.089	0.107	0.002	-0.017	-1.48
25	0.094	0.107	0.002	-0.013	-1.09
26	0.083	0.080	0.005	0.003	0.30
27	0.145	0.131	0.005	0.015	1.37

APPENDIX D

DUNCAN’S MULTIPLE RANGE TABLES

Table D1. Duncan’s Multiple Range table for palmitic acid (C16:0) composition of the apricot kernel oil fractions obtained at different time intervals during SC-CO_2 extraction and the oil extracted with hexane

```
Variable 3 (160)

      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of          Mean
          Freedom      Squares         Square          F-value    Prob.
---------------------------------------------------------------------------
Between       3          0.541           0.180           9.817    0.0047
Within        8          0.147           0.018
---------------------------------------------------------------------------
Total        11          0.688

          Coefficient of Variation = 2.45%

       Var.     V A R I A B L E   No. 3
        1      Number         Sum      Average          SD          SE
     ------------------------------------------------------------------
         1      3.00        17.130      5.710         0.10        0.08
         2      3.00        17.200      5.733         0.01        0.08
         3      3.00        16.280      5.427         0.22        0.08
         4      3.00        15.660      5.220         0.13        0.08
     ------------------------------------------------------------------
     Total     12.00        66.270      5.522         0.25        0.07
     Within                                           0.14


Error Mean Square = 0.01800
Error Degrees of Freedom = 8
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.3676
s_ = 0.07746    at alpha = 0.010
 x
_
     Original Order               Ranked Order

 Mean    1 =    5.710  A     Mean    2 =    5.733  A
 Mean    2 =    5.733  A     Mean    1 =    5.710  A
 Mean    3 =    5.427  AB    Mean    3 =    5.427  AB
 Mean    4 =    5.220   B    Mean    4 =    5.220   B
```

Table D2. Duncan's Multiple Range table for palmitoleic acid (C16:1) composition of the apricot kernel oil fractions obtained at different time intervals during SC-CO_2 extraction and the oil extracted with hexane

```
Variable 4 (161)


     A N A L Y S I S   O F   V A R I A N C E   T A B L E
        Degrees of    Sum of           Mean
         Freedom      Squares          Square          F-value    Prob.
---------------------------------------------------------------------------
Between       3          0.093           0.031           2.567    0.1274
Within        8          0.097           0.012
---------------------------------------------------------------------------
Total        11          0.190

          Coefficient of Variation = 15.21%

       Var.     V A R I A B L E   No. 4
        1      Number        Sum      Average          SD          SE
     ------------------------------------------------------------------
         1      3.00         2.340      0.780          0.01        0.06
         2      3.00         2.060      0.687          0.04        0.06
         3      3.00         2.490      0.830          0.22        0.06
         4      3.00         1.800      0.600          0.00        0.06
     ------------------------------------------------------------------
     Total     12.00         8.690      0.724          0.13        0.04
     Within                                            0.11


Error Mean Square = 0.01200
Error Degrees of Freedom = 8
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.3001
s_ = 0.06325    at alpha = 0.010
 x
_
     Original Order               Ranked Order

 Mean    1 =   0.7800  A    Mean    3 =   0.8300  A
 Mean    2 =   0.6867  A    Mean    1 =   0.7800  A
 Mean    3 =   0.8300  A    Mean    2 =   0.6867  A
 Mean    4 =   0.6000  A    Mean    4 =   0.6000  A
```

Table D3. Duncan's Multiple Range table for stearic acid (C18:0) composition of the apricot kernel oil fractions obtained at different time intervals during SC-CO_2 extraction and the oil extracted with hexane

```
Variable 5 (180)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of           Mean
          Freedom      Squares          Square          F-value    Prob.
---------------------------------------------------------------------------
Between       3          0.263           0.088           2.629    0.1220
Within        8          0.267           0.033
---------------------------------------------------------------------------
Total        11          0.531

          Coefficient of Variation = 17.45%

       Var.     V A R I A B L E   No. 5
        1      Number         Sum      Average          SD          SE
     ------------------------------------------------------------------
         1      3.00         3.890      1.297         0.08        0.11
         2      3.00         2.720      0.907         0.25        0.11
         3      3.00         2.970      0.990         0.26        0.11
         4      3.00         2.990      0.997         0.02        0.11
     ------------------------------------------------------------------
     Total     12.00        12.570      1.047         0.22        0.06
     Within                                           0.18


Error Mean Square = 0.03300
Error Degrees of Freedom = 8
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.4977
s_ = 0.1049     at alpha = 0.010
 x
_
     Original Order               Ranked Order

 Mean    1 =    1.297  A    Mean    1 =    1.297  A
 Mean    2 =   0.9067  A    Mean    4 =   0.9967  A
 Mean    3 =   0.9900  A    Mean    3 =   0.9900  A
 Mean    4 =   0.9967  A    Mean    2 =   0.9067  A
```

Table D4. Duncan's Multiple Range table for oleic acid (C18:1) composition of the apricot kernel oil fractions obtained at different time intervals during SC-CO_2 extraction and the oil extracted with hexane

```
     Variable 6 (181)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of           Mean
          Freedom      Squares         Square          F-value    Prob.
-----------------------------------------------------------------------------
Between       3          0.861           0.287           2.304    0.1535
Within        8          0.997           0.125
-----------------------------------------------------------------------------
Total        11          1.858

          Coefficient of Variation = 0.52%

       Var.     V A R I A B L E  No. 6
        1      Number         Sum      Average          SD          SE
     -------------------------------------------------------------------
          1      3.00       202.100     67.367         0.03        0.20
          2      3.00       202.480     67.493         0.21        0.20
          3      3.00       202.600     67.533         0.32        0.20
          4      3.00       204.200     68.067         0.59        0.20
     -------------------------------------------------------------------
     Total      12.00       811.380     67.615         0.41        0.12
     Within                                            0.35


Error Mean Square = 0.1250
Error Degrees of Freedom = 8
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.9686
s_ = 0.2041     at alpha = 0.010
 x
_
     Original Order              Ranked Order

 Mean    1 =    67.37  A    Mean    4 =    68.07  A
 Mean    2 =    67.49  A    Mean    3 =    67.53  A
 Mean    3 =    67.53  A    Mean    2 =    67.49  A
 Mean    4 =    68.07  A    Mean    1 =    67.37  A
```

Table D5. Duncan's Multiple Range table for linoleic acid (C18:2) composition of the apricot kernel oil fractions obtained at different time intervals during SC-CO_2 extraction and the oil extracted with hexane

```
     Variable 7 (182)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of          Mean
          Freedom      Squares         Square          F-value    Prob.
---------------------------------------------------------------------------
Between       3          0.258           0.086           0.617
Within        8          1.115           0.139
---------------------------------------------------------------------------
Total        11          1.373

          Coefficient of Variation = 1.49%

       Var.     V A R I A B L E  No. 7
        1      Number        Sum      Average          SD         SE
     -------------------------------------------------------------------
          1      3.00        74.520     24.840          0.01        0.22
          2      3.00        75.520     25.173          0.09        0.22
          3      3.00        75.650     25.217          0.14        0.22
          4      3.00        75.340     25.113          0.73        0.22
     -------------------------------------------------------------------
     Total     12.00       301.030     25.086          0.35        0.10
     Within                                            0.37


Error Mean Square = 0.1390
Error Degrees of Freedom = 8
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 1.021
s_ = 0.2153     at alpha = 0.010
 x
_
     Original Order              Ranked Order

 Mean    1 =    24.84  A    Mean    3 =    25.22  A
 Mean    2 =    25.17  A    Mean    2 =    25.17  A
 Mean    3 =    25.22  A    Mean    4 =    25.11  A
 Mean    4 =    25.11  A    Mean    1 =    24.84  A
```

Table D6. Duncan's Multiple Range table for palmitic acid (C16:0) composition of the apricot kernel oil fractions obtained at different pressures during SC-CO_2 extraction and the oil extracted with hexane

```
Variable 3 (160)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of           Mean
          Freedom      Squares          Square          F-value    Prob.
---------------------------------------------------------------------------
Between       2          1.628           0.814          34.275    0.0005
Within        6          0.143           0.024
---------------------------------------------------------------------------
Total         8          1.771

          Coefficient of Variation = 2.74%

       Var.     V A R I A B L E  No. 3
        1      Number        Sum      Average          SD          SE
     ------------------------------------------------------------------
         1      3.00        18.620      6.207          0.22        0.09
         2      3.00        16.270      5.423          0.09        0.09
         3      3.00        15.660      5.220          0.13        0.09
     ------------------------------------------------------------------
     Total      9.00        50.550      5.617          0.47        0.16
     Within                                            0.15


Error Mean Square = 0.02400
Error Degrees of Freedom = 6
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.4690
s_ = 0.08944    at alpha = 0.010
 x
_
     Original Order              Ranked Order

 Mean    1 =    6.207  A     Mean    1 =    6.207  A
 Mean    2 =    5.423   B    Mean    2 =    5.423   B
 Mean    3 =    5.220   B    Mean    3 =    5.220   B
```

Table D7. Duncan’s Multiple Range table for palmitoleic acid (C16:1) composition of the apricot kernel oil fractions obtained at different pressures during SC-CO_2 extraction and the oil extracted with hexane

```
     Variable 4 (161)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of          Mean
          Freedom      Squares         Square          F-value    Prob.
---------------------------------------------------------------------------
Between       2          0.082           0.041           1.855    0.2359
Within        6          0.133           0.022
---------------------------------------------------------------------------
Total         8          0.216

          Coefficient of Variation = 20.61%

       Var.     V A R I A B L E  No. 4
        1      Number        Sum      Average          SD          SE
     ------------------------------------------------------------------
         1      3.00        2.210      0.737         0.07        0.09
         2      3.00        2.500      0.833         0.25        0.09
         3      3.00        1.800      0.600         0.00        0.09
     ------------------------------------------------------------------
     Total      9.00        6.510      0.723         0.16        0.05
     Within                                          0.15


Error Mean Square = 0.02200
Error Degrees of Freedom = 6
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.4490
s_ = 0.08563    at alpha = 0.010
 x
_
     Original Order               Ranked Order

 Mean    1 =   0.7367  A    Mean    2 =   0.8333  A
 Mean    2 =   0.8333  A    Mean    1 =   0.7367  A
 Mean    3 =   0.6000  A    Mean    3 =   0.6000  A
```

Table D8. Duncan's Multiple Range table for stearic acid (C18:0) composition of the apricot kernel oil fractions obtained at different pressures during SC-CO_2 extraction and the oil extracted with hexane

```
     Variable 5 (180)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of          Mean
          Freedom      Squares         Square          F-value    Prob.
---------------------------------------------------------------------------
Between       2          0.617           0.309          28.149    0.0009
Within        6          0.066           0.011
---------------------------------------------------------------------------
Total         8          0.683

          Coefficient of Variation = 13.15%

       Var.     V A R I A B L E   No. 5
        1      Number        Sum      Average          SD          SE
     -------------------------------------------------------------------
          1      3.00        2.900      0.967          0.18        0.06
          2      3.00        1.280      0.427          0.04        0.06
          3      3.00        2.990      0.997          0.02        0.06
     -------------------------------------------------------------------
     Total      9.00        7.170      0.797          0.29        0.10
     Within                                            0.10


Error Mean Square = 0.01100
Error Degrees of Freedom = 6
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 0.3175
s_ = 0.06055    at alpha = 0.010
 x
_
     Original Order              Ranked Order

 Mean    1 =   0.9667  A     Mean    3 =   0.9967  A
 Mean    2 =   0.4267   B    Mean    1 =   0.9667  A
 Mean    3 =   0.9967  A     Mean    2 =   0.4267   B
```

Table D9. Duncan's Multiple Range table for oleic acid (C18:1) composition of the apricot kernel oil fractions obtained at different pressures during SC-CO_2 extraction and the oil extracted with hexane

```
     Variable 6 (181)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of          Mean
          Freedom      Squares         Square          F-value    Prob.
---------------------------------------------------------------------------
Between       2          2.115          1.057           2.679    0.1474
Within        6          2.368          0.395
---------------------------------------------------------------------------
Total         8          4.483

          Coefficient of Variation = 0.93%

       Var.     V A R I A B L E  No. 6
        1      Number        Sum      Average          SD         SE
     ------------------------------------------------------------------
         1      3.00       200.650     66.883         0.90        0.36
         2      3.00       202.680     67.560         0.15        0.36
         3      3.00       204.200     68.067         0.59        0.36
     ------------------------------------------------------------------
     Total      9.00       607.530     67.503         0.75        0.25
     Within                                           0.63


Error Mean Square = 0.3950
Error Degrees of Freedom = 6
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 1.903
s_ = 0.3629     at alpha = 0.010
 x
_
     Original Order              Ranked Order

 Mean    1 =    66.88  A    Mean    3 =    68.07  A
 Mean    2 =    67.56  A    Mean    2 =    67.56  A
 Mean    3 =    68.07  A    Mean    1 =    66.88  A
```

Table D10. Duncan's Multiple Range table for linoleic acid (C18:2) composition of the apricot kernel oil fractions obtained at different pressures during SC-CO_2 extraction and the oil extracted with hexane

```
     Variable 7 (182)


      A N A L Y S I S   O F   V A R I A N C E   T A B L E
         Degrees of    Sum of          Mean
          Freedom      Squares         Square          F-value    Prob.
---------------------------------------------------------------------------
Between       2          0.726           0.363           0.636
Within        6          3.426           0.571
---------------------------------------------------------------------------
Total         8          4.153

          Coefficient of Variation = 2.98%

       Var.     V A R I A B L E   No. 7
        1      Number         Sum      Average          SD          SE
     ------------------------------------------------------------------
         1      3.00        75.590     25.197         1.02        0.44
         2      3.00        77.260     25.753         0.38        0.44
         3      3.00        75.340     25.113         0.73        0.44
     ------------------------------------------------------------------
     Total      9.00       228.190     25.354         0.72        0.24
     Within                                           0.76


Error Mean Square = 0.5710
Error Degrees of Freedom = 6
No. of observations to calculate a mean = 3

Duncan's Multiple Range Test
LSD value = 2.287
s_ = 0.4363     at alpha = 0.010
 x
_
     Original Order              Ranked Order

 Mean    1 =    25.20  A    Mean    2 =    25.75  A
 Mean    2 =    25.75  A    Mean    1 =    25.20  A
 Mean    3 =    25.11  A    Mean    3 =    25.11  A
```

APPENDIX E

FIGURES

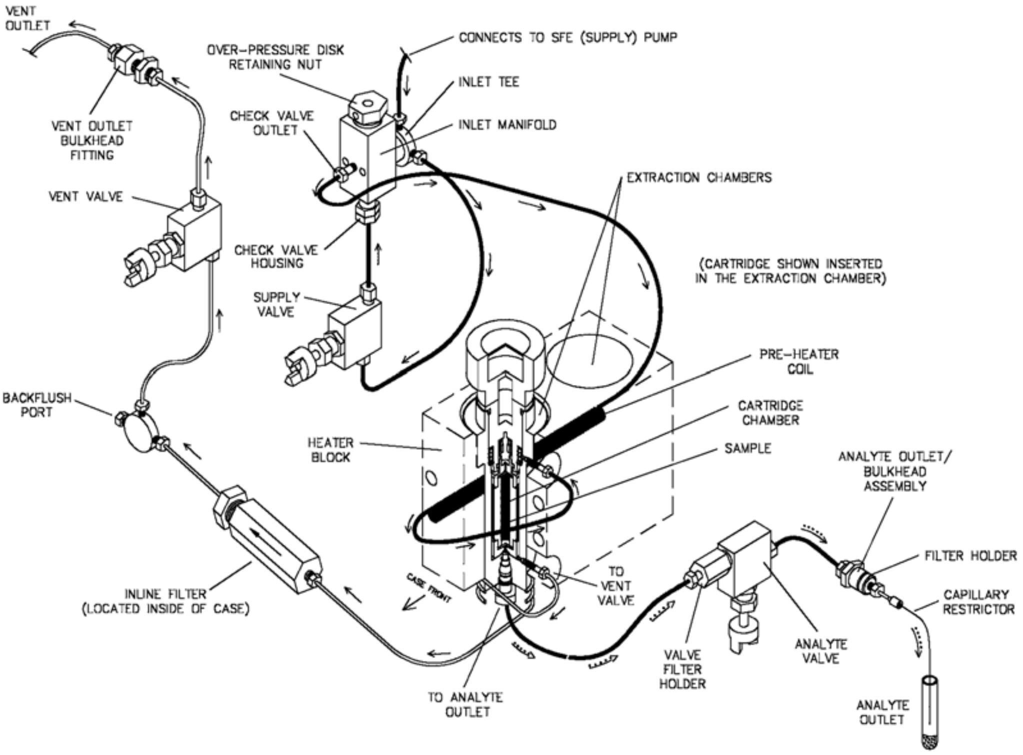

Figure E1. Fluid flow diagram of supercritical fluid extraction system.

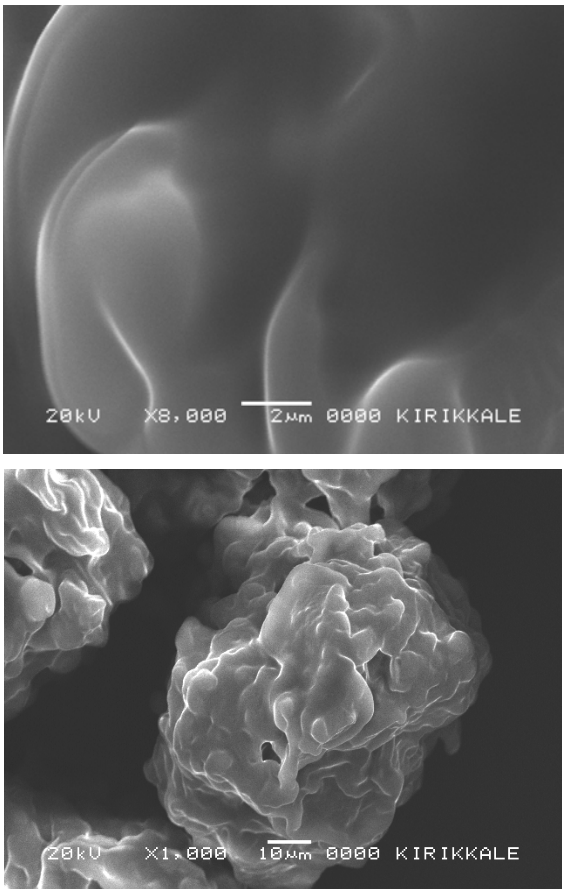

Figure E2. Scanning electron microscope images of the surface of an apricot kernel particle before extraction (particle size 2).

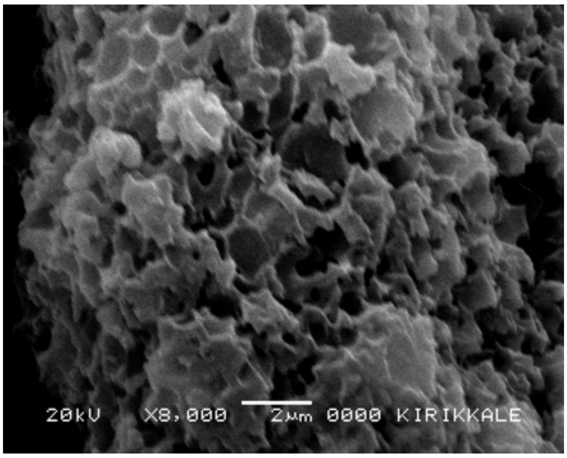

Figure E3. Scanning electron microscope image of the surface of an apricot kernel particle after SC-CO_2 extraction (particle size 2).

VITA

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