DEVELOPMENT AND UTILIZATION OF A METHOD FOR PECAN OIL EXTRACTION VIA SUPERCRITICAL CARBON DIOXIDE TO ENHANCE THE AMOUNT AND RATE OF OIL RECOVERY

By

WENDY ALEXANDER

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University of California, San Diego

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Thesis Approved:

Gerald H. Brusewitz

Thesis Advisor

Glenn Krazler

Neil Mann

Thomas C. Collins

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

The pecan industry began in the United States around 200 years ago. Pecans grown on wild trees along the Mississippi River were sold as early as 1802. Today's pecans are either native or an improved form. Improved pecans have been developed on trees that have been grafted or budded (seedlings). Native pecans are derived from trees without grafting or budding and are predominately grown along river beds in Oklahoma and Texas. Both native and improved pecans are commercially sold by distributors to bakers, retailers, and food service buyers. Bakers are the largest group using pecans (Santerre, 1994). Pecans are also used in ice cream products, cereal products, and confectionery products. Most pecan end users prefer to buy pecan halves and pieces. Pecan halves, pieces, and meal are used for a variety of baked products. Halves and pieces have been used for cookies, cakes, breads, muffins, and pies. Meal is mainly used for cookies and cakes.

Many of the uses for pecan halves in baked goods require heating. They may also be used raw after the baked product is cooked. The range of uses for raw pecan halves maintained at room temperature is limited by the short shelf life of this product. The high oil content of pecans (60-70% by weight) combined with the high percentage of poly-unsaturated fatty acids (25-27%) is the source of this problem. Specifically, the oxygen in air promotes oxidation of the oil, and the degenerative products formed lead to formation

of rancidity in pecans. The future growth of the pecan industry would be enhanced by the development of methods to prolong storage at room temperature of raw pecan halves.

Factors that may be controlled to prolong shelf life are temperature, moisture content, oxygen environment, lighting conditions, and externally applied antioxidants. Current use of room temperature storage methods that limit the exposure to oxygen delay the oxidation reaction, yet do not sufficiently prolong shelf life. They are also impractical for use in cereal products and baked products with uncooked pecans. New storage technology is needed to allow development of new products using pecans which may be stored at room temperature. This advance could help the pecan industry offset recent losses from a lack of high quality nuts.

A method proposed to extend shelf life combines reducing the oil content and storing in reduced oxygen environments. The rate of shelf life reduction of pecans from oil oxidation should decrease with a smaller quantity of the highly unsaturated pecan oil. The oil can be removed by a technique called supercritical fluid extraction (SFE). Supercritical fluid extraction is a non-destructive process that reduces the total oil content of the pecan.

As opposed to liquid solvent extraction, SFE uses a fluid in its supercritical state. The fluid commonly used for supercritical fluid extraction of food products is carbon dioxide (CO_2). It is Food and Drug Administration (FDA) accepted for use with food products because it is non-toxic to humans. Liquid extraction is performed using organic solvents (e.g. hexane) which may leave hazardous chemical residues in food products. The use of a safe fluid makes SFE a promising alternative to solvent extraction. Another

big difference between SFE and liquid extraction of pecans is the goal of the process. Liquid extraction is used to recover oil from the nuts. SFE is used to remove oil from the nuts and recover reduced-fat pecans. Thus, SFE produces two usable end products.

Other advantages of SFE as an extraction method for pecans are that the percentage of oil removed can be easily controlled, the recovered oil is a marketable product, and the pecan halves are left intact. A disadvantage is the requirement to operate above the critical pressure of the extraction fluid (7.38 MPa for CO_2). This constraint leads to high initial equipment costs for high pressure pumps, tubing, and extraction vessels. The new oil product and the extended shelf life of the pecans could be expected to offset some of the high equipment costs associated with SFE.

Another disadvantage of SFE is the lack of easy application to different foods and the lack of experimental data for different operating conditions. Experimental testing is therefore necessary to determine the information required for equipment and process system design. An important unknown parameter is the solubility of the potential extract. When CO_2 is used, an estimate of the degree of solubility of the extract in the fluid can be obtained from liquid CO_2 solubility charts. The solubility of the largest component in liquid CO_2 may be used for extracts composed of a mixture of substances.

SFE has been used for many food applications, including seed oil extraction, milk fat extraction, freeze-dried meat fat extraction, coffee and tea decaffeination, and hops organic acids extraction. Decaffeination of raw, soaked coffee beans was the first commercial SFE process. A commercial plant began operating in 1978 in Germany (Rizvi *et. al.*, 1986). Soaking in water was done to increase the selectivity of the supercritical

CO_2 for the caffeine. Initial caffeine levels in the coffee beans range from 0.7 to 3%. SFE reduced this value to less than 0.02% without harming the flavor and aroma of the coffee. Hops extraction was also first done in Germany (Rizvi *et. al.*, 1986). Milled hops are formed into pellets and then extracted with supercritical carbon dioxide. The carbon dioxide removes and concentrates the resulting extracts for use in manufacturing beer. This method supersedes liquid extraction with organic solvents that are being more heavily regulated by the Environmental Protection Agency (EPA) and that are hazardous to humans. However, it has been found to be less cost-effective.

The feasibility of SFE for pecans was demonstrated by Chao Zhang (1994). As much as 76.5% of the oil was removed in continuous flow extraction during a 3-h extraction at 80 °C, 68.9 MPa, and 2.0 standard liters per minute (slpm) gaseous CO_2 (slpm definition and conversion is given in Appendix). In static extractions, pecans halves did not break despite the use of high pressures, up to 10.3 MPa. Limitations of these experiments are that they were performed on small quantities of nuts (7 to 8 g), there was no control of fluid flowrate, and the results showed limited solubility of oil in supercritical CO_2.

Examination of the effect of CO_2 flowrate on the rate of extraction and the percentage of broken nuts (if any) is needed to provide information important for designing commercial plant-size operations. In addition, the use of larger quantities of pecans must be investigated. For laboratory experiments, a procedure must be developed that allows the amount of oil extract collected (which is a quantity easy to measure) to be an accurate measure of the oil removed from the pecans. This may be accomplished by

minimizing the difference between the final weight loss of the pecans and the total amount of oil collected.

Another unknown parameter is the change in the composition of the extract over time and for different processing conditions. This information is important to ensure that the poly-unsaturated fat responsible for reduced shelf life is being removed. The results of the experiments proposed will provide more information that may be useful in design and optimization of commercial pecan processing plant operations.

Objectives

This study was conducted to develop a method using continuous flow supercritical CO_2 for partial pecan oil extraction, and then to use this method to investigate extraction parameters. The specific objectives were:

1. To develop a method to minimize the difference between the oil removed from pecans and the oil collected during supercritical CO_2 extraction.
2. To determine the effect of micrometering valve temperature, collection vessel temperature, and CO_2 flowrate on oil recovery using supercritical CO_2 extraction.
3. To determine the effect of extraction temperature, pressure, time, and micrometering valve temperature on the fatty acid composition of oil recovered from pecans using supercritical CO_2 extraction.

4. To determine the effect of extraction temperature and pressure on the amount of oil extracted from pecans using supercritical CO_2.
5. To determine the factors controlling complete pecan oil extraction from whole pecan halves using supercritical CO_2.

CHAPTER II

LITERATURE REVIEW

Pecan Background

Pecans are classified as members of the walnut family. The word pecan is derived from the Native American word pegan, meaning bone shell (Coyle, 1982). Pecans are indigenous to North America and were originally found growing wild in the Mississippi Valley and river bottoms in Texas and Oklahoma. Pecan trees (Carya illinoinensis) are grown extensively in Oklahoma, Texas, Georgia, and New Mexico. Pecans are used in many food products including pies, cakes, ice cream, pudding, cookies, and cereals.

Oil Content

Pecans contain approximately 50-70% oil (by weight) depending on the variety, harvest year, harvest location, and level of maturity. Triglycerides make up over 95% of the lipids in pecan oil (Santerre, 1994). The oil contains mainly 16-18 carbon chain fatty acids with 0 to 3 double bonds. The main fatty acids with their carbon number, double bond number, and mole percentages (for low Nitrogen fertilized trees) are:

Palmitic acid	(16:0)	6.1%
Stearic acid	(18:0)	1.1%
Oleic acid	(18:1)	64.7%

Linoleic acid (18:2) 27.3%

Linolenic acid (18:3) 0.9%

Fatty acids with double bonds are unsaturated, while those without double bonds are saturated. Oleic acid and linoleic acid, which are mono-unsaturated and di-unsaturated, respectively, are the main components of pecan oil. Thus, pecan oil is highly unsaturated, with over 90% unsaturated fatty acids. Only canola and safflower oils have less saturated fat than pecan oil. It is also high in mono-unsaturated fat, exceeded only by olive oil. This composition makes pecan oil desirable from a nutritional standpoint, and also makes it an excellent candidate for a new cooking oil product.

Important quality factors for shelled pecans are size, color, aroma, texture, and flavor. Desirable pecans have a light amber color, are fairly large, and have a typical sweet odor and flavor (National Pecan Sheller's Association, 1988). Nut quality, as measured by flavor stability, relates to the chemical composition of the pecan oil as well as its total oil content. Oil content is therefore considered an important quality parameter for pecans (Woodroof and Heaton, 1961). High levels of poly-unsaturated fatty acids indicate high potential for rancidity and therefore poor flavor and low shelf life due to the presence of double bonds which are prone to attack by oxygen. A desirable pecan would store well for prolonged periods of time without going rancid. In terms of composition, this behavior necessitates a high oleic acid concentration (mono-unsaturated) and a low concentration of linoleic (poly-unsaturated) acid.

Among cultivars, the concentration of oleic and linoleic acid in the oil is inversely related. Studies have shown large variations of oleic/linoleic (O/L) ratios between the different

cultivars. However, a direct relation between oil content and flavor has not been substantiated (Rudolph *et. al.*, 1992a).

Fats

Fats, which are a significant part of pecans, are classified as the most abundant types of lipids. Lipids are generally defined as substances that are insoluble in water and can be extracted from cells by organic solvents of low polarity (Morrison and Boyd, 1987). Lipids are a class of organic substances that include triacylglycerols (fats), phospholipids, cholesterol, and free fatty acids (Santerre, 1994). Fats in the liquid state are called oils. Fats are chemically known as glycerides. Triglycerides may be broken into three fatty acids and a glycerol. Each fat has a characteristic fatty acid composition. Fatty acids are mainly straight-chain organic substances with 3 to 18 carbon atoms. They are mainly composed of an even number of carbon atoms, because they are formed in pairs in fat biosynthesis. The most common unsaturated fatty acids are oleic, linoleic, and linolenic. Each of these has previously been identified in pecan oil.

Unsaturated fatty acids may exist in either the cis- or trans- isomer forms. The configuration of hydrogen about the double bond in unsaturated fatty acids is usually cis-, although the trans-conformation is more stable (Morrison and Boyd, 1987). Saturated and trans-unsaturated fatty acid chains are straight, and therefore fit well with their own molecules and each other. Cis-unsaturated fatty acid chains contain a bend at the double bond. Therefore, they fit poorly with saturated chains and each other. The closer these molecules fit,

the stronger the intermolecular forces, and the higher the melting point of the fat. Thus, the poor fit of cis-unsaturated fatty acid chains leads to a lower melting point. For this reason, highly unsaturated fats, like those found in pecans, exist as liquids, and more saturated fats exist as solids at room temperature.

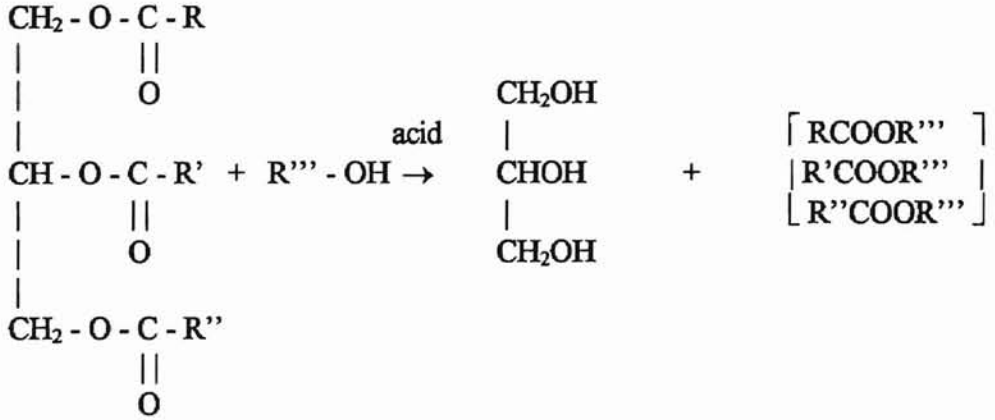
Methyl Ester Formation from Fatty Acids

Pecan oil is composed of fatty acids connected in triglyceride form as well as some free fatty acids. Fatty acid composition may be determined experimentally by converting the organic acids to esters and performing gas chromotography on the esters. The general form of the esterification reactions for both fatty acid forms is given below:

1. Free Fatty Acids

$$\underset{\text{organic acid}}{R\text{-}COOH} + \underset{\text{alcohol}}{R'\text{-}OH} \xleftrightarrow{\text{acid}} \underset{\text{ester}}{R\text{-}COO\text{-}R'} + \underset{\text{water}}{H_2O}$$

2. Glycerides



Glyceride Alcohol Glycerol Esters

The pecan oil is mixed with methanol in the presence of an acid catalyst. The reaction products are methyl esters corresponding to each fatty acid in the oil, glycerol, and water. The resulting mixture can be separated and analyzed with gas chromotography to determine the oil's fatty acid composition. The calculation of the fatty acid composition on a mole percent basis is performed by comparing the gas chromotography peak areas of the substance with those for a known quantity of an internal standard.

Tocopherol Content

Tocopherols are the most important natural antioxidants in fats and oils. Antioxidants are used to retard the rancidity process. Fats exposed to oxygen will go rancid in relation to the rate of depletion of natural antioxidants during storage. Pyriadi and Mason (1968) found a positive relationship between tocopherol content and pecan oil stability. This effect is due to the ability of tocopherol to protect fatty acids from free-radical attack. The free radicals are formed during auto-oxidation. Without the presence of tocopherols, the free radicals would be used in a series of chain reactions to cause fatty acid peroxidation. This deterioration process occurs during pecan storage and leads to rancidity and a reduction in shelf-life.

The γ-tocopherol accounts for over 95% of the total tocopherol content of pecans (Lambertsten *et al.*, 1962), i.e., between 12.3 and 17.4 mg /100 g oil (Fourie and Basson, 1989). It has the same antioxidant ability as α-tocopherol, yet can be oxidized to chroman-5-6-quinone, which has poor antioxidant properties. This leaves the unsaturated fatty acids vulnerable to free-radical attack.

Tocopherol content of pecans has been found to be related to pecan storage stability. Pecans were found to have better storability than macadamia nuts, but poorer than almonds (Fourie and Basson, 1989). The difference is due to the greater α-tocopherol concentration and total tocopherol content of the almonds and the smaller total tocopherol content of the macadamia nuts, relative to pecans. This effect shows the importance of both quantity and composition of tocopherol on retardation of rancidity. The total tocopherol content decreased in all three nuts during storage. This result may be due to the inhibitory function of tocopherols during auto-oxidation. They may act as hydrogen donors to stop the chain mechanism of auto-oxidation.

In a study of the chemical changes in extracted pecan oil, during oxidation tocopherol content decreased (Rudolph *et. al.*, 1992b). The tocopherol content remained constant until formation of peroxides. Tocopherol then began acting as an antioxidant and began to deplete. The fatty acids were found to oxidize as the tocopherols and pecan oil color disappeared. The color of the oil changed from yellow to reddish and finally became colorless. The color change was followed by a decrease in linoleic acid and oleic acid and an increase in rancidity products. Linoleic acid depleted more rapidly than oleic acid. This result indicates that linoleic acid is an important factor in oil degradation after harvest.

Monitoring the concentrations of both oleic and linoleic acid seemed to be a successful method of indicating oil storage potential. Pecan oil with higher amounts of oleic relative to linoleic acid was found to have higher keeping times (Rudolph *et. al.*, 1992b). It is possible that this approach is also applicable to the determination of pecan kernel storage potential. It may therefore serve as a suitable criterion for determination of extraction parameters when

reducing oil content for improved storage capability. This indication would be possible if different extraction conditions lead to different fatty acid compositions remaining in the extracted pecan. It is unlikely that poly-unsaturated fatty acids (linoleic, linolenic) would be separated by supercritical fluid extraction using only pure CO_2 due to the "small difference in the total double bond numbers of the triglycerides which consist of these fatty acids" (Saito *et. al.*, 1994). However, it may be possible to have at least minimal control over separation of poly-unsaturated (linoleic) and mono-unsaturated fatty acids (oleic).

Storage Ideas

Oxygen content and temperature are important parameters for storage of pecans. Commercial storage of pecan halves is done at room temperature (21-25 °C) in containers ranging from polyethylene bags to tin cans with storage lives extending from 3 to 6 months (Santerre, 1994). Storage in vacuum cans is often done by the snack food industry. This process is costly because of the evacuation process. Other methods used to reduce oxygen content include flushing with nitrogen or carbon dioxide, adding an oxygen absorbing compound to the package, or applying edible coatings to the pecans which create a modified atmosphere as the pecans respire.

Nitrogen flushing has been used to reduce oxygen contents to less than 5% (Dull and Kays, 1988) and is a method preferred over carbon dioxide flushing due to absorption of carbon dioxide by the pecan (Sacharow, 1971). Storage in packages impermeable to oxygen with low-oxygen environments (less than 2%) has been found to yield pecans with undesirable

flavors, darker color, and a softer texture. (Santerre, 1994). To avoid these problems, pecan storage is suggested in materials with oxygen transmission rates greater than 0.08 cc O_2 per 100 cm per 24 hr (Dull and Kays, 1988). Edible coatings have also been found to delay rancidity (Godkin *et. al.*, 1951) and are being used in the food industry to extend shelf life (Santerre, 1994). The expected shelf life extension for pecans is not sufficient to use this method alone. More research is needed to improve storage times using coatings.

Pecans are often packaged in clear bags made of polyethylene, cellophane, or different polymer substances so that consumers may see the product. These packages are typically exposed to fluorescent light and sunlight. The type of light incident on the packages has an effect on pecan color and shelf life. Pecan oil oxidation may be initiated by exposure to ultraviolet light (Santerre, 1994). Heaton and Shewfelt (1976) found that pecans exposed to both cool-white fluorescent light and sunlight became darker in color when stored in bags with high light transmission rates. The degree of darkening was lower for the pecans stored under fluorescent lights. Use of packages with lower light transmission rates produced no detectable darkening differences after 24 weeks of storage at 23 °C.

Another parameter that is important for pecan storage is moisture content. Water activities less than 0.68 are sufficient to prevent both mold and bacteria growth on pecans. The moisture content of the pecans required to achieve this water activity at 21 °C depends on oil content and ranges from approximately 4.5 to 5.7% (Santerre, 1994). Excessively low moisture contents (less than 2%) must be avoided, however, to prevent formation of surface cracks and disruption of membrane stability, which could lead to increased oil oxidation and therefore decreased shelf life.

Refrigeration is a viable method of deterring rancidity. Pecans stored at 0.6 °C and 75% RH (relative humidity) for 12 months yielded no changes in kernel color, oil quality, or tocopherol content (Yao *et. al.*, 1992). This result concurs with Woodroof and Heaton's (1979) determination that refrigeration is the most acceptable form of storage for pecans. Steam conditioning of nuts before cracking, heating the pecans to 80 °C followed by rapid cooling, and external application of antioxidants are also methods to retard rancidity, yet are less effective than refrigeration. These techniques are applicable to pecans that must be stored at room temperature, yet methods must be sought that effectively reduce rancidity without removing the flavor or destroying the texture of the pecan.

Supercritical Fluid Extraction

Extraction techniques which have been used to remove oil from pecans are by cold press and solvent extraction. The cold press method uses either a screw or hydraulic press to force the oil out of the pecans. A disadvantage of this procedure is the structural damage to the pecans. Solvent extraction is performed by contacting the pecan with a hot organic liquid (e.g. hexane). This technique does not reduce flavor, yet poses food safety concerns about potentially leaving toxic chemical residue. Supercritical fluid extraction using carbon dioxide has been proposed as a safe alternative to hexane extraction. This procedure uses a supercritical fluid as the solvent. A basic understanding of supercritical fluids is beneficial for optimum application of this technology.

Supercritical Fluid

A supercritical fluid is a fluid that exists above the critical point of a pure substance. Baron Cagniard de la Tour discovered the supercritical phenomenon in 1822 (Westwood, 1993). In the supercritical fluid region, there is no phase transition between a liquid and a gas. Figure 1 depicts the phase diagram for a pure substance. This graph shows the divisions between the solid, liquid, gas, and supercritical fluid phases. The saturation line extends from the triple point where solid, liquid, and gas coexist, to the critical point. Below the critical point, there is evaporation of a liquid to a gas and condensation of a gas to a liquid by crossing the saturation line. As the critical point is reached along the saturation line, density of the liquid phase decreases and density of the gas phase increases until they reach the same density and the distinction between liquid and gas disappears. At this point the substance is called a supercritical fluid. Since liquid and gas phases do not occur above the critical point, there can be no transitions between these phases in this region.

Since the supercritical fluid is formed from a 'melding' of a liquid and a gas, it retains properties of both phases. Specifically, it has a liquid-like density and gas-like diffusivity and viscosity. The density relates to its solute-holding power, diffusivity relates to mass transfer within the fluid, and its viscosity relates to flowrate during extraction. One of the primary advantages of supercritical fluid use is the ability to easily change its density, and therefore its solvating power, by changing the pressure at constant temperature. The solvating power of a supercritical fluid is increased by compressing the fluid, making its density more like that of a liquid (Saito *et. al.*, 1994). The compression causes molecular interactions to increase since there are shorter distances between the molecules and this proximity produces its solvating

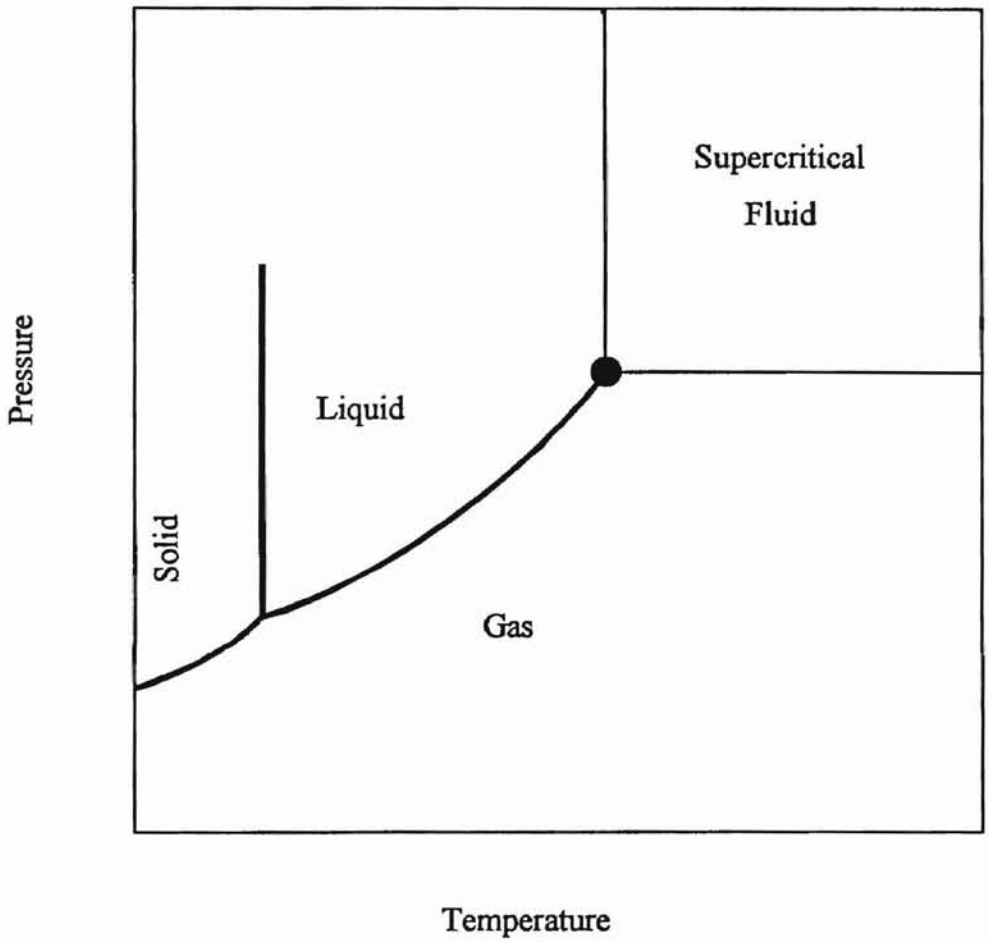


Figure 1: Phase diagram.

power. Selection of the fluid's density depends on the volatility and polarity of the compounds that require extraction. Generally, a low density is used to extract volatile, non-polar solutes and a higher density is used to extract less volatile and more polar solutes.

The overall solubility of a substance in a supercritical fluid is influenced by both the volatility of the solute, which is related to vapor pressure, and the solvating effect of the supercritical fluid, which is related to density (Westwood, 1993). The supercritical fluid solvent density is a function of both temperature and pressure. Pressure and density are directly related, while temperature and density are inversely related. The reduction in density due to an increase in temperature leads to a decrease in solubility. Temperature also effects the vapor pressure of the solute. As temperature increases, the solute's vapor pressure increases and the solubility increases. Thus, temperature causes both an increase and a decrease in solubility. These two competing effects lead to either a net increase or decrease in solubility. The area where the solubility decreases as temperature increases is called the retrograde region. Goodrum and Kilgro (1987a) found a retrograde region below a pressure of about 35 MPa for peanut oil extraction in the temperature range of 25 to 95 °C. Zhang (1994) did not report a retrograde region for pecan oil extraction at 40 to 80 °C and 41.3 to 68.9 MPa.

Carbon Dioxide

Many extractions, especially of foods, are performed with CO_2. CO_2 is non-toxic, non-reactive, non-flammable, abundant, inexpensive, and easily removed from the pecan and the

extract. The critical point of pure carbon dioxide is 31.05 °C, 7.38 MPa. Thermally labile products may be used with carbon dioxide due to its relatively low critical temperature.

At standard temperature and pressure (25 °C, 0.101325 MPa), CO_2 exists as a gas. CO_2 is modeled as a nonpolar, linear molecule with one carbon atom connected by a separate double bond to two oxygen atoms. It is classified as a quadropole since four charges (2 positive and 2 negative) are present, yet vectorially sum to a zero net dipole moment. (The four charges result from the unequal sharing of electrons in the carbon-oxygen double bonds. Specifically, oxygen has a greater affinity for electrons and receives a partial negative charge. The carbon atom receives a partial positive charge from each double bond.) By the rule that like dissolves like, it is logical that gaseous carbon dioxide can extract non-polar substances. Supercritical CO_2, however, can extract non-polar and slightly polar substances. The ability to dissolve slightly polar substances is due to the quadropole.

Supercritical CO_2 also provides increased solubilizing power over gaseous CO_2. This capability occurs because supercritical fluids exhibit liquid-like densities while maintaining gas-like diffusivities and viscosities. Another advantage of supercritical carbon dioxide is low surface tension. This quality allows it to penetrate the porous structure of a solid matrix to release the desired solute (McHugh and Krukonis, 1994). It can also be fine-tuned to selectively separate out different substances in a matrix, provided the substances have sufficiently different polarities, by increasing the extraction pressure at constant temperature. All these features make supercritical CO_2 an excellent solvent in extraction operations.

Modifiers

A chemical called a modifier may be added to a supercritical fluid to increase its solvent strength. Organic liquid modifiers are added to CO_2 to produce a solvent that can extract polar solutes. As discussed above, pure CO_2 is only capable of extracting non-polar and slightly polar solutes. A logical choice of modifier is a substance in which the desired extracts are soluble and with which other components of the extraction matrix do not react. Common modifiers are acetone, methanol, and ethanol (Singh and Rizvi, 1995). Wong and Johnston (1986) found that the solubility of cholesterol in CO_2 modified with 9% ethanol was 100 times greater than in pure CO_2.

It is important to realize that the addition of a modifier does change the properties of the extracting solvent. When organic modifiers are added to CO_2, the critical temperature of this mixture is greater than the critical temperature of pure CO_2 (Westwood, 1993). The critical temperature of the modifier/CO_2 mixture is between the critical temperatures of the pure components. The critical pressure of the mixture is greater than the critical pressures of the pure components (Singh and Rizvi, 1995).

Extraction

In food processing applications, three SFE operations that have been performed are total extraction, deodorization, and fractionation (Rizvi *et. al.*, 1986). The CO_2 phase diagram of Figure 2 depicts conditions used to perform these different functions. Total extraction is the

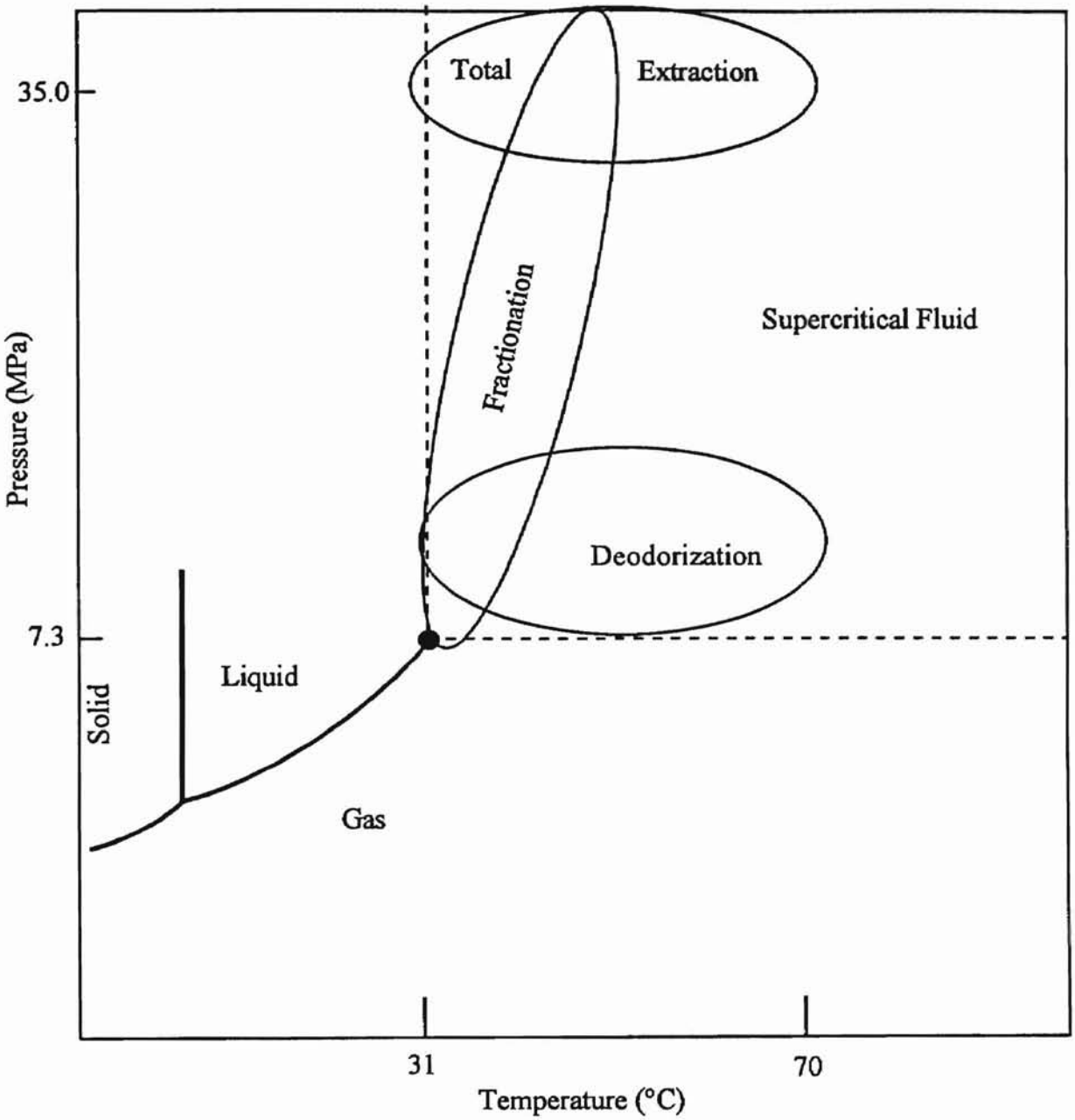


Figure 2: Pressure and temperature ranges for total extraction, deodorization, and fractionation with supercritical CO_2.

removal of all soluble compounds from a matrix and requires high pressures. Solubility of many solutes reaches the maximum levels at higher pressures. Pecan oil solubility increases with increasing pressure in the pressure range of 41.3 to 68.9 MPa (Zhang, 1994). As previously discussed, the effect of increasing temperature at constant pressure may increase or decrease solubility. For many products, like pecan oil, solubility is increased at higher temperatures. Increasing temperature was even found to have a greater effect than increasing pressure in the high-pressure region of 41.34 to 68.9 MPa for pecan oil (Zhang, 1994). The highest practical temperature used for extraction is limited, however, by the susceptibility of product to thermal degradation. For pecans, this occurs around 80 °C, when pecans begin to roast.

Deodorization is another SFE operation. Deodorization, as opposed to total extraction, involves the removal of odor components of a food product. The extraction is performed at much lower temperatures and pressures than total extraction because the compounds being removed are quite soluble near the critical point.

The third SFE operation on the diagram is fractionation. Fractionation is a slight variation of a total extraction. Fractionation separates components of a mixture with sufficiently different polarities. It is accomplished by changing the extraction pressure, and therefore solute holding power, of the supercritical fluid. Jojoba oil extracted with supercritical CO_2 at 80 °C was fractionated into components with different wax ester compositions by increasing the extraction pressure from 20.6 to 75.7 MPa (King, 1991).

Partial pecan oil extraction should be similar to total extraction using a temperature higher than the critical temperature to increase solubility and lower than the roasting

temperature to prevent product degradation and antioxidant destruction. The only difference is that only part of the extract is removed. Less time is required for a partial extraction than a total extraction. A commercial scale total extraction of whole pecan halves by SFE to simply recover oil is not expected to be economically feasible because of the required long times and large amounts of CO_2. For total extraction, when the nuts are not a desired end product, pecans can be ground as done by Maness *et. al.* (1995).

The bottom line in extraction is how much solute is removed from the extraction sample. This quantity relates to both solubility and mass transfer. Parameters that may be adjusted to control the extraction are temperature, pressure, flowrate, extraction vessel packing, extraction matrix, and amount of modifiers used. The temperature, pressure, and modifiers dictate the maximum solubility of the solute in the supercritical fluid. The amount of extractable solute relative to the amount of solvent used affects the observed solubility. The setpoint flowrate affects convection from the matrix surface to the flowing supercritical fluid and the overall rate of extraction. The extraction vessel packing affects the flow paths available to remove solute from the vessel. A very compressed arrangement can occlude the exit and prevent collection of solute.

A solid matrix is used to hold liquid solutes that need extraction. SFE generally involves removal of a liquid substance from a solid matrix. The matrix may be a nut that contains oil or sand that contains pesticides. Other possible matrices include glass wool or glass beads. If a substance is to be placed on a matrix, it is important that the matrix does not affect the ability of the supercritical fluid to extract the solute. It is undesirable for the solute to adsorb so strongly or diffuse so far into the matrix that it limits the rate of extraction. With

pecan oil extraction, there is no choice of matrix, and diffusion into the nut is not a limiting factor, because the oil is dispersed throughout the nut. Reducing the particle size of this matrix is a good way to reduce the influence of diffusion of oil out of the nut on the extraction time. Goodrum and Kilgro (1987a) obtained increased extraction rates for peanut oil by decreasing the peanut particle size.

Basic equipment required to perform an extraction is a solvent pump, an extraction vessel, a temperature/pressure control system, an exit system for removal of solvent from the extraction vessel, and a collection vessel. A typical setup schematic is shown in Figure 3. A high-pressure pump is used to bring the liquid carbon dioxide to the operating pressure and deliver it to the extraction vessel. The carbon dioxide flows into a packed extraction vessel housed in an oven. The vessel contents are heated to achieve supercritical conditions. The outlet valve is then opened and extraction begins. The exiting supercritical fluid/extract stream is then manipulated to cause a decrease in the solubility of the solute. The resulting gaseous carbon dioxide and extract physically separate in a collection vessel. The extract remains in the collection vessel and the carbon dioxide flowrate is measured and vented to the atmosphere. This arrangement can be altered to recycle the carbon dioxide by adding a tubing system, collection vessel, and a secondary compressor. Recycling usually is not done when using small volumes of carbon dioxide, as in most laboratory SFE units.

Solvent and extract may be separated by reduction in pressure, reduction in temperature, manipulation of both temperature and pressure, or use of an adsorption system like activated carbon. For depressurization to atmospheric conditions, the stream is passed through a pressure reduction valve. The extract precipitates out of the gaseous solvent

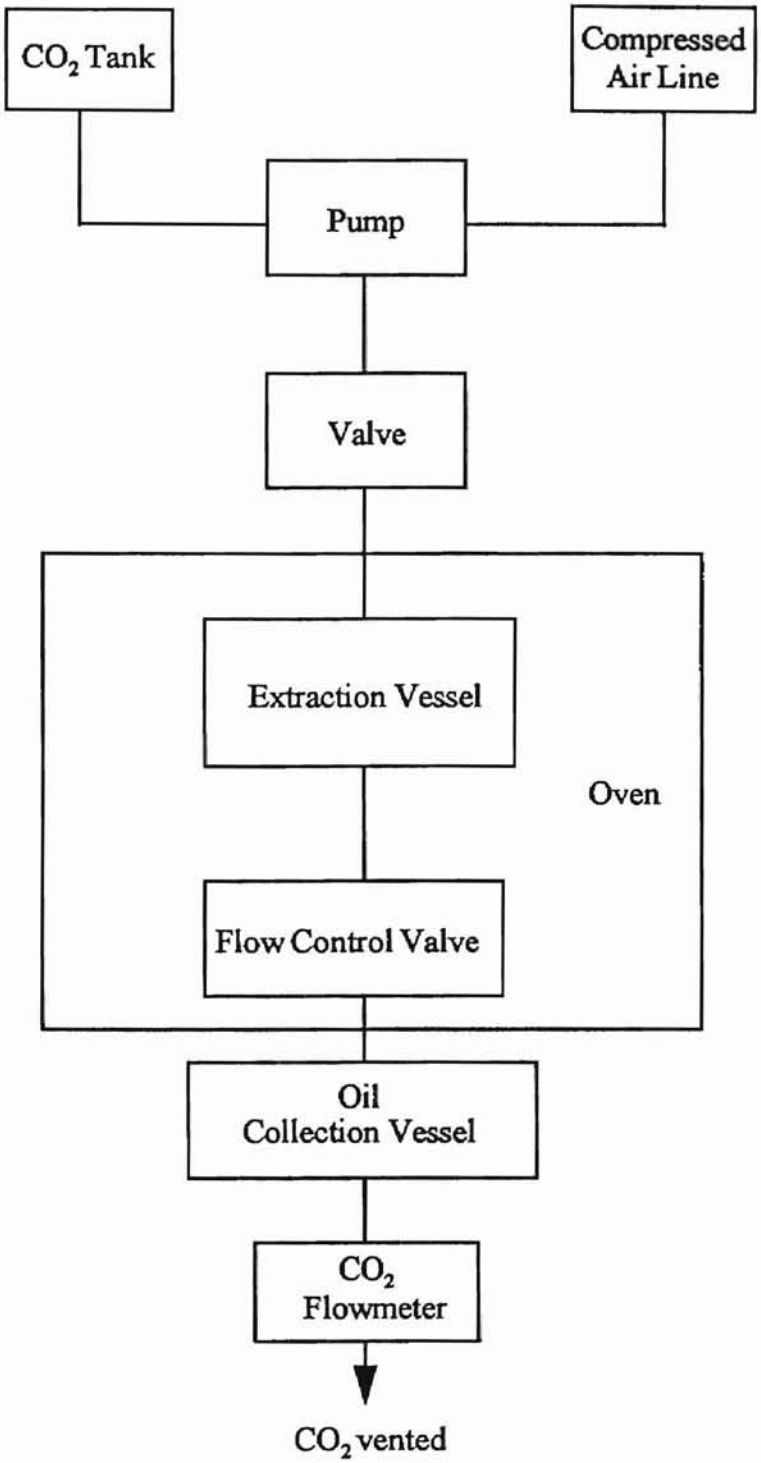


Figure 3: Schematic of SFE system.

because it is less soluble in this phase. Depressurization can be done by either fixed restrictors capable of depressurizing at a fixed flowrate or flow control valves capable of being set to depressurize at different flowrates. An important part of this setup is the heating block on the pressure reduction valve. Heating is performed to allow sample collection by preventing the fluid and extract from freezing in the tubing due to expansive cooling. The temperature of the valve depends on the flowrate used for depressurization. The ease of this separation is a distinct advantage of SFE over liquid solvent extraction.

Separation by temperature reduction requires the use of a temperature that minimizes the solubility of the solute in the solvent. As with pressure reduction, the resulting extract is collected in a collection vessel (Rizvi *et. al.*, 1986). There have also been experiments where a series of collection vessels at different temperatures and pressures were used to fractionate the extract and recover specific substances. Lim and Rizvi (1995) separated anhydrous milk fat into four fractions using collection vessel conditions of 60 °C/24.1 MPa, 80 °C/20.7 MPa, 80 °C/17.2 MPa, and 60 °C/ 6.9 MPa following supercritical CO_2 extraction at 40 °C/24.1 MPa. This procedure is a possible alternative to fractionation by changing the extraction pressure at constant temperature during an extraction.

For an adsorption system, solute is trapped in the adsorption system while solvent is not. The solute must therefore have a greater affinity for the adsorbing material than the solvent. Subsequent chemical steps are used to recover the extract. This method is less expensive for commercial processes than pressure reduction followed by recompression of the solvent in the recycle process. It is not advisable, however, for pecan oil extraction, since it would require the use of harsh chemicals to recover the oil. Use of these chemicals would

remove part of the advantage of SFE over liquid extraction if the oil extract was to be an edible product. As a result, depressurization or distillation are used for separation.

Three methods for collection during depressurization are neat collection, solvent collection, and solid-phase extraction cartridge collection. Neat collection involves recovering the liquid extract in an empty vial or test tube. A variation on this process is to add glass wool and/or a cold trap. The purpose of the glass wool is to provide a tortuous path to trap any liquid entrained in the exiting gas stream. The purpose of the cold trap is to further lower the solubility of the extract in the gaseous carbon dioxide. Solvent collection is performed using a test tube partially filled with an organic liquid (e.g. hexane) that contains the soluble extract. The liquid may be chilled to improve its trapping ability. This method is not recommended when the extract is the desired end product, since additional steps must be performed to separate the extract from the solvent trap. Solid-phase extraction trapping involves the use of a cartridge filled with solid packing to which the desired extract is attracted. The extract adsorbs onto the packing and the solvent flows through it. Extract elution is later performed using liquid chemicals. This arrangement is good for collection of trace amounts of extract. It is not recommended for pecan oil extraction because the chemicals involved are harmful, and elution adds extra steps to the SFE process.

Extraction Parameters

Studies have been conducted to determine optimum extraction parameters including temperature, pressure, flowrate, flow direction, extraction vessel orientation, and particle size

on other food products. Reduction in the particle size of soybeans (Snyder *et. al.*, 1984) and peanuts (Goodrum and Kilgro, 1987a) led to a decrease in extraction time. This result showed that the extraction process for these substances is limited by diffusion through the natural matrix. Flowrate had no effect on the amount of collected extract for evening primrose oil extraction (Favati *et. al.*, 1991). However, increasing the flowrate did decrease the amount of time required to collect extract for tomato seed extraction (Roy *et. al.*, 1994).

CO_2 flow direction has been studied extensively. Vertical orientation tends to remove extract from the extraction vessel better than horizontal orientation because of the formation of dead space at the top of the packed bed when horizontal. Vertical solvent flow may be either up or down. Upflow versus downflow was studied with peanuts, grapes, peppermint, and spearmint (Goodrum and Kilgro, 1987; Sovová *et. al.*, 1994; Barton, 1992). Downflow always yielded more extract. Goodrum and Kilgro (1987a) found uniform temperatures across the extraction vessel during downflow extraction. Modeling has been proven successful by Sovová *et. al.* (1994) in downflow using a plug-flow model with constant temperature and pressure. The channeling and thermal gradients found during upflow are more difficult to model. Another advantage of downflow is that gravity naturally directs extracted oil to the bottom of the extraction vessel where it can be removed by the turbulent flow of carbon dioxide.

Extraction vessel packing is also an important parameter. A void volume for the packed solid bed is required to allow the bulk fluid to contact the solid surface and remove the extract. Improper spacing will lead to inefficient solute removal and can be quite expensive. A

final practice used by many researchers is the use of glass wool plugs on each end of the solid bed to prevent solid particles entering and clogging the high-pressure tubing.

Extraction Equation

The total amount of solute removed for a given set of extraction conditions is given by the extraction equation. For solutes that do not suffer from adsorption kinetics, an exhaustive extraction may be divided into two parts. The first part is strongly influenced by the solubility of the solute in the supercritical fluid. The second part is strongly influenced by the diffusion of the solute to the matrix surface and the convection of the solute from the surface to the moving supercritical fluid. Solubility is not a dominating factor in the second section after removal of a good portion of the solute. The first part of the extraction is the faster period. The second part is slow, and the removal of extract follows an exponential decay rate. Singh and Rizvi (1995) have described the extraction as approaching a first-order system for the longer, slow period. As a result, the experimental data from the second half of many extractions follow a straight line relationship of the form:

$$\ln(m/m_o) = b - a\,(t/t_c) \qquad (2.1)$$

where:
m = mass of solute in matrix at time = t (kg)
m_o= mass of solute in matrix, initially (kg)
b = y-intercept
a = constant
t_c = characteristic time (s)
t = extraction time (s)

The form of the equation for the characteristic time depends on the geometry of the solid matrix. Characteristic time, t_c, for a sphere is $r^2/\pi^2 D$ and for an infinite slab is $l^2/\pi^2 D$, where r is

the radius of the sphere (m), l is the slab thickness (m) , and D is the effective diffusion coefficient out of the matrix (m^2/s).

For the specific case of extraction from a sphere-shaped matrix in which diffusion of the solute out of the matrix is the controlling step, and the solubility of the solute in the supercritical fluid is assumed to be infinite, the following form of equation (2.1) results:

$$\ln(m/m_o) = \ln(6/\pi^2) - t/t_c \qquad (2.2)$$

This equation was used to describe supercritical carbon dioxide extraction of caffeine from coffee beans with equivalent radii of 4.01 mm (Udayasankar *et. al.*, 1986). Many extractions documented involve matrices of less than 1 mm in terms of the size of the smallest dimension. Examples include extraction from tomato seeds (Roy *et. al.*, 1994) or grape seeds (Sovová *et. al.*, 1994). Models have been derived that describe extraction from these small particles. Sovová *et. al.* (1994) divided the extraction from a packed bed of grape seeds into sections describing solubility dominance, transition from solubility to diffusion dominance, and diffusion dominance. The diffusion dominance described was at the interface of the matrix surface and the solvating supercritical fluid. There was no mention of diffusion from the matrix to the solid surface. Reverchon and Osséo (1994) modeled a single spherical particle in a packed bed and applied the resulting equation across the entire length of the bed to obtain an overall extraction equation. His model curves did not fit his experimental data as well as Sovová's model. Reverchon hypothesized that the poor agreement could be caused by the lack of the matrix particles being identical and spherical.

The applicability of both of these extraction models was not presented for larger matrices. For larger particle sizes, the effect of diffusion out of the matrix increases and must

be accounted for in a suitable equation. It is asserted that extraction would be more efficient if pecan halves were ground to reduce the particle size and increase the surface area available for extraction. This may not be an option when whole pecan halves are the desired end product. Thus, an equation is desired that describes extraction from large particles. A straight-line equation has already been presented for the diffusion-dominant rate of extraction. Previous work by Zhang (1994) suggested that pecan oil extraction did not reach the diffusion dominance region in 160 minutes at gaseous CO_2 flowrates of 1 to 2 standard liters/minute (slpm). These extraction times removed 41 to 78% of the oil at 40 to 80 °C and 41.3 to 68.9 MPa. The amount of oil that is sufficient to reduce shelf life and maintain an edible pecan product has not been established. As a result, it is currently important to study the extraction in this solubility-dominant region and determine a relationship that describes the observed behavior.

CHAPTER III

MATERIALS, EQUIPMENT, AND METHODS

Extraction Equipment

Extraction experiments were conducted using a SPE-ED™ model 680-bar extraction unit (Applied Separations, Allentown, PA) as shown in Figure 4. The maximum operating temperature and pressure of the unit are 250 °C and 68.9 MPa, respectively, and it may hold up to two 1 L extraction vessels or one 2.5 L vessel. The main components are the 300 mL extraction vessel (rated to 68.9 MPa) (Thar Designs, Pittsburgh, PA) to hold the solid matrix, the oven to produce the necessary temperature, the air-driven pump to produce the required CO_2 pressure, the heated micrometering valve to allow control of CO_2 flowrate and prevent freezing of the exiting CO_2/extract stream, the collection vessel to hold the extracted solute, and the CO_2 cylinder to provide the source of extraction fluid. Air at 6.89×10^5 Pa for the pump is supplied from a compressor. A water trap is located before the extraction pump to remove moisture from the air.

Extraction parameters are monitored using temperature, pressure, and flow sensors. Thermocouples measure oven temperature, extraction vessel temperature, and the micrometering valve block temperature. The oven and micrometering valve thermocouples are connected to a temperature controller to maintain temperature setpoints at ± 1 °C. Pressure gauges monitor the line pressure for the CO_2 and air streams. The CO_2 pressure sensor has an alarm that sounds when the rated equipment pressure of 68.9 MPa is exceeded. If the pump exceeds 68.9 MPa and the situation is not corrected, a rupture disc will reduce the pressure at

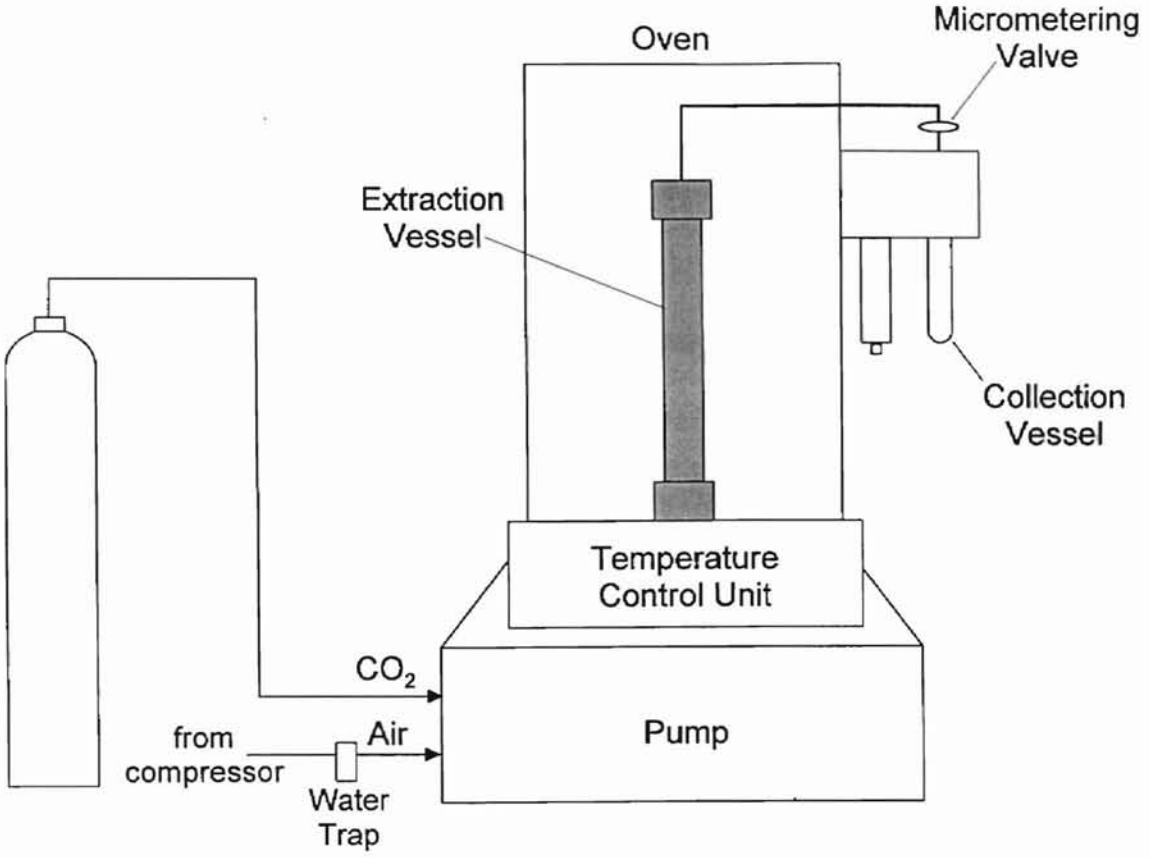


Figure 4: SPE-ED™ extraction unit.

the pump. An Omega model FMA1820 electronic flowmeter (Omega Engineering, Inc., Stamford, CT) measures the expanded CO_2 flowrate downstream of the extract collection vessel. The flowmeter is connected to an Omega model DPF66 flow totalizer (Omega Engineering, Inc., Stamford, CT) to monitor the amount of CO_2 used during extractions.

Experimental Procedure

Method Development

A standard procedure for extraction was developed to decrease the differences between extraction runs. The procedure is divided into the pretreatment, warm-up, extraction, depressurization, and cleaning steps.

Pretreatment

'Nance' native pecan halves with 4.79% moisture content (wet basis) and 63.9% oil content and 'Wichita' pecan pieces with 4.12% moisture content (wet basis) and 58.5% oil content were used for all experiments. The initial oil content was determined using a quantitative SFE extraction procedure for ground pecan samples developed by Maness *et. al.* (1995). The moisture content was determined by measuring the weight loss of 15 pecans dried in a forced-convection oven at 130 °C for 6 hours. The unextracted pecans were stored in Zip-Loc™ freezer bags at -17 °C to prevent sample degradation prior to experiments. Before an extraction run, the pecans were removed from the freezer and kept in sealed freezer bags for at

least 30 minutes to equilibrate at room temperature (22-25 °C). This step prevented an increase in pecan moisture content. Pecans that equilibrated in an open container were found to have moisture content values 0.5 to 1% higher than the pecans left in the freezer bags.

Filling the extraction vessel began by placing a piece of pre-weighed Pyrex™ glass wool in one end to serve as the bottom plug. The sample of pecans was weighed and placed in the extraction vessel, the preweighed top glass wool plug was inserted, and the cap was screwed on by hand. The glass wool plugs were used to trap the solid pecan pieces and prevent plugging of the extraction vessel or the tubing. The acceptable weight range for each glass wool plug was determined by filling the vessel with the same quantity of 'Wichita' pecans (70 g) and varying weights of glass wool plugs. Using greater than 2.6 g of glass wool on each side, extracted oil was not collected due to improper extraction vessel packing. Oil was collected when 0.5 to 2.6 g of wool was used on each side, and this weight range was used for all experiments.

After filling, the extraction vessel was set into the system oven and connected to stainless steel, high-pressure tubing (2.54×10^{-4}m I.D.). Coleman grade liquid CO_2 (Air Products and Chemicals, Inc., Allentown, PA) stored in a cylinder with a 14-MPa helium headspace and a dip tube was delivered to the vessel, and the system was examined for leaks. The extraction vessel and the micrometering valve were then heated to the desired setpoints. After reaching the appropriate temperature, the desired extraction pressure was set on a panel controlling the air-driven pump.

Warm-Up

Warm-up is the period in which the extraction vessel and pecans reached the setpoint temperature. Two warm-up factors that affect extraction are warm-up time and pressure increase scheme. Figure 5 shows the effect of a one-hour difference in warm-up time on extraction of 'Nance' native pecans at 75 °C, 62.0 MPa with an initial warm-up pressure of 13.7 MPa. Main experiments were conducted with warm-up times of 1 h to eliminate this difference.

The effect of initial pressure setting before the warm-up period was studied for a one-step and a two-step pressure scheme in preliminary experiments. The one-step pressure scheme is performed by continually increasing the extraction pressure to the desired value as the extraction vessel warms up. The extraction pressure was not increased to this desired value until the start of heating, because thermal expansion would have caused the actual vessel pressure to be greater than the desired pressure at setpoint temperature. The two-step pressure scheme involves setting the vessel pressure to about 13.7 MPa and increasing to the desired pressure after the vessel is about 3 °C below the setpoint temperature. The initial warm-up period was started at 13.7 MPa, based on the low solubility of fats at low-extraction pressures.

Extraction curves for 'Wichita' pecans run at 62 °C and 55.1 MPa (Figure 6) clearly show an initial lower extraction rate for a two-step warm-up pressure scheme. Results show that pecan oil is more soluble in supercritical CO_2 at pressures above 13.7 MPa than below 13.7 MPa. Table I presents the percent oil extracted after 165 minutes for both warm-up schemes. The data for the one-step warm-up scheme are always higher.

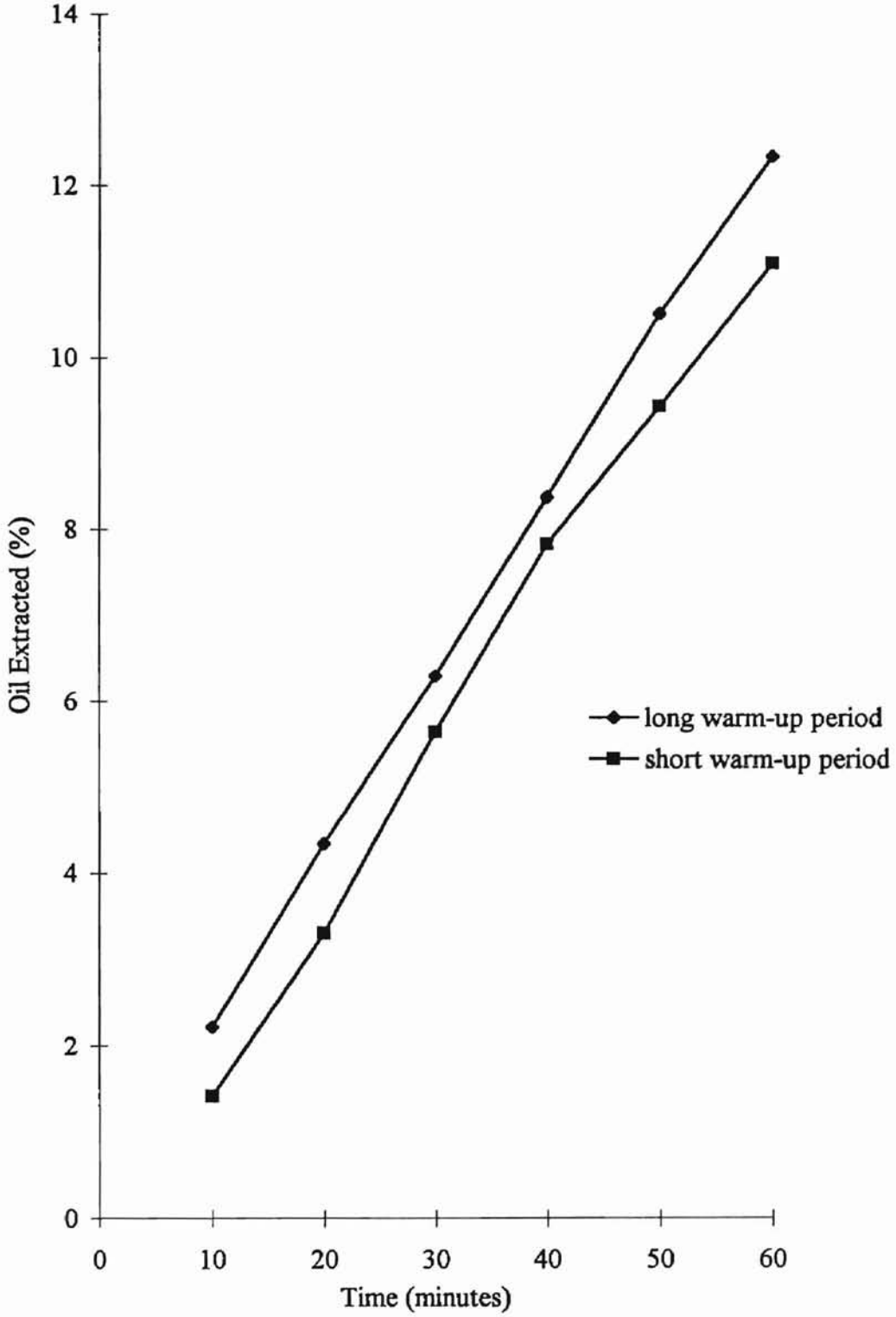


Figure 5: Effect of warm-up time on oil extracted from 'Nance' native pecans at 75 °C, 62.0 MPa, and 3.0 slpm CO_2.

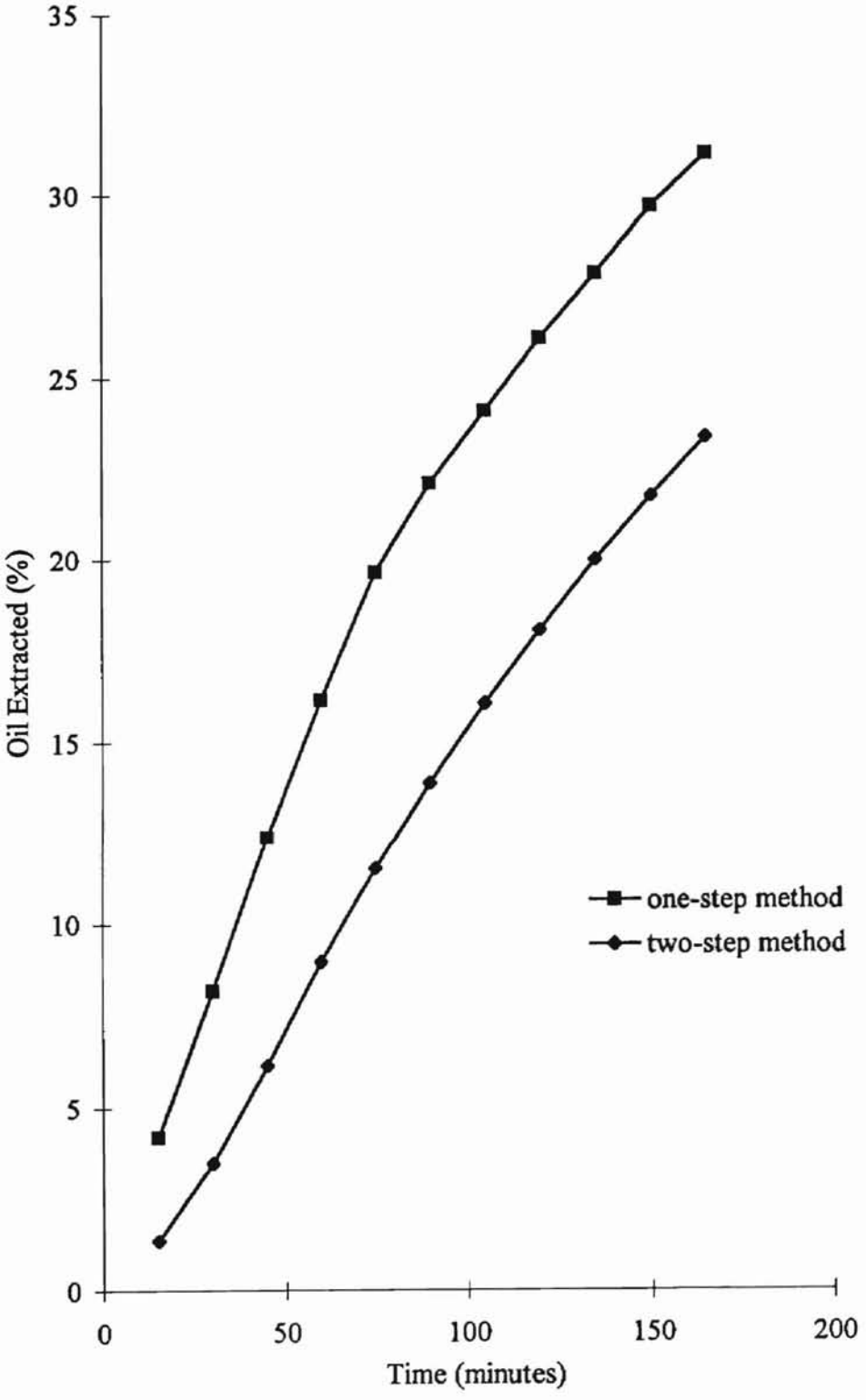


Figure 6: Effect of pressure increase method during warm-up on oil extracted from 'Wichita' pecans at 62 °C, 55.1 MPa, and 2.5 slpm CO_2.

Table I : Effect of pressure increase method during warm-up period on oil extracted after 165 minutes from 'Wichita' pecans at 62 °C and 2.5 slpm CO_2.

Temperature (°C)	Pressure (MPa)	Pressure Increase Method	Oil Extracted (%)
62	41.3	one-step	23.09
62	41.3	two-step	14.65
62	55.1	one-step	31.14
62	55.1	two-step	23.38

This response indicates that the method used to reach the setpoint pressure does affect the extraction run. Although the one-step warm-up scheme yields more oil, the two-step method was used for all experiments. This procedure was done so that experimental results would reflect the effect of pecan oil extraction without the influence of the warm-up period (which acts as a separate static extraction). Using the two-step pressure scheme, it will be assumed that extraction begins when both the setpoint temperature and pressure are reached.

Extraction

When the desired extraction conditions were reached (after 60 to 75 minutes), the outlet valve was opened and the micrometering valve was set to the desired flowrate. Extraction time is defined as the length of time the outlet valve is open. Extract was collected in a pre-weighed 13x100 mm test tube with a glass wool plug and a screw cap with a septum. The glass wool was positioned at the top of the test tube to trap any oil particles remaining in the exiting gas stream. The tubing that delivered the extract/CO_2 stream was placed below the glass wool, and the CO_2 vent tubing was placed above the glass wool. The oil collected in the test tubes was kept below a 'threshold' level of 1.5 cm from the bottom of the test tube to prevent excessive oil losses from the collection vessel. The combination of glass wool and low liquid level reduced loss of oil in preliminary experiments by approximately 50%.

The collection vessels were placed into position before extraction. Collection was performed both with and without cooling, depending on the experimental requirements. When cooling was not done, the collection vessels were maintained at room temperature. For cooling, the test tubes were placed in ice water baths before extraction to equilibrate. The ice baths were used during extraction to promote oil collection. The test tubes were changed frequently to maintain low liquid levels and improve oil recovery. The process of changing test tubes involved closing the outlet valve, removing the test tube with collected oil, connecting the new test tube, and re-opening the outlet valve. The removed test tubes were weighed to determine the amount of extract collected. The collection vessel changing procedure was repeated for the duration of the extraction process.

Depressurization

A slow method to depressurize the extraction vessel without breaking the pecans was developed and used for all runs. After completing an extraction run, the inlet valve to the extraction vessel was closed.. A new, tared collection vessel was inserted, and the outlet valve was opened to release CO_2 which was monitored by the flow totalizer to determine when the vessel was empty. The micrometering valve was left at the same flowrate as during the experiment, yet CO_2 flowrate decreased to 0 slpm as the extraction vessel was emptied Depressurization time was determined by the CO_2 flowrate. At least an hour was required for this step. When shorter times were used, CO_2 was found to remain in the extraction vessel and dissolve into the pecans.

After fully venting the CO_2, the outlet valve was closed and the heaters were turned off. The extraction vessel was allowed to cool overnight and was removed from the oven the next day. The top endcap was unscrewed, and the top wool, pecans, and bottom wool were removed and individually weighed. Weighing the entire extraction vessel, including the sample before and after each run, would be the simplest approach for determining the oil removed from the pecans, but the amount of oil extracted is less than 0.42 % of the vessel's weight, and this level would provide poor accuracy of oil weight measurements. The mass of the pecans weighed after incomplete venting (from short depressurization times) decreased with time due to the escape of the dissolved CO_2. Using the slow depressurization method, no CO_2 remained in the pecans, since the final weight did not fluctuate while being weighed. The slow method was therefore used for all main experiments.

Cleaning

The final step in the extraction procedure was cleaning the equipment. The main extraction vessel body was rinsed with soapy water, then pure water, and finally air dried. Using only this procedure, increased amounts of oil were collected during the first 15 minutes of preliminary experiments. Residual oil from the extraction tubing was found to be the source of these erroneous extract weights. A subsequent cleaning step was developed that corrected this problem. After the initial cleaning and prior to every new run, the empty vessel was connected to the experimental setup and cleaned in place by flushing the equipment with CO_2

at 75 °C and 62.0 MPa for 30 minutes. After venting the vessel and allowing it to cool, it was used for the next run.

Experiments

Experiments were conducted to determine the effects of micrometering valve temperature on oil recovery, collection vessel temperature on oil recovery, flowrate on oil recovery, extraction conditions and time on the fatty acid composition of extract recovered from pecans, and the factors controlling extraction from whole pecan halves. The conditions used to perform these experiments are described below.

Micrometering Valve Temperature

Whole 'Nance' native halves were used for determination of the effect of micrometering valve temperature on oil recovery. The criterion for the optimum valve temperature was the smallest difference between oil recovered (collected in test tubes) and weight loss of pecans. Approximately 90 g of pecans were packed between glass wool plugs in a 300 mL stainless steel extraction vessel. Each plug initially weighed 0.5-2.6 g. Experiments were conducted at 75 °C, 62.0 MPa, a CO_2 flowrate of 3.0 slpm, a run time of 1 h, and a collection vessel temperature of 0 to 2 °C. Micrometering valve temperature setpoints were 75, 100, 125, and 150 °C. Two replicates of each experiment were conducted. The collection vessels were changed every 10 minutes to maintain low liquid levels and therefore maximize oil

recovery. They were individually weighed and summed to determine total oil recovery. The standard depressurization method as previously described was used after each hour extraction, and the oil collected was included in the total recovery value. After cooling, the extraction vessel contents were removed and weighed. The standard cleaning procedure was then used to prepare the machine for a new run. Oil collected during the cleaning run was also included in the total recovery value. Thus, the total recovery value included oil collected during extraction, depressurization, and cleaning. The oil recovered during these steps accounted for approximately 95, 4.5, and 0.5%, respectively, of the total recovery value.

Collection Vessel Temperature

Two different approaches were used for collection vessel temperature tests. The optimum collection vessel temperature was based on the lowest difference between oil recovered and weight decrease of pecan pieces.

The first approach used two test tubes connected in series as the collection vessels (Figure 7). Pieces of 'Wichita' pecan halves were used for these experiments. A small piece of Tygon tubing connected the collection vessels. Extraction conditions used were 45 °C, 34.4 MPa, and 1.5 slpm CO_2. The first test tube was at room temperature (about 25 °C), and the second test tube was exposed to an ice water bath at 0 to 2 °C. Oil collected in the two test tubes and the connecting tubing at regular intervals was determined by weighing each component.

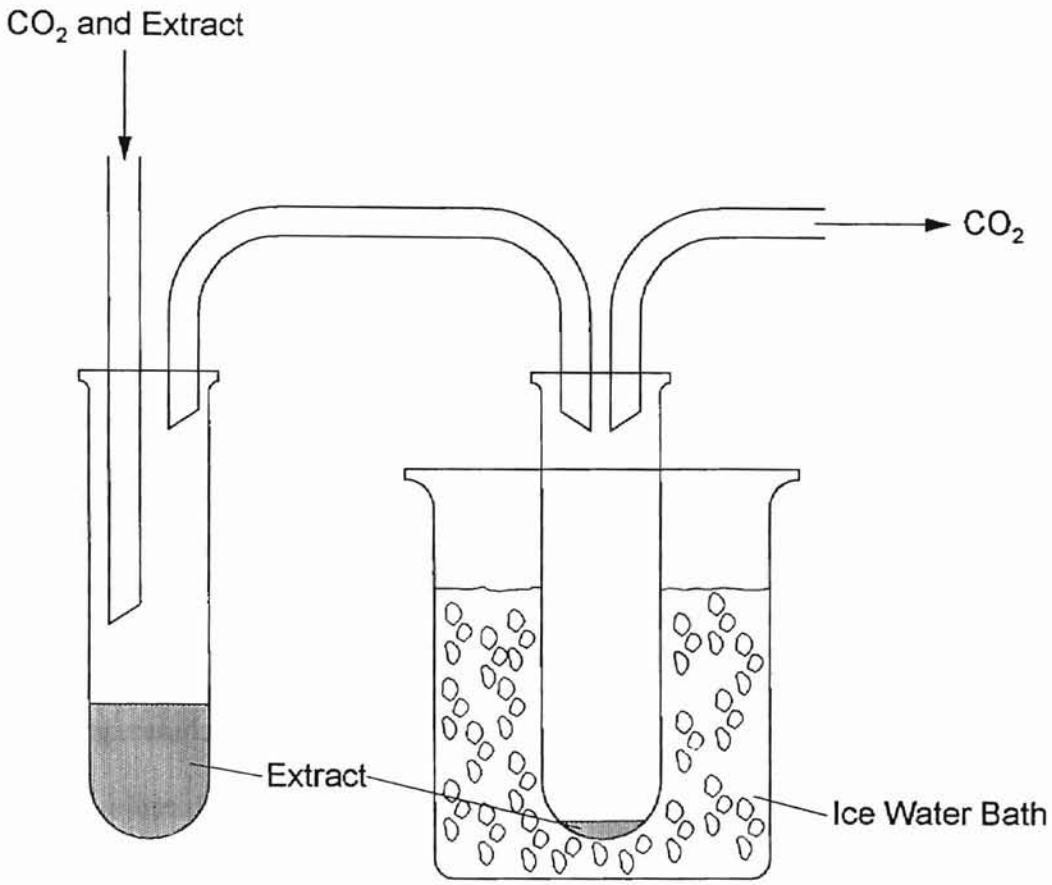


Figure 7: Two collection vessels in series.

The second approach used one test tube as a collection vessel. Whole 'Nance' native halves were used for these experiments. The first set of extraction conditions were 75 °C, 62.0 MPa, 3.0 slpm CO_2 with a micrometering valve temperature set at 100 °C, and collection vessel bath temperatures of 0 °C and 25 °C. Experiments were then conducted at 75 °C, 62.0 MPa with a higher CO_2 flowrate of 7.5 slpm, a micrometering valve temperature of 150 °C, and collection vessel temperatures of 0 °C and 25 °C. The two different valve temperatures used (100 °C and 150 °C) were chosen based on the study of extraction at a medium flowrate (3.0 slpm) and a high flowrate (7.5 slpm). These experiments were conducted for 30 minutes and the collection vessels were changed every 15 minutes. The collection vessels were weighed individually, and the oil collected during extraction was determined. Previously discussed depressurization and cleaning procedures were used for every run. Total oil recovery value included oil collected during extraction, depressurization, and cleaning.

CO_2 Flowrate

Whole 'Nance' native halves were used for the flowrate experiments. Approximately 90 g were added to a 300-mL stainless steel extraction vessel along with glass wool plugs. Each plug initially weighed 0.5-2.6 g. The experiments were conducted at 75 °C, 62.0 MPa, a micrometering valve temperature of 100 °C, and a collection vessel temperature of 0 to 2 °C. The CO_2 flowrates used were 1, 1.5, 2, 2.5, 3, 4, and 7.5 slpm. Two replicates of the 1.5, 2, 2.5, and 3 slpm experiments were conducted. The collection vessels were changed at regular intervals to maintain low liquid levels and therefore maximize oil recovery. After

depressurization and cooling, the vessel contents were removed and weighed. The standard cleaning procedure was then used to prepare the machine for a new run. The total recovery value included oil collected during extraction, depressurization, and cleaning.

Solubility and Fatty Acid Determination

Pieces from 'Wichita' pecan halves (i.e., one-quarter to one-half of a pecan half) were used for solubility and fatty acid composition experiments. These pecans had an initial oil content of 58.5%, by weight. Approximately 70 g were added to a 300 mL stainless steel extraction vessel for each run, and extractions were performed at 45, 62, and 75 °C. For each temperature, an extraction was performed at 41.3, 55.1, and 66.8 MPa. Dynamic extraction was performed at a CO_2 flowrate of 2.5 slpm, with a valve temperature of 100 °C and a collection vessel temperature range of 0 to 6 °C. High extraction pressure conditions were chosen, since previous experiments by Zhang (1994) demonstrated that more oil was extracted at higher pressures. The temperature range was selected so that it was above the critical temperature of CO_2 (31.05 °C) and below the roasting temperature of pecans (about 80 °C). Oil collected in the test tubes was weighed and stored in a freezer to await analysis. Only oil collected from the 45 °C and 62 °C extractions was used for fatty acid determination.

Gas chromotography was performed to determine fatty acid composition of the pecan oil. Fatty acids were converted into methyl esters which could be separated from the mixture and identified using gas chromotography. The methyl esterification procedure used followed that by Maness *et. al.* (1995).

The first step of the conversion procedure was to mix the pecan oil with methanol in the presence of hydrochloric acid which acted as a catalyst for the reaction. To prevent hydrolysis of methyl esters, methyl acetate, a water scavenger, was added to the reaction mixture. The reaction was performed at 90 °C for 2 hours in a-one dram vial containing 600 nmoles heptadecanoic acid as internal standard and sealed with a Teflon-lined cap. After the first fifteen minutes, the liquid in the vial was mixed by vortexing to ensure the oil samples were in a single phase for methanolysis. Upon completion, tert-butyl alcohol was added to the reaction mixture to coevaporate the hydrochloric acid. The mixture was evaporated for 30 minutes using nitrogen gas. The remaining liquid, containing the methyl esters, was diluted with hexane and injected into the Tracor Model 540 gas chromatography unit (Tracor Instruments, Austin, TX). The unit contained a split injection port (split ratio of 50:1) and a flame ionization detector. The injector temperature was maintained at 275 °C and the detector at 300 °C. A DB 23 (30 m x 0.25 mm; 0.25 μm film thickness) fused silica capillary column (J and W Scientific Inc., Rancho Cordova, CA) and helium carrier gas at a velocity of 20 cm/s were used for methyl ester separation. The initial column temperature was set at 50 °C for 2 minutes and increased at 10 °C/minute to 180 °C. A second ramp function of 5 °C/min was used to increase the column temperature from 180 °C to 240 °C. Temperature was held at 240 °C for 5 minutes. Peak areas corresponding to the individual fatty acid methyl esters were obtained from a Spectra-Physics 4990 integrator (Spectra-Physics Inc., St. Louis, MO). Three replicates were performed for each oil sample. Heptadecanoic acid was used as the internal standard for composition calculations using the resulting peak areas.

Extended Period Extraction

The extended period extraction experiment was performed to determine the factors controlling pecan oil extraction and the extraction times each factor dominated. The extraction vessel was filled with 90.26 g of whole 'Nance' native pecan halves. Extraction was conducted for 181 hours at 75 °C, 62.0 MPa, and 2.5 slpm, with a micrometering valve temperature of 100 °C and a collection vessel temperature of 0 to 2 °C. The collection vessels were replaced in regular intervals of every 10 minutes for the first 180 minutes, and intervals increasing from 20 to 730 minutes for the rest of the extraction to maintain low liquid levels in the vessels and maximize oil recovery. Previously discussed depressurization and cleaning procedures were used when the extraction was completed. Total extract recovery value included extract collected during extraction, depressurization, and cleaning.

CHAPTER IV

RESULTS AND DISCUSSION

Micrometering Valve Temperature

For the 3.0 slpm flowrate used in these experiments, a valve temperature of 100 °C was found to yield the smallest loss of extract, 6.54%, based on the percent difference between the weight of extract collected and the weight loss of the pecans (Figure 8). The average differences for 75 °C and 125 °C were 11.11% and 13.73%, respectively. The 22.74% extract loss at 150 °C may be higher due to the greater volatility of the oil at the higher temperature and aerosol formation. This problem may be enhanced by the short distance between the micrometering valve and the collection vessel. There may be insufficient time for the oil to cool and separate from the carbon dioxide. These values are based on a collection vessel temperature of 0 °C.

Collection Vessel Temperature

Two Collection Vessels

Using two collection vessels placed in series did not yield quantifiable results because most of the oil that escaped the first vessel became trapped in the small tubing between the two vessels. This tubing was later weighed to determine the oil loss. It provided a better estimate than the second collection vessel, yet was still an unreliable measure of extract

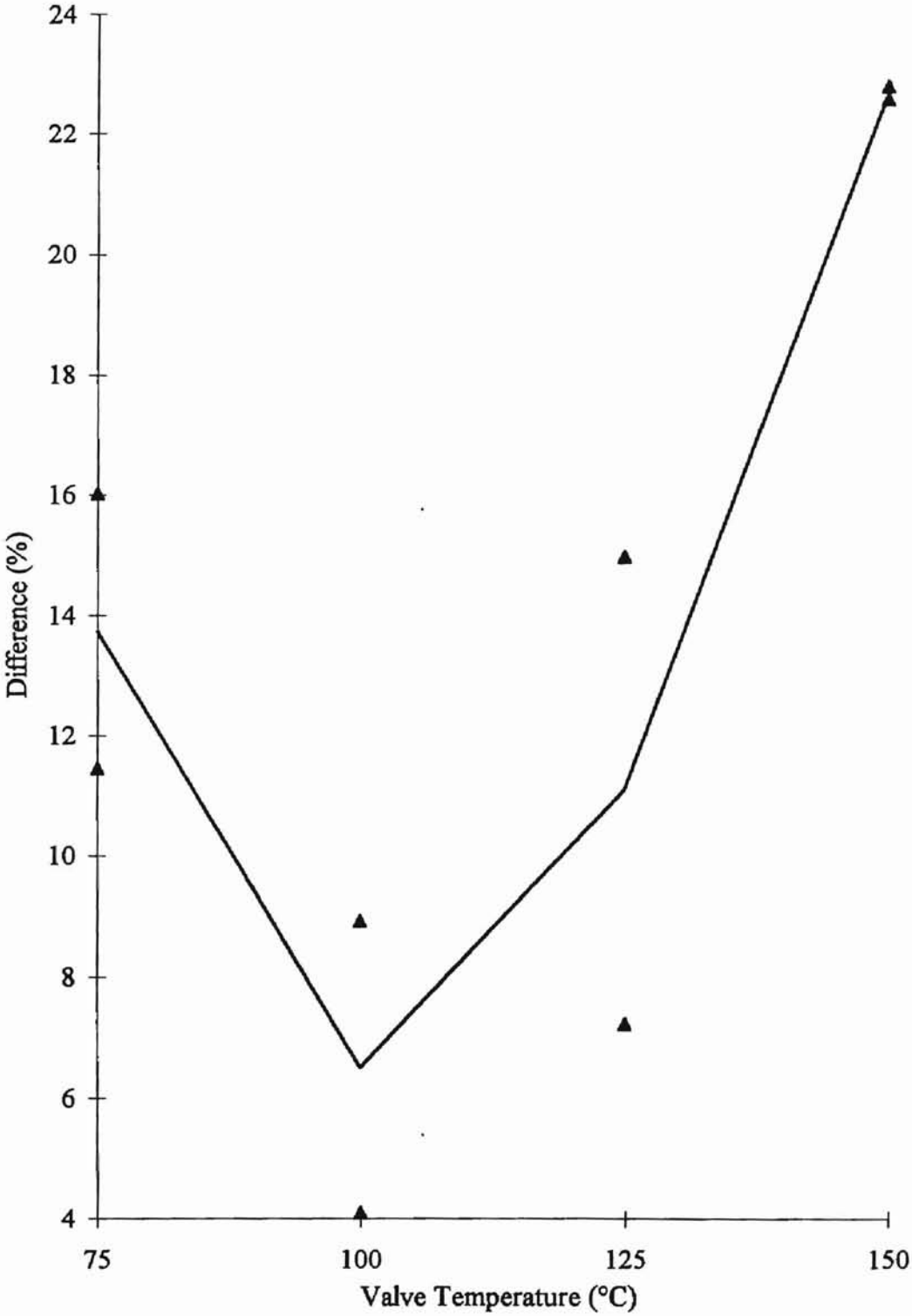


Figure 8: Effect of valve temperature on oil recovery from 'Nance' native pecans at 75 °C, 62.0 MPa, and 3.0 slpm CO_2.

$$\text{Difference (\%)} = 100\frac{\text{Pecan Weight Loss(g) - Oil Collected (g)}}{\text{Pecan Weight Loss(g)}}$$

removed during a specific time period. Also, the tubing only showed a weight change when the liquid level in the first collection vessel exceeded the previously mentioned 'threshold level'. Only qualitative data was obtained from these brief experiments.

Single Collection Vessel

The percent difference between the weight of extract collected and the weight loss of the pecans was used as a measure of the effectiveness of the four different collection vessel/valve temperature combinations. The 100 °C valve temperature experiments gave a 2.85% difference and a 19.81% difference at collection vessel temperatures of 0 °C and 25 °C, respectively. The temperature of the glass collection vessel increased during the 25 °C run, but did not change during the 0 °C run. Thus, cooling of the collection vessel is necessary to reduce extract loss when operating at 3.0 slpm. The 150 °C valve temperature weight differences were 15.42% at 0 °C and 13.15% at 25 °C. These similar results indicate that there is no benefit from external collection vessel cooling for the 150 °C processing conditions at the high flowrate of 7.5 slpm. The similar values at a valve temperature of 150 °C may be explained by the temperature of the wall of the glass collection vessel for the 25 °C run decreasing from 25 °C to 17 °C during the first 5 minutes and remaining at this temperature for the rest of each 15-minute collection interval. For the 0 °C run, the collection vessel temperature increased from 0 °C to 5 °C, yet returned to 0 °C after the first 5 minutes. It is also possible that aerosol formation at

the high flowrate was the largest problem and led to similar extract losses regardless of the collection vessel temperature.

A valve temperature of 100 °C was insufficient for a flowrate of 7.5 slpm. At this temperature, the expansive cooling of the exit stream caused the carbon dioxide/extract stream to freeze in the valve, and no extract was collected. The slightly high differences obtained at 150 °C indicate that a temperature between 100 °C and 150 °C should be investigated for processing conditions.

These experiments indicate that at lower flowrates, 100 °C for a valve temperature and 0 °C for a collection vessel temperature are sufficient to minimize extract losses. At higher flowrates, use of 150 °C for a valve temperature and 25 °C for a collection vessel temperature produces a difference around 10% .

CO_2 Flowrate

The effect of CO_2 flowrate on the amount of oil extracted during 120 minutes is shown in Figure 9, where the percent oil extracted term is determined by dividing the amount of extract collected by the total amount of oil in the 'Nance' native pecan halves (63.9% oil by weight). As flowrate increased from 1 to 4 slpm, the percent oil extracted increased from 8.81% to 21.52%. Increasing flowrate by a factor of four produced only 2.4 times as much extract collected. As flowrate increased from 4 to 7.5 slpm, the percent oil extracted changed only from 21.52% to 21.66%. This result indicates that there is no benefit from using a CO_2 flowrate higher than 4.0 slpm for approximately 90 g of pecans

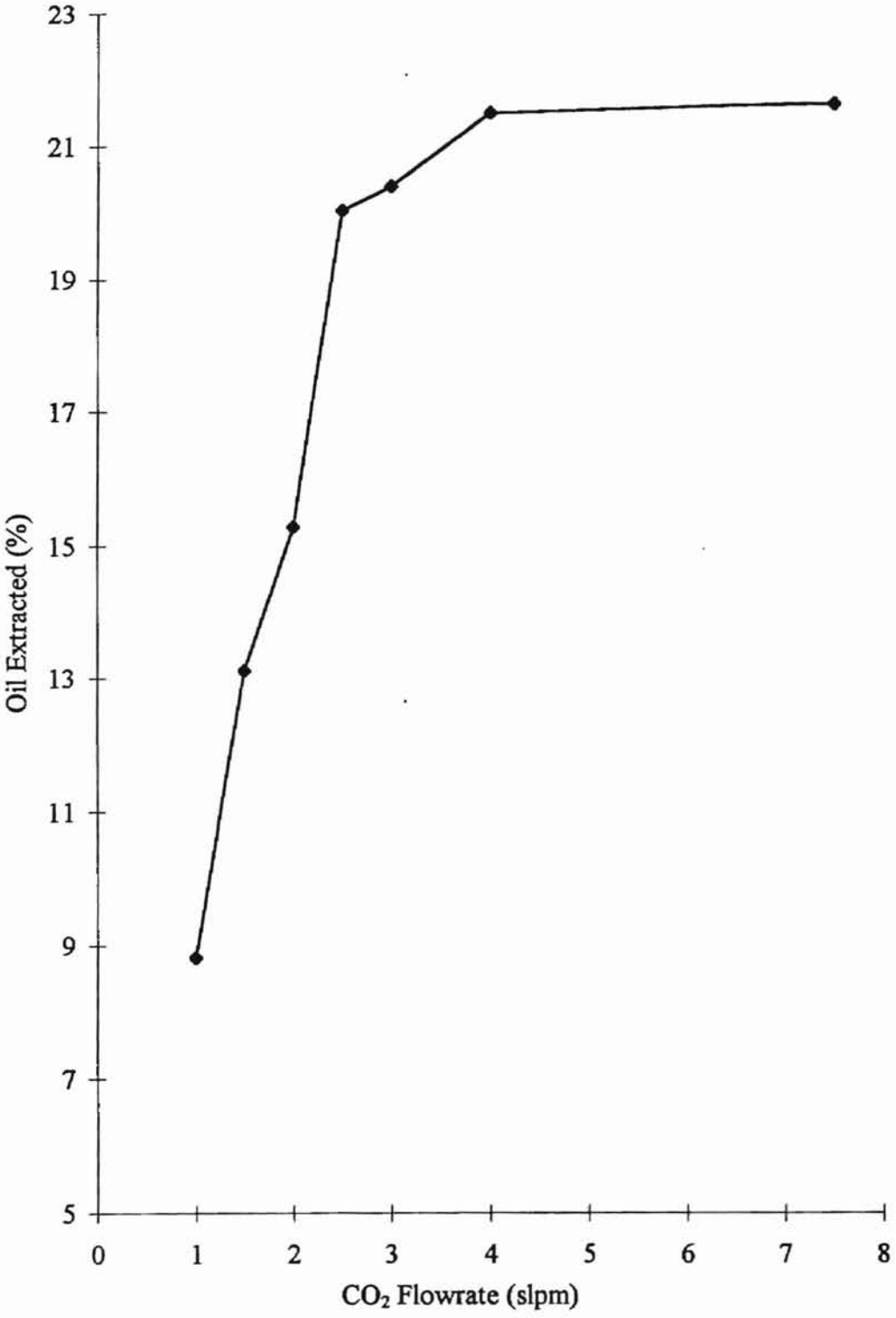


Figure 9: Effect of CO_2 flowrate on oil extracted from 'Nance' native pecans at 75 °C, 62.0 MPa, and 120 minutes.

in a 300 mL extraction vessel operated for 120 minutes at 75 °C and 62.0 MPa. At 120 minutes, the relationship between percent oil extracted and flowrate is given by the following equation:

$$\% \text{ Extracted} = 21.94 - 37.23\exp(-F) \qquad r^2 = 0.97 \qquad (4.1)$$

The percent difference between the oil collected and the weight loss of the pecans at the different CO_2 flowrates investigated is presented in Table II. The values range from 2.85% to 10.46%, which are all acceptable. The cause of the slightly higher value at 1.0 slpm may be due to the longer extraction time. Preliminary experiments conducted during development of the extraction method had suggested that more oil would be lost at higher flowrates. This trend did not prove true for the combination of low collection vessel liquid levels, glass wool in the collection vessel, and experimentally determined valve and collection vessel temperatures. This result indicates that the method developed is capable of yielding low loss of extract at flowrates of 1 to 7.5 slpm and therefore fulfills one objective of this project.

The amount of extract collected over time for the CO_2 flows of 1 to 7.5 slpm is shown in Figure 10. For 2 compared with 1 slpm, almost twice the amount of extract was collected at all times. This ratio did not continue with further increases in flowrate. Increasing CO_2 flow from 1 to 3 slpm yielded less than three times the amount of extract. Figure 10 also shows that for extraction times less than 105 minutes, the amount of oil extracted increases as CO_2 flowrate increases from 1 to 7.5 slpm. This trend does not continue at 120 minutes, as previously discussed.

Table II: Extract losses from collection vessel at different CO_2 flowrates for 'Nance' native pecans at 75 °C and 62.0 MPa.

Flowrate (slpm)	Difference * (%)
1	10.46
1.5	6.27
2	9.77
2.5	8.17
3	7.65
4	2.31
7.5	5.86

* Difference (%) = $100\frac{\text{Pecan Weight Loss(g) - Oil Collected (g)}}{\text{Pecan Weight Loss (g)}}$

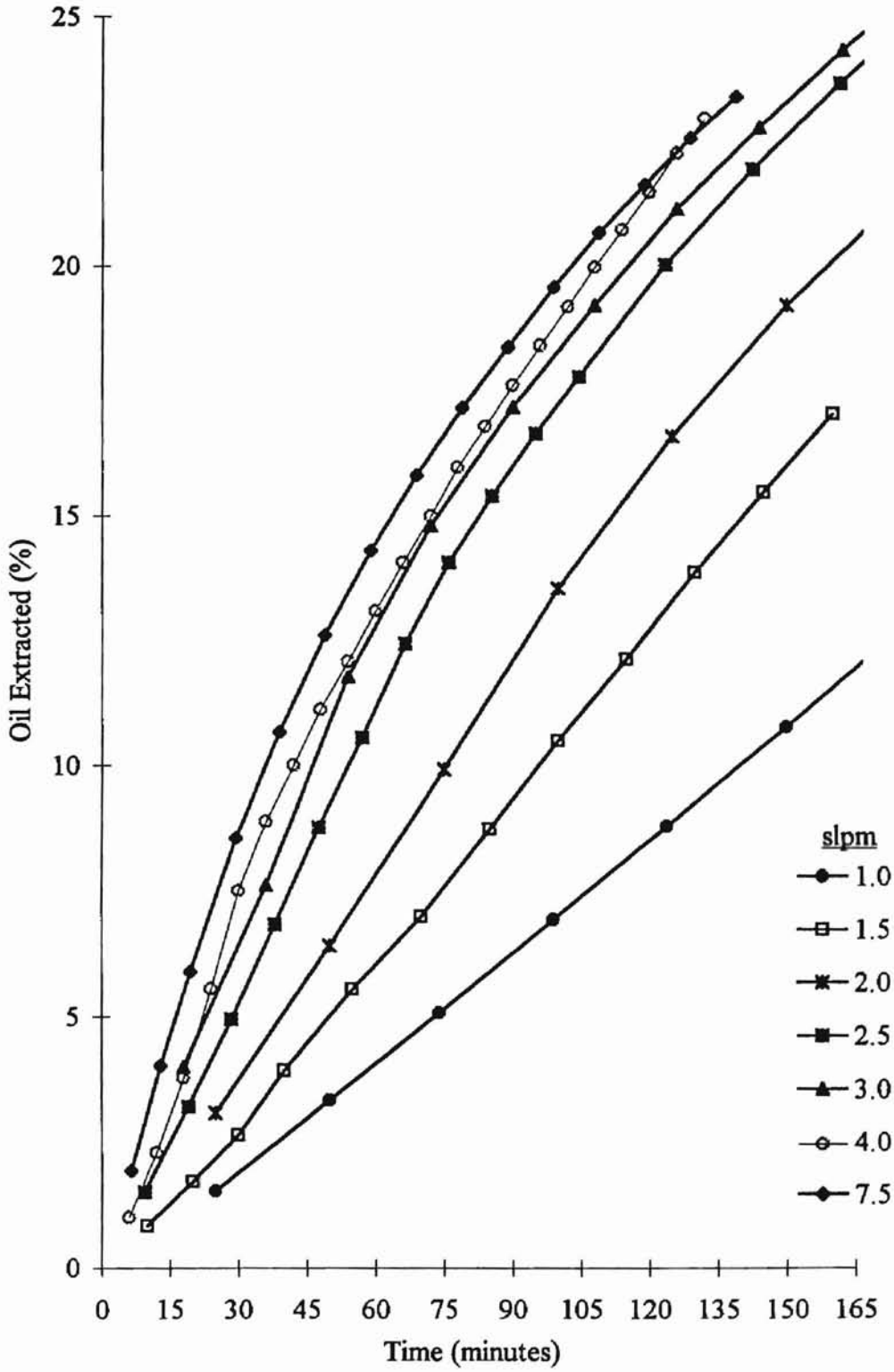


Figure 10: Effect of CO_2 flowrate on oil extracted from 'Nance' native pecans at 75 °C and 62.0 MPa.

The amount of oil extracted over time for the flowrates examined fits the following basic form:

$$W = (a/b)[1-\exp(-bt)] \quad (4.2)$$

where: W = weight oil collected (g)
t = time (minutes)
a = f(T,P,F)
b = f(F)
F = flowrate (slpm)
T = temperature (°C)
P = pressure (MPa)

The values for a and b increase as flowrate increases (Table III). The a/b values are the same order of magnitude for all extractions, except at 1.0 slpm. This exception may be because this extraction curve would be better represented using a straight line.

The a and b terms are composed of the following parameters for 'Nance' native pecan halves extracted at 75 °C, 62.0 MPa with a valve temperature of 100 °C and a collection vessel temperature of 0 °C for 1-4 slpm and a valve temperature of 150 °C and a collection vessel temperature of 0 °C for 7.5 slpm:

$$a = FC_i\rho/\alpha \quad (4.3)$$

$$b = (F/\alpha)[(1/V) + (1/K)] \quad (4.4)$$

where: F = flowrate (slpm)
C_i = initial slope of solubility curves (g_{oil}/g_{CO2})
ρ = density CO_2 (g/L)
α = void volume of pecan bed
V = volume of extraction vessel (L)
K = constant

The term C_i is a function of flowrate from these experiments. Figure 11 shows the solubility curves for the flowrates from 1- 7.5 slpm used to determine the C_i values. The

Table III: Coefficients in equation 4.2 at different CO_2 flowrates for 'Nance' native pecans at 75 °C and 62.0 MPa.

Flowrate (slpm)	a	b	a/b	r^2
1	0.043	7.95E-07	53900	0.998
1.5	0.073	0.001	50.673	0.997
2	0.083	0.002	35.007	0.999
2.5	0.126	0.005	23.581	0.998
3	0.138	0.006	21.607	0.997
4	0.153	0.007	21.576	0.998
7.5	0.192	0.011	16.765	0.999

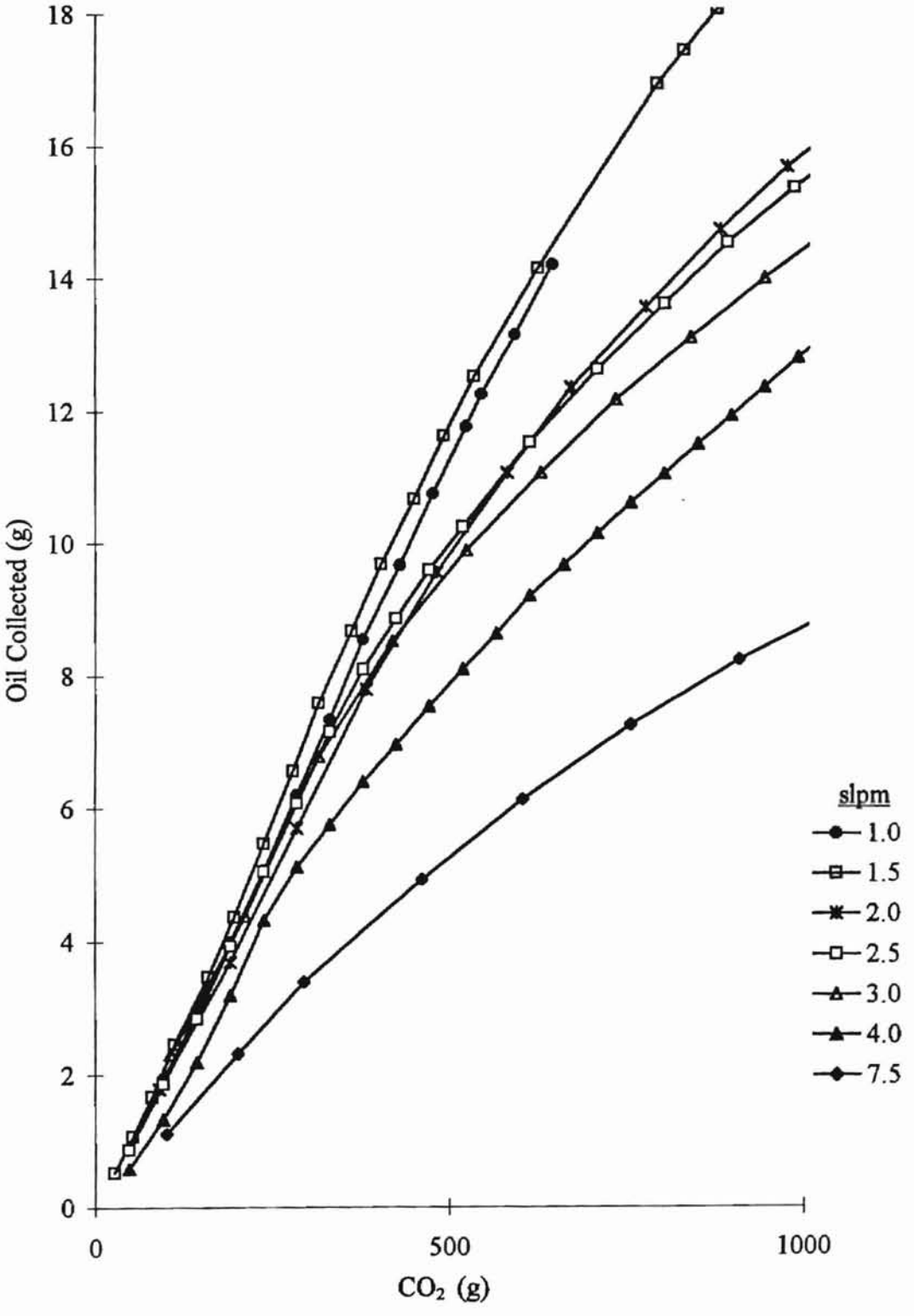


Figure 11: Oil solubility curves at different CO_2 flowrates for 'Nance' native pecans at 75 °C and 62.0 MPa.

relation between C_i and flowrate is shown in Figure 12. The straight-line equation describing this relationship is :

$$C_i = -0.0016F + 0.0244 \qquad r^2 = 0.95 \qquad (4.5)$$

Using this relation and the equations presented for each flowrate, extraction curves can be constructed at other flowrates in the range of 1-7.5 slpm and for extraction times up to 165 minutes. Different factors control the extraction rate during longer extraction periods. The factors controlling extractions in the times investigated are assumed to be solubility and external mass transfer of oil from the pecan to the supercritical fluid. At longer times, diffusion through the pecan is assumed to have a greater influence and the empirical equations presented may not apply.

Oil Composition

Pressure and Temperature Effect

Gas chromatography of the methyl esters formed from pecan oil was used to determine the fatty acid composition of oil extracts. The main fatty acids obtained in all extracts were found to be oleic, linoleic, palmitic, stearic, and linolenic. The mole percentages of the five main fatty acids in oil extracted appeared similar at different extraction temperatures and pressures as shown in Figure 13. ANOVA results indicate significant differences ($P < 0.05$) for all fatty acids except stearic. The O/L (oleic/linoleic) ratio also showed differences ($P < 0.05$) for different extraction conditions. The average

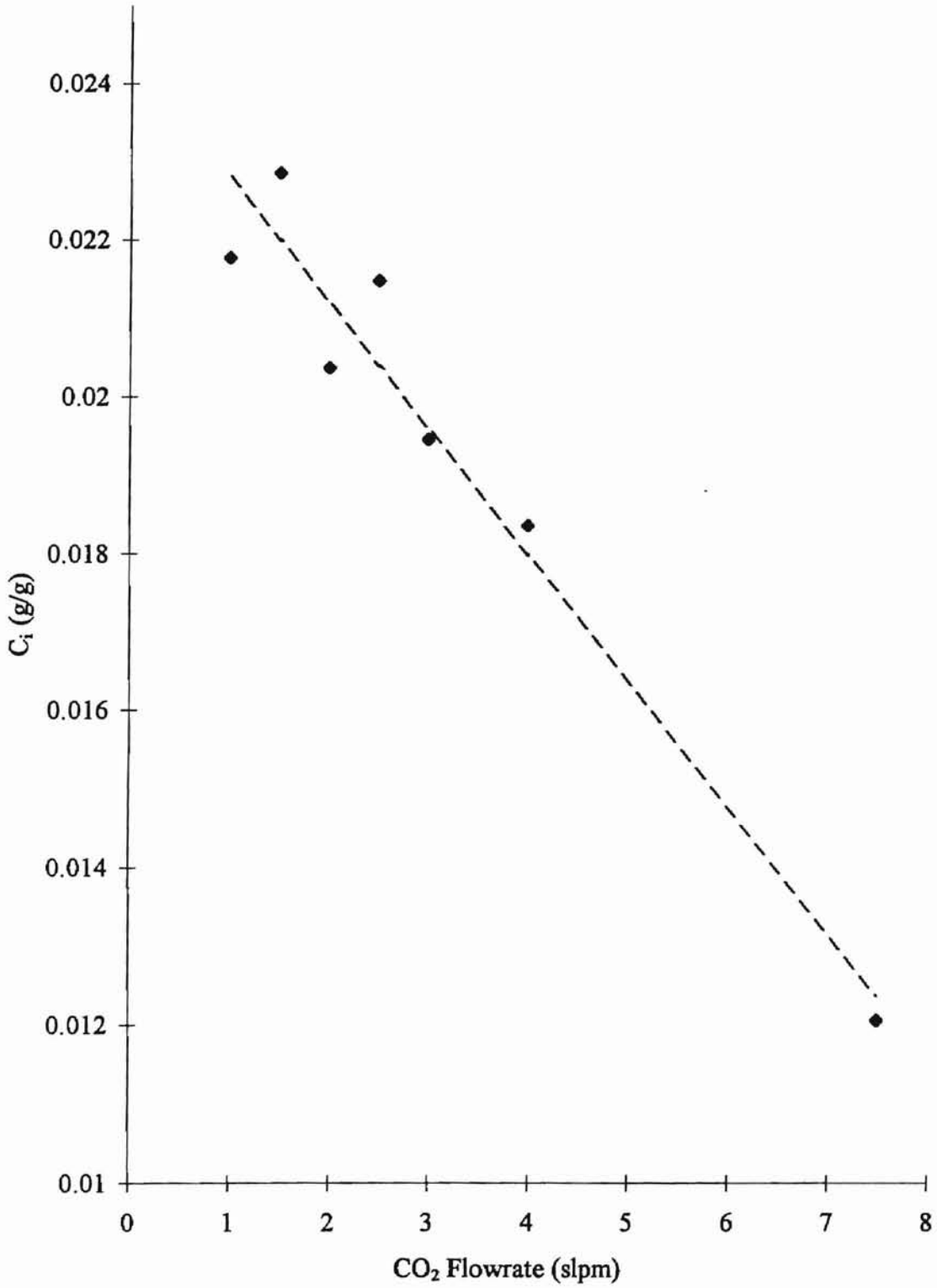


Figure 12: Initial solubility at different CO_2 flowrates for 'Nance' native pecans at 75 °C and 62.0 MPa.

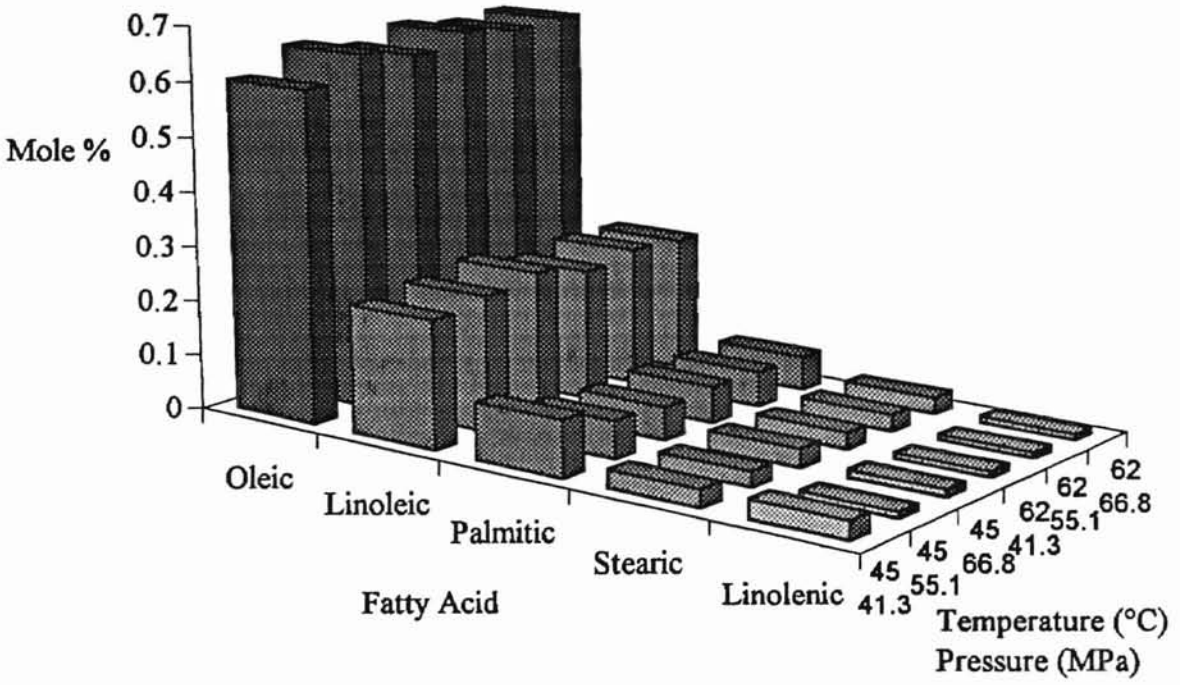


Figure 13: Fatty acid composition of pecan oil extracted from 'Wichita' pecans at 45 - 62 °C, 41.3 - 66.8 MPa, and 1 hour. Each bar is the average of two replicates.

O/L values for each temperature did not change by a quantity greater than 0.1 and ranged from 2.5 to 2.8 for all six extraction conditions. Apparently, fatty acid composition of the oil is slightly affected over the range of conditions of extraction. The same results were obtained from examination of differences between pecan oil obtained at 45 °C, but at 62 °C no differences were found ($P>0.05$) for all five main fatty acids. This result indicates that the differences observed for all pressure and temperature effects may result from the differences at 45 °C.

Analysis of data at the three pressures of 41.3, 55.1, and 66.8 MPa was also conducted. At 55.1 MPa, no differences were indicated ($P>0.05$) for all five main fatty acids. Differences were indicated ($P<0.05$) for linoleic acid and linolenic acid at 41.3 MPa and for oleic, linoleic, and linolenic acid at 66.8 MPa.

Time Effect

At extraction conditions of 45 °C, 41.3 MPa, and 2.5 slpm, there was no difference ($P> 0.05$) in the mole percentages of the five main fatty acids obtained for three extraction times as shown in Figure 14. At 55.1 and 66.8 MPa, there was no difference ($P>0.05$) in the fatty acid composition between 15 minutes and 250 minutes. Fatty acid composition was unchanged over time of extraction of oil from pecans.

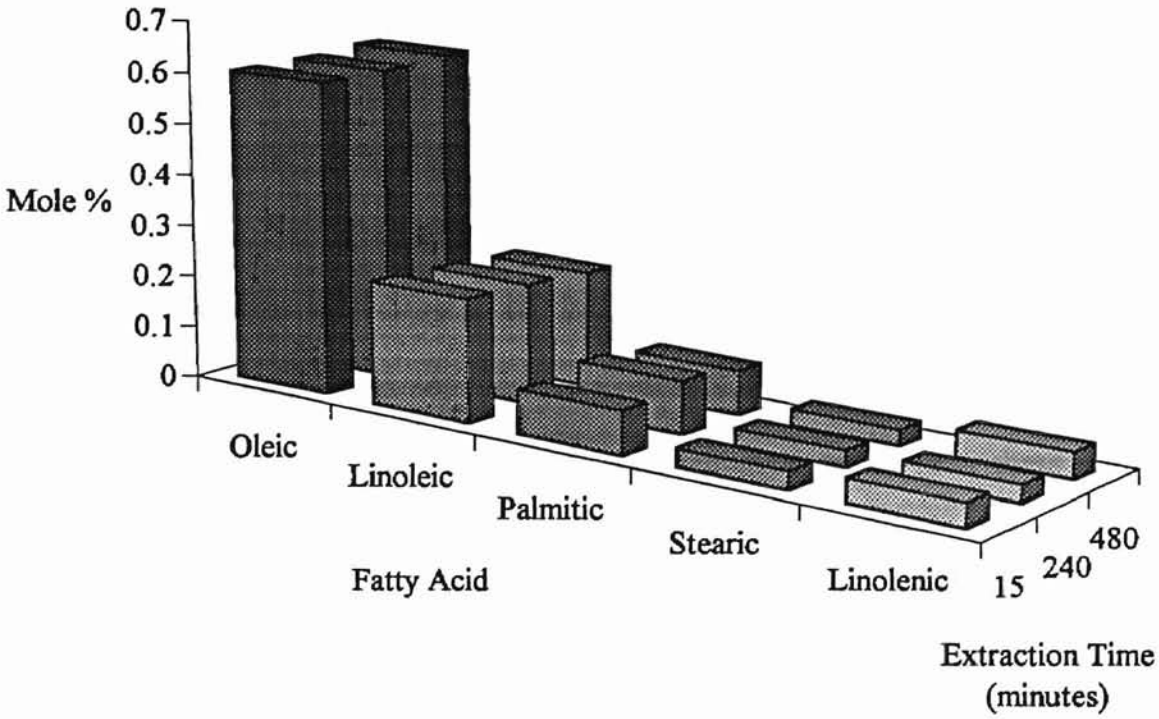


Figure 14: Fatty acid composition of pecan oil extracted from 'Wichita' pecans at 45 °C and 41.3 MPa. Each bar is the average of two replicates.

Cultivar Effect

At constant extraction conditions of 75 °C, 62.0 MPa, and 2.5 slpm, the extracted oil composition after 1 hour of extraction appeared similar from 'Nance' native and 'Wichita' pecans (Table IV). However, ANOVA results indicated significant differences ($P<0.05$) for the O/L ratio and for all main fatty acids except linolenic. The result for linolenic is not considered significant because its mole percentage in pecan oil is very low (around 1%). A difference in both oleic and linoleic acid is more noteworthy since they collectively contribute to about 90% of the pecan oil composition. Previous researchers (Senter and Horvat, 1976; Heaton *et. al.*, 1966; French, 1962) also found different fatty acid compositions for different pecan cultivars. The 'Nance' native and 'Wichita' pecan oil compositions were not presented in the compilation of results from these studies presented by Santerre (1994).

Valve Temperature Effect

At extraction conditions of 75 °C, 62.0 MPa, and 3.0 slpm, the fatty acid composition of pecan oil samples obtained after 1 hour using different micrometering valve temperatures appear similar (Table V). However, ANOVA results show significant differences ($P<0.05$) in the mole percentages of the palmitic, oleic, and linoleic acids and the O/L ratio. The difference may be due to either precipitation of different oil

Table IV: Fatty acid composition of pecan oil from different pecan cultivars at 75 °C and 62.0 MPa.

Cultivar	Palmitic (%)	Stearic (%)	Oleic (%)	Linoleic (%)	Linolenic (%)
Wichita	5.88	2.62	65.15	25.32	1.02
Nance	5.36	2.34	67.15	24.08	1.07

* Data are average of 3 replicates

Table V: Effect of micrometering valve temperature on pecan oil's fatty acid composition for 'Nance' native pecans at 75 °C, 62.0 MPa, and 3.0 slpm CO_2.

Valve Temperature (°C)	Palmitic Mole (%)	Stearic Mole (%)	Oleic Mole (%)	Linoleic Mole (%)	Linolenic Mole (%)
75	5.18	2.22	69.57	22.09	0.94
100	5.36	2.34	67.15	24.08	1.07
125	5.39	2.35	68.49	22.70	1.07
150	5.08	2.52	69.40	21.97	1.03

*Data are average of 3 replicates

components in the valve or volatilization of different components and subsequent loss with the vented CO_2.

Solubility Effect

Figure 15 shows the percent oil extracted after 165 minutes at three temperatures and three pressures. Pressures ranging from 41.3 to 66.8 MPa are necessary because fat has low solubility at low pressures. Low pressures are used to extract odiferous compounds from natural substances. More oil was extracted at 75 °C than at 62 °C and 45 °C. This trend concurs with the results obtained by Zhang *et. al.* (1995).

Increasing extraction temperature from 45 °C to 75 °C increased the percent oil extracted from 14.34% to 17.48% at 41.3 MPa, from 21.26% to 31.53% at 55.1 MPa, and from 21.51% to 32.37% at 66.8 MPa. Extraction pressure caused a significant increase in the oil extracted when raised from 41.3 to 55.1 MPa, but only a slight (62 °C) or negligible (45°C and 75 °C) increase from 55.1 to 66.8 MPa. Due to the higher cost of equipment for higher operating pressures, extractions at pressures above 55.1 MPa are not beneficial.

These results conflict with those of Zhang *et. al.* (1995), who indicated a positive pressure effect in the pressure range of 41.3 to 68.9 MPa and the temperature range of 40 to 80 °C. The difference may be explained by considering the extraction curves and the method used to obtain them. Figures 16, 17, and 18 show percent oil extracted from 'Wichita' pecans with time curves for nine pressure and temperature combinations. The

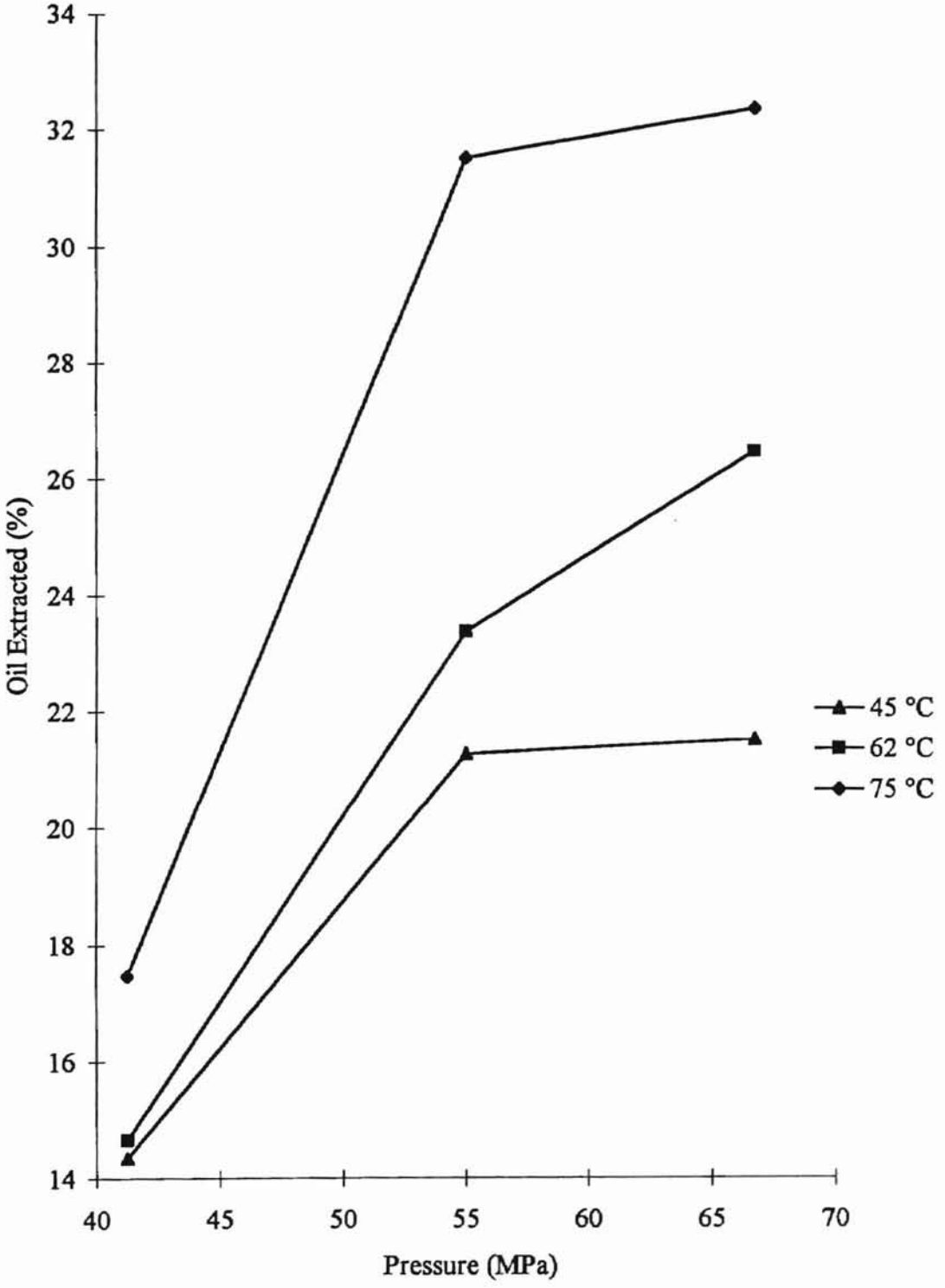


Figure 15: Effect of temperature and pressure on oil extracted from 'Wichita' pecans at 2.5 slpm CO_2 and 165 minutes.

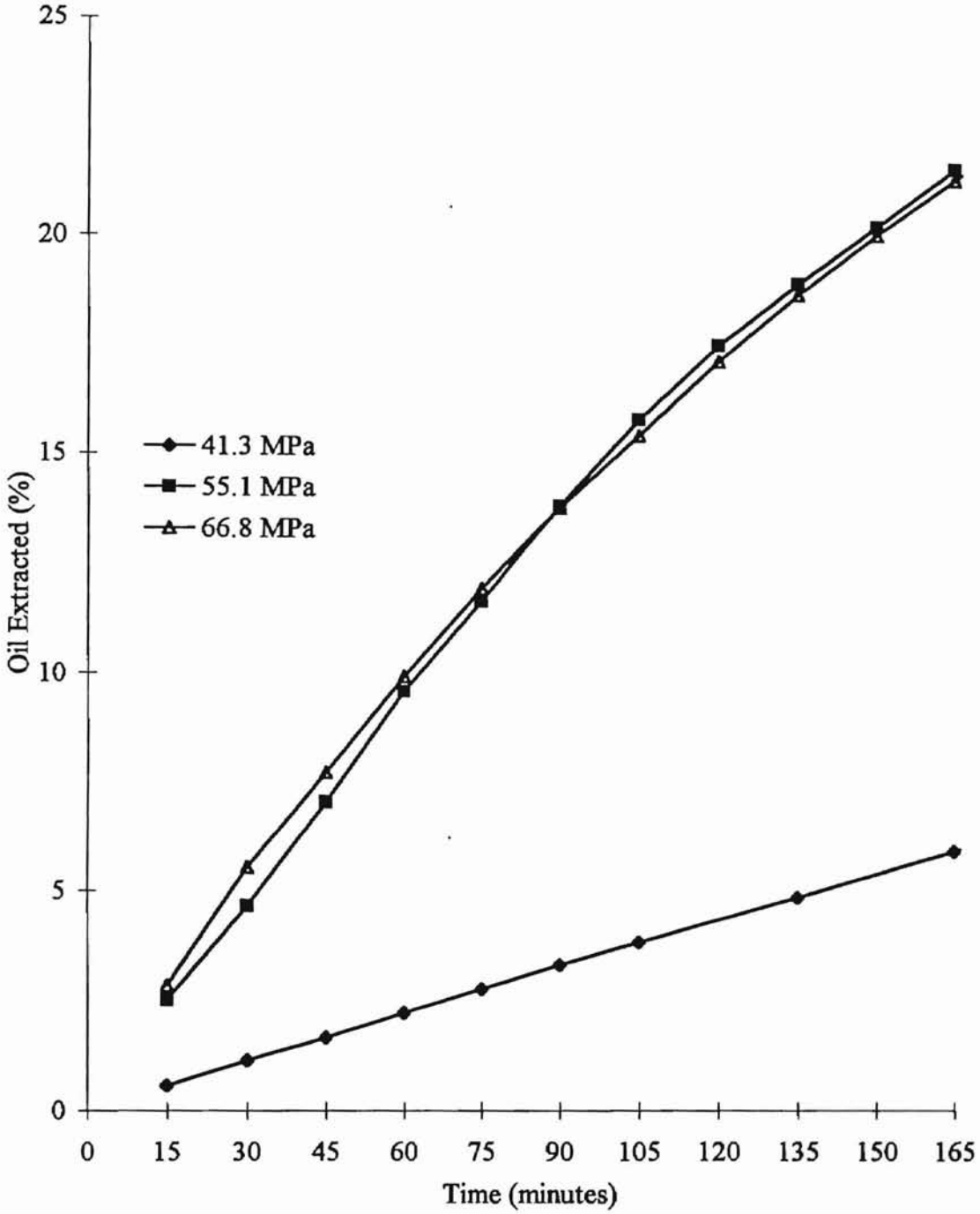


Figure 16: Extraction curves for 'Wichita' pecans at 45 °C, 41.3 - 66.8 MPa, and 2.5 slpm CO_2.

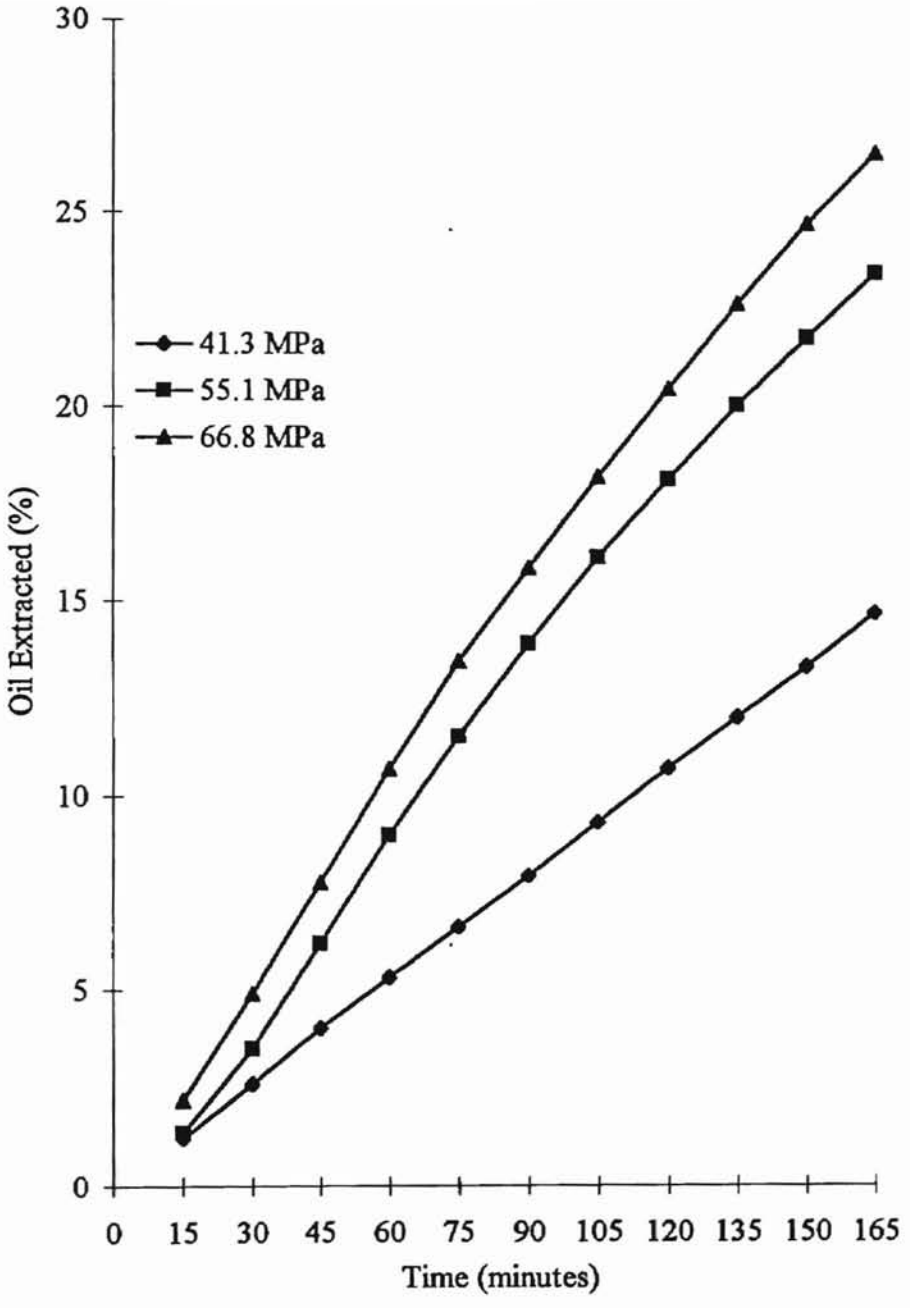


Figure 17: Extraction curves for 'Wichita' pecans at 62 °C, 41.3 - 66.8 MPa, and 2.5 slpm CO2.

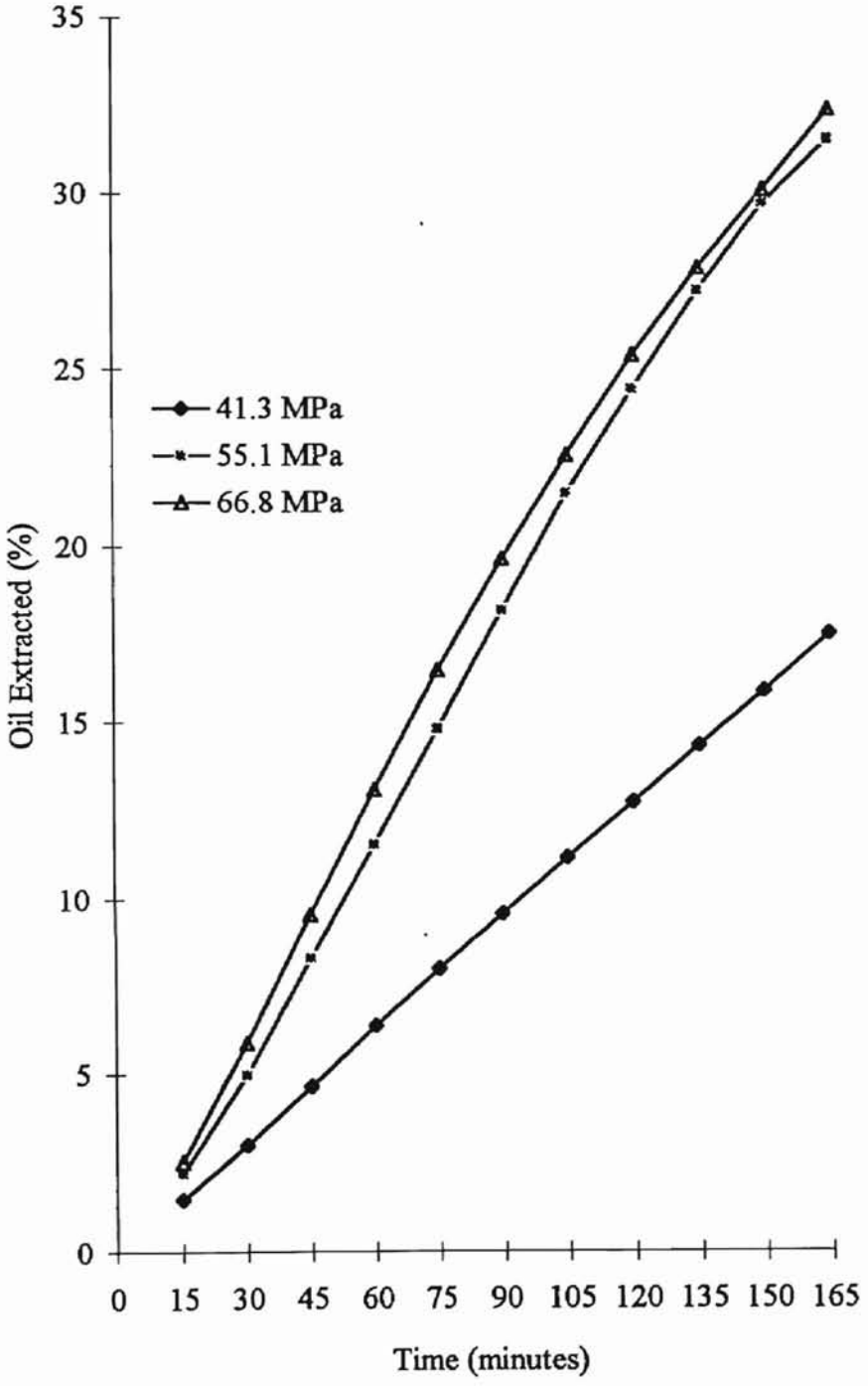


Figure 18: Extraction curves for 'Wichita' pecans at 75 °C, 41.3 - 66.8 MPa, and 2.5 slpm CO_2.

data are exponential at 55.1 and 66.8 MPa , but nearly linear at 41.3 MPa. The data may be fit to exponential equations as given in Table VI. The regression equations and the factors relating to the a and b values are identical to the equations determined from the flowrate experiments.

The curves presented by Zhang (1994) for small quantities of pecans (7 to 8 g) extracted at flowrates of 1.12 to 2.02 slpm at 41.3 to 68.9 MPa were linear for their entire extraction time of 160 minutes. The curves shown in Figures 16, 17, and 18 show exponential behavior at flowrates of 2.5 slpm and extraction pressures of 55.1 MPa and 66.8 MPa before 160 minutes. This difference in extraction curves may have led to the difference in determination of the amount of oil extracted at pressures ranging from 55.1 to 66.8 MPa.

An important difference between the experiments conducted in this research using the SPE-ED™ continuous CO_2 flow extraction unit and those conducted by Zhang (1994) was the lack of CO_2 flowrate control in his Dionex Model SFE-703 extraction unit. As the extraction pressure increased from 41.3 to 68.9 MPa in Zhang's experiments (1994), the flowrate increased from 1.12 to 2.02 slpm. Experiments conducted herein with the SPE-ED™ unit at 75 °C and 62.0 MPa produced different extraction curves at these different flowrates. Zhang (1994) used the data obtained at different flowrates to determine trends for different extraction temperatures and pressures. This flowrate control discrepancy is expected to explain the differences between the trends obtained from the two extraction units.

Table VI: Coefficients in equation 4.2 at different temperatures and pressures for 'Wichita' pecans at extraction times up to 165 minutes.

Temperature (°C)	Pressure (MPa)	a	b	a/b	r^2
45	41.3	0.038	0.001	45.723	0.999
45	55.1	0.080	0.005	15.210	0.999
45	66.8	0.074	0.004	18.742	0.998
62	41.3	0.035	5.6E-08	6.3E+05	0.999
62	55.1	0.066	0.001	58.725	0.993
62	66.8	0.078	0.002	42.379	0.998
75	41.3	0.044	3.5E-09	1.3E+07	0.999
75	55.1	0.082	3.4E-05	2431.989	0.996
75	66.8	0.097	0.002	46.151	0.997

Extended Period Extraction

An extended period extraction was performed to determine the shape of the extraction curve for pecans beyond 165 minutes. An extraction was performed at 75 °C, 62.0 MPa, 2.5 slpm, with the valve temperature at 100 °C and the collection vessel temperature at 0 °C for 181 hours (7.54 days), at which time it was determined that about 95% of the oil and water in the pecans had been removed, based on the amount of collected extract (Figure 19). The difference between the weight of extract collected and the weight loss of the pecans was 5.38 %. The extracted nuts were observed to be much darker in color than pecans extracted for times less than nine hours at the same temperature and pressure. They also seemed to be very brittle.

Figure 20 shows a semi-log plot of the natural log of the fractional loss of solute from pecans over time. After approximately 16 hours, the curve becomes linear and is given by the following expression:

$$\ln(m_o/m) = 0.542 + (0.0139)t \qquad (4.6)$$

where: t = time (hours)
m_o = amount of oil in pecans, initially (g)
m = amount of oil in pecans at time = t (g)

Data fit the line with an r^2 value of 0.999. The rate-limiting extraction step in the region where the above equation holds is assumed to be diffusion of oil to the surface of the pecans. An effective diffusion coefficient for this process may be obtained from the magnitude of the slope of the line using the following relation for a sphere:

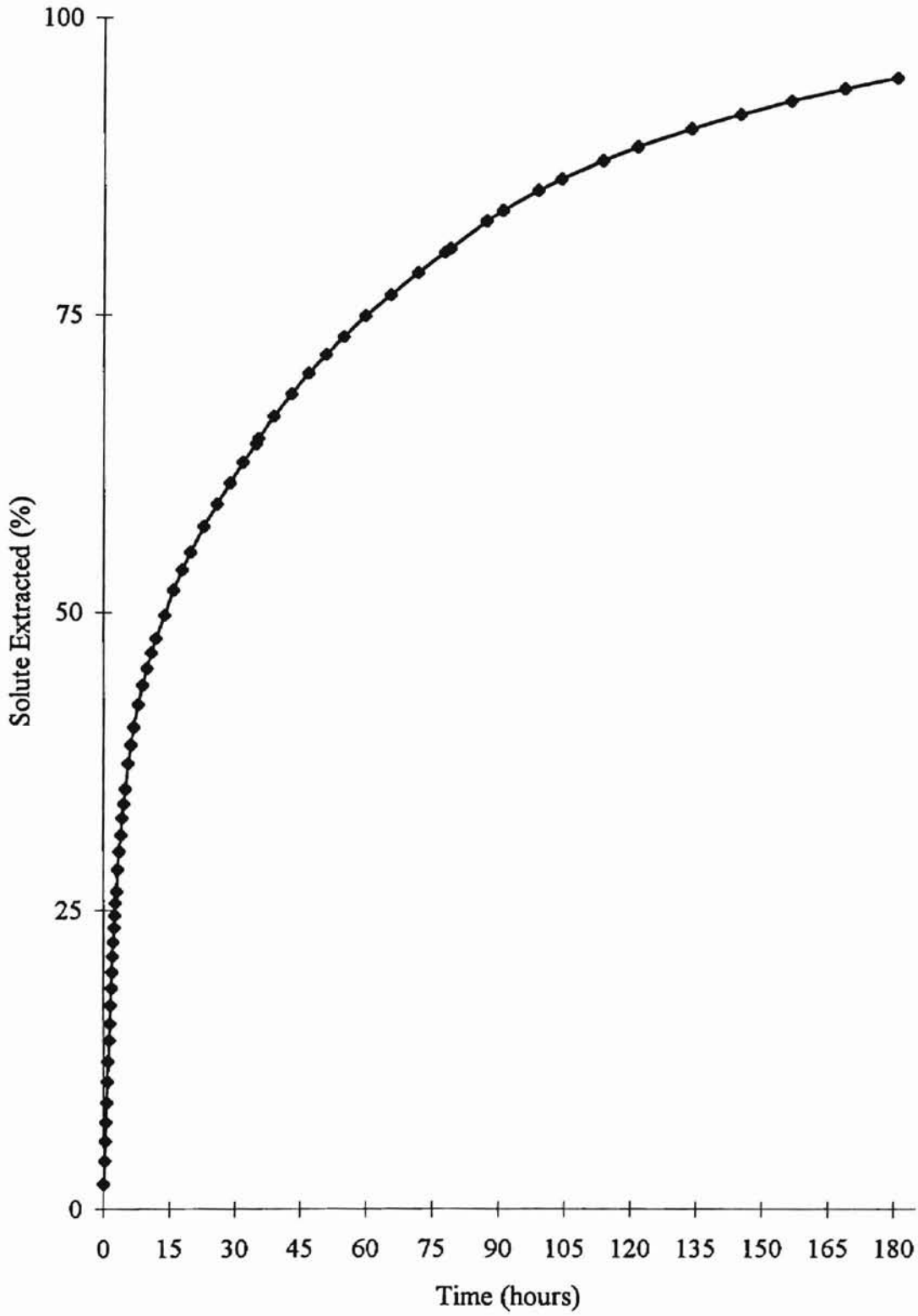


Figure 19: Extended period extraction curve for 'Nance' native pecans at 75 °C, 62.0 MPa, and 2.5 slpm CO_2.

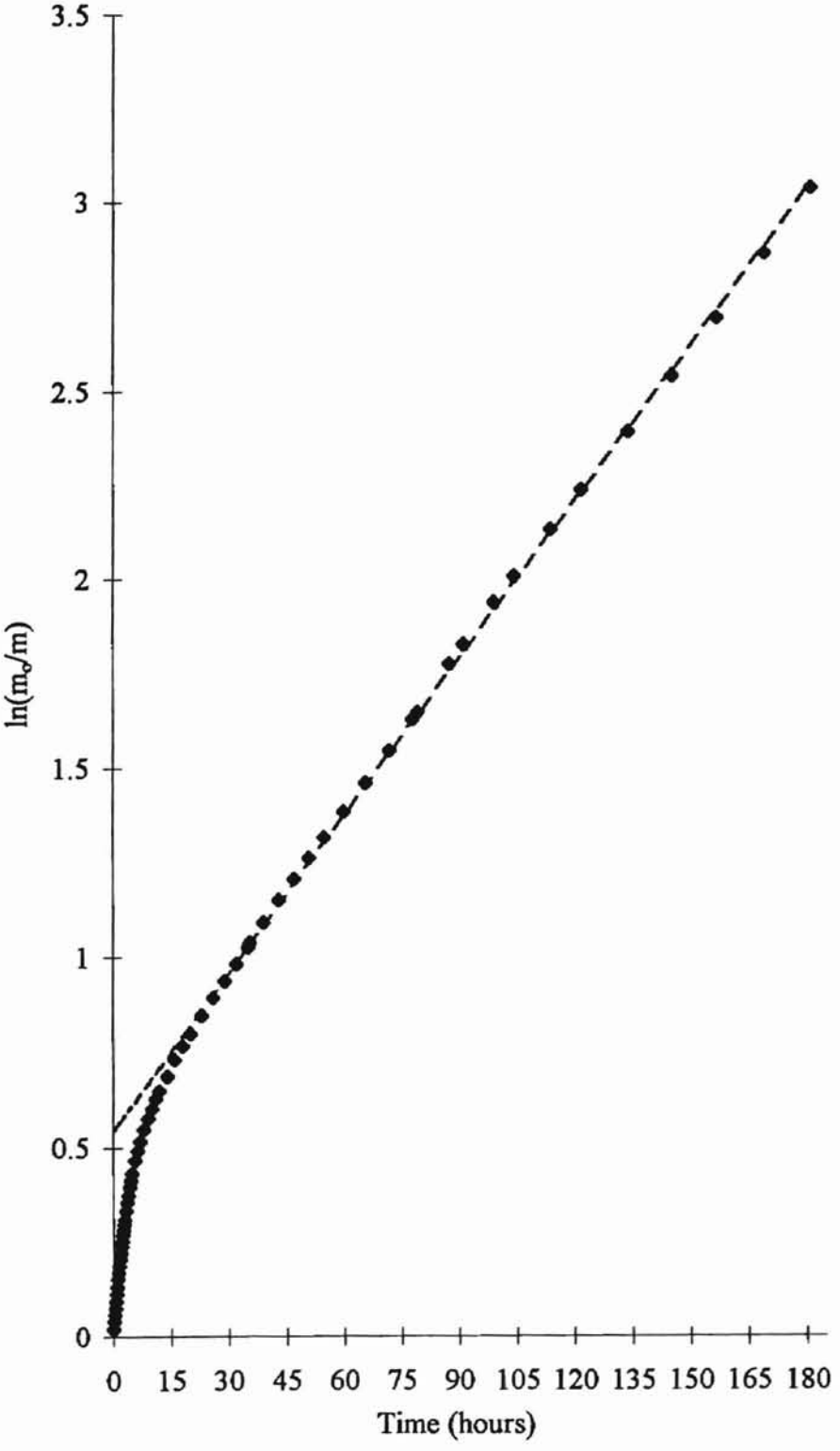


Figure 20: Ln(m_o/m) curve for extended period extraction of 'Nance' native pecans at 75 °C, 62.0 MPa, and 2.5 slpm CO_2.

$$a' = D\pi^2/r^2 \qquad \text{(Note : } a' = a/3600\text{)} \qquad (4.7)$$

where: a' = slope (s^{-1})
a = slope (h^{-1})
D = effective diffusion coefficient (m^2/s)
r = radius (m)

Using this equation, the effective diffusion coefficient is 9.76×10^{-12} m^2/s. The radius value for the 'sphere' was assumed to be 5 mm, which is one-half of the minor diameter of an average pecan. This can be compared with an effective diffusion coefficient of 2.53×10^{-10} m^2/s for extraction of caffeine from coffee beans with equivalent radii of 4.01 mm (Udayasankar *et. al.*, 1986).

Since a straight-line relationship described the data at long times, the total amount of solute in the pecan was estimated using Westwood's (1993) equation:

$$m_o = m_1 + [(m_2)^2/(m_2-m_3)] \qquad (4.8)$$

where: m_o = initial solute content of pecans (g)
m_1 = mass of solute collected for time at least equal to initial non-exponential period (g)
m_2 = mass of solute collected for time in exponential period (g)
m_3 = mass of solute collected for same extraction time as m_2 in exponential period (g)

Using the values of m_1, m_2, and m_3 as given in Table VII, the estimated value of m_o was 61.41 g. The initial weight of pecans used in the experiment was 90.26 g. The total estimated solute content of these pecans is 68.0%. This value consists of both the oil and water content of the pecans. The initial moisture content of unextracted pecans was 4.79% using an oven drying technique. The initial oil content of the pecans was 63.9% using a quantitative extraction of ground pecans. From these values, the initial solute content of the pecans was found to be 68.7%. This result agrees with the value obtained from the estimation equation (eq. 4.8). Thus, the long experiment achieved adequate

TableVII: Pecan oil and water content estimation from extended period extraction data for 'Nance' native pecans at 75 °C, 62.0 MPa, and 2.5 slpm CO_2.

Extraction Time (minutes)	Mass Component	Mass Extracted (g)
0 - 960	m_1	32.156
960 - 5950	m_2	20.925
5950 - 10860	m_3	5.959

Component	Actual	Estimated	Difference (%)
m_o	61.41	62.00	0.96
(Oil + Water) Content	68.04	68.69	0.95
Water Content	4.79	-	-
Oil Content	63.90	-	-

prediction of the total solute content in the pecans based on the amount of solute collected. The low loss of solute that was determined, based on the small percent difference (5.38%) between solute collected and solute removed from pecans, supports the reliability of this estimation procedure.

A limitation of this estimation method is the requirement that extraction time extends beyond the initial non-exponential extraction period. For pecan extraction, this requires an extraction time longer than would be commercially viable. The faster quantitative method designed by Maness *et. al.* (1995) is a more practical method for determination of oil content.

The inability to change, i.e., decrease, the size of the pecan limits the rate of extraction. This is why diffusion is the limiting factor during the extended extraction period (for times greater than 960 minutes). That 95% of the oil and water was removed indicates a rate-limiting factor like adsorption does not occur. If adsorption had been a factor, extraction would have leveled off at a value lower than the total solute content. This phenomenon has been observed in CO_2 extraction of pyrene from a wet petroleum waste sludge (Westwood, 1993). Use of a different solvent produced more effective extraction.

Another factor that contributed to the slow rate of oil removal is the low solubility of pecan oil in supercritical carbon dioxide, which is assumed to be the rate-limiting step for extraction between 0 and 16 hours. At 75 °C, 62.0 MPa, and 2.5 slpm, the maximum observable solubility (g extract/ g CO_2), which occurred only during the beginning of the extraction, was found to be 0.021. This value clearly shows that pecan oil and

supercritical carbon dioxide are not completely miscible under these extraction conditions. List *et. al.* (1989) found that soybean triglycerides are completely miscible in supercritical carbon dioxide at an extraction temperature of 70 °C and extraction pressure of 83 MPa. The lipids in pecan oil contain 95% triglycerides and the solubility of vegetable triglycerides may be considered identical (McHugh and Krukonis, 1994). Solubility at this high pressure for pecans was beyond the 68.9 MPa limits of our extraction equipment. Also, use of extraction conditions that yielded complete miscibility of triglycerides that were not bound to a natural matrix may lead to lower solubility when extracting from a pecan. Using "complete miscibility" extraction conditions of 90 °C and 83 MPa for soybean flakes (20 % oil by weight), List *et. al.* (1989) obtained a maximum initial solubility [g_{oil} /(g_{oil} + g_{CO2})] of only 20.5 %. This value resulted because the observed extraction solubility depends on the amount of oil in the natural matrix and the amount of supercritical carbon dioxide inside the extraction vessel. A higher pecan oil solubility and a lower processing time may be obtained by increasing extraction pressure to 83 MPa, yet the cost would be large for equipment capable of operating at pressures above 68.9 MPa.

CHAPTER V

CONCLUSIONS

1. Differences between pecan final weight loss and oil collected were less than 10%. Extract collected may therefore be used as a measure of the oil removed from pecans during supercritical CO_2 extraction.
2. Micrometering valve temperature and collection vessel temperature necessary to minimize extract lost from the collection vessel and to prevent micrometering valve clogging depend on CO_2 flowrate.
3. At 75 °C , 62.0 MPa, and 120 minutes, the solute extracted increases as CO_2 flowrate increases from 1 to 4 slpm, but not from 4 to 7.5 slpm. For extraction times less than 105 minutes, the amount of solute extracted increases as CO_2 flowrate increases from 1 to 7.5 slpm.
4. Amount of oil extracted increases with extraction temperature and pressure for 45 and 75 °C with pressures ranging from 41.3 to 55.1 MPa, but not from 55.1 to 66.8 MPa.
5. Amount of oil extracted increases at 62 °C for pressures ranging from 41.3 to 66.8 MPa.
6. Extraction temperature and pressure affect fatty acid composition of the collected pecan oil.
7. Extraction time does not affect fatty acid composition of the collected pecan oil.
8. Micrometering valve temperature affects fatty acid composition of the collected pecan oil.

9. Pecan oil extraction is initially influenced by CO_2 solubility and flowrate and later by diffusion from the pecan.

CHAPTER VI

SUGGESTIONS FOR FUTURE STUDY

A pecan quality factor that would be interesting to investigate is the effect on the tocopherol content of supercritical fluid extraction of pecans. This relationship is of interest because tocopherol has an inhibitory effect on pecan oil oxidation. It would be helpful to determine whether the ratio of tocopherol to triglycerides of the pecans changes during extraction and relate this possibility to the development of rancidity during storage after extraction.

A study is needed of the effect of pecan initial moisture content on extraction. Parameters that could be investigated include the rate of extraction and the final condition of the pecans. It would also be helpful to determine what moisture levels cause excessive breakage of pecans during depressurization after extractions for varying lengths of time.

Examination of the effect of pecan variety, kernel shapes, and sizes on extraction would also be useful to determine if there are any differences among varieties.

A study could be conducted of the rate at which extraction pressure should be achieved during the vessel warm-up. This rate can be examined for different extraction temperatures and pressures.

A study could be conducted of the effect of extraction method on pecan oil extraction. Passey (1991) described a static cycling technique for peanuts that could be applied for pecans. This method could be compared to continuous extraction.

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APPENDIX

APPENDIX A

MICROMETERING VALVE TEMPERATURE EXPERIMENT I

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 75 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	1.079	1.079	1.87
20	115.7	1.229	2.308	4.01
30	178.9	1.056	3.364	5.84
40	236.7	1.072	4.436	7.70
50	294.6	1.099	5.535	9.61
60	357.8	1.174	6.709	11.65
70	415.6	0.843	7.552	13.12
Depressurization	652.4	0.453	8.005	13.90
Cleaning	894.4	0.071	8.076	14.03

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.10	1.114	1.258
Final	80.98	1.534	1.685

APPENDIX B

MICROMETERING VALVE TEMPERATURE EXPERIMENT II

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 75 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	1.566	1.566	2.72
20	115.7	1.425	2.991	5.20
30	178.9	1.347	4.338	7.55
40	236.7	1.182	5.520	9.60
50	294.6	1.174	6.694	11.64
60	352.5	1.071	7.765	13.51
Depressurization	599.8	0.488	8.253	14.36
Cleaning	720.8	0.053	8.306	14.45

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	89.96	1.252	2.201
Final	80.07	1.553	2.875

APPENDIX C

MICROMETERING VALVE TEMPERATURE EXPERIMENT III

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	1.383	1.383	2.40
20	115.7	1.316	2.699	4.68
30	173.6	1.219	3.918	6.80
40	231.5	1.291	5.209	9.04
50	289.4	1.339	6.548	11.36
60	352.5	1.142	7.690	13.35
Depressurization	578.7	0.413	8.103	14.06
Cleaning	799.7	0.079	8.182	14.20

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.17	1.794	0.919
Final	81.64	2.032	1.211

APPENDIX D

MICROMETERING VALVE TEMPERATURE EXPERIMENT IV

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	0.877	0.877	1.52
20	115.7	1.176	2.053	3.57
30	173.6	1.448	3.501	6.09
40	236.7	1.362	4.863	8.45
50	289.4	1.000	5.863	10.19
60	352.5	1.044	6.907	12.01
Depressurization	647.1	0.547	7.454	12.96
Cleaning	857.5	0.071	7.525	13.08

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.02	1.123	0.717
Final	81.84	1.580	1.001

APPENDIX E

MICROMETERING VALVE TEMPERATURE EXPERIMENT V

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 125 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	1.049	1.049	1.82
20	115.7	1.035	2.084	3.61
30	173.6	1.174	3.258	5.64
40	231.5	1.186	4.444	7.70
50	289.4	1.368	5.812	10.06
60	352.5	1.144	6.956	12.05
Depressurization	578.7	0.412	7.368	12.76
Cleaning	694.5	0.062	7.43	12.87

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.37	1.212	1.481
Final	81.63	1.481	1.924

APPENDIX F

MICROMETERING VALVE TEMPERATURE EXPERIMENT VI

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 125 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	1.693	1.693	2.93
20	115.7	1.414	3.107	5.37
30	173.6	1.353	4.460	7.71
40	231.5	1.351	5.811	10.04
50	289.4	1.463	7.274	12.57
60	347.2	1.410	8.684	15.01
Depressurization	578.7	0.528	9.212	15.92
Cleaning	720.8	0.074	9.286	16.05

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.56	1.489	1.746
Final	80.55	1.823	2.296

APPENDIX G

MICROMETERING VALVE TEMPERATURE EXPERIMENT VII

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 150 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	0.975	0.975	1.68
20	115.7	1.063	2.038	3.52
30	173.6	0.900	2.938	5.07
40	231.5	1.021	3.959	6.84
50	289.4	1.002	4.961	8.57
60	352.5	1.021	5.982	10.33
Depressurization	599.8	0.473	6.455	11.15
Cleaning	757.6	0.018	6.473	11.18

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.61	1.780	1.356
Final	82.22	2.109	1.694

APPENDIX H

MICROMETERING VALVE TEMPERATURE EXPERIMENT VIII

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 150 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	57.9	0.916	0.916	1.58
20	115.7	0.990	1.906	3.29
30	173.6	0.999	2.905	5.01
40	231.5	0.997	3.902	6.73
50	289.4	1.003	4.905	8.46
60	347.2	1.018	5.923	10.22
Depressurization	626.1	0.561	6.484	11.19
Cleaning	820.7	0.069	6.553	11.30

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.72	2.765	1.559
Final	82.25	3.544	1.939

APPENDIX I

COLLECTION VESSEL TEMPERATURE EXPERIMENT I

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 25°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	84.2	1.358	1.358	2.13
30	173.6	1.735	3.093	4.85
Depressurization	363.0	0.685	3.778	5.92
Cleaning	584.0	0.039	3.817	5.98

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	99.90	0.828	0.876
Final	95.14	1.410	1.232

COLLECTION VESSEL TEMPERATURE EXPERIMENT II

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 0°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	84.2	1.579	1.579	2.49
30	173.6	1.815	3.394	5.35
Depressurization	363.0	0.631	4.025	6.35
Cleaning	584.0	0.026	4.051	6.39

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	99.19	0.630	1.142
Final	95.02	1.090	1.450

APPENDIX J

COLLECTION VESSEL TEMPERATURE EXPERIMENT III

'Nance' native pecans

75 °C, 62.0 MPa, 7.5 slpm

Valve Temperature = 150 °C, Collection Vessel Temperature = 25°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	215.7	3.153	3.153	4.96
30	436.7	2.933	6.086	9.58
Depressurization	683.9	0.353	6.439	10.14
Cleaning	904.9	0.028	6.467	10.18

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	99.41	1.205	1.077
Final	91.96	1.510	1.322

COLLECTION VESSEL TEMPERATURE EXPERIMENT IV

'Nance' native pecans

75 °C, 62.0 MPa, 7.5 slpm

Valve Temperature = 150 °C, Collection Vessel Temperature = 0°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	210.4	3.127	3.127	4.91
30	415.6	2.816	5.943	9.33
Depressurization	736.5	0.358	6.301	9.89
Cleaning	957.5	0.026	6.327	9.93

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	99.67	1.218	0.942
Final	92.22	1.541	1.181

APPENDIX K

FLOWRATE EXPERIMENT I

'Nance' native pecans

75 °C, 62.0 MPa, 1.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 1°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
25	47.3	0.878	0.878	1.53
50	94.7	1.052	1.930	3.36
74	142.0	0.993	2.923	5.08
99	189.4	1.061	3.984	6.93
124	236.7	1.085	5.069	8.81
150	284.1	1.129	6.198	10.78
175	331.4	1.146	7.344	12.77
200	378.8	1.206	8.550	14.87
225	431.4	1.118	9.668	16.81
249	478.8	1.082	10.750	18.69
274	526.1	1.025	11.775	20.47
281	547.1	0.487	12.262	21.32
306	594.5	0.898	13.160	22.88
331	647.1	1.061	14.221	24.73

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.51	2.169	1.244
Final	73.20	2.651	1.505

APPENDIX L

FLOWRATE EXPERIMENT II

'Nance' native pecans

75 °C, 62.0 MPa, 1.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 1°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	26.3	0.526	0.526	0.91
20	52.6	0.547	1.073	1.85
30	78.9	0.590	1.663	2.87
40	110.5	0.794	2.457	4.25
55	157.8	1.100	3.467	5.99
70	194.7	0.898	4.365	7.54
85	236.7	1.106	5.471	9.46
100	278.8	1.092	6.563	11.34
115	315.7	1.027	7.591	13.12
130	363.0	1.084	8.675	14.99
145	405.1	1.010	9.685	16.74
160	452.4	0.987	10.672	18.45
175	494.5	0.962	11.634	20.11
190	536.6	0.892	12.526	21.65
220	626.1	1.639	14.165	24.48
280	794.4	2.789	16.954	29.30
295	831.2	0.507	17.461	30.18
310	878.6	0.627	18.088	31.26
340	968.0	1.058	19.146	33.09

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.54	2.067	1.437
Final	69.62	2.317	1.742

APPENDIX M

FLOWRATE EXPERIMENT III

'Nance' native pecans

75 °C, 62.0 MPa, 2.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
12.2	47.3	0.705	0.705	1.22
24.3	94.7	0.954	1.659	2.88
36.5	142.0	0.969	2.628	4.56
49.5	189.4	0.969	3.597	6.25
61.7	236.7	0.991	4.588	7.97
73.8	284.1	0.943	5.531	9.60
86.0	331.4	0.836	6.367	11.06
98.2	378.8	0.860	7.227	12.55
109.3	426.1	0.823	8.050	13.98
121.3	473.5	0.758	8.808	15.30
133.3	520.8	0.764	9.572	16.62
145.2	568.2	0.733	10.305	17.89
158.2	620.8	0.747	11.052	19.19
170.3	668.2	0.679	11.731	20.37
182.8	715.5	0.648	12.379	21.50
194.8	762.9	0.612	12.991	22.56
206.8	810.2	0.578	13.569	23.56
219.0	857.5	0.576	14.145	24.56
231.0	904.9	0.548	14.693	25.51
243.0	952.2	0.540	15.233	26.45
254.8	999.6	0.504	15.737	27.33
268.2	1052.2	0.542	16.279	28.27

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.12	1.659	1.913
Final	71.05	1.949	2.289

APPENDIX N

FLOWRATE EXPERIMENT IV
'Nance' native pecans
75 °C, 62.0 MPa, 2.5 slpm
Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
9.5	47.3	0.869	0.869	1.51
19	94.7	0.986	1.855	3.23
28.5	142.0	0.992	2.847	4.95
38	189.4	1.083	3.930	6.83
47.5	236.7	1.122	5.052	8.78
57	284.1	1.024	6.076	10.57
66.5	331.4	1.088	7.164	12.46
76	378.8	0.938	8.102	14.09
85.5	426.1	0.764	8.866	15.42
95	473.5	0.726	9.592	16.68
104.5	520.8	0.652	10.244	17.81
123.5	615.5	1.292	11.536	20.06
142.5	710.2	1.102	12.638	21.98
161.5	804.9	0.996	13.634	23.71
180.5	894.4	0.915	14.549	25.30
199.5	989.1	0.836	15.385	26.75
218.5	1083.8	0.767	16.152	28.09
237.5	1178.5	0.722	16.874	29.34

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.32	1.679	1.414
Final	70.92	1.907	1.612

APPENDIX O

FLOWRATE EXPERIMENT V

'Nance' native pecans

75 °C, 62.0 MPa, 3.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
8.2	47.3	0.845	0.845	1.47
16.4	94.7	0.913	1.758	3.06
24.6	142.0	0.890	2.648	4.60
32.8	189.4	0.973	3.621	6.30
41	236.7	1.097	4.718	8.20
49.2	289.4	1.279	5.997	10.43
57.4	336.7	0.877	6.874	11.95
65.6	384.1	0.677	7.551	13.13
73.8	431.4	0.741	8.292	14.42
82	478.8	0.693	8.985	15.62
90.2	526.1	0.555	9.540	16.59
98.4	573.5	0.577	10.117	17.59
106.6	620.8	0.592	10.709	18.62
114.8	673.4	0.542	11.251	19.56
123	720.8	0.497	11.748	20.43
131.2	768.1	0.475	12.223	21.25
139.4	815.5	0.460	12.683	22.05
147.6	862.8	0.423	13.106	22.79
155.8	910.2	0.440	13.546	23.55
172.2	1010.1	0.803	14.349	24.95
180.4	1057.5	0.369	14.718	25.59

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.01	1.876	1.583
Final	72.78	2.082	1.827

APPENDIX P

FLOWRATE EXPERIMENT VI

'Nance' native pecans

75 °C, 62.0 MPa, 4.0 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
6	47.3	0.582	0.582	1.01
12	94.7	0.742	1.324	2.30
18	142.0	0.854	2.178	3.79
24	189.4	1.018	3.196	5.56
30	236.7	1.119	4.315	7.50
36	284.1	0.803	5.118	8.90
42	331.4	0.637	5.755	10.01
48	378.8	0.648	6.403	11.13
54	426.1	0.558	6.961	12.10
60	473.5	0.584	7.545	13.12
66	520.8	0.554	8.099	14.08
72	568.2	0.535	8.634	15.01
78	615.5	0.565	9.199	16.00
84	662.9	0.471	9.670	16.81
90	710.2	0.479	10.149	17.65
96	757.6	0.460	10.609	18.45
102	804.9	0.441	11.050	19.21
108	852.3	0.457	11.507	20.01
114	899.6	0.435	11.942	20.77
120	947.0	0.432	12.374	21.52
126	994.3	0.447	12.821	22.29
132	1041.7	0.395	13.216	22.98

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.07	1.737	1.251
Final	75.18	2.076	1.535

APPENDIX Q

FLOWRATE EXPERIMENT VII
'Nance' native pecans
75 °C, 62.0 MPa, 7.5 slpm
Valve Temperature = 150 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
6.5	100.0	1.110	1.110	1.93
13	199.9	1.205	2.315	4.03
19.5	294.6	1.073	3.388	5.89
29.5	463.0	1.541	4.929	8.57
39	605.0	1.209	6.138	10.67
49	757.6	1.126	7.264	12.63
59	910.2	0.975	8.239	14.33
69	1073.3	0.864	9.103	15.83
79	1220.6	0.783	9.886	17.19
89	1373.1	0.705	10.591	18.42
99	1525.7	0.687	11.278	19.61
109	1683.5	0.628	11.906	20.70
119	1841.4	0.552	12.458	21.66
129	1993.9	0.536	12.994	22.59
139	2146.5	0.483	13.477	23.43

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.37	1.297	1.337
Final	75.28	1.434	1.645

APPENDIX R

EXTRACTION PRESSURE AND TEMPERATURE EFFECT ON THE FATTY ACID COMPOSITION OF PECAN OIL

'Wichita' pecans

No.	Temperature (°C)	Pressure (MPa)	Palmitic (%)	Stearic (%)	Oleic (%)	Linoleic (%)	Linolenic (%)	O/L (%/%)
1	45	41.3	8.9	3.4	61.5	23.0	3.2	2.7
2	45	41.3	11.4	3.0	59.2	23.1	3.3	2.6
Avg.	45	41.3	10.1	3.2	60.4	23.1	3.3	2.6
1	45	55.1	6.3	3.0	65.7	23.9	1.1	2.7
2	45	55.1	6.2	2.9	65.7	24.1	1.0	2.7
Avg.	45	55.1	6.3	3.0	65.7	24.0	1.0	2.7
1	45	66.8	6.2	2.9	64.4	25.5	1.1	2.5
2	45	66.8	6.2	3.0	64.2	25.5	1.1	2.5
Avg.	45	66.8	6.2	2.9	64.3	25.5	1.1	2.5
1	62	41.3	6.6	2.9	64.7	24.9	1.1	2.6
2	62	41.3	5.9	3.1	64.3	25.7	1.0	2.5
Avg.	62	41.3	6.2	3.0	64.5	25.3	1.0	2.5
1	62	55.1	6.8	3.0	65.4	23.9	1.0	2.7
2	62	55.1	6.2	2.9	66.0	23.9	1.0	2.8
Avg.	62	55.1	6.5	2.9	65.7	23.9	1.0	2.7
1	62	66.8	6.3	2.7	65.1	24.8	0.0	2.6
2	62	66.8	6.0	3.1	65.1	24.8	0.0	2.6
Avg.	62	66.8	6.2	2.9	65.1	24.8	0.0	2.6

APPENDIX S

EXTRACTION TIME EFFECT ON THE FATTY ACID COMPOSITION OF PECAN OIL

'Wichita' pecans

No.	Time (minutes)	Temperature (°C)	Pressure (MPa)	Palmitic (%)	Stearic (%)	Oleic (%)	Linoleic (%)	Linolenic (%)	O/L (%/%)
1	15	45	41.3	8.9	3.7	60.2	23.2	4.0	2.6
2	15	45	41.3	8.4	3.4	60.3	23.5	4.3	2.6
Avg.	15	45	41.3	8.7	3.6	60.2	23.4	4.2	2.6
1	240	45	41.3	8.9	3.4	61.5	23.0	3.2	2.7
2	240	45	41.3	11.4	3.0	59.2	23.1	3.3	2.6
Avg.	240	45	41.3	10.1	3.2	60.4	23.1	3.3	2.6
1	480	45	41.3	7.1	2.3	62.9	22.6	5.2	2.8
2	480	45	41.3	9.9	3.7	59.7	22.0	4.6	2.7
Avg.	480	45	41.3	8.5	3.0	61.3	22.3	4.9	2.8
1	15	45	55.1	6.7	2.6	64.5	25.1	1.1	2.6
2	15	45	55.1	6.3	3.5	63.7	25.5	1.1	2.5
Avg.	15	45	55.1	6.5	3.0	64.1	25.3	1.1	2.5
1	250	45	55.1	6.3	3.0	65.7	23.9	1.1	2.7
2	250	45	55.1	6.2	2.9	65.7	24.1	1.0	2.7
Avg.	250	45	55.1	6.3	3.0	65.7	24.0	1.0	2.7
1	15	45	66.8	6.2	3.0	64.2	25.5	1.1	2.5
2	15	45	66.8	6.4	3.0	63.0	26.4	1.2	2.4
Avg.	15	45	66.8	6.3	3.0	63.6	26.0	1.1	2.5
1	250	45	66.8	6.2	2.9	64.4	25.5	1.1	2.5
2	250	45	66.8	6.2	3.0	64.2	25.5	1.1	2.5
Avg.	250	45	66.8	6.2	2.9	64.3	25.5	1.1	2.5

APPENDIX T

OIL EXTRACTION EXPERIMENT I
'Wichita' pecans
45 °C, 41.3 MPa, 2.5 slpm
Valve Temperature = 100 °C, Collection Vessel Temperature = 4°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	0.569	0.569	1.39
30	142.0	0.585	1.154	2.81
45	210.4	0.521	1.675	4.08
60	278.8	0.552	2.227	5.42
75	347.2	0.542	2.769	6.74
90	420.9	0.546	3.315	8.07
105	484.0	0.514	3.829	9.32
135	631.3	1.006	4.835	11.77
165	778.6	1.055	5.890	14.34
195	925.9	0.925	6.815	16.59
225	1083.8	0.778	7.593	18.49
255	1231.1	0.732	8.325	20.27
346	1699.3	2.240	10.565	25.72
421	2057.1	0.980	11.545	28.11
583	2604.2	1.215	12.760	31.07

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	70.21	-	-
Final	56.5	-	-

APPENDIX U

OIL EXTRACTION EXPERIMENT II
'Wichita' pecans
45 °C, 55.1 MPa, 2.5 slpm
Valve Temperature = 100 °C, Collection Vessel Temperature = 1°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	1.180	1.180	2.84
30	163.1	1.121	2.301	5.53
45	236.7	0.905	3.206	7.71
60	310.4	0.922	4.128	9.92
75	384.1	0.830	4.958	11.92
90	457.7	0.758	5.716	13.74
105	531.4	0.696	6.412	15.41
120	610.3	0.704	7.116	17.11
135	683.9	0.639	7.755	18.64
150	757.6	0.564	8.319	20.00
165	831.2	0.527	8.846	21.26
180	910.2	0.548	9.394	22.58

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	71.11	-	-
Final	59.67	-	-

APPENDIX V

OIL EXTRACTION EXPERIMENT III

'Wichita' pecans

45 °C, 66.8 MPa, 2.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 1°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	78.9	1.040	1.040	2.51
30	152.6	0.885	1.925	4.65
45	226.2	0.989	2.914	7.04
60	310.4	1.053	3.967	9.58
75	384.1	0.847	4.814	11.63
90	468.2	0.892	5.706	13.78
105	552.4	0.823	6.529	15.77
120	631.3	0.701	7.230	17.47
135	710.2	0.586	7.816	18.88
150	789.2	0.537	8.353	20.18
165	868.1	0.551	8.904	21.51

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	70.76	2.644	0.971
Final	55.43	3.294	3.503

APPENDIX W

OIL EXTRACTION EXPERIMENT IV

'Wichita' pecans

62 °C, 41.3 MPa, 2.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 0°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	68.4	0.503	0.503	1.22
30	142.0	0.566	1.069	2.60
45	215.7	0.580	1.649	4.01
60	289.4	0.528	2.177	5.29
75	363.0	0.529	2.706	6.58
90	441.9	0.542	3.248	7.89
105	515.6	0.575	3.823	9.29
120	594.5	0.577	4.400	10.69
135	673.4	0.537	4.937	12.00
150	736.5	0.529	5.466	13.28
165	826.0	0.561	6.027	14.65

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	70.34	2.258	1.316
Final	63.06	2.657	1.558

APPENDIX X

OIL EXTRACTION EXPERIMENT V

'Wichita' pecans

62 °C, 55.1 MPa, 2.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	0.565	0.565	1.36
30	147.3	0.885	1.450	3.49
45	221.0	1.107	2.557	6.15
60	299.9	1.175	3.732	8.97
75	373.5	1.059	4.791	11.52
90	447.2	0.986	5.777	13.89
105	526.1	0.909	6.686	16.07
120	599.8	0.836	7.522	18.08
135	673.4	0.801	8.323	20.01
150	747.1	0.724	9.047	21.75
165	820.7	0.679	9.726	23.38

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	71.10	2.640	1.802
Final	59.80	3.237	2.081

APPENDIX Y

OIL EXTRACTION EXPERIMENT VI
'Wichita' pecans
62 °C, 66.8 MPa, 2.5 slpm
Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	0.908	0.908	2.19
30	152.6	1.118	2.026	4.88
45	226.2	1.178	3.204	7.72
60	305.1	1.222	4.426	10.67
75	384.1	1.147	5.573	13.44
90	457.7	0.979	6.552	15.80
105	531.4	0.975	7.527	18.15
120	605.0	0.941	8.468	20.42
135	683.9	0.910	9.378	22.61
150	757.6	0.851	10.229	24.66
165	826.0	0.749	10.978	26.47

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	70.90	0.758	1.062
Final	57.56	1.594	1.504

APPENDIX Z

OIL EXTRACTION EXPERIMENT VII

'Wichita' pecans

75 °C, 41.3 MPa, 2.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	0.616	0.616	1.48
30	147.3	0.636	1.252	3.01
45	226.2	0.677	1.929	4.64
60	299.9	0.712	2.641	6.35
75	373.5	0.672	3.313	7.97
90	447.2	0.660	3.973	9.56
105	515.6	0.662	4.635	11.15
120	589.2	0.648	5.283	12.71
135	662.9	0.667	5.950	14.32
150	736.5	0.640	6.590	15.85
165	826.0	0.675	7.265	17.48

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	71.05	1.707	1.839
Final	62.10	1.900	2.390

APPENDIX AA

OIL EXTRACTION EXPERIMENT VIII

'Wichita' pecans

75 °C, 55.1 MPa, 2.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	0.920	0.920	2.21
30	147.3	1.146	2.066	4.97
45	221.0	1.374	3.440	8.27
60	294.6	1.356	4.796	11.53
75	368.3	1.353	6.149	14.79
90	441.9	1.395	7.544	18.14
105	515.6	1.381	8.925	21.46
120	589.2	1.214	10.139	24.38
135	662.9	1.161	11.300	27.17
150	736.5	1.039	12.339	29.67
165	826.0	0.772	13.111	31.53

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	71.09	2.562	2.322
Final	56.34	2.962	2.757

APPENDIX BB

OIL EXTRACTION EXPERIMENT IX
'Wichita' pecans
75 °C, 66.8 MPa, 2.5 slpm
Valve Temperature = 100 °C, Collection Vessel Temperature = 2°C

Time (minutes)	Total CO_2 (g)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
15	73.7	1.050	1.050	2.54
30	147.3	1.377	2.427	5.87
45	221.0	1.522	3.949	9.54
60	294.6	1.462	5.411	13.08
75	368.3	1.396	6.807	16.45
90	441.9	1.300	8.107	19.59
105	515.6	1.220	9.327	22.54
120	589.2	1.159	10.486	25.34
135	662.9	1.027	11.513	27.82
150	736.5	0.933	12.446	30.08
165	826.0	0.948	13.394	32.37

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	70.73	1.866	1.936
Final	55.14	2.455	2.666

APPENDIX CC

LONG EXTRACTION TIME EXPERIMENT

'Nance' native pecans

75 °C, 62.0 MPa, 2.5 slpm

Valve Temperature = 100 °C, Collection Vessel Temperature = 1°C

Time (minutes)	Total CO_2 (g)	Solute Collected (g)	Total Solute Collected (g)	Total Solute Collected (%)
10	47.3	1.304	1.304	2.10
20	100.0	1.185	2.489	4.01
30	147.3	1.014	3.503	5.65
40	199.9	0.966	4.469	7.21
50	247.3	1.032	5.501	8.87
60	294.6	1.114	6.615	10.67
70	342.0	1.046	7.661	12.36
80	394.6	1.108	8.769	14.14
90	441.9	0.885	9.654	15.57
100	494.5	0.932	10.586	17.07
110	541.9	0.886	11.472	18.50
120	594.5	0.797	12.269	19.79
130	641.8	0.836	13.105	21.14
140	694.5	0.748	13.853	22.34
150	747.1	0.725	14.578	23.51
160	794.4	0.655	15.233	24.57
170	841.8	0.629	15.862	25.58
180	894.4	0.602	16.464	26.56
200	994.3	1.115	17.579	28.35
220	1089.0	0.953	18.532	29.89
240	1183.7	0.843	19.375	31.25
260	1278.4	0.869	20.244	32.65
280	1373.1	0.732	20.976	33.83
300	1478.4	0.809	21.785	35.14
340	1673.0	1.345	23.130	37.31
380	1851.9	0.979	24.109	38.89
420	2046.5	0.904	25.013	40.34
480	2325.4	1.160	26.173	42.21
540	2604.2	1.019	27.192	43.86
600	2883.0	0.899	28.091	45.31
660	3167.1	0.816	28.907	46.62
720	3440.7	0.720	29.627	47.79

APPENDIX CC (CONTINUED)

Time (minutes)	Total CO_2 (g)	Solute Collected (g)	Total Solute Collected (g)	Total Solute Collected (%)
840	3935.3	1.221	30.848	49.76
960	4508.7	1.308	32.156	51.86
1080	5113.7	1.069	33.225	53.59
1200	5676.7	0.905	34.130	55.05
1380	6534.2	1.310	35.440	57.16
1560	7381.2	1.188	36.628	59.08
1740	8228.3	1.095	37.723	60.84
1920	9101.6	1.064	38.787	62.56
2100	9974.9	0.979	39.766	64.14
2130	10127.5	0.276	40.042	64.58
2340	11148.1	1.163	41.205	66.46
2580	12310.8	1.173	42.378	68.35
2820	13478.8	1.093	43.471	70.11
3060	14662.5	1.010	44.481	71.74
3300	15777.8	0.920	45.401	73.23
3600	17266.7	1.099	46.500	75.00
3945	18981.8	1.131	47.631	76.82
4320	20739.0	1.163	48.794	78.70
4680	22527.8	1.057	49.851	80.41
4755	22896.0	0.216	50.067	80.75
5250	25295.1	1.438	51.505	83.07
5470	26336.7	0.528	52.033	83.92
5950	28609.5	1.048	53.081	85.62
6265	30087.9	0.601	53.682	86.58
6835	32881.5	0.977	54.659	88.16
7315	35122.7	0.741	55.400	89.36
8045	40536.3	0.944	56.344	90.88
8720	43777.1	0.784	57.128	92.14
9410	47070.5	0.691	57.819	93.26
10140	50532.2	0.656	58.475	94.32
10860	54088.7	0.565	59.040	95.23

	Pecan Weight (g)	Top Wool Weight (g)	Bottom Wool Weight (g)
Initial	90.26	1.912	1.166
Final	27.89	1.926	1.185

APPENDIX DD

P VALUES FROM ANOVA OF THE FATTY ACID COMPOSITION OF PECAN OIL

Effect	No. Replicate	Palmitic	Stearic	Oleic	Linoleic	Linolenic	O/L
Temperature and Pressure	2	0.011	0.640	0.002	0.001	2.4E-08	0.008
Time	2	0.682	0.885	0.885	0.124	0.060	0.196
Variety	3	0.003	1.7E-04	0.010	0.032	0.423	0.024
Valve Temperature	3	0.030	0.207	0.001	2.7E-04	0.093	3.7E-04

P VALUES FOR TEMPERATURE EFFECT

Temperature (°C)	No. Replicate	Palmitic	Stearic	Oleic	Linoleic	Linolenic
45	2	0.047	0.373	0.022	1.2E-04	7.1E-05
62	2	0.648	0.964	0.063	0.066	0.192

P VALUES FOR PRESSURE EFFECT

Pressure (MPa)	No. Replicate	Palmitic	Stearic	Oleic	Linoleic	Linolenic
41.3	2	0.093	0.423	0.07	0.037	0.001
55.1	2	0.489	0.759	0.935	0.292	0.094
66.8	2	0.89	0.952	0.009	2.4E-04	0.011

APPENDIX EE

STANDARD LITER/MINUTE CONVERSION

The conditions for a standard liter/ minute (slpm) are:

$P = 0.101325$ MPa
$T = 25$ °C

To convert to a flowrate at different conditions (2), use the ratio of the fluid's density at the different conditions to the density at standard conditions (1). An example is provided below.

Fluid: CO_2 (g)

$T_1 = 25$ °C	$T_2 = 0$ °C
$P_1 = 0.101325$ MPa	$P_2 = 0.101325$ MPa
$\rho_1 = 1.964$ g/L	$\rho_2 = 1.978$ g/L
$F_1 = 1.0$ lpm	$F_2 = ?$

$$F_2 = F_1(\rho_1 / \rho_2)$$

$$F_2 = \frac{(1.0 \text{ L/min})*(1.964 \text{ g/L})}{(1.978 \text{ g/L})}$$

$F_2 = 0.99$ L/min

$F_2 = 9.9 \times 10^2$ mL/min

VITA

Wendy Alexander

Candidate for the Degree of

Master of Science

Thesis: DEVELOPMENT AND UTILIZATION OF A METHOD FOR PECAN OIL EXTRACTION VIA SUPERCRITICAL CARBON DIOXIDE TO ENHANCE THE AMOUNT AND RATE OF OIL RECOVERY

Major Field: Biosystems Engineering

Biographical:

Education: Graduated from Thousand Oaks High School, Thousand Oaks, California in June, 1988; received Bachelor of Science degree in Chemical Engineering from University of California, San Diego, La Jolla, California in March, 1994. Completed the requirements for the Master of Science degree with a major in Biosystems Engineering at Oklahoma State University in July, 1996.

Professional Memberships: Alpha Epsilon, Institute of Food Technologists, Tau Beta Pi.