

EFFECT OF MOISTURE CONTENT ON KERNEL
BREAKAGE AND EXTRACTED OIL FROM
PECANS USING SUPERCRITICAL CO₂

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CHAPTER I

INTRODUCTION

Pecan trees are native to North America and are planted extensively in Oklahoma, Georgia, California and western Texas (Santerre, 1994). Usually, pecans are shelled prior to sale, and shelled pecans are widely used in baked goods and confectionery foods such as pies, cakes, ice cream, and candies. High oil content (as much as 75%) in pecans contributes to the pecan flavor, but it is especially vulnerable to oxidation, causing rancidity (Santerre, 1994). This development of off-flavor and subsequent quality deterioration shortens pecan and pecan product shelf life, limiting the pecan market. To improve storage stability, removing part of the oil from pecan meats was proposed. Reducing the oil content extends pecan shelf life, prolongs pecan quality, and provides lower fat foods.

Oil extraction is traditionally done by either mechanical compression or solvent extraction. The primary disadvantage of mechanical compression is destruction of the pecan structure. Solvent extraction may leave toxic residues in the final edible product and is not effective without first grinding the pecan. For these reasons, supercritical fluid extraction (SFE) with carbon dioxide (CO_2) is being considered as an alternative to conventional procedures, because it is efficient and non-destructive to the pecan. SFE is performed in the critical region where the fluid has no phase difference between gas and

liquid, and exhibits significant solvent strength (McHugh and Krukornis, 1994). It is advantageous to use CO₂ as a solvent in the food industry since it is easily separated from the obtained mixture, inexpensive and nontoxic.

Application of supercritical CO₂ for food processing has expanded in recent years. Decaffeination of coffee with SFE began in 1978 and is now commonly used commercially (Rizvi et al., 1986). Use of supercritical CO₂ to extract essential oil, de-fat soybeans, extract peanut oil, and remove milk fat has been reported (Stahl and Gerard, 1985; Eldridge et al., 1986; Goodrum and Kilgo, 1987; Lim and Rizvi, 1995).

For longer pecan shelf life, Zhang (1994) studied the feasibility of reducing pecan oil by extraction with SC-CO₂ and investigated the effects of extraction temperature and pressure on oil recovery. Alexander (1996) further optimized some extraction parameters for pecan oil SFE. These studies established a method to reduce pecan oil without destroying the kernel shape. However, after extraction, short depressurization time causes pecan breakage, which limits the pecan's potential commercial value. Although prolonged depressurization time can decrease pecan breakage, it is a disadvantage in industrial production.

Water pretreatment to adjust texture has been employed in pecan nut cracking and shelling to reduce kernel shatter. Passey and Patil (1994) also used water conditioning to prevent peanuts from breaking during SFE. This evidence indicates that water pretreatment might be useful for preventing the breakage that occurs in pecans during depressurization. Water may serve two functions during SFE: swelling the pecan matrix and modifying the polarity of the CO₂ (Stahl et al., 1988). The expansion of the tissue structure creates more contact surface between the desired extracts and the solvent, and

the water polarity increases the selectivity of the SC-CO₂. Presoaking of feed material with water considerably increases the efficiency of caffeine extraction from coffee beans or tea leaves using SC-CO₂ (Luque de Castro et al., 1994). In canola flake oil extraction, water modification did not improve oil yield, but researchers found that some water co-extracted with the oil (Dunford and Temelli, 1997).

Although several studies have been conducted to optimize extraction of pecan oil with SC-CO₂, none have investigated the effect of moisture content. Therefore, this research was conducted and provided some information for rapid oil extraction (i.e., short depressurization period) while preserving the integrity of pecans.

Objectives

This study investigated the effects of initial moisture content of pecan kernels on pecan breakage and oil yield when extracting with SC-CO₂. The specific objectives were as follows:

1. To examine the effect of depressurization time on pecan breakage after supercritical CO₂ extraction.
2. To determine the effect of initial moisture content on pecan breakage and oil yield using supercritical CO₂ extraction.
3. To investigate the effect of water penetration time on pecan breakage and oil yield using supercritical CO₂ extraction.

CHAPTER II

LITERATURE REVIEW

Pecan Industry

As an indigenous U.S. food crop with rich flavor and crisp texture, the pecan is one of the most popular nuts in the United States and Western Europe. Native pecan trees grow primarily in Oklahoma and Texas, and along the river systems of central and eastern North America (Florkowski and Hubbard, 1994). There are over 1000 documented pecan varieties (Thompson and Young, 1985), but only a few of them are of high quality and high quantity. Usually large, thin-shelled nuts are desired and in high demand by consumers.

The commercial pecan industry is considered to be an important native contributor to the U.S. industry. The economic potential of the pecan was realized during the 1700s and early 1800s, when pecan nuts started to be sold as a commercial item and a small pecan industry was initiated (Wood et al., 1994). Many factors such as market, improved cultivars, and insect and disease control have propelled the growth of the pecan industry. Prior to being used in food manufacturing, pecans are cleaned, sized and shelled. Shelled pecans or halves are called half-kernels, which are further sorted and used for different food products according to their appropriate quality. To meet the demand for pecan pieces in food industry, the pecan halves are chopped into different

sizes on a custom-order basis. Also, during shelling a lot of pecan pieces are created, only when necessary are whole halves chopped into less valuable pieces. Pecan halves are mainly used in candy and chocolate-covered products, while pecan pieces and meals are extensively used in cookies and cakes.

Kernel Composition

The composition of pecan kernels varies greatly depending on cultivar and growing conditions. The predominant constituents of the pecan kernel are lipids (oils), which can be as high as 75% with 90% unsaturated fatty acids (Santerre, 1994). Additionally, pecans are composed of 12-15% carbohydrate, 9-10% protein, 3-4% moisture and about 1.5% minerals (Kays, 1987a).

Oil Content

Pecan oil is considered to be the most important factor relating to the pecan's quality. With 55-75% total oil content, pecan kernels are rich in pleasant flavor but susceptible to instability. The high percentage of polyunsaturated fatty acids that exist in the pecan oil is the main factor leading to pecan deterioration. Unsaturated fatty acids, such as oleic and linoleic, containing one and two double bonds respectively, are easily attacked by oxygen, developing staleness and rancidity. Polyunsaturated fatty acids such as linoleic are especially prone to oxidation since having multiple double bonds increases the chance of combination with oxygen. Therefore, pecans are semi-perishable at ambient temperatures with over 90% unsaturated fatty acids plus a high concentration of polyunsaturated fatty acids (27.3% linoleic). For this reason, pecans present problems

when used in food products, and their use is limited due to their short shelf life. Separation of oil from pecans can produce two edible products, pecans and pecan oil, and is considered to be an attractive method to improve the pecan storability.

Moisture Content

Moisture content is the second most important factor that influences pecan quality. Pecan kernels reach the optimum texture at about 5% moisture content. They are fragile with less than 4% moisture content, and are unattractively tender with over 8% moisture content (Heaton and Woodroof, 1965). Furthermore, the storage life of pecans is closely tied to its moisture content. The level of moisture influences the growth of molds and the rate of metabolic activity. Beuchat and Heaton (1980) indicated that low sap and low superficial moisture of pecan kernels provided less chance for fungal growth. A positive relationship between pecan moisture and respiration rate was reported by Beaudry et al. (1985). Respiration rate is monitored as an index of the general metabolic rate and is measured as carbon dioxide produced. They found a logarithmically linear increase of respiration at pecan moisture contents greater than 4.5%. Because detrimental biological and chemical changes are accelerated by the high rate of respiration, high moisture content leads to pecan degradation during storage. However, at extremely low moisture content (under 2%), pecan membrane stability is broken and the pecan surface fractures, which exposes more oil to the oxygen and accelerates the oil oxidation. Likewise, pecan kernel grade may suffer from breakage during subsequent handling since over dried pecans form too crisp a structure.

Instead of moisture content, water activity (a_w) is frequently used as an indicator for preventing mold growth. Water activity is defined as the ratio of the vapor pressure of the system to the vapor pressure of pure water, and is a crucial factor in mold growth (Santerre, 1994). Pecan drying is a way to decrease the water activity of pecans so that the growth of molds and bacteria are restricted. A water activity of less than 0.68 will preclude growth of organisms, and pecans between 4.5% and 5.7% moisture have $a_w < 0.68$. Therefore, pecans can be prevented from molding with moisture content from 4.5% to 5.7%, depending on the oil content of kernels (Santerre, 1994).

The moisture content of harvested pecan kernels varies widely with cultivar, and is affected by environmental conditions. To prevent molding, pecans should be removed from the field quickly, followed by proper drying. Generally, pecans need to be dried below a moisture content of 4.5% as rapidly as possible after harvest to preserve pecan quality (Heaton et al., 1977). However, low heat has to be used to prevent cracking. The process of pecan cracking and shelling requires water readjustment by adding water to reduce kernel breakage. Pecans are commonly soaked in 1000ppm chlorinated water for 1-2 hours, followed by draining and then holding for 12-24 hours prior to cracking (Forbus and Senter, 1976). An alternative method is to apply hot water (85 °C) to shorten the soaking period to 3-5 minutes. These processes usually increase kernel moisture content from around 4% to around 8%, which makes pecan kernels more pliable and reduces their breakage during cracking. Before storage, previously conditioned pecan kernels must be dried to at least 4.5% again.

Shult (1996) studied the effects of pecan moisture content and oil content on pecan texture. The Texture Profile Analysis (TPA) method was performed to quantify

food texture parameters by using a universal-testing machine. The results indicated that TPA parameters such as hardness, cohesiveness and springiness changed with the pecan's moisture and oil contents.

Pecan Quality and Storage

Pecan kernel quality is usually evaluated by color, flavor, size and the absence of insects and diseases (Kays, 1987b). The kernels of high grade have light color, good flavor with a crisp taste, large size with few defects and no insect damage. These qualities are hard to retain during handling and storing of pecan kernels. Pecan kernels are susceptible to darkening of color, development of off flavors and rancidity, shattering by mechanical processes and damage by insect infestation during storage.

The environmental factors such as temperature, concentration of oxygen, and light are important during pecan storage (Kays, 1987b). In general, decreasing the storage temperature can extend the pecan storage life since the rate of detrimental change is greatly reduced at lower temperature. Oxygen is a main factor causing rancidity of kernels along with unfavorable flavor production, especially for pecans stored at room temperature. However, since pecans are living organisms that require some oxygen to respire and remain in aerobic balance, a very low oxygen environment also leads to pecan quality losses (Dull and Kays, 1988). Thus, oxygen concentration of stored pecans should be properly controlled to minimize quality losses. Light is a factor that causes pecan kernel darkening. Heaton and Shewfelt (1976) showed that pecans stored under sunlight were significantly ($p = 0.05$) darker than those stored under cool white fluorescent light.

Hence, the strategies aimed at these environmental factors for extending shelf life of pecans are as follows:

1. Store pecans in a low temperature environment (i.e. below 0 °C).
2. Reduce oxygen concentration to a proper degree by evacuating, flushing with nitrogen or carbon dioxide, selecting proper packaging materials, or applying edible coatings to form a barrier.
3. Hold pecans in the dark and use low light transmission rate packages.

The pecan moisture content and oil content are the main factors that are crucial to pecan storage. As previously discussed, high water content creates an environment for mold growth, bacteria proliferation and chemical changes. Before storage, pecan moisture should be reduced to below 4.5% but above 2% to delay quality losses (Santerre, 1994). With high levels of unsaturated fatty acids, pecan oils are susceptible to oxidation, which deteriorates pecan kernels and thereby shortens shelf life. One efficient way to extend pecan shelf life is by reducing the oil content. There are many techniques that have been developed to extract oil from pecans, and these will be discussed in the next section. Extraction of the oil can serve two purposes: prolong the pecan shelf life and obtain oil as a new product, i.e., cooking oil.

Methods of Extraction

Extraction is defined as a separation process that removes a soluble component from solid or liquid materials by dissolving it in a solvent. Extraction processes can be grouped into liquid-liquid, solid-liquid (or leaching), and supercritical fluid extraction (SFE) (Singh and Rizvi, 1995). Both liquid-liquid and solid-liquid extraction are

conventional extraction methods, and supercritical fluid extraction is a relatively new extraction technology.

Before the unique characteristics of SFE were realized, solvent extraction had been widely applied in food processing. For instance, brewing tea from tea leaves is a solvent extraction process using hot water as a solvent to extract the soluble components from tea leaves. Since mechanical expression cannot separate oil from soybean, corn, and rice bran, solvent extraction has been used for oil recovery for a long time (Toledo, 1994). Extraction of vegetable oil from nuts and seeds is traditionally based on organic solvents, such as hexane, acetone, and alcohol. The general rule of solvent selection is "like dissolves like", but for the food industry, the most important criterion is non-toxicity. Since organic solvents may leave residues in foods, and most of them are toxic, solvent extraction is becoming more restrictive in the food industry. For food safety and environmental protection, other nontoxic solvents and methods for removing oil are being studied.

Supercritical fluid extraction (SFE) with Carbon Dioxide (CO_2) is recognized as a safe solvent extraction and has attracted the interest of the food industry. So application of SFE in food processing is a promising alternative to conventional solvent extraction.

Traditionally, the removal of oil from pecans is by expression and solvent extraction. Expression applies mechanical pressure to rupture the cells of pecans and force out the oil. In general, high quality oil can be obtained by this method if the oil seed contains more than 25% oil content (Heldman and Hartel, 1997). But for pecans, this procedure destroys their structure, causing nuts to lose value, and pecan oil is currently the only useable end product.

Solvent extraction typically removes the pecan oil by contacting the pecans with hot hexane solvent and further processing is needed to separate pecan kernels and oil from solvent. Although solvent residues are generally very low, there still remains the concern for safety due to many organic solvents are toxic or carcinogenic. Thus, supercritical carbon dioxide extraction (SC-CO₂) has been studied to remove oil from pecans.

Supercritical Fluid Extraction

Fundamental Principles

Supercritical Fluid Extraction (SFE) is similar to solvent extraction but uses a fluid in its supercritical state as the extractant. A gas, when compressed above its critical point (critical temperature and pressure), will have no phase difference between gas and liquid and is called supercritical fluid (SCF) (McHugh and Krukoni, 1994). The desirable transport properties of this supercritical fluid are attracting more and more attention in extraction processes.

The pressure-volume-temperature (P-V-T) phase diagram of a pure material is illustrated in Figure 1. This three-dimensional phase diagram presents the thermodynamic states of the solid, liquid, gas and supercritical fluid (Singh and Rizvi, 1995). The two-dimensional (P-V, T-V, and P-T) phase diagram (Figure 2) is made by projecting and plotting lines representing constant values of the third variable. From P-V, T-V graphs, we see that the density of the supercritical fluid can be easily changed with a small adjustment in temperature and pressure. The P-V phase diagram shows that the density (volume) of a fluid in the critical region can increase (decrease) greatly with

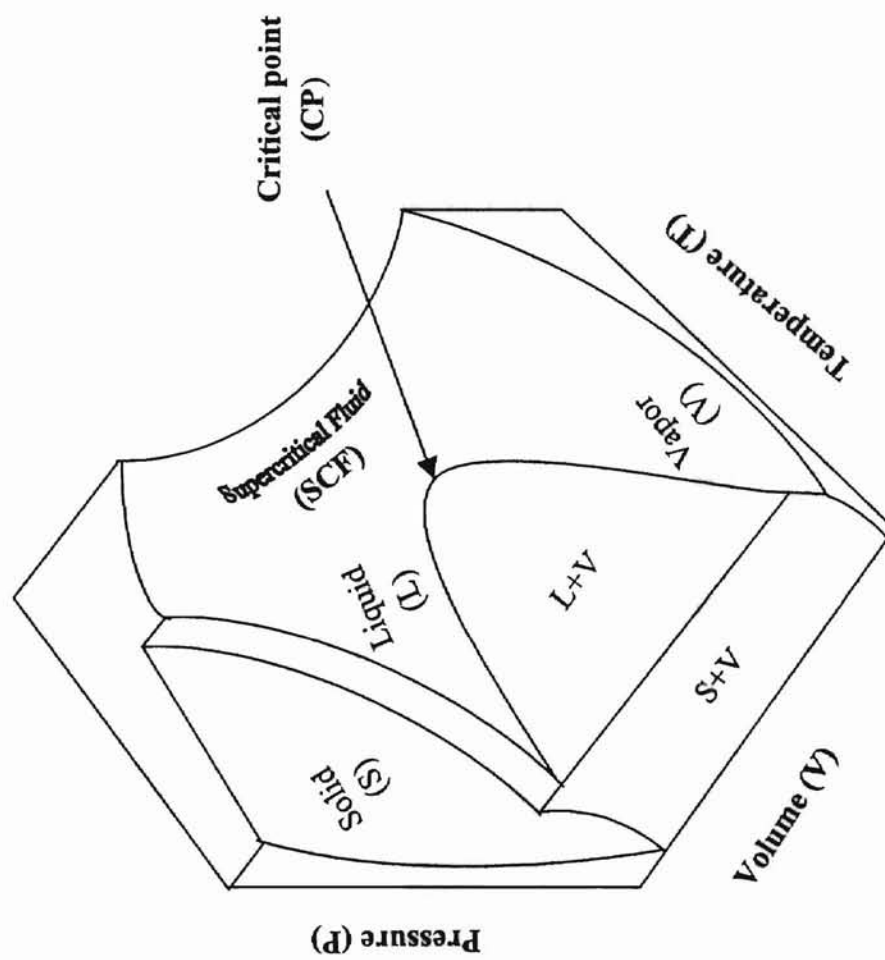
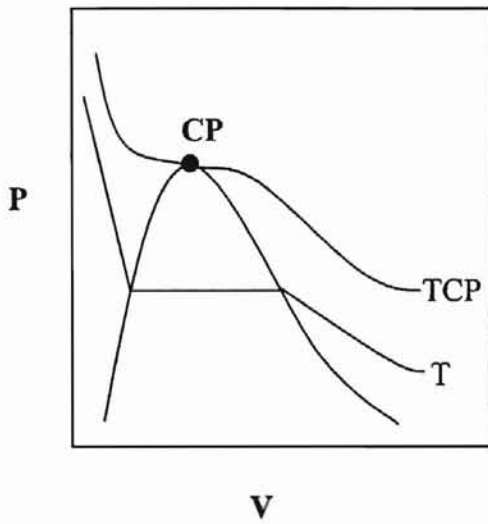
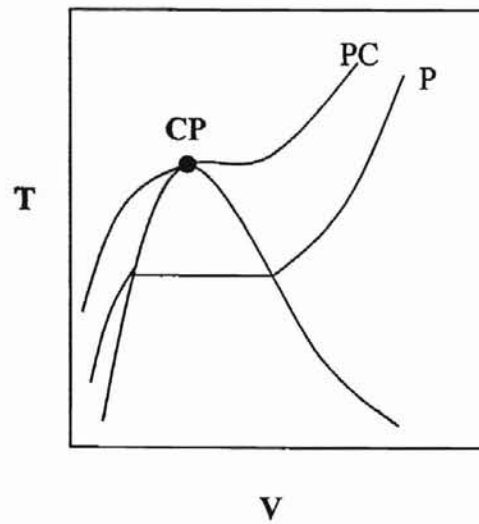


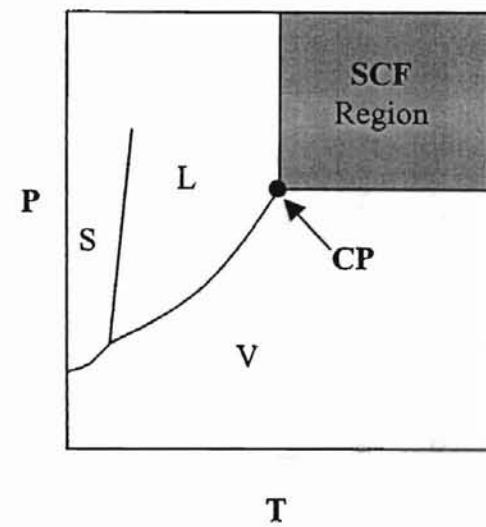
Figure 1. P-V-T Phase diagram.



a. P-V phase diagram



b. T-V phase diagram



c. P-T phase diagram

Figure 2. Two dimensional phase diagrams.

the pressure increasing at a constant temperature, while the T-V phase diagram indicates a decreasing density as the temperature increases along the line of a constant pressure. The familiar P-T phase diagram depicts the typical regions corresponding to the gas, liquid, and solid states. The vapor and liquid phases reach equilibrium along the saturation line from the triple point, and break at the critical point. The supercritical region originates from the critical point and is indicated in the P-T diagram. Only one phase exists in this supercritical region but it possesses the properties of both gas and liquid.

The fluid exhibits a significant enhanced solvent power when the critical point approaches. This can be explained by the unique transport properties of supercritical fluids. Since the distinction between gas and liquid disappears in the supercritical region, this gas-liquid fluid has a high density, similar to that of a liquid, and a high diffusivity and low viscosity, similar to that of a gas. Generally, for a solvent, the dissolving power depends on its density, the mass transfer rate depends on its diffusivity, and the dynamic features depend on its viscosity (Luque de castro, et al., 1994). Since the density of a SCF is positively proportional to the solvent power, and the high diffusivity and low viscosity of a SCF contribute to more efficient extractions, the mass transfer properties of a supercritical fluid are much more favorable than those of an ordinary liquid solvent. Furthermore, manipulating the pressure and temperature can alter the density of a supercritical fluid for useful purposes, which means the selectivity of extraction can be modified according to some requirements. As a result, the supercritical fluid has been extensively adapted as a solvent in extraction processes.

The typical supercritical fluid extraction (SFE) involves the following four basic operational steps: loading, adjusting extraction conditions, extraction, and separation. A simplified SFE system including recycling is depicted in Figure 3. In the loading step, the fluid and the sample material are brought into the extraction cell. A pressure pump and heater are used to set the extraction pressure and temperature to reach the critical region. Once the desired supercritical conditions approach, extraction starts by opening the outlet valve. The extract-loaded supercritical fluid is then separated by reducing the pressure and temperature in order to lower the dissolving power, after which the extract is collected in the receiver. The gas is either compressed back to the supercritical state to recycle or just vented out without recycling. After finishing one extraction process, depressurization takes place in order to empty the extraction cell and recharge the sample material. In this case, loading and emptying the extractor is a common batch operation. Batch operation is inefficient, whereas continuous SFE at high pressures is not yet practical. Friedrich and Pryde (1984) introduced a semi-continuous Supercritical CO₂ system for oil extraction of Jojoba. With a three-vessel system, a variety of extraction configurations can be adopted by manipulating the valve sequence and flow direction. This procedure represents one approach to improving the efficiency of the SFE process.

SC-CO₂

Supercritical Carbon Dioxide (SC-CO₂) is the most favorable solvent used in the food industry due to its safe nature. CO₂ is non-toxic, non-flammable, and readily available. It doesn't leave a residue in the food product and has a low critical point (critical temperature and pressure). Table 1 shows the critical parameters of some fluids

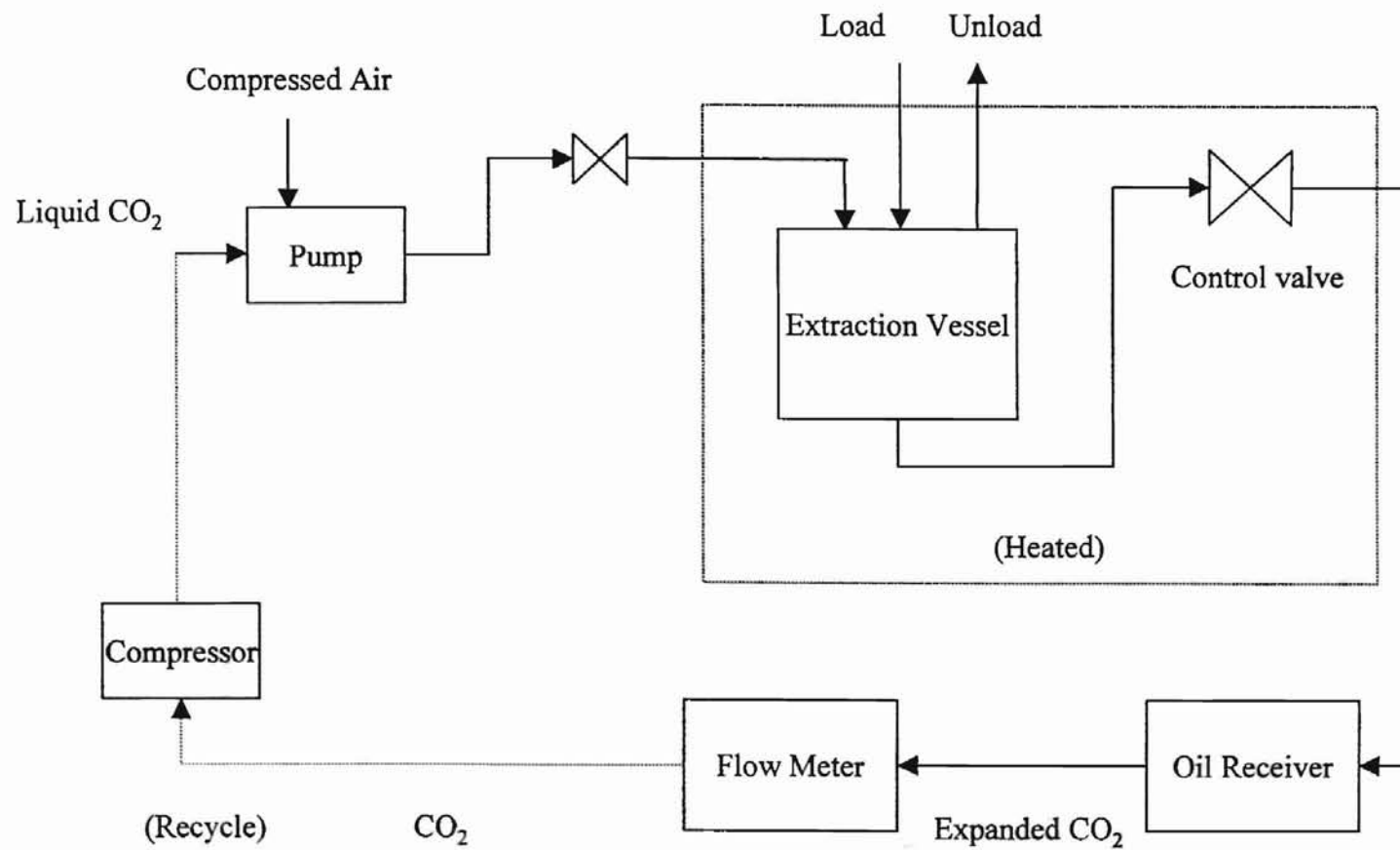


Figure 3. A simplified SFE system including recycling.

used for SFE. Since CO₂ has convenient critical parameters, the extraction equipment can be easily designed to satisfy the supercritical conditions at a lower cost, and can be used on thermally labile foods. CO₂ is classified as a non-polar solvent because of its non-polar distribution of molecules, but with the large molecular quadrupole, it also can slightly extract some polar compounds. Therefore, non-polar compounds such as oil can be extracted by SC-CO₂, while proteins, carbohydrates, and mineral salts are only slightly soluble in SC-CO₂ (Castera, 1994). Extraction of oils and fats from nuts or food with SC-CO₂ is of particular interest because oils and fats exhibit superior solubility in SC-CO₂.

Table I. Critical parameters of some fluids used for SFE.

	Critical temperature (°C)	Critical Pressure (MPa)	Critical density (g/ml)
Carbon dioxide	31.1	7.2	0.47
Ammonia	132.5	10.98	0.23
NO ₂	158	9.87	0.27
Acetone	235	4.70	0.279
Ethanol	243.4	7.2	0.276
Water	374.2	21.48	0.32

Source: From Luque de Castro, 1994.

Extraction Conditions

Pressure and Temperature

Pressure and temperature determine the mass transport properties of the supercritical fluid. As the pressure increases, the density and viscosity of the SF increase, and the diffusivity decreases at a constant temperature. Higher density leads to an increase in solubility, but decreased diffusivity and raised viscosity cause a lower solubility. The pressure plays double roles in SF solubility, but most often, solubility is increased through increased density. On the other hand, the increased temperature has the opposite effects as pressure on these three properties at a constant pressure. That is, it

decreases the density and viscosity and increases the diffusivity, influencing solvent power in both ways. Therefore, the overall solubility in SFE is the combined effects of temperature and pressure (Luque de Castro, et al., 1994). Friedrich and Pryde (1984) reported that the solubility isotherms of soybean oil at 50 °C and 60 °C were crossed at 41.4 MPa, and the extracted oil decreased with increasing temperature at low pressures. The similar relationship of solubility with pressure and temperature was also found in oil extraction from canola seeds (Fattori et al., 1988; Dunford and Temelli, 1997). These relationships came about because the effect of rapid decrease in SCF density overcomes the increased solubility effect with a rise in temperature at low pressure, whereas density changes with temperature are less sensitive and of less important at high pressure. For pecan oil extraction with SC-CO₂, Alexander (1996) stated that the extracted pecan oil increased with increasing pressures from 41.3 to 55.1 MPa, but did not from 55.1 to 66.8 MPa. At this point, increasing pressure above 55.1 MPa was not efficient for pecan oil extraction because CO₂ is already less compressible so that the solute power relating to CO₂ density has no more improvement.

Flow Rate and Particle Size

By controlling flow rate, supercritical fluid is transferred from the extractor to the collection cell and separated from extracts there. Using a high flow rate usually accelerates the transport of the extracts so the extraction time can be shortened. Very high flow rates should be avoided as they may decrease the collection and extraction efficiency. The decrease is due to high pressure drops along the extraction vessel (Luque de Castro, et al., 1994). A faster extraction rate occurred when flow rate was increased

during tomato seed extraction (Roy et. al., 1994). In one set of experiments by Alexander (1996), it was found that higher flow rates increased the pecan oil extraction rates. In addition, the flow orientation has influence on the extraction rate. Goodrum and Kilgo (1987) reported a higher oil recovery and more uniform extraction from peanuts with downward flow using vertical extraction than with upward flow or horizontal extraction.

Particle size affects the solute accessibility by SFE. Snyder et al. (1984) demonstrated that the soybean oil yield increased from 66% to 97% as the flake thickness reduced from 0.81mm to 0.10 mm. Flaking or grinding disrupts the cell wall and more oils are exposed to allow more SFE. The efficiency of SC-CO₂ extractions depended on the degree of the cellular disruption when canola seeds were pretreated in one of five methods (Fattori, et al., 1988).

Moisture Content

Water may function as a polar component to modify the polarity of CO₂, or to swell the solid matrix facilitating diffusion, affecting SFE selectivity and efficiency (Stahl et al., 1988). The extraction of caffeine from coffee or tea is a typical example of water application in SFE. Pre-soaking crude materials with water before extraction swells the matrix to make caffeine accessible, and also alters selectivity of SC-CO₂ to favor the solubility behavior of caffeine (Luque de Castro, et al., 1994).

As previously mentioned, pure CO₂ is an appropriate extraction solvent for nonpolar components but is often ineffective with polar components. Water added to a sample or saturated with CO₂ increases the extractability of polar components due to the enhanced polarity of CO₂. Stahl and Gerard (1985) proposed to strengthen selectivity of

SC-CO₂ with the addition of water in essential oil extraction. In their research, solubility of the polar components was changed by saturation of CO₂ with water. Increased moisture content in cardamom seeds did not affect the oil yield, but did increase the solubility of some polar volatiles with the moisture level increasing from 10% to 20% (Gopalakrishnan and Narayanan, 1991).

During swelling, water expands the sample porosity, increases the permeability of the cell membrane to improve the contact surface, and improves diffusion through the extracted sample (Stahl et al., 1988). At the same time, excess moisture content in the sample causes problems during SFE since it hinders the accessibility of the extracts. These two competing effects of moisture presence in solid samples yield different effects depending on the nature of the samples. Snyder et al. (1984) found that there was a small positive effect on soybean oil solubility when adjusting moisture content from 3% to 12%. To avoid high moisture problems in meat fat extraction, meat products were dehydrated from about 70% MC down to 2% MC, and more fat was extracted and extraction periods were shorter (King et. al, 1989). Dunford and Temelli (1997) found that moisture level had no influence on canola lipid extractability.

Water was observed to be co-extracted with oil during extraction by SC-CO₂ (Snyder et al., 1984; Chao et al., 1991; Reverchon et al., 1995; Dunford and Temelli, 1997). The solubility of pure water in SC-CO₂ was estimated to be 4-8 mg/g CO₂ at pressures of 2-5 MPa and 75 °C, converting from mole fractions of water vapor in the binary system (Coan and King, 1971). Snyder et al. (1984) stated that water extracted with vegetable oil was insignificant and only collected towards the end of extraction. The increased extractability of water with oil was observed during ground beef SFE

when pressure increased from 17.2 to 31.0 Mpa and higher temperature $> 50^{\circ}\text{C}$ (Chao et al., 1991).

Pecan oil Extraction and Breakage

Zhang (1994) discussed the feasibility of SFE to remove oil from pecans for extending their shelf life. Without disrupting the kernel cell, up to 77% of the initial oil was extracted from intact pecan halves during 160 minutes extraction at 80°C and 68.9 MPa. After extraction, serious breakage of pecan kernels occurred due to long extraction time or short depressurization time. Alexander (1996) examined the effects of the extraction pressure, temperature, and CO_2 flowrate on the amount and composition of pecan oil recovered. The temperatures of micrometering valve and collection vessel were investigated to reduce extract lost. As well, pecan breakage was observed during fast depressurization. Slow depressurization (at least 1 hour) was required to avoid kernel breakage. A method to analyze the total oil content of pecans, using supercritical CO_2 , was developed by Maness et al. (1995). Compared with the traditional extraction by organic solvents, extraction with SC-CO_2 produced no differences in either pecan oil yield or fatty acid composition.

Similar kernel breakage during SFE was found for peanut oil extraction. Passey and Patil (1994) indicated that peanut kernels should be pretreated to 8-11% moisture content before extraction to produce unbroken peanut kernels. This adjustment of peanut kernel moisture is similar to that during pecan shelling, which applies water to minimize pecan kernel breakage.

Borges and Peleg (1997) studied the effect of moisture content on the texture of nut kernels. As the water activity increased, the break deformation of the kernels of almonds or hazelnuts increased, which implied that higher moisture content softened the texture of nuts. Break deformation is a texture parameter used to measure plasticisation. The effect of moisture content on pecan kernel texture has also been examined (Shult, 1996). Consequently, there is a need to study the relationship between moisture content of pecan kernels and breakage during depressurization after pecan oil extraction, as well as the effect of moisture content on pecan oil yield.

CHAPTER III

MATERIALS, EQUIPMENT, AND METHODS

Pecan Kernels

'Western Schley' pecan halves were obtained from Young Pecan Company (Las Cruces, NM) and were kept in a refrigerator (4 °C) until use. Initially, pecan halves had 3.7% moisture content and 64.2% oil content (by weight). Moisture content was determined by oven drying pecans and oil content was measured by quantitative SFE of pecan oil from ground pecans (Maness et al., 1995). Moisture contents of pecan halves were modified by two methods (humidification and spraying water) to achieve design levels for extraction. Small pieces or damaged kernels were removed by hand to obtain intact pecan halves. After extraction, unbroken pecan halves and broken pieces were separated to determine the degree of kernel breakage.

Extraction Equipment

A Spe-ed™ SFE Model 680 BAR system (Applied Separations, Allentown, PA) was used for pecan oil extraction. This extraction unit consisted of a pump module, a control and collection module(C&C), an oven module and a 300 mL extraction vessel rated at 68.90 MPa (Thar Designs, Pittsburgh, Pa). Conditions could be set at pressures up to 68.90 MPa and temperatures up to 250 °C by the operation module. A CO₂

cylinder with a 14 MPa helium head pressure and dip tube was attached to the main extraction unit to provide liquid CO₂ (Air Products and Chemicals, Inc., Allentown, PA). Figure 4 shows the schematic view of this SFE system.

Pecan samples were loaded into the extraction vessel between glass wool plugs fitted into both ends of the vessel. The filled extraction vessel was vertically mounted into the oven and connected to the inlet valve and metering valve using high-pressure tubing. With the inlet valve open and fluid delivery control on, CO₂ flowed to the extraction vessel to the desired pressure by slowly turning the air pressure regulator. To prevent over-pressurization, the final pressure was not set until the temperature set points were achieved since thermal expansion could cause the system to exceed its pressure limits. An alarm and a rupture disc provided over-pressure protection for safe operation of the system. The extraction temperature was adjusted by setting the temperature on the control panel, and it was automatically maintained at ± 1 °C. Compressed air was supplied by a compressor-driven pump to reach the desired CO₂ pressure. The water trap was inserted to keep moisture out of the pump. Extraction parameters were monitored on the temperature panel, flowmeter, and pressure gauge. During extraction, supercritical CO₂ flowed through the pecan samples, dissolved the oil from pecans, and the mixture was separated at the collection tube. Glass wool plugged the top of the collection tube to sufficiently trap the extracted oil. Extracted pecan oil separated from CO₂ solvent and collected in the collection tube due to a reduction in pressure. At low pressure and temperature, SC-CO₂ changed back to the gas state and was then vented to the atmosphere. The micro-metering valve was heated to prevent freezing (Joules-Thompson cooling) of the exit line during sudden reduction in pressure.

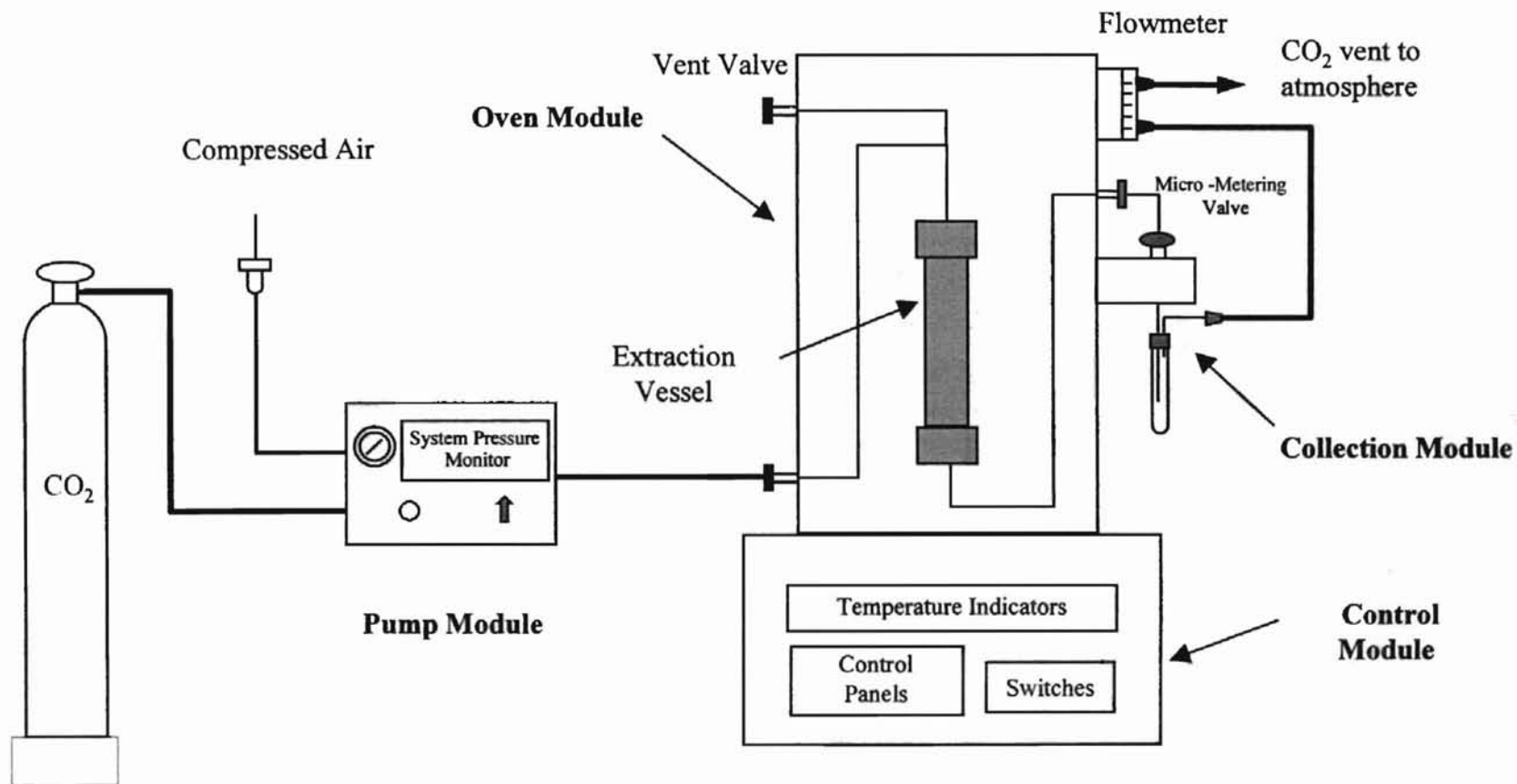


Figure 4. Schematic of the Spe-ed™ SFE extraction system.

Extraction Parameters

Thirty-five Western Schley pecan halves (around 20 gram) were used for each extraction. Based on results from Alexander (1996), a flowrate of 3.0 slpm and a metering valve temperature of 100 °C were used to minimize the amount of extract lost from the collection tube and to prevent the micro-metering valve from freezing. The collection tube was maintained at 0 °C in an ice-water bath. An extraction temperature of 75 °C was chosen since the amount of extracted oil increases with increasing temperature. A high extraction pressure (62 MPa) was selected to ensure sufficient kernel breakage after depressurization. The extraction time was set to 60 minutes, which is in the linear increasing time region of oil extracted (Alexander, 1996). Preliminary tests produced about 12% weight of pecan total oil after one hour extraction (Figure 5) similar to the experiments of Alexander.

Experimental Design

The independent variables in this study were pecan initial moisture content, depressurization time, and water penetration time. For the experiment on pecan initial moisture content, two depressurization times (10 minutes and 20 minutes) were chosen. The interaction of depressurization time and pecan moisture on pecan breakage was examined. Five levels of moisture content were planned with 3 replicates in each level. For the experiment on water penetration time, 2 levels of water penetration time (1 hour and 48 hours) were selected with 6 replicates in each pair. The resulting pecan breakage and oil yield were examined. The statistical differences were tested using analysis of variance and multiple comparisons of means. Analysis of variance of data was carried

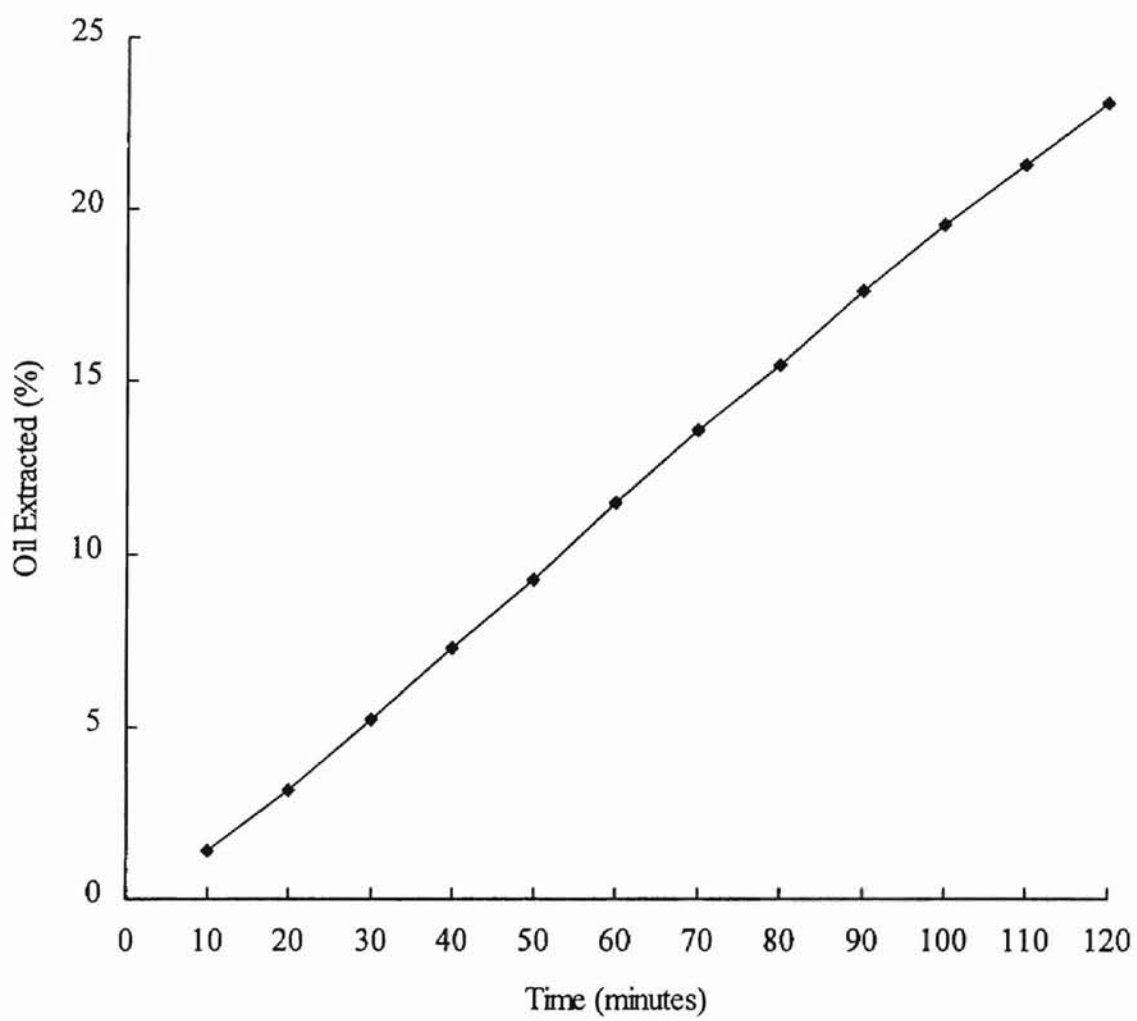


Figure 5. Western Schley pecan oil extraction at 75 °C, 62.0 MPa, and 3.0 slpm CO₂ flowrate.

out using the General Linear Model procedure of SAS (SAS Institute, Inc., 1989).

Multiple comparisons of means were tested by LSD (Least Significant Difference) at $\alpha = 0.05$.

Experimental Procedures and Methods

Adjustment of Pecan Initial Moisture Content

The moisture content of received pecans was 3.7% initially, and varied during storage time. Water was applied to pecans to adjust the moisture content. Two methods of moisture addition were used to condition pecan halves: humidification and spraying water.

Humidification: Pecans were placed in a screen bottom tray in an environmental chamber at 90% RH and 30 °C. After 9 hours, 2 days, and 5 days, moisture increased to 4.9%, 6.4% and 7.4%. Higher moisture contents could not be achieved by humidification as mold would appear after pecans had been in the chamber for more than 5 days. During humidification, the moisture content was monitored by measuring the weight and knowing the initial moisture content. When the desired moisture range was approached, the pecans were taken out of the chamber and sealed in Zip-Loc™ freezer bags. The actual moisture content of pecans was determined by drying in an oven at 130 °C for six hours. The pretreated pecan halves were stored in Zip-Loc™ freezer bags at 4 °C to maintain moisture content for the extraction tests.

Spraying water: This method was used to obtain moisture contents greater than 7.5%. Amounts of water were added to pecan halves by using a spray bottle. The water was sprayed to the kernel surface as uniformly as possible, and the excess water drained

through a screen bottom. Final moisture content of pecans could be estimated by calculating the ratio of water to dry matter. Sprayed pecan halves were then stored in Zip-Loc™ freezer bags for at least 24 hours to let them attain a uniform moisture content before extraction. Unextracted pecans were kept in a refrigerator for future experiments.

The following five levels of initial moisture were attained for pecan initial moisture content experiment: 3.5%, 4.9%, 6.4%, 7.4%, 11.0%.

Water Penetration Time

Water was added to pecan halves using a spray bottle to achieve a range of moisture contents. The desired moisture content was obtained by calculating the weights of dry matter and water, then adding determined amounts of water to the pecans. Pretreated pecans were sealed in Zip-Loc™ bags and kept at room temperature. Extraction was conducted after a short time (1 hour) and a long time (48 hours) to determine if there was a relationship between water penetration time and pecan breakage and oil yield. The test was repeated 6 times, with different moisture contents ranging from 6.1% to 11.6%.

Determination of Pecan MC

In each case, the moisture content was determined by drying pecans in a forced convection oven at 130 °C for 6 hours. To prevent pecan moisture content from changing, refrigerated pecans were placed at room temperature (around 25 °C) and kept in sealed freezer bags to equilibrate at least 30 minutes before extraction.

Extraction

Weighed pecans were filled into the 300 ml extraction vessel with Pyrex™ glass wool plugging at both ends to retain pecans and prevent clogging of the extraction system. About 2 g of glass wool were used on each side for all experiments to maintain consistent packing in the vessel. Improper extraction vessel packing can cause pecan pieces to plug the system or make the collection of extracted oil difficult (Alexander, 1996).

After the extraction vessel was mounted in the oven and connected to the system by high-pressure tubing (2.54×10^{-4} ID), the leaks were checked by delivering CO₂ to the extraction vessel. Then, a two step warm-up pressure scheme (Alexander, 1996) was conducted to ensure that extraction started at the same point. The vessel pressure was first set to about 13.8 MPa, and then was increased to 62 MPa after the vessel reached the setpoint temperature. This heating period took about 80 minutes, and then the extraction was run for 60 minutes.

The oven extraction conditions were held at 62.0 MPa pressure, and 3.0 slpm CO₂ flowrate. Temperatures throughout the system consisted of 75 °C for the vessel, 100 °C for the valve, and 0 °C for the collection tube. During extraction, the micro-metering valve was opened and served as a restrictor to control flow. A collection tube (13x100 mm) with a septum in the screw cap collected the extracted oil from expanded SC-CO₂. A glass wool plug was inserted at the top of the collection tube to trap entrained oil in the exiting CO₂. When pecan oil had been extracted for 60 minutes, the collection tube was removed and a 10 minute depressurization was conducted, unless otherwise stated.

Depressurization

The supercritical fluid extraction process consists of a pressurization period followed by depressurization. Pecan kernel breakage does not occur during application of high pressure but may occur during depressurization. It has been shown that the amount of kernel breakage increases as the depressurization time decreases (Zhang, 1994). Alexander (1996) used more than 60 minutes depressurization time with no pecan breakage.

To identify pecan breakage, two depressurization times of 10 minutes and 20 minutes were tested. The ability to control depressurization in this extraction unit was limited, so depressurization was adjusted by opening valves and unscrewing the top end of the extraction vessel. The pressure gauge indicated an approximate pressure drop because it measured the whole system pressure but did not exactly monitor the pressure drop through the extraction vessel. When fully opening all release valves, a pressure of 62 MPa in the extraction vessel dropped to 0 MPa after 20 minutes. The initial decrease from 62 MPa to about 7 MPa occurred rapidly in the first minute of depressurization, but was still around 2 MPa after 10 minutes. For the shorter depressurization test, the top end of the vessel was unscrewed after 10 minutes of depressurization to release the 2 MPa pressurized gas and the vessel pressure dropped to 0 MPa quickly. After depressurization, the vessel was removed from the oven and opened to access the pecans.

Analysis of Pecan Breakage

The extracted pecans were poured out of the extraction vessel and sealed in a plastic bag as they cooled to room temperature. To measure pecan breakage, the unbroken pecans were counted as they were taken out of the bag. A standard U.S. No.4 sieve and a No. 8 sieve were used in series to separate the pecan pieces into groups of larger, medium, and very small pieces. The pecans were sieved and shaken gently by hand for a few seconds to determine the particle size distribution (PSD) of the broken pieces.

Determination of oil yield

The weight of the collection tube was measured before and after extraction. Since water was co-extracted with oil during extraction, the pecan oil needed to be dried. A method was developed to remove the moisture from the extracted oil. The extracted oil in the tube was poured into an aluminium dish. The dish and tube were placed into a forced convection oven at 56 °C for at least 5 hours to drive off the moisture.

Peanut oil was tested first to determine the reliability of this method. A known amount of water was added to a known amount of peanut oil in the glass tube making a wet oil sample. This wet peanut oil was then oven dried. It was difficult to remove water from oil in the tube because the oil is less dense than water and floats on top of the water acting as a barrier to drying. Therefore, peanut oil with water was poured into an aluminum dish (ID 57 mm) to a depth of about 1 mm to increase the contact area of water with dry air. Dishes and the empty oil collection tubes were then dried in a convection

oven at a low temperature (56 °C) to avoid oil vaporization. After 6 hours, the weight of oil samples remained nearly constant (Figure 6), without losing any more mass during further drying for 80 hours. The residue of oil and water in the tube was slower to dry, but only a 0.02 gram decrease occurred after 6 hours, which was negligible. In a second experiment, this result was confirmed when the peanut oil and moisture content reached a nearly steady state after 5 hours while drying in a weigh dish. This is shown in Figure 7.

From the results with peanut oil, 5 hours of oven drying at 56 °C was selected as a method for removing co-extracted water from pecan oil. During oven drying at 56 °C, the pecan oil-water mixture reached a constant weight after 5 hours and lost no more than 0.005 gram in the next 76 hours (Table II).

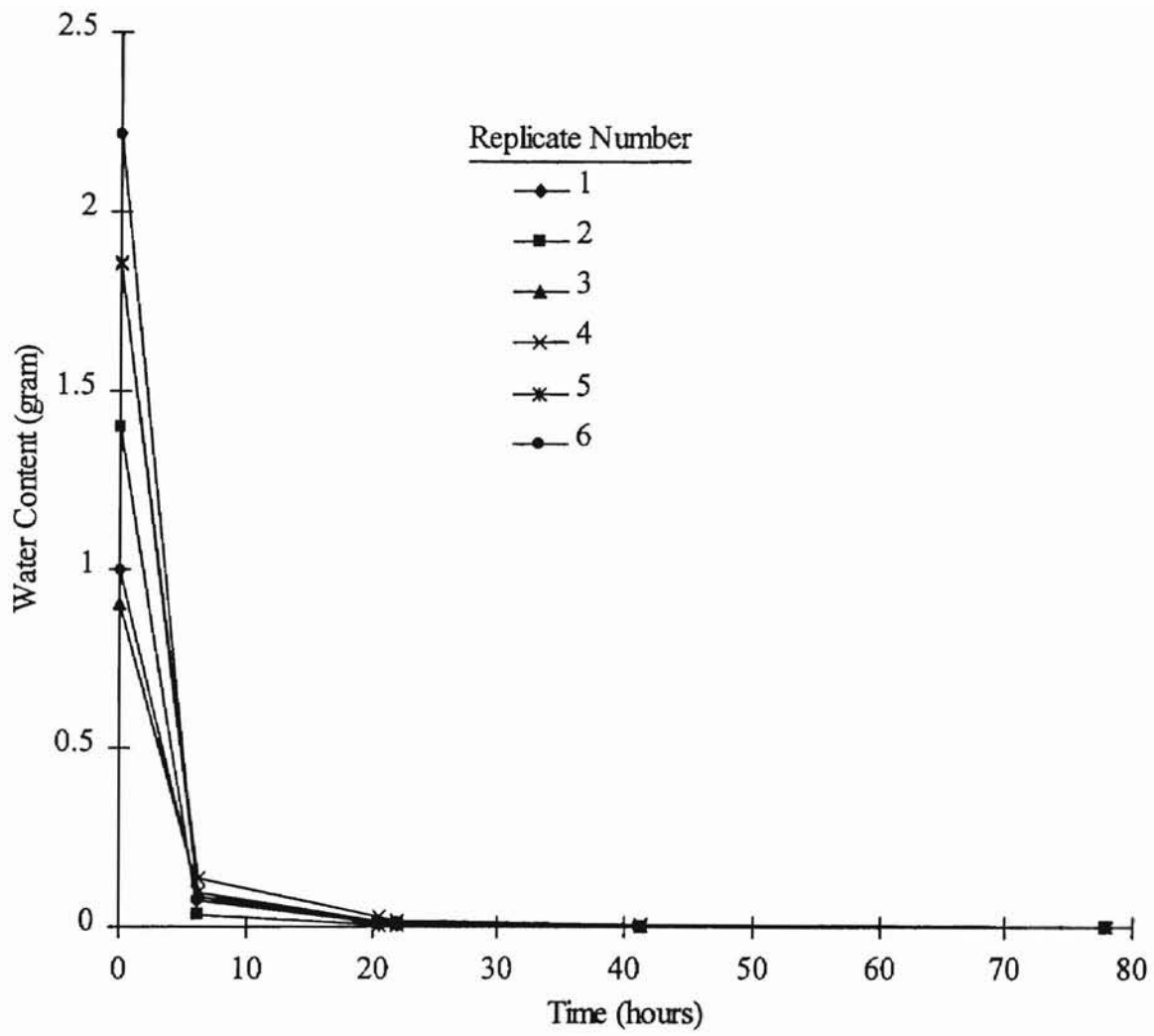


Figure 6. Drying of water-peanut oil mixture at 56 °C .

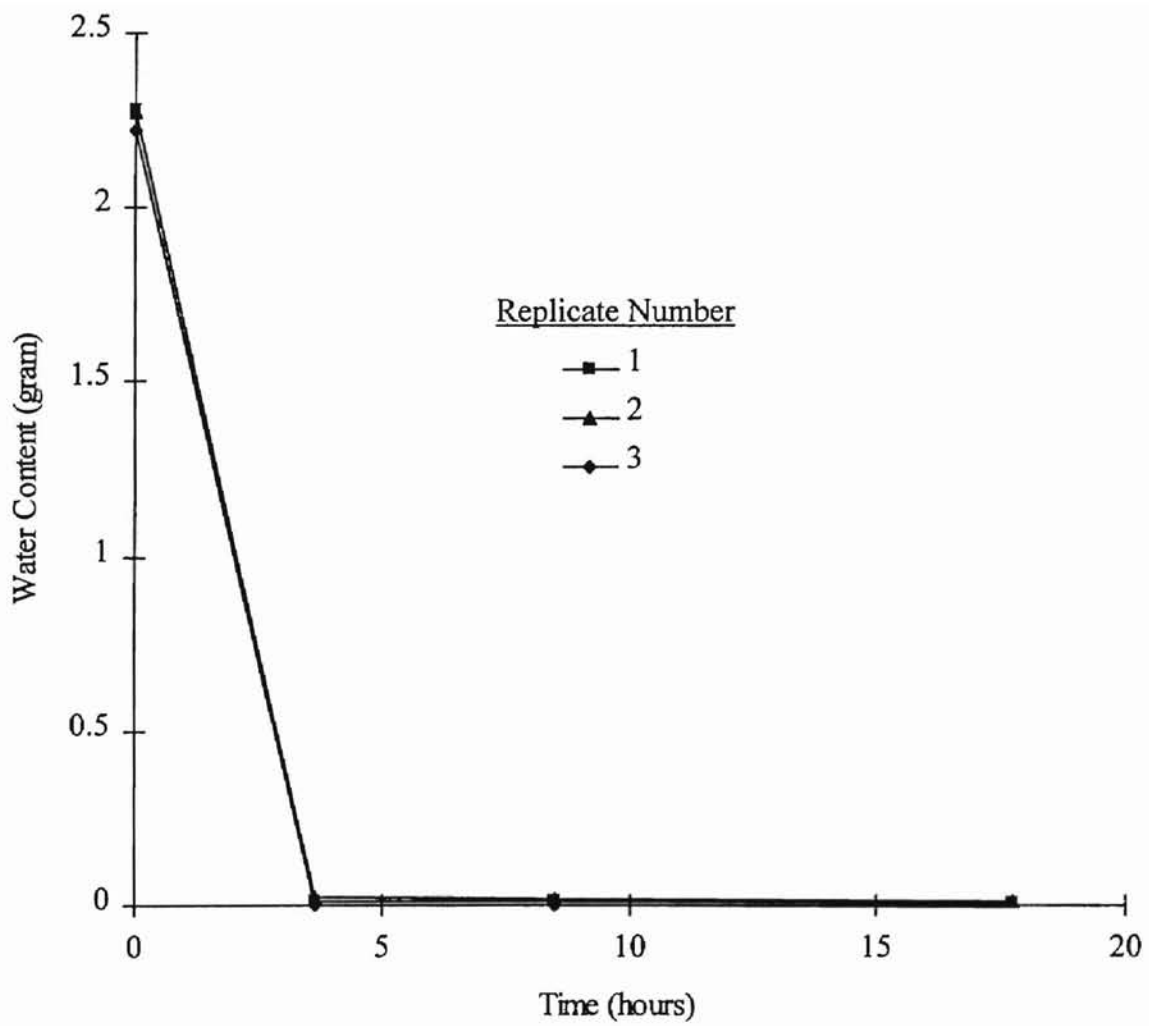


Figure 7. Drying of water-peanut oil mixture in an aluminum dish at 56 °C .

Table II. Pecan oil and water mixture weight loss in oven at 56 °C.

Time (hours)	Mixture Weight (gram)					
	Replicate Number					
	1	2	3	4	5	6
0	1.958	3.521	3.169	2.640	3.345	2.966
5	1.932	3.441	2.774	2.491	2.956	2.847
24	1.932	3.436	2.774	2.491	2.956	2.847
76	1.932	3.436	2.774	2.492	2.955	2.848

CHAPTER IV

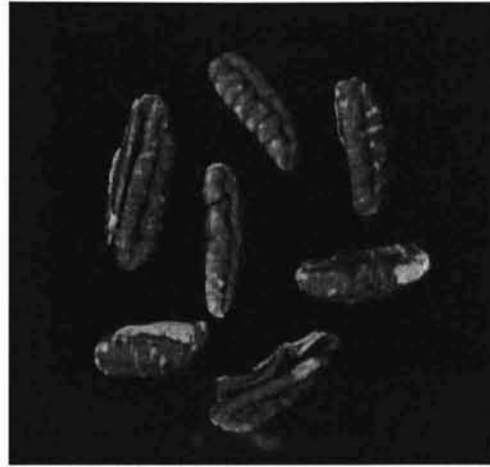
RESULTS AND DISCUSSION

This chapter contains a description of the results obtained from experiments involving depressurization time, pecan initial moisture content, and water penetration time. Pecan breakage, oil yields, co-extracted water and a mass balance were analyzed for each of the experiments.

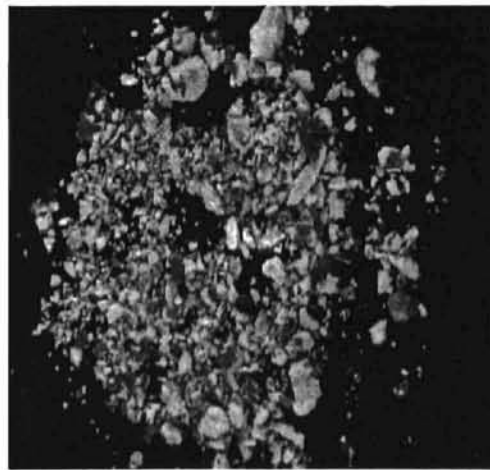
Depressurization Time

With a depressurization time of 20 minutes, virtually no pecan breakage was found. When extracted pecans were removed from the vessel, the pecan halves were entirely intact; only their color became darkened. However, significant pecan breakage occurred when using a 10 minute depressurization time. Pecan samples of broken and unbroken pieces are shown in Figure 8.

The fact that no kernel breakage occurred during 20 minute depressurization suggests that the end of the depressurization is crucial in causing pecan breakage, in spite of the 55.2 MPa pressure drop during the first minute of depressurization. Since depressurization was conducted above the critical temperature of CO₂, the supercritical CO₂ experienced a phase change from a liquid-like state to a gas state during high pressure release. The saturated CO₂ inside the pecan kernels may remain in a liquid-like



a. Sample of Unbroken Pecans



b. Sample of Broken Small Pieces

Figure 8. Pecan samples after depressurization.

state when pressure releases from 62 MPa to 7 MPa, but from 2 MPa to 0 MPa the liquid-like CO₂ will change to a gas state. During this latter depressurization, suddenly released pressure causes CO₂ to transition from a liquid state to a gas state rapidly so that gas flushes out substantially from the inside of kernels, inducing a strong internal mechanical stress on the structure of the pecans due to gas expansion. When the kernel structure cannot withstand this stress, pecan kernels will break. Therefore, a fast depressurization rate is inconsequential while CO₂ remains in a liquid state, but a slow rate is required in order to avoid breakage when the CO₂ depressurizes from a liquid state to a gas state.

Pecan breakage as affected by depressurization time and pecan initial MC is reported in Table III. The weight of pecans remaining on the No.4 sieve is used as an estimator of pecan breakage. From the table it can be seen that in 8 different experiments at 4 different moisture contents with the 20 minute depressurization time, no pecan breakage occurred. In similar experiments with the 10 minute depressurization time, severe pecan breakage occurred. The percentage of large No.4 pecan halves declined from 100% to as low as 15.77% upon shortening the depressurization time from 20 to 10 minutes.

For each data set, the coefficient of variation (CV) was calculated to measure variation among the treatments. The CV ranged from 3.85% to 23.73% at 5 pecan initial moisture contents for 10 minute depressurization. An analysis of variance indicated that there was a significant interaction ($P < 0.01$) between depressurization time and pecan initial moisture content (Table IV).

Since pecan breakage was found at 10 minutes depressurization, further tests were conducted with this depressurization time, except where otherwise indicated.

Table III: Effect of depressurization time on pecan breakage at different moisture contents.

Depressurization Time (minutes)	Pecan Initial MC (%)	Weight of Pecans on No.4 Sieve (%)					
		1	2	3	Mean	Standard Deviation	CV
10	3.5	27.42	27.45	37.06	30.64	5.56	18.13
	4.9	15.77	22.97	25.60	21.45	5.09	23.73
	6.4	41.68	32.30	46.54	40.17	7.24	18.02
	7.4	63.94	46.40	49.80	53.38	9.30	17.43
	11.0	97.90	90.64	94.37	94.30	3.63	3.85
20	3.5	100	100	-	100	0	0
	4.9	100	100	-	100	0	0
	6.4	100	100	-	100	0	0
	7.4	100	100	-	100	0	0

Table IV: Analysis of variance for effect of depressurization time (DT) and pecan initial moisture content (MC) on weight percent of pecans remaining on No.4 sieve.

Source	DF	SS	Mean Square	F Value	Pr>F
DT	1	16231	16231	583**	0.0001
MC	4	7070	1768	63**	0.0001
DT*MC	4	3889	972	35**	0.0001
Error	15	418	28		
Total	24	26370			

** Significant at $P < 0.01$

Effect of Initial Moisture Content

Pecan Breakage

The particle size distribution of the 35 pecans placed into the extraction vessel and the number of unbroken kernels after extraction at different moisture contents are reported in Table V. Almost all pecan kernels at lower initial moisture levels (3.5%, 4.9%) were broken after depressurization, and the testas of the few unbroken kernels were seriously damaged. The higher the pecan initial moisture content, the fewer broken pecan kernels, and the condition of the testa of the unbroken pecans was better. For 11.0% initial MC, 34 out of 35 pecan halves were unbroken and the kernel surface was intact.

The particle size distribution of the pecans (Figure 9) shows that increasing the pecan initial moisture content tends to increase the percentage of large particle sizes (No.4 sieve). Thus, pecan breakage was greater at lower moisture contents. The individual data points of the weight percent of pecans retained on the No.4 sieve at each moisture content is shown in Figure 10. There was a nearly linear increase in large particle sizes as moisture content was increased. When second order regression was performed, r^2 went from 0.86 to 0.92.

An analysis of variance shows that there was a significant difference among the five moisture contents (P-value < 0.01). The least significant difference (LSD) was used to test differences among means at five moisture contents (Table VI). For particles on No.4 sieves, the effects of 7.4% and 11.0% MC are different from each other and the other three moistures. The largest amount of large particles was attained at 11.0% MC,

Table V: Particle size distribution of pecans at different moisture contents after 10 minute depressurization.

Pecan Initial MC (%)	Particle Size Distribution (%)			Number of Unbroken Kernels	Degree of Unbroken kernels *
	No.4	No.8	Fines		
3.5	27.42	27.77	44.81	1	3
	27.45	24.14	48.41	0	
	37.06	22.37	40.57	4	
4.9	15.77	24.30	59.93	1	3
	22.97	30.94	46.09	1	
	25.60	22.54	51.86	3	
6.4	41.68	16.78	41.55	12	2
	32.30	20.69	47.01	9	
	46.54	15.15	38.31	19	
7.4	63.94	10.66	25.40	22	1
	46.40	15.17	38.43	18	
	49.80	13.84	36.36	18	
11.0	97.90	0.45	1.65	34	0
	90.64	3.00	6.36	34	
	94.37	1.70	3.93	34	

- * 0 No apparent damage on kernel surface
- 1 Kernel skin slightly cracked
- 2 Kernel skin cracked
- 3 Kernel skin seriously damaged

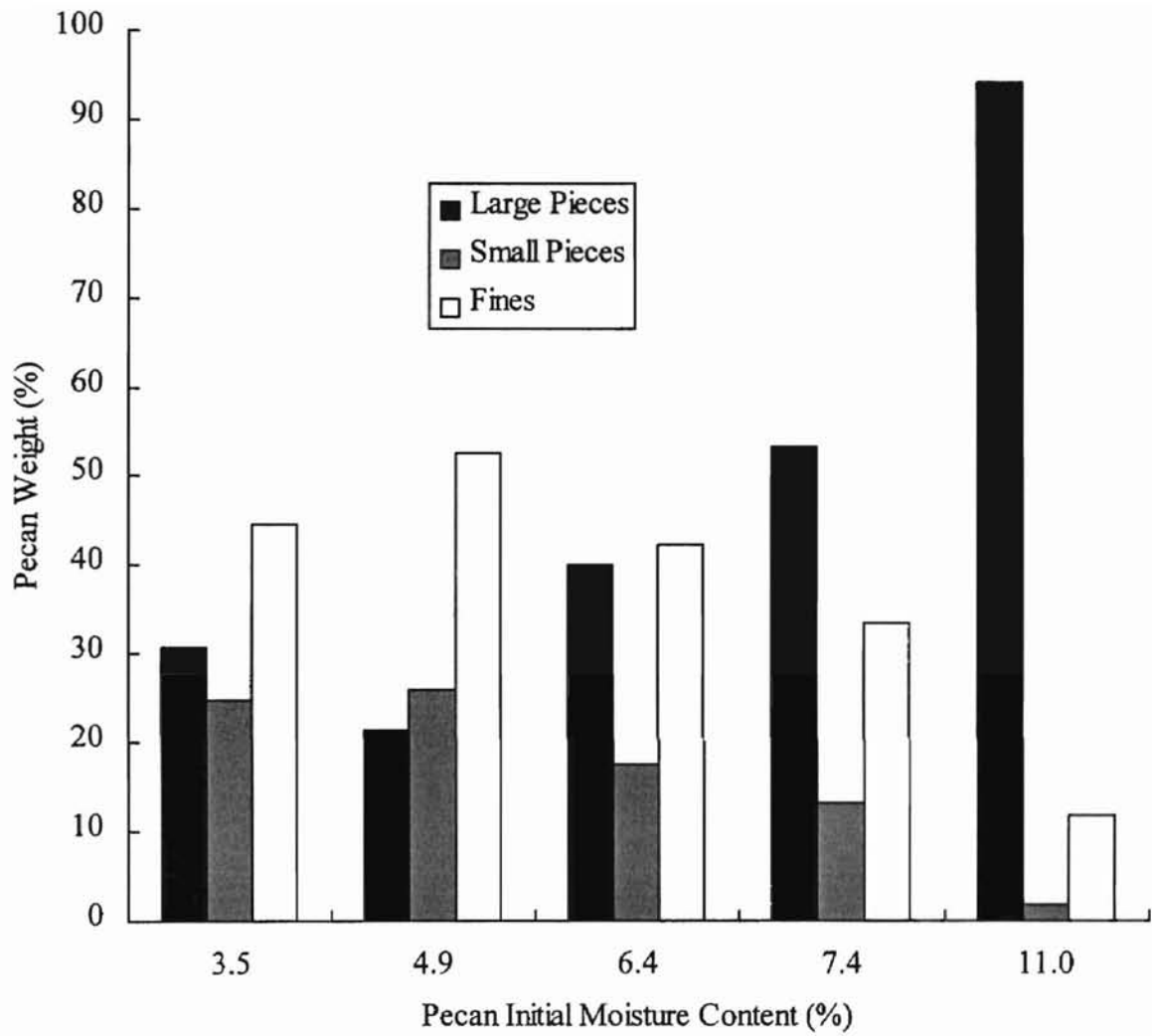


Figure 9. Particle size distribution of pecans after oil extraction.
 Depressurization time = 10 minutes; Average of 3 replications.

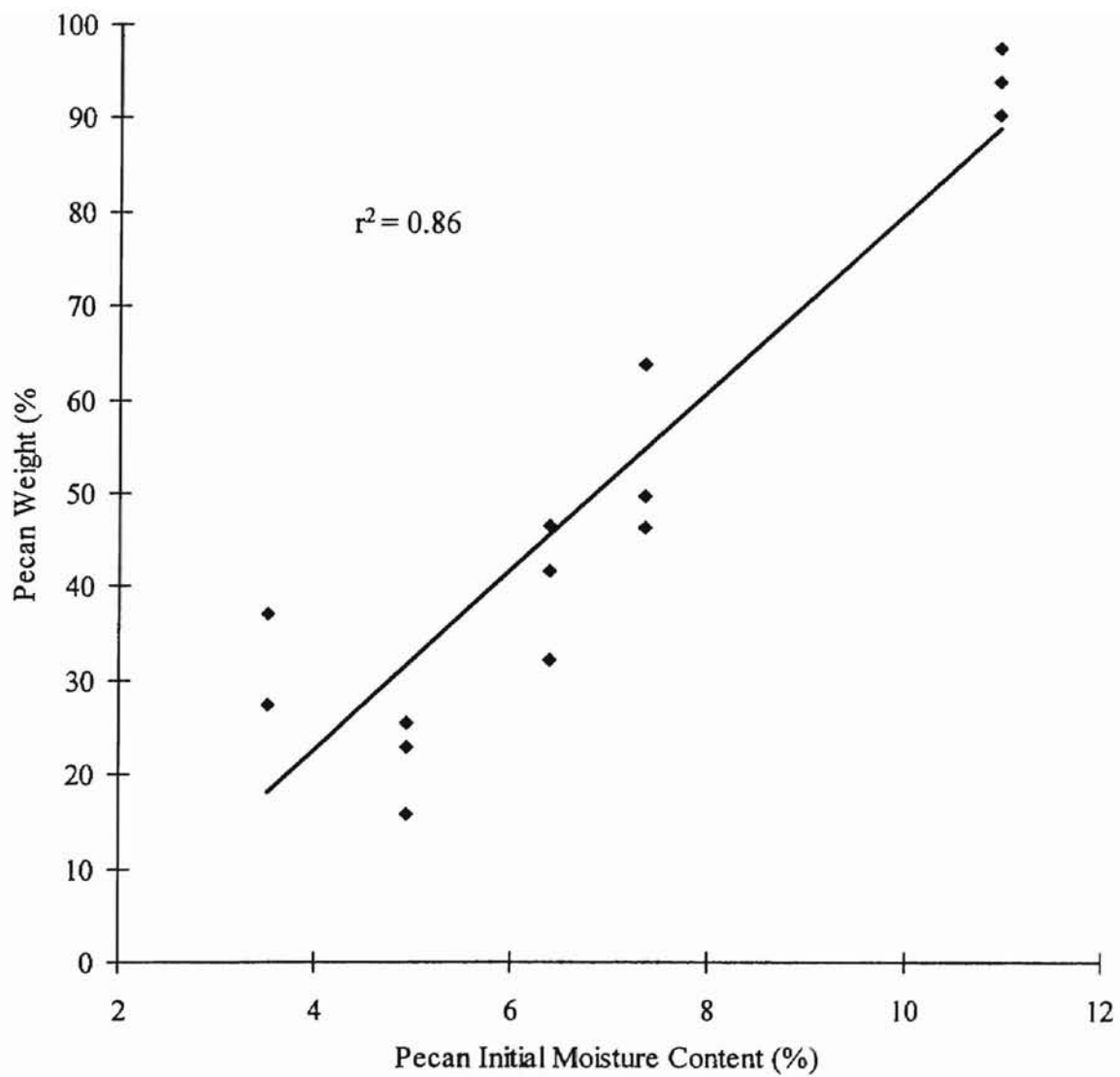


Figure 10. Weight percent of large pieces (remaining on No. 4 sieve).
Depressurization time = 10 minutes.

Table VI: Means of particle size distribution of pecans after oil extraction.

Pecan Initial MC (%)	Particle Size Distribution of Pecans (%)		
	No.4	No.8	Fines
3.5	30.64 ^{cd}	24.76 ^a	44.60 ^{ab}
4.9	21.45 ^d	25.93 ^a	52.63 ^a
6.4	40.17 ^c	17.54 ^b	42.29 ^{bc}
7.4	53.38 ^b	13.22 ^b	33.40 ^c
11.0	94.30 ^a	1.72 ^c	3.98 ^d

Depressurization time = 10 minutes

a-d: Means in a column with the same letter are not significantly different (LSD, $P > 0.05$)

while the smallest mean was at 4.9% MC. Particle size at 3.5% MC was not different from that at 4.9% MC and 6.4%.

In general, the initial moisture content of the pecans did affect the amount of breakage during the 10 minute depressurization time, and moisture modification before extraction may be beneficial for reducing pecan breakage.

The effect of water content on pecan breakage can be explained by the pecan texture change with water. The mechanical properties of pecans were found to vary with water content (Shult, 1996). After absorbing water, pecan kernels become soft and pliable, which may be attributed to a change in their tissue structure. Pecan tissues consist of proteins and carbohydrates, which are the main hydrophilic components of the structure. Changes in the moisture content affect the plasticisation of proteins and carbohydrates, and alter pecan tissues. The brittle and crunchy textural quality of nuts is lost as a result of taking up moisture (Hung and Chinnan, 1989; Borges and Peleg, 1997). A limber and more flexible pecan structure is formed at higher moisture contents, and its resistance to mechanical force is improved. This increased resistance reduced the amount of kernel breakage with high internal mechanical strain during rapid pressure release.

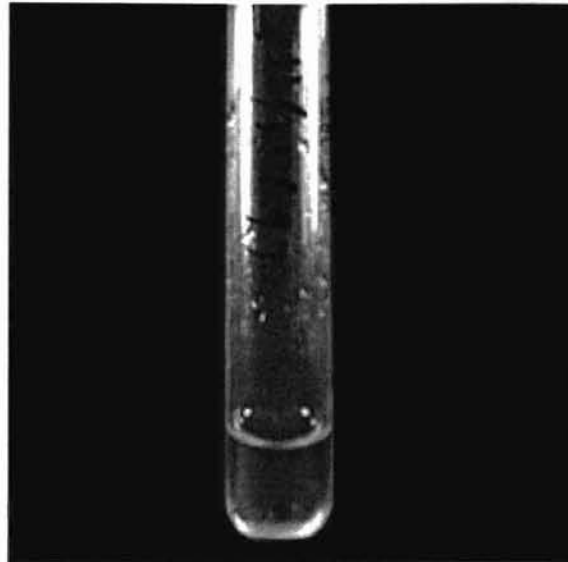
Oil Yield

During each extraction, oil was collected in a test tube for later analysis. The extracted oil from pecans with lower initial moisture content was very clear with a light brown color. During extraction of higher moisture content pecans, the collected oil contained more water, was cloudy and exhibited a yellow color due to the presence of

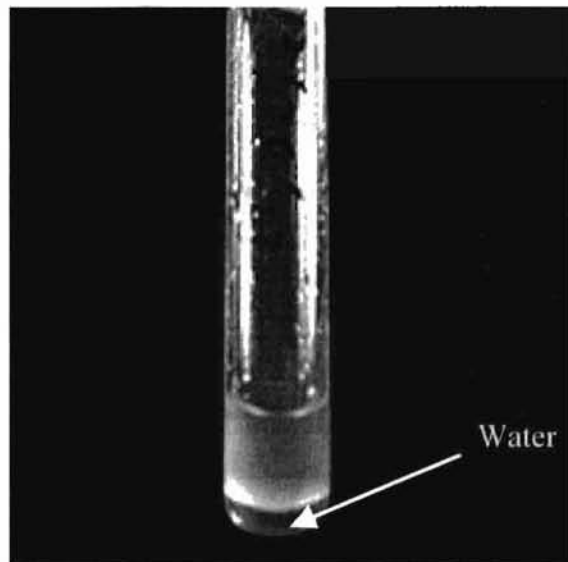
water. The oil and water eventually separated by gravity after a long time. About 2 mm of water were visible at the bottom of the collection tube when oil was extracted from pecans with 11.0% MC, and the oil floated on the top of the water. This is shown in Figure 11. Oil yield data were obtained after heating the mixture as described in the methods section.

The effect of pecan initial moisture content on the amount of oil extracted is shown in Figure 12, where the oil yield is defined as the weight of extracted oil on a dry pecan weight basis, and the percentage of extracted oil is defined by dividing the weight of extracted oil by the total amount of oil initially in the pecans. The oil recovery yields did not show much effect of moisture content. Although there was a slight increase in pecan oil yield with increasing moisture content, this trend was not significant ($r^2 = 0.24$), even though the CV ranged from 4.64% to 19.22% (Table VII). An F test shows that the P-value is equal to 0.31, indicating that there is no significant difference between the five moisture contents (Table VIII). Likewise, the mean values of oil yield were similar at five pecan initial moisture contents.

Water affects SC-CO₂ oil extraction primarily by swelling the pecan structure to change the oil accessibility, but not by increasing the selectivity of CO₂. This is because most oils are non-polar so that the polarity of the solvent has a minor influence on oil extraction. The addition of water and diffusion into the pecan causes an expansion of the pecan structure. Rai and Kumar (1995) demonstrated this expansion by measuring porosity and grain volume changes in moisture content. The expansion of cell walls makes the cell membrane more permeable so that both oil and SC-CO₂ can pass more easily. At this point, oil extractability should be improved by adding water because the



6.1% initial moisture content



11.6% initial moisture content

Figure 11. The extracted oil at different pecan initial moisture contents.

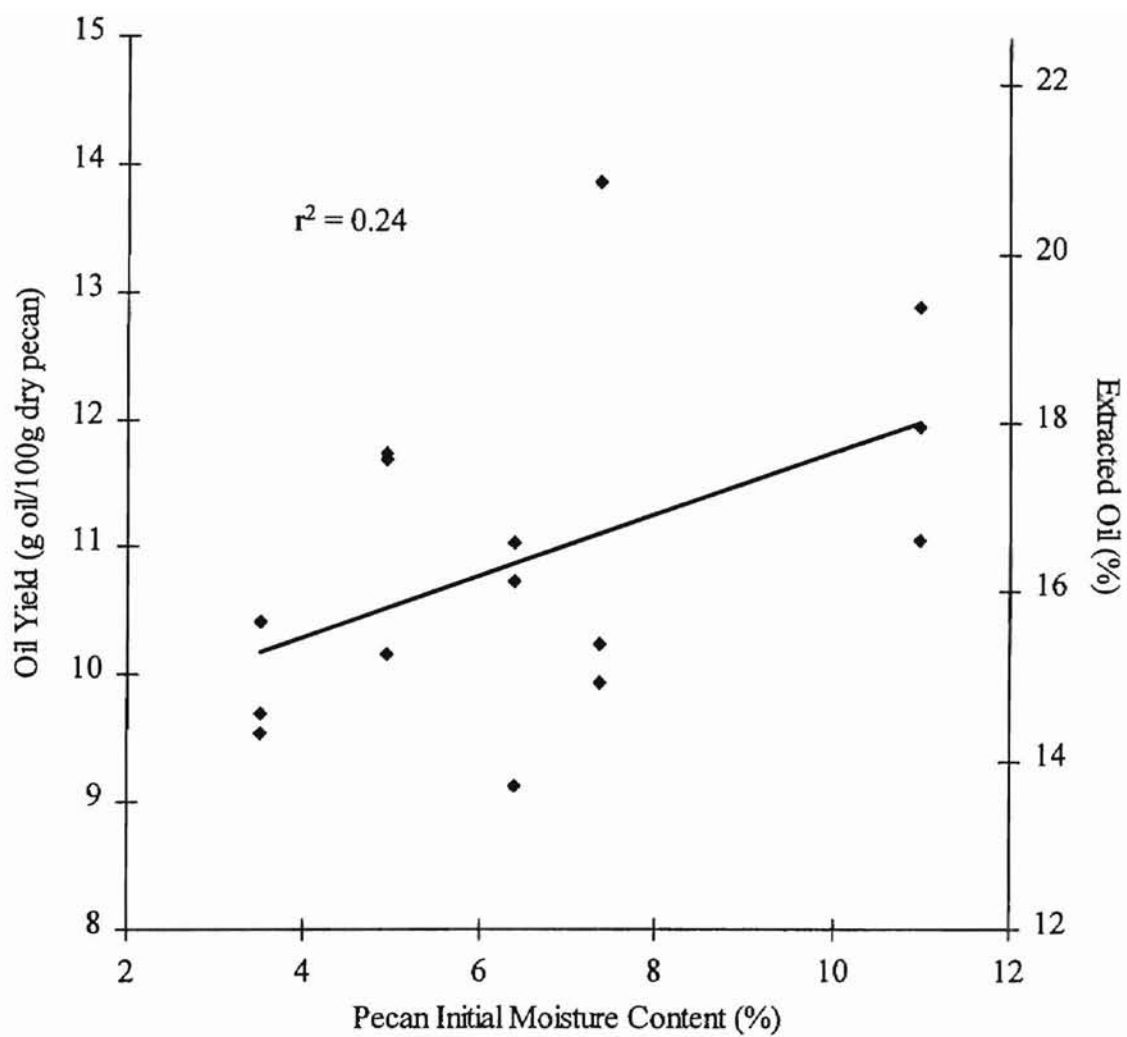


Figure 12. Pecan oil yield and percentage of extracted oil versus pecan initial moisture content.

Table VII. (a). Pecan oil yield at different moisture contents.

Pecan Initial MC (%)	Oil Yield (g oil /100g dry pecan)					
	1	2	3	Mean	Standard Deviation	CV
3.5	10.41	9.55	9.71	9.89	0.46	4.64
4.9	10.17	11.68	11.73	11.19	0.89	7.95
6.4	10.74	11.04	9.14	10.31	1.02	9.94
7.4	10.25	9.94	13.86	11.35	2.18	19.22
11.0	12.88	11.94	11.06	11.96	0.91	7.63

(b). The percentage of extracted oil at different moisture contents.

Pecan Initial MC (%)	Extracted Oil (%)					
	1	2	3	Mean	Standard Deviation	CV
3.5	15.70	14.41	14.64	14.92	0.69	4.64
4.9	15.34	17.62	17.70	16.89	1.34	7.95
6.4	16.20	16.65	13.78	15.55	1.54	9.94
7.4	15.46	14.99	20.91	17.12	3.29	19.22
11.0	19.43	18.01	16.68	18.04	1.38	7.63

Table VIII: Analysis of variance for effect of pecan initial moisture content (MC) on oil yield (g oil / 100g dry pecan).

Depressurization time (minutes)	Source	DF	SS	Mean Square	F Value	Pr>F
10	MC	4	8.33	2.08	1.37	0.313
	Error	10	15.23	1.52		
20	MC	4	14.78	4.93	1.54	0.335
	Error	10	12.81	3.20		

swelling effect of the water increases the contact between the oil and SC-CO₂. However, excess water in pecans also impedes the reciprocal diffusion of oil and SC-CO₂, and has a negative effect on oil accessibility. These two opposing effects of water on pecan oil extraction showed a slight net increase in oil yield at higher pecan initial moisture contents.

Effect of Water Penetration Time

Pecan Breakage

The results of pecan breakage for different water penetration times before SFE extraction are shown in Table IX. Fewer broken pecans resulted from the longer water penetration, 48 vs. 1 hour, especially at lower moisture levels. In addition, the unbroken kernel surface was less damaged during longer water penetration for all moistures. Figure 13 shows the percent of pecans remaining on the No. 4 sieve after extraction with short and long penetration times. Extraction of pecans after a long water penetration period produced less breakage than a short water penetration time. In the 6.1 - 7.7% MC range, the 48 hour water penetration period produced almost twice the amount of large pecan pieces as the 1 hour penetration time. These results imply that water changed the pecan texture as it penetrated further into the pecans. As moisture was increased to 8.5%, the effect of the water penetration time decreased, and the difference between 1 hour and 48 hours was negligible at 11.6% MC.

After spraying water on the pecan surface, a water concentration gradient is developed, and water starts to diffuse from the pecan surface to the interior. As water gradually penetrates towards the pecan interior, more of the microstructure of the pecan is

Table IX: Effect of water penetration time on particle size distribution of pecans after extraction.

Pecan Initial MC (%)	Water Penetration Time (Hours)	Particle Size Distribution (%)			Number of Unbroken Kernels	Degree of Unbroken Kernels *
		No.4	No.8	Fines		
6.1	1	30.98	20.73	48.29	3	3
6.1	48	55.70	10.08	34.22	21	2
7.0	1	37.78	20.20	42.02	6	3
7.0	48	63.94	9.73	26.33	26	2
7.5	1	38.35	19.87	41.77	6	3
7.5	48	50.14	11.26	38.60	20	2
7.7	1	34.80	20.47	44.73	4	2
7.7	48	72.81	7.51	19.68	30	1
8.5	1	52.05	14.90	33.05	14	2
8.5	48	64.39	9.13	26.48	30	1
11.6	1	96.81	0.46	2.73	34	0
11.6	48	97.43	0.49	2.08	34	0

- * 0 No apparent damage on kernel surface
- 1 Kernel skin slightly cracked
- 2 Kernel skin cracked
- 3 Kernel skin seriously damaged

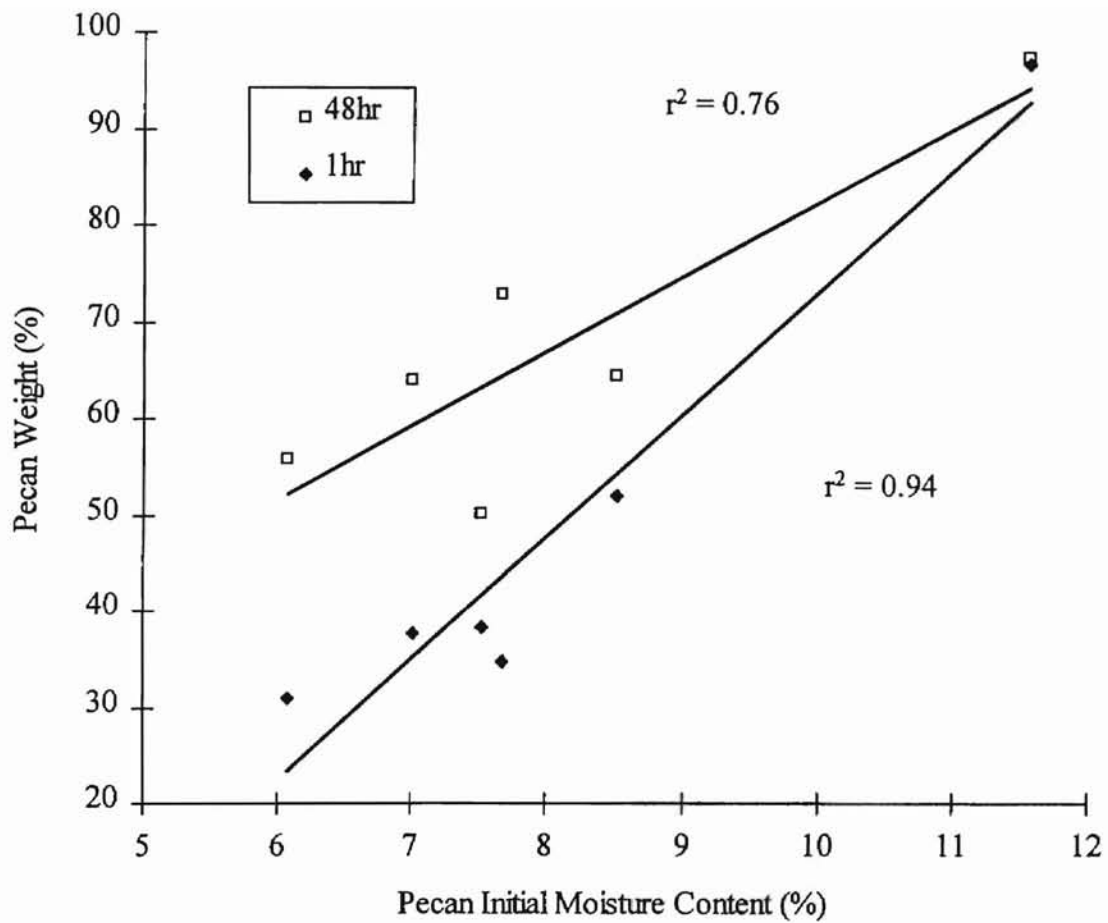


Figure 13. Percent of large pieces of pecans (remaining on No. 4 sieve) after oil extraction with short (1hr) and long (48hr) water penetration times.

modified. Eventually, equilibrium will be attained, and the amount of added water will determine the degree of structure modification. This equilibrium likely occurs within the 48 hour water penetration time, but not within the 1 hour water penetration time. As expected, less pecan breakage occurred after extraction with the 48 hour treatment due to the pecan structure being more altered than that of the 1 hour treatment. The amount of water sprayed on the pecans also affects the rate of arrival of equilibrium. A larger amount of water on the pecan surface accelerates the speed of water imbibition because of higher water osmotic pressure. Therefore, the number of unbroken pecans was almost the same at 11.6% MC for either longer or shorter water penetration time, indicating that the equilibrium state may be obtained after 1 hour for large amount of added water.

Oil Yield

Figure 14 shows the oil yields with long and short water penetration times for the six different moisture contents. The overall oil yields for 48 hours were 30% higher than those for 1 hour. The two oil yield trend-lines show an obvious difference between the two treatments, indicating that more oil was extracted after the longer water penetration time. Further, there was an increase in oil yield when the pecan initial moisture content increased for 1 hour water penetration time.

The higher oil yield after the longer water penetration time implies a positive swelling effect of water on the pecan structure. This can also be explained by the change in the pecan kernels' interior after adding water. The water in the kernels should be more evenly distributed after the longer time so that the whole kernel structure is expanded by water swelling, and oil is more accessible. Thus, more oil can be extracted from this

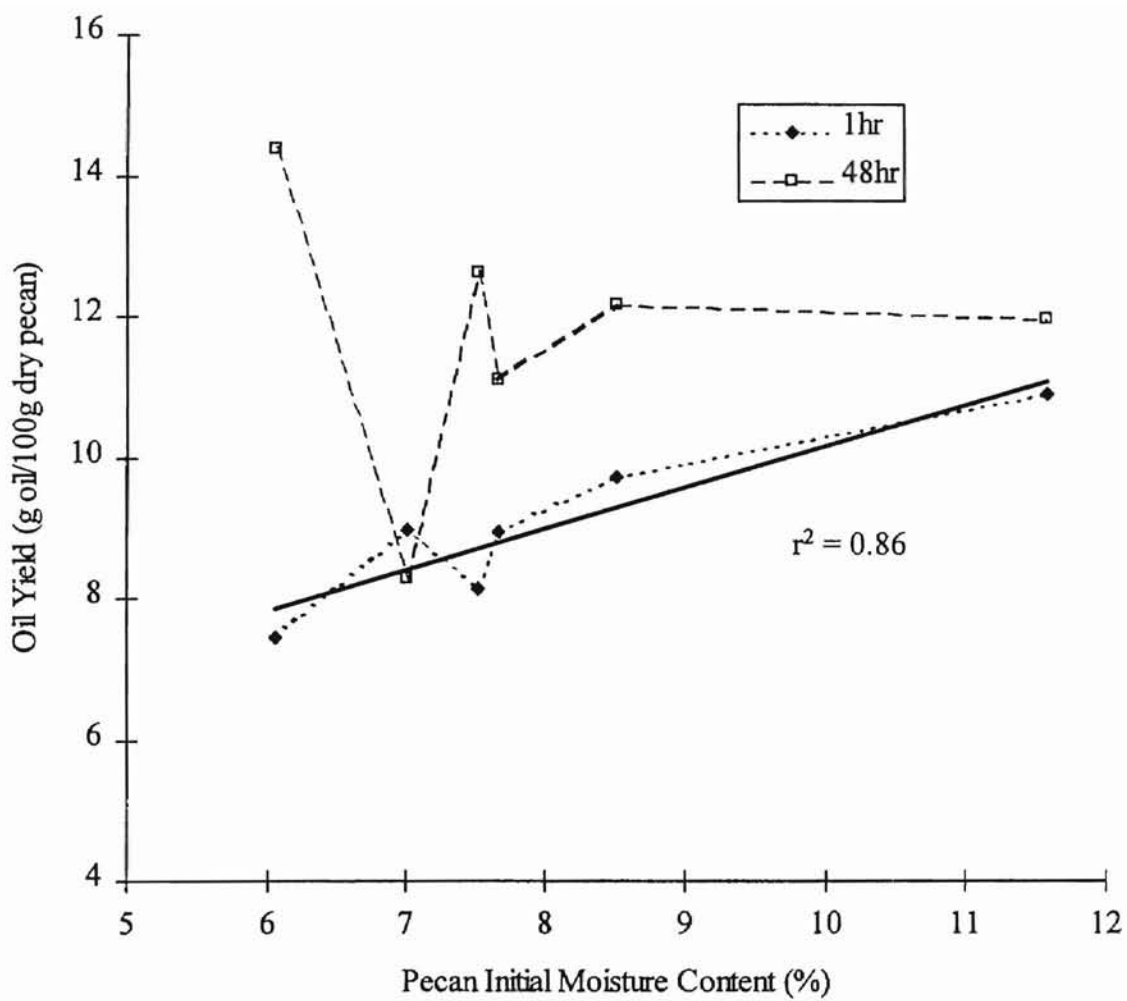


Figure 14. Effect of water penetration time and pecan initial moisture content on pecan oil yield.

wider pecan structure. In this case, the expansion effect presented no more increase in oil yield at higher moistures when uniform water distribution was achieved. The trend of increasing oil yield with increasing moisture at 1 hour water penetration may have also been because of the rate of water absorption before reaching equilibrium. The difference in water concentration is greater when spraying a larger amount of water on the kernel surface so that the water diffuses more rapidly and further expands the cell wall. This expansion rate is likely the main reason for the resultant increase in oil yield at higher moistures for the 1 hour water penetration time.

Water Co-extracted

The moisture content of pecans after oil extraction was lower than that of the initial pecans, suggesting that some water was co-extracted along with the pecan oil (Figure 15). The difference in moisture content before and after extraction indicates that an amount of water was released from the pecans during SC-CO₂ extraction. Figure 16 shows the amount of water in the extracted oil. As the pecan initial moisture content was increased, there was a linear increase in the amount of co-extracted water. The water content of extracted oil from pecans having initial moisture contents of 3.5% and 12.0% were 0.7% and 11.7% respectively, indicating that a large amount of water was extracted from pecans of higher moisture content. As was mentioned previously, a cloudy yellow color oil was collected due to mixing of oil and co-extracted water from pecans of high moisture, and a clear light brown oil came from pecans with low moisture. An increase in the amount of water co-extracted with increasing pecan initial moisture content indicates that water extraction is in an equilibrium-controlled phase extraction

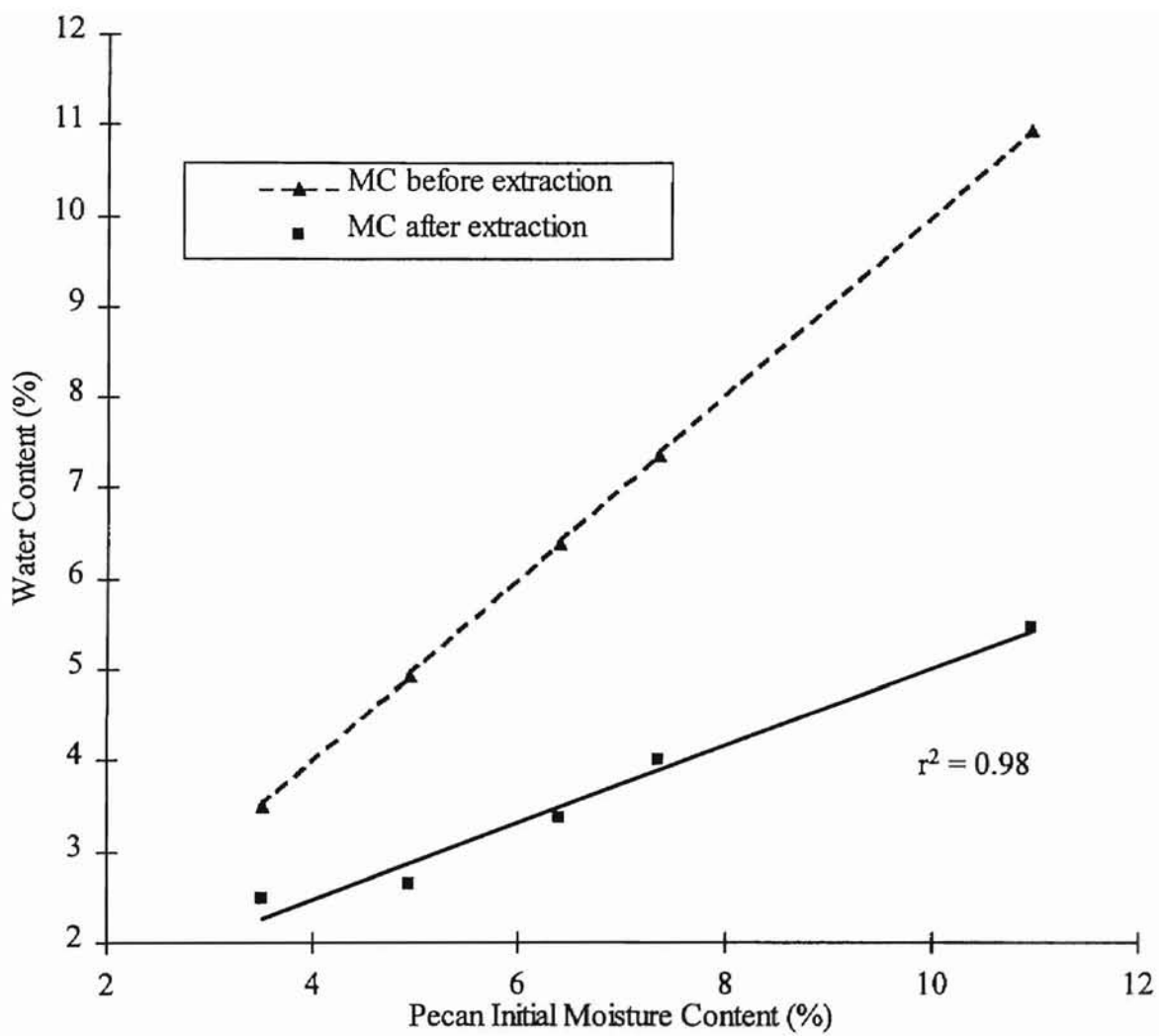


Figure 15. Pecan moisture content before and after extraction.
Average of 3 replications.

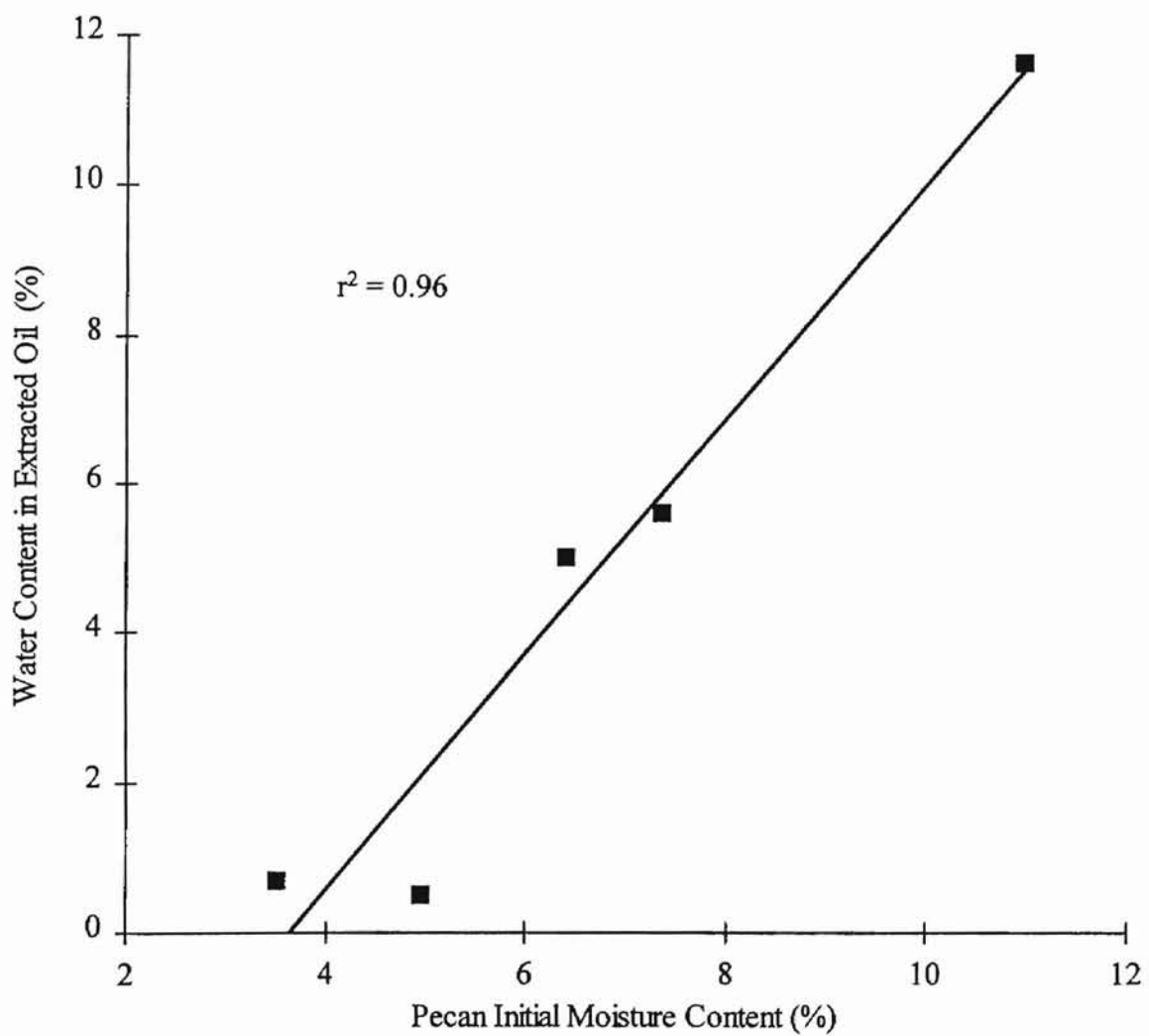


Figure 16. Effect of pecan initial moisture content on moisture in extracted oil.
Average of 3 replications.

process. In this case, the highest water solubility in SC-CO₂ was calculated to be about 0.12g of water for 100g CO₂. Reverchon et al. (1995) computed an equilibrium solubility of water to be 0.03g/100g CO₂ in sage oil extraction, which is about four times less than the water solubility in pecan oil extraction. This difference can be accounted for mainly in the different extraction conditions: sage oil was extracted at 200 bar, 40 °C while pecan oil was extracted at 620 bar, 75 °C. Since water vapor pressure increases with temperature, water solubility in the supercritical CO₂ was higher with pecan oil extraction.

Pecan Mass Balance

During extraction processes, there will always be some unaccountable loss of mass due to volatility of oil and aerosol formation. For the 3.0 slpm CO₂ flowrate, Alexander (1996) found that the temperatures of 100 °C valve and 0 °C collection vessel produced the smallest loss of extract to the ambient. During those experiments, the differences between pecan final weight loss and oil collected were less than 10% different. Therefore, the same optimum parameters were used in our tests, and it was assumed that the collected oil was reliable as a measure of the oil extracted from pecans. In addition, a very slow depressurization (at least 1 hour) was used in her experiments to prevent pecan breakage and collect all oil entrained in released CO₂.

An average of 20% difference between pecan final weight loss and extracted oil existed in our experiments. This difference is computed based on the difference between the weight of oil collected and the weight loss of the extraction vessel, instead of using the weight of oil collected and the weight loss of the pecans as Alexander did. We were

not able to accurately determine the weight loss of the pecans after the kernels were broken and sticking on the vessel wall or glass wool.

The oil contents of two samples of reduced oil pecans measured by the quantitative extraction method (Maness et. al, 1995) were 51.2% and 48.5% (Samples resulted from 1 hour supercritical CO₂ extraction at 3.5% and 7.8% MC respectively). From these oil contents, 13.5% and 16.3% oil yields were obtained by subtracting from the 64.2% initial oil content and adjusting for dry weight. Compared with the average of 9.9% and 11.4% oil yields at 3.5% and 7.4% MC, the oil yields calculated from reduced oil pecans are higher than those from the actual collected oil. The high unrecovered mass was likely due to water vapor and oil loss from opening valves during depressurization. A test using the same depressurization method as Alexander described yielded an 8.4% difference based on the weight loss of the pecans, which was consistent with her results.

CHAPTER V

CONCLUSIONS

This study provided further information about how to reduce pecan breakage during supercritical CO₂ extraction of pecan oil by adjusting the pecan's moisture content before extraction. The conclusions drawn from this study were as follows:

1. Pecan kernel breakage occurred during SC-CO₂ tests if the depressurization time was 10 minutes but no breakage occurred at a depressurization time of 20 minutes. The pressure release rate in the final stage of depressurization was crucial in causing pecan breakage.
2. The effect of pecan initial moisture content on pecan breakage was significant ($P < 0.01$). As pecan initial moisture content increased from 4.94 to 10.97%, the percentage of large particle sizes increased from 21.45 to 94.30%.
3. Over the initial moisture content range of 6.07 to 11.57%, the 48 hour water penetration time produced more large particles and an average of 30% higher oil yield than the 1 hour water penetration time prior to SFE.
4. The unbroken kernel surface was less damaged at higher pecan initial moisture content or after longer water penetration time.
5. Pecan oil yield was slightly higher at higher moisture contents, but the differences were not significant.

6. More water was co-extracted with oil from pecans at higher initial moisture contents.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDY

This study found that depressurization after oil extraction from the critical pressure to ambient pressure plays an important role in causing pecan breakage, but the pressure release rate was not precisely controlled or measured in this study. An experiment is needed to monitor the depressurization rate in the extraction vessel to determine the optimum depressurization rate for minimum pecan breakage.

Since pecan texture was altered by adjusting moisture content to reduce pecan breakage during SFE, further studies could be conducted to investigate the relationship among SFE process parameters, pecan texture and breakage. Varying lengths of extraction time could be tested as a factor influencing pecan breakage because oil content also affects pecan texture.

The method of adding water to pecans was not studied and it would be useful to examine whether different water conditioning methods similarly affect pecan breakage and extracted oil quality.

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APPENDIX

APPENDIX A.2

INITIAL MOISTURE CONTENT EXPERIMENT AT 4.9% MC

20 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	20.26	5504.3	2.03	2.02	15.89	15.66
	Final Weight, g	16.10	5501.5	2.64	2.56	17.89	15.78
2	Initial Weight, g	21.08	5505.5	2.26	2.19	15.92	15.87
	Final Weight, g	17.29	5502.9	2.75	2.68	17.72	15.97

	Unbroken Kernels	Pecan Breakage
1	35	No
2	35	No

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	4.94	2.63	0.60
2	4.94	2.49	0.89

APPENDIX A.3

INITIAL MOISTURE CONTENT EXPERIMENT AT 6.4% MC

20 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	20.30	5504.7	2.18	2.20	15.38	15.34
	Final Weight, g	16.41	5501.3	2.49	2.44	17.65	15.43
2	Initial Weight, g	20.40	5504.4	2.00	2.08	15.54	15.98
	Final Weight, g	-	5500.8	2.19	2.20	18.48	16.03

	Unbroken Kernels	Pecan Breakage
1	35	No
2	35	No

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	6.40	3.07	3.17
2	6.40	3.50	5.31

APPENDIX A.4

INITIAL MOISTURE CONTENT EXPERIMENT AT 7.4% MC

20 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	20.77	5505.1	2.15	2.15	15.05	15.68
	Final Weight, g	16.94	5502.5	2.72	2.59	16.69	15.80
2	Initial Weight, g	20.17	5504.2	1.93	1.98	15.33	15.66
	Final Weight, g	15.85	5501.2	2.36	2.39	17.67	15.77
		Unbroken Kernels	Pecan Breakage				
1		35	No				
2		35	No				
		Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %			
1		7.36	3.07	1.83			
2		7.36	3.50	5.77			

APPENDIX B.1

INITIAL MOISTURE CONTENT EXPERIMENT AT 3.5% MC

10 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	21.32	5505.0	1.88	1.87	15.35	15.45
	Final Weight, g	17.32	5502.8	2.20	2.70	17.50	15.57
2	Initial Weight, g	19.90	5503.8	2.01	2.00	15.82	15.68
	Final Weight, g	16.06	5501.8	2.63	2.50	17.68	15.84
3	Initial Weight, g	18.99	5502.8	2.00	1.91	16.185	16.094
	Final Weight, g	15.08	5500.6	2.61	2.53	17.970	16.183
<hr/>							
	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g			
1	1	4.73	4.79	7.73			
2	0	4.40	3.87	7.76			
3	4	5.50	3.32	6.02			
<hr/>							
	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %				
1	3.50	2.57	0.37				
2	3.50	2.68	1.40				
3	3.50	2.22	0.34				

APPENDIX B.2

INITIAL MOISTURE CONTENT EXPERIMENT AT 4.9% MC

10 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	18.54	5502.3	1.94	1.91	15.42	15.05
	Final Weight, g	14.66	5499.7	2.46	2.55	17.23	15.20
2	Initial Weight, g	17.35	5501.1	1.97	1.98	15.77	15.81
	Final Weight, g	12.79	5498.9	2.44	2.52	17.70	15.91
3	Initial Weight, g	19.726	5503.7	2.04	1.97	15.367	16.203
	Final Weight, g	15.06	5501.2	2.44	2.74	17.582	16.290
	Unbroken Kernels		No. 4 Sieves, g	No. 8 Sieves, g	Rest, g		
1	1		2.31	3.56	8.78		
2	1		2.91	3.92	5.84		
3	3		3.85	3.39	7.80		
	Pecan MC, % (Before Extraction)		Pecan MC, % (After Extraction)	Extracted Oil MC, %			
1	4.94		2.57	0.72			
2	4.94		2.68	0.16			
3	4.94		2.64	0.68			

APPENDIX B.3

INITIAL MOISTURE CONTENT EXPERIMENT AT 6.4% MC

10 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	20.00	5503.7	1.97	1.99	15.80	16.02
	Final Weight, g	15.38	5501.0	2.45	2.65	17.91	16.08
2	Initial Weight, g	19.14	5503.0	1.97	2.00	15.92	15.89
	Final Weight, g	14.38	5500.5	2.44	2.55	17.98	15.95
3	Initial Weight, g	22.229	5506.1	1.96	2.03	15.995	15.296
	Final Weight, g	17.84	5503.3	2.46	2.41	17.984	15.340
	Unbroken Kernels		No. 4 Sieves, g	No. 8 Sieves, g	Rest, g		
1	12		6.31	2.54	6.29		
2	9		4.59	2.94	6.68		
3	19		8.19	2.67	6.74		
	Pecan MC, % (Before Extraction)		Pecan MC, % (After Extraction)	Extracted Oil MC, %			
1	6.40		3.36	4.65			
2	6.40		3.31	4.12			
3	6.40		3.42	6.31			

APPENDIX B.4

INITIAL MOISTURE CONTENT EXPERIMENT AT 7.4% MC

10 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	21.01	5504.9	2.04	1.95	15.97	15.79
	Final Weight, g	16.26	5502.0	2.75	2.36	18.08	15.88
2	Initial Weight, g	20.32	5504.2	2.04	2.04	15.80	15.80
	Final Weight, g	15.88	5501.6	2.47	2.47	17.78	15.93
3	Initial Weight, g	19.910	5503.6	1.98	2.03	15.885	16.108
	Final Weight, g	15.16	5500.6	2.18	2.58	18.600	16.156
<hr/>							
		Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g		
1		22	10.32	1.72	4.10		
2		18	7.34	2.40	6.08		
3		18	7.45	2.07	5.44		
<hr/>							
		Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %			
1		7.36	4.20	5.58			
2		7.36	4.48	5.51			
3		7.36	3.34	5.82			

APPENDIX B.5

INITIAL MOISTURE CONTENT EXPERIMENT AT 11.0% MC

10 minutes depressurization time

Experiments		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	22.665	5506.5	1.96	1.95	15.372	16.226
	Final Weight, g	17.72	5502.5	2.32	2.35	18.388	16.291
2	Initial Weight, g	21.683	5505.4	1.96	1.93	15.440	15.502
	Final Weight, g	16.70	5502.1	2.41	2.37	18.043	15.546
3	Initial Weight, g	22.003	5505.7	2.05	1.91	15.263	16.056
	Final Weight, g	17.26	5502.1	2.44	2.28	17.663	16.121
<hr/>							
		Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g		
1		34	17.25	0.08	0.29		
2		34	15.10	0.50	1.06		
3		34	16.08	0.29	0.67		
<hr/>							
		Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %			
1		10.97	5.83	13.86			
2		10.97	5.17	11.45			
3		10.97	5.39	9.75			

APPENDIX C.1

WATER PENETRATION TIME EXPERIMENT AT 6.1% MC

10 minutes depressurization time

Water Penetration Time, hour		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	23.470	5505.2	2.02	2.00	15.414	15.817
	Final Weight, g	19.49	5502.7	2.57	2.53	17.093	15.881
48	Initial Weight, g	22.228	5503.8	2.05	2.03	16.065	15.990
	Final Weight, g	17.46	5500.3	2.20	2.40	19.200	16.048

	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g
1	3	5.98	4.00	9.32
48	21	9.62	1.74	5.91

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	6.07	2.46	2.26
48	6.07	3.22	4.08

APPENDIX C.2

WATER PENETRATION TIME EXPERIMENT AT 7.0% MC

10 minutes depressurization time

Water Penetration Time, hour		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	23.683	5507.5	1.95	2.08	15.582	15.723
	Final Weight, g	18.87	5504.8	2.58	2.64	17.692	15.805
48	Initial Weight, g	21.012	5505.0	2.09	1.96	15.365	16.357
	Final Weight, g	17.04	5502.6	2.64	2.41	17.025	16.385

	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g
1	6	7.05	3.77	7.84
48	26	10.78	1.64	4.44

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	7.01	3.19	6.40
48	7.01	3.68	2.35

APPENDIX C.3

WATER PENETRATION TIME EXPERIMENT AT 7.5% MC

10 minutes depressurization time

Water Penetration Time, hour		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	21.572	5505.1	1.92	1.98	16.080	15.279
	Final Weight, g	17.38	5502.6	2.39	2.58	17.753	15.361
48	Initial Weight, g	22.952	5506.7	2.02	1.98	15.291	15.888
	Final Weight, g	17.86	5503.4	2.34	2.37	18.167	15.947

	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g
1	6	6.62	3.43	7.21
48	20	8.86	1.99	6.82

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	7.52	2.70	2.93
48	7.52	3.57	6.71

APPENDIX C.4

WATER PENETRATION TIME EXPERIMENT AT 7.7% MC

10 minutes depressurization time

Water Penetration Time, hour		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	21.381	5505.2	1.98	2.08	15.126	15.848
	Final Weight, g	16.82	5502.5	2.44	2.87	16.969	15.923
48	Initial Weight, g	19.806	5503.6	2.04	2.00	15.360	15.409
	Final Weight, g	15.33	5500.4	2.49	2.49	17.490	15.481

	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g
1	4	5.78	3.40	7.43
48	30	11.06	1.14	2.99

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	7.67	2.87	4.12
48	7.67	3.39	4.60

APPENDIX C.5

WATER PENETRATION TIME EXPERIMENT AT 8.5% MC
10 minutes depressurization time

Water Penetration Time, hour		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	20.727	5502.0	1.91	1.96	15.804	15.585
	Final Weight, g	16.50	5499.6	2.26	2.36	17.823	15.643
48	Initial Weight, g	20.556	5502.1	1.97	2.05	16.153	15.454
	Final Weight, g	15.95	5499.1	2.26	2.68	18.595	15.520

	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g
1	14	8.49	2.43	5.39
48	30	10.09	1.43	4.15

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	8.52	2.95	8.72
48	8.52	3.97	6.31

APPENDIX C.6

WATER PENETRATION TIME EXPERIMENT AT 11.6% MC

10 minutes depressurization time

Water Penetration Time, hour		Pecans (35)	Extraction Vessel	Glass Wool		Collection Tube	Cleaning Tube
				Inlet	Outlet		
1	Initial Weight, g	22.785	5504.1	1.96	1.93	15.497	16.000
	Final Weight, g	17.87	5500.6	2.50	2.33	18.102	16.057
48	Initial Weight, g	21.019	5502.6	2.04	2.07	16.331	16.163
	Final Weight, g	16.61	5499.2	2.31	2.35	18.972	16.210

	Unbroken Kernels	No. 4 Sieves, g	No. 8 Sieves, g	Rest, g
1	34	17.02	0.08	0.48
48	34	15.95	0.08	0.34

	Pecan MC, % (Before Extraction)	Pecan MC, % (After Extraction)	Extracted Oil MC, %
1	11.57	4.96	15.74
48	11.57	6.27	15.71

APPENDIX D

'WESTERN SCHLEY' PECAN OIL EXTRACTION RATE TEST

75 °C, 62.0 MPa, 3.0 slpm, Valve: 100 °C, Collection Tube: 0 °C
 Depressurization Time: 1 hour, Extraction Time: 120 minutes, Pecan MC: 3.1%

Time (minutes)	Oil Collected (g)	Total Oil Collected (g)	Total Oil Collected (%)
10	0.189	0.189	1.432
20	0.232	0.421	3.190
30	0.268	0.689	5.221
40	0.272	0.961	7.282
50	0.261	1.222	9.259
60	0.299	1.521	11.525
70	0.272	1.793	13.586
80	0.251	2.044	15.488
90	0.288	2.332	17.670
100	0.252	2.584	19.580
110	0.234	2.818	21.353
120	0.243	3.061	23.194
Depressurization	0.225	3.286	24.899
Cleaning	0.036	3.322	25.171

	Pecans	Extraction Vessel	Glass Wool	
			Inlet	Outlet
Initial Weight (g)	20.544	5501.7	1.91	1.93
Final Weight (g)	16.339	5498.8	2.19	2.18

APPENDIX E.1

CALCULATION OF PECAN OIL YIELD AND
PERCENTAGE OF EXTRACTED OIL

Depressurization Time: 10 minutes, Extraction Time: 60 minutes

Pecan Oil Content: 64.2%

MC: 3.1 %

Pecan Initial MC (%)	Wet Pecan Weight (g)	Dry Pecan Weight (g)	Corrected Oil Content (%)	Total Oil Content (g)	Extracted Oil (g)	Extracted Oil (%)	Oil Yield (g oil / 100g dry pecan)
	21.32	20.57	63.97	13.64	2.14	15.70	10.41
3.50	19.90	19.20	63.97	12.73	1.83	14.41	9.55
	18.99	18.33	63.97	12.15	1.78	14.64	9.71
	18.54	17.62	63.02	11.68	1.79	15.34	10.17
4.94	17.35	16.49	63.02	10.93	1.93	17.62	11.68
	19.73	18.75	63.02	12.43	2.20	17.70	11.73
	20.00	18.72	62.05	12.41	2.01	16.20	10.74
6.40	19.14	17.92	62.05	11.88	1.98	16.65	11.04
	22.23	20.81	62.05	13.79	1.90	13.78	9.14
	21.01	19.46	61.42	12.90	2.00	15.46	10.25
7.36	20.32	18.82	61.42	12.48	1.87	14.99	9.94
	19.91	18.44	61.42	12.23	2.56	20.91	13.86
	22.66	20.17	59.02	13.37	2.60	19.43	12.88
10.97	21.68	19.30	59.02	12.80	2.31	18.01	11.94
	22.00	19.59	59.02	12.99	2.17	16.68	11.06

APPENDIX E.2
CORRECTION OF PECAN OIL CONTENT

The pecan oil content at 3.1% MC is: 64.24 %

To correct oil content at different moisture content based on 3.1% MC, the following equation was used:

$$\text{Oil Content at M2} = 64.24 \% * (1 - M2) / (1 - M1)$$

Where

M1 = 3.1%

M2 is the moisture content at which pecan oil content needs to be corrected

Proof

Let

OC1 -- Oil content at M1 (Known: Before water conditioning)

OC2 -- Oil content at M2 (After water conditioning)

Since

$$OC2 = OC1 * W / (W+X)$$

Where W -- Pecan total weight before water conditioning

X -- Weight of water change

And $M2 = (M1 * W + X) / (W+X)$

Therefore

$$W / (W+X) = (1 - M2) / (1 - M1)$$

$$OC2 = OC1 * (1 - M2) / (1 - M1)$$

Example

$$\begin{aligned} \text{Oil content at 10.97 \% MC} &= 64.24 \% * (1 - 0.1097) / (1 - 0.031) \\ &= 59.02 \% \end{aligned}$$

VITA

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