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I am submitting herewith a thesis written by Haizhou Li entitled “Ultrasound and Microwave Assisted Extraction of Soybean Oil.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Biosystems Engineering Technology.

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Ultrasound and Microwave Assisted Extraction of Soybean Oil

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Abstract

Soybeans, one of the world's leading cash crops, contain appropriately 20% lipid. Currently, soybean oil is the principal vegetable oil used in the U.S. and the world market, totaling 29% of the world vegetable oil production in 2001. Development of extraction technology that could increase oil yield would thus significantly enhance the profitability of the soybean industry and reduce processing costs significantly. It has been shown that both ultrasound-assisted and microwave-assisted extraction methods can enhance extraction of phytochemicals from plant sources while reducing processing time and solvent consumption. However, little is known about how ultrasound and microwave can affect the soybean oil extraction.

The main objectives of the research were to (1) determine the effect of ultrasound on soybean oil extraction, (2) determine the effect of microwave on soybean oil extraction, and (3) study the effect of different solvents on soybean oil extraction. Thus, this study aimed to compare the yield, composition, and quality of extracted soy oil obtained by traditional and ultrasound-assisted or microwave-assisted processing methods. The effects of different solvents and levels of ultrasound or microwave treatment on the extracted soybean oil were evaluated. Both laboratory-scale ultrasound-assisted and microwave-assisted soybean oil extraction procedures were developed in this research.

Ultrasound-assisted extraction was found to be a simpler and more effective alternative to traditional methods for soybean oil extraction. Two different soybean

varieties (TN 96-58, N 98-4573) were used in the experiments. Oil was extracted using different solvents [hexane, isopropanol, and mixed solvent (hexane:isopropanol 60%:40% v/v)] under either direct sonication by an ultrasonic probe at intensity levels ranging from 16.4 Wcm^{-2} to 47.6 Wcm^{-2} or using a traditional procedure without ultrasound application. It was found that the ultrasound-assisted extraction of oil from soybeans yielded greater oil than the traditional method regardless of soybean variety. Higher sonication intensity allowed for more efficient oil extraction (faster and greater oil yield). The solvent influenced the sonication enhancement, i.e., the oil yield extracted by this procedure was highest when using hexane:isopropanol solvent mixture. Fatty acid profile analysis measured by GC indicated that the oil quality did not appreciably change from traditionally extracted oil when ultrasound assistance was used.

Microwave-assisted extraction can increase the oil yield and extraction process rate. Three different solvents (hexane, isopropanol, and a mixed solvent (hexane:isopropanol 60%:40%, v/v)) were used to extract soybean oil after being irradiated with microwaves (2450 MHz) at increasing reaction times. Oil yield obtained with microwave irradiation was highest using the mixed solvent. Microwave-assisted extraction of oil from soybeans yielded markedly higher oil percentages than traditional method, i.e., oil yield of microwave-assisted group was 0.45 g higher than that of control group during a 2 hr. extraction time. Increased microwave reaction times increase oil as well. For the mixed solvent, 4.17 g more oil was extracted when the reaction time changed from 30 to 120 min.

Both ultrasound and microwave treatment had a positive effect on soybean oil extraction. Increases in soybean oil yield were achieved with the hexane:isopropanol mixed solvent. Further research is planned to evaluate the potential of ultrasound- and microwave-assistance in soybean oil extraction.

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1 Literature Review

1.1 Introduction

In the Far East, soybeans have been an integral part of people's diets for more than three thousand years (Li, 1994). In addition to traditional soy products, such as, fresh green soybeans and tofu, a large variety of new protein products, such as, defatted soy flours, soy protein concentrates, and their derivatives (e.g., hydrolyzed soy protein), became available to meet increasing nutritional and functional needs of foods (Chen et al., 2001; Ho et al., 2001; Henkel, 2000).

Soybeans are one of the world's leading cash crops (Dohlman et al., 2001). The plant is highly adaptable to regions with different environmental conditions (Khurana and Yadava, 1982). Furthermore, soybeans have the ability to fix large quantities of nitrogen (Keerio et al., 2001). Soybean has thus become an increasingly important agricultural commodity, which is illustrated by a steady increase in U.S. and worldwide annual production (Figure 1.1). The total global production is currently estimated at over 137 million metric tons, with the major producers being the United States, Brazil, China, Argentina, and India (Figure 1.2). In any given year, U.S. farmers produce about half of the total world soybean crop.

Soybeans are the dominant oilseed in both the U.S. and world markets (Figure 1.3). However, a report on the history of soybean oil (Dutton, 1981) stated that it was considered as a poor quality oil in the early 1940s, more appropriate for use in industrial paints rather than in food use. The increase in the popularity of soybean oil,

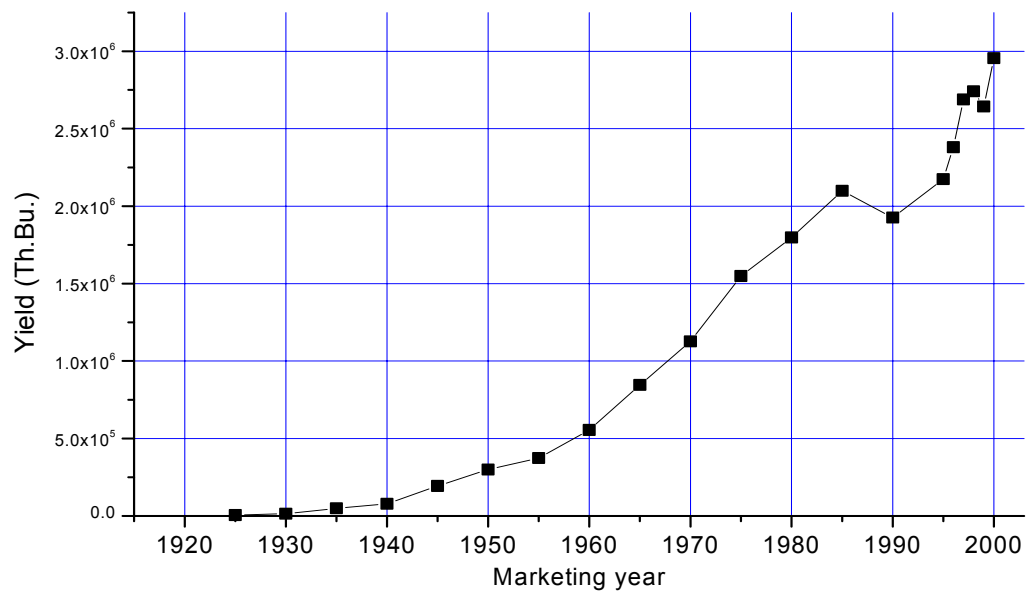


Figure 1.1 Total annual soybean production in the United States. Data adapted from Soya & Oilseed Bluebook (2001).

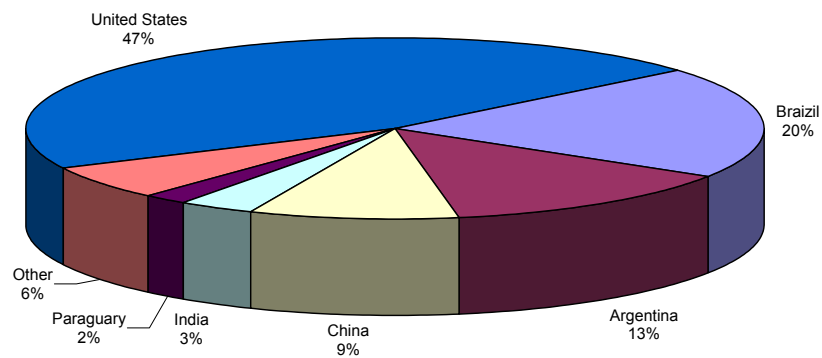


Figure 1.2 Market share of world soybean production between 2000 and 2001. Total estimated world production: 155.8 million metric tons. Data adapted from Soya & Oilseed Bluebook (2001).

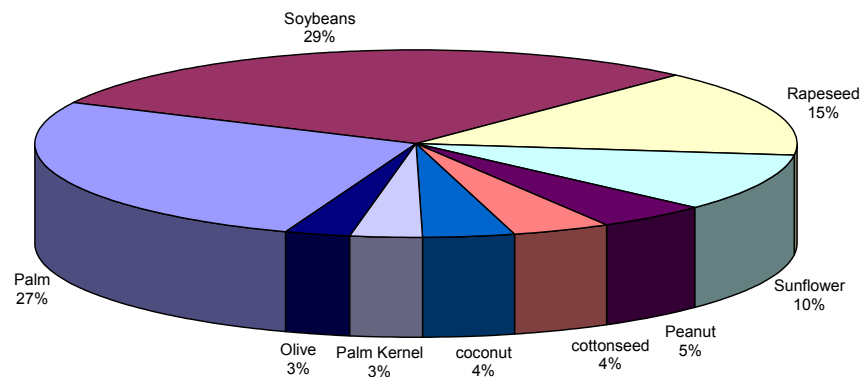


Figure 1.3 Market share of world vegetable oil production between 2000 and 2001.
Total estimated world vegetable oil production: 82.7 million metric tons.
Data adapted from Soya & Oilseed Bluebook (2001).

from the minor edible oil of the 1940s to the major food oil of the 1990s, was in part due to other desirable soybean characteristics, such as, the high quality of the soybean protein meal and the high soybean yields. The high yields led to reduced prices of soybean products. Above all, the improved understanding of lipid chemistry and the development of enhanced oil processing technology were the most vital factors promoting the success of soybean oil as a food grade product. Modern soybean oil is a stable, high quality triglyceride that is widely used in commercially processed foods. It is free of other lipids; i.e.; phosphatides; contaminants; and available at a reasonable cost.

1.2 Molecular properties of soybean oil

Soybean contains appropriately 20% oil. This is the second highest lipid content among all food legumes. The highest oil content is found in peanut, which is about 48% oil on a dry matter basis (Salunkhe et al., 1983). During seed development, soybeans store their lipids, mainly in the form of triglycerides, in an organelle known as the oil body. Refined soybean oil contains more than 99% triglycerides (Table 1.1). Triglycerides are neutral lipids that consist of three fatty acids linked via ester bonds to glycerol. Functional properties, such as, oxidative stability, and the nutritional value of edible oils in general and soybean oil in particular are determined by their fatty acid composition, molecular configuration, and position of fatty acids within the triglycerides. Like many other oils of plant origin, soybean oil contains primarily unsaturated fatty acids. The fatty acid with the highest percentage in soybean oil is linoleic acid, followed in a decreasing order by oleic, palmitic, linolenic, and stearic acid (Wang et al., 2001).

Table 1.1 Typical composition of crude and refined soybean oil. Data adapted from Pryde (1980).

Components	Unit	Crude oil	Refined oil
Triglycerides	%	95-97	>99
Phosphatides	%	1.5-2.5	0.003-0.045
Free fatty acids	%	0.3-0.7	<0.05
Unsaponifiable matter	%	1.6	0.3
Plant sterols	%	0.33	0.13
Tocopherols	%	0.15-0.21	0.11-0.18
Hydrocarbons	%	0.014	0.01
Trace metals			
Iron	Ppm	1—3	0.1-0.3
Copper	Ppm	0.03-0.05	0.02-0.06

Physical properties of soybean oil depend on its molecular properties, for example, the longer the chain length of a fatty acid, the higher its melting point. Introduction of a double bond into the fatty acid chain can significantly lower the melting point of the lipid (Cahoon et al., 1997). Oils that contain a high percentage of saturated fatty acids have a high melting point, giving a semisolid or solid appearance, whereas, those containing a high percentage of unsaturated fatty acids have a low melting point, thus giving them a liquid appearance.

The distribution of fatty acid within the triglycerides is another important parameter. The position of fatty acids in typical soybean triglyceride is not random. The position of the carbon atoms in the glycerol moiety of a triglyceride can be described using the stereospecifically number (SN) 1, 2, or 3 (Figure 1.4). According to Evans et al. (1969), it is based on the following rules: (1) saturated fatty acids (mainly palmitic and stearic acids) and those with chain length greater than 18 carbons are first distributed equally and randomly on positions 1 and 3; (2) oleic and linolenic acids are treated alike, or as a unit, and distributed randomly and equally on all three positions; and (3) all remaining positions are filled by linoleic acid.

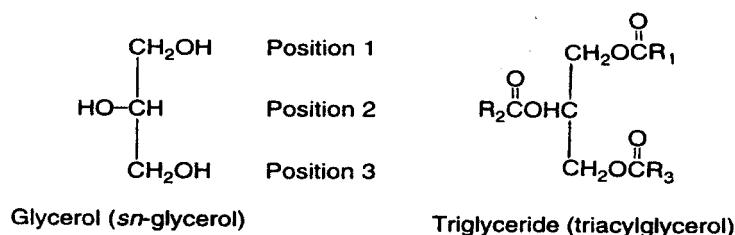


Figure 1.4 Molecular structure of glycerol and triacylglycerol showing their SN positions.

1.3 Methods of Soy Oil Extraction

1.3.1 Mechanical extraction

Mechanical extraction to remove the oil from seeds is often the preferred choice, especially, if a variety of oilseeds are to be processed (Hancock, 1995; Menconi and Bioli, 1998). Lipid is forced out from soybean seeds by the high pressure generated by the mechanical extraction equipment. This method can be applied for cold pressed oils and for seeds that have a high oil content (Irfan and Pawelzik, 1999). Low initial cost, the absence of solvent requirements, and a high operational safety are the obvious advantages. However, this method is not capable of obtaining a high oil yield from oilseeds. In many cases, the leftover oil content in the cake can be as high as 8% (Anderson, 1996).

In the mechanical extraction process, the main operational parameters are pressure and temperature: the higher the pressure and temperature, the more oil that can be extracted. If high pressure is applied at room temperature in the soybean oil extraction process, it is difficult to obtain more than 10% oil from the oil seeds (Li, 1999). This has been explained by the oil viscosity that cannot be significantly decreased at low temperature. Furthermore, the rate of oil extraction is also affected by the viscosity, a hydrokinetic property (Bredeson, 1978).

Mechanical extraction is based primarily on physical changes. Raw material volume is significantly reduced; the oil is forced out; trace water is evaporated; the oil viscosity decreases continuously; and the solids, pigment, and colloidal content in the oil increases gradually. In addition, a series of chemical changes occur: the colloidal structure is partially damaged; proteins are denatured and may react with other compounds. At the

same time, unstable compounds that are composed of protein and free fatty acid or phosphatide can decompose, which can increase the impurity of the oil.

1.3.2 Solvent extraction

In the western world, solvent extraction is the most widely used method to extract oil from oil seeds. Most commercial oil extraction plants currently use hexane as a solvent, but other solvents have recently been considered (Freidrich and Pryde, 1984; Baker and Sullivan, 1983; Karnofsky, 1981). Snyder and Kwon (1987) reviewed the desirable properties of an oil solvent. Ideal solvent properties would be high triglyceride selectivity, no toxicity of residues in the oil, a low specific heat, low heat of vaporization, and low reactivity with the oilseeds and the extraction equipment. The ideal solvent should not be flammable or explosive and should be available in large quantities at a low price.

Such an ideal solvent is nearly impossible to find, but hexane fulfills many of the requirements so as to be widely used for soybean oil extraction. A recent risk assessment of hydrocarbon solvents in oil processing claimed hexane to be as safe as other hydrocarbons (Galvin et al., 1995). However, it should be noted that hexane is explosive, flammable, and expensive. Studies over the past several years have thus focused on investigating alternative solvents.

Alcohols have been proposed as an alternative solvent to hexane, although the solubility of triglyceride in alcohol is very low. Oil solubility can be greatly improved by increasing the temperature. In this case, oil that is extracted at high temperatures can be

phase-separated from the solvent by cooling the system below the solubility line. The remaining residual oil in the solvent that can be stripped out at a lower cost less than that of solvent removal from the whole crude oil (Johnson and Lusas, 1983).

Aqueous isopropanol has been studied as an extracting solvent by Baker and Sullivan (1983). The authors showed that azeotrope of 87.7% isopropanol and water was effective at 77°C and the oil phase was separated by cooling to 30°C. The extracted oil contained less phospholipids and free fatty acid than oil obtained via hexane extraction. However, the efficiency of the process was limited by the inability to recover isopropanol in greater concentrations than the water azeotrope (Lusas et al., 1994). An integrated distillation process was proposed in 1994 to improve the recovery (Lusas et al., 1994). Later studies investigated the use of membranes to improve isopropanol recovery instead of plate and frame membranes (Lusas et al., 1995).

Supercritical carbon dioxide has been used as a potentially safe, nontoxic solvent at the USDA Northern Regional Center in Peoria, Illinois. Oil extracted with supercritical carbon dioxide contained less phospholipids than hexane extracted oil. Moisture content and particle size were shown to influence the extraction rate and oil yield at 50°C and 5.6×10^7 Pa (Snyder et al., 1984). However, supercritical carbon dioxide extraction is associated with high cost. The increased expense of carbon dioxide extraction is due to the required equipment and the need to generate high pressure (7×10^6 - 7×10^7 Pa). Efforts have therefore focused on reducing the costs of the process (Reverchon and Osseo, 1994).

1.4 Ultrasound

1.4.1 Introduction of ultrasound

Ultrasonics is the name given to the study and application of sound waves with frequencies higher than those to which the human ear can detect. It is mechanical waves with frequencies between 16 kHz and 100 MHz (Cains et al., 1998; Mason and Cordmas, 1996). Ultrasound has been utilized by animals for millions of years (Astrup, 1999). For example, bats and dolphins use low-intensity ultrasonic pluses to determine the size, shape, and velocity of insects and fishes. Furthermore, certain marine species use high-intensity pulses of ultrasound to stun their victims prior to capture. As in nature, the subject can be divided into two sections, one dealing with low-amplitude vibration and the other with high energies. Low-amplitude ultrasound is concerned with the effect of the medium on the waves; permanent changes in the media do not take place. In high-energy application, however, the waves cause changes in the physical properties of the medium. Ultrasound waves with low intensities in the MHz range are primarily used for diagnostic purposes. Ultrasound waves in the kHz range with large amplitudes are called power ultrasound or high-intensity ultrasound and are used to alter material properties. Applications include cleaning, drilling, acceleration of chemical reactions, and the production of emulsions. The effect through direct interaction with the ultrasonic waves or indirectly through cavitation.

1.4.2 The physics of ultrasound

The acceleration and initiation of chemical reactions in an ultrasonic field is closely related to the phenomenon of “cavitation” (Mason et al., 1996). “Cavitation” means the

formation of cavities in the liquid and their subsequent collapse, which is accompanied by intense hydraulic shocks. A cavitation bubble is formed if the pressure in a particular volume inside the liquid temporarily falls below the threshold of the vapor pressure of the liquid. The intense hydraulic shock waves resulting from the collapse of the cavities can have an enormous destructive pressure. For instance, cavitation on the blades of a rapidly rotating propeller screw of a ship or hydraulic turbines can destroy the material from which the screw is made.

When high intensity ultrasonic waves are propagated through a liquid, a disruption of the continuity of the liquid with the formation of a cavity may occur at sites of rarefaction (negative pressures). The cavity formed is the vapor of the surrounding liquid. Gases dissolved in the liquid can diffuse into the cavity. The gas bubble formed in the rarefaction phase collapses fairly rapidly in the next compression cycle.

Cavitation bubbles do not appear instantaneously at sites of rarefaction. An extremely short, but nevertheless definite, time is required. Hardcastle et al. (2000) reported that the bubbles grow and collapse within a few microseconds. The duration of the low-pressure phase, during which cavitation bubbles grow, decrease with increasing ultrasonic frequency. This explains why larger amplitudes of ultrasonic vibrations are required to generate cavitation at high frequencies. At very high frequencies (15 MHz), no cavitation is observed even when the ultrasonic intensity reaches several thousand watts per square centimeter (Noltingk and Neppiras, 1950).

Under the influence of ultrasound, gas bubbles suspended in a liquid medium undergo periodic compression and expansion, i.e., they pulsate with a specific frequency. This frequency is given by the equation:

$$f_0 = \frac{1}{2\pi R_0} \sqrt{\frac{3\gamma p_0}{\rho}} \quad (1)$$

where R_0 is the resonant cavity size, f_0 is the wave frequency, γ is the special heat ratio of the gas, p_0 is the total pressure, and ρ is the density of the media. This equation explains why high-intensity ultrasound equipment usually operates at low frequencies: cavitation bubbles can grow larger at low ultrasonic frequencies.

1.4.3 Applications in food technology

The application of ultrasound in the food industry has been a subject of intense research and development for many years. Until several years ago, the main application of ultrasound involved non-invasive analysis with particular reference to food quality assessment. For example, monitoring the attenuation of an ultrasound pulse can be used to determine the degree of homogenization of fat within milk (Miles et al., 1990). By measuring the ultrasound velocity in conjunction with attenuation, the particle size distribution in emulsions can also be determined (Javanaud et al., 1991). Recent researches on applications of ultrasound in food industry have been varied:

Measurement of thickness: Ultrasonic devices are commercially available that can accurately measure the thickness of materials, particularly, materials that are difficult to characterize using conventional techniques. Examples include pipes, chocolate layers on

confectionery, fat or lean tissue in meat, and liquids in a can, and egg shells. (Javanaud, 1988; Povey and McClements, 1988)

Determination of creaming and sedimentation profiles: The ultrasonic velocity and/or attenuation coefficient is a function of sample height and time. The ultrasonic parameters are then converted into the physical property of interest (e.g., particle concentration or size) using appropriate mathematical equations. This technique should be particularly useful for studying the instability of dairy emulsions, fruit juices, mayonnaises, cream liqueurs, and salad creams (Howe et al., 1986; McClements, 1995).

Effect on living cell: Prolonged exposure to high intensity ultrasound has been shown to inhibit the catalytic activity of a number of food enzymes. High intensity ultrasound has also been used to facilitate the microbial decontamination of various types of food products. This has been explained in terms of the intense pressures, temperatures and shear forces generated by the ultrasonic waves (Zhu, 1998).

Effect on extraction processes: The experiment conducted by Mason et al. (1996) on the use of ultrasound to extract tea solids from leaves showed that the efficiency of ultrasonic extraction was greater than simple thermal extraction and it also reduced the process time.

Tenderization of meat: High intensity ultrasound wave can lead to improved functional properties of meat products, such as, water-binding capacity, tenderness, and cohesiveness. It has been suggested that ultrasound releases myofibrillar proteins, which

are responsible for binding the pieces of meat together in formed meat products (Pohlman et al., 1997; Troy, 1994).

Ultrasonic emulsification: One of the basic applications of high intensity ultrasound in processing is emulsification. Such emulsions are often more stable than those produced with conventional method and often require less surfactant (Mongenot et al., 2000; Zayas, 1985).

1.4.4 Effects on extraction processes

Application of power ultrasound can significantly improve the kinetics of solvent extraction of organic compounds contained within the body of plants and seeds (Mason et al., 1996). For example, Wang and Goldblith (1974) showed that a continuous process in which the sonication of the slurry by a 550 W probe operating at a 20 KHz frequency was used to extract protein from defatted soybeans resulted in an efficient extraction that exceeded any previously used technology. The mechanical effects of ultrasound improve mass transfer process because 1) power ultrasound provides a greater penetration of solvent into cellular materials and 2) power ultrasound in extractive processes results in the disruption of biological cell walls and facilitates the release of contents (Chendke and Fogler, 1975).

1.5 Microwave

1.5.1 Introduction of microwave heating

Microwaves can be described best as radio waves with very short wavelength, between 300 MHz and 30 GHz. In relation to other radio frequencies, microwaves lie between television and infrared frequencies (Figure 1.5).

Microwaves thus have similar properties as infrared and light waves; they can be reflected, transmitted and absorbed. The energy of microwaves stems from electrical energy that is converted to microwave via a microwave power tube or generator. For commercial foodservice and for home use, a frequency of 2450 MHz is the current standard. The main application of microwaves in foodservice is based on their ability to heat products. The following is a list of advantages of microwave heating compared to conventional heating.

1. It is a fast process. Heating rate is significantly higher than for conventional heating.
2. Temperature profile is generally more uniform than in conventional heating.
3. It is a fast process. Heating rate is significantly higher than for conventional heating.
4. It is selective; moist areas are heated more rapidly than the dry spots. Such selectivity is absent in conventional heating.
5. It can be instantly turned on or off, unlike conventional heating.

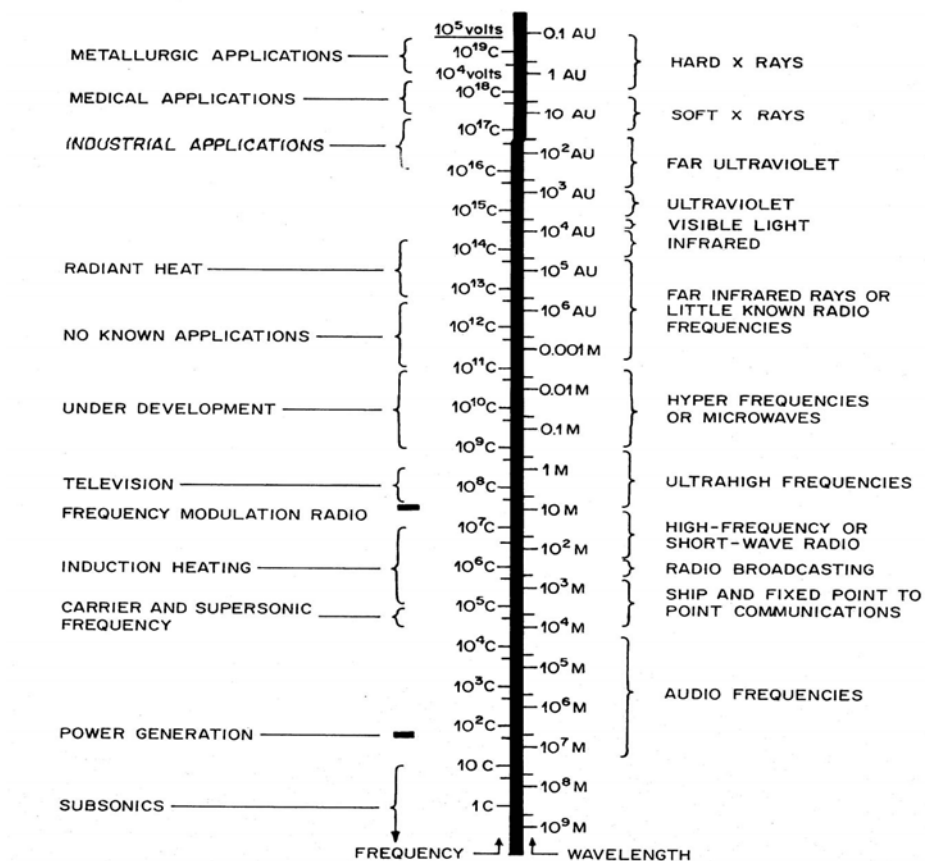


Figure 1.5 The electromagnetic frequency spectrum. [C-cycles per seconds; AU-Angstrom units ($1 \text{ \AA} = 10^{-10} \text{ m}$)]

Due to these special characteristics, microwave heating has become pervasive in commercial foodservice applications.

1.5.2 The physics of microwave heating

Materials absorb microwave energy which is then converted into heat. In foods, it is primarily polar molecules that interact with microwaves to produce heat.

Water is the most common polar molecule and is a major component in many foods. In the presence of a microwave field, water molecules attempt to orient themselves with

the microwave field in much the same manner as iron fillings become oriented with a magnetic field. Since the microwave field is reversing its polarity with every cycle, millions of times each second, the water molecules attempt to reorient themselves millions of times each second. In doing so, considerable kinetic energy is converted into frictional energy resulting in an increase in temperature.

Ionic conduction is another important microwave heating mechanism. Ions, being electrically charged, interact with microwave fields. Ions in solution move towards the direction of the electromagnetic field of microwave. Upon field reversal, the orientation is reversed. Ionic conduction can occur in cellular fluids when animal or vegetable tissues are exposed to microwave energy.

1.5.3 Microwave properties of foods

The energy that can be absorbed by a substance is expressed by the relationship

$$P = \sigma E^2 \quad (2)$$

where P is the energy absorbed in watts/cm³, σ is the equivalent dielectric conductivity and E is the voltage gradient in volts/cm. The dielectric conductivity, σ is given by

$$\sigma = 2\pi\epsilon_0\epsilon''f \quad (3)$$

where f is the frequency of the energy source, ϵ_0 is the dielectric constant of vacuum (8.85×10^{-12} farads/m), and ϵ'' is the dielectric loss factor of the substance. Since the field strength (E) and the frequency are essentially constant in industrial microwave ovens, the loss factor (ϵ'') is the only variable of importance. The loss factor depends on the material being processed. A “lossy” material is one that heats well in microwave field, while a

“low loss” material is one that heats poorly. The loss factor is a measurable quantity and a considerable amount of dielectric loss factors of different materials have been accumulated (Bengtsson and Risman, 1971; Kent, 1987; Mudgett et al., 1974; Ohlsson et al., 1974).

Wang and Goldblith, (1974) noted that the loss factor varies with temperature and frequency. They also pointed out that penetration of microwave power decreases dramatically at lower frequencies if the temperature increases, even though the temperature dependence at 2450 MHz is relatively small. Thus, the choice of 2450 MHz as a heating frequency has proven to be advantageous since at this frequency, there is less sensitivity to moisture and salt content as well as temperature.

The main difference between microwave heating and other heating methods is that microwaves penetrate deeply into food materials and the waves are converted to heat as they propagate through the material. Unlike in any other appliances, microwave heats food internally rather than just at the surface. Consequently, a great variety of new food products have been developed specifically for the microwave oven.

In addition to the dielectric properties of foods, the following other factors affect microwave heating performance.

Geometry: The shape of a food items is critical to the microwave heating results. When the diameter is increased beyond a critical value, it may be impossible for center heating to occur except via conduction. Risman and Ohlsson (1987) reported that

microwave heating at 2450 MHz can be concentrated in the center of spheres with diameters that measure between 20 and 60 mm.

Surface to volume ration: The greater the surface area, the faster that cooking occurs. Thus, foods can be cooked faster if they are diced.

Thermal conductivity: Thermal conductivity is a measure of a material's ability to transfer heat in response to a temperature difference. Microwave heating is able to raise the temperature in a frozen food. It should be noted that at some point, the product specific heat begins to increase rapidly so that external layers of the food become completely thawed. These outer food layers then behave as a resistance to further deep microwave heating.

1.5.3 Applications in Food Technology

Precooking: One of the most successful applications of microwave heating in food processing is the microwave precooking of bacon. There are now well over 30 continuous microwave bacon cookers operating in the United States, using large microwave power oven and having large product outputs (Venkatachalam et al., 2002).

Baking: Baking is one of the microwave processing operations that would be expected to be widespread in food industry (Nykvist and Decareau, 1976). An early application of microwave to baking was described by Fetty (1966) as part of a proof-baking system. A highly successful commercial proofing procedure was developed by DCA Food Industries (Schiffmann, 1992). This process replaces the usual, slow,

inefficient batch or continuous conventional proofers with a straight-line microwave conveyor, which reduced the total proofing time from 45 to 4 min.

Drying: One of the great advantages of microwave drying is fast rate of the process. Materials can often be dried in less than 10% of the normal drying time. Microwave drying involves a completely different mechanism compared to the traditional oven drying or natural sun drying. As a result of the internal heat generated by the microwave field, there exists an internal pressure gradient which effectively pumps water to the surface. In conventional drying, drying rate is limited by the rate at which water or other solvents diffuse from the interior of the food material to the surface from where it evaporates. It is usually not a good idea to try to dry too quickly since the surface may overdry, case harden, or crack because the interior water cannot reach it quickly enough.

Sterilization: Microwave sterilization can deliver products returning good flavor because microwaves are able to heat the product 3-5 times faster than conventional sterilization systems. The microwave-sterilized product is not temperature abused, so the food looks better, has better texture, and tastes better than products processed by any other available technology (Harlfinger, 1992).

1.6 Gas Chromatography

Chromatography is a separation method that relies on differences in partitioning behavior between a flowing mobile phase and a stationary phase to separate the components in a mixture. A column holds the stationary phase and the mobile phase carries the sample through it. Sample components that partition strongly into the

stationary phase spend a greater amount of time in the column and are separated from components that stay in the mobile phase predominantly and pass through the column faster.

As the components elute from the column they can be quantified by a detector and/or are collected for further analysis. An analytical instrument can be combined with a separation method for on-line analysis. Examples of such "hyphenated techniques" include gas and liquid chromatography with mass spectrometry (GC-MS and LC-MS), Fourier-transform infrared spectroscopy (GC-FTIR), and diode-array UV-VIS absorption spectroscopy (HPLC-UV-VIS).

Gas chromatography (GC) involves a sample being vaporized and injected into the head of the chromatographic column. The sample is transported through the column by the flow of an inert, gaseous mobile phase. Most columns contain a liquid stationary phase on a solid support (Figure 1.6).

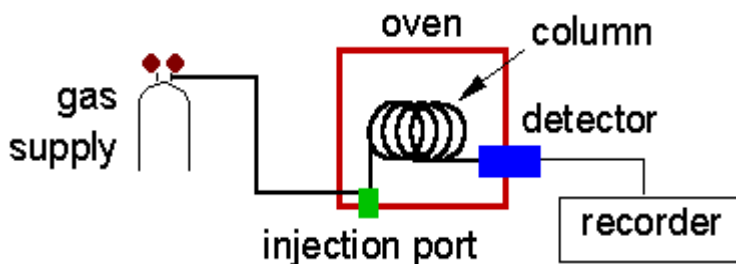


Figure 1.6 Schematic diagram of gas chromatography.

Mobile phases are generally inert gases such as helium, argon, or nitrogen. The injection port consists of a rubber septum through which a syringe needle is inserted to inject the sample. The injection port is maintained at a higher temperature than the boiling point of the least volatile component in the sample mixture. Since the partitioning behavior is dependant on temperature, the separation column is usually contained in a thermostat-controlled oven. Separating components with a wide range of boiling points are accomplished by starting at a low oven temperature and increasing the temperature over time to elute the higher-boiling point components. Separation of low-molecular weight gases is accomplished with solid adsorbents.

For any GC analysis, the sample must be volatile and in many cases requires that a suitable derivative be obtained before analysis. GC has been well established as a powerful tool in lipid research. The high resolving power, speed of analyses, sensitivity and adaptability to automation make GC a highly desirable technique. Since all of the fatty acid (FA) components are similar in structure, the boiling point is largely determined by the molecular weight (MW). Thus, retention time is primarily determined by the MW of the component. In any given analysis, the temperature is initially low, and so higher MW components condense first at the column head. As the temperature is increased, the components are vaporized at their effective boiling points and carried through the column. The efficiency of the separation is such that glyceride components that differ by only two carbon atoms can be completely resolved.

Accurate determination of fatty acid (FA) compositions of different matrix-bound FAs is a predominant problem in total fat extraction. The classic steps to determine FAs

include extraction of a particular sample with organic solvents, followed by transesterification of the isolated lipid to form fatty acid methyl esters (FAME) and quantification of FAMEs by gas-liquid chromatographic analysis.

2 Methods

2.1 Moisture Conditioning

Soybeans can be safely stored at less than 10% moisture content (Moisture content is in percent wet basis unless otherwise stated.); however, in industry and laboratory processing, moisture content is between 10% and 14%. If the moisture content exceeds 14%, soybeans are hard to grind; at moisture content below 14%, ground soybean particles are not be uniform with a large amount of fine particles that are not suitable for oil extraction.

A single kernel moisture tester (Shizuoka Seiki CRT-160E Single Kernel Moisture Tester, Japan) was used to measure the soybean moisture. The system allowed for quick testing of batches of grains while individually measuring each grain. Samples were placed within the unit and then fed through rollers where they were crushed. Moisture was then measured through their electrical resistance.

2.2 Extraction

Extraction is the key step in this research that ultimately evaluates the effects of ultrasound and microwave assistance, different extractants, and different soybean varieties. Two essential problems are important in the investigation of extraction processes: the choice of the extractant and the effect of process variables on the extraction. The solution of the first problem, apart from stability of the extractant and certain specific requirements relevant to technological application, such as specific gravity, boiling point and viscosity, lies in the investigation of the extractive capacity of

various compounds as a function of their molecular structure and their active functional groups. During this research, hexane, isopropanol, and a mixture (60%:40% v/v) of the foregoing two solvents were used as extractant.

2.2.1 Ultrasound-assisted extraction

A generator converts electricity into the required high frequency alternating current, which is then used to drive the transducer assembly. The transducer element (Figure 2.1) converts the high-frequency alternating current into mechanical vibrations. Design of the transducer is based on piezoelectric technology. The geometry of a piezoelectric crystal changes with applied electric current. The shape and dimensions of the sandwich transducer assembly is dependent on its working frequency thus, a 20 kHz assembly is twice the length of a 40 kHz transducer due to wavelength considerations. The power available through a given transducer changes inversely with the square of the frequency. Thus high power equipment usually operates at lower frequencies.

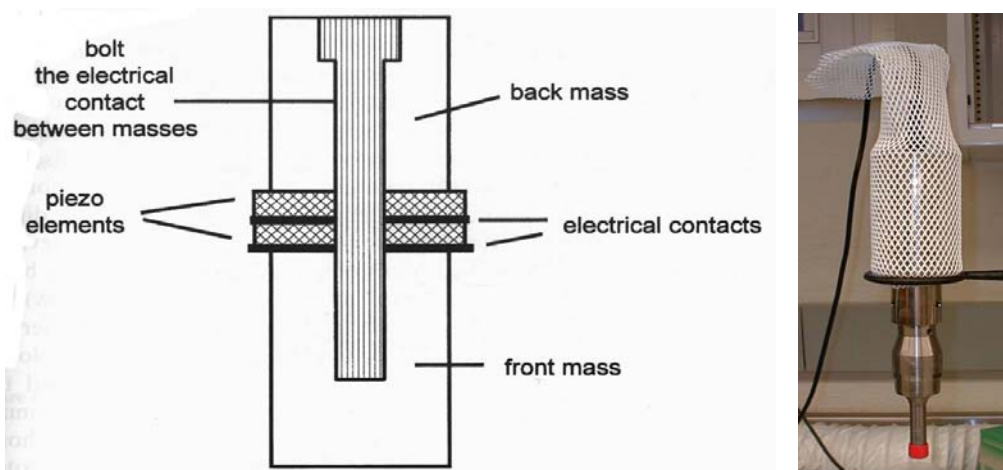


Figure 2.1 Principle setup of the high-intensity ultrasonic transducer unit.

2.2.3 Microwave-assisted extraction

Microwave heating results from interactions of the chemical constituents of foods with an electromagnetic field. These interactions lead to instantaneous heat generation within the product due to “molecular friction.” This friction results from the disruption of weak hydrogen bonds associated with the dipole rotation of free water molecules. The friction is also caused by the electrophoretic migration of free salts in an electrical field of rapidly changing polarity. These effects are predominantly related to the aqueous ionic constituents of food and their associated solid constituents.

2.3 Gas Chromatography Analysis

Oil quality was analyzed by a Hewlett-Packard 6890 gas chromatograph (Agilent Tech. Inc., Wilmington, DE, U.S.) (Figure 2.2) with cold on-column injection on a capillary column HP-2980 (30 m × 0.25 mm × 0.1 μm) and with detection by flame ionization.



Figure 2.2 Hewlett-Packard 6890 gas chromatograph.

Fatty acid methyl esters (FAME) were prepared by AOCS official method Ce 2-66 (AOCS, 1998):

1. Accurately weigh a test portion of sample (approximately 200 mg) into a stoppered-glass centrifuge vial.
2. Add 2.0 mL of hexane followed by 0.1 mL of 2 N methanolic KOH.
3. Close the vial and shake well for 30 s then centrifuge.
4. Remove two drops of the upper layer and dilute with 2.0 mL of hexane.
5. The concentration of the FAME in hexane is approximately 0.5%.

For GC, a temperature program was set with injection at 130°C, rising at 3°C/min. to 210°C and with a 10 min. holding. The detector temperature was set at 250°C. Helium carrier-gas column flow rate was 1.8 mL/min., and make-up gas flow rate was 30 mL/min. The flow rate of hydrogen and air was 40 mL/min. and 400 mL/min., respectively. Prepared FAME (2 µl) was introduced into the GC with split ratio of 1:10. Peak areas were then calculated with data collection being managed by HP Chem. Station software. The soybean oil quality change was reflected by unsaturated fatty acid and saturated fatty acid content ratio. The fatty acid content in oil was the integrated peak area in GC graph.

3 Ultrasound-assisted Extraction of Oil from Soybeans

3.1 Abstract

A laboratory-scale ultrasound assisted soybean oil extraction procedure was developed and evaluated. Ultrasound-assisted extraction was found to be a simpler and more effective alternative to conventional methods for soybean oil extraction. Two different soybean varieties (TN 96-58, N 98-4573) were used in the experiments. Oil was extracted using three different solvents [hexane, isopropanol, and mixed extractant (hexane:isopropanol 60%:40%, v/v)] under direct sonication by an ultrasonic probe at intensity levels ranging 16.4 Wcm^{-2} to 47.6 Wcm^{-2} and also using the traditional solvent extraction procedure without ultrasound application. It was found that the ultrasound-assisted extraction of oil from soybeans yielded distinctly more oil than the traditional method regardless of soybean variety. A higher sonication power intensity level allowed for greater oil extraction than the lower power intensity level. The solvent influenced the effectiveness of sonication enhancement, i.e., the oil yield extracted by this procedure was highest when using the isopropanol-hexane solvent mixture. Fatty acid profile analysis measured by GC indicated that the oil quality did not appreciably change from conventionally extracted oil when ultrasound assistance was used.

3.2 Introduction

According to the a survey in Soya & Oilseed Bluebook (Soyatech, Inc., 2001), soybean has already become the dominant oilseed in the world vegetable oil market due to its high oil content and low cost accounting for 29% of vegetable oil production in

2000. Therefore, any improvement in soybean oil processing technology can lead to a market increase in the soybean industry efficiency and profitability.

Currently, Solvent extraction is the most widely used method for obtaining high quality oil in the world oil industry. The traditional techniques of solvent extraction of lipid materials are primarily based on the appropriate choice of solvents and the use of heat and agitation to increase the solubility of lipid compounds and improve mass transfer.

It is well known that the choice of solvent used in extraction can have a marked influence on the results of the process. Snyder and Kwon (1987) reviewed the desirable properties of solvents and concluded that the ideal solvent should be a triglyceride selective suitable for oil extraction only, leave only nontoxic residues in the oil, have a low specific heat and a low heat of vaporization, be unreactive with both oilseeds and extraction equipment, will not explode or ignite, and be cheap and readily available in large quantities.

Most solvents do not fulfill all these criteria. However, hexane, a nonpolar solvent, has most of the desirable properties and is widely used for soy oil extraction. Unfortunately, hexane is explosive, flammable, and expensive, which are significant drawbacks in large scale extraction processes. Other solvents have been considered in both laboratory and industry, for example, alcohol (Karnofsky, 1981), isopropanol (Baker and Sullivan, 1983), and carbon dioxide (Freidrich and Pryde, 1984).

Long extraction times and low efficiency are the most obvious disadvantages of the traditional extraction method. Recently, various investigators have shown that application of high intensity or power ultrasound can be used to enhance the extraction of phytochemicals from plant sources while reducing processing time and solvent consumption (Mason et. al., 1996; Vinatoru et al., 1997; Schafer, 1998). High intensity ultrasound (20-100 kHz, 10-100 Wcm⁻²) is an efficient processing technology that is increasingly used in the food industry, such as, in sterilization, homogenization, emulsification, and extraction. Although ultrasound technology has been widely used in chemical engineering and material science, not much research has been conducted to investigate the potential of using power ultrasound to improve soybean oil extraction.

Based on the research of Leadley and Williams (2001) and Ren and Allen (2001) on the ultrasound-assisted extraction, it appeared that ultrasound could also be used to enhance extraction of lipids from plant seeds like soybean. An improved oil extraction yield could enhance profits to soybean farmers and reduce processing costs. Thus, the objective of this study was to compare the yield, composition, and quality of extracted soy oil obtained through traditional and ultrasound-assisted oil extraction methods. The effects of different solvents and ultrasound intensities on the ultrasound-assisted extracted soybean oil were evaluated.

3.3 Materials and Methods

3.3.1 Materials

Two soybean varieties, TN 96-58 and N 98-4573, were used in this study. TN 96-58 is one of the most popular varieties planted in Tennessee while N 98-4573 is a special

variety with a modified fatty acid profile being bred by researchers in North Carolina. Both varieties were obtained from the crops laboratory at The University of Tennessee. Soybean moisture content was determined using a single kernel moisture tester (CRT-160E, Shizuoka Seiki, Japan).

AOCS Mix No.3, A fatty acid standard, was purchased from Alltech Corp. (Deerfield, Illinois, U.S.). This was used in the GC analysis. The standard was diluted to 10 mg/mL in hexane and kept in a well-closed container in refrigerator (4 °C).

Hexane and Isopropanol used in the oil extraction were purchased from Fisher Scientific (Fair Lawn, New Jersey, U.S.).

Power ultrasound applied in this research was generated by sonicator (S3000, Misonix Incorporated, Farmingdale, New York, U.S.)

3.3.2 Methods

1 Soybean Cleaning

During harvesting, drying, transportation, and storage, foreign material, such as small stones, sand, and plant leaves, may unavoidably be mixed with soybeans. These foreign materials affect extraction efficiency, and oil quality, in addition to potentially damaging equipment. Raw soybeans were therefore cleaned using the grading procedure of the Federal Grain Inspection Service (FGIS, 1999). Cleaning was done in 125 g units using a sieve set consisting of a 10/64-in. x 3/4-in. slot-hole sieve placed on top of an 8/64-in. round-hole sieve. The soybeans were poured into the center of the top sieve. The sieves and bottom pan were then held level. Using a steady motion, the sieve set was

moved from right to left approximately 10 in. five times to complete one sieve operation. All soybeans on the 8/64-inch round-hole sieve and on the 10/64 x 3/4-in. slotted-hole sieve were collected and used in the subsequent experiments.

2. Soybean Conditioning

Moisture content is a critical parameter in soybean processing both in industry and laboratory. Moisture content for oil extraction should be between 10% and 14%. If the moisture content exceeds 14%, soybeans are hard to grind; at a moisture content below 10%, ground soybean particles will not be uniform. The presence of a large amount of fine particles is not suitable for oil extraction processing.

The cleaned, raw soybeans at a moisture content of about 8% were packaged 2 kg/bag and kept in an environmental chamber adjusted to room temperature. Moisture content of soybeans was measured every two hr using the single kernel moisture tester until final moisture of 11% was reached. The conditioned soybeans were then kept in a sealed, insulated box that was adjusted to room temperature for future use.

3. Grinding

The cleaned and conditioned soybean seeds were ground using a hammer mill (Standard Model No.3, Arthur Thomas Co., Philadelphia, PA, U.S.A.) running at 478 RPM. A stainless steel screen with a mesh size of 4 mm was used to obtain a uniform soybean particle size. The ground soybeans consisting of both the ground seed and hull were kept in air tight plastic bags until used.

Table 3.1 Experimental treatment factors in ultrasound-assisted extraction evaluation.

Soybean Variety	Solvent Variety	Power Level	Reaction Time (hr)					
			0.5	1.0	1.5	2.0	2.5	3.0
TN 96-58	Hexane	16.4 Wcm ⁻²	✓	✓	✓	✓		✓
		20.9 Wcm ⁻²	✓	✓	✓	✓	✓	
		47.6 Wcm ⁻²	✓	✓	✓	✓		✓
		Control	✓	✓	✓	✓		✓
	Isopropanol	20.9 Wcm ⁻²	✓	✓	✓	✓		✓
		Control	✓	✓	✓	✓		✓
	Mixed Solvent	20.9 Wcm ⁻²	✓	✓	✓	✓		✓
		Control	✓	✓	✓	✓		✓
N 98-4573	Hexane	20.9 Wcm ⁻²	✓	✓		✓		✓
		Control	✓	✓		✓		✓

4 Extraction and Sonication Procedure

Experimental treatment factors investigated in this study are listed in Table 3.1. All extraction tests were undertaken in triplicate. Levels of ultrasonic wave intensity used were 16.4 Wcm⁻², 20.9 Wcm⁻², and 47.6 Wcm⁻². Extraction using the traditional procedure served as the control. The solutions were sonicated for 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 hr, respectively.

The intensity of the generated ultrasonic wave was determined using a calorimetric method with water as the test solution (Mason, 1990). For each solution, the temperature T was recorded with a thermal couple as a function of time under adiabatic conditions. From temperature versus time data, the initial temperature rise dT/dt was determined by polynomial curve fitting. The absolute ultrasonic power P was then given by

$$Q = mc_p \left(\frac{dT}{dt} \right) \quad (4)$$

where m is the mass (100 g) and c_p is the heat capacity of water ($4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$). The intensity of ultrasonic power dissipated from a probe tip with radius r is then given by (Mason et al., 1996)

$$I = \frac{P}{\pi r^2} \quad (5)$$

For input power levels of 90, 120, and 180 W, the calculated intensities were 16.4 Wcm^{-2} , 20.9 Wcm^{-2} , and 47.6 Wcm^{-2} , respectively.

The 150 mL solvent was mixed with 100 g ground soybean in a 600 mL plastic beaker. The ultrasound probe was lowered into the mixture about 2/3 depth below the mixture surface for ultrasound pretreatment. The solution was gently and constantly stirred by means of a laboratory stirrer.

5. Distillation Procedure

After extraction, the oil was separated from the solvent mixture using a simple countercurrent distillation set-up with water as the coolant. The heat source was set to $110 \pm 5^\circ\text{C}$. At 120°C , the optimum oil can be obtained (Li, 1999)b.

6. Fatty Acid Profile Determination by GC

Fatty acids (FAs) are widely dispersed in nature as constituents of lipid-containing material. The most significant characteristic of dietary lipids is the content of different FAs and different types of FAs. Thus, FAs are often chosen as the indicator of dietary

lipid quality. The classic steps to determine FAs include extraction of a lipid sample with organic solvents, followed by transformation of the isolated lipid to fatty acid methyl esters (FAME) and quantification of FAME by gas chromatographic analysis. The AOCS official methods (AOCS, 1998) describe a detailed procedure for the preparation of FAME (Ce 2-66) and GC analysis (Ce 1-62). Thus, oil quality change due to the application of ultrasonic energy can be measured by this official method. Oil quality was analyzed using a Hewlett-Packard 6890 gas chromatograph with cold on-column injection in a capillary column (HP-2980 (30 m $\times$ 0.25 mm $\times$ 0.1 μ m)) and by flame ionization detection.

For GC, a temperature program was set with injection at 130°C, rising at 3°C/min. to 210°C and with a 10 min. holding. The detector temperature was set at 250°C. Helium carrier-gas column flow rate was 1.8 mL/min., and make-up gas flow rate was 30 mL/min. The flow rate of hydrogen and air was 40 mL/min. and 400 mL/min., respectively. Prepared FAME (2 μ L) was introduced into the GC with split ratio of 1:10. Peak areas were then calculated with data collection being managed by HP Chem. Station software. The soybean oil quality change was reflected by unsaturated fatty acid and saturated fatty acid content ratio. The fatty acid content in oil was the integrated peak area in GC graph.

3.4 Results

3.4.1 Effect of solvent extraction without sonication

The oil extraction capabilities of different solvents in the traditional process at different process times are shown in Figure 3.1. Three different solvents: hexane, isopropanol, and hexane:isopropanol mixture (60%:40% v/v), were used in this research to evaluate their efficiency. When the reaction time was increased from 30 min. to 3 hr., 0.89 g, 1.14 g, and 1.73 g more soybean oil was obtained in the isopropanol, hexane, and mixed solvent groups, respectively. This result indicates that oil yield increased with treatment time regardless of the solvents used. Notably, the mixed solvent resulted in the greatest oil yield increase (1.73 g), while the increase with isopropanol was the least (0.89 g).

After 30 min., the oil yield from the mixed solvent was 0.77 g higher than that of hexane, which was in turn 0.44 g higher than that of isopropanol. When the reaction time was increased to 3 hr, the oil yield of mixed solvent was 1.02 g higher than that of hexane, which was in turn 1.03 g higher than that of isopropanol. So, it can be concluded that isopropanol is not an effective solvent in traditional soybean oil extraction process. With ultrasound assistance, the mixed solvent showed promise as a potential replacement for hexane, the solvent currently used in the soybean oil industry.

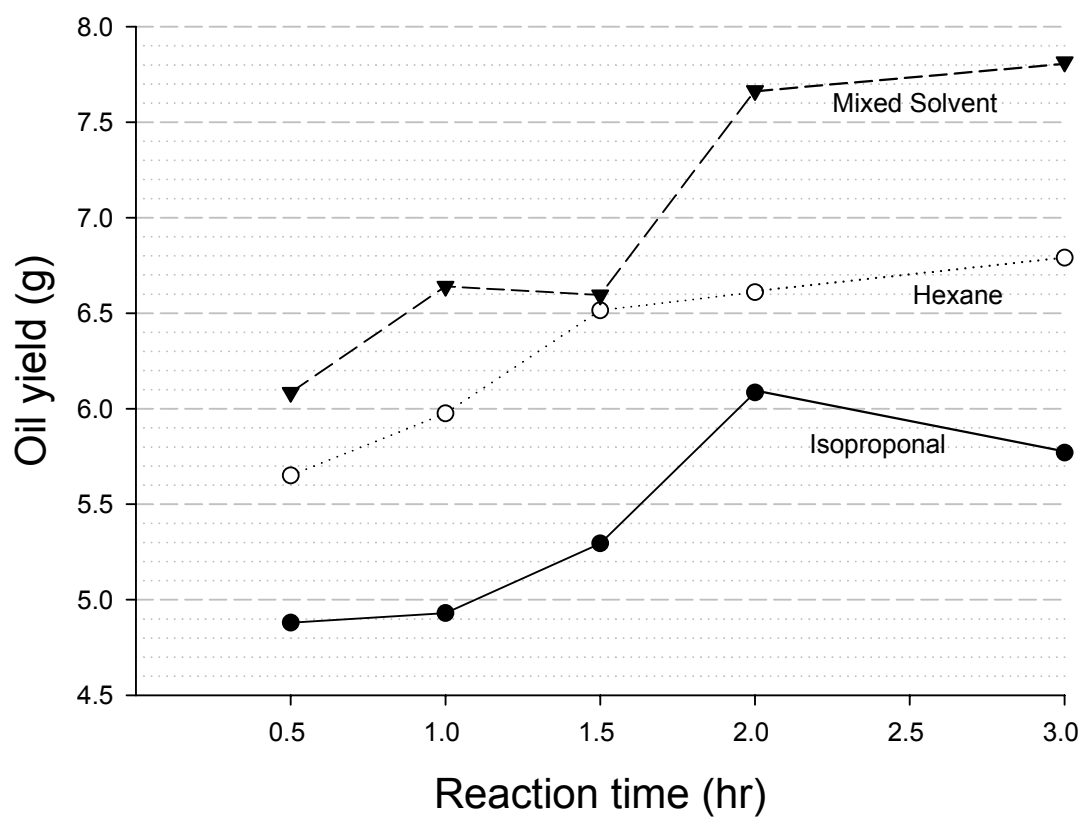


Figure 3.1 The ability of different solvents to extract oil from TN 96-58 using the traditional extraction process.

3.4.2 Effect of ultrasonic intensity on oil yield

The influence of different ultrasound intensity levels is shown in Figure 3.2. Three levels of ultrasonic power intensity, 16.4 Wcm^{-2} , 20.9 Wcm^{-2} , and 47.6 Wcm^{-2} , were tested. The results showed that in general, increased power intensity increased oil yield. With reaction time of 2 hr and ultrasound intensity of 47.6 Wcm^{-2} , the increase in oil yield was 7% higher than that at 20.9 Wcm^{-2} which in turn was 18% higher than that at 16.4 Wcm^{-2} .

As shown in Figure 3.2, the oil yield after a 2 hr. reaction time at 16.4 and 47.6 Wcm^{-2} was 0.25 and 2.04 g higher than that of the control, respectively. The oil yield increase at 47.6 Wcm^{-2} was approximately 8 times higher than the yield increases obtained at 16.4 Wcm^{-2} . This result indicates that increased oil yield is not linear with the increased ultrasound power at a specific reaction time. After 30 min. at 47.6 Wcm^{-2} , the oil yield was 1.04 g higher than that of the control. This was only 2 times the oil yield difference between 16.4 Wcm^{-2} sonication and the control (0.5 g). This result illustrates that application of ultrasound was more effective with a longer extraction time. Oil yield difference between the 16.4 Wcm^{-2} and 47.6 Wcm^{-2} at 30 min. reaction time was 0.5 g , whereas at reaction time 2 hr., the difference increased to 1.79 g . These results show that the effect of ultrasound on the oil yield was not a linear relationship with the reaction time. Thus, in general, longer sonication can yield more soybean oil.

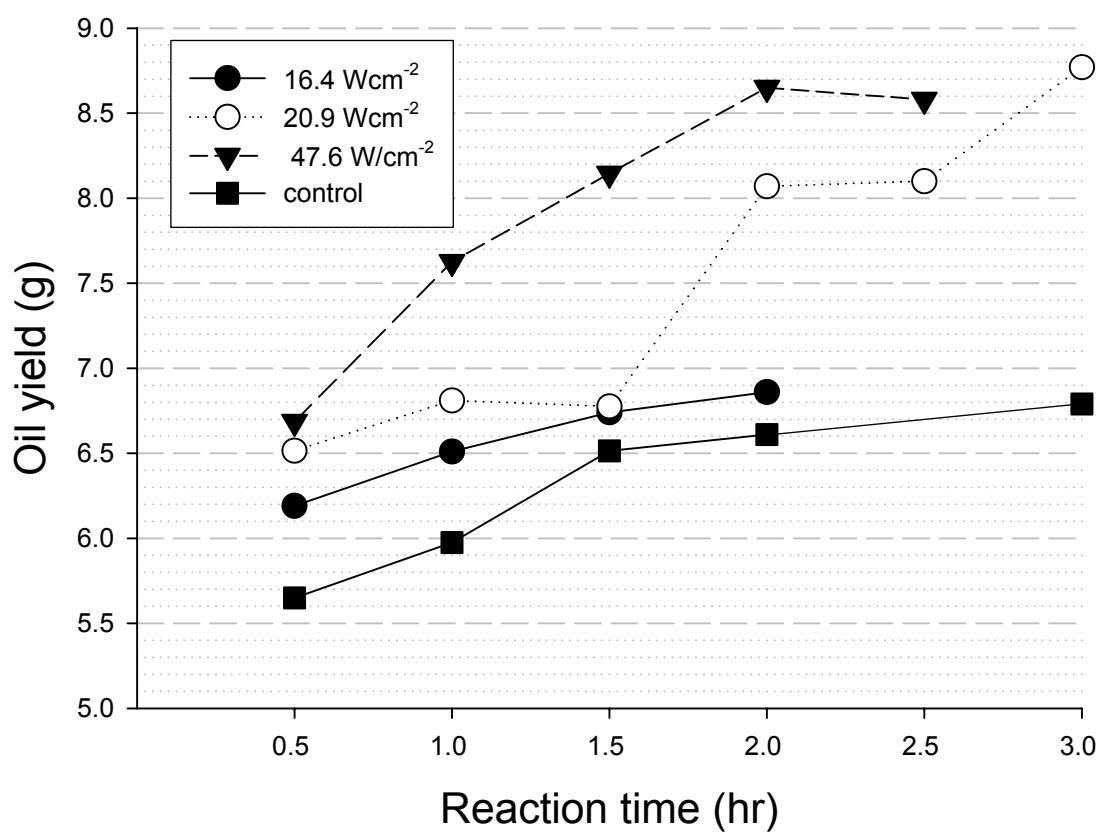


Figure 3.2 Effect of ultrasound intensity on soybean oil extraction with hexane.

3.4.3 Oil yield of soybean varieties obtained with ultrasound-assisted extraction

In general, the oil yield of both varieties of soybeans increased with the application of ultrasound (Figure 3.3). Reaction time is also one of the factors that can increase the yield of soybean oil during solvent extraction because all four lines in the Figure 3.3 increased when the reaction time increased. However, the increase in oil yield for these two soybean varieties of soybean with reaction time was different. For TN 96-58 variety, the difference between the control group and the ultrasound-assisted group was 0.97 g at a reaction time of 30 min., while the difference was 1.98 g after 3 hr. For this variety, ultrasound had a more pronounced effect on the yield in the latter stage of extraction. In contrast, for N 98-4573, the oil yield difference between the control and the ultrasound-assistance group was 1.4 g at a reaction time of 30 min. and 0.63 g at 3 hr. For this variety, ultrasound apparently enhances oil yields in the early stage of the extraction process.

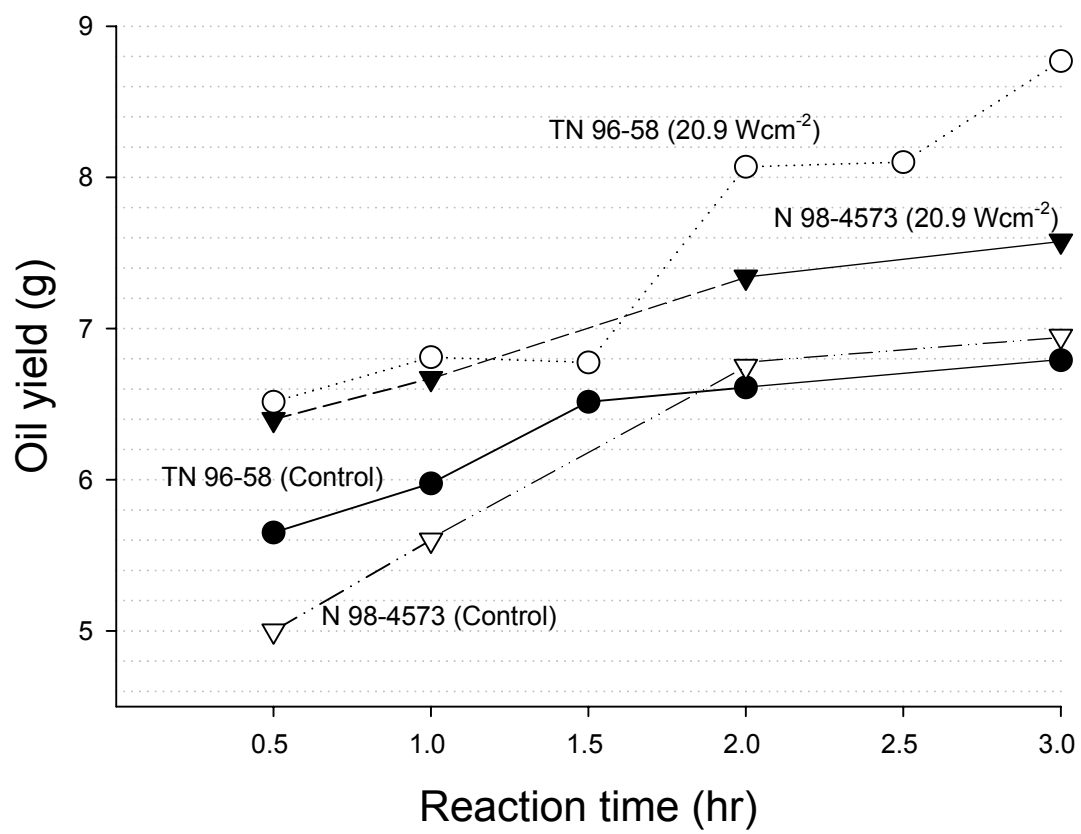


Figure 3.3 Effect of ultrasound on oil extraction on two different soybean varieties at intensity 20.9 Wcm^{-2} .

3.4.4 Oil yield as a function of solvents applied in the extractions

As illustrated in Figure 3.4, the difference between the oil yield obtained with hexane and isopropanol as solvents after 30 min. in the traditional extraction process was 0.77 g. When the reaction time was increased to 3 hr., the difference was 0.98 g. Over the levels of reaction time investigated, the average oil yield obtained by extraction using hexane was about 0.92 g higher than the yield obtained using the isopropanol.

Comparison of the trend lines for the control treatment shows that the selection of solvent influences on the final oil yield. However, it is not clear whether the same conclusion can be drawn when hexane and isopropanol are used as solvent in the ultrasound-assisted operation. After 30 min. reaction time, the oil yield of hexane extraction was 0.48 g higher than that of isopropanol extraction. When the reaction time was increased to the 3 hr, the oil yield obtained with isopropanol was 0.23 g higher than that using hexane as a solvent. At the 30 min. reaction time, the difference between the ultrasound-assisted and the control process both using hexane was 0.87 g while the difference between the two processes using isopropanol as the solvent was 1.16 g. Remarkably, at a reaction time of 3 hr, the difference increased to 1.98 g and 3.23 g, respectively. It is apparent in Figure 3.4 that in the ultrasound-assisted extraction operation where isopropanol was used as solvent, there was a greater increase in oil yield than when hexane was used. This result indicates that the efficiency of ultrasound-assisted soybean oil extraction depends on the solvent used in the extraction process.

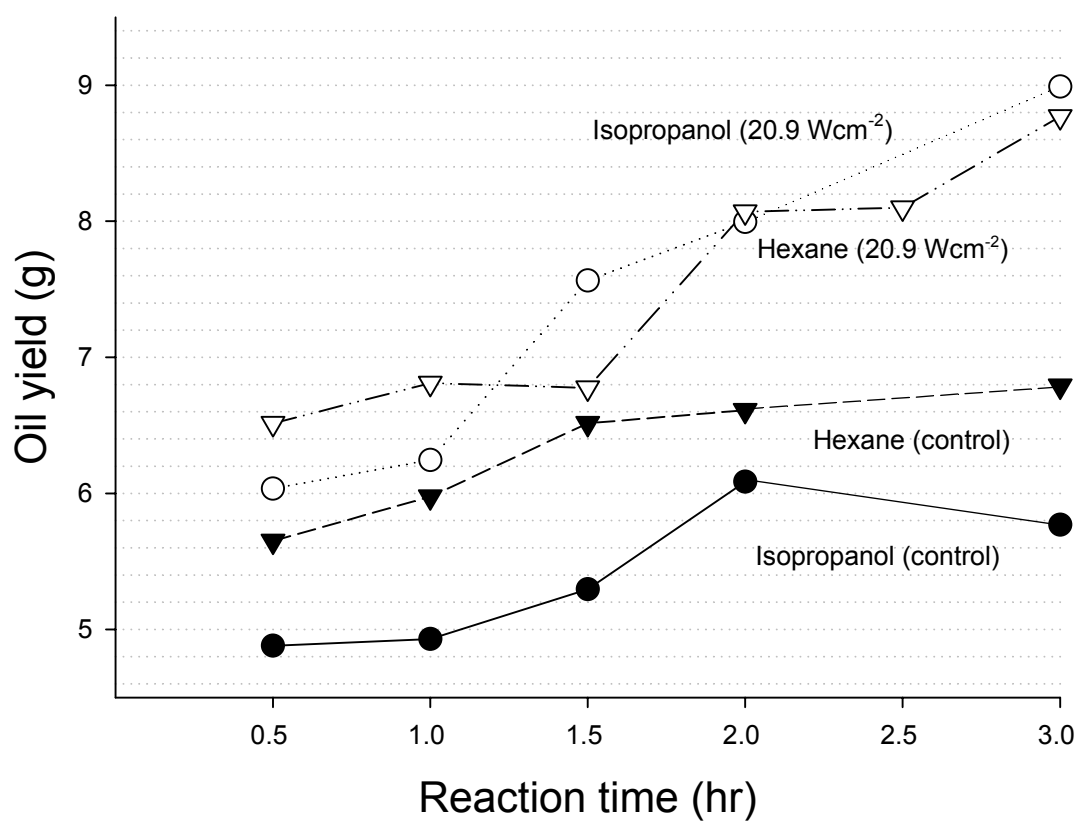


Figure 3.4 Effect of solvent on soybean oil extraction with ultrasound assistance at 20.9 Wcm⁻².

3.4.5 Extraction with a mixed solvent

A solvent mixture was prepared by mixing hexane and isopropanol at a ratio of 60%:40% (v/v). Oil yields obtained with the three solvents (hexane, isopropanol and the solvent mixture) both with and without ultrasound assistance are shown in Figure 3.5. The enhanced extraction performance of the mixed solvent can be readily seen in the figure. When the reaction time was 30 min., the oil yield from the mixed solvent was 0.44 g higher than from hexane and 1.21 g higher than from isopropanol. When the reaction time was increased to 3 hr., the oil yield from the mixed solvent group was 1.03 g higher than from hexane and 2.05 g higher than when isopropanol was used. The excellent extraction capability of the mixed extractant was further enhanced by the application of ultrasound. The oil yield was 6.29 g after 30 min. and which increased to 12.21 g after 3 hr when the mixed solvent was used in combination with ultrasound. The difference between the ultrasound-assisted group and the control group was only 0.2 g at the beginning of the extraction. However, when a reaction time of 3 hr was used, the difference increased to 4.39 g. These results indicate that for the mixed solvent, reaction time is an important processing parameter affecting the final oil yield.

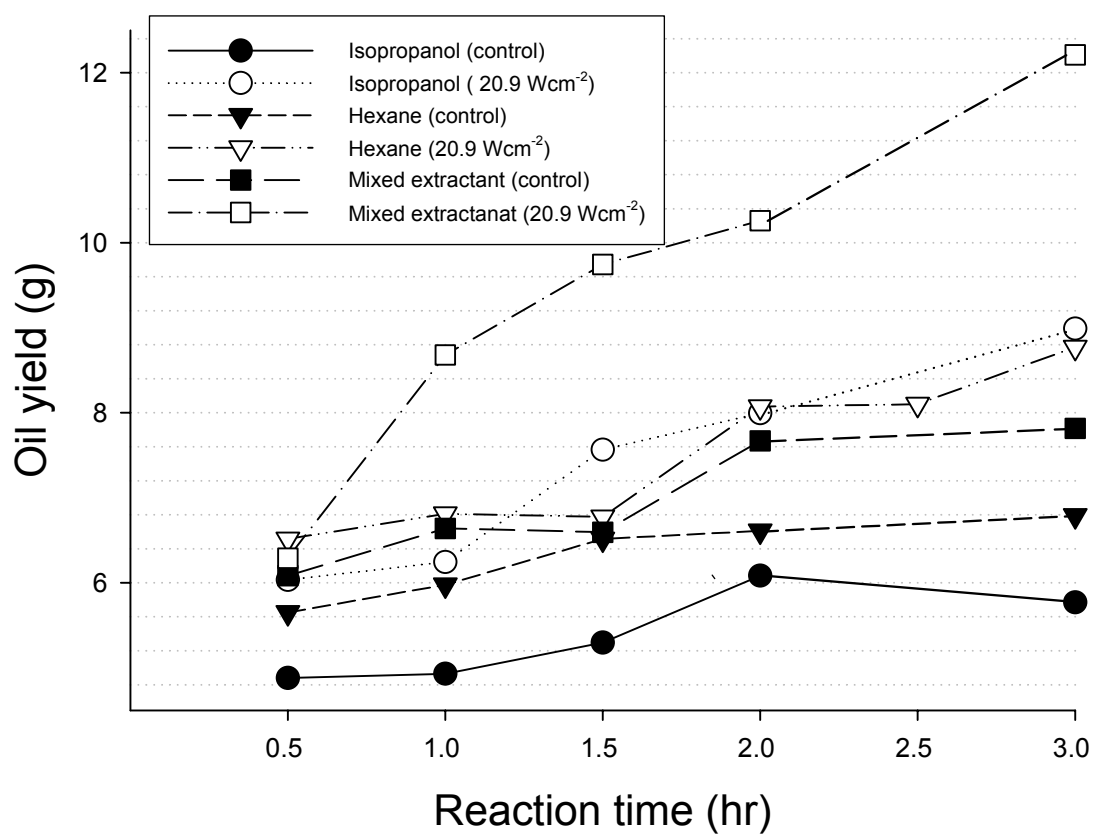


Figure 3.5 Oil yield increase with the use of hexane:isopropanol (60%:40% v/v) mixture as the solvent at an ultrasound treatment intensity of 20.9 Wcm⁻².

3.4.6 Oil quality measurement

Figure 3.6 generated by GC shows the typical fatty acid profile of soybean oil. Results of the GC analysis shown in Table 3.2 reflect a decrease in the relative percentage of unsaturated fatty acids and an increase in the percentage of saturated fatty acids when ultrasound-assisted extraction was used. This ratio is used as an indicator of the extent of fat deterioration because unsaturated fatty acid is more susceptible to oxidation, whereas saturated fatty acid is more stable to oxidation. In the control group, the C18:1/C16:0 ratio was 1.5376 while in ultrasound-assisted extraction group it

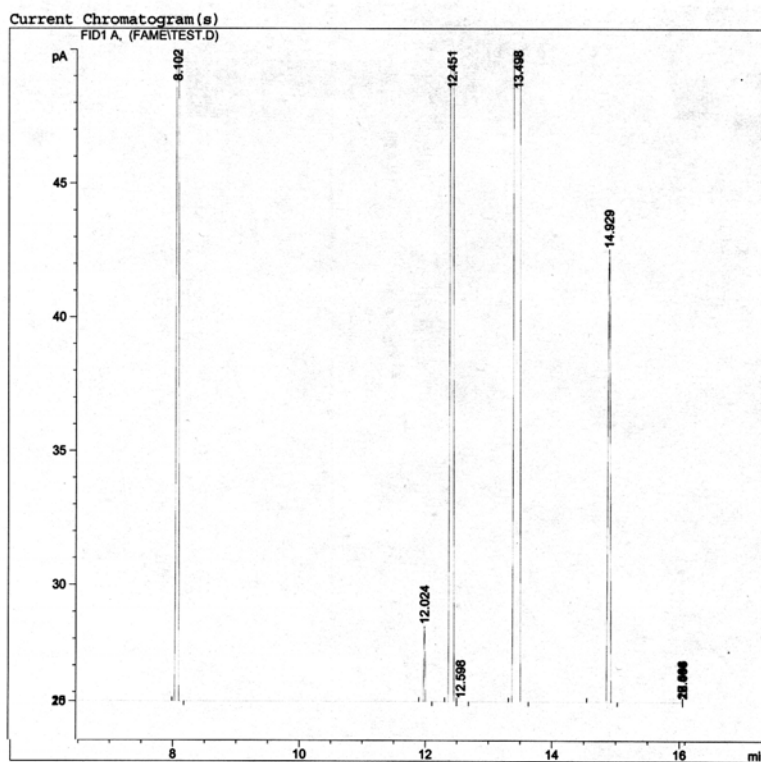


Figure 3.6 Typical chromatogram for soybean oil.

Table 3.2 Ration between unsaturated and saturated fatty acid (C18:2/C16:0, C18:1/C 16:0) in oil from ultrasound-assisted and traditional extraction.

Retention time (min)	ultrasound-assisted		control group	
	peak area	ratio	peak area	ratio
8.02 ± 0.01 (16:0)	128.29	1	130.02	1
11.92 ± 0.02	39.52	0.3080	38.6	0.2969
12.35 ± 0.02 (18:1)	197.27	1.5376	193.11	1.4852
12.49 ± 0.02	16.03	0.1250	15.96	0.1228
13.34 ± 0.05 (18:2)	651.14	5.0756	656.48	5.0491
14.82 ± 0.02	89.7	0.6992	90.46	0.6957
16.46 ± 0.02	3.83	0.0299	3.6	0.0277
16.90 ± 0.02	2.4	0.0187	2.4	0.01855
22.33 ± 0.03	4.77	0.0372	4.5	0.03461

decreased to 1.4852. The oxidation percentage was 3.4%. The ratio of C18:2/16:0 was 5.0756 and 5.0491 in the control and ultrasound-assisted group, respectively. Due to oxidation, there was a difference of 0.52% in the linoleic acid content.

The difference in the GC analysis between the ultrasonicated and the control group was deemed small indicating that ultrasonication had very little effect on the quality of the extracted oil

3.5 Conclusions

The application of high power ultrasound for soybean oil extraction showed a positive effect on the oil yield. The following conclusions were drawn from this research:

- Ultrasound had a significant influence on soybean oil extraction.
- Sonication power intensity level affected the final soybean oil yield.
- Application of ultrasound increased oil yield regardless of soybean variety. However, the relative oil yield increase was a function of soybean variety.
- The mixed hexane: isopropanol (60%:40% v/v) solvent system was more efficient in extracting soybean oil than hexane or isopropanol only.
- The choice of solvent influenced the efficiency of the ultrasound to improve yield.
- Application of ultrasound-assistance in oil extraction had a negligible effect on oil quality, i.e., a high oil quality was still obtained.

The results obtained in this study have important implications for future applications in the soybean oil industry. This study showed that ultrasound has the potential to be used in oil extraction process to improve efficiency and lower the processing cost. The hexane and isopropanol mixed solvent (60%:40% v/v) can potentially be applied in soybean oil extraction because of its excellent oil extraction performance: less cost and better safety characteristics. Future studies will concentrate on finding the optimum combination of process parameters (ultrasound intensity, temperature, solvent, etc.) that can improve the efficiency of oil extraction.

4 Microwave-assisted Extraction of Oil from Soybeans

4.1 Abstract

A laboratory-scale microwave-assisted soybean oil extraction procedure was developed and evaluated. The microwave-assisted extraction was found to be a simpler and more effective alternative to conventional extraction methods for the productions of soybean oil. Soybean samples were extracted with different solvents [hexane, isopropanol, and a mixed solvent (hexane:isopropanol 60%:40% v/v)] after being pretreated with microwave exposure (2450 MHz) at increasing times. Oil yields were compared to the conventional hexane extraction procedure. Microwave-assisted extraction yielded significantly higher oil percentages than the conventional method, specifically, oil yield of microwave-assisted group was 0.45 g higher than that of control group during the first 2 hr. Increased microwave reaction times increased oil yield as well. For the mixed solvent, 4.17 g more oil was extracted when the reaction time was increased from 30 min. to 2 hr. Oil yield obtained with microwave assistance was highest using a mixed solvent. Fatty acid from conventionally extracted oil profile analysis measured by GC indicated that the oil quality did not appreciably change when microwave assistance was employed.

4.2 Introduction

Microwaves are best described as radio waves with very short wavelength. They occupy the portion of the electromagnetic spectrum between 300 MHz and 30 GHz. Microwave heating is one of the most commonly used methods of food preparation today because of its convenience, short processing time, selectivity, and economy. Due to these

characteristics, microwave ovens have been quickly adapted in a large number of commercial foodservice applications. In the food industry, microwave heating has been successfully used with increasing success in baking, blanching, cooking, drying, pasteurization, sterilization, and thawing of various food products (Rosenberg, 1987). Recent research has indicated that microwave radiation can be applied to the oil industry to aid in the processing of lipids (Yoshida and Takagi, 1997).

The most widely used extraction methods currently in the oil seeds industry involve solvent extraction, especially in the western world with hexane the most popular solvent. However, an ideal solvent does not exist based on the reviews by Snyder and Kwon (1987). Hexane fulfills most requirements of the ideal solvent but it has its drawbacks. Hexane is explosive and flammable, so other solvents have been considered in both laboratory and industrial applications, for example, alcohol (Karnofsky, 1981), isopropanol (Baker and Sullivan, 1983), and carbon dioxide (Freidrich and Pryde, 1984).

Based on the survey in Soya & Oilseed Bluebook (Soyatech, Inc., 2001), soybean has already become the dominant oilseed in the world vegetable oil market due to its high oil content and low cost accounting for 29% of vegetable oil production in 2000. Therefore, any improvement in soybean oil processing technology can increase the soybean industry profitability markedly. Although microwave technology has been widely used in food area, not much research has been done to investigate the efficiency of the application of microwave for soybean oil processing industry,

One of the objectives of this study was to compare the yield, composition, and properties of the extracted soy oil obtained through conventional and microwave-assisted extraction. The effectiveness of microwave assisted extraction was also investigated.

4.3 Materials and Methods

4.3.1 Materials

Two soybean varieties, TN 96-58 and N 98-4573, were used in this study. TN 96-58 is one of the most popular varieties planted in Tennessee while N 98-4573 is a special variety being bred by researchers in North Carolina. Both varieties were obtained from the crops laboratory at The University of Tennessee. Soybean moisture content was determined using a single kernel moisture tester (CRT-160E, Shizuoka Seiki, Japan).

AOCS Mix No.3, A fatty acid standard, was purchased from Alltech Corp. (Deerfield, U.S.). This was used in GC analysis. The standard was diluted to 10 mg/mL in hexane and kept in a well-closed container in refrigerator (4 °C).

Hexane and isopropanol used in the oil extraction were purchased from Fisher Scientific (Fair lawn, New Jersey, U.S.).

4.3.2 Methods

1. Soybean Cleaning

During harvesting, drying, transportation, and storage, foreign material, such as small stones, sand, and plant leaves, may unavoidably be mixed with soybeans. These foreign materials affect extraction efficiency, and oil quality, in addition to potentially increasing wear on equipment. Raw soybeans were therefore cleaned following the using

the Federal Grain Inspection Service grading procedure (FGIS, 1999). Cleaning was done in 125 g units using a sieve set consisting of a 10/64-in. x $\frac{3}{4}$ -in. slot-hole sieve placed on top of an 8/64-in. round-hole sieve. The soybeans were poured into the center of the top sieve. The sieves and bottom pan were held level. Using a steady motion, the sieve set was moved from right to left approximately 10 in. five times to complete one sieve operation. All soybeans retained on the 8/64-inch round-hole sieve and the 10/64 x $\frac{3}{4}$ -in. slotted-hole sieve were collected and used in the subsequent experiments.

2. Soybean Conditioning

Moisture content is a critical parameter in soybean processing both in industry and the laboratory. For extraction, soybean moisture content should be between 10% and 14%. If the moisture content exceeds 14%, soybeans are hard to grind; at moisture content below 10%, ground soybean particles will not be uniform. The presence of large amount of fine particles is not suitable for oil extraction processing.

The cleaned, raw soybeans at a moisture content of about 8% were packaged into 2 kg bags and kept in an environmental chamber adjusted to room temperature. Moisture content of soybeans was measured every two hr using the single kernel moisture tester until final moisture of 11% was reached. The conditioned soybeans were then kept for future use in a sealed, insulated box that was adjusted to room temperature.

3. Grinding

The cleaned and conditioned soybean seeds were ground using a hammer mill (Standard Model No.3, Arthur Thomas Co., Philadelphia, PA, U.S.A.) running at 478

RPM. A stainless steel screen with a mesh size of 4 mm was used to obtain a uniform soybean particle size. The ground soybeans consisting of both the ground seed and hull was kept in air tight plastic bags until used.

4 Microwave Pretreatment

Prior to actual extraction, the ground soybean was pretreated by heating in a microwave oven. A 100 g sample was weighed and spread out as a 3.8 cm ring of material on the outer edge of 25.4 cm diameter glass turn table. The heating times used in this study were 30, 60, and 120 s. A 600 W microwave oven with a 0.6 ft³ cavity and equipped with a turntable was used for the soybean pretreatment.

The power of the microwave field where the samples were placed was determined using a calorimetric method (Mason, 1990). This was done by heating 100 g water in a 250 mL glass beaker in the microwave oven at the different treatment times. The initial temperature of the water was recorded using a thermocouple. The microwave heating time was 30 and 60 s, respectively. The final temperature after heating was recorded using the same thermocouple. The absolute microwave power P was computed as:

$$P = \frac{mc_p(T_f - T_i)}{t} \quad (6)$$

where m is the mass (100 g) and c_p is the specific heat of water (4.184 J g⁻¹ °C⁻¹), T_i is the initial temperature, T_f is the final temperature, and t is the microwave heating time. For heating times of 30 and 60 s, the calculated power at the point of sample placement was 413 and 379 W, respectively.

5. Extraction

Extractant (150 mL) was mixed with microwave heated ground soybean in a 600 mL plastic beaker. Stirring was accomplished at room temperature with the use of a laboratory stirrer. Stirring time (extraction time) was an experimental treatment factor investigated with 0.5, 1.0, 1.5, and 2.0 hr evaluated.

6. Separation

The miscella was separated from the mixture through a vacuum filter. The oil was then separated from the solvent using a vacuum oven, which also kept the oil from oxygen exposure and resultant oxidization. The oven temperature was set at $120 \pm 5^{\circ}\text{C}$ and the air pressure was set at -60 KPa. The best quality oil for food applications can be obtained at 120°C . A pressure of -60 KPa was used because it was the maximum available for the vacuum oven employed in separation.

4.4 Results

4.4.1 Effect of different extraction time

The effect of 1 min. microwave pretreatment on soybean oil yield using hexane at increasing extraction times (0.5-2.0 hr.) is shown in Figure 4.1. The difference between the control group and microwave-assisted group was a constant 0.45 g up to 90 min. extraction. At 120 min., it increased to 0.62 g. As shown in the figure, microwave pretreatment basically increased oil yield at a constant rate in both conventional and microwave assisted extraction. It can be seen that there is a linear relationship between the extraction time and the oil yield during the maximum 2 hr extraction time tested when microwave assistance is employed.

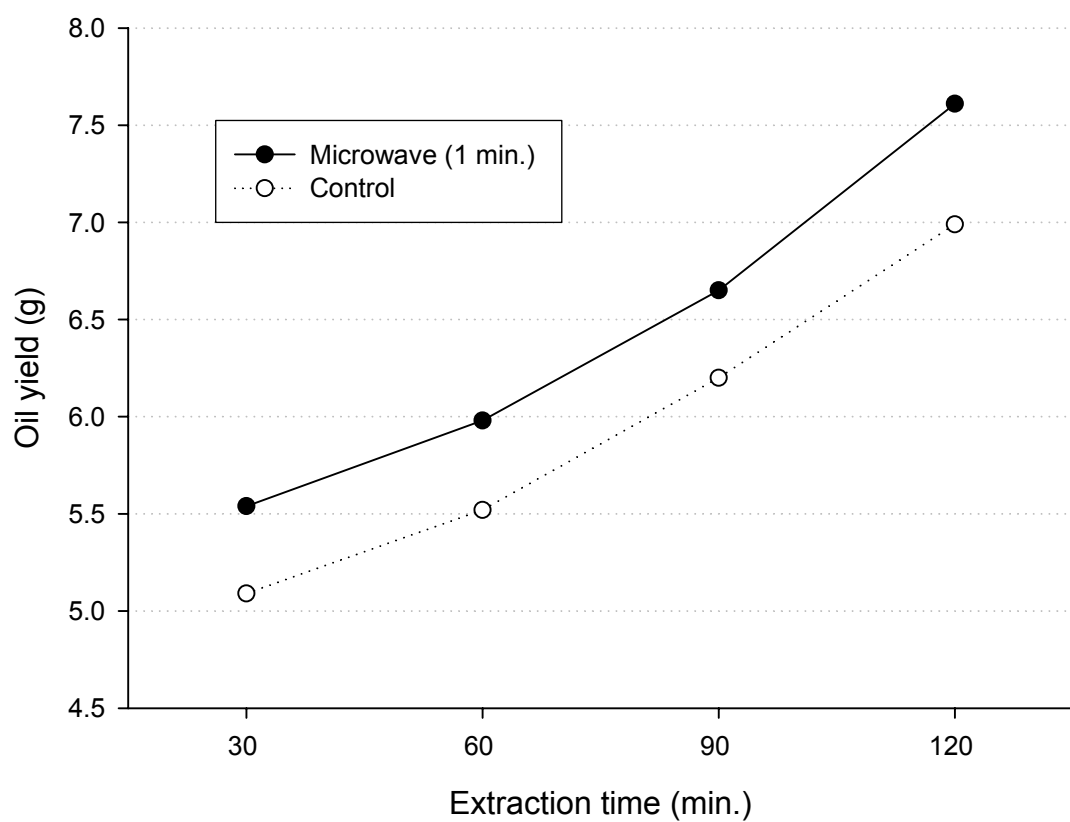


Figure 4.1 Effect of 1 min. microwave pretreatment on soybean oil yield at increasing hexane extraction times.

4.4.2 Effect of different microwave reaction time

Figure 4.2 shows the influence of different solvents at different microwave pretreatment times on the soybean oil yield when the extraction time was 120 min. The mixed solvent consistently had the highest oil yields followed by hexane and then isopropanol. The increase between 30 and 120 s reaction time was 4.17 g and 3.78 g, respectively, for both mixed extractant and hexane while it was only 1.81 g for isopropanol. Evidently, isopropanol was not an ideal solvent for this procedure.

As shown in the figure, microwave reaction time clearly affected the oil yield. The longer the reaction time, the higher the oil yields obtained. For the mixed solvent, 4.17 g more oil was extracted when the reaction time was increased from the 30 to 120 s. The increase in oil yield was 2.03 g when the microwave treatment was increased from 30 to 60 s. When the reaction time increased from 60 to 120 s, the increase was greater at 2.14 g. This result illustrates that the effect of microwave pretreatment is greatest at the initial moments of exposure. Longer exposure times (pretreatment times) continued to improve yield but at a diminishing rate.

The effect of microwave treatment is simply product heating. No cell or intercellular disruption occurs as would be the case when ultrasound is used. Temperatures of the ground soybean samples at different microwave treatment times should have been measured. There would be a limit to the microwave treatment time because it is likely that longer exposure times would lead to thermally induced chemical transformations resulting in a reduction in the oil yield and quality.

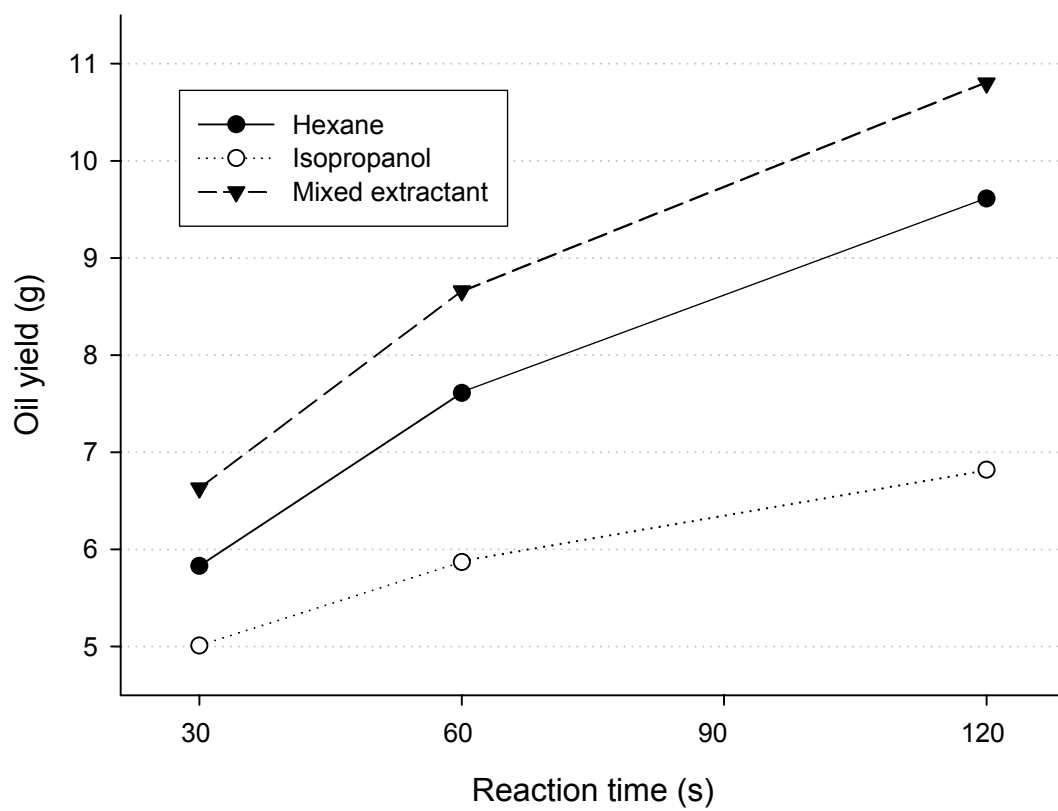


Figure 4.2 Effect of microwave pretreatment time on soybean oil extraction using different solvents.

4.5 Conclusions

The application of microwave pretreatment in soybean oil extraction show positive effect on the oil yield and time cost. The following conclusions were obtained from this research:

- Microwave has a significant influence on soybean oil extraction
- The microwave reaction time affected the final soybean oil yield.
- The mixed solvent system, hexane:isopropanol (60:40% v/v), was more effective in extracting soybean oil than either hexane or isopropanol alone.

The results obtained positively indicate the potential of using microwave-assistance to improve chemical extraction of soybean oil. The mixed solvent shows promise as a replacement for hexane when microwave-assistance is used because of its good soybean oil extraction performance. Future studies will concentrate on finding the optimum experimental parameters (microwave reaction time, temperature, solvent etc.), which can help industry to obtain maximum profit.

5 Conclusions

The application of both power ultrasound and microwave for soybean oil extraction show positive effect on the oil yield and processing time. The following conclusions were from the research conducted:

- Ultrasound-assistance had a positive influence on soybean oil extraction.
- Microwave pretreatment had a positive influence on soybean oil extraction
- The sonication power level affected the final soybean oil yield.
- The microwave reaction time affected the final soybean oil yield.
- Application of ultrasound increased oil yield regardless of soybean variety, however, the relative oil yield increase was affected by variety.
- The mixed solvent system, hexane:isopropanol (60%:40% v/v), was more effective in extracting soybean oil than hexane or isopropanol only in both microwave-assisted and ultrasound-assisted systems.
- Application of ultrasound had a negligible effect on oil quality, i.e., there was no difference in the fatty acid profile compared to conventionally extracted oil.

The results have important implications in the soybean oil industry. Both ultrasound and microwave have the potential to be used in oil extraction process to improve efficiency and lower processing cost. The hexane and isopropanol mixed solvent (60%:40% v/v) show promise as a replacement for hexane in soybean oil extraction because of its good oil extraction performance, especially, with ultrasound and microwave-assistance. Future studies should concentrate on finding the optimum

experimental parameters (ultrasound intensity, temperature, solvent, etc.) which can optimize the oil extraction process.

References

- Anderson, D. 1996. A primer on oils processing technology. *In: Bailey's Industrial Oil and Fat Products*, Vol. 4. John Wiley & Sons Ltd., Chichester, UK.
- AOCS. 1998. Official Methods and Recommended Practices of the American Oil Chemists' Society. American Oil Chemists Society, Champaign, IL.
- Astrup, J. 1999. Ultrasound detection in fish: a parallel to the sonar-mediated detection of bats by ultrasound-sensitive insects. *Comparative Biochemistry and Physiology*. 124(1):19-27.
- Baker, E. C. and D. A. Sullivan. 1983. Development of a pilot-plant process for extraction of soy flakes with aqueous isopropyl alcohol. *J. Am. Oil Chem. Soc.* 60(7):1271-1276.
- Bengtsson, N. E. and P. O. Risman. 1971. Dielectric properties of foods at 3 GHz as determined by a cavity perturbation technique. *J. Microwave Power* 6(2):107-123.
- Bredeson, D. 1978. Mechanical extraction. *J. Am. Oil Chem. Soc.* 55(11):762-764.
- Cains, P. W., P. D. Martin, and C. J. Price. 1998. The use of ultrasound in industrial chemical synthesis and crystallization. 1. Applications to synthetic chemistry. *Organic Process Res. Dev.* 2(1):24-48.
- Cahoon, E. B., Y. Lindqvist, G. Schneider, and J. Shanklin. 1997. Redesign of soluble fatty acid desaturases from plants for altered substrate specificity and double bond position. *Proc. U.S. Nat. Acad. Sci.* 94(10):4872-4877.
- Chen, C., X. Wang, D. Chen, G. Li, A. Ronnenberg, and H. Watanabe. 2001. Tofu consumption and blood lead levels in young Chinese adults. *Am. J. Epid.* 153(12):1206-1212.
- Chendke, P. K. and H. S. Fogler. 1975. Microsonics in industry. *Ultrasonics* 13(1):31-37.
- Dohlman, E., R. Schnepf, and C. Bolling. 2001. Soybean production costs and export competitiveness in the United States, Brazil, and Argentina. *Oil Crops Situation and*

Outlook Yearbook. No.OCS-2001. Economic Research Service, U.S. Department of Agriculture, Washington, D.C.

- Dutton, H. J. 1981. History of the development of soy oil for edible uses. J. Am. Oil Chem. Soc. 58(3):234-236.
- Evans, C. D., D. G. McConnell, G. R. List, and C. R. Scholfield. 1969. Structure of unsaturated vegetable oil glycerides: direct calculation from fatty acid composition. J. Am. Oil Soc. 46(8):421-424.
- Federal Grain Inspection Service. 1999. Inspecting grain: Practical procedures for grain handlers. USDA, Washington, D.C.
- Fetty, H. 1966. Microwave baking of partially baked products. In: Proc.Am. Soc. Bakery Engineers, pp. 145-166. American Society of Bakery Engineers, Chicago, IL.
- Fleming, H. 1944. Effect of high frequency on microorganisms. Electrical Eng. 63 (18):1034-1042.
- Freidrich, J. P. and E. H. Pryde. 1984. Supercritical CO₂ extraction of lipid bearing materials and characterization of the products. J. Am. Oil. Chem. Soc. 61(2):223-228.
- Galvin, J.B., C. J. Kirwin, and D. W. Kelly. 1995. Risk assessment of hydrocarbon solvents. Inform 6(8):951-952.
- Gedye, R. N., F. E. Smith, and K. C. Westway. 1988. The rapid synthesis of organic compounds in microwave ovens. Can. J. Chem. 66(1):17-26.
- Gedye, R. N., F. E. Smith, and K. C. Westway. 1991. Microwave in organic and organometallic synthesis. J. Microwave Power 22(1):3-17.
- Hancock, J. 1995. A look at processing specialty oils. Inform 6(7):812,814-817.
- Hardcastle, J. L., J. C. Ball, F. Hong, R. G. Compton, S. D. Bull, and S. G. Davies. 2000. Sonoelectrochemical and sonochemical effects of cavitation: correlation with

- interfacial cavitation induced by 20 KHz ultrasound. *Ultrasonics Sonochemistry* 7(1):7-14.
- Harlfinger, L. 1992. Microwave sterilization. *Food-Technol.* 46(12):57-59,61.
- Henkel, J. 2000. Soybean Health claims for soy protein, questions about other components. *FDA Consumer* 34(3):13-15,18-20.
- Ho, S. C., S. Chan, Q. Yi, E. Wong, and P. Leung. 2001. Soy intake and the maintenance of peak bone mass in Hong Kong Chinese women. *J. Bone Mineral Res.* 16(7):1363-1369.
- Howe, A. M., A. R. Machie, and M. M. Robins. 1986. Technique to measure emulsion creaming by velocity of ultrasound. *J. Dispersion Sci. Technol.* 7(2):231-243.
- Irfan, I. and E. Pawelzik. 1999. The effect of rapeseed treatment by microwave and radio-frequency application on oil extraction and oil quality. II. Influence on oil quality. *Lipid* 101(5):168-171.
- Javanaud, C. 1988. Applications of ultrasound to food systems. *Ultrasonic* 26(1):117-123.
- Javanaud, C., N. R. Gladwell, S. J. Gouldby, D. J. Hibberd, A. Thomas, and M. M. Robins. 1991. Experimental and theoretical values of the ultrasonic properties of dispersions: effect of particle state and size distribution. *Ultrasonics* 29(1):331-337.
- Johnson, L. A. and E. W. Lusas. 1983. Comparison of alternative solvents for oil extraction. *J. Am. Oil Chem. Soc.* 60(2):229-242.
- Karnofsky, G. 1981. Ethanol and isopropanol as solvents for full-fat cottonseed extraction. *Oil Mill Gaz.* 85(10):34-36.
- Keerio, M. I., S. Chang, M. Mirjat, M. Lakho, and I. P. Bhatti. 2001. The rate of nitrogen fixation in soybean root nodules after heat stress and recovery period. *Int. J. Agric. Biol.* 3(4):512-514.
- Kent, M. 1987. *Electrical and Dielectric Properties of Food Materials.* Science and Technology Publishers, Ltd., London.

- Khurana, S. and T. P. Yadava. 1982. Stability and adaptation in soybean. *Indian J. Agric. Sci.* 52(5):292-296.
- Li, F. 1994. Study on origin and evolution of soybean. *Soybean Sci.* 13(1):61-66.
- Li, W. 1999. *Oil Processing Technology and Equipment*. Chinese Economic Pub., Beijing, China.
- Leadley, C. and A. Williams. 2001. Current and potential applications for power ultrasound in the food industry. *New Food.* 4(3):23-26.
- Lusas, E.W., L. R. Watkins, S. S. Koseoglu, K. C. Rhee, E. Hernandez, M. N. Riaz, W. H. Johnson, Jr., and S. C. Doty. 1994. Replacing hexane with isopropyl alcohol as an oil extraction solvent. IV. Progress on cottonseed and soybean extraction. Paper presented at the 85th Am. Chem. Soc. Annual Meeting, Atlanta, Georgia, May 8-12.
- Lusas, E. W., S. S. Koseoglu, L. R. Watkins, K. C. Rhee, E. Hernandez, M. N. Riaz, W. H. Jr. Johnson, and S. C. Doty. 1995. Replacing hexane with isopropyl alcohol as an oil extraction solvent. V. Pervaporation IPA recovery, materials energy balances, meal feeding trials. Presented at the 86th Am. Oil Chem. Soc. Annual Meeting, San Antonio, Texas, May 7-11.
- Mason, T. J. 1990. *Sonochemistry: the uses of ultrasound in chemistry*. Royal Society of Chemistry, Cambridge, England, U.K.
- Mason, T. J. 1992. Industrial sonochemistry: potential and practicality. *Ultrasonics* 30(3):192-196.
- Mason, T. J. and E. D. Cordmas. 1996. Ultrasonic intensification of chemical processing and related operations - a review. *Trans. Inst. Chem. Eng.* 74:511-516.
- Mason, T. J., L. Paniwnyk, and J. P. Lorimer. 1996. The uses of ultrasound in food technology. *Ultrasonic Sonochemistry* 3(3):253-260.
- McClements, D. J. 1995. Advances in the application of ultrasound in food analysis and processing. *Trends Food Sci. Technol.* 6(9):293-299.

- Menconi, M. and P. Bioli. 1998. Process for extracting an oil mixture and oil mixture obtained by said process. PCT-International-Patent-Application. Patent No. WO 98/38268 A1.
- Miles, C. A., D. Shore, and K. R. Langley. 1990. Attenuation of ultrasound in milks and creams. *Ultrasonics* 28(6):394-400.
- Mongenot, N., S. Charrier, P. Chalier. 2000. Effect of ultrasound emulsification on cheese aroma encapsulation by carbohydrates. *J. Agric. Food Chem.* 48(3):861-867.
- Mudgett, R. E., S. A. Goldblith, and P. O. Risman. 1974. The frequency and temperature dependence of dielectric food data as determined by a cavity perturbation technique. *J. Microwave Power* 9(2):129-145.
- Noltingk, B. E. and E. A. Neppiras. 1950. Cavitation produced by ultrasonics. *Proc. Phys. Soc.* 63(8):674-681.
- Nvkvist, W. E. and R. V. Decareau. 1976. Microwave meat roasting. *J. Microwave Power* 11(1):3-24.
- Ohlsson, T. and N. E. Bengtsson. 1975. Dielectric food data for microwave sterilization processing. *J. Microwave Power* 10(1):93-108.
- Pohlman, F. W., M. E. Dikeman, and D. H. Kropf. 1997. Effects of high intensity ultrasound treatment, storage time and cooking method on shear, sensory, instrumental color and cooking properties of packaged and unpackaged beef pectoralis muscle. *Meat Sci.* 46(2):89-100.
- Povey, M. J. W. and D. J. McClements. 1988. Ultrasonics as a probe of food emulsions and dispersions. *J. Food Eng.* 8(1):285-327.
- Povey, M. J. W. 1998. Ultrasonics of food. *Contemporary Physics* 39(2):467-478.
- Pryde, E. H. 1980. Composition of soybean oil. *In: Handbook of Soy Oil Processing and Utilization*, eds. S. R. Erickson, E. H. Pryde, O. L. Brekke, T. L. Mounts, and R. A. Falb, Ch. 2. American Oil Chemists Society, Champaign, IL.

- Ren, Y. and S. E. Allen. 2001. Ultrasound treatment acceleration of solvent extraction for fumigant residues from wheat. *J. AOAC Int.* 84(5):1551-1554.
- Reverchon, E. and L. S. Osseo. 1994. Comparison of processes for the supercritical carbon dioxide extraction of oil from soybean seeds. *J. Am. Oil Chem. Soc.* 71(10):1007-1012.
- Risman, P. O. and T. Ohlsson. 1987. Principles and models of power density distribution in microwave oven loads. *J Microwave Power* 22(4):193-198.
- Rosenberg, U., and W. Bogl. 1987. Microwave thawing, drying, and baking in the food industry. *Food Technol.* 41(6): 85-91.
- Salunkhe, D. K., S. K. Sathe, and N. R. Reddy. 1983. Legume lipids. In: *Chemistry and Biochemistry of Legumes*, ed. S. K. Arora. Edward Arnold Publishers, Ltd., London.
- Schafer, K. 1998. Accelerated solvent extraction of lipids for determining the fatty acid composition of biological material. *Analytica Chimica Acta* 35(8): 69-77.
- Schiffmann, R. F. 1992. Microwave processing in the U.S. food industry. *Food Technol.* 46(12):50-51,56.
- Snyder, J. M., J. P. Freidrich,, and D. D. Christianson. 1984. Effect of moisture and particle size on the extractability of oils from seeds with supercritical CO₂. *J. Am. Oil Chem. Soc.* 61(12):1851-1861.
- Snyder, H. E. and T. W. Kwon. 1987. *Soybean Utilization*. AVI Van Nostrand Reinhold Co., New York.
- Soyatech, Inc. 2001. *Soya & Oilseed Bluebook*. Soyatech, Inc., Bar Harbor, ME.
- Troy, D. J. 1994. Increasing meat tenderness through endogenous systems. *Farm and Food* 4(1):15-17.
- Venkatachalam, M., S. S. Teuber, K. H. Roux, and S. K. Sathe. 2002. Effects of roasting, blanching, autoclaving, and microwave heating on antigenicity of almond (*Prunus dulcis* L.) proteins. *J. Agric. Food Chem.* 50(12):3544-3548.

- Vinatoru, M., T. Maricela, R. Otilia, P. I. Filip, D. Lazurca, and T. J. Mason. 1997. The use of ultrasound for the extraction of bioactive principles from plant materials. *Ultrasonics Sonochemistry*. 4:135-139.
- Wang, D. I. C. and S. A. Goldblith. 1974. Dielectric properties of food materials. *J. Microwave Power* 9(4):303-316.
- Wang, T., L. A. Johnson, and T. Wang. 2001. Survey of soybean oil and meal qualities produced by different processes. *J. Am. Oil Chem. Soc.* 78(3):311-318.
- Yoshida, H., and S. Takagi. 1997. Microwave roasting and positional distribution of fatty acids of phospholipids in soybeans. *J. Am. Oil Chem. Soc.* 74(2):117-124
- Zayas, J. F. 1985. Structural and water binding properties of meat emulsions prepared with emulsified and unemulsified fat. *J. Food Sci.* 50(3):689-692.
- Zhu, S. 1998. A preliminary enquiry into sterilizing experiment by ultrasonic wave. *Sci. Tech. Food Ind.* 1(1):12-14.

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