Comparison of Alternative Solvents for Oils Extraction

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ABSTRACT

A comprehensive review of the literature about use of solvents for extraction of oilseeds is presented. Mention has been found of over 70 solvents. Currently, hexane is the major solvent in use, but recent price increases and safety, environmental and health concerns, have generated interest in alternatives. Solvents vary considerably in chemical and physical properties which affect their performance in oil extraction. The choice of solvent depends upon the primary end product desired (oil or meal). Recent research on alternative solvents has focused on ethanol, isopropanol, methylene chloride, aqueous acetone, and hexane/acetone/water mixtures.

INTRODUCTION

Solvent extraction has been defined as a process for transporting materials from one phase to another for the purpose of separating one or more compounds from mixtures. In the case of oilseed extraction, crude vegetable oil is separated by solvent from meal comprising proteins and carbohydrates. Various solvents have been used commercially, and others have been proposed, based on encouraging laboratory results; but currently, hexane is the solvent of choice by oilseed processors. Operating losses of solvent range between 0.2 and 2.0 gallons per ton of seed processed, and a 6- to 8-fold increase in price during the last decade, has made hexane costs a major factor in oilseed milling. Occasional scarcities of hexane, toxicological and environmental concerns, and several catastrophic explosions and fires have motivated searches for alternative solvents. Listings of references for various solvents and their usage were published on two occasions in this journal (1,2); and Hron et al. (3) recently discussed biorenewable solvents. However, a comprehensive review of alternative solvents for oilseeds extraction has not been published.

DISSOLUTION THEORY

Solvent extraction dissolution theory, based on the laws of thermodynamics, has been explained by Sedine and Hasegawa (4). During dissolution, two separate substances, the solute and the solvent, form a molecular mixture. Dissolution is always accompanied by a negative free energy change. Free energy (ΔG) is related by the Gibbs equation to enthalpy (or heat content (ΔH)), absolute temperature (T), and entropy (or amount of disorder (ΔS)) as:

$$\Delta G = \Delta H - T\Delta S$$

Because dissolution involves mixing of two substances and an increase in their disorder, a positive entropy change, occurs.

Dissolution involves two endothermic processes and one exothermic. First, solute molecules (whether solid or liquid) separate into isolated molecules. This is an endothermic process. Its energy is called "lattice energy," "heat of sublimation," or "heat of vaporization," and is small when the solute molecules are nonpolar. The separated solute molecules are next dispersed into the solvent. Energy is required to dissociate the solvent molecules, in preparation to accommodate the solute molecules. The energy required increases with increasing intermolecular interactions in the pure solvent in the following order: nonpolar solvents < polar solvents < hydrogen-bonded solvents. The energy required is also greater when the solute molecule is larger, since more intermolecular bonds must be disrupted between solvent molecules to make room for the solute. In the third process (which is exothermic), the dispersed solute molecules interact with neighboring solvent molecules. Energy released increases in the following order of solute-solvent interactions: both solvent and solute molecules are nonpolar < one is polar and the other is nonpolar < both molecules are polar < solute molecules are solvated by the solvent molecules.

The overall enthalpy change is more negative (exothermic) if energy losses of the solute-solute and solvent-solvent interactions are greater than the energy gain in the solute-solvent interaction. When solute molecules are strongly bonded to each other, they are highly soluble only in solvents whose solute-solvent interactions are also large. When solvent molecules are highly interassociated, as with water, the solute dissolves well only if dissolution results in a stronger solute-solvent interaction. Thus, the solubility of triglyceride in water is small because triglyceride molecules interact with water only weakly and energy gained from the triglyceride-water interaction cannot compensate for the large amount of energy required to break the intermolecular hydrogen bonds of water. However, solubility of oil in *n*-hexane is high because of stronger solute-solvent interactions which compensate for energy losses in the first and second stages.

A general principle for the dissolution of materials, is that "like dissolves like"; i.e., a nonpolar solute is more soluble in a nonpolar solvent, while a polar solute is more soluble in a polar solvent. However, some polar solvents can dissolve certain nonpolar solutes, such as methanol dissolving triglycerides. The energy required for disruption of solvent-solvent interactions may be large; but, the gain of energy in the solute-solvent interaction is still larger.

The solubility of one liquid in another is usually increased by elevating the solution temperature. Solubility is low at low temperatures, but increases at higher temperatures until the critical solution temperature is reached where the liquids become miscible in all proportions. Vegetable oil and acetone behave in this manner.

EXTRACTION

Mechanisms of Extraction

Chemical engineers have applied leaching theory (5,6), diffusion theory (7-9), soaking theory (10) and Hagen-Poiseuille laws for viscous flow in capillaries (11,12) to correlate extraction rate data, predict extraction time and design extractors. However, oilseed extraction involves several mechanisms for removing a liquid from a solid: leaching, washing, diffusion and dialysis (13-15). Seeds or press cakes are usually prepared by cracking, heating and flaking prior to direct solvent extraction, or are conditioned, expeller-pressed, ground and flaked prior to extraction. These operations distort cells (16,17), and rupture cell walls and the natural compartmentalization of oil in spherozomes within the cell. Flaking also reduces particle

thickness and the distance required for transfer of oil into bulk solvent. The larger portion of the readily available oil derives from ruptured cells. The transfer mechanism is probably governed by capillary flow; and rate of oil transfer is partly dependent upon viscosities of the solvent and miscella. A smaller portion of oil is contained within unruptured cells, and must be transferred by osmosis. This transfer has been shown to be very slow in oilseed extraction (11), and the rate is dependent upon molecular sizes of the oil and solvent.

Properties of Ideal Solvents for Oilseed Extraction

The desirable properties of a solvent suitable for extracting vegetable oil from oilseeds are numerous (18,19); and experience tells us that the ideal solvent probably does not exist. Nearly all known oilseed extraction plants are currently using hexane; however, industry is constantly looking for a better solvent. The definition of "better" depends upon what our objectives are, and the available practical alternatives. When hexane became scarce and prices rose quickly during 1972, a "better" solvent would have been one which was plentiful and lower priced. When a fire or explosion occurs in an extraction plant, a "better" solvent is one which is nonflammable. When governmental regulatory agencies act to curb solvent emissions, a "better" solvent is one to which they will not object. However, when we say "better", we do not mean "better at any cost".

In selecting the "better" solvent, other requirements should be considered, including: ability to use the new solvent in existing equipment or with low costs of retrofitting, and possible effects on profitability of operations which result from changes in extractor capacity, solvent and energy costs, product yields and market value. The ability to fulfill many of these requirements depends in part upon physical and chemical properties of the solvent.

High solvent power for triglycerides at elevated temperatures is the single most important property of a solvent. Obviously, if the oil is not soluble in the solvent, there would be no extraction. A method for correlating and predicting solubility data for fatty materials in various solvents has been reported by Skau and coworkers (20-24). Generally, elevated temperatures are used to facilitate more rapid extraction (25). A solvent having high solubility at elevated temperature and low solubility at ambient temperature may be desirable, because phase separation of oil from solvent would occur without necessity for evaporation. The lower alcohols exhibit this characteristic.

The second most important characteristic is that the solvent be nontoxic to workers at the mill, and nontoxic to animals or humans when the meal is used as feed or food. Some potential solvents have been shown to be lethal, mutagenic, carcinogenic and/or narcotic.

Selectivity of a solvent is also a very important characteristic; but, the desired selectivity may vary for different oilseed crops and desired end products. Where the concern is only about oil, it is desirable to use solvents which extract only triglycerides and leave phosphatides, free fatty acids, waxes, and pigments in the meal. Only occasionally are phosphatides economically recovered from crude oils as lecithin for use as emulsifiers. Usually, these compounds must be removed during refining, but have much lower value than triglycerides, and increase refining loss. However, phosphatides, free fatty acids, waxes, and pigments are not desired in the meal if it is to be used for preparation of food protein flours, concentrates or isolates. In some cases, it may be desirable to extract other components along with triglycerides, such as gossypol, aflatoxin, alkaloids and flavor compounds, because they cause problems if left in the meal.

Gossypol in crude cottonseed oil can cause red color in the oil if the oil is not miscella or conventionally refined shortly after extraction.

Most cottonseed processors heat treat cottonseed meats to bind gossypol to protein, thereby reducing its extraction with oil. But this practice also reduces feeding efficiency, and the residual free gossypol is still sufficient to be toxic to nonruminants. Cottonseed oil millers are, therefore, interested in solvents which would extract free gossypol from the meal, and make the meal suitable for feeding to poultry and swine, or for use as food protein ingredients.

Ever since the early 1960s, when large numbers of turkeys were killed in England by feeding moldy peanut meal, the presence of aflatoxins in oilseeds and their products has attracted wide attention. Hexane does not extract aflatoxins which, consequently, become concentrated in the meal. Cottonseed and peanuts are particularly susceptible to aflatoxin producing molds. Meals exceeding 20 ppb aflatoxin are generally not permitted as food and feed ingredients, and may be relegated to fertilizer use. Solvents which extract aflatoxins with the oil have been sought (26), since aflatoxin is removed from oil or inactivated by alkali refining and bleaching (27) and has not been found in refined vegetable oils. Other solvents are used to extract alkaloids from lupine meal and off-flavor compounds from soybean meal.

The solvent should be easily recovered from meal and oil. Physical properties such as specific heat, latent heat of vaporization, boiling point, oil solubility, viscosity, specific gravity, and polarity affect the ease and amount of energy required to recover the solvent. However, the more polar solvents may become strongly absorbed by protein through hydrogen bonding, making it difficult to achieve low levels of residual solvent.

Nonflammability, or low flammability within a narrow range of explosive limits, are desirable to reduce the hazard of fire and explosion. Despite close surveillance by management, and compliance with recommended practices of fire protection associations, building codes and governmental regulatory agencies, about one major accident occurs per year, worldwide, and reminds us of hazards associated with hexane extraction.

Solvent stability is desired. Extraction solvents should be stable to heat, light and water. Recycling is necessary, and the solvent must withstand repeated cycles of heating, vaporizing and cooling. Stability is also required to prevent contamination of meal and oil with potentially hazardous decomposition products.

Extraction solvents should be nonreactive with oil and meal. An example of solvent-product interaction problems occurred in the development of trichloroethylene for extraction of soybeans. Apparently, this solvent reacted with proteins to form compounds which were toxic to cattle and caused numerous deaths. In addition to the loss of animals, the tragedies of the trichloroethylene experience were that doubts were cast on safety of all solvent-extracted meals during the emerging years of the industry, and some of these concerns still haunt the credibility of all halogenated hydrocarbon solvents.

The solvent should not react with equipment. Some solvents are corrosive to piping and metal components, and solubilize metalic ions which can cause discoloration and off-flavors in oil. Gaskets and seals may be deteriorated, and plastic parts and tubing may become brittle by contact with some solvents.

A good solvent should have high purity. The more pure the solvent, the more uniform the operating characteristics. Solvents, which are mixtures of several compounds, boil or distill over temperature ranges inclusive of the boiling

points of the components. High losses are experienced when using solvents with wide boiling ranges. A high concentration of low boiling compounds may result in losses due to leaks and escape through the condensor; whereas, a high concentration of high boiling compounds may result in losses due to solvent residuals in oil and meal. Increasing the heat to remove these residual solvents is costly in energy, and can adversely affect feed value of the meal and oil color. High purity is also important from the standpoint of toxicity. For example, the benzene content of commercial hexane has been of concern.

Slight solubility in water is desired, since live steam is frequently used to strip trace residuals of solvent from meal and oil. But separation of solvent from the solvent-water mixture is enhanced if solubility of solvent in water is low.

Finally, the ideal solvent would be available in adequate quantities at low prices. Although considerable effort has gone into reducing leaks, spills and residual levels in meal and oil, some losses are inevitable, and solvent must be replaced.

HISTORY OF SOLVENTS USED IN OILSEED EXTRACTION

Patents were issued in France to E. Deiss in 1855 for a process to extract fat from bones and wool using carbon disulfide, and a year later for extraction of oilseeds (28). Several years later, Deiss built a plant at Marseilles for extracting oil from olive press cake, and the process quickly expanded across France and Italy (29).

Batch solvent extraction was well established as an industrial process in Europe by 1870 (30). In addition to carbon disulfide, petroleum naphthas, trichloroethylene and ethanol were used as early commercial solvents for oilseed extraction.

Hydrocarbon Naphthas

During the early years of the petroleum industry, the major emphasis was on making medicinals, lubricants, heating oils and lighting oils (31). The more volatile fractions (naphthas of natural gas and gasoline refining) were considered to be nuisances by refiners since there were few commercial uses for them. However, acceptance of the internal combustion engine and automobiles increased the commercial value of these fractions. About 1905-10, the volatile petroleum naphthas and gasoline became the desired principal products, rather than unwanted byproducts.

The shortage of fats and oils in Europe for food, explosives, and industrial uses, which occurred during and immediately after World War I, led to development of more efficient and complete processes for recovering oil from oilseeds (32). Prior to 1920, solvent extraction was batchwise; but, in the early 1920s, continuous and countercurrent extractors were developed in Germany by Bollman and Hildebrandt to extract soybeans imported from Manchuria. By 1928, the Hansa-Muhle Company was extracting 1,000 tons of seed per day in four Hildebrandt extractors at its central plant in Hamburg, Germany (33). The earliest solvent extraction trials in the United States were on corn germ in Cedar Rapids, IA, in 1915, and at Southport Mills, New Orleans, where aviation-type gasoline and later benzene were used to recover oil from cottonseed cake, copra, palm kernel and other materials in 1917-19 (34).

During the Depression, the automobile giant, Henry Ford, became instrumental in developing soybeans as a cash crop for farmers (28). He perceived farmers as a market for his Model T automobile and decided that he had to find a way for industry to become a customer of farmers. Ford established the Edison Institute, where it was found that soybean oil could be used as a base for enamel paints and the meal for plastic parts for his cars if the oil could be removed to less than 2%. Mechanical presses in use at that time left 5-10% residual oil in the meal. Edison staffers, envisioning that farmers could run a simple extractor on the farm during the winter to produce oil and meal, began to develop a suitable extractor. Publicity about soybeans, and new uses of soy products developed by the Edison Institute and others, contributed to the considerable growth in soybean production in the 1930s and 1940s. In 1934, the Archer-Daniels-Midland Co. and the Glidden Co. each opened plants in Chicago using Hildebrandt U-tube extractors and hexane-type petroleum naphthas for solvent. These were the first large-scale oilseed extraction plants in the USA, and each processed ca. 100 tons daily of soybeans.

Prior to the 1940s, most of the naphthas available to oilseed extractors had been developed for the rubber, lacquer and other industries. Although cheap, they often did not meet even the loose specifications of the time, and had variable physical properties. Most of the extraction naphthas were made directly from crude petroleum, and contained large amounts of sulfur, nitrogen and high boiling compounds which were greasy and polymerized or gummed during use. Extractors using these solvents required considerable steam, time and labor for desolventizing oil and meal. Often high residuals caused unstable oil and unacceptable flavors and odors in oils and meals. (Even ordinary gasoline, which contained high boiling fractions (boiling range 39-204 C), had been used (34).) Extending the desolventizing time to remove the high boiling components greatly impaired oil color, and palatability and feeding efficiency of the meals for livestock. It was little wonder that general opinion during the 1930s was that solvent extracted oils and meals were inferior to mechanically expressed products.

The oil extraction industry began to demand purer solvents, which boiled and distilled within narrower temperature ranges. This led to development of pentane-type naphthas (boiling range 35-59 C), hexane-type naphthas (boiling range 63-69 C), cyclohexane-type naphthas (boiling range 89-98 C) from natural gas. The newer solvents significantly improved the qualities of crude oil and meal recovered by extraction, and all have been commercially used for oilseed extraction. Hexane became the major solvent because of high stability, low evaporation loss, low corrosion, low greasy residue, and better odor and flavor of mill products.

Hexane comes from the same feedstock as gasoline and its bulk adds to the volume of gasoline, even though its octane value is low (35). To justify its production, hexane must sell at a premium over gasoline. Therefore, its price has been determined by the supply and demand for gasoline.

Trichloroethylene

Flammability of hydrocarbon naphthas has been a major obstacle in commercial development of solvent extraction processes. Only large centralized facilities can afford the capital investment and obtain the highly skilled labor required to extract oilseeds with hexane. During the period 1930-55, economics favored establishment of extraction operations close to the supply of seed and markets for livestock and poultry feed in order to save freight costs (36). A nonflammable solvent was critical to establishment of a decentralized oilseed processing industry, and led to interest in trichloroethylene. Like several other halogenated hydrocarbons, this compound is nonflammable and nonexplosive, and therefore appealing because of safety considerations

and reduced costs of extraction equipment and fire-fighting provisions. Trichloroethylene was particularly attractive because it was readily available (being used in quantity for degreasing metal parts (37) and dry cleaning (38)); and moisture of the flakes had little effect on extraction rate (39). Industrial supplies of trichloroethylene have boiling points of about 87 C, which are low enough for easy evaporation without excessive volatility. Also, being a single compound rather than a mixture, no stripping of high boiling compounds was required from the oil and meal. Trichloroethylene has a low heat of vaporization which results in low evaporation costs, and low water solubility and solvent losses during solvent-water separation. For these reasons, a major research and development effort was begun at Iowa State University in the early 1940s to develop a solvent extraction process using trichloroethylene which could be used in a decentralized soybean extraction industry.

Besides the cited advantages for trichloroethylene, it was understood that this solvent had some disadvantages which were perceived to be insignificant. Cost was high compared to hydrocarbon napthas, and more complete recovery from oil and meal was required. Although trichloroethylene had a high solvent capacity, it was less selective and extracted more pigments than hexane. Consequently, yield of crude oil was higher but the color was poorer; however, good color could be achieved without excessive refining loss (38). At that time, trichloroethylene vapors were thought to be toxic; this was believed to be due to presence of impurities (40). Periodically, some concern had been expressed about a report by Stockman (41) in 1916 that soybean meal extracted with trichloroethylene ("trimeal") had caused "bloody nose disease" (or hemorrhagic aplastic anemia) and cattle deaths in Southern Scotland. Stockman had first presumed that residual trichloroethylene was the cause; but he and others (36,42) could not induce the toxic effect by adding the solvent to hexane-extracted meal. During the period that research was being conducted at Iowa State, one large English mill had used trichloroethylene to minimize fire hazards during air raids of World War II and continued to do so, until at least 1952, without incident. However, the meal was fed at very low levels (0.5 lb/animal/day) in mixed rations. Believing that the cattle deaths were the result of contaminants in the early preparations of trichloroethylene (29), US researchers did not seriously consider the Stockman report in developing a trichloroethylene extraction process.

After Iowa State had perfected an extractor and a process for extracting soybeans with trichloroethylene, an equipment manufacturer was licensed to sell the extractor and construction of ten plants using trichloroethylene began. As these plants came on stream in 1951, meal began to be fed to cattle at 2-3 lb/animal/day as a protein supplement, rather than in mixed feeds. Cattle quickly began to die of "bloody nose disease". By 1952, most of the mills had closed or were selling the meal for swine or poultry feeding, since apparently only ruminants were affected (43). The plants were converted to hexane and production of the developed extractor continues today.

Despite considerable research (44,46) the precise toxic mechanism involving solvent, meal and cattle was never identified. However, it was hypothesized that trichloroethylene reacted with sulfhydryl groups of the amino acid cysteine, because S-(*trans*-dichloro-vinyl)-L-cysteine produced the same symptoms when fed to calves. Unfortunately, a search of foreign literature, through which it was learned in the USA that widespread cattle deaths had also occurred in Germany, France and Holland during the 1920s and more recently in Italy and Japan, was not conducted until the crisis developed.

Ethanol

While work in the USA was being directed at trichloroethylene, the Japanese-controlled Manchurian Soybean Company in Darien, Manchuria was developing the "hot ethanol process" (47,48) because of shortage of petroleum distillates. Solubility of oil in ethanol is dependent upon temperature and water content (Fig. 1) (49-53). At temperatures higher than 70 C, soybean oil is miscible in all proportions with near absolute ethanol. At lower alcohol concentrations, oil solubility is greatly reduced and complete miscibility is not achieved even at the boiling point. However, solubility of oil in 95% ethanol (azeotropic mixture with water) can be brought into a practical range by operating at sufficient pressure to bring the temperature to 90 C.

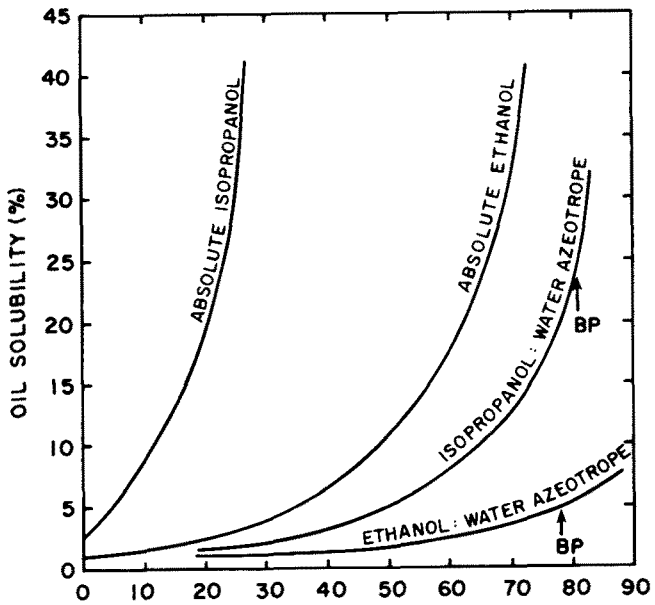

FIG. 1. Solubilities of cottonseed oil in alcohols. (Plots of data from references 50-53, 99, 112.)

The installation at Darien had a capacity of 100 tons of soybean per day. The beans were flaked and dried to 3-5% moisture. Since absolute ethanol has dehydrating properties, predrying of beans was important to reduce uptake of water and the consequent loss of solvent power. Had the beans been dried to 3% moisture or less, no absorption of moisture would have occurred (54). The dried flakes were charged into a battery of batch extractors with hot 99% ethanol under pressure. Miscella was drawn off, cooled, and pumped to a conical separating tank. Cooling the hot solution of oil in ethanol resulted in the formation of two layers; the lower, heavier phase consisted of ca. 95% oil and 5% ethanol, while the lighter, upper phase was chiefly ethanol with a small amount of oil. The oil phase was sent to an evaporator, and the ethanol phase was recycled to the same extractor until the oil content of the meal was reduced to 0.5-1.0%. After extraction and oil separation, the final alcohol phase was sent to a still for rectification and recovery of residual oil and byproducts

(sugars, saponins and phosphatides). The recovered oil was light yellow and suitable for edible purposes without further refining. The quality of meal was greatly improved over meals extracted with hexane, and was suitable for food and industrial uses. The meal was characterized as being absent of bitter and beany flavors, whiter in color (55), and free of flatus-causing sugars. The high cost of ethanol relative to hydrocarbons, and the higher latent heat of vaporization, have been deterrants to further development of alcohol extraction. However, more competitive prices, possibility of nondistillation solvent recovery (54), and mounting interest in use of renewable resources (including alcohol produced from agricultural residues), have led to renewed interest in ethanol as an extraction solvent.

Other Solvents

The literature contains limited reports (48) on use of ethanol-benzene and methanol-benzene mixtures for processing soybeans where phosphatide recovery was important. These mixtures were used commercially by the Hansa-Muhle Co. in Hamburg, Germany in the late 1920s. Also, at about the same time, a small extraction plant in Monticello, IL, operated for a period on benzene (48). Despite wide explosive limits in air, which made it an undesirable solvent, carbon disulfide was used on a limited basis to extract olive oil from olive press cake in Europe; however, it was never used in the US crushing industry.

MEANINGS OF CHEMICAL AND PHYSICAL CONSTANTS

Chemical and physical constants of many solvents are presented in Table I. Since these properties largely determine the relative suitability for vegetable oil extraction, it is necessary to understand their meaning in selecting a solvent.

The boiling point of a solvent is an easily determined constant and is indicative of solvent purity. A moderately low boiling point (35-65 C) is desired to reduce the amount of sensible heat required for evaporation. A narrow boiling range also reduces solvent residuals in products.

The latent heat of vaporzation is the quantity of energy (cal) required to convert a mass of liquid (g) to vapor without a change in temperature. A low latent heat of vaporization is desired to minimize intermolecular interaction and evaporate solvent from oil and meal. Evaporation in an oil mill consumes more energy than any other unit operation. Small differences in latent heat of vaporization can significantly affect energy costs.

Specific heat is a measure of the quantity of energy (cal) required to raise the temperature of one gram of solvent by one degree centigrade. Low specific heat values are also desired to reduce energy costs in heating solvents.

Specific gravity (or density) is an easily obtained constant, which is important in controlling solvent purity. Specific gravity is a measure of the mass (weight, g) of solvent relative to its volume (cm^3). Since solvents expand in volume with increases in temperature, specific gravity is usually determined at a standard temperature of 20 C. Wide variations in specific gravity occur among the different solvents. For example, hydrocarbon fractions have specific gravities of 0.60-0.75 g/cc, while some halogenated hydrocarbons can be as dense as 1.7 g/cc. Extractors designed for more dense solvents require heavier construction materials, and more energy for pumping for the same volume.

Viscosity is a measure of internal molecular friction, which hinders flow. A low viscosity is desirable. Since extraction is in part governed by capillary flow, solvents with high viscosities may have slower rates of extraction. Viscosity of miscella also affects the rate of solvent drainage and percolation. The more viscous solvents also require more energy for pumping. Viscosity is lower at higher temperatures, and is usually reported at a standard temperature of 20 C.

Surface tension is a property indicative of the contraction of an exposed surface of solvent to the smallest possible area due to intermolecular cohesion. A high surface tension can impede penetration of solvent into oilseed flakes, and reduce the rate of extraction.

Dielectric constant is a dimensionless quantity, which indicates the electrical insulating properties of the solvent. The higher the dielectric constant, the more polar the solvent and, generally, the lower its solubility of oil.

Flash point (closed-cup) and explosive limits define the fire hazard of a solvent. The flash point is the temperature at which vapors over the solvent will ignite when exposed to a flame or spark in a confined space. Lower flash points indicate greater fire hazard (64). Explosive limits are the range of solvent concentrations (volume percent in air) that can be ignited or exploded. Upper and lower explosive limits occur because both solvent vapors and oxygen are required for combustion. The higher the lower limit, and the narrower the range, the lower the fire hazard.

Many solvents form azeotropic mixtures with water. An azeotrope is a specific ratio which has a constant boiling point, and whose components cannot be separated by distillation. The azeotropic mixture always has a lower boiling point than either of the pure components. Stripping of solvents from meal and oil is often eased by sparging steam to form the azeotropic mixture.

The solubility of water in solvent indicates the relative ease of separating water and solvent from vapors condensed from desolventization of oil and meal. Low levels of water solubility are desired.

The hazard of a solvent to health of employees working in extraction plants is given by threshhold limit value-time weighted average (TLV-TWA) (63). These levels indicate the concentrations in the work environment at which it is believed that nearly all workers may be repeatedly exposed, for a normal 8-hr workday and 40-hr workweek, without adverse effect. The limits are not regarded as definitions of safe and dangerous conditions. Low hazard levels are undesirable because solvent leaks, spills and losses are inevitable.

ALTERNATIVE SOLVENTS FOR OIL EXTRACTION

Aqueous Extraction

Water can be used as a processing aid for physical separation of oil from oilseed solids by the aqueous extraction process developed at Texas A&M University (65-71). The process includes comminuting the seed and dispersal in hot water, followed by centrifugal separation, which divides the dispersion into emulsion, solid residue and soluble aqueous phases. The cream emulsion is then broken to recover the oil, and the solids concentrated by drying. Edible protein products, such as protein isolates and concentrates, may be simultaneously recovered. Extraction of oil from other seed components by this process is based on insolubility of oil rather than on dissolution of oil.

Petroleum Hydrocarbons

Hydrocarbon fractions are petroleum distillates and, as such, are mixtures of various hydrocarbons. Each component has its own individual boiling point, solvency and other properties. It is possible to have two or more fractions with practically identical boiling ranges, but which

TABLE I

Chemical and Physical Properties of Extraction Solvents

Solvent	Boiling point (C)	Latent heat of vaporization (cal/g)	Specific heat (cal/g C)	Specific gravity @ 20 C (g/cc)	Liquid viscosity @ 20 C (cp)	Surface tension (dyne/cm)	Dielectric constant	Flash point (C)	Explosive limits (% vol in air)	Water solubility @ 25 C (g/L)	Water azeotrope		TLV-TWA (ppm)
											Water (% wt)	Boiling pt. (C)	
Water	100.0	540.1	1.018	1.000	1.005	72.75	80.36	NF	NF	–	–	–	–
Petroleum fractions													
Gasoline	39-204			0.72-0.76				-45	1.3- 6.0				300
Petroleum ether	35-60			0.62-0.66				-40	1.4- 8.0				
Pentanes	32-37			0.62-0.63				-54					600
Methyl pentanes	56-62			0.65-0.67				-32					500
Hexanes	65-69			0.67-0.72	0.32			-22	1.1- 7.5				50
Heptanes	88-99			0.72-0.74	0.47			-5	1.2- 6.7		10.3	80-85	400
Cyclohexane	65-85												300
Alkanes													
n-Propane	-41.7	101.6	0.520[bp]						2.4- 9.5				
n-Butane	0.5	92.2	0.550[bp]						1.9- 8.5				800
n-Pentane	36.2	85.3	0.542	0.626	0.234	16.05	1.84	-49	1.4- 8.0	0.36			600
Isopentane	27.8	81.7	0.535	0.620	0.224	15.00	1.84	-5	1.4- 8.3	0.14			
n-Hexane	69.0	79.9	0.533	0.659	0.312	18.40	1.89	-23	1.2- 7.7	0.05	5.0		50
Isohexane	60.3	77.4	0.533	0.652	0.299	15.84		-7	1.2- 7.0	0.00			500
n-Heptane	98.4	75.5	0.528	0.684	0.417	20.14	1.92	-4	1.0- 7.0	0.05	13.0	79.4	400
Cycloparafins													
Cyclopentane	49.5	92.9	0.422	0.751	0.438	22.42	1.97	-37	1.4-	0.00			600
Cyclohexane	80.7	77.2	0.433	0.778	0.977	24.98	2.02	-18	1.3- 8.4	0.00			300
Aromatic Hydrocarbons													
Benzene	80.1	94.0	0.410	0.879	0.647	28.88	2.28	10	1.3- 7.9	0.82			10
Toluene	110.6	86.7	0.402	0.867	0.585	28.53	2.38	6	1.2- 7.1	0.47			100
Mixed xylenes	138.7	81.1	0.408		0.65	28.31	2.4	29	1.0- 5.3	0.00			100
Halogenated Hydrocarbons													
Dichloromethane	39.8	78.7	0.276	1.326	0.513	28.00	9.08	NF	NF	20.00	1.5	38.1	100
Ethyl chloride	12.3	92.5	0.370[bp]	0.923[bp]			6.29	-50	3.6-14.8				1000
Chloroform	61.2	59.0	0.234	1.477	0.562	27.10	4.81	NF	NF	0.00	2.8	56.1	10
Carbon tetrachloride	76.7	46.5	0.200	1.585	0.971	26.84	2.24	NF	NF	0.80	4.1	66.0	5
1,2-Dichloroethane	83.6	77.3	0.310	1.255	0.78	37.50	10.50	15	6.2-15.9	8.69	8.2	70.5	200
1,2-Dichloroethylene	60.3	73.0	0.270	1.282	0.467	28.00	9.20	14		0.00			200
1,1,1-Trichloroethane	74.1	68.7	0.240	1.324	0.858	25.12	7.50	NF	NF	0.00	4.3	65	350
1,2,2-Trichloroethylene	86.7	57.3	0.300	1.456	0.550	32.00	3.27	NF	NF	1.00	5.4	73	50
1,1,2,2-Tetrachloroethylene	121.0	50.1	0.210	1.618	0.90	29.3	2.20	NF	NF	0.00	15.9	87.8	50
1,2-Dichloropropane	95.9	72.2	0.310	1.157	0.865	31.40	8.93	21	3.1-14.5	2.7			75
n-Butyl bromide	101.4			1.274			7.07	24	2.6- 6.6	0.00			
1,1,2-Trichloro 1,2,2-triflouroethane	47.6	35.1	0.213	1.574	0.694	19.0	2.44	NF	NF	0.27			1000
Alcohols													
Methanol	64.7	473	0.599	0.792	0.59	22.53	31.2	11	6.0-36.5	INF	NONE	NONE	200
Ethanol	78.3	204	0.61	0.785	1.22	22.1	25.7	12	3.3-19.0	INF	4	78.2	1000
n-Propanol	97.2	162.6	0.586	0.805	2.256	23.8	20.1	22	2.6-13.5	INF	29.1	87.7	200
Isopropanol	82.5	159.3	0.596	0.786	2.4	20.8	18.6	11.7	2.5-12.0	INF	12.3	80.4	400
n-Butanol	117.7	141.3	0.563	0.811	2.948	24.6	16.1	37	1.5-11.3	79	42.5	92.7	50
Isobutanol	107.9	138.0	0.716	0.803	6.68	22.8	17.7	28	1.7-10.9	95	33.0	89.8	50
Allyl alcohol	96.9	163.8	0.665	0.850	1.072	25.7	21.6	21	2.5-18.0	INF	27.7	88.9	2
Furfuryl alcohol	171			1.129				79	1.8-16.3	INF	43	94	5
Aldehydes													
Furfural	161.7	107.5	0.401	1.161	1.49	40.7	41.9	60	2.1-	83	35	97.9	2
Ketones													
Acetone	56.1	124.5	0.51	0.791	0.316	23.7	21.5	-16	2.2-13.0	INF	NONE	NONE	750
Methyl ethyl ketone	79.6	106.0	0.55	0.806	0.423	24.6	18.51	-4	2.0-10.2	353	11.3	73.4	200
Esters													
Methyl acetate	56.9	104.4		0.958	0.381	24.76	7.3	-10	3.1-16		3.5	56.4	200
Ethyl acetate	77.0	102.9		0.897	0.473	23.75	6.02	0	2.3-11.4		8.5	70.4	400
Ethers													
Ethyl ether	34.5	84.0	0.548	0.715	0.233	17.0	3.88	-40	2.3- 6.2	75	1.1	34.1	400
Isopropyl ether	68.4	68.2	0.526	0.722	0.379	32.0	2.21	-28	1.4-21	2	4.5	62.2	250
Dioxane	101.1	97.0		1.033	1.439	34.45	16.3	5	2.0-22.0	INF	18.4	87.8	25
Ethylene glycol monomethyl ether	124.2	129.6	0.534	0.966	1.53	30.8		43		INF	77.8	99.9	25
Ethylene glycol monoethyl ether	134.7		0.530	0.931	1.84	28.2		40	2.6-15.7	INF	71.2	99.4	
Amines													
*Ethanol*amine	172.2	197.1		1.018	24.1	48.3	5.3	90	1.7- 9.8	INF			3
Butylamine	77.0	104.8		0.741	0.68	24.0			1.2- 8.0	INF			5
Triethylamine	89.5			0.733		20.66	12.3		1.8-12.4	15	10	75	10
Pyridine	115.3	59.6		0.982	1.038	37.25		23		INF			5
Other solvents													
Carbon disulfide	46.5	84.1	0.24	1.263	0.363	32.25	2.64	-30	1.0-50.0	2.2	2.8	42.6	10
Solvent mixtures													
Hexane/acetic acid (96:4)	68												
Hexane/methanol (45:25)	51												
Hexane/ethanol (79:21)	58.6												
Hexane/isopropanol (77:23)	62.7												
Hexane/allyl alcohol (95:5)	65.5												
Aromatic hydrocarbon/ethanol (90:10)													
Ethanol/water (96:4)	78.2		0.598	0.805				18					
Isopropanol/water (87.7:12.3)	80.4	204.1	0.770	0.818	2.106	21.1	27.0	17					
Methanol/trichloroethylene (75:25)													
Ethanol/trichloroethylene (75:25)													
Acetone/water (90:10)	59												
Acetone/hexane/water (54:44:2)	49												

[1]Data from references 57-64.

may be quite different in chemical composition (72). No two oil pools yield petroleum and natural gas which are exactly alike in chemical composition, and no two refiners process crude oil and natural gas in exactly the same manner.

Propane and butane gases, which boil at ambient temperatures, may be used in pressurized extractors (73-76). Extraction may be conducted at low temperatures where phosphatides, free fatty acids and pigments have relatively low solubility compared to triglycerides. Removal of solvent from oil and meal is easily accomplished by reducing pressure and applying slight heat.

Pentanes, hexanes and heptanes have been the principal constituents of extraction solvents used in the USA (77, 78). Solvents high in hexane content are now preferred; and typical purchase specifications are shown in Table II. Hexane-extracted meals are essentially free of odor and taste. The unsaponifiable content of hexane-extracted oil is low, since there are no high boiling components which resist desolventization. Heptanes are more difficult to desolventize and require more steam. Cyclohexane has been used in Europe, but is more difficult to desolventize than hexane.

The petroleum fraction commonly referred to as "hexane" can vary in the range of 45-90% *n*-hexane. Other major constituents are 2- and 3-methyl pentane, methyl cyclopentane and cyclohexane. Studies using different grades of hexane (79,80) indicate that the rate of oil extraction by pure *n*-hexane is slower than that of less pure hexane when extracting soybeans, but equal when extracting cottonseed. Also, the purer hexane extracted less free fatty acids and less color pigments from both. One study (79) compared pure grades (99% pure) of isopentane, *n*-pentane, cyclohexane, *n*-heptane, benzene; technical grades (95% pure) of neohexane, diisopropyl, 2-methyl pentane, 3-methyl pentane, *n*-hexane, methyl cyclohexane; and commercial grades of *n*-pentane, isohexane, *n*-hexane, isopentane and *n*-heptane. Oil yields were shown to decrease and color became darker as the boiling point of the solvent increased. Commercial quality hydrocarbons gave larger oil yields. Methyl pentane was shown to be the best hydrocarbon for extraction, and its moderately high concentration in commercial hexane, probably explains the improved solvent properties.

One of the early recognized and debated topics in hexane extraction is the search for a breakeven point for incremental extraction of soybean oil. The best quality oil (which is high in triglycerides) is extracted first and poor quality oil (which is high in phosphatides) is extracted later (13). The breakeven point between the incremental value of the later extracted oil, and incremental costs of extraction and refining losses of the later fractions, might be determined on a cost accounting basis.

Hexane only partially extracts phosphatides; and residuals in soybeans have been claimed to cause bitter and "beany" flavors in edible protein ingredients. The soy protein industry has used secondary extraction to remove flavor compounds from concentrates and isolates. Hexane partially extracts gossypol from cottonseed and, unless cottonseed is heat-treated prior to extraction to bind gossypol to protein, poor color results unless oils are refined immediately after extraction. The residual free gossypol in hexane-extracted cottonseed meal precludes its use as feed for nonruminant animals.

Aromatic hydrocarbons are unsaturated compounds with a six-carbon (benzene) ring structure. They are regarded as the most powerful solvents of the hydrocarbon family (57). Benzene, toluene and xylenes are effective; but, benzene is the only family member which has been used in commercial extraction of oilseeds. Oil extracted with benzene has lower neutral oil content and poorer color, and also lower free fatty acid content than hexane-extracted oil. A considerable portion of the gossypol can be extracted from cottonseed with benzene (83).

Halogenated Hydrocarbons

Halogenated solvents are hydrocarbons which contain fluorine, chlorine and bromine. Halogenation of hydrocarbons was discovered in 1840 by photochemical chlorination of methane (57). Despite relative high cost, halogenated hydrocarbons have had immense appeal as extraction solvents, because many are nonflammable. Trichloroethylene, as previously discussed, has been used commercially for extracting oilseeds, and extracts oil at a higher rate than

TABLE II

Typical Purchase Specifications for Hexane for Oilseed Extraction

Property	Value	Test
Specific gravity @ 25 C (g/cc)	0.6705 to 0.6805	ASTM D 1963-61
Distillation range (760 mm)		
Minimum initial boiling point (C)	65.0	ASTM 1078-63
Typical 10% distillation (C)	67.1	
Typical 50% distillation (C)	67.7	
Typical 90% distillation (C)	68.2	
Maximum dry point (C)	70.0	
Maximum nonvolatile residue (g/100 mL)	0.001	
Acidity of distillation residue	Neutral	
Closed-cup flash point (C)	-32 to -58	ASTM D 56-61
Maximum sulfur	10	ASTM D 1266-62T
Maximum vapor pressure (psia @ 35 C)	6.0	ASTM D 323-58
Composition (GLC, % area)		
n-Hexane	45-70	
Methyl cyclopentane	10-25	
Total *n*-hexane and methyl cyclopentane	60-80	
Total 2-methyl pentane; 2,3 dimethyl butane; and 3-methyl pentane	18-36	
Maximum cyclohexane	2.5	
Maximum benzene	0.1	
Maximum APHA color	15	ASTM D 1209-62
General appearance	Free of foreign material	

some other chlorinated hydrocarbons (84). Although use of trichloroethylene resulted in meals which were toxic to cattle, other halogenated compounds, which are effective solvents, may be nonreactive. Halogenated hydrocarbon solvents usually have wide variations in boiling points (-50 to 150 C), low latent heats of vaporization, low specific heats, and high specific gravities, viscosities and dielectric constants.

Fluorinated hydrocarbons such as the "freon" products, are widely used as refrigerants and aerosol propellants. Some can be used as liquid solvents, and others as liquified gases and supercritical fluids. 1,2,2-Trifluorotrichloroethane has been examined in laboratory extractions of soybean flakes (85,86). Trifluortrichloroethane extracts nearly equivalent quantities of oil and free fatty acids as hexane, but, slightly more phosphatides.

Although attempts to use trichloroethylene as a solvent for vegetable oil extraction have been abandoned, other chlorinated hydrocarbons have shown potential usefulness. Chlorinated hydrocarbons are currently used in a number of food industries (82). Dichloromethane (methylene chloride) is used to prepare hops extracts used in making beer. Coffee has been decaffeinated with dichloromethane and trichloromethylene. Dichloromethane has a high solubility for waxes and its use has been proposed as an aid in caustic peeling of fruits.

Dichloromethane is an excellent solvent for oils and is nearly as effective as trichloroethylene (88,89). Its low boiling point (39.8 C) results in easy desolventization of oil and meal; and the meal is believed to be nontoxic to animals (90). Suitability of methylene chloride as an oil extraction solvent was recognized in the 1940s, but high costs prevented serious consideration by oil millers. However, its relative price differential from hexane has decreased, making dichloromethane more competitive. Additional advantages in solvent selectivity have recently been recognized. Dichloromethane has good solubility for aflatoxins, and is used in analyses for extracting aflatoxins and purifying them for assay. Additionally, dichloromethane will extract gossypol from cottonseed. Cherry and Gray (91,92) have shown that dichloromethane, used for secondary extraction of hexane-extracted cottonseed meal, can produce food-grade meal (< 0.045% free gossypol). High solubility of gossypol in extraction solvents has been considered a major disadvantage resulting in oil with poor color. However, recent unpublished data (93) have shown that oils with excellent color can be produced from dichloromethane-oil miscellas by miscella refining. Data (94) have also shown that simultaneous extraction of oil, aflatoxin and gossypol from cottonseed flakes is possible.

Although the other chlorinated hydrocarbons are good solvents for oil (49,88), certain disadvantages make them less attractive. Ethyl chloride has a very low boiling point and is flammable. 1,2-Dichloroethane, 1,2-dichloroethylene, 1,2-dichloropropane and 1,2,3-trichloropropane are flammable also. 1,1,1-Trichloroethane and 1,1,2,2-tetrachloroethylene are nonflammable, but have high boiling points which make solvent recovery difficult. Chloroform and carbon tetrachloride are nonflammable, have similar boiling points, and produce oil with quality similar to hexane, but have low health hazard limits. A British patent was granted in 1938 for a process using carbon tetrachloride to extract castor oil (95). All chlorinated hydrocarbons give darker crude oil but the oils can be refined to good color without greater refining loss (88).

Brominated hydrocarbons have limited potential as oil extraction solvents (12). The boiling point of *n*-butyl bromide (101.4 C) is not conducive to efficient commercial extraction.

Alcohols

Alcohols have long been attractive alternative solvents to hexane for oil extraction in Asian countries, because petroleum is expensive, often scarce, and must be imported. Development of a process in Manchuria in the late 1930s for extracting oil from soybeans with anhydrous ethanol has already been discussed. The major problem in this application is maintaining solvent in the dry anhydrous state. Methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol and allyl alcohol are all good solvents at temperatures close to their boiling points, provided they remain anhydrous. Because solubility of oil is low, reduction of temperature is an effective means of recovering solvent from miscella. Use of this nondistillation method for solvent recovery in alcohol extraction requires 25-30% less energy than extraction with hexane (54). Since alcohols are more polar than hexane, they tend to extract more nontriglyceride compounds. Usually, the extracted oils contain more phosphatides and nonsaponifiables. When the chill-separated alcohol phase is recirculated, many of the soluble compounds reach an equilibrium between the oilseed and solvent and very little is extracted thereafter.

Alcohol/Water Mixtures

Most alcohols (methanol being an exception) form azeotropic mixtures with water, which have different properties than either pure solvent. Alcohol/water azeotropes of ethanol and isopropanol are 95% and 91% by volume, respectively. While other alcohol/water mixtures have been considered, the azeotropic mixtures have the most commercial potential (96,97). As water content increases, alcohol solvents become more polar and solubility of oil decreases (Fig. 1) (98,99). Conversely, capacity to extract nonlipids (phosphatides, pigments, sugars, etc.) increases as water content of the mixture increases. In laboratory experiments, anhydrous ethanol extracted 1.9 times as much lipid materials from soybean flakes, and one-half as much nonlipid materials, as 90% ethanol (50).

Solubilities of a variety of oils in aqueous alcohol solutions have been determined at various temperatures (50-53). The solubility of each oil in aqueous alcohol increases with temperature until the critical solution temperature is reached. The critical solution temperature increases linearly with moisture content of the alcohol. The critical solution temperature for oil in 95% ethanol is ca. 90 C, and requires pressurized vessels, since the boiling point is 78.2 C. While it is not practical to operate today's commonly used extractors under pressure, it is possible to operate within 1-2 C of the boiling point, where 95% ethanol has a solution capacity of ca. 8% oil. Efficient separation of oil from solvent occurs at 25 C or below, where oil solubility is less than 1%. After separation, the alcohol phase can be repeatedly recycled into the process with an equilibrium concentration of solubles varying from 4.3% at 0 C to 5.5% at 20 C. About 97% of the alcohol in the miscella can be recycled (100). Several processes have been devised to remove alcohol solubles remaining in the light phase (101, 102) and to recover phosphatides (103,104). Solvent stripped from the oil phase is recycled to the extractor for final washing of flakes. Moisture control during flaking becomes important when extracting with 95% ethanol in order to preserve oil solubility. The flakes are in moisture equilibrium with 95% ethanol when they contain 7-9% moisture. More moist flakes increase the water content of the alcohol. Pilot-plant extractions have shown that oil extracted from cottonseed with ethanol has free fatty acid content, refining loss and color within grade standards for prime oil (105).

Solubility properties of isopropanol/water mixtures, and feasibility of using 91% isopropanol as a solvent for cottonseed extraction, were first studied by Harris and coworkers in the late 1940s (99,106,108). The solubility of oil increases as it is heated until the critical solution temperature is reached (109). The critical solution temperature of isopropanol also increases with moisture content, and is ca. 82 C for 91% isopropanol. Only slight pressure is required for miscibility, since the boiling point is 80.4 C. When the extractor is operated with a solvent temperature within 1-2 C of the boiling point, solubility of oil is ca. 20% by weight. The oil can then be separated from miscella by chilling. The equilibrium solubles content varies from 4.7% at 0 C to 5.9% at 20 C. Free fatty acids, phosphatides, sugars and other extractables tend to concentrate in the alcohol phase upon phase separation, leaving relatively pure oil in the heavy phase. Further purification of the alcohol phase can be achieved by liquid-liquid extraction (99). The oil phase is ca. 88% oil, and is then stripped by evaporation and steam sparge. Flakes with 8-11% moisture seem to be in equilibrium with 91% isopropanol, and do not affect the water content of the recycle solvent. The crude oil extracted with 91% isopropanol is generally superior to crude oil obtained by hexane, and is much lower in free fatty acid content and phosphatides. Incorporation of minor amounts (0.1-1.0%) of hydrogen peroxide reportedly improves the color of oil extracted with isopropanol azeotrope (110). Residual oil levels, in the range of 0.3-0.7%, have been achieved in extracting soybean flakes with a pilot-plant extractor (111).

One of the objectives of the original research by Harris was to develop a process for simultaneous extraction of oil and gossypol from cottonseed. Harris reported that the isopropanol/water azeotrope extracted gossypol (106); more recently, it has been shown that gossypol is not extracted, but, rather becomes bound to protein (112). Crude oil has excellent color and is yellow rather than red, as is typical of hexane extraction. Free gossypol contents of the meal were reduced by 97%; and preparation of meals suitable for monogastric animals may be possible.

Both ethanol/water and isopropanol/water mixtures have been shown to be effective in removing aflatoxins. Higher concentrations of water are more effective. Reductions of 96-98% were achieved by extracting cottonseed and peanut meals with 90% ethanol, and 93-96% with 95% ethanol (113). In laboratory extractions at 60 C, 80:20 (w:w) isopropanol/water reduced aflatoxin content from cottonseed meal by 100%; isopropanol/water azeotrope achieved 79% reduction; and anhydrous isopropanol achieved 39% reduction (114). Simultaneous extraction of aflatoxin and oil from cottonseed flakes has been demonstrated in laboratory scale (112). Six stages of batch extraction (12 min contact time, 3 min drain, 2:1 solvent/flake) with isopropanol azeotrope were completed (Fig. 2). A 90% extraction of aflatoxin, with 97% extraction of oil, was achieved. In pilot-plant extractions of flaked meats having 350 ppb aflatoxin, the aflatoxin level in the meal was 6 ppb (115). The aflatoxin level in prepressed cottonseed meal was reduced from 300 ppb to 2 ppb.

Lupine, an emerging crop in South American and Mediterranean areas, contains up to 25% oil and 45% protein; but, its use in these countries, as a much needed food protein, is limited by the presence of bitter tasting, poisonous alkaloids (116). Alkaloids can be removed from hexane defatted meals by secondary extraction with ethanol/water and iospropanol/water mixtures (117). It is also likely that alkaloids and oil can be simultaneously extracted.

Because of increased interest in bland soybean protein

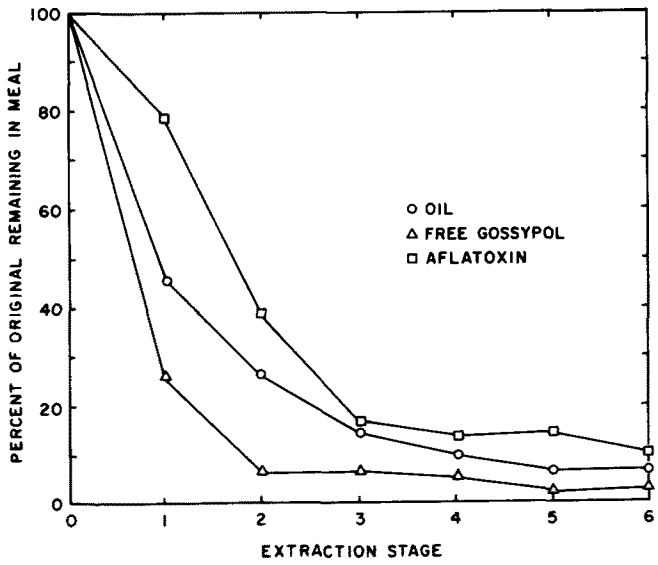

FIG. 2. Laboratory simulation of cottonseed extraction with isopropanol/water azeotrope (112).

food ingredients, it is desirable to find a solvent which will completely remove undesirable flavor compounds along with the oil. These compounds might then be removed from oil during refining and deodorization. About 1960, several soybean concentrates appeared in the market which were prepared by aqueous ethanol leaching of defatted flakes (118). Use of aqueous methanol (119), aqueous isopropanol (120), ethanol/acetone/ethylacetate (33:33:33, w/w/w) (121), and ethanol/chloroform (50:50, w/w) (122), have also been reported for preparing bland soy concentrate. Sources of many undesirable flavors has been associated with residual phosphatides. Simultaneous recovery of oil and these compounds may require evaporation of the miscella rather than phase separation of the solvent, and would increase energy costs (123). Ethanol-extracted flakes and extrudates have been shown to have superior color and flavor, reduced levels of flatus-causing sugars, and different functional properties (124-130). Peanut meal extracted with 90% isopropanol also has bland flavor (131). Protein dispersibility and trypsin inhibitor and urease levels are much lower in ethanol and isopropanol extracted meals than in hexane-extracted meals.

Two extraction processes have been developed for using ethanol/water and isopropanol/water mixtures (Fig. 3). In the Shell Process tested at the Texas A&M University pilot plant, soybeans are countercurrent-extracted with isopropanol azeotrope (78 C). The full miscella is cooled, and the oil phase-separated and sent to the oil stripper. The alcohol phase, together with alcohol from the oil stripper, are recycled to the extractor (132). It has been found that more isopropanol/water remains held up in gravity drainage than occurs in hexane extraction (111). By using a screw press to mechanically reduce solvent hold-up, considerable savings are achieved in energy and otherwise lost oil. Higher solvent:flake ratios (3:1 to 4:1) are used in isopropanol extraction than typical in hexane extraction (1:1). This process routinely has achieved 0.3-0.7% residual oil in the meal.

The Karnofsky Process (133-135) extracts gossypol, phosphatides, fatty acids, aflatoxin and oil in four sequential countercurrent extraction steps. In the first step, 60%

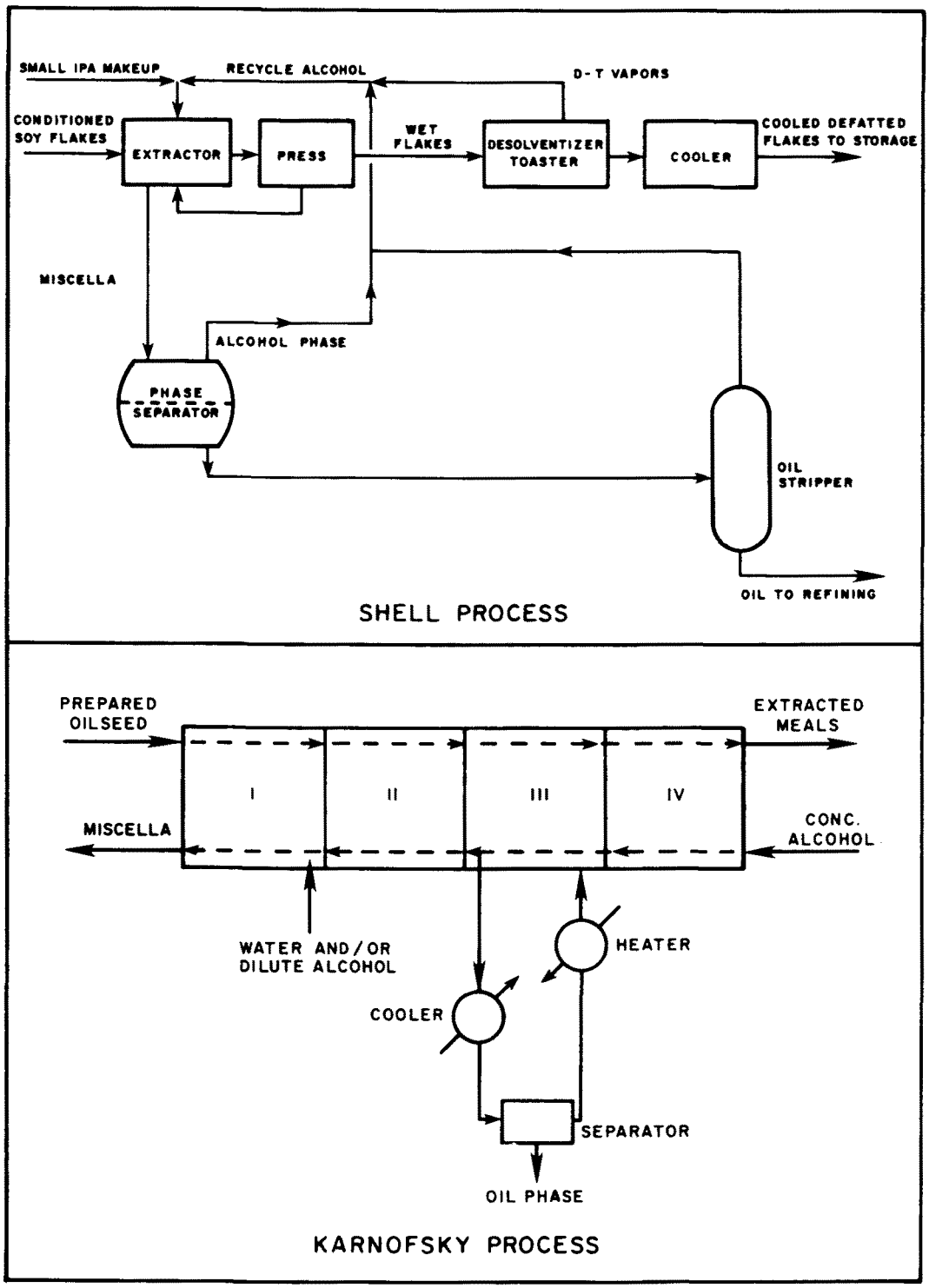

FIG. 3. Alcohol extraction processes (111,135).

ethanol selectively extracts carbohydrates, fatty acids and phosphatides. (Aflatoxin and gossypol can also be extracted if 85% ethanol is used.) The second step is a buffering stage to displace dilute alcohol with concentrated alcohol. Step three is essentially the oil extraction process developed by Harris. Oil extraction is completed in step four, where the flakes are extracted with azeotropic alcohol. The type of alcohol (ethanol or isopropanol), water content, temperature, and flow retention times at each stage, affects the properties of the meal. Use of low temperatures in the first step favors extraction of gossypol and higher protein solubility. As low as 0.29% total gossypol and 0.019% free gossypol have been achieved. Use of higher temperatures favors aflatoxin extraction.

Aldehydes

Fufural (an aldehyde solvent) and furfuryl alcohol have received cursory interest by the oil extraction industry (136). Furfural has excellent capacity for solubilizing oil at warm temperatures, and the solvent can be separated from crude oil by chilling the miscella or by adding water. Oils extracted with furfural contain high quantities of phosphatides. Furfural can be made from agricultural residues.

Ketones

Although a variety of ketones are available as industrial solvents, only acetone and butanone (methyl ethyl ketone) have been of interest in oil extraction. Eaves and coworkers (137) evaluated these solvents in pilot-plant batch extraction of cottonseed, and found that both solvents recovered as much oil from cottonseed flakes as did hexane. Gossypol content of meal was low; but crude and alkali refined oils had poorer color than hexane-extracted oils. Although free fatty acids are soluble in acetone, phosphatides are insoluble. Cottonseed meal extracted to low levels of gossypol with butanone have been shown to have higher nutritional value than hexane-extracted soybean meal.

Both butanone and acetone have high solubilities for water. Addition of water, either purposefully or through dissolution of seed moisture, affects solubility of various seed components (Fig. 4). Oil is substantially soluble only up to 10% water (138,139) and adding water to acetone miscella is one means used to recover oil from miscella. Extracting cottonseed with 70-75% acetone will remove 96-98% of the aflatoxin, essentially all the free gossypol, most free fatty acids and much of the sugars, but, negligible quantities of neutral oil. Therefore, sequential extraction of cottonseed with 30% aqueous acetone followed by hexane has been proposed (139,140). A mixture of 10% water in acetone has also been shown to be effective in removing aflatoxin from hexane-extracted peanut meal (141) and peanut and cottonseed press cakes (142), and has been used in preparative extraction for quantitative analyses (143).

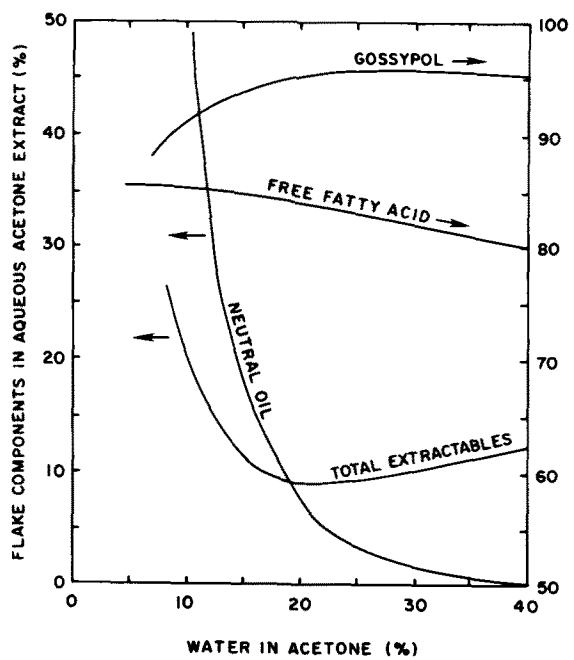

FIG. 4. Solubilities of cottonseed flake components in aqueous acetone (139).

The extracted peanut meal gave good feed conversion rates in ducklings and rats. Since oil is substantially soluble at 10% water, it would seem that a single extraction step with 10% aqueous acetone might achieve nearly the same objectives as sequential extraction with 30% aqueous acetone followed by hexane.

The Vaccarino Process (144) was developed to commercially extract cottonseed meal with acetone. The process includes countercurrent extraction of cottonseed flakes with acetone (0-1% water), miscella refining to prevent color fixation, phase separation of oil from solvent by adding water, and rectification of acetone before recycling to the extractor. This process has been used in a commercial mill of G&S Vaccarino, and reportedly produces excellent quality oil with low refining losses since the soap is dissolved without entraining neutral oil.

Other Pure Solvents

Various other compounds have received cursory interest as oil extraction solvents. Several patents have been issued for use of methyl and ethyl acetate esters to defat soybeans if the protein is used in industrial applications (145-147). Among the ethers, ethyl ether has received the most consideration; it has been found to be as effective as hexane in extracting neutral oil, but also extracts more free fatty acids and gossypol. A US patent (148) has been granted for using ethylene glycol monomethyl ether (methyl cellosolve) and ethylene glycol monoethyl ether (ethylene cellosolve). The amines have been found to produce soybean meal toxic to chickens (149), and are no longer considered. Carbon disulfide was once used to extract olive oil, but its use has been discontinued due to high explosion hazard. Interest in liquified gases and supercritical fluids has been rekindled in the last several years (150-152).

Mixed Solvents

Mixtures of various compounds exhibit chemical and physical properties different from the individual components, and in some cases retain the benefits of each solvent without the disadvantages. Aqueous ethanol, aqueous isopropanol and aqueous acetone are but a few examples which have already been discussed. Numerous other mixed solvents have potential as oil extraction solvents.

One of the earliest solvent mixtures used for extracting oils was a mixture of 10% ethanol in an aromatic hydrocarbon (benzene, toluene, xylene) (153,154). The ethanol helped to extract lecithin, and thereby improved quality of the protein in the defatted meal.

Methanol/trichloroethylene and ethanol/trichloroethylene were evaluated in the late 1940s (102). A mixture of 75:25 (w/w) ethanol/trichloroethylene was found to have good solvent properties, and was used successfully in continuous extraction of soybeans (155). The mixed solvent was considerably less explosive than pure ethanol or hexane and less expensive than pure trichloroethylene. At trichloroethylene concentrations above 10%, the critical solution temperature was reduced to 60 C. Flakes had to be dried to 6% moisture to prevent moisture uptake and reduction of solvent capacity for oil. Development of this solvent system ceased with the recognition of toxic problems associated with trimeal.

Researchers at the USDA Southern Regional Research Center developed a mixture of acetone/hexane/water (54:44:2, w/w/w) for extraction of cottonseed (156). The original objective was to upgrade cottonseed meal for poultry feed and food protein ingredients by extracting gossypol; however, it was also shown that aflatoxin could be extracted (142,157,158). These solvents form an azeotrope

at 56.5% acetone, 42.1% hexane, and 1.4% water, which boils at 49 C. The higher water content in the solvent mixture is for maintaining equilibrium between solvent and flakes (159). Although gossypol is extracted with the oil, and might be expected to result in poor oil quality, the lower boiling point enables evaporation of miscella and oil recovery at temperatures much lower than hexane (48-52 C vs 67-71 C), and without color fixation of oil. Alternatively, oil may be recovered by treating the miscella with six times as much water to cause separation into an acetone-water phase, and a hexane-oil miscella which may be miscella refined. Acetone/hexane/water extracts 5% more oil from cottonseed than does hexane; but concentrations of other nontriglyceride components double (160). Excellent quality refined oils are produced by both processes (161). The extraction is very rapid and follows dilution law (162). Organization within the cells is destroyed almost instantaneously.

The meal is low in free gossypol (0.00-0.03%) and total gossypol (0.25-0.40%), has high nitrogen solubility and nutritive quality and has no cyclopropenoid fatty acids (163). Feed efficiency of meals extracted with acetone/hexane/water is ca. 40% greater than for the best hexane-extracted meals (164); and the resulting protein is of nearly the same quality as milk protein (168). However, the meal has a "catty" flavor and odor which has prevented its use in food protein products. The odor has been attributed to diacetone and trace reaction products of mesityl oxide and sulphur-containing amino acids (165-168). Acetone/hexane/water has been used for simultaneous extraction of oil and aflatoxin from peanut press cake (158,169). Aflatoxin was reduced by 90% in pilot-plant immersion extractor trials (157). Acetone/hexane/water has also been used in analytical methods for quantitative extraction of aflatoxin (170).

A new process, in which countercurrent extraction is accomplished with a vibrating screen, was developed specifically for acetone/hexane/water (171,172). Extraction of oil and gossypol is most efficient when the solvent mixture is saturated with water, and the flakes contain 12% or more moisture. Moist flakes and marcs have a tendency to swell and form a plastic mass, and deep-bed extractors are not suitable. The vibrating screen process keeps the marc loose and facilitates drainage of miscella.

Mixtures of alcohols (methanol, ethanol, isopropanol and allyl alcohol) with hexane show potential as oil extraction solvents (173), and form azeotrope at 29% methanol, 21% ethanol, 23% isopropanol, and 4.5% allyl alcohol. Hexane/alcohol azeotropes have been widely used for secondary extraction of residual lipids from hexane-extracted meals in order to improve flavor and odor (174). "Grassy" and "beany" flavors in direct hexane-extracted soybean (175-177) and peanut meals (178) have impeded their acceptance as food ingredients. These flavors have been attributed to residual phosphatides which are easily extracted with hexane/alcohol mixtures. Hexane/ethanol azeotrope extraction has minimal effect on protein solubility (175,178), and has been used to remove oil and aflatoxin from peanut press cakes (179). Hexane/methanol is particularly effective in removing aflatoxin. Mixtures of 20-30% ethanol in hexane are effective in simultaneously extracting oil and reducing gossypol content of cottonseed meal (180). Free gossypol was reduced to 0.013-0.04%, total gossypol to 0.32-0.55%, and residual oil to less than 0.5% (181). A US patent was recently issued for use of hexane/alcohol mixtures for simultaneous extraction of vegetable oil and debittering of meal (182). Lecithin is recovered from the miscella by addition of aqueous ethanol, which causes phase separation of hexane-oil from alcohol-lecithin.

Mixtures of hexane and 2-25% acetic acid have been used for extraction of oil and protein from cottonseed (183,184). As the ratio of acetic acid to hexane is increased, total lipid, neutral oil, phosphatide and gossypol contents of the miscella increased; but free fatty acid content did not change significantly. Apparently, cell membrane components are labile to acidic aqueous solvents, and their disruption allows more complete extraction. About 4% acetic acid in hexane is the upper desired level, because higher levels discolor the oil and solvent recovery becomes difficult.

FUTURE TRENDS

Current interest in isopropanol and methylene chloride is high. Simultaneous removal of undesirable components, such as aflatoxin, gossypol, "beany" flavors and alkaloids, offers the potential for upgrading meal products for use as nonruminant feeds and human foods.

Oil extraction is an energy-intensive industry, and energy costs are often two-thirds of the processing cost. Much of the energy consumed in extraction is needed for evaporation. Solvents which allow nonevaporative methods of solvent recovery from miscella result in considerable reduction in operating costs. Solvents which pose less health and fire hazards, greater ability to extract neutral oil, gossypol and aflatoxin, but less ability to extract phosphatides, free fatty acids and nontoxic pigments, will always be of interest.

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