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 inter-

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

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

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

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 propor-
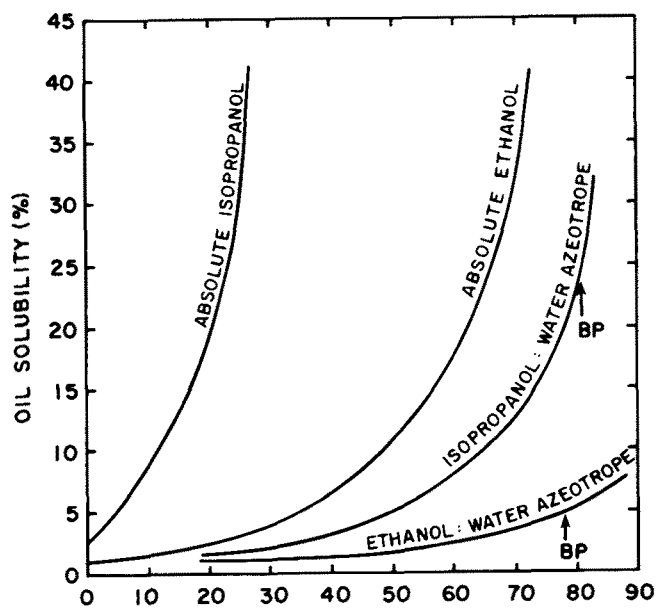

FIG. 1. Solubilities of cottonseed oil in alcohols. (Plots of data from references 50-53, 99, 112.)

tions 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.

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

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 frac-

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