ical aspects are being investigated at the Universities of Bochum (G.M. Schneider) and Karlsruhe (E.U. Franck).

There is still some doubt whether the use of supercritical fluids will be competitive with traditional methods of processing oilseeds and oils. In the near future, the use of supercritical carbon dioxide and other dense gases will probably be limited to a few special applications, such as the de-oiling of crude lecithin and the fractionation of butter fat. Yet, if the price of hexane should increase dramatically and if large-scale equipment should become available at reasonable cost, the deodorization of oils, and eventually the extraction of oilseeds with supercritical carbon dioxide, may become competitive with steam deodorization and hexane extraction, respectively.

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Biorenewable Solvents for Vegetable Oil Extraction[1]

R.J. HRON, Sr., S.P. KOLTUN and A.V. GRACI, Jr., Southern Regional Research Center, Agricultural Research Service, USDA, PO Box 19687, New Orleans, LA 70179

ABSTRACT

A review of the literature pertaining to possible alternatives for hexane as solvent in the extraction of vegetable oils was made. The review was restricted to solvents obtainable from renewable resources and included the most recent technological advances in oil extraction processes. The most promising systems surveyed were based on the use of water, alcohols, ketones, halocarbons, or of liquified and supercritical gases as solvents for oils.

INTRODUCTION

Over 14 billion lb of edible vegetable oils (soybean, cotton-seed and sunflower) was produced in 1979 in the U.S. mostly by direct solvent or prepress-solvent extraction methods (1). The major portion (86%) of this oil was produced from soybeans with hexane as the extraction solvent. With a crush of over 1 billion bushels of soybeans in 1979 and a conservative estimated solvent loss of 0.15% of the total soybeans processed (2), ca. 16 million gal of hexane was lost. A report (3) in the spring of 1980 confirmed the fact that hexane was in short supply and demonstrated to edible oil producers that an alternative solvent, less dependent on petroleum for its source, was needed. Additionally, with the price of hexane approaching $1.70/gal and both federal and state authorities enforcing emission standards, solvents and/or extraction systems once considered uneconomical have begun to attract renewed interest. McGee (4), in 1947, and Price (5), in 1965, reviewed a list of potential vegetable oil extraction solvents; now it is timely to update their work and to concentrate on the potential of renewable solvents or extraction systems currently available to processors.

This is a review of potential biorenewable solvents, the basic processes for each, and the advantages and disadvantages of the proposed solvents compared to the present hexane system.

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Water

Water, known as the universal solvent, is immiscible with vegetable oil and therefore is a poor solvent for the oil. Nevertheless, many researchers have used water systems in the extraction of oil and protein from soybeans, cotton-seed, peanuts, sunflowers and coconuts (6-14). The aqueous process, as shown in the flow diagram (Fig. 1) consisted basically of the following steps—grinding, mixing, and extracting with water-containing additives, solid-liquid and liquid-liquid separations, and drying. The mechanics of oil extraction with aqueous solutions are unique in that it is critical to all the processes that a majority of oil cells in the raw material be ruptured during the grinding step. This is necessary to free the oil globules and to allow them to emulsify with water, under agitation, and thus be "extracted." Insufficient grinding results in low oil recoveries and corresponding high residual oils in meal or protein fractions. Excessive grinding yields "mayonnaise-like" emulsions that are difficult to break and call for specialized
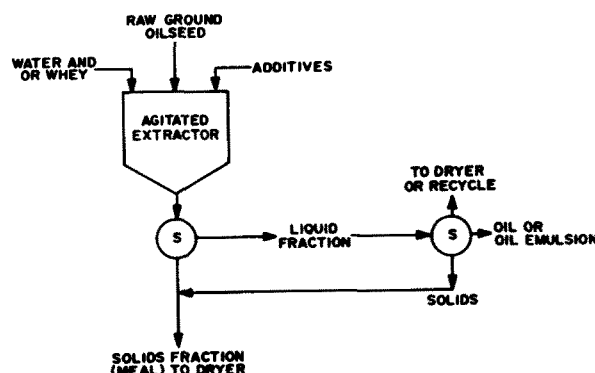

FIG. 1. Simplified flow diagram for aqueous extraction of vegetable oil.

techniques, such as those described by Sugarman (13) and Hagenmaier et al. (14). They claim that stable oil-in-water emulsions can be broken by controlling both moisture and pH and the application of shearing agitation and heat prior to centrifugation. The water used in oil extraction may be acidic, basic or contain added salts or chemicals, depending on the undesirable substances to be removed and the type of final protein product (concentrate or isolate) desired. An acidic pH is used in the production of normal meals, whereas a basic pH is used to produce protein isolates. As an additional benefit with sunflower seeds, acidic solutions reduce chlorogenic acid content of the extracted meals (15). Hydrogen peroxide or sodium hypochlorite added to the extractant is effective in the destruction of aflatoxins (16). At the completion of extraction, solid-liquid separation is accomplished using vibrating screens, presses or centrifuges. The resulting solids are washed and the slurry is separated again. Normally, 3-phase centrifuges are used in another key step in the process, to produce oil, aqueous, and solids phases. The oil phase may contain free oil or an emulsion, depending on the raw material and process used. The emulsion may be treated as previously described to produce a high-quality oil requiring very little treatment besides drying. The aqueous or whey phase can be spray-dried or used directly as the water source in subsequent extractions. It can be processed also by reverse osmosis and ultrafiltration techniques to recover protein isolates and produce water which is suitable for reuse (9). The solid, or meal, phase needs only to be drum- or spray-dried to produce edible protein products.

Pilot-plant scale-ups of aqueous extraction processes have been demonstrated at Texas A&M for soybeans, peanuts and coconuts (6,7), and limited peanut commercializations have been reported for the Bhatia, Chayen and Peana processes (10-12,17).

The advantages and disadvantages of aqueous processing are shown in Table I.

TABLE I

Advantages and Disadvantages of Aqueous Processing

Advantages	Disadvantages
Plentiful supply	Less efficient in oil extraction (recovers only about 95%)
Nonflammable and non-explosive, vapors are nontoxic	Whey fractions easily contaminated by bacteria
Can remove antinutritional factors such as gossypol and chlorogenic acid	Normally have to demulsify oil fractions
Can increase returns on cottonseed by producing edible meals and isolates	Highly dependent on centrifuges which necessitate high maintenance and energy consumption
Normally do not have to dry raw material before extraction	Uses more BTUs per ton of seed in evaporation and desolventization (drying) operations
Vapors are nonpolluting	Usually high residual oil content (4+%) in edible concentrates or isolates could cause storage problems
	Normally produced meals or isolates have to be dried in energy-intensive drum or spray drying equipment

Alcohol

Methyl, ethyl and isopropyl alcohols are good solvents for vegetable oils, but methyl alcohol is of little interest commercially for this purpose due to its toxicity. Both ethyl and isopropyl alcohols can be produced by the fermentation of biorenewable resources. Ethyl alcohol is a direct fermentation product, whereas isopropyl alcohol is produced indirectly by reducing acetone obtained from the Weizmann corn fermentation process (18,19). The solubility of vegetable oil in these alcohols varies greatly with temperature and alcohol concentration. Oils are essentially completely soluble in each alcohol at its boiling point and only very slightly soluble in alcohol at ambient temperature. Also, as concentration of an alcohol decreases with the addition of water, the solubility of the oil in the alcohol also decreases.

Based on these solubility characteristics, the Central Laboratory of the South Manchuria Railway Company in Darien, Manchuria, developed and built, during the 1930s, the first successful commercial ethyl alcohol extraction plant to process soybeans (20-22). During the late 1940s and early 1950s, Beckel and coworkers at the USDA's Northern Regional Research Center, also using these solubility characteristics, developed a continuous circulation process to extract soybean oil. They claimed this process eliminated distillation, thereby reducing energy requirements by 25% over a comparable hexane process (23). This development, along with their other significant improvements, advanced the aqueous ethanol-soy oil extraction process as far as possible without its commercialization in this country (23-28). Karnofsky in 1979 and 1980 added to the existing knowledge with a novel, 4-step, sequential extraction variation that uses dilute aqueous ethanol to extract carbohydrates and phosphatides and, subsequently, boiling absolute ethanol to extract the soybean oil (29,30). The use of absolute ethanol as a solvent for cottonseed oil was also reported by Satyan and Rao in pilot-plant studies in India in 1952 (31,32). About this time, Magne and Skau published extensive solubility data for cottonseed oil in absolute alcohol and in various aqueous alcohol solutions (33). This research was followed up by Rao and coworkers in 1955 who reported extensive solubility studies on cottonseed, peanut, sesame and sunflower seed oils in aqueous ethanol (34-37). Their work culminated in a report detailing studies of pilot plant cottonseed extractions with 91.5, 95.4 and 99.9% ethanol, and included a hypothetical flow chart for a complete extraction process (37). Karnofsky, in 1981, presented laboratory data showing the application of his four-step soybean extraction procedure for cottonseed oil extraction (38). He claimed his process can be used to extract aflatoxin, fatty acids, phosphatides and most of the gossypol to produce semirefined oils and meals containing less than the maximum allowable edible level of free gossypol. Karnofsky's claim of removal of aflatoxins was in reference to research previously reported by Rayner and coworkers (39,40). They claimed up to 96 and 98% removal of aflatoxins from cottonseed and peanut meals, respectively, with 90% ethanol.

The use of isopropyl alcohol as a solvent in vegetable oil processing is demonstrated best by Harris and coworkers who developed a complete pilot plant isopropyl alcohol-cottonseed extraction process (41-44). The process is very similar to the one developed by Beckel for ethanol-soybean except that it also removes gossypol from cottonseed. The "Cavsol" process is another which uses isopropyl alcohol to extract oilseeds. It was developed through the pilot-plant stage in Australia but, like all others, has yet to be commercialized (45).

A flowsheet for a typical alcohol extraction process is shown in Figure 2. In this process, the oilseed is hulled, flaked and dried to 3% or less moisture to prevent solvent dilution (if the 95% ethanol azeotrope is used). Normally,

constant boiling mixtures of alcohol and water (azeotropes) are used in the extraction process to avoid special processing and the excessive energy needed to produce absolute alcohols. The azeotrope concentrations for ethanol and isopropyl alcohol and water are 95 and 91%, respectively. For efficient extraction, the temperature of the azeotrope should be as close as possible to the boiling point of the alcohol.
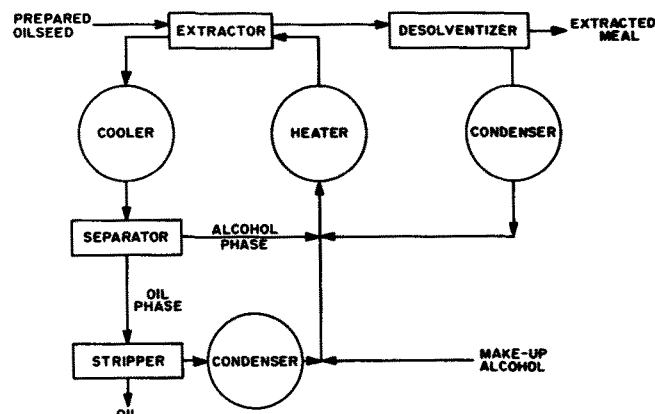

FIG. 2. Simplified flow diagram for alcoholic extraction of vegetable oil.

The hot miscella is circulated through the extractor, after which it is cooled and allowed to separate into oil-rich and alcohol-rich phases. The oil-rich phase is stripped of its remaining alcohol to produce a semirefined oil. The alcohol-rich phase from the separator is combined with alcohol recovered from the desolventizer and stripper condensers, and make-up alcohol. This mixture is then heated to boiling and recycled through the extractor. Beckel and coworkers claim a 25% reduction in energy requirements over a conventional hexane process by recycling the alcohol solvent (bypassing distillation) (23).

n-Propyl and n-butyl alcohols also extract vegetable oil and can be obtained from renewable resources. However, they cannot be considered seriously because of their high boiling points (over 200 F), which result in excessive energy for recovery and increased refining loss in the case of cottonseed oil, and also because of their toxicity.

The advantages and disadvantages of alcohol processing are shown in Table II.

TABLE II

Advantages and Disadvantages of Alcohol Processing

Advantages	Disadvantages
25% reduced energy consumption by the use of recirculation techniques which minimize distillation requirements	May have to purify miscellas of phosphatides, carbohydrates and other nonglyceride extractives
Can remove antinutritional factors such as gossypol, aflatoxins and chlorogenic acid	Repeated recirculation of solvent could impart undesirable odors to protein products
Can produce high-quality oil with low free fatty acids	Because of polar and hydrogen bonding, alcohols absorb strongly on most meals and are difficult to remove
Can produce additional by-products such as lecithin, sterols and saponins	In some cases, oil-bearing materials must be dried prior to extraction to minimize dilution of solvent
Greater industrial safety	Lower solvent power
Lower toxicity	

Ketones

The vegetable oil solubility characteristics of the ketones are similar to those of the alcohols in that both ketones and alcohols at high concentrations are good oil solvents and form two-phase miscellas when diluted with water. Acetone and methyl ethyl ketone are the only low boiling ketones (134 F and 175 F, respectively) of commercial interest. Acetone is the only one presently obtainable from a renewable resource (Weizmann fermentation process) (18,19). Laboratory and pilot-plant data for the acetone extraction of both oil and gossypol from cottonseed (43,45-48) and oil from soybeans (49) are readily available. Pons and Goldblatt have shown that acetone is also an effective solvent for aflatoxins (50). Limited commercialization of an acetone extraction process has been reported by Vaccarino in Sicily where a 50-ton/day batch process plant (51,52) is in operation.

The flow sheet for one possible acetone extraction processing scheme is shown in Figure 2, in which acetone could be substituted for alcohol. Another scheme is shown in Figure 3 which is a simplified version of the Vaccarino process.
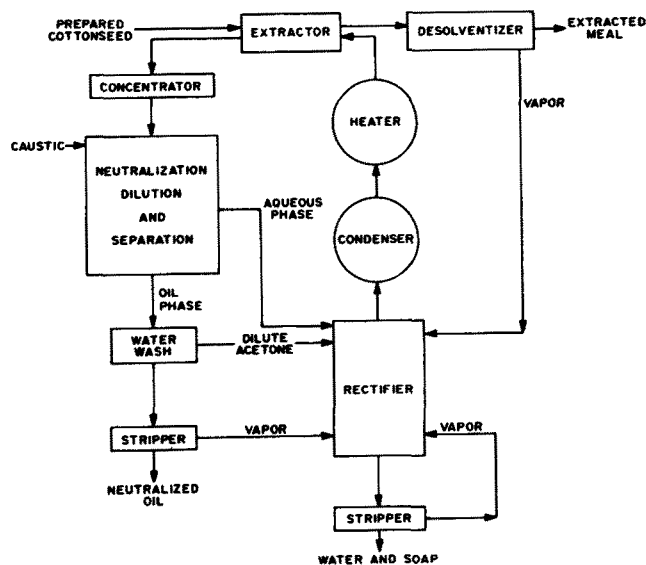

FIG. 3. Simplified flow diagram for the Vaccarino process for acetone extraction of cottonseed oil.

In the Vaccarino process, cottonseed flakes are extracted with 96% acetone to produce a homogenous miscella containing 25% oil. The miscella is then concentrated and treated with cold alkali. Upon subsequent dilution with water, two phases are produced—an aqueous phase containing soap, gossypol and acetone and an oil phase containing extremely clear neutral oil and ca. 9% acetone. The oil phase is washed with water and stripped with superheated steam and the resulting oil is sent to bleaching and deodorizing operations. The aqueous phase and other process streams are sent to a rectifier and the resulting high boiling fraction or "bottoms" are stripped and the solvent and soap, or "foots," are recovered.

The advantages and disadvantages of ketone solvents are shown in Table III.

Liquified and Supercritical Gases

Of the alternate solvents reviewed, liquified and especially supercritical gases have recently attracted the most attention. When a gas such as carbon dioxide is compressed and maintained below its critical temperature (88 F), it be-

TABLE III

Advantages and Disadvantages of Ketone Processing

Advantages	Disadvantages
Can be concentrated easily by rectification	Normal refining operations produces abnormally dark cottonseed oil which is difficult to bleach
Phosphatides and gums are insoluble and remain with the meal	Extracted meals have a disagreeable cat-like odor upon standing
Can remove antinutritional factors such as aflatoxins and gossypol in cottonseed	
Extracted cottonseed meals are light colored and have high protein solubility	
Although they have low flash points, ketone fires can be extinguished easily with water	
Can reduce energy consumption up to 25% by the use of recirculation techniques	

comes a liquid. If, during compression, the liquified gas is heated and allowed to exceed its critical temperature, it will revert to a gas and no amount of additional pressure will reliquify it. The gas is now "supercritical" and has the properties and extractive capacity of a liquid. The use of liquified and/or supercritical gases to fractionate oils can be traced back to the 1930s (53,54), when it was shown to be an energy saver. However, the abundant supply of cheap energy and the necessity of using expensive high pressure equipment (2,500-10,000 psi) hindered its development, relegating it to the recovery of aroma and flavor essences from fruits, coffee and tea (55,56). Grimmet reviews in detail (57) the broad extractive uses of liquid carbon dioxide. Although liquid and supercritical carbon dioxide gas, obtainable from alcohol fermentation, has been used in the extraction of many different materials, only recently has its use in vegetable oil extractions been documented. Stahl and coworkers in Germany have described the parameters influencing the extraction and fractionation of soybean, sunflower seed and rapeseed oils with liquid and supercritical carbon dioxide (58). During the same period in this country, Friedrich, Christianson and coworkers at the USDA's Northern Regional Research Center reported on the use of supercritical carbon dioxide in the extraction of soybean and corn germ oil (59,60). Various low boiling hydrocarbons, such as propane, butane and ethylene, that are gases at atmospheric conditions, have been proposed as vegetable oil solvents. These were proposed initially by Rosenthal and Trevithick (61,62), and in vegetable oil refining, as in the Solexol process (63). At present, they are either unobtainable or uneconomically obtainable from renewable resources and, more importantly, are extremely hazardous compared to carbon dioxide.

A simplified flow diagram for a typical liquified or supercritical gas extraction is shown in Figure 4. In this process, usually the gas is compressed well above its supercritical pressure (1,073 psi for CO_2) to between 5,000 and 10,000 psi and then passed through the extractor containing the flaked, oil-bearing material. The extracted oil is recovered by reducing pressure in either one or two stages. In a two-stage process, the pressure is reduced first to an intermediate pressure between the supercritical value and 10,000 psi with or without a temperature change. In the second stage, the pressure is reduced to a value slightly

below the critical pressure, while temperature is maintained above the critical value (104 F for CO_2). The temperature requirement is necessary in order to keep the solvent in a gaseous state. In this manner, two liquid oil fractions can be separated by precipitation from a supercritical gas phase. In a single-stage process, either one of the pressure reductions, above or below critical pressure, can be used to effect oil precipitation. The oil products then are recovered by simple evaporation of the CO_2 gas at ambient conditions. Depending on the individual solubility characteristics of the gases and oils used, various combinations of temperatures and pressures can produce significantly different extraction and separation effects. Although no commercial CO_2-vegetable oil extraction plants are known to be in operation, there is a report of a large-scale commercial application of the process for the batch decaffeination of coffee by Hag A.G. in Germany (57).
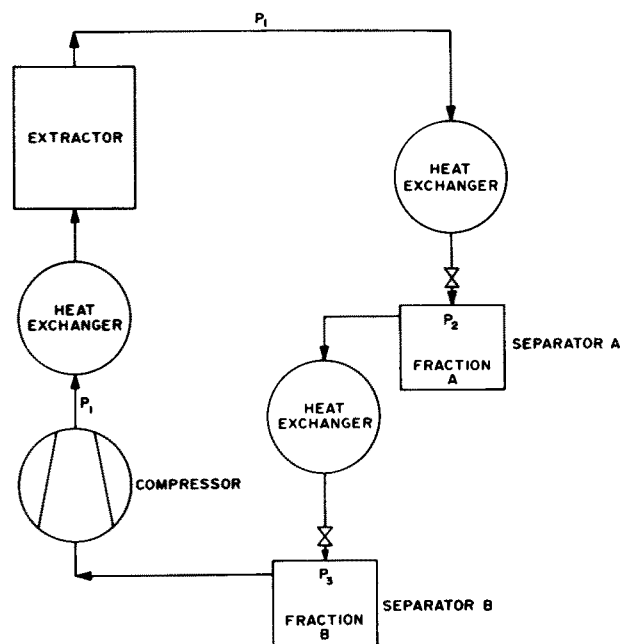

FIG. 4. Simplified flow diagram for the liquified or supercritical gas extraction process.

Several other gases besides CO_2 have good oil solvent properties in either the liquified or supercritical states. These include ammonia, carbon disulfide, sulfur dioxide, ethylene and nitrous oxides, and various freons. However, they are not suitable for commercial application because of various reasons, such as the corrosive effect on the respiratory system, flammability or nonapproval by FDA for food use.

Table IV compares the advantages and disadvantages of using supercritical CO_2 vs hexane in a solvent extraction process.

Miscellaneous Solvents

In addition to the solvents already discussed, a diverse number of individual solvents exist that also have good oil solubility and can be obtained from renewable resources. At the present time, however, they have significantly less appeal as alternatives for hexane. These solvents can be found in the aldehyde, ether, ester and chloro/fluorocarbon chemical groups.

Of the aldehydes, furfural is probably the best known and the only one of practical significance. It can be obtained readily from cereal grasses, corn cobs, cottonseed

TABLE IV

Advantages and Disadvantages
of Liquified and Supercritical Gas Processing

Advantages	Disadvantages
Lipids may be selectively fractionated during extraction or recovery to produce high-quality oils with low free fatty acids	High operating pressures of 1,000 to 10,000 psi necessitates expensive processing equipment
Solvent easily removed from oil and meal products by evaporation	Batch processing results in low capacities
Inexpensive raw material obtained as byproduct from alcohol fermentation	
Extracted cottonseed meals are light-colored; low working temperatures result in little protein denaturization	
Nonflammable, nonexplosive, nontoxic and does not contribute to environmental pollution	
Can be energy saving	

and rice hulls, and bagasse. Freeman found it to be an excellent solvent at temperatures around 104 F for soybean and cottonseed oils (64,65). The solvent properties of furfural are similar to those of alcohols and ketones; upon cooling, the miscella separates into two phases—one containing saturated glycerides and the other unsaturated glycerides. The problem with furfural and the limiting factor, as with all aldehydes, is its toxicity.

Methyl, ethyl and isopropyl ethers, and dioxane have also been shown to be excellent direct oil extraction solvents (45,66). All of these ethers are highly flammable and, except for methyl ether, form explosive peroxides. Also, ethyl ether and dioxane can be ignited by contact with a high-pressure steam line. Therefore, it is not surprising that none of these ethers have been considered practical for commercial use.

Ethyl acetate, and ester which can be produced by reacting ethyl alcohol with acetic acid, was one of a series of solvents evaluated in the Cavsol process, it was dropped in favor of aqueous isopropyl alcohol because of the latter's advantage in regard to meal properties (45). Although ethyl acetate is an excellent solvent and has low toxicity, it cannot be considered seriously because it is a narcotic.

A group of the chloro/fluorocarbons consisting of trichloroethylene methylene chloride, chloroform, methyl chloroform and the freons have been considered as possible alternatives to hexane. They are excellent solvents for oil, have low boiling points, and are not easily ignitable (49,67, 68). Trichloroethylene was reported in 1949 by Sweeney and Arnold to be an excellent solvent for soybean oil (69). An extraction equipment supplier commercialized the process. Shortly thereafter, he converted all plants to hexane because of the sudden death of cattle that had eaten trichloroethylene-extracted meal (70). McKinney and coworkers attributed the deaths to a toxic reaction product of the amino acid cysteine and the solvent (71). Of the remaining chlorocarbons, methylene chloride, the solvent of choice in the decaffeination of coffee beans, has ideal solvent properties required in direct vegetable oil extraction process. Its delayed acceptance is probably due to the suspicion of chlorocarbons being carcinogens. Chloro/fluorocarbons or freons also have been reported to be excellent solvents for soybean oil (68). Their general use

has been deferred until their safety in food production and the question of whether they deplete the atmosphere of ozone can be completely resolved (72).

There are many binary and tertiary biorenewable solvent systems that have excellent oil solvency characteristics. However, because of the sophisticated equipment required and the additional costs entailed in such systems, they are not as economically feasible as single solvent processes.

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