Membrane Applications and Research in the Edible Oil Industry: An Assessment

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Commercial sources of edible oils and fats include oilseeds, fruit pulps, animals and fish. Oilseeds processing typically consists of the following steps: i) seed preparation; ii) solvent extraction of flakes and/or extruded collets; iii) desolventization of the meal; iv) recovery of solvent by distillation; and v) degumming, refining, bleaching, and deodorizing of the crude oil. The process consumes large amounts of energy—in the forms of electricity, natural gas and fuel oils—to heat and cool the oil between individual processing steps and to generate high vacuum. Steam requirements for producing edible oil from crude oil range from 2000 to 4000 Btu/lb depending on the type of oil processed. The processing of cottonseed, corn, peanut and soybean oils alone consumes approximately 64.7 trillion Btu/yr of energy in the United States (based on 15.1 × 10^9 lb crude oil processed). Electricity requirements for a typical refinery are between 120,000 kWh and 160,000 kWh/yr (based on 1400 to 1800 kWh/22,000 lb crude oil processed/hr). Current membrane separation research, as applied to miscella distillation; vapor recovery; condensate return; wastewater treatment; degumming, refining, and bleaching; hydrogenation catalyst recovery; oilseed proteins; and nitrogen production, is reviewed in this paper.

The greatest potential for energy savings of 15 to 21 trillion Btu/yr exists in replacing or supplementing conventional degumming, refining, and bleaching processes. Decreased oil losses and decreased bleaching earth requirements are other potential advantages of membrane processing.

Approximately 2 trillion Btu/yr could be saved using a hybrid membrane system to recover solvents in extraction of crude oils. Although marginal success has been reported to date, the development of hexane-resistant membranes may make this application viable.

Oilseed processing and edible oil refining. Typically, oilseeds are cleaned and, depending on the type of seed, may be processed in one of two ways. High-fat content seeds may first be pre-pressed before solvent extraction. However, low-fat content seeds usually are flaked and directly extracted by solvent (Fig. 1). Although many hydrocarbon solvents have been investigated for extracting oilseeds, commercial hexane has become the most widely used solvent. During processing, hexane is recovered from the oil by distillation and reused; solvent also is recovered from the meal in the desolventizer-toaster.

After solvent extraction, miscella contains 25–30% oil. Figure 2 illustrates the details of miscella distillation and a solvent recovery system. Miscella is pumped from the miscella tank into the evaporator, where a majority of the solvent is removed at this stage, and concentrated miscella (90% or more oil) next flows into the vacuum stripper. Hexane content of the oil is brought to less than 1% by high vacuum at the top of the stripper. The remaining solvent then is stripped by counter current live steam during its movement through a series of trays. The solvent and steam are condensed in the oil stripper condenser, and the mixture is separated by decanting. Process efficiency is affected by vacuum level, cooling water temperature, configuration of the stripping unit and the temperature of the incoming oil.

Solvent recovery is one of the most crucial steps in processing edible oils because of economic, environmental and safety implications, and more than 2 million tons are estimated to be recovered each year in the processing of edible oils (1).

Crude soybean oil is refined to remove free fatty acids, phosphatides, gums, settlings, coloring matters such as chlorophyll, xanthophyll, and miscellaneous unsaponifiable materials (Fig. 3).

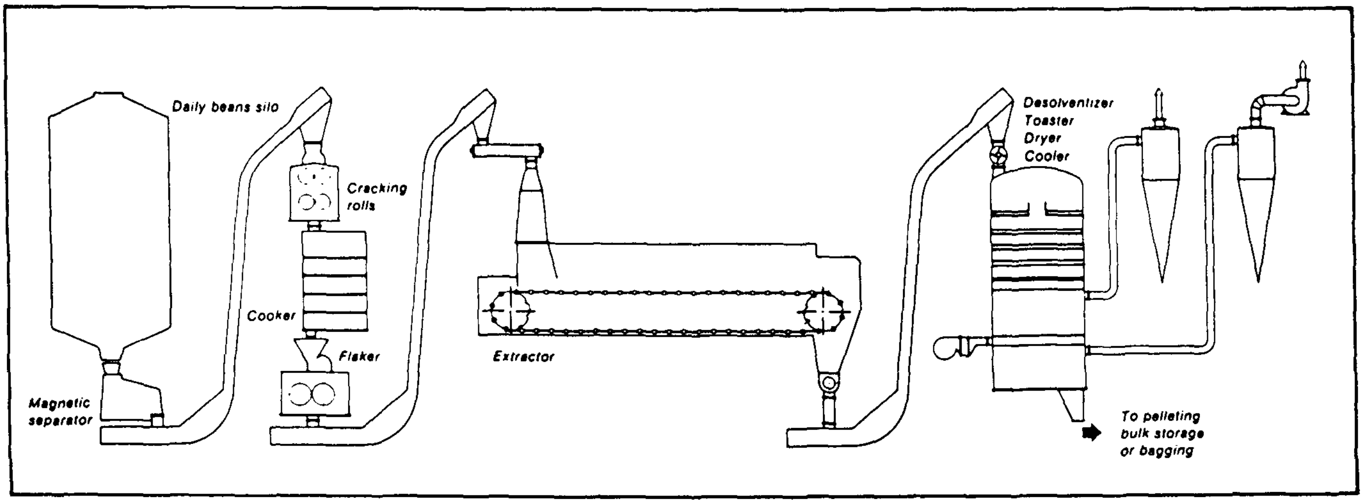

FIG. 1. Simplified flow diagram for soybean preparation, solvent extraction and meal desolventization.

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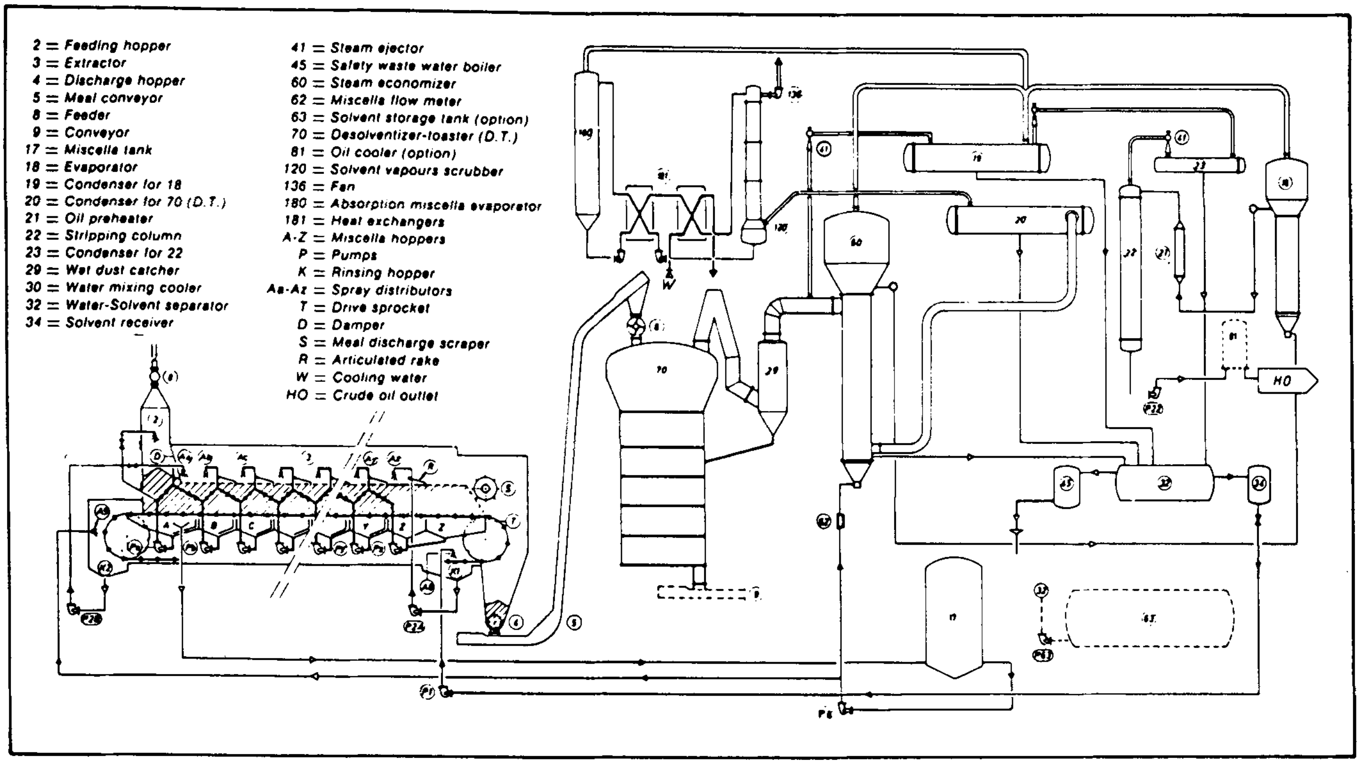

FIG. 2. Detailed flow diagram of a solvent extraction and recovery system.

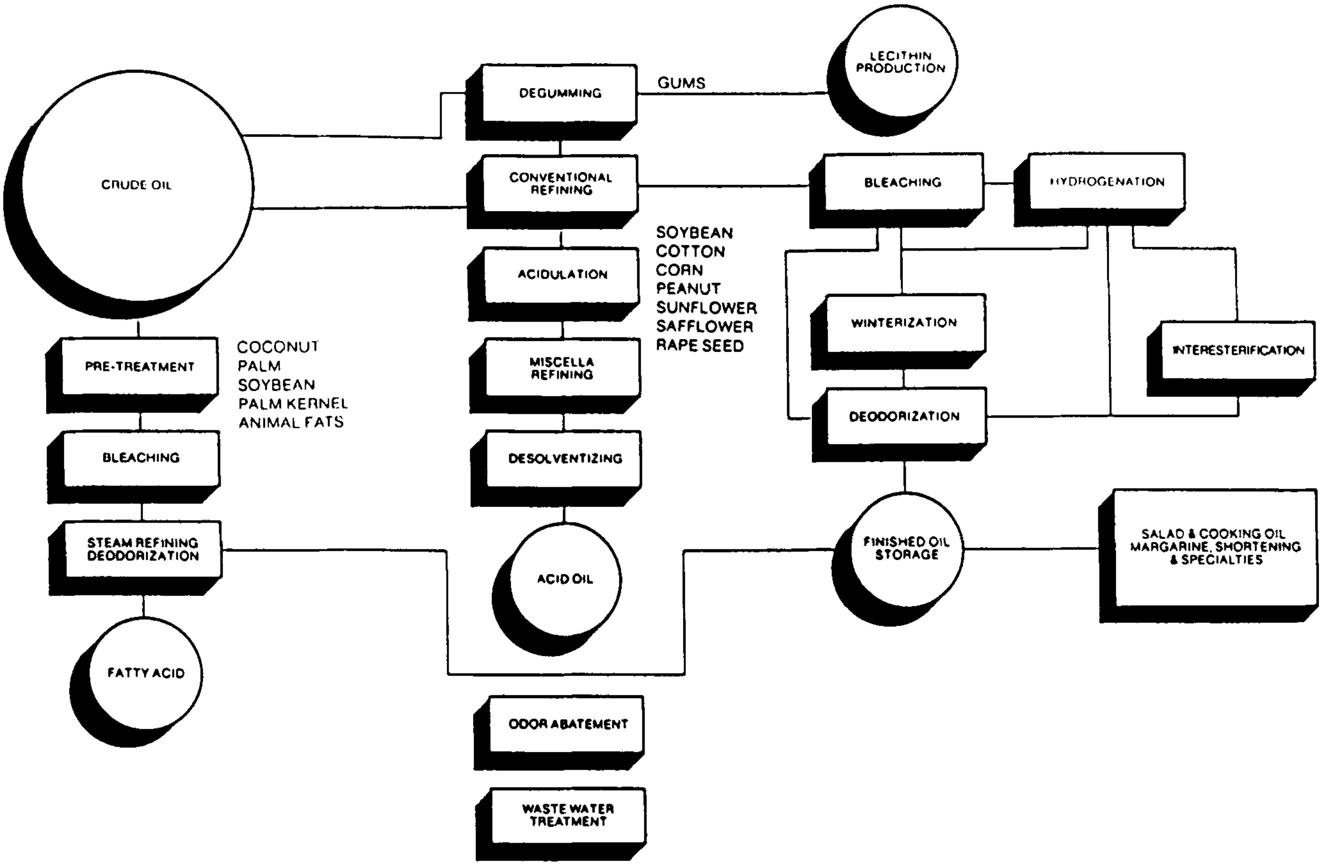

FIG. 3. Simplified flow diagram for crude vegetable oil processing.

The first step in crude oil refining is the degumming process, during which phospholipids that may act as emulsifiers or precipitate in shipment and storage are removed. Lecithin, often used as a food ingredient, is a by-product of this process. In the following step, the degummed oil is treated with aqueous sodium hydroxide to react and precipitate free fatty acids as soaps, and at the same time to remove the remaining trace amounts of phospholipids. Neutral oils are recovered from extraneous materials by centrifugation. At this point, the oil still contains pigments, in addition to very small amounts of unreacted free fatty acids that will be completely removed with odor- and color-causing fractions during deodorization. The next step is a bleaching process, which uses acid-activated bleaching clays and/or carbon to absorb and remove chlorophyll, xanthophyll, peroxides and their breakdown products, to improve flavor and produce oils with acceptable color and stability. Bleached oil is separated from the adsorbents by filtration.

The final step of the refining process is deodorization—oils are heated with steam sparging under high vacuums to strip trace amounts of free fatty acids, aldehydes and ketones and other volatile materials that have not been removed during previous steps. These impurities may impart undesirable flavors and odors if the refined and bleached oil is not properly deodorized.

Considerable amounts of energy in the form of steam or electricity are required in these processes and each step only removes one or two undesirable components. If crude oil is not properly processed, treatments during the following steps will be more difficult and time- and labor-consuming. In addition to the energy costs, oil refining and hydrogenation processes produce various waste streams such as acidic wastewater, used bleaching clay and catalyst suspended in filter aid that either needs to be treated or recovered because of economical or environmental reasons.

Process engineering and design of refining equipment have been improved considerably during the last ten years, primarily by reduction of energy requirements and reduction of neutral oil losses. However, the basic principles of edible oil processing have not changed for almost sixty years.

Energy consumption in oilseed crushing. Approximately 15.1 billion lb of soy, corn, cottonseed, and peanut oils were produced during 1986-1987 in the U.S. oil mills (Table 1).

TABLE 1

1986-1987 U.S. Production and Stock of Major Crude Oils at Oil Mills[a]

Production	1986-1987 Production millions pounds
Soybean oil	12,798.1
Cottonseed oil	781.3
Peanut oil	144.2
Corn oil	1,400.1
Total	15,123.7

[a] U.S. Department of Commerce, Bureau of Census.

The extraction step in Figure 1 involves several unit operations. The approximate steam consumption per ton of processed soybeans for each operation is given in Table 2 (1,2). These numbers are an estimate of energy consumption by each unit operation in an extraction plant. The energy requirements pattern for soybeans is well-known and is used as a basis to calculate energy consumption for other oilseed sources. Soybean processing accounts for more than 75% of the total energy used in U.S. oilseed production and is the most standardized.

Processing data in Table 2 and annual energy consumption data (1,3) for each of the subcategories of the fats and oils industry were used to estimate energy use patterns in Table 3. Assumptions and data used for the process energy calculations are given in Tables 1-3, 6, 7 and in the cited references.

Energy consumption in oil refining. Large amounts of energy are used in heating and cooling oil between process steps and in generating the required vacuum levels during the degumming, refining, bleaching, and deodorizing processes. Steam requirements for producing edible oil from crude oil range from 2000 to 4000 Btu/lb depending on the type of oil being processed (3). This corresponds

TABLE 2

Steam Consumption Per Ton of Processed Seed (1)

Processing step	lb/ton
Seed preparation - preheating (20° to 60°C)	90
Extractor heating	20
Desolventizer-toaster (75°C dome-vapor-temperature)	280
Distillation	50
Meal drying according to various systems	80 to 160
Hexane recovery according to various systems	30 to 60
Estimates of losses by radiation (varies with plant size)	20 to 50
Total	570-710[a]
Electric energy consumption[b]: 26-32 kWh/metric ton of processed seed	

[a] Steam consumption for degumming and lecithin drying are not included in the crude oil production process, but are treated under refining.

[b] The major operations consuming electric energy include materials handling, cracking mills, mechanical screw presses, and solvent extractors.

TABLE 3

Energy Use Patterns in the Production of Crude Oils (1)

	Trillion Btu/yr				
Processing steps	Cotton	Soy	Vegetable	Shortening	Total
Seed preparation	0.6	4.2	0.3	1.9	7.0
Extractor heating	0.1	0.9	0.1	0.4	1.5
Desolventizer-toaster	1.8	13.3	0.8	5.9	21.8
Distillation	0.3	2.4	0.1	1.1	3.9
Meal drying	0.8	5.7	0.3	2.6	9.4
Hexane recovery	0.3	2.1	0.1	0.9	3.4
radiation losses	0.2	30.2	1.8	13.5	45.7

to $\sim$64.7 trillion Btu/yr energy consumed annually in the U.S. (based on 15.1×10^9 lb crude cottonseed, peanuts, corn and soybean oil per year) (1). Electricity requirements for a typical refinery are between 120,000 kWh and 160,000 kWh/yr (based on 1400 to 1800 kWh/22,000 lb crude oil processed/hr) (Koseoglu, S.S., unpublished data, Texas A&M University, August 19, 1987).

Membrane processing. The basis for separation during membrane processing is illustrated in a simplified form in Figure 4. When a pressurized feed stream containing a mixture of large and small molecules passes through a tube, only those molecules smaller in size than the membrane pores pass through as permeate. The remaining mixture "retentate" of larger molecules passes through the tube and is collected at the end. However, the mechanism of separation is more complex. Many other variables—such as composition of membrane; method of membrane manufacturing; shape and configuration of the molecules; their interactions with each other and the membrane surface; fluid dynamics of the membrane unit; pressure, temperature and velocity of the mixture—influence the separation process.

Membrane separations can be divided into three different categories. Microfiltration (MF) covers separation of micron or submicron particles of 0.02–2.0 μ range in a solution. The perpendicular flow mode is very common in this separation method. However, recently there has been considerable interest in a cross flow configuration.

Ultrafiltration (UF) generally includes the 0.002 to 0.2 μ range, which corresponds to 500 to 300,000 molecular-weight cut-off (MWCO). Both structure and performance of ultrafiltration membranes are different from microporous membranes. Because of the nature of the mixture and differences in pore size, UF is always run in a cross flow mode.

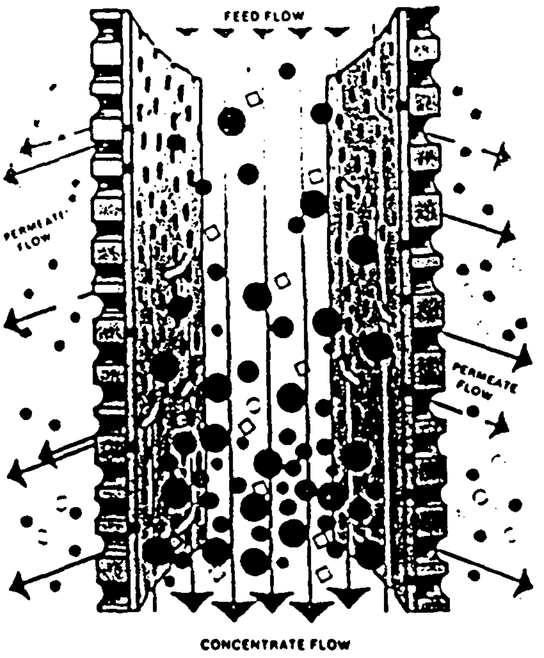

FIG. 4. Schematic representation of ultrafiltration process.

Reverse osmosis (RO) is the most complex separation technique in membrane technology. It is affected by salt concentration of the mixture, composition of membrane materials, interactions between the molecules and membrane surface, and associated charges. Pore sizes of reverse osmosis membranes range from 5 to 15 Å. The lower limit corresponds to a MWCO of less than 250.

A simplified diagram of a batch ultrafiltration system is shown in Figure 5. Membrane cartridges are the heart of the UF system. Other components, including manifolding in various arrangements, pump(s), tankage, instrumentation, valves, and cleaning subunits complete the overall system. The UF system can be designed in various modes: including single pass; batch; feed and bleed and multistage feed and bleed.

The main limitations of conventional membranes processing are short membrane life; low temperature and pressure ranges; sensitivity of membranes to chlorine; and stability of membranes at high and low pH ranges (4,5). Earlier UF/RO membranes were made primarily of cellulose acetate and various polyamide materials which are sensitive to chlorine and organic solvents, and were limited in applications to aqueous mixtures (4). In recent years, new membranes (that have increased chemical stability, pressure, and temperature ranges) have become available. Membranes made of polysulfones, zirconia-coated carbon, extruded alumina "ceramics," and alumina coating on inert support materials are being introduced in UF applications (5), but are not yet available in RO pore sizes.

Commercial membranes are available in various forms such as tubular, spiral wound, hollow fiber, flat, and flat leaf. The proper membrane selection can be made by examining concentration and type of the extract, pressure and temperature range of separation, chemical stability of the membranes and sanitation requirements.

DISCUSSIONS

Presently used commercial membrane separation processes. Membranes are used in limited fashion in the processing of fats and oils, and applications used by other industries could be adopted by the fats and oils industry.

(A) Nitrogen production. Nitrogen blanketing is used in the fats and oils industry to decrease oxidative deterioration during the packaging process. Conventional gas separation processes to produce nitrogen are based on adsorption/desorption or cryogenic fractionation. Pressure swing adsorption (PSA) is a batch process requiring

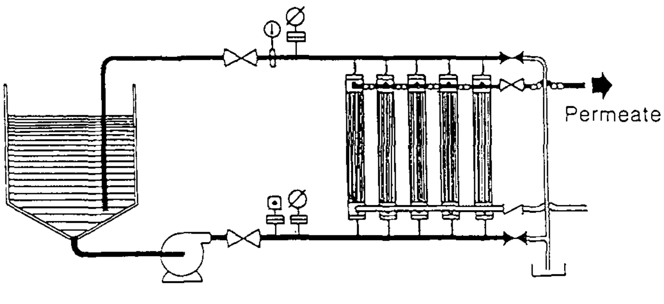

FIG. 5. Typical batch ultrafiltration process.

heavy, bulky columns. Cryogenic processes occur at temperatures much below 0°C, and are economical only at large capacities.

Membrane air separation processes are not difficult to operate and can be operated continuously. Membrane technology is best applied to processes where high purity N_2 is not required. Membrane air separation processes can produce nitrogen with purities of 90 to 97% (6), at pressures of 100 psi or higher, and in volumes up to 35,000 standard cubic feet per hour (scfh) (7). Membrane processes are well-suited in situations where portability, equipment size and weight, and low maintenance are factors. A list of suppliers who offer commercially-available nitrogen generating systems is shown in Table 4. Nitrogen production for blanketing and packaging with membranes is currently being considered by several vegetable oil processors (Farr, W.E., personal communication, Anderson Clayton/Humko Products, Inc., May 19, 1987).

(B) Wastewater treatment. In many cases, wastewaters from vegetable oil processing mills are discharged to municipal treatment systems or are treated on-site and discharged directly to rivers or streams. Direct on-site discharge treatment typically includes pH adjustment to an acidic state, gravity separation, pH re-adjustment to near neutrality, chemical coagulation with dissolved air flotation, biological treatment and, in some cases filtration through granular media (8). Many plants have found that discharge to municipal systems (despite high costs) is more economical than on-site treatment.

Several membrane companies now offer systems to concentrate oily waste streams. Membrane modules are compact and in many cases the permeate or purified water is recycled. Companies active in this technology include Osmonics, Norton, Koch, and Alcoa.

Osmonics has RO/UF systems that utilize the OSMO spiral wound membrane module to concentrate oils. The OSMO modules have concentrated standard oils to over 50% concentration in water, and corn oil to over 15% (Osmonics Bulletin). The most common application of the membrane system follows a conventional waste treatment plant skimmer.

Norton offers a tubular ceramic membrane that separates oils from waste streams. The membrane is a high purity alumina that can be operated at temperatures up to 150°C, is resistant to solvent and strong chemicals, and tolerates a pH of 1 to 12. A Norton system has been installed at a DOE installation at Savannah River, Georgia. Operating capacity is 100 to 200 gal/min (GPM). This system handles radioactive waste and removes 85 to 100% of the hydrocarbons present in the waste stream.

TABLE 4

Nitrogen-Generating System Suppliers (1)

Company	Configuration
A/G Technology	Hollow fiber
Ashai Glass	Plate and frame
Dow (Generon)	Hollow fiber
Monsanto	Hollow fiber
Air Products	Spiral wound
Permea, Inc.	Hollow fiber
Union Carbide	Hollow fiber

Typical costs for ceramic membranes are \$200 to \$500/ft^2 (Michaels, S., personal communication, Norton, July 1987).

Koch offers polymeric membranes packaged in various configurations. A typical system can process 25,000 to 100,000 gal/day with membrane life of 3 to 5 years. Commercial applications include coolant streams in the metals industry, wash water from mayonnaise and oleo packaging, and industrial laundries.

Alcoa offers inorganic UF and MF membranes under the trade name Membralox®. Cross-flow modules produce a water product containing 5 mg/l oil from a vegetable oil wastewater feed containing 450 mg/l. At this feed, the flux was 325 GFD/ft^2. This application uses an alpha-alumina (Al_2O_3) membrane with a pore diameter of 2000 angstroms (9).

Barriers to wide-scale use of the above systems include capital costs, lack of dependable cleaning procedures, and unfamiliarity of membrane systems to potential customers. The literature does not contain any information on adsorptive properties of ceramic/metallic membranes which affect both membrane life and selectivity. Long-term studies are needed to identify and solve the problems associated with ceramic membranes.

Developing applications. This subsection describes membrane applications that have been studied in fats and oils processing. It also discusses applications that have been applied in other industries and have potential in the fats and oils industry.

(A) Solvent/vapor recovery. Solvent extraction of vegetable oils and other liquid-solid extraction processes in the U.S. recover 2 million ton/yr of solvent (1). Solvent recovery in fats and oils processing is principally by evaporation with vapors recovered from noncondensible gases by mineral oil absorption. Membrane separations have been studied for both solvent and vapor recovery.

(1) Miscella distillation. The recovery of solvents used in the extraction step is required for economic, environmental, and safety considerations. The miscella (mixture of extracted oil and solvent) exits the extractor at 70 to 75 wt% solvent content (10) and currently, the solvent is recovered by distillation.

We have studied separation of vegetable oils from commercial extraction solvents using various RO and UF membranes (11). A list of membranes evaluated is shown in Table 5. The membranes were tested for their abilities to separate mixtures of hexane, ethanol, or isopropanol and 25 wt% cottonseed oil.

A laboratory scale membrane separation unit obtained from Abcor, Inc. (now Koch Membrane Systems) was used to determine solvent permeation rates and separation performances of 10 membranes. Using ethanol as the solvent, one membrane exhibited a flux of 200 GFD with 1% oil remaining in the permeate. However, hexane rapidly deteriorated all but one of the membranes tested. The membrane that was compatible with hexane had a low flux and unacceptably low oil retention.

Industrial scale membranes procured from Romicon, Osmonics, and Patterson Candy International (PCI) were evaluated. A hexane separation was attempted with a hollow-fiber Romicon unit, and it was noted that the pores of the fibers swelled almost closed. The Sepralator unit (Osmonics) was not able to retain oil from either the isopropanol/oil mixture or the hexane/oil mixture.

TABLE 5

Commercial Membranes and Their Specifications (14)

Company	Membrane	Estimated MWCO	Polymer
Romicon, Inc.	PM 1	1000	Polysulfone
Osmonics, Inc.	OSMO Sepa 0 (PA)	500-1000	Polyamide
	OSMO Sepa S-20 (VF)	20,000	Fluorinated polymer
	OSMO 192T-89 (PA)	300-400	Polyamide
	OSMO 192T-0 (PA)	500	Polyamide
	OSMO 192T-97 (CA)	150-200	Cellulose acetate
Paterson Candy International Ltd.	PCI ZF-99	<400	Composite
	PCI RO (CA)	<400	Cellulose acetate

However, some of the PCI and Abcor membranes selectively removed solvent (ethanol or isopropanol) from the miscella.

In related work, polysulfone membranes were studied for the separation of hexane, pentane, or heptane from hydrocarbons obtained in the deasphalting process. This work was performed by Allied/Signal and sponsored by the DOE Office of Industrial Programs. Deasphalting is the upgrading of heavy oils into high-grade petroleum oils (12,13). A spiral wound element, aided by formation of a dynamic gel layer, recovered pentane from the hydrocarbon mixture. Experiments in which crude oil was dissolved in pentane at an average pentane/oil ratio of 4 demonstrated average selectivities of 9 (pentane to oil) and fluxes of 10 to 15 GFD. Allied Signal has suggested that this work could be extended to food processing. Further on-site type testing is needed to verify that this concept is applicable to edible oil processing.

A conceptual design of a combined membrane/distillation process proposed by Allied/Signal for solvent recovery is shown in Figure 6. The solvent-rich stream that exits the membrane unit is recycled to the extractor and the oil-rich stream is processed by distillation to recover the remaining solvent. Assuming a 43% reduction in the quantity of oil and solvent to be distilled (as achieved in Allied/Signal's research), energy savings of 2 trillion Btu/yr is estimated for the combined-membrane/distillation recovery operation.

It was discovered (12,13) that pretreating the polysulfone membranes with solvent significantly increased the flux. One pretreatment procedure involved soaking the membranes in solvents of decreasing polarity: 50/50 solution of isopropanol/water followed by a 50/50 solution of isopropanol/pentane and finally pentane. Allied/Signal researchers suggested that pretreatment prevented the collapse of membrane pores that occurs upon direct contact of the membrane with a hydrocarbon feed. Pretreatment can be an important step in membrane systems involving feedstocks containing hydrocarbons.

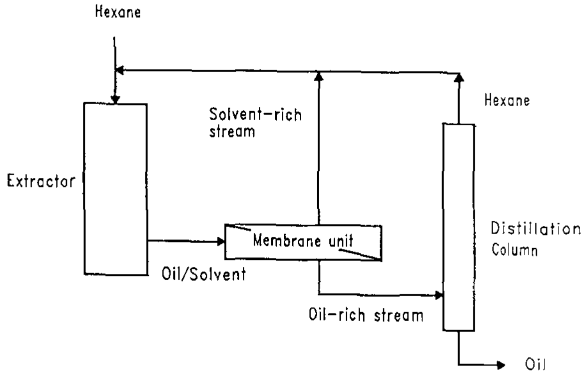

FIG. 6. Membrane recovery of extraction solvent in oil production.

Forsaie *et al.* (14) discussed the possibility of using a vegetable oil/diesel fuel mix in the event of a shortage of conventional diesel fuel. If vegetable oils were to be used as fuels, the energy saving potential of using membranes for solvent recovery would greatly increase. This savings potential assumes that processing techniques similar to those currently used in edible oil production will be used.

(2) Vapor recovery. Most of the hexane losses in a vegetable oil plant occur because of the high solvent content of meal exiting the desolventizer-toaster and in noncondensible vent gases leaving the plant (2). The air/solvent streams from the extractor, desolventizer-toaster, and evaporators go to a vent system where the hexane is absorbed from the vapor into mineral oil. The solvent is then stripped from the mineral oil by steam distillation (Fig. 7). This process requires approximately 3.4 trillion Btu/yr (Table 2).

Membrane Technology Research Inc. (MTR) has investigated recovery of solvent from waste air streams using gas permeation (15). In the MTR process, solvent-laden exhaust air is separated into a solvent-rich stream and a solvent-depleted (air) stream using spiral wound membrane modules. A partial vacuum is applied to the permeate side of the membrane to provide the driving force for solvent vapor permeation. The organic vapor is then compressed and condensed to recover the solvent while the solvent-depleted air is recirculated to the process. In some applications, the recirculated air is hot, and the recovered energy associated with its sensible heat is greater than the energy required to compress the solvent vapor.

Of the membrane materials tested (15), silicone and neoprene rubbers demonstrated the best solvent permeabilities. Nitrogen permeabilities were 250 × 10^{-10} cm^3 (STP)/cm^2 sec-cm Hg for silicon and 3 to 5 × 10^{-10} cm^3/cm^2 sec-cm Hg for neoprene. Solvent permeabilities were between 100 and 10,000 times higher. Typical solvent fluxes with silicone membrane ranged from 0.05 to 0.25 GFD. A gas permeation membrane system could be used to recover vaporized solvent directly from the

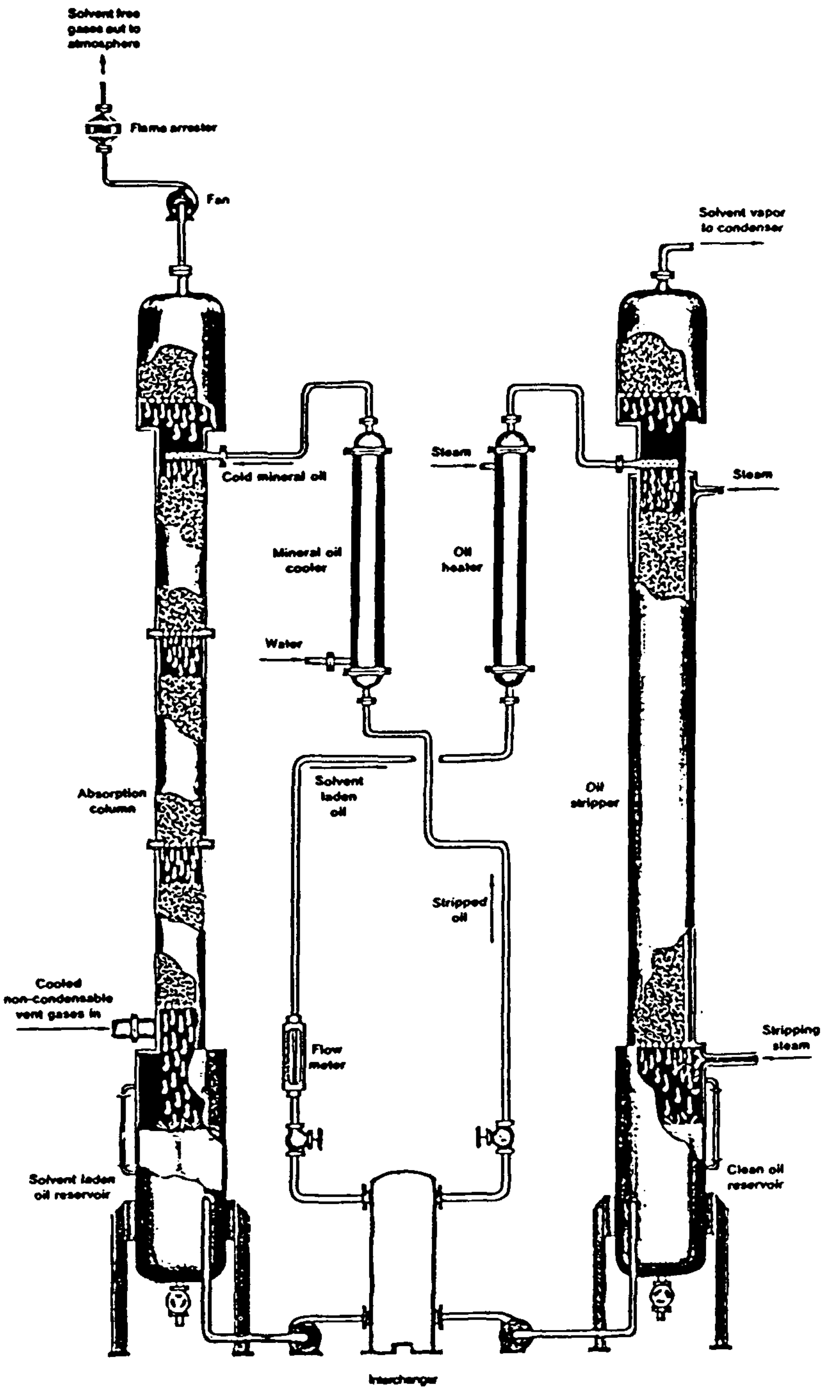

FIG. 7. Mineral oil scrubbing system for recovery of solvent from air.

air/solvent stream. The large amount of fines present in the air/solvent stream may present a problem and would have to be removed if a membrane system is to replace the conventional mineral oil system.

(B) Degumming, refining, and bleaching. Commercial sources of edible oils and fat include oilseeds, fruit pulps, animals, and fish (16). Various combinations of degumming, bleaching, and chemical or physical refining steps are used in processing crude oil into edible products. However, each step removes only one or two undesirable components and requires high capital cost equipment. We have recently reported initial studies using a high pressure UF technique to degum and decolorize crude oils in preparation for physical refining (17). Cottonseed, soybean, peanut, palm, and meadowfoam oils have been tested, and the results are promising. The replacement of several processing steps with a single membrane process has potential for saving both capital cost and energy.

Energy savings from applications of membrane processing can come from two main areas. First, membrane processing combines bleaching and degumming

TABLE 6

Thermal Balance of a Typical Refinery and Expected Energy Savings by Employment of a Membrane Processing[a]

Processing section	Thermal consumption (000,000) Kcal	Percentage of total consumption	Expected energy savings (000,000) Kcal
Oil storage[b]	2,241.6	2.96	224.0
Refining and bleaching[c]	10,244.5	13.52	5,122.3
Hydrogenation #1	3,382.8	4.46	—
Hydrogenation #2	476.2	0.63	—
Deodorization semi	16,929.0	22.34	—
Deodorization batch	31,286.8	41.30	—
Soapstock, glycerine and sharpless[d]	10,524.5	13.89	10.524.5
Packaging	678.1	0.9	—
Total consumption	75,763.5	100.0	15,870.8

[a] From an energy audit of a refinery (name not disclosed at request of the company) (100,889 MT/year processing capacity).

[b] Conservatively, it was assumed that use of the membrane system reduces oil storage costs by 10% because caustic refining has been replaced by physical refining.

[c] Since the membrane system reduces coloring pigments drastically, and completely in some cases such as peanuts and cottonseed, minimal bleaching is required. However, it was conservatively estimated that membrane processing will reduce bleaching time and the amount of clay use by half.

[d] There is no need for soapstock acidulation if physical refining is used.

into a single energy-efficient step. This would allow domestic oils to be physically refined, an advantage that palm oil has enjoyed. Physical refining has the following advantages over conventional caustic refining processes: installation costs are 22% lower; steam usage is 28% lower; cooling water is 7% lower; process makeup water is 85% lower; wastewater treatment is 63% lower; electrical power is 62% lower; and refining losses are 60% lower.

The second area is reduction in use of steam. Operating temperatures for membrane processing are lower than conventional processing, and we estimate that steam requirements can be decreased by 28% using physical refining as opposed to chemical refining (17). In physical refining, the free fatty acids and undesirable flavor compounds are removed by steam stripping rather than by alkali used in chemical refining. If a range of 25 to 35% steam savings is used, potentially 15 to 21 trillion Btu/yr can be saved if membrane processing is used to prepare the oil for physical refining.

Table 6 shows the thermal energy balance of a typical refinery. Expected energy savings from membrane processing are given in column three, and indicate that at least 21% savings (corresponds to 64.7 trillion Btu/yr in US) could be obtained by utilizing a combination of membrane technology and physical refining. The additional costs for physical refining will be offset by savings from the elimination of the oil drying costs. Estimates for the energy requirements of oil processing and potential savings were based on information found in Bollheimer and Campbell (18), Gavin (19), Dada (20), and Koseoglu, S.S., unpublished data, Texas A&M University, August 19, 1987).

German and Japanese workers have been active in the development of nonaqueous separations technology for oils and fats processing (21-28). However, because of the large economic potential of this technology, most of the information has been published in the patent literature.

In chemical refining, a considerable amount of oil is lost because of saponification of neutral oils. Ordinarily 1 to 4 times the free fatty acid (FFA) content is lost in refining oils such as cottonseed and soybean. For example, soybean oils containing 0.9 to 2.8% FFA suffer a 3.6 to 11.2% loss (29). Based on U.S. annual production of 15.1 billion lb of crude oil (soybean, cottonseed, and corn), up to 1.4 billion lb of oil is lost each year. These losses could be decreased by 60% using membrane refining. Calculations based on data available from the energy audits of various oil mills and refineries, and publications of U.S. Department of Commerce (Table 1) indicate that refining losses due to entrapment of neutral oil in soapstock and hydrolysis of the neutral oil during the caustic refining are about $163.3 million/year (Table 7).

Bleaching earth or clay requirements and associated waste treatment costs also would decrease with membrane processing. During bleaching, usually 0.75% bleaching clay is mixed with crude oil for removing coloring pigments and decomposition of peroxides. Each pound of bleaching clay absorbs at least 0.4 lb of oil which cannot be recovered economically. This amounts to about $13.6 million/year neutral oil that is lost with the bleaching clay. The used bleaching clay also creates waste disposal problems.

(C) Condensate return. Condensate recovery and reuse in the boiler has become a common energy conservation method for many industries. The sensible heat of the condensate is recovered, and wastewater treatment costs are reduced. Some refiners object to returning condensate to the boiler because of the possible oil contamination, but many refiners solved this problem through use of oil detection devices. If oil is detected, the condensate must be sent to waste treatment and cold makeup water is used to replace the hot condensate.

A high temperature-resistant membrane system could be applied to condensate clean-up. When oil is detected, the condensate could be diverted to a membrane system

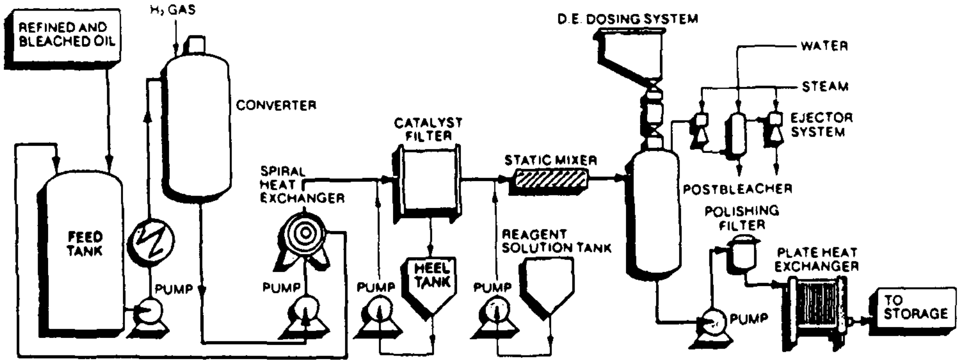

FIG. 8. A flow diagram of a hydrogenation system.

TABLE 7

Refining Losses Due to Entrapment of Neutral Oil in the Clay and Soapstock and Hydrolysis of Neutral Oil During Refining and Expected Savings Due to Membrane Processing

Processing	Oil losses (lbs)	Losses (dollars)
Conventional processing		
Bleaching	45,371,100	13,611,330
Caustic refining	544,453,200	163,335,960
Total	583,824,300	176,947,290
Membrane processing and physical refining		
Bleaching	22,685,550	6,805,665
Physical refining	217,781,280	98,001,576
Total	240,466,830	104,807,241

that separates the oil and condensate. The condensate would then be returned to the boiler (Farr, W.E., personal communication, Anderson Clayton/Humko Products, Inc., May 19, 1987). Several companies have systems available to treat oily streams. These systems are discussed in the wastewater treatment section of this paper.

(D) Catalyst recovery. Oil hydrogenation is usually performed in batch reactors equipped with gas-dispersing agitators, heating and cooling coils, gas handling systems, and catalyst introduction and removal equipment (Fig. 8). Normally, a supported nickel catalyst is added at a predetermined concentration depending on the product (16). Catalysts are normally dispersed on a carrier, e.g., diatomaceous earth.

When hydrogenation is complete, the catalyst is recovered by recirculating the oil through a high capacity filter until the oil is free of nickel (16). The cake that contains the catalyst is recovered manually from the filter and can be reused a number of times. Exhausted catalyst can be processed to recover its nickel content.

Ceramic membranes are able to withstand the high operating temperatures of hydrogenation and could be used to replace the filters used in catalyst recovery. Norton filters have been studied extensively in a similar application to recover activated carbon and other finely divided heterogeneous catalysts (Michaels, S., personal communication, Norton, July 1987). With catalyst particle size ranging from 1 to 100 microns, the catalyst will not penetrate into the filter media. Also, the tangential flow design of Norton's system lifts the catalyst from the surface, thus decreasing membrane fouling. Use of ceramic membranes could reduce the amount of oil lost in catalyst recovery.

Preliminary work (Michaels, S., personal communication, Norton, July 1987) has demonstrated that hydrocarbons behave differently than esters in the presence of alumina. A reaction between the glycerides and the alumina causes waxes to form along the membrane surface. Further work to find a surface treatment to prevent wax formation is needed. Straight chain hydrocarbons can be treated with these membranes as discussed in the wastewater treatment section. However, ceramic membrane module costs are high relative to polymeric membranes, thereby limiting their use and acceptability.

(E) Oilseed proteins. Most of the meal obtained in the production of crude oils is used as protein supplements in animal feeds (30). In the last decade, increasing amounts of soy flour have been converted into products for human consumption, and the estimated annual U.S. usage has increased from 1.9 lb/capita in 1977 to nearly 5 lb/capita in 1987 (31). Vegetable food proteins have been prepared from as many as 50 different species with the most common products being soybean and peanut proteins, wheat gluten, and some products of peas and beans (32). Isolated vegetable protein products generally have good nutritional value and are used in breakfast cereals, pet foods, confections, dairy-like products, and nutritional and dietary beverages.

Isolated protein processing plants are designed similarly to plants used for making cheese and processing whey. A typical process flow sheet for production of isolated soy protein is shown in Figure 9 (32).

The protein is extracted from defatted, untoasted flakes with a dilute alkali solution. The insolubles are separated by centrifugation and the extracted protein is precipitated by acidification to pH 4.5. The resulting curd is then washed, dissolved, re-precipitated, and rewashed before drying. A disadvantage of this process is that some acid-soluble protein (vegetable whey protein) is lost in the process and becomes a disposal problem.

Several processes have departed from this standard practice. Aqueous systems have been employed to extract

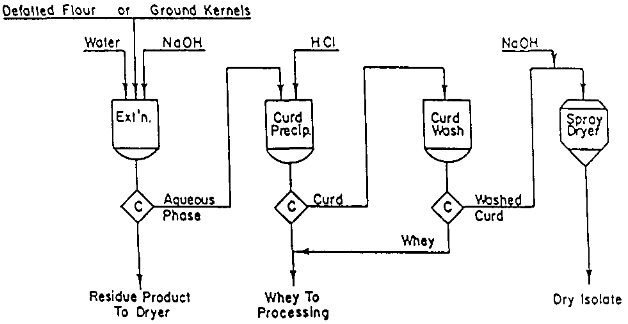

FIG. 9. Simplified flow diagram of commercial protein isolate production.

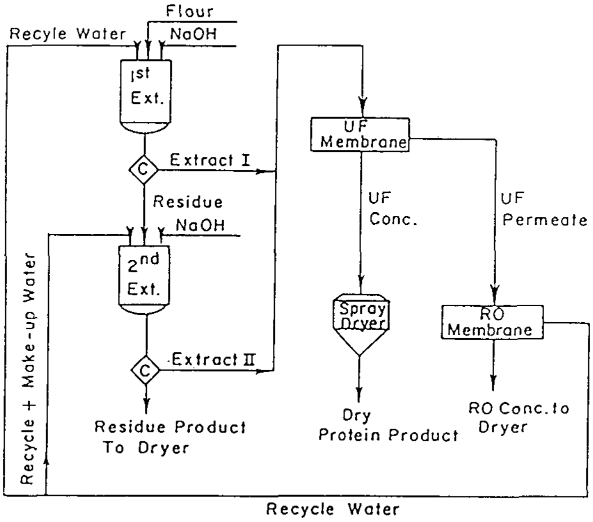

FIG. 10. Simplified flow diagram for membrane isolation of oilseed proteins.

both oil and proteins instead of the solvent extraction method (33). Also, UF has been used to recover protein from defatted soy flakes instead of isoelectric precipitation.

A recent review by Koseoglu and Lusas (32) gives the summary of aqueous, membrane and adsorptive separations of vegetable proteins. Aqueous extraction and membrane processing have been combined in a patented process developed at their laboratories. This approach offers several improvements over conventional methods of protein isolation. A flow diagram of the membrane process is shown in Figure 10 (32). In this process, proteins are recovered directly from the aqueous extract by UF to avoid generation of whey. The RO step recovers any product that may have passed the UF membrane, and also allows for reuse of the effluent water. This process has been tested on soy, glandless cottonseed, and peanuts (34-36).

The UF unit used in these tests was an internally-coated tubular membrane manufactured by Abcor, Inc. (Wilmington, MA). The unit contained 22 ft^2 of noncellulosic membrane, and produced fluxes ranging from 20 to 43 GFD (37). Diafiltration was employed to purify the protein. The UF membrane was cleaned by flushing with an acid solution (pH 3) and a detergent solution. The RO system used was an externally coated tubular system manufactured by Western Dynetics, Inc. (Newbury Park, CA).

Similar work has been reported by Nichols and Cheryan (38), Cheryan (39) and Cheryan *et al.* (40-43). A Romicon hollow-fiber UF produced soy protein concentrates of 60% protein, 35% fat, and very low oligosaccharide content (44-46). In this work, whole soybeans were used as the starting material rather than defatted soy flakes.

Another advantage of using membranes in soy protein processing is removal of undesirable, low molecular weight components. Soybeans contain both off-flavor and anti-nutritional components that must be reduced for production of a high quality protein product. UF has been investigated as a means of removing low molecular weight compounds such as phytic acid and oligosaccharides while retaining the desired protein and fat components (39).

Soy protein production using membranes is well-developed and ready for industrial implementation. One possible advantage to industry acceptance of this application is its similarity to the dairy industry, which has a large amount of membrane experience. The economics of this process were discussed by Hensley and Lawhon (47) and Lawhon *et al.* (36).

Continuous membrane bioreactors have been used to produce hydrolyzed vegetable proteins in the form of amino acids and peptides which can be used in medical diets, infant formulas, and nutritional fortification of beverages and foods (39). Yields in excess of 90% protein are obtainable in a UF reactor using a 10,000 molecular weight cut-off membrane. This system recycles the hydrolyzing enzyme that increases productivity 20- to 50-fold over that of batch reactors (conventional method hydrolyzing proteins). Details and operating characteristics of this system have been published by Cheryan and Deeslie (40-42) and Deeslie and Cheryan (48-50).

Energy savings. The greatest potential for energy savings exists in replacing or supplementing conventional degumming, refining, and bleaching processes. Energy savings approach 15 to 21 trillion Btu/yr. Reduced oil losses and bleaching earth requirements are other potential advantages of membrane processing. Work to date has been preliminary, and additional studies are needed to better define the limits and feasibility of this membrane application.

Approximately 2 trillion Btu/yr could be saved using a hybrid membrane system to recover solvents used in the extraction step of crude oil production. Studies to date report marginal success. The development of hexane-resistant membranes may make this application viable. Further testing is needed.

Membrane preparation/pretreatment can be an important factor in hydrocarbon system performance. Studies have shown pretreatment increases flux with little decrease in selectivity (12,13). More studies are needed to determine optimum pretreatment strategies. This need can be expanded to include looking at the surface phenomena of a variety of membranes, and, in turn, to determine the fouling characteristics of membranes. It naturally follows that cleaning processes need to be better outlined for a variety of membrane types.

The negative perception of the industry toward non-technical aspects of membrane processing must be overcome in order to gain acceptance in food processing. Membrane separations are less familiar to the oils and fats industry, and are considered to be expensive, requiring unusual cleaning procedures and frequent membrane replacement in order to correct flux loss or module failure. These misunderstandings developed because experiments with early membranes yielded unfavorable results. However, during the last ten years, extensive work has been done to overcome these technical problems and, fortunately, membranes finding acceptance in various food processing applications where their use leads to increased product yield and quality and considerable energy savings.

Several membrane applications in the fats and oils industry can benefit from research in these areas: for example, solvent recovery from miscella, wastewater treatment, and degumming, refining, and bleaching.

ACKNOWLEDGEMENTS

The work presented was performed by DOE Contract number AC07-76IDO 1570 (DOE Report DOE/ID10210) and supported in part by the Texas Food and Fiber Commission.

The authors would like to credit the following sources (references)—51, 52, 35, 1, and 53 for the figure information—Figure 1 and Figure 2; Figure 3 and Figure 8; Figure 4, Figure 5, Figure 9, and Figure 10; Figure 6; and Figure 7—respectively.

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[Received August 14, 1989; accepted November 20, 1989]
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