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# Distillation of Natural Fatty Acids and Their Chemical Derivatives

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## 1. Introduction

Well over 1,000 different fatty acids are known which are natural components of fats, oils (triacylglycerols), and other related compounds (Gunstone & Norris, 1983). These fatty acids can have different alkyl chain lengths (typically ten or more carbon atoms), 0-6 carbon-carbon double bonds possessing *cis*- or *trans*-geometry, and can contain a variety of functional groups along the alkyl chain (Gunstone et al., 2007b). Of these, there are approximately 20-25 fatty acids that occur widely in nature, are produced from commodity oils and fats, and find

Fat/Oil	Fatty acid length and unsaturation												
	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1
Canola				0.1	4.1	1.8	60.9	21.0		0.7		0.3	
Coconut	7.8	6.7	47.5	18.1	8.8	2.6	6.2	1.6		0.1			
Cottonseed				0.7	21.6	2.6	18.6	54.4	0.7	0.3		0.2	
Crambe					1.7	0.8	16.1	8.2	2.9	3.3		2.2	59.5
Cuphea (PSR-23)	0.8	81.9	3.2	4.3	3.7	0.3	3.6	2.0	0.3				
Palm			0.2	1.1	44.0	4.5	39.1	10.1	0.4	0.4			
Palm kernel	3.3	3.4	48.2	16.2	8.4	2.5	15.3	2.3		0.1	0.1		
Rapeseed					2.7	1.1	14.9	10.1	5.1	10.9		0.7	49.8
Soybean			0.1	0.2	10.7	3.9	22.8	50.8	6.8	0.2			
Sunflower					3.7	5.4	81.3	9.0		0.4			
Lard		0.1	0.1	1.5	26.0	13.5	43.9	9.5	0.4	0.2	0.7		
Tallow			0.1	3.2	23.4	18.6	42.6	2.6	0.7	0.2	0.3		

Table 1. Fatty acid composition of selected fats and oils (Evangelista & Cermak, 2007; Knapp, 1993, O'Brien, 2004; Stauffer, 1996)

major use for food and nutrition applications with the remainder being used by the oleochemical industry to produce soaps, detergents, personal care products, lubricants, paints, and more recently, biodiesel. Approximately 17 commodity fats and oils are obtained from various domesticated plants and animals. The largest vegetable oil sources are the oilseed crops (soybean, rapeseed, sunflower, and cottonseed) grown in relatively temperate climates. Another major oil source are oil-bearing trees (palm, coconut, and olive) grown in tropical or warm climates (O'Brien et al., 2000). The triglyceride-containing oils are extracted from oilseeds by mechanical pressing or by using solvent extraction (*n*-hexane). Seeds containing high oil contents are usually mechanically extracted first to reduce the oil content in the seed by 60% before solvent extraction. Animal fats are obtained by rendering inedible animal by-products like fat trim, meat, viscera, bone, and blood, generated by slaughter houses and meat processing industry and mortalities on farms (Dijkstra & Segers, 2007; Hamilton et al., 2006). World fat and oil production in 1998 was 101 million tons, of which 14.2% (14.3 million tons) was used as basic oleochemicals (Hill, 2000). In 2009, the global production of fats and oils increased to 137.5 million tons with 21.2% (29.3 million tons) used for non-food industrial purposes (Gunstone, 2011). This growth was driven by the high petroleum prices as well as the growing demand for natural or renewable products (de Guzman, 2009).

Symbol	Systematic Name	Trivial Name	Melting Point <sup>a,b</sup> (°C)		Boiling Point <sup>c</sup> (°C/(10 mm Hg))	
			Acid	Methyl Ester	Acid	Methyl Ester
Saturated fatty acids			Acid	Methyl Ester	Acid	Methyl Ester
10:0	decanoic	capric	31.0	-13.5	150	108
12:0	dodecanoic	lauric	44.8	4.3	173	133
14:0	tetradecanoic	myristic	54.4	18.1	193	161
16:0	hexadecanoic	palmitic	62.9	28.5	212	184
18:0	octadecanoic	stearic	70.1	37.7	227	205
20:0	eicosanoic	arachidic	76.1	46.4	248 <sup>d</sup>	223 <sup>d</sup>
22:0	docosanoic	behenic	80.0	53.2	263	240
24:0	tetracosanoic	lignoceric	84.2	58.6	---	198(0.2) <sup>e</sup>
Unsaturated fatty acids <sup>f</sup>						
16:1	9-hexadecenoic	palmitoleic	0.5	-34.1	180(1) <sup>a</sup>	182
18:1	9-octadecenoic	oleic	16.3	-20.2	223	201
18:2	9,12-octadecadienoic	linoleic	-6.5	-43.1	224	200
18:3	9,12,15-octadecatrienoic	linolenic	-12.8	-52.4	225	202
20:1	9-eicosenoic	gadoleic	23.0	---	170(0.1) <sup>a</sup>	154(0.1) <sup>e</sup>
20:4	5,8,11,14-eicosatetraenoic	arachidonic	-49.5	---	163(1) <sup>a</sup>	194(0.7) <sup>a</sup>
22:1	13-docosenoic	erucic	33.5	-3.5	255	242

Table 2. Nomenclature of selected fatty acids and their respective melting and boiling points. <sup>a</sup>Gunstone et al., 2007b. <sup>b</sup>Knothe & Dunn, 2009. <sup>c</sup>Budde, 1968. <sup>d</sup>Farris, 1979. <sup>e</sup>Ethyl ester. <sup>f</sup>Double bonds in the all *cis*- geometry.

The fatty acid composition of fats and oils varies widely depending on the source (Table 1). Coconut and palm kernel oils contain high amounts of medium chain saturated fatty acids like lauric and myristic acids (Table 2). Palm, tallow and lard oils are high in longer saturated fatty acids (palmitic and stearic acids) and monounsaturated oleic acid. Canola, and sunflower oils are high in oleic acid while soybean oil has more linoleic acid. Rapeseed and crambe are good sources of long chain fatty acids like erucic acid.

The first step in fatty acid production (Fig. 1) is the splitting or hydrolysis of the triglyceride molecules of fats and oils in the presence of water to yield glycerine (10% yield) and a mixture of fatty acids (96% yield), (Gunstone et al., 2007a).

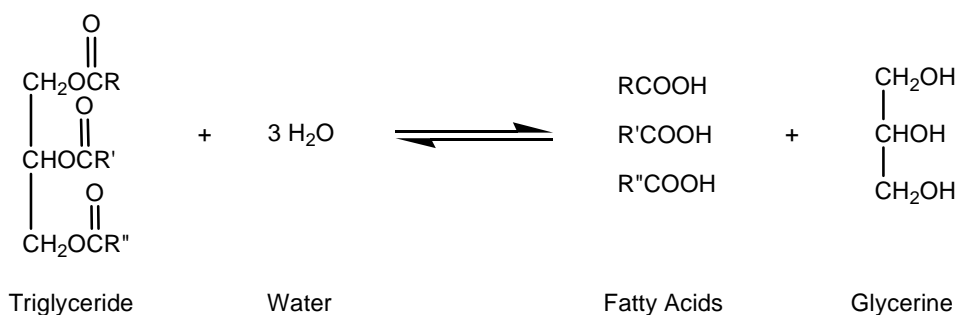


Fig. 1. Splitting or hydrolysis of fat or oil triglycerides to fatty acids and glycerine

This can be done batch-wise using the Twitchell process (Ackelsberg, 1958; Twitchell, 1898) or continuously at high pressure and temperature like the Colgate-Emery process (Barnebey & Brown, 1948). Typically, the crude fatty acids obtained by the Colgate-Emery process are considerably lighter in color in comparison to those obtained by the Twitchell process. The degree of triglyceride hydrolysis is important as residual mono-, di-, triglycerides and free glycerol in the fatty acid prior to distillation will result in more distillation pot residue (Potts, 1956). The fatty acids from the fat splitting process are relatively dark in color and contain various impurities. The fatty acids are subsequently purified or separated into fractions by distillation and fractionation.

## 2. Distillation methods used in fatty acid industry

Purification of fatty acids by distillation has been practiced for well over a hundred years and is still the most common and most efficient means of producing high purity fatty acids. Distillation removes both the low and high boiling impurities as well as odor substances. Distillation of fatty acids may be either batch or continuous process, at atmospheric pressure or under reduced pressure. It may be simple distillation involving purification of mixed fatty acids or fractional distillation consisting of both purification and separation of fatty acids according to chain length (Gervajio, 2005; Muckerheide, 1952; Potts & White, 1953). Because of the inherent sensitivity of fatty acids toward heat, the distillation methods employed should be conducted at as low a temperature as practically and economically feasible while maintaining the shortest residence time of the fatty acid in the distillation unit. Today's, modern distillation units rely upon high vacuum, effective heating, short contact times, effective mass transfer between vapor and condensate, and steam economy (Lausberg et al., 2008).

## 2.1 Batch distillation

Batch distillation at atmospheric pressure is probably the oldest of the commercial processes used in fatty acid distillation. It uses a direct-fired still pot fitted with a steam sparger. The pot is charged with fatty acids and heated to 260° to 316°C and sparged with saturated steam at 149°C. The ratio of steam to fatty acid vapor is typically 5 to 1. The steam and fatty acid vapor are condensed separately. The economics of this type of distillation is poor due to the large amount of steam used. Considerable amounts of fatty acids are also entrained in the steam condensate. Distillation is further complicated because of the prolonged heating of the fatty acids at high temperatures and the inherent thermal instability of the fatty acids. This combination often results in considerable decarboxylation and polymerization with consequently large amounts of viscous residue and pitch. Tall fatty acids of about 95% hydrolysis when distilled in this manner yield 15 to 20% entrained fatty acids and 10 to 15% residue. Re-splitting the residue and distillation yields low quality fatty acids and a final pitch residue of 5 to 8% (Muckerheide, 1952). Later improvements in this distillation technique included working at reduced pressure (5-50 mm Hg) and lowering the amount of injected steam. The water from the steam is desirable as it suppresses anhydride formation (Potts, 1956).

## 2.2 Continuous distillation

Probably the first fatty acid still to use continuous distillation was developed by Wecker (1927). A simplified diagram of this process is illustrated in Fig. 2. Preheated fatty acid feed enters through pipe *c* and flows through a series of reaction chambers *a* interconnected by pipe *b*. The reaction chambers are heated at the bottom by gas or oil burners. Superheated steam is introduced through pipe *l* and injected into the feed in each chamber by a sparger (*m* and *n*). The low pressure imposed in the reaction chamber and the high temperature of the feed caused the superheated steam to evaporate vigorously resulting in an instantaneous distillation of the fatty acids. The vapor are led to a pipe header *g*, condensed by a water-cooled condenser *h*, and collected in *i*. The steam passes on to the barometric condenser through *k* and the non-condensable gases are removed by a vacuum pump. The residue leaving the last reaction chamber is cooled in *d* and into collector *e*. Vacuum on the still is maintained at 30-35 mm Hg and the temperature in the still chambers ranged from 196° to 260°F. Residence time of fatty acids is about 30 min.

One disadvantage of steam distillation of fatty acids is the formation of emulsions in the last stage of condensation where a water spray is used. The calcium and magnesium salts in the water spray react with the fatty acids forming soaps. To recover the fatty acids, the soap is acidified and redistilled if desired. This can be avoided by employing dry distillation, i.e., distillation without using steam or any gaseous medium as carrier of the fatty acids. Such process was developed by Mills (1942) who employed a combination of dry and flash distillation to recover fatty acids from hydrolyzed fats and oils (Fig. 3). The fatty acid to be distilled is rapidly heated using a heat exchanger (4) to the boiling point corresponding to the operating pressure ( $\leq 12.7$  mm Hg absolute) in the still (10). When the heated feed is introduced to the bottom of the tube (13) and exposed to the lower pressure in the still, the fatty acids vaporizes immediately. The vapors lift the undistilled residue (11) from the bottom of the still up the tube and splashes against the bottom of the baffle (15) creating a continuous curtain of liquid undistilled material. The vapor proceeds to the condensers (17

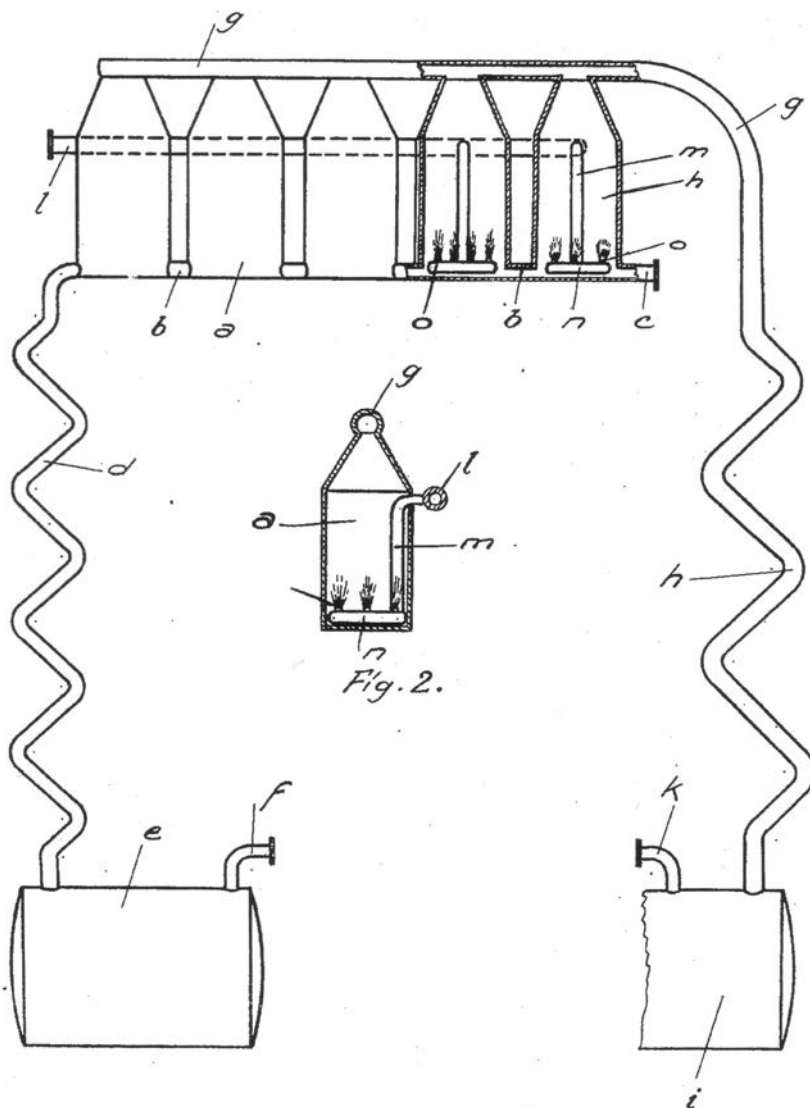


Fig. 2. Continuous distillation (Wecker, 1927)

and 18) and the fatty acid condensates are collected in the receivers (20 and 21) which can be withdrawn continuously or intermittently. The undistilled material is withdrawn continuously through pipe (30) which can be directed by valve (35) back to the heat exchanger or by valve (34) to the residue collector (31).

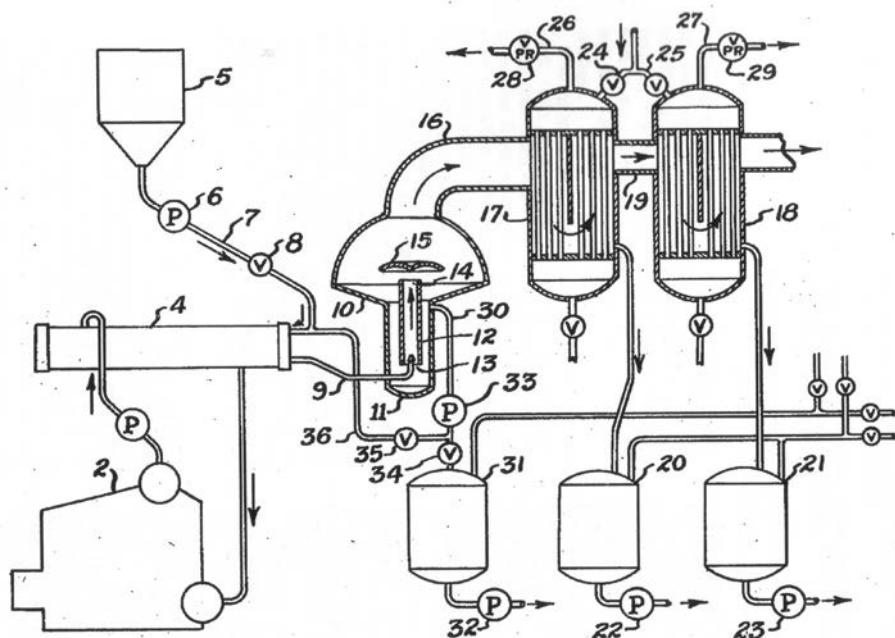


Fig. 3. Continuous dry distillation (Mills, 1942)

### 2.3 Fractional distillation

Because fatty acids are derived from natural sources, their initial and distilled compositional mixtures tend to vary even when the same type of fat or oil is used. Users generally prefer pure fatty acids or mixtures of fatty acids of consistent composition and known properties. Fractional distillation separates fatty acids based on their boiling points. Fatty acids which differ in chain length by two carbons are easily separated, thus; fatty acid fractions of 90% or better purity are obtained (Potts & White, 1953; Ruston, 1952). Fundamentally, fractional distillation is carried out in the same manner as continuous distillation. The main difference is in the design of the main fractionating column which is fitted with several bubble cap trays, means for removal of side stream distillates of fatty acids and return part of these streams as reflux (Muckerheide, 1952; Stage, 1984).

In the fractionating column, vapors move upwards through the column and condensed at the top. A portion of the condensate is returned as reflux downwards through the column where it is brought into more or less intimate contact with the ascending vapors. Heat is exchanged between the rising warmer vapor and the cooler descending condensate. The more volatile fraction in the condensate is vaporized and the easily condensable fraction in the vapor is condensed. Under ideal conditions, the heat lost by the rising vapor is gained by the descending condensate, with no heat loss or gain from the outside. The net result is

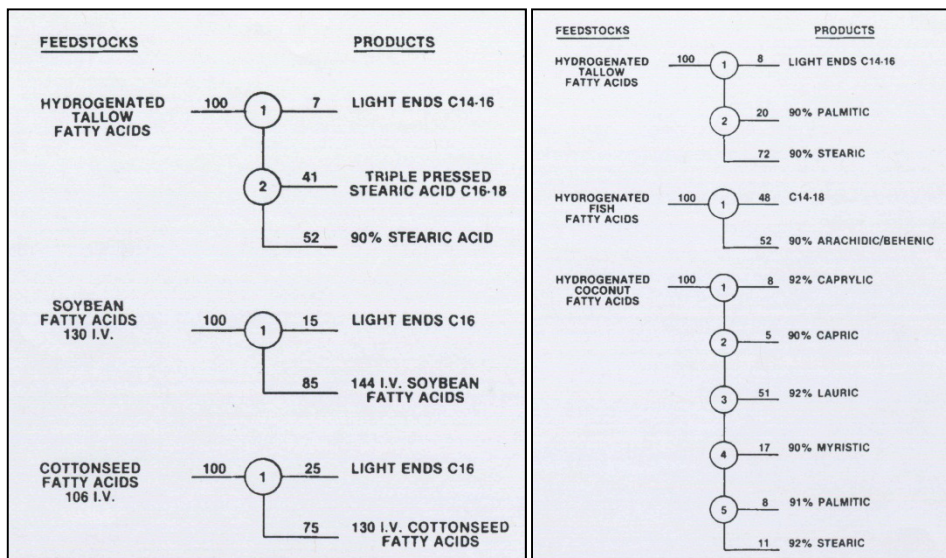


Fig. 4. Partially fractionated hydrogenated tallow, soybean and cottonseed fatty acids and fully fractionated hydrogenated tallow, fish, and coconut fatty acids (Berger & McPherson, 1979)

the concentration of more volatile fractions on top of the column and the increasing concentration of less volatile fraction at the bottom of the column (Norris & Terry, 1945). Fractionating stills are custom designed to suit the feedstock and product requirements. With lauric type fatty acids from coconut and palm kernel oils, up to 30 fractionating trays can be used for highest purity fraction because of the higher volatility and greater stability of the shorter chain fatty acids. Long chain fatty acids like erucic (C22:1) in rapeseed oil have much lower vapor pressure and would need a limited number of fractionating trays to keep the reboiler below the decomposition temperature (Berger & McPherson, 1979). Commercial fatty acid products that can be obtained by fractional distillation are shown in Fig. 4.

The first continuous fractional distillation unit for the separation of a fatty acid mixture was installed by Armour and Company in 1933 (Fig. 5). The system consisted of the main fractionating tower, two smaller side stripping towers, conventional air ejectors and boosters, condensers, coolers, and a direct-fired fatty acid heater. The direct-fired fatty acid heater was susceptible to coking and corrosion from the fatty acids which resulted in operation downtime. Shell and tube heaters using condensing Dowtherm vapor as source of heat replaced the direct-fired heater in subsequent installations (Potts & White, 1953).

Fractional distillation was also employed by General Mills in their fat and oil processing plant which started operation in 1948. The feed stock is introduced into the first distillation tower and heated by the rising vapours from the base of the tower (Fig. 6). This eliminated the problem of fouling in heating tubes when preheating incoming feed. Also, to conserve space and construction cost, the second distillation tower was superimposed on the third. Fractionated fatty acids, fatty acid esters, and their derivatives were produced from low grade fats, oils, acid oils, and tall oil.



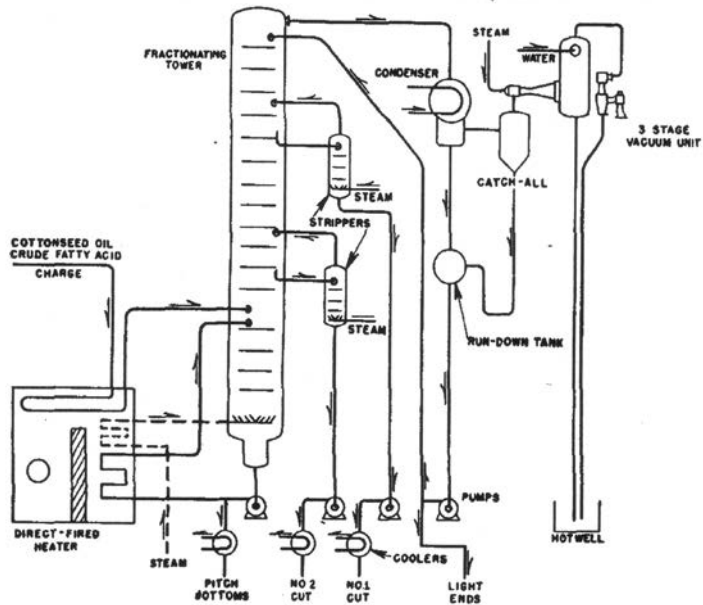


Fig. 5. Flow diagram of fractional distillation employed by Armour and Company in 1933 (Potts & White, 1953)

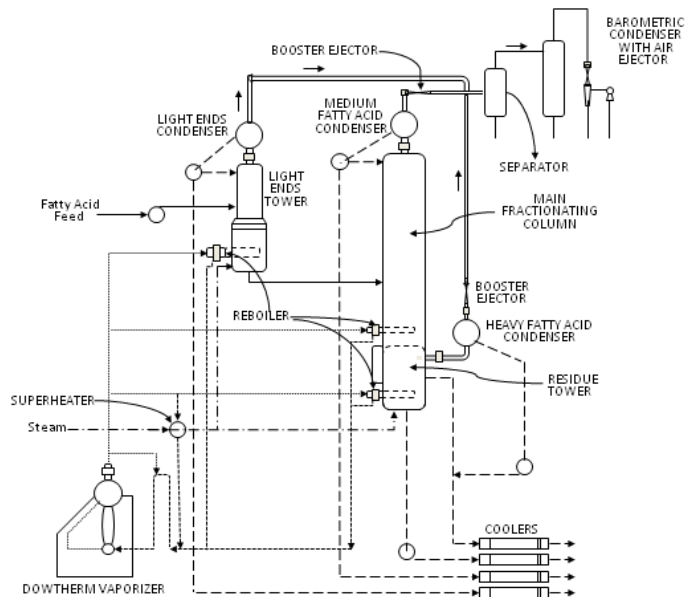


Fig. 6. Flow diagram of fractional distillation employed by General Mills in 1948 (Potts & White, 1953)

## 2.4 Molecular distillation

Molecular distillation is industrially useful in the purification of unstable or highly oxidatively unstable fats, oils and their derivatives. Molecular distillation consists of at least the following types: wiped film molecular distillation unit (Fig. 7) and centrifugal molecular distillation unit (Fig. 8).

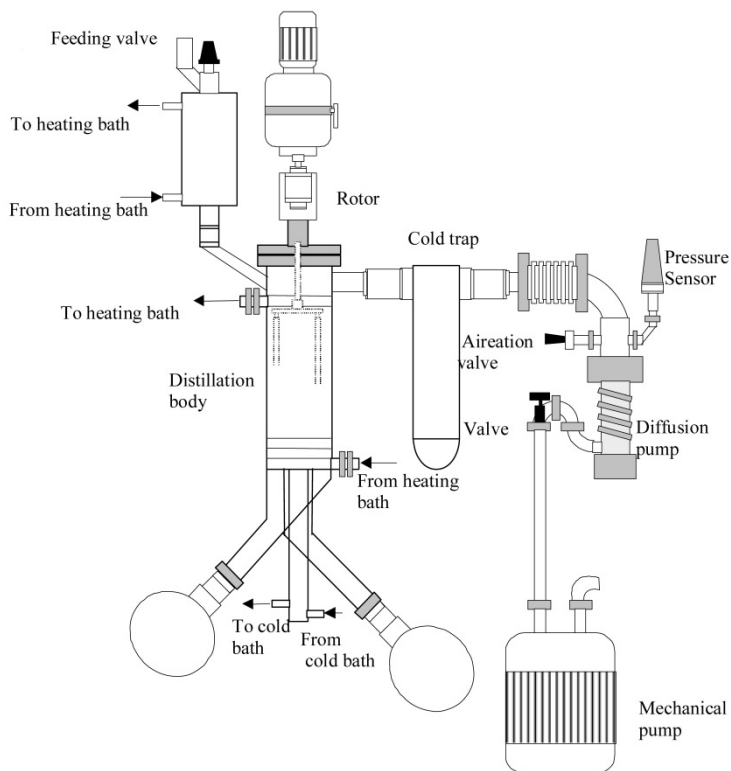


Fig. 7. Wiped film molecular distillation unit (Marttinello et al., 2008)

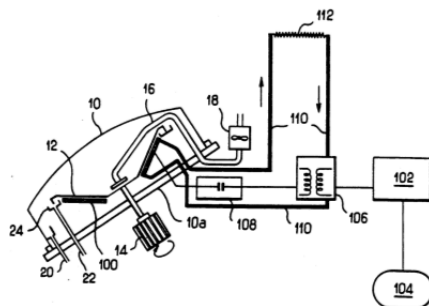


Fig. 8. Centrifugal film molecular distillation unit (Nuns et al., 1994)

Molecular distillations are conducted under vacuum conditions, which allows for reduced distillation temperatures compared to conventional distillation techniques thus reducing the risk of oxidative damage. Separating the oil's components by weight allows contaminants to be reduced far below industry standards. Current industrial applications include cosmetic applications, the concentration of omega-3 fatty acids (EPA and DHA) and corresponding esters in fish oil (Rossi et al., 2011), and contaminant removal. Additionally, Vitamin E (Pramparo et al., 2005), Vitamin A, cocoa butter, dimer acids, epoxy resins, lubricants, monoglycerides, insecticides, pharmaceuticals, perfumery and flavours, essential oils, Azadirachtin (Neem based pesticides) and its formulations as well as many other natural & herbal products have been distilled on an industrial scale using this process. Additional applications and information on fatty acid molecular distillation will be reported in Section 3.3 Distillation.

### 3. New crops and products

Development of new crops in the United States is based on a history of screening and identifying plants for novel chemicals, germplasm development of a select few unique plants, isolation of raw materials (processing, refining and distilling), product development, evaluation, and scale-up to commercial production and, finally, the transfer of knowledge to industrial partners and farmers. In most cases, these new crop identifications initially begin with the individual selection based on oil composition and unique fatty acid profiles, followed by continued evaluation and development based on novel raw materials, industrial applications of the raw materials and agronomic potential. From this extensive survey, two crops were selected to focus on (Cuphea and Meadowfoam). Additionally, these crops have had been converted into industrial products which require some degree of purification. Thus separations of both the new crop fatty acids and new products have undergone distillations.

#### 3.1 New crop examples

##### 3.1.1 Meadowfoam

One example of a successful new crop is meadowfoam (*Limnanthes alba*). In the 1960's, USDA scientists identified this plant as a potential new crop out of hundreds of others that needed further research. In the 1970's, a meadowfoam breeding program began the daunting task of domesticating this plant. By the 1990's, numerous varieties had been released and meadowfoam reached commercial scale (approximately 8000 acres in 1997) in the Willamette Valley of Oregon located in the Northwestern US. The unique long chain fatty acids of meadowfoam [5-eicosenoic acid (62%); 5,13-docosadienoic acid (19%); 5-docosenoic acid (3%); and 13-docosenoic acid (10%)] helped advance its development (Phillips et al., 1971). Finally, the  $\Delta 5$  unsaturation itself has enhanced resistance to oxidative degradation as evidenced by the high OSI of the oil (246.9 h @ 110°C) which makes meadowfoam oil one of the most stable oils available on the market (Isbell et al., 1999). Meadowfoam oil is found in numerous cosmetic applications, such as hair shampoos and conditioners, skin creams, hair setting aids, permanents, hair relaxers, and hair colors.

### 3.1.2 Cuphea

Cuphea (*Lythraceae*) is a large genus of over 200 species of herbs and shrubs that produces a small seed with oil that is rich in saturated medium-chain triacylglycerols (which can be converted to medium chain fatty acids, MCFAs) (Graham et al., 1981; Knapp, 1993; Miller et al., 1964; Wolf et al., 1983). MCFAs (C8:0-C12:0) are used primarily in soaps (Nandi et al., 2004), detergents (Molly & Bruggeman, 2004), cosmetics (Brown et al., 2008), lubricants (Nagaoka & Ibuki, 2000), and food applications (Tholstrup et al., 2004). One-half of the MCFAs used by the US soap and detergent industry are obtained from coconut and palm kernel oils, while the other half is from petroleum (Hardin, 1991).

With the need for higher seed yields, oil content, and less seed shattering, Steve Knapp (1993) at Oregon State University began developing promising cuphea crosses. Cuphea PSR-23 is a hybrid between *Cuphea viscosissima* (a species native to the US) and *Cuphea lanceolata* (a species native to Mexico). One of these new germplasm lines, PSR-23, with partial seed retention and high in C10:0, decanoic acid, was developed and has been planted in the Midwest and mechanically harvested and dried (Cermak et al., 2005) by researchers at USDA since 2000. The seeds weighed 538 g/L (3.3 g/1,000 seeds) and contain up to 35% oil (Table 1). The oil typically contains around 82% capric, 4% oleic, 4% palmitic, 2% linoleic, 4% myristic, and 3% lauric acids (Evangelista & Manthey, 2004; Gesch et al., 2005; Kim et al., 2011).

Recent seed increases in Cuphea provided sufficient amounts of seed to conduct oil extraction studies and, at the same time, produce much needed oil for product development and applications testing. The first report on full press oil extraction from Cuphea seeds was also optimized in a pilot-scale study (Evangelista & Cermak, 2007). Oil extracted by pilot plant screw pressing of whole Cuphea seeds produced dark green colored oil. Chlorophyll content of the oil, ranging from 200-260 ppm, had been reported, but levels up to 326 ppm have recently been observed (Evangelista & Cermak, 2007). About 6.5-8% bleaching clay had been used in the bleaching step to bring the chlorophyll level in the refined oil to 0.5 ppm. Aside from the added cost of the bleaching clay, more oil is also lost as these adsorbents retain between 50-75% their weight of oil. With a supply of cuphea oil a series of new products could be developed from this new oil or corresponding fatty acids ranging from biodiesel (Geller et al., 1999), to cosmetics (Brown et al., 2008) to lubricants (Cermak & Isbell, 2004a,b; Cermak et al., 2008).

### 3.2 Estolides

Estolides have been used to help develop new products from industrial crops (Cermak & Isbell, 2001b). Estolides are formed by the formation of a carbocation that can undergo nucleophilic addition with or without carbocation migration along the length of the chain. The carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters. The extent of oligomerization is reported by estolide number (EN) which is defined as the average number of fatty acids added to the base fatty acid. The estolide carboxylic acid functionality can be converted *in situ* under esterification conditions with the addition of an alcohol to yield the corresponding estolide ester (Fig. 9).

Estolides from a number of fatty acids have been shown to have desirable low-temperature properties (Cermak & Isbell, 2001a,b; Isbell et al., 2000a) making them suitable for lubricants. However, the current market price of meadowfoam precludes its use in these markets.

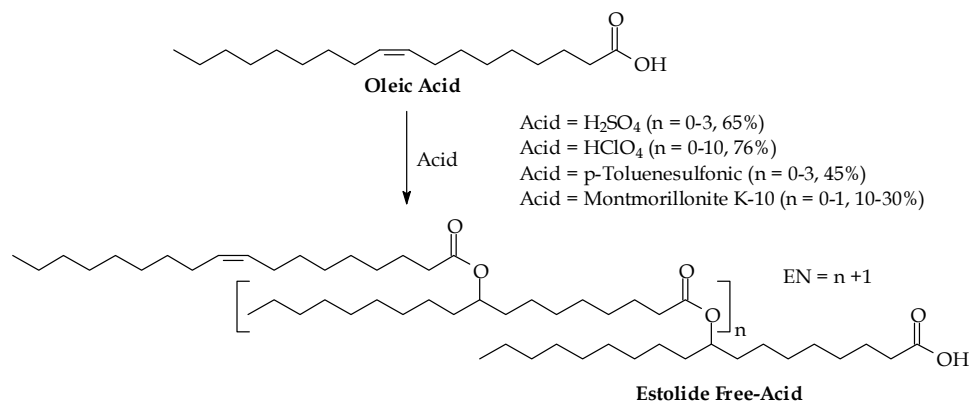


Fig. 9. General Oleic Estolide Free-Acid Synthesis

Therefore, meadowfoam has been marketed into cosmetics where the estolide has shown good properties for use in hair conditioners (Isbell et al., 2000b), but dark colored products have limited the estolides use. Frykman and Isbell (1999) have shown that some color reduction is possible by bleaching with sodium borohydride, but further color reduction may be required. A second method for estolide purification was reported based on chromatography, but this method only provided trace quantities of individually purified oligomers for qualitative characterization (Isbell & Kleiman, 1994 and 1996) and would not serve as a means for industrial-scale estolide production.

### 3.3 Distillation

Coconut and palm kernel oils alone provided more than 450 thousand tons of decanoic acid to the global market in 2006, where it is used as a wood preservative (Yoshida & Iinuma, 2004) cosmetic agents for hair (Hoppe & Engel, 1989), activity against termites (Goettsche & Borck, 1994), dental compositions (Velamakanni et al., 2006), lubricants (Cermak & Isbell, 2004a), fabric softeners (Hohener & Frick, 2003) and cosmetics (Ishii & Mikami, 1995).

Cuts of saturated fatty acids can be successfully distilled from coconut and palm kernel fatty acids at relatively low temperatures to produce nearly colorless fatty acids. There are many compounds that are sensitive to heat such as high vacuum oils (Rees, 1980), vegetable oils (Cermak & Isbell, 2002; Isbell & Cermak, 2004), pharmaceuticals, and cosmetics (Batistella & Marciel, 1996) which prohibit the use of conventional distillation techniques. Molecular or short-path distillation, which has been known for some time (Biehler et al., 1949), uses a high vacuum to achieve distillation of thermally unstable materials, and is often the most economically feasible method of purification. Centrifugal and falling films are two basic types of molecular distillation units which use a short exposure of the distilled liquid to the evaporating cylinder. The high temperature exposure time in these stills is on the order of a few seconds to tenths of seconds as the liquid is spread evenly in the form of a film (Micov et al., 1997). These types of distillation units have been used successfully to demonstrate and compare the distillation of many different compounds, such as carotenoids from palm oil (Batistella & Marciel, 1998), cuphea fatty acids (Cermak et al., 2007), and estolides (Isbell & Cermak, 2004).

At the USDA laboratory, estolides and new crop fatty acids have been distilled on both the Myers Lab 3 and Myers Pilot 15 molecular distillation units (Myers Vacuum, Kittanning, PA), the simpler of the two being the Myers Lab 3 (diagram illustrating the operational features of this unit is presented in Fig. 10). The condenser temperature can be set to the desired temperature, rotor speed was constant at 1725 rpm, and cold tap water was used to cool the diffusion pump and rotor bearing. Vacuum pressure is usually maintained at  $6 \times 10^{-4}$  -  $3 \times 10^{-3}$  mm Hg at both the chamber and foreline pressure sensors.

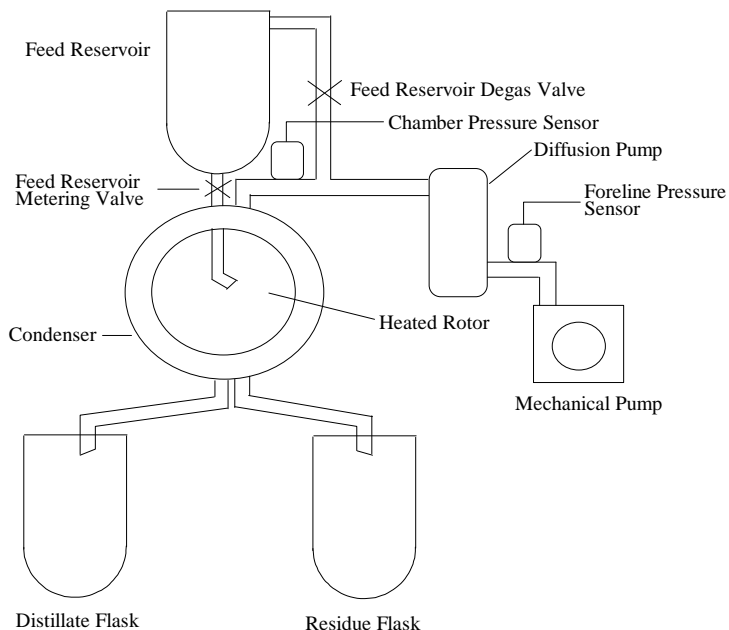


Fig. 10. Schematic diagram of Myers Lab 3 short path molecular distillation unit

The more complex unit, a Myers Pilot-15 distillation unit (Fig. 11), was used for pilot scale distillations (Cermak & Isbell, 2002). It is a continuous, centrifugal 38.1 cm molecular still that contains all of the components needed for distilling raw feedstock. Raw feedstock is delivered with a metering valve and a gear pump. It first enters a degasser unit which is maintained at pressures between  $5.4 \times 10^{-3}$  -  $6.8 \times 10^{-2}$  mm Hg. It then enters the heated evaporator cone or distillation chamber, where the molecular distillation takes place. The distillate and residue are continuously removed by transfer pumps. The material is passed to and from each station through stainless steel transfer lines, which are traced with heating tapes. This unit was designed for use in extended or large scale distillations of ~50 gals/day.

The major component of the Myers Pilot-15 distillation unit is a concave, heated evaporator cone, which rotates within the distillation chamber and is maintained at pressures as low as  $<6.8 \times 10^{-5}$  mm Hg (Fig. 12). Degassed and/or stripped feedstock is metered by the feed pump into the center of the spinning evaporator cone (1700 rpm) and is spread rapidly and evenly outward in a thin film over the entire surface by centrifugal forces. As the film spreads and is heated, part of the feedstock reaches a temperature at which it vaporizes and

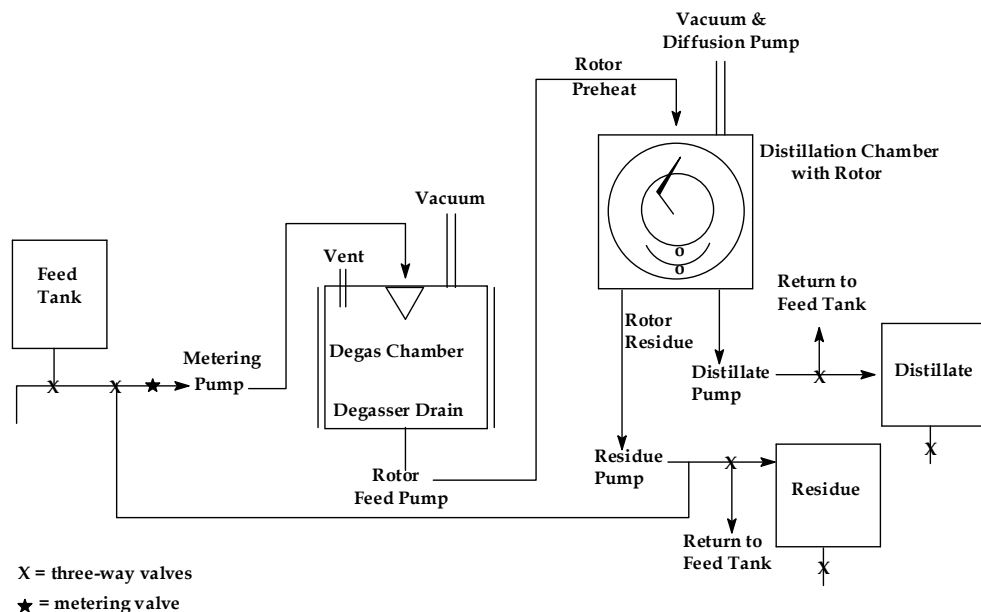


Fig. 11. Operational Flow Diagram for the Myers Pilot-15 Distillation Unit

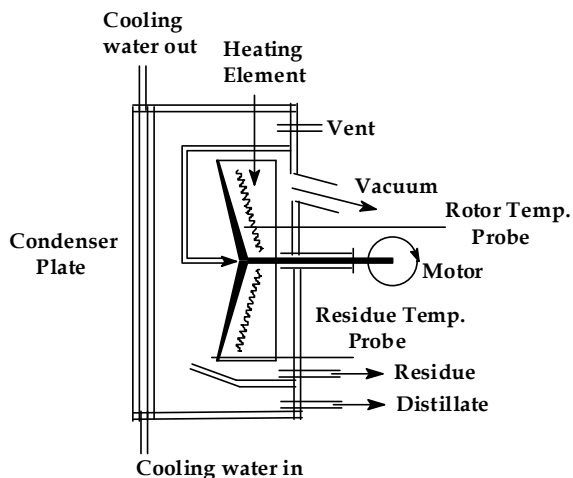


Fig. 12. Side View of Myers Pilot-15 Distillation Chamber

leaves the rotor surface to condense on the cooler surface of the condenser plate. With the help of centrifugal force the unvaporized feedstock, the residue, is spun into a gutter, where it is removed from the still by a constant-speed transfer pump. The condensed vapor, the distillate, flows by gravity into a removal pipe located at the bottom of the distillation chamber and then pumped from the still by another constant speed transfer pump. The operational distillation unit has two temperature sensors in the distillation chamber. The

first sensor, which monitors the temperature of the rotor, is located by the electric heating elements just beneath the 38.1 cm rotor. This first temperature corresponds to the temperature of the heating element, not the temperature of the rotor. The actual temperature of the rotor can be varied by varying the flow of feed material without affecting the element temperature. The second and most important temperature sensor measures the temperature of the residue. This sensor is located in the gutter where the residue is collected during distillation. The residue sensor provides the closest temperature of the rotor, since it is a measurement of the temperature of the material that was just in contact with the rotor.

All the transfer lines and pumps are wrapped with heating tapes. The heating tape and electrical elements are controlled with digital controllers either based on percent power demand or actual measured temperature. Each region of the transfer line and pump has internal temperature probes that measure the temperature of the material as it passes the sensors.

These two distillation units common to industrial processes have allowed new crop fatty acids and products to be distilled at levels acceptable for industrial purposes. These materials have than been used in commercial products such as cosmetics (Brown et al., 2008; Isbell et al., 2000b) and lubricants (Cermak & Isbell, 2004a,b; Cermak et al., 2008).

### 3.3.1 Cuphea

Estolides have been previously synthesized by USDA's National Laboratory in Peoria, IL, from C10:0 decanoic acid, cuphea oil, Table 1 (Cermak & Isbell, 2004a). These estolides have useful properties as lubricants based on the physical properties exhibited by these C10:0 materials. An issue associated with the decanoic estolides is the color of the final product. Commercial decanoic acid is not as refined as other mid-chain fatty acids, so removal of the color bodies is necessary for light colored estolides. The measurement of the color of a material is designated as the Gardner color. The Gardner color scale is from 1 to 18 with 1 containing the least amount of color and 18 with the maximum amount of color. Lubricant manufacturers and consumers would prefer lubricants with colors similar to current petroleum oils, lower numbers i.e. Gardner 1 to 3. To obtain these properties, the starting material must be distilled, which is costly and can lead to undesired additional color bodies with certain distillation techniques. The ability to achieve a fast and mild distillation of short-chain fatty acids could be used to obtain oil with low Gardner color while the residue would not be darkened by the distillation process. These improvements with decanoic acid would help with the commercialization of cuphea as a new oil seed and give US farmers a valuable rotation crop. This studies objective was to investigate the general conditions necessary for laboratory molecular distillation of decanoic acid or enrichment from cuphea fatty acids. Fatty acid profiles, Gardner colors, and flow rate requirements were examined to determine the best set of operating conditions.

The basic experimental conditions for the two different flow rates, high and low, over eight different rotor temperature settings, their effects on split ratio determined by mass, Gardner colors, and percent short saturated fatty acids are reported in Table 3. The split ratios of the high and low flow rates across the rotor are similar (Fig. 13A). However, as the rotor temperature was increased to 110°C and greater, the split ratios increased with the lower flow rate. The increased mass in the distillate fraction would be expected at the lower flow



Trial	Rotor temp <sup>a</sup> (°C)	Flow (g/min)	Split flow	C8 and C10 FAs (%) <sup>b</sup>		Gardner color	
				Distillate	Residue	Distillate	Residue
1	40	1.49	0.03	98.9	81.9	1-	1
2	40	0.49	0.03	98.9	81.5	1-	1
3	50	1.36	0.30	98.5	77.4	1-	2
4	50	0.54	0.12	98.8	80.3	1-	3
5	55	1.65	0.93	97.0	69.5	1-	1
6	55	0.49	0.37	98.3	76.9	1-	1
7	60	1.99	1.30	96.5	63.4	1-	1
8	60	0.52	0.85	96.2	69.2	1-	2
9	65	2.23	1.47	95.5	62.7	1-	1
10	70	1.36	1.44	95.1	62.3	1-	3-
11	70	0.46	0.98	96.1	67.9	1-	2
12	90	1.72	1.79	88.2	58.9	1-	1
13	90	0.50	1.97	89.8	66.6	1-	1
14	110	1.87	4.63	83.8	69.1	1-	6-
15	110	0.54	4.92	83.3	66.9	1-	7

<sup>a</sup>Heated rotor spinning at 28.75 Hz under a high vacuum ( $6 \times 10^{-4}$  –  $3 \times 10^{-3}$  mm Hg)

<sup>b</sup>Saturated fatty acids determined by GC (SP-2380, 30 m x 0.25 mm i.d.)

Table 3. Effects of molecular distillation parameters on fatty acids, split ratio, and color

rate because heat transfer to a smaller amount of material passing across the rotor would be more efficient (Isbell & Cermak, 2004). Data points are not reported past 110°C because the saturated fatty acids in this study had distilled before that temperature.

As the rotor temperature was increased the split ratios of distillate to residue increased and affected what was being distilled. At increased temperatures, more unsaturates and higher chain saturated fatty acids were distilled affecting the purity of the sample. The purity of the distillate as defined by the percent of octanoic (C8:0) and decanoic (C10:0) fatty acids is shown in Fig. 13B. Both the high and low flow rates gave similar results as the temp was increased. All temperatures 70°C and less provided materials that were greater than 95% enriched in C8:0 and C10:0 FAs. With a lower rotor temperature a greater quantity of short saturated fatty acids was present in the distillate fraction. As the rotor temperature was increased, both the low and high flow rate distillates contained lower percentages of the short saturated fatty acids, but the amounts of distillate increased over the amount of residue.

As the rotor temperature was increased, the distillate to residue split ratio increased, but the percent of short-chain fatty acids decreased in the distillate samples. The split ratios of the multiple-pass distillations increased with each consecutive distillation from 2.50 (Table 4, Trial 16) to 16.59 (Trial 19). The distillate percents of C8:0 and C10:0 and overall saturates all increased as expected as the distillate was further purified to obtain high percents of total

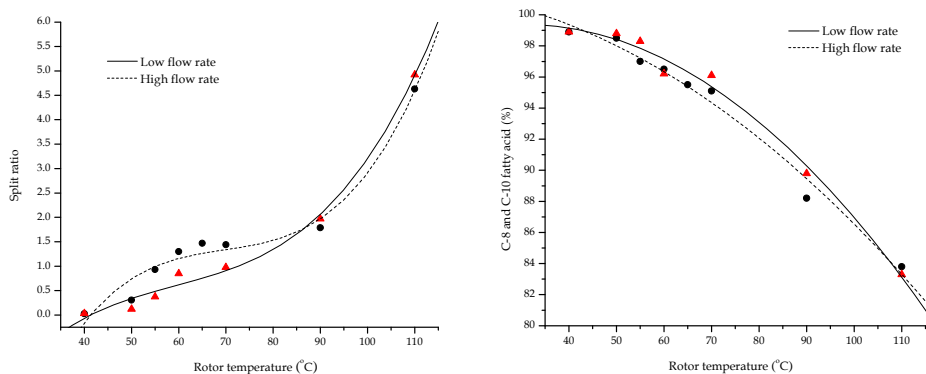


Fig. 13. A) Effect of rotor temperature on split ratio or B) Effect of rotor temperature on C8:0 and C10:0 fatty acids

Trial	Distillation (pass)	Split Flow Ratio	Fatty acid (%) <sup>a</sup>							
			8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2
16	First	2.50	0.8	89.8	3.1	3.0	1.6	0.0	1.0	0.6
17	Second	11.33	0.7	91.4	3.0	2.6	1.2	0.0	0.6	0.4
18	Third	15.50	0.7	92.4	2.9	2.4	0.9	0.0	0.4	0.3
19	Fourth	16.59	0.6	92.9	2.9	2.2	0.8	0.0	0.4	0.2
20	Fifth	11.79	0.6	93.8	2.7	2.0	0.6	0.0	0.2	0.0

<sup>a</sup>Determined by GC (SP-2380, 30 m x 0.25 mm i.d.) and standard deviation < + 0.10

Table 4. Fatty acid profile of distillate distillations at 70°C

saturates (99.8 %, Trial 19). The fatty acid profile for the multiple-pass distillation is shown in Table 4. After the first pass (Trial 16), stearic and linolenic fatty acids were removed and each additional pass started to remove the linoleic and oleic fatty acids. The final pass yielded a material that contained only 0.2% oleic as the only unsaturation in the fraction.

Single-pass distillation is the simplest and least expensive mode of distillation, but some applications require additional distillations to achieve difficult separations. Separating materials that are very close in molecular weight or have very similar boiling points can require multiple-pass distillations. One of the main reasons for performing single or multiple-pass distillations is to aid in the removal of color bodies. All the cuphea FA distillates had very excellent Gardner colors of 1-, which is the lowest color rating (Table 3). The residues varied in the amount of color bodies in the samples depending on whether the residue was a single or multiple-pass distillation. A multiple-pass distillation of a distillate is prime example to explore the removal of color bodies. The first distillation gave a distillate with a Gardner color of 1-, however, when that material was re-distilled, the residue led to a Gardner color of 6+ (Cermak et al., 2007). Each consecutive distillation had higher split flow

rates and showed that most of the material was being distilled. This increase was expected as only small amounts of saturates and/or color bodies were left to be removed with each distillation. This multiple-pass distillate would be very desirable for very color sensitive applications.

With the Myers 3 being primarily a laboratory molecular distillation unit, one of the main goals was to have a high throughput while collecting quality saturated material. This equipment would meet these high throughput conditions when the rotor temperature was set to 65°C with a high flow rate of 2.2 g/min while maintaining a distillate to residue split ratio of about 1.5 as demonstrated in Table 3 (Trial 9). The distillate produced would contain high percents of C8:0 and C10:0 as well as no unsaturates. The Gardner color values were excellent under these conditions as well. Thus, cuphea fatty acids were effectively separated with the Myers 3 lab-scale centrifugal molecular distillation unit.

### 3.3.2 Meadowfoam

Previous studies of meadowfoam oil and the corresponding fatty acids have resulted in several novel compounds, i.e., estolides (Isbell & Kleiman, 1994 and 1996) and lactones (Isbell & Cermak, 2001). Meadowfoam estolides have cosmetic applications as they improve conditioning, shine, and comb-out compared with existing conditioners (Isbell et al., 2000b). One of the biggest problems with meadowfoam estolides is their color. Ideally, cosmetic ingredients should be colorless (Gardner=0). Crude meadowfoam fatty acids are very dark (Gardner=15+), which leads to very dark estolides (Gardner=18+). If crude meadowfoam fatty acids could be purified to a low Gardner color at a low cost, this would lead to a lower colored estolide and eliminate post-distillation decolorization (Frykman & Isbell, 1999). Color improvements in meadowfoam estolide and fatty acids would help the commercialization of this new oil seed and give US farmers a valuable rotation crop.

Crude mixtures of meadowfoam fatty acids were separated using a Myers Pilot-15 molecular centrifugal distillation unit. A series of conditions were examined to identify the optimum operating conditions including: rotor temperature, degas temperature, rotor preheat, and flow to the rotor (Cermak & Isbell, 2002). The main heating source for the distillation unit is the rotor element, which is located beneath the rotor and can range anywhere from room temperature to 800°C (Fig. 12). Thus, the easiest place to make a significant impact on heat available for distillation is in the distillation chamber. A set of conditions where the rotor temperature was varied while other system conditions remained constant is shown in Table 5. The flow rate of the feed stock was set at 100 g/min. The rotor temperature was changed from 275 to 475°C as the data points were collected. As the temperature increased, the distillate to residue ratio also increased, which was expected. At a rotor temperature of 475 °C, most of the material was distilled and only a small fraction was collected as residue. With the increased temperature, color bodies also distilled. The Gardner color for the distillation products with varying rotor temperature are reported in Table 5. The 475°C distillation had a Gardner color of 4, whereas the ideal Gardner color is 1.

The increased rotor temperature, unfortunately, maximized the amount of distilled material at the sacrifice of color. The fatty acid profile of both the residue and distillate are reported in Table 5. The crude meadowfoam main components were 5-eicosenoic acid (59.9%), 5,13-docosadienoic acid (17.3%), 5-docosenoic acid (4.3%), and 13-docosenoic acid (11.9%). The distillation at a rotor temperature of 425°C resulted in the closest percent composition to the

Rotor Temp	C20:1 (%)		C22:1 (%)				C22:2 (%)		Gardner color
	$\Delta 5$ -d	$\Delta 5$ -r	$\Delta 5$ -d	$\Delta 5$ -r	$\Delta 13$ -d	$\Delta 13$ -r	$\Delta 5,13$ -d	$\Delta 5,13$ -r	
°C									Distillate
S.M.	59.9		4.3		17.3		11.9		15
275	72.0	56.9	2.0	4.9	5.8	13.4	10.1	18.9	3
325	69.2	54.1	2.6	5.6	7.3	15.3	11.9	20.2	1
375	69.6	40.1	2.8	7.4	7.9	20.2	12.9	26.1	1
400	63.2	38.2	3.4	8.9	9.4	23.7	14.6	27.1	1
425	59.7	35.0	4.3	7.1	12.0	19.4	17.4	23.8	1
475	59.2	35.2	4.4	6.6	18.0	18.0	17.5	21.9	4

Table 5. Fatty acid profile - varying rotor temperature

crude meadowfoam fatty acids. Different ratios of fatty acids were distilled depending on the rotor temperature. For the two rotor temperature extremes of 275 and 475°C, the amount of 5-eicosenoic acid was enriched in the distillate to 72.0% at 275°C from 59.2%, whereas the 5,13-docosadienoic acid was enriched in the distillate to 17.5% at the upper temperature of 475°C from 10.1%.

Meadowfoam fatty acids were effectively separated by a Myers Pilot-15 molecular distillation unit. The precise distillation conditions were determined by varying conditions to obtain material that was light in color, Gardner color of 1. Conditions were then chosen to minimize high energy demands on any one element of the system. The varying conditions described were used to determine the ideal distillation conditions (Cermak & Isbell, 2002). All of the conditions played a vital role in conducting a successful distillation. The rotor temperature and flow rate had the greatest impact on the Gardner color and the fatty acid composition of the distillate. After the ideal conditions were determined, an additional larger volume (95 L) of meadowfoam fatty acids was distilled to verify the conditions.

Additionally, meadowfoam estolides can be distilled on the Myers Lab 3 (Fig. 10) to separate the monoestolides (EN=1) and polyestolides (EN>1) (Fig. 9). Table 6 shows experimental conditions for two flow rates over seven different temperature settings and their effect on split ratio, which was determined by mass. The split ratio for both high and low flow rates across the rotor are similar. However, at the low flow rate (0.32 g/min) and high temperatures (300°C), the split ratio is nearly twice that of the high flow rate (1.79 g/min). The increased mass in the distillate fraction would be expected at the lower flow rate because heat transfer to a smaller amount of material passing across the rotor would be more efficient. However, these higher split ratios lowers monoestolide purity which decreases beyond 275°C (Fig. 14). The highest distillate purity occurs for both the low and high flow rates at 200°C (Fig. 14). At 325°C, splatter from the feed stock bumping as it comes into contact with the hot rotor became a significant problem and contaminated the distillate. Therefore, the sample at high flow rate at 325°C was not collected.

Myers Lab 3 distillation unit proved effective. Color from the distillate was effectively removed from the monoestolide fraction with a Gardner color of 1 for those fractions below 250°C (Table 6). This corresponds well with the optimum distillation temperature of 225°C.

Set point (°C)	Temperature (°C)		Isolated mass (g)		Rate (g/min)	Split ratio	Gardner color	
	Rotor	Distillate	Residue	Distillate			Residue	Distillate
Low flow rate								
175	174	29.3	0.9	19.2	1.01	0.05	12	1
200	201	29.4	2.4	15.9	0.92	0.15	12	1
225	226	29.8	2.7	12.9	0.78	0.21	12	1
250	249	29.9	3.6	9.5	0.66	0.38	12	1
275	274	29.8	5.2	9.5	0.74	0.55	12	4
300	299	30.1	3.0	3.3	0.32	0.91	12	5
325	322	30.2	8.1	6.2	0.72	1.31	12	6
High flow rate								
175	174	29.7	4.0	39.9	2.20	0.10	12	3
200	198	29.5	7.6	34.2	2.09	0.22	13	1
225	225	30.2	7.5	31.0	1.93	0.24	14	3
250	248	30.5	8.7	18.7	1.37	0.47	14	4
275	274	29.7	8.2	20.2	1.42	0.41	14	4
300	299	30.4	13.8	21.9	1.79	0.63	14	6

Table 6. Effect of Myer Lab 3 distillation parameters on split and color

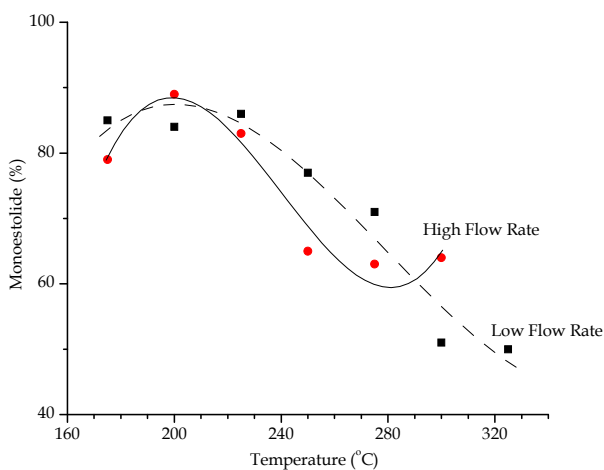


Fig. 14. Effect of rotor temperature on monoestolide composition in distillate fraction

Higher temperatures show degradation in color values as a result of co-distillation and splatter from the color bodies found in the polystolide fraction. This color improvement from the starting material (Gardner color of 12) should greatly enhance the value of this material for cosmetic applications where product color is an important factor.

## 4. Fatty acid alkyl ester derivatives

Industrially, mono-alkyl fatty acid esters can be prepared by reacting fat and oil triglycerides with an alcohol using alkaline-catalyzed interesterification (alcoholysis) or from the direct esterification of fatty acids (Farris, 1979; Sonntag, 1982). Although a variety of alcohols can be utilized, fatty acid methyl esters (FAME) prepared using methanol are most common based on price and availability. These fatty acid esters not only serve as specialty chemicals but are also used extensively in various oleochemical processes as intermediates to produce fatty alcohols, alkanolamides, and  $\alpha$ -sulfonated methyl esters (Gervajio, 2005; Gunstone et al., 2007a). Additionally, fatty acid esters, particularly fatty acid methyl esters, are used extensively for the burgeoning biodiesel industry (mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats).

### 4.1 Distillation

With regards to distillation, mono-alkyl fatty acid esters have several significant advantages when compared to the distillation of fatty acids (Budde, 1968; Farris, 1979). Because the acid moiety is in the ester form, the fatty acid esters are less corrosive. Therefore, expensive corrosion resistant equipment may not be necessary. Since the ester group cannot participate in hydrogen bonding the esters have lower boiling points, are oftentimes easier to fractionate, and require less energy for their fractionation, Table 2. As can be seen from Table 2, the esters tend to boil approximately 30°C below their corresponding fatty acids. As a result of the two aforementioned properties, the esters are also less susceptible to color formation, decarboxylation and degradation during the distillation. Finally, the fatty acid methyl esters are more amenable to fractional distillation and separation since they follow Raoult's law more closely than their corresponding fatty acids, which show significant deviation from Raoult's law making it difficult to fractionally distill and separate fatty acids differing by two carbon atoms in chain length (Budde, 1968; Markley, 1964).

Careful control of the distillation parameters allows the advantages inherent to the fatty acid esters to be exploited and used advantageously especially when attempting to fractionate thermolabile materials such as highly unsaturated esters derived from marine oils. Fractional distillation has been performed for some time on a variety of saturated and highly unsaturated fatty acid ester mixtures at reduced pressures on the laboratory scale as a method to purify fatty acid esters. Early reports examined the separation of various fatty acid methyl esters of corn (Baughman & Jamieson, 1921), sunflower (Baughman & Jamieson, 1922b), soybean (Baughman & Jamieson, 1922a), and menhaden oils (Brown & Beal, 1923) by fractional distillation into their various components. Later spinning band columns improved distillation fractionation; for example, Weitkamp (1945) reported the isolation of 32 compounds into four main compound classes (fatty acids, 2-hydroxy acids, and two types of branched iso and anteiso acids) from wool wax by distilling fatty acid methyl esters. Privett and coworkers (1959) distilled several fractions of methyl esters derived from pork liver lipids. Fractional distillation of unsaturated C20 esters from rapeseed (Haeffner, 1970) and herring oil methyl esters (Ackman et al., 1973) have also been reported. Methyl docosahexaenoate (C22:6) was fractionated from a fatty acid methyl ester mixture derived from tuna oil using spinning band distillation at a pressure of 0.025-0.030 mm Hg (Privett et al., 1969). Unique to this method, an amplified distillation process was used, wherein a mixture of carrier components based on long chain acetates (3 g myristyl, 7 g palmitoleyl, 7

g oleyl, 5 g of 11-eicosenoyl, and 3 g erucyl acetates) was employed to facilitate the fractionation of minor components and minimize artifacts arising from C22:6 methyl ester degradation by keeping the distillation temperature from rising sharply during fractionation. The carrier acetates were present in two-to three-fold excess over the fatty acid methyl esters and were chosen to have a range of boiling points covering that of the sample, not form azeotropes and could be separated easily with any sample components. Distillation gave fractions containing mixtures of the enriched methyl esters and acetates. These separate fractions containing the desired methyl esters and carrier acetates were then saponified to give long chain alcohols (from carriers) which were extracted from the soaps as nonsaponifiable matter. The sodium acetate was converted to acetic acid by acidification and separated from the desired fatty acids by extraction with distilled water. By this method a cut of tuna oil containing 84% C22:6 was obtained.

The development of molecular distillation techniques characterized by short exposure of the sample to high temperatures, short path length for the distillate, and high vacuum led to better column efficiencies. Many reports on the molecular distillation of fatty acid esters from sunflower and soybean esters (Pramparo et al., 2005), rapeseed fatty acid esters and tocopherols (Jiang et al., 2006), eicosapentaenoic (EPA) and docosahexaenoic acid ethyl esters (Brevik et al., 1997), and squid visceral oil ethyl esters (Liang & Hwang, 2000; Rossi et al., 2011) have been reported. Vázquez and Akoh (2010) reported a detailed study on the fractionation of short and medium chain fatty acid ethyl esters via short-path distillation that were obtained from a blend of coconut oil and dairy fat. They examined feed rates, temperatures, and single or multiple steps. They were able to obtain fractions containing a high purity of specific fatty acid ethyl esters with a desired composition and yield.

On an industrial scale, a recent set of patents describe a continuous process (~2,000 kg/h) whereby fractional distillation of palm kernel fatty acid methyl esters is done to produce technical grade oleic acid methyl esters (~75 wt%) containing low levels of saturated methyl palmitate (< 5 wt%) and methyl stearate (<2 wt%) (Heck et al., 2000; Heck et al., 2005). This method avoids additional crystallization steps currently used by other processes. The resulting enriched methyl oleate fraction could then be reduced to obtain the corresponding unsaturated fatty alcohols. In this process, the starting palm kernel methyl esters are first fractionally distilled to separate the C8-C14 esters from the C16-C18 esters. The bottom C16-C18 ester fraction is subsequently fractionally distilled to separate the C18 esters (saturated and unsaturated) from the C16 esters. Finally, the C18 esters are fractionally distilled to obtain an enriched C18 unsaturated fraction (methyl oleate) while reducing the saturated C18 ester (methyl stearate) to less than 2 wt%.

A 1999 patent describes the large scale fractional distillation of rapeseed methyl esters, among other fats and oil esters, to obtain a colorless fraction enriched in C22 (behenic) methyl esters with low acid value and purity of at least 86 wt% (Kenneally et al., 1999). The starting rapeseed methyl esters composition was C16-3.5%, C18-38.0%, C20-9.7%, C22-47.4%, C24-1.4%. Batch fractional distillation at 232-274°C of the rapeseed methyl esters using a packed column with 10 theoretical stages, overhead condenser, receiver, and vacuum pump operating between 5-25 mm Hg gave a 32% yield of the C22 methyl ester cut containing 92.6% C22 and 1.8% C18.

The explosive growth of the biodiesel industry has focused attention on mono-alkyl esters of long-chain fatty acids. Typically, biodiesel is comprised of fatty acid methyl esters, although

ethyl, propyl, butyl esters, etc. might be used for either B100 or blending applications. Because various esters may be used and these higher esters likely have boiling points higher than the methyl esters, focus on the distillation characteristics of these fatty acid esters with regards to biodiesel specifications are important. Accordingly, Schober and coworkers (2010) have examined the distillation characteristics for a series of fatty acid ethyl esters derived from various feedstock following ASTM D1160 specifications. They found the ethyl esters exceeded the maximum limit set for in the ASTM specifications which has important implications for higher esters to be used as biodiesel.

## 4.2 Reactive distillation

Reactive distillation has been known since the 1920's but has gotten renewed interest in recent years. The complexities of reactive distillation have been thoroughly reviewed (Malone & Doherty, 2000; Sharma & Singh, 2010; Taylor & Krishna, 2000). Reactive distillation is the simultaneous implementation of reaction and distillation within a single column unit, whereby the reactants are converted to products in a reaction zone in the presence of catalyst with simultaneous distillation of the products and recycling of unused reactants to the reaction zone (Doherty & Buzad, 1992; Kiss et al. 2008, Malone & Doherty, 2000; Omota et al., 2001; Omota et al., 2003ab; Sharma & Singh, 2010; Taylor & Krishna, 2000). A diagram comparing a conventional reaction and distillation process to a reactive distillation process is shown in Fig. 15.

Briefly, as seen in Fig 15a., the reaction in the presence of catalyst takes place in a separate reactor. The crude products are transferred to a sequence of distillation columns are required to produce pure C and D by the conventional process. The unreacted components, A and B, are recycled back to the reactor. In contrast, Fig 15b shows that by combining the reaction and distillation operations, A and B continuously react in the reaction zone while products C and D are removed from A and B in the rectifying and stripping sections at the top and bottom, respectively (Taylor, & Krishna, 2000). This technique can reach 100% conversion and potentially minimize operational and equipment costs and decrease waste energy. Reactive distillation is especially suited for the chemical reactions limited by thermodynamic and equilibrium constraints, since one or more of the products of the reaction are continuously separated from the reactants (Kiss, 2011; Nguyen & Demirel, 2011).

With regards to fatty acid ester production and purification, and more specifically to large scale production of biodiesel, it would appear that reactive distillation could provide an efficient and integrated approach to obtain the desired fatty acid esters. However, to date most studies have focused on computer aided modeling, simulation and economics of reactive distillation to produce fatty acid alkyl esters (Bhatia et al., 2007; Kiss, 2011; Kiss et al., 2006; Nguyen & Demirel, 2011; Omota et al., 2001; Omota et al., 2003ab) while more recent experimentally based studies are not as prevalent (Bhatia et al., 2006; He et al., 2006; Silva et al., 2010; Steinigeweg & Gmehling, 2003).

Steinigeweg and Gmehling (2003) reported the development of a reactive distillation process for the pilot plant production of decanoic acid methyl esters. The reaction was catalyzed heterogeneously using a strong acidic ion-exchange resin and supported by structured corrugated wire mesh sheets (Katapak-S) in the columns and reaction parameters such as



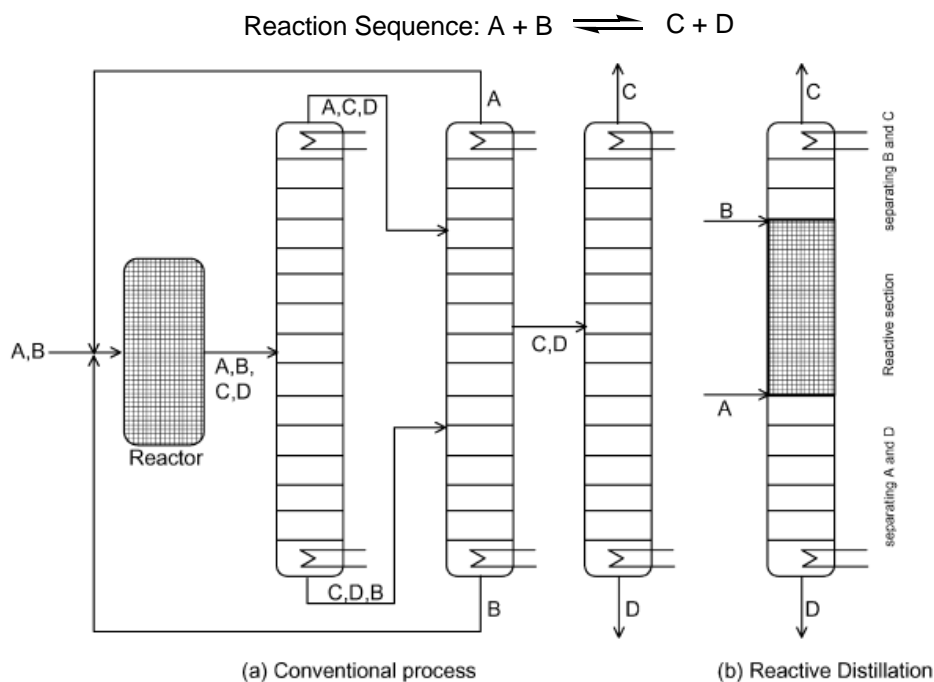


Fig. 15. Scheme comparing the reaction sequence where A and B are reactants and C and D are the desired products. (a) conventional reactor and distillation process; (b) reactive distillation column. Adapted from Taylor & Krishna (2000)

reflux ratio and reactant ratios were examined (Steinigeweg & Gmehling, 2003). They found that a low reflux ratio of 0.01, a (1:2) decanoic acid:methanol in feed stream, distillate to feed ratio of (1:2), 393K and 3 bar resulted in good fatty acid conversion to the corresponding methyl decanoate. Recently, computer simulation for the esterification of decanoic acid with methanol using reactive distillation has been carried out by Machado and coworkers (2011) using the experimental data obtained Steinigeweg and Gmehling (2003) to validate their models. Furthermore, Machado and coworkers modeled experimental results obtained for the esterification of oleic acid with methanol (Silva et al., 2010; Kiss et al., 2006) and lauric acid with ethanol (De Pietre et al., 2010). They found good agreement between their modeling and the experimentally determined esters found in the literature and predict conversions above 98%.

Bhatia and coworkers performed a thorough study on the esterification of palmitic acid with isopropanol in a reactive distillation column using zinc acetate supported on functionalized silica gel as a catalyst in Katapak-SP structured packing (Bhatia et al., 2006). The column performance was evaluated by varying the operating parameters such as feed flow rate, reboiler temperature, palmitic acid feed composition, palmitic acid feed temperature, molar ratio of isopropanol feed to palmitic acid feed and reflux ratio. From their work they proposed a technically optimized reactive distillation process for the production of isopropyl palmitate.

Using a laboratory scale continuous flow reactive distillation apparatus, He, Singh, & Thompson, (2006) examined a combined process which used a conventional pre-reactor coupled to a reactive distillation column to convert canola oil into its corresponding fatty acid methyl esters, Fig. 16.

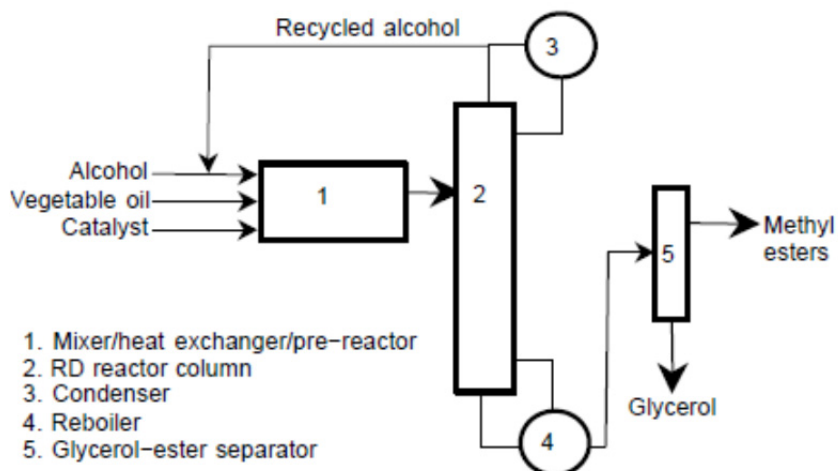


Fig. 16. Schematic of reactive distillation reactor system used to convert canola oil into its corresponding fatty acid methyl esters (He et al., 2006)

Reaction parameters such as methanol:canola oil, feed rate of canola oil and potassium hydroxide catalyst, and temperature were examined for runs with and without the pre-reactor. A 95% conversion with a 94% yield (esters contained 1.1%, 2.0%, and 2.0% mono-, di-, and triglyceride, respectively) was obtained using a column temperature of 65°C and a 4:1 methanol:canola oil molar ratio with the pre-reactor. They were able to reduce reaction times 10 to 15 times while also reducing methanol consumption by 66% over conventional biodiesel processes.

Recently, Brazilian researchers used a pre-reactor (with sodium hydroxide catalyst) coupled to a reactive distillation column in a semi-batch system to examine the preparation of fatty acid methyl esters from soybean oil and bioethanol (Silva et al., 2010). They used experimental design to optimize the catalyst concentration (from 0.5 wt% to 1.5 wt %) and the ethanol/soybean oil molar ratio (from 3:1 to 9:1). The reactive column reflux rate was 83 ml/min, and the reaction time was 6 min. Their best conversion to esters was 98.18 wt% with 0.65 wt% of sodium hydroxide, ethanol/soybean oil molar ratio of 8:1, and reaction time of 6 min. The reaction time of 6 min means: 1 min in the pre-reactor and 5 min in the reactive distillation column.

A recently patent published application demonstrated a process to produce mixed fatty acid esters with a variety of heterogeneous catalysts. Again, a pre-reactor coupled to a reactive distillation column was used (Asthana et al., 2009). Crude fatty acid methyl esters are first prepared in the pre-reactor much like a conventional biodiesel process. After a crude separation of glycerol and other components the fatty acid methyl esters are transferred to the reactive distillation column where they undergo further reaction with different alcohols

from 2-8 carbon atoms to give a fatty acid alkyl ester mixture upon exiting the reactive distillation column.

Although the results described above are promising and represent good first steps toward implementation of reactive distillation for fatty acid ester production, as concluded by Taylor and Krishna in their 2000 review on reactive distillation, and with particular focus towards production and separation of fatty acid esters, they state:

...There is a crying need for research in this area. It is perhaps worth noting here that modern tools of computational fluid dynamics could be invaluable in developing better insights into hydrodynamics and mass transfer in RD columns. Besides more research on hydrodynamics and mass transfer, there is need for more experimental work with the express purpose of model validation...

There remains more work to be done in the use of reactive distillation to produce and purify fatty acid alkyl esters.

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