Efficient Removal of Environmental Contaminants: Comparing Multi-Stage Thin-Film Evaporation with Gas Stripping and Short-Path Distillation

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Edible oils are processed to remove impurities and contaminants that meet regulatory standards, acceptable palatability and shelf life. Crude edible oils normally have some non-triglyceride components and other impurities that are removed during refining. These components include free fatty acids, phospholipids, color components, peroxides, carboxylic compounds, metals, and harmful environmental contaminants such as PCBs, dioxins, furans and pesticides.

- Marine oils are closely monitored for quality and harmful environmental contaminants, and regulatory agencies have established maximum permitted levels for such contaminants in food and animal feed ingredients.
- Some of the more volatile contaminants can be removed by steam deodorization in conventional edible oil processing. However, higher-efficiency technologies are needed to remove less volatile components.

Most edible oils undergo four basic processing steps (O'Brien et al., 2000):

1. Refining/neutralization
2. Bleaching
3. Winterization
4. Deodorization

The last step, deodorization, is a stripping process that uses steam to remove undesirable odors or flavors along with other impurities, such as peroxides, carboxylic compounds, and free fatty acids (FFAs). Deodorization also partially removes environmental contaminants and destroys color compounds, which has a bleaching effect on the oil. Depending on the type of oil being processed, most deodorizers operate at temperatures above 200°C, and pressures between 2 and 5 Torr.

FFAs are typically reduced to 0.2 to 0.5% by weight, but this also varies based on the type of oil. Desirable compounds, such as tocopherols and other antioxidants, are also removed. Deodorization can reduce the content of tocopherols in the final RBD (refined, bleached, and deodorized) oil by as much as 60% (Norris, 1985). Typically, a small amount of tocopherols is added to the final product to prevent oxidation after deodorization.

Regulatory agencies have established maximum permitted levels (MPLs) for such contaminants in food and animal feed ingredients (SCAN, 2000; SCF, 2000). The FDA and the European Commission (EC) have implemented food and feed legislation concerning polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (DL-PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs). Fish, and consequently fish oil, has been identified as one of the most important contributors to the level of PCDD/Fs and DL-PCBs in feed and food products (Table 1).

Table 1. Quality Parameters for Fish Oil (GOED, 2017)

Acid value	**3 mg KOH/g Max**
Peroxide value	**5 meq/kg max**
Anisidine value	**20 max**
TOTOX	**26 max**
PCDDs and PCDFs	**2 ppt max**
Dioxin like PCBs	**3 ppt max**
TOTAL PCDDs/PCDFs/DL PCBs	**4 ppt max**
Total PCBs	**90 ppb max**

Marine oils are closely monitored for quality and harmful environmental contaminants, such as dioxins, furans, and polychlorinated biphenyls (PCBs). Dioxins have been shown to be extremely harmful to humans and animals, and have been implicated in disrupting endocrine (hormone) systems in humans and wildlife. PCBs are a group of closely related chemicals, and some dioxin-like PCBs exhibit toxicities similar to those of toxic dioxins.

Some of the more volatile PCBs and PAHs can be removed by steam deodorization in conventional edible oil processing. However, for the less volatile components, the higher efficiency of processes, like short-path distillation (SPD) and thin-film evaporation, are necessary to remove these compounds, to levels required by regulatory agencies, and are both processes are generally ran after bleaching and winterization. (Breivik and Thorstad, 2005).

The uses of thin-film evaporation and short path distillation technologies will be compared to Artisan's evaporation/stripping technology (combining thin- film evaporation and gas stripping) and how Artisan's process solution is a more efficient and economical alternative to short path distillation.

Short Path Distillation

The terms “short-path” and “molecular distillation” are often used interchangeably. However, molecular distillation normally refers to the use of a distillation apparatus, where the gap between the evaporator and condenser is equal to or less than one mean free path of the molecules evaporated. thus facilitating collision-free diffusion transport. This is not usually the case in commercial SPD equipment where the evaporation/condensation gap is larger than that required to meet these molecular mass transfer conditions.

Equation 1.

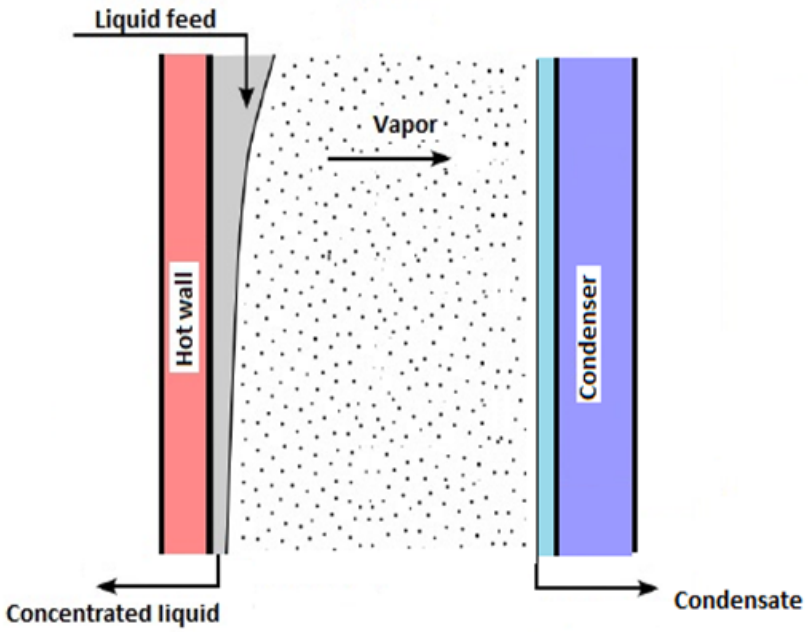
The mean free path, j_i, can generally be estimated using Equation 1, where pi^0 is the vapor pressure, M_i is the molar mass, R is the gas constant, and T is the temperature (Arzate-Martínez et al., 2011).

$$j_i = p_i^0 \sqrt{\frac{1}{2\pi M_i RT}} \quad (1)$$

Short-path distillation units generally consist of jacketed vessels. Within these vessels, an agitator, commonly referred to as the rotor, spreads the product on the wall of a heated surface. As various components evaporate from this heated surface, they are condensed a short distance away, as shown in Figure 1. The process is normally operated under deep vacuum (micron range) conditions and is commonly used for high-boiling, viscous, and heat-sensitive materials. The forced circulation of the evaporating fluid at higher velocities (6–30 ft./s), results in higher heat-transfer coefficients and allows for smaller heat-transfer areas. The forced circulation is particularly useful in high-evaporation applications.

Short path distillation (SPD) units generally consist of large-diameter jacketed tubes, in which the product is spread on the wall of the heated surface by an agitator, commonly referred to as the rotor, and the evaporated components are condensed a short distance from the heated surface as shown in Figure 4. This process is normally operated under high vacuum conditions. These evaporation and distillation units are commonly used for extremely viscous and heat-sensitive materials. The forced circulation of the evaporating fluid at higher velocities (6-30 ft/s) results in higher heat-transfer coefficients and allows for smaller heat transfer areas.

Figure 1. Short-Path Distillation/ Evaporation



Short-path distillation is generally characterized by the combination of a very short residence time in the evaporator (1–10 seconds), high vacuum levels (0.001–0.02 Torr), and a short distance between the evaporator and condenser (10–50 mm). In SPD, efficient mass transfer rates are achieved due to the feed forming a thin film on the inner wall of the distillation unit. The vaporized components are condensed immediately on a cold surface in the interior of the unit. In other words, the vapor stream travels a "short path" directly to the condenser, which is located within the evaporator chamber. Rapid condensing of the vapor stream that is generated precludes the vapor pressure of this stream from adding to the system's operating pressure. SPD typically operates at relatively low distillation rates of 100–200 kg/hr. per square meter of evaporator surface area.

There are two types of short-path distillation plants in commercial use. The more common configuration includes thin films generated using devices such as rollers, wipers, fixed clearance blades, or pitched blades rotating inside the column to spread out the film. A second method for the formation of a thin film is to use a rotating disk that spreads a film through the use of centrifugal force on a heated disc. Film thickness and residence time are controlled by the rotation speed of the evaporator disc and the feed rate. The condenser of an SPD system is normally located at the center of the apparatus to minimize pressure drop by internally condensing the volatile components that evaporate, as described above, allowing operation in the micron range of vacuum.

Some commercial lipid applications of short path distillation include purification of monoacylglycerols (Szelag and Zwierzykowski, 1983), recovery of carotenoids from palm oil (Batistella & Wolf-Maciel, 1998), recovery of tocopherols (Bruegel et al., 1996), and the reduction of cholesterol in butter and lard (Lanzani, et al., 1994).

Thin-Film Evaporation with Gas Stripping

Two different designs of the thin-film evaporation with gas stripping system are used to overcome the problems associated with film distribution in falling-film evaporators. In the standard design, the feed introduced at the top of the unit cascades down as a thin film through a series of tube-and-disc trays where the volatile components are stripped off by the rising vapor under vacuum. Evaporation takes place through several stages where each tube-and-disc tray creates a fresh liquid film at each stage, providing a new surface for evaporation and stripping, as shown in Figure 2. The basic design has semi-cone solid distribution discs for moderate vacuum (10 and higher Torr) applications. For high vacuum applications (0.5 to 5 Torr), the discs are replaced with chimneys to achieve extremely low pressure drops. A cross section of each design is shown in Figures 3a and 3b.

Figure 1. Thin-Film Evaporation with Gas Stripping: **The Artisan Evaporator/Stripper® System**

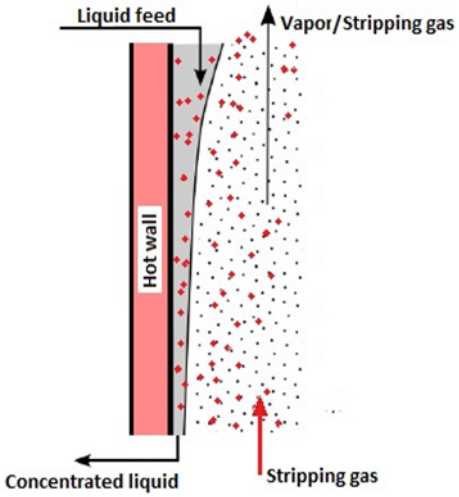


FIG. 3. a) Standard Stripper Tray Design; b) Ultra-Low Pressure Drop Stripper Tray Design

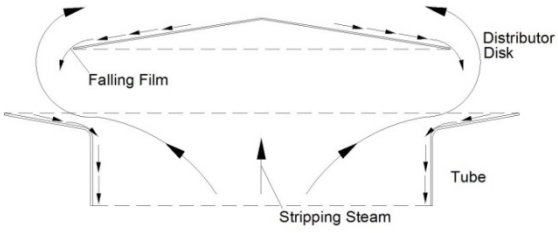


FIG 3.a

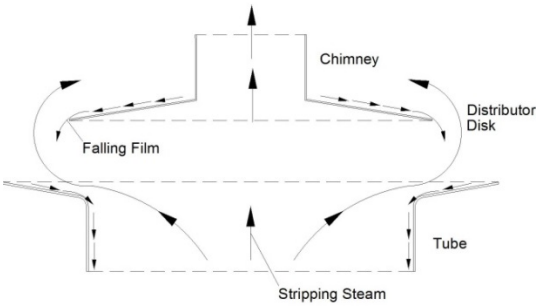


FIG. 3.b

Residence time is generally measured in 1 to 3 seconds per stage, and pressure drop in the chimney tray design is generally less than 0.02–0.05 Torr per stage, which allows for the distillation process to take place at very high vacuum and reduced operating temperatures at the bottom of the stripping column, where the most difficult part of stripping takes place. Nitrogen and more typically dry, superheated steam is used as the sparging medium flowing through each stage in the column to further enhance mass transfer. For applications which require higher percentage of volatiles to be removed, each tube can be individually jacketed to provide additional heat transfer.

However, in most applications, such as solvent recovery, deodorization of fats and oils, or in the removal of environmental contaminants, the trays are not heated due to the relatively small amount of volatiles being removed by the stripping gas.

The thin-film evaporation system can achieve extremely low residual levels of contaminants by taking advantage of the role of the carrier effect of lights in multicomponent separations. The "carrier effect," which is well-known in the petroleum industry, is when the addition of light hydrocarbons enhances the separation of heavy cuts, such as gas oil from residue. Stichlmair and Fair (1998) presented data obtained numerically, showing that the liquid yield in a flash is lowered when light components are added to the mixture, which is equivalent to feeding stripping gas, such as steam, to the system. The vapor-liquid phase behavior is assumed to follow Raoult's law. For simplicity, we define **K =Y/X,** which is commonly referred to as the "Separation Factor", where Y is the vapor mole fraction and X is the liquid mole fraction of the light component to be removed. In general, if one assumes ideal vapor liquid equilibrium **(ϒ=1),** this term can be defined by the ratio of the partial pressure of the light component to the system pressure (K=VP/π), where VP is the vapor pressure of the light component and **π** is the system pressure. Now if we add stripping steam into the simplified equation, $\mathrm{K} = \frac{\mathrm{VP}}{\boldsymbol{\pi}-\mathbf{P}}$, where **P** is the partial pressure of steam in the vapor phase. As can be seen from this equation, "injecting stripping steam is equivalent to reducing the system pressure."

Removal of Contaminants from Edible Oils

If heat sensitive oils, such as marine oils, are processed at conditions similar to those used for vegetable oils, losses of up to 30% of the valuable omega-3 fatty acids; eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) can occur during the long periods of heating in the deodorizer. The main advantages of both short-path distillation and thin-film evaporation for physical de-acidification of edible oils are lower operating temperatures and shorter processing times, enabling treatment of heat-sensitive oils without degradation.

Furthermore, the removal of less volatile components, such as PCDD/F, and PCBs from fish oils, is significantly more challenging than simply reducing the FFA concentration of the oil. As such, the higher efficiency of processes like short-path distillation and thin-film evaporation with steam stripping is more suited to remove these contaminants, while preserving the quality standards shown in Table 1.

Figure 4 depicts the experimental set-up used for the pilot plant stripping trials conducted on crude fish oil using the thin-film evaporation with gas stripping system described above. Both three and four equilibrium stage, partially heated, as well as unheated disc and tube trays were tested to determine the stage efficiency under various operating conditions.

Figure. 4. Drawing of the experimental setup used during the pilot trials for the removal of contaminants from fish oil using thin-film evaporation with gas stripping.

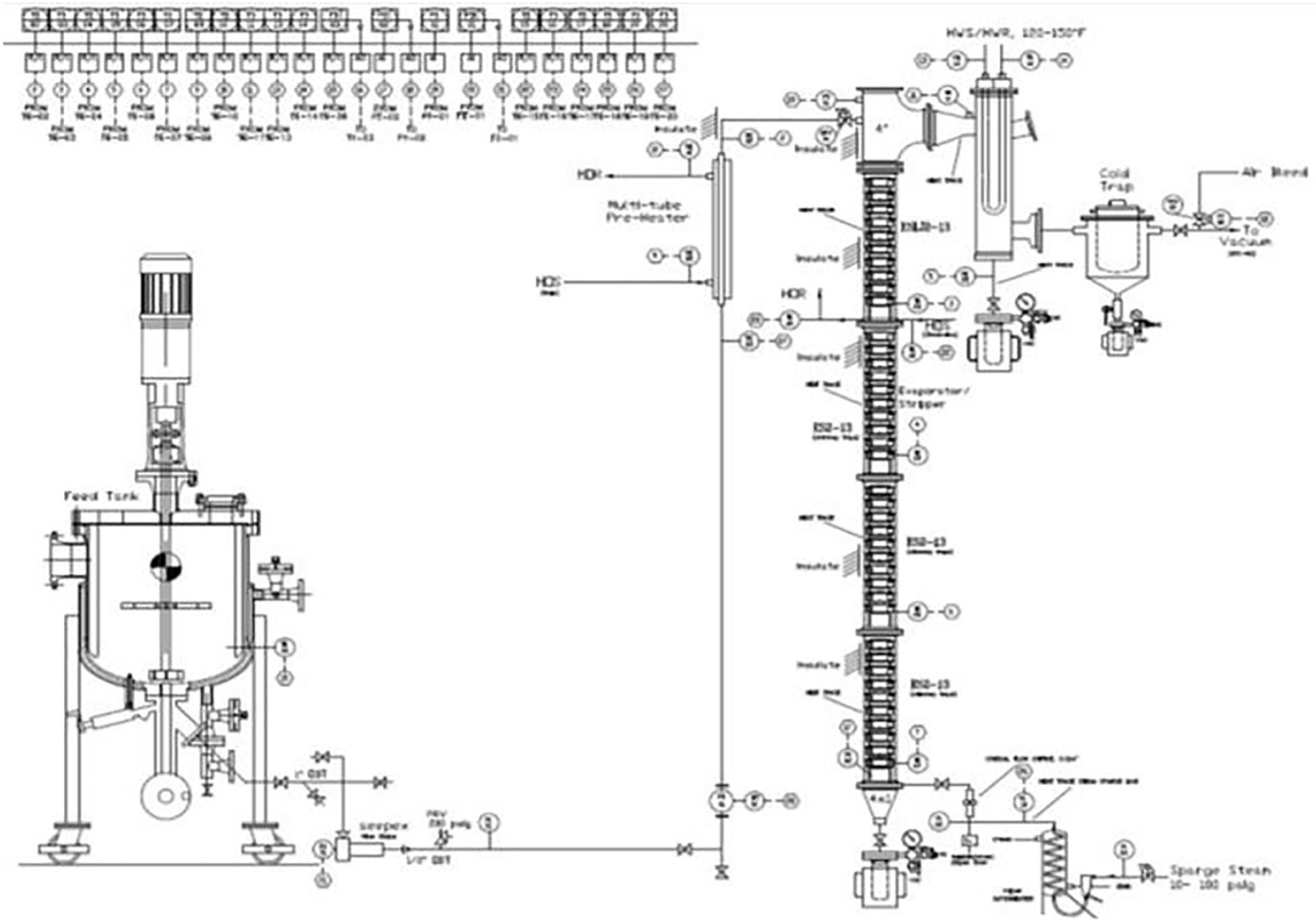


Figure 4. The trials took place over a period of roughly three months, and more than 50 combinations of critical operating parameters were tested to optimize the process. Feed rate, sparge steam rate, operating temperature, and pressure were the primary variables examined.

Analytical test results for samples of the stripped oil collected during the trials were subsequently used to validate process simulations created using ChemCAD® software. Simulations were performed using various different vapor-liquid equilibrium (VLE) models to determine the model that best fit the data. The results predicted by the simulations were typically within a margin of error of between 5 to 10%, depending on the particular model. Table 2 is a sample of three operating conditions and associated analytical results from the test campaign.

Table 1. Sample of Operating Conditions & Analytical Results from Artisan's Fish Oil Stripping Test Campaign

	Condition #	1	2	3
Operating Conditions	Feed rate [lb/hr]	25	25	20
	Operating temperature [F]	402	429	442
	Top pressure [torr]	1	2	3
	Bottom pressure [torr]	4.8	5	7.6
	Steam sparge: feed mass ratio [%]	5.00%	5.00%	9.85%
Analytical Results for Stripped Oil	FFA concentration [wt%]	0.23	0.2	0.25
	PCDD/F [pg/g or ppt]	1.4	0.79	0.27
	DL-PCBs [pg/g or ppt]	0.5	0.08	0.007
	Total PCBs UB [ng/g or ppt]	11.2	2.75	0.42

Table 2. Removal of Environmental Pollutants in Fish Oil. Test results from Artisan's test campaign indicated ZERO LOSS of DHA and EPA in the refined oil. Table 3 shows results comparing short-path distillation with thin-film evaporation with steam stripping for the removal of environmental contaminants from fish oil.

	Sum PCBs (pg/g or ppt) (Before stripping)	**Sum PCBs (pg/g or ppt) (After stripping)**	**Sum PCDD/F (pg/g or ppt) (Before stripping)**	**Sum PCDD/F (pg/g or ppt) (After stripping)**
Short-Path Distillation	427	7.78	33.09	2.65

Thin-film evaporation with steam stripping	370,000	420	8	0.27

Advantages & Disadvantages of Available Distillation/ Evaporation Technologies

For large volume operations, continuous deodorizers are typically preferred over batch units due to higher efficiencies and lower energy consumptions. The standard deodorizers commonly available, from a number of manufacturers, such as Desmet Ballestra and Alfa Laval, are either tray columns or come with structured packing to promote stripping. However, both types, particularly the tray deodorizers, carry a high retention time and pressure drop; thus the oil is exposed to high temperatures for up to 30 minutes or longer depending on the type of oil and the desired product specifications.

Furthermore, to achieve extremely low FFA content in the refined oil, since higher temperatures are not desirable, the process would need to operate at very low pressures. However, as the operating pressure is reduced, vapor volumes expand, causing higher pressure drop across the column for a given stripping steam rate. Thus the pressure at the bottom of the column would be too high to achieve high FFA removal at lower operating temperatures.

Although, FFA removal or conventional deodorization can be effectively carried out in tray or packed columns, the same does not hold true when the objective is the removal of the closer boiling contaminants, such as PCB's, dioxins, and the like. These compounds have a lower vapor pressure than FFAs, and are more difficult to strip to extremely low residual levels.

There are two other alternatives to conventional deodorizers: One is short-path distillation, and the other is the Artisan Evaporator/Stripper, which is a multi-staged, ultra-low pressure drop thin-film deodorizer.

Short-path evaporators are commonly used for distillation of high-boiling, heat-sensitive materials, such as tocopherols and other antioxidants. This technology is manufactured by a number of companies, such as VTA, Buss-SMS-Canzler GmBH, GIG Karasek GmBH, Pfaudler, and others. The technology has also been used occasionally in stripping operations, where the objective is to remove only a very small amount of undesirable odorous compounds, color bodies, or other contaminants**.**

Although, equilibrium prevailing stripping separations can effectively be carried out in short-path evaporators, in nearly all applications where ppm or ppb level purity is desired, multiple passes or evaporation units in series are employed at a significant capital and installation cost to reach extremely low levels of impurities. In addition, there is a potential for significant yield loss due to the very low operating pressures which causes the oil itself to evaporate.

Thin-film evaporation with gas stripping is a more suitable and economical solution to short-path evaporation in difficult stripping applications, such as contaminant removal and physical refining of edible oils.

This multi-stage, disc and tube falling film tray design provides ample surface area and has no moving parts. The system can be designed with over 4 to 5 theoretical stages to achieve extremely low

residual levels of undesirable contaminants as compared to a short-path evaporator, which is only a single-stage unit operation. The increased separation efficiency due to multiple stages and the use of stripping gas allows the evaporator/stripper to achieve similar product purity at higher operating pressures, resulting in little or no yield losses. Table 4 illustrates the advantages and disadvantages of thin film-stripping versus short path evaporation systems.

Table 4. Advantages & Disadvantages of Thin-Film Vs. Short- Path Evaporation Systems

Type	Advantages	Disadvantages
Short-Path Systems	• Suitable for highly viscous materials • No hot, dry spots • Operates at a micron range vacuum • Low-temperature operation • High heat transfer rates • Suitable for fouling service	• Poor separation efficiency • Product yield loss • High capital investment • Expensive to maintain • Costly vacuum system • Throughput limited • Single-stage operation
Thin-Film Evaporation with Steam Stripping	• High throughput capability • Multi-staged operation • No moving parts • Moderate capita investment • Little to no maintenance • Low pressure drop • Operates as low as 0.5 mmHg vacuum • Virtually no product yield loss	• Viscosity limited to 10,000 cP • Limited evaporation capacity • Low heat transfer rates • Not suitable for fouling service

Typical cost ranges for the conventional fish oil processing steps, including refining, bleaching, winterizing, molecular distillation, and deodorizing, are outlined in Table 5.

Table 5. Processing costs for fish oil based on conventional processing techniques [$/lb.]

Refining	Bleaching	Winterizing	Molecular Distillation	Deodorization
0.10-0.20	*0.10-0.30*	*0.08-0.10*	*0.11-0.20*	*0.18-0.20*

As discussed, Artisan's multi-stage thin-film stripping process can be used in place of the physical refining, short-path, or molecular distillation and deodorization processing steps listed above. Furthermore, the Artisan process is comparable to standard deodorization, just one of the three processing steps it replaces, in terms of cost**.**

Consequently, the use of this thin film stripping process for fish oil purification results in a cost reduction of 0.21 to 0.41 $/lb. as shown in Table 6.

Table 6. Processing costs for fish oil based on Artisan's newly developed processing technique [$/lb.]

Bleaching	Winterizing	Thin Film Stripping
0.10-0.30	*0.08-0.10*	*0.18-0.20*

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