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I. BACKGROUND

Omega-3 polyunsaturated fatty acids (PUFA) are becoming more commonly useddietary supplements, as studies have shown positive human health impacts resulting from regular consumption of Omega-3 PUFA [1].Studies by Robertson et al.[2] and Kromhoutet al.[3] have shown that people who have a high intake of Omega-3 fatty acids often show decreased risks of cardiovascular and inflammatory diseases. With the increased usage of Omega-3 PUFA, production requirements of high-purity products with eicosapentaenoic acid (EPA)/ docosahexaenoic acid (DHA) contents exceeding 55% have also increased. In the process of extracting Omega-3 PUFA, fish oil ethyl ester (EE) is used as the feedstock, which contains complex mixtures of fatty acids with varying degrees of unsaturation. A number of processes designed to concentrate and separate Omega-3 PUFA from fish oils are being exploredin an effort to improve extraction efficiency and it is important to determine which of these processes would be economically viable for large-scale production.

Previously reportedseparation methods for extracting Omega-3 PUFA from fish oils include adsorption chromatography, molecular distillation, enzymatic splitting, low-temperature crystallization, supercritical fluid extraction and urea complexation.This work analyzes the feasibility of an industrial Omega-3 recovery process using silver-based solvent extraction as the separation method. One advantage of using solvent extraction is the ability to obtain a high purity product while being able to recover and reuse the solvent to minimize material costs, compared to more expensive techniques such as supercritical fluid extraction. Another advantage is the ability to perform the separation at moderate temperatures and pressures, compared to other methods which require significant changes in temperature/pressure to isolate the Omega-3 PUFA. Urea precipitation has been a commonly employed method of extracting Omega-3 PUFA from fish oils.However, the extraction efficiency of urea precipitation is lower than that of solvent extraction, and may lead to the formation of toxic byproducts.

While previous work in this field has focused on extraction of Omega-3 PUFA from synthetic mixtures of EPA and DHA [4-6], it is desirable to determine the feasibility of extracting Omega-3 directly from winterized 18/12 EE fish oils. This work concentrates on the conceptual design and economic feasibility analysis of an industrial extraction process using a silver-based solvent to selectively separate the Omega-3 PUFA from natural fish oils. Solvent extraction using a silver-based solvent is a commonly used technique for purification of fatty acid ethyl esters, which utilizes the complexation between the double bonds of EPA/DHA and silver ions [5,6]. Belarbi*et al.*[4] achieved success with this separation technique in a laboratory setting using idealized mixtures of EPA and DHA, and a desire to expand on this work led to the completion of laboratory experiments to study the effectiveness of silver-based solvent extraction using 18/12 EE fish oils [7].The results from these laboratory experiments using a mini-fluidic reactor and a continuously stirred tank reactor (CSTR)showed that the recovery of Omega-3 PUFA in silver-based liquid-liquid extraction (LLE) was greater than 75%, enabling the design of a conceptual industrial

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sized application of this process. This work compares the extraction capability and economic viability of a batch-wise process using three CSTRs with those of a continuous plug-flow reactor (PFR)which offers inventory reduction opportunities.The two processes are identical apart from the reactors and downstream surge tank, and so from an economic standpoint, the main difference is in the capital cost and operating cost of the different types of reactors, as well as the solvent inventory cost for filling the reactor vessels.

In practical silver-based solvent extraction, it is economically important to recover and reuse/sell the silver as part of the process. In this work, three solvent recovery and recycle methods have been analyzed and compared from an economic perspective:multi-effect evaporation, electrochemical oxidation, and chemical reaction-based recovery of silver. In the analysis, it was assumed that all of the silver nitrate and silver oxide remains in the aqueous phase, allowing it to be recovered from a single process point and tobe fed back to the reactor.

II. Liquid-liquid Extraction of Omega-3 Pufa Using a Silver Nitrate Solvent

Solvent extraction is a common mass transfer operation used for separation of various biological compounds from their feedstocks [8-10]. In this application of solvent extraction, the silver ions in the silver nitrate solvent undergo a fast reversible chemical reaction in which they form complexes with the five and six unsaturated sites in EPA and DHA, respectively. This silver-based solvent extraction of highly unsaturated fatty acids was proposedon a laboratory scale as a new method by Yazawa*et al.* [11] and has since been explored by a number of other authors using idealized extraction systems and lab-scale analyses [12].

The reported experiments on extraction using silver salts have primarily focused on laboratory based separation of Omega-3 PUFA from synthetic EPA/DHA mixtures at mini/micro scale and in batch processes. There remains a need however, for validation of an industrial process aimed at extracting and concentrating Omega-3 fatty acids from natural fish oils. The proposed application of silver-based solvent extraction in this report consists of five main steps. First, the heterogeneous fatty acid oil mixture is sent to a reactor where it is contactedwith a silver salt solution to form an emulsion including an aqueous phase and an organic phase. In the aqueous phase, the silver ions form complexes with the double bonds of EPA and DHA, increasing the miscibility of these compounds in the aqueous phase. These complexes are of the charge-transfer type where the EPA/DHA acts as an electron donor and the positive silver ion acts as an electronacceptor [13]. Next, hexane orhexene is added as an emulsion-breaker, which separates the organic phase from the aqueous phase inside a gravity settler. The aqueous phase is then extracted either by mixing it with a displacement liquid or increasing the temperature of the aqueous phase to at least 30°C, or a combination of the two methods. The aqueous phase is then diluted with water or extracted with supercritical CO_2 to dissociate the complex, where the silver ions' affinity for the double bonds of EPA/DHA is no longer strong enough to hold the complex in the aqueous phase. In the final step, the diluted aqueous phase containing the silver nitratesolution is separated from the concentrated Omega-3 fatty acids – the desired product of the process. The silver is recovered by a variety of chemical precipitation processes and either sold or regenerated and recycled into the extraction process after verifying the concentration and purity of silver nitrate solution.

The mechanism by which the silver ions and double bonded compounds form complexes has been the subject of significant scientific research; however quantitative data such as equilibrium constants exist for only a small number of short chain mono- and di-olefins [14]. As the Omega-3 fatty acids of interest have five and six double bonds, there is a need for experiments producing quantitative data related to these compounds. The stability of a complex with an organic compound decreases with the increasing chain length. Generally, the rate of complexation is very rapid but the complexes are unstable and exist in equilibrium with the free form of the olefin. The coordination forces between Omega-3 PUFA and silver ions are weak, and these properties of complexation between a double bond and a silver ion are favorable for use in chromatography/LLE [13].Due to the high cost of silver, it is important to accurately determine the ratio of silver ions to DHA and EPA moles required to form the complexes. For the purpose of this work, it was assumed that a silver ion is required for each double-bond:

1 mole of DHA (356g) + 6 moles of silver ions = 1 mole of DHA–Ag complex

1 mole of EPA (330g) + 5 moles of silver ions = 1 mole of EPA–Ag complex

III. Case Description

Mukoma [15] developed a hierarchical procedure for conceptual process design, which has been applied to compare the economics of the CSTR system with the PFR system. The following economic analysis is based on a fish oil processing facility capable of processing ten tons of fish oils per shift, where one shift is assumed to be eight hours. A simplified conceptual process diagram is shown in Figure 1, demonstrating an integrated process of three main operations involved in the production of EPA/DHA-Ethyl Esters (EPA/DHA-Et): solvent extraction, de-emulsification and de-complexation for the recovery and recycle of silver nitrate to the solvent extraction process.

In Figure 1, the oil layer leaving the first gravity settler is a combined stream of a residual oil layer which does not form an emulsion or complex with the silver nitrate solution, and an organic phase dissolved in hexane, referred to as fraction 1. The hexane-free oil layer is the combination of the residual oil and fraction 1, after the hexane is boiled off in a distillation column. The aqueous layer exiting the bottom of the gravity settler contains the majority of the Omega-3 content as well as the silver nitrate solvent. The organic Omega-3 PUFA stream leaving the second distillation column is referred to as fraction 2.

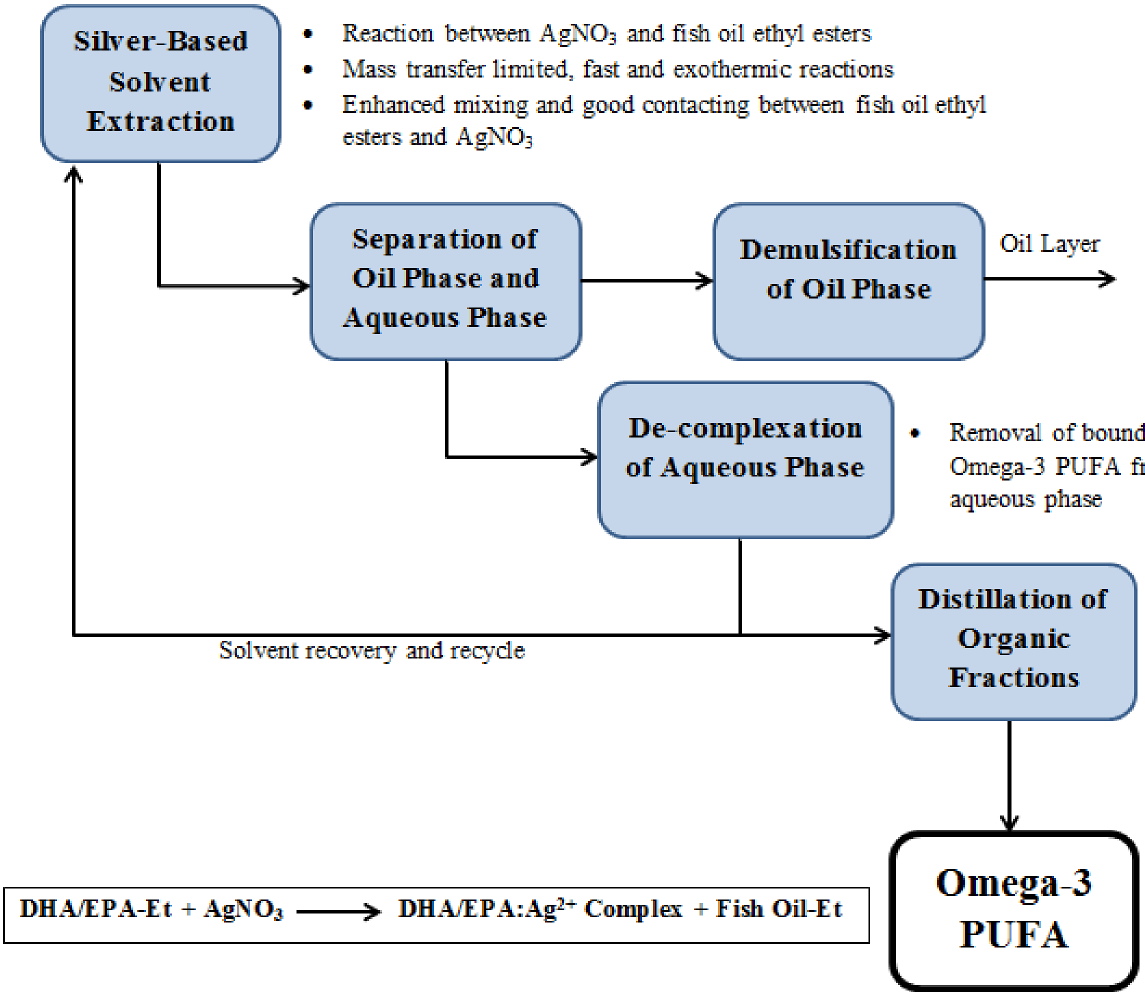

Figure 1 : Overview of silver-based solvent extraction of Omega-3 PUFA from fish oil EE

The two distillation columns in the process were simulated in UniSim to determine the energy requirement to evaporate the hexane out of the oil and organic phases, and recycle the hexane back to the process. Anevaporator which could potentially be used to recover and recycle the $AgNO_3$ solution was also simulated in UniSim for the same purpose. In a conservative approach to this economic analysis, the evaporator was modeled as a single-effect evaporator. In an industrial process, the unit would be operated as a multi-effect evaporator as this multi-effect configuration maximizes efficiency and steam economy.

a) *Comparison between Batch and Plug-Flow Processes*

Previous research by Kamio*et al.* [5,6] using a plug-flow micro reactor demonstrated that contact times of 10-20 seconds was sufficient for the system to reach equilibrium after contacting the silver salt solution with pure synthetic DHA and an organic carrier (heptane). Experiments completed with commercial raw trans-esterified fish oils using a mini-fluidic reactor in a laboratory setting demonstrated that a ~36 second residence time was more than sufficient to reach equilibrium. [7] This resulted in an 80 to 90% pure EPA/DHA product being formed, comparable to that in abatchsystem after 15 minutes. This mini-fluidic reactor would scale commercially as a double pipe heat exchanger to be considered as plug flow reactor. Similardistribution ratios between the aqueous $AgNO_3$ extraction phase and the organic carrier (hexane in these experiments) were alsoreported by Teramoto*et al.*[16]

The yield of Omega-3 PUFA from each product stream of LLE in both the plug flow reactor system and the batch reactor system are detailed in Table 1. The weight percentages of Omega-3 in each stream were taken as an average often experimental measurements; five from the batch system and five from the plug flow reactor system at various contacting times. The weight percentages were then used to determine the recoveries of Omega-3 in each stream, which were normalized to account for some material loss in the experimental measurements. Table 1 shows that the Omega-3 PUFA recovery in the mini-fluidic contacting system is 75.0% based on laboratory experiments, which is only slightly lower than that in the idealized batch process where the Omega-3 PUFA recovery is 76.5%. The Omega-3 purity in the organic layer was found to be close to 80%. Based on the results from these laboratory experiments, a conceptual process design for LLE of Omega-3 PUFA in the PFR configuration has been developed. The mass balance and sizing of equipment in the conceptual industrial sized process have been completed based on these laboratory yields of Omega-3 PUFA from fish oil ethyl esters.

Table 1 : Recovery of Omega 3 PUFA from each stage of LLE experiments

Product Stream	Stream Flow Rate (kg/min)	Omega-3 wt.%	Omega-3 Flow Rate (kg/min)	Normalized Omega-3 recovery (%)
18/12 Fish Oil EE Feed	20.67	30.9	6.39	100.0
Residual Oil from Gravity Settler		3.0		
PFR system	13.48		0.40	6.9
Batch system	9.84		0.30	4.5
Oil Layer (Fraction 1)		24.8		
PFR system	0.94		0.23	4.0
Batch system	2.27		0.56	8.5
Hexane-Free Oil Layer (Residual Oil + Fraction 1)		5.8		
PFR system	14.42		0.83	14.1
Batch system	12.12		0.70	10.5
Organic Layer (Fraction 2)		79.3		
PFR system	5.54		4.39	75.0
Batch system	6.39		5.07	76.5

In order to compare the batch process with the continuous mini-fluidic reactor process, the batch process has been designed so that in one eight-hour shift, the same amount of fish oil ethyl ester feedstock can be processed as in eight hours of operation in the continuous system. In the batch process, in order to minimize equipment size and cost, it is assumed that three CSTRs are operated in parallel to meet the equivalent capacity of the PFR process. Figure 2 shows the proposed batch process with eight-hour batch sizes indicated for the industrial process. The CSTR products are recombined into one stream and sent to the storage tank, which is blanketed with nitrogen to avoid oxidation of Omega-3 PUFA. In the plug-flow system, the fish oil ethyl ester feedstock is continuously fed to the reactor along with the concentrated $AgNO_3$ solvent, after which the mixture is sent to a gravity settler in continuous operation. After this stage, the post-extraction processing is performed in continuous processes which have equivalent flow rates in both systems.The conceptual process flow diagram for the continuous plug-flow reactor system is displayed in Figure 3.

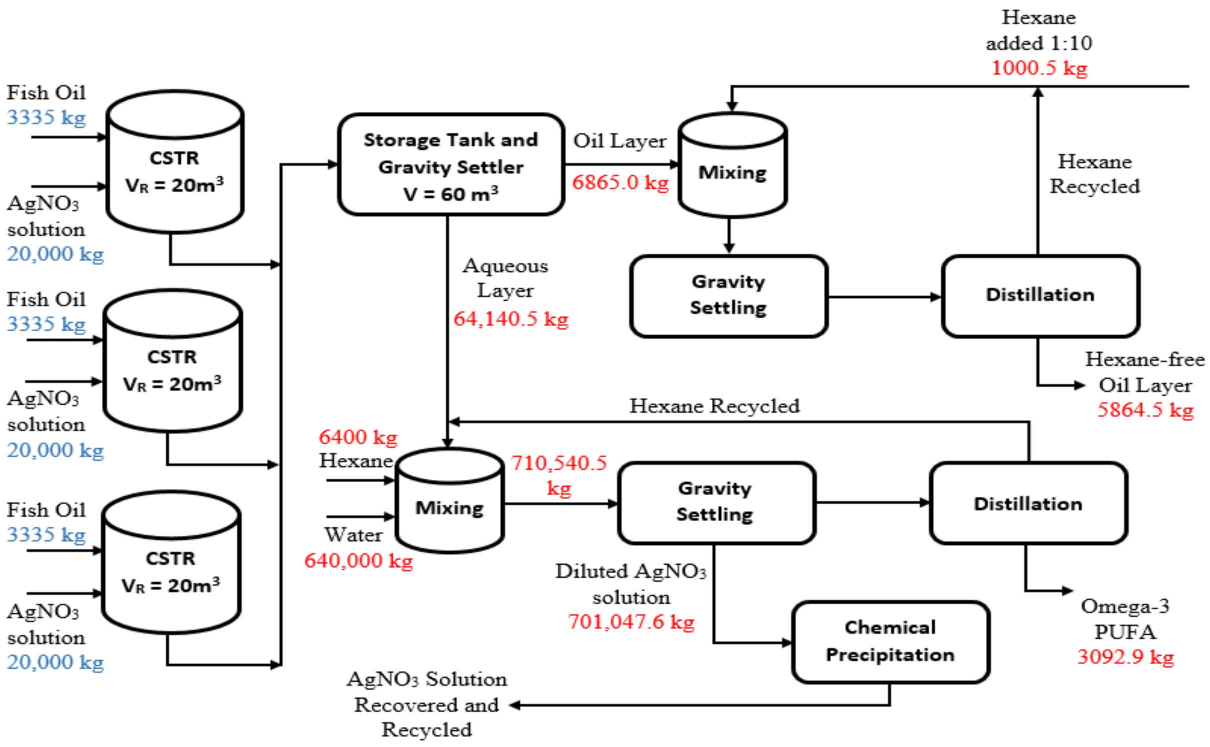

Figure 2 : Process flow diagram of multiple CSTR reactor system with reactors in parallel in order to meet production capacity of the equivalent continuous process

The application of mini-fluidic based extraction of Omega-3 PUFA using a concentrated silver nitrate solution is promising because of its simplicity, short residence time within the reactor and improved mixing compared to conventional systems. As can be seen in Figure 2 and Figure 3, the yield of Omega-3 PUFA is roughly 25% of the fish oil ethyl ester feedstock fed to the LLE reactor (78 to 82% recovery), which means for a processing rate of ten tons of fish oil per shift, roughly 2.5 tons of Omega-3 PUFA can be produced.

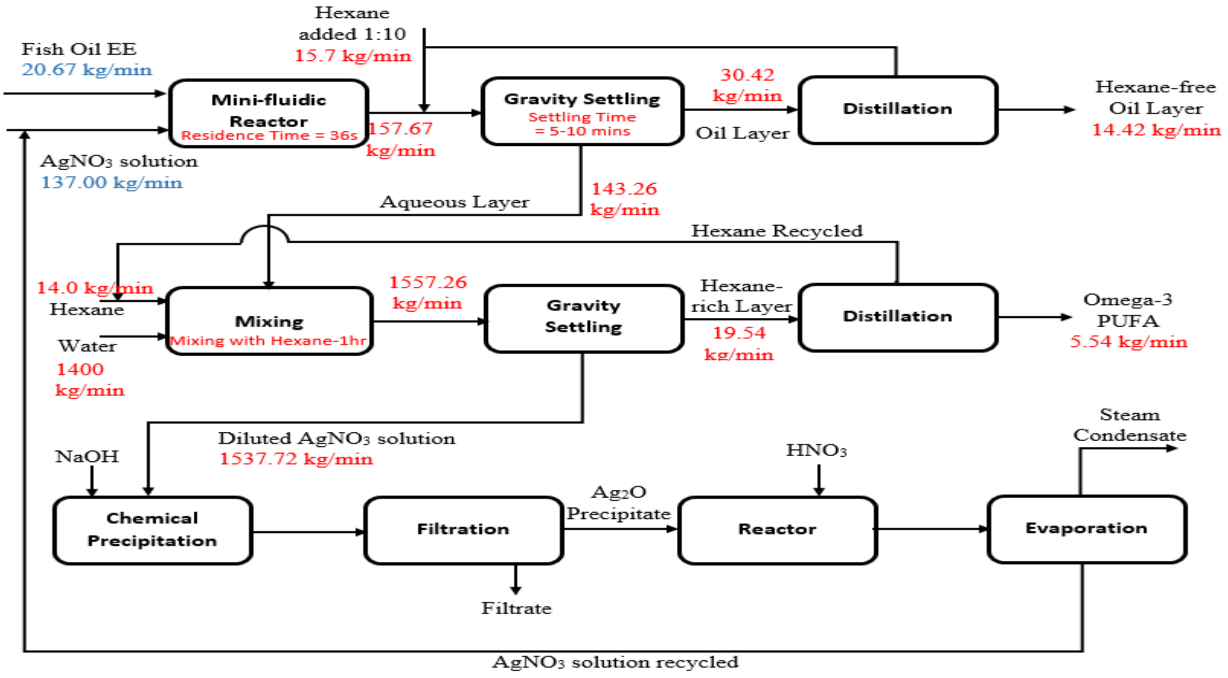

Figure 3 : Process flow diagram for Omega-3 PUFA extraction in continuous plug-flow reactor system using silver-based solvent extraction

b) *Recycle or Generation Method for Silver Nitrate Solution*

Silver-based solvent extraction of Omega-3 PUFA from fish oil ethyl esters is an expensive process due to the high cost of silver nitrate salts; minimum $US 300 per kg in July 2015 [17], if bought in large quantities. Silver nitrate is used because it is effective in the separating the Omega-3 PUFA from the fish oils, however practical recovery of silver nitrate or generation of new silver nitrate solution via a cost-effective process is necessary to minimize the operating cost of the process and make the process economically feasible on an industrial scale. As part of the process, some of the silver nitrate in the diluted aqueous phase will naturally oxidize forming Ag_2O. The simplest option for regenerating $AgNO_3$ solution to be used in the LLE reactor is to sell any Ag_2O that precipitates, and buy new $AgNO_3$ with which to make up the necessary volume to be fed to the reactor. This is the method on which this economic analysis is based, however other options include recovery processes to avoid the buying and selling of expensive silver compounds. The feasibility of this buy-and-sell method in an industrial process would greatly depend on the market price of these silver compounds.

Available processes for the recovery of silver nitrate solution include purifying the silver nitrate stream by using a multi-effect evaporator (MEE), chemically removing the silver from the solution so that it can be recovered and regenerated, and recovering the silver nitrate by electrolysis using copper electrodes. Rawat [18]reported experimental recoveries of silver nitrate from laboratory waste solutionsof 85-91% for five samples, using a combination of ion exclusion and ion exchange procedures. Murphy [19] further developed several chemical reaction-based recovery techniques, reporting experimental recoveries of greater than 98%. For the purpose of this economic analysis, it was assumed that the majority of the unrecoverable silver losses would be in the small amount of silver oxide that dissolves in the dilute water stream, preventing it from being converted back into silver nitrate. This quantity of silver loss was determined from the solubility of silver oxide in water to be ~78 g/min. While this is only a small fraction of the original mass of silver, the expensive price of buying new silver nitrate to replenish the original solution results in an annual operating cost of US $29.6 million, and so an efficient solvent recovery method should be used to avoid these losses.

The first solvent recovery method considered is that in which the silver nitrate stream is attempted to be purified, first by evaporating most of the water out of the diluted solution in a multi-effect evaporator (MEE) to bring the solution to the desired 50 wt.% $AgNO_3$. In this process, the significant thermal energy and the possibility of increased oxidation of silver nitrate as the temperature is increased is concerning. Using a single effect evaporator, with a 20% additional energy requirement for preheating the water to its boiling point, ~706,000 tonnes of steam would be required annually. This results in an annual operating cost of the single stage evaporator, assuming 24 hours per day operation for 350 days per year, of ~US $5.60 million. This is significantly lower than the US $29.6 million required to replenish the silver losses with new silver nitrate solution. The use of a multi-effect evaporator could further reduce this energy requirement to less than 50% of that of a single-effect evaporator. The benefit to this technique is that there would be limited use of chemicals relative to the other options for recovery of silver nitrate.

The second silver nitrate recovery option would be to chemically remove the silver nitrate by purposefully oxidizing all of the silver, causing it to precipitate out as Ag_2O. This could be done by reacting the silver nitrate solution with sodium hydroxide or potassium hydroxide, forming sodium (or potassium) nitrate, solid silver oxide and some additional water. The solid silver oxide would precipitate out of the solution and collected via filtration, thus eliminating the energy requirement from the first solvent recovery method. This silver oxide would then be stored and reacted with nitric acid (HNO_3) as needed to regenerate silver nitrate solution. One disadvantage to this method is the creation of a $NaNO_3$waste stream containing a significant portion of the water from the diluted aqueous phase, which would then need to be treated and concentrated. This process would likely still require a multi-effect evaporator to concentrate the sodium nitrate solution. In addition, the nitric acid would need to be purchased in this option. A simplified flow diagram of this process is shown in Figure 4.

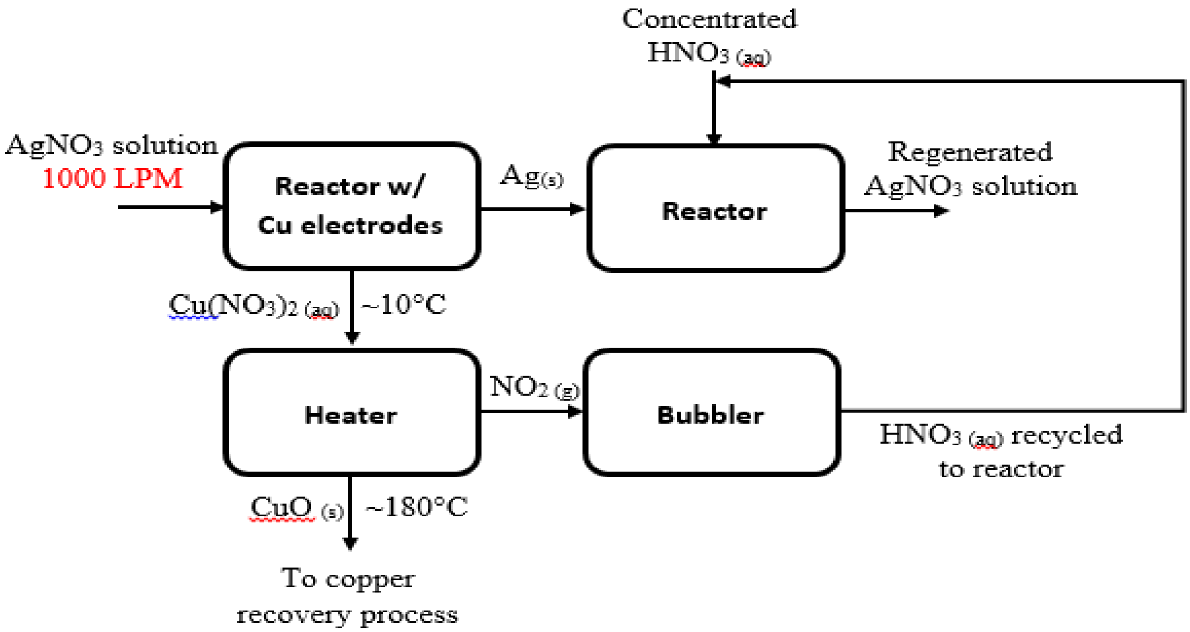

Figure 4 : Process design for the concentration of silver nitrate solvent solution by evaporation

An alternative to purchasing the nitric acid would be to use the sodium nitrate stream to generate nitric acid for the process. This could be done by reacting $NaNO_3$ with sulphuric acid (H_2SO_4) to produce HNO_3 and $NaHSO_4$. The disadvantage with any of these methods is that a byproduct will be generated in any case, with either $NaHSO_4$ or $NaNO_3$ requiring disposal. The relative advantage of reacting the sodium nitrate with sulphuric acid would depend on the availability of the two acids in the region of operation.

Finally, the third silver nitrate recovery method considered is to electrochemically extract the silver through the use of copper electrodes as shown in Figure 5. In this process, the silver would deposit on the copper electrode, with some copper metal dissociating into the solution, forming $Cu(NO_3)_2$. This copper nitrate can then be heated to 180°C, which converts the compound to copper oxide (CuO), releasing NO_2 and O_2 gases. The NO_2 gas can then be passed through water, which generates nitric acid to be used in the process. This reaction also produces NO, which can be bubbled through water to produce additional HNO_3. As with the chemical removal and recycle of silver, this method produces a stream requiring further processing – where CuO is converted back to elemental copper. This reaction is relatively slow, and would therefore require a large amount of copper in an industrial system to sufficiently handle the large throughput required.

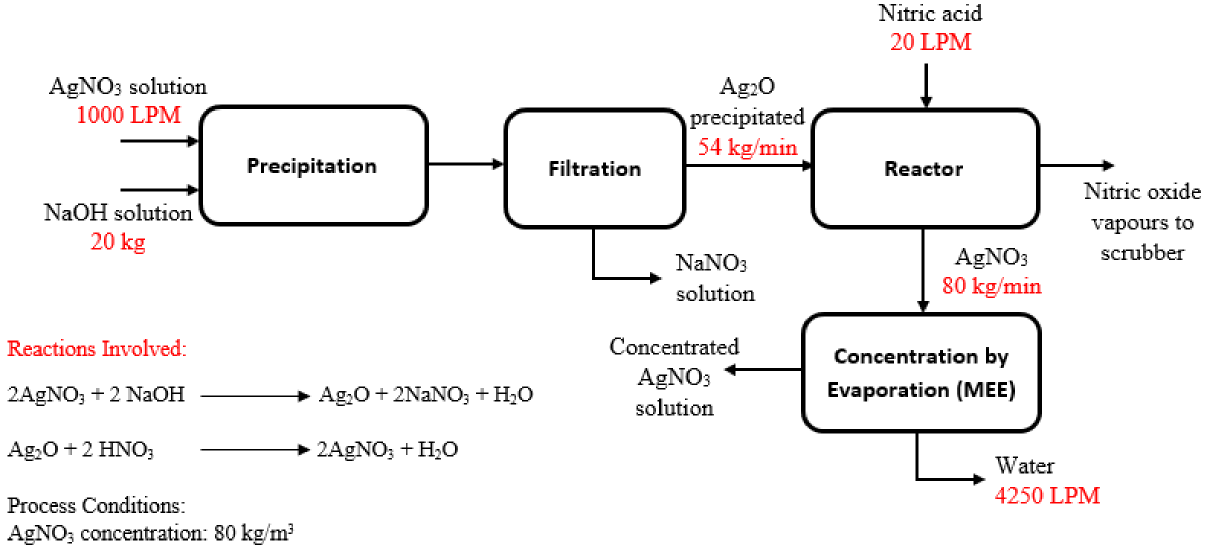

Figure 5 : Process design for the concentration of silver nitrate solvent solution by electrochemical extraction using copper electrodes

Other solvent recovery methods include a chemical reaction-based method involving salt, producing a silver chloride precipitate, which can then be converted to sodium nitrate to be used in the LLE reactor. This option is likely not viable for large scale production as it would involve the use of large quantities of harmful halides, which would then have to be processed and removed safely. Another option is to reduce the silver solution using formic acid, producing silver nitrate and sodium formate. This is also an unlikely option for large scale operation due to the toxic and harmful nature of the formic acid involved and the production of a formate stream which would require additional processing.

IV. DISCUSSION AND EVALUATION

The feasibility of this industrial-sized process depends greatly on the purchase and sale price of the compounds involved. For example, if the price and demand of silver oxide is high relative to the price of silver nitrate, it may be economically beneficial to sell the silver oxide precipitate and purchase new silver nitrate solution, rather than trying to recover the original solution. Furthermore, the price of sulphuric acid, nitric acid, sodium nitrate, and sodium bisulfate ($NaHSO_4$) all affect which process is the most economically efficient to apply to an industrial sized plant. Currently, Tianjin Yinlida Chemicals Co., Ltd. [20] is advertising an average bulk price of silver oxide (99% purity) of ~US $1000/kg, while the price of silver nitrate from the same company is advertised at ~US $750/kg.Recognizing that there would be operating costs associated with the units in an industrial plant, it appears likely that selling the silver oxide and purchasing new silver nitrate would be economically viable. This method eliminates the need for a multi-effect evaporation unit to evaporate a large quantity of water, requiring a significant energy input which would hinder the feasibility of the process from an economic standpoint.

a) *Solvent Inventory Comparison*

In the process of liquid-liquid extraction of Omega-3 PUFA, the use of concentrated 50 wt.% silver nitrate solution as a solvent is expensive and minimal consumption is important in order to decrease the operating cost of the extraction process. Based on the process design, the required solvent inventory for the continuous plug-flow system is much less than that for the batch process. Due to the continuous nature of the PFR, the necessary reactor volume is much smaller. In both designs, it is assumed that the reactor and the gravity settler will be filled at all times. This means that for the batch process (Fig. 2), 120,000 kg of $AgNO_3$ solution would be required, as 20,000 kg are required for each of the three CSTRs, and then that same amount is required to fill the gravity settler. Comparing this to the continuous design, where the mass of solvent required to fill the reactor and settler was determined by knowing the flow rate of $AgNO_3$ solution and the vessel capacities. For the reactor, with a residence time of 36 seconds (Fig. 3), 82.2 kg of $AgNO_3$ solution would fill the reactor. For the gravity settler in the continuous process, using a conservative estimate of ten minutes for the residence time, 1370 kg of $AgNO_3$ solution would fill the settler. Thus the continuous process requires only 1452.2 kg of solvent inventory – roughly 1% of that required for the batch process. Based on this information, the operating cost of the continuous process would decrease by requiring less solvent for the liquid-liquid extraction process.

Silver nitrate comprises 50 wt.% of the solution and using a standard bulk cost of $AgNO_3$ of ~$750 per kg, the cost of the silver nitrate in the batch process would be ~$40 million, while that in the continuous process would be ~$484,000.

b) *Operating Cost and Energy Requirement*

In solvent extraction of Omega-3 PUFA from fish oil ethyl esters, there are several units requiring energy to heat, cool or cause a phase change to the various streams in the process. The first of these units is the distillation column which takes the hexane carrier and the oil phase as input and raises the temperature to the boiling point of hexane (68.5°C), effectively separating the oil phase from the organic carrier. For this economic analysis, it was assumed that steam would be used to heat the mixture to the boiling point and evaporate the hexane. The LLE reaction is approximately isothermal, operating at 10°C, and so it was assumed that the hexane/oil mixture would enter the distillation column at this temperature. To obtain the specific heat capacity of the mixture, a mass average specific heat capacity between the oil and the hexane was calculated. For this calculation, the specific heat capacity of the oil fraction was assumed to be that of vegetable oil at 10°C, reported by Clark *et al.*[21]. After the mixture reached the boiling point, only the hexane fraction would then need to be evaporated. This resulted in the calculation of an energy requirement for the column, from which the amount of low pressure steam (LPS) required to supply the necessary heat to the column was calculated. A study done by the United States Department of Energy[22] reports that the cost of LPS is approximately $3.00/klb, from which the operating cost of this distillation column could be calculated. The flow rates used in this calculation are shown in Figure 2.

The next unit requiring a significant amount of energy input in this process was the second distillation column, which again evaporates hexane for recycle, separating the organic carrier from the desired Omega-3 PUFA product. The energy requirement calculation for this unit was done similarly to that of the first distillation column, with the properties of the Omega-3 fatty acids replacing those of the oil in the first column. Sathivel [23] reported experimentally observed specific heat capacities in the range of 0.8-2.3 kJ/kg-K for red and pink salmon oils. Research by Young [24], Morad*et al.* [25] and the Fisheries and Aquaculture Department of the Food and Agriculture Organization of the United Nations [26] all report fish oil specific heats between 2.1-2.5 kJ/kg-K at 25°C. Further research by Sathivel [27] showed that the specific heat of catfish visceral oil is between 1.7-2.0 kJ/kg-K. For this analysis, an Omega-3 PUFA specific heat capacity of 2.0 kJ/kg-K was assumed. It was determined that the annual cost of steam required to heat the distillation columns is ~\$26,700, assuming continuous, 24 hours per day operation for 350 days per year.

Once the hexane streams leave the distillation columns, they are recycled back into the process. The hexane leaving the distillation column must be condensed and cooled to 10°C before recombining with the process solutions. It was assumed that cooling water would be used to condense the hexane and lower the temperature from its boiling point to approximately 40°C. The cooling water was assumed to enter the heat exchanger at 30°C and leave at 45°C. After this initial cooling, refrigerated cooling water would be used to achieve the rest of the heat transfer. The temperature change of the refrigerated cooling water was assumed to be ~11°C. Using a cost of water of \$0.020/m^3 and a refrigeration cost of \$4.00/GJ,the annual cost of cooling water for the proposed facility is ~\$50,100.

c) Economic Comparison between Plug-Flow and Batch Systems

For this economic evaluation, correlations from Seider*et al.* [28],Turton*et al.* [29], and Ulrich [30] were used, corrected for a Chemical Engineering Plant Cost Index (CEPCI) of 573.4 for January, 2015. These correlations provide an estimate of the cost of the major unit operations, equipment and materials involved in the proposed facility, which can be used as a basis for estimating the potential profitability of the plant.

A summary of the grass-roots fixed capital investment (FCI$_{GR}$), the manufacturing cost (COM$_d$) and the revenues expected from the proposed process are outlined in Table 2, for both the CSTR and PFR systems. For this analysis, a selling price of \$8.00/kg Omega-3 PUFA was assumed. The selling price of Omega-3 PUFA of \$8.00/kg represents an average of various products, grades and quantities available, with prices ranging from \$4.00/kg to higher than \$12.00/kg. Furthermore, it was assumed that the profit gained by selling the silver oxide precipitate and buying new silver nitrate would be consumed by the processing of the dilute silver nitrate waste stream.

Table 2 : Summary of key parameters in economic comparison between PFR and CSTR systems

Equipment	\$ Millions – PFR System	\$ Millions – CSTR system
Grass-roots fixed capital investment by equipment type		
Pumps	0.850	0.850
Heat exchangers and reactors	0.271	1.531
Towers (Distillation columns)	0.448	0.448
Vessels and storage tanks	1.124	2.704
Raw Materials	2.248	41.956
Total FCI$_{GR}$	**4.941**	**47.489**
Cost of Manufacturing		
Direct manufacturing cost (DMC)	6.021*	6.021*
Fixed manufacturing cost (FMC)	0.935	1.124
General expenses (GE)	0.712	0.747
Total COM less depreciation (COM$_d$)	**7.668**	**7.892**
Revenues		
Omega-3 PUFA sales (2.625 ktons at 8000\$/ton)	**21.000**	**21.000**

**This cost is based on a single-effect evaporator. In an industrial process, multi-effect evaporation would reduce this cost greatly.*

The data in Table 2 shows clearly that the biggest difference in cost between the CSTR system and the PFR system is the raw materials cost, which is mainly comprised of the solvent inventory cost for silver nitrate. The 99% reduction in solvent inventory provides the PFR system with a distinct advantage over the CSTR system in terms of potential profitability in an industrial-sized process. Furthermore, the PFR system has a lower grass-roots fixed capital investment, due mainly to the smaller reactor and gravity settler required for the continuous process. With annual revenues of ~US \$21 million from the sale of Omega-3 PUFA, a cost of manufacturing of ~US \$7.9 million, and a fixed capital investment of ~US \$47.5 million, the CSTR process would likely not be economically viable on an industrial scale. Conversely, the PFR system has a cost of manufacturing of ~US \$7.7 million, a moderate fixed capital investment of ~US \$4.9 million and the same revenues as the CSTR design, making it more economically feasible.

The economic analysis completed in this work was done assuming that all silver oxide precipitated could be sold and silver nitrate purchased at the prices listed previously. This work aimed to compare the feasibility of the plug-flow reactor system to that of the CSTR system, and in both processes, the same solvent recovery/generation system would be applied. If the solvent was recovered and recycled via chemical reaction-based methods using sodium hydroxide and nitric acid, the profitability of the process would depend highly on the selling price of the chemicals involved in the process. Likewise, if the solvent was recovered via electrochemical oxidation using copper electrodes, the purchasing price of copper would be important to the potential profitability of the proposed plant.

V. Conclusions

The proposed facility offers a practical method of extracting Omega-3 PUFA from fish oil ethyl esters on an industrial scale by solvent extraction in a continuous plug-flow reactor using a silver-based solvent. The economic analysis presented in "Economic Analysis and Discussion" demonstrates that the profitability of this process is highly sensitive to the selling price of silver oxide and silver nitrate, as well as efficiencies in the solvent recovery operation. The economic benefit to the proposed plug-flow reactor configuration is that the solvent inventory required for this continuous system is much smaller than that of the batch process, as the vessels can be built much smaller. Due to the high cost of silver-based compounds, any reduction in solvent inventory results in significant savings related to raw material costs. Considering the increased global consumption of Omega-3 fatty acids and the research into the health benefits of these products, there is an increasing need for an economically viable process of producing Omega-3 PUFA on an industrial scale. While additional research into silver recovery methods and deactivation rates is required to implement this design into an industrial-sized plant, there is an incentive for continuing to pursue efficient methods of recovering Omega-3 directly from fish oil feedstock.

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