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Procedure for the Selection among Technologies. Treatment of Deodorizer Distillate Oil

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ABSTRACT: With the aim of both adding value by recovering tocopherols from a natural source and promoting environmental care, this work studies how to select among available technological alternatives for the processing of deodorizer distillate oil (DDO), which is a residue of the edible oils refining industry. The work focuses on how to generate a first set of promising alternatives (we propose to follow an established process design procedure based on heuristics, combined with a screening of the literature, with criteria to narrow the large number of alternatives published). The final selection among them is an established approach: we propose to implement a multiobjective optimization mixed integer linear program maximizing the net present value (NPV) and minimizing the generation of greenhouse gases measured as kilogram-equivalent of CO_2. For a given case study of soybean DDO the first step generated a set of six technologies for the treatment of DDO with different processing capacities plus two additional alternatives for the final destination of DDO. The Pareto set of solutions constructed with the results provides information to adopt a both economic and environmentally sound choice of a processing technology. For the particular case analyzed, the technology that maximizes NPV within the Pareto set of solutions was esterification of free fatty acids with ethanol in acid medium followed by a separation of the esters by molecular distillation, at the largest production capacity (576,000 kg/year). This technology gives the maximum NPV of $19,574,000 generating 5,142,500 kg of CO_2-equiv. The results obtained are useful for decision making in the industry, to give an adequate final destination to the residue DDO.

1. INTRODUCTION

Deodorizer distillate oil (DDO) is a byproduct of edible oils refining processes. It is the fraction of volatile compounds of the oil obtained by steam stripping it at a pressure in the order of 1−5 mmHg. This byproduct is mainly composed by free fatty acids (and even more volatile substances responsible for the musty odor), and in lesser proportions by heavier compounds: tocopherols, sterols, and some entrained oil, among others. DDO represents between 0.1 and 0.4% of the oil to be refined, and its composition varies according to the type of oil (e.g., sunflower, soybean, and so on) and the process conditions of the deodorization.[1,2] If it were disposed of as a residue, treating the effluent would be expensive for this byproduct, due to its large oxygen demand (biodegradable organic matter). On the other hand, the content of some commercially valuable components encouraged many proposals (academic research reports as well as patents) for implementing extraction and purification treatments. Moreira and Baltanas[3] and afterward Dumont and Narine[4] review a large amount (more than 100 in each article) of alternative processing proposed in the literature. The higher price component is tocopherols (vitamin E) which are natural antioxidants and find large application in food, pharmaceutical, and cosmetic industries.[5] Sterols are also high valued and, depending on the oil, free fatty acids (FFAs) may also have a good price. If DDO is sold as raw material for this recovery, its price is based on its vitamin E content.[6] Depending on the edible oil refined, the content of tocopherols in the DDO varies; e.g., in the case of soybean oil the DDO contains up to 10% tocopherols, while the DDO from sunflower oil has only up to 5%.

To generate the set of alternative processing to be considered, we may start by accounting for those proposed in the literature, or a subset of them selected by some criteria: we here propose to consider only those currently available at the industrial scale, i.e., successfully implemented. This will discard many alternatives which, even if promising, still need further development work, besides the fact that we lack economic data to assess them. Another way for generating alternatives is to design them: we here apply the hierarchical procedure proposed by Douglas[7,8] for designing a new process, to check if it generates some extra promising alternative. The design procedure makes decisions progressively (e.g., input−output structure of the flow sheet and then the recycle of streams and design of the separation system) guided by heuristics. Once we define an initial set of alternative processing, which we believe includes the optimal processing route, we may proceed to mathematical programming to make the decision based on the mass and energy balances involved in each alternative and on performance indices (based on these balances) that weight how good it is for us (we propose to consider both an economic and an environmental metric).

Deciding among alternative technologies is a multiple choice problem, which has been approached in the recent literature by addressing two presently active areas of research: supply chain optimization and mass integration. In both cases the problem is modeled as a mixed integer linear program (MILP) where the technology selection is done through binary variables that adopt the value "one" in the case in which the technology is adopted and "zero" otherwise.

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The supply chain optimization literature deals with optimizing the multiple echelon supply chain composed of production, storage, and market sites, usually considering their spatial distribution and transportation costs. The work of Mele et al.,[9] who optimize the sugar chain in Argentina, and Giarola et al.,[10] who approach the design and planning of the biofuels refinery chain in Italy, are examples of this type of work. On the other hand, the mass integration literature deals with optimizing the allocation of material streams seeking to reduce both the consumption of fresh resources and generation of residual streams. The original source−sink programming technique optimizes the allocation of mass sources to mass sinks.[11] Mass sources are available streams (fresh resources from outside the process or streams that exit process units) while mass sinks are sites that need or admit streams. Each mass source is split into exiting streams which are fed to the mass sinks (that pose flow rate and composition constraints to admit them); then the MILP selects the optimal allocations.

A work that takes this approach to solve a problem much like the one we are interested in solving here is reported by Haslenda and Jamaludin[12] who seek minimizing waste from palm oil refining through an "industry to industry byproducts exchange". Their mass sources are the soapstock, deodorization distillate oil, and spent bleaching earth residual streams from the palm oil refining industry, and their mass sinks are the animal feed, biodiesel, lubricant, and soap industries. In this approach the mass sources splitters render streams with the same composition as the mass source. To overcome this limitation, El-Halwagi[11] proposes alternative splitters named "interceptors" which carry out separation operations exchanging mass from a rich stream toward a lean stream resorting to an external mass separating agent (MSA). These pieces of equipment are typically absorbers or strippers and usually require some recovery system for the external MSA regeneration. The composition change of mass sources thus enhances the possibility that exiting streams be admitted by mass sinks, thus improving mass integration. Fischer and Iribarren,[13] who seek mass integrating a new biodiesel process to an existing industrial environment, further extended the idea of interceptors proposing "operators" to condition the mass source streams to allow their integration, where operator is any process able to transform a source stream rendering a stream acceptable for a mass sink: any unit operation, or a combination of them (a complete process), including the interceptors proposed by El-Halwagi.[11] We will here follow this last approach, i.e., a source−sink formulation with operators, taking as operators the set of processing alternatives generated in the first step of the here proposed procedure.

The remainder of this work is organized as follows. Next we generate the set of processing alternatives by first screening the literature and selecting among the processing routes proposed there, and then using process design heuristics to check if they generate some new alternative or provide some new insight into the problem formulation. Following, we present the mathematical formulation of the problem. The focus then turns to the application to our case study, for which we describe with more detail each of the alternative processing routes implemented in the model and report the product yields, energy consumptions, water usage, CO_2 generation, and cost data for each alternative. Afterward, we analyze the results and draw conclusions about the approach proposed in this work.

2. GENERATION OF THE SET OF DDO PROCESSING ALTERNATIVES

2.1. Screening of Processing Alternatives Proposed in the Literature. Analyzing the separation technologies reported in the reviews by Moreira and Baltanas[3,15] and Dumont and Narine[4] focusing on those currently available at industrial scale, or for which economic feasibility has been reported, we find that they correspond to formerly "emerging" technologies: molecular distillation first and supercritical extraction with CO_2 more recently that found their way into industrial scale production.

Molecular distillation (or short path) is a partial evaporation under very high vacuum in the order of a few micrometers of Hg.[5,16,17] The equipment is mechanically designed such that the condensing surface is very close to the evaporating surface, thus presenting a short path for molecules that escape from the evaporating surface and are captured by the condensing surface. This unit operation allows the separation of high boiling point (yet thermally sensitive, such as tocopherols and sterols) substances, at relatively low temperatures. The technology is well established for a variety of high boiling natural compounds and specifically for the concentration of tocopherols, and several contractor companies offer the equipment. We took the technical and economic data for this processing alternative from a local contractor company.[18,19] Molecular distillation could be implemented with just one stage separating the FFA and leaving a product concentrated in tocopherols or feeding this last stream to a second stage to separate triglycerides (oil entrained in the DDO) as the heavy product.

Supercritical fluid extraction technology (SCFE) has emerged as a competitive alternative to conventional techniques (liquid−liquid or solid−liquid extraction with organic solvents) for the extraction of natural products in food and pharmaceutical industries. Supercritical CO_2 is an excellent solvent for the extraction of tocopherols and sterols present in DDO.[20,21] The technology is well established at the industrial scale for the extraction of caffeine from coffee, while Mendes et al.[22] performed an economic evaluation of an industrial process to concentrate tocopherols and concluded that this process is technically and economically viable.

Other processing alternatives considered in the literature arise from resorting to a first chemical reaction step that modifies the less valuable components, without altering the most valuable (tocopherols and sterols) and facilitates their separation: hydrolysis of the glycerides into FFA, saponification of FFA and glycerides into soaps, and esterification of FFA into biodiesel. From these alternatives, we will consider here esterification of the FFA followed by molecular distillation. This alternative is presented by Moreira and Baltanas[15] as having the advantage that boiling points of FFA esters are lower than of FFA which facilitates the posterior distillation and afterward were studied and recommended by Facioli and Barrera-Arellano[24] and Pramparo et al.[2] This process obtains a product concentrated in tocopherols plus a technical (not purified) grade fatty acids ethyl esters (FAEE) named pre-biodiesel with a reported good selling price (it finds application in some robust machinery, or it is sold to biodiesel production plants that purify it into automotive grade biodiesel). Furthermore, this alternative is especially attractive for soybean oil DDO because its FFAs are low priced (e.g., in comparison with FFA from sunflower oil DDO) and because soybean oil refineries used to be integrated to a biodiesel process.

2.2. Process Design Procedure. After getting this first set of processing alternatives from a literature search, we resort to the hierarchical process design procedure of Douglas[7,8] to check if it generates some other promising alternative or contributes some extra insight into the problem formulation. The design procedure makes decisions progressively guided by heuristics. We restrict the following analysis to those applicable to our case; e.g., we do not have a product formation reaction or gaseous separations.

At the higher hierarchy level of designing the input−output structure of the flow sheet, the input is already defined to be DDO and the procedure helps to decide about the number and destination of products: a list is made of components ordered by increasing boiling points and then classified as either: reactant, primary product, valuable byproduct, fuel, or waste. Reactants are recycled; this is the case of excess ethanol in the case of the esterification−molecular distillation processing route. Any exiting stream concentrated in tocopherols should be considered a primary product. The classification of valuable byproducts could be applied to biodiesel and the oil fraction exiting the two stages molecular distillation. The soybean FFA in the light stream exiting the first molecular distillation is low priced and does not warrant further purification (this stream also carries the more volatile substances responsible for the musty odor). The same happens with the FFA plus oil stream exiting the SCFE processing alternative. Thus, these streams could be given the destination code "fuel" or "waste". As they do have a good combustion heat and there is no environmental hazard in giving them this destination, they will be considered "fuel".

Next in the hierarchy of process design decisions comes defining the recycle structure and design of the separation system. Our only recycle is ethanol in the esterification−molecular distillation processing alternative. With respect to separations, the heuristic for liquid separations is to first consider distillation (a single stage distillation or flash if applicable, or common distillation with reflux) whenever the differences in relative volatilities are greater than or equal to 1.1. The components present in DDO meet this rule, so we shall consider this technology. While distillation at atmospheric pressure must be excluded due to thermal damage of tocopherols, the molecular distillation proposed in the literature overcomes this problem. Also, there is an alternative distillation operation overlooked in the technologies offer reported in the literature: hydrodistillation, i.e., steam stripping with partial reflux of the light fraction FFA stream. In hydrodistillation the total pressure is given by the summation of water and volatile organic components. Thus, the separation of FFA can be performed at a moderate vacuum. Actually, steam stripping is the same operation that produced the DDO and can be used in situ to separate the FFA with the same utilities (steam quality and vacuum level) of the oil refinery, at the same temperature and pressure conditions of the deodorization.[25]

At typical conditions of deodorization, e.g., 180 °C and 5 mmHg, only FFA can be separated from the heavier components, so this processing alternative is only competitive with the single step molecular distillation. Separation of heavier components would require larger temperatures (not allowed because of thermal damage) or lower pressures. So, resorting to the hierarchical process design procedure did contribute the extra processing alternative hydrodistillation and highlighted the fuel destination of two of the exiting streams, which will serve to price them in the problem formulation.

2.3. Final Set of Processing Alternatives. Summarizing the result of this section, six technologies for processing DDO were preselected: one stage molecular distillation and hydrodistillation that produce FFA and a mixture of tocopherols−sterols−oil; esterification followed by molecular distillation that produces pre-biodiesel and the mixture tocopherols−sterols−oil; two stages molecular distillation and hydrodistillation followed by molecular distillation that produce FFA, a mixture of tocopherols−sterols, and a fraction of oil that can be returned to the refinery; and finally SCFE that produces a mixture of tocopherols−sterols and a mixture of FFA−oil. Also, we considered two alternatives that do not process the DDO at all: burning it in the refinery boiler or selling it to a vitamin E producing factory located 790 km away from the refinery. These last two alternatives were included in the set for completeness; the problem formulation including only the selection among available technologies would have been biased toward processing, while we knew these alternatives are the ones presently adopted when deciding about disposition of DDO as a residue: both of them are good economic alternatives if compared to processing it in a waste treatment plant.

The tocopherols in the mixture tocopherols−sterols have a higher price than in the mixture tocopherols−sterols−oil because it finds more applications, and the price of these mixtures also depends on its tocopherols concentration, which is different depending on the technology used to produce it. Pre-biodiesel and oil have their respective prices as valuable byproducts, while FFA and the mixture FFA−oil are priced as boiler fuels depending on their heat of combustion.

3. MATHEMATICAL FORMULATION

The model has been formulated as a multiobjective MILP optimization involving the selection of the most appropriate technology for processing the DDO depending on the plant capacity and assessing the trade-off between their economic and environmental performances. One objective is maximizing the NPV (net present value) shown in eq 1, and the other is minimizing the production of greenhouse gases measured as CO_2-equivalent (eq 2). While not explicitly considered in the optimization, we tracked the energy and water consumption of each alternative as additional assessment data.

objective functions:

$$\text{obj}_1 = \text{NPV} = \sum_t (\text{CF}_{k,t} \times \text{df}_t) - \text{TCI} \tag{1}$$

$$\text{obj}_2 = -\text{TCO}_2 = \sum_t \text{CO}_{2(k,t)} \tag{2}$$

The NPV is computed as the summation of the cash flows (CF) over a horizon time of 10 years, and discounting the capital investment (TCI) for each technology depending on the size of the plant, df_t is the discount factor at time period t shown in Table 5. Objective two TCO_2 is the total production of carbon dioxide computed over the horizon time.

constraints:

$$\text{CF}_{k,t} = \text{TP}_{k,t} - \text{TAX}_{k,t} + D_{k,t} \quad \forall\ k, t \tag{3}$$

The cash flows in eq 3 are computed as the total profit (TP) before tax minus taxes (TAX) and adding the depreciation of CI for each technology, which was obtained from eq 5 were dk_t is a fixed quota shown in Table 5. The total profit is obtained in eq 4 as sales revenue income (INC) minus variable costs

(CVAR) and fixed costs (CFIX) for each technology analyzed and time period.

$$\mathrm{TP}_{k,t} = \mathrm{INC}_{k,t} - \mathrm{CVAR}_{k,t} - \mathrm{CFIX}_{k,t} - D_{k,t} \quad \forall\, k, t \tag{4}$$

$$D_{k,t} = \mathrm{TCI}_k \times \mathrm{dk}_t \quad \forall\, k, t \tag{5}$$

The fixed costs are computed as a fixed factor (Tf, taken here to be 15%) times the sales revenue (eq 6). The variable costs are computed as raw material cost plus operative costs and transportation cost (eq 7) for each alternative analyzed and time period. The raw material cost is the raw material price times the amount of raw material used by each technology, depending on the capacity of the plant (eq 8). The operative costs (COP) were computed (eq 9) adding the energy consumption and water consumption contributions, (both per kilogram of raw material processed) times the plant capacity. Coefficients one and two (C_1 and C_2) are the energy and water consumption displayed in Table 2. The transportation cost CTRANS$_{k,t}$ is obtained with the equation proposed by Mele et al.[9] as a function of the distance between the factories and using the coefficients presented in Table 6.

$$\mathrm{CFIX}_{k,t} = \mathrm{Tf} \times \mathrm{INC}_{k,t} \quad \forall\, k, t \tag{6}$$

$$\mathrm{CVAR}_{k,t} = \mathrm{CRM}_{k,t} + \mathrm{CPO}_{k,t} + \mathrm{CTRANS}_{k,t} \quad \forall\, k, t \tag{7}$$

$$\mathrm{CRM}_{k,t} = \mathrm{PRM}_t \times \mathrm{CAP}_k \quad \forall\, k, t \tag{8}$$

$$\mathrm{COP}_{k,t} = C_1 \times \mathrm{CAP}_k + C_2 \times \mathrm{CAP}_k \quad \forall\, k, t \tag{9}$$

The sales revenue incomes (INC$_{k,t}$ were computed (eq 10) as the summation of the sales accounting each of the products delivered by each technology. The sales corresponding to each product are obtained (eq 11) as the amount produced prod$_{j,k,t}$ times its price.

$$\mathrm{INC}_{k,t} = \sum_j \mathrm{SALE}_{j,k,t} \quad \forall\, k, t \tag{10}$$

$$\mathrm{SALE}_{j,k,t} = \mathrm{prod}_{j,k,t} \times \mathrm{price}_{j,t} \quad \forall\, k, t \tag{11}$$

The tax was computed (eq 12) as a tax ratio (Tr) of 0.3[9] times the total profit TP$_{k,t}$. TAX$_{k,t}$ is applicable only for positive TP$_{k,t}$, so if PT$_{k,t}$ is positive, eq 13 imposes $V_{k,t} = 0$ and eq 12 holds; otherwise if TP$_{k,t}$ is negative, eq 14 assigns $V_{k,t} = 1$ and TAX$_{k,t}$ = 0.

$$\mathrm{TAX}_{k,t} \geq (\mathrm{Tr} \times \mathrm{TP}_{k,t}) - (V_{k,t}M) \quad \forall\, k, t \tag{12}$$

$$\mathrm{TP}_{k,t} \leq M(1 - V_{k,t}) \quad \forall\, k, t \tag{13}$$

$$\mathrm{TP}_{k,t} \geq -MV_{k,t} \quad \forall\, k, t \tag{14}$$

$$\mathrm{TAX}_{k,t} \geq 0 \quad \forall\, k, t \tag{15}$$

The plant capacity (eq 16) is selected by computing the binary variable $X_{p,k}$ times the plant size SIZE. The total production prod$_{j,k,t}$ of each product is computed (eq 17) as the capacity of the plant times a conversion factor $\delta_{k,j}$. The conversion factors are displayed in Figure 1, given as mass fractions of the raw material.

$$\mathrm{CAP}_k = \sum_p \mathrm{SIZE}_{p,k} \times X_{p,k} \quad \forall\, k \tag{16}$$

$$\mathrm{prod}_{j,k,t} = \mathrm{CAP}_k \times \delta_{k,j} \quad \forall\, j, k, t \tag{17}$$

The total capital investment was computed (eq 18) as the summation of individual capital investments depending on the plant size times the binary selection variable $X_{p,k}$. The production of carbon dioxide $\mathrm{CO}_{2(k,t)}$ was computed (eq 19) as an emission factor for thermal energy Fi$_k$ times the capacity of the plant and the energy consumption E_k for each process. For thermal energy we took into account that the refinery boilers are fed with wood, while for electric energy we assumed it was generated by natural gas fed power plants. Equations 20 and 21 are logical constraints for technology and plant size selection variables.

$$\mathrm{TCI}_k = \sum_p \mathrm{CI}_{p,k} \times X_{p,k} \quad \forall\, k \tag{18}$$

$$\mathrm{CO}_{2(k,t)} = \mathrm{CAP}_k \times E_k \times \mathrm{Fi}_k \quad \forall\, k, t \tag{19}$$

$$\sum_k Y_k = 1 \tag{20}$$

$$\sum_p X_{p,k} = Y_k \quad \forall\, k \tag{21}$$

4. STUDY CASE

Our study case is the disposition of DDO from a soybean oil refining factory located in the north of the Province of Santa Fe, Argentina. This plant processes 4500 tons of soybean oil per month, generating 100 tons per year of DDO residue, with an average composition of 9% tocopherols, 50% FFA, 17% sterol esters, and 24% oil.[24,5,1]

4.1. Technologies Taken into Account. *Technology 1: Hydrodistillation.* This technology works at the same temperature and pressure of the deodorization process, using the same steam and vacuum utilities (180 °C and 5 mmHg) of the oil refinery and requires a small investment cost: a distillation column and a partial condenser that returns the FFA. The effective relative volatility between FFA and tocopherols was taken from Winters.[6] The loss of product in the distillate fraction was specified to be 0.5%, and the content of FFA in the bottom product was specified to be 0.5%, i.e., the same figure as that allowed in refined edible oil. The sizing of the equipment was done following Faccioli et al.,[25] who optimized the reflux ratio and number of stages for this separation. The investment cost was estimated using Douglas[8] methodology updated with the Marshall & Swift index published by *Chemical Engineering* (see Appendix A).

Technologies 2 and 3: Molecular Distillation of One and Two stages. This technology was implemented with either a single module to separate FFA or with two modules, where the second one separates the oil from the lighter fraction which contains the mixture tocopherols−sterols. The process conditions were for the first (or single) module 110 °C and for the second 170 °C with a pressure of 10^{-2} mbar in both cases. The yields for each module were reported by Pramparo et al.[2] The investment costs and the consumption of energy and water were taken from a local constructor[19] and are reported in Appendix A.

Technology 4: Hydrodistillation followed by Molecular Distillation. Steam stripping to separate the FFA and molecular distillation to separate the oil fraction: the product obtained in technology 1 is the raw material for the molecular distillation.

This technology combination has an a priori high potential because it makes it possible to separate FFA more effectively (hydrodistillation is a multiple stages operation while molecular distillation implements a one separation stage) with a lower cost of investment than molecular distillation.

Technology 5: Esterification followed by Molecular Distillation. First the FFA is esterified with ethanol in acid medium, and afterward the esters are separated by molecular distillation. The working conditions were taken from Pramparo et al.[2] Investment cost for the esterification reactor was estimated using Douglas[8] methodology, and investment cost for molecular distillation was taken from a local constructor.[19]

Tecnology 6: Supercritical Fluid Extraction with CO_2. Tocopherols and sterol esters are extracted from DDO with supercritical CO_2. We adopted the working conditions reported by Chang et al.,[26] a temperature between 70 and 90 °C and a pressure of 31 MPa. Investment cost was estimated using the formula proposed by Lack et al.[23] for three extractors in series. The extractor size was computed with a ratio of solvent to feed of 14.2 as in the work of Vertero.[27]

Besides the six technological alternatives analyzed previously, two extra alternatives for DDO final disposition were considered, which do not include processing it. One (alternative 7) is using the DDO directly as boiler fuel in the same oil refining factory. And the other (alternative 8) is to sell the DDO to a vitamin E producing factory located 790 km far away from the oil refinery.

4.2. Level of Detail of Process Alternatives "Models" Used in This Screening. Following Douglas[8] the goal of preliminary design is to screen out undesirable projects quickly. If a project passes this initial screening, the material balances will be recalculated more rigorously at a later stage. For the technologies discussed here, the information available in the literature comes from quite different kind of "models", e.g., rigorous simulations[5,16] for molecular distillation, experimental studies for molecular distillation,[2,17] and supercritical extraction[20,21] and short cut models using constant relative volatilities[6,25] for hydrodistillation; in all cases the balances reported are a result of a process optimization, either numerical or experimental.

Figure 1 outlines the alternatives analyzed displaying the product yields obtained from the literature given as mass fractions, and with the composition of products presented in Table 1. Alternative 7 (DDO going to boiler fuel) and alternative 8 (selling DDO to another industry) do not involve processing: the DDO is sent to these destinations without modification. Products 1−5 in Figure 1 contain tocopherols; its concentration in each product is shown as mass percentage in Table 1, which also presents the prices taken here for each product.

The price of DDO as a raw material for tocopherols recovery is an updated estimation from a local constructor[18] \$600/(ton of DDO) with a minimum 5% tocopherols plus \$140/ton for each additional 1% tocopherols. The tocopherols in products prod1 and prod2 are higher priced than in DDO (these products lack FFA and the lower molecular weight components), which can be used in formulations where the oil content does not jeopardize the product such as in cosmetic creams or many foods. By the same token, the tocopherols in products prod3, prod4, and prod5 have the higher price as they also lack the heavy oil fraction, which enables new applications. Raw (not purified) FFA and FFA−oil fractions were priced as boiler fuel, according to their heats of combustion following Garbini.[28] FAEE (the not purified biodiesel product) was priced as a raw material for the biodiesel industry, taking an up to date reported local price.[29]

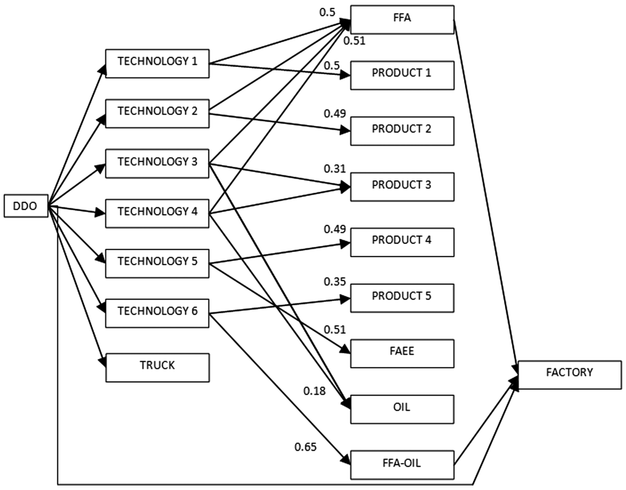

Figure 1. Alternatives analyzed, showing product yields obtained from the literature (technology 1, ref 6; technology 2, ref 5; technology 3, ref 16; technology 4, refs 6 and 16; technology 5, ref 2; technology 6, ref 26).

Table 1. Price and Tocopherols Composition (Mass %) of the Different Products

product	% tocopherols	price (\$/kg)
FFA		0.51
FAA-OIL		0.51
OIL		1.00
FAEE		1.099
DDO	9	4.00
product 1	18	10.80
product 2	19	11.40
product 3	32	19.20
product 4	33	19.80
product 5	40	24.00

The operating costs were estimated by performing energy and mass balances for each technology analyzed. For molecular distillation we used data from a local contractor company,[19] and for supercritical fluid extraction we used the data published by Brunner.[30] The operating costs taken into account were the consumption of energy and the consumption of cooling water, reported in Table 2 as consumptions per kilogram of DDO processed. The prices of energy and cooling water were \$0.07/kWh and \$0.01/(1000 L), respectively. Most of the large water consumption computed for molecular distillation is to condense the steam used in a four stages steam ejectors vacuum system, which is also responsible for the relatively large

Table 2. Energy and Cooling Water Consumption of Each Technology

technology	energy (kWh/(kg of DDO)	water (L/(kg of DDO))
technology 1	1.0	20
technology 2	2.0	500
technology 3	4.0	1000
technology 4	3.0	520
technology 5	2.8	504
technology 6	2.3	

energy consumption. Supercritical fluid extraction is also a large energy demanding technology due to CO_2 recompression.

We considered three plant capacities, corresponding to the minimum, medium, and maximum productions of DDO of oil refinery factories in this study case. These capacities are 108,000.0, 360,000.0, and 576,000.0 kg/year. We considered a production schedule of 300 working days/year, 24 h/day and a time horizon of 10 years.

For the computation of the environmental impact we took the greenhouse gas (GHG) emissions. This is the usually taken indicator in the technology selection literature as in Mele et al.[9] and Giarola et al.,[10] even if other authors such as Martin and Grossmann[14] choose computing energy and fresh water consumption. In our case the technologies analyzed do not generate polluting effluents but valuable byproducts or oily streams that can be safely burned in the oil refinery boiler. Also fresh water consumption is quite small, none uses process water but some consume (a small fraction) water makeup for the steam and cooling water facilities. The main difference among the technologies analyzed is their energy performance, i.e., uptake as heat, electricity, and transportation or delivery by burning a byproduct. All of these interactions with the environment can be added into the single GHG metrics using the factors reported by the U.S. Environmental Protection Agency.[31] These emission factors are shown in Table 3 and were used to consider burning the DDO (alternative 7), FFA and oily products (here encompassed by the term olefins), and wood (the presently used fuel at the refinery) in the factory boiler, fuel for transportation, and electricity (assumed to be produced from natural gas) consumed by each technology.

Table 3. Emission Factors Reported

source	emission factor (CO_2-equiv)
wood	1.44^{-3} kg of CO_2-equiv/kg
oleins	2.8 kg of CO_2-equiv/kg
gas oil	2.7 kg of CO_2-equiv/L
natural gas	5.45^{-2} kg of CO_2-equiv/(ft^3(STP))

Then, even if our case study is a specialty production with a relatively small (compared with the oil refinery) capacity and its contribution to global climate change will be minimal, GHG emissions were found to be an appropriate index to discriminate the alternatives considered here, based on their environmental performance.

Table 4 shows the capital investment CI required by each technology for each size analyzed; these values were obtained as shown in Appendix A. The Table highlights that the largest CI corresponds to technology 6, supercritical fluid extraction. Table 5 shows the evolution of cash flow and depreciation of CI, the latter during a period of 5 years at a rate of 20% as usually applied in the chemical industry. Table 6 shows the parameters valid for Argentina used to compute the transportation cost by truck in the alternative where the DDO is sold to a factory far from the oil refinery, to be used in the cost model presented by Mele et al.[9]

5. RESULTS ANALYSIS

The solution of the optimization problem as formulated in this work is given by a set of Pareto alternatives solution representing the optimal trade-off between the economic and environmental objectives considered. The Pareto solution is determined via the ε-constraint method[32,9] and considered six alternative processing methods at three production rates, plus two alternatives that do not process the DDO: it is sold to another industry or burned as boiler fuel in the same refinery. The results obtained are presented in Figure 2, which shows the selected technologies that exhibit the maximal NPV for a given interval of greenhouse gases emission. The technology that generates the largest NPV is $K = 5$, esterification plus molecular distillation, at the highest production capacity considered in our analysis. However, it is also the one that generates the highest environmental impact.

The left-hand side of Figure 2 only displays points corresponding to alternative 8, selling the DDO to a vitamin E production factory: the only GHG emissions involved in this alternative correspond to the fuel for transporting DDO which is smaller than in the alternatives that process it. The right-hand side displays two points corresponding to alternative 5, esterification plus molecular distillation at the higher production rates P2 and P3: the NPV at the larger plant capacities allow this technology entering into the optimal NPV vs GHG trade-off. Also technologies K1 hydrodistillation and K6 supercritical fluid extraction have points in the Pareto set, only at the larger production rate.

Several alternatives were discarded in the Pareto solution presented in Figure 2 because they have a lower NPV for the same CO_2 interval considered. Figure 3 displays the complete set of alternatives considered (all of the technologies analyzed, in the three studied production capacities) in the same NPV vs GHG coordinates graph used in Figure 2, which will permit one to get a broader insight into the trade-offs involved in this technology selection problem. The three points corresponding to the same alternative at different production capacities where connected by straight lines to facilitate the analysis and do not imply knowledge about the behavior of the two objectives between the points in the set.

Alternative 8, selling the DDO, renders the best environmental performance, while alternative 7, burning DDO, results in the worst one. The alternatives that process DDO lie between these extremes; they burn a fraction of the DDO processed: the FFA or FFA–oil byproducts produced by the separations. This outcome agrees with the intuitive perception that recycling materials as valuable products is the most environmentally friendly alternatives.

Alternative 5, esterification plus molecular distillation, is by far the most competitive in economic terms, but this conclusion depends strongly on the relative prices between pre-biodiesel (which was priced here as a valuable byproduct) and the FFA

Table 4. CI ($) Used As Data in the MILP Model for Each Technology and Size Analyzed

size	T1	T2	T3	T4	T5	T6
P1	10,000	120,000	160,800	130,000	145,000	2,600,000
P2	19,332	201,393	269,867	220,725	249,723	4,191,700
P3	27,300	250,000	335,000	277,300	318,255	4,812,700

Table 5. Value of df_t and dk_t for Each Time Period Utilized in the Model

time t (years)	1	2	3	4	5	6	7	8	9	10
df_t	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	0.42	0.39
dk_t	0.2	0.2	0.2	0.2	0.2					

Table 6. Parameters for the Computation of Transportation Cost

parameter of transportation	value
truck capacity (tons per trip)	20
average speed (km/h)	60
average fuel consumption (km/L)	5
fuel oil price ($/L)	0.85
driver wage ($/h)	10

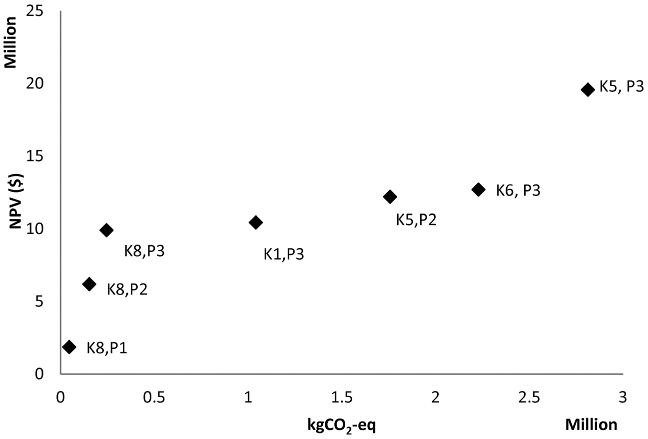

Figure 2. Pareto set of solutions considering the maximization of the economical objective NPV ($) and minimization of the GHG emissions measured as kilograms of CO_2-equiv: K = technology and P = size.

fraction (which was priced as a boiler fuel) produced by the other technologies. For example if FFA could be sold to a biodiesel factory (implementing the acid biodiesel process, such as, e.g., when using spent oil as raw material) at a higher price than boiler fuel, technology 5 would cease to be that competitive.

Leaving technology 5 aside from the analysis, we may draw some general conclusion about the other technologies from Figure 3: it can be noted that there is no significant difference between NPVs for different technologies at the same production capacities, but a significant difference does exist with respect to their CO_2 releases. This is valuable information for selecting a technology in the face of environmental policies.

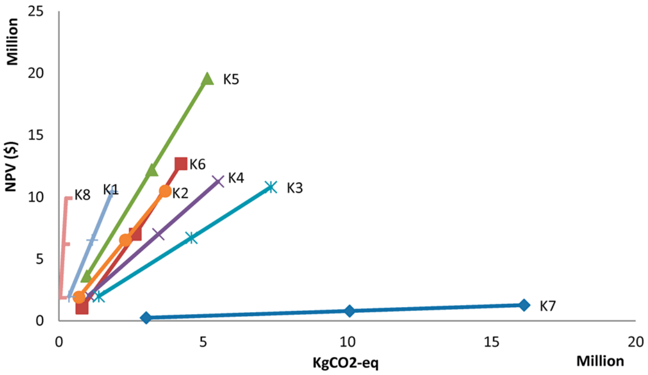

Figure 3. Analysis of all of the alternatives considered, in the three production capacities studied.

Another general conclusion is that the technologies that implement a one step separation for getting rid of the light FFA fraction (hydrodistillation and one stage molecular distillation) produce about the same economic revenue with less environmental impact than the technologies that implement a two steps separation (two stages molecular distillation and hydrodistillation plus molecular distillation) that also separate the heavy end oil fraction. This outcome could be interpreted as follows: a second separation increases environmental burden (associated with the energy required to perform it) without a significant economic reward. Technology 6, supercritical fluid extraction, is an intermediate case: it is a one step operation that concentrates the tocopherols−sterols fraction by separating it (dissolving it in the supercritical fluid) from both the FFA and oil fractions.

Again, this conclusion strongly depends on the price taken for the concentrated tocopherols product that lacks both the light and heavy ends: if this price were larger than that taken here, this conclusion should be revisited. In this case the second separation would have an economic reward and supercritical fluid extraction would have a good chance of being the technology of choice, because it is the one that performs the two separations in one step, generating less greenhouse gases than the technologies with two separation steps.

It should be noted that the products we are dealing with here are not shelf products but intermediate ones which are traded among companies. So, even if we were able to find price estimations for them, they are actually agreed among stakeholders and may be different from the prices listed in Table 1, depending on local conditions.

A disturbing (or at least uncomfortable) feature in Figure 3 is that, for every technology considered, the NPV shows an almost linear behavior with respect to the production capacity (CO_2 emissions are strictly proportional to production capacity), even if the capital investment CI is not linear with respect to plant size (see Figure 4 in Appendix A): the power law behavior of CI is almost not reflected in the NPV due to the large relative influence of the cash flow CF, which does have a linear dependence on production capacity.

6. CONCLUSION AND FURTHER WORK

The original goal of this work was to select the optimal technology for treating DDO to recover the valuable fraction of tocopherols while minimizing the environmental impact of the new process, but also to arrive at this target in an as systematic as possible decision procedure. This last objective is, we believe, the most general contribution of this work. We propose to do a screening of the alternatives presented in the literature by applying some criteria (proven economic feasibility in this case) to narrow the large number of them and resort to the hierarchical process design procedure of Douglas to check if it generates some extra promising alternative.

For the set of alternatives previously generated we perform the mass and energy balances, equipment sizing and costing needed to compute the economic NPV and environmental GHG performance indices. These data permit one to obtain a Pareto set of suboptimal solutions that provide information to adopt a both economically and environmentally sound choice of processing technology.

For the DDO processing case analyzed (with the economic data taken here, valid for this particular case), the technology that maximized the NPV was esterification of the FFA followed by separation through molecular distillation, at the largest production capacity.

A more comprehensive analysis of the whole set of alternatives considered gave a better insight into the trade-offs involved in this technology selection. The cash flow CF has a large relative influence in the NPV compared with the capital investment (CI) amortization, so technologies which produce about the same CF render about the same NPV. This occurs for example for K1, hydrodistillation, and K2, molecular distillation of one stage, and again for K3, molecular distillation two stages, and K4, hydrodistillation plus molecular distillation. The products that exit these processes are similar in amounts and compositions, yielding quite similar NPV.

There is no significant difference between NPVs for different technologies at the same production capacities, but a significant difference in their CO_2 releases: a two steps separation technology increases environmental burden (associated with the energy required to perform it) without a significant economic reward.

The products we are dealing with here are not shelf products but intermediate ones which are traded among companies. So, their prices are actually agreed among stakeholders and may differ widely depending on local conditions. So, the outcome about esterification plus molecular distillation being the optimal technology should not be taken as general, but be revised with the actual prices at hand. The methodology proposed for selecting a technology and the insights found on the trade-offs involved in this technology selection are, we believe, general.

Analyses as performed in this work may be a powerful tool for making decisions in industry: in the case study solved here alternative 7 that uses DDO as boiler fuel is the alternative presently implemented by the oil refinery, while the study shows that it is the worst choice from both the economical as well as environmental points of view.

As further work, we will consider the convenience of collecting DDO from several oil refineries, to be processed in a single plant, considering transportation costs and optimizing plant location.

■ APPENDIX A

The capital investment (CI) of each technology was estimated with independent nonlinear NLP models and the outcome figure fed as input data of the MILP model. The main features of these models are briefly described next, to illustrate the level of detail adopted for the analysis done in this work.

Technology 1

The capital investment for hydrodistillation corresponds to the column itself and a partial condenser that returns the FFA, letting go to the vacuum system the lighter organic components and steam. The facility lacks a boiler: it is fed at the bottom with live steam. This model was already used to optimize the reflux ratio and number of stages for the separation of FFA from heavier components in DDO by Faccioli et al.[25] and consists of a Fenske−Underwood−Gilliland distillation model plus a constraint accounting that the total pressure is given by the summation of the partial pressures of water and volatile organic components and incorporating water into the mass balances. Briefly summarized

$$N_m = \frac{\ln\left[\frac{\eta_l(1-\eta_h)}{\eta_h(1-\eta_l)}\right]}{\ln(\alpha_{l,h})} \quad (A1)$$

$$R_m = \frac{1}{(\alpha_{l,h}-1)}\left[\frac{\eta_l}{\eta_t} - \alpha_{l,h}\frac{\eta_h}{\eta_t}\right] \quad (A2)$$

$$H = 1.5 + (0.8N_m) \quad (A3)$$

$$D = (0.105(1.2R_m + 1))^{0.5} \quad (A4)$$

$$CI = ((M\&S) \times 4.7 \times (D)^{1.55} \times H \times 3.1) \quad (A5)$$

$$A = \frac{D_{FFA} \times CP \times \Delta T \times (1 + 1.2R_m)}{730\Delta T} \quad (A6)$$

$$CI = ((M\&S) \times 101.3 \times (A^{0.65}) \times 5.062) \quad (A7)$$

Equations A1 and A2 estimate the minimum number of stages and the reflux ratio as a function of the recoveries (moles in distillate per moles in feed) of the light key component, *l*, which was taken to be FFA and the heavy key component, *h*, which was taken to be tocopherols. These values are used to estimate the height, *H*, and diameter, *D*, of the column with eqs A3 and A4 which assume that the actual reflux ratio is 1.2 times the minimum and the number of stages is 2 times the minimum. Then, the CI of the column is estimated with eq A5 from Douglas[8] where *D* has an exponent of 1.55. Taking into account that the size of the column (its processing capacity) is proportional to D^2 (with *H* constant for the same separation), this means that the CI power law has a scale exponent of 0.775; eq A6 sizes the condenser and A7 estimates its CI again with Douglas[8] where the power law for CI as a function of the size (the area) is 0.65. The summation of the costs of both pieces of equipment gives the total CI for alternative 1, hydrodistillation, shown in Table 7. The model is used to optimize (in GAMS) the number of stages and reflux ratio specifying that the bottom product contained less than 0.5% FFA. The optimization results for a plant capacity of 108,000 kg/year DDO with a feed composition of 50% FFA, 9% tocopherols, 5% sterols, 15% sterols−esters, and 21% oil are shown in Table 7. The relative volatility values used were those published by Winters and Corp.[6]

Table 7. Sizing of the Hydrodistillation Facility for a Plant Capacity of 108,000 kg/year

D (m)	H (m)	N_m	R_m	A (m^2)	CI ($)
0.5	10	11	0.96	0.8	10,000

Technologies 2 and 3

For molecular distillation, the mass balances (yields and composition of products) were taken from either rigorous simulations[5,16] or experimental reports[2,17] from the literature, whose results very much agree after optimizing the feed flow rate. We didn't find a model for estimating CI in the literature, so took costs data from a local constructor[19] who reported a CI of $250,000 for a feed flow rate of 80 kg/h and CI of $120,000 for 15 kg/h. With these figures we calculated the power law exponent e to estimate the CI for other production capacities:

$$\frac{\mathrm{CI}_1}{\mathrm{CI}_2} = \left(\frac{\mathrm{CAP}_1}{\mathrm{CAP}_2}\right)^e \tag{A8}$$

Technology 4

Hydrodistillation followed by molecular distillation uses the mass balances and CI estimation approaches just described previously.

Technology 5

The material balances for the esterification were obtained following Pramparo et al.[2] with regard to reaction conditions: a temperature of 65 °C, atmospheric pressure, the acid medium, and the ratio of alcohol to raw material of 6.4 The reaction proceeds involving 1 mol of FFA/(per each mol of ethyl alcohol) with a conversion of 96% for a residence time of 1.5 h. The facility consists of a stirred vessel reactor sized with a geometrical ratio $H/D = 2$ plus an evaporator to vaporize the excess of ethyl alcohol and a condenser to return it to the liquid phase and cool to storage temperature.

The CI of the equipment were again obtained following the methodology of Douglas[8] and updated with the Marshall & Swift (M&S) index. The cost of heat exchangers is estimated with the same eq A7 while for the reactor we took the equation given by Douglas for pressure vessels:

$$\mathrm{CI} = (\mathrm{M\&S})(101.9 \times D^{1.066} \times H^{0.82} \times 3.1) \tag{A9}$$

The equations to perform the mass balances, equipment sizing, and estimation of CI were implemented as a NLP model in GAMS, which in this case has no degrees of freedom: no variable was optimized, but the reaction conditions recommended by Pramparo et al.[2] were taken as optimal. The summation of the CI costs of all pieces of equipment (reactor, evaporator, and condenser), plus the CI of one stage molecular distillation provides the total CI for alternative 5 presented in Table 4.

Technology 6

Capital investment for supercritical fluid extraction was estimated following Lack and Gamse[23] who consider three extractor tanks with 3 h extraction time each. The relation solvent to feedstock was 14.2 which determined the volume of the extractor. They propose eq A10 for estimating the capital investment:

$$\mathrm{CI} = 1.0163 \ln(V_T) - 4.9147 \tag{A10}$$

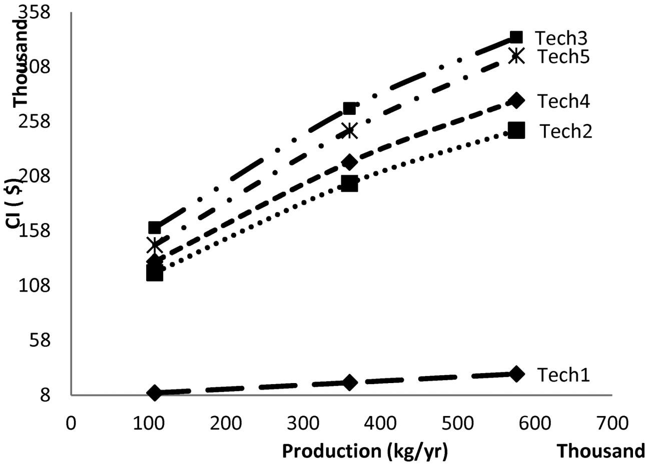

Figure 4. Investment cost vs production capacity of the technologies studied in this work.

Figure 4 presents the capital investment vs production capacity for all but one of the technologies studied; the CI of technology 6 is not presented because it overranges the other technologies (it is in the order of millions). In this figure it can be seen that technology 1 hydrodistillation has a marked difference with the others, being the least expensive. Technology 3 molecular distillation with two stages is the most expensive. In this figure it can be clearly seen that the capital investment vs plant size meets the typical power law form, for all the technologies analyzed.

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Notes

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NOTATION

Subscripts

j = product
k = technology
p = production capacity (kg/year)
t = time periods (years)

Parameters

$\delta_{k,j}$ mass fraction of feed converted into product j by technology k
$\mathrm{CI}_{p,k}$ capital investment required by technology k at plant capacity p (dollars)
E_k energy consumption by technology k [KWh/(kg of DDO)]
Fi_k emission factors for greenhouse gas computation (kg of CO_2-equiv)
PRM_k price of raw material k [dollars/(kg of DDO)]
$\mathrm{price}_{j,t}$ price of product j (dollars/kg)
$\mathrm{Size}_{p,k}$ plant capacity (kg/year)

Variable

A area of the condenser in the hydrodistillation (m^2)
CAP_k production capacity (kg/year)
$\mathrm{CF}_{k,t}$ cash flow (dollars/year)
CI cost of Investment of equipment (dollars)
$\mathrm{CO}_{2(k,t)}$ production of GHG by technology k in period t measured as kg of CO_2-equiv (kg/year)
D diameter of equipment (m)
D_{FFA} distillate flow of FFA in hydrodistillation (kg/h)
η_i recovery of component i moles in distillate/(mol in feed), $i = \{l,h\}$
H height of equipment [m]
N_{m} minimum number stages in the hydrodistillation
NPV net present value (dollars)
$\mathrm{prod}_{j,k,t}$ production rate of product j with technology k in time period t (kg/year)
R_{m} minimum reflux ratio in the hydrodistillation
TCI_k total capital investment (dollars)

$TCO_{2,k}$ total emission of greenhouse gases by technology k (kgof CO_2-equiv)

V_T total volume of the extractor in SCF and reactor in esterification (m^3)

Binary Variables

Y_k 1, if technology k is selected; 0, otherwise

$V_{k,t}$ 1, if taxation does not apply (negative income); 0, otherwise

$X_{p,k}$ 1, if size p is selected; 0, otherwise

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