FOOD AND BIOPRODUCTS PROCESSING 101 (2017) 177–183

Contents lists available at ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Selection among alternative processes for the disposal of soapstock

Daniela S. Laoretani*, **Carlos D. Fischer**, **Oscar A. Iribarren**

Instituto de Desarrollo y Diseño INGAR, UTN - CONICET, Avellaneda 3657, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form 5 October 2016
Accepted 31 October 2016
Available online 9 November 2016

Keywords:
Selection from alternative processes
Soapstock disposal
Process design

ABSTRACT

In this work a model is proposed to select among process alternatives that take soapstock as raw material, with the aim of maximizing economical performance, as well as disposing soapstock in an environmentally conscious way. This aim has been approached in previous literature using the traditional source-sink methodology that splits streams (with the same composition). In the present work, mass sources are connected with mass sinks through alternative "operators" (processes) whose exit streams are of different compositions. A superstructure is constructed that embeds economically feasible processes proposed in the literature, that produce intermediate goods salable to other factories or that can be recycled to the same refinery.

The optimal solution for our case study was the selection of a process to obtain pre-soap to be sold to a neighbor factory that produces industrial detergents. Afterward, the price of pre-soap was halved, pretending that the closest detergent factory is located way far from the refinery. In this case, the model selects a process that separates oil to be recycled to the refining process, and FFAs to be used as fuel in the same refinery. Thus, the optimal solutions found are valid for the particular case studied, while the main contribution of this paper is the approach proposed to make a decision.

1. Introduction

The soapstock is a by-product of the edible oil refining industry, which is generated in large quantity and contains a significant amount of free fatty acids (FFAs). This residue amounts to a 5–6%, or in some cases up till 20%, of the crude oil to be refined (Woerfel, 1983; Hass, 2005). The soapstock is generated when adding a solution of sodium hydroxide to neutralize the FFAs present in the crude oil. Its composition is a function of the type of oil and of the operating conditions of the refining. It consists in an aqueous emulsion of lipids due to the presence of soap. This stream is an important trouble for the refining industry if disposed as a residue due to its high organic load: about a 50% is lipid compounds.

There are many proposals published with the aim of adding value to the soapstock, while simultaneously reducing the oil refinery effluents. The process most widely adopted is for obtaining acid oil (Dorsa, 2008; Woerfel 1994, 1983;Tood and Morren, 1965). This process is easy to implement and obtains as primary product acid oil, a very versatile product, and acid wastewater which is easy to biodegrade after pH adjustment. Acid oil can be used as a feedstock for animal feed (Dumont and Narine, 2007; Haslenda and Jamaludin, 2011), as a raw material for the production of biodiesel (Hass, 2005; Li et al., 2010), or can also be used as boiler fuel. Rajkumar et al. (2010) too consider processing of soapstock with a strong acid for producing acid oil and do an economic assessment of acid wastewater treatment to minimize its environmental impact.

On the other hand in recent years there has been a boom in the manufacture of biodiesel, for which soapstock can be considered an attractive and economical raw material because it contains a large amount of FFAs (Atadashi et al., 2012; Keskin et al., 2008). Another alternative for processing soapstock is to obtain industrial soaps. In this case, the soapstock is a cheap raw material but the product obtained is not of very good quality. The quality of soap is a function of properties of the FFAs as the carbon chain length and unsaturation (Woerfel, 1994; Dorsa, 2008).

Besides the industrial processes already mentioned, there is a variety of possible processes with soapstock as raw material, which involve

* *Corresponding author.*
E-mail address: danielalaoretani@hotmail.com (D.S. Laoretani).
http://dx.doi.org/10.1016/j.fbp.2016.10.015

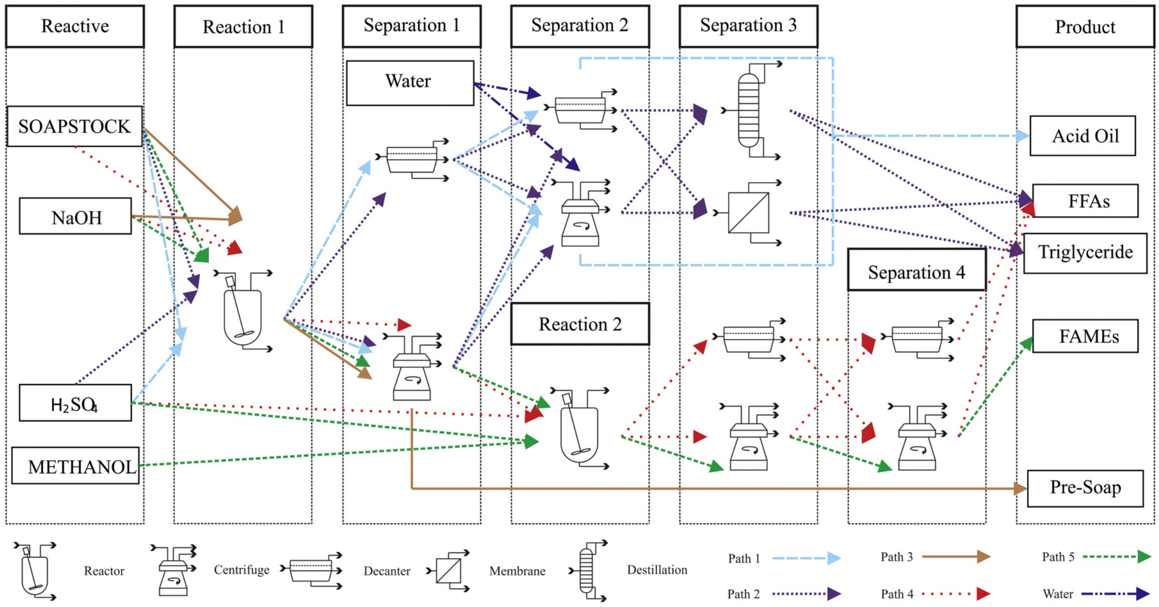

Fig. 1 – Alternative processes for the disposal of soapstock.

e.g. biological processes, solvent extractions, separating specific FFAs, the production of edible films used as a semi permeable covering in fresh produce such as peppers, apples and tomatoes to prolong its shelf life (Kuk and Ballew, 1999; Beaulieua et al., 2009) among many other options, but their economic viability in most cases remains unproven.

With respect to formulating the selection problem as a Mixed Integer Non Linear Program MINLP, the work of Haslenda and Jamaludin (2011) also takes this approach to solve the problem of selecting the destination of wastes from palm oil refining. These authors analyzed the destination of three residues: soapstock, deodorization distillate and spent bleaching earth and four sinks that admit limited amounts of these sources: animal feed, biodiesel, lubricant and soap industries. They do not select among process alternatives yielding different products, but considered mass sources splitters that render streams with the same composition as the mass source. Our approach here will be more complex: connect a mass source (soapstock) with different mass sinks (products) through alternative "operators" (processes) that render exiting streams with different composition than the inlet stream, as proposed by Fischer and Iribarren (2011).

The objective in the present work is deciding between different alternative processes (consisting of chemical reactions and separation operations) for the treatment of soapstock of soybean oil, rendering not yet shelf products but streams processable by other industries without a pretreatment.

The rest of this work is organized as follows. Section 2 presents a more in detail description of the problem to be solved. Section 3 describes the mathematical MINLP model. Section 4 presents the case study: the figures used for the parameters of the mathematical model (feed flow rate and composition, the cost of utilities, products prices). Section 5 presents and discusses the results for this base case, while Section 6 redoes the calculations in a scenario different than the base case, because one product changed its price. This section is intended to show the sensitivity of the optimal solution to changes in the model parameters. Finally Section 7 presents a general discussion and draws the conclusions of this paper.

2. Description of the problem

The problem to be solved can be stated as selecting the optimal processing route, from a process superstructure (shown in Fig. 1) that embeds the processing alternatives reported in the literature that were found most appealing: those that have been technically proven and were once assessed economically attractive, so that they reached industrial implementation. The alternatives analyzed involve the use of soapstock as feedstock to produce acid oil, free fatty acids (FFAs), fatty acids methyl esters FAMEs (a pre-biodiesel product) and pre-soap, where "pre" means able to be sold to industries that produce the "final" product.

They involve chemical reactions: either total saponification with sodium hydroxide to convert the remaining oil in FFAs, acidification with sulfuric acid to free the fatty acids (or both). And separation unit operations: we considered the options centrifugation or settling tank for the separation of aqueous and oily phases, and membrane or hydro-distillation (steam stripping) for the separation of free fatty acids from triglycerides. FFAs can be destined for food formulations: for animals but also for human diet e.g. soybean fatty acids are rich in linoleic acid. The destination of triglycerides is to return to the edible oil refining process. Following, we describe separately each of the five alternative processing routes considered.

2.1. *Acidification for the production of acid oil (Path 1 in Fig. 1)*

In this process, the sodium salts are converted back to free fatty acids with the addition of a strong acid. This breaks the emulsion and thus, the aqueous phase can be separated easier. Here we used sulfuric acid in a 10% weight/weight ratio of acid to soapstock and allow a reaction time of 4 h (Tood and Morren, 1965). After the aqueous phase is separated, the final product is a mixture of free fatty acids and triglycerides called acid oil. Two alternative equipments were considered to separate the phases: centrifuge and decanter (a settling vessel). The efficiency of this process is highly influenced by the content of gums (phospholipids) in the soapstock which produce a high degree of emulsification, in this case only the centrifuge will do the job. Otherwise, the centrifuge is not attractive because of its higher cost, especially considering the highly corrosive material to be treated (Woerfel, 1994). The settling vessel continues to be implemented in small and medium industries, since the cost is less and the material can be wood, stainless steel or reinforced plastic (Woerfel, 1994). After a first separation, the oily phase is washed with 25% water, and the phases are separated again.

2.2. *Acidification for the production of FFAs and triglycerides (Path 2 in Fig. 1)*

After obtaining acid oil with the process described in point 2.1, it was analyzed to separate in situ the free fatty acids from the triglycerides through either hydro-distillation or a membrane separation, which are unit operations also proposed for physical refining of the crude oil.

The difference in molecular sizes between fatty acids and triglycerides allows that membranes be effective to separate these components (Steffens et al., 2000). Several works propose crude oil deacidification via membrane, as an alternative to alkaline neutralization, among them Kumar and Bhowmick (1996), Hafidi et al. (2005), Kale et al. (1999), Raman et al. (1996). This alternative needs to incorporate a solvent to act as a carrier; in this case, it was considered the addition of methanol at a ratio of 25% of the feed flow entering the membrane. After membrane separation, evaporators and condensers are also needed to recover the methanol present in both the FFAs and oil streams.

In the case of hydro-distillation (steam stripping), the relative volatility between FFAs and triglycerides allows a good separation with the operative variables (temperature and pressure) normally used in the deodorization step of the oil refinery (Winters, 1994).

2.3. *Total saponification for the production of soap (Path 3 in Fig. 1)*

In this alternative process, a strong alkali is added with the objective of converting the mono, di and triglycerides too to sodium salt. First, this alternative was considered to obtain a feedstock for the production of soap as final product. The soap obtained has a lower price than if using bovine fat as feedstock (Dorsa, 2008; Haslenda and Jamaludin, 2011), but this alternative anyway fulfills our objective of adding value to the soapstock. Sodium hydroxide is added in a mass ratio of 10% of the soapstock and allowing a reaction time of 4 h (Hass, 2005; Keskin et al., 2008; Li et al., 2010; Pereda Marin et al., 2003). The reaction step is followed by phase separation to yield the aqueous soap product and an oily residual stream of unsaponificable compounds plus sodium salts. In this case, only centrifugation can be used for the separation, settling tanks are not adequate.

2.4. *Total saponification for the production of FFA (Path 4 in Fig. 1)*

After converting all the glycerides into sodium salts with the process described in point 2.3 the addition of a strong acid permits to recover the FFAs, which are an attractive feedstock for several processes (Frederick et al., 1955; Woerfel, 1994). Here sulfuric acid was used as in process 2.1 for producing acid oil. Thus, sodium sulfate is obtained as a precipitate and the emulsion is broken so the aqueous phase can be separated easier. This process has a higher yield in FFAs than the process described in point 2.2 while it does not produce triglycerides: it has two reaction steps but needs not the separation of FFAs from the oil.

2.5. *Total saponification for the production of FAMEs (Path 5 in Fig. 1)*

After obtaining the FFAs as in the process described in point 2.4 the addition of methanol in a ratio 70% of the feedstock in acid media (sulfuric acid 5% of the feedstock) and allowing a reaction time of 2 h (Pereda Marin et al., 2003) produces the esterification of FFAs that yields FAMEs. The next stages are separating the aqueous phase, washing with water and separating the aqueous phase again to eliminate the alcohols and acid which are soluble in water.

3. Mathematical models

To solve the problem described in the previous section, we developed a mathematical model: a mixed-integer nonlinear program (MINLP) with two levels of discrete decisions. The first level involves the selection of a product, while the second level of discrete decisions was for equipment selection. The model was implemented in GAMS 23.6 (General Algebraic Modeling System). The objective of the model was maximizing economic performance, assessed with Douglas (1988) index "Profit" through Eq. (1). The net profit is obtained as incomes from sales of products j ($Ing_{(j)}$) minus operative costs of process k for producing product j ($Op.c._{(k,j)}$) and annualized investment cost for buying the equipment involved in process k ($AIC_{(k)}$) as shown in Eq. (2).

$$Obj = Profit \tag{1}$$

$$Profit = Ing_{(j)} - Op.c._{(k,\,j)} - AIC_{(k)} \tag{2}$$

The sales revenue of product j ($Ing_{(j)}$) are obtained as the amount of product j produced in a year ($prod_{(j)}$) times its price ($Price_{(j)}$) in Eq. (3). Eq. (4), computes the operative cost of process k to produce product j ($Op.c._{(k,j)}$), as the summation of: the raw materials consumption to produce product j ($RM_{(j)}$), the utilities required by equipments eq to process product j ($Utility_{(eq,j)}$), the manpower consumption (Labor) and the cost for treatment of wastes generated by equipments eq to process product j ($TW_{(eq,j)}$), all these terms are computed on a 1 year basis. The annualized investment cost of process k ($AIC_{(k)}$) is computed in Eq. (5) as the summation of the costs $EC_{(eq)}$ of all the equipment involved in process k multiplied by a capital charge factor of 0.325. The investment costs of individual equipment were obtained following Douglas (1988).

$$Ing_{(j)} = \sum_{j} prod_{(j)} * Price_{(j)} \tag{3}$$

$$Op.c._{(k,j)} = RM_{(j)} + \sum_{eq} Utility_{(eq,j)} + Labor + TW_{(eq,j)} \tag{4}$$

$$AIC_{(k)} = \sum_{eq} EC_{(eq)} * 0.325 \tag{5}$$

The total and components mass balances are represented by Eqs. (6) and (7), where $Q_{(j)}$ is the mass flow rate of stream j (kg/h) and $W_{(i,j)}$ is the mass fraction of component i in stream j and the streams j belong either to $int_{(eq,j)}$ or $out_{(eq,j)}$ the sets of streams entering and exiting equipment eq respectively.

$L_{(r,i)}$ represents the generation by reaction of component i in reaction r.

$$\sum_{j \in ent(eq,j)} Q_{(j)} * W_{(i,j)} + L_{(r,i)} = \sum_{j \in sal(eq,j)} Q_{(j)} * W_{(i,j)} \; \forall (eq,i) \quad (6)$$

$$\sum_i W_{(i,j)} = 1 \forall (j) \quad (7)$$

Eqs. (8) and (9) represent the two levels of discrete decisions. Eq. (8) involves binary variables $Y_{(j)}$ that take the value 1 if stream j containing component i participates in reaction r, or 0 otherwise. The reaction $L_{(r,i)}$ takes place in the reaction equipment eq, $PM_{(i)}$ is the molecular weight of component i and $\mu_{(r,i)}$ is the conversion of component i in reaction r. Eq. (9) involves binary variables $X_{(eq)}$, that take the value 1 if the equipment eq is selected, or 0 otherwise. If the equipment is adopted, its cost $EC_{(eq)}$, is obtained as a function of its capacity cap raised to an exponent α and updated with the Marshall & Swift (M&S) index. The actual functional form of the expressions for computing the costs $EC_{(eq)}$ are shown in the Appendix A for every type of equipment involved in the model. The utility costs $Utility_{(eq,j)}$ exist if the equipment was selected and depend on the capacity multiplied by a cost factor $k_{(j)}$.

$$\bigvee_{r \in R_{(eq)}} \begin{bmatrix} Y_{(j)} \\ \sum_{i \in I_r} \frac{\mu_{(r,i)}}{PM_{(i)}} * L_{(r,i)} = 0 \\ L_{(r,i)} = 0 \forall i \notin I_r \end{bmatrix} \forall eq \in reactor \quad (8)$$

$$\begin{bmatrix} X_{(eq)} \\ EC_{(eq)} = cap_{(eq)}{}^{\alpha} * M\&S \\ Utility_{(eq,j)} = cap_{(eq)} * \kappa_{(j)} \end{bmatrix} \vee \begin{bmatrix} \neg X_{(eq)} \\ EC_{(eq)} = 0 \\ Utility_{(eq)} = 0 \end{bmatrix} \quad \forall (eq,j) \in ent \quad (9)$$

4. Case study

This section presents the figures fed as parameters to the model. The feed composition of soapstock was considered to be 50% water, 35% FFAs and 15% triglycerides and diglycerides (Atadashi et al., 2012). The flow rate of soapstock was 400 kg/h, taken from a local refining factory. The time horizon was 7200 h/year. The reagents employed were sulfuric acid, sodium hydroxide, and methanol for the etherification reaction. Table 1 presents their molecular weights and prices. The utilities required by the processes are water for washing stages, electric energy for reactor agitation and operating the centrifuges, and steam for the hydro-distillation. The other operating costs are manpower to operate the processes and wastes disposal. Their prices or costs are also shown in Table 1; the cost for treatment of wastewater was taken from Rajkumar et al. (2010).

The products obtained from the alternative processes analyzed here are shown in Table 2 with their respective selling prices.

Table 1 – Molecular weight (MW) and price of reagents and raw material.

Reactive	MW (kg/kmol)	Price ($/kg)
Soapstock	–	0.06[a]
H_2SO_4	98.0	0.95[b]
NaOH	40.0	0.30[e]
Methanol	32.0	0.44[b]
Utility	**Price**	
Electric energy ($/KWh)	0.106[c]	
Steam ($/kg)	0.019[c]	
Operator ($/h)	10.0[d]	
Water ($/m^3)	0.048[c]	
Wastewater Treatment ($/m^3)	1.79[e]	

[a] Hass (2005).
[b] ICIS pricing (2014).
[c] Ulrich and Vasudevan (2006).
[d] Mele et al. (2011).
[e] Rajkumar et al. (2010).

Table 2 – Price of products involved in analysis model.

Product	Price ($/kg)
Acid oil	0.30[c]
FAMEs	0.90[a]
FFAs	0.60
Triglycerides	0.41[b]
Pre-soap	0.40[d]

[a] Secretaria de Energía Rep. Argentina.
[b] SAGPyA.
[c] Local industry.
[d] Vaso et al. (2010).

Table 3 – Mass balances with compositions in mass fraction for the optimal process.

	Flow rate (Kg/h)	Water	FAS	Trig	NaHO	Glyc
F1	400.00	0.5	0.35	0.15	–	–
F2	40.00	–	–	–	1.0	
F3	440.00	0.45	0.46	–	0.07	0.01
F4	201.99	0.04	0.96	–	–	–
F5	238.01	0.84	–	–	0.13	0.03

FAS: sodium salt of fatty acids, Trig: triglyceride, Glyc: glycerin.

5. Results for the case study

For this case study, the model predicts that the optimal process is the one that obtains pre-soap. As shown in Fig. 2, the optimal process equipments are just a reactor and a centrifuge; this process did not have optional separation equipment: the centrifuge is necessary to break the emulsion while the decanter tank cannot manage this job.

Table 3 displays the mass balances for this process. Stream F5 is a process effluent as shown in Fig. 2. It was considered that it is not worth to recover the glycerin.

Table 4 shows the size and investment costs of the equipment involved in the process. Also, the annualized investment cost $AIC_{(k)}$ is shown, which has units $/year. The reactor has a diameter of 1 m and a height of 3 m and is made of stainless steel due to handling a caustic solution. The centrifuge was sized to process stream F3, this flow does not demand a large centrifuge. The total investment cost is $ 40,343, this small figure is an attractive feature of this simple process.

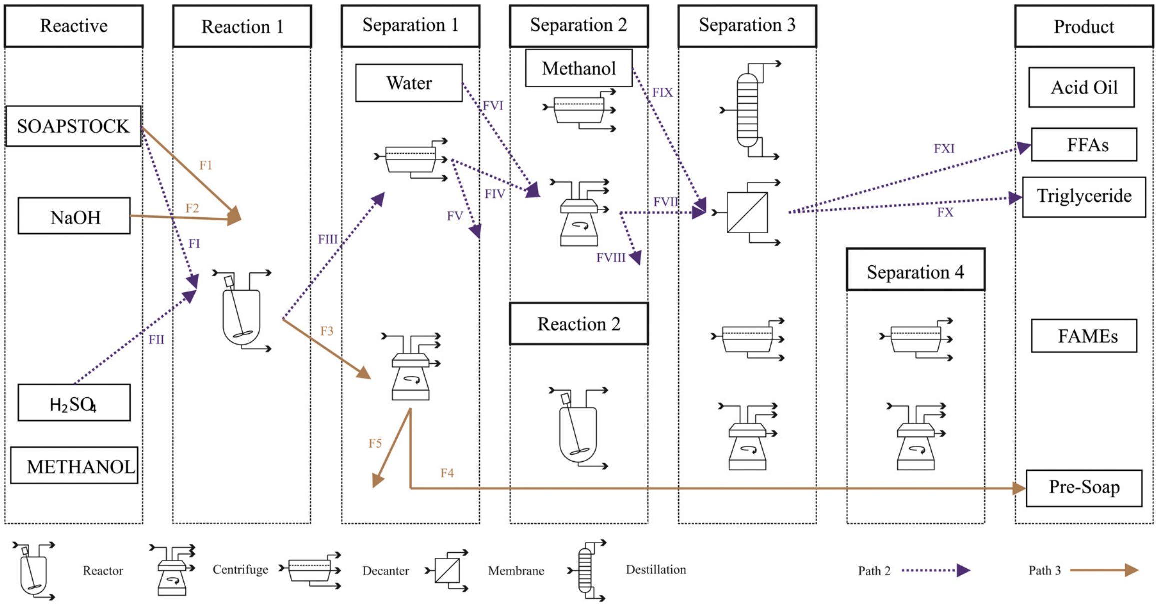

Fig. 2 – Optimal processes for the treatment to soapstock, depending on the prices scenario.

Table 4 – Size and cost of the equipment involved in the process.

Equipment	Size	$EC_{(eq)}$ ($)
Reactor	1.95 m^3	29,858.0
Centrifuge	0.12 hp	10,485.0
$AIC_{(k)}$	–	13,111.47

Table 5 – Operative Costs for Process 1.

Component of cost	Process 1
Electric Energy ($/year)	915
Raw material ($/year)	259,200
Cost of reagents ($/year)	156,040
Cost for wastewater treatment ($/year)	3068
Labor ($/year)	72,000
Total operative cost ($/year)	**491,223**

Table 5 shows the operative costs of the process. It can be seen that the higher costs are associated with the raw material and reagents. The labor cost considers one operator. The cost involved in treating the process waste is not that large and enables compliance with mandatory environmental regulations.

Table 6 shows the economic assessment of the process. There is a large positive income by sales of an annual production of 1,454,400 kg of pre-soap, even if this product is not high priced. The next figure is the raw material which is the same for all processes, and then reagents. That this process is the optimal makes sense: besides having a low investment cost, the price of sodium hydroxide is lower than sulfuric acid. The total investment capital is recovered in six months; a quite attractive result.

Table 6 – Economic assessment of the pre-soap process.

Economic component	Value
Product	PRE-SOAP
Sales revenue ($Ing_{(j)}$) ($/year)	581,510.
Operative cost ($Op.c._{(k,j)}$) ($/year)	491,223.
Annualized investment cost ($/year)	13,111.
Profit (/year)	**77,176.**

6. Scenarios with other product price

After the results obtained in the case study it was decided to analyze the effect of the variation of the selling price of the product, to find out the sensitivity of the optimal solution to changes in the model parameters. Pre-soap is not a shelf product, but an intermediate one which is traded among companies. So, its price is actually agreed among stakeholders

Table 7 – Mass balances with compositions in mass fraction for the FFAs process.

	Flow rate (Kg/h)	Water	FFS	Trig	Acid	FFAs	Solid	Methanol
FI	400.00	0.5	0.35	0.15	–	–	–	–
FII	40.0	–	–	–	1.0	–	–	–
FIII	440.0	0.45	–	0.14	0.04	0.29	0.08	–
FIV	189.77	–	–	0.32	–	0.68	–	–
FV	250.23	0.80	–	–	0.07	–	0.13	–
FVI	47.44	1.0	–	–	–	–	–	–
FVII	189.76	–	–	0.32	–	0.68	–	–
FVIII	47.44	1.0	–	–	–	–	–	–
FIX	47.44	–	–	–	–	–	–	1.0
FX	60.0	–	–	1.0	–	–	–	–
FXI	177.21	–	–	–	–	0.73	–	0.27

FFS: sodium salts of fatty acids, Trig: triglyceride, Solid: sodium sulfate.

Table 8 – Size and cost for equipment involved in the FFAs process.

Equipment	Size	$EC_{(eq)}$ ($)
Reactor	$1.95\,m^3$	29,859
Decanter tank	$2.93\,m^3$	10,334
Centrifuge	0.063 hP	4,525.4
Membrane	$3.93\,m^2$	2,165.9
Evaporator	$0.25\,m^2$	3,862.2
Condenser	$0.1\,m^2$	2,096.85
$AIC_{(k)}$	–	17,173.81

Table 9 – Economic evaluation of the FFAs process.

Economic component	Value
Product	FFAs and triglyceride
Sales revenue ($Ing_{(j)}$) ($/year)	737,720
Operative cost ($Op.c._{(k,j)}$) ($/year)	700,710
Annualized investment cost ($/year)	17,173.81
Profit ($/year)	**19,836.15**

and may differ widely depending on local conditions, e.g. the distance between the factories.

It was analyzed if a reduction of 50% in the price of pre-soap changes the selection of product and process. Taking a price for pre-soap of 0.20 $/kg, the result is the selection of the process to obtain FFAs and Triglyceride, with membrane equipment (Path 2 in Fig. 2). The mass balances for this process are shown in Table 7. The process involves acid reaction of soapstock with sulfuric acid (stream FII). In this case, the product obtained is FFAs (stream FXI) and triglycerides (stream FX). The oil is returned to the refining process and the FFAs used as fuel in the boiler of the same refinery. Methanol is used as carrier in the membrane operation (stream FIX), recovered by evaporation and recycled.

Table 8 displays the sizes and investment costs of the equipment. It includes the methanol evaporator and condenser, which are not shown in Fig. 2. In the first separation stage the MINLP selected a decanter tank while in the second separation stage it selected a centrifuge. This may be because while in both cases the size is proportional to the feed flow rate, the cost of the centrifuge is a function of its size raised to a much larger exponent than in the settling tank (see the Appendix A) and the feed flow rate in the second separation stage is lower.

The $AIC_{(k)}$ is larger than in the previous process because it involves a larger number of equipments. This jeopardizes the economic performance resulting in a lower profit, as shown in Table 9. The income from product sales is largest because the price of the product is largest in comparison with soap but the operative cost is also larger.

7. Discussion and conclusions

This work analyzed several process alternatives that obtain different products from soapstock as raw material. The objective was to select the alternative that maximizes the economical performance of the oil refinery, as well as solving the problem of disposing soapstock in an environmentally conscious way.

A superstructure was constructed that embeds different processes (proposed in the literature, with proven economic feasibility) which take soapstock as raw material to produce intermediate products salable to other factories. This MINLP model was implemented in GAMS to optimize the objective function "Profit" proposed by Douglas (1988). The optimal solution for our case study (data from a local soybean oil refinery) was the selection of the process to obtain pre-soap to be sold to a factory located in the same industrial park that produces industrial detergents. This company can convert pre-soap into the final product, with low processing costs and minimal raw material transport cost.

Afterwards we cut to half the price of pre-soap, pretending that this neighbor factory did not exist (if the closest detergent factory is located way far from the refinery, the price must be lowered to allow transportation cost), to show the sensitivity of the optimal solution to changes in the model parameters. Now the model selects as optimal the process that performs an acid reaction of soapstock for producing triglycerides and FFAs: the oil is returned to the refining process and FFAs is used as fuel in the boiler of the same refinery.

Thus, the main contribution of this paper is not the optimal solution found, which is valid only for the case study (the local factory), but the approach proposed to make a decision about the destination of soapstock. The same approach should also be useful to make future decisions (if market conditions change or new processing routes are available), to maintain the competitiveness of the refinery.

This work pursues the same basic idea of Haslenda and Jamaludin (2011) in the sense of generating an industry to industry by-products exchange, towards maximizing profit while minimizing environmental impact. The difference reside in the approach: these authors used the traditional source-sink model that just splits streams (retaining the same composition), while in the present paper mass sources are connected with mass sinks through alternative "operators" (processes) that render exit streams of different composition than the inlet stream, as proposed in Fischer and Iribarren (2011). Besides, in the present approach, the destination of the products may be the same factory, as happened in the case when the optimal process was for producing FFAs and triglycerides.

The process alternatives included in the superstructure in all cases consider a cost of treatment of effluents to achieve proper final disposal. The membrane technology used a solvent as carrier, but it is recovered and recycled to the process. The hydro-distillation consumes steam and thus generates condensed water, and also the water contained in the soapstock exits the processes as a residue. The biggest concerns about the processes analyzed here are the aqueous output streams: after correcting the pH of these streams, they can be treated easily to avoid damaging the environment.

Acknowledgements

We acknowledge financial support from Consejo Nacional de Investigaciones Científicas y Técnicas through Grant PIP 0688 for the Project "Optimization of Supply Chains in Biorefineries".

Appendix A.

The expressions to predict equipment capital costs $EC_{(eq)}$ are shown below, most of them were taken from Douglas (1988), but Eq. (A3) for the centrifuge was taken from Perry and Chilton (1973), and for the membrane modules we used the linear expression A5. In all cases, we used M&S the Marshall and Swift index published by Chemical Engineering Journal to update the prices. $D_{(eq)}$ [ft] and $H_{(eq)}$ [ft] are the diameter and height of vertical vessels. These were computed for the reactors with the feed flow rate and residence (reaction) time and for the distillation column considering 2 times the minimum number of stages and 1.2 times the minimum reflux ratio to perform the separation. In Eq. (A2), the bulk volume [m^3] of the settling tank was obtained computing the area necessary to perform the phase separation and a height of 1.5 m. In Eq. (A3), the $EC_{(eq)}$ is a function of the power $PW_{(eq)}$ [hp] necessary to process the inlet flow rate [gal/min]. In Eq. (A4), the area $A_{(eq)}$ [m^2] was obtained from the permeate flow rate and the price of the membrane module *Pricemem* [$/$m^2$] is 500 $/$m^2$ (already updated). In Eq. (A5), the factor Fc considers the material of construction and the working pressure.

$$EC_{(eq)} = M\&S * \left(101.9 * D_{(eq)}{}^{1.066} * H_{(eq)}{}^{0.82} * 3.1\right) \quad \text{Pressure vessels (Reactors)} \tag{A1}$$

$$EC_{(eq)} = M\&S * 190 * Bulk_{(eq)}{}^{0.5} \quad \text{Settling tanks (Decanters)} \tag{A2}$$

$$EC_{(eq)} = M\&S * \left(5200 * PW_{(eq)}{}^{0.68}\right) \quad \text{Centrifuges} \tag{A3}$$

$$EC_{(eq)} = A_{(eq)} \cdot Pricemem \quad \text{Membrane Modules} \tag{A4}$$

$$EC_{(eq)} = M\&S * 4.7 * D_{(eq)}{}^{1.55} * H_{(eq)} * Fc \quad \text{Distillation Column} \tag{A5}$$

References

Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R., Sulaiman, N.M.N., 2012. Production of biodiesel using high free fatty acid feedstocks. Renew. Sustain. Energy Rev. 16, 3275–3285.

Beaulieua, J.C., Parkb, H.S., Ballew Mimsa, A.G., Kuka, M.S., 2009. Extension of green bell pepper shelf life using oilseed-derived lipid films from soapstock. Ind. Crops Prod. 30, 271–275.

Douglas, James M., 1988. Conceptual Design of Chemical Processes. McGraw Hill, New York.

Desdoblamiento de las borras obtenidas en el proceso de neutralización de aceites vegetales. Aceites y Grasas. 2008, 71. XVIII, 2, 260–263.

Dumont, M.-J., Narine, S.S., 2007. Soapstock and deodorizer distillates from North American vegetable oils: review on their characterization, extraction and utilization. Food Res. Int. 40, 957–974.

Fischer, C.D., Iribarren, O.A., 2011. Synthesis of a mass integrated biodiesel process. Ind. Eng. Chem. Res. 50 (11), 6849–6859.

Frederick Jr., W.K., Vincent, G.B., Fred, H.S., 1955. Continuous purification and acidulation of vegetable oil soapstock. AOCS 32, 517–519.

Hafidi, A., Pioch, D., Ajana, H., 2005. Membrane-based simultaneous degumming and deacidification of vegetable oils. Innov. Food Sci. Emerg. Technol. 6, 203–212.

Haslenda, H., Jamaludin, M.Z., 2011. Industry to industry by-products exchange network towards zero waste in palmoil refining processes. Resour. Conserv. Recycl. 55, 713.

Hass, M.J., 2005. Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. Fuel Process. Technol. 86, 1087–1096.

ICIS pricing, http://www.icis.com/ 10th January 2014 report.

Kale, V., Katikaneni, S.P.R., Cheryan, M., 1999. Deacidifying rice bran oil by solvent extraction and membrane technology. JAOCS 76, 723–727.

Keskin, A., Gü rü, M., Altiparmak, D., Aydin, K., 2008. Using of cotton oil soapstock biodiesel–diesel fuel blends as an alternative diesel fuel. Renew. Energy 33, 553–557.

Kuk, M.S., Ballew, A.G., 1999. The potential of soapstock-derived film: cottonseed and safflower. JAOCS 76, 1387–1392.

Kumar, K.N.S., Bhowmick, 1996. Separation of fatty acids/triacylglycerol by membranes. JAOCS 73, 399.

Li, Y., Zhang, X., Sun, L., 2010. Fatty acid methyl esters from soapstocks with potential use as biodiesel. Energy Convers. Manage. 51, 2307–2311.

Mele, F.D., Kostin, Andrew M., Guillen-Gosalbez, G., Jimenez, L., 2011. Multiobjective model for more sustainable fuel supply chains. A case study of the sugar cane industry in Argentina. Ind. Eng. Chem. Res. 50, 4939–4958.

Perry, R.H., Chilton, C.H., 1973. Chem. Eng. Handbook, 5th edition. McGraw-Hill.

Pereda Marin, J., Barriga Mateos, F., Alvarez Mateos, P., 2003. Aprovechamiento de las oleinas residuales del proceso de refinado de los aceites vegetales comestibles para la industria del biodiesel. Grasas y aceites 54, 130–137.

Rajkumar, K., Muthukumar, M., Sivakumar, R., 2010. Novel approach for the treatment and recycle of wastewater from soya edible oil refinery industry—an economic perspective. Resour. Conserv. Recycl. 54, 752–758.

Raman, L.P., Cheryan, M., Rajagopalan, N., 1996. Deacidification of soybeanoil by membrane technology. JAOCS 73, 219–224.

Secretaria de Energía 20/03/2013. http://energia3.mecon.gov.ar/home/.

Steffens, M.A., Fraga, E.S., Bogle, E.S., 2000. Synthesis of bioprocesses using physical properties data. Biotechnol. Bioeng. 68, 218–230.

Tood, D.B., Morren, J.E., 1965. Continuous soaptock acidulation. Am. Oil Chem. Soc. 42, 172A–178A.

Ulrich, G.D., Vasudevan, P.T., 2006. How to estimate utility costs. Chem. Eng. (April), 66–69.

Vaso, K., Dema, M., Marku, J., 2010. Production of the anionic surfactant from soapstock of sunflower oil. Nat. Montenegrina, 773–783.

Winters, Robert L., 1994. Valor y utilización de los destilados del proceso de desodorización en el procesamiento de aceites comestibles Aceites y Grasas –54.

Woerfel, J.B., 1983. Alternatives for processing of soapstock. JAOCS 60 (2), 262A–265A.

Woerfel, J.B., 1994. Alternativas para el procesamiento y utilización de las borras de neutralización. Aceites y Grasas, 66–73.