Study of degumming and neutralization units

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Abstract

The purpose of this work was the study of the pre-treatment processes of vegetable oils existing in Iberol to produce biodiesel (the water degumming step and the chemical degumming and neutralization unit), to identify factors that could be improved and suggest hypotheses of optimization.

To meet this objective:

(i) The historical data of degumming and neutralization unit have been analyzed;
(ii) Experiments were conducted in the water degumming step;
(iii) Laboratory experiments of water degumming and chemical degumming and neutralization were made.

In these experiments the influence of various process parameters was analyzed:

(i) On the degummed oil loss and efficiency of degumming in the case of water degumming;
(ii) On the losses of neutral oil and the final parameters of the oil (acidity, phosphorus and soaps) in case of the degumming and neutralization unit.

It was concluded that it is advisable to install a heat exchanger for cooling the oil before water degumming, which it is anticipated to promote an income of 120.093 euros/year. The preferable investment was estimated to be 3.711 euros, by resorting to existing equipments in storage (three shell and tube heat exchangers, arranged in series with the power needed for desired oil cooling), with a "payback" time of about 1 month of operation, so this can be economically viable.

Keywords: vegetable oil, water degumming, chemical degumming, neutralization

1. Introduction

Water degumming involves mixing hot water with the oil at 70 to 80ºC, followed by a centrifugation step, which allows the removal of gums, constituted by water, hydratable phosphatides and other impurities. This process significantly reduces oil losses in the next process, alkali refining (degumming and neutralization unit), since phosphatides potentiate the formation of emulsions.

Degumming and neutralization unit allows the removal of non-hydratable phosphatides and free fatty acids present in the oil. The oil is preheated up to 75ºC and then phosphoric acid is mixed for conditioning of non-hydratable

phosphatides to a hydratable form. The extent of reaction is promoted for 5 minutes in a holding tank. Then, a caustic soda solution is added through a static mixer, which allows the neutralization of free fatty acids. Simultaneously, hot water is added to promote phosphatides agglomeration, which occurs after in a slow stirring tank for 30 minutes. The mixture is then heated and separated in a first centrifugation step. Neutral oil is obtained as light phase and "soapstock" as heavy phase, which contains phosphatides and soaps formed during neutralization step. The neutral oil still has a high content of soaps, for what is performed a washing step by adding a solution of citric acid. The soapy wash water is separated by centrifugation and neutral oil is vacuum dried.

2. Experimental procedures

Several types of experiments were performed and these require some laboratory tests of the oil:

- Free fatty acids content;
- Moisture (by Karl-Fischer method);
- Soap content;
- Phosphorus content (by ICP).

Three experiments were performed in water degumming facility. In the first, the process was monitored for six days. Changes in water flow were imposed and their values were recorded, as well as the values of oil flow and degumming temperature, once per shift. Furthermore, samples of crude oil before entering degumming process and dry degummed oil were taken for phosphorus content analyses.

In a second experiment, the flow of gums was measured by collecting of these into a container, timing its filling time. These measures were done for different water flows so it was possible to see how water flow affects the flow of gums. Oil samples were taken immediately after the centrifugation for moisture analysis.

The third experiment was very similar to the previous one, but phosphorus content was analyzed in the centrifuge samples and in a crude oil sample taken before the experiment, in order to estimate the oil losses of the process.

Water degumming was also simulated at the laboratory with crude oil from the facility. Different kinds of trials were carried out: variation of water quantity, variation of water type, variation of temperature and variation of time of mixture. In these trials was used a hotplate with magnetic stirring Yellow Line Mag HS7, with numerical indication of speed from 0 to 6, with temperature sensor and a centrifuge *Ecco.*

Soybean oil was taken from water degumming facility for these trials, with a content of phosphorus of 522 ppm (temperature trials) and 583 ppm (remaining trials). Hot water was added to 25g of soybean oil at 75ºC and the mixture was done for 7 minutes. The mixture was then centrifuged for 10 minutes at 2200 rpm. The degummed oil produced was analyzed for phosphorus content.

Due to impossibility of conduction trials on degumming and neutralization unit, its parameters were analyzed using historical data of operation and the process was simulated at the laboratory. For that propose, degummed soybean oil produced in the facility was used (191 ppm of phosphorus, 0,83% of free fatty acids and 0,16% of moisture), as well as rapeseed oil (232 ppm of phosphorus, 2,53% of

free fatty acids and 0,11% of moisture) degummed at the laboratory from virgin oil stored at the facility. Each trial required 127 g of degummed oil and phosphoric acid, agglomeration water (distilled water) and wash water solution were added according to the specific consumptions of the plant. The caustic soda solution was added according to the amount of free fatty acids present in the oil plus the excess practiced at the plant.

The mixture steps were made with the same hotplate with magnetic stirring used on water degumming trials and with a kitchen blender *Moulinex Turbomix 2*. For these trials was important to know which agitation speed was possible to accomplish with these devices, therefore an estimation was performed using an optical tachometer with probe *TMO-T6 Maintenance Product*. The centrifugation steps were made with the same centrifuge used in water degumming trials at 2700 rpm for 10 minutes. On the neutral oil free fatty acids, moisture, soap content and phosphorus content were evaluated.

3. Results and discussion

3.1. Water degumming

Process monitoring

It was found that the operating temperature was 98°C rather than about 75°C, as would be suited for this process. This has the disadvantage of increasing the solubility of phosphatides in oil, which reduces degumming efficiency. Theoretically, soybean oil has about 90% hydratable phosphatides and in practice efficiencies were between 57,0 and 82,4%. Besides the high temperature, other factors may be detrimental to the process, such as a possible poor contact between oil and water and addition of water in inadequate amount.

Flow measurement of gums

As expected, there is a relation between the water added and the gums flow rate.

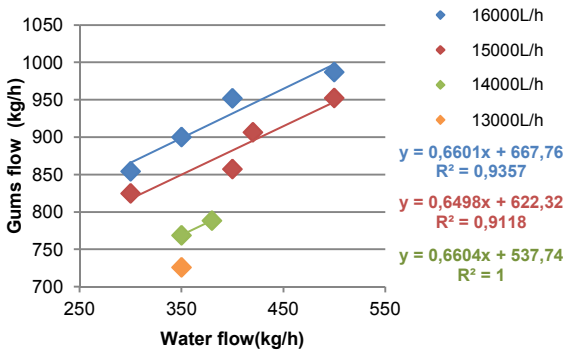

Figure 1 – Gums flow as function of water flow

Knowing the moisture content in degummed oil, the flow of gums in dry basis was obtained by material balance.

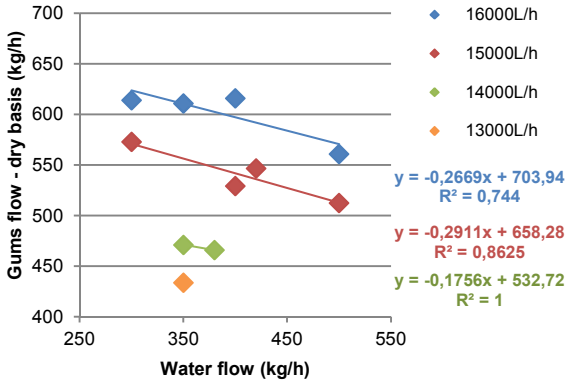

Figure 2 - Gums flow (dry basis) as function of water flow

Since the flow of gums in dry basis decreases as the water flow increases, it is noticeable that total losses will also decrease, but in the absence of phosphorus data, is not

possible to say if that decrease is due to less oil loss or due to a worse degumming.

Oil losses in water degumming

The same procedure was made, but phosphorus content was evaluated.

Table 1 – Results for degumming efficiency and losses

Oil (kg/h)	Water (kg/h)	Efficiency (%)	Total loss (%)	Oil loss (%)
13500	550	79,5	4,03	1,63
13500	500	81,1	4,20	1,76
13500	450	81,8	4,25	1,79
13500	350	82,2	4,49	2,01
12600	550	80,8	3,73	1,30
12600	500	81,2	3,83	1,39
12600	450	80,7	3,88	1,45
12600	350	78,9	4,13	1,75

Table 1 show that degumming efficiency is barely affected by water flow, so losses decrease with increasing water flow. In accordance with the literature [1] the oil losses should be 30% of total losses, which means 1,43 times the hydratable phosphatide content. As the crude oil contained 1005 ppm of phosphorus, the total loss should be 3,88% and 1,16% of oil loss.

Although water flows are greater than the theoretically necessary, it appears that in the range of flow rates tested, the greater the water flow, the lower are losses of the and lower is the representativeness of oil in total losses.

Water degumming laboratory trials

For these trials crude soybean oil with 583 ppm of phosphorus was used. At the plant, the corresponding degummed oil had 186 ppm of phosphorus.

Table 2 - Results from type of water, quantity of water and mixing time trials

Trial	Phosphorus (ppm)
1 (control)	151
2 (water from condensates)	152
3 (water from equipment 45)	149
4 (50% of the water required)	570
5 (115% of the water required)	155
6 (agitation for 30 minutes)	547

It appears that neither the contaminants of water from equipment 45 (oil and hexane) or the treatment compounds of water from condensates adversely affect the degumming. The addition of less water than required resulted in a decrease of the degree of degumming, as expected. With agitation for 30 minutes the degree of degumming also decreased.

For temperature trials, crude soybean oil with 522 ppm of phosphorus was used. The correspondent degummed oil at the plant had 162 ppm of phosphorus.

Table 3 - Results from temperature trials

Trial	Phosphorus (ppm)
7 (control – 75ºC)	108
8 (98ºC)	153

Temperature is an important factor in degumming processes, as expected. A decrease of temperature to 75°C promotes an increase in degumming efficiency of 8.6%.

3.2. Chemical degumming and neutralization

Chemical degumming and neutralization unit operation study

Process losses are a major factor to evaluate. They can be obtained by data of amount of oil that enters and leaves the process and by the flows expected by planning, but also through Wesson Loss factor, W (eq. 1 and 2) that can be determined by laboratorial analyses. In addition, a theoretical expression for this kind of processes can be used, where theoretical loss is 0,3% plus the sum of free fatty acids (%), phosphatides (%), moisture (%) and impurities (%) of degummed oil [1].

$$\text{Loss (\%)} = 0{,}3+1{,}25W \quad \text{if } W<3\% \quad \text{(eq. 1)}$$

$$\text{Loss (\%)} = 1{,}35W \quad \text{if } 3\%<W<10\% \quad \text{(eq. 2)}$$

Process losses occur mainly in the first centrifugation, where the heavy phase is "soapstock". Soaps are formed by reaction of free fatty acids with caustic soda, so it is reasonable that there is a linear relationship between free fatty acids (FFA) and process losses. Losses can also be related to phosphatide content (PL's) of degummed oil. Therefore, it was verified the relationship between these three parameters with the program Table Curve 3D. For soybean oil, for instance, with the loss verified at the plant, the relationship found is in equation 3.

$$\text{Loss}(\%)=0{,}2124+2{,}2608PL's_{(\%)}+0{,}8786FFA_{(\%)} \quad \text{(eq.3)}$$

$$(R^2 = 0{,}8231)$$

Chemical degumming and neutralization laboratory trials

In order to have a good chemical degumming, is very important that phosphoric acid is well dispersed in the oil, which is influenced by the rate of mixing.

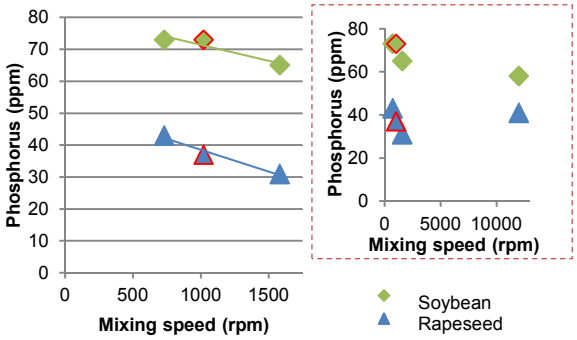

Figure 3 – Neutral oil phosphorus content as function of speed in phosphoric acid mixing. Magnetic stirring trials only (left) and including kitchen blender trial (right)

It is observed an increase in efficiency of degumming with increasing of mixing speed. However, the kitchen blender trial resulted in higher phosphorus content, for rapeseed, which may mean that the optimal speed is not in the range studied on this trial (1580 – 12000 rpm).

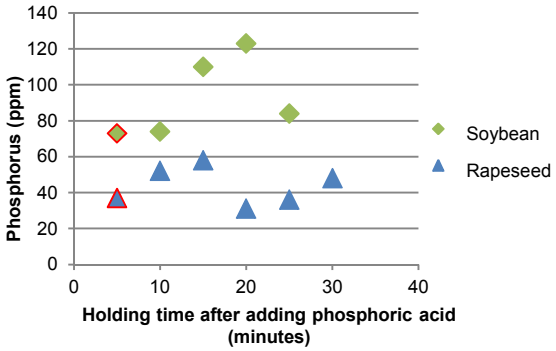

Figure 4 - Neutral oil phosphorus content as function of holding time after adding phosphoric acid

The results reveal no benefit in increasing the residence time after adding phosphoric acid. Most similar industrial processes practice a residence time of about 5 minutes, which is considered sufficient to promote the extent of reaction. In the literature [2] studies were performed about elimination of phosphatides as function of time, after addition of phosphoric acid, with sunflower oil and it was found that most of the phosphatides are removed after 5 minutes.

At the point of mixing caustic soda and agglomeration water, the better the contact between the water and oil, the better the removal of phosphatides, but is necessary to have into consideration that due to the neutralization of free fatty acids soaps are formed, which promote the formation of emulsions and may further take place side reactions, such as saponification of triglycerides. Given the potential formation of emulsions is thus relevant to assess whether it is advantageous to promote an increase in mixing rate and to what extent this increase is beneficial.

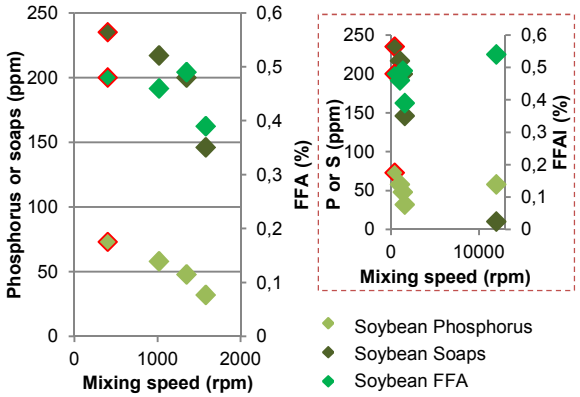

Figure 5 - Neutral oil phosphorus, soaps and free fatty acids as function of mixing speed in addition of caustic soda and agglomeration water

In tests conducted with soybean oil with magnetic stirrer there was an improvement of degumming, neutralization and soaps, with the increase of agitation speed. With mechanical stirring performance did not follow the trend of the previous points, revealing a decrease in the degree of neutralization. The lower content of soaps can be associated precisely with the lower degree of neutralization, since the neutralization promotes the formation of soaps.

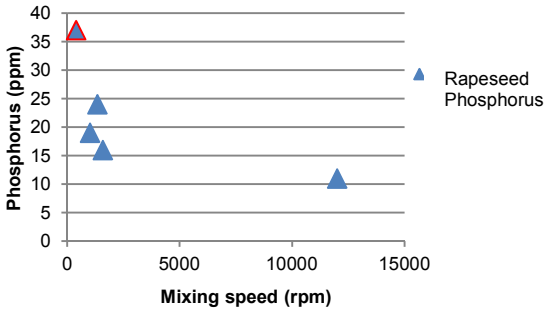

Figure 6 – Neutral oil phosphorus as function of mixing speed in addition of caustic soda and agglomeration water

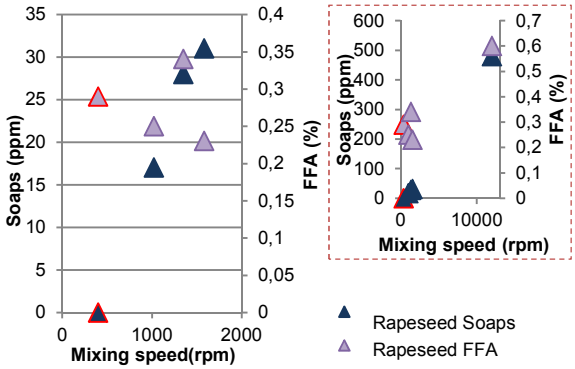

Figure 7 – Neutral oil soap and free fatty acids as function of mixing speed in addition of caustic soda and agglomeration water (rapeseed oil)

For rapeseed oil was observed a similar behavior, except for mechanical stirring when soaps and free fatty acids increase, which means saponification of triglycerides occurred.

4. Proposal for installation of a heat exchanger in water degumming

It was seen that cooling of crude oil before water degumming would be beneficial for degumming. It is thus necessary to estimate the investment to be made for the implementation of a heat exchanger, as well as evaluate the advantages and disadvantages of this option.

The advantages are:

- Improved efficiency of water degumming, since it is removed a greater amount of phosphatides, which are sold in meal;
- Lower consumption of raw materials in chemical degumming and neutralization, although only quantifiably after implementation of the modification;
- Lower neutral oil losses in chemical degumming and neutralization, because there are fewer phosphatides and therefore lower drag of neutral oil.

Also, the disadvantages must be taken into consideration:

- Higher losses of degummed oil, which will be sold at the price of meal (which is lower than the price of oil) due to drag by larger amount of phosphatides removed;
- Greater expense on water circulation for crude oil cooling and steam for degummed oil heating (before drying);
- Reduction of the amount and depreciation of "soapstock", whose price depends on fat percentage, which will be lower than at present.

For this analysis, were assumed degummed oil losses for a typical operation condition at the plant (Table 1, 13500kg/h of oil flow rate and 550 kg/h of water flow rate). For chemical degumming and neutralization unit, equation 3 was used for loss estimation. The results were as follows:

Table 4 - Comparison between the current situation and the situation with a heat exchanger

Parameters	Currently	With a heat exchanger
Water degumming efficiency (%)	81,0	89,6
Water degumming total loss (%)	4,03	4,54
Water degumming oil loss (%)	1,63	1,84
Neutralization total loss (%)	2,24	1,66
Neutralization oil loss (%)	0,90	0,57
Degummed oil loss increase (ton/year)	---	145
Neutral oil loss decrease (ton/year)	---	271
Oil savings (ton/year)	---	126

Knowing the current prices of products and utilities, the increase in income or expense for each item was estimated.

Table 5 - Income from heat exchanger implementation

Incomes (€/year)	Meal	7.581
	Neutral oil	283.152
	Total	**290.723**
Expenses (€/year)	Degummed oil	91.631
	Water circulation	9.263
	Steam	19.058
	"Soapstock"	50.678
	Total	**170.629**
Total income (€/year)		**120.093**

Two hypotheses of equipment to be installed were considered. One possibility was the use of

plates existing in storage for rebuilding a plate heat exchanger. On the other hand, shell and tube heat exchangers also exist in storage.

Although a plate heat exchanger is more compact, crude oil has high dissolved solids content, which can damage this kind of equipment. Furthermore, a rebuilt plate heat exchanger may present sealing problems. Operationally, shell and tube heat exchangers will be easier to maintain, taking into consideration oil characteristics. For the necessary cooling it will be required to take advantage of three existing shell and tube heat exchangers.

To estimate the investment was necessary to consider the costs of 2 inches carbon steel material (pipes, elbows, flanges and valves) and workforce. Also, for plate heat exchanger, nitrile gaskets and a support body were considered.

Table 6 - Investment estimation

Portions of investment	Price (€) (plate)	Price (€) (shell and tube)
Support body	2000,00	---
Gaskets	996,30	---
Pipes	101,40	101,40
Elbows	11,12	33,36
Flanges	31,20	93,60
Valves	636,08	2522,84
Workforce	576,00	960,00
Total investment	**4.352,10**	**3.711,20**

A simplified economic analysis for preliminary evaluation of the feasibility of equipment implementation was performed. For that propose a prediction rate for unexpected of 10%, a cash flow actualization of 1%, a loan for 3 years and an equipment lifetime 8 years were considered.

Table 7 - Economical analysis

Heat Exchanger type	Plate	Shell and tube
Income (€/year)	120.093,15	
Investment (€)	4.352,10	3.711,20
NPV (€)	843.124,64	843.689,20
IRR (%)	1919	2249
Payback time (months)	1	

This analysis result on a Net Present Value (NPV) and an Internal Rate of Return (IRR) more favorable for shell and tube heat exchanger implementation. The investment payback time was of about one month of operation. With these results it is expected that the investment may be economically feasible.

5. Conclusions

On water degumming, it is concluded that the currently temperature is detrimental to process efficiency. With laboratory trials was verified that cooling the oil to 75°C (suggested temperature in literature), implies an improvement of 8,6% in process efficiency. This improvement involves only, for the preferable situation, taking advantage of three existing shell and tube heat exchangers (estimated investment of 3.711 euros), which translates into an annual income increase of 120.093 euros, being the payback time of about 1 month of operation, implying an economically viable solution. Although degummed oil loss will increase with this improvement, a much higher benefit in degumming and neutralization will be achieved due to reducing on neutral oil losses. For a case study was determined a reduction of 0,59% on total loss and 0.33% on neutral oil. This is what is often noted by the authors of studies on such

processes, that the better the performance of water degumming, the better is the operation of degumming and neutralization (lower degree of emulsion, less losses, lower consumption of acids and alkali, which reduces operation problems reported from degumming and neutralization unit). It is thus essential to evaluate firstly what may improve water degumming, which is a simpler process, and then improve degumming and neutralization process unit, starting from a raw material already more refined. The type of water used on water degumming process and the introduction of a holding tank between the mixer and the centrifuge should be evaluated.

On degumming and neutralization unit, some improvements should be evaluated regarding mixture efficiency, which could be beneficial on reducing neutral oil losses and consumption of raw materials. Three mixture points should be evaluated: phosphoric acid addition, caustic soda and agglomeration water addition and wash water addition. However, the highly prone environment to form emulsions must be taken into consideration, therefore must be assessed to what extent is beneficial the increase on mixtures efficiencies.

6. References

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