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# Màster en Enginyeria Química

## Treball Final de Màster

**Conditioning of waste cooking oil for bioethylene production**

**Acondicionamiento del aceite usado de cocina para la producción de bioetileno**

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## 1. SUMMARY

The cracker is the unit where ethylene and polyethylene, among other products, are produced. The conventional cracker unit has had a feed that comes from crude oil, the main raw material being naphtha, but it is a non-renewable source. For this reason, the aim is to reduce the amount of traditional raw material and add one that is recycled and also comes from a renewable source, such as used cooking oil (WCO).

The main disadvantage of using WCO as a raw material is the limitations that the feed has to be processed by the cracker, as the restrictions are aimed at reducing the poisoning of the catalyst present in the cracker, at reducing corrosion, and also at reducing the formation of coke, as if the amount deposited is considerable, the cracker must be stopped.

Therefore, it is necessary to develop a pre-treatment to reduce the components limited by the cracker and for this reason, the present project is developed with the objective of developing a process for the pre-treatment of second-generation vegetable oil (called as WCO, waste cooking oil), so that such raw material fulfils the requirements to be processed without limitations in the cracker unit to produce ethylene.

To achieve the objective, the WCO has been characterised based on a literature search and with the oil characterised, the necessary pre-treatment operations can be selected to meet the specifications for the cracker feed.

The pre-treatment must have operations that remove metals, chlorides, nitrogen, ash and solid particles, free fatty acids, phosphorous, oxygen and water.

The processes selected to remove metals are degumming, bleaching, desalting, membrane extraction, ion exchange, and settling with skimming. The processes selected to remove chlorides are degumming, desalting, membrane extraction and settling with skimming. For the removal of nitrogen, they are deodorization and hydrotreating. For the removal of ash and solid particles, the processes are degumming, desalting, membrane extraction and settling with skimming. Free fatty acids are removed by degumming and deodorization. Phosphorus is removed by degumming, bleaching and desalting. Oxygen is removed by bleaching, deodorization and hydrotreating. Finally, to remove water there are the processes of degumming, deodorization, desalting and settling with skimming.

The future steps for the development are to check experimentally if the proposed pre-treatment is enough to achieve the requirements of the cracker, furthermore, experimentation will give a clearer picture and it is preferable to do this before industrial scale-up.

In addition, an economic study should be carried out to check whether or not the pre-treatment process is viable with the proposed processes. Furthermore, the economic study together with the experimental verification will allow to decide whether all the operations are necessary or not, as the components can be removed by different processes.

On the other hand, the economic viability is favoured by the use of processes that are well known in petroleum refining such as desalting, membrane extraction and hydrotreatment.



## 2. INTRODUCTION

Plastic materials such as polyethylene have become essential to achieve the needs of society. The traditional plastics value chain is based on petroleum, which is processed in refineries to obtain raw materials such as ethylene. However, the use of plastics is currently controversial for environmental reasons, as they are sometimes not biodegradable and/or recyclable. For this reason, petrochemical companies are emphasizing finding alternative feedstocks and developing processes to produce "green" polymers and are encouraged by legislative requirements.

In particular with polyethylene, the trend in the EU is to produce plastic from the reuse of landfill plastic. However, it is still not a green plastic, because the original raw material is crude oil, and it is for this reason that it is intended to produce the polyethylene feedstock, ethylene, from used vegetable oils. However, limitations have been found due to the quality of the oils, which prevent the consumption of more types of oils and in greater quantities due to the requirements set by the refinery cracker.

There is an immediate need to address this limitation in order to comply with upcoming legislation, which requires a minimum of recycled raw material.

Moreover, the interest in the development of production processes based on the use of waste as raw materials is increasing due to the reduction of environmental impact and the revaluation of waste as raw material, since waste generally generates costs because it must be treated for disposal or must be managed, however, if it is used as raw material, its acquisition is cheaper than the original raw material. In addition, it is very competitive that the end product from waste as raw material has the same characteristics as that produced by the "original" raw material.

Due to the above, much of the research is focussed on the use of waste as raw material, thus formulating new processes or adapting existing ones.

In this way, the project of the present document is in line with the current global trend, as it wants to use a raw material considered as waste, such as used oil, and it is also pioneering because it wants to propose a series of processes to comply with the specifications for the production of petrochemical products and to replace petroleum as a raw material.

This project is important because, at the date of its development, there is no defined pre-treatment for used oil to meet the requirements of the reaction unit for obtaining petrochemical products. As such, the project is aimed at the petrochemical sector, as this project proposes a more environmentally friendly way of obtaining plastics.

### 3. OBJECTIVES

This project aims to produce polyethylene based on vegetable-origin ethylene. Therefore, vegetable oils, preferable waste cooking oils (WCO) will be used as a raw material for the cracker unit to produce ethylene.

The objective of this project is to develop a process for the pre-treatment of second-generation vegetable oil (called as WCO, waste cooking oil), so that such raw material fulfils the requirements to be processed without limitations in the cracker unit to produce ethylene.

The inside battery limit is from the reception of the waste oils to the introduction of the waste oil into the cracker; therefore, the operating conditions of the cracker are excluded from the project.

To achieve the objective of this project, the following steps will be taken:

1. Set cracker requirements.
2. Characterisation of the used cooking oil.
3. Selection of operations for pre-treatment to achieve the requirements of the cracker.

### 4. METODOLOGY

The methodology followed to achieve the objectives of this project is using a bibliographic search of patents and studies of processes to remove components such as metals, alcohols, aldehydes and other organic components. Information is also searched from operational sources in refineries.

## 5. BACKGROUND

### 5.1. Cracker and steam cracking

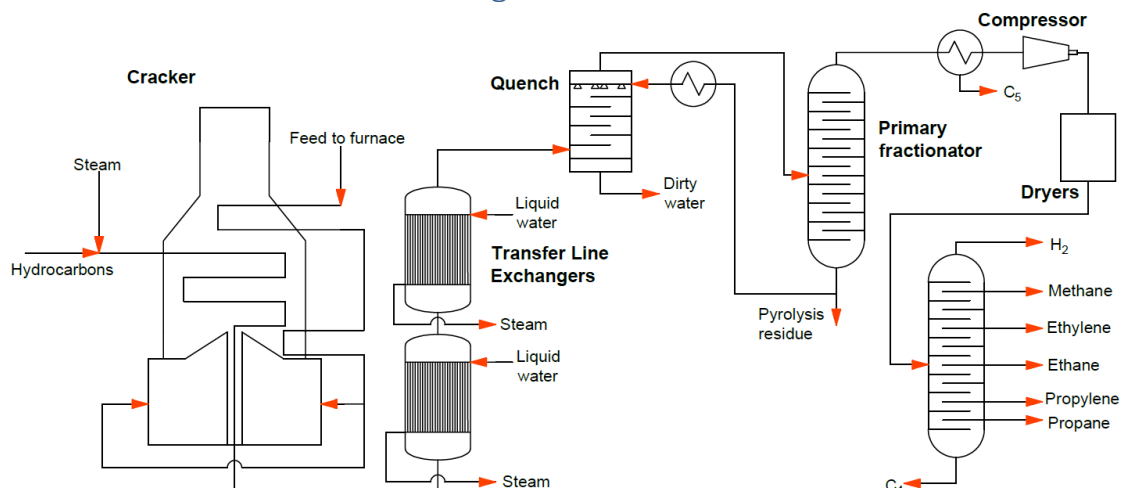


Figure 1. Steam cracking diagram. Adaptation from source [56].

A diagram of steam cracking is shown in Figure 1, but the process of separating of  $H_2$ , methane, ethane, propane, ethylene, propylene and  $C_4$  has been summarised. The equipment necessary to remove the waste generated during steam cracking is not shown.

The steam cracking process consists of two areas: a hot area where cracking and primary fractionation of the cracking products takes place, and a cold area where the separation of ethylene, propylene and the  $C_4$  fraction takes place [56, 62]

The cracker is a set of furnaces through which tubes pass with the feed, which is basically constituted by both light and heavy naphtha; kerosenes, gasoil and water vapour are also part of the feed to the cracker. The hydrocarbons that feed the cracker come from atmospheric distillation, vacuum distillation, or hydrocracking. A diagram of the cracker feed is shown in Figure 2.

The tubes in which the feed circulates are at high temperatures and this is where thermal cracking takes place. The tubes in which the feed circulates are at high temperatures and this is where thermal cracking takes place. The cracker has different zones, there is a convection zone in which the hydrocarbons and steam circulating through the tubes are preheated. After the convection zone, the radiation zone is where the cracking temperature is reached.

The reaction produced in the cracker is a thermal cracking, which is carried out with steam at temperatures between 800 and 850°C at a pressure slightly above atmospheric.

The catalyst used in the reaction is coated on the inside of the tubes. The catalyst is based on calcium-aluminate ( $Al_2O_3/CaO$ ) compounds in which the  $12CaO \cdot 7Al_2O_3$  (mayenite) prevails.

The chain-breaking process produced during thermal cracking consists of three stages:

1. Breakage of carbon-carbon bonds to give rise to free radicals.

2. Propagation of the chains by regrouping the radicals.
3. Termination reactions are reactions where chains are completed from radicals.

Operating temperature and pressure, residence time and vapour/hydrocarbon ratio are variables of thermal cracking.

The temperature depends on the feed to the cracker, as for ethane the operating temperature will be between 840 - 865°C, for naphtha between 825 - 850°C and heavier fractions between 810 - 835°C. The wall temperature of the cracker tubes is about 950°C at the beginning of the operation, but increases progressively in the course of the operation, due to the sedimentation of the coke inside the tubes. This leads to temperatures of 1,150°C, and this temperature is set by the limit of the material of which the cracker tubes are made. When the maximum permissible tube wall temperature or maximum pressure drop is reached, the cracker must be stopped and a decoke process carried out, which is the removal of the settled coal from a mixture of air and steam that allows it to be burned.

As mentioned above, the operating temperature increases the lower the number of carbons in the hydrocarbon due to the reaction rate for the decomposition of hydrocarbons, as it depends on the type and number of carbons. The rate of decomposition is higher as the number of carbon atoms increases.

The residence time is 0.2 to 1.2s for ethane/propane and 0.2 to 0.08s for naphtha and heavier feeds. Too long a residence time favours secondary reactions as well as the formation of liquids and coke.

The tube pressure ranges between 1.5 and 1.9 bar.

The vapour/hydrocarbon ratio is important because a low concentration disfavours coke-forming reactions, so that a suitable ratio allows not only more selective cracking, but also reduces carbon formation and thus reduces the time between shutdowns for decoking [56, 62]

**Table 1. Vapour/hydrocarbon ratios according to the principal hydrocarbon in the feed [61].**

Feed	kg vapour / kg hydrocarbon
Ethane and LPG	0.35 – 0.4
Naphtha	0.5
Gasoil and hydrocracking residues	0.8 – 1.0

At the end of the tubes, at the cracker outlet, the product is cooled to prevent further reaction and secondary reactions. There are two ways to cool the products: firstly, the heat of the products is used to produce very high-pressure steam and this is achieved using heat recuperators called Transfer Line Exchangers, these are heat exchangers in which there is water so that there is a heat transfer between the products and the water present in the heat exchangers to cool the products and generate steam. Subsequently, further cooling is done by a quench with liquids from the bottom of the pre-cooled fractionation tower.

Once the outlet steam from the cracker has cooled, it is passed through a "primary" fractionation column where the heavier fraction (pyrolysis residue) is separated at the bottom and the gas-phase hydrocarbon mixture and vapour are

separated at the head. The overhead extraction is cooled to condense the remaining hydrocarbons to C<sub>5</sub> and above. The non-condensed gas consists of hydrocarbons at C<sub>4</sub> and below, hydrogen and contaminants produced during steam cracking (mostly H<sub>2</sub>S, CO and CO<sub>2</sub>).

The outlet gas at the column head is compressed to 35 bar and dried to subsequently separate the hydrogen, methanol, ethane, propane in the corresponding units that are recycled to increase the conversion of ethylene and propylene, and the C<sub>4</sub> fraction is also separated.

In the cracker, there is pyrolysis with water vapour, also known as steam cracking, which is a process to obtain products to be used in petrochemicals such as ethylene, propylene, butadiene, benzene, toluene, and xylene. On the other hand, there are products obtained that are not strictly petrochemical, for example, hydrogen, the butanes fraction (once the butadiene has been extracted, which is a petrochemical product), where the latter is used as a feed for the MTBE (methyl tert-butyl ether) and ETBE (ethyl tert-butyl ether) units.<sup>1</sup>

Pyrolysis gasoline is also obtained, which is rich in aromatics, especially benzene, toluene and xylenes, and once debenzenised can be used in the formulation of gasoline.

Finally, the pyrolysis residue, which is a highly naphthenic product used as furnace fuel due to its low sulphur content, because before entering the cracker, the feedstock with a high sulphur content has undergone a desulphurisation process.

### 5.1.1. Steam cracking process with used vegetable oil

The objective of this project is to condition second-generation oil with the aim of substituting part of the feed that comes from the crude oil raw material with pre-treated used oil to meet the specifications of the cracker feed. This is done in order for the products obtained from the cracker to have a fraction of the feedstock of green origin and at the same time be reused, as the oil is second generation.

Figure 2 shows the cracker feed with the addition of the treated used vegetable oil.

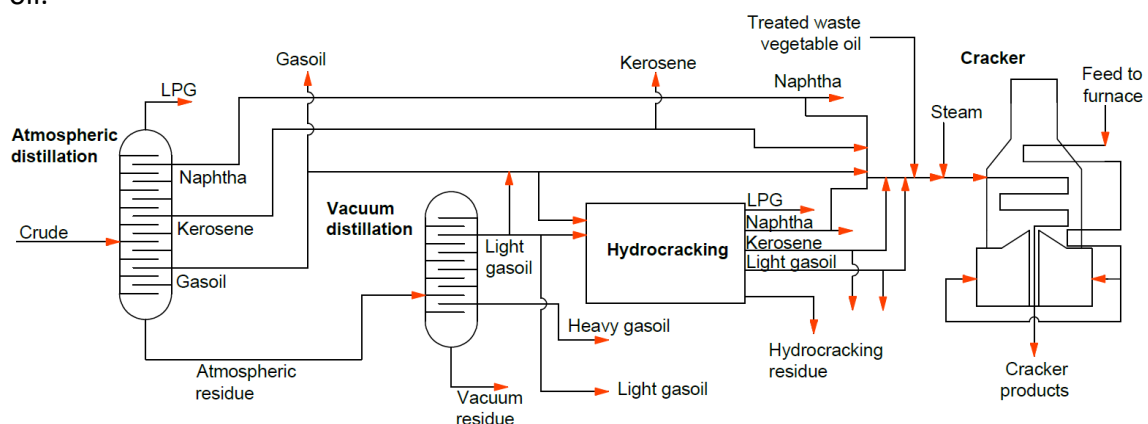


Figure 2. Conventional cracker feed also is added waste vegetable oil. Adaptation from source [62].

The hydrocracking process is fed with gasoil from atmospheric distillation (topping) and vacuum distillation.

<sup>1</sup> Both MTBE and ETBE are used in the formulation of gasoline as octane additives.

For feeding the cracker, basically, naphtha (both light and heavy) and paraffin (light and heavy) from the atmospheric column are used, diesel oil is also used and, differing from the conventional process, it is also fed with pre-treated waste oil.

Hydrocarbons from crude oil have been widely treated in conventional cracker design for years. Otherwise, processing WCO in such a cracker unit is a novel objective, which presents several handicaps. The main concern about WCO composition is its oxygen content, which can deal with CO and CO<sub>2</sub> formation, which is a poison for the catalyst. Also, with regards to constructive materials, conventional cracker units have been built in stainless steel, which could be damaged by pitting because of the chlorides content in the WCO. Also, WCO contains metals, which, in some cases reduce the catalyst activity. Also, the quality of the products may be reduced due to the nitrogen content because nitrogen forms ammonia and would come out with the more volatile products. Therefore, supplying WCO as a novel feed stream to conventional nowadays existing crackers requires conditioning such feed stream, so that is compatible with the cracker design.

Further on, the problems of this cracker feedstock are dealt with one by one in the section on used cooking oils. Table 2 sets the specifications that the feed must achieve when it enters the cracker:



Table 2. Cracker input specification [43,60].	
Item	Maximum concentration
Total metals	2 ppm wt.
Lead	50 ppb wt.
Sodium	10 ppb wt.
Copper	500 ppb wt.
Arsenic	5 ppb wt.
Iron	20 ppb wt.
Potassium	10 ppb wt.
Vanadium	25 ppb wt.
Aluminium	50 ppb wt.
Zinc	25 ppb wt.
Mercury	2 ppb wt.
Chlorides	50 ppb wt.
Phosphorous	5 ppm wt.
Carbonyl sulphide	3 ppm wt.
Asphaltenes	5 ppb wt.
Styrenes	500 ppb wt.
Ammonia	5 ppm mol
Amine	5 ppm mol
Carbon dioxide	~ 1000 ppm mol
Sulphur compounds	$100 \leq x \leq 500$ ppm wt.

These requirements have been taken from different sources that coincide with these same parameters and values.

## 5.2. Ethylene

Ethylene is a hydrocarbon with carbon-carbon double bonds ( $C_2H_4$ ), at room temperature, it is a colourless gas.

For physicochemical description, the properties of ethylene are shown in Table 3.

**Table 3. General data of ethylene. [49]**

Parameter	Data
CAS number	74-85-1
CE number	200-815-3
Hazards statements	H220: Extremely flammable gas – Category 1A. H280: Contains gas under pressure: may explode if heated. H336: May cause drowsiness and dizziness – Category 3.
State of matter	Gas or liquefied gas.
Appearance	Colourless
Molar mass	28.054 g/mol
Melting point	-169 °C at 101.3 kPa
Boiling point	-103.77 °C at 101.3 kPa
Lower and Higher Flammable Limit	Lower Flammable Limit: 2,7 %vol. Higher Flammable limit: 36 %vol.
Autoignition temperature	450 °C at 101.3 kPa
Vapour pressure	212.4 kPa (378 °C)
Relative density	0.978 at 20 °C

### 5.2.1. Uses

Ethylene is used as a raw material in the production of polymers such as high- and low-density polyethylene (HDPE and LDPE). From ethylene, dichloroethylene can be obtained, which in this case is an intermediate product for the synthesis of vinyl chloride, which is polymerised to obtain polyvinyl chloride.

If ethylene is reacted with benzene, styrene is obtained, allowing styrene to be obtained first and then polystyrene to be obtained.

It is also used for copolymers such as EVA (ethylene vinyl acetate) and EBA (ethylene butyl acrylate), where they are used for bollards, footwear, toys, gym floors, construction, packaging.

The most popular uses of the polymers described above are for packaging, construction, automotive, electrical and electronics, among others. [55]

### 5.2.2. Production processes

#### 5.2.2.1. Ethylene from crude oil

The process of production of ethylene from crude oil is explained in chapter 5.1 Cracker and steam cracking.

#### 5.2.2.2. Alternative processes to crude oil

a) Ethanol: The production of bioplastics from ethanol is a widely used route in Brazil, thanks to the availability of large areas of crop fields.

The basis for the production of plastics from ethanol is glucose. Glucose can be obtained from different sources, for example from sugar cane, sugar beet, corn starch, etc.

To obtain glucose, the raw material must first be cleaned, cut, crushed and ground to obtain two phases, the liquid phase which contains the sucrose, which is the product of interest, and the solid phase where the fibres of the raw material remain.

The sucrose is fermented anaerobically to obtain ethanol, then distilled to remove the water and the result is an azeotropic solution of hydrated ethanol at approximately 95% by volume, and a by-product called vinasse is also obtained. From a catalysed dehydration and at high temperature, ethylene is obtained, which is then polymerised into a monomer to obtain plastics. The properties of the polymer obtained would be the same as if it were produced from crude oil.

The process is the same regardless of where the ethanol comes from, i.e., it will be the same process both to produce ethanol from corn and to produce ethanol from sugar cane, for example. [55]

A schematic of the production of bioplastics from ethanol is shown in Figure 3.

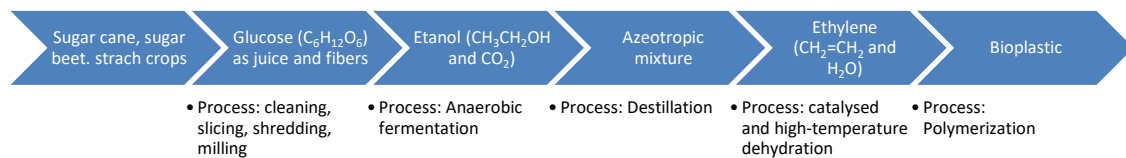


Figure 3. Scheme for bioplastic production from ethanol. [55]

One advantage compared to production using crude oil is the reduction of CO<sub>2</sub> emissions. On the other hand, however, the disadvantage is the dependence on the amount of raw material required, which translates into large areas of land for cultivation, as well as the dependence on favourable weather conditions, because a bad harvest year means that the price of ethanol will rise and consequently the profit margin will decrease.

b) **Landfill:** The landfill plastics are selectively collected and then used as raw material.

**Recycling:** In the extrusion stage, landfill polyethylene is added to the newly produced polyethylene.

The advantages for this production alternative are based on the amount that can be recycled from landfills, because the higher the amount from landfill the higher the percentage of recycling, however, it is necessary to invest in actions to achieve a good sorting and selection of the plastic. Also, the price of the raw material is lower, as waste is used as raw material.

On the other hand, plastic collected from the landfill and not treated afterwards has the disadvantage that its market is reduced due to the biological risk acquired in the landfill, as it is mixed directly with the virgin material to be added in the extrusion stage.

The plastic produced by this process has no market in the pharmaceutical or food industry.

**Circular:** With the selected landfill plastic, it is introduced to a pyrolysis stage to obtain pyrolysis oil, subsequently this pyrolysis oil feeds the cracker. [39]

Unlike the previous one, with the pyrolysis stage, the biological risk is eliminated, which means that its market is wider, as the biological risk is eliminated and its use in the pharmaceutical and food industry is suitable.

c) From vegetable oils: The vegetable oil is mixed with the crude oil before entering the cracker, and consequently, the monomer produced has a bio percentage. This alternative is under development and the future steps are to increase the percentage of vegetable oil and decrease the percentage of crude oil introduced into the cracker, thus achieving a higher bio percentage, and complying with future European regulations.

First-generation oil: The main disadvantage is due to competition for the raw material, as the food market means that there is a high demand and consequently the price of the raw material is high. This option is discarded as an alternative due to the high costs.

Second generation: In contrast to first-generation oils, second-generation oils are residues, which means that the price of the raw material is lower.

A good supply of this raw material requires investment in actions to recover second-generation oil, as a high percentage of this oil ends up in the environment in an uncontrolled manner. Therefore, this alternative would reduce the negative impact on the environment.

In conclusion, the alternatives based on the collection of landfill plastic are the most common in the EU, thanks to the low cost of acquiring the raw material, landfill plastic, and the fact that, unlike the alternative of bio-ethanol production, it does not require large areas of crops.

The present project is carried out according to the alternative based on second-generation vegetable oils because it goes one step further than alternatives based on landfill plastic collection, as the trend in European regulations is to demand that plastics must be green, so the raw material cannot be crude oil, at least not in its entirety.

### 5.3. Raw material

The raw material selected for this project is used vegetable oil (UVO), which is equivalent to used cooking oil (WCO), whereby used cooking oil is understood to be the oil of vegetable origin that has been used at least once in frying, boiling, seasoning and/or has been used, for example, in canning. Animal fats are therefore not included.

It is chosen as a raw material because it is a material of low acquisition value as it is considered a waste, indeed, there are currently production processes where used cooking oil is used as raw material, as in the case of biodiesel or biolubricants, for example. Even so, currently, in the EU, around 4 million tonnes of used oil are generated per year (cooking, thermal, engines, lubricants, etc.) of which a quarter comes from used cooking oil, so it has an important weight. On the other hand, around 190 million tonnes of used vegetable oils are generated worldwide each year. [34]

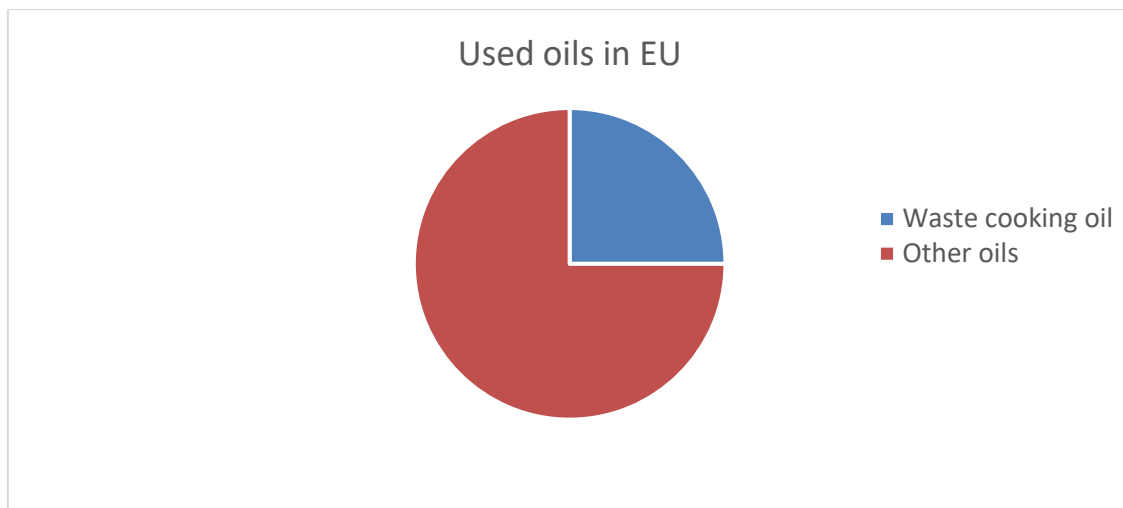


Figure 4. Used oils in the European Union. [34]

The volume of recovery of used vegetable oils is expected to increase as it will be increasingly needed as raw material and this will be possible thanks to investments in recovery and public awareness, because if it is not recovered or treated it can go to the environment being very harmful since one litre of used cooking oil pollutes a million litres of water [25], so it is necessary to make a good collection and try to minimise uncontrolled emissions of used cooking oil.

### 5.3.1. Waste cooking oils (WCOs)

#### 5.3.1.1. Composition

WCOs are triglycerides, and a triglyceride is a glycerol molecule linked to three fatty acid molecules.

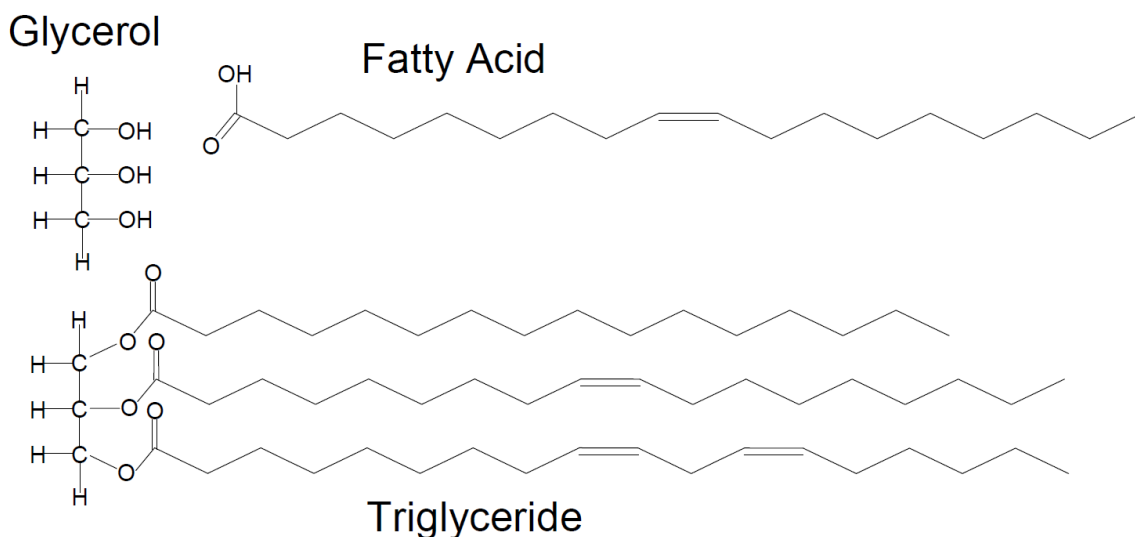


Figure 5. Glycerol molecule, fatty acid (oleic), triglyceride composed of palmitic (C16:0), oleic (C18:1) and linoleic (C18:2) acids.

Fatty acids (FAs) can be saturated or unsaturated depending on the carbon-carbon bond.

Saturated fatty acids are carboxylic acids with single carbon-carbon bonds with a length of generally 12 to 24 carbons. These fatty acids are less reactive due to their single bond, and increasing the number of carbons, the higher the melting temperature. Examples of saturated fatty acids are, for example, capric acid, lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachidic acid, behenic acid). [4]

Unsaturated fatty acids can be monounsaturated or polyunsaturated. Monounsaturated fatty acids are those with a single carbon-carbon double bond, while polyunsaturated fatty acids are those with more than one carbon-carbon double bond.

Examples of unsaturated fatty acids are:

- **Monounsaturated:** oleic acid, caproic acid, lauroic acid, elaidic acid, myristoleic acid and palmitoleic acid.
- **Polyunsaturated:** linoleic acid (two double bonds), linolenic acid (three double bonds), arachidic acid (four double bonds), eicosapentaenoic acid (five double bonds), docosahexaenoic acid (six double bonds).

Unsaturated acids can have cis- or trans- configuration. The trans-configuration is formed by hydrogenation or other processes, whereas the cis- configuration is found naturally in unsaturated acids.

Reactivity is higher in unsaturated than in saturated acids because unsaturated acids have one or more double bonds. Polyunsaturates are more reactive than monounsaturates, as reactivity increases with the number of double bonds. [4]

Oils are contaminated by particles, which can already be traces of metals from fryers and frying pans or by the release of organic matter from the food but can also be contaminated by the generation of new substances during the frying process, e.g., by compounds resulting from the Maillard<sup>2</sup> reaction.

The reactions that occur in the cooking process are listed below: [44]

- **Hydrolysis:** The water content in the food interacts with the frying oil at high temperatures, and there is also interaction with the water in the environment. This reaction increases the formation of polar molecules, i.e., the formation of free fatty acids and glycerols (monoglycerides, diglycerides, triglycerides), where free fatty acids are harmful to the cracker, as they are acidic and would promote corrosion pitting of the cracker.
- **Thermal degradation:** Degradation of triglycerides at high temperature in the absence of oxygen. The consequence of thermal degradation is the formation of ketones, alkanes, alkenes, oxopropyl ester, CO and CO<sub>2</sub>. Special care must be taken with the formation of CO and CO<sub>2</sub>, as they sleep the catalyst present in the cracker. In addition, care must also be taken with oxopropyl esters because in the cracker the oxygens present in these molecules could form CO and CO<sub>2</sub>.
- **Oxidation:** Reaction with atmospheric air, specifically with oxygen. Due to this reaction hydroperoxides are formed and special care must be taken because again in the cracker the oxygens present in these molecules could form CO and CO<sub>2</sub>.
- **Polymerisation:** The polymerisation is due to the reaction that occurs with unsaturated fatty acids at high temperatures. Due to polymerisation, structural changes

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<sup>2</sup> The Maillard reaction consists of a series of chemical reactions produced between proteins and sugars in food at high temperatures that generate compounds that modify the colour, smell, and taste of food. Overcooking generates toxic and/or mutagenic compounds, e.g., acrylamide.

occur in the triglyceride chains. This can result in an increase in acidity if free fatty acids are generated, or an increase in viscosity if monounsaturated fatty acids react to form polyunsaturated fatty acids.

Other factors that modify the properties of the WCO are:

- Salt, it is frequent to add salt to food when cooking or even to preserve it. This changes the viscosity and density of the oil, so that the used oil will have a higher viscosity and density than the oil before it was used. If large amounts of salt are added it can have effects on viscosity and density. If large amounts of salt are added it can have effects on the viscosity and density, as indicated below. Viscosity is increased due to the addition of a solid to the liquid medium, and solids are considered to have infinite viscosity. On the other hand, density is increased because salt (NaCl) is denser than oil.

Salt increases the water activity in the oil and consequently increases hydrolysis which, in turn, increases the formation of free fatty acids, which are detrimental to the cracker, as they are acidic and would promote corrosion pitting to the cracker.

- The water content comes from the water in the food itself, from defrosting or washing. This water passes into the oil and increases its solubilisation in the cooking process as the temperature increases. The addition of water to the oil is likely to increase the density of the oil, as water is denser, but on the other hand, as it is less viscous, it is also likely to decrease the viscosity of the oil.

Water interacts with the oil causing hydrolysis and consequently, the formation of free fatty acids is favoured. Free fatty acids are detrimental to the cracker, as they are acidic and would promote corrosion pitting of the cracker.

- The working temperature of the oil is equivalent to the cooking temperature of the oil. Viscosity decreases the higher the cooking temperature, as the number of saturated fatty acids increases and these do not have any carbon-carbon double bonds, so there is less packing, which results in greater fluidity. Temperature also decreases the density of the used oil.

Cooking temperature favours hydrolysis and consequently favours the formation of free fatty acids, which, as indicated above, are detrimental to the cracker, as they are acidic and would favour corrosion pitting to the cracker.

- The lifetime of the oil, this is equivalent to talking about the cooking time of the oil or the number of uses of the oil. Viscosity decreases, because as indicated with temperature, the number of saturated fatty acids increases and these do not have any carbon-carbon double bonds, so there is less packing, and this results in lower viscosity. This occurs because it is subjected to higher temperatures several times or for longer periods. The density of used oil also decreases with temperature.

As the duration of use of the oil increases, the formation of free fatty acids increases.

Also, the longer the exposure time of the oil to the metal of the cookware, the greater the amount of metal dissolved in the oil. [10]

#### 5.3.1.2. *Characterisation*

For the characterisation of the used reference oil, the reference oil being understood as that which has been taken as a starting point for conditioning. This oil must be representative of the way oils from different sources have been acquired, as it would not be realistic or competitive to have only one supplier of raw materials,

therefore oils from different countries have been used, e.g., Spain, Morocco, Malaysia, Japan, Turkey, Finland, Sweden, Nigeria, Saudi Arabia. In addition, different oils have also been characterised, e.g., olive oil, rapeseed oil, palm oil, sunflower oil, soybean oil, sesame oil, corn oil, among others.

Table 4 below shows the characterisation of the used cooking oil used for the selection of unit operations for conditioning and subsequent entry into the cracker.

<b>Table 4. Reference characterised used vegetable oil.</b>				
	<b>Average value</b>	<b>Range</b>	<b>N° Data</b>	<b>Standard deviation</b>
Free fatty acid content [%wt]	3.27	0.02 – 16.90	10	-
Water or moisture content [%wt]	0.0957	0.0441 – 0.1700	36	0.0338
Ash [%wt]	0.122	0.003 – 0.24	2	-
Density (15 °C) [g/cm <sup>3</sup> ]	0.9173	0.8232 – 0.9311	30	0.0257
Density (20 °C) [g/cm <sup>3</sup> ]	0.9163	0.9043 – 0.9232	10	-
Density (40 °C) [g/cm <sup>3</sup> ]	0.90195	-	1	-
Density (60 °C) [g/cm <sup>3</sup> ]	0.88844	-	1	-
Density (110 °C) [g/cm <sup>3</sup> ]	0.873	-	1	-
Kinematic viscosity (20 °C) [mm <sup>2</sup> /s]	124.00	-	1	-
Kinematic viscosity (30 °C) [mm <sup>2</sup> /s]	62.826	-	1	-
Kinematic viscosity (40 °C) [mm <sup>2</sup> /s]	38.738	31.381 – 51.440	40	4.630
Kinematic viscosity (60 °C) [mm <sup>2</sup> /s]	26.28	-	1	-
Kinematic viscosity (110 °C) [mm <sup>2</sup> /s]	3.8	-	1	-
Congealing temperature [°C]	2.84	-6.3 – 14.7	6	-
Iodine value [g I <sub>2</sub> / 100 g oil]	106.83	52.17 – 141.26	40	23.505
Peroxide value [meq/kg of oil]	44.13	7.13 – 200.38	32	35.04
Total polar material [%]	17.73	11.50 – 30.00	30	4.37
Acid value [mg KOH/g of oil]	2.75	0.17 – 28.70	41	5.38
pH	5.86	5.13 – 6.10	6	-
C [%wt]	74.75	71.58 – 77.91	2	-
H [%wt]	10.92	10.14 – 11.69	2	-
N [%wt]	0.05	0.04 – 0.06	2	-
S [%wt]	0	-	2	-



Table 4. Reference characterised used vegetable oil.				
	Average value	Range	N° Data	Standard deviation
O [%wt]	14.04	10.36 – 17.71	2	-
Al [mg/kg]	0.114	0.02 – 0.25	8	-
Br [mg/kg]	3.70	-	1	-
Na [mg/kg]	63.7	2.6 – 110.6	9	-
P [mg/kg]	302.4	4.8 - 600	2	-
Cr [mg/kg]	0.1750	0.0007 – 0.84	16	-
Ni [mg/kg]	0.5893	0.0041 – 1.1	9	-
Cu [mg/kg]	0.0773	0.0097 – 0.321	26	-
Co [mg/kg]	0.0000	-	1	-
Zn [mg/kg]	1.2288	0.0521 – 3.1	11	-
Mn [mg/kg]	0.2449	0.0006 – 0.910	26	-
Mg [mg/kg]	1.5	-	1	-
Ca [mg/kg]	5.3	-	1	-
Fe [mg/kg]	21.9867	0.0236 – 57.8	11	-
Pb [mg/kg]	0.0831	0 – 0.4	25	-
Cd [mg/kg]	0.4890	0.0013 – 2.77	27	-
As [mg/kg]	0.015	0.011 – 0.018	7	-
Caprylic acid (C8:0) [%wt]	2.5	-	1	-
Lauric acid (C12:0) [%wt]	0	-	1	-
Myristic acid (C14:0) [%wt]	3.70	0.13 – 10	3	-
Myristoleic acid (C14:1) [%wt]	0.26	-	1	-
Pentadecanoic acid (C15:0) [%wt]	0.04	-	1	-
Palmitic acid (C16:0) [%wt]	19.72	4.85 – 39.02	6	-
Palmiticoleic acid (C16:1) [%wt]	0.215	0.20 – 0.23	2	-
Stearic acid (C18:0) [%wt]	19.17	1.93 – 60.95	7	-
Oleic acid (C18:1) [%wt]	36.28	0.5 – 64.38	9	-
Linoleic acid (C18:2) [%wt]	22.37	6.54 – 50	9	-
Linolenic acid (C18:3) [%wt]	5.00	0.2 – 14.3	7	-
Arachidic acid (C20:0) [%wt]	0.57	0.15 – 1.14	5	-
Gadoleic acid (C20:1) [%wt]	0.70	0 – 1.1	3	-

Table 4. Reference characterised used vegetable oil.				
	Average value	Range	N° Data	Standard deviation
Behenic acid (C22:0) [%wt]	0.46	0.15 – 0.75	4	-
Erucic acid (C22:1) [%wt]	0.3	-	1	-
Lignoceric acid (C24:0) [%wt]	0.285	0.27 – 0.3	2	-
Monoglycerides [%wt]	1.2	0.1 – 2.2	2	-
Diglycerides [%wt]	4.70	1.8 – 7.65	5	-
Triglycerides [%wt]	87.77	79.1 – 96.43	2	-
Hexanal [mg/kg]	2.7287	-	1	-
Heptanal [mg/kg]	0.7503	-	1	-
Limonene [mg/kg]	0.7684	-	1	-
Furan, 2-pentyl [mg/kg]	1.8623	-	1	-
Nonanal [mg/kg]	4.0382	-	1	-
1-octen-3-ol [mg/kg]	0.8284	-	1	-
Furfural [mg/kg]	0.6783	-	1	-
Cyclohexanol-dimethyl [mg/kg]	0.5625	-	1	-
Benzaldehyde [mg/kg]	0.4908	-	1	-
2-Nonenal [mg/kg]	0.6348	-	1	-
2-Furan-methanol [mg/kg]	0	-	1	-
2-Decenal [mg/kg]	1.4988	-	1	-
2-Undecenal [mg/kg]	1.0504	-	1	-
2,4 Decadienal [mg/kg]	1.2092	-	1	-
Pyridine [mg/kg]	0.28	-	1	-
Pyrazine [mg/kg]	0.42	-	1	-
Tocopherol	1100	600 – 1600	2	-
Phytosterols	426.5	-	1	-
Carotenoids	600	-	1	-
Chlorophyll	30	-	1	-
Sources: [1, 3, 4, 5, 7, 10, 11, 12, 13, 18,19, 21, 25, 26, 27, 28, 29, 31, 33, 35, 38, 42, 44, 46, 52, 59, 61]				

### Phospholipids

Crude oils have a high amount of phospholipids, around 400 to 600 mg/kg calculated as phosphorus in the oil. There are indeed different oils with their particularities, so the raw material must be well characterised before storage and processing. Table 5 below shows different types of oil and the percentage of phospholipids in each of them.

Type of feedstock	Triglyceride content [%]	Phospholipid content [%]
Soybean oil	90-93	1.0 – 3.0
Canola oil	94.4 – 99.1	1.25 – 2
Rapeseed oil	98.5	1.25
Palm oil	~ 90.35	0.03 – 0.1
Cotton seed oil	92 – 98	0.7 – 0.9
Rice bran oil	81.3 – 84.3	3.6 – 6.0
Rice bran oil	98.0 - 99.5	0.5 – 1.5
Ground oil	98.0 – 99.7	0.3 – 0.7

There are two types of phospholipids, hydratable and non-hydratable, which often found together with different cations like magnesium, calcium, iron. Phospholipids which have metal cations must be removed because they are responsible for the deterioration of the oil and therefore the loss of quality.

Hydratable phospholipids are easily removable from water to form hydrated gums, which can then be removed by centrifugation or settling. This removed hydrated gum (hydratable phospholipids) has lecithin (phosphatidylcholine).

More difficult is to remove the non-hydratable phospholipids, because chemical reagents are required to hydrolyse them into hydratable phospholipids and metallic cations, which are further removed by the water degumming process. These chemical reagents are acids, e.g., citric acid, phosphoric acid, etc.

Table 6 below shows the different phospholipids in non-gummed oils, as well as the percentage present and whether they are hydratable or not.

Name of constituents	Nature	Percentage
Phosphatidylcholine (PC)	Hydratable	29.0 – 39.0
Phosphatidylinositol (PI)		13.0 – 17.5
Phosphatidylserine (PS)		5.9 – 6.3
Phosphatidic acid (PA)	Non-hydratable	5.0 – 9.0
Phosphatidylethanolamine (PE)		20.0 – 26.3

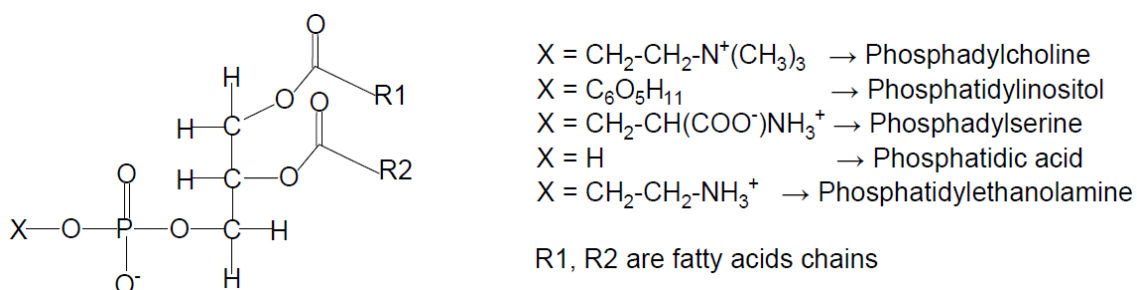


Figure 6. Molecular structure of phospholipids. Adaptation from source: [54]

When water is added to the oil, the hydratable phospholipids move to the interface between the aqueous phase and the oil phase and this occurs as a result of the weak dipole-dipole interaction (hydrophilic) between the polar head group of phospholipids and the water molecules. This interaction results in phase transitions, in

this case, oil-soluble hydratable phospholipids transform into oil-insoluble lamellar liquid crystals (gum).

The lower the amount of residual phosphatides after the degumming stage, the better or easier the subsequent refining stages will be, because less bleaching clay will be required in the bleaching stage, so it will have a positive impact from an economic point of view.

### Carotenoids and chlorophyll

Carotenoids are classified into two groups, xanthophylls and carotenes. The xanthophylls, unlike the carotenes, do have oxygen in their molecule, so they must be removed, as oxygen in the cracker can form CO and CO<sub>2</sub>, and so the lifetime of the catalyst is enhanced.

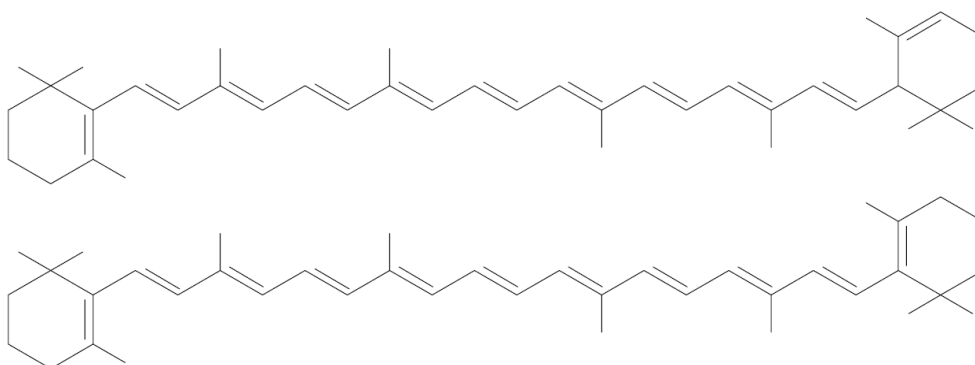


Figure 7. Molecular structure of alpha-carotene (on top) and beta-carotene (on bottom). Adaptation from source: [16]

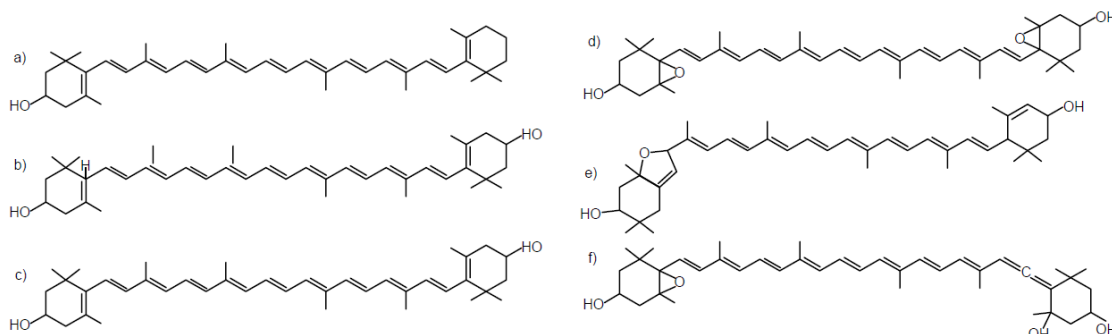


Figure 8. Molecular structure of xanthophylls: a) Cryptoxanthin, b) Lutein, c) Zeaxanthin, d) Violaxanthin, e) Flavoxanthin, f) Neoxanthin. Adaptation from source: [17]

Like xanthophylls, carotenes are removed by bleaching, and although these are not harmful to the cracker, as they have no elements such as oxygen, nitrogen, or other elements, they are removed collaterally by bleaching because the products that want to be removed are the xanthophylls and chlorophyll, as they have oxygen in the molecule as well as nitrogen and magnesium, in the case of chlorophyll.

The removal of chlorophyll and xanthophylls is important because their removal reduces the poisoning of the catalyst caused by the reaction of oxygen in the cracker, they can form CO and CO<sub>2</sub>, so the lifetime of the catalyst is enhanced.

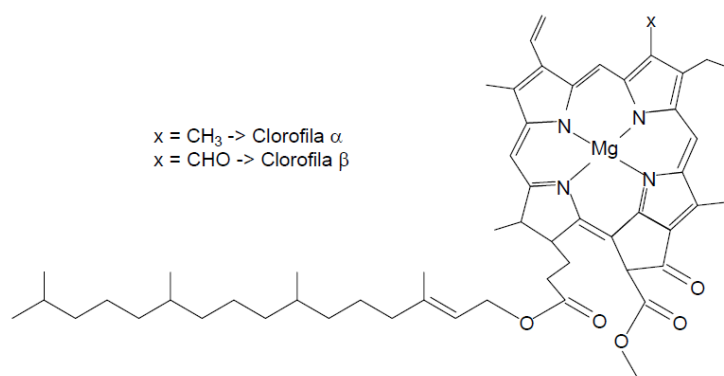


Figure 9. Molecular structure of chlorophyll. Adaptation from source [32]

### Ketones and aldehydes

Ketones and aldehydes some are in the oil itself, others are by-products of thermal degradation in the oil due to the use of vegetable oil. They are also present before it is used in cooking, frying, etc.



Figure 10. General molecular structure of ketones and aldehydes.

Its molecular structure as shown in Figure 10 has oxygens present which must be removed to avoid poisoning of the catalyst in the cracker, as it can be transformed into CO<sub>2</sub> and CO.

### Phytosterols

Phytosterols reduce the polymerisation that can occur in the oil when heated, i.e. they reduce the effect of thermal degradation in the oil.

Phytosterols can be found free (sterols) or esterified (sterol ester). Their molecular structure has oxygens present so they must be minimised as much as possible before entering the cracker.

Some of the sterol isomers have applications in the pharmaceutical and food industries. For example, they are used to treat excess cholesterol.

### Tocopherol

Tocopherol is an antioxidant inherent to the oil and in particular the α-tocopherol isomer is a type of vitamin E. Its molecular structure as shown in Figure 11 has oxygens present, and although the main objective of deodorization for this project is not its removal, since being an antioxidant it protects the oil from oxidation. However, it is true that, as it contains oxygen in its molecular structure, it must be reduced, as it should be remembered that in the cracker the oxygen present can be transformed into CO<sub>2</sub> and CO, which is harmful, as mentioned above.

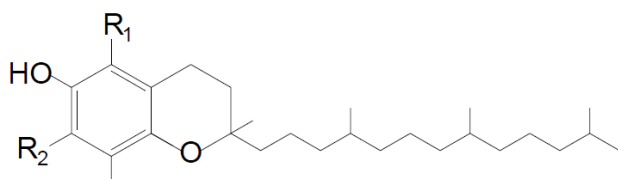


Figure 11. Molecular structure of tocopherol isomers.[18]

Tocopherol	R <sub>1</sub>	R <sub>2</sub>
α	CH <sub>3</sub>	CH <sub>3</sub>
β	CH <sub>3</sub>	H
γ	H	CH <sub>3</sub>
δ	H	H

Table 8 below shows a comparison between the requirements defined in the objective of this project and those of the feedstock of reference.

Table 8. Cracker requirements and used oil as feedstock.

Component	Used vegetable oil [ppm wt.]	Cracker requirements [ppm wt.] [49, 52]
Total metals	96	2
Lead	0.083	0.05
Sodium	64	0.02
Copper	0.077	0.5
Arsenic	0.015	0.005
Iron	22	0.1
Potassium	-	0.05
Vanadium	-	0.025
Aluminium	0.114	0.05
Zinc	0.123	0.025
Mercury	-	0.002
Chlorides	64	0.05
Phosphorous	302.4	5
Carbonyl sulphide	-	3
Asphaltenes	-	5
Styrenes	-	0.5
Ammonia	-	0.2
Amine	-	0.3
Carbon dioxide	-	53
Sulphur compounds	-	100 ≤ x ≤ 500
Nitrogen	418	0.03
Water or moisture content	962	5.
Alcohols	1.39	*1
Aldehydes	15	*1
pH	5 – 6	-
Ash	1215	*1
Iodine index	107 g I <sub>2</sub> / 100 g oil	-
Peroxide index	44 meq / kg oil	-
Acid index	3 mg KOH / g oil	-

\*1: Alcohols and aldehydes must be removed because of the oxygen content in their molecular structure which can form CO and CO<sub>2</sub> but no limit values have been found in the literature. Also no limit values have been found for ash.

It is evidenced in Table 8 that pre-treatment must be done to meet the requirements of cracker.

The reasons why the parameters indicated by the cracker should be reduced are given below. [43,60]

**Lead**: Lead poisons the nickel-based catalyst in the hydrogenation catalysts, and also contaminates the pyrolysis of heavier ethylene fractions.

**Sodium, potassium, and vanadium**: Sodium and potassium accelerate the corrosion caused by vanadium, where the most problematic compound is  $V_2O_5$ .

Moreover, sodium sticks to the cracker walls reducing the performance because it becomes a catalyst for the formation of carbon in the cracker tubes so that it obstructs the tubes and consequently causes a pressure drop. This can cause mechanical failure of the tubes.

The sodium comes from the sodium chloride added during cooking.

**Nitrogen**: Reduces catalyst life and also reduces ethylene quality because it comes out with ammonia.

If the amount of nitrogen present is large enough, it can break acetylene structures into  $C_2$  and  $C_3$  fractions in hydrogenation reactors.

Nitrogen can be found both in light fractions, e.g., in refinery gas, but also in heavy fractions, as it forms cyclic compounds such as pyridines, pyrroles, quinolines, indoles, carbazoles, pyridine, pyrazine etc., and these compounds are thermally very stable.

**Arsenic**: Forms arsine ( $AsH_3$ ) and leaves the column head with the  $C_2$  fractions, i.e., with ethylene. Arsenic poisons the palladium catalyst.

**Iron**: It sticks to the cracker walls, reducing performance because it becomes a catalyst for the formation of carbon in the cracker tubes so that it obstructs the tubes and consequently causes a pressure drop. This can cause mechanical failure of the tubes. On the other hand, iron is a pyrophoric material, which when transported through the cracker tubes and hitting the cracker walls can produce small splinters and/or sparks.

**Aluminium**: Deposits of aluminium so that it clogs and consequently there is pressure drop. This can cause mechanical failure of the tubes. Experience shows that the processing of polyethylene oils/waxes containing aluminium alkyls results in aluminium deposition in the convection section.

**Mercury**: Amalgamates with the deposited aluminium and weakens the metal components of the cracker. Water or moisture accelerates this process of embrittlement of metals.

Due to its high vapour pressure, it is found predominately in  $C_3$  and  $C_4$  fractions especially at low point drains in  $C_4$  processing area.

Even if used cooking oil does not contain mercury, it should be remembered that not only used oil but also the corresponding crude oil fraction enters the cracker, so it is through the crude oil that mercury will be introduced.

It is important to remove as much mercury as possible from the feed streams, as it causes damage due to clogging and where most of these accidents occur is in the cold box, as it accumulates, and the melting temperature of mercury is  $-38.87^\circ C$

**Zinc**: Promotes the negative effects of mercury.

**Chlorides**: These come from salts added in cooking. Chlorides form HCl, which dissolves in quench water. This may prompt under-deposit corrosion in the quench system. Any chlorides carried downstream can result in stress cracking of stainless-steel equipment. This may cause mechanical failure of the cracker.

**Sulphur and sulphur compounds**: These come from disulfides and thiols (R-SH) and react to form hydrogen sulphide with high conversion.

These compounds reduce the activity of the catalyst (they poison it), and also produce compounds such as iron sulphide, which is deposited, as it has long residence times in the cracker and cannot be removed by filtration. Centrifugation is necessary.

Sulphur is concentrated in the heavier fractions, so it reduces their quality, and there are also products where the sulphur content is a quality factor, and exceeding the permitted content makes it out of specification.

Hydrogen sulphite and sulphates react with the metals present in the cracker tubes, forming metal sulphides, and this compound has a low melting temperature and melts with the high fractions in the furnace, thus reducing the quality of the fractions with which it leaves.

On the other hand, the sulphur content in the feedstocks has a beneficial part for the cracking operation, as it passivates the metal in the cracker tubes, reducing the carbon, CO and CO<sub>2</sub> generated in the tubes. It is recommended to add dimethyl sulphide, dimethyl disulfide or thiols to control coking if the sulphur content is below 200 ppm.

**Phosphorus**: Phosphorus hydrolyses into phosphoric acid. Phosphorus can come from the raw material and/or from additives added to control the carbon in the cracker. In this case, the feedstock, as WCO contains phosphorus, and if you want to add an additive to control the coking formed, this would be a second source of phosphorus.

Care must be taken with the high use of raw materials with phosphorus and or additives, since, when phosphoric acid is formed, it attacks the metal tubes of the furnace, causing the thickness to decrease.

**Copper**: Adheres to the cracker walls, reducing performance because it becomes a catalyst for the formation of carbon in the cracker tubes so that it clogs the tubes and consequently there is pressure drop. This can cause mechanical failure of the tubes.

**Amines**: They decompose into NH<sub>3</sub> and HCN and are very soluble in water. The ammonia formed is retained with quench water, but in case of excess ammonia, it would come out through the ethylene fraction, thus reducing the quality of the product.

**Fatty acids**: Oxygen must be removed from the fatty acid chains because it produces CO<sub>2</sub> and CO, and the formation of these must be monitored, as it reduces the activity of the catalyst present in the cracker. So, hydrogenation is necessary to remove the molecules present in the fatty acids. With hydrogenation, water will be generated, which interacts with the oil causing hydrolysis and consequently the formation of free fatty acids is increased. Free fatty acids are detrimental to the cracker, as they are acidic and promote pitting of the cracker.

**Alcohols, glycerols, aldehydes**: As with fatty acids, oxygen must be removed from the carbon chain because in the cracker it generates CO<sub>2</sub> and CO, these compounds in the cracker poison the catalyst present in the cracker. In the same way as with fatty acids, hydrogenation is used, where oxygen is captured to generate water. The main drawback again is the same as in the previous case, the hydrolysis that will occur.



**Water:** Although there is no restriction in the bibliography on the water content allowed to enter the cracker, it must be reduced, since, as has been indicated throughout this project, the water interacts with the oil producing hydrolysis and consequently the formation of free fatty acids is increased, and free fatty acids are harmful to the cracker, since they are acidic and favour pitting due to corrosion of the cracker.

In addition, care must be taken with the water content, as it can cause clogging of pressure regulating valves and other similar equipment caused by the change in the state of the water. Another consequence of the presence of water in the feed to the cracker is the formation of hydrates, mainly with ethane and propane, and consequently, it could deposit solids in the pipelines, which would result in a blockage with a corresponding pressure drop. This could lead to mechanical failure of the pipeline.

**pH:** The pH is an indicator of the quality of the oil because if it is very used, in other words, it is poor quality, it will have a greater quantity of free fatty acids than if the oil is virgin, as there will be no presence of free fatty acids.

In addition to being an indicator of the quality of the raw material, the pH must also be controlled, as it enhances the pitting caused by corrosion from chlorides and fluorides, so at lower pH, fewer chlorides are needed to produce the same damage in the cracker.

**Solid residues:** Solid residues cannot enter the cracker, as this would increase the amount of carbon formed and would end up being deposited in the cracker, as well as operationally it could cause equipment blockage.

**Iodine value:** This measures the degree of unsaturation of the used oil. At higher the value, more unsaturated fatty acids it has and the higher the viscosity of the oil, as these fatty acids are more tightly packed than saturated fatty acids. In addition, as it is a used oil, it is possible that polymerisation has taken place and, therefore, there have been structural modifications in the triglyceride chains. This may increase acidity if free fatty acids are generated or an increase in viscosity if monounsaturated fatty acids react to form polyunsaturated fatty acids.

**Peroxide value:** This measures the oxidation of the oil and therefore the deterioration of the oils. Since oxidation will have taken place and due to this reaction hydroperoxides are formed, special care must be taken because again in the cracker the oxygens present in these molecules could form CO and CO<sub>2</sub>.

**Acid value:** This measures the amount of free fatty acids, at higher the acidity index, the greater amount of free fatty acids presents in the used oil, so it has poorer quality because high acidity means greater corrosion caused by chlorides and fluorides.

## 6. STATE OF THE ART

The different operations to be carried out in order to select a pre-treatment to meet the cracker feed requirements set out above are described below. The operations have been ordered according to the component being reduced.

### 6.1. Metals removal

The removal of metals is important as they can cause fouling, corrosion, catalyst poisoning, erosion of pipes and equipment, and can cause the product to be out of specification or promote the formation of coke in the cracker.

Metals are present in salts, as well as in particles from cooking utensils, from oil production processing or from the soil in which the raw material for oil production has been ground.

The processes used to remove metals from the oil are desalting, membrane extraction, ion exchange resin, degumming, bleaching, settling with skimming.

#### 6.1.1. Desalting

The objective of desalting is to precipitate salts and traces of metals released from the utensils used in the cooking process and intrinsically in the oil. In other words, this operation will remove inorganic chlorides and metals such as chromium, nickel, copper, cobalt, zinc, manganese, lead, cadmium, arsenic and aluminium. This process also removes solids from food residues remaining in the oil. It also removes part of the waxes and hydratable phospholipids.

This operation is important because, in addition to reducing the metal content, it also reduces the chloride content, thus not only avoiding problems of fouling, corrosion, catalyst poisoning, erosion of pipes and equipment, out-of-spec product or favouring the formation of coke in the cracker but also reducing the corrosion problems generated by the chlorides, as hydrochloric acid could be formed.

In addition, the removal of the waxes reduces the viscosity, so that the pumping costs will be lower.

The block diagram for the desalting process is shown in Figure 12 below.

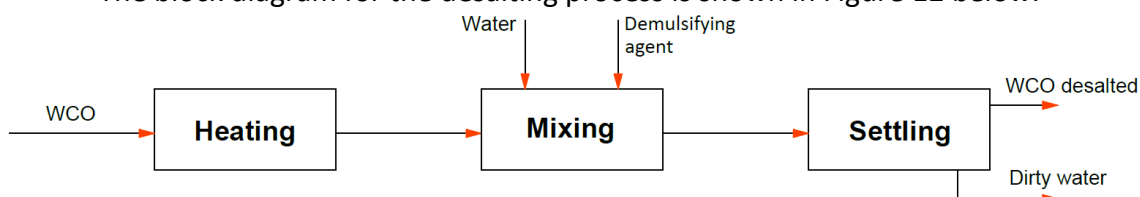


Figure 12. Block flow diagram of desalting process.

The diagram in Figure 12, where the desalting process is based on [6], is described in more detail below.

First of all, the WCO is heated to 115 - 150°C, depending on the density and viscosity of the raw material. After pre-heating the WCO, water is added in the range of 3 - 10% (v/v of the oil). Using a stirrer, the oil and water are mixed.

While mixing, a demulsifying agent, e.g., an amine, is added as described in patent US 4,992,210 [41], in an amount between 5 and 10 ppm. The purpose of adding

a demulsifying agent is to reduce the separation time of the two phases of the water-in-oil emulsion formed by the addition of water. Additionally, an electric field can be added to the mixture to reduce the stabilisation times of the aqueous and oily phases, as this favours the coalescence of the water droplets with the residues from the oil. In this way, the separation times between the phases are shorter. This is due to the fact that water is a polar fluid, unlike oil, which is not.

For the electric current, a voltage of 15 kV to 35 kV is used to promote coalescence.

Once the phases have stabilised, the water is decanted. If there is an excess of oil in the withdrawn water, it is advisable to do centrifugation to recover the oil, which is our raw material.

This is followed by a critical discussion of the desalting process.

The efficiency of the operation depends on the density and viscosity of the oil, but it also depends on the amount of water added, the agitation and the operating temperature.

As for the density, the higher the density of the oil, the more difficult it will be to separate the oil phase from the water phase, as the density of the oil will be closer to that of water and therefore more time will be required to stabilise the phases, as the difference in density is one of the factors favouring the "sedimentation" of the water phase.

The higher the viscosity, the more difficult the phase separation is, as salts and other solids have a higher resistance to flow through the oil and consequently the longer the phase stabilisation time. In addition, the higher the viscosity of the oil, the longer it takes for the water droplets to coalesce and eventually form a phase distinct from the oil. This is because it has less fluidity between the oil phase due to its high viscosity.

Agitation may not seem to be important, but care must be taken, as too much agitation can cause the water droplets in the oil to break up so that they will be very small and of equal size. This is not conducive to agglomeration of the water, as coalescence is favoured if the droplet sizes are different. On the other hand, agitation facilitates homogeneous heating of the oil and increases the contact between water and oil.

The operating temperature should be sufficient to reduce the viscosity and density, but not too high, as this would cause thermal degradation of the oil to form ketones, aldehydes, which are components that do not want to enter the cracker.

It is important to add the right amount of water, as we want water in oil emulsion and not oil in water, in order to reduce the phase separation time. Because the longer the phase stabilisation time, the longer the occupancy time of the equipment, as a longer residence time must be left in the equipment if the components are to be removed in the ranges of the water in oil and not in water.

It is recommended to carry out this process before any other, as it reduces the inorganic chlorides and metals, and consequently reduces the corrosion that the equipment may suffer after this process. It is important to remove the chlorides, as they could form hydrochloric acid, which together with the free fatty acids will promote corrosion in the pre-treatment units and of course also attack the cracker.

The wash water containing dissolved hydrocarbons, free oil, dissolved salts and suspended solids is further treated in an effluent treatment plant. If the oil losses are

significant in the separation of oil and water, it can be considered to add centrifugation to recover the oil entrained in the water. [14]

Table 9 shows typical desalting operation conditions used in the oil refining field. As can be seen, these variables are a function of crude oil density. It should be noted that the increase in water as density increases is due to the higher amount of salts and/or metals present in the crude oil and it is important to remember that the objective of this operation is to remove these salts and metals.

The operating temperature with increasing density of the crude oil is due to the fact that the sedimentation of the water with the salts and metals is favoured. In addition, volatile compounds are removed.

Crude oil density [kg/m <sup>3</sup> at 15°C]	Water wash [% v/v]	Temperature [°C]
< 825	3 – 4	115 – 125
825 – 875	4 – 7	125 – 140
> 875	7 – 10	140 – 150

### 6.1.2. Membrane extraction

The aim of membrane extraction is to remove ash and metals present in the oil as particles or in the form of salts.

This operation is important to reduce the metal content and avoid problems of fouling, corrosion, catalyst poisoning, erosion of lines and equipment, out-of-specification product or the formation of coke in the cracker. On the other hand, the salts removed contain chlorides so, that the chloride content is also reduced, which favours a reduction of corrosion along with the equipment.

The block diagram for the membrane extraction process is shown in Figure 13 below.

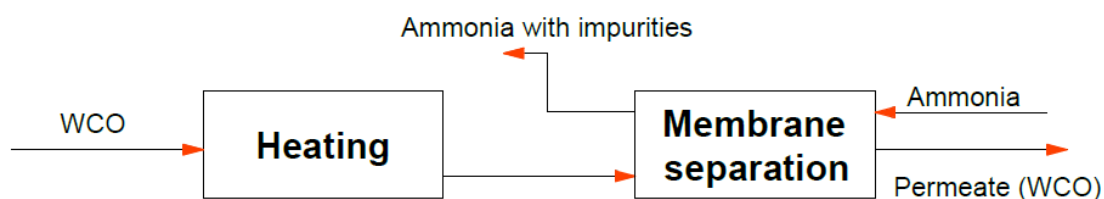


Figure 13. Block flow diagram of membrane extraction process.

The diagram in Figure 13 is described in more detail below, where the membrane extraction process is based on [50].

The process starts by heating the oil to a temperature of 50 to 250°C. The membranes used for this process are tubular as stated in patent US 6,024,880 [50]. The pore size is of the order of 0.005 m to 10 m and may be comprised of alumina (Al<sub>2</sub>O<sub>3</sub>), zirconia (ZrO<sub>2</sub>), silica (SiO<sub>2</sub>), titania (TiO<sub>2</sub>) or mixtures thereof.

The oil is passed through the inside of the membrane at a pressure of 1 to 17 atm absolute. The oil will be loaded from below, i.e., the inside of the membrane will be filled from bottom to top, thus providing a larger contact surface between the oil and the membrane.

The extracting phase circulates on the outside of the membrane. This extracting phase is hydrophilic and it is recommended to use an aqueous solution of ammonia.

This extractive phase is enriched in residues removed from the oil, i.e., it is enriched in salts, metals and ash. [23]

Once the oil permeance through the membrane had decayed by approximately 70 to 80% of the starting value, the membrane is considered fouled and membrane cleaning should be carried out. The method proposed by patent US 6,024,880 [50] to clean the membrane is from chloroform since it has been observed that with this solution the best results in terms of membrane permeability recovery have been obtained since, the permeability of the cleaned membrane was only 20% lower than that of the original fresh membrane, well above the other methods tested, which are from acetone, hot water, hot water and detergent, aqueous solutions of water and nitric acid and aqueous solutions of NaOH.

The results were that the permeability of the cleaned membrane was less than 50% of that of the original fresh membrane.

In addition to cleaning the membrane with chloroform, the membrane was also cleaned with demineralised water before being used again.

We proceed with a critical discussion of the membrane extraction process.

The operating pressure must be sufficient to circulate the oil inside the fibres, but not too high because between the oil and the extracting phase there is a membrane that is in contact with these two phases and a small emulsion could form.

This extracting phase is hydrophilic and must also be able to dissolve the salts because if they precipitate, they could clog the membrane. The most economical extractor is water, but the possibility of clogging the membrane is considerable due to the formation of an emulsion between the water and the oil. For this reason, it was decided to use an aqueous ammonia solution, as this is the one with which the best results were obtained according to the study. [23]

There is a considerable pressure drop in this operation, so a possible solution is to divide the flow into several smaller ones so that the clogging of the membranes is smaller, and the flow rate is lower.

The permeability of the membrane must be increased after rinsing, as about 20% of the permeability is not recovered. The process, if used, will be done with more than one membrane, i.e. there will be at least two in parallel since while one is being used in the process, the other(s) will be being cleaned. Furthermore, doubling in the proposed way would also allow operating with lower flow rates for each of the membranes, since if, for example, four membranes are operated, i.e. two being used in the process and the other two being washed, the flow rate that would treat each of the membranes would be lower, and consequently the cleaning would be extended and there would be more time to wash the membranes.

### 6.1.3. Ion exchange resin

The objective of the ion exchange resins process is to remove metals and anions from oil. For anions, this operation is of great importance to remove chlorides and thus reduce corrosion of equipment.

This operation is important because it can allow the reduction of chlorides and metals to very low values, so it is a final removal operation, i.e. it is not used to treat all the chlorides and metals that come into the oil but rather to finish reducing the levels of these two impurities.

The block diagram for the ion exchange process is shown in Figure 14 below.

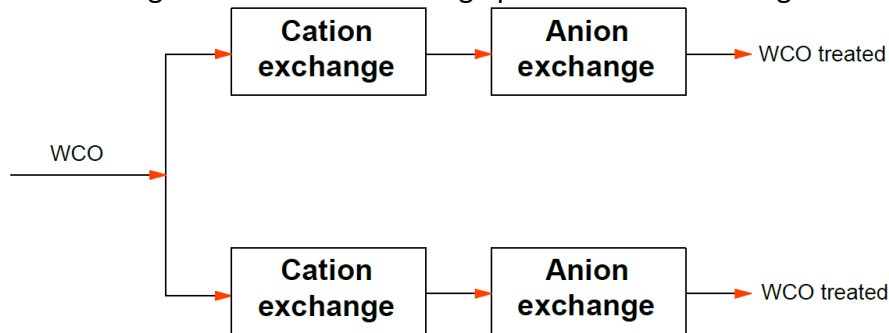


Figure 14. Block flow diagram of ion exchange process. A pair of ion exchange processes (one for cations and one for anions) in parallel.

The number of resins used for each ion exchange process is not shown in the Figure 14

The diagram in Figure 14 is described in more detail below, where the membrane extraction process is based on [8].

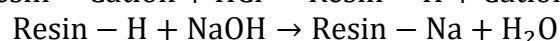
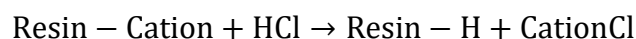
With this process, the oil is passed through a resin in order to remove ions from the oil and exchange them for other ions in the resin. This process is carried out in a column where there is a bed of ion exchange resin so that the fluid passes through the resin.

It is common to use columns of ion exchange resin beds in series and parallel. At least 1 should be used for each cation valence and there are cations of valence one, two and three. To remove chlorides, an anion removal resin will be required.

One of the options for the regeneration of cation exchange resins is to use an HCl solution. It is circulated through the exchange column dropwise for a sufficient time to regenerate the resin. The HCl solution replaces the cations adsorbed on the resin, as they are replaced by hydrogens. To finish removing the exchanged metals, which have been bound to the chlorides from the HCl, the bed is washed with countercurrent water (to avoid channelling) and dried. In this step, the metals present in the resin are recovered from the oil.

One of the options for the regeneration of anion exchange resins is from a NaOH solution. It is allowed to flow through the exchange column dropwise for a sufficient time to regenerate the resin. The NaOH solution replaces the anions absorbed on the resin as they are replaced by hydroxides. Again, to remove the sodium salts, which have been formed by the exchange of OH ions with those adsorbed on the resin, the bed is washed with countercurrent water (to avoid channelling) and dried.

The regeneration to sodium form of resin loaded with a cation from metals would proceed as follows:



To know the sufficient regeneration time, it is necessary to control the pH at the inlet and outlet of the column, since when the pH at the inlet and outlet is the same, it means that the column has been regenerated.

Some distributors of these resins are DUPONT with the different Amber models and BIO-RAD Laboratories with the Chelex models. [8]

This is followed by a critical discussion of the ion exchange process.

The variables of pH, residence time, flow rate, initial residue concentration, bed dimensions, viscosity, resin lifetime and membrane porosity are all important.

The pH is important to monitor because its variation at the outlet of the column may indicate that the breakpoint or depletion point has been reached. When the breakpoint is reached, the pH at the column exit varies rapidly because the effectiveness of the resin is starting to be reduced, as there is little resin contact surface left without depletion. At the point of exhaustion, the pH at the column outlet is practically identical to that at the column inlet because there is no ion exchange in the resin.

The residence time must be sufficient to remove the residues from the oil stream, if it is less than required, the output stream will still have metals at a higher value than desired. A shorter residence time than required may be due to preferential pathway channelling that may occur in the bed. On the other hand, if it is longer than required, the output stream will leave with adequate residue requirements, but the oil is being held longer than necessary, and may also promote pore blockages in the resin.

The flow rate is one of the aspects to be discussed, as it is possible to operate with downward or upward flows. Each alternative has its pros and cons, starting with the downward direction. It can be done by gravity or with the help of a pump, the fact is that it is common to produce channelling so that the efficiency of the resin would be reduced, and it would also be exhausted sooner as more flow would pass through the same  $m^2$  of resin in the case that this channelling occurs. Therefore, it is a more economical option a priori, as it can be done by gravity (or with the help of a pump, but the consumption will not be as great as if it has to be pumped upwards), but the efficiency is lower.

On the other hand, if the flow is upward, the requirements of the pump are greater, as the pressure losses are higher, since a microporous resin with a considerable viscosity has to be passed through. On the other hand, the efficiency is higher, as the oil has no channels in order to warrant perfect wetting of resin and, accordingly, to maximize the contact between resin and heavy metal ions in the feed solution. [15]

The quality of the raw material influences the operating variables, since, if sufficient metals and chlorides have been removed in previous operations, the contact and exchange time may be shorter than if they have a higher content. This is achieved by increasing or decreasing the velocity of the fluid passing through the column, i.e. the fluid pressure.

The dimensions of the bed depend on the initial concentration of waste, since the greater the amount of waste to be adsorbed, the greater the surface area of ion exchange required, so the greater the height of the bed. It is true, however, that when designing the ion exchange bed communities, they are made narrower to reduce the number of possible channels that can form.

Sufficient fluidity is required for this process, because if the fluid is too viscous, it will have great difficulty flowing through the resin, which may end up clogging. Ion-exchange technology from resins already has the difficulty of the large pressure drop that the system suffers due to the passage through the resin, but if the fluid is also considerably viscous, the operation is even more difficult, so there are two alternatives.

One of them is to increase the temperature of the fluid in order to reduce the viscosity, the disadvantage of the oil is that if the temperature is increased, the fatty acids polymerise, and thermal degradation is also favoured, so that a poorer quality oil



is obtained. In addition, too high operating temperatures shorten the lifetime of ion-exchange resins because many resins on the market have a maximum operating temperature of 60 - 100 °C. [65]

For the reasons described above, the operation should be carried out at room temperature.

On the other hand, to reduce the viscosity of the oil, an organic solvent can be used with characteristics such as being miscible with the oil, not producing any reaction, not causing any additional problems to the cracker, having a low viscosity, being economically viable to use and being reusable. Some of these solvents are e.g., alcohols, ketones. [65]

Another drawback of ion exchange resins is that they have a short lifetime, as they are easily exhausted, so they need to be regenerated frequently, so that it will be necessary (at least) to double the amount of resins so that when one is operating the other is regenerating, i.e. they will be placed in parallel. In this way, regeneration downtimes are reduced or non-existent for this process.

On the other hand, it is worth mentioning that this operation replaces metal cations with other metal cations contained in the resin, which is used for ion exchange. Consequently, it is possible to reduce the amount of a series of metals that can damage the cracker, so that this requirement would be reduced, but the "Total Metals" requirement would be increased. In conclusion, this operation serves to remove a metal cation that particularly damages the cracker or hinders its operation, but subsequently the metal that has been exchanged must be removed.

In addition to the above, it is also important to note that the columns with the ion exchange resin are placed in series because they have greater selectivity with those ions that have the same valence as the ion coming from the resin, for example, you want to remove Na cations, which have +1 charge, but you also want to exchange Zn cations, which have +2 charge, so at least 2 resins will be required in series, since the selectivity of the resin for sodium cations will also be adequate for cations of valence 1, and the selectivity for cations of different valence will be lower, therefore, to remove cations of valence 2, another resin must be added, which in addition to removing zinc cations will also be adequate to remove calcium and magnesium, for example.

Another reason to put ion exchange resins in series is because you also want to exchange anions, to remove chlorides.

#### 6.1.4. Degumming

The objective of degumming is to remove the phospholipids present in the oils, both the hydratable and non-hydratable ones, in addition to removing the non-hydratable phospholipids, metals are also removed, as indicated in the section on "5.3.1.2. Characterisation, Phospholipids", as these are attached to the chains of the non-hydratable phospholipids. In this case, the metals removed are calcium, magnesium and sodium. The amount of free fatty acids is also reduced. Waxes are also removed.

This operation is important because it reduces the amount of phosphorus in the oils, thus reducing the formation of phosphoric acid and consequently reducing corrosion. In addition, the reduction of the amount of metals reduces the oxidation of the oil, as metal hydroxides can form with oxygen. Finally, the reduction of fatty acids reduces the acidity of the oil, thus reducing the corrosion caused by chlorides in the oil.



In addition, the removal of waxes lowers the viscosity so that pumping costs will be lower.

Figure 15 below shows the block diagram for the degumming process applied in the pre-treatment.

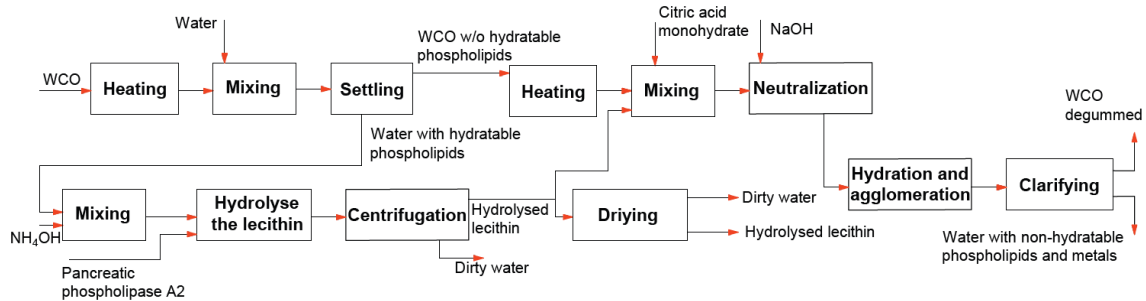


Figure 15. Block diagram of the process used for degumming.

The process of degumming on which Figure 15 is based is described in detail below. [45, 55, 63]

The first step is to describe the degumming process with water, followed by chemical degumming with hydrolysed lecithin.

The oil is heated to 80°C and 2.2% deionised water (by weight of the oil) is added. It is left for 20 minutes with stirring to ensure interaction between the oil and water. After the time has passed, the gums (hydratable phospholipids) are removed by settling to separate the oil phase from the aqueous phase. In addition, lecithin from the hydratable phospholipids is present in this sludge and is treated for later use in the process of removing the non-hydratable phospholipids.

For the process of obtaining lecithin, first of all, the pH of the aqueous phase is raised to pH = 8 from an ammonium hydroxide solution. Then a quantity of pancreatic phospholipase A2 equal to 0.15% by weight of the lecithin present is added. This mixture is left in a storage tank for 12 hours to allow the enzyme to hydrolyse the lecithin. Once this mixture contains the hydrolysed lecithin, the quantity required for the subsequent process of removing non-hydratable phospholipids can be added, since in the aqueous phase from settling or centrifugation to 80% by weight is lecithin. On the other hand, the excess lecithin is dried for its commercialisation, as it must have a quantity of less than 1% in water and cannot have a quantity of more than 20% in oil.

For the removal of the non-hydratable phospholipids, the oil is heated to 80°C and 0.12% (by weight of oil) of citric acid monohydrate from a 50% solution with deionised water is added. An amount equal to 2.2% (by weight of oil) of hydrolysed lecithin is also added. During the addition of acid and lecithin, the oil is kept under intense agitation for 20 minutes. Subsequently, an amount equivalent to 15% by weight of free fatty acids from a 2 - 3M solution of sodium hydroxide in deionised water is added. A more or more than the amount necessary to neutralise the added citric acid monohydrate is added. Stirring is reduced for 3 hours and the temperature of the mixture is reduced to 25-30°C. This allows hydration and agglomeration.

Finally, to improve the flowability, the mixture is heated to 65°C and rapidly clarified with about 7 flow rates per hour.

If necessary, rinsing with deionised water can be done to remove the formed gums and soapstock. Subsequently, to reduce the water content in the oil, vacuum drying can be carried out.

As a result of this process, the following oil specifications are expected to be obtained:

<b>Oil characteristics</b>	<b>Before degumming</b>	<b>After degumming</b>
Phosphalipids	302 ppm wt.	1 ppm wt.
Free fatty acids	3.27 % wt.	0,81 % wt.
Calcium	5.3	0.3 ppm wt.
Magnesium	-1.5	0.1 ppm wt.
Iron	22 ppm wt.	< 0.1 ppm wt.
Sodium	64 ppm wt.	4.3 ppm.

This is followed by a critical discussion of the degumming process with water to remove the hydratable phospholipids.

A suitable amount of water is added to the preheated oil and stirred. The hydratable phospholipids pass into the aqueous phase in about 5 - 45 minutes, as they pass to the interface between the aqueous phase and the oil phase, and this occurs as a result of the weak dipole-dipole interaction (hydrophilic) between the polar head group of phospholipids and the water molecules. Removal requires centrifugation or decantation. After separation of the hydratable phospholipids, the phospholipids are reduced to 100-200 mg/kg. These phospholipids contain lecithin (phosphatidylcholine) so a by-product is obtained in this treatment.

In order to further reduce the phospholipid content, a further process is required after degumming with water.

A critical discussion of the degumming process to remove non-hydratable phospholipids by addition of acid is given below.

To remove the non-hydratable phospholipids, proceed as follows:

To the preheated oil a suitable amount, between 0.1 - 0.5% (by weight of the oil) of a 50% solution of citric or malic acid or 0.1% (by weight of the oil) of phosphoric acid from a 75% solution is added. Good agitation is required for better contact between the acid solution and the oil to improve reaction times. These acids act as chelating agents to the nonhydratable phospholipids resulting in oil-insoluble salts, and hydratable phospholipids, which can be easily removed. It is estimated that the reaction can take from a few minutes to 30 minutes. [45, 63]

After the reaction time has elapsed, the non-hydratable phospholipids become hydratable due to the reaction between the acid and the non-hydratable phospholipids, as indicated above. [45]

To remove them, an appropriate amount of water is added. After the addition of water, the mixture is stirred further to promote agglomeration of salts (magnesium, calcium or iron salts formed) and hydratable phospholipids formed which are insoluble in water. Subsequently, separation is carried out by settling.

This is followed by a critical discussion of the process of degumming by neutralisation to remove non-hydratable phospholipids and neutralise free fatty acids.

Chemical degumming is suitable if the oil has been degummed with water and is also usually carried out if there has been a previous acid degumming process. Alkaline refining is carried out to lower the phospholipid content of the oil to levels in the order of 20 - 50 mg/kg. [63]

An acid, usually concentrated phosphoric acid, citric acid or malic acid, is added to the tempered oil and the mixture must be shaken vigorously in order to precipitate non-hydratable phospholipids left after the previous degumming.

The added acid is neutralised with a 2 - 3M sodium hydroxide solution. In addition, the sodium hydroxide must be stirred when adding the sodium hydroxide so that there is a good interaction between the mixture and the alkaline solution. It is also kept at a certain temperature to increase fluidity and facilitate contact between the mixture and the alkaline solution. On the other hand, the amount of sodium hydroxide must be sufficient to neutralise the added acid and free fatty acids, so the amount will depend on the quality of the oil. [36, 37]

When sodium hydroxide is added, neutralisation takes place, but at the same time, the saponification reaction takes place, thus consuming part of the raw material for soap formation. The result is a soapstock, which is removed together with the phospholipids and salts by centrifugation or decantation.

Depending on the soapstock formed, it is advisable to wash with water to ensure the removal of the soap from the oil, which has been formed by the saponification reaction. Finally, the remaining water in the oil is removed using a vacuum dryer, where the water is reduced to about 0.1% (by weight) of water.

When water is added to the oil, the hydratable phospholipids move to the interface between the aqueous phase and the oil phase and this occurs as a result of the weak dipole-dipole interaction (hydrophilic) between the polar head group of phospholipids and the water molecules. This interaction results in phase transitions, in this case, oil-soluble hydratable phospholipids transform into oil-insoluble lamellar liquid crystals (gum).

The lower the amount of residual phospholipids after the degumming step, the better or easier the subsequent refining steps will be, because less bleaching clay will be required in the bleaching step, so it will have a positive impact from an economic point of view.

Hydrolysed lecithin plays a very important role in removing phospholipids from the oil, so a critical discussion of the importance of its addition is given below to justify its addition to the process.

The hydratable phospholipids are formed among others by phosphatidylcholine also known as lecithin and hydrolysed lecithin offers many advantages for oil refining since it facilitates the elimination of phospholipids, and other impurities such as glycerol, waxes, etc. It also allows to reduce the loss of oil due to being dragged by the aqueous phase in the separation of the aqueous phases.

Hydrolysed lecithin is defined as lecithin in which the phosphatidylcholine has been hydrolysed to 20-80% by weight. Examples of hydrolysed phospholipids on the market are Bolec K and Solec K, which are obtained from soybean and sunflower oils, respectively, have been enzymatically hydrolysed to between 45 and 55%. [45]

A lecithin-containing slurry portion and/or a lecithin-containing aqueous phase, which can be subjected to acid, basic or enzymatic hydrolysis to produce hydrolysed phospholipids for use in the refining process.

Obtaining lecithin starts with separation by centrifugation or decantation to obtain the aqueous phase where the hydratable phospholipids are present, as it is in the sludge from degumming with water that the vast majority of phosphatidylcholine is present.

The procedure for the enzymatic hydrolysis of lecithin described in the patent US 4,584,141 is then developed: [45]

Start by tempering the sludge obtained by centrifugation to 70 - 90°C. The pH of the aqueous phase is raised to a basic pH around 7 - 9 from an ammonium hydroxide solution. Next, a solution containing phospholipase A2 is added to the sludge or aqueous phase and mixed thoroughly therewith. The mixture is left long enough for the phospholipase to act, an indicated time would be between 2 - 20 h.

Once this mixture contains the hydrolysed lecithin, the required amount can be added for the subsequent process of removal of non-hydratable phospholipids, since in the aqueous phase from centrifugation or decantation up to 80% by weight is lecithin. This crude lecithin is processed for further use in the process of removing non-hydratable phospholipids. On the other hand, the excess lecithin is dried for marketing in the food industry.

It should be noted that for lecithin to be used in the food industry it is important not to use inedible acids. For this reason, citric acid is used instead of phosphoric acid, for example.

The first step is to heat the sludge obtained by centrifugation to 70 - 90°C. The pH of the aqueous phase is raised to a basic pH around 7 - 9 from an ammonium hydroxide solution. Next, a solution containing phospholipase A2 is added to the sludge or aqueous phase and mixed thoroughly therewith. The mixture is left long enough for the phospholipase to act, an indicated time would be between 2 - 20 h.

Once this mixture contains the hydrolysed lecithin, the required amount can be added for the subsequent process of removal of non-hydratable phospholipids, since in the aqueous phase from centrifugation or decantation up to 80% by weight is lecithin. This crude lecithin is processed for further use in the process of removing non-hydratable phospholipids. On the other hand, the excess lecithin is dried for marketing in the food industry.

It should be noted that for lecithin to be used in the food industry it is important not to use inedible acids. For this reason, citric acid is used instead of phosphoric acid, for example.

#### 6.1.5. Bleaching

Bleaching is the process of removing pigments (mainly carotenoids and chlorophyll) and also compounds remaining in the neutralised oil, such as soaps, phospholipids and metal ions. This is achieved by the use of bleaching clays from adsorption on the clay.

This operation is important to remove the carotenoids and chlorophyll present in the oil, since as indicated above in chapter 5.3.1.2 "Characterisation, Carotenoids and chlorophyll" there is a type of carotenoids the xanthophylls that have oxygen in their

molecular structure, so they must be removed, as oxygen in the cracker can form CO and CO<sub>2</sub>, and so the lifetime of the catalyst is enhanced. Chlorophyll has nitrogen, magnesium and oxygen in its molecular structure, so again in the cracker, it can generate CO and CO<sub>2</sub> and also with nitrogen it can react to form ammonia, which causes corrosion in the equipment. Magnesium must also be reduced, as the amount of metals entering the cracker should be as small as possible, as shown in Table 2 "Cracker input specification" in chapter 5.1. Cracker and steam cracking.

On the other hand, the removal of soaps reduces the viscosity.

Furthermore, carotenoids and chlorophyll are unsaponifiable matter, so they cannot be removed by the process of degumming.

The block diagram for the bleaching process applied in the pre-treatment is shown in Figure 16

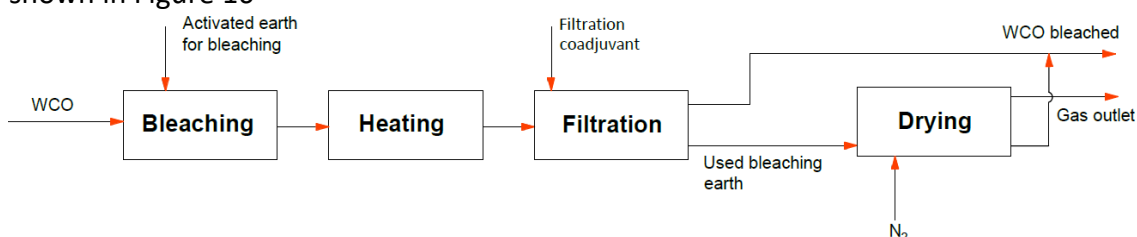


Figure 16. Block diagram of the process used for bleaching.

The bleaching process on which Figure 16 is based is described in detail below.

To bleach the oil, start by adding a quantity of activated bleaching earth equal to 1.0% by weight of the oil. Also, 0.2% (by weight of the oil) of filtration adjuvant is added in order to favour the removal of the bleaching clay with the adsorbed matter in the subsequent filtration. Following the addition of the clay and the adjuvant, the oil temperature is increased to 120°C under vacuum conditions of 266 Pa (equivalent to 2 mm Hg) absolute pressure, and agitation is also required to increase the contact between the oil and the clay. The temperature increase, pressure reduction and agitation are carried out for 20 minutes. Subsequently, the oil is filtered in order to separate the oil from the bleaching clay with adsorbed solutes. The cake is dried by steam blowing or nitrogen to lower amount of remaining oil in the bleaching clay. Nevertheless, 20 - 40% of the cake consists of oil. So, with the oil remaining in the clay it can be removed using an inert gas, e.g., nitrogen and returned with the oil separated by filtration. [57]

The bleaching earth used for the process described is from Filtrol Corporation under the brand name Filtrol@ 105. The filtration aid used in the process is from Johns-Manville Corporation under the brand name Filtercel@.

Some of the adsorbed compounds can be processed to be used as by-products, such as chlorophyll and carotenoids. [58]

The results are shown in Table 11 together with the deodorization results, as the selected patent EP 0,077,528 B1 [57] indicates the results obtained for the bleaching process together with the deodorization process.

Oil characteristics		Before bleaching and deodorization	Before bleaching and deodorization
Phospholipids		1 ppm wt.	1 ppm wt.
Free fatty acids		0,81 % wt.	0,010 % wt.
Iron		< 0.1 ppm wt.	< 0.1 ppm wt.
Tocopherols		1100 ppm	940 ppm
Colour	Red	9.1	0.1
	Yellow	42	1
Chlorophyll		30 ppm wt.	< 1.3 ppm wt.
Carotenoids		600 ppm wt.	Note 1
Ketones		Note 1	Note 1
Aldehydes		15 ppm wt.	Note 1
Phytosterols		5,200 ppm wt.	Note 1
Alcohols		1.39 ppm wt.	Note 1
Pyridine		0.28	Note 2
Pyrazine		0.42	Note 2
<p>Note 1* No values have been found as a result of the process described above for bleaching and deodorization, but it is mentioned as being reduced in the following bibliographies: [18, 38]</p> <p>Note 2: No literature has been found that states the values that are reduced after the bleaching and deodorization process.</p>			

This is followed by a critical discussion of the bleaching process.

It is important to ensure a good reduction of phospholipids before bleaching, otherwise a larger quantity of bleaching clay will be required to adsorb the unremoved phospholipids as well as the pigments, the latter being the reason for bleaching.

The bleaching process is based on the interaction between the adsorbent material (the clay) and the solute. The interaction between the adsorbent material and the solute is by the formation of Van der Waals bonds in the case of pigments and ionic bonds for metal ions. It should be noted that acid-activated bleaching clays have a higher adsorption capacity than natural ones, due to increased electrostatic adsorption.

There may be an increase in free fatty acids in the oil after bleaching, this is due to the operating temperature of the bleaching and the humidity of the activated bleaching clays, as it favours hydrolysis in the oil and therefore the formation of polar molecules.

In this process, chlorophyll and carotenoids are obtained as a by-product, which if processed can be marketed, since chlorophyll has well-known uses and carotenoids, specifically  $\beta$ -carotene has antioxidant and colouring properties, so that it can be used in the food industry. In addition, the  $\beta$ -carotene isomer is the most abundant in the oil.

#### 6.1.6. Settling with skimming

With this process, metals are reduced in the form of salts and particles because these precipitate and are extracted by decantation. In case there are very small metal

particles that remain suspended in the oil, they are also retained by the arrangement of the baffles.

The process and critical discussion of the process are developed in chapter 6.2.3. Settling with skimming.

## 6.2. Ash and particles removal

The removal of ash and suspended solids is important, as they can cause fouling, corrosion, catalyst poisoning, erosion of pipes and equipment, and can cause clogging of pipes and coke formation in the cracker.

Ash comes from food debris left in the used oil and solid particles come from metals due to the detachments on cooking utensils or from refining to obtain edible oil, as there may also be detachments of metal particles from the processing equipment.

The methods used to remove ash and solid particles from the oil are desalting, settling with skimming, degumming, membrane extraction

### 6.2.1. Desalting

Ash that is polar precipitates with water, but non-polar ash settles at the water-oil interface. In addition, some ash has a tendency to remain dissolved or on the surface, especially those with very small particle sizes, as they have a very low settling velocity. The process and critical discussion of the process are developed in chapter 6.1.1. Desalting.

### 6.2.2. Degumming

In degumming, water is added first, so that polar ash settles in the aqueous phase, but on the other hand, non-polar ash will remain at the oil-water interface. With degumming by adding acid, a greater amount of ash sediments, but there will still be a significant part of the ash that will not precipitate, as some ash tends to remain dissolved or on the surface, especially those with a very small particle size, as they have a very low sedimentation velocity. The process and critical discussion of the process is developed in chapter 6.1.4. Degumming.

In order to check if desalting and degumming water would also remove ash, a test is carried out. The process followed in the test to remove the ash is detailed below.

Firstly, a vessel is filled with used vegetable oil. In this case, the used oil is olive oil and has been used for canning, frying and cooking in the oven. Figure 17 (a) and (b).

Then a small amount of water is added and mixed. Figure 17 (c).

Heat the oil and water mixture for 10 min. Figure 17 (d) and (e).

Allow resting for 30 min. Figure 17 (f).

The results obtained are as follows:





(a)



(b)



(c)



(d)



(e)



(f)

Figure 17. Set of photos from the ash test. (a) Not used oil on the left. Used oil on the right, (b) Used oil with a close-up view, (c) When water is added, (d) Heating the mixture of used oil and water, (e) Result of heating, (f) Result of heating and leaving to repose.



As can be seen in Figure 17 (a), there is a noticeable colour change in the used oil and the unused oil. This is due to the carotenoid content, which gives the orange-yellow colour as they are basically pigments. Figure 17 (b) shows how there are particles both at the bottom that have already precipitated and how there are also particles that have not precipitated. Furthermore, in this same Figure it can also be seen that there are very small droplets in the oil, this is due to the water content in the oil. The water comes from the food and the cooking process.

Figure 17 (b) and (c) shows that when water is added, part of the ash precipitates into the aqueous phase but the other part remains at the interface, this is because there is polar ash and non-polar ash.

When the oil-water mixture is heated, the evaporating water passes to the surface of the oil, i.e. it crosses the oil-water interface and passes to the surface of the oil. It carries ash particles with it, which is detrimental if the ash is to be decanted with the water, as the ash is dissolved throughout the oil and even remains on the surface of the oil, as can be seen in Figures 17 (d) and (e).

In addition, it is also observed that the finer particles remain suspended in the oil and it is more difficult for them to precipitate and some of them even remain on the surface.

It has also been observed that if the agitation is faster, the emulsion formed of water and oil takes longer to stabilise and that the addition of water at the beginning is also decisive for the stability of the emulsion, since if it is added carefully, the two phases separate well, whereas if water is added under pressure, the emulsion formed of water in oil is more difficult for the phases to separate.

### 6.2.3. Settling with skimming

As can be seen in the desalting and water degumming test. Some solids remain suspended in the oil as they have a low sedimentation rate, some solids remain precipitated in the oil and other solids remain at the oil-air interface, i.e. they remain on the surface of the oil.

Indeed, the main objective of desalting and water degumming are not to remove the ash, but it is important to remove it at the beginning of the process, as these residues can cause clogging, reductions in performance in chemical processes, erosion, etc.

Therefore, the following device is proposed to remove most of the ash in the WCO.

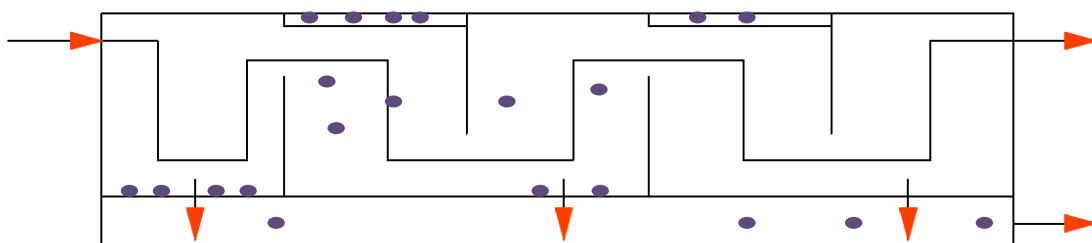


Figure 18. Proposal to remove ash from WCO. The ash at the bottom is decanted, while the ash at the top is removed by skimming.

On reception of the WCO, it is passed through a tank with a series of vertical baffles interspersed in such a way that the baffles encourage the settling solids to stay

at the bottom and the solids remaining on the surface to stay at the top, as shown in Figure 18. The solids that are suspended in the oil and have a lower precipitation velocity would remain still in the baffle interlayers.

To remove the solids that remain in the upper part of the oil, skimmers are used and the solids that precipitate in the lower part are decanted through a discharge outlet. The clean ash oil overflows, as shown in Figure 18.

In order for the proposed process to remove the necessary amount of ash, it is important to ensure an adequate process flow rate so that the residence time is sufficient to settle the ash located in the lower parts of the oil and so that the ash located near the surface agglomerates on the surface and can be removed by skimming.

There are different options to remove the ash, such as centrifuging or filtering, but the proposed option is the least expensive and operationally the simplest.

#### 6.2.4. Membrane extraction

The ash and solid particles are extracted from the oil through the membrane with the extractor fluid. It is desirable that the ash content in this operation is not too high, because a high ash content will lead to a higher pressure drop, and the efficiency of removing dissolved salts and metals will be reduced, as there will be fewer extraction pores due to the clogging caused by the ash and metal particles.

The process and critical discussion of the process is developed in chapter 6.1.2. Membrane extraction.

### 6.3. Chlorides removal

The removal of chlorides is important, as they can cause mechanical failure of equipment due to corrosion caused by the formation of hydrochloric acid and must therefore be reduced.

Chlorides present in oil are in inorganic form, as they are present as an anion forming salts.

The methods used to remove chlorides from the oil are desalting, membrane extraction, ion exchange resin, settling and skimming.

#### 6.3.1. Desalting

Chlorides are removed by precipitation of salts in the water used in desalting. The process and critical discussion of the process is developed in chapter 6.1.1. Desalting.

#### 6.3.2. Membrane extraction

The chlorides are removed by extraction of the salts through the membrane with the extraction fluid, which is an aqueous solution of ammonia. The process and critical discussion of the process is developed in chapter 6.1.2. Membrane extraction.

#### 6.3.3. Ion exchange resin

Chlorides are removed by ion exchange between the resin and the chloride anions. The process and critical discussion of the process is developed in chapter 6.1.3. Ion exchange resin.

#### 6.3.4. Settling and skimming

Chlorides have been removed because this process removes salts. The process and critical discussion of the process is developed in chapter 6.2.3. Settling and skimming

### 6.4. Phosphorous removal

The phosphorus present in the oil must be removed because phosphoric acid can be formed, which attacks the metal tubes of the furnace, causing the thickness to decrease.

Phosphorus is present in the oil in the form of hydratable and non-hydratable phospholipids, i.e. there are phospholipids where the addition of water to the oil is sufficient to bring them into the aqueous phase, whereas non-hydratable phospholipids require the addition of a chemical agent, such as an acid, to make them water soluble.

The methods used to remove phosphorus from the oil are desalting, degumming, bleaching.

#### 6.4.1. Desalting

Phosphorus is removed when water is added to precipitate salts, hydratable phospholipids also precipitate. The process and critical discussion of the process is developed in chapter 6.1.1. Desalting.

#### 6.4.2. Degumming

Degumming is the operation par excellence for phosphorus removal as both hydratable and non-hydratable phospholipids are removed. The process and critical discussion of the process is developed in chapter 6.1.4. Degumming.

#### 6.4.3. Bleaching

Phospholipids can be absorbed in bleaching earth. The process and critical discussion of the process is developed in chapter 6.1.5. Bleaching.

### 6.5. Oxygen removal

The removal of oxygens is very important for the correct functioning of the cracker because with oxygen in the cracker CO and CO<sub>2</sub> are formed, where CO is the most problematic as it numbs the cracker catalyst and is also the most important of the two carbon oxides, as it is the one that causes the most damage to the cracker catalyst.

Metals are present in salts, as well as in particles from cooking utensils, from processing for oil production or from the soil in which the raw material for oil production has been processed.

The methods used to remove oxygens from oil are bleaching, deodorization, hydrotreatment.

#### 6.5.1. Bleaching

Oxygen is removed in the bleaching process because the amount of xanthophylls and chlorophyll is reduced. These two components have oxygen in their molecular

structures. The method of removal of these components is by adsorption on the bleaching earth. The process and critical discussion of the process is developed in chapter 6.1.5. Bleaching.

### 6.5.2. Deodorization

The aim of deodorization is to reduce the content of free fatty acids and oxygen due to oxidation products during the cooking process (such as aldehydes, ketones), also alcohols, phytosterols and tocopherol, thanks to their vapour pressure, as they are more volatile compounds than fatty acids, so they can be separated by taking advantage of this characteristic.

Deodorization also removes organic nitrogen compounds such as pyridine and pyrazine, as these have boiling temperatures below the operating temperature of the deodoriser.

During deodorization, bleaching also takes place, as compounds such as carotenoids and lecithin are sensitive to heat, so their content is also reduced in the deodorization process. [21]

This operation is important because it reduces the corrosion caused by the free fatty acids which are removed, and also reduces the amount of oxygen in the oil by the removal of aldehydes, ketones, alcohols, tocopherol, etc.

The block diagram for the deodorization process is shown in Figure 19.

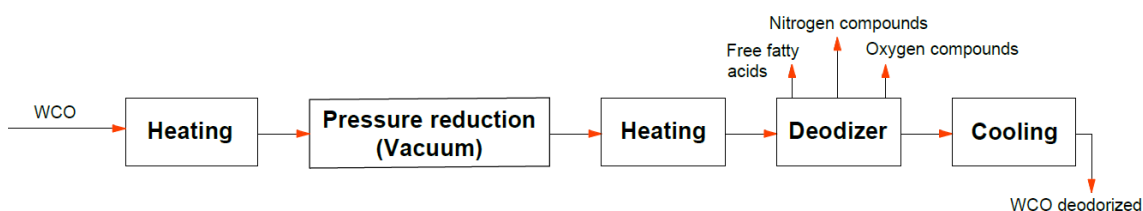


Figure 19. Block flow diagram of deodorization process. Fatty acids, pyridine and pyrazine (nitrogen compounds) and aldehydes, alcohols, ketones, phytosterols and tocopherol are removed in the deodorizer.

The diagram in Figure 19, where the deodorization process is based on patent EP 0,077,528 B1 [57], is described in more detail below.

The deodorization process starts with a deaeration. The oil is first heated to about 85 - 90°C and then distributed through a distribution ring and nozzles into a deaerator which is maintained at the same vacuum as the deodorizer. Deaeration is not done in the deodoriser.

After the deaeration stage, the oil is heated to the operating temperature of the deodorizer. The deodorization takes place for 90 minutes at 240°C and under vacuum pressure conditions of 26.6 Pa (equivalent to 0.2 mmHg) absolute pressure using 1.5% water vapour, i.e., 15 kg water vapour per tonne of oil. Finally, the oil is cooled to a temperature of 60 - 80°C at absolute pressures below 1 atm. [18]

The expected results during the deodorization process are listed in Table 11 “Oil from bleaching and deodorization process.” in chapter 6.1.5. Bleaching, as the results found were with the bleaching operation.

A critical discussion of the deodorization process follows.

First of all, deaeration is the first step because oxygen must be removed from the deaerator to minimise oxidation and polymerisation that would occur during deodorization, since when working at high temperatures and low pressures, it is necessary to remove as much oxygen as possible from the environment because it favours oxidation. In addition, polymerisation is favoured by high temperatures.

Deaeration is carried out in an external deaerator, i.e. it is not carried out in the same equipment as deodorization. The mixture is heated and then distributed through a distribution ring and nozzles into a deodoriser which is maintained at the same vacuum as the deodoriser.

Then, the oil is heated and then introduced into the deodoriser for the deodorization operation.

In the deodoriser, the oil enters through the upper part of the equipment and descends through the holes in trays, while the steam or inert gas used is introduced from the lower part of the equipment. By operating in this way, a higher extraction is achieved as it operates in countercurrent.

Finally, the oil is cooled and the pressure is lowered to absolute pressures below 1 atm in order to reduce the effects of thermal degradation, polymerisation and oxidation, since reducing the pressure reduces the possible interaction of oxygen from the environment with the oil and reduces the temperature reduces the thermal degradation and polymerisation of the triglycerides.

Also, it is highly recommended that an inline gas diffuser be used to inject nitrogen gas into the deodorized oil as it leaves the deodorizer. The combination of nitrogen diffusion and nitrogen blanket in the storage tank protects the oil from oxidation.

On the other hand, the deodoriser distillates can be collected in a scrubber cooler where it is separated from the steam and can be recovered to produce vitamin E in the case of tocopherols. The deodoriser distillate can be valuable if high levels of tocopherols and phytosterols are present in the composition.[21]

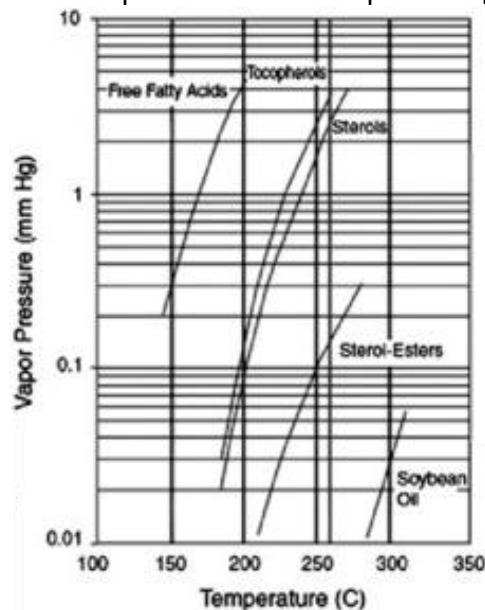


Figure 20. Relative volatility of some compounds in vegetable oils. [18]

**Table 12. Volatility and molecular weight of some components removed during deodorization. [18, 21]**

Component	Molecular weight	Relative volatility
Free fatty acid	280*	2.5*
Tocopherol	411	1
Sterol	410	0.6
Sterol ester	675	0.04
Oil	885	↓↓↓

\* The molecular weight is variable depending on the free fatty acids, so the volatility will also be variable, the figure of 2.5 corresponds to the linoleic acid of 280 g/mol,  $C_{18}H_{32}O_2$

From Figure 20 it is evident that these compounds can be removed with a suitable operating temperature and pressure, as they are more volatile than oil. The temperature and pressure must be adequate as this operation is critical, as it degrades the oil considerably due to oxidation, thermal degradation and polymerisation.

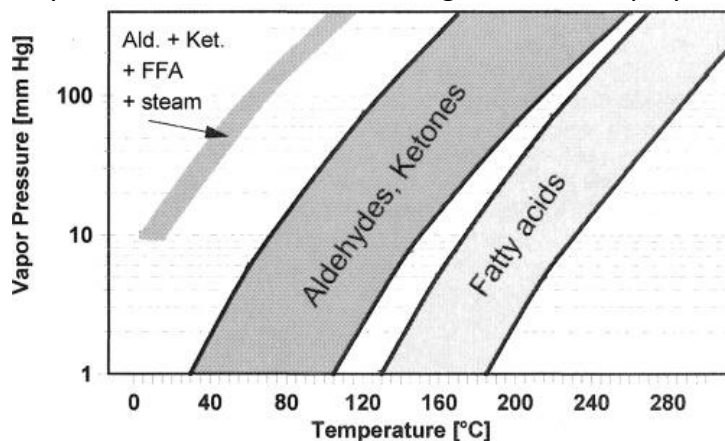


Figure 21 Vapour pressure as a function of operating temperature. [9]

Figure 21 shows that aldehydes and ketones can be removed from the oil under the right operating conditions. It also corroborates those free fatty acids can be removed.

### 6.5.3. Hydrotreatment

Hydrotreating aims to remove oxygens and nitrogen from the organic chains because otherwise the lifetime of the catalyst in the cracker would be reduced due to the presence of CO and CO<sub>2</sub> formed from the oxygen in the fatty acid chains. In addition, due to the presence of nitrogen, ammonia would be formed in the cracker, which would come out of the upper extractions such as ethylene and propylene, so that it would come out with a lower quality and ammonia is corrosive.

The block diagram for the hydrotreatment process is shown in Figure 22 below.

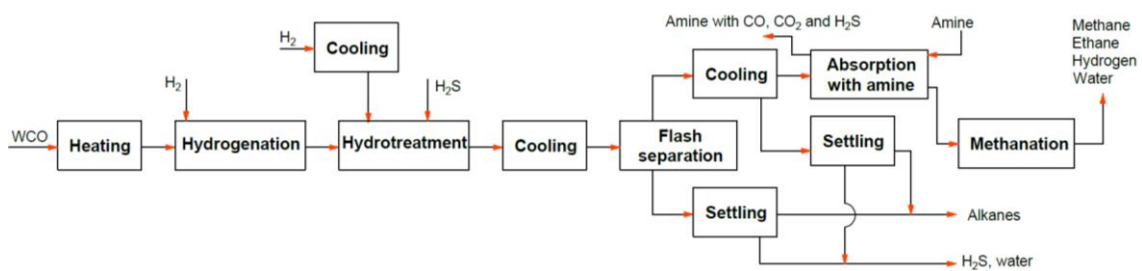


Figure 22. Block flow diagram of hydrotreatment process. The hydrotreatment operation includes hydrogenation, hydrodeoxygenation, decarboxylation, decarbonylation, and organic chain breaking.

The diagram in Figure 22 is described in more detail below.

First, the hydrogenation process takes place and consists of the saturation of the double bonds of the fatty acid chains by the addition of hydrogen in the presence of a catalyst under certain operating conditions of temperature and pressure. For each double bond, one molecule of hydrogen is required. Hydrogenation is carried out under the following conditions: The reactor is a fluidised bed reactor, so that the catalyst enters with the oil and is suspended in the oil when the hydrogen enters at the bottom of the reactor [2, 53]. When the catalyst is exhausted, the hydrogen pressure is increased to remove the catalyst.

As an example, if we take a triglyceride with the following fatty acids: linoleic, oleic and stearic, [C18:2], [C18:1] and [C18:0] respectively. Once the hydrogenation process is completed, the unsaturated fatty acids (linoleic and oleic) become saturated, so that there are three stearic fatty acids, i.e. two of them go from [C18:2] and [C18:1] to [C18:0].

After hydrogenation comes hydrotreating, which consists in adding hydrogen, which causes the separation and breakdown of the glycerol present in the triglyceride, giving rise to propane and a carboxylic acid chain attached to the fatty acid, as well as simultaneous reactions for the removal of oxygen and nitrogen. These processes are described below. [64]

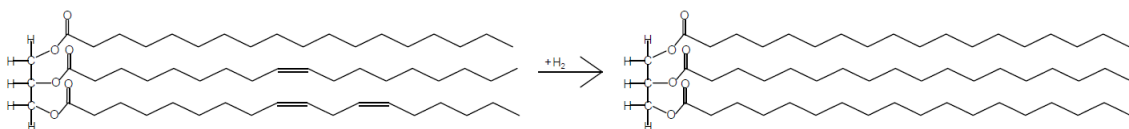


Figure 23. Saturation of the double bonds for a triglyceride formed with the following fatty acids: linoleic, oleic and stearic, [C18:2], [C18:1] and [C18:0]. Saturation of the double bonds requires one hydrogen molecule for each double bond. Adaptation from source: [64]

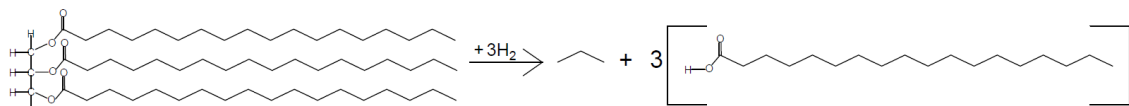


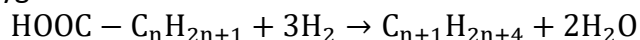
Figure 24. Separation and breakdown of the glycerol present in the triglyceride, resulting in propane and a carboxylic acid chain attached to the fatty acid. Adaptation from source: [64]

For oxygen removal. The remaining carboxylic acid attached to the fatty acid must be treated because it contains oxygen in the molecule, so hydrotreating follows to remove them. There are now three simultaneous reactions for oxygen removal:



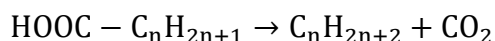
- Hydrodeoxygenation, carboxylic acid reacts with hydrogen to produce a hydrocarbon with the same number of carbon atoms as the fatty acid chain and two moles of water.

The hydrodeoxygenation reaction is:



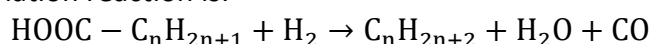
- Decarboxylation produces a mole of hydrocarbon with one less carbon atom than the fatty acid chain as it passes into the mole of CO<sub>2</sub> that is formed.

The decarboxylation reaction is:



- Decarbonylation, produces one mole of hydrocarbon with one less carbon atom, as well as one mole of CO and water.

The decarbonylation reaction is:



Although these operations occur simultaneously, they can be favoured over each other depending on the operating conditions and the catalyst selected. The operation of interest is hydrodeoxygenation, since alkanes and water are obtained, whereas in the other two reactions CO<sub>2</sub> and CO are obtained, in addition to the alkanes. For this reason, the operating conditions will be to favour hydrodeoxygenation. These reactions take place in a fixed bed reactor containing the catalyst and at operating conditions of 300°C, 92 bar and using a metal sulphide catalyst, NiMo supported on  $\gamma$ -alumina, where the metals deposited on the catalyst are in sulphide form. The sulphide combination chosen is NiMoS, with the content of the metal deposited on the nickel catalyst ranging from 0.5 wt.% to 10 wt.% and molybdenum ranging from 5 wt.% to 20 wt.%. [30, 48, 64]

However, this catalyst requires an amount of sulphur in the reactor feed stream and the WCO does not have it, consequently to meet the sulphur requirement H<sub>2</sub>S is added during the hydrotreating process, furthermore, H<sub>2</sub>S is also added after regenerating the catalyst in order to activate the catalyst, as it is carried out by reacting the metal oxides with hydrogen sulphide in the presence of hydrogen. In the catalyst activation process, water is generated as a by-product and is removed through a discharge valve at the bottom and the temperature is increased to dry the reactor.

Without the required sulphur content and addition, this can lead to catalyst deactivation, and the formation of water from the hydrotreating reaction also promotes catalyst deactivation. The addition of H<sub>2</sub>S during the hydrotreatment process extends the life of the catalyst before it is regenerated.

Another factor that favours hydrodeoxygenation is the removal of heat during the reaction, as it is an exothermic reaction. This also favours decarboxylation, but it disfavours decarbonylation, which is endothermic. In order to favour hydrodeoxygenation, hydrogen is brought in at a low temperature so that when it comes into contact with the oil, heat is removed.

H<sub>2</sub>S leaves the hydrotreating reactor in both gas and liquid phases, as it is polar, so it is miscible with water.

Last but not least, hydrodenitrogenation is another hydrotreating operation. With the hydrodenitrogenation operation, nitrogen is removed from the organic molecules since, if it is not removed, it reduces the useful life of the catalyst and also



reduces the quality of the ethylene since it would come out with ammonia. It should be noted that the ammonia formed is also harmful to equipment as it is corrosive.

The catalyst used is again metal sulphide NiMo, supported on  $\gamma$ -alumina, as this catalyst also has a high selectivity for hydrodenitrogenation. [30, 48]

Nitrogen is one of the most complex elements to remove, as there are nitrogen-containing compounds, such as pyridine, pyrazine, which nitrogen has a double bond and a single bond, so for denitrogenation to take place, these bonds must be broken, unlike oxygen, which needs to break a double bond or two single bonds. However, the content of these compounds is also reduced during deodorization, so hydrodenitrogenation reduces the amount of these nitrogen containing organic compounds. [2, 62]

To break these bonds, saturation by the addition of hydrogen is required.

An alternative to the catalyst used for hydrodenitrogenation is the metal sulphide catalyst NiW (Nickel - Tungsten) supported on  $\gamma$ -alumina, it has higher conversion but is more expensive, so NiMo is more often used. [47, 64]

Hydrodenitrogenation is an exothermic operation so heat must be removed for good reaction performance. In order to increase conversion, hydrogen is introduced into the fixed-bed reactor at low temperature, so that when it comes into contact with the WCO, heat is removed.

### **Products and separation of the hydrotreating products**

After hydrotreating, there is a mixture of hydrogen, carbon oxides, hydrogen sulphide and mainly C<sub>1</sub>-C<sub>4</sub> alkanes (in the gas phase) and alkanes (higher than C<sub>5</sub>), water (formed during hydrotreating) and hydrogen sulphide in the liquid phase. The alkanes are then separated from the other components by means of two separations, firstly a gas-liquid separation by means of a flash and then a liquid-liquid separation to separate the alkanes from the water.

Before the flash separation, the mixture is cooled in order to reduce the amount of alkanes in the gas phase (thus reducing it to C<sub>2</sub>). Once the mixture is cooled, the flash separation is carried out, where the pressure and temperature conditions must be adequate to remove the hydrogen and carbon oxides and to maintain the greatest amount of alkanes in the liquid phase, since the liquid phase is the one of interest.

The operating conditions of the flash are 50°C and 50 bar. Under these conditions, the gas stream exiting the flash represents 15% by weight of the flash input stream. On the other hand, the liquid phase has an organic phase content of 90% by weight and the remaining 10% is the aqueous phase. The organic phase contains the alkanes, and the aqueous phase contains the formed water and hydrogen sulphide. [24]

Once the gas phase has been separated from the liquid phase, the water is decanted together with the hydrogen sulphide in the liquid phase, this is possible because alkanes are not polar and water is, so they are immiscible. On the other hand, hydrogen sulphide, like water, is also polar, so it is miscible.

On the other hand, to prevent some of the lighter alkanes from passing into the gaseous state, decantation is carried out at the same pressure as the flash. In order to reduce the amount of alkanes in the gas phase, a droplet collector is installed at the top of the flash, as this retains the alkanes entrained (in the form of droplets) by the incondensable. [64]

Next, the treatment performed for the gas phase after flash separation is presented. The gases are passed through a heat exchanger to condense light alkanes that have come out in the gas phase. Thus, it is expected to reduce the percentage of alkanes in the gas phase and thus increase it in the liquid phase.

This is done to remove carbon oxides and hydrogen sulphide from the alkanes and hydrogen, as the latter can be used as feedstock for hot utilities (furnaces and boilers) or can be separated so that the hydrogen can be used again in the process, and the methane and ethane can be used as feedstock in the cracker for ethylene production.

The ammonia formed in the hydrotreater is in the gas state together with  $H_2S$ ,  $CO_2$ ,  $CO$ ,  $H_2$ , and mainly  $C_1$ - $C_4$  alkanes. The gas phase is separated from the liquid phase by a flash and the separated gas is then passed through a heat exchanger, as shown in Figure 22. The heat exchanger is used to reduce the temperature to condense alkanes in order to reduce the amount of alkanes in the gas phase, and the temperature reduction also precipitates ammonia. Water is added to the condensate from this heat exchanger to remove the ammonia from the condensed alkanes. Subsequently, it is decanted to separate the aqueous phase from the organic phase.

On the other hand, for the traces of ammonia in the liquid phase, it is removed by decantation, since this ammonia remains in the water that is formed in the hydrodeoxygenation and is polar like water so that the ammonia remains dissolved in the water.

#### Absorption with amine

To remove  $H_2S$ ,  $CO$  and  $CO_2$  from the gas stream, it is done by using aqueous amine solutions, e.g. MEA (Mono ethanolamine), DEA (Di ethanolamine), DIPA (Di isopropylamine), MDEA (Methyl di ethanolamine). In addition, these solvents can be regenerated. The choice of amine depends on the composition of the gas stream, as illustrated in Table 13. [62]

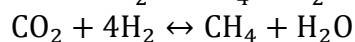
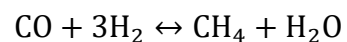
Table 13. Types of amines to be used in refining according to the composition of the stream coming from the flash. [62]	
Amine	$H_2S$ richness % wt.
Monoethanolamine (MEA)	15 -20
Diethanolamine (DEA)	25-30
Diisopropylamine (DIPA)	27-54
Methyl diethanolamine (MDEA)	24-50

The process is carried out in the countercurrent passage of the flash gas with the solvent in an absorber. This absorber is a plate column. The amine solution with  $H_2S$  is heated by heat exchange with the already regenerated solvent and is sent to the regeneration column where  $H_2S$ ,  $CO$  and  $CO_2$  are desorbed from the solvent by the decrease of the pressure in the regenerator. In addition, the solvent comes into contact in countercurrent with water vapour, so that there is greater interaction, i.e. there are greater shocks for the desorption of  $H_2S$ ,  $CO$  and  $CO_2$  to take place.

### Methanation

After the amine process, methanation is carried out to react the CO and CO<sub>2</sub> not absorbed by the amine, as it should be noted that the amine process has a higher selectivity for H<sub>2</sub>S than for carbon oxides.

The methanation reaction for carbon oxides is:



This reaction is carried out at low temperatures between 50 - 150°C or between 50 - 250°C, but in the latter case two reactors are required in series, and between reactors, there is cooling to achieve high conversion, as can be seen in Figure 25.[20]

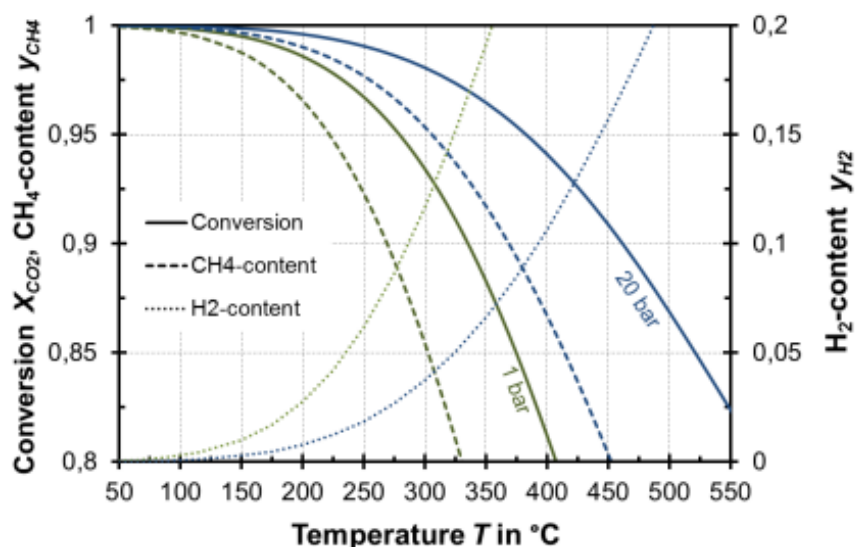


Figure 25. Equilibrium calculation for methanation (feed gas: H<sub>2</sub>/CO<sub>2</sub>/CH<sub>4</sub> = 4/1/1). [20]

With the incorporation of the methanation process, it is possible to have methane, ethane, hydrogen and traces of CO and CO<sub>2</sub> in the gas phase stream that has not been absorbed by the amine and have not reacted in the methanation.

Subsequently, if alkanes are to be separated from hydrogen, this can be done using membranes that allow hydrogen to pass through, but not alkanes [40]. After separation, the methane and ethane should be condensed so that they can be added to the petrochemical cracker as a single phase, together with the other alkanes obtained.

In the following, a critical discussion of the process is given and alternatives to the hydrotreatment process are mentioned.

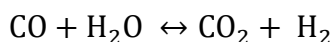
Regarding the operating conditions of hydrogenation. Special attention must be paid to the ratio of H<sub>2</sub>/WCO that is added as well as the pressure at which the H<sub>2</sub> enters since if it is too high the hydrogen can drag the catalyst and therefore it would no longer be a fluidised bed reactor and would become a moving bed reactor. On the other hand, the particle size of the catalyst is important, since the larger the particle size, the higher the H<sub>2</sub> pressure required to fluidise the catalyst in the oil.

As for the catalyst used for hydrotreating. Another alternative metal sulphide catalyst is CoMo supported on  $\gamma$ -alumina, but it has better selectivity for decarboxylation and decarbonylation reactions than for hydrodeoxygenation and hydrodeoxygenation is preferable because it is better that more water is formed as a by-product than CO<sub>2</sub> and

CO, as they must be removed to avoid poisoning of the petrochemical cracker catalyst. Again, with the CoMoS<sub>2</sub> catalyst, H<sub>2</sub>S is required. [64]

Another alternative to the NiMoS<sub>2</sub> catalyst (used in the process described above) and in general to metal sulphide supported on  $\gamma$ -alumina catalysts, are noble metal catalysts. Noble metal catalysts are platinum, palladium, rhodium, iridium, osmium. These catalysts give very good results and do not require a sulphur content in the feed, so that the amount of amine solvent is reduced, since in amine absorption it is not necessary to add so much amine because H<sub>2</sub>S does not have to be removed. In short, the costs of this operation are reduced, but on the other hand, they are increased on the other hand because the noble metal catalysts are more expensive. [24, 39]

Regarding the separation operations. The shift reactor could be an alternative to amine absorption if the noble metal catalyst is used since in the shift reactor the carbon monoxide from the flash is reacted with water to form hydrogen and CO<sub>2</sub>. [24]



Subsequently, methanation could be carried out. To obtain methane from carbon dioxide. Methanation is an exothermic reaction so it will be favoured at relatively low temperatures.

Cryogenic distillation is not used for the separation of H<sub>2</sub>S, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, because it is a very expensive process.

Although methanation is an equilibrium reaction, high conversions can be achieved as shown in Figure 25. In addition, the formation of methane is favoured, which can be used for the hot services of the process.

Hydrotreating is a process that requires demanding operating conditions as well as a high amount of hydrogen, as can be seen in the reactions for triglyceride cleavage and subsequently for decarbonylation and hydrodeoxygenation. In addition, it should be remembered that for each double bond in the fatty acid, one mole of hydrogen is required during hydrogenation.

A very important factor during the saturation of the double bonds is to have the oil well characterised, since, depending on the fatty acids in the triglyceride, there will be a greater or lesser number of unsaturated bonds, so that the lesser the number of unsaturated bonds, the lesser the demand for H<sub>2</sub>; on the contrary, the greater the number of unsaturated bonds, the greater the demand for H<sub>2</sub> to saturate them.

An indicator of the degree of unsaturation is the Iodine value, a high value indicates a higher number of double bonds in the triglycerides. If the raw material has a low Iodine value, the hydrogenation process will be less costly, as less hydrogen will be required.

Relative to the amine absorption process. The amount of solvent and the number of absorber plates will depend on the H<sub>2</sub>S, CO<sub>2</sub> and CO content of the flash stream and the amount of these in the desired purified off-gas.

Another aspect that should be highlighted is the interest in separating H<sub>2</sub> from the alkanes because if the objective is the production of ethylene, short-chain alkanes give higher yields, ethane being the one that gives the highest yield as can be seen in Table 14 [62]. In addition, if only the alkanes are to be separated from hydrogen, a distillation process can be carried out in which the hydrogen comes out through the column head and the alkanes come out through the plates and the bottom of the column.

**Table 14. Petrochemical cracking yields. [62]**

Yield % weight	Ethane	Naphtha		Gasoil
		Light	Heavy	
Hydrogen	3.6	1.1	0.8	0.7
Fuel gas	4.1	20.3	14.7	12.5
Ethylene	47.5	30.5	21.6	18.5
Propylene	41.6	21.1	17.1	15.2
C <sub>4</sub> fraction	1.5	9.2	8.8	7.5
Pyrolysis gasoline	1.7	14.9	27.1	29.7
Pyrolysis fuel oil	0.0	3.0	10.0	16.0

To avoid the accumulation of NH<sub>3</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>S, the hydrogen, methane and ethane stream is purged to avoid the accumulation of these. Since the ethane, methane and hydrogen stream can be used both as feed for the hot services and to separate the ethane and methane from the hydrogen and be condensed to be used in the cracker for ethylene formation since as mentioned above short-chain alkanes have a higher yield for ethylene formation, Table 14.

### 6.6. Nitrogen removal

Removing nitrogen is important, as it can cause the cracker output to be out of specification as it can come out with ammonia, as this is formed in the cracker and the formation of ammonia also promotes corrosion in the equipment.

Nitrogen is mainly present in chlorophyll and in pyrazine and pyridine compounds.

The methods used to remove metals from the oil are bleaching, hydrotreatment and deodorization.

#### 6.6.1. Bleaching

Nitrogen is removed in the bleaching process because the amount of chlorophyll is reduced. The molecular structure of chlorophyll contains nitrogen. By reducing the amount of nitrogen, ammonia corrosion is reduced, and the cracker output quality is increased, as there will be no hydrogen in the lighter fractions. The process and critical discussion of the process is developed in chapter 6.1.5. Bleaching.

#### 6.6.2. Hydrotreatment

Nitrogen is one of the most complex elements to remove, as there are nitrogen-containing compounds, such as pyridine, pyrazine, which nitrogen has a double bond and a single bond, so for denitrogenation to take place, these bonds must be broken. To break these bonds, saturation by the addition of hydrogen is required.

The process and critical discussion of the process is developed in chapter 6.5.3. Hydrotreatment.

#### 6.6.3. Deodorization

Deodorization also removes organic nitrogen compounds such as pyridine and pyrazine, as these have boiling temperatures below the operating temperature of the

deodoriser. The process and critical discussion of the process is developed in chapter 6.5.2. Deodorization.

### 6.7. Water removal

The removal of water is important as it promotes corrosion because hydrochloric acid and ammonia can dissolve in water. In addition, the water content promotes hydrolysis of the oil so that the oil is degraded.

Water is present in the oil because water is added in the process of using the oil, i.e. foodstuffs release water when they are cooked. In addition, there are operations in which water is added to remove water-soluble components.

The methods used to remove water from the oil are desalting, degumming, settling with skimming, hydrotreatment, deodorization.

#### 6.7.1. Desalting

Water, in addition to the oil, is also added for the desalting process, but this water is subsequently decanted to separate it from the oil. The process and critical discussion of the process is developed in chapter 6.1.1 Desalting.

#### 6.7.2. Degumming

Water, in addition to that in the oil, is also added for the degumming process, but this water is subsequently removed by clarification. The process and critical discussion of the process is developed in chapter 6.1.4. Degumming.

#### 6.7.3. Settling with skimming

The water comes with the oil as raw material and is removed by decantation. The process and critical discussion of the process is developed in chapter 6.2.3. Settling with skimming.

#### 6.7.4. Hydrotreatment

Water, in addition to the oil, is also added for the hydrotreatment process, but this water is subsequently removed by decantation to separate the organic phase with the alkanes from the aqueous phase. The process and critical discussion of the process is developed in chapter 6.5.3. Hydrotreatment.

#### 6.7.5. Deodorization

Water is removed due to the operating conditions, it is removed in the gas phase together with free fatty acids, aldehydes, ketones, alcohols, nitrogen compounds (pyridine and pyrazine), phytosterols and tocopherol. The process and critical discussion of the process is developed in chapter 6.5.2. Deodorization

### 6.8. Free fatty acids removal

The removal of free fatty acids is important as they cause pitting.

Free fatty acids originate from the oil due to hydrolysis and polymerisation during use. In addition, during the pre-treatment process they can also be generated due to the high process temperatures.

The methods used to remove metals from the oil are degumming and deodorization

### 6.8.1. Degumming

Free fatty acids can be removed by chemical degumming, i.e. if a base is added to neutralise the free fatty acids. The process and critical discussion of the process is developed in chapter 6.1.4. Degumming.

### 6.8.2. Deodorization

Free fatty acids are removed because they have a higher volatility than the fatty acids in the oil, which is why they can be removed during deodorization. The process and critical discussion of the process is developed in chapter 6.5.2. Deodorization.

## 6.9. Other non-selected processes

### 6.9.1. AXENS

The company Axens has developed a stepwise process based on the removal of chloride ions from the organic chains to form HCl. At the same time, nitrogen are also removed from the organic chains to form  $\text{NH}_3$ . HCl and  $\text{NH}_3$  are reacted at the appropriate conditions to form ammonium chloride, which is a salt and is deposited on the equipment. Additionally, it has been found that, at high temperatures, ammonium chloride readily dissociates into HCl and  $\text{NH}_3$ , but below  $100^\circ\text{C}$ , the compound is stable as  $\text{NH}_4\text{Cl}$ . Thus, for the formation of ammonium chloride by the Axens method, conditions below  $100^\circ\text{C}$  are used.

Finally, to remove the deposition of these formed ammonium chloride salts, they are washed with water to solubilise them in water and then removed by decanting or centrifugation.

This alternative is very promising according to operational information from refineries, but because no further knowledge and know-how is available because the services have to be contracted out to Axens.

### 6.9.2. Physical degumming

Physical degumming has many advantages, because there is less loss of raw material since, in chemical refining, part of the oil is consumed with the addition of NaOH. Also, the number of processes involved is reduced, so operating and equipment costs are lower.

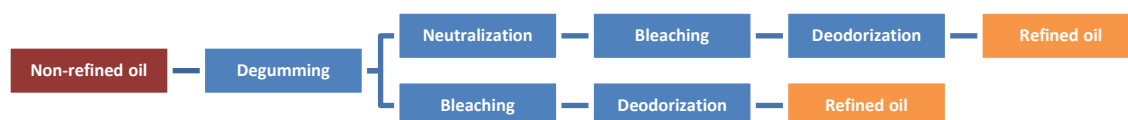


Figure 26. Scheme of chemical refining and physical refining.

The upper part of Figure 26 shows the chemical refining, which consists of neutralisation, bleaching and deodorization. The lower part shows the physical refining consisting of bleaching and deodorization stages.

Physical refining is the alternative to chemical refining. Physical refining consists of steam stripping, where the oil is heated at high temperature ( $230\text{-}240^\circ\text{C}$ ) and absolute pressures below 1 atm, typically operating in the range of 0.4 - 0.6 kPa for 3 -

5 h [18]. In turn, a vapour is passed through the oil phase to help carry away volatile compounds and to agitate the oil to increase the contact between the oil and the vapour. Generally, 1.5% steam by weight of the oil is used, i.e., a ratio of 15 kg of steam per tonne of oil is used. [36, 37]

Deodorization is very important if physical refining has been performed because in this process free fatty acids are removed, but a higher operating temperature and consequently higher levels of polymerised fatty acids will be had after deodorization.

The main drawback of this process is that the phospholipid levels must have been lowered in the previous degumming, otherwise the phospholipid content will not be removed until the bleaching stage and consequently a larger amount of bleaching clay will be required.



Summary of processes carried out

Table 15. Used vegetable oil treatment processes.			
Process	Removed components	Operation variables	
Degumming	Free fatty acids, water, phosphorous, metals, chlorides, ash and particles	Chemical reagent, stirring, temperature, contact time between phases, amount of water added	
Bleaching	Oxygen, metals, nitrogen, phosphorous	Bleaching earth selected, contact time between bleaching earth and oil, temperature, pore size in filtration	
Deodorization	Oxygen, water, nitrogen, free fatty acids	Temperature, pressure, ratio vapour/oil	
Desalting	Metals, chlorides, ash and particles, phosphorous, water	Temperature, amount of water added, stirring, demulsifying agent added, stabilisation time	
Membrane extraction	Metals, chlorides, ash and particles	Membrane selected, temperature, flow rate, pressure	
Ion Exchange resins	Chloride anions, metal cations	pH, time, flow rate, bed height	
Hydrotreatment	Hydrodeoxygenation	Oxygen, nitrogen, water	Ratio H <sub>2</sub> /oil, pressure, temperature, catalyst
	Decarboxylation		
	Decarbonylation		
	Hydrodenitrification		
Absorption	Hydrogen sulphide added for hydrotreatment, carbon oxides during hydrotreatment	Amine solution used, absorber	

Table 15. Used vegetable oil treatment processes.		
Process	Removed components	Operation variables
Methanation	Carbon oxides during hydrotreatment	Ratio H <sub>2</sub> /CO and CO <sub>2</sub> , temperature, pressure, recirculation
Settling with skimming	Ash and particles, metals, chlorides, water	Flow rate, residence time

### 6.10. Operations selected for pre-treatment process

The order of the operations selected for pre-treatment are (1) Settling and skimming, (2) Desalting, (3) Membrane extraction, (4) Ion exchange resin, (5) Degumming, (6), Bleaching, (7) Deodorization, (8) Hydrotreatment

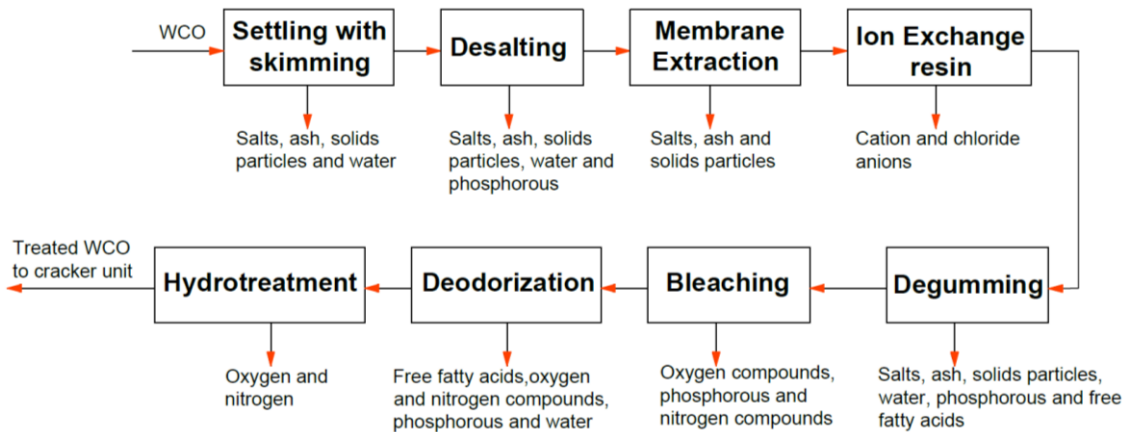


Figure 27. Block flow diagram of pre-treatment process for used cooking oil.

Figure 27 shows the block diagram with the selected operations for the proposed pre-treatment process.

It starts with operations capable of removing ash and solid particles because these particles increase the pressure drop and there is already enough pressure drop in a fluid such as oil which has a high viscosity. In addition, the solid particles that are not ash, are metal particles, which can cause erosion, clog pipes and equipment, and cannot reach the cracker as these residues poison the catalyst and promote the formation of coke in the cracker pipes, which would increase the stoppages to remove the deposited coke.

For these reasons, we start with the Settling with Skimming process. After all, it is a process that is expected to remove the ash to a large extent because it is designed to remove both the ash that remains precipitated and the ash that remains on the surface (oil-air interface) as well as the ash that remains suspended in the oil. In addition, this operation not only removes ash but also metal particles.

The operations capable of removing chlorides are the operations that follow ash removal. It is very important to place the removal of chlorides at the beginning because in this way the corrosion caused downstream will not be so great. It should be remembered that these chlorides come from inorganic sources, either from cooking salts or from salts in the soil in which the oil feedstock has been grown.

With the above mentioned, after settling with skimming comes desalting, which in addition to removing ash, salts are removed, since when water is added the salts pass into the aqueous phase. With the removal of salts, chlorides, which promote corrosion, are also removed. With this operation, a large part of the salts are removed and therefore the corrosion that the oil can cause to other processes is greatly reduced.

To continue with the reduction of ash and metals, the pre-treatment process continues with membrane extraction, which is used as the third process because there is no longer enough ash to clog the membrane pores and thus it does remove metal particles and salts. This process also removes chlorides.

The third pre-treatment process is the Ion Exchange resin. This process is expected to reduce the amount of metals and chlorides to very low levels, so that corrosion is considerably reduced. It should be noted that membrane extraction is prioritised over ion exchange resins because the latter process is more delicate as the resin is easier to degrade and the ash, could clog the oil passageways through the resin, causing the break point to be reached more quickly because if the passageways are clogged, there will be resin that is not in use, so that the resin that is exchanging will be processing more raw material than it was designed for, and it is not until regeneration that they can be unclogged.

Once the chlorides and most of the metals have been removed, degumming, bleaching and deodorization are carried out.

Degumming removes free fatty acids and hydratable and non-hydratable phospholipids. The better this process is done, the less bleaching earth will be needed in the bleaching stage. Furthermore, if a good neutralisation of the fatty acids is achieved, less steam will be needed for the deodorization and it should be noted that deodorization and bleaching have high operating conditions in the sense that it is easy to degrade the oil since it is operated at temperatures below 1 atm and high temperatures so that it is easy for polymerisation, oxidation or hydrolysis of fatty acids to occur and consequently, more free fatty acids, alcohols, ketones, aldehydes, etc. are generated.

Bleaching and deodorization are processes that should be the last ones, as they remove the oil antioxidants such as carotene and tocopherol.

It is important to remember that throughout the process that has been explained so far, there are operations dedicated to removing water, such as desalting, degumming and settling with skimming.

And the last process before feeding the cracker with the used oil is hydrotreating, which involves saturating the bonds in order to remove nitrogen and oxygen, and in turn, break the organic chains to form smaller ones, which is beneficial if the objective is to produce plastics since ethylene and propylene have higher yields in the cracker if the feed is C<sub>2</sub>-C<sub>4</sub>.

Finally, it should be noted that, throughout the process, three main by-products have been generated, hydrolysed lecithin, which is treated to be used in the degumming process; -carotene and tocopherol, which are antioxidants. In addition, some of the sterol isomers have applications in the pharmaceutical and food industries. For example, they are used to treat excess cholesterol.

## 7. CONCLUSIONS

In the present project, we have a reference oil that has been obtained by averaging the used vegetable oils found in the bibliography. It is true that this has been done in order to have an oil with more varied characteristics, but it may be interesting to restrict certain oils such as not having so many metals or so many chlorides or being saturated in order to reduce hydrogen consumption. The selection of the feedstock may be economically advantageous because it may not require all the pre-treatment operations listed in the present project. So, a good characterisation of the oil is required for good modelling of the pre-treatment process. Depending on the quality of the waste oil, more or less addition of this feedstock to the cracker will be allowed and the use of feedstock will be restricted depending on the origin. This will be determined by the bottleneck component.

The present project is a selection of operations to treat used cooking oil, but experimental confirmation is necessary in order to check that the operations and operating conditions are set to achieve the expected values to meet the requirements at the cracker inlet, which is the objective of the present project. In addition, an economic analysis must also be carried out to check its viability, since, throughout the pre-treatment process, raw material is lost due to decanting, secondary reactions and blockages. The economic and experimental analysis would give a much more realistic view of what this oil pre-treatment could end up being because it would show whether all the processes are necessary.

In order to achieve the requirements of cracker, different operations have been used to remove the same component as can be seen, because this is more likely to meet the cracker's specifications. For greater precision in the selection of operations, laboratory tests, CFD simulations and pilot plant testing are required before industrial implementation. With the proposed operations it is expected that the reductions of the components limited by the cracker will be obtained.

In terms of equipment and processes, there are those that have been selected for the pre-treatment of used vegetable oil that is already currently used for the refining of crude oil, such as desalting, hydrotreating and membrane extraction, as well as methanation and adsorption with amines to treat H<sub>2</sub>S, CO and CO<sub>2</sub>, which are also used. So, these are well known processes that need to be adapted to the new feedstock.

It should be noted that oxygen is the component that causes the most problems, as it poisons the catalyst by the formation of CO and CO<sub>2</sub> and furthermore, to remove it, bleaching, deodorization or hydrotreatment or a combination of these is needed and in both bleaching and deodorization antioxidants are removed, so that the oil is more likely to degrade into free fatty acids and/or compounds with oxygen due to the oxidation of the fatty acids. A possible solution to this problem would be the development of a new catalyst so that oxygen does not poison the catalyst.

Last but not least, water treatment is required for the polluted streams generated in the pre-treatment process so that a purification process will be required and it must also be verified that the treatment plant available at the refinery is capable of treating these new waste streams.

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