E.T.S. de Ingeniería Industrial, Informática y de Telecomunicación

LIFE CYCLE ASSESSMENT COMPARISON BETWEEN DISTILLATION AND MEMBRANE SYSTEM FOR BIOETHANOL PURIFICATION.

Grado en Ingeniería en Diseño Mecánico

Final degree work

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SUMMARY

This study is going to compare two different ways for the bioethanol purification. Distillation is nowadays the technique used by industry, but recent studies have demonstrated that more than 60 % of the energy used for bioethanol production is due to the distillation. In order to find a more efficient technique to separate bioethanol from water, there has been developed several techniques; among them membrane system is the best situated because their low energy requirements. However, for the manufacture of the membrane several chemical products are used and this could create environmental impacts that have to be studied previous its implementation.

The main objective of this study is to determine by Life Cycle Assessment (LCA) which technique has lower environmental impacts. Related with this main objective it’s going to be studied the membrane synthesis process in detail. The membrane system used in this work is a hollow-fiber that consists in thousands of membranes with diameters of 0,1 mm inside a steel vessel. The membrane is silicalite-1 zeolite and its synthesis process is going to be studied to quantify materials and energy requirements.

KEY WORDS

Ecodesign · Life Cycle Assessment · Life Cycle Comparison · Environmental impact · Ethanol · Ethanol purification · Distiller · Zeolite · Zeolite membranes · Silicalite-1

INDEX

1. - Introduction

1.1. - Definition and objectives

The objective of this study is the explanation of the distiller's use and to evaluate if the use of a new membrane system is better in terms of environmental impacts. Life Cycle Assessment (LCA) is going to be used to quantify environmental impacts of both systems and to compare them. ISO 14006:2011 that standardizes LCA process is going to be followed and GaBi 6.0® education software is going to be used to model the life cycle of the processes.

1.2. - Bioethanol Production

1.2.1. - Bioethanol and its characteristics

Bioethanol is the ethanol with renewable origin and it has the same characteristics that ethanol from fossil fuels. Ethanol or ethyl alcohol (CH_3CH_2OH) is a colorless, volatile and flammable liquid, with molecular weight of 46.07 g and density of 789 kg/m^3 at 294 K. Thermal properties are given in Table 1.

Boiling point	351.37 K
Flash point	289.6 K
Auto-ignition temperature	698 K
Heat of combustion	26,800 kJ/kg

Table 1. Primary properties of ethanol.

It burns with a smokeless blue flame, generally invisible in normal light. The auto-ignition temperature is the lowest temperature at which ethanol will spontaneously ignite in a normal atmosphere without an external source of ignition, such as a flame or spark.

Mixtures of water and ethanol are important throughout the bio-ethanol process. The knowledge of mixture flash points, as presented in Fig. 1, is needed for their safe handling, storage and transportation: the flash point is one of the most important physical properties used to determine the potential for fire and explosion hazards of liquids, used for the classification and labeling of dangerous substances and preparations. The flash point of a given liquid is the experimentally determined temperature adjusted to standard temperature and pressure at which a substance emits sufficient vapor to form a combustible mixture with air. A lower flash point value indicates that a given liquid is more hazardous relative to a different liquid with a higher value. [1]

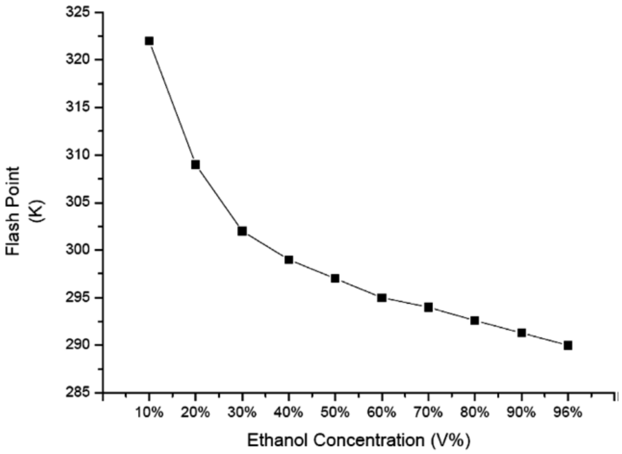

Fig. 1. Flash points of ethanol-water mixtures.

1.2.2. - Uses of bioethanol fuel

Ethanol fuel is ethanol (ethyl alcohol), the same type of alcohol found in alcoholic beverages. It is most often used as a motor fuel, mainly as a biofuel additive for gasoline. Recently, cars able to run using 100% ethanol have been introduced in Brazil. Ethanol fuel has a "gasoline gallon equivalency" (GGE) value of 1.5 US gallons (5.7 L), which means 1.5 gallons of ethanol produces the energy of one gallon of gasoline. But other ethanol fuel characteristics, including a high octane rating, result in increased engine efficiency and performance.

Ethanol fuel is widely used in Brazil and in the United States, and together both countries were responsible for 87.1% of the world's ethanol fuel production in 2011. Most cars on the road today in the U.S. can run on blends of up to 10% ethanol, and ethanol represented 10% of the U.S. gasoline fuel supply derived from domestic sources in 2011. Since 1976 the Brazilian government has made it mandatory to blend ethanol with gasoline, and since 2007 the legal blend is around 25% ethanol and 75% gasoline (E25). By December 2011 Brazil had a fleet of 14.8 million flex-fuel automobiles and light trucks and 1.5 million flex-fuel motorcycles that regularly use neat ethanol fuel (known as E100).

For the ethanol to be usable as a fuel, the majority of the water must be removed. Most of the water is removed by distillation, but the purity is limited to 95–96% due to the formation of a low-boiling water-ethanol azeotrope with maximum (95.6% m/m, 96.5% v/v) ethanol and 4.4% m/m (3.5% v/v, water). This mixture is called hydrous ethanol and can be used as a fuel alone, but unlike anhydrous ethanol, hydrous ethanol is not miscible in all ratios with gasoline, so the water fraction is typically removed in further treatment, by molecular sieves, to burn in combination with gasoline in gasoline engines.

The cost of producing ethanol remains significantly higher than the cost of producing fuels from petroleum. The federal government, since 1978, has given tax incentives intended to make ethanol competitive with gasoline in the motor fuel marketplace. Continued progress with both conventional and advanced ethanol production technologies could someday result in ethanol production costs competitive with petroleum fuels. [2]

1.2.3. - Current bioethanol production technology

The annual bioethanol production capacity in the United States has reached 34 billion liters as of July 2008, exceeding the 2008 biofuel production mandate of 32 billion liters under the Energy Independence and Security Act (EISA). Under the EISA, conventional biofuel production will have needed to further increase to 57 billion liters by this current year of 2015. The corn dry-grind process is the most widely used method in the U.S. for generating fuel ethanol by fermentation of grain. Increasing demand for domestically produced fuel and changes in the regulations on fuel oxygenates have led to increased production of ethanol mainly by the dry-grind process. Fuel ethanol plants are being commissioned and constructed at an unprecedented rate based on this demand, though a need for a more efficient and cost-effective plant still exists.

A simplified flow diagram of the process is shown in Fig. 2. The actual process contains more than 100 pieces of equipment and unit operations. It is not intended to replicate any fuel ethanol plant in existence, but rather a generic plant design containing equipment and unit operations necessary to convert corn into fuel ethanol.

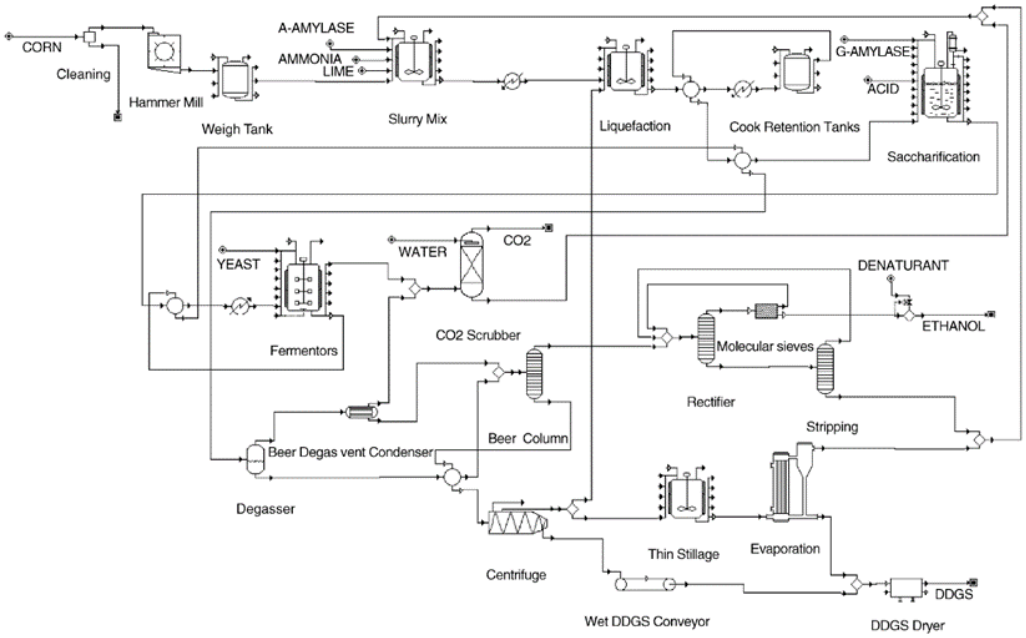

Fig. 2. Simplified flowchart of the dry-grind ethanol from corn process.

1.2.3.1. - Grain receiving

Corn is brought into the facility and held in storage silos prior to cleaning, where broken corn, foreign objects, and finer materials are removed using a blower and screens. A portion of the stream may be recovered and added back to the distillers dried grains with solubles, but the current setting is for the broken corn and foreign objects to go to waste. These silos are sized to hold sufficient corn for 12 days of plant operation. The cleaned corn is ground in a hammer mill and sent through weighing tanks to control the feed rate to the process.

1.2.3.2. - Liquefaction, saccharification, and fermentation

To begin this section, the measured ground corn is first sent to a slurry tank along with approximately 83,000 l/h of process water, thermostable alpha-amylase, ammonia, and lime. Alpha-amylase is added at 0.082% (db) of corn brought to the slurry, while ammonia and lime are added at 90 kg/h and 54 kg/h, respectively. After the slurry is prepared, the mixture undergoes liquefaction, where starch is gelatinized using a “jet-cooker” (steam injection heater) and hydrolyzed (broken down) with thermostable alpha-amylase into oligosaccharides also known as dextrins. During the gelatinization step, there is a sharp rise in the slurry viscosity that is rapidly decreased as the alpha-amylase hydrolyzes the starch. Liquefaction is done at pH 6.5 and is initially held for 60 min at 88ºC with agitation. The output from the initial liquefaction step is combined with “backset”, a recycled stream taken from the liquid portion of the “stillage” separated by centrifugation later in the process. The backset provides critical nutrients for the yeast later in fermentation. These combined streams are “cooked” and held at 110ºC for 15 min, and transferred to the saccharification tank after some heat is recovered using the process streams.

Further conversion of the oligosaccharides by glucoamylase to glucose is referred to as saccharification. Sulfuric acid is used to lower the pH in this tank to 4.5 and the slurry is held under these conditions for 5 h. Glucoamylase is added at 0.11% (db) during the saccharification step, and the starch is further hydrolyzed from dextrins into glucose at a temperature of 61ºC. During this incubation, almost all of the dextrins are converted to glucose although the glucoamylase continues to be active and can continue hydrolysis during fermentation if there are any unhydrolyzed dextrins remaining. Following the saccharification reaction, the slurry is transferred to the fermentation vessel with heat being recovered from the outlet stream, and cooled to 32ºC prior to fermentation.

Fermentation is the conversion of glucose to ethanol and carbon dioxide using yeast. The fermentation simulated in the process model is a batch process with six fermentors of approximately 1.9 million L (504,000 gal) each. The residence time is set at 68 h, with a working volume of 83% in the fermentors. Cooling is continuous as the conversion of glucose to ethanol produces 1200 kJ/kg of ethanol produced (516 Btu of heat per pound of ethanol). The extent of conversion is set according to experimental or process data, and the current fermentor output is 10.8% ethanol (w/w). A portion of the glucose (5 wt %) is converted into other solids (yeast cells).

The beer from the fermentation is heated using the process stream inlet to the saccharification tank, and then sent through a degasser drum to flash off the vapor. The vapor stream is primarily ethanol and water with some residual carbon dioxide. The ethanol and water vapors are then condensed and recombined with the liquid stream prior to distillation. Any uncondensed vapor is combined with the carbon dioxide produced during fermentation and sent through the carbon dioxide scrubber prior to venting or recovery.

1.2.3.3. - Distillation and ethanol recovery

The first step in ethanol recovery is the beer column, which captures nearly all of the ethanol produced during fermentation. An almost equal amount of water is also distilled that must be separated from the ethanol in the next stage of rectification/stripping. The outlet from the bottom of the distillation column contains a considerable amount of water and non-fermentable material such as protein, oil, fibers, and residual chemicals unconsumed during fermentation.

Recovery of the ethanol from the beer column distillate is accomplished through the combined action of the rectifier, stripper, and molecular sieves. Over 99% of the ethanol goes out of the top of the rectifier as distillate. The remaining bottoms product is fed to the stripping column to remove additional water, with the ethanol distillate from stripping being recombined with the feed to the rectifier. The distillate of the rectifier, containing primarily ethanol, feeds the molecular sieves, which captures the last bit of water, creating 99.6% pure ethanol.

Molecular sieves are composed of a microporous substance, designed to separate small molecules from larger ones via a sieving action. Water molecules are trapped and adsorbed inside the microporous beads, whereas the larger ethanol molecules flow around them. The water produced when the molecular sieves are regenerated by heating in an offline operation, is combined with the process condensate stream used to slurry the incoming ground grain.

1.2.3.4. - Stillage processing

A mixture of the non-fermentable material at 15% solids from the bottom of the beer column is fed to the whole stillage tank at the beginning of the stillage processing section. About 83% of the water present in stillage is removed during centrifugation, producing wet distiller's grains at 37% solids. The liquid product from centrifugation, known as thin stillage, is split and used as backset, with the rest going on to the thin stillage tank. Approximately 21,000 kg/h (6000 gal/h) of backset is fed back into the second step of the liquefaction process, with 59,000 kg/h (16,862 gal/h) remaining for thin stillage processing.

The thin stillage tank helps to maintain a constant feed to the evaporator, where water is recovered and the concentrate is dried further. The concentrate from the evaporator, at approximately 35% solids, is mixed with the wet distiller's grains coming from the centrifuge and sent to a large rotary drum dryer. The four-effect evaporator uses the overhead vapors from the rectifier instead of steam to provide heating for the first effect of the evaporator. The heated process streams are used in following effects of the evaporator. Outgoing vapor from the evaporator is condensed and mixed with the rest of the process condensate, which is used to slurry the ground grain at the beginning of the process. The drum dryer reduces the moisture content of the mixture of wet grains and evaporator concentrate from 63.7% to 9.9%, and this becomes the coproduct known as distiller's dried grains with solubles (DDGS). The volatiles produced during drying are treated with a thermal oxidizer prior to exhaust from the facility.

1.2.3.5. - Final products

The main product, fuel ethanol, is produced after mixing the refined ethanol with approximately 5% denaturant (gasoline), and is held in the product tank prior to transport out for sale as a motor fuel additive. The simulated product rate of denatured ethanol is 119 million kg/year (39.9 million gal/year), or 0.422 l/kg (2.83 gal/bu). The DDGS produced is sold as an animal feed with its value based largely on protein content. The DDGS normally has a protein content of 27.8% and is produced at a rate of 119 million kg/year (131,000 metric tonnes/year). [3]

1.2.4. - Bioethanol production improvements.

The production of bioethanol currently requires large amounts of energy, raising its cost and compromising its environmental benefits. In fact, separation and purification of bioethanol from fermentation broths by means of conventional distillation may account for 60-80 % of the total production cost. Currently, the fractional distillation of the water/ethanol mixture up to the azeotropic composition requires about 6.5 MJ/kg ethanol and the energy consumption is even higher to produce anhydrous ethanol. So it can be concluded that to reduce bioethanol costs and environmental impacts with respect to other fossil combustibles, different separation techniques have to be used.

Many alternative separation techniques have been explored to save energy consumptions such as adsorption, liquid-liquid extraction, gas stripping, and pervaporation being the last one the most promising technique because it has the advantage of easy operation, low energy consumption and small carbon footprint. However, a comparison in terms of economic and environmental benefits between pervaporation and distillation bioethanol separation has to be considered. In this work a comparison between distillation and pervaporation in terms of environmental impacts is going to be done. [2]

In this study LCA assessment is going to be done following the 14044:2006 standard and with the objective of comparing distillation with a hollow-fiber steel system made with silicalite-1 zeolite membranes. The final objective is to determine which system has less environmental impact.

1.3. - Zeolite Membrane

1.3.1. – Zeolite

Zeolites are micro-porous aluminosilicate minerals characterized by their ability to reversibly hydrate and dehydrated. Until October 2012 have been identified 206 types of zeolites according to their structure, of which more than 40 occur in nature; the rest are synthetic. [4]

The term zeolite was by the first time used in the 18th century by a Swedish mineralogist named Cronstedt who observed, upon rapidly heating a natural zeolite that stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils," he called this material zeolite. Technically, we speak of a zeolite as a crystalline hydrated aluminosilicate whose framework structure encloses cavities (or pores) occupied by cations and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. This definition places it in the class of materials known as "molecular sieves." [5]

Zeolites are crystalline aluminosilicates with open 3D framework tetrahedral structures built of SiO_4 and AlO_4 linked to each other by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimensions. A defining feature of zeolites is that their frameworks are made up of 4-coordinated atoms forming the tetrahedron. These tetrahedron are linked together by their corners and make a rich variety of beautiful structures. The framework structure may contain linked cages, cavities or channels, which are big enough to allow small molecules to enter. The system of large voids explains the consistent low specific density of these compounds. In zeolites used for various applications, the voids are interconnected and form long wide channels of various sizes depending on the compound. These channels allow the easy drift of the resident ions and molecules into and out of the structure. The aluminosilicate framework is negatively charged and attracts the positive cations that reside in cages to compensate negative charge of the framework.

1.3.1.1. - Types of zeolite

i) "Low-silica" or aluminium rich zeolites A and X (ratio Si/Al ≈ 1).

Zeolites A (Fig. 3) and X (the most common commercial adsorbents) discovered by R. M. Milton represent a fortunate optimum in composition, pore volume, and channel structure. Both zeolites are nearly "saturated" in aluminum in the framework composition with a molar ratio of Si/Al ≈ 1, which is considered as highest aluminum content possible in tetrahedral aluminosilicate frameworks. As a consequence they contain the maximum number of cation exchange sites balancing the framework aluminum, and thus the highest cation contents and exchange capacities. These compositional characteristics combined give them the most highly heterogeneous surface known among porous materials, due to exposed cationic charges nested in an aluminosilicate framework which results in high field gradients. Their surface is highly selective for water, polar and polarizable molecules which serves as the basis for many applications particularly in drying and purification.

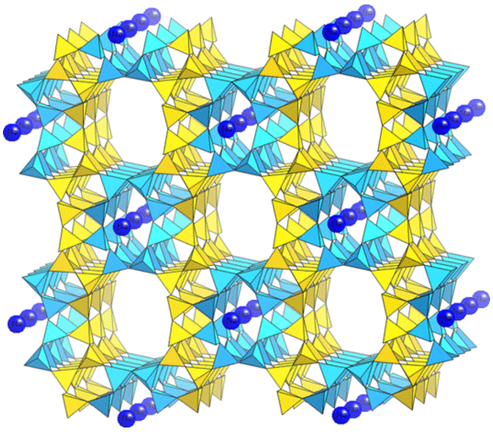

Fig. 3. Representation of zeolite A

ii) "Intermediate silica" zeolites: zeolite Y, mordenite, zeolite L, natural zeolites (ratio Si/Al =2÷5).

It was recognized that the tetrahedral aluminum positions in the zeolite frameworks provide a site of instability for attack by acid and water vapor of steam that make synthetic zeolites A and X less stable than their natural analogs, which have superior stability characteristics reflecting higher Si/Al molar ratio of 3-5. Therefore, zeolites with higher content of silicon were needed, primarily to improve stability characteristics, both thermal and to acids. The third commercially important molecular sieve zeolites type Y, with a Si/Al ratio from 1.5 to 3.0, and a framework topology like that of zeolites X and the rare zeolites mineral faujasite, represented the first successful discovery in that row of compounds. Besides improvement in stability moreover the differences in composition and structures had a striking, unpredicted effect on properties making zeolites Y based catalysts valuable in many important catalytic applications involving hydrocarbon conversion since their initial commercial introduction in 1959.

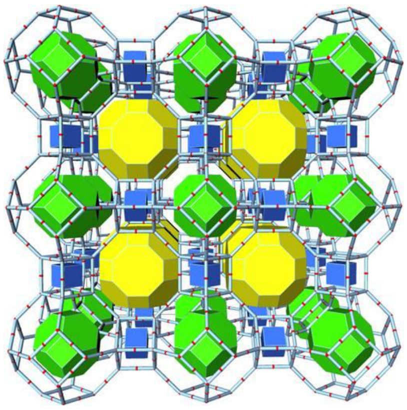

Fig. 4. The zeolite mineral mordenite. (MOR)

iii) "High silica" zeolites: zeolite beta, ZSM-5 (ratio Si/Al ≥ 10).

The most recent stages in the quest for more siliceous molecular sieve compositions was achieved in the late 1960's and the early 1970's with the synthesis of the "high silica zeolites". First in that row was zeolite beta (Fig. 5), and later ZSM-5 (Fig. 6). These are molecular sieve zeolites with Si/Al ratious from 10 to 100 or higher, with different surface characteristics. In contrast to the "low" and "intermediate" silica zeolites, representing heterogeneous hydrophilic surfaces within a porous crystal, the surface of the high silica zeolites is more homogeneous with an organophilic-hydrophobic selectivity. They adsorb stronger the less polar organic molecules and only weakly interact with water and other polar molecules. [6]

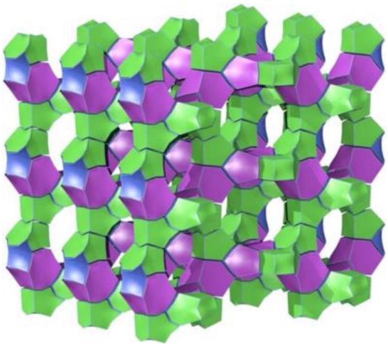

Fig. 5. Zeolite beta (BEA).

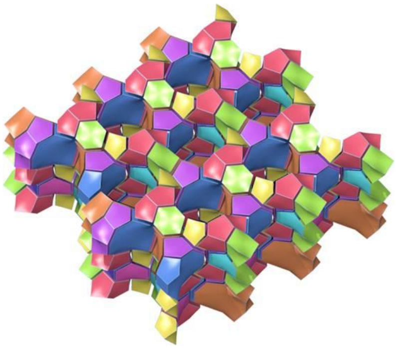

Fig. 6. The ZSM-5 zeolite (MFI).

1.3.2. - Silicalite-1 zeolite

The silicalite-1 is the type of membrane used in this study. Silicalite is a very common synthetic zeolite. It has many applications in the petroleum and petrochemical industries as catalysts or selective adsorbents. For example, silicalite and its analogue ZSM-5 are used for xylene isomerization, calalytic dewaxing, or conversion of methanol to gasoline.

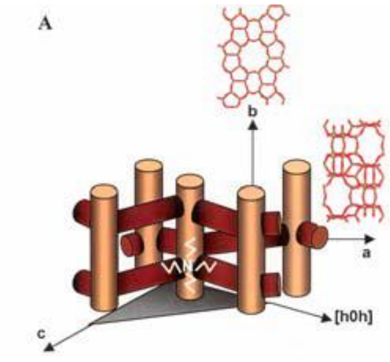

Fig. 7. Schematic representation of an MFI crystal. Zigzag channels in the a direction are interconnected with straight channels in the b direction.

Silicalite-1 presents interesting properties for the adsorption of ethanol, while exhibiting hydrophobic features. This pronounced hydrophobicity is due to the low aluminium content rather than the framework structure. One should note that theoretically there are no aluminium atoms in the silicalite framework which means that there are no cations that compensate for the extra charge.

Silicalite belongs to the family of pentasil zeolites, so called because their frameworks can be regarded as being built up from five-membered oxygen rings. The unit cell of silicalite contains 96 tetrahedral (SiO_2) units. One unit cell is composed of two straight channels and four sinusoidal or zigzag channels with four channel intersections, as shown in Fig. 7. [7]

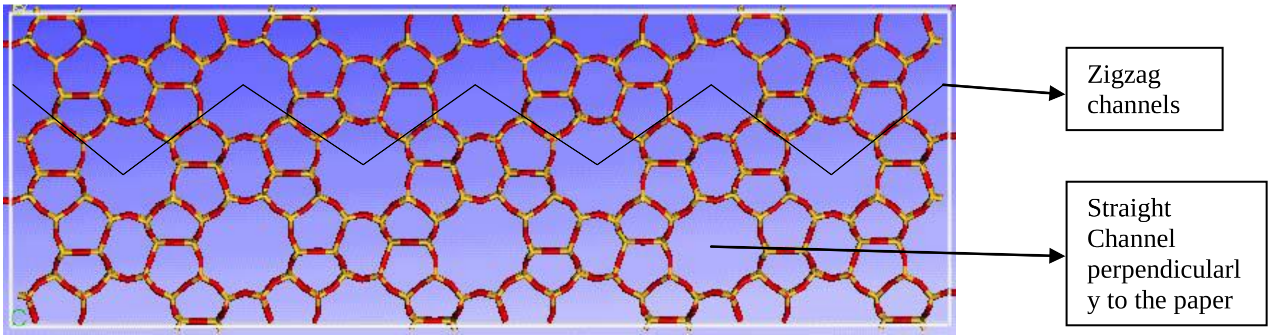

Fig. 8. Several unit cells elongated in x direction.

Fig. 9 illustrates the XRD patterns of the as-synthesised samples, confirming that silicalite-1 exhibit the peaks corresponding to the MFI zeolitic structure.

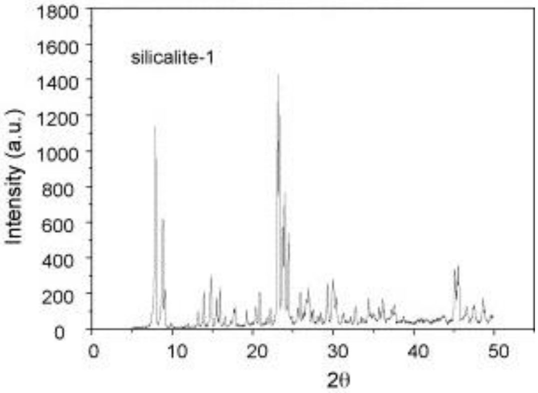

Fig. 9. XRD spectra of the silicalite-1.

Fig. 10 shows the TPD profiles obtained for ethanol and water with the silicalite-1 normalized per gram of adsorbent material. [8]

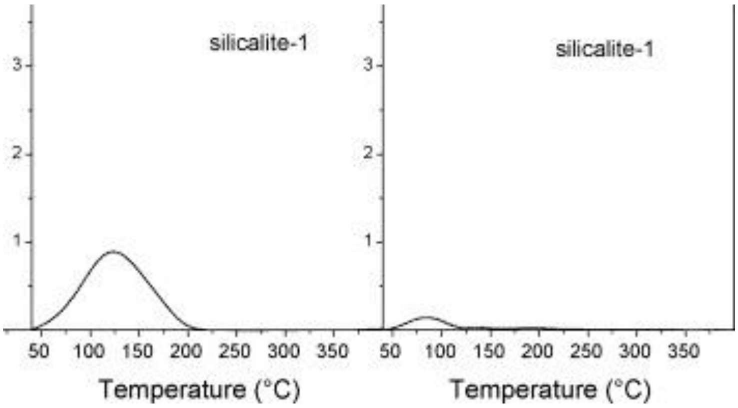

Fig. 10. TPD curves ethanol and water absorption for silicalite-1.

1.3.3. - Zeolite membrane

Separation processes are widely used in industry since the chemical conversions are often incomplete. Membrane technique is one of the most attractive separation methods because of its low cost and high selectivity. A membrane is an intervening phase acting as an active or passive barrier between phases adjacent to it under a driving force. Zeolitic membranes have gained considerable attention during the last decade. Detailed information can be found in the current literature and in several excellent reviews dealing with the subject of zeolitic membranes which have appeared over the last five years.

The regularly structured pores and cages make the zeolites a unique material for designing thin films, coatings and membranes that can be utilized for a variety of purposes. Since the early 1990s, intensive research efforts have been underway to develop the synthesis and separation applications of zeolitic membranes. The specific properties of zeolite membranes which have attracted the attention of academic and applications scientists are: (i) long-term stability at high temperature, (ii) resistance to harsh environments, (iii) resistance of high pressure drops, (iv) inertness to microbiological degradations, and (v) easy cleanability and catalytic activation.

One of the most challenging problems in the preparation of zeolitic membranes is the complete exclusion of pinholes from the membranes, particularly under conditions of severe thermal cycling.

Silicalite-1 membranes, due to its hydrophobic character, have been used in systems for the dehydration of liquids. In this work are going to be used for the dehydration of ethanol-water mixtures. [9]

As it has been said before, in this work silicalite-1 membranes have been used. Membrane synthesis process is going to be explained later in this study, but it's worth mentioning that the layer of silicalite-1 that serves as membrane grows from seeds or silicalite-1 previously synthesized. This process is highly complex and its study and environmental quantification by LCA are out from the objective of this project. Although it is not going to be studied, here it's explained briefly synthesis process of these silicalite-1 seeds. Multilamellar silicalite-1 was synthesized using the diquaternary ammonium surfactant $[C_{22}H_{45}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{12}\text{-}N^{+}(CH_3)_2\text{-}C_6H_{13}](OH)_2$ or $C_{22\text{-}6\text{-}6}(OH)_2$ as reported by Choi et al. [8] $C_{22\text{-}6\text{-}6}Br_2$ was synthesized by alkylation of N,N,N',N'-tetramethyl-1,6 hexanediamine with 1-bromodocosane at 70 ^{0}C followed by alkylation of the resultant product by 1-bromohexane at 85 ^{0}C. $C_{22\text{-}6\text{-}6}(OH)_2$ was obtained by ion exchange of the bromide salt. For the synthesis of multilamellar silicalite-1, tetraethyl orthosilicate (TEOS) was hydrolyzed in the presence of $C_{22\text{-}6\text{-}6}(OH)_2$ and distilled water to obtain a gel composition of 100 SiO_2 : 15 $C_{22\text{-}6\text{-}6}(OH)_2$: 4000 H_2O: 400 EtOH. After hydrolysis for 24 hours at room temperature, the resultant gel was transferred to a rotating Teflon-lined steel autoclave at 150 ^{0}C. Crystallization was stopped after 5 days and the product was obtained by centrifugation. The cake was washed with distilled water to reduce the pH to 9 and dried in a vacuum oven at 130 ^{0}C. [10]

1.4. – Pervaporation

Pervaporation is a process in which a liquid stream containing two or more miscible components is placed in contact with one side of a non-porous polymeric membrane or molecularly porous inorganic membrane (such as a zeolite membrane) while a vacuum or gas purge is applied to the other side. The components in the liquid stream sorb into/onto the membrane, permeate through the membrane, and evaporate into the vapor phase (hence the word 'pervaporate'). The resulting vapor, referred to as 'the permeate', is then condensed.

A schematic diagram of the pervaporation process is shown in Fig. 11 As depicted in Fig. 11, by separating the extracting vapor phase from the feed liquid with a membrane which is selective for Species 1, the permeate vapor is enriched in Species 1 relative to the feed liquid.

The properties of the membrane material dictate the separation achieved in the process. For example, if the membrane is hydrophobic, then the membrane will preferentially permeate organic compounds relative to water and the permeate will be enriched in the organic compounds. Alternatively, if the membrane is hydrophilic, then water will be enriched in the permeate and the organic compound in the feed liquid will be dehydrated. In this study pervaporation is going to be applied for the dehydration of an ethanol/water mixture and the membrane used has therefore to be hydrophobic. [11]

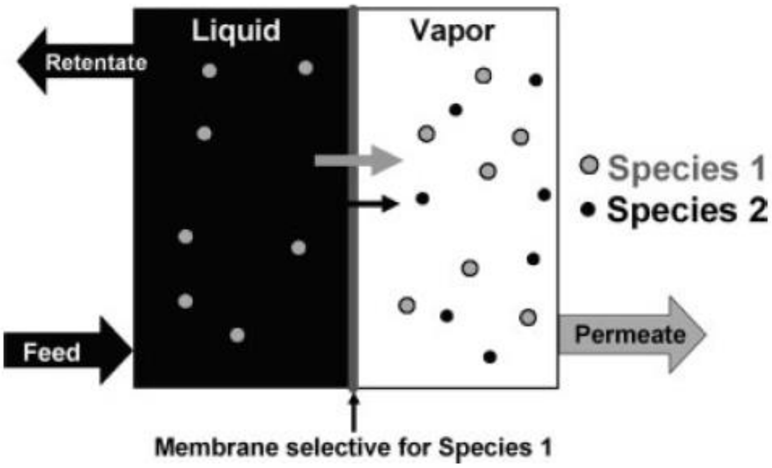

Fig. 11. Schematic diagram of pervaporation process.

1.4.1. - Hollow-fiber zeolite membranes for pervaporation

Hollow fiber configuration is used with the main objective of making easier the use of zeolite membranes by industry. One of the main problem related with zeolite membranes is its low permeation flux. To solve this problem it is possible to use numerous membranes in one system. If the area of permeation is multiplied by a factor of thousands of million, the flux will be multiplied also and the application of membrane systems in industry will be easier.

In a hollow fiber, several membranes are introduced in carcass like it is showed in Fig. 12. A mixture of water/ethanol is introduced as process feed flow and pure ethanol is going to be obtained in the permeate side. A mixture enriched with water is going to exit the system as retenate.

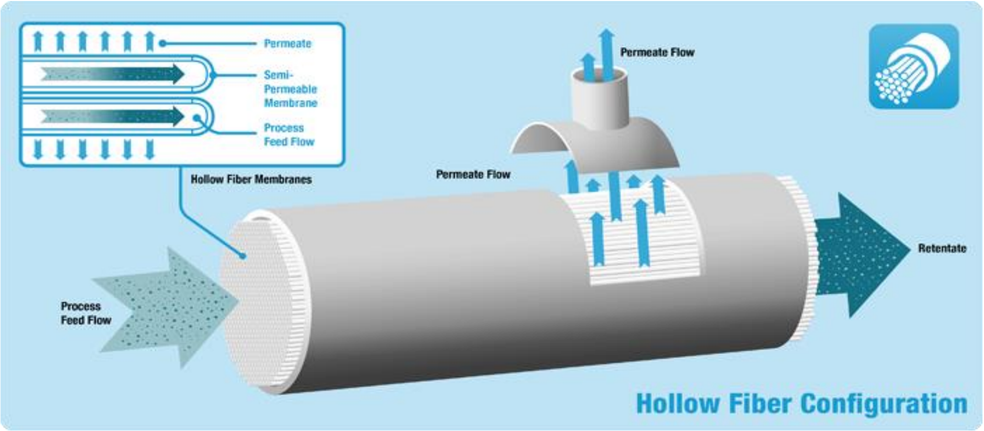

Fig. 12. Hollow fiber configuration.

2. -Life Cycle Assessment

It is defined as a tool to quantitatively evaluate the environmental burdens associated with a product process. Life Cycle Assessment (LCA) identifies and quantifies both the material and energy use and emissions to the environment, determines the impacts, and assesses and implements environmental improvement strategies.

The main characteristic of the LCA if that considers the impacts of the product-system along its life cycle, from its origin as a raw material to final as waste. All intermediate stages as transportation and repair of raw materials, manufacturing, transportation to markets, distribution, use, etc. are taken into account.

In a full LCA all environmental effects arising from the consumption of raw materials and energy needed for manufacturing, emissions and waste generated in the production process as well as the environmental effects from the end of product life are attributed to the products when this is consumed or unusable.

LCA is therefore an environmental account that is charged to products properly quantified. The general categories of environmental impacts needing consideration include resource use, human health and ecological consequences (International Standard ISO 1997). ISO 14044: 2006 systematize the steps throughout LCA study and is going to be followed in this study

2.1. - LCA methodology

According to the methodology proposed by the ISO standard 14044: 2006 LCA project it should be divided into four phases: Study objectives and scope, inventory analysis, impact analysis and interpretation.

As illustrated in Fig. 13, these four phases are not simply sequential. LCA is an iterative technique to be increasing the level of detail in successive iterations.

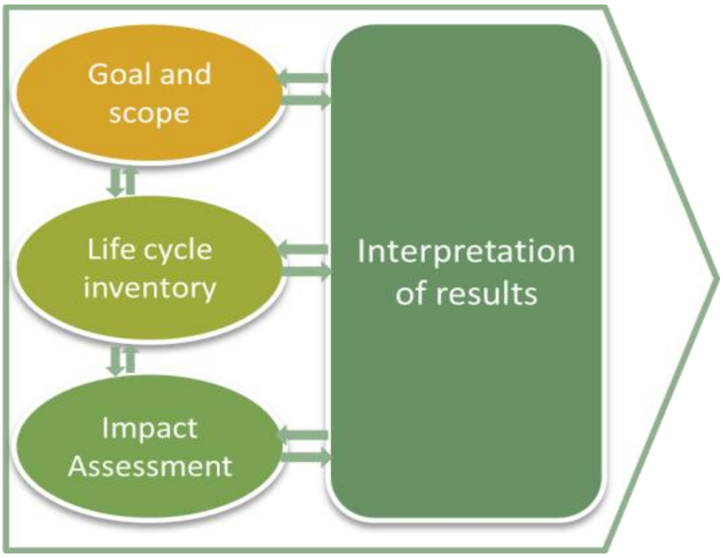

Fig. 13. LCA steps

STEP 1. PURPOSE AND SCOPE OF THE STUDY

In this phase the subject matter is defined and reasons leading to realize and establishing functional unit are included. The functional unit describes the main function of the system analyzed. A LCA does not serve to compare products with each other, but services and / or quantities of the product to carry out the same function. For example, it is not valid to compare two kilograms of different paint that does not serve to perform the same function, cover an area with a similar duration.

Because of its global nature, a complete LCA can be very extensive. For this reason we must set limits that should be clearly identified. The system boundaries determine which unit processes shall be included within the LCA. Several factors require system boundaries, including the intended use of the study, the hypotheses, the exclusion criteria, data and economic constraints and the intended recipient.

STEP 2. LIFE CYCLE INVENTORY ANALYSIS (LCI)

This phase involves data collection related with the functional unit and calculation procedures to identify and quantify all adverse environmental effects. In a generic way we will call these environmental effects as "environmental load". This is defined as output or input of matter or energy of a system that cause negative environmental impact. With this definition greenhouse gas emissions, water effluents and solid waste, consumption of natural resources, noise, radiation, smells, etc. are included. When working with systems involving multiple products, we will proceed to allocate at this stage, the flows of matter and energy and environmental emissions associated with each product or subproduct.

STEP 3. LIFE CYCLE IMPACT ASSESSMENT (LCIA)

The structure of this phase is determined by the ISO 14042 standard, distinguishing between mandatory elements and optional elements.

Required elements are considered:

- Selection of impact categories, category indicators and models.

- Classification. At this stage the data from the inventory are assigned to each impact category depending on the expected environmental effect. An impact category is a class that represents the environmental consequences generated by the process or product systems.

- Characterization. It consists of modeling with the factors of the inventory data for each of these categories of impact.

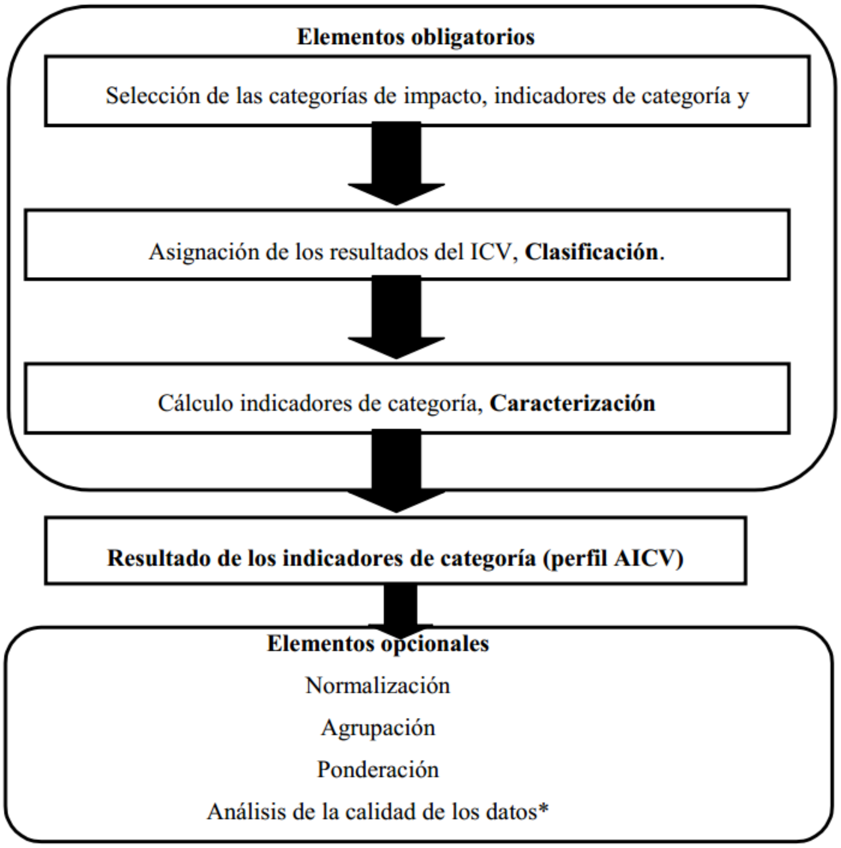

Fig. 14. Mandatory and optional elements of the LCIA in accordance with the ISO 14042 standard.

There are also a number of optional items that can be used depending on the purpose and scope of the LCA study.

- Normalization. It means to give relative importance to an impact category regarding a depending on geographic and/or temporary scale.

- Grouping, sorting and cataloging of possible indicators.

- Weighting. It is to establish factors that give a relative importance to different impact categories regarding economic, politic and social criterion and then add them together and get a weighted result as a single comprehensive environmental index system.

- Analysis of data quality. It will help to understand the reliability of the results of the LCIA. It is considered binding in comparative analyzes.

STEP 4. LIFE CYCLE INTERPRETATION

Interpretation is the phase of a LCA in which the inventory analysis results are combined with the impact assessment. The results of this interpretation may take the form of conclusions and recommendations for decision-making. It allows to determine which stage of the product life cycle has higher environmental impacts and therefore, to evaluate points system that could or should be improved. In the case of comparison of different products you can determine which has a better environmental performance.

In our study as Life Cycle analysis comparison is going to be done to determine which system (distillation or membrane) is better in terms of environmental impacts.

2.2. - LCA Software

In recent years, based on LCA methodology, it has been developed several programs to facilitate its implementation. Most of these programs include databases that can vary in size and quality of the data. Databases of public inventory are built into most commercial programs.

These softwares model the life cycle of a product system and quantify material and energy inputs and outputs. Then automatically transform all these data to environmental indicators. Some of these programs also perform sensitivity analysis and uncertainty examples of software on the market can be cited Gabi (IKP), LCAiT (Chalmers), ProMES (PréConsultants), TEAM (ecobilangroup), Umberto (IFEU). In this work the GaBi® 6.0 education program is used. [12]

3. - Purpose and scope of the study

In this paper two different ways of purification of ethanol are going to be compared through LCA. For this, first of all, both systems are going to be simulated. Once we have the results of the LCAs they have to be compared between them and in this manner is possible to know which of the two ways is better to the environment.

3.1. - Functional unit

The functional unit describes the main function of the system analyzed. For a LCA comparison the functional unit of both systems has to be the same. For example, when a study that compares environmental impact of two different milk packages is performed, the functional unit should be the same, e.g. to package one liter of milk from the factory to the final consumer. In this study the functional unit is the amount of a continuous flux of bioethanol in the distiller: 3.04 kg/s during 10 years. [13]

As it has been explained above, in this work is going to be compared a distillation system with a hollow-fiber system with membranes of diameter 0.1 mm and length of 1 m. Three different systems are going to be compared with the distillation, each of them with different permeation flux. The permeation flux is defined as the flux that permeate from retenate per area of permeation and depends on the wide and porosity of the zeolite layer over the support. Membrane selectivity is defined as the capacity of a membrane to separate from the retenate one compound. Membrane selectivity can be calculated with equation:

$$S_{i/j} = \frac{Y_{i/j}}{X_{i/j}}$$

being i the compound that is going to be separated and j the compound that is going to be retenated, $Y_{i/j}$ the molar fraction of i in the permeate side, and $X_{i/j}$ the molar fraction of i in the retenate side.

Permeation flux has influence on the selectivity of the membrane because as higher is the permeation flux, lower is the selectivity. In this work units of kg/h*m^2 are going to be used for the bioethanol permeation flux and values of 2.5, 5 and 10 kg/s*m^2. Ideal selectivity are going to be considered for the three cases because it has been considered for all the permeation fluxes that all the bioethanol which enters into the membrane system is going to permeate.

Taking all above into account, it is possible to calculate the number of membranes of the hollow-fibers for each permeation fluxes.

Flux (kg/hm2)	Flux (k/s m2)	m2 necessary	Nº of membranes	Length	Diameter of tubes	Nº of tubes
2,5	6.94E-04	4.38E+03	1.99E+07	1	1.00E-04	1.39E+07
5	1.39E-03	2.19E+03	9.95E+06	1	1.00E-04	6.97E+06
10	2.78E-03	1.09E+03	4.97E+06	1	1.00E-04	3.48E+06

Table 2. Data per functional unit for membranes.

The Table 2 shows the results of the calculations. Once the flux is in the same unit as the distiller flux the area of the membrane is calculated to obtain the same flux. Membrane synthesis data have been extrapolated from the membrane disc synthesis process explained on bibliography (Fig. 15 in the next section). The criteria used for the extrapolation was the permeation area considering that pressure difference between feed and permeation side is 1 atm and constant for all the membranes inside the hollow-fiber. 4377.6, 2188.8, and 1094.4 m^2 of permeation area of the hollow-fiber will be necessary when permeation flux is 2.5, 5, and 10 kg/h*m^2, respectively. Following this criteria and knowing that the permeation area of the disc membrane is 2.2 cm^2, materials and energy for the synthesis of the membrane disc are going to be multiplied by 1.99e+7, 9.95e+6, and 4.97e+6, to obtain materials and energy used during synthesis of hollow-fiber with permeation fluxes of 2.5, 5, and 10 kg/h*m^2, respectively.

3.2. - Synthesis of silicalite-1 membrane

The synthesis process and material quantities that appear on Fig. 15 are for the membrane disc synthesis. As it has been said before, all the quantities are going to be multiplied by a numerical factor to simulate material requirements of hollow-fiber membrane

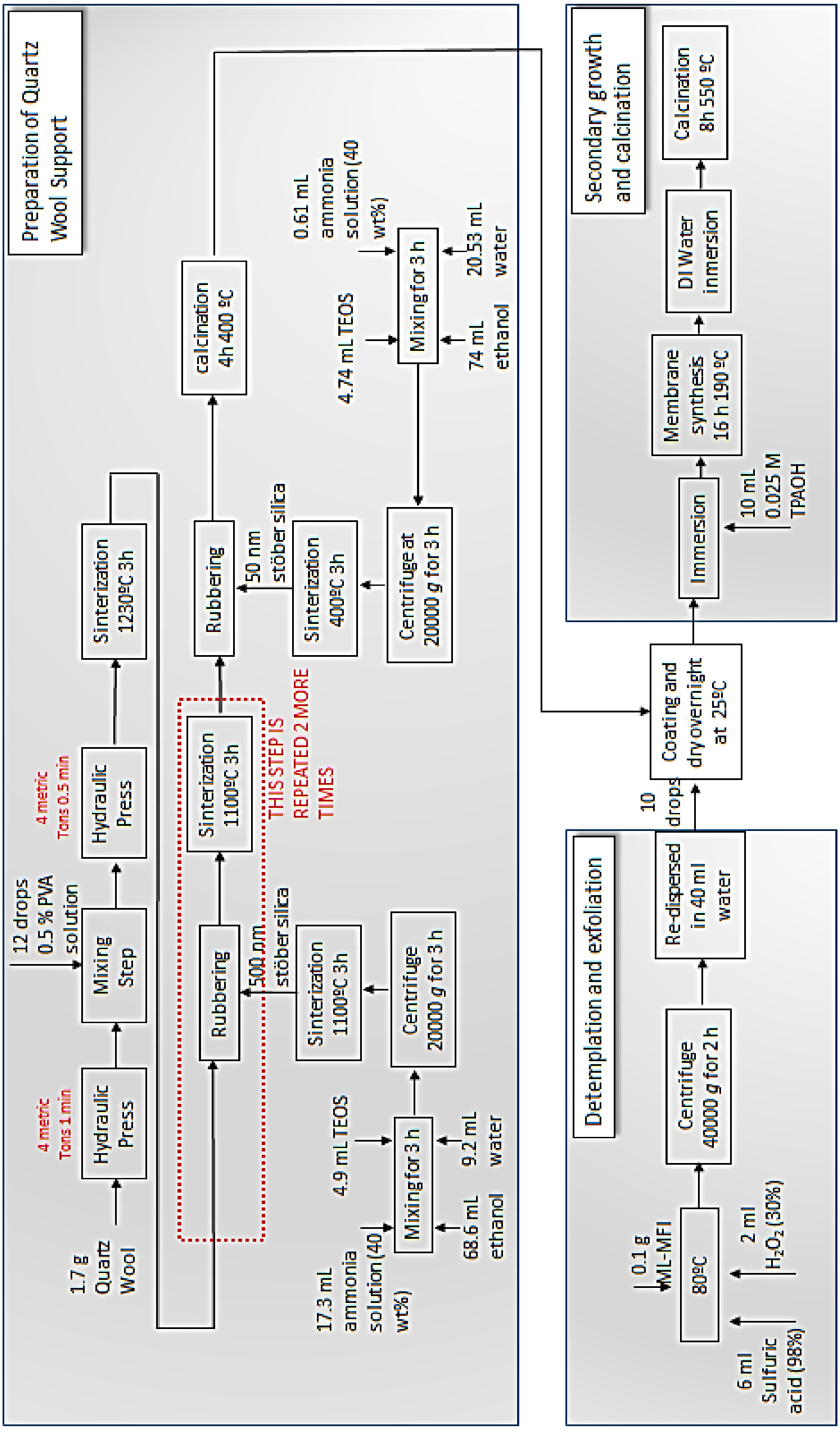

Fig. 15. Membrane fabrication process.

In the first part of the synthesis the support is prepared. First, glass wool was compressed. Then it proceeds to add silica on the wool. This silica will be a source of silicon for further growth silicalite. The addition of silica is done by rubbering, a technique of deposition of silica on the glass wool by friction. There are two types of silicas, 500 nm and 50 nm. The two different silicas are different in size and are prepared by sintering TEOS also ethanol, ammonia and water.

Furthermore, once prepared the support with silica particles inside, silicalite zeolite seeds are prepared. It is the detemplation stage and exfoliation. These seeds are dispersed in a liquid medium and have surfactant to prevent aggregation. These seeds are introduced also in the support (coating stage and dry overnight). Finally the support was put into an autoclave with 10 mL of 0.025 M TPAOH, a structuring agent which directs the crystal growth of silicalite. These seeds act as nucleation points from which grow silicalite crystals. Growth it occurs during 16 hours at 190 degrees. Finally, the membrane is calcined to remove the structuring agent which blocks the pores of the membrane.

4. - Life Cycle Inventory

This phase involves data collection related with the functional unit and calculation procedures to identify and quantify all adverse environmental effects. In a generic way we will call these environmental effects as "environmental load".

4.1. - Distiller data

Energy Used

This is the energy that the rectifying consume in the functional unit chosen, it is going to be a big amount because for the purification of ethanol a lot of energy is needed because it has to heat the mix enough to evaporate the water.

$E = 4.22$ MW $\qquad \eta = 80\%$

$E_{100\%} = E/0.8 = 5.27$ MW

$T = 10y*330d*24h = 79200$ h

$E_T = E_{100\%}*t = 4.18E^5$ MW/h

Rectifying Column Weight

It has been separated the rectifying column in three parts the top of the column, the body of the column and the bottom of the column. The top and the bottom are semicircles with diameter of the column, so we can calculate these two parts as a circle.

$V_o = 4/3*\pi*r_1{}^3-4/3*\pi*r_2{}^3 = 4/3*\pi*(2.95/2)^3-4/3*\pi*(2.93/2)^3 = 0.2716\ m^3$

$V_\square = \pi*(2.95/2)^2*(16.61-2.95*2)-\pi*(2.93/2)^2*(16.61-2.95*2) = 0.989\ m^3$

$V_{plates} = 1/4*\pi*(2.93/2)^2*0.007*28 = 0.33\ m^3$

$V_T = V_o+V_\square+V_{plates} = 1.5906\ m^3$

$$M_{Re} = V_T*\rho = 1.5906*8000 = 12724.48 \text{ kg}$$

Stripping Column

It has been separated this column as the same that the last.

$$V_o = 4/3*\pi*r_1^3-4/3*\pi*r_2^3 = 4/3*\pi*(0.58/2)^3-4/3*\pi*(0.56/2)^3 = 0.01021 \text{ m}^3$$
$$V_{\square} = \pi*(0.58/2)^2*(12.34-0.58*2)-\pi*(0.56/2)^2*(12.34-0.58*2) = 0.2002 \text{ m}^3$$
$$V_{plates} = 1/4*\pi*(0.56/2)^2*0,007*27 = 0.0116 \text{ m}^3$$
$$V_T = V_o+V_{\square}+V_{plates} = 0,222 \text{ m}^3$$
$$M_{Si} = V_T*\rho=0,222*8000 = 1776.08 \text{ kg}$$

4.2. - Membrane data

Table 3 shows the amount of each material for the synthesis of the membrane depending the flux of the membrane and also the data shown in Fig. 15. This figure shows material data for the calculation of the 2.2 cm^2 permeation area. Table 3 shows these data classified (first column) and also in the next columns multiplied by each corresponding scaled factor (Section 3.1) for the different fluxed in the hollow fiber system. It's worth mentioning that energy required for pervaporation has not been considered in this study. Vacuum is necessary in permeate side to remove ethanol gas flow from membrane in pervaporation system. Also energy is necessary to condensate this flow to liquid ethanol and this energy was neither considered.

Material mass	g	Flux 2.5 (kg)	Flux 5 (kg)	Flux 10 (kg)
Quartz wool	1.70	3.38E+04	1.69E+04	8.46E+03
0.5% PVA	0.75	1.49E+04	7.46E+03	3730.91
Ammonia 40%wt	39.38	7.84E+05	3.92E+05	1.96E+05
TEOS	18.14	3.61E+05	1.80E+05	9.02E+04
Ethanol	264.19	5.26E+06	2.63E+06	1.31E+06
Sulfuric acid	10.80	2.15E+05	1.07E+05	5.37E+04
H2O2 (30%)	2.80	5.57E+04	2.79E+04	1.39E+04
ML-MFI	0.10	1989.82	994.91	497.45
TPAOH	10.00	1.99E+05	9.95E+04	4.97E+04
water	48.13	9.58E+05	4.79E+05	2.39E+05

Table 3. Mass of material for each flux.

4.3. -Vessel data

At the same way the table 4 show all the information about the vessel and the amount of material needed for each flux.

Flux	**2,5(kg/h*m2)**	**5(kg/h*m2)**	**10(kg/h*m2)**
Rectangular pitch (1,25*OD)	1.25E-04	1.25E-04	1.25E-04
Diameter of Vessel [m]	0.47	0.66	0.33
Volume of Vessel (assume no end pieces) [m3]	0.17	0.34	0.09
Surface area of steel (assume hemispherical end pieces) [m2]	2.15	3.44	1.38
Thickness [m]	0.05	0.05	0.05
Volume of steel [m3]	0.11	0.17	0.07
Density of steel [kg/m3]	8050	8050	8050
Mass of Steel [kg]	864.84	1384.20	554.56

Table 4. Vessel data.

4.4. - Hypothesis

It is necessary to do several hypothesis because GaBi 6.0 doesn't have in its database all the process that are needed. For this reason most of the chemicals have been studied and it has been calculated the raw materials and energy for their production.

4.4.1. -Distiller hypothesis

- The thickness of the columns is 1 cm.
- The thickness of the plates is 0.7 cm.
- The plates of the columns have the same diameter of the columns and its area is a quarter of the total area of the plate.
- It has been considered a steel density of 8 g/cm^3.
- The top and the bottom of the column have been welded to the body of the column
- The steel of the column is the same as the steel sheet process by default of GaBi.

4.4.2. - Membrane hypothesis

- It has been used glass wool instead of quartz wool.
- In this study all the process are going to be placed in Europe, as much as GaBi allow.
- All the parts of the membrane, the vessel and the membrane go to the landfilled at end of life.
- For this membrane process silicalite-1 seeds are used. This seeds are used as nucleation points in the synthesis of zeolite. But in this study it hasn't be simulated because stay out the limits of objectives and time of the work.

4.5. – TEOS

Tetraethyl orthosilicate (TEOS) is the chemical compound with the formula $Si(OC_2H5)_4$ (Fig. 16). Often abbreviated TEOS, it is a colorless liquid that degrades in water. TEOS is the ethyl ester of orthosilicic acid, $Si(OH)_4$. It is a prototypical alkoxide.

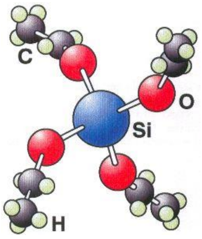

Fig. 16. TEOS molecule.

TEOS is a tetrahedral molecule. Like its many analogues, TEOS is prepared by alcoholysis of silicon tetrachloride, so is a source of silicon. [14]

To simulate the TEOS fabrication process is needed the amount of all inputs to produce 1 g of TEOS and as GaBi doesn’t have all the chemicals in its database. To simulate the synthesis of TEOS is needed to set off the chemicals until one which GaBi database has. All the reactions are with 90% efficiency.

$\rho = 0.933$ g/ml PM(TEOS) = 208.3322g/mol

$$SiCl_4 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 4HCl \quad (1)$$

$$Si + 2Cl_2 \rightarrow SiCl_4 \quad (2)$$

$$Si + 2Cl_2 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 4HCl \quad (3)$$

$n_{TEOS} = 1/208.332=4.8*10^{-3}$ mol

$n_{Si} = 4.8*10^{-3}/0.9=5.333*10^{-3}$ mol

$n_{Cl2} = 2*4.8*10^{-3}/0.9=0.010667$ mol

$n_{ethanol} = 4*4.8*10^{-3}/0.9=0.02133*10^{-3}$ mol

Mass of each chemical is obtained multiplying each mol by each molecular weight.

	Mol	PM(g/mol)	g
Si	5.33E-03	28.0855	0.14978
Cl_2	0.010667	70.906	0.75635
Ethanol	0.02133	46.0684	0.98264

Table 5. Inputs for 1g of TEOS.

4.6. – TPAOH

Tetrapropylammonium hydroxide (TPAOH) is a quaternary ammonium salt, act like a surfactant. All information is taken from bibliography. [15] The next Table 6 shows the material needed for the production of 1 g of TPAOH. All the inputs can be simulated in GaBi except PCl_3.

Inputs	**g/g TPAOH**
C_2H_4	0.55
Syngas	1.15
NH_3	0.08
PCl_3	0.68
NaOH	0.59

Table 6. Inputs for 1 g TPAOH

The chemicals have to be disaggregated which one there is in GaBi 6.0 database. All of the compounds on Table 6 are in GaBi except PCl_3. Its synthesis process has been studied and disaggregated until reactants that appear in GaBi database. All reactions has been considered with a molar efficiency η=90%.

$PM(P_4) = 123.895$ g/mol $PM(Cl_2) = 70.096$ g/mol $PM(PCl_3) = 137.3328$ g/mol

$$P_4 \quad + \quad 6Cl_2 \quad \rightarrow \quad 4PCl_3$$

$n_{PCl3} = 0.68/137.3328=4.9515*10^{-3}$ mol

$n_{P4} = 4.9515*10^{-3}/(4*0.9)=1.3754*10^{-3}$ mol

$n_{Cl2} = 6*4.9515*10^{-3}/0.9=8.2524*10^{-3}$ mol

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \quad \rightarrow \quad 6CaSi_3O_3 + 10CO + P_4$$

$n_{Ca3(PO4)2} = 2*4.9515*10^{-3}/0.9=3.0564*10^{-3}$ mol

$n_{SiO2} = 6*4.9515*10^{-3}/0.9=9.1693*10^{-3}$ mol

$n_c = 10*4.9515*10^{-3}/0.9=0.01528$ mol

Now Table 6 can be completed with PCl_3 materials synthesis required and in Table 7 is shown all the inputs for the getting 1 g of TPAOH.

	mol	**PM(g/mol)**	**g**
C2H4			0.55
Syn-gas			1.15
NH3			0.08
NaOH			0.59
Cl2	8.253E-03	70.096	0.5785
Ca3(PO4)2	3.056E-03	310.1767	0.9480
SiO2	9.169E-03	60.0843	0.5509
C	0.015	12.0107	0.1835
Energy(MJ)	2.575		

Table 7. Inputs for 1g of TPAOH

So the only thing left is link all this data and carry it to a process in GaBi, but we need for the process TPAOH 0,025M so we have to add, a process to mix the TPAOH and water.

4.7. - Energy consumption in membrane fabrication

The Table 8 shows the energy consumption of each device used in the membrane fabrication. The consumption of the devices have been obtained from a devices used in a laboratory except the sinterization oven (HT 450/18) [16] which it was disposed from a web site which sells industrial oven for this kind of process, because was needed an oven defining specific volume. An oven of smaller volume has been used for the sinterization at 400ºC (HT 450/16). [16]

Device	Consumption(KW/h)	Time (h)	Energy (KW)
Hydraulic Press(1)	7.5	1.67E-02	0.13
Hydraulic Press(2)	7.5	8.33E-03	0.06
Sinterizacion 1250ºC	44.4	3	133.2
Centrifuge(1)	1.2	3	3.6
Sinterization 1100ºC(1)	8.25	3	24.75
Sinterization 1100º(2)	39.1	9	351.9
Centrifuge (2)	1.2	3	3.6
Sinterization 400ºC	3	3	9
Calcination 400ºC	14.22	4	56.88
Centrifuge 40 Kg	2.4	2	4.8
Coationg and dry overnight	0.888	8	7.104
Membrane synthesis	6.75	16	108
Calcination 800ºC	19.55	8	156.4

Table 8. Energy consumption in membrane synthesis.

5. – Life Cycle Impact Assessment

Once inventory data have been collected, they are transformed and summed up in the various environmental impact indicators by characterization factors. On bibliography appears information about what each indicator measures and how it has been calculated. [17][18]

- Acidification (mol N or S-Equiv.)
- Resource Depletion (kg Sb-Equiv.)
- GW, excl biogenic carbon (kg CO_2 Equiv.)
- Particulate matter (kg PM2, 5-Equiv.)
- Terrestrial eutrophicatrion (mol N or S-Equiv.)
- Freshwater consumption (kg)

6. – Life Cycle Interpretation

6.1. - Distiller environmental impacts

Table 9 shows environmental impacts for the distiller in all their steps as the LCA requires. The use has the higher impact into the environment because the enormous quantity of energy needed for the distiller. During natural gas combustion it is emitted NO_x and SO_2 responsible of the high values of the acidification indicator at the use phase. In the use phase is taken into account the resources depletion impact caused by natural gas extraction and because of this, resource depletion indicator has higher value in this step. Global Warming potential value is due to the CO_2 emissions during natural gas combustion. The responsible of the high value of the particulate matter are the SO_2 and the Dust(PM 2.5) emitted to air. Terrestrial eutrophication value is due to the SO_2 and NO_x emissions. The high value of the freshwater consumptions is due for the process is needed huge quantities of water.

Distiller	Raw Materials Extraction	Manufacturing	Use	End of life
Acidification (mol N or S-Equiv.)	45.51	0.19	5.72E+04	0.29
Resource Depletion (kg Sb-Equiv.)	2.29	0.01	285.21	1.99E-03
GW, excl biogenic carbon (kg CO_2 Equiv.)	3.32E+04	429.13	2.23E+08	149.43
Particulate matter (kg PM2, 5-Equiv.)	24.08	0.03	9233.51	0.40
Terrestrial eutrophication (mol N or S-Equiv.)	524.96	1.96	4.72E+05	2.44
Freshwater consumption (kg)	1.51E+04	169.84	6.97E+07	145.93

Table 9. Environmental impacts of distiller LC.

6.2. - Membrane environmental impact

In this paragraph is going to be show the environmental impacts of the membrane life cycle, at first only is going to be show for Flux 2.5 and later in the step of comparison will be show all flux together. It is possible to see in Table 10 and Figure 17 that the "Preparation of Quartz Wool Support" step has the highest contribution on each impact value. Because of that it is necessary to disaggregate it in all their processes to see which one has the highest impact.

Flows (Flux 2,5)	Preparation of Quartz Woll Support	Detemplation and exfoliation	Secondary growth and caltincation	Vessel Fabrication	Membrane Use
Acidification (mol N or S-Equiv.)	4479.97	515.58	4.06	2.72	1.19
Resource Depletion (kg Sb-Equiv.)	87.27	5.15	0.27	0.14	0.01
GW, excl biogenic carbon (kg CO_2 Equiv.)	6.12E+06	9.6E+04	4.26E+03	2004.01	476.56
Particulate matter (kg PM2, 5-Equiv.)	833.90	97.16	6.57	1.44	4.22
Terrestrial eutrophication (mol N or S-Equiv.)	4.96E+04	7.51E+03	46.83	31.36	11.87
Freshwater consumption (kg)	2.75E+06	4.17E+04	2.35E+03	910.29	943.55

Table 10. Environmental impacts of membrane flux 2.5 LC.

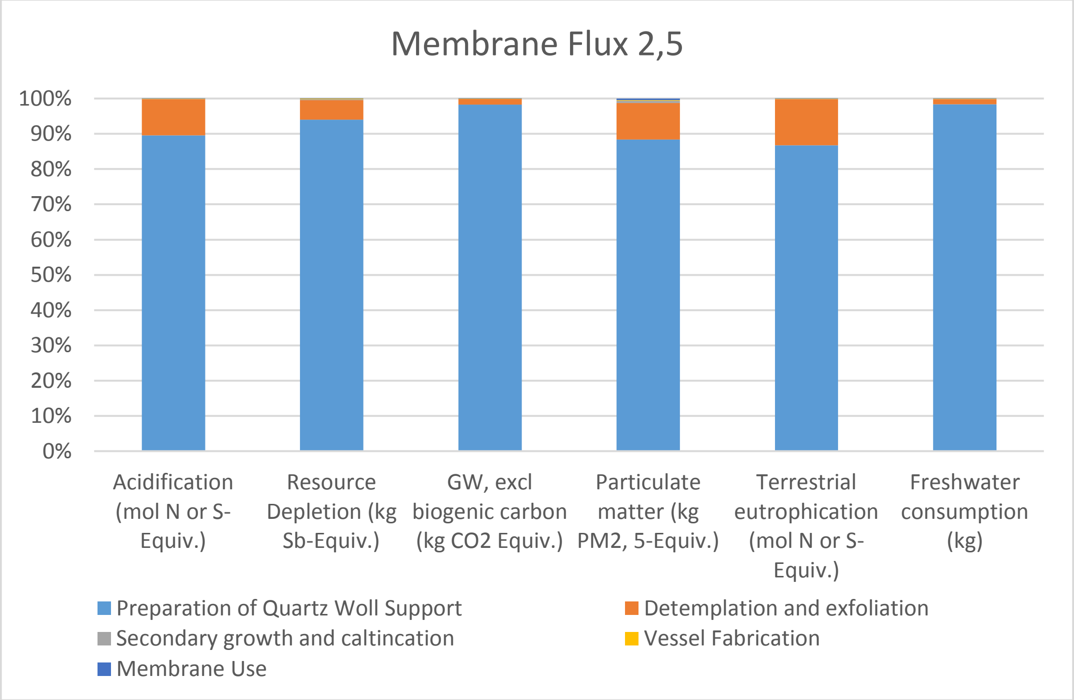

Fig. 17. Contribution in % of each step of the membrane hollow fiber preparation to the different indicator for the 2.5 kg/h*m2 membrane flux.

The next graphs show the different impacts of the different processes that performs the “preparation of quartz wool support”. In Fig. 18 it can be seen that the obtention of the Ethanol is the process with highest contribution to Acidification indicator because during its manufacture NO_x and SO_2 are released to the air.

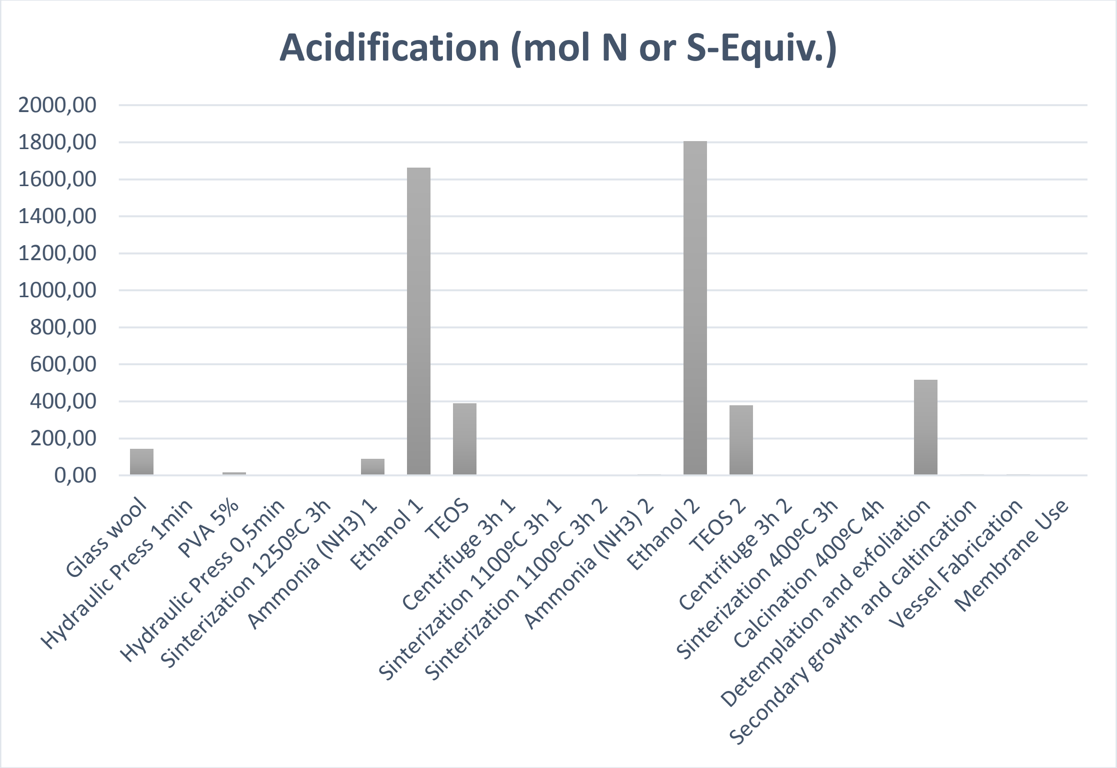

Fig. 18. Acidification of membrane flux 2.5 (Preparation disaggregate) LC.

In Fig. 19 it can be seen that the obtention of the Ethanol and TEOS are the processes with highest contribution to Resource Depletion indicator because of the use of natural gas and inorganic resources to produce them.

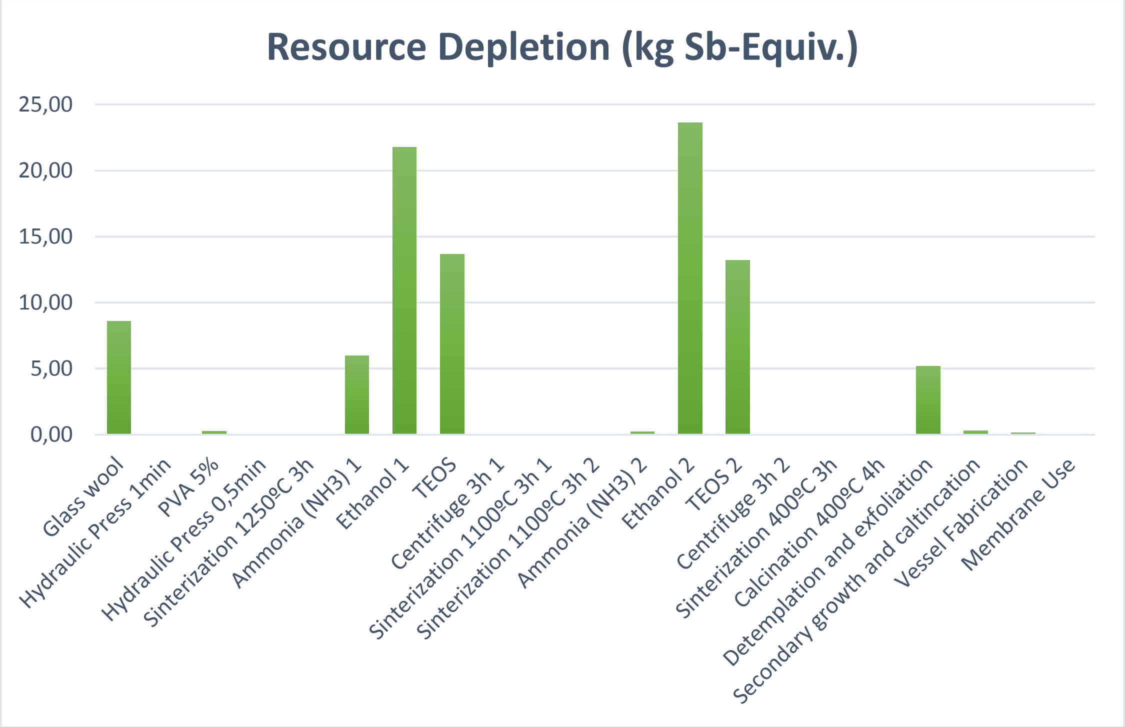

Fig. 19. Resource Depletion of membrane flux 2.5 (Preparation disaggregate) LC.

In Fig. 20 is represented the values of the indicator Global Warming and it can be seen that the production of the Ethanol is the process with highest contribution to this indicator because the emissions of CO_2 and CH_4 to the air during its manufacture.

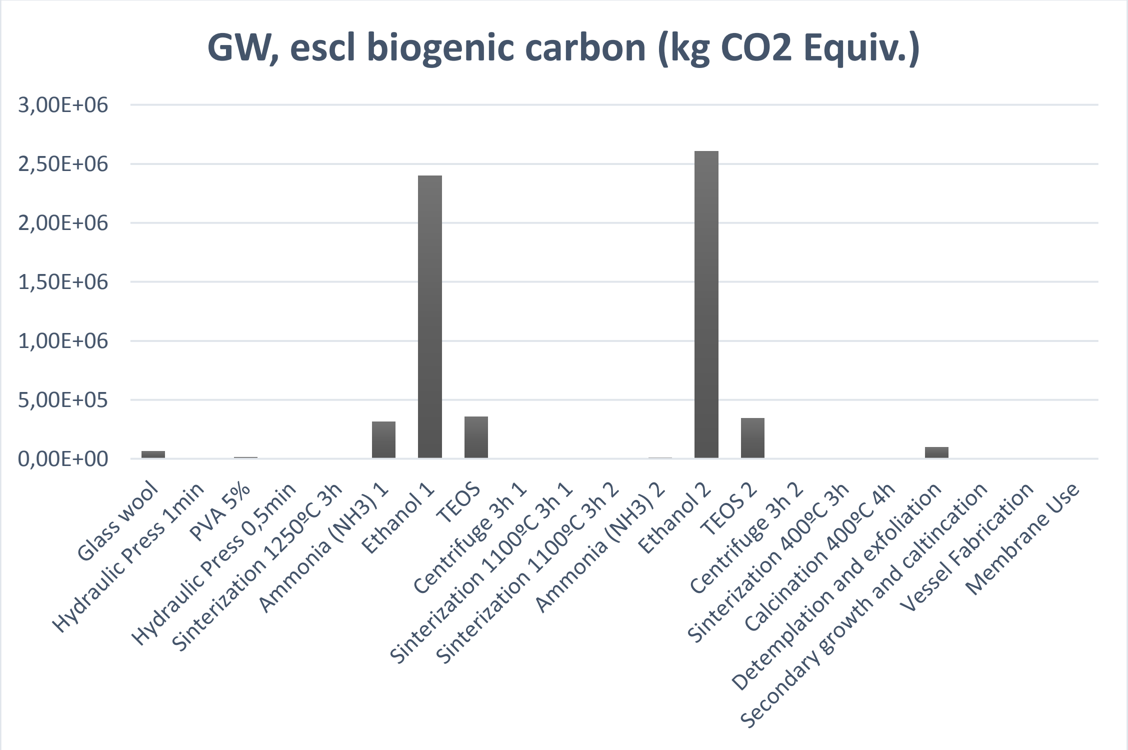

Fig. 20. GW, escl biogenic carbon of membrane flux 2.5 (Preparation disaggregate) LC.

In Fig. 21 it has been represented the Particulate Matter indicator and it can be seen that the fabrication of the Ethanol and TEOS are the processes with highest contribution to this indicator because during its manufacture SO_2 and Dust(PM 2.5) are released to the air.

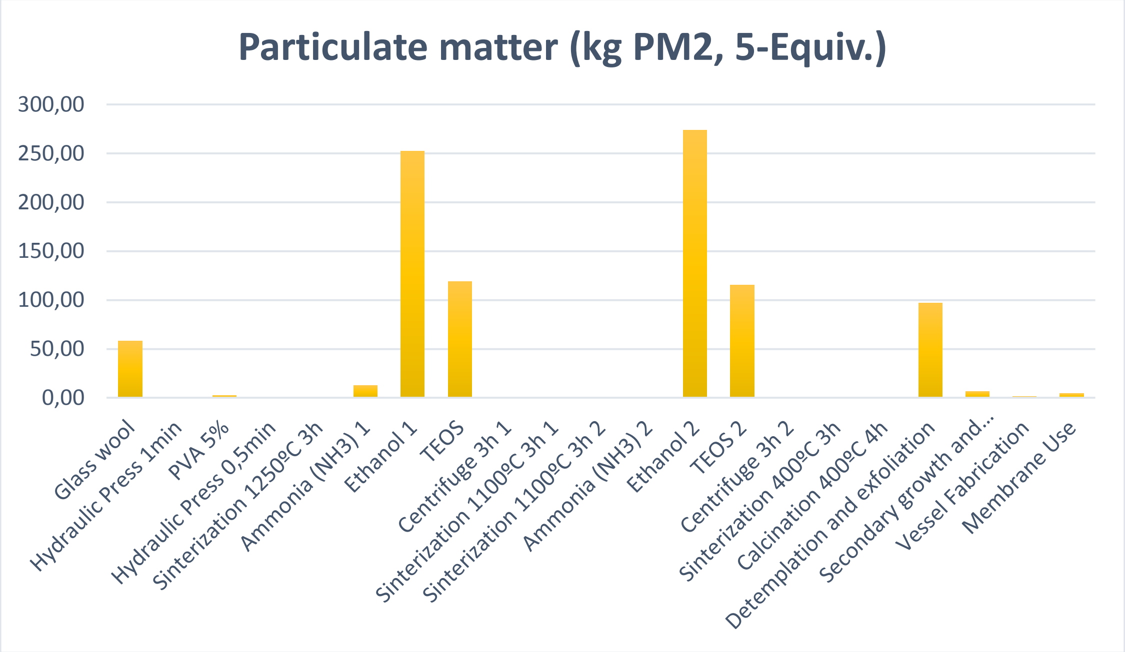

Fig. 21. Particulate matter of membrane flux 2.5 (Preparation disaggregate) LC.

In Fig. 22 it can be seen that the obtention of the Ethanol and detempation and exfoliation step are the processes with highest contribution to this the Terrestrial Eutrophication indicator because during Ethanol manufacture NO_x and SO_2 are released to the air. Also these gases are emitted during sulfuric acid used in detemplation and exfoliation step.

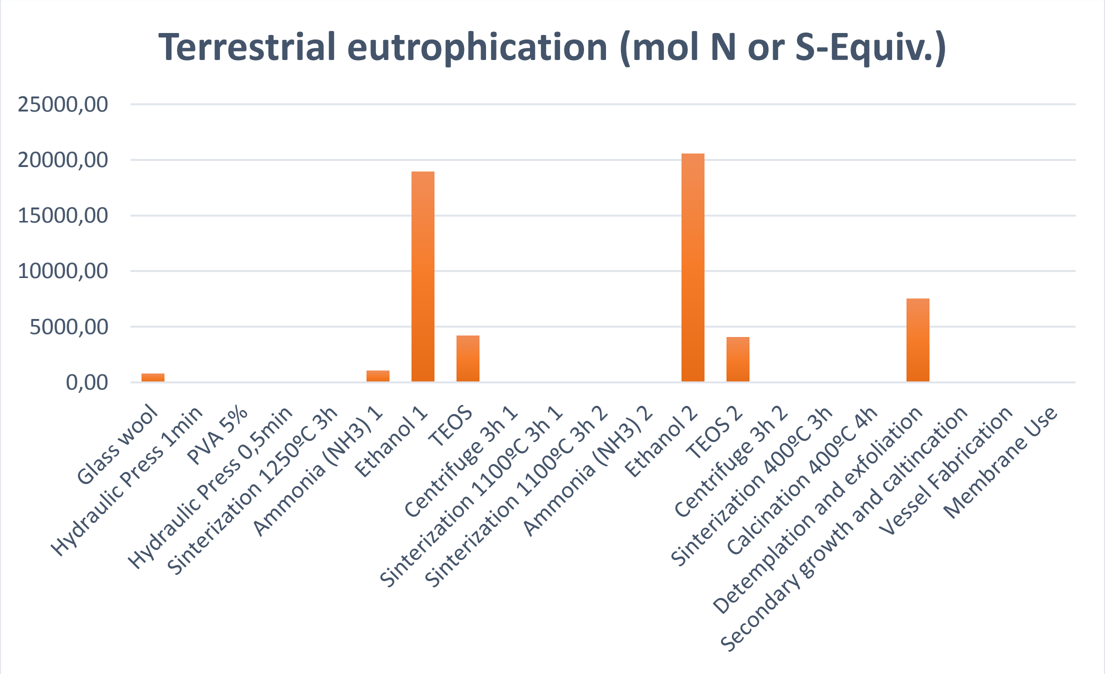

Fig. 22. Terrestrial eutrophication of membrane flux 2.5 (Preparation disaggregate) LC.

In Fig. 23, that represent the values for the Freshwater consumption, it can be seen that the obtention of the Ethanol and PVA are the processes with highest contribution to this indicator because during its manufacture huge quantities of river water is consumed.

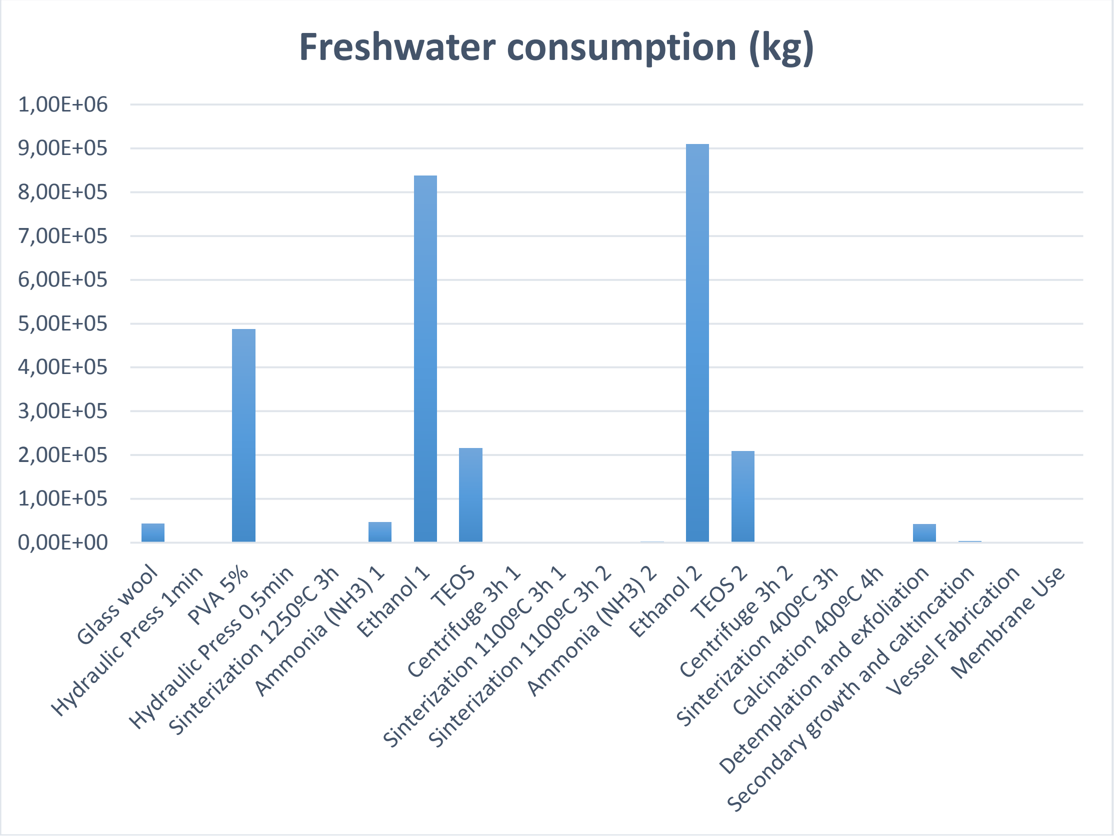

Fig. 23. Freshwater consumption of membrane flux 2.5 (Preparation disaggregate) LC.

6.3. – Life Cycle Comparison

Finally, distillation and Membrane system are going to be compared in terms of environmental impacts. Table 11 shows the values for each indicator for the four cases studied. It is possible to appreciate that the use of membranes reduces the value of each indicator. Because the main objective of the membrane system is the reduction of the EIIs of current distillation system for the bioethanol purification, in Fig. 24 has been represented the % of reduction of the 6 EEIs.

Comparison Table	Distiller	Flux 2.5	Flus 5	Flux 10
Acidification (mol N or S-Equiv.)	5.73E+04	5.00E+03	2496.89	1249.54
Resource Depletion (kg Sb-Equiv.)	287.51	92.70	46.91	23.52
GW, excl biogenic carbon (kg CO_2 Equiv.)	2.23E+08	6.22E+06	3.12E+06	1.56E+06
Particulate matter (kg PM2, 5-Equiv.)	9.26E+03	937.64	468.09	235.70
Terrestrial eutrophication (mol N or S-Equiv.)	4.72E+05	5.72E+04	2.85E+04	1.43E+04
Freshwater consumption (kg)	6.97E+07	2.79E+06	1.40E+06	7.01E+05

Table 11. LCC between all devices.

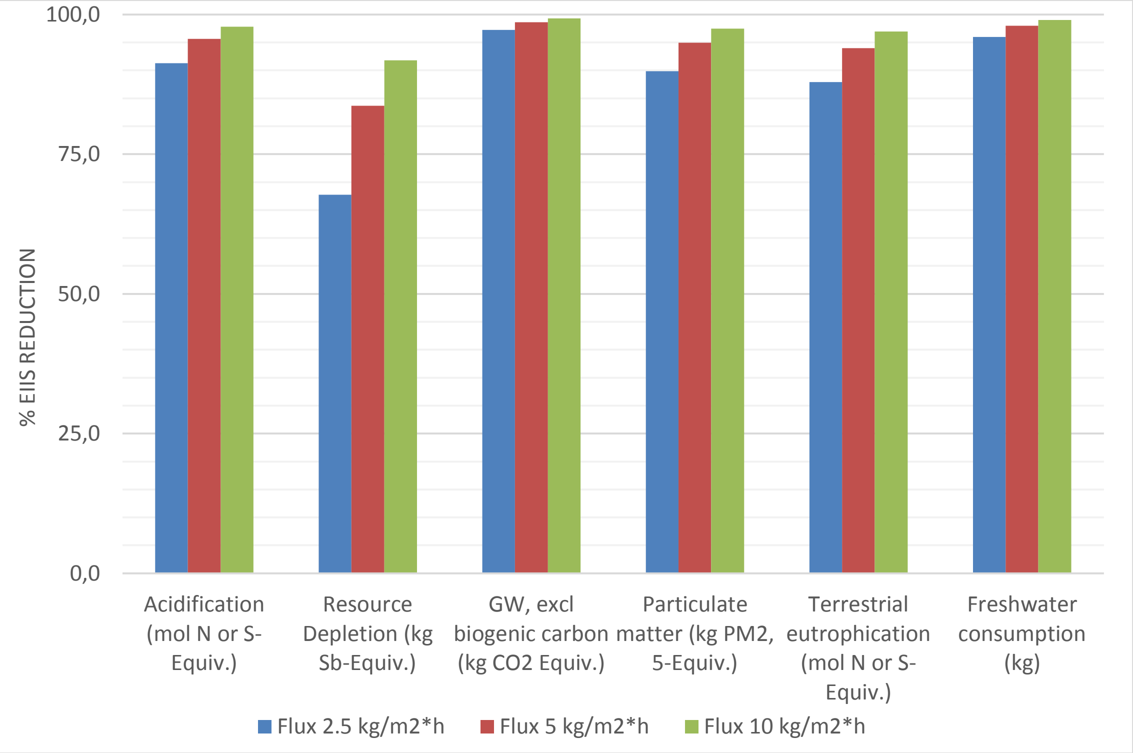

Fig. 24. % of reduction of the 6 EEIs.

It can be seen that for 5 of 6 indicators the % of reduction using membrane system is higher than 80 %. For the Resource Depletion indicator, the % of reduction is smaller because the ethanol and TEOS fabrication need a lot of fossil resources and inorganic material.

Obviously, the % of reduction is higher for the membrane system with higher fluxes because the amount of materials used for their synthesis is smaller. As it has been said before, in this study it has been considered that the selectivity doesn’t depends on the flux of permeation, in other words, pure ethanol is obtained in the permeation side not depending on the permeation flux value. This is an ideal situation because as higher is the flux of the membrane, lower is the selectivity.

7. - Conclusions

- A simulation of the synthesis process of a hollowfiber system of silicalite-1 and distillation process have been achieved, both for the bioethanol purification process.

- Inside the distillation process, the gas natural consumption has proved to be the most damage for the environment.

- Inside the membrane process, the obtention of ethanol for the synthesis of nanoparticles has proved to be the most damage for the environment.

- When both systems are compared, it is demonstrated that the use of the membranes reduces 5 of the 6 environmental indicators more than 80%.

- The environmental impacts for the membrane process is reduced according more flux have the membrane.

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ANEXO I

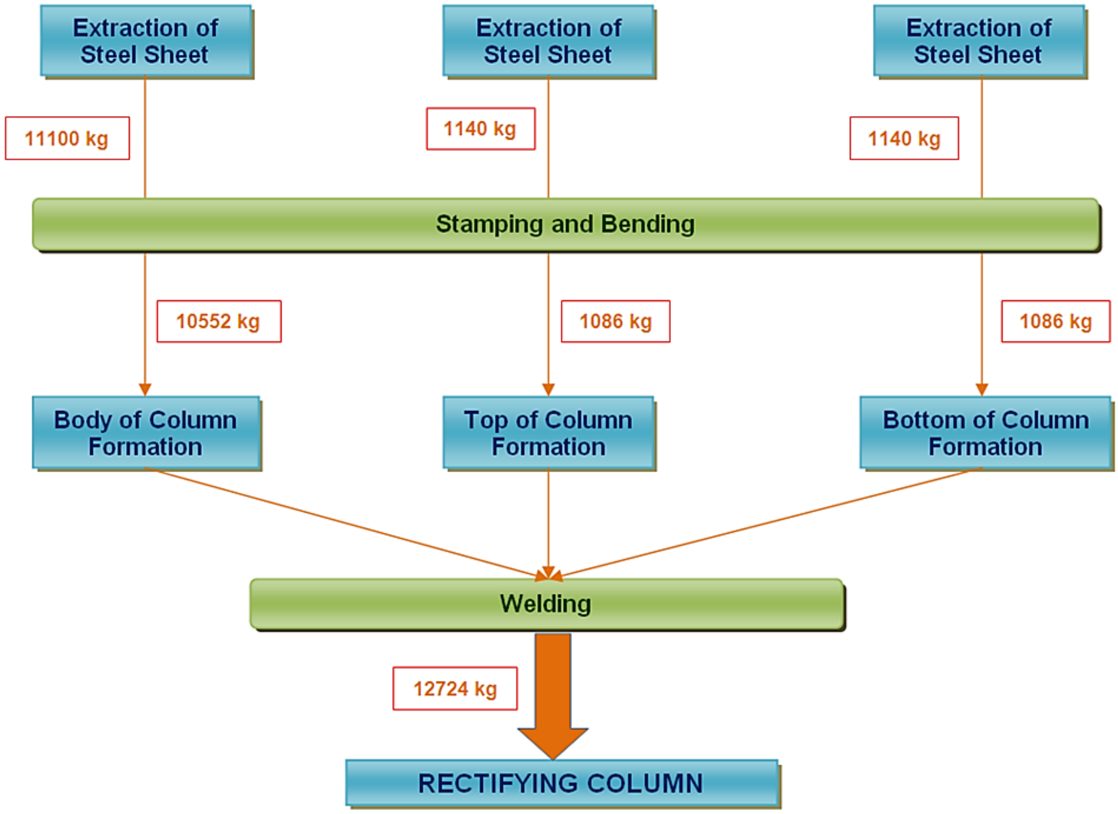


Fig. 25. Simulation of rectifying column fabrication.

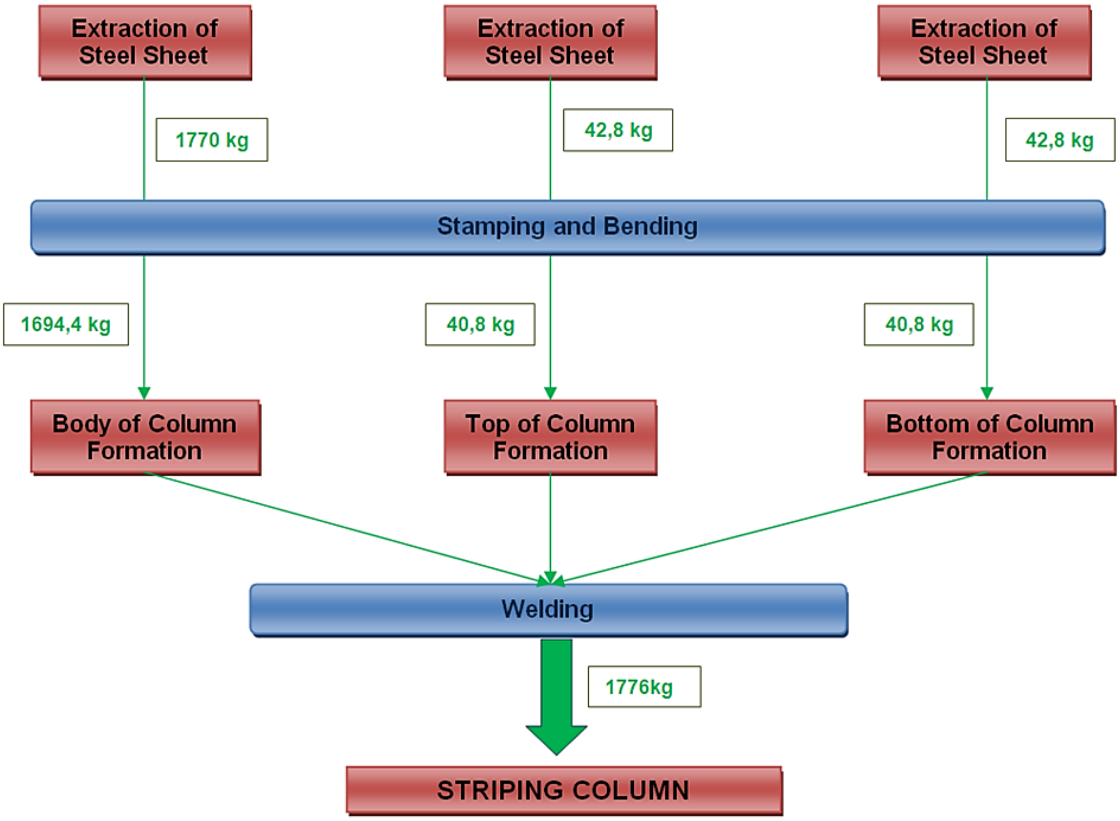


Fig. 26. Simulation of striping column fabrication

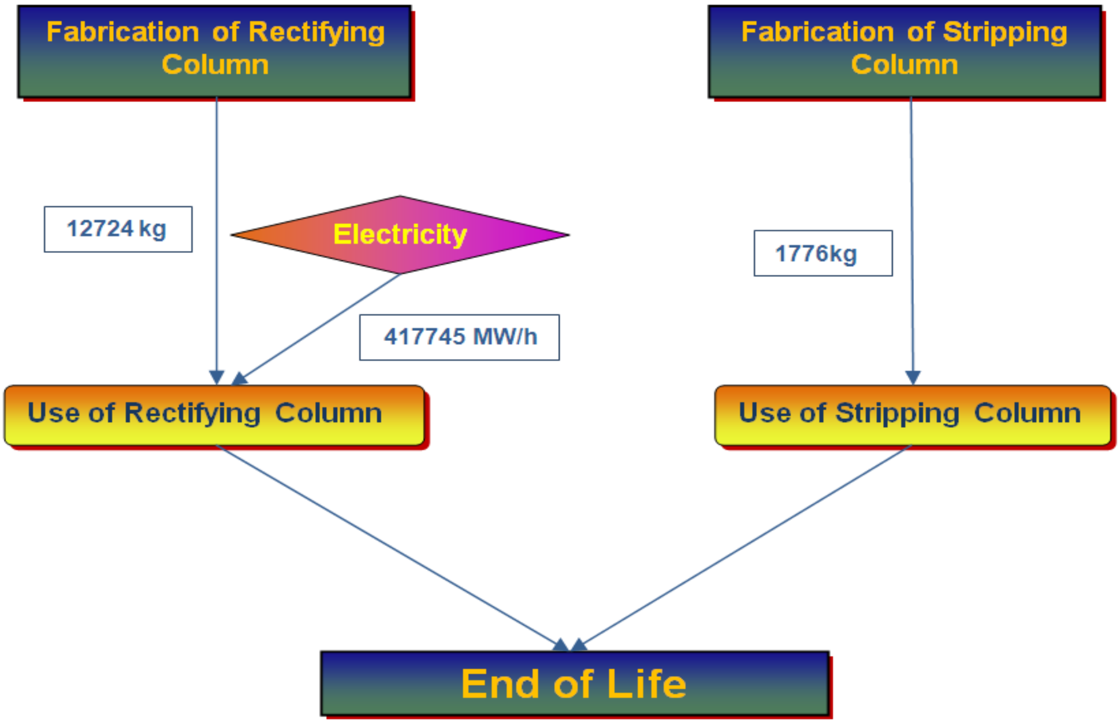


Fig. 27. Simulation of distiller use.

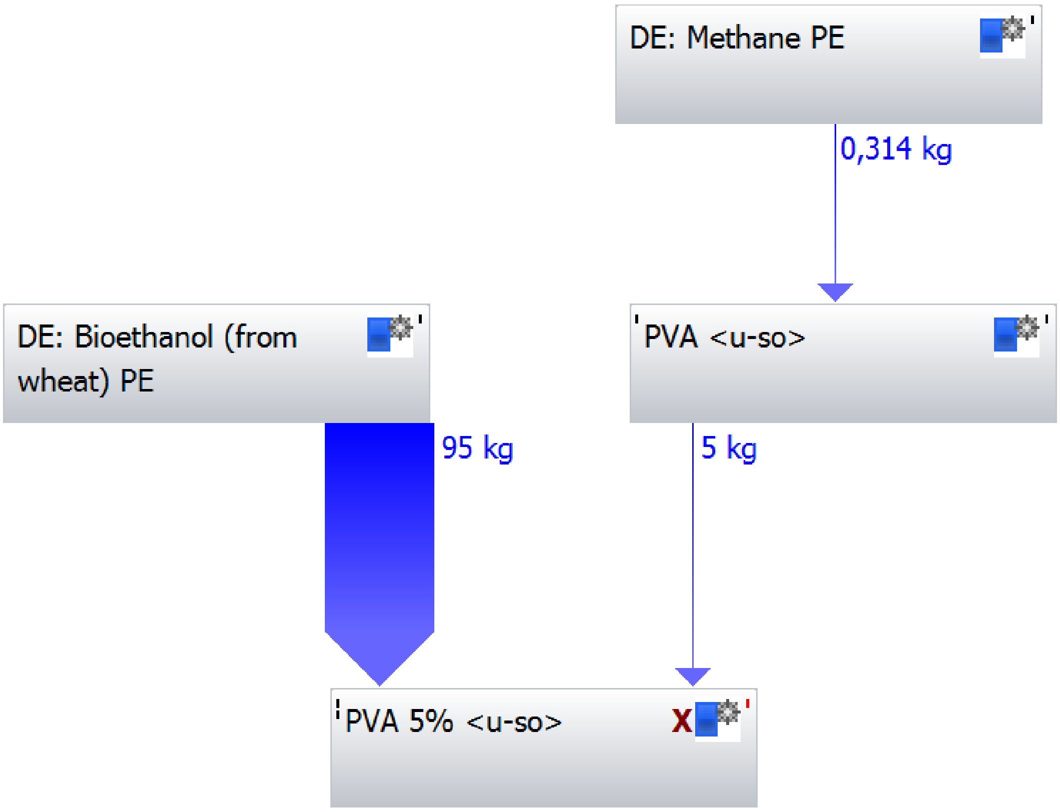


Fig. 28. PVA 5% synthesis.

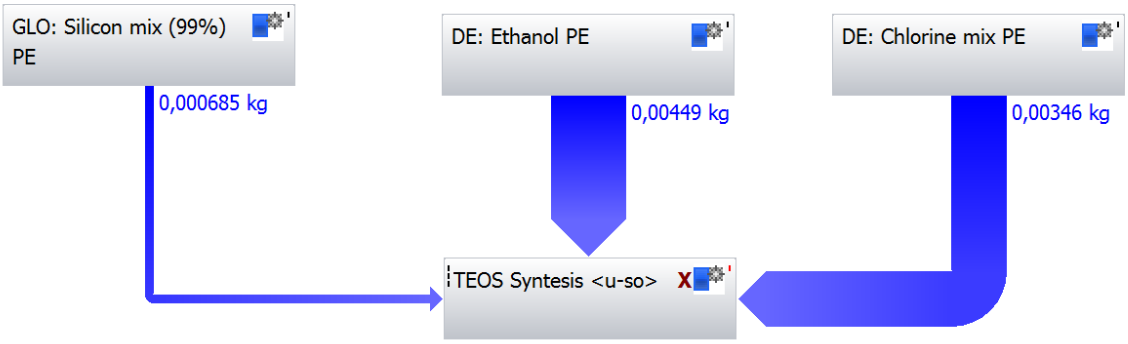


Fig. 29 TEOS synthesis

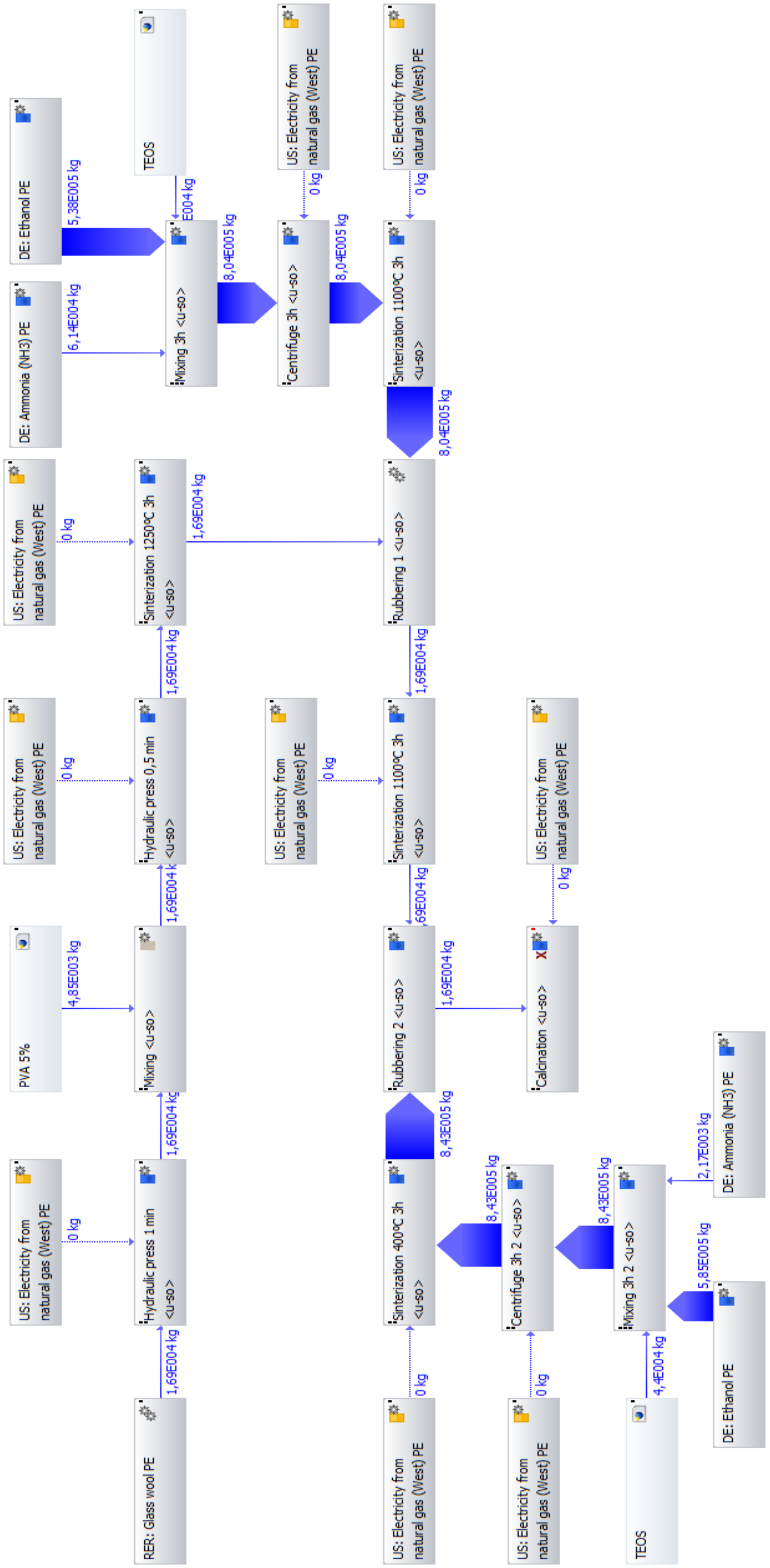


Fig 30. Preparation of Quartz Wool Support synthesis.

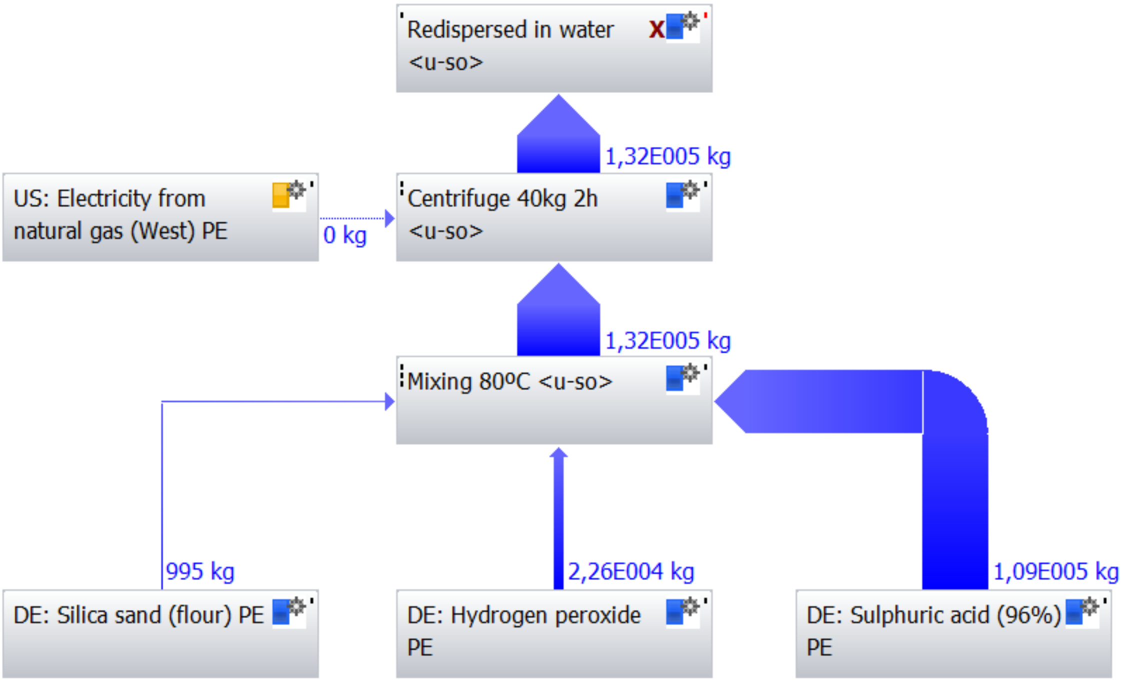


Fig. 31. Detemplation and exfoliation synthesis.

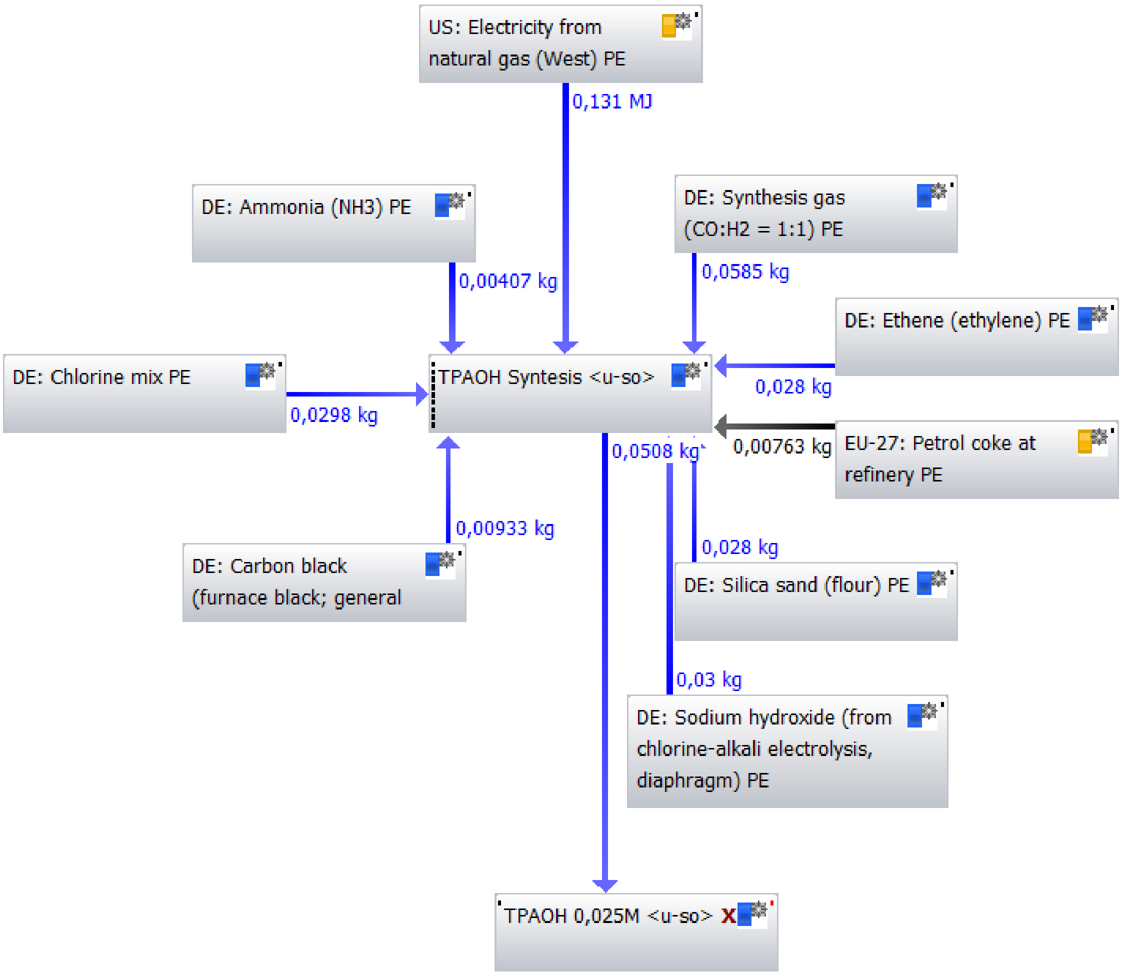


Fig. 32. TPAOH 0.025 M synthesis.

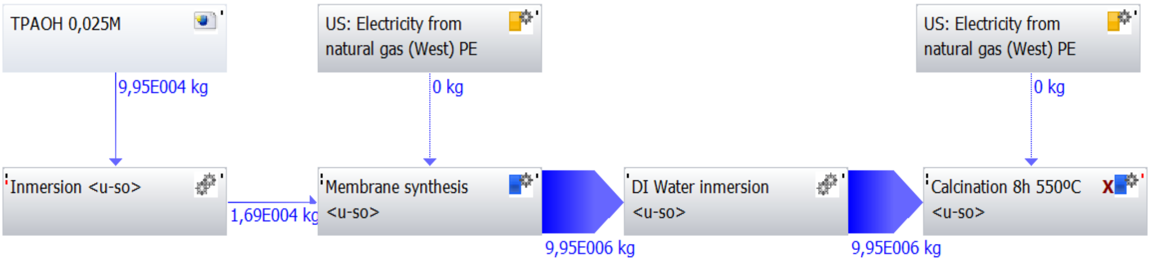


Fig. 33. Secondary growth and calcination synthesis.

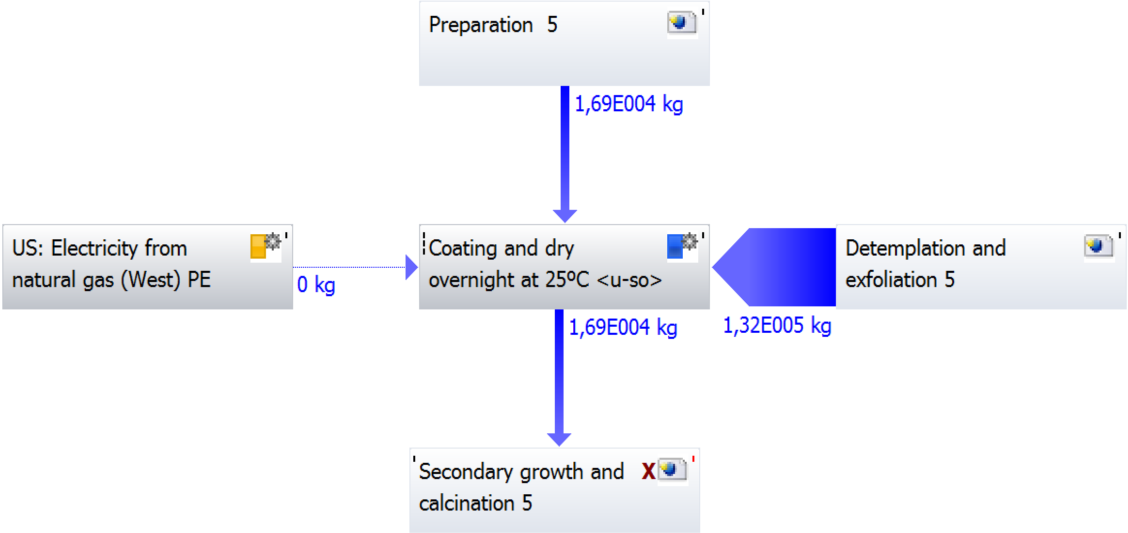


Fig. 34. Membrane fabrication synthesis.

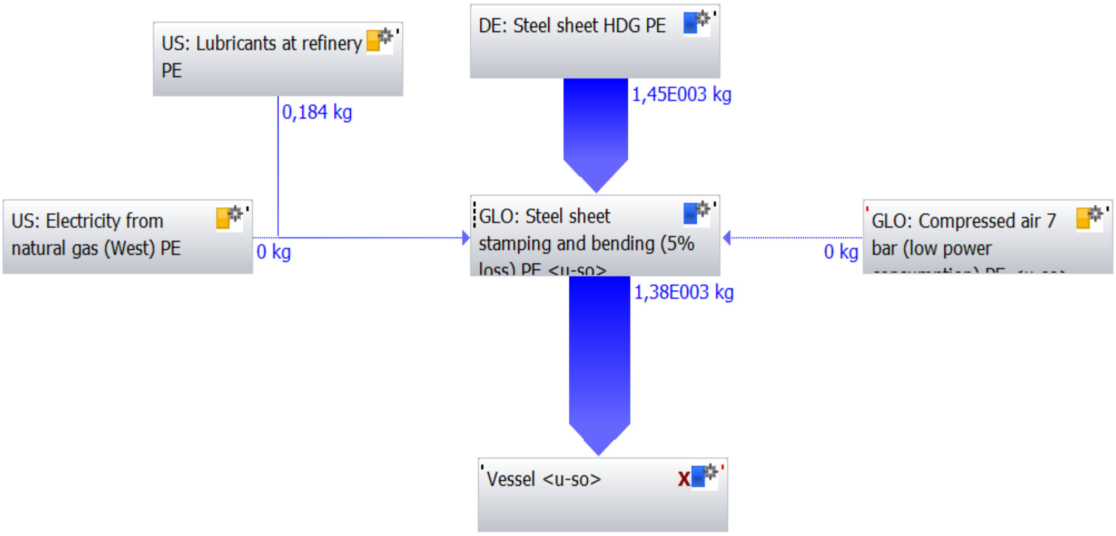


Fig. 35. Vessel fabrication synthesis.

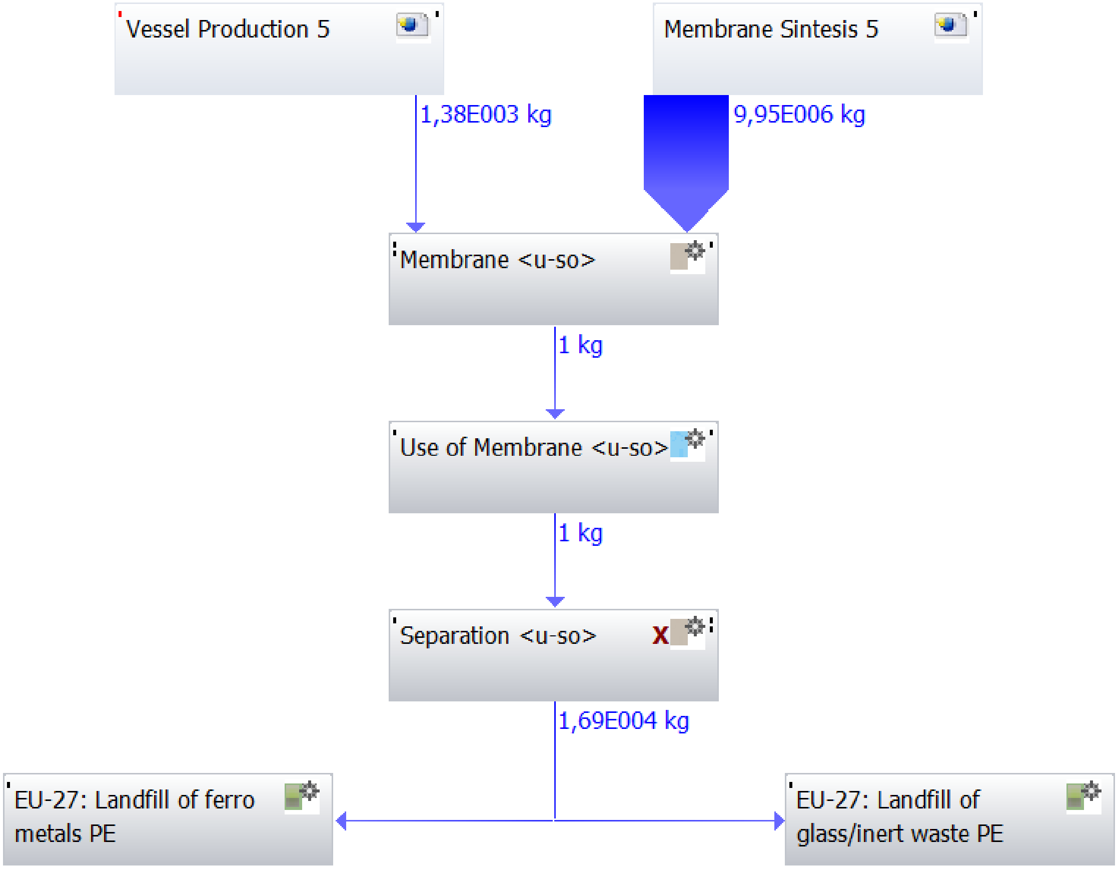


Fig. 36. Membrane LC synthesis.

ANEXO II

Distiller	Distiller LCA	Raw Materials Extraction	Manufacturing	Use	End of life
Acidification (mol N or S-Equiv.)	5.73E+04	45.51	0.19	5.72E+04	0.29
Resource Depletion (kg Sb-Equiv.)	287.51	2.29	6.30E-03	285.21	1.99E-03
GW, excl biogenic carbon (kg CO2 Equiv.)	2.23E+08	3.32E+04	429.13	2.23E+08	149.43
Particulate matter (kg PM2, 5-Equiv.)	9258.02	24.08	0.03	9233.51	0.40
Terrestrial eutrophication (mol N or S-Equiv.)	4.72E+05	524.96	1.96	4.72E+05	2.44
Freshwater consumption (kg)	6.97E+07	1.51E+04	169.84	6.97E+07	145.93

Table 12. Environmental impacts of distiller LC.

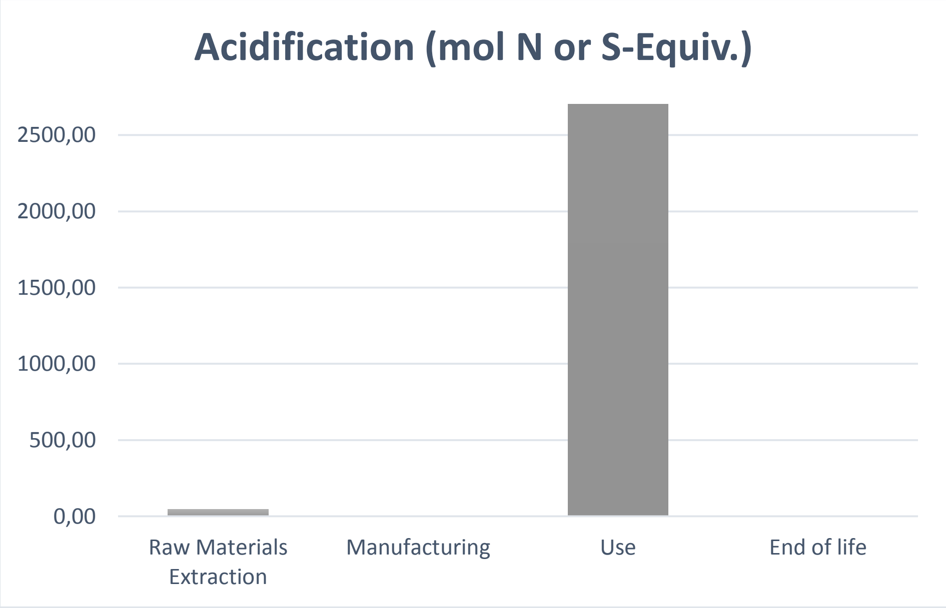


Fig. 37 Acidification of distiller LC.

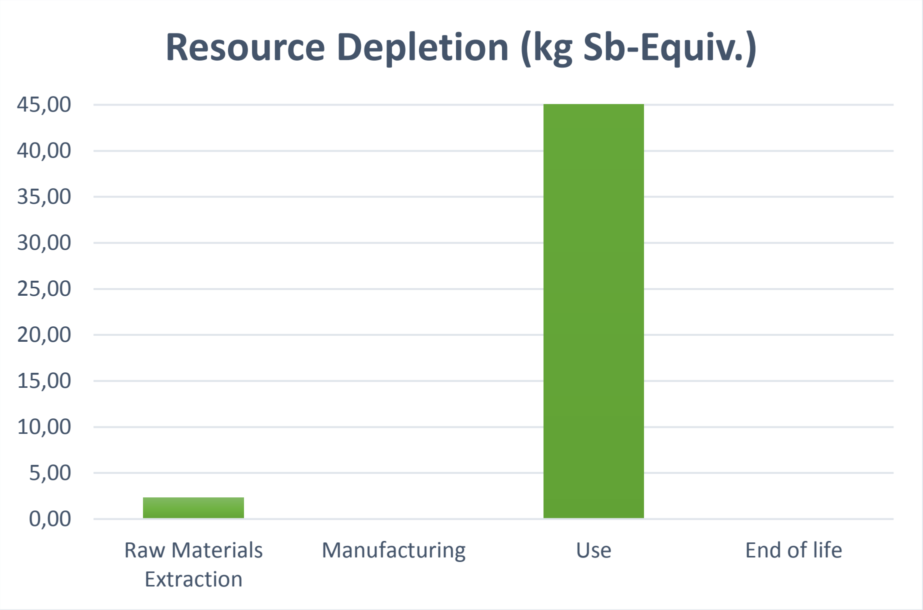


Fig. 38. Resource Depletion of distiller LC.

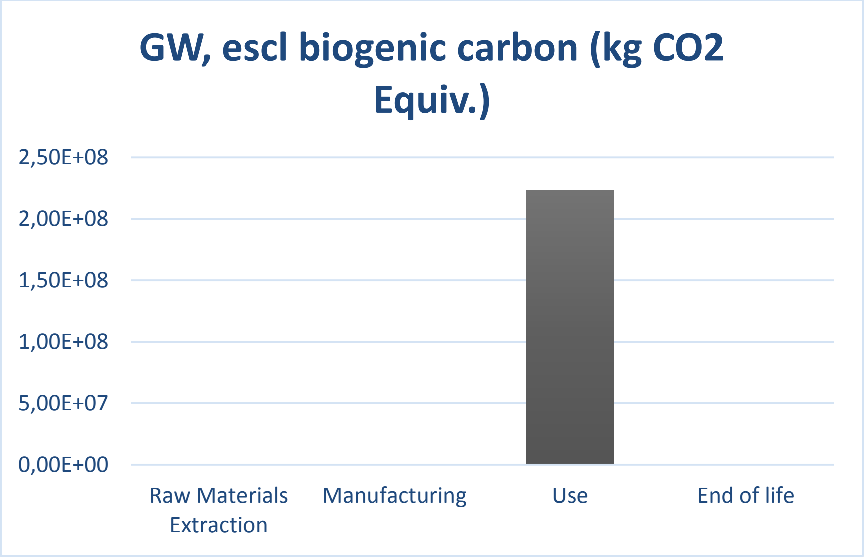


Fig. 39 GW, escl biogenic carbon of distiller LC.

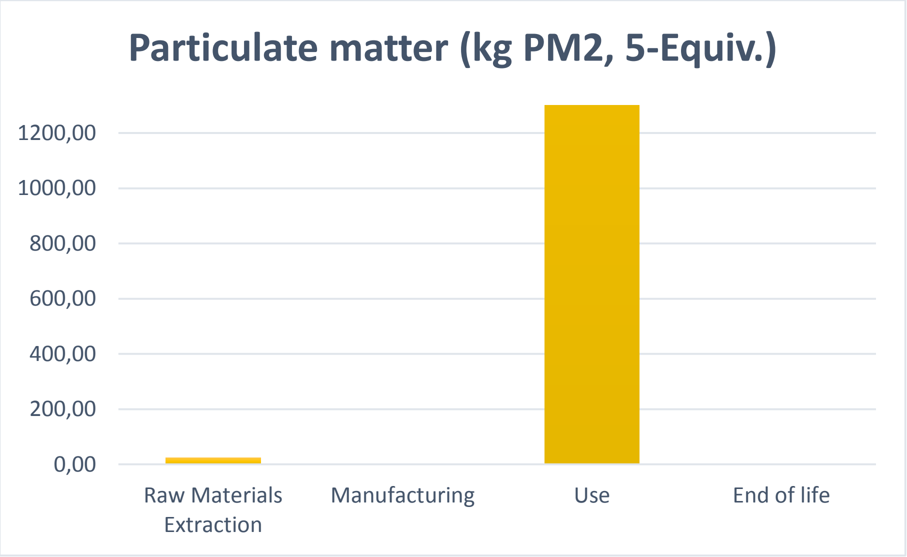


Fig. 40. Particulate matter of distiller LC.

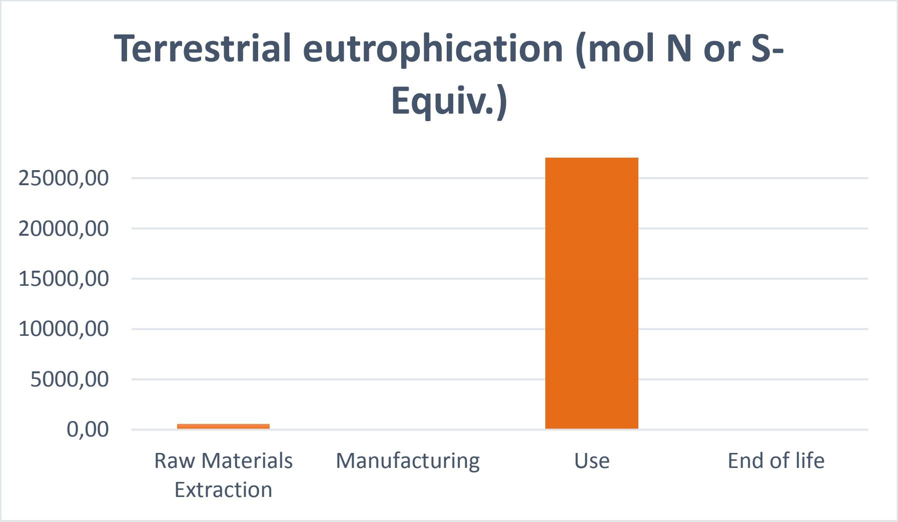


Fig. 42. Terrestrial eutrophication of distiller LC.

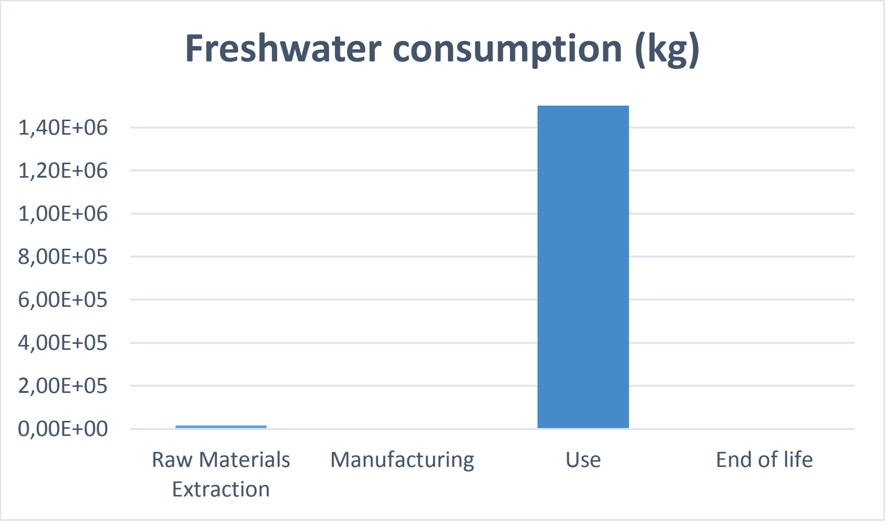


Fig. 43. Freshwater consumption of distiller LC.

Flows (Flux 5)	Membrane Synthesis	Preparation of Quartz Woll Support	Detemplation and exfoliation	Secondary growth and caltincation	Vessel Fabrication	Membrane Use
Acidification (mol N or S-Equiv.)	2496.89	2239.99	254.85	2.05	4.35	0.61
Resource Depletion (kg Sb-Equiv.)	46.91	43.64	3.13	0.14	0.22	4,94E-03
GW, excl biogenic carbon (kg CO2 Equiv.)	3.12E+06	3.06E+06	5.91E+04	2200.55	3207.48	248.09
Particulate matter (kg PM2, 5-Equiv.)	468.09	416.95	47.85	3.29	2.30	2.14
Terrestrial eutrophication (mol N or S-Equiv.)	2.85E+04	2.48E+04	3.69E+03	23.56	50.19	6.10
Freshwater consumption (kg)	1.40E+06	1.37E+06	2.49E+04	1.20E+03	1456.95	481.35

Table 13. Environmental impacts of membrane flux 5 LC.

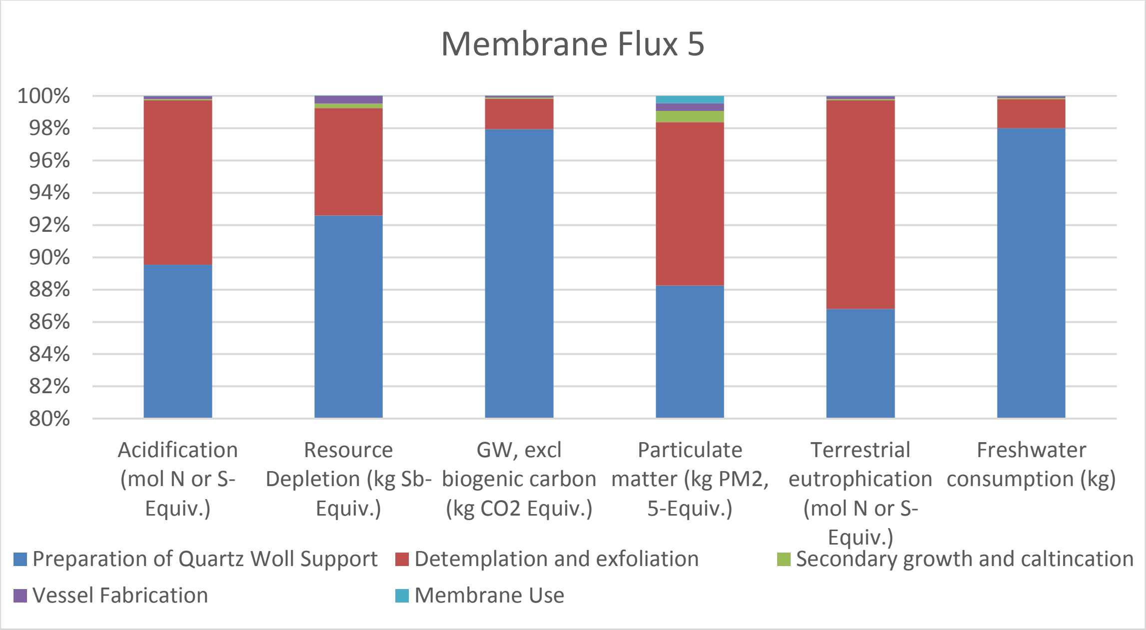
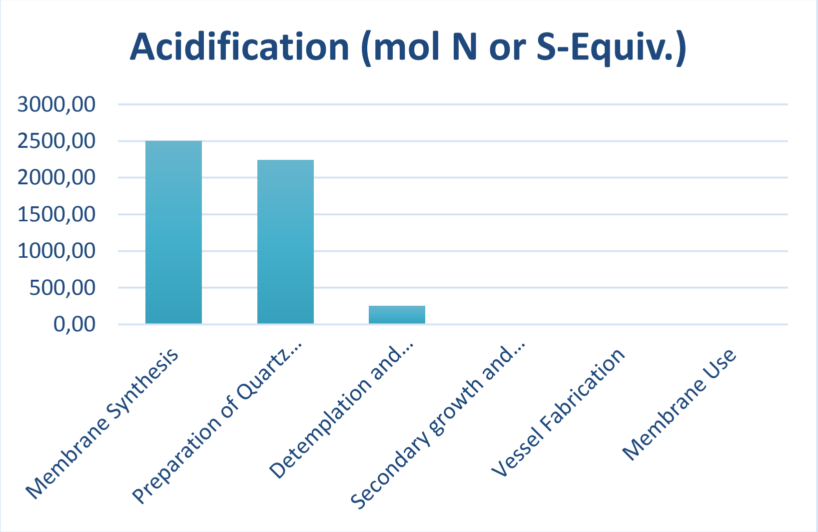


Fig. 44. Environmental impacts of membrane flux 5 LC.



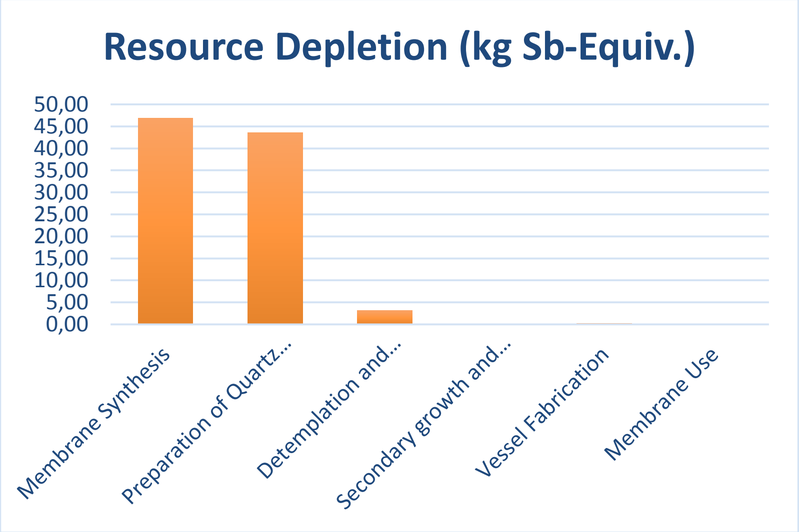
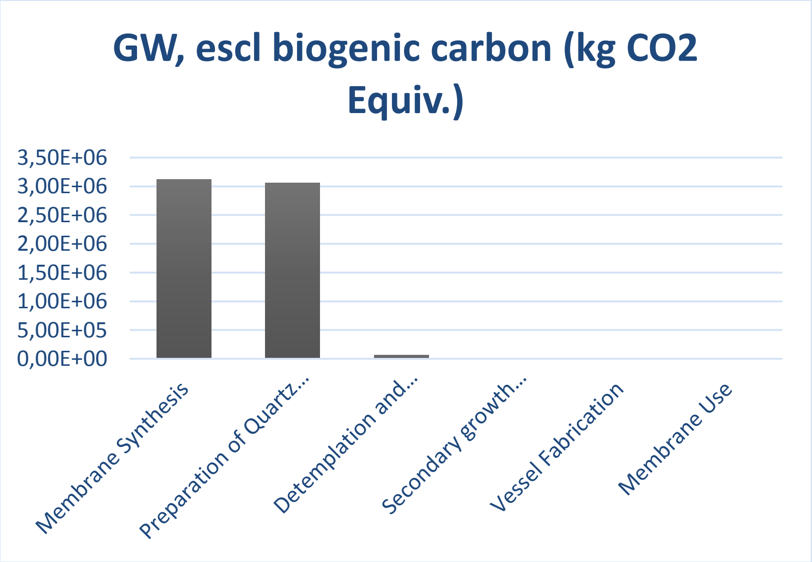


Fig. 45. Acidification of membrane flux 5 LC.

Fig. 46. Resource depletion of membrane flus 5 LC.



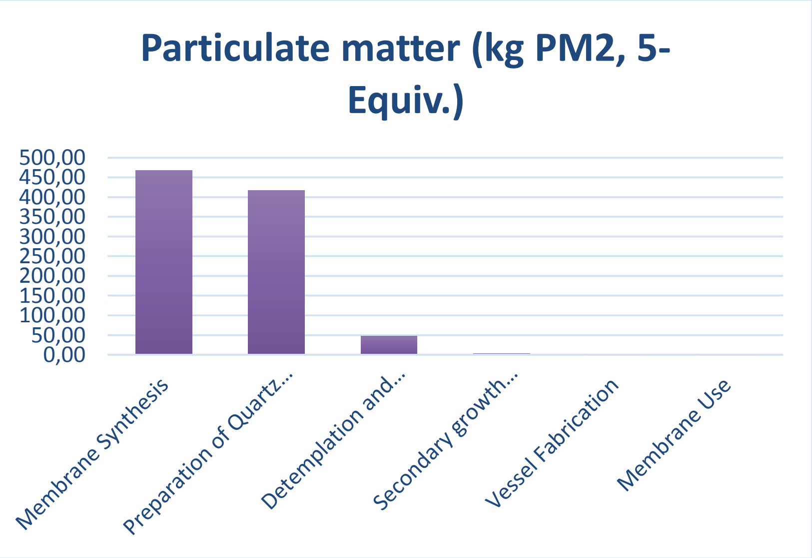


Fig. 47. GW, escl biogenic carbon of membrane flux 5 LC.

Fig. 58. Particulate matter of membrane flux 5 LC.

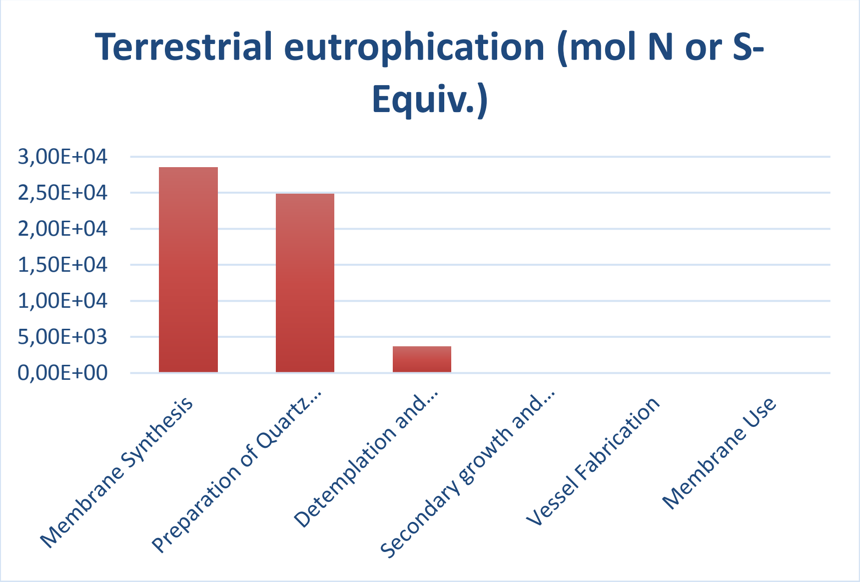


Fig. 49. Terrestrial eutrophication of membrane flux 5 LC.

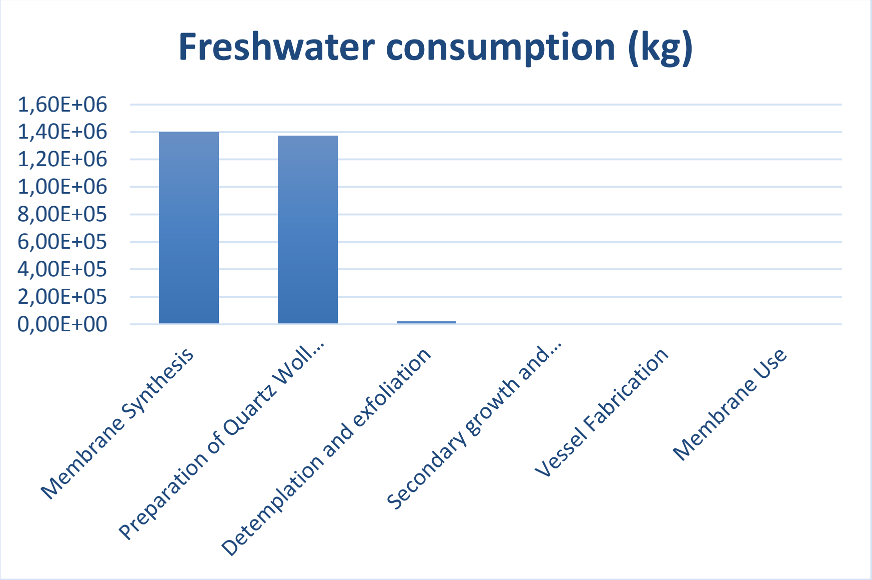


Fig. 50. Freshwater consumption of membrane flux 5 LC.

Flows (Flux 10)	Membrane Synthesis	Preparation of Quartz Woll Support	Detemplation and exfoliation	Secondary growth and caltincation	Vessel Fabrication	Membrane Use
Acidification (mol N or S-Equiv.)	1249.54	1120.06	127.42	2.05	1.74	0.30
Resource Depletion (kg Sb-Equiv.)	23.52	21.82	1.57	0.14	0.09	2,45E-03
GW, excl biogenic carbon (kg CO2 Equiv.)	1.56E+06	1.53E+06	2.95E+04	2200.55	1285.04	122.63
Particulate matter (kg PM2, 5-Equiv.)	235.70	208.49	23.93	3.29	0.92	1.06
Terrestrial eutrophication (mol N or S-Equiv.)	1.43E+04	1.24E+04	1846.00	23.56	20.11	3.03
Freshwater consumption (kg)	7.01E+05	6.87E+05	1.24E+04	1196.71	583.71	239.29

Table 14. Environmental impacts of membrane flux 10 LC.

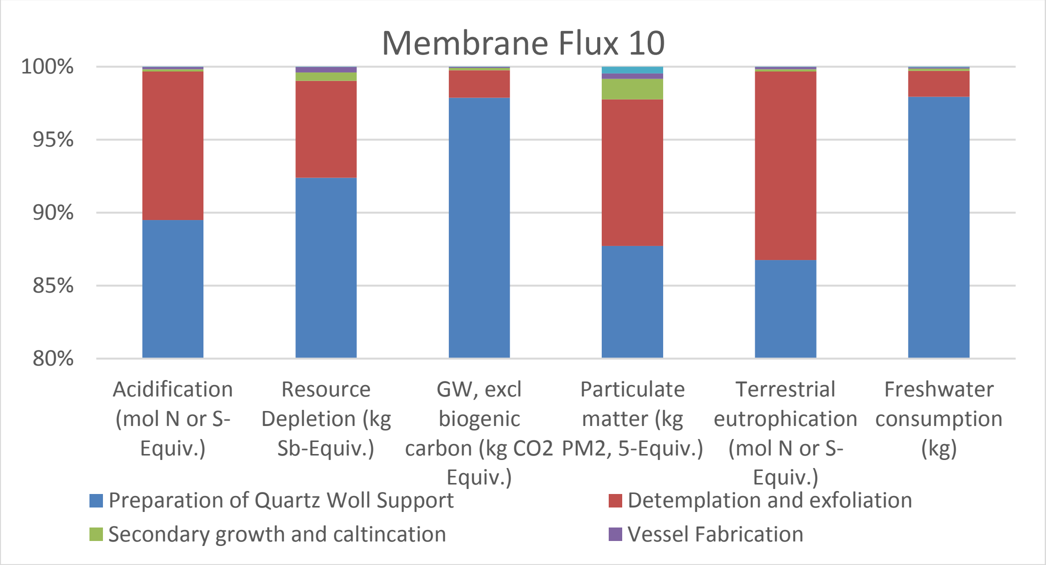
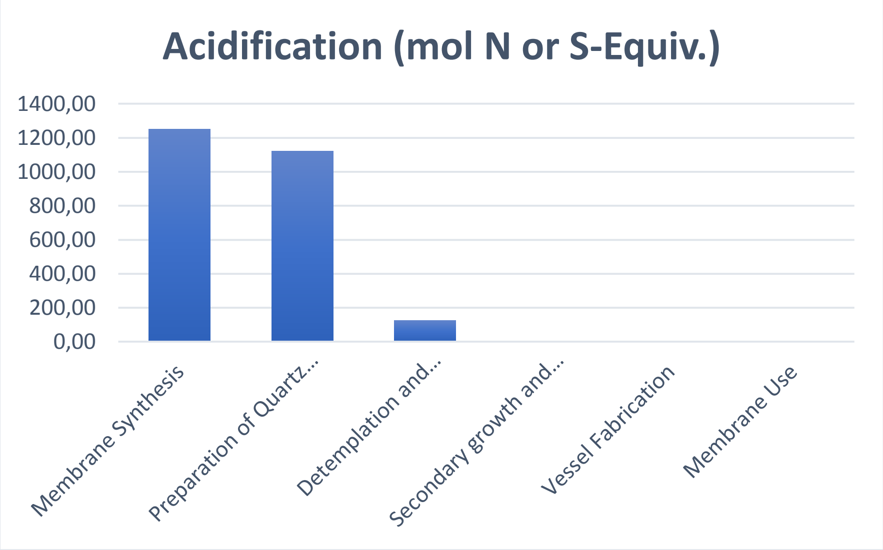


Fig. 51. Environmental impacts of membrane flux 10 LC.



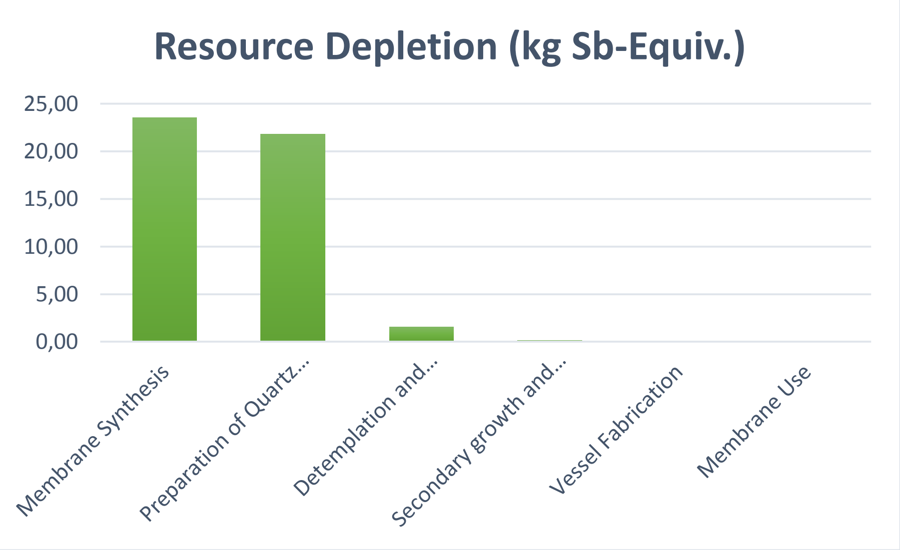
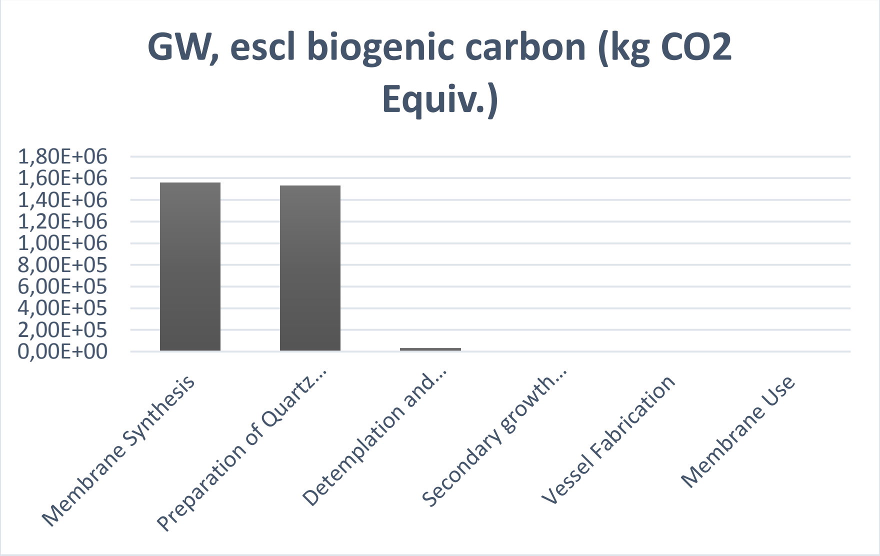


Fig. 52. Acidification of membrane flux 10 LC.

Fig. 53. Resource depletion of membrane flux 10 LC.



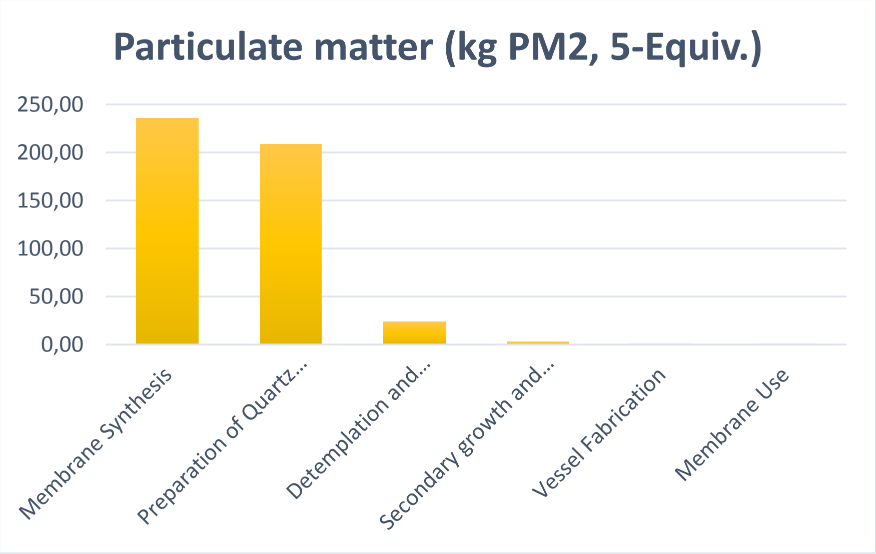
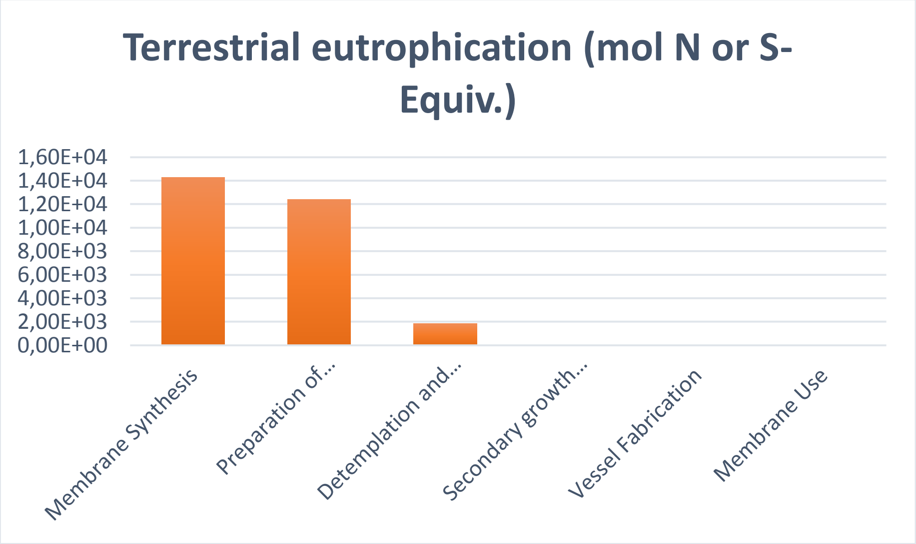


Fig. 54. GW, escl biogenic carbon of membrane flux 10 LC.

Fig. 55. Particulate matter of membrane flux 10 LC.



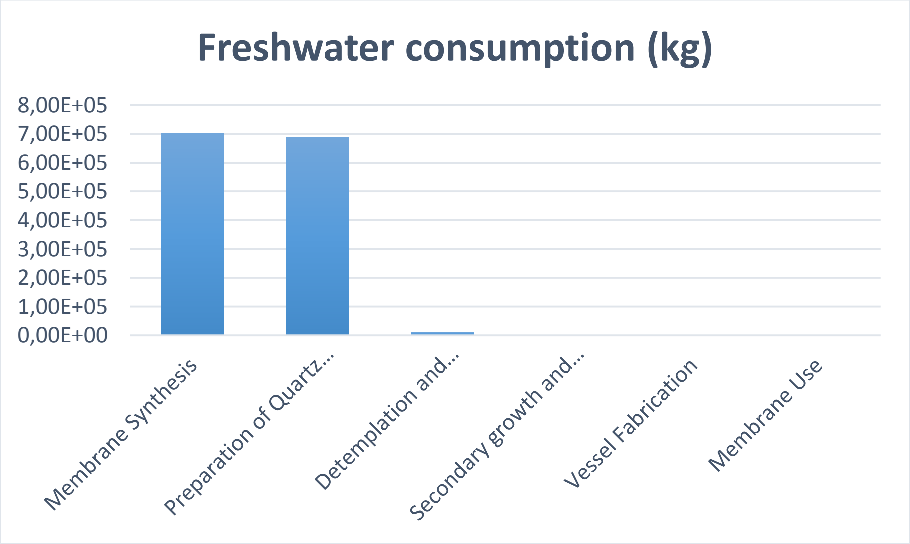


Fig. 56. Terrestrial eutrophication of membrane flux 10 LC.

Fig. 57. Freshwater consumption of membrane flux 10 LC.

All devices	Distiller	Flows (Flux 2.5)	Flows (Flux 5)	Flows (Flux 10)
Acidification (mol N or S-Equiv.)	5.73E+04	5.00E+03	2496.89	1249.54
Resource Depletion (kg Sb-Equiv.)	287.51	92.70	46.91	23.52
GW, excl biogenic carbon (kg CO2 Equiv.)	2.23E+08	6.22E+06	3.12E+06	1.56E+06
Particulate matter (kg PM2, 5-Equiv.)	9.26E+03	937.64	468.09	235.70
Terrestrial eutrophication (mol N or S-Equiv.)	4.72E+05	5.72E+04	2.85E+04	1.43E+04
Freshwater consumption (kg)	6.97E+07	2.79E+06	1.40E+06	7.01E+05

Table 15. Environmental impacts of all devices LC.

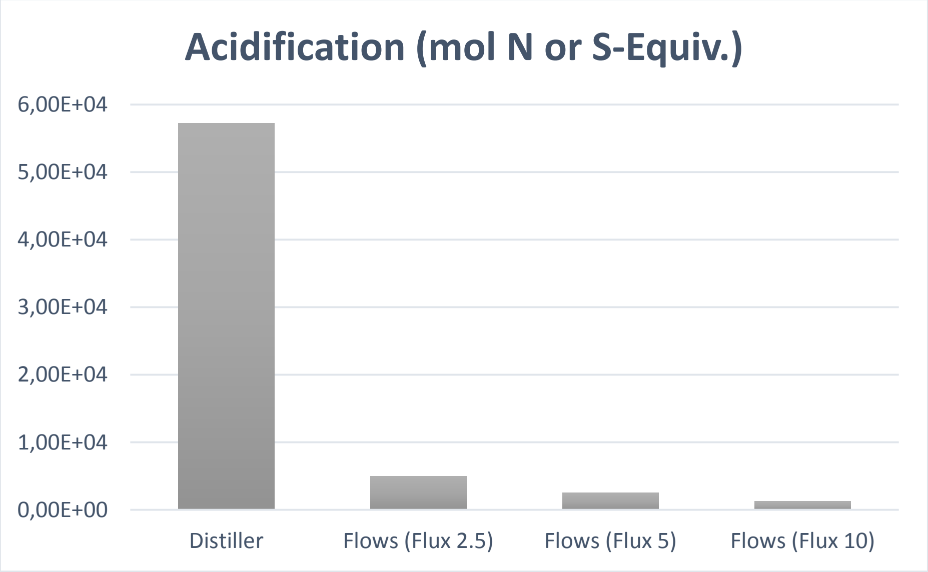


Fig. 56. Acidification of all devices LC.

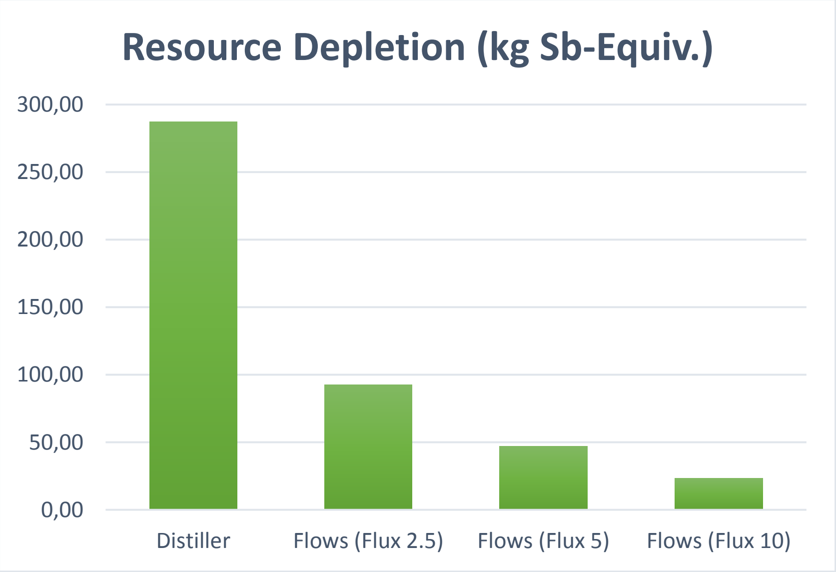


Fig. 57. Resource depletion of all devices LC.

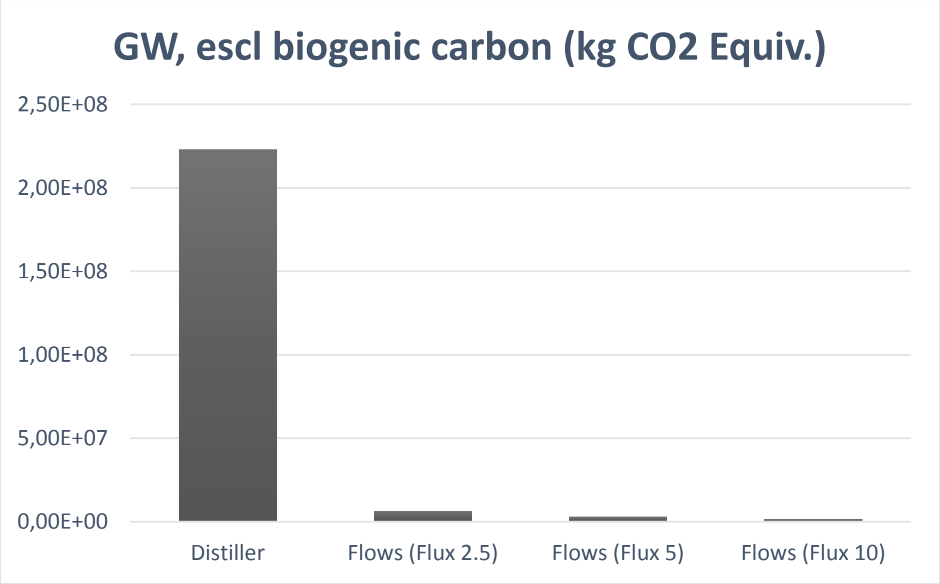


Fig. 58. GW, escl biogenis carbon of all devices LC.

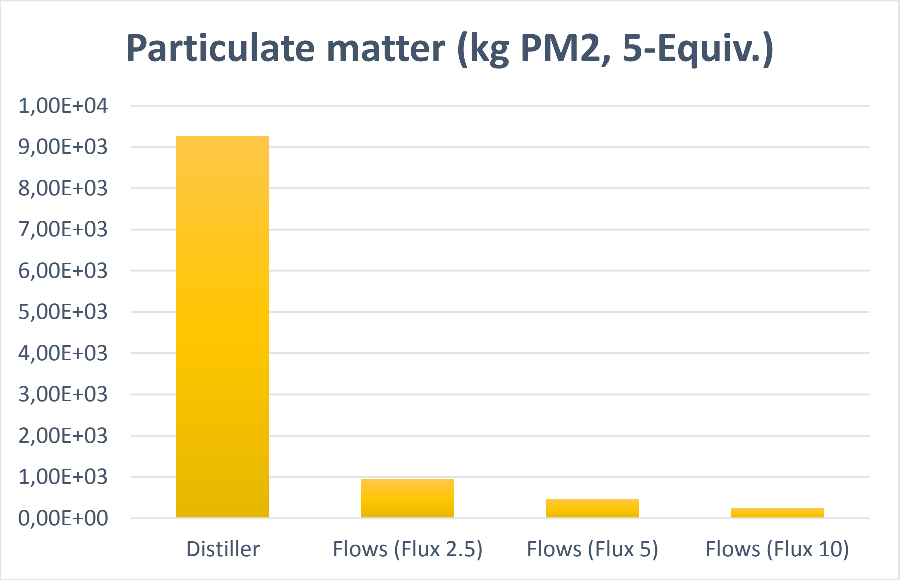


Fig. 59. Particulate matter of all devices LC.

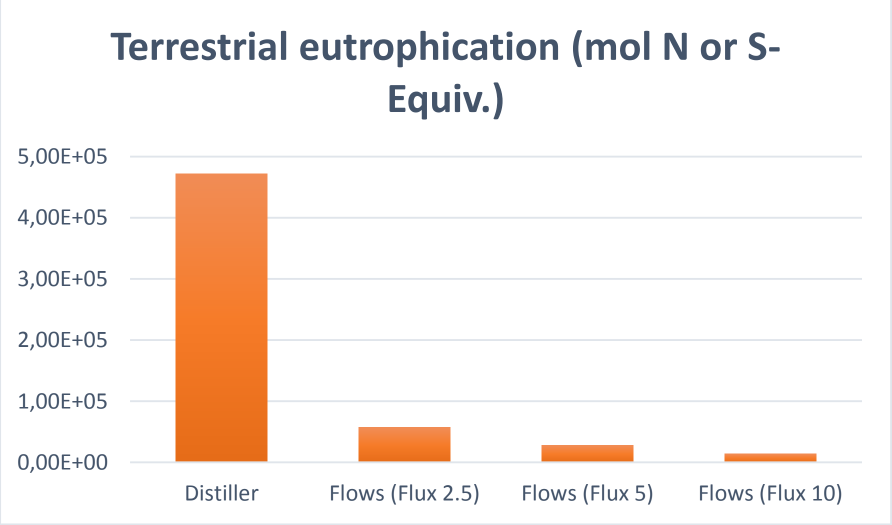


Fig. 60 Terrestrial eutrophication of all devices LC.

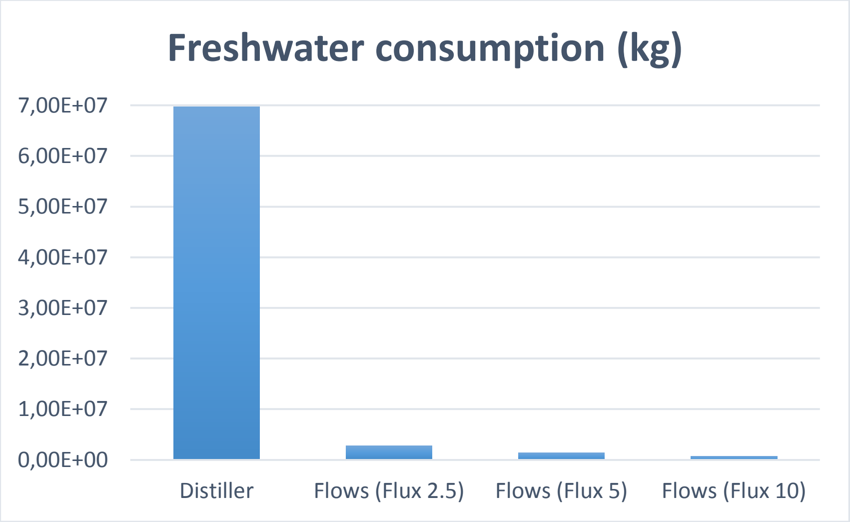


Fig. 61. Freshwater consumption of all devices LC.

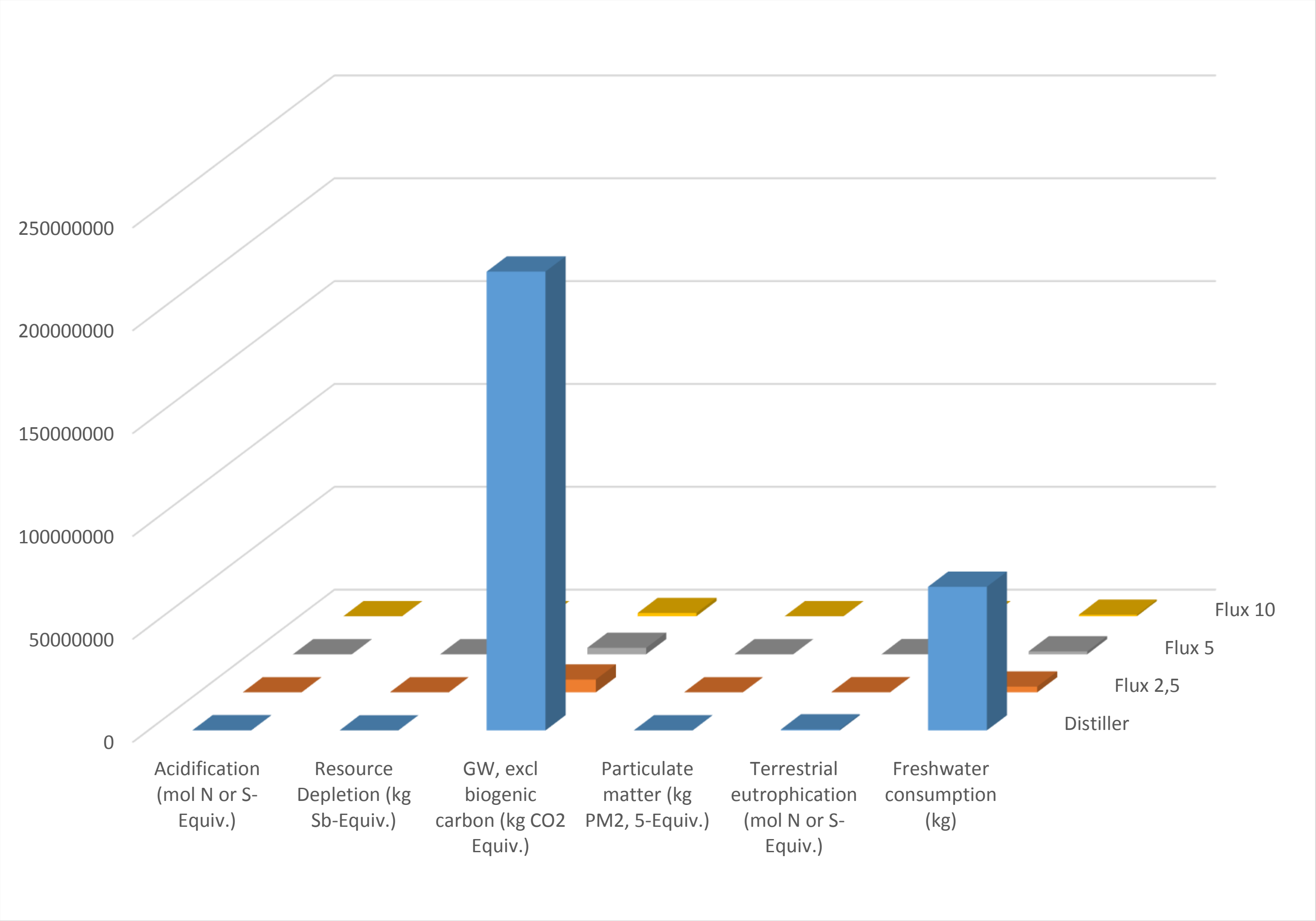


Fig. 62. Environmental impacts of all devices.