Water – energy nexus in biofuels production and renewable based power

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Abstract

In this paper, the water–energy nexus for renewable based processes is evaluated. Process synthesis and integration techniques are used to synthesize the processes and integrate the energy and water, optimizing the consumption of both natural resources. In the analysis of water consumption, it was found that cooling needs and water using technologies are major drivers. Currently, contaminated water is fairly well treated for further use. Therefore, the more the energy is integrated, the lower the cooling needs are reducing the water consumed accordingly. In terms of efficient processes in water–energy consumption, the best one is the FT-fuels, with other options being second generation bioethanol via gasification and catalytic synthesis, biodiesel production from cooking oil and the integrated process that produces biodiesel and glycerol ethers, as long as the rainfall water is not included in the analysis. Otherwise, solar based fuels are more efficient.

Keywords: Energy, Alternative fuels, Water, Water-Energy nexus.

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1. Introduction

Water and energy are two interrelated natural resources (Azapagic and Perdan, 2014). Typically, not much attention has been paid to the consumption of water due to its low price and relative availability. However, generally the production of energy, requires a considerable amount of water. For instance, the production of power in thermal plants requires around 1.8 L/kWh (Torcellini et al., 2003). In this particular case the water consumed is mostly the one lost by evaporation in the cooling tower. In the production of petrol or diesel, there is a certain amount of water injected to extract the crude, around 2.5 L/L (Wu et al., 2009). These two examples show that, although there is a strong link between both resources, each product and process determine the actual value, and most importantly, where it is possible to implement further water and energy saving technologies. The renewable sources of energy, i.e. solar, wind, biomass, to mention the three most important ones, can be processed in a number of ways to obtain power and fuels. Furthermore, the production of biomass itself requires special consideration. If the biomass is not native to a certain region and there is no enough natural irrigation, there is a large amount of water needed to grow the biomass (Wu et al., 2009). Although this point is controversial, sugar cane in Brazil grows with no artificial irrigation, whereas in many cases there is need for a supply of water to produce the biomass, the raw material of the biofuels.

While on the one hand, energy production (or fuels) requires energy, on the other hand, energy is required to treat and transport water. The water used in any process comes out with increased levels of chemicals, particles, etc. This water needs to be reintegrated in the system, and for that the levels of contaminants must be reduced to levels established by environmental regulations.

In this work, we analyze different primary renewable sources of energy such as biomass, solar and wind and a number of processes that transform them into power and a number of common fuels, not restricted to bioethanol and biodiesel, discussing the sinks and sources of water and energy for each case, and how process design and integration help to reduce energy and water consumption. We present results on the operation of such processes and the efficiency in water used per MJ energy produced.

2. Methodology

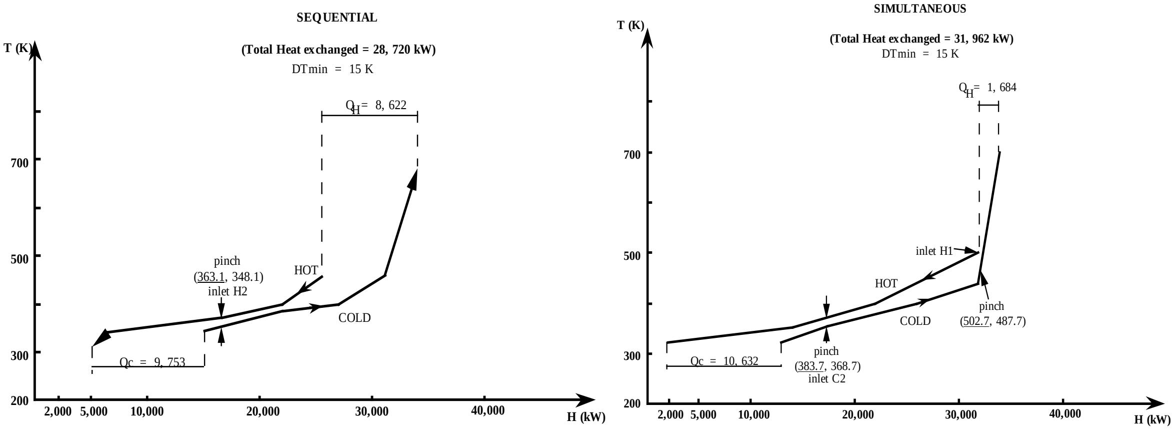
The optimization of water and energy is a well studied area within the process engineering community. The seminal papers on energy integration for process design deal with the development of pinch technology (Linhoff and Hindmarsh, 1983), the use of mathematical optimization techniques for the simultaneous optimization and heat integration (Duran & Grossmann, 1986), or the design of heat exchanger networks (Yee & Grossmann, 1990). With regards to water consumption, major works include Takama et al paper in 1980 formulating the first water network, to the heuristics presented by Wang & Smith (1994) developing the water pinch, and the novel formulations and solution procedures for the water network as in Galán & Grossmann (1998), Karuppiah and Grossmann (2006), Ahmetovic and Grossmann (2011). Traditionally, previous studies have considered each resource, water and energy, independently. One reason for this is that the problems by themselves are quite difficult. Water networks (WN) and heat exchanger networks (HEN) lead to non-convex mixed-integer nonlinear programming problems for which global optimal solutions are hard to obtain. Furthermore, large mixed-integer nonlinear programming models arise when a number of alternative technologies is considered for the processing of a certain raw material into a desired product (i.e. Martín & Grossmann 2011).

Except for few integrated approaches or targeting methods (Yang and Grossmann, 2013), the optimal design of renewable based fuels and power production is carried out using a sequential approach for optimizing first the topology and energy, and in a second step, optimizing the water consumption (Grossmann and Martín, 2010). In the first stage the process is designed, including simultaneous optimization and heat integration in those cases where models for the reactor conversions are available. Once the topology of the process is fixed and the optimal operating conditions are determined, models such as the one by Yee and Grossmann (1990) are used to develop a heat exchanger network, minimizing simultaneously the utilities and the investment cost. Finally, water is integrated by designing a water network by using the model developed by Ahmetovic and Grossmann (2011). We need to bear in mind that process decisions and flowsheet topology could incorporate water optimization within the first stage. In the next subsections we describe such an approach.

2.1.-Process synthesis and energy optimization

A superstructure optimization approach is a powerful tool to evaluate a large number of alternatives in a systematic way. First, each of the units must be modeled. There is a trade-off between accuracy and simplicity. For optimization purposes, the large problem size when the complete superstructure is formulated suggests the use of simple models based on mass and energy balances, rules of thumb, thermodynamic principles (kinetics and species equilibrium) and experimental results and trends (Martín & Grossmann, 2012).

Once the units are modeled, the superstructure optimization model is put together. Furthermore, we can incorporate Duran & Grossmann's (1986) formulation for simultaneous optimization and heat integration. The formulation is based on a search of the pinch point among candidates from each of the streams involved in the process. Compared to the sequential approach, the overall conversion can increase as well as the profit if simultaneous integration is considered in together with the design. In terms of heat integration, Figure 1 shows the comparison between the composite curves in using a sequential approach (a), and the simultaneous approach (b) by the formulation. As can be seen, a significant reduction in the energy required to for the process is achieved.



a) Sequential approach b) Simultaneous approach

Figure 1.- Compasiron of the use of simultaneous optimization and heat integration

At this point, the optimal topology and operating conditions result from solving a large MINLP. The second step is to use the Yee and Grossmann (1990) model for the streams computed in the process flowsheet optimization to design the heat exchanger network and minimize the utilities. Figure 2 shows a two stage superstructure for the synthesis of a heat exchanger network (HEN) for two hot streams and two cold streams.

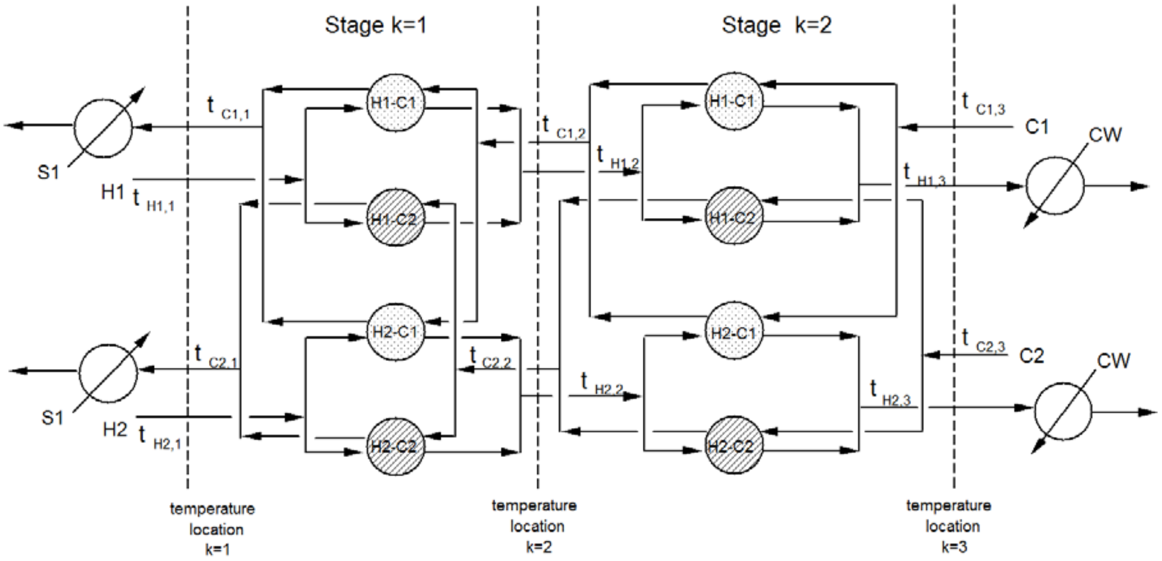


Figure 2.- Superstructure for heat exchanger network.

2.2. Water network superstructure and model

Once the superstructure has been optimized simultaneously with heat integration and the HEN obtained, the next step is to synthesize the water network to minimize the freshwater consumption. For this purpose, a superstructure is postulated that consists of one or multiple sources of water of different quality, water-using processes, and wastewater treatment operations. All possible interconnections are considered and incorporate process units, treatment unites as well as sources and sinks of water. Figure 3 presents a scheme of the superstructure. The model for the superstructure is a nonconvex nonlinear programming (NLP) which can be solved to global optimality (Ahmetovic and Grossmann, 2011). The objective function is to minimize the total network cost consisting of the cost of freshwater, the investment cost on treatment units and the operating cost for the treatment units subject to splitter mass balances, mixer mass balances (bilinear), process units mass balances and treatment unit mass balances.

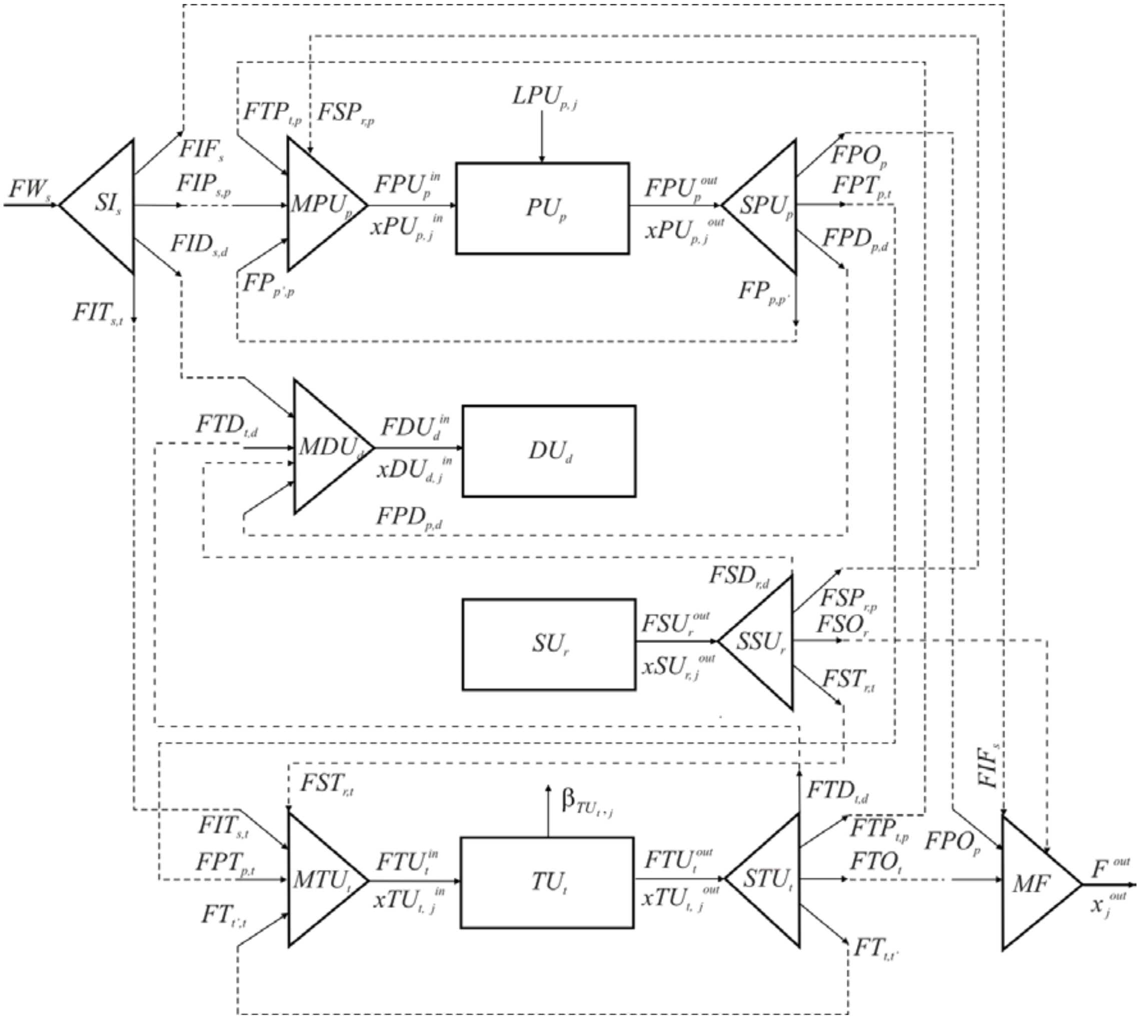


Figure 3. Generalized superstructure for the design of integrated water networks. Ahmetović and Grossmann [68]
PU: Process Unit; DU: Demand Unit; SU: Source Unit; TU: Treatment Unit.

To synthesize the optimal water network for a production facility, the interconnections of the process and treatment units, and their corresponding flowrates must be identified. Three main contaminants are considered: total suspended solids (TSS), total dissolved solids (TDS) and organics (BOD and COD) which are known to be the most important ones. Below we describe the main units involved in the WN.

2.2.1.- Treatment Units.

-Solids removal: Suspended solids such as straw or sand are typically removed using screens.

-Organics removal: Biochemical processes involve large amounts of water, that once the main product is recovered, it still contains a number of organic species. For instance, the water from the distillation columns requires a system of anaerobic and aerobic treatment to remove the traces of glycerol, organic acids and ethanol that has not been recovered.

-Total dissolved solids removal: One of the most important contaminants in the operation of boilers and cooling towers are the total dissolved solids (TDS) since they do not allow the complete recirculation on the blowdowns due to the build-up of salts. In order to partially remove the total dissolved solids, a reverse osmosis is commonly used. The literature reports removal ratios of 90% at the most, better than ion exchange or nanofiltration.

2.2.2.-Utility units: Demand and sinks.

-Cooling tower: The use of the cooling tower depends on the actual process, either cooling down the water used as cooling agent or to condense the extraction of the lower pressure turbine in power plants. The flowrate treated by the tower and the cooling needed, ΔT, determine the losses by evaporation (Perry and Green, 1997). The amount of water lost by drift, which is the liquid water in the tower discharge vapors, typically, varies between 0.1 and 0.2 percent of the water supplied to the tower. Therefore, the makeup requirements for the cooling tower consist of the evaporation loss, drift loss, and blowdown. The cycles of concentration (COC) are the ratio of the concentration of salts or dissolved solids in the circulating water/blowdown to that in the makeup water. In industrial practice, the cycles of concentration normally range from three to seven. We need to maintain the concentration of pollutants within some limits that are reported in the literature, which determines the actual fresh water fed. The total suspended solids (TSS) in the outlet stream of the cooling tower is typically 50 ppm, while the TDS are 2500ppm (APHA , 1989) The regulations require that the concentration of TDS in the effluent not to exceed 500 ppm (Patoczka, 2007).

-Boiler: The steam generated in the boiler is used to supply heat in the heat exchanger network, while the steam condensate is returned to the boiler. In the case that there is no steam consumption in the process or loss in the heat exchanger network, the flowrate of the generated steam in the boiler and returned steam condensate is the same. In addition, makeup requirements for the boiler system will be equal to the discharged blowdown. The American Boiler Manufacturers Association specifies that the concentration of TSS in the blowdown water from boilers is typically 10ppm, while the TDS will be 500ppm (ABMA, 2015)

3.-Processes

In this section we describe several process technologies for the production of promising biofuels and power using renewable sources of energy. We divide the section into bioethanol, FT-liquids, biodiesel, integrated processes based on algae and solar and wind based processes.

3.1.-Bioethanol

-**Bioethanol from corn**: The first section of the process involves the pretreatment of the corn grain to break its physical and chemical structure. In this stage water in the form of steam is added to the process. The process units are grinding, direct contact with steam, saccharification and liquefaction. Next, the sugars are exposed for fermentation. The second section is the fermentation of the sugars, mainly glucose, into ethanol. Water and starch are fed to the reactor. The amount of water required is such that the concentration of ethanol at the end of the fermentation is below the toxic levels for the yeast, 15% of ethanol in water. CO_2 is also generated in the fermentation. One of the challenges when it comes to energy integration is the low operating temperature of the fermentors, 32-38ºC. Although the reaction is exothermic, that energy cannot be further used, requiring cooling water. After fermentation, a beer column followed by the use on rectification, adsoprtion in corn grits and molecular sieves are used in parallel. Ethanol dehydration is an energy intense step. Furthermore, together with steam, cooling is also required. Multieffect columns are a useful technology to reduce energy and cooling needs. The complete flow is treated at the molecular sieves to reach fuel grade ethanol. Both distillation columns discharge water with organics. After proper treatment, water can be reused within the process, reducing the freshwater needed (Karuppiah et al 2008), see Figure 4. In Table 1 we summarize the main operating parameters of this process.

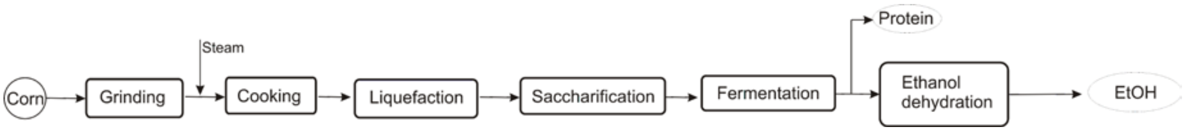


Figure 4.- Block diagram for the corn based ethanol

-Bioethanol from switchgrass via hydrolysis: The switchgrass is pretreated to expose the sugar polymers using dilute acid pretreatment. This treatment requires a certain amount of steam and operates at moderate temperature, 140-180ºC. However, part of the steam can be recovered in a flash after the breakage of the biomass and can be reused, reducing the water needs of the process. Next, the mixture is hydrolyzed to breakdown the polymers into sugar monomers which are fermented into ethanol. The inhibition of the production of ethanol due to its presence in the liquid phase results in the need for a large amount of water in the fermentor. Ethanol cannot exceed 8%. Finally, the ethanol is dewatered using a multieffect beer column followed by molecular sieves. The dilute mixture to be separated increases the energy consumption of the process, since we evaporate water with steam (Martín & Grossmann, 2012a). In terms of water consumption, it is assumed, based on literature results (Wu et al., 2009), that if the switchgrass grows in native regions there is no need for irrigation. See Figure 5 for a block diagram of the process. Table 1 reports the water and energy consumptions as well as economic information on the process.

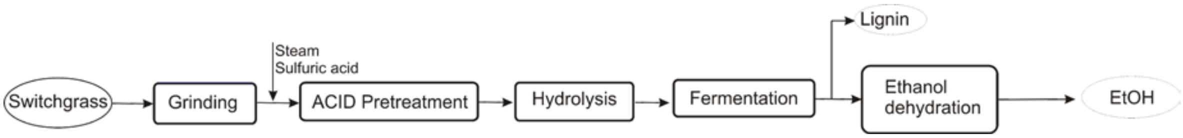


Figure 5.- Block diagram for biochemical based second generation bioethanol

-Bioethanol from switchgrass via Gasification: The switchgrass is pretreated to break the solids into fine particles that are gasified into raw syngas using direct gasification, which requires a large amount of steam and pure oxygen. Next, the gas is reformed with steam to eliminate hydrocarbons. Subsequently, the gas composition is adjusted by removing the excess of hydrogen using a membrane-PSA system. At this point, sour gases are removed using a PSA system to eliminate the majority of the CO_2 followed by the use of ethanolamines (MEA) to remove the last traces of it as well as the H_2S by absorption. In this way, energy is saved in the recovery of the ethanolamines since it is an expensive distillation that is required to be able to regenerate the MEA for further use. In Figure 6 we present a block diagram for gasification based processes to produce syngas.

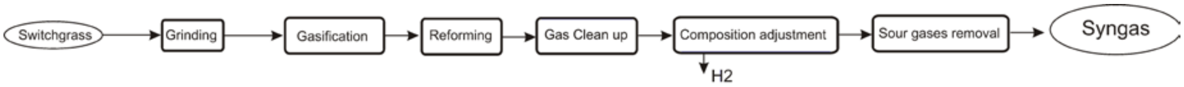


Figure 6.-Block diagram for the production of syngas from switchgrass

Finally, two synthetic paths are considered. a) Fermentation of syngas followed by dehydration of ethanol as for the hydrolysis path. In this case the energy consumption is high due to the need to dehydrate a very dilute water-ethanol mixture. Furthermore, the low operating temperature of the fermentor, 32-38 ºC, does not allow the reuse of the energy generated. b) Catalytic synthesis followed by a sequence of distillation columns. This second alternative provides another interesting feature from the energy integration point of view. The synthesis is FT-type, exothermic and occurs at 300ºC. Therefore, the energy released in the production of the ethanol can be reused within the process as seen in Martín & Grossmann (2011a),b. Figure 7 for the use of syngas to produce chemicals. See Table1 for the main operating data of the process.

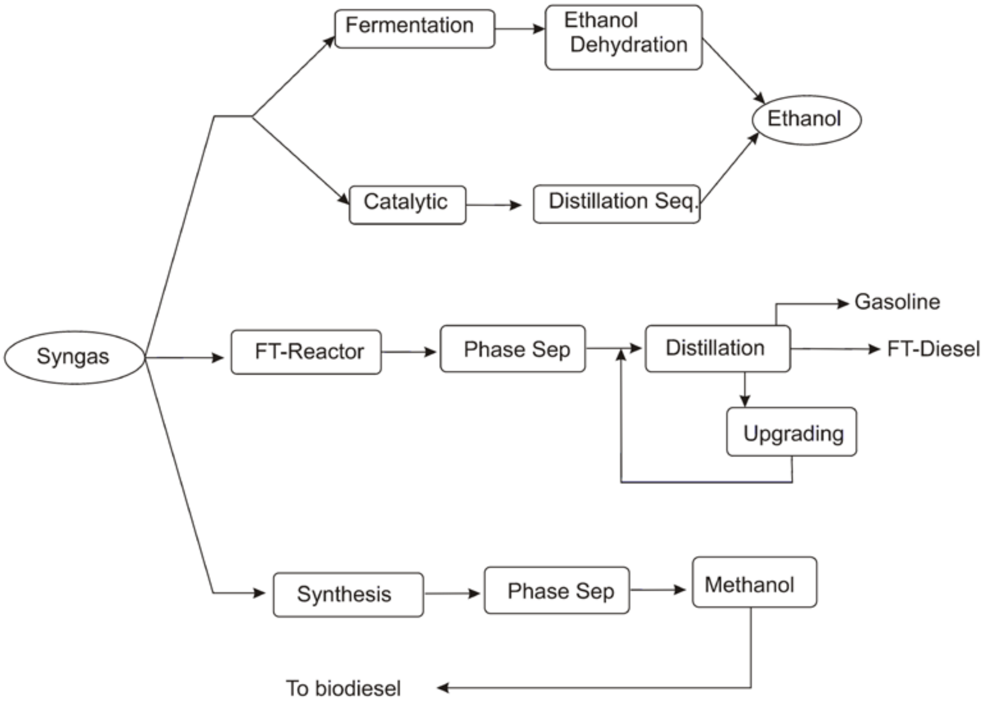


Figure 7.- Block diagram for the production of chemicals from Syngas.

3.2.-Synthetic fuels from switchgrass.

-FT-fuels from lignocellulosic switchgrass. Similar to the previous case until the syngas is obtained and purified, its composition and temperature is adjusted for the optimal production of FT-diesel. As in the catalytic synthesis of ethanol, the reactor is exothermic and operates at moderate temperature, which allows heat integration. Furthermore, a certain amount of water is produced in the reaction. Next, the gas and liquid products are separated and the liquid phase distilled. Liquid–liquid separation between the hydrocarbons and the water allows a source of water within the process. The bottoms are upgraded, hydrotreated, to increase the yield towards FT-gasoline and diesel (Martín & Grossmann, 2011c). See Figures 6 and 7 for the block diagram of the process. In Table 1 we report the energy and water consumption of the process as well as economic data.

3.3.-Biodiesel production

-Biodiesel from algae. The algae are grown in a pond. Water consumption depends on the source of the water used in the pond. While the use of freshwater was the first option, lately and with the aim of reducing water consumption, waste water has been evaluated with good results. Water is also lost by evaporation from the ponds. Again, the source of that water determines the impact of this loss on freshwater consumption. Next, the algae are harvested. Subsequently, the oil is extracted using an organic solvent and mechanical action The oil is next transesterified. Out of the five catalysts evaluated, alkali catalyst gave the best results. After the transesterification, the methanol is recovered by distillation, where most of the energy of the process is used. However, the lower operating temperature of the column to avoid glycerol decomposition, allows certain integration. Note, that in biodiesel production the reaction is in equilibrium. Apart from the catalyst load, the temperature and the excess of methanol are used to drive the equilibrium to products. Next, the biodiesel is separated from the glycerol using gravity separation. Subsequently, the removal of the catalyst is carried out using a washing step. The water used here must be treated to be reused. Finally, the glycerol and the biodiesel are purified by distillation. The high operating temperatures results in the need for high temperature sources of energy, and therefore reduces the possibility of energy integration (Martín & Grossmann, 2012b). Table 1 summarizes the energy and water consumption of the process.

-Biodiesel from cooking oil. Similar to the previous process, in this case we have to determine the effect of the impurities accompanying the oil on the reaction removing them if necessary. The optimization performed suggests the use of heterogeneous catalysts, since they are not so vulnerable to impurities in the feedstock, and simplifies the methanol recovery and biodiesel purification, reducing the investment cost of the plant and the energy consumption (Martín & Grossmann, 2012). The advantage is that no washing step is needed, reducing the water needed in the process. Table 1 presents the data with a clear advantage in water consumption compared to the process that uses algae.

<u>3.4.-Algae based biorefineries</u>

Note that the integrated processes have certain common characteristics to the individual ones that are integrated. For the sake of reducing the length of the paper, we do not describe again the individual features, but the advantages and disadvantages of the integration. Table 2 shows the main operating parameters. Each process is described in the table by the main products. Figure 8 shows a block diagram presenting the all the alternatives described in section 3.4.

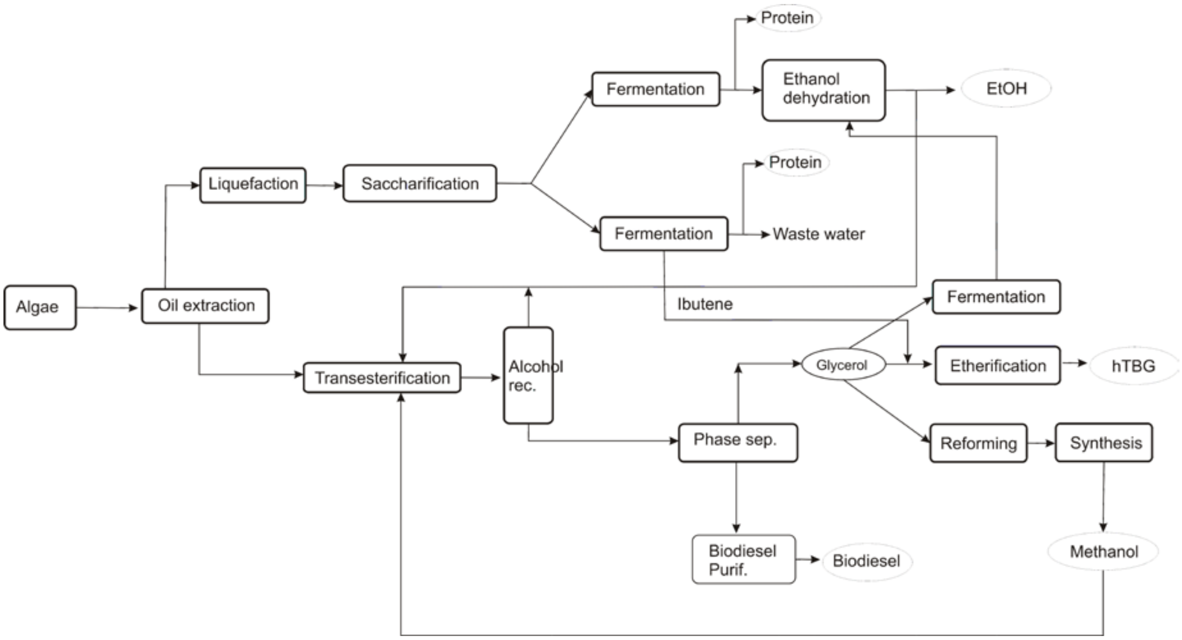


Figure 8.- Block diagram fro algae based biorefineries

-Integrated production of FAEE and ethanol. This process consists of integrating the algae based production of biodiesel with a first generation bioethanol technology to process the starch contained within the algae. Thus, algae are grown in ponds. Next, by using an organic solvent in an almost closed cycle and mechanical action, the oil is extracted and the starch is separated. The starch is broken down into glucose via liquefaction and saccharification. Subsequently the glucose is fermented into ethanol. Finally, the ethanol is dehydrated. In parallel, the oil is transesterified using the dehydrated ethanol. The use of homogeneous catalysts implies the need of a washing step. Heterogeneous catalysts, although typically require larger excess of alcohol to reach the same conversion, with the corresponding consumption of energy to recover it, simplifies the purification of the product. The ethanol is recovered, recycled and mixed with part of the ethanol produced from the starch. The glycerol is separated from the biodiesel and sold as byproduct (Martín & Grossmann, 2013a). See Table 2. Figure 8 shows the block diagram for algae based processes including all the alternatives evaluated.

-Use of glycerol to produce methanol. Although the use of methanol is widespread due to its lower cost and faster reaction times compared to other alcohols, its source is typically not sustainable. Methanol is mainly produced from coal or natural gas steam reforming consuming energy (steam reforming is endothermic) and water. However, the production of glycerol together with biodiesel, is potentially promising to reduce the need for fossil based methanol. Based on the facility that produces biodiesel from cooking oil, it is possible to consider glycerol reforming to produce syngas and with it methanol. Reforming can be endothermic, steam reforming, or adiabatic, autoreforming, which reduces the energy needs but consumes pure oxygen. Once the syngas is produced, it has to be cleaned from hydrocarbons, but mainly CO_2. A concentration of around 8% of CO_2 is needed for the catalysis to be efficient. We use PSA based on the studies in bioethanol production to reduce the energy needs of the process. The production of methanol is an equilibrium reaction controlled by the ratio H_2 to CO and the temperature. The reaction is exothermic and the moderate operating temperature allows heat integration. Furthermore, water can be generated, and then after treatment, reused within the process. By using glycerol as a source of methanol, the fossil based methanol is reduced by almost half (Martín & Grossmann, 2013b). See Table 2 and Figure 8 for the block diagram

-High ethers production. Starting with the same basic process as before, we can increase the production of diesel substitutives by glycerol etherification. The glycerol is etherified with ibutene for the production of hTGB, high glycerol ethers. Energy is consumed in the purification steps since, after a liquid-liquid separation, two distillation columns are used to recover the ibutene and the hTGB's, while recycling the monoethers and the glycerol. The low operating pressures at these columns reduce the operating temperatures allowing energy integration (Martín & Grossmann, 2014b). In Table 2 the main operating parameters are presented and in Figure 8 the block diagram is shown

-**Integrated production of FAEE and ethanol using glycerol to enhance ethanol production**. The basic process corresponds to the simultaneous production of biodiesel and bioethanol. The glycerol produced can also be fermented to ethanol, and thus increasing the production of ethanol. We consider the integrated process that produces biodiesel and ethanol from algae. The glycerol is then further processed to ethanol. The dehydration steps are already needed since we obtain ethanol from sugar fermentation. Therefore, although the energy consumption due to the dehydration of a larger stream increases, so does the yield from algae to biofuels (Martín & Grossmann, 2014a). The other advantage is the economies of scale due to the common section for ethanol dehydration. See Table 2 and Figure 8 for the block diagram

3.5-Wind and Solar based processes.

While wind and solar energy has been devoted to the production of power, the main challenge so far is the storage. The availability of solar and wind energy results in volatile power production with time. However, we can store that power as chemical energy by synthesizing chemicals. i.e. methane, using CO_2 as carbon source. In this section we describe the production of power from concentrated solar power facilities and the production of methane from wind and solar energy. See Table 3 for the summary of the results

-**Concentrated solar power facilities** (CSP). Concentrated solar power facilities consist of three sections: The heliostat field, including the tower collector and the molten salts storage tanks, a regenerative Rankine cycle, that includes the steam turbine, and the cooling system. A fraction of the flow of salts is used to superheat the steam before it is fed to the first stage of the turbine. The rest is used to reheat the steam before it is fed to the second stage. In the second stage of the turbine, a fraction of the steam is extracted at medium pressure and it is used to heat up the condensate. Finally, the rest of the steam is expanded to an exhaust pressure, condensed and recycled. In order to condense the exhaust, wet or dry facilities can be used. The consumption of water is clearly dependent on the technology selected. The use of a cooling tower results in the losses of water mentioned above due to evaporation and drift (Martín & Martín, 2013). While the consumption of water in thermal plants is a concern, when solar thermal plants are considered, it all becomes more important since these facilities are typically located in regions where the solar incidence is high, and by default, the water availability is low. Therefore, the use of dry cooling (Martín, 2015 submitted) is an interesting option to reduce water consumption in energy production. We need to bear in mind that there is a small amount of water that it is typically used to clean the mirrors, but it is nothing compared to the losses by evaporation. See Figure 9 for a block diagram.

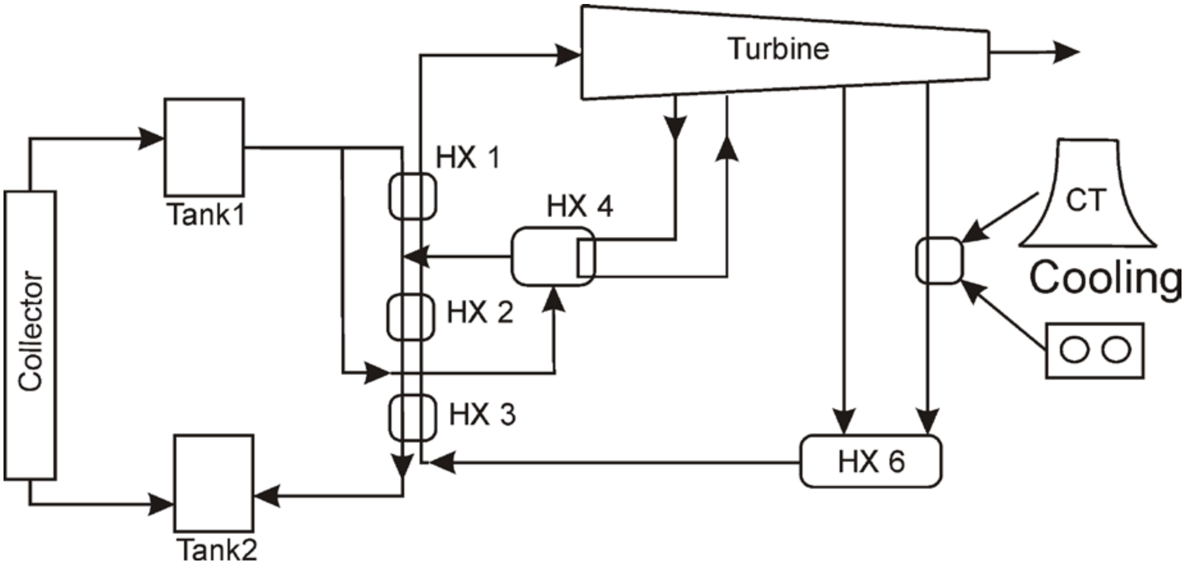


Figure 9.- Block diagram for CSP facilities.

Apart from the production of power, we can use that power to produce hydrogen through electrolysis and with it methane, a drop-in fuel.

-Methane production using CO_2 and hydrolytic H_2. Either a solar field (Davis & Martín, 2014b) or a wind farm (Davis & Martín, 2014a) can be used to provide the electricity needed for the electrolysis of water. In this process water is the raw material, and thus it is consumed as such. Out of its breakage, oxygen and hydrogen are produced. The oxygen is compressed and dehydrated. The hydrogen stream is purified to remove the traces of oxygen and next dehydrated. Subsequently, CO_2 is fed to the system generating methane and producing water that is recycled. The reactor is exothermic and operates over 350ºC, which provides integration opportunities. See Figure 10 for the block diagram.

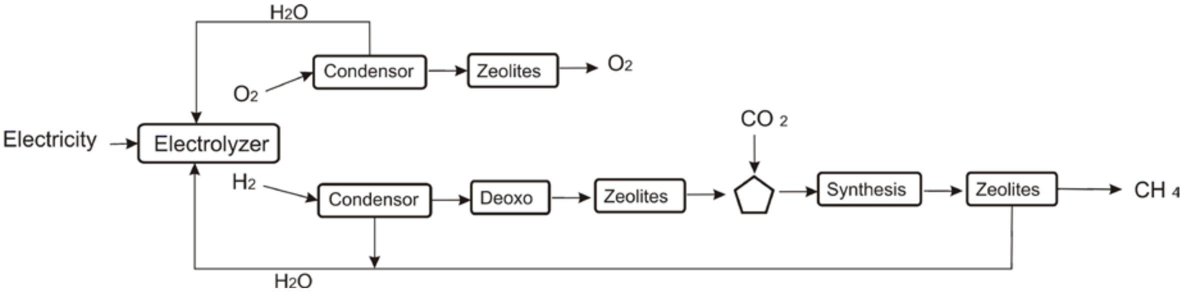


Figure 10.- Block diagram for synthetic methane production

3.6-Identification of process units

The identification of the process units, demand units and source units for the processes under consideration is presented in the list below. The flows and the level of contaminants of source units are given by the mass balances. It is assumed that washing only generates solid contaminants, while distillation columns and condensation mainly generate organic contaminants. Scrubbing, on the other hand, generates both organics (NH_3) and solids (Char and Olivine). For all the processes described in section 3 we consider:

Sources: Beer and rectification columns, Condensation processes.

Demand units: Gasifier, Electrolyzer, Fermentors, Dilution tanks, Boiler, Cooling tower.

Process Units: Pretreatment, Scrubbers, Boiler, Cooling tower

4.- Water energy nexus

4.1.-Water and energy consumption in renewable based processes.

Going back to the processes that has been described, recall that water is lost when the cooling water is processed through the cooling tower. The lower the flowrate of cooling water to be processed the lower the losses. Also, any reduction in cooling water flowrate, also reduces water consumption. Therefore, water can be saved by energy integration and/or air cooling as discussed above.

Energy integration allows reuse of the excess of energy in certain units of any process to be provided to those that demand energy. The integration of the energy leads to reduction in the amount of energy that we need to remove from the process using cooling utilities. Furthermore, the waste energy remaining is already at low temperature. An example of this direct link and the implication of water consumption were presented by Ahmetovic et al. (2010). The authors reported the improvement in energy consumption when mathematical optimization techniques were applied to the optimization of first generation corn-based ethanol. They first performed the superstructure optimization, followed by the synthesis of the HEN, and finally the substitution of the distillation columns by multieffect columns. Following this scheme, the energy consumption was reduced form 79 MW to 35.9 MW; i.e. almost half the energy consumption was reduced. In parallel to this, because of the reuse of the energy available within the process, the cooling needs of the process decreased from 59 MW to 21.5 MW, see Figure 11 for the relationship. As a result, the flow of water to be treated in the cooling tower decreased by two thirds, resulting in a decrease in the water consumption from around 4.1 gal/gal to 1.5 gal/gal. In Figure 12 shows the direct relationship between the energy consumed and the water consumed in the production process for bioethanol production from corn,

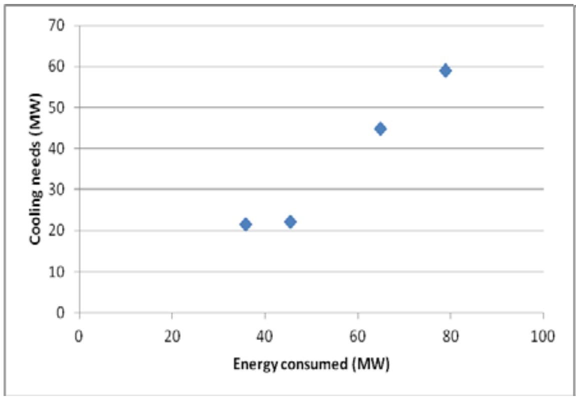


Figure 11.- Energy vs cooling needs in the corn ethanol process

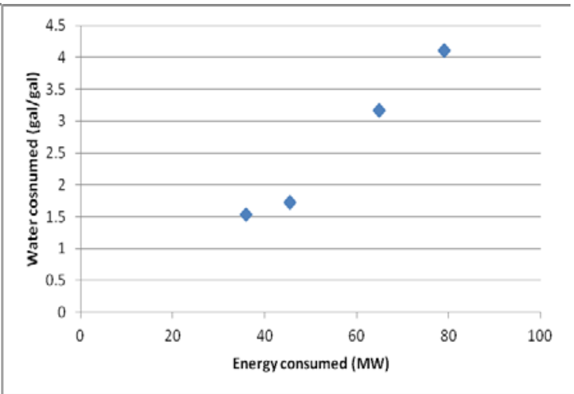


Figure 12.- Energy – water link in the corn ethanol process.

The second option corresponds to the use of air cooling. In this case Martín et al. (2010) for the second generation bioethanol production discussed the advantages of using air cooling to reduce the use of water as a cooling agent. Air cooling could be used for thermal based processes to a larger extent due to the higher operating temperatures across the flowsheet. In those cases, water savings of 10-50 % were obtained by replacing water by air. More significant were the savings in power production. Concentrated Solar Power technologies using cooling towers require 2.1 L/kWh for cooling (Martín & Martín, 2013). However, If dry technologies are used, instead of using cooling water, 5-10 % of the power produced was used by the fans of the air cooler for the condensation of the steam (Martín, 2015).

The similar analysis was conducted for all the processes presented in section 3, and Tables 1-4 summarize the operating data. Table 1 summarizes the information related to each of the individual processes, those which produce one main product such as ethanol, biodiesel. FT diesel, using different raw materials. We see that only second generation bioethanol or FT diesel report negative consumptions of energy. In terms of water consumption, good energy integration is possible in thermal based processes, since they operates at high pressures and temperatures, thereby reducing the water needs. Thus, ethanol production from gasification of switchgrass and FT-diesel production show reduced water consumption values. Only slightly above, is the water consumption for the production of biodiesel from cooking oil. It is important to note that the simultaneous optimization and heat integration used in the biodiesel process design, resulted in operating conditions at the reactors that were different than the ones reported in the literature. Actually the reason was that the reactor was optimized alone targeting the highest conversion, without taking into consideration the energy consumption to recover the excess of alcohol used to drive the equilibrium to products (Martín & Grossmann, 2012). Table 2 shows the comparison for the alkali and acid homogeneous catalyst. Note that for the integrated process KOH was used, to improve the removal of the catalysis by precipitation by forming K_2PO_4. This was not considered in previous work either.

Table 1.- Summary of the main features of the optimized processes

	Ethanol (Corn)	Ethanol (Hydrolysis)	Ethanol (Gasification & Catalysis)	Ethanol (Gasification & Fermentation)	FT-Diesel	Biodiesel (Cooking)	Biodiesel (Algae)
Investment ($MM)	90	169	335	260	216	17	110
Capacity(MMgal/yr)	60	60	60	60	60	72	69
Production cost ($/gal)	1.24	0.80	0.41	0.81	0.72	0.66	0.42
Water consumption(gal/gal)	1.5	1.66	0.36	1.59	0.15	0.33	0.60
Energy consump. (MJ/gal)	11.5	-10.2	-9.5	27.2	-62.0	1.94	1.94

Table 2.- Comparison of operating conditions at the reactor: simulation vs simultaneous optimization and heat integration

	Simulation		Optimization	
	Alkali [a,b]	Acid([a,b]	Alkali	Acid
(Algae / Cooking Oil)	H_2SO_4 */NaOH		H_2SO_4/KOH	
Temperature(ºC)	70*/60	80	45/45 (64.6)*	47.5/47.5
Pressure (bar)	4*/4	4	4/4(4)^{f}	4^{f}
Alcohol : oil ratio(mol/mol)	6:1*/6:1	50:1	6.6/6.6(1)*	20/20
Residence time(h)	1* / 4	4	2/2(2.45)*	48
Catalyst	1*/1(%w/w)	1.3:1 molar to oil	1.06/1.063(0.4)*	2/2

(Zhan et al 2003, West et al 2008) (*) Pretreatment (^{f}) fixed

Table 3 summarizes the information of the integrated processes where either glycerol is further used to produce methanol, ethanol or ethers or the raw material, algae, are used to simultaneously produce ethanol and biodiesel. We see that in most of the cases the water consumption remains within a small range. The main product is biodiesel, and therefore, all the processes share a large portion of the flowsheet. Only when oil is used as raw material for the production of FAEE and glycerol ethers, and not considering the water used for ethanol production, good heat integration results in lower water consumption. In terms of energy consumption, the use of homogeneous alkali catalysts for oil transesterification show higher consumptions. In spite of the lack of energy sources within algae based biorefineries, the advantage is that they have good energy integration.

Table 3.- Summary of alage based integrated processes

	EtOH+FAEE+ Gly (Alkali)	EtOH+FAEE+ Gly (Enzymes)	EtOH+ FAEE (Enzymes)	EtOH+ FAEE (Alkali)	FAME+MetOH Autoref	FAME+MetOH Steam Ref	EtOH+FAEE+ hTBG	FAEE+ hTBG	FAME+ hTBG
Investment ($MM)	175	180	211	198	118	121	167	27.2	30
Capacity(MMgal/yr)	91	90	94 (13 EtOH)	96 (13 EtOH)	69	69	105 (9 EtOH)	81	84
Production cost ($/gal)	0.32	0.35	0.45	0.38	0.66	0.69	1.00	1.33	1.26
Water consumption(gal/gal)	0.77	0.59	0.59	0.84	0.79	0.79	0.59	0.29	0.65
Energy consump. (MJ/gal)	6.72	4.00	4.20	7.65	3.65	3.71	3.36	2.54	1.71

Finally, Table 4 shows the main operating parameters for solar and wind based power and chemicals production. We present one case where no water is used, CSP using dry cooling. Even though water for mirror cleaning is reported, it is neither process water nor water to produce the raw material. The wet cooling CSP process, as thermal plants, consumes water due to the evaporative losses in the cooling tower and the value, 2.1 L/kWH, is very similar to the one reported for coal based thermal plants (Torcellini et al., 2003). Apart from that, we see the relative large water consumption for the production of methane. Even though water is produced together with the methane and recycled, cooling needs for the electrolyzer and for the rest of the process, increase water consumption. Furthermore, in this case water is also a raw material for the production of hydrogen.

Table 4 Summary of the main operating parameters of the solar and wind based processes.

	CSP (wet)	CSP (Dry)	Solar CH_4	Wind CH_4
Investment ($MM)	260	265	240	375
Capacity	See Energy	See Energy	33.7 M m3 CH_4 111 Mkg O_2	33.7 M m3 CH_4 111 Mkg O_2
Production cost (€kWh)	0.15	0.16	0.33	0.48 (€/m^3)
Water consumption(L/kWh)	2.1	0	13.5	13.5 kg/m^3
Energy(GWh)	117	111	0	0

4.2.-Water- Energy link in renewable based processes

For a number of fuels and sources of power we evaluate the link between the energy, the net energy including that needed in the process, and the one obtained when we burn the fuel, and the water consumed to evaluate the more efficient fuel and process among those studied. See Figure 13 for the summary of the results. Bear in mind that the use of CSP with dry cooling does not require process water, and thus the ratio presented should be infinite. Among the other processes, we see that FT is the most efficient. As seen in Table 1, this process produces a large amount of energy. Part of the energy is due to the production of flue gas, and the rest because of the high operating temperatures and exothermic reactions. Furthermore, the yield to fuels is medium to high among the alternatives. If we evaluate the bioethanol production processes, the most efficient is the one that follows the thermo-catalytic path. In this case, apart from producing energy from ethanol, we can produce it from hydrogen. Furthermore, the process has a net energy balance itself as in Table 1. The cooling can be carried out with the use of air as cooling agent to reduce water consumption as presented by Martín et al (2010).

The production of ethanol from corn, or using other technologies to process the switchgrass, results in very similar efficiencies in water consumed per MJ produced. In the case of the corn-based ethanol, we do not include the irrigation water for corn. The process itself requires energy, but the ethanol produced and the reduced water consumption due to proper energy integration and WN design, results in competitive efficiencies compared to the production of bioethanol via hydrolysis of switchgrass. In this particular case, although the process is in itself quite similar to the corn based one, the operating temperatures in the pretreatment are higher and so is the steam consumption for breaking up the biomass structure. Switchgrass, and in general lignocellulosic biomasses, are more robust than corn grain, which requires more energy to expose the sugars. Furthermore, the fermentation allows lower concentration of ethanol in the reactor compared to the first generation one as presented before, which result in larger energy consumption for dehydration. The advantage is the presence of lignin that can provide energy for the process, resulting in a positive net energy balance. On the contrary, if the thermal-biochemical path is selected, the energy balance of the process is not positive as seen in Table 1. The concentration of ethanol in the syngas fermentor is typically lower than 5%. Therefore, the water-ethanol mixture is rather dilute, requiring a large amount of energy for the separation. Although the biomass gasification section has several streams that can provide energy to the system because of the high temperature, there is not enough energy available in the process. Furthermore, the exothermic reactor operating as in all other fermentations around 32-38ºC, results in the need for a certain amount of water for cooling. In summary, the water efficiency of this process is similar to corn-ethanol and biochemical switchgrass based ethanol, but not competitive with the use of the thermo-catalytic path.

As efficient in terms of water consumption as second generation bioethanol via thermo-chemical path, is the production of diesel from waste cooking oil and the production of biodiesel, bioethanol and high glycerol ethers. In the first case, we use a residue, cooking oil. Note that we do not consider the water consumption in the production of the waste. This process requires little energy, only in the recovery of the methanol and the purification of the products, but the yield to biodiesel is high and the water consumption is reduced, 0.33 gal/gal. The use of algae as raw material decreases the water efficiency by half. There are a number of reasons. First, the catalyst used is homogeneous, and therefore washing is required to remove the ions increasing the water consumption. Furthermore, the process requires cooling for a distillation column that recovers the solvent used in the extraction of the oil form the algae. As a result, the water consumption is twice that when cooking oil is used, and the yield to products does not change. Most of the other processes that have algae as raw material, have as upper bound this as water efficiency. For instance, the use of glycerol to produce methanol. Even though it reduces the dependency on fossil fuel, it does not increase the yield to biofuels resulting in water efficiencies in the level of not using the glycerol at all. The simultaneous production of ethanol and biodiesel and the further use of glycerol to increase the production of ethanol also present similar values in terms of water efficiency. In this case, we increase the yield form algae to fuels, since not only biodiesel but also ethanol is produced. On the other hand, the production of ethanol increases the energy consumption in the dehydration step. Finally, the production of glycerol ethers shows an interesting result. When we use cooking oil as raw material, ethanol as transesterifying agent and later the glycerol is etherified to produce glycerol ethers, the energy integration is efficient and the water consumption of the process is low resulting in high water efficiency. In other alternatives such as starting from algae and producing ethanol, biodiesel and glycerol ethers or from cooking oil but using methanol instead of ethanol as transesterifying agent, the water efficiency is around 50 MJ/L. We need to bear in mind that when methanol, ibutene or another raw material is included, the water consumed in the production of this raw material is not included in the study, and therefore the overall efficiency can be lower. Furthermore, in this analysis we have not included the water needed in case switchgrass requires irrigation, assuming it Is native to the regions where it grows (Wu et al 2009), or if freshwater was used in the ponds. In the end, even if no irrigation is needed, water from rainfall has actually being consumed.

Finally, we see that the solar and wind based processes are not that efficient compared to biomass based processes. Actually no more that 6 MJ are produced per L of water used in the process but in the case of the dry cooling CSP facility in which case we could claim almost infinity water efficiency. However, no additional water is actually needed for “producing” the raw material, contrary to the case for the biomass based fuels where even if it is waste water or rainfall, more water is involved in the process.

We now add the consumption of water in irrigation for corn, 7-14 gal/gal (Wu et al , 2009). We assume 7 gal/gal since it is an old range and agricultural methods have improved, while for algae it is reported that from 3.15 to 3650 gal/gal are needed (NSC, 2009). We consider the average. The production of switchgass does not require irrigation as it is native. Therefore, no change in the efficiency is expected. Figure 14 updates Figure 13 accounting for irrigation. We can see that the water efficieny of algae based processes and corn ethanol are really low compared to lignocellulosic based fuels or even solar and wild based ones.

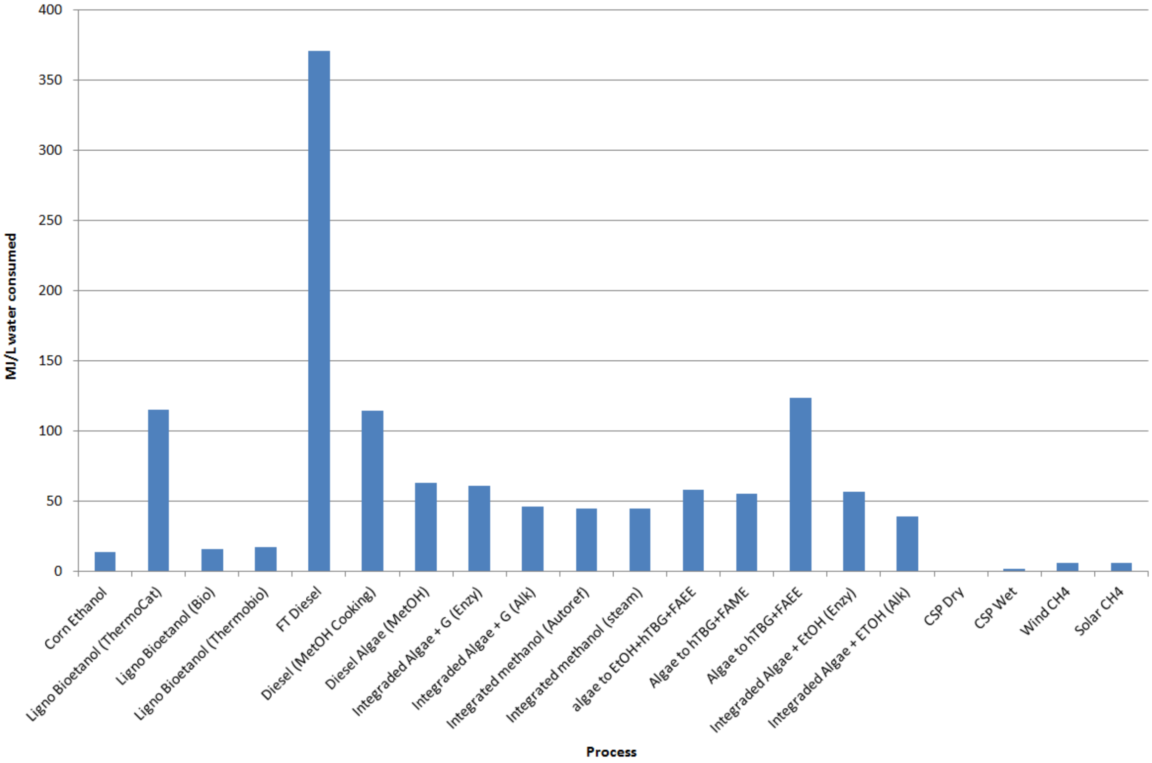


Figure 13- Water-energy nexus at the process level in renewable based processes

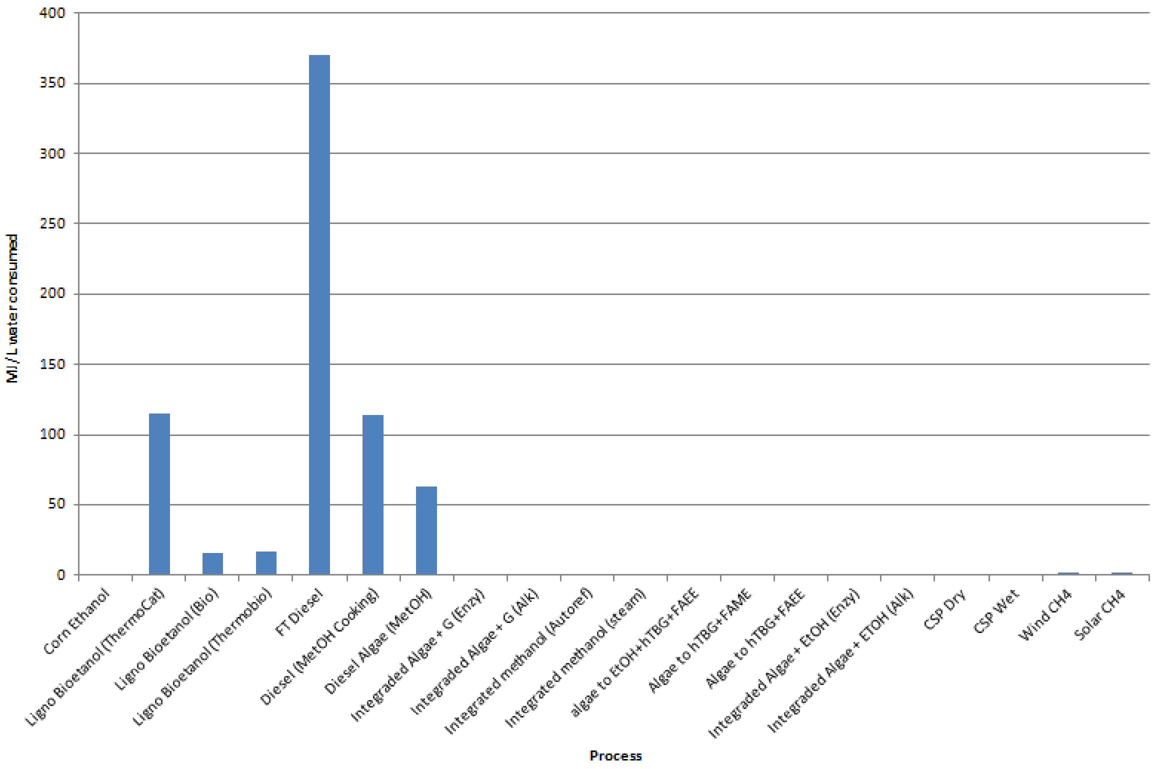


Figure 14- Water-energy nexus in renewable based processes: Process level and Irrigation

Accounting for rainfall is challenging. Actually even if we do not use freshwater in growing crops, that does not mean that no water has been consumed to produce the raw material. 1mm of rain represents 1L per m^2. In the native regions of the US where switchgrass is produced, around 1.27 m of rain per year are collected (Linacre and Geerts, 1998). With a typicall 10-18 t/hectare of swichgrass and the current yield from the biomass to ethanol, we can assume about 5119 L of rain fall per L of ethanol produced and 3065 L of rain per L of FT fuel produced. In terms of corn, the typicall rain fall is about 75 mm average raining in the cornwall of the US (www.holiday –weather.com) with an average yield of 8 t/hectare, 245 L of rain per L of ethanol. With these rough estimations we complete Figure 15 where all the water involved in the production of each fuel is accounted for. We see that there are no longer large differences, since rainfall, even if it is free, is water consumed to produce the biomass. From Figure 16 we can conclude that CSP dry is the more efficienct since no water is used for the production of power. Among the other proceses, the use of cooking oil does not require that much water either. Apart from these two exceptions where the raw material or the process does not use water at all, most of the processes are similar in the water efficiency, FT and all the algae based ones, see the detail in Figure 16. Second generation ethanol is not much more efficient. The only advantage is that nature provides for that water and not human such in the case of algae or corn.

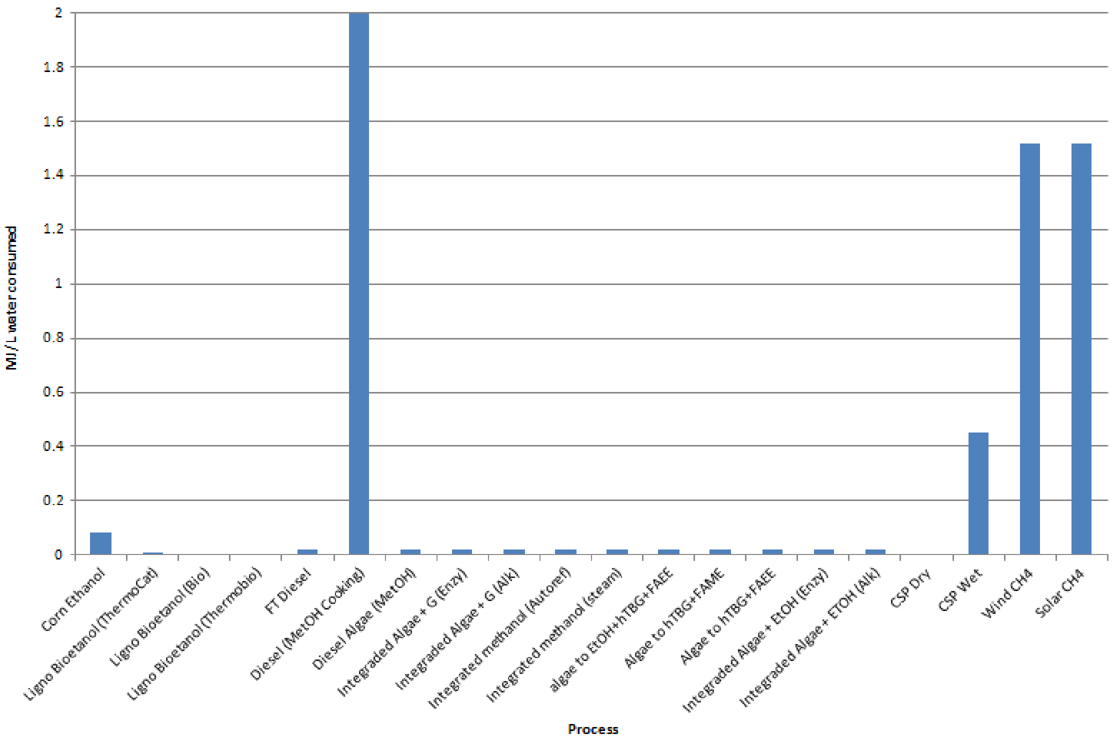


Figure 15- Water-energynexus in renewable based processes: Irrigation water and rainfall

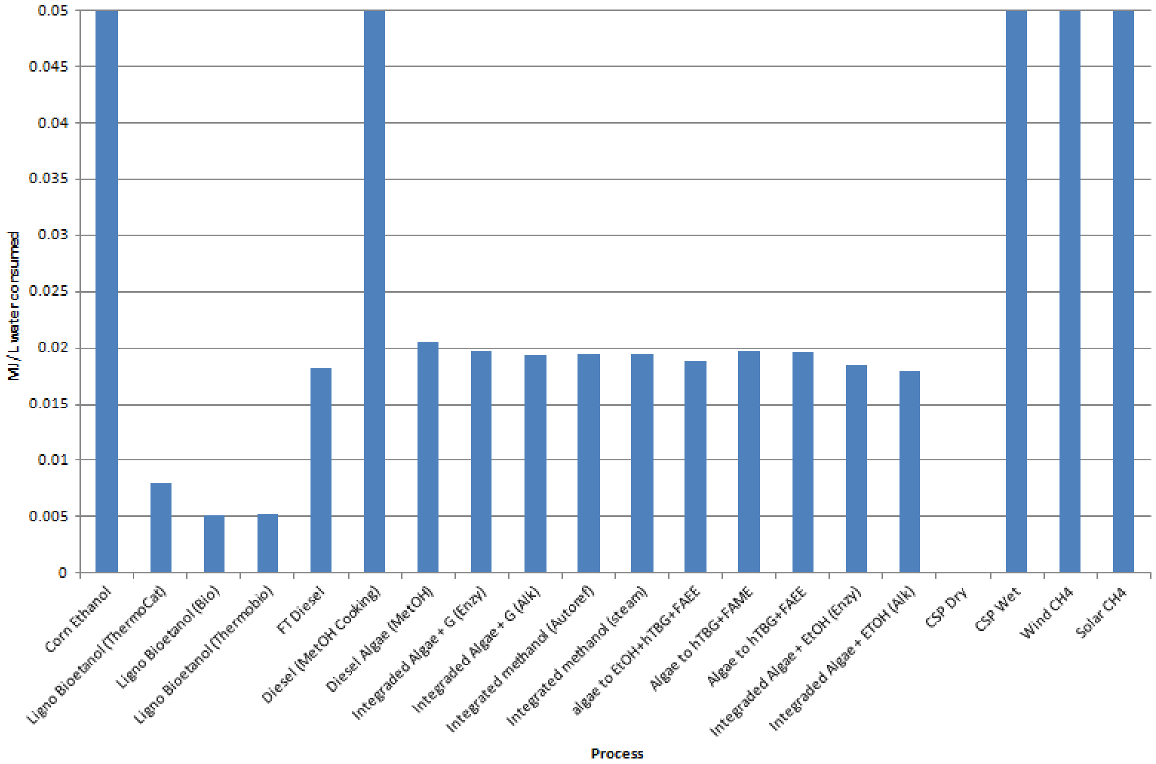


Figure 16- A detail of the Water-energynexus in renewable based processes: Irrigation water and rainfall

5.- Conclusions

In this work, the water – energy nexus for the production of renewable based power and fuels has been evaluated. A number of different processes from various raw materials to obtain bioethanol biodiesel, FT fuels, among others have been described in terms of their energy and water consumption.

There is a strong link based on the losses of water by evaporation in the cooling tower. The smaller the cooling needs requiring water, the lower the water consumption of the process. Air cooling and energy integration are both technologies for reducing the water consumption.

Among the number of processes evaluated we have considered the energy consumed by the process and that obtained, either as power or thermal energy, and if the fuel produced is burned. We see that only four processes produced over 100 MJ per L of water consumed, FT fuels being the most efficient because of a number of reasons such as the fact that the synthesis produced water itself, that there is a large excess of energy within the process and the FT fuels are produced with high yield from the biomass.

Finally, when rain fall is accounted for in the water consumption for the production of fuels, no large differences among raw materials or products are found. Water efficiency is low in general, and avoiding water for raw material production improves the overall water efficiency of the particular fuel.

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