Optimization of Water Consumption in Second Generation Bioethanol Plants

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Abstract

In this work we address the water consumption optimization of second generation bioethanol production plants from lignocellulosic switchgrass when using thermo-chemical, thermo-biochemical or biochemical routes considering corn-based ethanol as a eference. In order to optimize the water consumption a three stage method is used. First, energy consumption is optimized in the production processes, which reduces the cooling needs of the processes and thus, the water looses by evaporation and drift in the cooling tower. Next, a number of technologies are considered to partially substitute the use of water as cooling agent . Finally, the optimal water networks for each of the ethanol production processes are designed by determining water consumption, reuse and recycle and the required treatment using a superstructure optimization approach. The resulting water consumption ratios range from 1.5 to 3 gal/gal, which are in the range or even below the amount of water needed for gasoline production and with low or no water discharge depending on the process. Further reduction can be obtained by stressing the use of air cooling and if the water released from the crop can be properly recovered and treated. Under these conditions the water consumption ratios range from 0.6 to 1.7 gal/gal and with no or low water discharge.

Keywords: Energy, Biofuels, Alternative fuels, Water, Ethanol

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1. Introduction

Current industrial production and population demands are placing extra pressure on natural resources. Concerns related to overconsumption and depletion of these resources have focused on energy sources like crude oil, carbon and natural gas[1] . Water has been overlooked from that list mainly due its wide availability in many regions of the world. As a result, water is inexpensive compared to any other raw material, in spite of an average annual increase of 6.7% over the last years according to the 2008 GWI/OECD[2]. However, the industrial growth and the development suggests that by 2025 the industrial water usage (including utility cooling and heating, processing, transportation, air conditioning, cleaning, etc.) will account for about 11% of the total world water consumption [3,4] which can cause water stress in several regions of the world. The increasing concern towards water resources[5,6] and the green policies supported by many governments are making the management of water consumption and wastewater treatment an important topic with new economic incentives for implementing technologies that are more environmentally friendly, and that can ensure efficient use of water resources including the treatment and recycling of wastewater. [7]

In the recent past systematic methods for minimizing water consumption have focused on the optimal synthesis of process water networks. In order for these networks to be more effective in reducing water consumption, energy optimization has a large impact in decreasing the cooling needs and reducing the water loss by evaporation and drift in the cooling tower as shown recently for Ahmetović et al. [8] Energy optimization for biofuel plants involves superstructure optimization, the implementation of multieffect columns together with the design of optimal heat exchanger networks [9,10] When a sequential approach is used, the design of the water network is presented after the energy optimization. The design of water networks can be performed using two different approaches: (a) conceptual engineering approach[11-16] or (b) systematic methods based on mathematical programming.[17-23] Simultaneous minimization of energy and water was first addressed by Savelski and Bagajewicz [24] although this was only in the context of water networks without considering the process itself. Since then, conceptual techniques[25-31] and mathematical approaches have been applied on a variety of problems. [32-39]

To further reduce the consumption of cooling water different technologies that substitute water as cooling agent may also be implemented such as air cooling [40]. Thus, the implementation of these technologies together with the energy optimization and the design of optimized water networks are the key for the economic and technical feasibility of new production processes like the ones involving bioethanol production from switchgrass.

2. Problem statement

In this paper we analyze the impact that water saving technologies and methods have on a number of new processes for the production of ethanol from lignocellulosic material, the so called second generation bioethanol, by applying to conceptual designs of these processes the water network optimization method by Ahmetovic and Grossmann[68] we compare these results with the water consumed in corn-based ethanol plants as well as in the production of gasoline to provide further insight into the important topic of the water consumption in biofuel production processes.

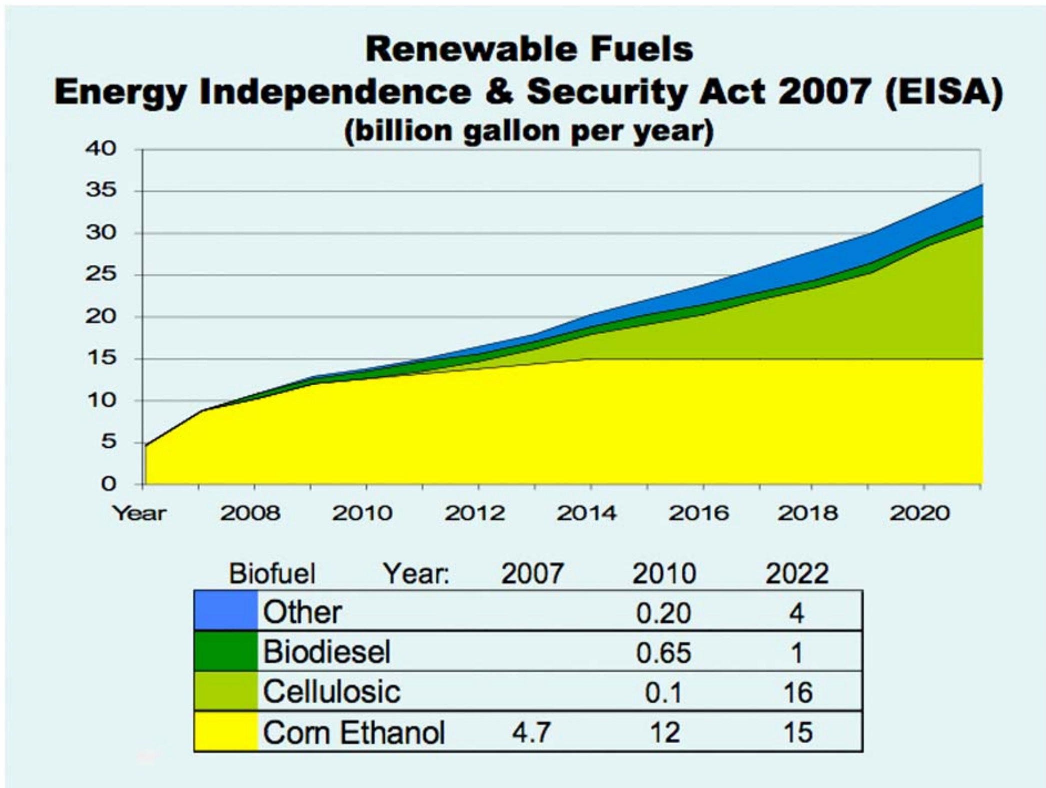
The low price of freshwater makes it difficult to take into account the effect of water consumption in the economic optimization of biofuel plants. Thus, the optimization of water consumption is performed sequentially. The first stage consists of reducing the energy consumption of the process through heat integration. In this paper we used data from previous papers [41-43]. Philips et al.[40] proposed the use of air cooling in order to replace water as cooling agent in the condensers of the distillation columns and in the intercooling stages of gas compression. Thus, in a second stage we assume that the cooling of the condensers and the inter cooling stages of gas compression are not treated with a cooling tower. Finally an optimal design of the water network is developed for each of the processes under consideration using mathematical programming techniques.

The paper is organized as follows. In section 3 we discuss the water consumption in bioethanol plants. We present a brief explanation of the optimal conceptual design of the different production processes from corn and switchgrass[41-43] to identify the water requirements and wastewater production. In section 4 we present the impact that the implementation of cooling water saving technologies like air cooling and energy optimization have on the cooling needs of the different flowsheets under consideration. In section 5 we design optimal water networks for each of the processes. Finally, in section 6 we discuss the effect of the simultaneous production of hydrogen not only on the economy of the process (see Martin & Grossmann)[42] but also on the water consumption together with the possibility of further reducing in the consumption of water by stressing the use of air cooling and recovering the water that is extracted from the crop in the pretreatment stages.

3. Ethanol production processes

The compatibility of ethanol with the current gasoline based transport system has supported its production to become the most important alternative fuel so far. However, the expected increase in the volume of ethanol production from corn and lignocellulosic raw materials in order to meet the governmental policies in the US [44] (see Fig 1) or in the EU[45], has raised concerns regarding their technical feasibility in terms of land usage, energy and water consumption.[46-47] In this paper we focus on the problem of water consumption in the production of first and second generation of ethanol where water is needed at two stages of the process, irrigation, which depends on the raw material[3] and the production process itself.

The expected increase in the production of biofuels as a result of the current policies supporting biofuel industry[3,44,45] has raised questions regarding its impact on the water consumed for irrigation. Thus, departments of agriculture of different countries have analyzed the effect of those policies on the share of water needed to grow the crops devoted to biofuel production. It is reported that the impact of biofuel production policies can be important in certain regions but on the whole, it will affect less than 5%. In contrast, if the amount of biofuel to be produced is far larger, the production regions as well as the raw material must be carefully selected so as not to have a big impact on food production and water availability. The use of different raw materials, rather than corn, that do not compete with the food supply chain and that require less irrigation as well as the proper location of the plantations will also reduce the water consumption for the production of biomass. [48]



Biofuel	Year: 2007	2010	2022
Other		0.20	4
Biodiesel		0.65	1
Cellulosic		0.1	16
Corn Ethanol	4.7	12	15

Figure 1. US. Renewable fuels production and requirements. (Source US dept of energy)

The second stage in water consumption for the production of ethanol is in the production process itself. Ethanol production processes can be classified into first generation, like those based on sugar or corn, and second generation, such as those based on lignocellulosic raw materials. In this paper we compare the water consumption of the corn based process with the values calculated for the second generation of ethanol production plants. The first data available in the literature regarding water consumption in ethanol plants reveal values from 3 to 15 gal $_{water}$ / gal $_{ethanol}$ for the corn based process. According to the literature [46,49,50,51] the best possible water consumption for corn based ethanol is 2.85 gal $_{water}$ / gal $_{ethanol}$ and a mean industrial value for the newest plants is 3.4 gal water per gal of ethanol. However, Ahmetović et al [8], showed that it is possible to go as low as 1.5 gal $_{water}$ / gal $_{ethanol}$ in case of the corn ethanol process, confirming the claims by companies like Delta T. For the second generation of ethanol production processes from lignocellulosic raw materials, different values have been reported depending on the raw material such as 6 to 9.8 gal_{water} / $gal_{ethanol}$ for switchgrass[51], or 1.94 - 2 gal_{water} / $gal_{ethanol}$ for hybrid poplar [40, 51,52].

For a further evaluation and comparison with these values, in this paper we optimize water consumption in second generation bioethanol plants. In order to identify the needs of water in the different processes and the sources of wastewater, we briefly discuss first the flowsheet of four different production routes: corn-based ethanol, thermo-chemical, thermo-biochemical and biochemical. Further details of the processes can be found in previous papers by the authors. [41, 42,43]

3.1. First generation: Corn-based ethanol.

Karuppiah et al. [41] proposed an optimal conceptual design for the production of ethanol from corn using the dry grind process by optimizing a superstructure for producing 60M gal ethanol/yr. As presented in a previous paper by the authors[8], the plant consists of three different sections. The first section involves the pretreatment of the corn grain to break its physical and chemical structure making the sugars accessible for fermentation. The process units employed are grinding, direct contact with steam, saccharification and liquefaction. The second section is the fermentation of the sugars, mainly glucose, into ethanol using a yeast, *Saccharomyces cerevisiae*. 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. CO_2 is also generated in the fermentation. After fermentation, two alternatives were proposed for the separation of solids from the slurry exiting the fermentor: a) mechanical separation before the beer column (BC1), or b) after the beer column. The third section comprises the technologies used for the purification and dehydration of ethanol to fuel grade, and involves the following choices: (1) A rectification column which can concentrate ethanol to the azeotropic composition, (2) adsorption of water in corn grits, and (3) molecular sieves. The superstructure is optimized in terms of energy consumption. The separation of the solids takes place before the beer column, while the dehydration stage consists of the rectification column together with adsorption in corn grits with final stage in the molecular sieves. For further details we refer to previous papers by the authors. [8,41]

3.2. Second generation: Lignocellulosic ethanol

There are mainly two different technological routes to transform lignocellulosic raw materials into ethanol. The first one is based on the hydrolysis of the raw material to expose the sugars that are fermented to ethanol. Due to its similarity with the corn-based production of ethanol and the expected lower capital cost, this technology has received a great deal of attention by many researchers.[53-57] The second possible technology is the gasification of the raw material into syngas and the synthesis of ethanol either as via mixed alcohols synthesis, a modification of the Fischer-Tropsch process, or by means of the fermentation of the syngas. [40,45,58,59] Here we briefly discuss optimal conceptual designs of the processes based on the results by Martín and Grossmann[42-43] to identify the water consumption and wastewater generation.

3.2.1. Thermo-chemical process

The process described below is the optimal conceptual design of a thermo-chemical process for the production of ethanol from switchgrass as proposed by Martín & Grossmann[42]. The process consists of three different parts. The first one is the production of syngas from biomass. The raw material is washed, its size is reduced by grinding and it is partially dried using a mechanical press in the pretreatment. Next, high pressure direct gasification with steam and oxygen is the best option. The gas generated at the gasifier is cleaned from solids as well as other compounds like hydrocarbons, NH_3, CO_2 or H_2S. The hydrocarbons are partially removed using steam reforming. Next, the solids are removed in a ceramic filter and the gas is expanded generating energy. The last traces of hydrocarbons are removed in a Pressure Swing Adsorption (PSA) system with a bed of Silica gel. PSA systems work at low temperature and thus water condenses before these process units. At this point the composition is adjusted to a molar ratio CO : H_2 of 1 separating the excess of hydrogen using a hybrid PSA-membrane system. The hydrogen generated as byproduct is a major source of income for the process. After the composition adjustment, sour gases such as CO_2 and H_2S are removed using a PSA system with a bed of zeolites followed by MEA to remove the H_2S, which is poisonous for the catalysis. Water condenses before these operations due to the low temperatures and high pressures and is withdrawn from the system. Finally, the synthesis of ethanol is carried out using high alcohols synthesis production. A catalyst based on the one used for the production of methanol is used.[40] The light hydrocarbons and the unreacted gases are recycled back to the cleanup section of the process, while the purification of ethanol is carried out using a direct sequence of distillation columns where the methanol is recycled back to the reactor. Figure 2 shows the flowsheet of the process. [42]

In this process wastewater is generated mainly in the condensation before the PSA and the MEA systems, where different organics may accompany the water, while the water used for raw material washing contains suspended solids that must be removed for the water to be reused.

We have also considered another alternative, closer to the one presented in Philips et al [40]. The optimized flowsheet is presented in Martin & Grossmann [42] under the label of subproblem C. This production process uses low pressure indirect gasification, steam reforming of the gas followed by wet removal of solids, and catalytic synthesis of ethanol which is purified using direct distillation sequence. Thus, wastewater is generated not only in the condensation previous to the PSA systems, but also from the scrubber. It is assumed that from the stream leaving the scrubber, basically char (particles) and NH_3 are the most important contaminants. Organics are the contaminants accompanying the condensed water.

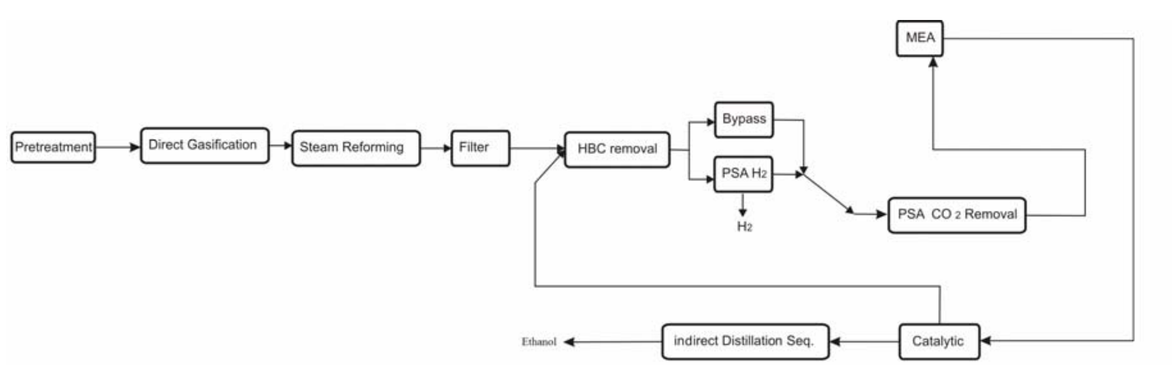


Figure 2. Thermo-chemical ethanol production from biomass

3.2.2. Thermo-biochemical.

Based on the studies by Martín and Grossmann [43] the optimal conceptual design for the production of ethanol via gasification of switchgrass followed by the fermentation of syngas is as follows. The raw material is washed to remove solids and partially dried using a mechanical press. The gasification of the raw material takes place at high pressure with steam and oxygen using a direct gasifier. In order to remove the hydrocarbons obtained in the gasification, the gas is reformed with steam. Later a ceramic filter is used to remove solids. The composition of the gas may be adjusted since the CO: H_2 ratio of 1 is the preferred one in the reactor. The bacteria used for the fermentation of the syngas, *Z. Mobilis*, do not require separation of the excess of hydrogen, but the economy of the hydrogen favors its separation from the gas stream since it is a valuable byproduct. The gas must then be cleaned from sour acids. The bacteria, *Z. Mobilis*, can handle concentrations of H_2S up to 2.5% in volume. Thus, the treatment for this gas is only to avoid build up of H_2S in the process. The optimal process requires that the stream coming from the composition adjustment is first treated in a PSA system to remove most of the CO_2 and later only half of the stream will be treated in the MEA system to remove H_2S. PSA and MEA work at low temperature and thus water condenses and is withdrawn from the system before these process units. The syngas is then fermented in a stirred tank reactor in water, which has to be fed to the fermentor. The unconverted gases are recycled to the purification stages, while the ethanol / water mixture is sent to distillation and later to molecular sieves to dehydrate the ethanol to fuel quality. Figure 3 shows the flowsheet.

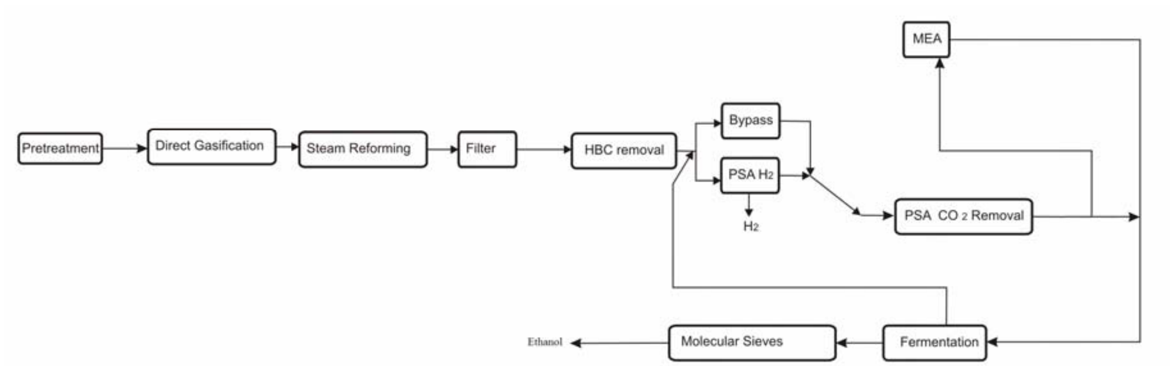


Figure 3. Thermo – biochemical production of ethanol from lignocellulosic biomass

In this process, wastewater is generated before any PSA system as well as from the distillation column where organics are the main contaminants. Moreover, the water used for the raw material washing contains suspended solids the must be removed for the water to be reused.

3.2.3. Production of ethanol from switchgrass via hydrolysis

The last alternative considered to produce ethanol from lignocellulosic raw material is via hydrolysis of the biomass. In order to pretreat switchgrass to make the cellulose and the hemicellulose sugar accessible for hydrolysis, two methods have been found to be competitive for industrial production of ethanol due to the high yield towards the liberation of cellulose and hemicelluloses from the matrix of the plant: (1) dilute acid (H_2SO_4) pretreatment [45,55,60-61] and (2) ammonia fibre explosion (AFEX)[62-64]. Martín & Grossmann[43] proposed an optimal conceptual design for ethanol production via hydrolysis in which the dilute acid pretreatment was cheaper aside from being more environmentally friendly as it consumes less energy and less cooling water. Moreover, Čuček & Kravanja[65] presented the LCA results revealing that the dilute acid has less impact on the environment. Once the physical structure of the switchgrass has been broken to allow the contact between the polymers and the enzymes, hydrolysis of the polymeric sugar takes place. This process is carried out in stirred tank reactors at 50 ºC where the accessible cellulose and hemicellulose are broken into fermentable sugars [45,53-55,66-67] The sugars, mainly glucose and xylos, are fermented in water into ethanol. The reactions are different in terms of yield and rate. The optimal ceonditions are 38 ºC so that both sugars are fermented at the same time. A number of different products are obtained together with ethanol such as different acids product of the metabolic paths of the microorganisms used (Z mobilis bacterium) and cells are grown as well.[45,55,67] The purification stages consist of the removal of solids, lignin and cells, from the liquid slurry coming out of the fermentor. The lignin is used to obtain energy for the process. Finally, ethanol is dehydrated by means of a beer column followed by molecular sieves to achieve fuel grade. Figure 4 shows the flowsheet from Martín & Grossmann. [43]

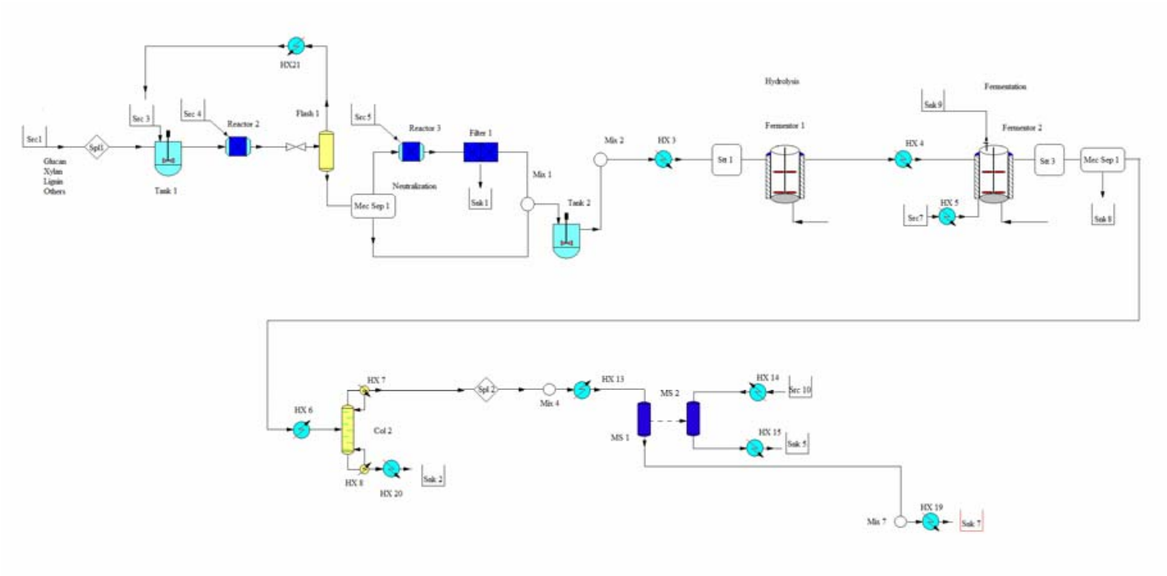


Figure 4. Production of ethanol from swichgrass via Hydrolisis

In this process, wastewater is generated from the distillation column, where organics are the main contaminant, while water is required in the pretreatment stages (raw material washing and dilute acid pretreatment) for the hydrolysis and fermentation.

4. Effect of energy optimization and the implementation of energy saving technologies on water consumption.

Following the optimization of the flowsheet based on minimum energy consumption, multieffect columns are introduced and heat integration of the streams is performed. It turns out that the use of multieffect columns is very effective in order to reduce the cooling requirements. For the case of the thermo-biochemical or biochemical process, the use of multieffect columns for the beer column saves up to 90% in cooling water while in case of the separation of alcohols, a reduction up to 60% in each of the condensers is obtained.[42-43] Heat integration also plays an important role in reducing the cooling needs since the energy available in the streams is recovered, thereby reducing the heat to be removed from the process by cooling. As a result of implementing multieffect columns and performing heat integration, the cooling needs are greatly reduced which results in lower losses of water by evaporation in the cooling tower. The optimized processes (with multieffect columns and heat integration) feature the energy and cooling requirements as shown in Figure 5.

We have also included data from two reports by the NREL[40,52,67]. In general, it can be seen that the cooling requirements for all the processes are larger than in the case of the corn-based ethanol. The more aggressive pretreatments needed to break the structure of the crop imply higher temperatures and pressures in the process resulting in larger cooling needs. Furthermore, the lower concentration of ethanol in the fermentor of the thermo-biochemical process also increases the demand of water for the processes. Furthermore, the optimized processes presented by Martin & Grossmann[42,43] show a large reduction in cooling needs compared to the ones presented in the NREL reports [40,52,67] as a result of the energy optimization in particular for the biochemical process based on hydrolysis of the raw material.

In order to further reduce the use of cooling water, air can be used as cooling agent in the condensers of the distillation columns as well as the inter coolers between compression stages, as proposed by Philips et al. [40] As a result of the implementation of this technology, the cooling requirements using water as cooling agent are reduced and so is the amount of water that is lost by evaporation and drift at the cooling tower. In Figure 6 we show the decrease in the water cooling requirements when air cooling is used. The results from the NREL [40,52,67] show larger impact of the air cooling larger because they do not use multieffect columns. It is important to highlight that substituting water by air as cooling agent has only a large impact in the energy to be removed by cooling water in production processes based on gasification. This is due to the fact that the high pressures used across the process flowsheet result in high cooling needs in the compression stages where air cooling can be implemented. However, for the rest of the processes, the use of multieffect columns is very effective in reducing the consumption of cooling water [41-43] . Air cooling is extensively used in the case of the process presented by NREL [40] to reduce cooling water consumption.

Once the cooling needs are established, we proceed to design the water network for the different processes under consideration.

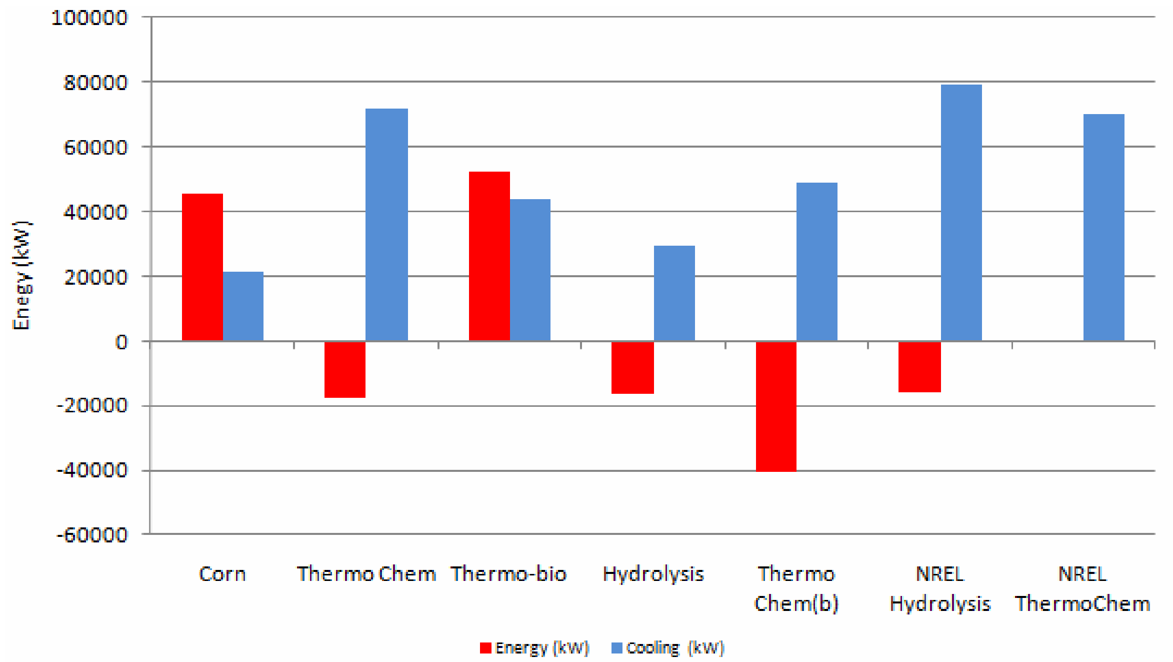


Figure 5.- Energy and cooling needs for different ethanol production processes.

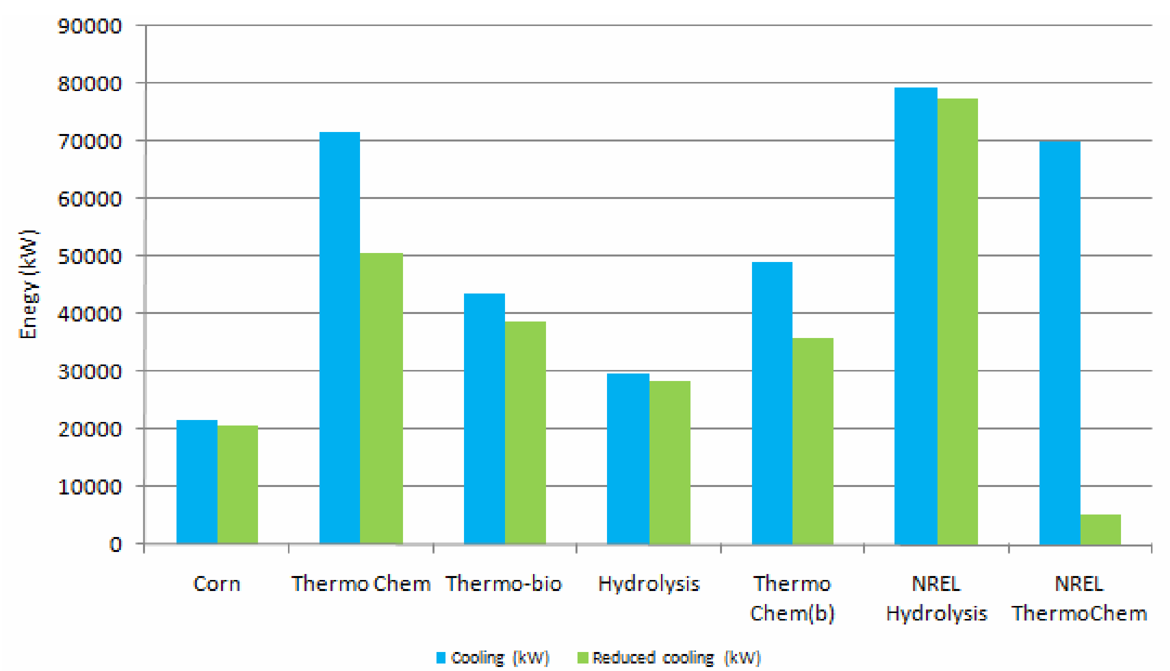


Figure 6.- Cooling needs of different bioethanol production processes

5. Water consumption optimization by implementation of water networks

5.1. Water network superstructure and model

In order to synthesize the optimal water networks for the bioethanol production plants together with the cooling water and stream loops, we optimize the general superstructure of integrated process water networks shown in Figure 8 which has been proposed recently by Ahmetović and Grossmann. [68]

The superstructure consists of one or multiple sources of water of different quality, water-using processes, and wastewater treatment operations. The unique feature is that all feasible connections are considered between them, including water re-use, regeneration, recycling, local recycling around process and treatment units and pre-treatment of feedwater streams. Multiple sources of water include water of different qualities that can be used in the various operations, and which may be sent first for pre-treatment. The superstructure incorporates both mass transfer and non-mass transfer operations.

The model is formulated as a nonconvex nonlinear programming (NLP) which is solved to global optimality. 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 units mass balances. The detailed model for the design of water networks can be found in previous papers [8, 68]

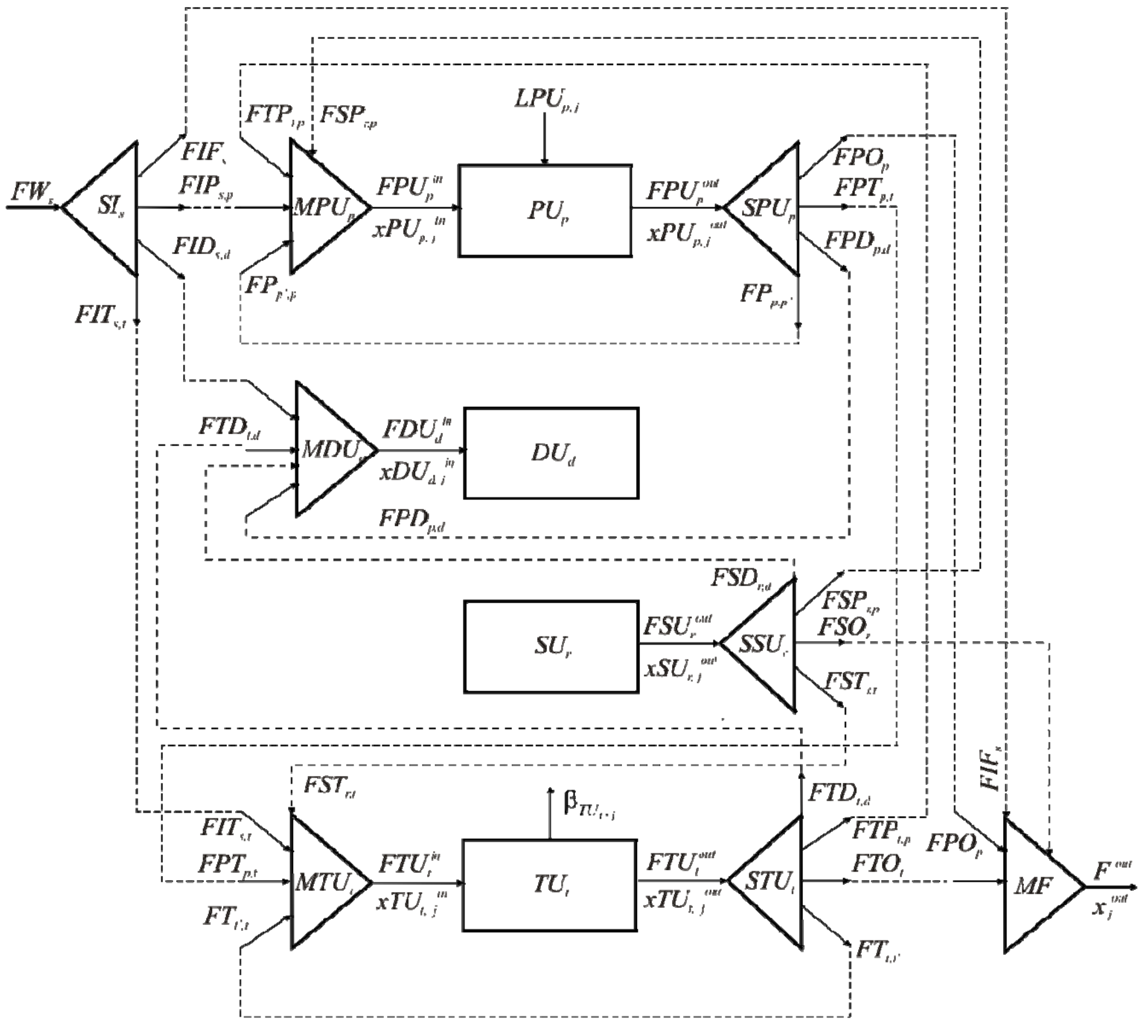


Figure 7. Generalized superstructure for the design of integrated water networks. Ahmetović and Grossmann [68]
PU: Process Unit; DU: Demand Unit; SU: Source Unit; TU: Treatment Unit.

5.2. Application of water network

To synthesize the optimal water network for the bioethanol production plant using the generalized superstructure described above, the process and treatment units, and their corresponding flowrates must be identified. For all the processes described in section 3 we consider:

Sources: Beer and rectification columns, Condensation processes.

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

Process Units: Pretreatment, Scrubbers, Boiler, Cooling tower

The application of the water network to a particular case also requires the specification of the treatment units in accordance with the contaminants. Wastewater streams are generated from the boiler, cooling tower, and beer columns, discharge from condensations. 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. [69] Suspended solids are present in the water used for washing the raw material; the organics are the main contaminants in the streams coming out of the distillation columns and the scrubber, while the dissolved solids include the concentration of salts as a result of the evaporation processes in the boiler and the cooling tower. Furthermore, the water fed to the fermentor must have no ethanol, which is toxic for the bacteria or yeast. We assume that there are three different wastewater treatment units as well as the fact that fresh water has no contaminants at all. In the next section we present the models for the treatment units and for the boiler and cooling tower.

5.2.1. Models for process and treatment units.

5.2.1.1. Solids removal (TU1)

In order to remove suspended solids such as straw or sand screens are widely used. The removal rates vary depending on the size of the solids.[70] We assume 99.9% removal for suspended solids.

5.2.1.2. Organics removal (TU2)

The water from the distillation columns, the condensed water and the stream coming from the scrubber require a system of anaerobic and aerobic treatment to remove the organic matter. The anaerobic stage removes 90% of the organics generating biogas rich in methane that can be reused to obtain energy. Later, the water is treated in an aerated lagoon to obtain relatively clean water that can be recycled to the process according to the results presented by Zhang et al.[55] Thus, for this study, both treatments are integrated and modeled as a single treatment unit whose removal efficiency is assumed to be 100%.[55]

5.2.1.3. Cooling tower.

The model for the cooling tower is similar to the one used in the previous paper by the authors[8] and it is based on typical design equations [71,72,73] and mass balances (See appendix 1 for more details). Currently, the main issue is to improve the operation of the cooling towers to reduce the water losses. New developments in the drift-eliminator design make it possible to reduce drift loss below 0.1 % [71] to values of 0.005 %[74] . In this work we assume a value of 0.1%. By reducing the drift it is possible to further reduce the global consumption of water. The concentration of total suspended solids (TSS) in the outlet stream of the cooling tower is typically 50 ppm, while the TDS are 2500ppm [75].

5.2.1.4. Boiler.

We use the same model for the boiler as presented in the previous paper by the authors[8]. See appendix 2 for more details. 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 [76].

5.2.1.5. Total dissolved solids removal (TU3)

One of the most important contaminants in the operation of boilers and cooling towers are the total dissolve 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 dissolve solids, a reverse osmosis system is considered. The literature reports removal ratios of 90% at the most, better than ion exchange or nanofiltration.[69,77] The regulations require that the concentration of TDS in the effluent not exceed 500 ppm. [78]

5.2.1.6. Cost correlations.

The cost correlations for the equipment involved in the network, screens,[79] aerobic and anaerobic treatment,[80] boiler,[81] cooling tower,[82] and the reverse osmosis (RO)[83] are the same as used in Ahmetovic et al [8] and they can be found in appendix 3.

The relative optimality tolerance was set to zero, and we used the general purpose optimization software BARON[84] to solve global optimization of the nonconvex NLP problem.

5.2.2. Water networks

Table 1 shows the identification of the process units, demand units and source units for each of the processes under consideration. The flows and the level of contaminants of source units are given by the mass balances presented in previous papers by the authors. [40,42-43] 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).

In the next sections we show the design of the optimal water networks with flow rates in t/h, calculated for each of the processes under consideration (corn-based ethanol, thermo-chemical, thermo-biochemical, biochemical (hydrolysis) and NREL-based thermo-chemical lignocellulosic bioethanol) assuming the implementation of air cooling for intercompresion stages and distillation column condensers. Thus, only the reduced cooling needs presented in Figure 6 will be treated in the cooling tower. We then summarize the effect of the implementation of air cooling and the impact of the production of hydrogen as byproduct in the water consumption for all the processes.

Table 1.- Inventory of units for the water networks of the bioethanol processes.

Process	Process Units	Demand Units	Source Units
Corn	P1: Washing P2: Boiler P3: Cooling Tower	D1: Fermentor D2: Boiler D3: Cooling tower	S1: Rec Column S2: Beer Column
Thermo-chemical	P1: Washing P2: Cooling Tower	D1: Gasifier D2: Cooling Tower	S1: Condensation
Thermo-biochemical	P1: Washing P2: Boiler P3:Cooling Tower	D1: Fermentor D2: Boiler/Gasifier D3: Cooling tower	S1: Beer Column S2: Condensation
Hydrolysis	P1: Washing P2: Boiler P3:Cooling Tower	D1: Fermentor D2: Boiler D3: Cooling tower D4: Acid treatment	S1: Beer Column
Thermo-chemical (NREL)	P1: Washing P2: Cooling Tower	D1: Gasifier D2: Cooling Tower D3: Scrubber	S1: Scrubber & Condensation

5.2.2.1. Corn- based process.

The reduced cooling needs due to the use of air cooling for the condensers of the distillation columns, together with an updated water price (5.7 $/MT) results in a lower consumption of water 38.968 t/h compared to the value obtained previously, 40.822 t/h (Ahmetović et al.) [8], which represents 5% decrease. The increase in the price of water (from 0.0087 $/ton[8] to 0.057 $/ton[42]) modifies the optimal network towards lower fresh water consumption (1.47 $gal_{water}/gal_{ethanol}$ vs. 1.54 $gal_{water}/gal_{ethanol}$[8]). The optimal water network for corn-based ethanol process is shown in Fig. 8.

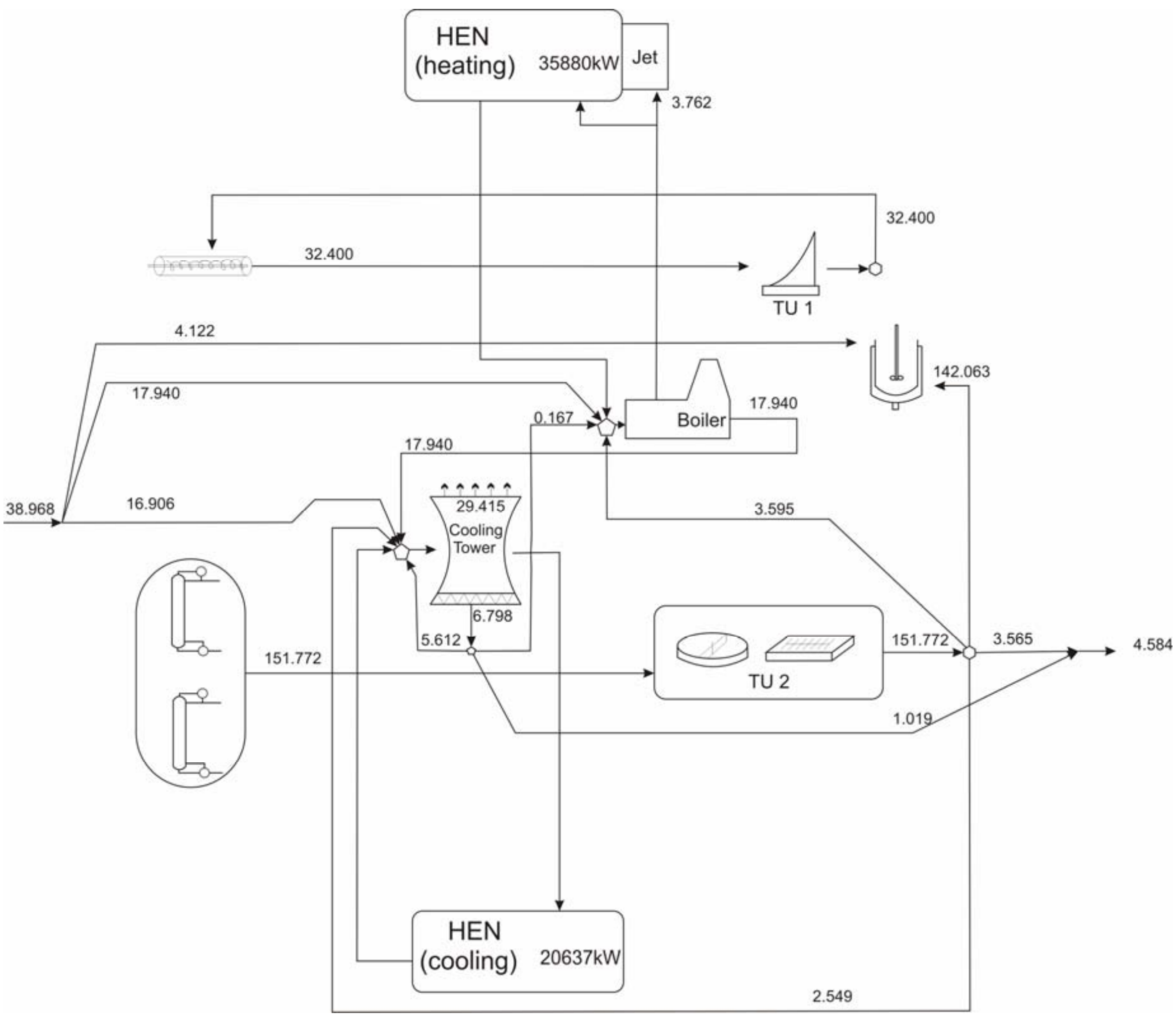


Figure 8. Water network for the Corn ethanol process.

Figure 8 shows the optimal design of the water network for the corn ethanol process implementing air cooling technologies. Freshwater is used in the cooling tower and in the boiler to dilute the TDS below the operating levels. Meanwhile, the water containing solids or organics can be treated and reused. It is not possible to achieve zero discharge due to the higher cost of freshwater and the low flowrates within the network. The water discharged is 4.584 t/h.

5.2.2.2. Thermo Chemical: Lignocellulosic Gasification Catalytic

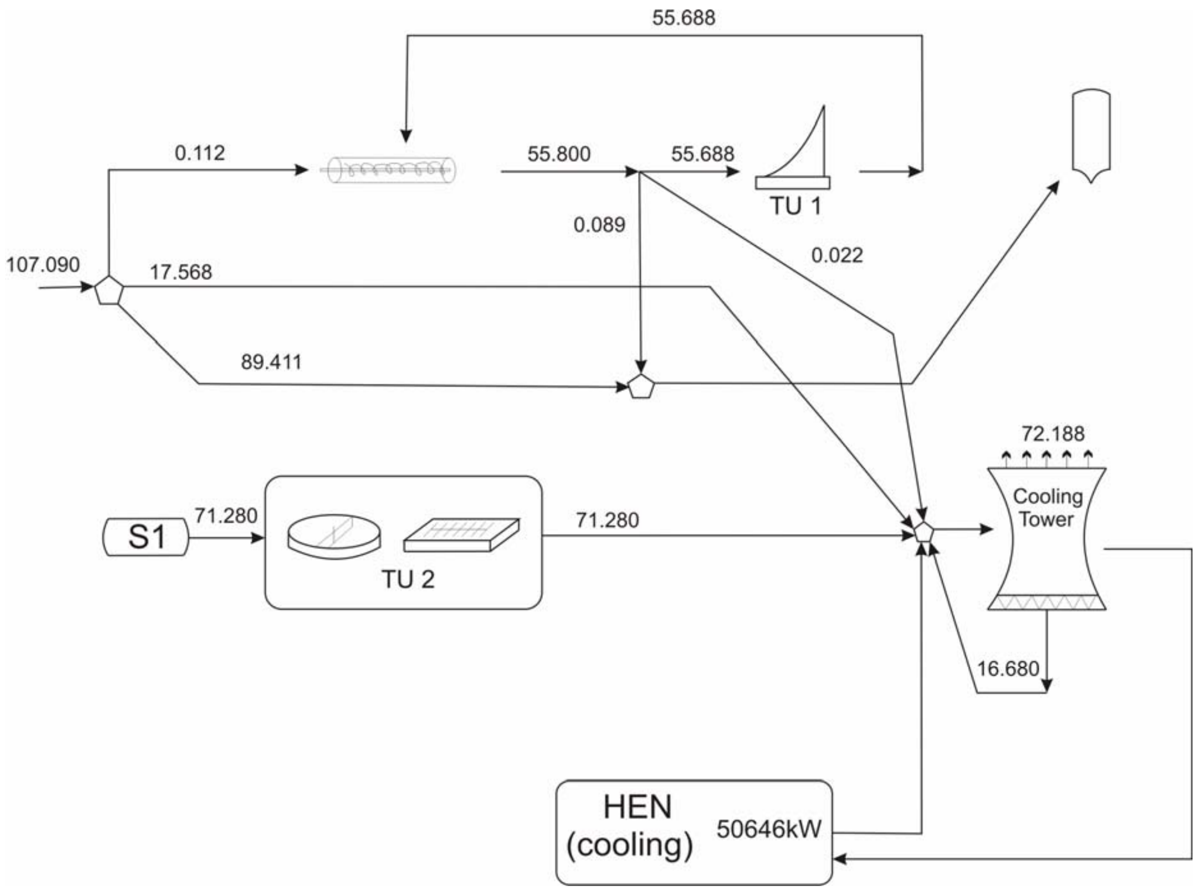


Figure 9. Water network for the Catalytic production of ethanol from syngas

The production process of ethanol from switchgrass via gasification and catalytic synthesis requires a large amount of cooling water mainly due to the high temperatures and pressures in order to break the structure of the crop, to clean the syngas from different chemicals, to prepare the gas for the catalytic reaction, and due to the large amount of water consumed in the form of steam in the gasifier. The implementation of air cooling technologies after energy optimization represents a reduction of cooling water around 30%, since the compression stages require large cooling needs, resulting in a decrease in the water consumption from

120.425 t/h to a value of 107.090 t/h, 4.0 $gal_{water}/gal_{ethanol}$. Further reduction in the use of cooling water could be obtained by extending the use of air coolers to any cooler apart from condensers and compression interstage coolers. Figure 9 shows the optimal water network for the thermo-chemical process when air cooling is used since the HEN only accounts for the cooling water. There is no water discharge and the reverse osmosis is not used because the large flowrates used in the plant allow TDS dilution below the operating limits.

5.2.2.3. Thermo biochemical: Lignocelulosic Gasification Fermentation

The thermo-biochemical process is less water demanding that the thermo-chemical one due to the lower working pressures in the synthetic part of the process. Thus, the impact of air cooling in the overall water consumption represents a reduction of 11% in cooling water needs resulting in a total freshwater reduction from 110.110 t/h (without air cooling) to 85.370 t/h (implementing air cooling), 3.2 $gal_{water}/gal_{ethanol}$, which is in the range of the current corn based ethanol plants.[8] The freshwater is used in the fermentor, while treated water is used as make up in the cooling tower and in the boiler. No water is discharged to the environment. Figure 10 shows the optimal water network for this process with air cooling technology in operation.

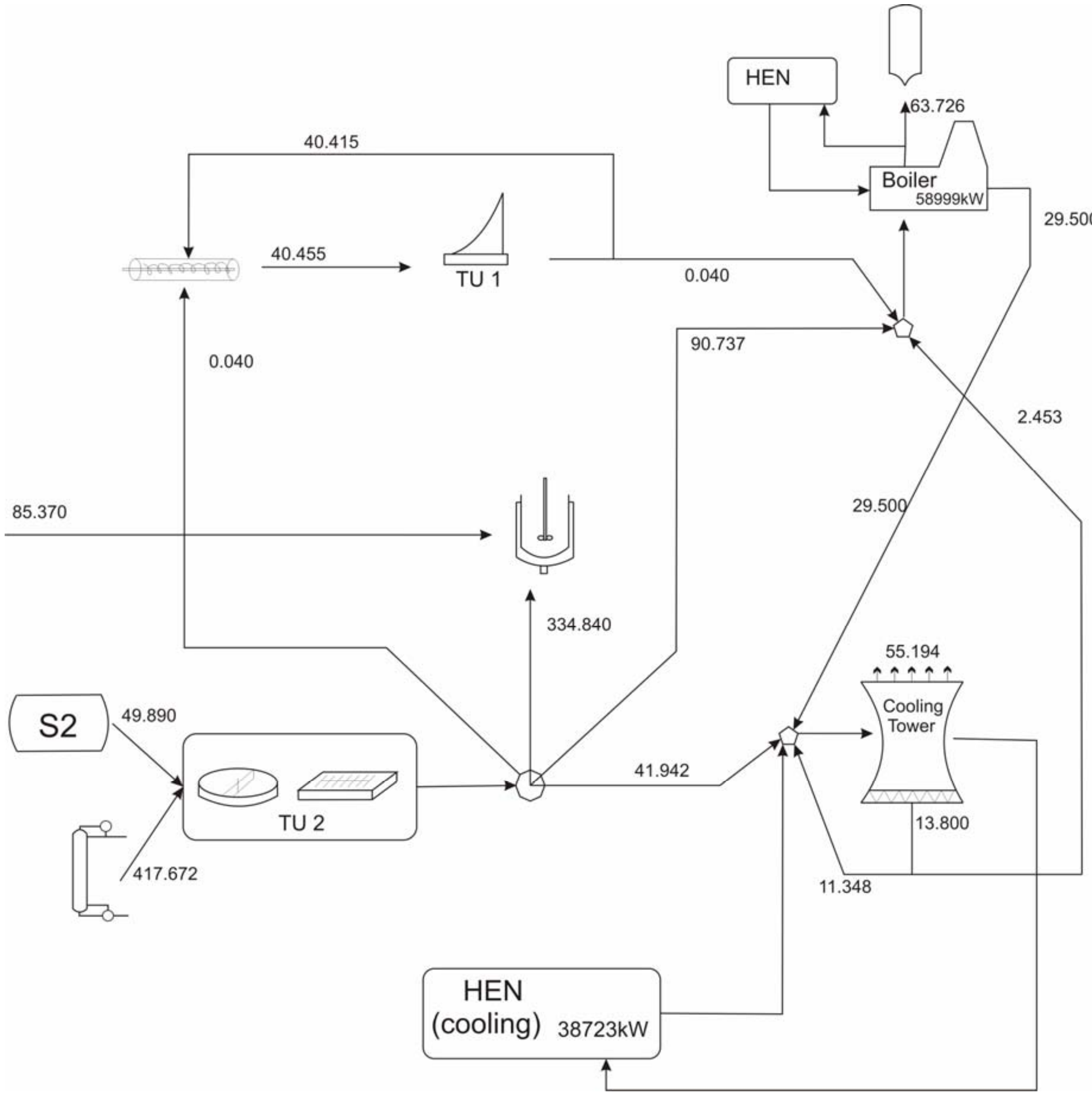


Figure 10. Water network for the production of ethanol from syngas via fermentation.

5.2.2.4. Biochemical: Lignocellulosic Hydrolysis

The production of ethanol from hydrolysis of switchgrass is a more moderate process compared to the two previous ones in terms of operating pressures and temperatures. As a result, cooling requirements are less than half the ones for the thermo-chemical process, as seen in Fig 6. For this process, the implementation of air cooling reduces only 5% of cooling water due to the optimization of the distillation columns by means of the implementation of multieffect columns. The total consumption of fresh water after the implementation of air cooling technologies is 54.088 t/h which results in a consumption of 2.0 $gal_{water}/gal_{ethanol}$. However, the wastewater discharged is far larger than in the precious processes, 10.528 t/h. The lower flowrates in the water network do not allow TDS dilution and the high cost of reverse osmosis. Figure 11 shows the optimal water network.

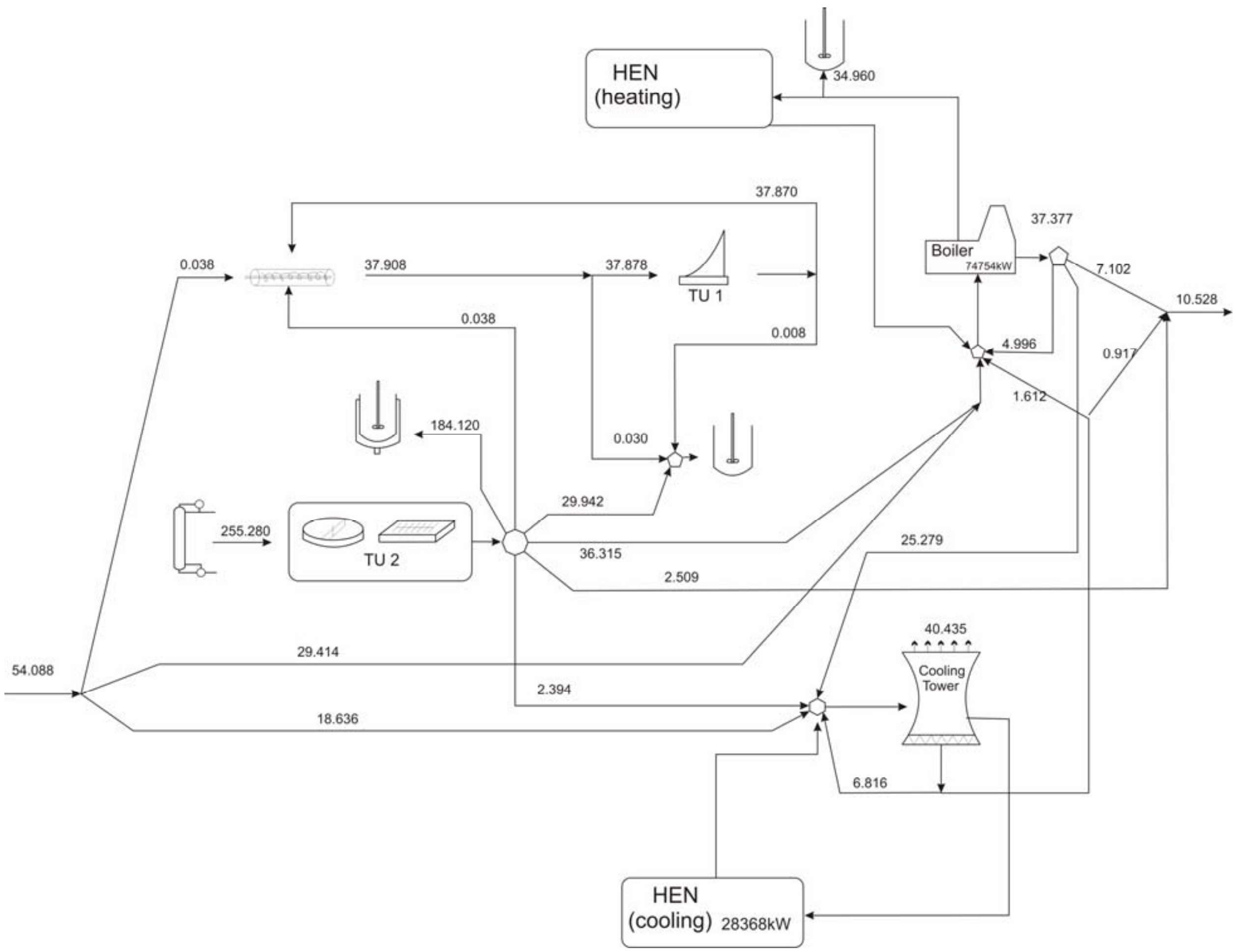


Figure 11. Water network for the production of ethanol from lignocelluloses via hydrolysis

5.2.2.5. Thermo Chemical b (NREL comparison)

Finally, we used an optimal flowsheet using the same gasifier and synthetic technologies as the ones presented by the NREL from a previous paper by the authors [42] to design the optimal water network. In this case, the scrubber generates two types of contaminants (solids and organics). The optimal flowsheet developed by Martin and Grossmann[42] shows a smaller impact when the air cooling technologies are implemented due to the energy optimization. The implementation of air cooling reduces 20% the cooling needs versus the 60% reduction in the case of the NREL based process. The freshwater needs after energy optimization and the implementation of air cooling technologies are 87.534 t/h for a 3.3 $gal_{water}/gal_{ethanol}$ also in the range of the current corn based ethanol plants.[8] The water discharged to the environment is 5.964 t/h. Figure 12 shows the optimal water network.

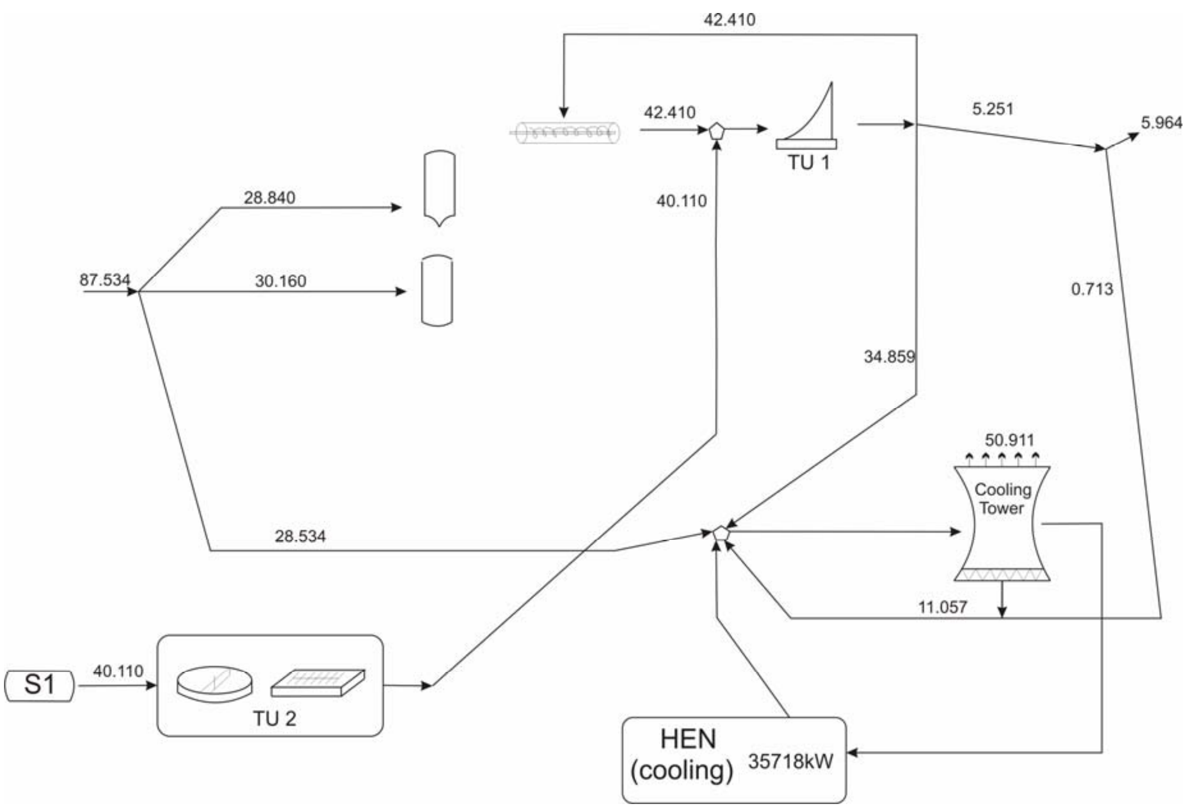


Figure 12. Water network for the optimized case of the production of ethanol NREL process.

6.-Results and discussion.

Figure 13 summarizes the water consumption before and after the implementation of air cooling (first two columns of each group). As we mentioned before, air cooling is only interesting for gasification based processes due to the high cooling needs in the inter-compression stages. Furthermore, most of the processes evaluated show values of water consumption below the one reported for gasoline production. However, some of the values are somehow misleading. The cooling requirements for the thermo-chemical and thermo-biochemical processes not only account for the production of ethanol, but also for the production of a significant amount of hydrogen. In order to compare with the other ethanol production plants we should also consider the water consumption and cooling requirements of hydrogen production plants from the gasification of raw materials. Martin & Grossmann[85] optimized the production of hydrogen from biomass. Using the data regarding the cooling needs and the water consumption for the optimized production of hydrogen, we can also discount that amount to show the net cooling requirements for ethanol production only. Using this idea we discount the water consumed for the production of hydrogen. In this way it is possible to determine the consumption of water just for the production of ethanol as shown in the third column of each group in Figure 13. It can be seen that the water consumption for producing ethanol is lower than the amount needed to produce gasoline in most of the cases, particularly for corn-based ethanol plants. On the other hand, the most promising process for producing ethanol from lignocellulosic biomass from the water consumption standpoint consists of the hydrolysis of the biomass and the fermentation of the liberated sugars into ethanol with a total consumption of 2gal/gal, while the reported values in the literature range from 1.94 (hybrid poplar)[52] to 5.9-9.8 (Switchgrass).[51] In the case of the thermo-chemical plants, the water consumption reported in the NREL report (based on hybrid poplar)[40] only accounts for the water that is lost in the cooling tower and the boiler.

The water discharged from the processs is summarized in Figure 14 whether we use air cooling or not. It turns out the large amounf of water used in the case of the production of ethanol via gasification allows dilution of the streams so that water can be recycled. In the case of processes with lower consumption, water is discharged due to the high cost of treating TDS.

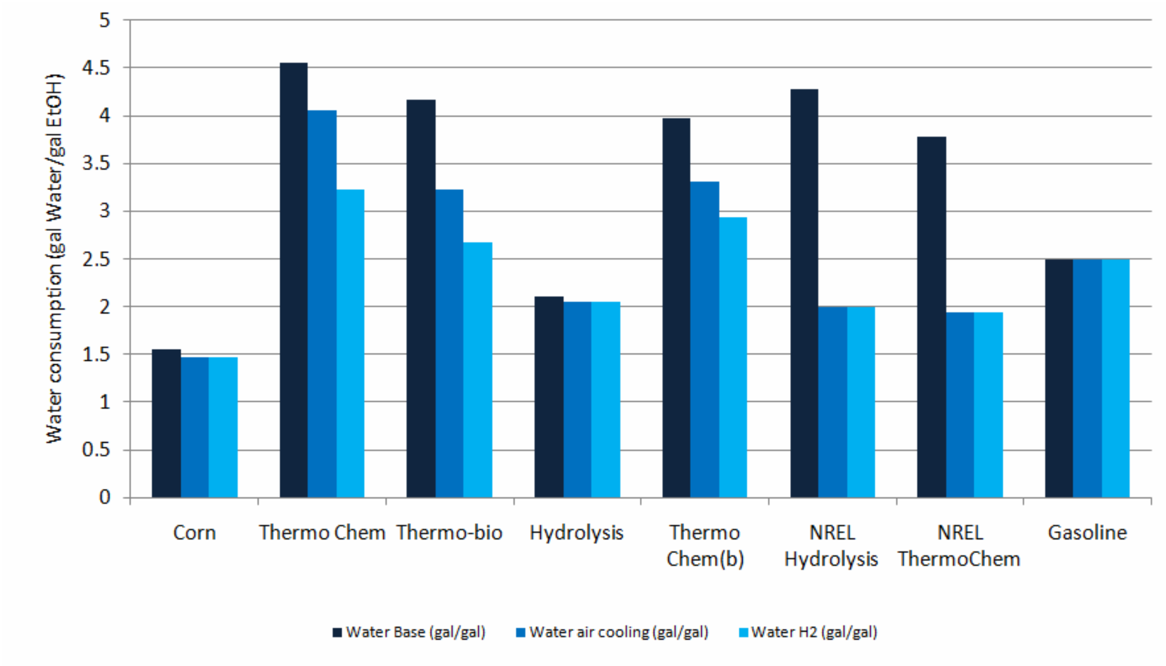


Figure 13. Water consumption.

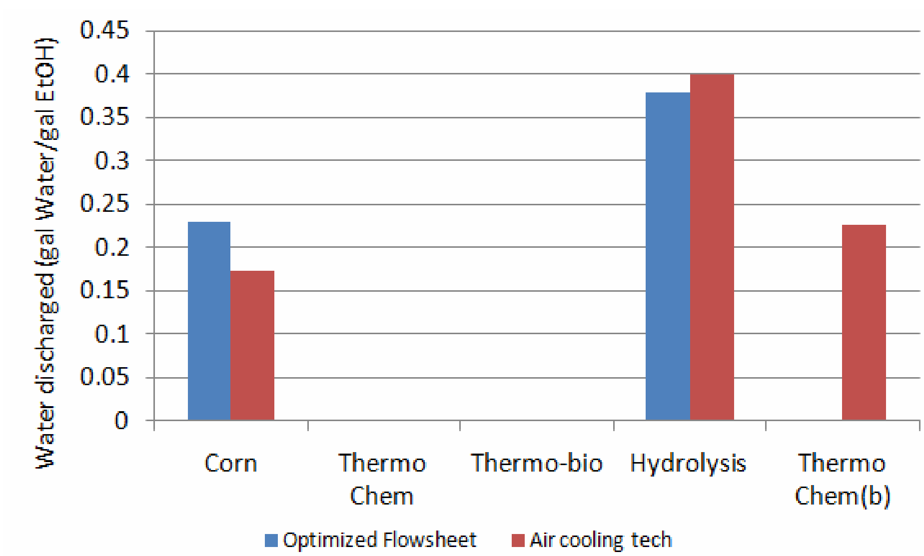


Figure 14. Water discharge

It is possible to reduce the water consumption even further. If for the case of the thermo-chemical process we extend the use of air cooling not only for condensers of the distillation columns and compression stages but for any other equipment so that cooling water is only used below 40ºC, only 21MW need to be removed using cooling water. Thus, it should be possible to reach water consumptions levels of 2 gal/gal. If the water used in the production of hydrogen is discounted, the net water consumed is 1.23 gal/gal. These processes also present no discharge. For the case of the hydrolytic based process, extending the use of air cooling such that water is used to cool down below 40ºC requires removing only 29 MW with which water consumptions as low as 1.66 gal/gal can be obtained (discharging 0.52 gal/gal). In the case of the thermo-biochemical process, cooling water is used to remove 21 MW and the water consumption can be reduced even further to 2.01 gal/gal (discounting the water consumed in the production of hydrogen) with a discharge of 0.03 gal/gal. Although a promising value, it is higher than the ones claimed by Coskata which is in the range of 1 gal/gal.[51] Finally, in the case of corn based ethanol, water consumption can be as low as 1.17 gal/gal since only 14MW of heat must be removed using cooling water. However, the discharge almost doubles, increasing from 0.17 gal/gal to 0.27 gal/gal due to the fact that lower water available within the network is not capable of diluting the blowdowns which are discharged since the cost of removing TDS using reverse osmosis is high.

Finally, there is another source of water in the thermo-chemical and thermo-biochemical processes that we have not considered yet because its composition is complex. It is the water that is released from the mechanical drying of the crop. This water cannot be recovered in case of using a dryer with air or flue gas instead of a mechanical press. When using a mechanical press, by compressing the biomass the water leaves with salts and other components. We assume that these contaminants can be removed using a combination of the aerobic and anaerobic treatment. Thus, the results for water consumption and discharge, after discounting the water used for hydrogen production, are presented in Figure 15. Values from 0.58 gal/gal, in the case of the corn-based process, to 1.66 gal/gal in the case of the hydrolytic based one, were found well below the water consumption for the production of gasoline.

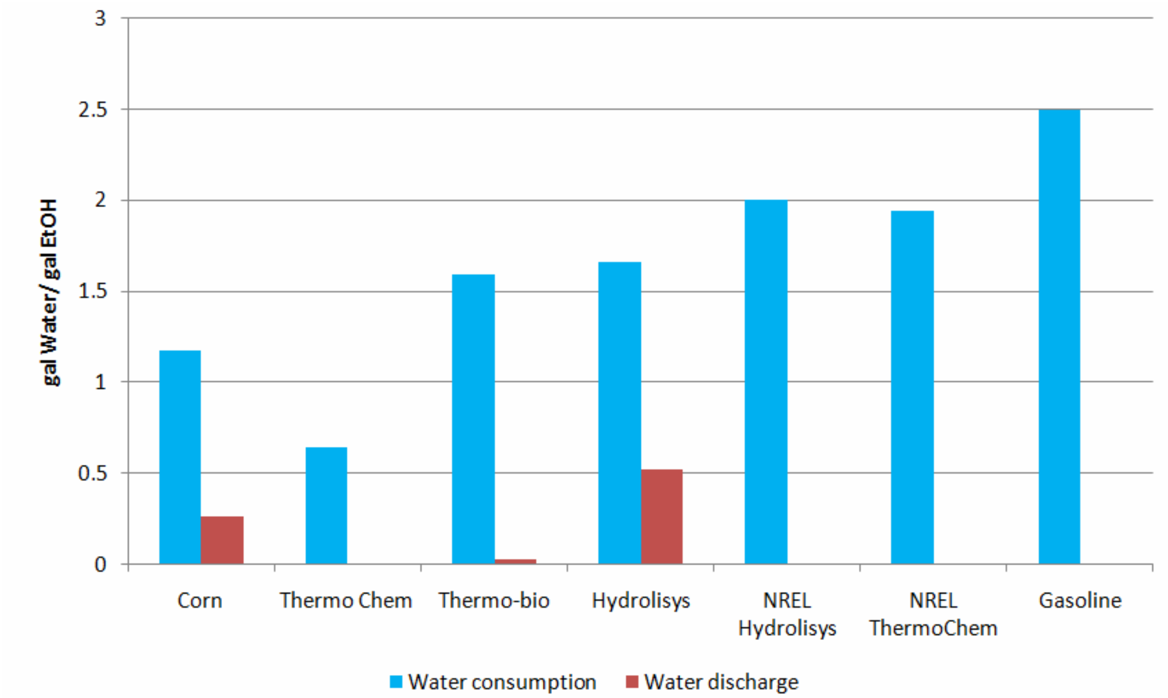


Figure 15.- Minimum water consumption and discharge in ethanol production processes

7. Conclusions.

In this paper we have studied the water consumption of different bioethanol production plants from corn and switchgrass. Water consumption in bioethanol plants can be reduced by energy optimization, by the use of technologies that substitute water as a cooling agent together and by recycling and reusing process and cooling water and steam. A superstructure optimization approach has been used to develop the optimal conceptual designs of water networks for different bioethanol production processes yielding water consumption values in the range of the ones required for gasoline production.

We have shown that by optimizing the energy consumption, implementing cooling water saving technologies and treating and reusing the water within the process, the water consumption falls below the one required for the production of gasoline for all the cases studied. However, in terms of water discharge the biochemical processes from corn or lignocellulosic materials show higher discharges due to the lower water flowrates within the water network and the high cost of treating certain contaminants. On the other hand, thermal based processes have more water in the network which allows contaminant dilution and lower water discharge. In these cases, the use of air cooling is recommended in order to keep the freshwater consumption at reasonable levels.

In order to further reduce water consumption a number of alternatives should be pursued. First, cooling technologies that do not use water as cooling agent should be extensively studied and implemented to reduce the use of cooling towers. Next, cheaper and more efficient treatment technologies must be developed. Finally, the optimization of the operation of the cooling towers must be addressed, since it represents the equipment with highest water losses. Very promising values can be obtained, from 0.6 gal/gal to 1.7gal/gal, below the water consumption for the production of gasoline.

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Appendix 1: Cooling tower

The cycles of concentration (COC) are defined as the ratio of the concentration of salts or dissolved solids in the circulating water or blowdown to that in the makeup water [71,72]. In industrial practice, the cycles of concentration normally range from three to seven, and they are important in the design and operation of cooling towers[73]. Fig. A1 shows a closed loop of circulating water between the heat exchanger network and the cooling tower.

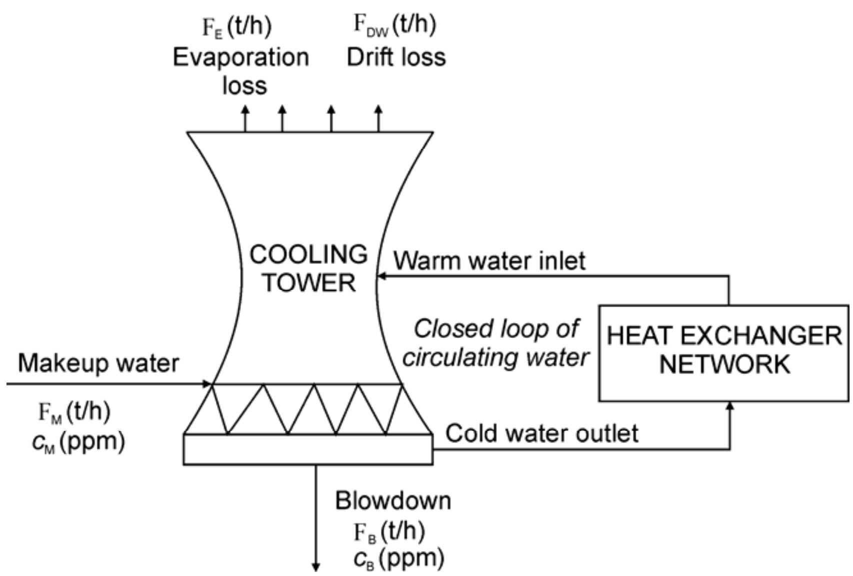

Figure A1. Closed loop for circulating water in cooling tower system.

From the cooling requirements in the heat exchanger network (heat rejected in cooling tower) $Q_C(kW)$, the flow rate of circulating water F_{REC}, in the cooling tower and heat exchanger network can be calculated from the equation:

$$Q_C = F_{REC} \cdot c_{p,W} \cdot \Delta T \qquad \text{(A.1)}$$

where c_p = specific heat capacity of water (kJ/(kg ºC)), ΔT= temperature difference between inlet and outlet water in cooling tower (ºC).

To calculate the evaporation loss in the cooling tower, which is the amount of water evaporated in the tower, an empirical correlation that is often used is the one by Perry and Green[71]:

$$F_E = 0.00085 \cdot \Delta T \cdot F_{REC} (m^3 / h) \cdot 1.8 \qquad \text{(A.2)}$$

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. New developments in the drift-eliminator design make it possible to reduce drift loss below 0.1 percent [71] to values of 0.005 %[74] By reducing the drift it is possible to further reduce the global consumption of water. A value of 0.1 is considered in the calculations.

The makeup requirements for the cooling tower consist of the evaporation loss, drift loss, and blowdown:

$$F_M = F_E + F_{DW} + F_B \qquad \text{(A.3)}$$

As mentioned earlier, the cycles of concentration (COC) are the ratio of the concentration of salts or dissolved solids in the circulating water/blowdown c_B (ppm) to that in the makeup water c_M (ppm).

$$COC = \frac{c_B}{c_M} \qquad \text{(A.4)}$$

Appendix 2: Boiler

Fig. A.2 shows a simplified utility system consisting of a boiler, heat exchanger network (steam-using operations) and deaerator. For simplicity we assume that a single level of steam is generated.

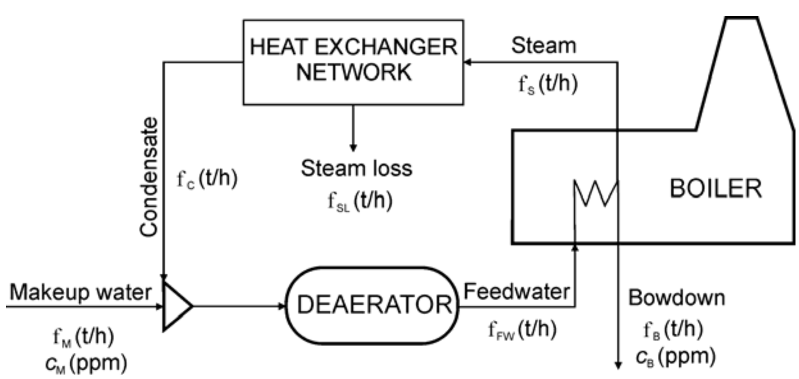

Figure A2. A simplified boiler system.

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 f_{SL} in the heat exchanger network, the flow rate of generated steam in the boiler and returned steam condensate is the same, $f_S = f_C$. In addition, makeup requirements for the boiler system will be equal to the discharged blowdown.

According to this water balance for the boiler system, the mixer, and the heat exchanger network is given by the equations:

$$f_M = f_{SL} + f_B \tag{A.5}$$

$$f_{FW} = f_M + f_C \tag{A.6}$$

$$f_S = f_{SL} + f_C \tag{A.7}$$

$$f_B = \frac{1}{COC - 1} f_S \tag{A.8}$$

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 [76]. Assuming the simplified utility system in Fig. A2, the generated steam in the boiler can be calculated from the heat requirements in the heat exchanger network.

$$Q_H = f_S \cdot \Delta H_v \tag{A.9}$$

where ΔH_v=latent heat of steam condensation (kJ/kg) for a given temperature and pressure.

In order to control the buildup of contaminants in the closed boiler system, the blowdown has to be discharged and fresh makeup water supplied to the boiler so that none of the contaminants exceeds its limit.

Appendix 3. Cost correlations

$$C_{Coolingtower} = 3229 \cdot (E(kW))^{0.59} \quad \text{(A.10)}$$

$$C_{Furnance} = 2328.3 \cdot (E(kW))^{0.7} \quad \text{(A.11)}$$

$$C_{Screens} = 10085 \cdot A(m^2)^{0.43} \quad \text{(A.12)}$$

$$A = \frac{Q(m^3/s)}{v(m/s)} \quad \text{(A.13)}$$

v(m/s)=1.6 (depends on sedimentation velocity)

$$C_{Screens} = 4750 \cdot (m(ton/h))^{0.43} \quad \text{(A.14)}$$

$$C_{\text{biological treatment}} = C_{\text{Aeration tank}} + C_{\text{Anaerobic treatment}} \cong 1500(m(ton/h))^{1.13} \quad \text{(A.15)}$$

$$C_{RO} = 3024 \cdot m(ton/h) \quad \text{(A.16)}$$

The annualized factor for investment on the treatment units (AR) is taken to be 0.1, and the total time for the network plant operation in a year is assumed to be 8640 h.