On the systematic synthesis of sustainable biorefineries

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Abstract.

In this paper, we review the current effort towards the design of production processes from different sources of biomass including first, second and third generation of biofuels such as bioethanol, biodiesel, hydrogen, FT-diesel. We review results of the design of these processes using mathematical programming techniques to systematically evaluate a large number of alternative technologies, by optimally integrating the use of raw material, energy and water in order for the process not only to be economically feasible but also sustainable. Integration of processes is the future of biorefineries to exploit synergies to reduce the production cost.

Keywords: Bioethanol, Biodiesel, Hydrogen, Mathematical programming.

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1.-Introduction

The production of biofuels has become a short and medium term solution to the increase in the demand for fuel in the transportation sector due to their compatibility with the supply chain of the crude based fuels as well as with the current automobiles, which can use biodiesel, bioethanol or a blend with crude based fuels with few or no changes in their design. However, the first generation of ethanol and biodiesel, based on the use of raw materials such as sugar, corn or wheat grain or vegetable oils, presented a number of ethical problems related to the use of the raw materials for food or fuel as well as the competition for the use of land devoted to the production of those raw materials. Those concerns, largely due to social pressure, have been addressed in the second generation of biofuels, which use waste from the forest industry, cooking oil, lignocelluslosic raw materials or third generation, biofuels based on algae.[1-3] However, there are also concerns on the actual sustainability of the production process of biofuels mainly due to the consumption of energy and water. While energy consumption has always been a top priority in any production process as a result of its direct impact on the production cost, water consumption has also become a major concern due to its increasing shortage in certain parts of the world. For instance, some of the first generation bioethanol production facilities could not operate in the mid-West of the US due to the shortage of this relatively cheap utility. The studies from the first production facilities for ethanol using corn have not been encouraging since they report large values of water and energy consumption compared to the production of crude based gasoline.[4-6] Therefore, the operation of the first generation of bioethanol plants has presented a series of challenges that also put to the test the design of the processes for second generation of biofuels. However, there are still reasons for optimism. The first biorefineries for the production of bioethanol[4] and biodiesel were designed without making use of tools long applied in the petrochemical industry. More recently, the use of case study based simulation has provided a more systematic approach to the evaluation of the process and its economics. [7-13] However, bioprocesses pose special features such as exothermic fermentation reactions that operate at low temperature and are not a source of heat as in traditional petrochemical plants. Furthermore, bioprocesses tend to require a large amount of water or large energy demand in distillation columns for separating highly diluted mixtures. All these pose an important number of challenges[14] that require the use of advanced process synthesis and optimization methods in order to ensure that these processes are economically viable, energy efficient

and with minimum environmental impact. Therefore, an improvement in the water and energy efficiency of biofuel production processes is expected so long as systematic methods are used.

To introduce the available systematic techniques for process design, integration and optimization, we first briefly review the advances in the area of process systems. Process synthesis is a relatively new area within Chemical Engineering that deals with the selection of the topology of a process in order to convert a set of inputs into a desired set of outputs.[15] The objective is to find designs with minimum cost or maximum profit, even though objectives such as maximizing efficiency or minimum usage of a resource (e.g. energy or freshwater) can also be considered. Major approaches to synthesize optimal process flowsheets that meet the desired objectives include the use of heuristics, physical insights (commonly based on thermodynamics and first principles), and the optimization of superstructures of alternatives. Major contributions in the first two approaches have been the hierarchical decomposition[16] and the pinch analysis[17] that has proved to be very successful in industrial applications. The more recent trend has been to combine some of these concepts with the mathematical programming approach,[18] which consists of three major steps. The first is the development of a superstructure representation of alternatives from which the optimum solution is selected. The second is the formulation of a mathematical program that generally involves discrete and continuous variables for the selection of the configuration and operating levels from the superstructure. The third is the solution of the optimization model (commonly a mixed-integer nonlinear programming, MINLP, or a generalized disjunctive programming, GDP, model) from which the optimal solution is determined. While superstructures can be developed in a systematic way for subsystems, e.g. for heat exchanger networks (e.g. see Yee and Grossmann[19]), their development for general process flowsheets is more complex,[20] and graph theory has also been applied to this task.[21] Chemical and physical principles and engineering know-how of the process must be understood to postulate alternative technologies for carrying out the transformations. As for the problem formulation, it is important to note that synthesis models can be formulated at three major levels of detail: (a) high level aggregated models that are expressed in terms of major features like mass and energy flows (e.g. LP transshipment model for HEN by Papoulias and Grossmann[22]; NLP heat and mass exchanger model by Papalexandri and Pistikopoulos[23]; (b) short-cut models that involve relatively simple nonlinear models for cost optimization (investment and operating costs)

(e.g. MINLP heat exchanger networks by Yee and Grossmann[19] ; MINLP process flowsheets by Kocis and Grossmann[24]; (c) rigorous models that rely on detailed and complex models for predicting the performance of the units (e.g. MINLP synthesis of distillation sequences[25] and GDP models. [26]

It should be noted that at the level of process synthesis two major subproblems that have had major significance for sustainability are optimization of energy recovery and water management. Here the calculation of the minimum utility cost can be determined with the LP model by Papoulias & Grossmann[22], while the specific network can be synthesized with the MINLP model by Yee and Grossmann.[19] Furthermore, the simultaneous optimization and heat integration of a process can be modeled with the constraints by Duran and Grossmann.[27] However, this method is restricted to nonisothermal streams. Grossmann, Yeomans, and Kravanja[28] have extended this model for handling isothermal streams that undergo change of phase using a disjunctive programming approach. On the problem of synthesizing water process networks, there has been significant work reported in the literature using both pinch (Wang and Smith[29]) and mathematical programming approaches (e.g. Karuppiah and Grossmann[30]), for reviews see Bagajewicz,[31] Bagajewicz and Faria,[32] Jezowski.[33] Since the pinch approach is restricted to problems with a single contaminant, the mathematical programming approaches have emerged as the preferred choice in water networks. These models, aside from optimizing the cost, have as major goal to minimize the consumption of freshwater. Ahmetovic and Grossmann[34] have recently developed a model that allows the handling of multiple sources of freshwater, recycle in units, and sources of sinks of water in a process, while allowing to control the complexity of the network by limiting the number of piping connections with 0–1 variables.

Finally, it should also be pointed out that systematic methods for synthesizing separation systems have also had a very important role to play in the design of sustainable chemical processes. At this point there are still very few papers that have reported the use of process synthesis techniques with the explicit incorporation of sustainability issues.[35-39] Some of them have applied optimization methods to the molecular design of solvents and the synthesis of the associated separation processes,[40-41] and more recently, for the design of biorefineries as we show later in the paper[42-50] as well as integrating the different processes for the optimal operation of biorefineries.[51-55]

In this paper we review the design of sustainable biorefineries from different raw materials such as corn, for the production of first generation bioethanol, lignocelluslosic materials, second generation of biofuels or cooking and algae oil, second and third generation of biodiesel. The study of these processes using a systematic approach based on mathematical programming techniques allows defining benchmarks for comparing different biofuels in terms of energy and water consumption so as to address concerns on sustainability of the production of alternative fuels. Furthermore, this approach also yields production and investment costs evaluating tradeoffs as well as evaluating the production of byproducts that may be of interest within the biorefinery complex such as fertilizers, hydrogen and glycerol.

2.-Background on biofuel production processes.

The history of the biofuels is linked to the automobile industry since the very beginning back in the 19th century. In 1876, Nicklaus Otto invented the internal combustion engine. Otto's engine mixed fuel and air before their introduction to the cylinder. A flame or spark was used to ignite the fuel-air mixture. The combustion engine was adopted by the automobile industry making use of ethanol as fuel. The first car produced in an assembly line, the ford Model T (1908-1927), can be also regarded as the first flexible fuel vehicle since it had an adjustable carburetor so that the car could be run on gasoline, ethanol or a blend. Furthermore, by the time the Diesel engine was patented in 1893, Rudolf Diesel stated, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time".[42] In fact the diesel engine was originally conceived for the use of peanut oil. Biofuels are in fact gentler with the engines due to their cleansing or detergent effect resulting in cleaner filters, strainers and nozzles, which improve the combustion efficiency and also because of the absence of sulfur in the fuel. However, the ready availability of crude based fuels displaced the use of biofuels for decades, and the use of renewable resources was focused more on pulp and paper production from wood, saccharification of wood, nitration of cellulose for guncotton and viscose silk, production of soluble cellulose for fibers, fat curing, and the production of furfural for Nylon.
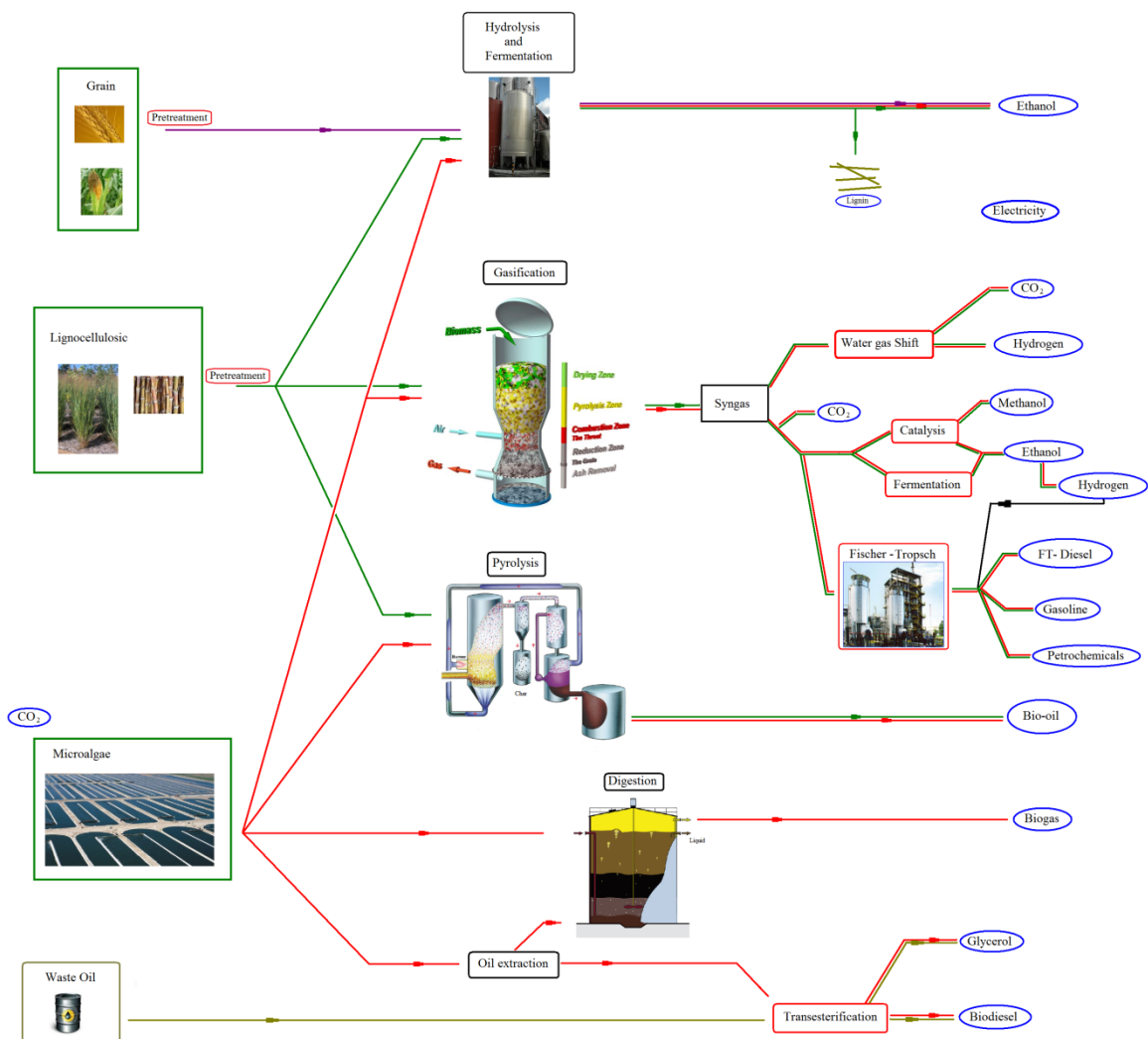
Figure 1.-Raw materials and technologies for production of biofuels

Nowadays, the increasing shortage of energy resources and the increasing demand and dependency on fossil fuels, as well as the growing concern about the environment, have led to consider alternative and renewable energy sources. Presently, the entire world is on a race for developing alternative energy resources which must be cheap, renewable and do not cause pollution, and whose emissions can be regarded as being neutral. In the case of the transportation sector, the most challenging one due to the need for high density energy sources, only biomass provides an alternative that can be implemented in the short-term.[56] Thus, bioethanol and biodiesel have become the most promising alternatives. Today's biorefinery technologies are based: (1) on the utilization of the whole plant or complex biomass, and (2) on integration of traditional and modern processes for utilization of biological raw materials. Figure 1 provides an overview of the different processing

alternatives using biomass and waste as raw material and possible process integration. In the next sections we present the evolution of the biosources of fuel and the effort towards reducing energy and water consumption for the production of ethanol, biodiesel and other biobased fuels from first, second and third generation of raw materials, as well as the contribution of systematic design to design the production processes.

3.-Synthesis of biofuel production processes.

3.1.-Corn and sugar cane based bioethanol: First generation bioethanol.

The production of ethanol from corn or sugar cane has been around for many years,[57] particularly in the US and in Brazil. In Brazil sugar cane accounts for three quarters of the feedstock used to produce ethanol and covers 50% of the country's transportation needs.[58] The production process from sugar cane is simple because once the sugar is extracted from the cane it can be directly fermented to obtain ethanol. Fermentation occurs with the addition of yeast and the ethanol is recovered through distillation and dehydration.[59,60] The production of ethanol from sugar is limited to regions where sugar cane is widely available and easy to grow, and those are directly related to the proper climate and water availability. In the United States, alcohol fuel was produced in corn-alcohol stills until the production of ethanol was prohibited in 1919.[61,62] Later, ethanol was used as a fuel during the WWII for domestic army vehicles. However, the low prices and availability of oil after the war made the government to abandon the use of ethanol. The use of ethanol came to light again in 1957 due to the production of a cheap sweetener, high-fructose corn syrup (HFCS), which is produced by the corn wet milling process. The prevalence of this sweetener in the market in 1974 generated a need for finding a market for the ethanol, which is a byproduct of this process. Currently only 5% of the ethanol produced follows the wet milling process while 95% is produced using the dry grind process.[7]

For quite some time corn based ethanol was deemed to have a negative net energy balance[63] and a vigorous debate took place between various authors and the USDA[64] on whether the production of corn-based ethanol was reasonable. Table 1 presents a summary of the values for energy consumption reported in the literature.

Table 1.- Energy consumption in corn-based ethanol plants

Author (year)	Energy consumption (Btu/gal)
Pimentel (2001) [65]	75,118
Keeney and DeLuca (1992) [66]	48,470
Wang et al. (1999) [67]	40,850
Shapouri et al. (2002)[64]	51,779
Wang et al (2007) [68]	38,323

Karuppiah et al.[43] considered the energy optimization of the "dry-grind" process. In such plants, fuel ethanol is produced using corn-kernels as the feedstock. Fuel grade ethanol has to be very close to 100% pure before it can be blended with gasoline for its use in automobiles. However, conventional distillation columns produce an azeotropic mixture of ethanol and water (95% ethanol–5% water, %w/w), which has to be purified further for making fuel ethanol. The main challenge in the way of producing fuel ethanol commercially is that the process is very energy intensive, and requires large amounts of steam for use in the rectifiers to obtain an azeotropic mixture of ethanol and water, and requires the use of expensive molecular sieves to obtain 100% pure ethanol. Karuppiah et al.[43] developed a simplified model to predict the performance of the bio-ethanol flowsheet that includes grinding, scarification, fermentation, centrifugation and drying operations (see Fig. 2). A limited superstructure was also postulated in which some of the major alternatives include separation by molecular sieves and/or corn grits, and different ways to accomplish the drying for the dried grains solids either before or after the beer column, a by-product used as cattle feed. The objective was to optimize the flowsheet, determining the connections in the network and the flow in each stream in the network, such that the energy requirement of the overall plant is minimized. The MINLP optimization model without heat integration led to a decrease of the manufacturing cost from $1.50/gal (base case) to $1.36/gal. In the next step heat integration was considered. However, it became clear that the scope of heat integration was limited by the relatively low temperature in the fermentor. In order to improve the potential for heat integration the authors considered multi-effect distillation in the "beer" column and in the azeotropic column as alternatives for the optimization (see Fig. 2). This finally led to a 65% savings in steam consumption, leading to an energy consumption of 22,000 Btu/gal (including electrical energy) and cooling water with a cost reduction down to $1.24/gal. Figure 6, which is shown later in the paper, shows the energy consumption and cooling needs of the process. This example

illustrates the potential for cost reduction in biofuel plants by using an optimization approach.
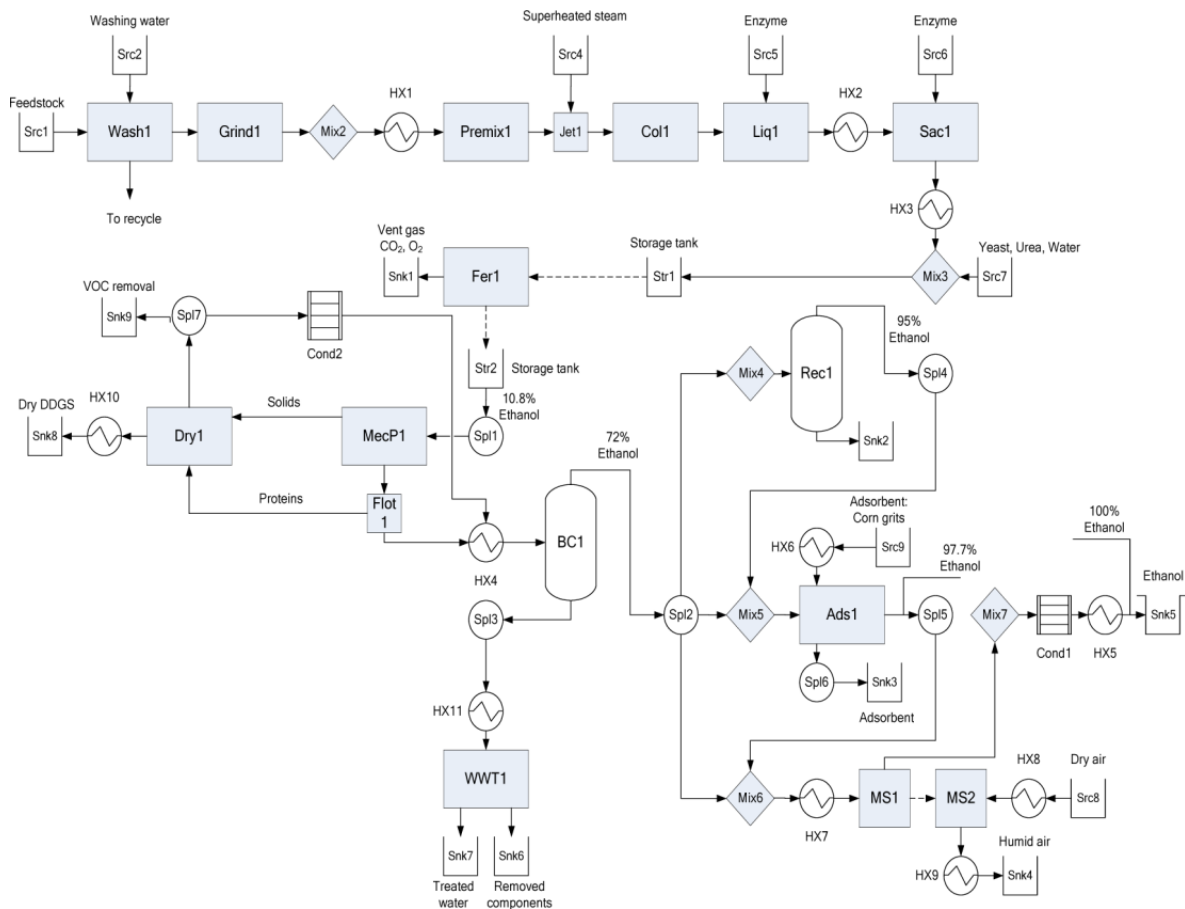
HX: Heat exchanger; Dry: Dryer; Fer1: Fermentor: BC: Beer Column; Rec1: Rectification column; Mix(i): Mixer; Spl(i): Splitter; MS: Molecular sieve; MecP(i): Mechanical Press.; Wash1: Raw Material Washing; Grind1: Grinding Unit; Col1: Column; Liq1: Liquefaction; Sac1: Saccharification; Src(i): Source; Snk(i): Sink; Cond(i): Condenser; Ads1: Adsorption;Flot: Flotation Unit.

Figure 2.- Corn based ethanol production process

However, sustainability is concerned for more than just energy consumption. Corn-based ethanol has been criticized not only for its energy balance, but also because of its high demand of water. The first data available in the literature regarding water consumption in ethanol plants reveal values from 3 to 15 $gal_{water}/gal_{ethanol.}$[69] Over the last decades there has been an improvement to reach the current industrial mean value for the newest plants of 3.4 $gal_{water}/gal_{ethanol.}$[4] Based on that, the suggested best possible water consumption for corn process is 2.85 $gal_{water}/galethanol.$[69,70] By developing the optimum water network for the cases in which Karuppiah et al.[43] optimized the energy consumption, it is worth pointing out that energy optimization plays a very important role in reducing the water consumption since the cooling needs are greatly reduced and so are the losses in the cooling tower. In this way, by coupling energy optimization and the design of optimal water networks, where waste water is treated and recycled, and using air cooling to

partially substitute water as cooling agent, the water consumption in the corn-based ethanol plant can be reduced down to only 1.17 gal$_{water}$/gal$_{ethanol}$ as seported by Ahmetovic et al.[71] see Fig. 7 later in the paper. This is lower than the data published in the literature while certifying the technical feasibility of the claims by the company Delta T, which has reported consumptions of 1.5 gal/gal.[72] Furthermore, the energy optimization and water network design also play an important role towards zero discharge of water achieving discharge values of 0.27 gal$_{water}$/gal$_{ethanol}$[73]. However, better and cheaper wastewater technologies are needed to reach the goal of zero discharge. Figure 3 shows the water network for this example. The main water loss is due to the evaporation at the cooling tower. While the water stream with solids is treated in the screen, TU1, and recycled, the fresh water and treated water at TU2, from the distillation columns is used to feed the different units demanding water such as the fermentor, the boiler or the cooling tower.
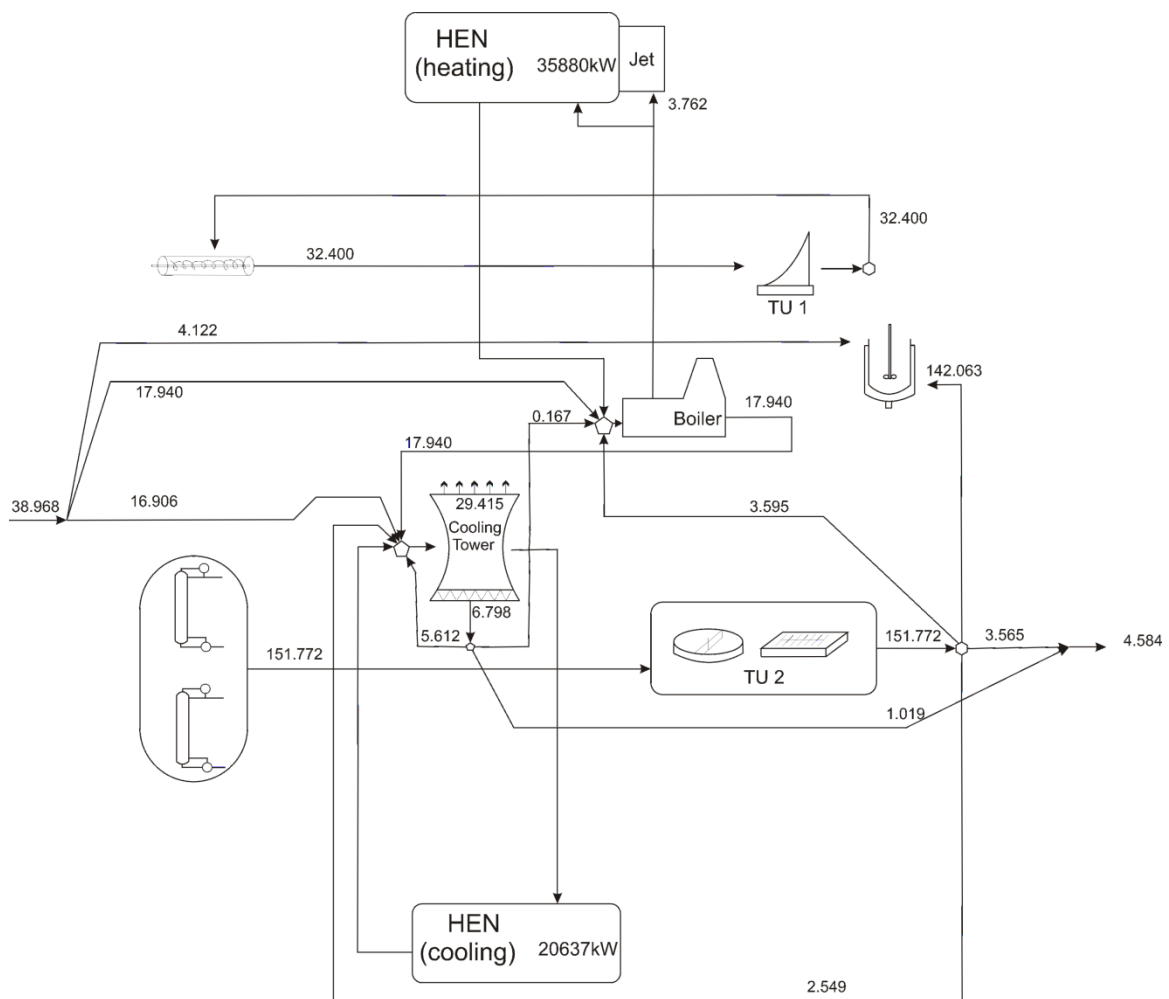

Figure 3.-Water network for the optimal production of corn base ethanol. Flows in t/h. TU 1: Solids removal. TU2: Secondary treatment for organics. HEN: Heat exchanger network.

3.2.- Lignocellulosic based biofuels

In this section we focus on ready to use biofuels that can substitute gasoline and crude based diesel directly, such as bioethanol, FT diesel and gasoline and the production of hydrogen due to the increasing importance of fuel cell technology.

3.2.1.-Second generation of bioethanol

Corn based ethanol has the disadvantage that it competes with the food chain in terms of the land needed for its growth as well as in the final destination of the grain. Thus, the second generation bioethanol has focused on overcoming this disadvantage by using lignocellulosic materials whose yield from the ground to the liquid fuel (see Fig 4[74-77]) is higher than that using corn, especially switchgrass, and that have smaller or even no footprint on the food supply chain. Among the wide spectra of lignocellulosic raw materials, the use of corn stover can be considered as a medium term case in which it is possible to take advantage of the already established corn industry, while the forest industry cannot be considered as a substitution for fuel in the long term, but only for the recycle and reuse of waste. Switchgrass, on the contrary, is a non-food related lignocellulosic raw material that can be produced in non-arable lands in most of the US territory with high yield to ethanol.

There are two paths to obtain ethanol from lignocellulosic raw materials, gasification or hydrolysis. So far detailed studies on the process from corn stover or hybrid poplar have been published, mainly by the National Renewable Energy Laboratory (NERL), for both paths using ASPEN as a process simulator.[8,10,78-82] In general, the similarity between the hydrolysis path and the first generation of bioethanol together with the lower investment cost compared to the thermal-based process has attracted the attention of many researchers. Martín & Grossmann[44,45] presented studies for gasification and hydrolysis of switchgrass based on superstructure optimization to evaluate a large number of alternatives in a systematic way using mathematical programming techniques.
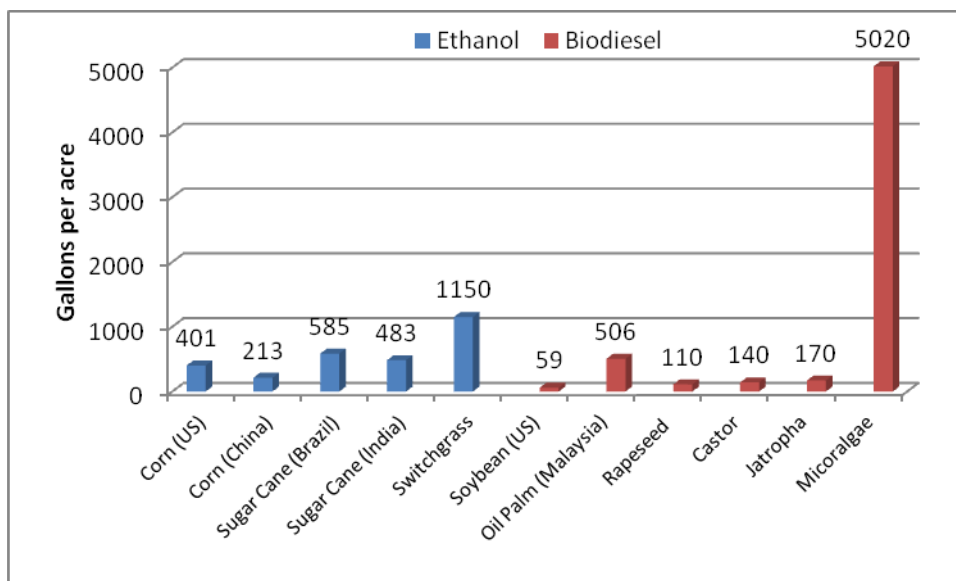
Figure 4.- Yield to ethanol and diesel form different raw materials[74-77]

a) Gasification

The NERL reports[10,78] and some academic papers[81,82] have evaluated the production of bioethanol from corn stover, wood chips or hybrid poplar through case studies using ASPEN as the simulation tool. Phillips et al.[10] and He & Zhang[82] considered indirect gasification, which allows the use of air since the combustion takes place in a different chamber, and mixed alcohols synthesis. On the other hand Dutta & Phillips[78] and Piccolo & Bezzo[81] evaluated the use of direct gasification, which requires oxygen to avoid the dilution of the syngas produced, but while Dutta & Phillps[78] selected mixed alcohols synthesis that takes place at high pressure and temperature allowing better energy integration, Piccolo & Bezzo[81] decided on the use of syngas fermentation. The different assumptions make difficult the direct compassion from one study to the other. The only pilot plant at the moment, which is by Coskata,[83] has selected gasification and syngas fermentation, while Abengoa is performing pilot plant studies on the biochemical process.[84]

In order to evaluate all these alternatives in a systematic manner, and to avoid the use of raw materials that do not offer a promising future, Martín and Grossmann[44] developed the optimal conceptual design of the production process of 60 MMgal/yr ethanol from switchgrass by optimizing the energy consumption of a superstructure that involves all the alternative designs considered so far plus a number of alternative cleanup technologies, see Figure 5.
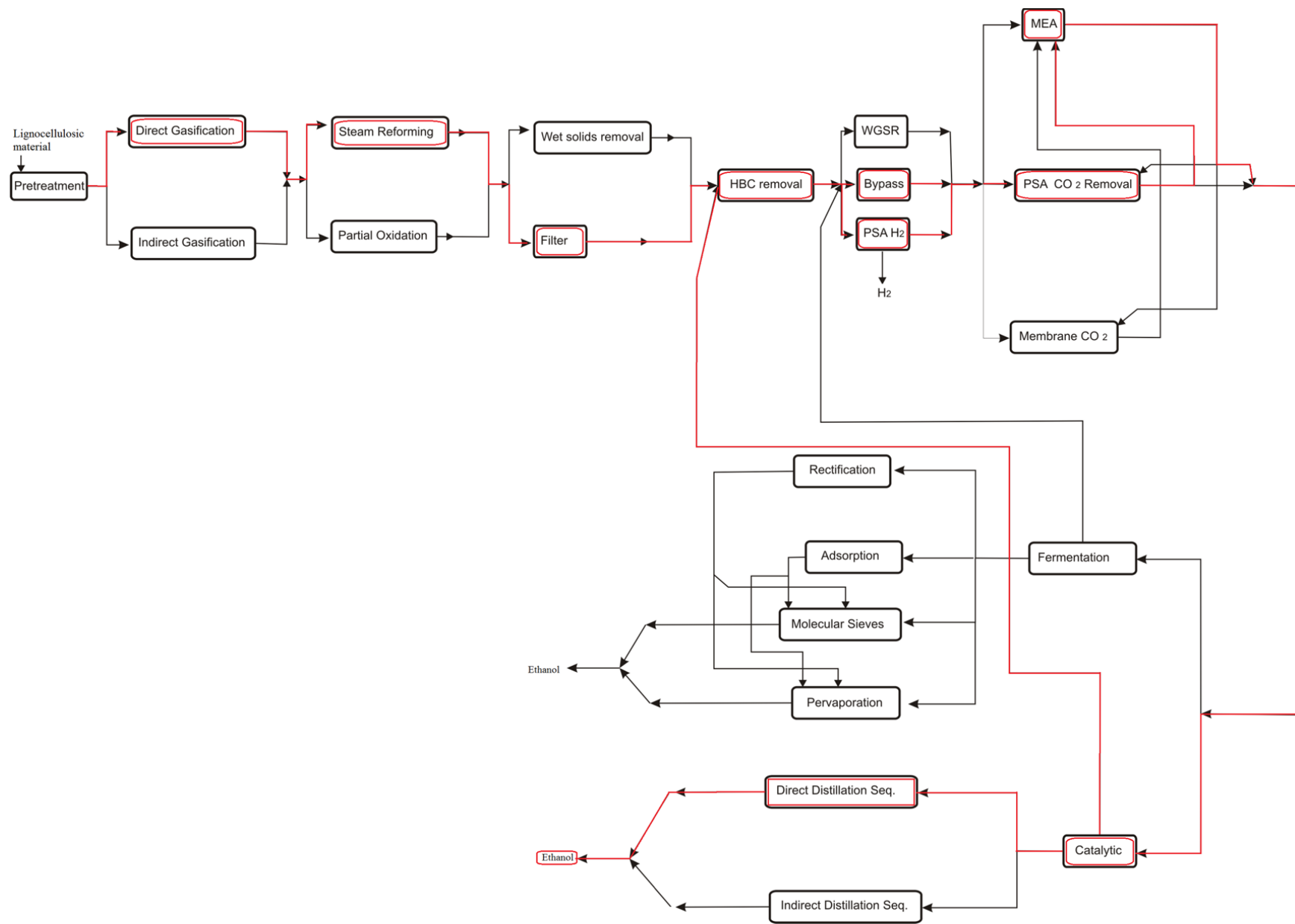
Figure 5.-Superstrucure for the production of bioethanol via gasification of biomass and optimal path

The process consists of four different parts: gasification (followed by gas cleanup), concentration adjustment, sour gases removal and ethanol synthesis and purification. Two alternatives are evaluated for gasification, indirect[10] (it allows the use of air since the combustions takes place in a second chamber and requires less steam but generates higher concentration of hydrocarbons) or direct (requires the use of pure oxygen to avoid syngas dilution, requires more steam but generates lower concentration of hydrocarbons).[78,85] The gas obtained is treated using either steam reforming (endothermic but with higher yield to hydrogen) or partial oxidation (exothermic allowing steam production but lower yield to hydrogen) to remove hydrocarbons, and subsequently it must be cleaned from solids as well as other compounds like NH_3 using either hot or cold cleaning. Next, the gas composition is adjusted to a CO/H_2 ratio of 1. Three technologies (bypass, membrane-PSA and water gas shift) are evaluated. Then, the removal of sour gases, CO_2 and H_2S, is required. Three alternatives, membrane separation (capable of removing CO_2 only), absorption in ethyl-amines (energy demanding process) and PSA (capable of removing CO_2 only) are considered for this task. Once the syngas is prepared, two synthetic paths are evaluated: (1) high alcohols catalytic process with two possible distillation sequences (direct and indirect), and (2) syngas fermentation followed by four possible dehydratation processes: distillation, water adsorption in corn grits, molecular sieves and pervaporation. The number of alternative designs is large, and thus systematic process design methods are a powerful tool to design the production process. The superstructure is modeled as an MINLP problem which is solved by partial enumeration of the integer variables in terms of gasification technologies, reforming modes and synthetic paths, generating 8 subproblems.[44] For each of the subproblmens the cleanup stages and separation processes are optimized to minimize energy consumption. Subsequently, multieffect columns and the design the optimal HEN are implemented in each of the subproblems. Finally, an economic evaluation to account for the contribution of hydrogen as byproduct, raw material consumption and utilities yields the flowsheet with lowest production cost that is shown in Figure 6. Figure 8 shows the energy consumption and cooling needs of the process.[44]
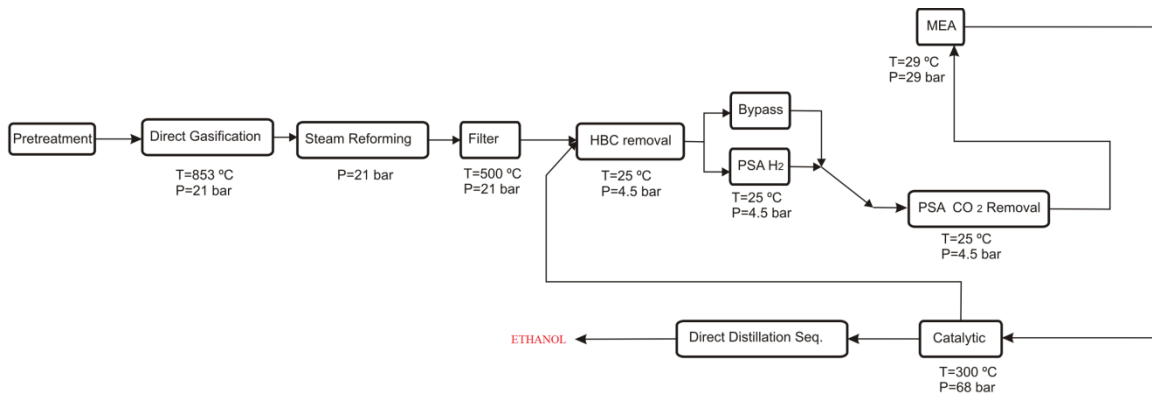
Figure 6. Thermo-chemical ethanol production from biomass

The most profitable process uses high pressure direct gasification, followed by steam reforming, which increases the production of hydrogen. The composition adjustment is carried out by removing the excess of hydrogen from the stream using PSA and membranes. Then sour gases are removed in two steps, PSA to remove CO_2 and MEA to get rid of H_2S. Finally, the catalytic path is selected followed by a direct distillation sequence. The facility for producing 60MMgal/yr of bioethanol generates 17 MW of energy and requires 70 MW of cooling. The production cost of this design turned out to be 0.41 $/gal due to the contribution of hydrogen as byproduct and the investment for the plant is $335 million. The fermentation path is not economically attractive due to the low concentration of ethanol in the reactor, which results in high consumption of energy to dehydrate the water-ethanol mixture. It is estimated that if the concentration of ethanol reaches values of 15%[44] this synthetic path becomes promising too. Several studies focus on increasing the concentration of ethanol in the fermentor by removing it from the liquid phase using adsorbents.[86]

Even though the comparison of these results with the literature is not entirely consistent, it is still useful. For example, Phillips et al[10] proposed the use of indirect gasification of lignocellulosic materials followed by steam reforming and high alcohols synthetic path reporting a price for ethanol of $1.22/gallon (with a reduction down to $1.01 /gallon due to byproduct credits) with an investment of $190 million for 2000 MT/day of dry biomass producing 60MMgal/yr of ethanol. He & Zhang[82] reported 0.19€/L also for the indirect gasification and autoreforming scenario. On the other hand, Dutta and Phillips[78] reported a price of $1.95/gallon for the use of direct gasification followed by steam reforming and high alcohols synthesis with an investment of $254 million for processing 2000 MT/day of dry biomass to produce 60MMgal/yr of ethanol. The use of

fermentation of the syngas has received industrial and academic attention, and Huhnke[87] reported the production of ethanol via gasification–fermentation at \$1.2 /gal, while Piccolo and Bezzo[81] reported 0.65 €/L. The Coskata process,[83] based also on the fermentation of syngas, claims production costs under \$1 /gallon for a pilot plant production scale, but none of these processes considers the possibility of obtaining hydrogen as byproduct.

The production process of ethanol from switchgrass via gasification requires a large amount of water in the form of cooling water, due to the high pressures and temperatures in the entire process, and in the form of steam to perform the gasification. Values of 5.9-9.8 $gal_{water}/gal_{ethanol}$ have been reported in the literature when using switchgrass as raw material,[5] or 2 $gal_{water}/gal_{ethanol}$ from hybrid poplar.[10] Due to the high cooling needs, some authors support the implementation of air cooling technologies to substitute part of the use of cooling water.[10] Making use of this technology after the energy optimization and heat integration, Martín et al.[73] presented the fact that it is possible to reduce the cooling water use to a total freshwater consumption below 1.5 $gal_{water}/gal_{ethanol}$. This value also accounts for the production of a significant amount of hydrogen which is produced in part due to the decomposition of steam. Discounting the water consumption due to the co-production of hydrogen in Fig. 9, the water consumption for the production of ethanol reveals a value of only 0.65 gal/gal.[73] There is no water discharge because the large amount of water circulating within the process allows enough dilution of the total dissolved solids (TDS) and reuse of the stream.

b) Biochemical

To produce ethanol from lignocellulosic raw material another route possible is the biochemical one. For that we need to pretreat the biomass, switchgrass, to expose the hemicelluloses and cellulose for further treatment, among the number of technologies for biomass pretreatment,[88] two methods have been found to be competitive for the 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[79,81,89,90,93] and (2) ammonia fibre explosion (AFEX). [80,88,91-92] Most of the papers either study the pretreatment, mainly from an experimental point of view,[89,88,91-82] or deal with the production of ethanol from the liberated sugars.[81,90] The most complete studies are the ones produced by the NREL,[79,80,93] where using a scenario based approach, they analyze the

production of ethanol from corn stover.[79,80,93] Even though this raw material is interesting as a bridge between first and second generation of bioethanol, the use of a hydrolytic path is sensitive to the composition of the lignocellulosic biomass, and thus it is not easy to apply it to any other raw material. Swichgrass is a promising lignocellulosic raw material in the US due to the production capacity in US soil. From the industrial point of view, currently Abengoa[84] is testing the biochemical path for the production of second generation bioethanol at large scale in their facility at Salamanca in Spain.

To evaluate different pretreatment and dehydration options, Martín & Grossmann[45] proposed an optimal conceptual design for ethanol production via hydrolysis of switchgrass by postulating a superstructure that embeds both pretreament alternatives (AFEX and dilute acid) together with hydrolysis of the biomass, fermentation of the sugars and four technologies for the dehydratation of ethanol (rectification, adsorption using corns grits, molecular sieves and pervaporation). By solving the MINLP model minimizing the energy consumption, the optimal flowsheet uses dilute acid pretreatment, which is cheaper and more environmentally friendly since it consumes less energy and requires less cooling water. The process consists of pretreating the switchgrass to reduce the particle size and break the physical structure. 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.[81,90,94-96] The sugars, mainly glucose and xylose, are fermented in water into ethanol. The reactions are different in terms of yield and velocity. The optimal temperature is 38 ºC so that both are fermented at the same time. A number of different products are obtained together with ethanol such as different acid products of the metabolic paths of the microorganisms used (*Z mobilis* bacterium).[81,90,96] 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 fuel grade quality. Next, heat integration is performed. Figure 7 shows the flowsheet from Martín & Grossmann,[45] while Figure 8 presents the energy consumption and cooling needs of the process.
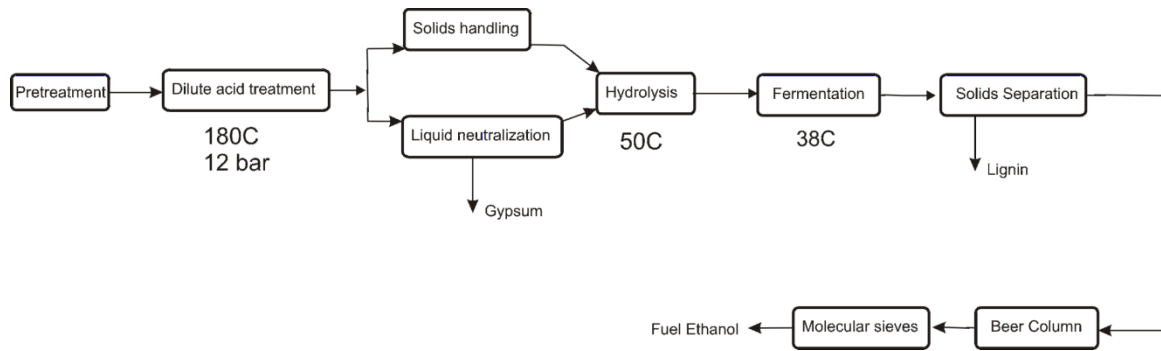
Figure 7.- Hydrolysis based production process of ethanol from switchgrass

The production cost reported in the literature for the acid/enzymatic hydrolysis process by NREL is $1.33 /gal from corn stover with an investment of $200 million for 2000 TM/day of dry biomass producing 60MMgal/yr of ethanol,[79] while others are more optimistic aiming at values lower that $1.10 per gallon ethanol.[87] However, a recent study by Kazi et al.[80] reports a production cost much higher than the ones in the literature based on the different price for the feedstock and the assumptions in the model (e. g. conversions, yield). The estimate of the current commercial scale for lignocellulosic materials is at $2.43 /gal with an investment of $156-$209 million for installed equipment and a total capital investment of $327-$501 million for 2000 MT/day of dry biomass to obtain 60MMgal/ty of ethanol. In Martin & Grossmann's study[45] a production cost of $0.8/gal is reported with an investment cost of $169 million for the same production rate.
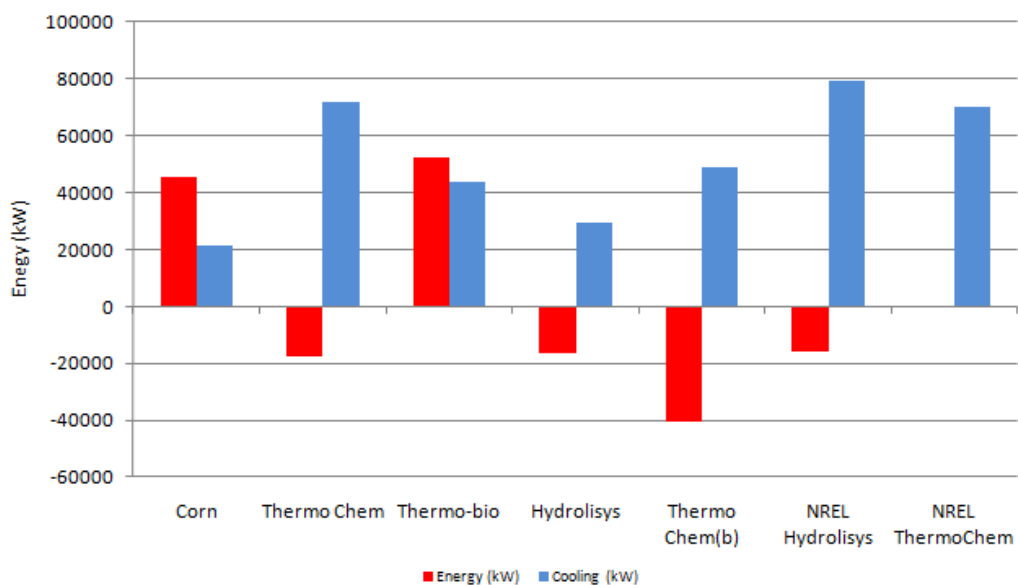

Figure 8.- Energy consumption and cooling needs for the ethanol production processes.
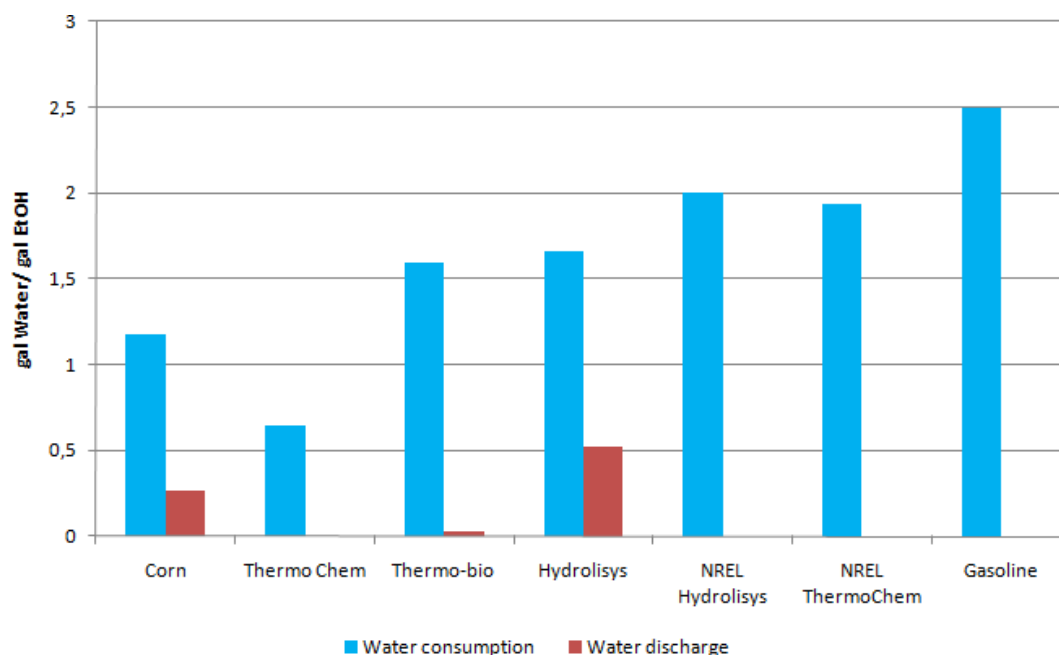
Figure 9.- Water consumption ethanol production processes.

The production of ethanol from hydrolysis is a more gentle process in terms of operating pressures and temperatures compared to the gasification process resulting in less than half the cooling requirements for the thermo-chemical process (see Figure 8). However, the lower temperatures prevent from an extensive use of air cooling to substitute water as cooling agent, while the exothermic fermentation at 38ºC prevents from good energy integration. The results in the literature show values of 2 $gal_{water}/gal_{ethanol}$.[69] By designing the optimal water network,[73] the total consumption of freshwater turns out to be 1.66 $gal_{water}/gal_{ethanol}$ (see Fig. 9) and wastewater is discharged, 0.52 $gal_{water}/gal_{ethanol}$, since the lower flowrates in the water network do not allow TDS dilution and the high cost of removing TDS results in discharging water instead of treating it.

3.2.2.- FT-diesel and green gasoline

Not only bioethanol can be produced from lignocellulosic materials but also diesel or hydrogen. The history of the Fischer-Tropsch synthesis can be traced back to the beginning of the 20th century, when in 1902 Sabatier and Senderens discovered that CO could be hydrogenated over Co, Fe and Ni to methane. Later in 1925 professor Franz Fischer, founding director of the Kaiser-Wilhelm Institute of Coal Research in Mülheim an der Ruhr, and Dr. Hans Tropsch reported synthesis of hydrocarbon liquids and solid paraffins on Co-Fe catalyst under mild conditions of 250-300°C. Fischer-Tropsch technology was extensively developed and commercialized in Germany during World War

II when it was denied access to petroleum-rich regions of the world. Likewise, when South Africa faced a world oil embargo during their era of apartheid, it employed Fischer-Tropsch technology to sustain its national economy. Fischer-Tropsch liquids can be refined to various amounts of renewable (green) gasoline, diesel fuel, and aviation fuel depending upon selected process conditions. Depending on the types and quantities of Fischer-Tropsch products desired, either low (200–240 °C) or high temperature (300–350 °C), and synthesis at pressures ranging between 10 to 40 bar, are used with either cobalt or iron based catalysts.[97] Despite the extensive work in Fischer-Tropsch technology using coal, not much work has been reported for the use of lignocellulosic raw materials mainly using a scenario based approach [13,98-101]. Tijmensen et al[99] used ASPEN to simulate the production of FT –fuels reporting investments of MM$ 280–450 for a production plant capacity of 366 MW. Swanson et al.[13] presented a simulation based study using ASPEN process simulator for the production of FT – diesel from the gasification of corn stover, syngas treatement, Fischer-Tropsch synthesis and hydroprocessing. The plant requires 300MM$ of installed cost (2000 MT/day of dry biomass) and produces FT-diesel at $4/gal. Tock et al [98] performed a techno-economical analysis for the production of liquid fuels including FT diesel, methanol and dimethyl eter from wood comparing a number of alternatives in a systematic way for a number of case studies of plant capacities and with fixed operating conditions at the main units. For the case of FT-diesel, they report from 19MM€ to 300MM€ for plant capacities from 20 MW to 400MW and production costs from 70 to 90 €per MWh of fuel.

Martín and Grossmann[102] proposed a superstructure embedding alternative technologies for the optimization of the production of FT-diesel from switchgrass. The process starts with the gasification of the biomass. Two different alternatives are evaluated, direct and indirect gasification. The gas obtained is reformed, cleaned up and its composition may be adjusted in terms of the ratio CO/H_2 for the optimal production of diesel fraction using up to three possible technologies (bypass, PSA and water shift). Next, the removal of CO_2 and H_2S is performed by means of two clean up processes such as absorption in ethyl-amines and PSA, see Figure 5 for this part of the flowsheet. Then the Fischer-Tropsch reaction is conducted and the products are separated. Hydrocracking of the heavy products is also considered to increase the yield towards diesel. Again, a number of alternative processes and trade-offs makes it difficult to propose a flowsheet without the help of a systematic approach. The optimization of the system is formulated as a Mixed-

integer Non-linear Programming (MINLP) problem where short cut models, reduced order models, design equations and mass and energy balances are used for the different units involved in the production process with special focus on the FT reactor, the hydrocraking unit and the CO/H_2 adjustment. The MINLP is solved for the optimal production of the FT-diesel fraction while minimizing the energy and hydrogen consumption. Energy integration and an economic evaluation are also performed.
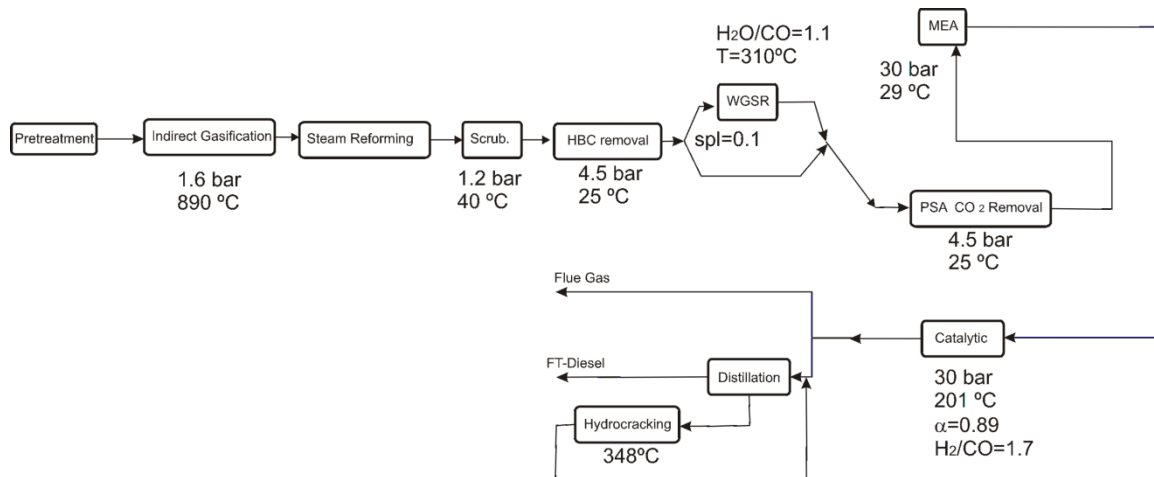

Figure 10.- Optimal flowsheet for the production of FT- Diesel.

The optimal solution requires the use of indirect gasification followed by steam reforming. The ratio CO/H_2 is slightly modified to match the experimental minimum, while adjusting the temperature of the FT reactor and of the hydrocracker to increase the biodiesel production results in a promising production cost of 0.73 \$/gallon and an investment cost of \$216 million for producing 60MMgal/yr of biofuels (green gasoline and diesel). Figure 10 shows the optimal flowsheet. For this design the consumption of water can be as low as 0.15gal/gal as long as air cooling is used together with water treatment, recycle and reuse.

3.2.3.-Hydrogen production

The syngas obtained from biomass is an interesting building block for a number of chemicals. In this paper, we do not describe the production of high value products like fine chemicals or polymers, but we focus on hydrogen. Hydrogen is a clean and renewable source of energy with the highest gravimetric energy density of any known fuel with the

advantage of zero carbon emissions that can be used for fuel cell powered vehicles, or as an intermediate needed in the production of crude oil-based chemicals.[103-105]

Hydrogen can be produced by generating syngas via gasification, cleaning up of the gas and shifting the energy value of the CO to H_2 using the water gas shift reaction (WGSR).[106-108] Recent studies have evaluated the production of hydrogen from gasification of biomass using a dynamic simulation approach,[109] or steady process simulation using ASPEN or HYSYS[102-113] in which the process technologies are fixed upfront in terms of gasification, either direct gasification[102,110] or indirect gasification,[111,112] steam reforming, gas clean up using PSA/scrubbers and water gas shit reaction[102-112]. The production costs reported in the literature from tree forest biomass in Western Canada are $1.14/kg of H_2 [114] while the NERL obtained values in the range of $1.18 –$ 1.78 /kg[111] and the only value they obtained below $1/kg resulted from assuming zero cost for the raw material. Lau et al.[110] obtained values form $0.65/kg -$1.33/kg for switchgrass depending of the plant size and similar values for other raw materials such as bagasse (0.75-1.50$/kg) or nutshell (0.90-1.33$/kg). For the near future the DOE suggests a price of $1.58 /kg, and in the long run this price is expected to decrease to $1.10/kg with the corresponding decrease in the investment from $150Million to $110 Million for treating 2000 ton/day of dry biomass.[112] In order to reduce the current production cost, a new reactor design, capable of separating the hydrogen produced through a permeable membrane has been proposed.[102, 115-118]

Martín and Grossmann[119] coupled the newly developed reactor design using membrane technology[102] with two different gasification technologies, direct and indirect gasification, and two reforming modes, partial oxidation or steam reforming creating a superstructure formulated as an MINLP. The tradeoffs to be resolved are that indirect gasification can use air and consume less steam but produces more hydrocarbons than the direct one, while steam reforming is endothermic with higher yield to hydrogen and partial oxidation which is exothermic and lower yield to hydrogen. The operating conditions in the gasifiers and at the WGSR are optimized for hydrogen production in each of the four alternative technologies while minimizing the energy consumption. Next, energy is integrated to design the heat exchanger network. Finally, an economic evaluation is performed to determine the production cost. It turns out that indirect gasification with steam reforming is the preferred technology providing higher production yields (0.13 $kg/kg_{dryBiomass}$) than the ones reported in the literature for hydrogen from natural gas and at

a lower and promising production cost of 0.68 $/kg with an investment cost of $148 million. Figure 11 presents the block flowsheet diagram for the process. The disadvantage of using biomass to obtain hydrogen is that the biomass fixes carbon from the atmosphere, and thus it should be considered as a source of carbon too, not only a source of hydrogen. This fact can be alleviated if we inject the CO_2 generated in the ponds or photoreactors for the production of microalgae.
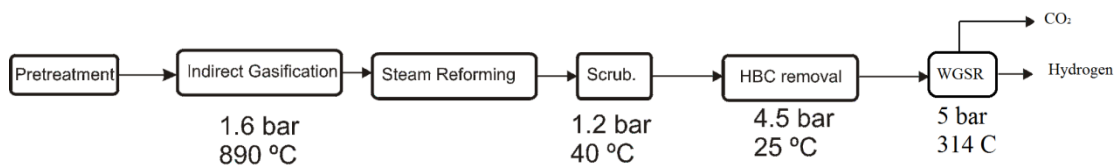

Figure 11.- Optimal flowsheet for the production of hydrogen from biomass

3.2.4.-BioOil and fuel gases via fast pyrolysis

We have described above the two opposite alternatives with regard to the conversion of lignocellulosic biomass into different biofuels, either the complete breakdown of the biomass into syngas (gasification) or the partial breakdown into sugars (biochemical route). There is an intermediate process by which biomass is thermally decomposed at temperatures around 400 to 500ºC in an oxygen free atmosphere generating three kinds of products: solid (biochar), gas (light hydrocarbons and syngas), and liquid (pyrolysis oil or bio-oil). While the gases can be readily used as fuels, the liquids must be further processed before they can be used as transportation fuels, for which hydrocracking or catalytic cracking is needed, or as heavy fuels for thermal plants, due to the presence of acid compounds and water as well as the particular physical properties of the bio-oil, high viscosity and thermal and storage instability. [120-124]

In the literature we can find a number of papers dealing with the conceptual design of fast pyrolysis plants, mainly addressing the type of the pyrolysis reactor used, fluidized beds, ablative reactors, cyclonic reactors, circulating fluid beds (CFB), or vacuum pyrolysers and the effect of the operating conditions on the products yield[122-125]. Only few papers actually perform a techno-economic evaluation of the process using a scenario based simulation approach with ASPEN, even though some models rely on built on

modules whose performance relies on experimental data. However, not all of them include the upgrading step[125,128]. The DOE in 2009 presented a study based on 2000 t/yr of wood chips for the production of 76MMgal/yr of synthetic gasoline and diesel evaluating a process involving fast pyrolysis, hydrotreating, hydrocraking, distillation of the resulting liquid and hydrogen production in-situ for the autonomous operation of the plant. The investment turned out to be $303MM with a production cost of liquid fuel of $2.04/gal. The NREL studies are also based on a 2000 dry ton/year feedstock, reporting production yields of 134-220 MML/yr with expected investments of $287MM-$200MM and production costs of $3.09-$2.11/gal of gasoline equivalent [126-127], where the range depends on the hydrogen, either produced in-situ for fuel upgrading or for selling purposes. Some [128] report total direct investments of $360MM, and total capital investments of $504MM for a 600 t/day feedstock treatment capacity but they do not include the hydrocraking step. Brown et al. [129] evaluated a number of scenarios for different upgrading technologies for a feedstock of 2000 t/day of biomass. They consider either fluid catalytic cracking (FCC) of whole pyrolysis oil (WPO); one-stage hydrotreating and FCC of WPO; FCC of the aqueous phase of pyrolysis oil (APPO); one-stage hydrotreating and FCC of the APPO; and two-stage hydrotreating followed by FCC of the APPO based on ASPEN simulation. In this paper they report capital costs from $99 MM to $112MM depending mainly on the upgrading steps installed, operating costs from $70MM to $90MM. As a result of their study, it is claimed that the technologies do not have a positive internal rate of return (IRR) unless they include hydrotreating. However, an optimization based approach is still missing. Furthermore, better physicochemical understanding of the pyrolysis process[122] is needed to be able to select the operating conditions for the optimal product distribution

3.3.-Oil based biofuels

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines.[130,131] However, using raw vegetable oils for diesel engines can cause numerous engine-related problems.[132] The increased viscosity, low volatility, and poor cold flow properties of vegetable oils lead to severe engine deposits, injector coking, and piston ring sticking.[133,134] Thus, research has focused on developing transformation products like pyrolysis, micro-emulsion and transesterification. The process of transesterification has been the most widely used. It removes glycerol from the

triglycerides and replaces it with radicals from the alcohol used for the conversion process.[135] This process decreases the fuel's viscosity but maintains the cetane number and heating value. The monoesters produced by transesterifying vegetable oils with alcohol are known as *biodiesel.*[136,137]

3.3.1.-Raw materials

a) Vegetable oils: First generation of biodiesel.

Biodiesel is obtained using vegetable oils such as sunflower, cottonseed oil, rapeseed oil, soybean oil, palm oil, peanut oil and canola oil as raw materials.[138,139] Their use is distributed across the globe depending on the production capabilities of different countries. For example, Canola is the preferred one in Canada, cottonseed oil is abundantly produced in Pakistan, palm oil is frequently used in Malaysia, while soybean with 56% of the world's oilseeds represents the biggest oilseed crop produced. However, biodiesel can be twice as expensive as crude based diesel (biodiesel form soybean is estimated around 2-2.5 \$/gal) but the capital investment for a biodiesel plant is far lower.[140] Moreover, the competition with the food chain and the cost of the raw material is directing the focus to the use of alternative sources of oil.

b) Cooking oil based diesel: Second generation of biodiesel.

Among oils, waste cooking oil is a promising alternative to vegetable oil for biodiesel production because it is much less expensive than pure vegetable oil. Waste oils have been traditionally sold commercially as animal feed. However, since 2002 the EU has enforced a ban on feeding these mixtures to animals, because, during frying, many harmful compounds are formed. The high temperatures during frying (from 160-200 ºC) cause major physical and chemical changes to the oil, which differs from oil to oil, depending on their composition. Basically three types of reactions occur during frying: thermolytic, oxidative, and hydrolytic which result in changes in the vegetable oil such as: (i) an increase in the viscosity, (ii) an increase in the specific heat, (iii) a change in the surface tension, (iv) a change in color, and (v) an increase in the tendency of fat to foam. As a combined result of all these chemical reactions, many undesirable compounds are formed,

increasing the polar fraction and preventing the use of waste cooking oil as an additive to feeding mixtures for domestic animals because it could result in the return of harmful compounds back into the food chain through the animal meat.[141] Hence, the waste cooking oil must be disposed of safely, or be used in a way that is not harmful to human beings.

The quantity of waste cooking oil generated per year is of the order of several kg per person in industrialized countries.[141] The disposal of waste cooking oil is problematic because disposal methods may contaminate the water. Therefore, many developed countries have set policies that penalize the disposal of waste oil through the drainage. Therefore, the production of biodiesel from waste cooking oil is one of the better ways to reuse and dispose it efficiently and economically obtaining added value from dangerous wastes.[142-144] However, the high demand of diesel fuel and the availability of waste cooking oil [11, 141, 145, 146] indicates that biodiesel from cooking oil cannot replace diesel fuel, but it can at least contribute to reducing the dependency of crude oil based diesel. The properties of the biodiesel from waste cooking oil would be largely dependent on the physicochemical properties of these feedstocks.

3.3.2.-Production process of biodiesel from oil.

Biodiesel is obtained via transesterificastion of oil with alcohols. The yield of the reaction depends on a number of parameters such as reaction temperature and pressure, reaction time, rate of agitation, type of alcohol used and molar ratio of alcohol to oil, type and concentration of catalyst used, and concentration of moisture and free fatty acids (FFA) in the feed oil. Methanol is the most widely used alcohol because of its low price, but ethanol has also been tested. There are five main alternatives to perform the transesterification of the oil towards biodiesel depending on the catalysts used: homogeneous acid-catalized, alkali-catalyzed, heterogeneous (acid or basic), enzymatic and no catalyzed under supercritical conditions. The alkali-catalyzed reaction is limited because of the formation of soaps between the catalysis and the free fatty acids (FFA) and the negative effect of the presence of water in the oil by favoring saponification although the reaction is quick. The acid catalyzed reaction is not limited by the purity of the reactants but by the reaction time, which is around 4 days. The enzyme catalyzed reaction is insensitive to water and FFA, and it is easier to purify the products. However, the

catalyst is more expensive and its conversion is lower than the previous two processes. Heterogeneous catalytic processes are a promising alternative due to the simplified purification stages. Finally, it is also possible to transesterify the oil with supercritical methanol. Although the yield of methyl ester is high, the molar ratio of methanol to oil is high (1:42), and the operating conditions are extreme (350ºC and 45 MPa).[11, 141,146-154]

A number of authors have developed and evaluated the production process based on those technologies from a technical and economical point of view following a case study based simulation approach using ASPEN or HYSYS.[11,12, 148, 154-163] The use of heterogeneous catalyzed processes (enzymatic, basic or acid based) or supercritical based processes, are gaining support due to the reduced separation stages resulting in a very competitive prices,[12,160,162] which compete with the previously denoted as most economical, the acid catalyzed process, because it is less affected by the impurities of the raw material reducing the purification pretreatment stages.[11,155] The range of investment and production cost reported in the literature is large due to the different plant sizes considered in the studies and the individual costs and assumptions. Even though, we find interesting to present some results as benchmark. The investment cost for the production of biodiesel is around $7 million for 36,000 MT/year[148] to $8.5 to 27 million for 8,000 MT/yr to 200,000 MT/yr[148] with production costs of $0.5/kg[148], $0.63/kg[12] or $0.74/kg[11,154] for a 8,000 MT/yr for the best catalytic process in each of those studies, 0.05-2.38€/kg for the enzymatic case depending on the cost of the enzyme[162] or $0.26/kg for the supercritical process, for a production capacity of 80,000 Ton/yr.[160] Furthermore, the production of biodiesel is less water intense than bioethanol, consuming around 1 gal/gal.[164]

However, the recycle of methanol and the number of variables involved in the operation of the reactor indicates that a systematic study may yield interesting results in terms of energy and water consumption. Recently, Martín and Grossmann[165] have simultaneously optimized the production of biodiesel in terms of technology (homogeneous alkali and acid catalyzed, heterogeneous enzymatic or basic and non catalyzed under supercritical conditions) and operating conditions (using surface response models for the reactors), and performing simultaneous optimization and heat integration at the process flowsheet using Duran & Grossmann's approach.[27] The model was formulated as an MINLP where each of the flowsheets was simultaneously optimized and heat integrated, see Figures 12 & 13, using as objective function a simplified operating cost

involving the cost of the different chemicals and the energy consumption. The result is that for cooking oil the heterogeneous catalyzed reaction is the best process yielding a production price of 0.66$/gal, with an energy consumption of 1.94 MJ/gal (half the best estimates) and the water consumption is 0.33 gal/gal of biodiesel, almost a third of the one reported in the literature.[164]
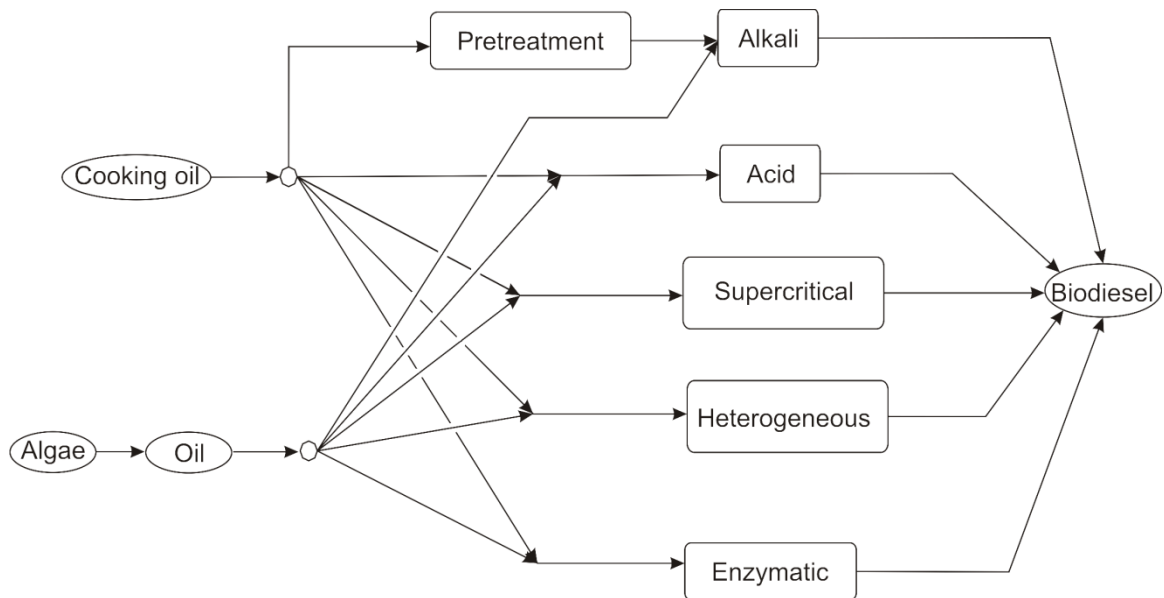

Figure 12.- Superstructure for the optimal production of biodiesel from oil
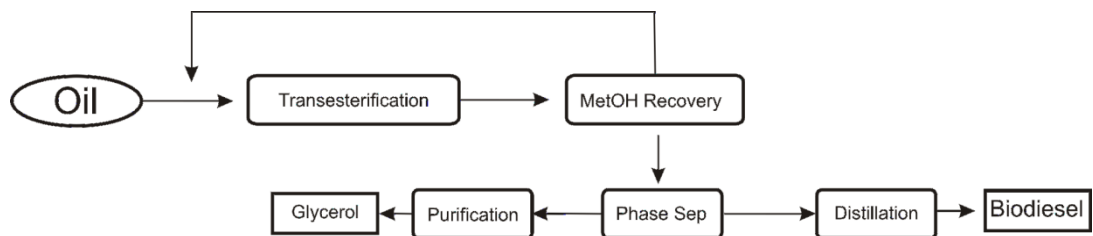

Figure 13.- Basic structure of the trasnesterification process.

3.3.3.-Glycerol: Valuable byproduct.

The byproduct of the transesterification of oil is glycerol. Due to the expected increase in the production of biodiesel, research has focused on the use of glycerol to produce different added value chemicals to improve the economic balance of biodiesel production.[147, 166-173] For instance, it is possible to synthesize *1,3-propanediol* which can be used in composites, adhesives, laminates, powder and UV-cured coatings, mouldings, novel aliphatic polyesters, co-polyesters, solvents, anti-freeze and other end uses[174], *1,2 propanediol,* a major commodity chemical with an annual production of over 1 billion

pounds in the United States,[175] *dihydroxyacetone,* used in cosmetics industries as a tanning agent,[176] *succinic Acid that* can be used for the manufacture of synthetic resins and biodegradable polymers and as an intermediate for chemical synthesis,[177] polyglycerol esters which find their utilization as antifogging and antistatic additives, lubricants, or plasticizers,[178] as well as *polyesters, polyhydroxyalkonates.*[179] However, it is also possible to obtain H_2 or syngas from the reforming of glycerol [173, 180-183] that can be used as raw material for other biofuels or chemicals.

3.4.-Algae based biofuels.

Microalgae are also a source of biomass with great potential. The algae convert sunlight, saline water, nutrients and CO_2 into proteins carbohydrates and lipids with a growth rate that doubles their biomass up to five times a day. Subsequently, growth is stopped by limitation of the nutrient so that lipids are produced. Algae can grow not only on normal carbon sources, such as glucose, fructose, etc, but on waste from agriculture and food industries, and using saline water or wastewater, thus lowering the cost of microalgae oil while it can also be a good for water treatment.[184] Next, the algae are harvested to eliminate the water that accompanies them, which can be recycled, using either flotation or settling (helped by flocculation), centrifugation or filtration. Finally, the oil is extracted and either transesterified (using the same processes as for any other oil), or it can be catalytically converted into gasoline.[185] Microalgae oils are believed to be a promising feedstock for biodiesel production since the oil they generate has a fatty acid composition similar to that of vegetable oils.[184,186] In order to produce a fair amount of oil, microalgae must be carefully selected so that they are capable of producing large quantities of lipids while being tolerant to fluctuation in the operating conditions. [187-189]

The main problem with producing biodiesel from algae is that to make it commercially viable, the algae need a concentrated and plentiful source of CO_2, and furthermore it is necessary to reduce the high harvesting costs.[190] The current microalgae oil price is high ranging from 0.25 \$/lb to \$15/gal, [187-190] but it is expected that it could be as low as 0.07\$/lb.[190] However, certain processes for the production of ethanol, hydrogen or FT-diesel via gasification generate a fair amount of CO_2 that can be used for this process as well as power facilities. Furthermore, new technologies are in development to reduce the harvesting costs of microalgae.[191] The potential yield of biofuel from microalgae is one

or two orders of magnitude higher than with any other crop and 5 times larger than the best yield switchgrass as seen Fig. 4. The use of microalgae as feedstock for the production of biodiesel has been sponsored by the US Department of Energy. It is reported that microalgae can be produced using salt water (eliminating the problem of water usage) and that with 1 to 3 million acres, about 2-5% of the cropland used currently in the US, it would be possible to meet the US diesel needs. Furthermore, the production of diesel from algae could be achieved at a lower cost than the current one for diesel. [192]

In the study by Martín and Grossmann[165] the oil from algae can be produced at $0.065/lb as long as the new technology released by Univenture[191] is implemented and operates as claimed. Next a MINLP involving five different technologies (homogeneous alkali or acid catalyst, heterogeneous enzymatic or basic catalyzed and under supercritical conditions) is solved to determine the best production process among the five alternatives commented before, homogeneous acid or alkali catalyzed, heterogeneous enzymatic or basic and non catalyzed under supercritical conditions, simultaneously optimizing and heat integrating each process similar to the case that uses cooking oil. For this type of oil the best process is the alkali catalyzed with a production cost of 0.42 $/gal requiring 1.94 MJ/gal of energy and 0.60 gal/gal of water. The second best process is quite close, only $0.02/gal more expensive and is the heterogeneously basic catalyzed, which may be selected in order to have a flexible process capable of processing cooking oil or algae oil.

The potential of the microalgae is not limited to the use of the oil they generate, but they can also be used to obtain ethanol by fermenting the starch and cellulose contained in them, hydrogen by gasification or biological conversion, liquid fuels by pyrolysis following similar processes as commented in section 3.2.4, or thermal liquefaction and methane by digestion or high value products.[193-195] It is also possible to use the oil for biodiesel production while the residues are used to obtain ethanol via fermentation. [196-197]

4.- Biorefineries.

The chemical process industry often constructs large integrated production sites, namely integrated chemical complexes[198-200] hat are composed of many interconnected processes and a number of chemicals. The operation of these complexes is based on exploiting the synergies of vertical integration, reuse of byproducts, and energy integration

among processes. NREL has defined a biorefinery as a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. Therefore, biorefineries also represent networks of this kind (see Figure 14) that are capable of producing a wide variety of products from fuels to chemicals or even energy. [194, 201-203]
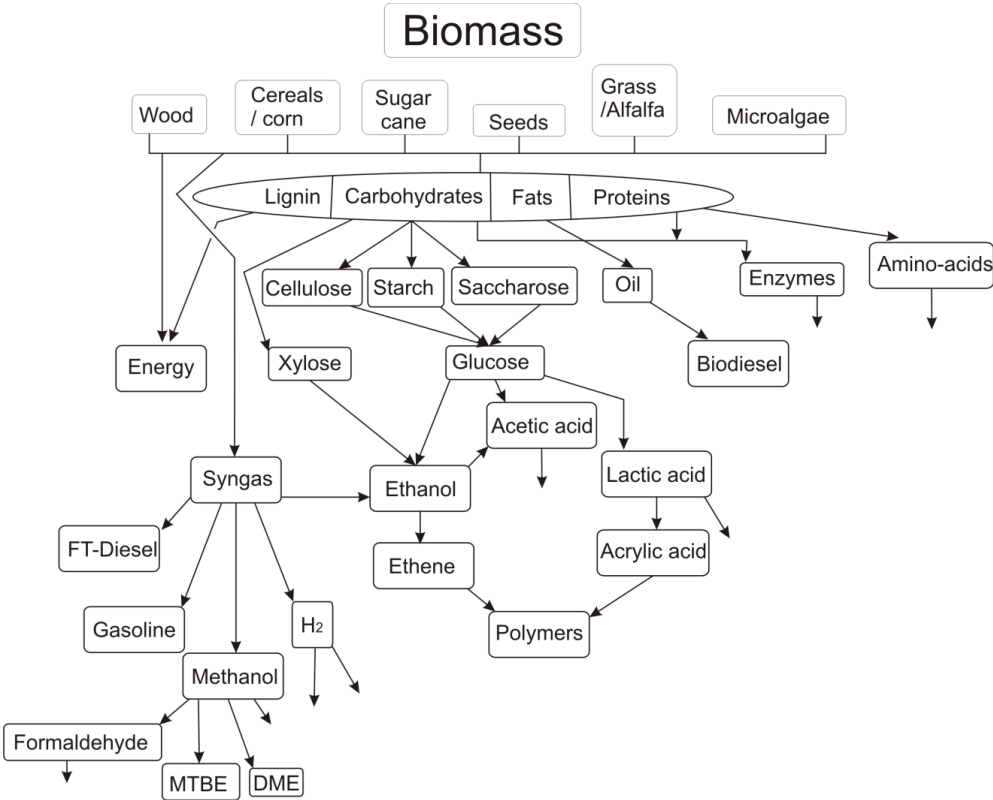

Figure 14.- Biorefineries as integrated sites

To evaluate the integration of the processes, we first need to study them separately to identify synergies. Table 2 shows the summary of the economics of the different second and third generation biofuel processes and their byproducts based on lignocellulosic switchgrass, cooking oil and algae for late 2010 early 2011 prices. We assume that the taxes on the fuels are around \$0.6/gal [204] and the selling prices correspond to gasoline, diesel and hydrogen, in which case instead of gal we consider kg. As it can be seen, there are a number of tradeoffs in terms of investment versus production cost. Furthermore, most of the lignocellulosic based processes produce energy, as well as byproducts such as hydrogen, a mix of alcohols and CO_2 or green gasoline that can be used as fuel. On the other hand, biodiesel requires energy and CO_2, in the case when microalgae are used to obtain the oil, while producing a series of byproducts such as fertilizers or glycerol.

Up to date, three types of biorefineries have been defined as phase I, II and III. The phase I and II use grain (corn and wheat) as feedstocks, the only difference is that phase I produces a fixed amount of ethanol and other products with fixed processing capabilities based on the corn dry milling process, while phase II has the capability of producing a number of products based on the corn wet milling process. The phase III biorefinery combines whole crop and lignocellulosic materials.[205]

Table 2.- Summary of the main features of the optimized processes[40,41, 88, 105, 151]

	Ethanol (Hydrolysis)	Ethanol (Gasification & Catalysis)	Ethanol (Gasification & Fermentation)	FT-Diesel	H_2	Biodiesel (Cooking)	Biodiesel (Algae)
Total investment ($MM)	169	335	260	216	148	17	110
Capacity(MMgal/yr)	60	60	60	60	60*	72	69
Biofuel yield (kg/kg_wet)	0.28	0.20	0.33	0.24	0.11	0.96	0.48
Production cost ($/gal)	0.80	0.41	0.81	0.72	0.68*	0.66	0.42
Water consumption(gal/gal)	1.66	0.36	1.59	0.15	--	0.33	0.60
Energy consump. (MJ/gal)	-10.2	-9.5	27.2	-62.0	-3.84*	1.94	1.94
ROI (%)	44.91	26.15	29.08	36.25	16.86	565.4	91.27
PayOut (yr)	1.02	1.66	1.51	1.24	2.40	0.09	0.52
Byproduct	Energy CO_2	Hydrogen Mix alcohols Energy CO_2	Hydrogen CO_2	Green Gasoline Energy CO_2	Energy CO_2	Glycerol	Glycerol Fertilizer

(*) For Hydrogen instead of gal, kg is used

In order to design a biorefinery that is capable of fully using the entire corn plant and serve as a bridge between the first and second generation of bioethanol, an integrated design of dry grind and gasification technologies has been proposed using the process simulation tool MIPSYN, Mixed-Integer Process SYNthesizer[206] which is an implementation of the modeling and decomposition (M/D) strategy developed by Kocis and Grossmann[207] and the outer-approximation and equality-relaxation algorithm (OA/ER) by Kocis and Grossmann[24]. MIPSYN enables automated execution of simultaneous topology and parameter optimization of processes enabling the solution of large scale

MINLP problems. For the simultaneous optimization and heat integration, the model by Duran and Grossmann[27] is also implemented in MIPSYN. The aim is to optimize the integrated biorefinery that uses the entire corn plant by integrating the technologies required to process the corn grain and the corn stover in such a way that equipment can be shared and most importantly, energy can be integrated due to the high demand of energy in the dry-grind process.[55] Figure 15 presents the flowsheet for the integration of the processes. In this way we can evaluate the trade-offs that arise between both processes:

- The dry-grind and thermo-biochemical processes require energy because of the need for ethanol dehydration. Furthermore, since they cannot take advantage of the exothermic fermentations because they occur at low temperature, they increase the cooling water consumption. In contrast, the thermo-chemical process generates energy due to the exothermic synthesis reaction at high temperature which can provide energy for the dehydration of the ethanol coming from the dry grind path.

-The ethanol-water mixture from the fermentors, either syngas or sugars fermentor, can be dehydrated using the same technologies and, thus, economies of scale can be exploited with this technology integration.

- If the thermo-chemical path is selected, the only common part is the technology for CO_2 capture, while both processes run in parallel.
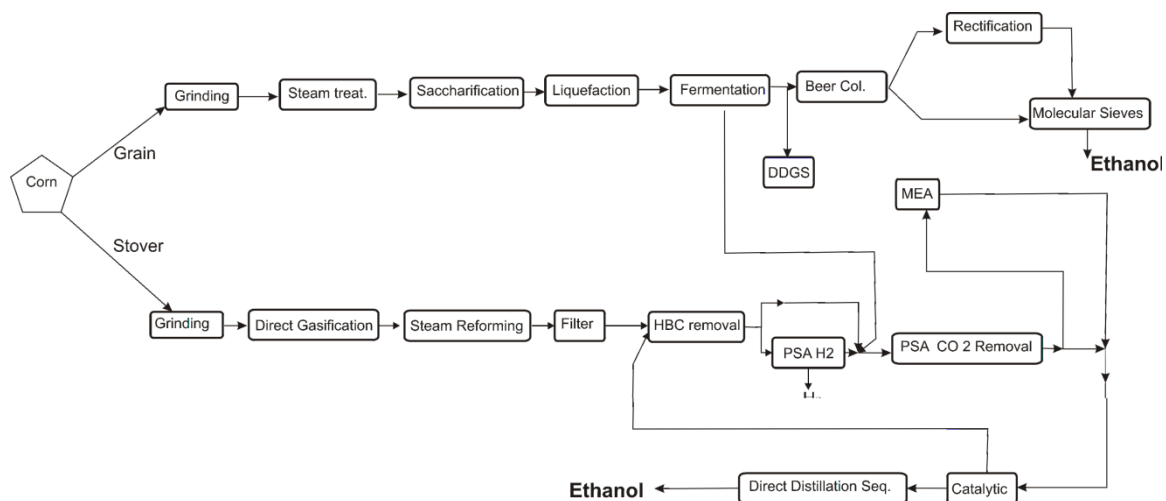

Figure 15.- Process integration for the simultaneous production of food and ethanol from corn

The lowest cost integrated process, uses the thermo-chemical path for transforming the lignocellulosic material into ethanol, especially due to good heat integration in spite of

a lower yield towards ethanol (0.28 $kg_{ethanol}/kg_{biomass}$ vs. 0.30 $kg_{ethanol}/kg_{biomass}$). In constrast, the flowsheet with the highest profit consists of the dry-grind process and thermo-biochemical route. For this process treating 18kg/s of corn grain and the correspondent stover that can be harvested together with it, the water consumption is 1.37gal/gal requiring 17MW of steam.

5.-Conclusions

The strong competition in the energy market requires for alternative fuels based on biomass (e.g. bioethanol, biodiesel) to be produced in an efficient and sustainable way. Mathematical optimization techniques together with conceptual design have been traditionally used in the petrochemical industry to improve the performance and operation of the processes. Therefore, there is scope for the use of these process systems engineering tools to optimize the design and operation of future biorefineries as has been shown in this paper. A sustainable design must include a process optimized in terms of energy and freshwater consumption as the two most important indicators for good operation. Mathematical programming techniques and the newly developed technologies have been used to develop attractive conceptual designs for the production of bioethanol, biodiesel, hydrogen and other chemicals. We would like to point out that while the heat exchanger network design has been solved as a global optimization problem, as well as water network design, the process flowsheet superstructure optimization has been locally optimized, due to the size and nonlinearities of the problem. Although comparison with other work and reports is always difficult, and ultimately validation is required with more detailed studies or pilot plant data, the results that we have obtained point to production costs and water usages that are often below the current industrial practice. Finally, for the sake of further reducing the operating costs, biorefineries should be operated as multiproduct facilities. Their operation is complex and mathematical programming techniques can also be used to help in the decision making process of which product to obtain and how much to produce.

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