Optimal production of Furfural and DMF from algae and switchgrass

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Abstract.

In this paper we develop a conceptual design of optimal integrated processes for the production of DMF and furfural from biomass, switchgrass and algae. The processes consist of four stages, (1) biomass pretreatment into intermediates such as oil and glucose from algae and, glucose and xylose from switchgrass, (2) dehydration of the sugars, (3) HMF and furfural purification, and (4) synthesis of DMF out of HMF and FAEE synthesis from oil in the case of using algae. We formulate mixed integer non linear programming models, for which simultaneous optimization and heat integration is performed for both raw materials. For switchgrass, the use of AFEX pretreatment is recommended for a production of cost of DMF and furfural of \$3/kg (\$570MM of investment cost). For algae, the composition is 60% oil, 30% starch and 10% protein to obtain 98 MMgal/yr of biofuels, 16% of DMF, at a cost of \$1.98/gal (\$693 MM of investment). If the sugar concentration in the dehydration reactor increases from 10 to 30%, we can reduce the production costs by 25% and the investment cost up to 50%.

Keywords: Energy, Biodiesel, glycerol, ethers, process integration

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1.-Introduction

In recent years, an increasing effort has been devoted to find paths to utilize biomass as feedstock for the production of organic chemicals because of its abundance, renewability and worldwide distribution. Sugars are valuable intermediates to value-added chemicals. The transformation of sugars to furans is interesting not only as building block to other chemicals but as fuels themselves, (Tong et al., 2010). Unlike lignocellulosic raw materials that are source for mostly pentoses and hexones, algae composition comprises lipds apart from starch, glucose, and protein (Keshwani & Cheng, 2009). Therefore, it is expected that while from switchgrass we should be able to obtain not only dimethyl furfural (DMF) but also furfural, from algae we should be able to produce DMF out of the starch. Lately, a number of papers have evaluated the production of furan and 5-(hydroxymethyl)furfural (HMF) and DMF from sugars, xylose, fructure or glucose, but all of them start with the sugars without evaluating the production of those sugars from energy crops (Kazi et al., 2011; de Ávila & Guiradello, 2012).

The basic process to obtain either HMF or furfural from sugars consists of their dehydration. There is extensive research in the literature evaluating the effect the operating conditions for these reactions, not only to produce furans, but also to separate them from the reaction mixture. Therefore, most of the analysis is based on evaluating the mixture of reaction involving one or two phases, aqueous phase, with or without salts, and organic phase or the use of ionic liquids. If we focus first on the dehydration of hexoses, much of the work uses fructose as raw material. The use of pure water is limited because the dehydration of fructose is generally non-selective, leading to a range of byproducts besides HMF. Thus, biphasic systems are used for fructose dehydration, where a water-immiscible organic solvent is added to extract continuously the HMF from the aqueous phase. The challenge is the poor partitioning coefficient of HMF into the organic phase, requiring large amounts of solvent, and hence large energy consumption for product purification. Lately the addition of salts to the aqueous phase has increased the partition coefficients (Roman -Leshkov 2007, Pagan Torres et al 2012). However, most of the natural raw materials contain glucose instead of fructose. Typically, the dehydration of glucose has been reported to have lower reaction rate and selectivity to 5-HMF compared to those of fructose (Tong et al., 2010). However, It is possible to simultaneously isomerize the glucose into fructose and dehydrate the sugar (Pagán Torres et al., 2012). Different solvents have been tested in glucose dehydration with mineral acids as catalyst (Binder et al., 2010). In addition to the use of glucose and fructose to produce HMF, researchers have studied xylose as a feedstock for the production of furfural. The basic principles are similar, the use of a biphasic system in order to continuously separate the furfural produced from the organic phase. A number of organic phases have been tested in the literature using different catalysts including mineral acids, zeolites, acid-functionalized materials and heteropolyacids (Xing et al., 2010).

Various combinations of solvents and catalysts have been tested to produce HMF and furfural from one of the multiple feedstocks. So far, to the best of our knowledge, there is no experiment reporting simultaneous dehydration of glucose, fructose, and xylose into HMF and furfural (Chheda et al., 2007). However, recently the same catalyst has proved to work for both sugars (Binder et al., 2010; Marcolutilo & de Jong 2010; Xing et al., 2010). Furthermore, there is still no integrated process for the production of HMF, furfural and DMF directly from biomass. Thus, in this paper we evaluate the optimal production of furfural and DMF from lignocellulosic raw materials, and DMF and biodiesel from algae. The paper is structured as follows: the processes that transform the algae and switchgrass into furans are described in section 2. Next, the main modeling issues are discussed in section 3, followed by the results and the discussion. Finally, conclusions are drawn and suggestions for further experimental development are presented.

2.-Problem statement

2.1.-Sugars from biomass

We consider two different raw materials, algae and switchgrass. The first one is comprised of lipids, useful for the production of biodiesel, starch, which is a polymer of glucose, and thus can be used for the production of HMF and later DMF, and protein. The lignocellulosics composition consists of cellulose, a polymer of glucose which is the raw material for HMF and DMF, hemicelluloses, a polymer of xylose, which can be used for the production of furfural, and lignin, which can be used to provide energy to the system or to obtain higher value products.

2.1.1 Algae to oil and glucose for DMF

Algae allows the simultaneous production of biodiesel and DMF. Figure 1 shows the flowsheet for the production of glucose and biodiesel. The section corresponding with the algae growing, harvesting and oil extraction is similar to previous papers by the authors (Martin & Grossmann, 2012&2013) where further details on the models can be found. CO_2 is injected in the ponds and fertilizers are added (Pate , 2008) to grow algae at 50g/m^2 d (Sazdanoff, 2006). Saline or wastewater are considered to reduce the need for freshwater. The dry algae biomass is assumed to be composed of oil, up to a maximum of 60%w/w, starch and protein with a minimum of 10%w/w to be consistent with realistic values. Together with the algae, oxygen is produced and water is evaporated, (Pate, 2008). Next, the algae are harvested from the pond using a capillarity based technology developed by Univenture inc. obtaining a cake of algae with 5% wet moisture. The biomass is mixed with cyclo-hexane and compressed so that oil is extracted and the biomass (starch and protein) is separated from the oil.

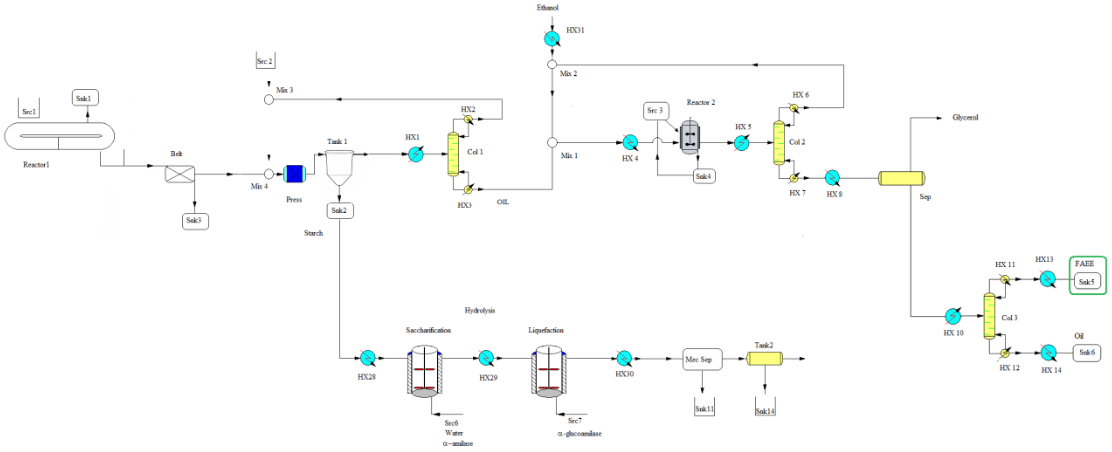


Figure 1.- Algae growing, oil and starch extraction and biodiesel production

The production of biodiesel can use either methanol or ethanol (Martín & Grossmann, 2012, Severson et al., 2013). Due to the expected integration of this plant in the biofuel supply chain, we will assume the use of ethanol as the alcohol of choice. Following Severson's et al. (2013) work, the oil is transesterified with ethanol using an enzymatic catalyst. A surface response model is used to predict the conversion of the oil. After the reaction, the excess of ethanol is recovered and the glycerol is separated from biodiesel by gravity using a phase separator. The glycerol can be sold or further used as raw material while the biodiesel is purified in a distillation column. The main process constraints can be seen in Table 1.

Table 1.-Main operating constraints. (Martín & Grossmann, 2012; Severson et al., 2013)

Equipment	Temperature limit
Alcohol separation column	Bottoms $\leq 150^oC$ Reflux ratio 1-3
Biodiesel purification column	Top: $\leq 250^oC$ Bottoms: $\leq 350\text{-}375^oC$ Reflux ratio 2-3
Phase separation	30-40ºC

On the other hand, the starch requires liquefaction (85ºC) and saccharification (65ºC) to break down the polymers into glucose. The solid phase, mainly protein, is separated from the liquid phase and can be sold. Next, the glucose can be used for the production of HMF and DMF

2.1.2.-Lignocellulosics to sugars for Furfural and DMF

Grinding is the first stage to reduce the size of the raw material and to increase the contact area before pretreatment. There are a number of alternative pretreatments. However, based on previous studies in the literature, we will focus on AFEX and dilute acid (Martín & Grossmann, 2012; Keshwani et al., 2009; Sun & Cheng, 2002; Taherzadeh & Karimi, 2008; Alvira et al. 2010). We use surface response models to determine the optimal operating conditions of the pretreatments and the yield to xylose and glucose. The models can be found in Martin & Grossmann (2014). Once the physical structure of the switchgrass has been broken down, the cellulose and lignocellulose are hydrolyzed. Figure 2 shows the flowsheet for the production of xylose and glucose from switchgrass.

Some studies, Zhang & Runge (2011), Shigh et al. (1984) evaluated the fractionation of pentoses and hexoses. However, based on the experimental data in the literature, the catalysts for the dehydration of the xylose and the operating conditions are similar to those used for the dehydration of the glucose (fructose) (Binder et al., 2010; Marcolutilo & de Jong, 2010; Xing et al. 2010; Pagán –Torres et al., 2012). Moreover, the same reaction medium can be used for both. Next, the sugars are dehydrated for the production of furfural from xylose and HMF, and subsequently, DMF from glucose.

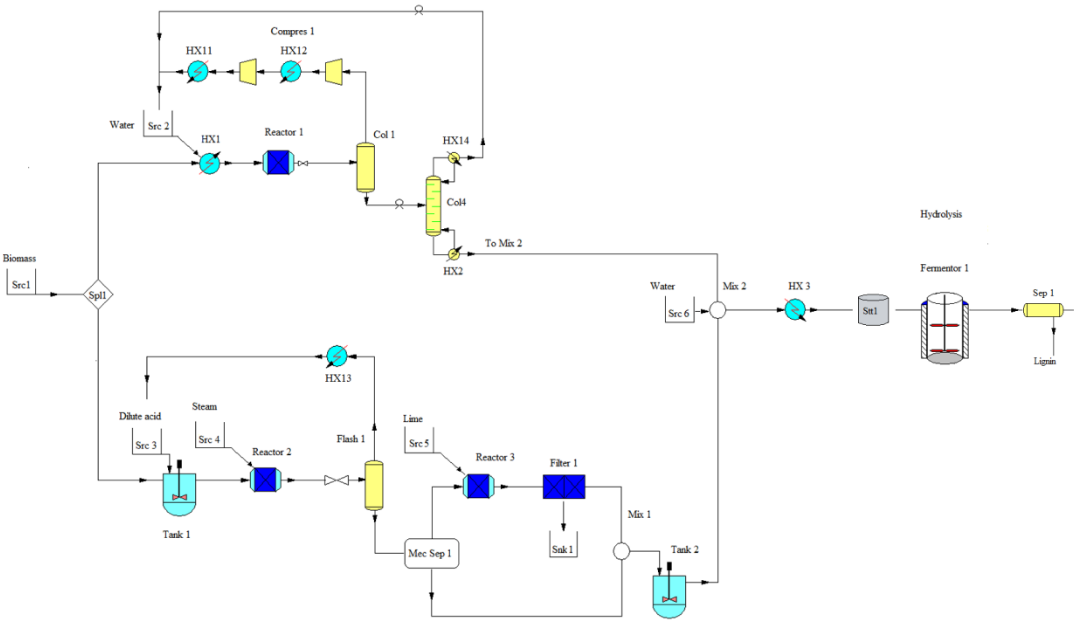


Figure 2.- Alternative pretreatments, Dilute acid and AFEX, for the production of sugars from switchgrass

2.2.-Sugar dehydration.

2.2.1.-Glucose dehydration

The chemical reaction that takes place for glucose dehydration is presented in Figure (3)

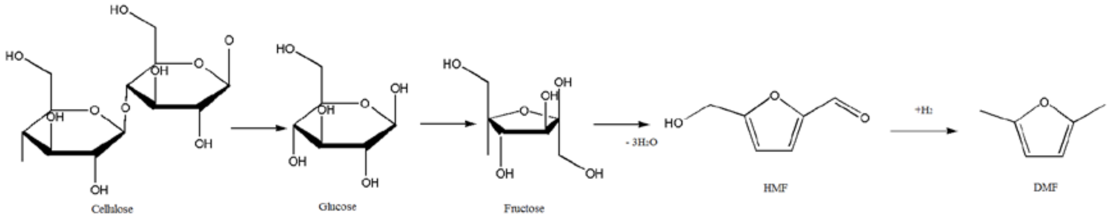


Figure 3.-Glucose dehydration scheme

The easiest dehydration of six carbon sugars to HMF occurs for fructose. When the starting material is glucose, an isomerization (epimerization) step from glucose to fructose is needed prior to the acid catalyzed dehydration. Efficient isomerization catalysts are, for example, $CrCl_3$ and $CrCl_2$ (Binden & Raines, 2009). The interesting point of using these catalysts is that they have also proved to be efficient for the dehydration of xylose to furfural (Binden et al., 2012). Pagán-Torres et al. (2012) and Biden (2010b) experimentally proved the dehydration of glycose in a biphasic system using and acid aqueous phase (using HCl) with salts, NaCl, where the produced HMF was continuously extracted using an organic solvent. Even with an initial concentration of fructose as high as 50 wt% and using HCl as the catalyst, remarkable results with selectivity of 77% and a conversion of 90% at 180ºC have been reported. Different solvents have been tested in the literature such as THF, DMSO, butanol operating as 160ºC to 180ºC and high pressure (Roman-Leshkov et al., 2009). Although various extracting solvents can generate high HMF selectivity, the use of 1-butanol as a solvent is advantageous for biomass applications. For instance, while solvents such as 2-butanol are obtained from petroleum-derived products, 1-butanol can be produced by the fermentation of biomass-derived carbohydrates. Also, unlike unsaturated solvents such as toluene or methylisobutylketone, 1-butanol is inert in the hydrogenolysis step of our process (Roman-Leshkov et al, 2007).

2.2.2.-Xylose dehydration

The dehydration of xylose follows a mechanism similar to the one presented for glucose, see Figure (4):

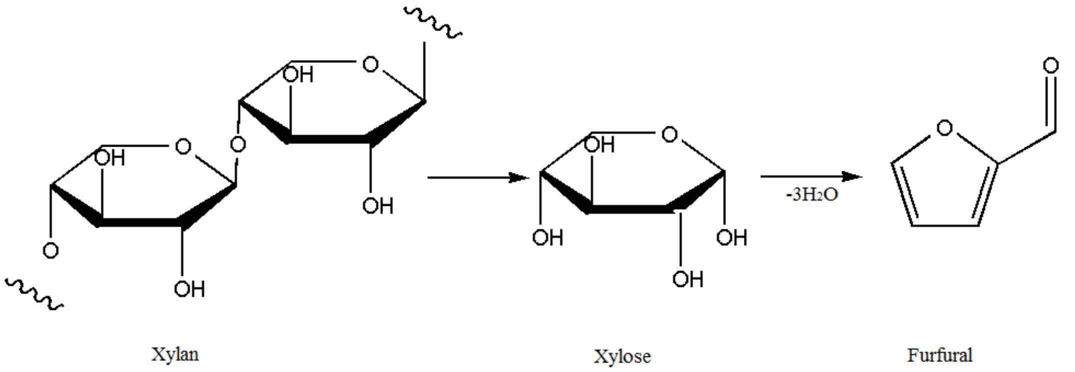


Figure 4.-Xylose dehydration scheme (Binder et al. 2010)

Several authors have evaluated this reaction using as catalysts HCl, $CrCl_x$ using mono or biphasic sistems. (Binder 2010b; Marcotulio & De Jong 2010; Xing et al. 2010; Weingarten et al., 2010; Karinen et al., 2011). In particular Marcotulio & De Jong (2010) proved that the use of NaCl and HCl results in up to 80% selectivity, using similar catalysts than the ones used by Pagan-Torres et al. (2012) for glucose. Actually, the furfural selectivity increases from 12.6% to 80.7% as the HCl / Xylose molar ratio increases from 0.6 to 2.4. This suggests that high acid concentration is necessary to obtain high selectivity of furfural. However, further increasing the ratio of HCl to xylose to 3:1 improves the selectivity by only 3% (Xing et al., 2010). Different organic phases have also been tested, most of them are the same as the ones used when dehydrating hexoses. The operating temperature ranges from 160ºC to 200ºC. Note that this range is also similar to the one used for the dehydration of the hexoses.

3. Modeling issues

The units are modeled using reduced order models based on experimental data from the literature, mass and energy balances, rules of thumb and design equations. The superestructure is formulated in terms of the total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network. The components in the system include those in the following list: {Water, Ethanol, Glycerol, FAEE, FFA, Oil, Hexane, Starch, Glucose, Xylose, Maltose, Protein, Succinic Acid, Acetic Acid, Lactic Acid, Urea, NH_3, H_2SO_4, KOH, K_2SO_4, H_3PO_4, K_3PO_4, Algae, Biomass, CO_2, O_2, Buthanol, Hydrogen, NaCl, HCl, $CrCl_3$, NaOH, HMF, DMF, furfural }.

For the production of sugars from lignocellulosic raw materials and the algae growing, harvesting, oil extraction and starch processing to glucose, we refer to previous papers by the authors where the details of the modelling can be found. (Karuppiah et al., 2008; Martín & Grossmann, 2012; Martín & Grossmann, 2014; Severson et al., 2013). Here we focus on the dehydration stage of the glucose and xylose, and the subsequent separation and purification stages. We assume adiabatic stream mixing.

3.1.- Switchgrass to furfural and DMF

Algae only contain starch as carbohydrate. Thus, one can only expect to obtain HMF and DMF from them. However, the lignocellulosic raw materials contain cellulose and hemicelluose, apart from lignin. Therefore, the production of furfural and DMF, via HMF, simultaneously should be possible (Yemis & Mazza, 2012; Singh et al., 1984; Chheda et al., 2007). In Figure 5 we present the detail for the flowsheet that converts xylose and glucose to furfural and HMF or DMF. We briefly describe below the models for the different units involved.

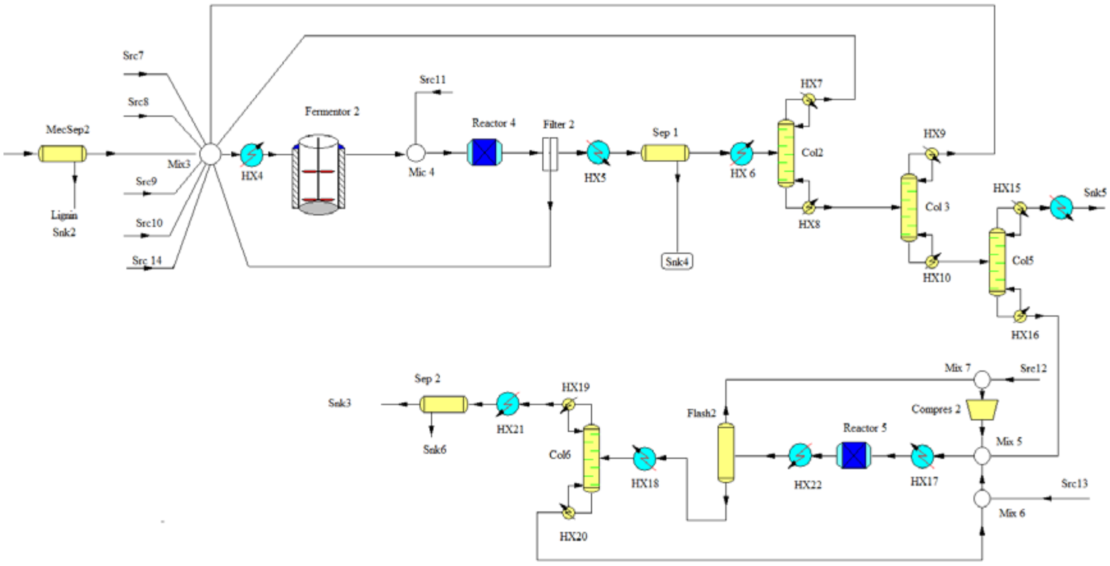


Figure 5.- Production of Furfural and DMF from pentoses and hexoses

The different ingredients are mixed in Mix 3 with the solution of sugars coming from biomass processing. We add butanol, HCl, $CrCl_3$ and NaCl together with recycled streams coming from different separation stages such as the Filter 2, where the solid catalyst is recovered, the first distillation column (column 2), where mainly water and butanol are recycled, and the distillate of column 3 consisting mainly of the same species. The streams are mixed adiabatically and heated up in heat exchanger 4 up to the reaction temperature. At this point the different species must meet certain concentrations for the reaction to reach high conversion from glucose to HMF and from xylose to furfural. Based on experimental results reported in the literature, the catalyst added ($CrCl_3$) should be 0.06 molar ratio to the sugars (Bider et al., 2010). The NaCl added corresponds to that needed to saturate the water (Roman-Leshkov et al., 2007). It is also assumed that the butanol represents twice the aqueous phase (Pagán Torres et al., 2012), the HCl added is 0.12 mol/L (Roman-Leshkov et al, 2007). Finally, we consider that the sugar concentration in water is 10% at the most, (Binder and Raines, 2009). This is a mayor assumption in terms of energy consumption since the higher the concentration the lower the energy consumption in the subsequent separation stages. However, based on the fact that phase separation allows the removal of most of the aqueous phase and that higher concentrations are not typically evaluated experimentally, we prefer to use this value as representative to be on the safe side. The model for the mixing is given by eqs. (1)-(5).

$$\frac{\mathrm{m(CrCl3, Mix3, HX4)}}{\mathrm{MW(CrCl3)}} = 0.06 \cdot \left(\frac{\mathrm{m(Gluc, Mix3, HX4)}}{\mathrm{MW(Gluc)}} + \frac{\mathrm{m(Xylo, Mix3, HX4)}}{\mathrm{MW(Xylo)}} \right); \tag{1}$$

$$\mathrm{m(NaCl, Mix3, HX4)} = 0.359 \cdot \mathrm{m(Wa, Mix3, HX4)} \tag{2}$$

$$\begin{aligned} &\mathrm{m(ButOH, Mix3, HX4)} = 2 \cdot (\mathrm{m(Wa, Mix3, HX4)} + \mathrm{m(NaCl, Mix3, HX4)} \\ &+ \mathrm{m(HCl, Mix3, HX4)} + \mathrm{m(CrCl3, Mix3, HX4)} + \mathrm{m(Gluc, Mix3, HX4)} + \\ &\quad \mathrm{m(Xylo, Mix3, HX4)}); \end{aligned} \tag{3}$$

To be on the conservative side,

$$\mathrm{m(Gluc, Mix3, HX4)} + \mathrm{m(Xylo, Mix3, HX4)} = 0.1 \cdot \mathrm{m(Wa, Mix3, HX4)}; \tag{4}$$

$$\mathrm{m(HCl, Mix3, HX4)} = 0.12 \cdot 0.001 \cdot 36.5 \cdot \mathrm{m(Wa, Mix3, HX4)}; \tag{5}$$

The operating temperature and pressure at the reactor are fixed at 180ºC and 11 bar since they are common for both sugars to be dehydrated. Further optimization studies of the reactor are encouraged to modify this temperature within typical operation ranges are from 160-200ºC (Marcotulio et al., 2000; Roman –Leshkov et al., 2007). Under these operating conditions, the total conversion from glucose to HMF becomes 0.67 (Roman –Leshkov et al., 2007) and from xylose to furfural to 0.56 (Marcotulio et al., 2010). The energy involved in the reaction is calculated based on an enthalpy balance. The reactor is modeled based on the stoichiometry and the energy balance as eqs. (6) - (13)

$$C_6H_{12}O_6 \rightarrow C_6H_6O_3 + 3H_2O \tag{6}$$

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O \tag{7}$$

$$\mathrm{m(Gluc, Fermentor2, Reactor4)} = (1 - \mathrm{Sel\_g} \cdot \mathrm{Conv\_g}) \cdot \mathrm{m(Gluc, HX4, Fermentor2)}; \tag{8}$$

$$\mathrm{m(HMF, Fermentor2, Reactor4)} = \mathrm{Sel\_g} \cdot \mathrm{Conv\_g} \cdot \mathrm{m(Gluc, HX4, Fermentor2)} \cdot \frac{\mathrm{MW(HMF)}}{\mathrm{MW(Gluc)}}; \tag{9}$$

$$\mathrm{m(Xylo, Fermentor2, Reactor4)} = (1 - \mathrm{Sel\_x} \cdot \mathrm{Conv\_x}) \cdot \mathrm{m(Xylo, HX4, Fermentor2)}; \tag{10}$$

$$\mathrm{m(furfural, Fermentor2, Reactor4)} = \mathrm{Sel\_x} \cdot \mathrm{Conv\_x} \cdot \mathrm{m(Xylo, HX4, Fermentor2)} \frac{\mathrm{MW(furfural)}}{\mathrm{MW(Xylo)}}; \tag{11}$$

$$\begin{aligned} &\mathrm{m(Wa, Fermentor2, Reactor4)} = \mathrm{m(Wa, HX4, Fermentor2)} + \\ &\mathrm{Sel\_g} \cdot \mathrm{Conv\_g} \cdot \mathrm{m(Gluc, HX4, Fermentor2)} \ \frac{\mathrm{MW(Wa)}}{\mathrm{MW(Gluc)}} + \\ &\mathrm{Sel\_x} \cdot \mathrm{Conv\_x} \cdot \mathrm{m(Xylo, HX4, Fermentor2)} \cdot \frac{\mathrm{MW(Wa)}}{\mathrm{MW(Xylo)}}; \end{aligned} \tag{12}$$

$$\mathrm{Q}(\mathrm{Fermentor2}) = \sum_{prod} \Delta H_f - \sum_{react} \Delta H_f; \tag{13}$$

Before attempting any product separation, HCl is neutralized. Due to the fact that NaCl has been used in the phase separation, NaOH is used. The energy from the reaction is removed from the jacketed reactor using cooling water. Apart from the species involved in the chemical reaction, the rest of the components advance to the filter. The neutralization is modeled by eqs. (14)-(17),

$$\mathrm{m(NaOH)} = \mathrm{m}(\mathrm{HCl, Fermentor2, Reactor4})\frac{\mathrm{MW(NaOH)}}{\mathrm{MW}(\mathrm{HCl})}; \tag{14}$$

$$\begin{aligned}\mathrm{m}(\mathrm{NaCl, Reactor4, Filter2}) &= \mathrm{m}(\mathrm{NaCl, Fermentor2, Reactor4}) \\ &+\mathrm{m}(\mathrm{HCl, Fermentor2, Reactor4})\frac{\mathrm{MW}(\mathrm{NaCl})}{\mathrm{MW}(\mathrm{HCl})};\end{aligned} \tag{15}$$

$$\begin{aligned}\mathrm{m}(\mathrm{Wa, Reactor4, Filter2}) &= \mathrm{m}(\mathrm{Wa, Fermentor2, Reactor4}) + \\ \mathrm{m}(\mathrm{HCl, Fermentor2, Reactor4})&\frac{\mathrm{MW}(\mathrm{Wa})}{\mathrm{MW}(\mathrm{HCl})};\end{aligned} \tag{16}$$

$$\mathrm{Q}(\mathrm{Reactor4}) = \Delta H_{neutra} \tag{17}$$

Next, the filter is expected to recover the solid catalyst, $CrCl_3$, at reaction temperature, while the rest goes to the heat exchanger.

After the filter, a phase separation is performed. Based on experimental results from the literature, an operating temperature of 37ºC is selected (de Álvila et al., 2012). Thus, we cool down the mixture in heat exchanger 5 from reaction temperature to 37ºC. The partition coefficient of the HMF and furfural is taken to be 3, in volume ratio, towards the organic phase (Roman-Leshvok et al. 2009; Roman-Leskov et al., 2007). The water accompanying the organic phase is considered to be lower or equal than 6%, and the butanol in the aqueous phase lower or equal to 1% (Roman – Leshkov et al., 2007). We also assume that all the NaCl exits with the aqueous phase (de Ávila et al., 2012). Note that a minimum amount may remain in the organic phase but is its neglected (Roman-Leshkov et al., 2007), and that 50% of the remaining sugars end at each phase. The separation stage is modeled using eqs. (18) – (27),

$$\mathrm{m}(\mathrm{J, Filter2, HX5}) = \mathrm{m}(\mathrm{J, HX5, Sep1}) \ \forall J \tag{18}$$

$$\mathrm{Q}(\mathrm{HX5})=\sum_{j}\mathrm{m}(\mathrm{J},\mathrm{Filter2},\mathrm{HX5})\cdot\mathrm{c\_p\_ind}(\mathrm{J})\cdot\left(\mathrm{T\_phasesep}-\mathrm{T}(\mathrm{Filter2},H\mathrm{X5})\right); \tag{19}$$

$$\mathrm{m}(J,\mathrm{HX5},\mathrm{Sep1}) = \mathrm{m}(J,\mathrm{Sep1},\mathrm{HX6}) + \mathrm{m}(J,\mathrm{Sep1},\mathrm{Snk4}) ; \tag{20}$$

$$\mathrm{m}(NaCl,\mathrm{Sep1},\mathrm{HX6}) = 0 \tag{21}$$

$$\mathrm{m}(J,\mathrm{Sep1},\mathrm{HX6}) = \mathrm{m}(J,\mathrm{Sep1},\mathrm{Snk4}); J = Gluc\,\&\,Xylo \tag{22}$$

$$\mathrm{m}(\mathrm{Wa},\mathrm{Sep1},\mathrm{HX6}) \le 0.06\cdot\mathrm{MT}(\mathrm{Sep1},\mathrm{HX6}); \tag{23}$$

$$\mathrm{m}(\mathrm{ButOH},\mathrm{Sep1},\mathrm{Snk4}) \le 0.015\cdot\mathrm{MT}(\mathrm{Sep1},\mathrm{Snk4}) ; \tag{24}$$

$$\begin{gathered}\mathrm{m}(\mathrm{HMF},\mathrm{Sep1},\mathrm{HX6})\cdot\left(\begin{array}{l}\dfrac{\mathrm{m}(\mathrm{HMF},\mathrm{Sep1},\mathrm{Snk4})}{\rho_{\mathrm{hmf}}}+\dfrac{\mathrm{m}(\mathrm{furfural},\mathrm{Sep1},\mathrm{Snk4})}{\rho_{\mathrm{fur}}}\\ +\dfrac{\mathrm{m}(\mathrm{Wa},\mathrm{Sep1},\mathrm{Snk4})+\mathrm{m}(\mathrm{Gluc},\mathrm{Sep1},\mathrm{Snk4})+\mathrm{m}(\mathrm{Xylo},\mathrm{Sep1},\mathrm{Snk4})}{\rho_{Wa}}\end{array}\right)=\\ \mathrm{Recov}\cdot\left(\mathrm{m}(\mathrm{HMF},\mathrm{Sep1},\mathrm{Snk4})\cdot\left(\dfrac{\mathrm{m}(\mathrm{HMF},\mathrm{Sep1},\mathrm{HX6})}{\rho_{\mathrm{hmf}}}+\dfrac{\mathrm{m}(\mathrm{furfural},\mathrm{Sep1},\mathrm{HX6})}{\rho_{\mathrm{fur}}}+\dfrac{\mathrm{m}(\mathrm{ButOH},\mathrm{Sep1},\mathrm{HX6})}{\rho_{\mathrm{but}}}\right)\right);\end{gathered} \tag{25}$$

And similarly for the furfural

$$\begin{gathered}\mathrm{m}(\mathrm{furfural},\mathrm{Sep1},\mathrm{HX6})\cdot\left(\begin{array}{l}\dfrac{\mathrm{m}(\mathrm{HMF},\mathrm{Sep1},\mathrm{Snk4})}{\rho_{\mathrm{hmf}}}+\dfrac{\mathrm{m}(\mathrm{furfural},\mathrm{Sep1},\mathrm{Snk4})}{\rho_{\mathrm{fur}}}\\ +\dfrac{\mathrm{m}(\mathrm{Wa},\mathrm{Sep1},\mathrm{Snk4})+\mathrm{m}(\mathrm{Gluc},\mathrm{Sep1},\mathrm{Snk4})+\mathrm{m}(\mathrm{Xylo},\mathrm{Sep1},\mathrm{Snk4})}{\rho_{Wa}}\end{array}\right)=\\ \mathrm{Recov}\cdot\left(\mathrm{m}(\mathrm{furfural},\mathrm{Sep1},\mathrm{Snk4})\cdot\left(\dfrac{\mathrm{m}(\mathrm{HMF},\mathrm{Sep1},\mathrm{HX6})}{\rho_{\mathrm{hmf}}}+\dfrac{\mathrm{m}(\mathrm{furfural},\mathrm{Sep1},\mathrm{HX6})}{\rho_{\mathrm{fur}}}+\dfrac{\mathrm{m}(\mathrm{ButOH},\mathrm{Sep1},\mathrm{HX6})}{\rho_{\mathrm{but}}}\right)\right);\end{gathered} \tag{26}$$

$$\mathrm{m}(\mathrm{ButOH},\mathrm{Sep1},\mathrm{Snk4}) \ge 0.005\cdot\mathrm{MT}(\mathrm{Sep1},\mathrm{Snk4}) ; \tag{27}$$

The organic phase from the phase separator is distilled. Based on offline simulation results in CHEMCAD, we fix the reflux ratio at 1.5. The column operates at low pressure, 0.5 atm, to avoid species decomposition. From the distillate we recover 99,9% of butanol and the water in the feed together with the sugars. The boiling temperature of the mixtures with sugars may be affected by their presence, 0.51 ºC/M. The low composition in sugars supports the assumption that the effect is negligible. From the bottoms we obtain HMF, furfural and the rest of butanol. Short cut models (Biegler et al., 1997) and the input from the rigorous simulation in CHEMCAD have been used to model the distillation columns. All the columns have total condensers and operate in sequence so that the bottoms of one column correspond to the feed operating conditions for the next one. The second column recovers butanol as distillate and HMF and furfural at the bottoms. We assume sharp distillation based on the large difference in the boiling points between butanol and the other two compounds. Finally, the third column separates furfural to be sold from the HMF that is further used for the production of DMF.

The production of DMF from HMF is carried out in a catalytic reactor at 120 ºC and 16 bar using CuRu as catalyst. We feed HMF and butanol so that the concentration of the first one is 5% of the liquid mixture. The reactor operates with an excess of hydrogen, 12 times the one given by the stoichiometry (Kazi et al., 2011). Next, the mixture is heated up to 120ºC in heat exchanger 17 before being fed to the reactor. The hydrogenation reactor is modeled using eqs. (28) –(33)

$$\mathrm{m}\left(\mathrm{J},\mathrm{Compres2},\mathrm{Mix5}\right) + \mathrm{m}\left(\mathrm{J},\mathrm{Mix6},\mathrm{Mix5}\right) + \mathrm{m}\left(\mathrm{J},\mathrm{Col5},\mathrm{Mix5}\right) = \mathrm{m}\left(\mathrm{J},\mathrm{Mix5},\mathrm{HX17}\right); \tag{28}$$

We assume that the mix is adiabatic

$$\mathrm{m}\left(\mathrm{H2},\mathrm{Compres2},\mathrm{Mix5}\right) = 12\cdot 4\cdot \mathrm{m}\left(\mathrm{HMF},\mathrm{Col5},\mathrm{Mix5}\right)\frac{\mathrm{MW}\left(\mathrm{H2}\right)}{\mathrm{MW}\left(\mathrm{HMF}\right)}; \tag{29}$$

$$0.05\cdot \mathrm{m}\left(\mathrm{ButOH},\mathrm{Mix6},\mathrm{Mix5}\right) = \mathrm{m}\left(\mathrm{HMF},\mathrm{Col5},\mathrm{Mix5}\right); \tag{30}$$

$$\mathrm{Q}\left(\mathrm{HX17}\right) = \sum_j \mathrm{m}\left(\mathrm{J},\mathrm{Mix5},\mathrm{HX17}\right)\cdot\left(\lambda + \int_{T(Mix5,HX17)}^{T(HX17,\mathrm{Re}actor5)} Cpdt\right) \tag{31}$$

In the reactor the following reaction takes place:

$$C_6H_6O_3 + 4H_2 \rightarrow C_6H_8O + 2H_2O \tag{32}$$

The conversion is reported to be 100% (Kazi et al., 2011) and the mass balance is calculated based on the stoichiometry of the reaction. The heat of reaction is calculated based on an enthalpy balance.

$$\mathrm{Q}\left(\mathrm{Reactor5}\right) = \sum_{prof} \Delta H_f - \sum_{reac} \Delta H_f \tag{33}$$

The excess of hydrogen is recovered in a flash operating at 30 ºC and 2 atm to avoid the losses on the main compounds, and so that the hydrogen is almost dry for recycling. The stream exiting the reactor is cooled down and the vapor condensed at heat exchanger 22. The hydrogen recycled is mixed with fresh hydrogen to maintain the operating ratio and are compressed using a two stage compressor with intercooling.

$$\mathrm{Q}\left(\mathrm{HX22}\right) = \sum_j \mathrm{m}\left(\mathrm{J},\mathrm{HX22},Flash2\right)\cdot\left(-\lambda + \int_{T(Mix5,HX17)}^{T(HX17,\mathrm{Re}actor5)} Cpdt\right) \tag{34}$$

The DMF, butanol and water are sent to column 6. The column is modelled based on short-cut methods (Biegler et al 1997). We fix the reflux ratio at 1.5 and operate the column at 1 atm. We recover DMF and water as distillate. Both are separated using a phase separator. From the bottoms of the column we obtain butanol that is recycled to the reaction stage where it is mixed with fresh one to maintain the concentration of HMF at the entrance of the reactor at 5% by weight.

3.2.- Algae to biodiesel and DMF

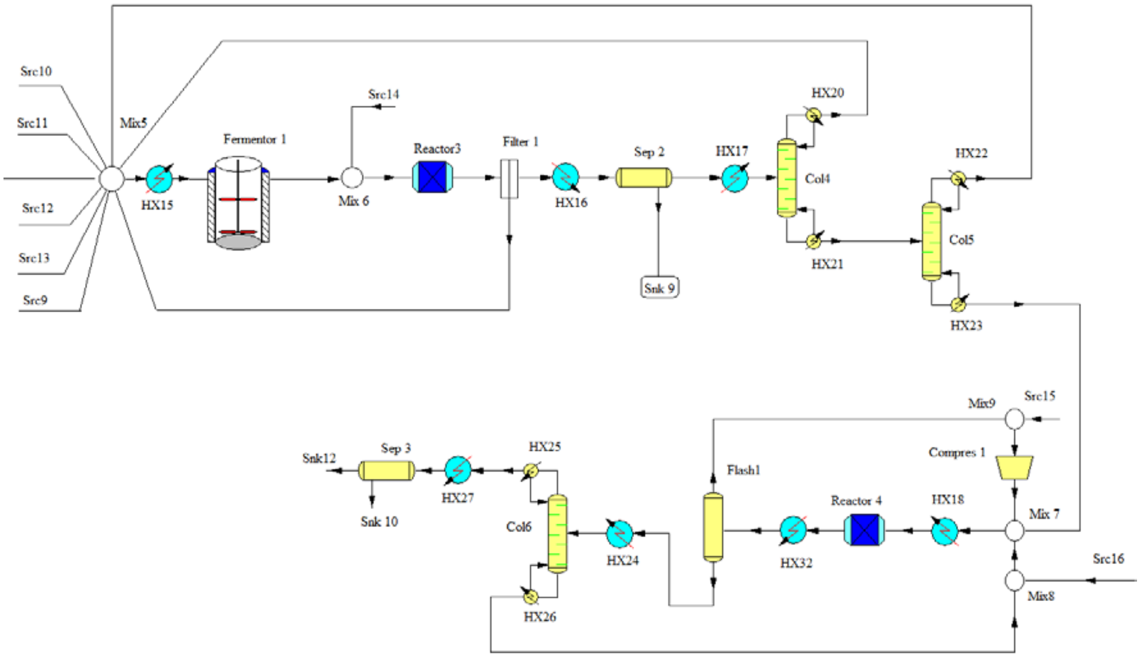


Figure 6.- Production DMF from glucose

In Figure 6 we see the process for the conversion of the glucose from algae to DMF. The process is similar to the previous one, but simpler, since the only sugar present is glucose. Therefore, in this case we will only be able to produce one HMF and from it, DMF. In this sense, after the fermentation and neutralization of the mixture, we proceed to catalysts separation. Next, we separate the aqueous phase including the salts. The mixture, mainly butanol, HMF and a small amount of water and glucose is distilled so that most of the glucose, butanol and water is recovered. In the second distillation column we separate the rest of the butanol, which is recycled to the reactor from the HMF that is fed to the synthesis stage where we add butanol again and hydrogen. In the reactor, similar to the previous case, DMF is produced and the excess of hydrogen is recycled, while the liquid phase, butane, water and DMF is distilled. The butanol is recovered and recycled to Mix8 in the figure, and the DMF together with water goes as distillate. The two phases, water and DMF, are separated by gravity.

3.3.-Problem formulation and solution procedure

We formulate the problem for the use of switchgass as raw material as an MINLP, where the objective function is a simplified production cost involving the income due to the furfural and the DMF, assumed to have a price of $2/kg, and the energy consumed in the process. Due to the fact that there is only one integer variable, we decompose the problem into two NLP with 3000 equations and 3600 variables each to simultaneously optimize the operating conditions of the pretreatment and heat integrate the entire flowsheet using Duran & Grossmann's (1986) model. In the case of the use of algae, the problem is formulated as an NLP with 4100 equations and 5400 variables where the main decision variables are the algae composition, the operating pressures of the distillation columns and the operating conditions of the transesterification reactor. Again simultaneous optimization and heat integration is performed. We use multiple starting points to solve the problems with CONOPT 3.0 as the preferred solver.

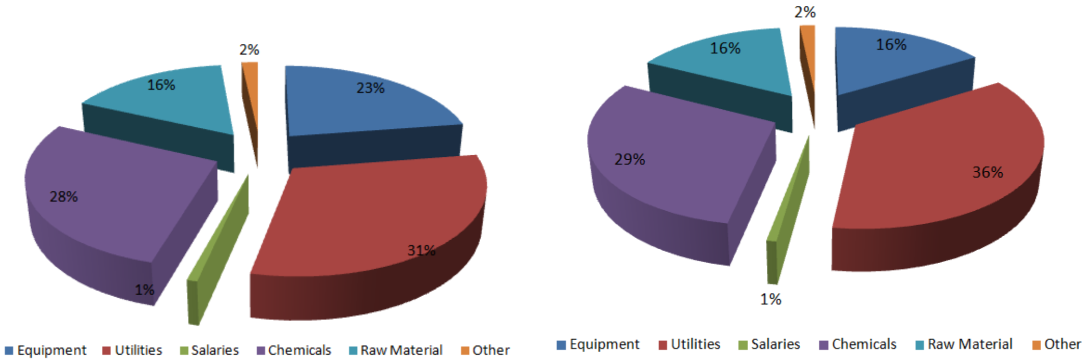
Next, we develop the optimal heat exchanger network using SYNHEAT (Yee & Grossmann 1990). Finally, the cost analysis is performed involving raw material cost (biomass, ethanol), maintenance, cost of utilities and chemicals (fertilizers, hydrogen, butanol, salt, glycerol and protein), labor, annualized equipment cost and the cost for the management of the facility, following Sinnot´s (Sinnot, 1999) method; see also previous papers by the authors (Martín & Grossmann, 2011) for further details on the cost functions. In the case of the algae based process, we will also determine the water consumption so that it is possible to make a more complete comparison with previous work. We use Ahmetovic´s et al. (2010) approach

4.-Results

4.1.- Lignocellulosic based DMF and furfural

If we use lignocellulosic switchgrass as raw material, we have as main products DMF and furfural and as byproduct lignin. We consider a price for the switchgrass of $75/t (http://cropwatch.unl.edu/), assuming $0.1/kg of profit for the glycerol produced, according to the current price (www.icispricing.com) and the target from the DOE, $0.2/kg of protein, 1.6 $/kg of Hydrogen (DOE target) and 1.23 $/kg ButOH, (http://en.wikipedia.org/wiki/Liquid_fuels), 0.2 $/kg for HCl (http://www.icis.com/) and $0.1/kg for NaCl (ttp://www.alibaba.com)

Of the two pretreatments considered, AFEX turns out to provide the better performance for a production cost of $11.4/gal ($3/kg) versus $12.15/gal ($3.20/kg) for the acid based pretreatment with an investment cost of $570 MM (vs. 764MM). The optimal operating conditions are of 180ºC, low contact time, 0.5 kg of water added per kg of dry biomass and 2 kg of ammonia per kg of dry biomass. We would like to highlight that the process is large in terms of operations involved in the pretreatment of the biomass to extract the sugars and the transformation of the xylose and glucose into furfural and DMF, respectively results in high investment costs together with relatively low conversion since we obtain 24MMgal of products, 9.3 MMgal/yr of furfural and 14.7 MMgal/yr of DMF, representing 15% by weight of the initial biomass for the best of the two processes. Due to the need of energy for the process, the lignin produced is fully used to provide part of it (representing around 25% of the total energy required assuming 78% of efficiency in the boiler). Figure 7 presents a breakdown of the production costs for both alternatives where we can see the large contribution of the utilities and the chemicals such as H_2, HCl, and butanol. The main consumption of energy is due to the separation of the solvent that is used to extract the HMF and the furfural as well as the high temperature of operation of the dehydration reactor.



Acid AFEX

Figure 7.- Production cost breakdown for the production of DMF and furfural from switchgrass

There are only a couple of techno-economical studies for the production of these chemicals and both start with the sugars whose price is based on market studies. However, the production prices we obtain are in line with the results provided by de Ávila Rodriguez & Guirardello (2012) for the production of

DMF from fructose alone, and also of the same order of the ones reported by Kazi et al (2011), who also produced only DMF from pure glucose. Therefore, in those studies the cost involved in processing the biomass is assumed to the included in the cost of the sugars.

4.2.-Algae based DMF

In this case we have as variable the algae composition to produce as main products FAEE and DMF, while as byproducts we can obtain glycerol and protein. The algae composition that yields the optimal production facility corresponds to 60% oil, 30% starch and 10% protein, as in previous studies. The reason is that the production of biodiesel is cheaper in terms of energy consumption and investment cost, while the use of starch as raw material is much more expensive. The operating conditions of the transesterification reactor are also similar to the ones in previous papers for integrated processes; see Table 2 where only small changes can be seen.

Table 2.- Operating conditions at the FAEE transesterification reactor. Enzyme catalyst.

	Enzymatic			
	Alone (*) (ethanol $1/gal)	Integrated E + biodi (**)	Enhanced ethanol (***)	FAEE + DMF
Temperature(ºC)	45	30	30	30
Pressure(bar)	4^f	4^f	4^f	4^f
ratio_et	8.9	4.1	4.2	4.2
Time (h)	6.9	8.0	8.0	8.0
Cat/lipase(%)	14.0	13.0	13.1	13.0
Water added	0.0	0.0	0.0	0.0

(*) Severson et al 2012, (**) Martin& Grossmann 2012 (***) Martín & Grossmann 2013

The total production capacity of biofuels is 98 MMGal /yr where 81MMGal/yr correspond to biodiesel (FAEE) and 17 MMGal/yr to DMF. The investment cost for this facility is high, $693 MM, even higher than the one that uses switchgrass as raw material based on the need for algae growth and oil extraction, as well as biodiesel production steps. The production cost for the main products, namely FAEE and DMF, is $1.98/gal. Figure (8) presents the breakdown of the production cost where utilities (steam, cooling water and electricity) represent the major contribution.

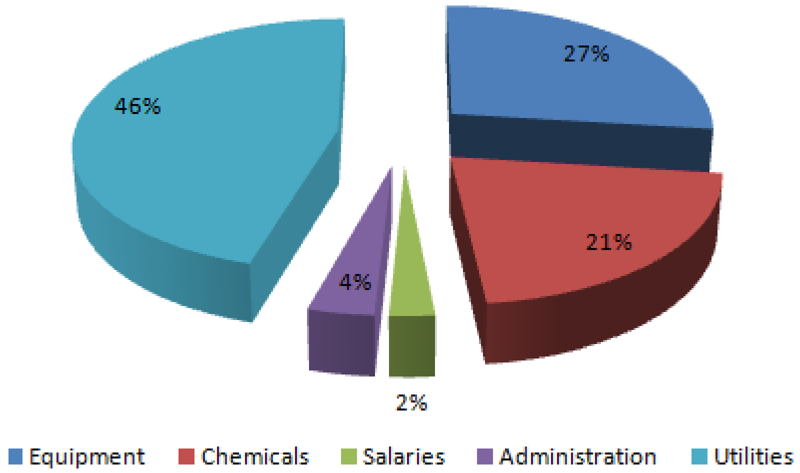


Figure 8.- Production cost breakdown for the production of FAEE and DMF from algae

This production cost ($1.98/gal), the investment, the water and the energy consumption, see Table 3, are higher than any of the other previous designs for the production of biodiesel. However, we are not only producing biodiesel but also a useful intermediate for the industry from renewable sources.

Table 3 .-Summary of results with different integration alternatives

	Enzymatic (Ethanol and Gly)	Integrating MetOH (AR)	Enzymatic EtOH + D&TTBG & FAEE	Enhanced ethanol	FAEE + DMF & Glycerol
$\$/\text{gal}_{\text{biofuel}}$	0.35	0.66	1.00	0.45	1.98
Energy (MJ/gal$_{\text{biofuel}}$)	4.00	3.65	3.36	4.20	79
Water (gal/gal$_{\text{biofuel}}$)	0.59	0.79	0.59	0.60	18
Investment(MM$)	180	118	167	211	693
Capacity (Mgal/yr)	90	69	105 (96 biod/9bioet)	94 (81biod/13bioet)	98 (81 Biod/17 DMF)

4.3.-Stragetegies to reduce energy consumption and production cost.

Based on the results for the different processes evaluated, either using switchgrass or algae, we identify the distillation column used to separate the buthanol from the HMF and / or furfural as the most energy intensive equipment. There are two main reason for this. On the one hand, the amount of butanol that is needed. Based on experimental data discussed in the development of the model, typically the amount of organic phase is a number of times that of the aqueous phase. Furthermore, the amount of water needed in the process depends heavily on the concentration of sugars in the dehydration reactor. Most of the experimental results presented in the literature comment on glucose concentrations around 10% total or with respect to the water phase (de Ávila et al., 2012). On the one hand, some studies reveal that it is possible to use a solution up to 30% by weight of sugars in the water phase (Pagán and Torres, 2006), and the butanol used is typically several times the aqueous phase, more than 4, (Kazi et al., 2012), while for concentrations of xylose higher than 10%, the yield to furfural decreases (Rong et al., 2012). Therefore, there is quite a significant disagreement between the maximun coencentration of sugars in the reacting mixture, which results in the amount of butanol to be removed. Therefore, there is an opportunity for reactor optimization that will lead to important energy and water consumption reductions which will reflect upon the production cost.

If we start from pure glucose and xylose, it is possible to easily decide on the composition of the feed to the dehydration reactor. However, if we start with raw biomass, the process is more complex due to the fact that in biomass processing, water is added and it will carry the sugars dissolved. From the conservative results presented above, we can see that water is in fact added to the reactor to adjust the sugar concentration below 10% in the water. We can reduce this water concentration, while maintaning the rest of the ratios constant including that related to buthanol given by eq (3).

For the two cases we have evaluated, the use of switchgrass and the use of algae, we report the possible savings as long as the dehydration reactor is feasible. Due to the fact that we are cannot experimentally validate the feasibility, we prefer not to include a detailed cost analysis, but only the general trend and relative savings in case the fraction of sugars in the reactor can be increased until 30% of the water amount added. It is important to keep in mind that while Roman Leskov et al. (2007) claim that it is possible to increase the concentration of glucose in the mixture, Rong et al. (2012) report a decrease in the yield of the dehydration as the xylose concentration increases.

For the use of swichgrass, based on the AFEX pretreatment, Figure 9 presents the relative energy consumption in the synthesis area, from the feed to the dehydration reactor to the columns where butanol is separated from HMF and furfural. It can be seen that energy can be reduced up to 60%, which can be translated into savings of $55MM in hot utilities and $11 MM in cooling utilities as well as in raw materials such as HCl or butanol, which can result in a production cost of $1.5/kg of HMF and furfural if we can recover the NaCl that comes out with the aqueous phase. The investment cost of the plant is also reduced due to the smaller size of a number of equipment in the synthesis by almost half, $370MM.

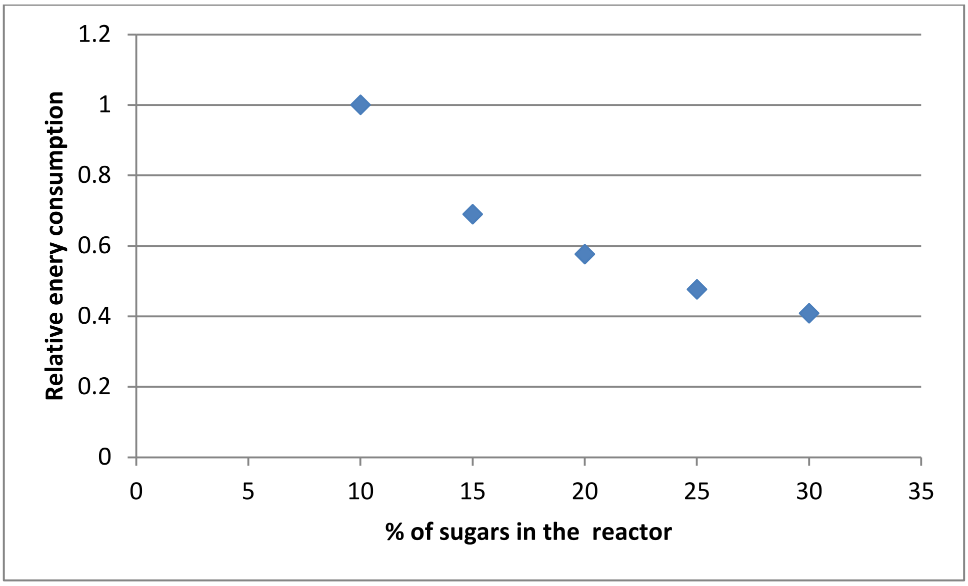


Figure 9.-Effect of the sugar content in the dehydration reactor. Switchgrass

For the use of algae, we only have glucose in the dehydration reactor. We follow the same approach as for the previous case reducing the water that can be fed to the dehydration reactor to see the effect of that on the separation stages of the product HMF, see Figure 10. More than 60% of energy can be saved by increasing the sugar concentration in water. These savings can be translated into utilities savings of up to $30MM/yr of hot utilities and around $8MM in cooling utilities together with a decrease in raw materials, resulting in a decrease of around $0.5/gal with respect to the base price presented above, $1.98/gal. This value is becoming competitive with the production of different substitutes of diesel and gasoline as presented in Table 3, with the advantage that HMF and DMF can have different added valued uses. Furthermore, the investment in the plant can be reduced down to $415MM, representing two thirds of the original base case based on 10% of sugars in water.

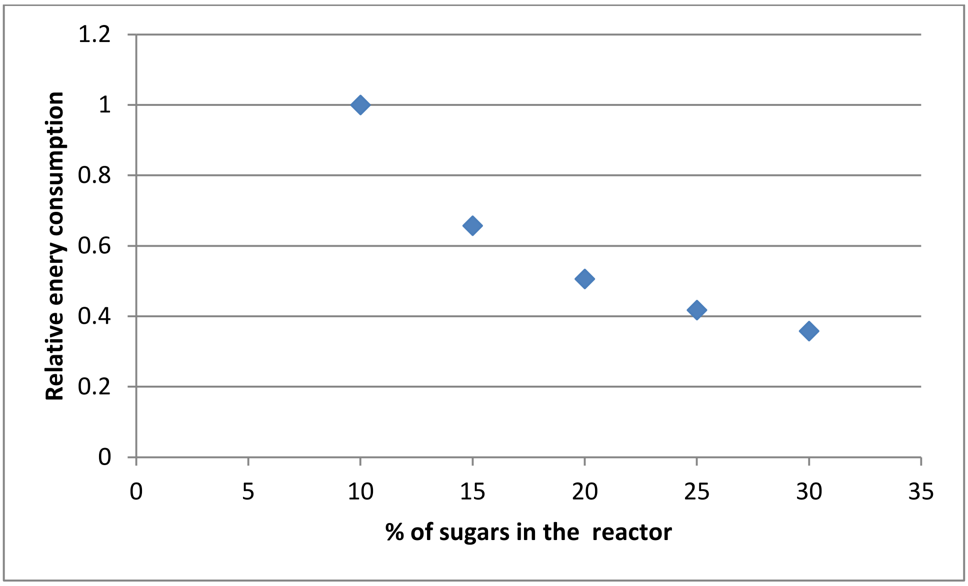


Figure 10.-Effect of the sugar content in the dehydration reactor. Algae based

5.-Conclusions

In this paper we have explored the production of DMF and furfural from switchgrass and algae developing optimal conceptual designs for the corresponding production facilities.

When switchgrass is used, the preferred pretreatment is AFEX followed by hydrolysis so that the xylose and glucose are available for dehydration. If algae are used, we cannot only produce DMF, due to the starch within the algae, but also biodiesel that we assume is FAEE for which we need ethanol.

The resulting optimal processes yield promising production prices, around $2.3/kg if swichgrass is used and $1.7/gal in the case of producing biodiesel and DMF from algae. However, in the last case the energy consumption as well as the water consumption are really high due to the purification and separation stages for the intermediates. It is technologically feasible to produce furfural and DMF out of algae and switchgrass but at a high cost.

For further experimental studies, this paper suggests the experimental optimization of the dehydration based on the use of lower amount of the second phase in the dehydration reactor (in this case butanol) so that the separation of the products from the separating agent is less expensive, and /or the use of a different agent that has a lower vaporization heat. This can somehow be obtained if the concentration of sugars in the aqueous phase is increased.

Nomenclature

Conv_g: Conversion ot glucose /0.82/
Conv_x: Conversion to xylose /0.7/
Cp: Heat capacity (kJ/kg K)
m(J,unit, unit1) : Mass flow rate (kg/s)
Q(unit): Heat involved in unit (kW)
T_phasesep: Temperature of phase separators (ºC)
Recov: Partition coefficient /3/
Sel_g: Selectivity to glucose /0.85/
Sel_x: Selectivity to xylose /0.8/

Simbols:
λ: Latent heat (kJ/kg)
ρ: Liquid I density (kg/m3)
ΔH: Reaction enthalpy (kJ/kmol)

Units
Col: Column
Compres: COmpressor
HX Heat Exchanger
Mix: Mixer
Press: Mechanical Press
Sep: Separator
Snk: Sink

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