Biomass as source for chemicals, power and fuels

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Abstract

In this chapter we discuss on the possible routes to process biomass for the production of chemicals, fuels and power. Once the individual processes are described, we present several alternatives for the use biomass to produce a number of products simultaneously taking advantage of synergies between processes, the possibility of producing intermediates out of the same raw materials, and process integration opportunities among processes and energy sources. The methodology used is based on mathematical optimization techniques to allow for solving tradeoffs and identifying the best integrated operation of multiproduct plants.

8.1. Introduction and method.

Biomass has been used as a source of energy and construction materials for centuries. However, the easy access to crude oil in the late 70's and its cheap price reduced the use of biomass and limited its applications (BP, 2014). The unstable situation in many producing countries and the expected depletion of the resources has encouraged the search for alternative fuels. Actually, it has been more a "back to the past" trend rather than a step forward. For instance, the Ford T, the first car produced in an assembly line, was meant to run on ethanol, while vegetable oil fed diesel engines in the beginning. Over the last decades, research has focused on the use of biomass to substitute fuels by sustainable ones and lately other chemicals have been included in the portfolio. In this chapter we start with individual processes that transform various types of biomass into products. Next, we comment on the properties and composition of the biomass that will allow evaluating the possibilities for integrated production processes. Finally, biomass, unlike solar or wind energy, can be stored for a certain period. This is an important property to have since it allows using biomass as back up renewable energy source in the operation of solar and/or wind based facilities.

The design of individual or integrated processes for the transformation of biomass into different fuels can benefit from process system engineering approaches. Conceptual design based on superstructure optimization (Martín & Grossmann, 2013) is a powerful tool to select among technologies, i.e. biodiesel

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catalysts, gasification alternatives, and determine the optimal operating conditions. Basically, the approach consists of modeling the different options using simple but reliable models, formulating the superstructure of alternatives in the form of mixed integer non linear programming problems and solving it. Simultaneous optimization and heat integration can be included in the formulation (Duran & Grossmann, 1986). Next, for a given process topology, we can design the heat exchanger network (HEN) to reduce the utilities consumption based on the model presented by Yee & Grossmann (1990). Water consumption issues can be addressed either at the design stage of the flowsheet and/or by .designing the optimal water treatment and reuse network (Ahmetovic and Grossmann, 2011).

Typically, individual processes do not operate independently but as a part of chemical complexes. In order to identify integration opportunities and evaluate non obvious tradeoffs, systematic analysis and process design using mathematical programming techniques is again a powerful ally. Once the process or the integrated complex is established, rigorous simulation using commercial software such as ASPEN plus or CHEMCAD, can be used to simulate the performance of the process (i.e. Zhang et al. (2003) for biodiesel production, de la Cruz et al. (2014) for integrated production of diesel substitutes).

8.2 Individual processes

8.2.1 Grain based

Grain, corn or wheat, consists mainly of starch which is a polymer of glucose units. Therefore, they both are used within the food chain. However, by proper breakage of the polymer, grain can be a source of glucose. This is the basis for first generation bioethanol.

In order to extract the starch out of the grain, it is processed through grinding and cooking with steam. Next, the biomass is subjected to liquefaction and saccharification at 90ºC and 65ºC, respectively, over 30 min each, so that the starch breaks into maltose and then into glucose, as presented in the following reactions. Apart from the proper temperature, enzymes, amylases and glucoamylases, catalyze the process (Jacques et al., 1999).

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\alpha-amylase} nC_{12}H_{22}O_{11}$$

$$\mathrm{C_{12}H_{22}O_{11} + H_2O \xrightarrow{glucoamylase} 2C_6H_{12}O_6}$$

At this point glucose is available as a raw material in a dilute stream with water. There are a number of chemicals that can be produced out of glucose fermentation such as acetone, butanol but ethanol is the easiest one. The fermentation of glucose to ethanol takes place isothermally at 32-38 ºC under anaerobic conditions. We need to ensure that the ethanol concentration in the mix is always below 15%, so that the fermentation is not inhibited. Ethanol is toxic for the *saccharomices cerevisiae*, the bacterium catalyst.

$$\mathrm{C_6H_{12}O_6 \xrightarrow{\mathit{yeast}} 2C_2H_6O + 2\,CO_2}$$

While ethanol is the main product, there are a number of secondary reactions whose conversions and stoichiometry are presented in Table 8.1

Table 8.1 Main reactions in the production of corn based ethanol

Reaction	Conversion
glucose $\xrightarrow{yeast}$ 2 ethanol + 2 carbon dioxide	0.92
$C_6H_{12}O_6 + 2\,H_2O \xrightarrow{yeast} 2C_3H_8O_3 + O_2$	0.034
$C_6H_{12}O_6 + 2\,CO_2 \xrightarrow{yeast} 2C_4H_6O_4 + O_2$	0.01
glucose $\xrightarrow{yeast}$ 2 lactic acid	0.002
glucose $\xrightarrow{yeast}$ 3 acetic acid	0.0024
glucose + 1.2 ammonia $\xrightarrow{yeast}$ 6 cell mass + 2.4 water + 0.3 oxygen	0.0316

The fermentation takes place for 24-72 h for the ethanol to be produced. After that, and before further treatment, Karuppiah et al. (2008) showed that solids separation is the best option. A flotation unit operation is used to recover the protein that will be dried to produce the so-called dried distiller grains and soluble that can be used as cattle feed. The liquid is now sent to a distillation column to concentrate the ethanol. One of the main disadvantages of the process is the energy intensive distillation in the beer column. In order to reduce the energy and cooling needs at that column, a multi effect distillation system can be used. It consists of splitting the feed into a number of columns so that the reboiler of the lower pressure column acts as condenser of the higher pressure column. A three effect system is used (Karrupiah et al 2008) to reduce the energy needs with a limited increment in the investment cost. The bottoms of the column contain mainly water, but a number of organic species follow such as lactic acid, acetic acid, glycerol, etc. This stream is actually a good source of water to reduce the overall water consumption, (Ahmetovic et al., 2010) but it has to be properly treated to remove the organics. Ethanol fuel cannot contain more than 0.03% water. Therefore, a dehydration step follows the beer column. Rectification is the typical option (Jacques et al., 1999) but it is more energy intensive. Therefore, a combination between adsorption in corn grits and molecular sieves allows reducing the energy consumption while securing fuel quality. Energy integration in this process is crucial for a positive net energy balance and a competitive price of 1.24 $/gal (Karuppiah et al., 2008). The advantage of energy integration is twofold. First, it reduces the energy consumption in a challenging process since the operating temperatures are low, and reusing the energy is a difficult task. Furthermore, the fermentation is exothermic, but operates at low temperatures increasing the cooling needs. As a result, energy integration also reduces the cooling needs for a minimum of 1.5 gal of water per gal of ethanol produced (Ahmetovic et al 2010). Figure 8.1. shows a scheme of the process.

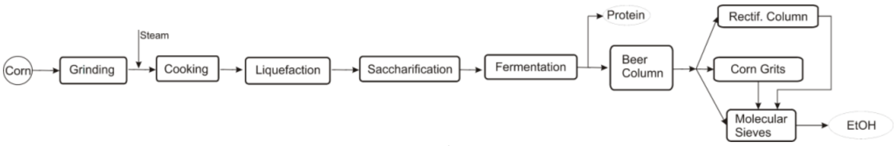

Fig. 8.1 Block diagram for corn based ethanol

8.2.2 Oil Based

The second main biofuel is biodiesel. First generation biodiesel has traditionally been produced from oil seeds. The oil is extracted from the seed using mechanical operations, providing heat and typically using a solvent. There are a number of procedures, but most of them make use of any of these three options. Therefore, once the oil is extracted, it has to be separated from the solvent using flash distillation. The high difference in the boiling point between the oil and the solvent simplifies the process. As in the case of the bioethanol, seeds and grain are both food. The ethics behind their use as a source of fuels have pushed the industry towards substituting the source of oil to non edible seeds such as jatropha or cooking oil. In this last case, the impurities must be taken into account before processing the oil.

The production of biodiesel from oil is based on the transesterification reaction of the oil with alcohols. Basically the oil consists of three chains of hydrocarbons whose viscosity is difficult to process. Therefore, the idea is to break it down into three chains. By doing this, we not only reduce the viscosity of the mixture, but also the properties of the product match those of the crude based diesel.

The transesterification is an equilibrium reaction between the oil and alcohols. For economic reasons, methanol has been used for a long time. From the technical point of view, it provides high yield to biodiesel, fatty acid methyl ester (FAME), and quick reaction times. Martín & Grossmann (2012) evaluated a number of catalysts, homogeneous acid and basic, heterogeneous, enzymatic and non-catalyzed under supercritical conditions. In order to drive the equilibrium to products, an excess of alcohols is typically used as well as the proper amount of catalysts and the operating pressure and temperature (Meher et al., 2006). The impurities in the oil, water and Free Fatty acids, pose on the use of alkali catalyst an extra challenge since pretreatment must be used to esterify them using an acid catalyst. When comparing the different catalysts, the actual process flowsheet structure changes from one to another. After the transesterification, a distillation column is typically used to recover the excess of methanol. If homogeneous catalysts are used, a washing step is needed to separate the catalyst with the polar phase from the biodiesel. Next, the polar phase is neutralized before the glycerol is purified. The organic phase containing the biodiesel is distilled to eliminate the unconverted oil. However, the use of heterogeneous catalysis or supercritical conditions simplifies the purification steps since a solid liquid separation removes the catalyst after the reaction, and after the polar – organic phase separation, the products have higher purity. Figure 8.2 shows the block diagram from purified oil. Units and streams in discontinuous boxes and lines are optional depending on the catalyst used.

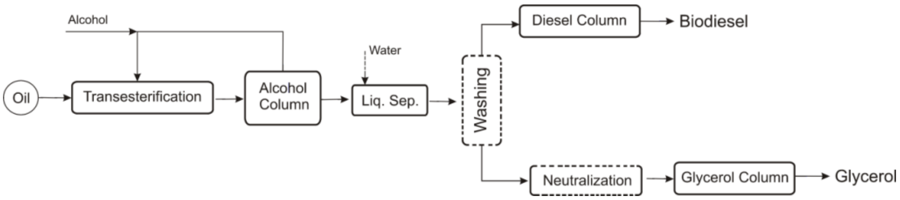

Fig. 8.2 Oil based biodiesel.

Martín & Grossmann (2012) optimized the production of biodiesel using methanol providing the optimal operating conditions at the reactor and suggesting the use of alkali catalyst for oil with a limited amount of impurities and heterogeneous catalyst for cooking oil. The formulation they used in the optimization, Duran and Grossmann's Model (1986) for simultaneous optimization and heat integration, allowed determining tradeoffs related to the excess of methanol used in the transesterification versus the energy that is to be spent in the recovery stage. In this way, the optimal operating conditions at the reactor are computed. Note, that the results are different to the ones reported in the literature (Zhang et al 2003). The values used by Zhang et al. (2003) are based on experimental evaluation of the reactor aiming at the highest conversion, but they do not account for the trade-off between an increase in the conversion and the energy cost for recovery the excess of alcohol. The optimization of the energy consumption also reduces water consumption. The work shows promising production costs of \$0.42/gal, and reduced energy and water consumption values of 1.94 MJ/gal and 0.6 gal/gal using the alkali catalyst when the oil is clean, and values of \$0.66/gal, 1.94 MJ/gal and 0.33 gal/gal respectively using the heterogeneous catalyst, when we use cooking oil. Note that the use of heterogeneous catalyst reduces water consumption since there is no washing step. The higher cost is due to the cost of cooking oil according to literature values.

Not only is methanol competitive as alcohol, but also ethanol. Severson et al. (2013) evaluated the use of ethanol as transesterifying agent. The reason is the availability of ethanol within biorefineries, and therefore the reduced dependency on fossil based raw materials. The process flowsheet is similar to the one in Figure 8.2 for oil sources with limited amount of impurities. It turned out that the alkali homogeneous catalysis is preferred yielding production costs of \$0.51/gal, water consumption values of 0.47 gal/gal and energy consumption of 2.81 MJ/gal.

8.2.3 *Lignocellulosic biomass*

8.2.3.1 The biomass.

In our race towards sustainability we look for alternative raw materials that provide the same building blocks as grain or seeds, but with no interference with the food supply chain. Lignocellulosic raw materials such as corn stover, miscanthus or switchgrass are an alternative source of sugars and biobased chemicals. The structure of all these resources is similar. They have a structure of lignin to support the plant, and within that structure, we can find cellulose and hemicellulose binding it. Cellulose and hemicellulose are sugar polymers. In order to get to them we need to break the structure. Its stability results in the need for energy intensive pretreatments. Figure 8.3 shows the structure of the biomass.

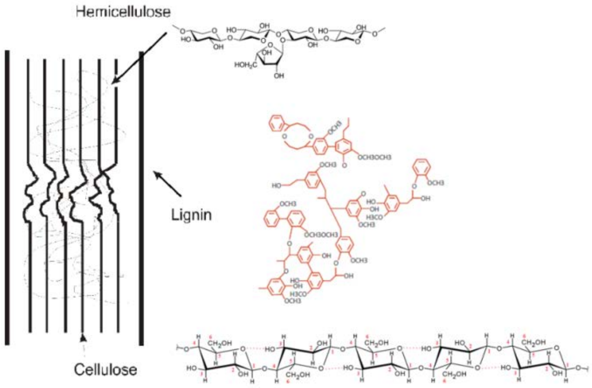

Fig. 8.3 Lignocellulosic structure

8.2.3.2.-The pretreatment.

Pretreatments are developed depending on the target intermediates. We can aim at the production of liquids, using fast pyrolysis at medium temperature, sugars, for which we need to break the physical structure using moderate pressures and temperatures, or produce syngas at high temperatures, a very versatile building block. For this last option we use gasification. In this section we briefly discuss the path to sugars and to syngas. Pyrolysis is a complex process that results in a wide range of products difficult to tackle due to their corrosivity and viscosity, hence and further upgrading is needed (Brown et al., 2012)

To sugars: As we presented above, the production of sugars out of lignocellulosic raw materials is a challenging process since we just need to break the physical structure. We first grind the material to small pieces for the pretreatment to be effective, (Mani et al 2004). Next we can use a number of alternatives at moderate temperatures, 100-180 ºC, and pressures, 12-20 bar, adding different chemicals such as sulfuric acid, ammonia, CO_2, Ozone etc. With this stage we can break the biomass into its polymers. There are a number of interesting reviews commenting on different pretreatments (Sung and Chen, 2002, Keshwani and Chen 2009). Among them the use of dilute sulfuric acid, developed by the NREL (Aden and Foust, 2009; Kazi et al., 2010), the Ammonia Fiber Explosion, AFEX, (Alizadeh et al., 2005) or organosolv pretreatments (Zhao et al., 2009) are the most widely used. Organosolv uses a number of solvents, mainly alcohols, to fractionate the lignocellulosic biomass extracting the lignin. Different variants are available such as organic acid, organic peracid, peracetic acid or high boiling point alcohols pretreatment (Zhao et al 2009). AFEX consists of using a solution of ammonia and water at 20 bar and 90-180 ºC so that in the expansion of the ammonia, the biomass breaks down, (Alizadeh et al., 2005). Until recently, ammonia recovery was the most expensive part of the process. The dilute acid consists of the use of steam and a solution of 0.5-2% of sulfuric acid to break the lignocellulosic structure operating at 12 bar and 140-180 ºC. Sugar dehydration may occur generating inhibition species such as furans (Aden and Foust, 2009; Kazi et al. 2010).

After any pretreatment, the polymers are exposed to the enzymes to break them into glucose, xylose and other sugars. The hydrolysis takes place at 50 ºC. It is characterized by endothermic reactions, eqs. (4)-(5). The sugars are a basic building blocks for a number of chemicals as we will see later.

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6 \qquad \Delta H=22.1n\ \ kJ\cdot mol^{-1} \qquad (4)$$

$$(C_5H_8O_4)_m + mH_2O \longrightarrow mC_5H_{10}O_5 \qquad \Delta H=79.0m\ \ kJ\cdot mol^{-1} \qquad (5)$$

To Syngas: This type of pretreatment is the extreme one in the sense that we use high temperature, 850-1000 ºC, to obtain carbon monoxide and hydrogen as building blocks. See Figure 8.4 for a scheme of the process and the alternatives. Actually, syngas is quite a versatile building block. Based on Fischer Tropsch (FT) type of catalysis, alcohols and hydrocarbons can be obtained (Dry, 2002). To produce syngas, biomass is gasified. A number of technologies are available based on the design of the gasifier and the operation (Brigdwater, 1995). For biomass processing, we can highlight the use of direct gasification (Dutta and Phillips, 2009) and indirect gasification (Phillips et al., 2007). Indirect gasification is based on the use of the Ferco Battelle Gasifier. The system consists of a fluidized bed gasifier, using steam as gasification agent, and sand, olivine, to provide the energy for the gasification. The char generated in the gasification and the sand are transferred to a combustor where, by burning the char, energy is obtained to reheat up the sand. Hot sand is sent back to the gasifier to provide the energy for gasification. The gasifier operates close to atmospheric pressure but yields high throughput per unit volume of the reactor. The gas generated is rich in small hydrocarbons though. The direct gasification uses the Renugas gasifier from the Gas Technology Institute (GTI). Steam and oxygen are used to gasifier the biomass. The gas contains larger proportion of CO_2 but lower concentration of hydrocarbons. It typically operates at 20 bar.

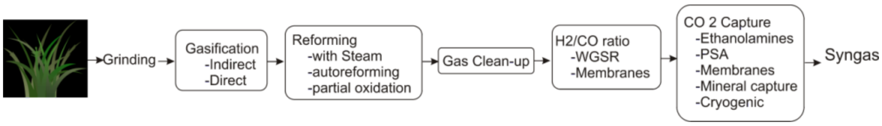

Fig. 8.4 Alternatives to process lignocellulosic biomass into syngas.

Once the raw syngas is produced, the hydrocarbons are eliminated via reforming. Steam reforming, partial oxidation or autoreforming are available technologies. Steam reforming is endothermic but with higher yield to hydrogen. Partial oxidation, on the other hand, is exothermic but with lower yield to hydrogen. Autoreforming is adiabatic combining exothermic and endothermic reactions. After reforming the syngas, it must be purified from solids, using filters or scrubbers, and its composition may need to be adjusted depending on the final use. For instance, methanol production requries a H_2 to CO ratio of around 2, as well as the production of FT-liquids. Ethanol or DME production, on the other hand, require a ratio of 1 (Martín & Grossmann, 2013). In all the cases the CO_2 and the H_2S must be removed to avoid poisoning the catalyst.

CO_2 capture is a topic of increasing interest and a number of technologies are available (USDOE, 2015). Absorption in ethanol amines (with chemical reaction), absorption in physical solvents, adsorption using pressure swing adsorption systems, membranes, mineral capture, are among the most widely used. Chemical absorption requires a large amount of energy to recover the solvent. In terms of physical absorption, there are a large number of solvents such as methanol, dimethyl ether of propylene glycol, etc. that operate at high pressures and low temperatures to improve the capture process. Adsorption beds have lower capacities than chemical absorption. The use of membranes for CO_2 capture requires the use of a carrier, such as ethanol amines that must be later regenerated. Cryogenic recovery typically results in high compression and cooling costs, while the use of mineral capture is attracting attention due to the reversible reaction involving CaO, CO_2 and $CaCO_3$.

8.2.4.3.-Sugar based products

Sugars are fermented by a number of microorganisms, or dehydrated to obtain higher value products. Figure 8.5 shows the main products from sugars in the biofuels industry. We can think of the production of wine or beer. In this work we focus on biofuels, and thus our aim is to comment on alternative fuels based on sugars, but lately, the tight benefits have lead to extending the scope. Actually, we could have described some of these products from grain as sugar source. However, the move from first generation to second generation to avoid competition with the food chain has stopped the development of processes from grain based glucose.

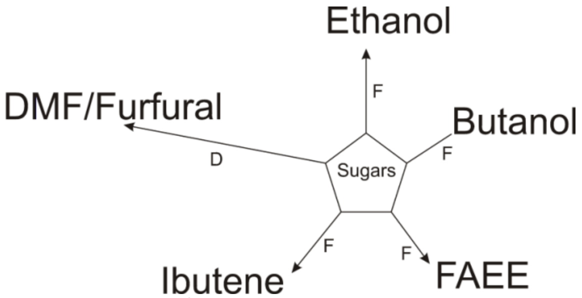

Fig 8.5 Main products from sugars. D : Dehydration; F: Fermentation.

Bioethanol: The production of ethanol from lignocellulosic based sugars, mainly glucose and xylose, takes place at 32-38 ºC anaerobically and 1.2 bar, to avoid air from entering the fermentor. It is an exothermic reaction catalyzed by *Zymomonas Mobilis*. The ethanol generated inhibits the process and concentrations from 6-8% of ethanol in water are typically obtained, although values up to 12 % are expected (Dimian, 2008). Apart from ethanol, a number of other chemicals are produced. Table 8.2 shows the reactions and the conversions to each one.

Once the ethanol-water mixture is obtained, the dehydration step is similar to first generation ethanol, see Figure 8.1. It consists of a multieffect distillation column, followed by molecular sieves to produce fuel grade ethanol. The lignin is not degraded in the process, and it can be used as energy source for the process. Martín & Grossmann (2012) optimized this process resulting in a net positive energy balance, by using the lignin to provide energy. The flowsheet involved dilute acid pretreatment followed by hydrolysis, sugar fermentation and ethanol dewatering. A production cost of 0.8 $/gal was reported together with $169 MM of investment for 60MMgal/yr of ethanol. The water consumption of this process turned out to be 1.7 gal/gal (Martín et al., 2010), due to the energy intense pretreatment and dehydration step together with an exothermic reaction operating at low temperature (fermentation).

Table 8.2 Main reactions in the production of second generation ethanol

Reaction	Conversion
Glucose → 2 Ethanol + 2 CO_2	Glucose 0.92
Glucose + 1.2NH_3 → 6 Z. mobilis + 2.4 H_2O + 0.3 O_2	Glucose 0.04
Glucose + 2 H_2O → Glycerol + O_2	Glucose 0.002
Glucose + 2 CO_2 → 2 Succinic Acid + O_2	Glucose 0.008
Glucose → 3 Acetic Acid	Glucose 0.022
Glucose → 2 Lactic Acid	Glucose 0.013
3 Xylose → 5Ethanol + 5 CO_2	Xylose 0.8
Xylose + NH_3 → 5 Z. mobilis + 2 H_2O + 0.25 O_2	Xylose 0.03
3Xylose + 5 H_2O → 5Glycerol + 2.5 O_2	Xylose 0.02

3 Xylose + 5 CO_2 → 5 Succinic Acid + 2.5 O_2	Xylose 0.03
2 Xylose → 5 Acetic Acid	Xylose 0.01
3 Xylose → 5 Lactic Acid	Xylose 0.01

FAEE. Recently Paap et al. (2013) presented interesting results for the production of biodiesel, FAEE, from aerobic fermentation of sugars at 32-38 ºC. The main reactions shown in Table 8.3 are based on the evaluation of the fermentation products and their yield (Martín & Grossmann, 2015). The advantage of the production of biodiesel is the inexpensive separation of the product from water using a centrifuge. On the other hand, currently the conversions to biodiesel are low, and the yield to other products such as ethanol or glycerol results in a loss in raw material since it is not economically interesting to recover them. The production cost of biodiesel is 3.6 $/gal with an investment of $178 MM for current yields for 10 MMgal/yr of FAEE.

Table 8.3 Main reactions in the production of FAEE

Reaction	Conversion	DH_r (kJ/mol)
9Glucose + $2O_2$→$2C_{18}H_{36}O_2$+$18CO_2$+$18H_2O$	Glucose 0.3*	-405
Glucose → 2 Ethanol + 2 CO_2	Glucose 0.3	-84,394
Glucose + 1.2NH_3 → 6 Z. mobilis + 2.4 H_2O + 0.3 O_2	Glucose 0.1	NA
Glucose + 2 H_2O → 2 Glycerol + O_2	Glucose 0.3	504
27 Xylose + $5O_2$→$5C_{18}H_{36}O_2$+$45CO_2$+$45H_2O$	Xylose 0.2*	-338
3 Xylose → 5Ethanol + 5 CO_2	Xylose 0.2	-74,986
Xylose + NH_3 → 5 Z. mobilis + 2 H_2O + 0.25 O_2	Xylose 0.2	NA
3Xylose + 5 H_2O → 5Glycerol + 2.5 O_2	Xylose 0.2	418

Ibutene. The interest in the production of ibutene is not that much in the biofuel industry but as intermediate for polymerization or for diesel substitutes production. Typically obtained from the C4 fraction of crude, ibutene has recently been used in the production of glycerol ethers (Cheng et al., 2011) In order to avoid the use of raw materials from fossil resources in the production of alternative fuels, Van Leeuwen et al (2012) presented the production of ibutene from glucose fermentation. The reaction is as follows:

$$6C_5H_{10}O_5 \xrightarrow{yeast} 5C_4H_8 + 10CO_2 + 10H_2O + 12ATP \qquad \Delta H = -26\ \mathrm{kJ \cdot mol^{-1}}$$

It takes place at 32-38 ºC at atmospheric pressure using *S. Cerevisiae*. The reaction time is around 24 h. The advantage of this chemical, compared to ethanol or even FAEE is that the product is a gas. Therefore, the separation from the reaction medium is straighforwared. Next, ibutene and CO_2 are separated using PSA or membranes. The economics of the process depends on the possibility of using glucose and xylose to obtain this chemical. There is no experimental evidence of the fermentation of xylose to ibutene. Switchgrass contains cellulose and hemicellulose that can be used to obtain a source for glucose and xylose. If we can use only glucose to produce ibutene, the cost per kg of ibutene is \$0.75. If we can use both sugars, the production cost drops by almost half to \$0.45/kg. Another possibility is to use the xylose for the production of ethanol, and therefore in this case we have a multiproduct facility. The production cost of ibutene can be as low as \$0.39/kg considering the credit from ethanol (Martín & Grossmann, 2014) The investment cost of the three options discussed are \$122M, \$143M and \$188M respectively using the same flowrate of raw material than that used for 60MMgal/yr of ethanol via hydrolysis.

Butanol: Sugars can be fermented to produce a mixture of butanol, acetic acid and ethanol. It is the so called ABE fermentation. Clostridium is used as the microorganism to produce such a mixture via two steps acidogenesis and solventogenesis (Patakova et al., 2013) The mixture produced out of the fermentation is complex and the separation involves liquid-liquid separation and several distillation stages (Kraemer et al., 2011)

HMF and DMF: In the attempt to look for higher added value products, advanced fuels and intermediates, Dumesic's group has extensively worked on the dehydration of sugars, glucose and xylose, to produce hydroxymethyl furfural (HMF) and dimethyl furfural (DMF) from glucose and furfural from xylose (Roman-Leshkov et al. 2007; Roman –Leshkov and Dumesic, 2009). The dehydration of C6 sugars is easy when fructose is the raw material. However, glucose is the C6 is naturally obtained. Isomerization using catalysts such as $CrCl_3$ and $CrCl_2$ is a feasible alternative. The advantage of these catalysts is that it is possible to use them in the dehydation of xylose too. Typically the dehydration takes place at around 160-180ºC using different acids as catalyst and a two phase system to help separate the product. Various organic solvents such as butanol, THF can be used. Once furfural and / or HMF are produced, a complex purification sequence is followed to recover the solvent and the products involving liquid – liquid separation, and several distillation steps. Subsequently, DMF can be produced from HMF by hydrogenation. The reaction takes place using an organic solvent and an excess of hydrogen operating at 120 ºC and 16 bar (Kazi et al., 2011). Martín and Grossmann (2015) evaluated the production of DMF and furfural from algae and switchgrass as source for sugars. Using switchgrass as raw material the production of cost of DMF and furfural is \$3/kg (\$570MM of investment cost), while for algae we present the results later in the chapter.

8.2.4.4 Syngas based products

Syngas is a very versatile raw material or building block to produce chemicals. In this section we present the major uses of the lignocellulosic based syngas. In Figure 8.5, the block diagram is presented. We also include the production of methanol that will be described later from glycerol.

Bioethanol. The mechanism to produce sugars is similar to that presented for Fischer-Tropsch hydrocarbons. Actually the idea is to grow the carbon chain by constantly adding CO to the previous piece on the surface of the catalyst. The production of a particular chemical is based on controlling the growth and the termination of the chain. Thus, the production of ethanol from syngas is known as mixed alcohols synthesis. The main reactions can be seen below. The reactor operates at 300 ºC and 68 bar. Higher temperature favors the production of shorter chemicals. The reactions and conversions of the mixed alcohols synthesis can be seen below (Phillips et al., 2007). As can be seen, a part from ethanol, methanol, propanol and butanol are produced. This fact reduces the yield since, while the unreacted syngas can be recycled and reused, the alcohols must be separated using a distillation column sequence and sold to the market as a mixture. Dutta et al (2009), Phillips et al. (2007) simulated the production of ethanol via this path, but using two different gasification schemes (direct and indirect respectively) showing promising productions costs for ethanol around $1/gal. Later Martín and Grossmann (2011) optimized the production of bioethanol from switchgrass and the best option found was the use of direct gasification followed by steam reforming of the hydrocarbons for a production cost of $0.41/gal based on the credit that the production of hydrogen could provide. The investment cost turned out to be $335 MM for a 60 MMgal/yr of ethanol. The facility showed a net positive energy balance of 8.5 MJ/gal.

$$CO + H_2O \longrightarrow H_2 + CO_2; \quad \text{Con\_CO2} = 0.219$$
$$CO + 2H_2 \longrightarrow CH_3OH; \quad \text{Con\_MetOH} = 0.034$$
$$CO + 3H_2 \longrightarrow CH_4 + H_2O; \quad \text{Con\_CH4} = 0.003$$
$$2CO + 4H_2 \longrightarrow C_2H_5OH + H_2O; \quad \text{Con\_EtOH} = 0.282$$
$$2CO + 5H_2 \longrightarrow C_2H_6 + 2H_2O; \quad \text{Con\_C2H6} = 0.003$$
$$3CO + 6H_2 \longrightarrow C_3H_7OH + 2H_2O; \quad \text{Con\_PropOH} = 0.046$$
$$4CO + 8H_2 \longrightarrow C_4H_9OH + 3H_2O; \quad \text{Con\_ButOH} = 0.006$$
$$5CO + 10H_2 \longrightarrow C_5H_{11}OH + 4H_2O; \quad \text{Con\_PentOH} = 0.001$$

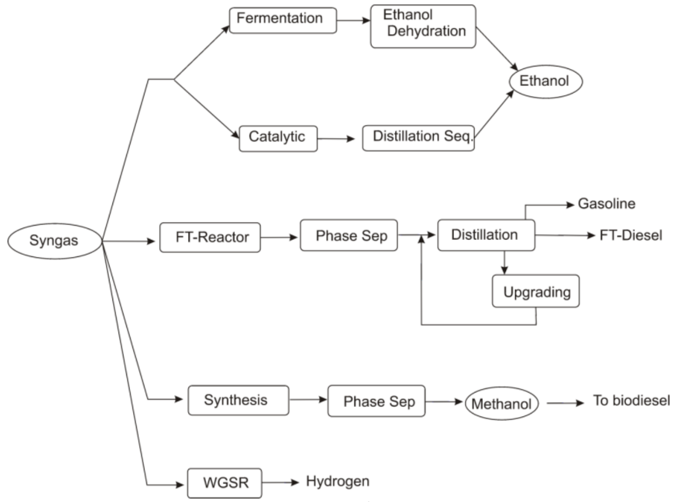

Fig. 8.5 Uses of syngas.

However, syngas can also be fermented (Klasson et al., 1991). The fermentation, as any other fermentation for the production of ethanol presented above, takes place at 32-38 ºC following the reaction below

$$3CO + 3H_2 \longrightarrow C_2H_5OH + CO_2$$

The H_2 to CO ratio needed is 1 and, as a result, there is an excess of hydrogen in the syngas that, if recovered, can provide a promising credit. The concentration of ethanol in the water mixture is 5% at the most, which is an important burden in terms of energy consumption for the process. After the fermentation, the ethanol must be dehydrated. The same scheme described above is used, a mutieffect distillation column followed by molecular sieves. The low concentration of ethanol in the water is a drawback for this option. The net energy balance of this process is negative, 27MJ/gal, and the production cost $0.81/gal using direct gasification and steam reforming with an investment required of $260 MM for a 60 MMgal/yr of ethanol (Martín & Grossmann, 2011).

FT Fuels: The production of FT fuels is an interesting alternative for the use of syngas. The composition and the operating conditions at the reactor determine the main product, from gasolines, to diesel or heavier oil. The Anderson - Schulz -Flury model is a simple approach to predict the products distribution (Schulz et al., 1999). For instance, the production of diesel fraction requires lower temperatures, 200 ºC, 30 bar, a H_2 to CO ratio of 1.7, and the proper catalysts based on cobalt or iron. Gasoline products are typically obtained at higher temperatures and using iron based catalysts. Apart from hydrocarbons, water and flue gas are produced. Liquid – liquid separation withdraws water from the mixture before hydrocarbon fractionation into gasoline and diesel. To increase the yield of the process to lighter fractions, the heavy products can be upgraded using catalytic cracking, hydrocracking or similar (Dry 2002). The net energy balance of the process is positive based on the production of flue gas. The production cost of fuels is higher than that of ethanol, \$0.72/gal, but the investment cost is lower, \$216 MM, for the same biofuels production capacity.

Hydrogen: In the previous examples we have presented the production of syngas as a mixture of CO and hydrogen; we can use the WGS reaction to drive the mixture of gases to H_2 and CO_2. By using a membrane reactor (Ji et al., 2009) and taking into account that the small size of the hydrogen plays an important role, it is possible to obtain a fairly pure stream of hydrogen with a reduced number of purification stages. Therefore, it is possible to produce hydrogen at \$0.68/kg and with a reduced investment, \$148 MM for 60 MMkg/yr (Martín & Grossmann, 2013).

8.2.5 Algae.

Algae are a rich raw material with a high yield compared to other biomass sources (Chisti 2007). Its composition as biomass consists basically of carbohydrates (starch), lipids, and proteins. The biodiesel industry has pushed the development of methods to increase the oil accumulated by modifying the algae growth. However, algae can also be used to produce ethanol due to the starch content. As a result, algae can be a good source for ethanol. During the 70's the aquatic program of the US government studied the production of algae as a source for fuels. Their conclusions were simple; the low cost of crude oil and the easy access to it resulted in closing the program (Sheehan et al., 1998). The main problem is therefore the cost for growing and harvesting the algae. There are a number of options to grow the algae. We can distinguish between raceway Ponds (circular, tanks, paddlewheel raceways) or photo reactors (airlift, tubular, bag cultures). The first ones are simple civil engineering structures with small depth that are filled with water where the algae grow using CO_2 or other carbon source and nutrients (Sazdanoff, 2006). The algae growth depends on the solar incidence and the carbon intake. They have important evaporation losses, poor control and contamination. Furthermore, the concentration of algae in the pond is quite low, 0.1-0.5 h per L, and the energy required to harvest the algae is so high that the production cost per gallon is prohibitive. Another option is the use of photoreactors. The design of this equipment is more complex to allow for solar energy to reach the algae. They are transparent pipes or bags of small diameter allocated in structures to provide large volumes. The advantage of this system is the controllability. They are closed units not subjected to direct atmospheric contamination as the ponds are. The main drawback is the higher cost and more complex design for high volume production, and the fact that the growth of algae in the walls blocks the light. In both cases, algae harvesting is carried out using flotation tanks and a drier to reduce the water content to 5 -10% so that we can extract the oil from the biomass (alfalaval.com, Brennan and Owende (2010), Mata et al., 2010). The higher concentration of algae in the case of using photoreactors reduces the processing costs.

Algae can be used as such via gasification to produce syngas. From that, we can use it as described above in the case of lignocellulosic raw materials. Another option is the thermochemical liquefaction producing liquid fuels directly at 300-350 ºC and 5-20 MPa. Pyrolysis is also an option to produce bio-oil form algae operating at 350-700ºC, but has the same drawbacks related to the wide range of products and the complex composition. A part from these thermal processing we can follow biochemical conversion either anaerobic digestion, alcoholic fermentation, photobiological hydrogen production and biodiesel production.

The Anaerobic fermentation (AD) of any biomass generates the so-called biogas consisting of methane and CO_2. The AD is a process consisting of three steps: hydrolysis, fermentation and methanogenesis, so that the biomass is broken into sugars, then fermented into alcohols, acetic acid and gas, mainly H_2 and CO_2 and finally the mixture is metabolized to produced methane and CO_2. Typically 50-70% of methane by volume can be obtained. The presence of protein in the algal biomass reduces the yield, but it can be mitigated by adding another biomass with a high C to N ratio.

Algae, because of its content of starch, can be fermented into ethanol. The ethanol water mixture, typically between 10-15% ethanol, must follow the same dehydration process discussed for any other biomass presented in the chapter. The solid residue can be use as cattle fed. Thus, algae species with high starch content are good for this option (Brennan and Owende, 2010). We have seen in the case of lignocellulosic that the sugars can be used to produce a number of other chemicals such as FAEE, ibutene for its further use (de la Cruz et al., 2014), DMF at the cost of $1.98/gal ($693 MM of investment) (Martín & Grossmann, 2015).

We can also produce hydrogen. During photosynthesis, microalgae produce protons and oxygen from water. Hydrogenase enzymes convert the protons into hydrogen (Brennan and Owende, 2010).

Apart from all these options, algae are typically devoted to the production of oil for biodiesel production. Oil has to be extracted from the algae biomass. The extraction is similar to that employed for seeds consisting of mechanical action and the use of solvents. As a result, the price per gallon of algae oil is high (Klise et al., 2011); however it is expected that values of $0.07/lb could be reached (Pokoo et al., 2010). Actually, the use of capillarity based harvesting, proposed by Univenture Inc can help achieve values of $0.06/lb (Martín & Grossmann, 2012). Once the oil is available, we can produce biodiesel via transesterification as described above. The production cost of biodiesel from algae actually depends heavily on the cost of harvesting. The use of advanced harvesting methods can reduce the production cost to $0.42/gal with investment cost dominated by algae growing around 110 MM$ per 72 Mgal/yr of biodiesel. (Martín & Grossmann, 2012).

8.2.6 Wastes: Biogas.

Anaerobic digestion is one of the most energy efficient and environmentally friendly processes for the production of energy from biomass. Anaerobic digestion is a biological process performed by many classes of bacteria on a large number of biomass types from algae, as indicated above, to wastes. It consists of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In particular, it is an interesting technology to obtain further energetic value from water treatment sludge, cattle manure and others. The process can be mesophilic, running at 20-40ºC for more than a month, or thermophilic, at 50-65ºC. It consists of hydrolysis, fermentation and methanogenesis. The entire process lasts for several days. The actual biogas composition, from 50-70% in methane and 30-40% CO_2, with small amounts of N_2, O_2, H_2S and NH_3 depends on the raw material, as well as the yield from biomass to biogas, Gunaseelan 1997, Steffen et al (1998).

8.3 Integrated processes.

For many years process design was focued on the transformation of a biomass type or source into one main product, i.e. bioethanol, as some byproducts from the same process. The tight margins and the competitive fuels and energy markets have altered that trend. Actually, chemical complexes consist of a large number of processes operating in a symbiotic way to take advantage of the excess of energy, the possible use of the byproducts and the integration of technologies. Thus, the biofuels industry has followed the same trend, and with the help of process system engineering techniques, a number of integrated processes have been developed. In this section we discuss some of those processes paying special attention to the integration of energy, raw materials and technologies.

8.3.1 First and second generation bioetanol

Bioethanol has been produced from corn in the US for the last decades (Jacques et al., 1999). The concerns related to the use of food as a raw material for the production of fuels have led to the development of technologies to process biomass that do not interfere the food market such as lignocellulosic energy crops. Among them, let us focus on corn stover. In the production of corn, grain represents 45% of the total biomass produce. The remaining 55% is stover, a lignocellulosic type of biomass that can be used as lignocellulosic raw material for sugars. In order to maintain minerals in the ground, it is not recommended to harvest more than 70% of this mass. Therefore, around 85% of the biomass grown in the production of corn can be used in an integrated facility, (Atchinson, 2003; Nielsen, 2009). The integrated process that uses the entire corn plant can benefit from the symbiosis of first and second generation production processes. In the first place, it will increase the production capacity by almost 100%. Typically, second generation bioethanol presents a positive net energy balance. The excess of energy, either due to the exothermic reactions at high temperature from the gasification or the synthetic reactor, or the use of lignin as source for energy, can provide the energy for the dehydration of the ethanol produced in the fermentation of glucose from corn grain. In case the bio-path is followed from the lignocellulosic part of the biomass, there are a number of steps, the dehydration involving beer column and molecular sieves, that are common, and thus economies of scale improve the economics of the process. Cucek et al. (2011), integrated first and second generation technologies to process the grain and the stover to evaluate the integrated biorefinery. The most economical process used the thermo chemical route for processing the stover so that the excess of energy could be used to feed the beer column used in dehydration of the grain based ethanol. Ethanol was produced at $1.22/gal. Water consumption was also limited to 1.56 gal/gal.

8.3.2 Algae based fuels

In the previous section the rich composition of the algae, typically starch, up to 40%, lipids, up to 75 %, and protein (Mata et al., 2010). There is a large number of species that can be grown in marine or freshwater. This composition allows for integration of the production of several products within the same biorefinery complex so that no fossil based chemical or raw material is needed. The basic process is the production of ethanol and biodiesel from algae (Martín & Grossmann, 2013). Figure 8.6 shows a scheme of the processes described below.

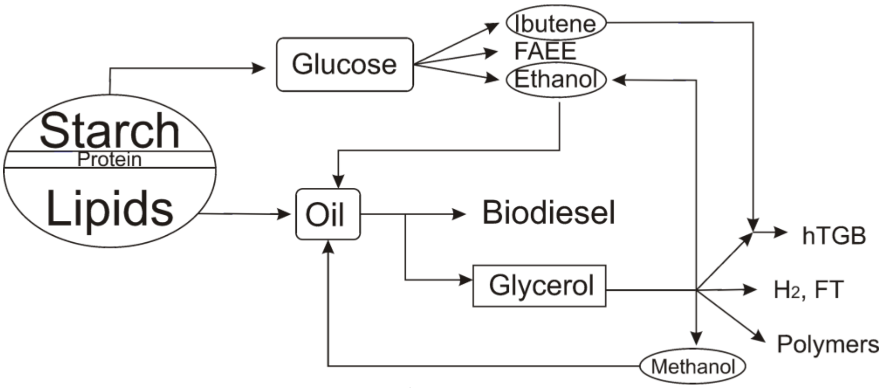

Fig. 8.6 Biorefinery based on algae

8.3.2.1.-Ethanol and Biodiesel.

Severson et al. (2013) showed that the production of biodiesel, Fatty acid ethyl ester or FAEE, was not only technically feasible, but also competitive for certain prices of ethanol as transesterifying agent. Algae provide the opportunity to produce ethanol from the starch, and oil from the lipids. Therefore, we have all the ingredients to obtain FAEE from algae with no need to buy fossil based methanol. One thing remains open, what is the optimal composition of the algae in terms of starch and lipids, for the operation of such an integrated facility. Again, the PSE approach provided the tools to come up with a model that allowed computing the optimal algae composition for the simultaneous production of ethanol and biodiesel. The equilibrium that governs the transesterification of the oil suggests including simultaneous optimization and heat integration within the formulation (Duran and Grossmann, 1986). Thus, the biorefinery consists of algae growing. Next, the oil is extracted using mechanical action and hexane. The starch is sent to be processed following first generation bioethanol technologies, namely, liquefaction followed by saccharification and glucose fermentation to ethanol. Once the ethanol is produced, proteins are removed from the liquid stream to be sold and the ethanol is dehydrated using a multieffect column and molecular sieves. Part of the ethanol is sold, if there is an excess, and the rest is used in the transesterification of the oil extracted from the algae. The high energy required in ethanol dehydration, and the high yield from oil to biofuels suggested a composition of 60% lipids, 30% starch and 10 % protein dry biomass basis. Biodiesel is the main product of the integrated facility .The production cost of biodiesel was \$0.35/gal using 4 MJ/gal for a production capacity of 90 Mgal/yr using enzymatic catalysts. Ethanol represented 9% of the total biofuels sold since part of it was internally used. The investment of such a plant added up to 180 MM\$. The use of alkali catalyst was cheaper by 3c\$/gal, but the energy consumption was 50% higher. (Martín and Grossmann, 2013) This process has two main byproducts, protein and glycerol. High added value products can be obtained from protein, the glycerol represents an interesting source of carbon for the production of chemicals.

8.3.2.2 Use of glycerol

Production of methanol. One of the main drawbacks of the production of biodiesel in current industrial processes is the use of methanol as transesterifying agent. Methanol is typically produced from coal or natural gas via syngas production. However, the bioproduct of the process, glycerol can be reformed to produce syngas, see Figure 8.5. Therefore, we can reduce the dependency on fossil based ethanol by using the glycerol as raw material for the production of methanol. The process consists of glycerol reforming with steam, with a mixture of pure oxygen and steam (autoreforming) or aqueous phase glycerol reforming with water in liquid phase to produce syngas. Next, the syngas must be cleaned up for hydrocarbons removal, its composition adjusted to achieve a H_2 to CO ratio of 2, and the CO_2 is partially removed, since the catalyst works better with concentrations of CO_2 from 3 – 8% in volume. Methanol synthesis is governed by two main reactions in equilibrium. The production can be carried out in gas phase at low pressure, or liquid phase, at high pressure.

$$CO + H_2 \leftrightarrow CH_3OH$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

Finally, the unreacted gas is recycled and the methanol-water mixture separated. The optimal process allowed saving 50% of fossil based methanol using autoreforming. However, the production cost of biodiesel increased with respect to its production alone by 0.15$/gal and the energy consumption went up to 3.55 MJ/gal and the investment cost by less than 10% (Martín & Grossmann, 2013).

Hydrogen and FT fuels: The syngas from glycerol can also be used to increase the yield to fuels by producing hydrogen and FT fuels. The processing technologies have already been described above. However, this use is not competitive with the use of switchgrass for the production of the same fuels (Martín & Grossmann, 2014).

Production of ethanol: Glycerol can be fermented anaerobically at 38ºC to ethanol using E. Coli for 60h. Ethanol can reach 10% in water (Dharmadi et al., 2006)

$C_3H_8O_3 \rightarrow C_2H_6O + H_2 + CO_2$ (98%)
$CO_2 + C_3H_8O_3 \rightarrow$ Succinic Acid + H_2O (1%)
$C_3H_8O_3 \rightarrow$ 3.0075(Biomass) + H_2O (1%)

The water-ethanol mixture is, in some sense, similar to the production of ethanol from sugars. Therefore, we can develop an integrated process that produces ethanol from the algae starch as well as from glycerol. The dilute ethanol mixture from both sources is dewatered using a beer column and molecular sieves. Economies of scale are an asset for this process. On the other hand, the high energy consumption required for ethanol dehydration is the drawback of this option. Part of this ethanol is used internally to transesterify the oil from the algae lipids and the rest is sold. The optimal algae composition for the operation of this facility consists of 60% lipids, 30% starch and 10 % protein, dry biomass basis. Ethanol production increases by 50% using the glycerol, compared to the option that does not further uses it, while the cost of biofuels adds up to $0.45/gal. The energy consumption increases up to 4.2 MJ/gal and the investment goes up to 211 MM$ (Martín & Grossmann, 2014).

Production of high glycerol ethers: To increase the yield from oil to fuels it is possible to use the glycerol to obtain glycerol ethers. The reaction is an equilibrium that typically uses ibutene to etherify the crude glycerol, (Behr and Obendorf, 2001).

$$Glycerol + iButene \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MTBG$$

$$MTBG + iButene \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} DTBG$$

$$DTBG + iButene \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} TTBG$$

Several papers (Cheng et al., 2011; Vlad et al., 2010; Martín & Grossmann, 2014) have proposed processes to transform glycerol into di and tri-tertbutyl glycerol (hTBG), since both can be used as diesel substitutes. The process actually uses glycerol as separation agent of the mixture of ethers, mono, di and tri. The glycerol and monoether are recycled back to the reactor, while the ibutene with the di and tri ethers are further separated recycling the ibutene and purifying the hTBG. The initial drawback of this process is the use of ibutene, a typical C4 chemical. However, as presented above, we can produce it from sugars. That possibility opens the opportunity to synthesize a process based on algae with no need for fossil based chemicals. We grow the algae in such a way that we produce starch to be used to obtain glucose. 50% of the glucose will be used for ethanol production and the rest to produce ibutene, while the ethanol once dehydrated as before, is used to transesterify the oil, the ibutene is later used to etherify the glycerol. In this way, we do not need any fossil based chemical for the production of diesel substitutes, biodiesel (FAEE) and hTBG's. Furthermore, the integrated facility is not only environmentally more friendly, but it also reduces the production cost from $1/gal (Martín & Grossmann, 2014) to $0.46/gal (de la Cruz et al., 2014). On the other hand, the investment cost of the facility increases from $167MM (Martín & Grossmann, 2014) to $205MM (de la Cruz et al., 2014) if ibutene is internally produced.

Polymers: In the last examples we have seen that the use of glycerol for enhancing the production of fuels is an interesting option but has no economic incentive. There are other possibilities such as the use of glycerol for the production of high added value products out of glycerol. For instance, we can produce polyesters from glycerol using adipic acid. Out of glycerol and adipic acid liquid or solid polymers can be produced for paintings or as adsorption materials (Bueno et al., 2015) This alternative is more profitable; the production cost is around 1.7€/kg and the selling price adds up to 5€/kg Apart from this PHB can also be produced via fermentation (Ibrahim and Steinbüchel, 2009). Economic evaluations of this option are still in progess.

8.3.3 Multiproduct processes from lignocellulosic biomass

Actually this topic is not new. FT production processes discussed above are capable of producing a wide range of products, and among them, substitutes for crude based gasoline and diesel. However, extend this study to those other processes that generate ethanol, FAEE and ibutene. In a second step, since syngas is a building block that can be produced from several renewable and non renewable sources alike, in this section we discuss the use of shale gas and biomass to produce FT fuels.

Simultaneous production of ibutene, FAEE and ethanol: The production of ethanol from lignocellulosic biomass is the base case for second generation biorefineries. However, such a process is not flexible to meet the demand for fuels in the biorefinery since with ethanol we only substitute gasoline. Furthermore, the economics of biofuels is not still competitive with crude based fuels. Based on the versatile use of sugars, as presented in the previous section, we can find in the literature two integrated biorefineries of interest. On the one hand, we can simultaneously produce FAEE and ethanol from switchgrass (Martín & Grossmann, 2015). In this sense the integrated facility can produce substitutes for gasoline and diesel at the same time. The tradeoff involved in this facility is simple. Ethanol dehydration is energy intensive, but the yield from biomass to ethanol is moderate. On the other hand, the separation of FAEE from an aqueous mixture is easy, but the yield to FAEE is low. Therefore, the analysis presented was to evaluate what was the optimal production of both fuels. It turns out that the yield from biomass had larger impact on the economics than the energy savings in product purification. Only if the demand requires the production of both, it is technically feasible to do so, but it is economically not attractive. The production of ethanol and glycerol together with FAEE reduces the yield, but those components were very diluted in water, and therefore recovering them was not economically interesting.

Since the economics of the ethanol is tight and the production of ibutene from xylose has not yet been experimentally validated, it is an interesting possibility to simultaneously produce ibutene and ethanol from switchgass. The glucose in the biomass is used for ibutene production, while the xylose is devoted to ethanol. In this way, the facility is not only able to produce ethanol at a reasonable price and amount, but the ibutene, whose price from crude oil is close to \$2/kg, is possible to be produced below \$0.4/kg using renewable raw materials.

Renewable and non renewable source for syngas. In this chapter we have presented the production of syngas from biomass, lignocellulosic and glycerol. In 2009 there was a large increase in the production of natural gas from shale gas. The availability of this non-conventional natural gas changes the energy market affecting the electricity price. Since shale gas is widely available in the US, and in the same region switchgrass grows natively, it is interesting to evaluate the possibilities of using one and/or the other in order to produce FT liquids. Martín & Grossmann (2013) used a mathematical programming approach to evaluate the limit in the price of biomass and shale gas for economically producing FT liquids from either feedstocks. A large sensitivity analysis was performed using a base production capacity of 60 Mgal/yr. Using as target price for the liquid fuels \$1/gal, the study showed that the price of biomass below \$100/t is competitive, but above that shale gas is preferred to meet the liquid fuels demand. On the other hand, the price of the shale gas must be below \$11.5/MMBTU for it to be an attractive source. By using biomass and shale gas, the dependency of US on foreign crude could be reduced, while all the effort into second generation biofuels is still useful.

8.3.4 Integrated solar, wind and biomass.

So far we have focused mainly on the production of fuels or chemicals; however biomass can be used to produce energy too. Here it is where the properties of biomass can be of great advantage compared to solar and wind and thus complement each other. Biomass can be stored. Energy crops are typically perennial, and thus harvesting can be done when biomass is needed. On the other hand, solar and wind energy are available only a certain times of the day or the year, as it has been discussed in other chapters of this book. Therefore, it is natural to integrate biomass with solar and wind in order to secure the production of power, and with it chemicals and fuels.

CSP- Biomass: The variability of power production from solar energy means that along the year favorable months produce even more than twice the power, then in less favorable seasons. While the demand for power does not follow the production term, and the processes operate better at a constant flow, the integration between a biomass based polygeneration system and a concentrated solar power facility allows constant production of power over a year. The excess of energy can be chemically stored. For instance, hydrogen can be produced when solar energy is capable of meeting the demand and the production capacity of hydrogen will vary over the year. By doing this, we reduce the idle sections of the process. The biomass based polygeneration system consists on the generation of syngas from biomass. The same technologies for biomass processing as those used for the production of second generation bioethanol apply in this case. After syngas clean-up, we use a Brayton cycle to generate power. Furthermore, there is an excess of energy at different parts of the process. For instance, the gases from the combustor or the gasifier, the partial oxidation can provide part of the energy to reheat up the salts within the CPS facility. Figure 8.7 shows a scheme of the integrated process.

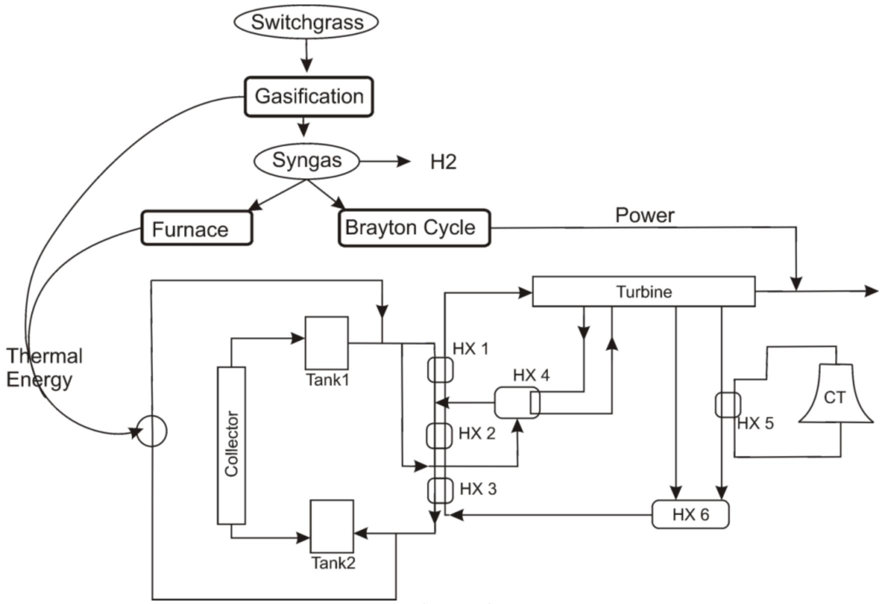

Fig 8.7 Integrated CSP-Biomass facility for constant power production

Vidal and Martín (2015) used a mathematical optimization approach to evaluate the operation of such integrated facility. The biomass is processed using indirect gasification followed by steam reforming. The reason is that the syngas produced in this way has more energy within for its use in the Brayton cycle. The streams from the combustor are used to provide heat to the salts, taking advantage of the high temperature of the gases. On the other hand, the CSP facility consists of the solar field, a regenerative Rankine cycle and a wet cooling tower. For the constant production of 340 MW, the production cost of electricity is €0.073/kWh, obtaining together with the electricity, 97 kt/yr of hydrogen. The investment for the integrated plant adds up to 2305M€. Furthermore, in order to maintain electricity costs below 0.1 € /kWh, we need to assure biomass costs below 100 € /t, and/or hydrogen prices above 0.58 € /kg. Similar facilities to the one evaluated are being currently built worldwide.

PV- Wind – Biomass: Solar, wind and biomass can also be integrated for the production of chemicals using CO_2 as carbon source. One of the alternatives to use CO_2 to produce methane, methanol or others is to reduce it with hydrogen, For the process to be environmentally friendly, so that CO_2 is not only captured but also reused, the hydrogen must be renewable. We can produce renewable hydrogen from biomass, as was seen in this chapter before, but we can also produce it from water splitting. In this case, the power must be renewable for the hydrogen to be it too. Therefore, Solar photovoltaics, PV solar, Wind energy and biomass can be integrated for the production of hydrogen so that it can be further used to obtain for instance methane. The advantage of producing methane is that we are storing solar and wind energy in the form of a chemical that it is easy to handle and ready to use as fuel. By integrating the three sources, it is possible to maintain constant production of methane independently of the solar or wind availability. See Figure 8.8 for a scheme of the integrated process. The excess of energy can be sold into the market. Martín and Davis (2015) evaluated this integrated facility, again, using mathematical programming techniques. The study allowed determining the optimal combination of the three as a function of the biomass price and the cost for the solar and wind energy. Biomass was processed via indirect gasification, and steam reforming to produce syngas. Instead of using it to obtain hydrogen, the model suggested its use to produce power through a Brayton cycle. In parallel, solar was recommended to complement the biomass as long as the biomass price is below 50€/t, and the investment in the biomass section is below 1500€/kW, and the solar incidence is above 1200 kWh/m^2 yr. The use of wind is restricted to low solar incidence, wind velocities above 9 m/s and high prices for biomass.

8.4 Conclusions

Biomass, due to its rich composition, is a versatile raw material for the production of chemicals that can be used as biofuels. There are a number of alternatives to substitute crude based gasoline and diesel, but most importantly, the technologies are becoming available and industrially feasible. Furthermore, the production costs are becoming competitive. Although the first attempt was to produce the fuels on their own, the development of integrated processes presents several advantages that exploit the synergies of several processes. Although the price of crude are still low for biomass based fuels to be used, there is no doubt that sustainability requires the use of alternative sources. Among them, biomass is a powerful ally since we can store it for some time and can be processed to meet large demand of fuels.

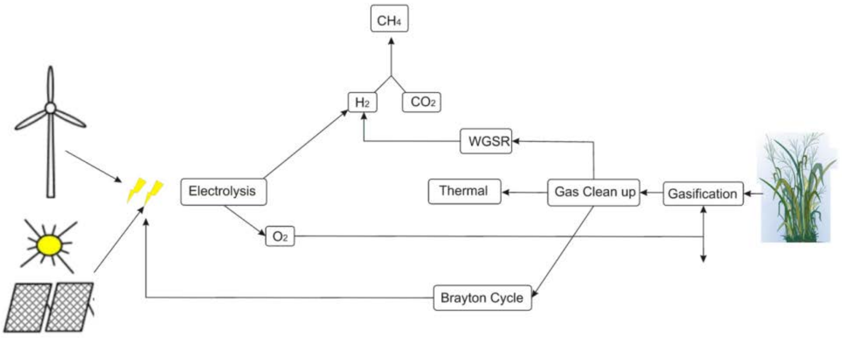

Fig. 8.8 Integrated system for constant methane production .Reproduced with permission

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