Biomass refineries: relationships between feedstock and conversion approach

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Abstract

For conversion purposes, biomass can be classified into three main categories: homogeneous biomass (ex.: corn grains), quasi-homogeneous biomass (ex.: forest residues, straws and plantations in marginal lands) and non-homogeneous biomass (ex.: mixed forest residues, MSW, etc.). In North America homogeneous biomass costs (FOB plant) are over 100 $US/tonne in 2009 (anhydrous basis; 1 tonne = 18 GJ), therefore its conversion to biofuels requires subsidies. As well, alternate and added value uses (food and fibre) compete for such category of feedstock. Quasi-homogeneous biomass, whose cost (FOB plant) 30 - 60 $US/tonne in 2009 (anhydrous basis) for forest residues and straws and estimated between 80 and 100 $US/tonne for plantation biomass (i.e. willows, switchgrass, etc.), is suitable for bio-refineries aiming at co-products biofuels, green chemicals and fibres. However, the availability of large quantities of quasi-homogeneous residual biomass is strongly linked to the existing biomass industrial sector since mills processing sugar cane, corn, wheat and wood also have access to such biomass category whose competing use is the generation of bioenergy (process heat and, in some cases, power). It is however possible to integrate a pre-treatment (a better term is “fractionation”) of the quasi-homogeneous biomass to produce useful fractions for biofuels, green chemicals and fibres while using the residual fractions for bioenergy. Non-homogeneous biomass is available in all urban centers of the planet and constitutes a major opportunity for biofuels and green chemicals since its cost is negative (i.e. it is a disposal cost paid by municipalities to landfills or incineration facilities) and a sustainable society ought to aim at zero residues. Non-homogeneous biomass can be prepared and converted into a homogeneous and clean syngas intermediate. The latter contains typically two thirds of the carbon in the feedstock and technologies to convert it into biofuels and green chemicals are being developed.

Keywords: biodiesel, biorefineries, cellulose, ethanol, extractible, gasification, hemicelluloses, homogeneous biomass, lignin, quasi-homogeneous biomass, non-homogeneous biomass.
1 Introduction

The utilization of biomass as a source of energy products requires considering its nature, cost, availability and the potential conversion approaches. Biomass cost is directly influenced by the quality of the carbon structures. As an example, homogeneous biomass obtained from a selected tissue of a defined tree species will be logically more expensive than an ensemble of different tissues from mixed plant species as well as more heterogeneous carbon matrices (such as municipal solid waste). In North America, cost of biomass ranges (2009) from more than 100 $US per anhydrous tonne (ex.: debarked wood chips) to -50 $US per anhydrous tonne (ex.: MSW). Three distinctive categories of biomass can be considered: homogeneous, quasi-homogeneous and non-homogeneous biomass. Plantations can also be considered for energy products, even though their biomass cost will likely be higher than forest or agricultural straws. Their eventual use is of interest since they may help to reduce the pressure on the forest, particularly when such plantation biomass is grown on marginal lands.

1.1 Homogeneous biomass

Lignocellulosic homogeneous biomass has as key example the wood chips from debarked single species used in the pulp and paper mills. Such a biomass has a cost (FOB plant) higher than 100 $US per anhydrous tonne (> 6 $US/GJ), thus rendering it difficult to consider for energy products. Only with co-products from specific fractions of the biomass, can such high-grade biomass be considered for this purpose.

1.2 Quasi-homogeneous biomass

Quasi-homogeneous biomass refers to mixed tissues of a single species or of a mixture of closely related species such as residual straws and forest residues. Non-limiting examples are: corn stover [1,2], bagasse and straw from sugar cane plantations [3,4], straw from wheat [5], residual grape biomass [6] and residues from olives processing [7]. Also included in this category is “whole biomass” planted in marginal land: Arundo donax, Cynara cardunculus, Miscanthus sinensis, Panicum virgatum, Sorghum bicolor [8], Eucalyptus gunnii, Populus trichocarpa, Salix viminalis [9,10] and Miscanthus x Giganteus [11] among others.

The forest residues produced during forest operations are also included in this category. Such forest residues have been estimated to about 6.9 million tons (anhydrous) per year in the province of Quebec alone [12]. Degraded biomass forest such as the large quantities of pines killed by the mountain pine beetle [13] fall within the quasi-homogeneous biomass category as well.

Quasi-homogeneous biomass is composed of chemical structures derived from several types of tissues, thus more complex than homogeneous biomass which comes from specific tissues. Cost for this quasi-homogeneous biomass varies, in North America (2009) from 30 to 60 $US per ton (anhydrous base)
when residues are considered. Such biomass is a readily available feedstock for conversion processes whether biological, thermo-chemical or in combination.

1.3 Non-homogeneous biomass

Non-homogeneous biomass is a category for which the cost ranges from 30 $US/ton (anhydrous basis) to negative values (tipping fee) for “waste”. Such negative value is related to the avoided cost of landfills. The key example of such biomass is municipal solid wastes (MSW) which comprise (i) residential residues (the «garbage»); (ii) institutional, commercial and small industries (ICI) wastes; and (iii) construction and demolition wood (C&W). Included in the latter are contaminated woods such as spent poles and railroad ties and sludge from rendering operations and wastewater treatment plants. These residues are available in large volumes and could become a significant source of carbon for which the supply would be local and recurrent. It is estimated that in the western world each person “produces” close to 1.0 kg of residential MSW per day with an equal amount of ICIs also generated. Only a fraction of such residual materials can be effectively recycled and biocomposted, leaving about half available for conversion processes.

Since such materials are highly heterogeneous (MSW contains food remnants, paper, cardboard, plastics, glass and metals), the production of a homogeneous intermediate that can be better used than the original material limits the conversion technologies to a few options. Among these options, biogasification (i.e. anaerobic digestion) of sludge often preceded by a pre-treatment to improve digestibility and thermal gasification of sorted, dried and shredded solid wastes are efficient techniques which allow the production of a homogeneous gas (biogas or syngas). Purification of this gas and neutralization of contaminants allows its utilisation for heat and power production or in catalytic synthesis.

2 Choice of conversion process

The choice of an appropriate conversion technique very much depends on the availability, category and composition of the biomass. With quasi-homogeneous biomass a co-products strategy is possible. Such strategy is related to chemical pulping which is, overall, the isolation of the cellulose fibre from a lignocellulosic matrix. Most of the pulping processes used in the industry co-produce fibres and energy from the residues. The approach implies further separation/isolation of the macromolecular compounds and their conversion to “green chemicals” and/or alternative fuels from the lignin, hemicelluloses and the short chain cellullosic fibres. On the other hand, non-homogeneous and often heterogeneous biomass can, via higher severity conversion processes (pyrolysis or gasification) be transformed to intermediate uniform feeds (char and bio-oil via pyrolysis or syngas via gasification) which are more suitable that the original material for additional conversion into final products.
2.1 Biorefineries based on fractionation

A general illustration is depicted in Figure 1.

Figure 1: Illustration of the biorefinery concept (courtesy of CRB) that could be used for the conversion of forest and agricultural quasi-homogeneous biomass into biofuels and added value products.

The key goal in fractionation is to isolate the constitutive chemical families present in the feedstock. Thermocatalytic processes of low severity such as solvolysis or steam treatments accomplish this. The fractions produced will subsequently be transformed into defined chemicals and fuels. Any residue is used as source of heat and/or power.

2.1.1 Removal of extractives

The quasi-homogeneous biomass contains a certain amount of extractives. These molecules are not part of the structural macromolecules in lignocellulosic plants and are often categorized as secondary metabolites. Extractives are used by plants against insects, fungus and bacteria [14]. They range between 3 to 10 wt% of the dry weight of the biomass. Removal and recovery of the extractives is the first unit operation to consider. Liquid-solid extractions are generally used [15]. Extracts are usually a complex mixture of molecules. Isolation and purification of extractives has lured researchers and industrial groups given the potential applications from aroma chemicals to the pharmaceutical potentials. However the purity required in fine chemicals has limited the use of “bulk extractives” as raw material. The simplest utilization of the bulk extractives in a generic biorefinery would be as input to a cogeneration plant.

2.1.2 Aqueous/steam and organo-solvolytic treatments

After removal of bulk extractives, the fractionation of lignocellulosics into constitutive macromolecular families is central to the biorefinery concept.
Aqueous/steam treatments, of which steam treatments are a well known variation dating back to the beginning of the 20th century [16] are, essentially, hydrolytic processes (with or without soluble catalysts) applied for a few minutes in the temperature range from 170 to 230°C and at a steam pressure equal or higher than the vapour pressure of water at the chosen temperature. In the simplest application, the heated biomass saturated with water is suddenly depressurized and flown at high speed through an appropriately designed nozzle. The downstream side of the nozzle is at lower pressure than the upstream side and thus sudden vaporization of water occurs. The force generated by the sudden vaporization separates the fibres inducing a partial hydrolysis of the hemicelluloses. This technique is actually used as pre-treatment for the production of low cost fermentable sugars [17] for the production of paper [18] and for the production of fiber for board (masonite board as an example).

Organo-solvolysis is a process by means of which an organic solvent, mixed generally with water, is used to solubilise specific macromolecules (a large fraction of the hemicelluloses and lignin) liberating cellulose. This technique (also called organosolv pulping) has been demonstrated using acidic water/alcohols media but it has not gained commercial status. The “liquefaction” of cellulose in a mixture of water, acetone and HCl has also been proposed [19]. The utilization of acid ethylene glycol [20] and formic acid [21] has also been studied as organosolv approaches.

In both steam treatment and organosolv approaches, the process can be tuned for optimal results on the production of cellulose or sugars depending on severity. Steam treatments allow separation of hemicelluloses and cellulose fractions. Solvolysis usually allows recuperation of native lignin with little modification of the original macromolecule.

2.1.3 Hemicelluloses

The hemicelluloses are macromolecules that are produced following a branched polymerization of C5 and C6 carbohydrates. Usually, the hemicelluloses found in ligneous plants are composed of xylose and glucose but also, in lower concentrations, of arabinose and mannose. The constraint concerning this heterogeneous composition of sugars is that the pentoses (xylose and arabinose) are difficult to ferment when using classical micro-organisms. Nevertheless, it has been shown in the last few years that it is possible to ferment xylose using genetically modified organisms [22]. The latter are promising but they are difficult to be used given inhibitors present in the hydrolyzates at industrial level. An alternative is to ferment C6 sugars using known microorganisms (such as yeasts), then use the C5 for dehydration to furfural with simple acid catalysts. At high temperatures, the hexoses are converted to 5-hydroxymethyl-2-furfural while pentoses are converted to furfural (see Figure 2). Furfural could serve as an added value chemical for polymerisation or, through conversion (mainly selective hydrogenation), could yield furanic oxygenates which blend well with established hydrocarbon fuels. The 5-hydroxymethyl-2-furfural is a relatively unstable compound in presence of water and acid catalyst and tends to be converted to levulinic acid and formic acid (see Figure 2). While formic acid
could be used as a green chemical, esterification of levulinic acid could lead to the production of biodiesel grade esters. Most of the previously mentioned molecules will likely be significant as a forthcoming generation of ‘green’ chemicals and biofuels [23].

Figure 2: Dehydration of glucose to 5-hydroxymethyl-2-furfural and then to levulinic acid and formic acid (A) and dehydration of xylose to furfural (B).

2.1.4 Delignification
In case of solvolysis, lignin is directly solubilised during the treatment. When using steam treatments, delignification of the cellulose-rich fibres obtained from the removal of the hemicelluloses can be performed using either an organosolv method or, as in the Kraft pulping process, with NaOH at concentrations varying in the range 5-20% (wt). Abundance of the hydroxide ions will produce partial hydrolysis (the extent of which depends upon severity) of the C-O-C bonds in the lignin macromolecule thus generating monomeric, dimeric and trimeric structures. The alkaline solution allows the solubilisation of the lignin fragments and of the residual lignin itself. The dissolved dimers, trimers and the lignin itself can then be recovered after neutralization of the basic solution using a common acid as H\textsubscript{2}SO\textsubscript{4}. The latter will provide a proton to the aromatic structures thus rendering them un-miscible with water. The recovered mix (dimers, trimers and residual lignin) could be used as a source of energy via cogeneration. However, its subsequent secondary hydrolysis (at higher severities than those used in the delignification) could provide (i) additional monomeric units to those initially produced in the delignification step: catechols or aldehydes (vanillin or syryngaldehyde) could thus be isolated; and (ii) dimeric and trimeric compounds which both posses carbon-carbon bonds between the aromatic rings which could be transformed in high octane fuels via hydro-treatment techniques available in petroleum refineries.

2.1.5 Cellulosic fibers and fines
Cellulosic fibres are the product derived from biomass having the most important market as a non-food material. In general, steam treatments and organosolv processes provide fibres that have a quality comparable or even better than the classical chemical pulps. Along with the (long) fibres required for pulp, the
accompanying short fines are of interest. They could readily be brought to their microcrystalline structure which contains cellulosic chains at polymerization levels not exceeding 220 units. Such chains are linked together with hydrogen bonds. Although the crystalline system is highly polar because of the numerous alcohol functions found on the macromolecules, it is also highly resistant to aqueous solvation because the functional groups are generally oriented toward the center of the crystal. It is therefore usually difficult to attack the bond linking the glucose units and force the depolymerization of cellulose into its monomeric units (glucose). Enzymes are prime candidates as biocatalysts for the depolymerization [24]. Alternatively cellulose can be swollen by water or organic solutions having sufficient ionic strength to break the H-bonded matrix. Once cellulose is swollen its depolymerization (i.e. hydrolysis) to glucose, fermentation to ethanol or other end products is possible.

2.2 Pyrolysis and Gasification

Non-homogeneous biomass is a complex and often variable mixture of numerous carbon-based structures. The amount of different compounds renders this type of feedstock difficult to fractionate. The biorefinery approach needs to yield homogeneous intermediates that can be upgraded to defined and marketable end products. Pyrolysis and gasification accomplish such goal by forcing major changes in the carbon-based structures.

Pyrolysis (also known as thermal decomposition or thermal cracking), produces three streams: gas (normally used to fuel the process itself), a “bio-oil” (a complex mixture of dehydration water, organic compounds derived from carbohydrates, lignin and their cracked carbon structures) and residual charcoal (char as it is commonly known). In rapid pyrolysis processes, bio-oil (50 –70 wt% of the biomass) and char (10 – 20 wt% of the biomass) are the two intermediates that can be conveniently transported (they have higher bulk energy densities than the original solid feedstock) and used directly for their energy content (case of bio-oil replacing petroleum-based products in furnaces) and char as a soil additive. The bio-oil can also be fractionated into an essentially water-free oligomeric lignin-rich fraction and an aqueous fraction which contains carbohydrate-derived compounds (aldehydes to a large extent). The oligomeric lignin fraction can be used very much like a near-petroleum feedstock (oxygenated since it has a phenolic structure) in crackers and hydrocrackers located in petroleum refineries. Alternatively, the oligomeric lignin-rich fraction can be catalytically converted into oxyaromatics having value as green chemicals (for instance, catechols) and biofuels (for instance, alkoxyaromatics). The aqueous fraction containing carbohydrate-derived compounds can also be upgradable to simpler intermediates, such as hydrogen. It can also be concentrated, via membranes, and used directly as fuel.

With heterogeneous feedstock (such as “urban biomass”: sorted municipal solid waste residues), the pyrolysis route is constrained because of possible contaminants in the bio-oil. With such feedstock, synthetic gas is by far the best alternative because independently of the nature of the biomass used, it is essentially a homogenous intermediate. When oxygen and steam are used as
partial oxidation agents, the synthetic gas becomes syngas, which can be used for chemical synthesis if its conditioning and purification reaches levels that make it compatible with catalysts. Gasification is thus attractive because of its flexibility regarding feedstock. Urban biomass is a preferred input material because of its negative cost (i.e., the avoided landfill cost). Gasification of bio-oil can also be carried out. Biomass can thus be pyrolyzed in regional plants, the bio-oil transported and converted in a larger gasification and synthesis plant. Economies of scale may thus offset the high cost of the quasi-homogeneous biomass.

Gasification of biomass is usually performed at temperatures close to 800°C [25]. However, the choice of temperature as well as the process conditions leading to the formation of syngas are highly dependent on the nature of the feedstock given the presence of inorganic salts (recognized as ‘ash”) having low softenings points often at near or lower temperatures than 800°C. Chlorides are particularly low melting point salts. Temperatures in the thermal decomposition zone thus need to be adjusted to the nature of the inorganics present in the raw material. The chemistry of the reactions involves the following sequence: dehydration, thermal decomposition, partial oxidation and steam-driven and, to a lesser extent, CO2-driven reactions. The initial products of this complex process will be gas, intermediates and char. Such a mixture undergoes the reactions shown in Table 1.

Table 1: Identification of the major chemical reactions associated with the gasification of carbon-based compounds.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + ½O₂ = CO</td>
<td>1</td>
</tr>
<tr>
<td>CO + ½O₂ = CO₂</td>
<td>2</td>
</tr>
<tr>
<td>H₂ + ½O₂ = H₂O</td>
<td>3</td>
</tr>
<tr>
<td>C + CO₂ ↔ 2CO</td>
<td>4</td>
</tr>
<tr>
<td>C + H₂O ↔ CO + H₂</td>
<td>5</td>
</tr>
<tr>
<td>C + 2H₂ ↔ CH₄</td>
<td>6</td>
</tr>
<tr>
<td>CₙHₘOₖ + aO₂ + bH₂O = cCO + dCO₂ + eH₂</td>
<td>7</td>
</tr>
</tbody>
</table>

Among these reactions it is possible to identify oxidation reactions (1,2,3), the Boudouard reaction (4), the water-gas shift (5), the methanation reaction (6) and the autothermal reforming reaction of the oxygenated compounds produced by dehydration and by thermal decomposition (7). The latter reaction (7) includes the shift reaction [CO + H₂O ↔ CO₂ + H₂]. All these reactions permit to understand the importance of an oxygen input when feedstock as coal or plastic is gasified. Reactions 4, 5, 6 and 7 shows that it should be possible to control the composition of the syngas by partial oxidation of the char produced during its thermal decomposition. This particularity is important when it is necessary to homogenize the composition of the syngas independently of the gasified feedstock. The reforming of the oxygenated compounds is also an important aspect allowing the generation of a syngas with a limited amount of chemical
compounds as output. Carbon monoxide and hydrogen are the key compounds for synthesis and will also allow the utilization of advanced concepts such as coupling gasification with fuel cells. In equation (7), the coefficients a-e will depend upon the temperature and the composition of the oxygenated intermediates.

Yields of synthetic gas vary within a range of 1.8 – 2.2 Nm³/kg biomass (dry) for air gasification and 0.8 to 1.0 Nm³/kg biomass (dry basis) for O₂/steam gasification. The dry synthetic gas contains about 75% of the energy in the biomass being gasified. In addition heat recovered from the hot synthetic gas adds about 10% for a total of 85% as recovered energy. Low grade heat accounts for 5% and the rest and the remaining energy balance is due to the endothermic reactions and losses.

Gas composition varies somewhat with technology and operating conditions. Table 2 shows typical compositions from Enerkem’s gasifiers operated with air and O₂ / steam. Note the beneficial effect of reforming in reducing the gas mix components.

The gasification technologies are usually categorized in three families; the slowly moving (often named “fixed”) bed reactor (in either downdraft or updraft

<table>
<thead>
<tr>
<th>Gas compound</th>
<th>Air Gasification (Low severity)</th>
<th>Air gasification (Low severity) + steam reforming</th>
<th>O₂ / steam Gasification (Low severity)</th>
<th>O₂ / Steam Gasification (Low severity) + steam reforming</th>
<th>O₂ / Steam Gasification (Low severity) + steam reforming + CO₂ scrubbing (partial removal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>55.8</td>
<td>35.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Ar</td>
<td>0.8</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>H₂</td>
<td>9.5</td>
<td>35.2</td>
<td>11.8</td>
<td>47.0</td>
<td>65.0</td>
</tr>
<tr>
<td>CO</td>
<td>10.3</td>
<td>17.9</td>
<td>20.4</td>
<td>23.2</td>
<td>32.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>14.1</td>
<td>10.9</td>
<td>41.1</td>
<td>29.4</td>
<td>2.4</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.2</td>
<td>0.5</td>
<td>10.0</td>
<td>traces</td>
<td>traces</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>2.2</td>
<td>0</td>
<td>8.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C₅H₇ (C₂-C₅)</td>
<td>2.1</td>
<td>0</td>
<td>6.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C₆H₇ (C₆ and higher)</td>
<td>1.0</td>
<td>0</td>
<td>0.7</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Composition can be varied by adjusting the reforming step with steam and CO₂ for specific applications.
mode), the fluidized bed reactor and the entrained flow gasifier with or without slag formation. The fixed bed gasification relies on establishing a “pile” of solid material that is reacting progressively, and thus slowly moving downwards due to gravity. Addition of oxidant and of steam is done at strategic zones of the “pile”. Such approach, with numerous geometrical variations and feeding systems is the most ancient configuration used for the formation of synthesis gas.

Coke or anthracite which are relatively pure carbon structures were used early on readily producing “water gas”. Lignocellulosic biomass can also be used as a feedstock but due care is needed for the management of the intermediate tar. Downdraft gasifiers where the gas is flown through a hot incandescent char zone permits to reach low tar levels in the synthetic gas produced. Fluidized beds imply inert solids (sand, alumina or olivine) being fluidized by air or oxygen/steam. The carbonaceous material is inserted in or just on top of the bed where the heat and mass transfer coefficients are high (200 – 500 watts/m²). This technique was identified as the most suitable for the gasification of biomass [25]. It requires that the size of the biomass particles that are introduced in the reactor is not superior to a few centimetres. The fine carbon particles that exit the bed entrained by the gas undergo additional conversion in the upper part of the reactor. A cyclone permits to recycle unconverted solids. The entrained flow gasifier is well developed for the gasification of fine coal particles and could also be used for biomass. In this type of process, the grinded feedstock is converted co-currently with the oxidizing agent and steam in essentially a flow reactor. If the temperature at which the conversion is done is sufficiently high, the biomass will not produce any char residues and the slag will be solidified by contacting it with a liquid phase from which the solids are recovered.

Unwanted components of synthetic gas comprise tars (composed of polyphenolics and poly-aromatics compounds), chlorine-based compounds (as HCl), sulphur (as H₂S and COS), un-converted carbon particles as well as metal salts (mainly oxides). For further use the synthetic gas (syngas), needs to be purified. The sequential treatment used for the purification of the syngas is directly related to the utilization that is intended for it. When the gas is produced for the synthesis of alcohols or alkanes, removal of particulates and tar, as well as reduction of chlorine-based and sulphur-based compounds must reach essentially zero levels. As well carbon dioxide levels need to be compatible with desired synthesis strategies. In the last few years, numerous papers have been published on the purification of syngas. Experimental data points to sequential hot gas conditioning and wet scrubbing techniques capable of producing a clean syngas ready to be used for catalytic synthesis. Neutralization of chlorine using CaO is an efficient technique that permits to get rid off residual HCl. But reducing sulphur to sub-ppm levels (ppm = mg/Nm³) is a difficult task and thus catalytic reforming of the tar and low molecular weight hydrocarbons has not, to our knowledge (2009) been successfully implemented for long period of times (in excess of 200 h). If thermal reforming (without catalyst) is used, the destruction of the tar is not complete yet its removal can be achieved via scrubbing techniques. The latter use either aqueous or oil-based systems or a combination. The H₂/CO ratio is adjusted during the thermal reforming step by
conducting such step at appropriate severities and steam/carbon ratios. Particulate levels are lowered to ppm levels via a combination of cyclones and scrubbers. Alternatively metal and ceramic filters have been tested. Final purification of the syngas for catalytic synthesis uses CaO and ZnO filters as well as chilled methanol (other solvents can also achieve the same result) which permits, as well, to adjust the CO₂ concentration in the syngas to the desired level. Nitrogen gases, namely NH₃ and HCN are not an issue since during the thermal reforming and subsequent scrubbing they are removed. Cleaning and recirculating the scrubbing liquids is an inherent component of the gas conditioning strategy. It implies stripping the dissolved gases and vapours and, as well, precipitating out as sludge the fine particulates present in the liquid phase.

3 Conversion of syngas to biofuels

Production of methanol from syngas is industrially practiced. Copper/zinc oxide-based catalysts show high productivities up to 2 kg of MeOH per kg of catalyst per hour [26] with selectivities reaching near the 100% level.

Production of ethanol and long chain alcohols is one of the most researched areas currently (2009) in this field. Conversion of syngas to ethanol can be done using two distinct pathways: the direct catalytic conversion (associated with drastically lower conversion yields if compared to the methanol synthesis) or via the separate homologation of methanol. The latter pathway allows one to take advantage of high production yields associated with methanol synthesis yet it has a higher complexity than the direct pathway because of the additional synthesis steps required.

Production of alkanes from synthesis gas is known as the Fisher-Tropsch synthesis (FT). At the industrial level, cobalt and iron are used as catalysts at temperatures close to 340°C. Such conditions allow converting close to 40% of the syngas into gasoline and 20% in propene and butene which can be partially inserted in synthetic fuel to increase its octane level [27]. The yields of useful product that can be commercialized as gasoline or as diesel following a FT synthesis are lower than those observed in the methanol synthesis [28]. The latter can be converted to gasoline via catalytic oligomerization, which constitute an alternative to the FT synthesis.

4 Conclusions

For the conversion of lignocellulosics to biofuels a decision on the technological route to be followed very much depends on the type and cost of biomass and availability within a reasonable transportation distance that does not exceed 100 km, as the norm in North America. For this purpose biomass can be categorized as follows: homogeneous biomass (>100 $US/t), quasi-homogeneous biomass (30-60 $US/t) and non-homogeneous biomass (≤ 0 $US/t, dry basis). Among the biofuel production techniques that are actually entering the market, gasification is by far the most versatile because it can be applied to all the different types of
biomass previously mentioned. However, because of the biomass availability and cost, the feedstock targeted by gasification will be preferentially non-homogeneous biomass which permits moderate capacity plants (100 000 t biomass input, dry basis, per day) and, as well, quasi-homogenous biomass, the latter requiring, via gasification, large economies of scale. The homogeneous and quasi-homogeneous biomass, because of their higher costs (about 100 $US for homogeneous to a range of 30-60 $US per anhydrous tonne for quasi-homogeneous) could be adapted to a co-product strategy. The biorefinery concept, using fractionation approaches, will allow the isolation and the utilization of the constitutive fractions of the biomass. Such approaches should also be designed to be self-sufficient in terms of energy. The isolated constitutive fractions are the “secondary biomass feedstock” for upgrading to marketable end products” green chemicals, biofuels and fibres.

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