

PART II

NEEDS AND TECHNOLOGICAL CAPABILITIES

6 LARGE TECHNOLOGICAL AREAS

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6 LARGE TECHNOLOGICAL AREAS

6.1 Feedstock

Four main large technological areas were identified (**Table 18**) that contribute to achieve the critical system requirements listed in **Table 15** (see section II.2). The most important areas are plant breeding and improvement, and crop management.

Table 18 Large technological areas for feedstock production.

AREA	LIST OF THE RELEVANT TOPICS
1) Plant breeding/ improvement	new traits, transgenic technologies, tolerance to adverse climatic conditions, tolerance to pests, superior genotype selection, cloning systems, hybridization, new crop varieties, specific varieties for biomass production.
2) Crop management	no-tillage, minimum tillage, fertilization, precision agriculture, harvesting systems, mechanization, soil management and farm practices, water use efficiency
3) Residue use and by-products	alternative uses for residues, recycling of nutrients, development and use of by-products, equipment for application of by-products.
4) Residues and wastes collection and management	in-site collection (where the residue is produced), transportation and logistics of residue, storage, pretreatment, machinery/equipment, landfill emissions.

6.2 Refining Technologies

6.2.1 Pre-treatment processes

The use of lignocellulose materials (lignin, hemicellulose and cellulose) for second generation biofuels has not yet become an industrial reality due to the lack of efficiency and low cost technologies (DIAS, 2011). Even massive use of the first generation fuels (from sugars and vegetable oils) from biomass have not yet reached their full potential, due to a series of difficulties, mainly related to sustainability, food versus fuel competition and land use. The heterogeneity of lignocellulosic material and the broad variation in chemical composition of the raw material can be overcome by a variety of pretreatments to produce a more uniform structured material, which only then would be transformed into desirable intermediates via secondary conversion processes.

An effective pre-treatment, according to Galbe and Zacchi (2010), must yield high concentration of soluble carbohydrates; achieve high digestibility for hydrolytic enzymes; produce low concentration of degraded products of sugar and/or lignin; offer high solids content, require low energy requirement and/or allow energy recycling; and low capital and operational costs.

Amongst these are physical or also named mechanical (fractionation, crushing, extraction), chemical (acid, alkaline, organosolv), physicochemical (steam explosion, hydrothermolysis)

and biological (enzymes, microorganisms) or a combination of pretreatments that prepare large volumes of biomass and condense them to lower volumes. Small pretreatment units can be installed at the feedstock production farms to initially transform the biomass and its products can be then transported or used immediately by the conversion plant.

6.2.2 Conversion Technologies

6.2.2.1 Gasification

The gasification of carbonaceous materials has been commercially done for over 50 years; however the synthesis gas has to be catalytically transformed into liquid fuels. To do this in an economical way, the gasification has to be done under pressure which represents some technical risks and needs larger plants. Another possible route for lignocellulosic biomass is to start with pyrolysis, obtaining bio-oil and bio-char, intermediate products that could be transported economically through larger distances, to be then submitted to gasification and synthesis by the Fischer-Tropsch process. The investment cost for the FT alternative is given as high (1€/L for a 200 million liters/year capacity) (KUMAR et al., 2009).

6.2.2.2 Fast Pyrolysis

Fast pyrolysis converts biomass into a liquid product (pyrolysis oil or bio-oil) which needs to be upgraded to produce liquid fuels. According to Mohan et al. (2006), fast pyrolysis of biomass produces bio-oil, which is easily transported and stored and could then be upgraded by hydroprocessing or fractionation (distillation) and commercialized according to the properties of each fraction obtained. Bio-oil could also be transported to a Syngas refinery to be further processed by Fischer-Tropsch technologies (ZHANG et al., 2012).

Charcoal processing is also considered a pretreatment that increases the energy density of the biomass. Therefore, pretreated material is more easily stored and transported (i.e. bio-oil, hemicellulose hydrolysates, charcoal) and potentially better distributed to larger refineries. Fast pyrolysis is preferred. There are several demonstration plants being tested outside Brazil. Bio-char is a very valuable active carbon source (VAMVUKA, 2011).

6.2.2.3 Liquefaction

Biomass conversion to liquid fuels (bio-oil) via solvent liquefaction, pyrolytic processes and catalytic hydroprocessing achieves good yields of liquid hydrocarbons but this is mostly experienced on a bench scale and small pilot plants. Improved understanding of process steps and properties still needs to be developed, since process economics are promising in the current economic environment. Solvent liquefaction seems to be promising as no hydrogen or catalysts are needed and the conversion conditions are rather moderate. Patents have shown that the level of upgrading of bio-oil depends on the final use of the product, which will depend on the properties of the desired liquid fuel (MOHAN et al., 2006). **Figure 50** presents a bio-platform scheme.

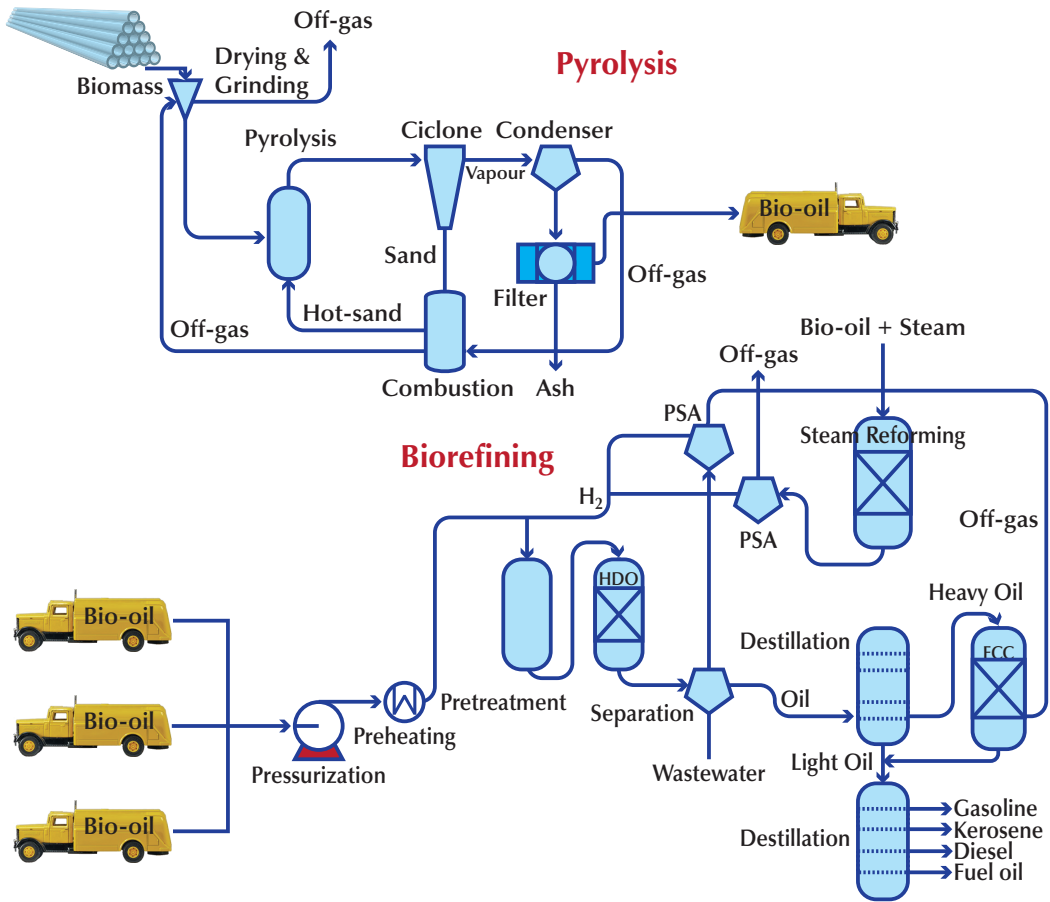


Figure 50 Bio-oil platform. Source: Elliot, 2010.

6.2.2.4 Hydrolysis

Hydrolysis with a low concentration of acid and steam explosion processing is able to disrupt the hemicellulose fraction and release lignin and cellulose to some extent and two main products obtained are the lignin + cellulose fraction and the hemicellulose-rich hydrolysate. Acid hydrolysis is valuable for pre-hydrolysis. The pre-hydrolyzed cellulose can then be hydrolyzed enzymatically. A large number of pilot and demonstration plants exist throughout the world. There are different technological concepts aiming to increase the amount of solids in the reactors (**Figure 51**) (MOSIER et al., 2005).

Byproducts as furfural, hydroxymethylfurfural, organic acids and others can be formed during hydrolysis, which inhibit fermentation (**Figure 52**). The concentration of inhibitory byproducts and as well of the desired sugars (pentose sugars in monomeric or oligomeric forms) in the hydrolysis streams, obtained after the steam explosion pretreatment, can be adjusted by setting the process conditions. Therefore, hemicelluloses sugars would be released in the liquid phase and the solid cellulose is further enzymatically treated. Despite the differences in acid pretreatments (inorganic, organic acids, impregnation) and steam treatments, it is possible to find a set of pretreatment conditions that allows the biomass

processing or mixture of them to be converted with satisfactory yields of streams, and offering the solid cellulose ready for enzymatic treatment.

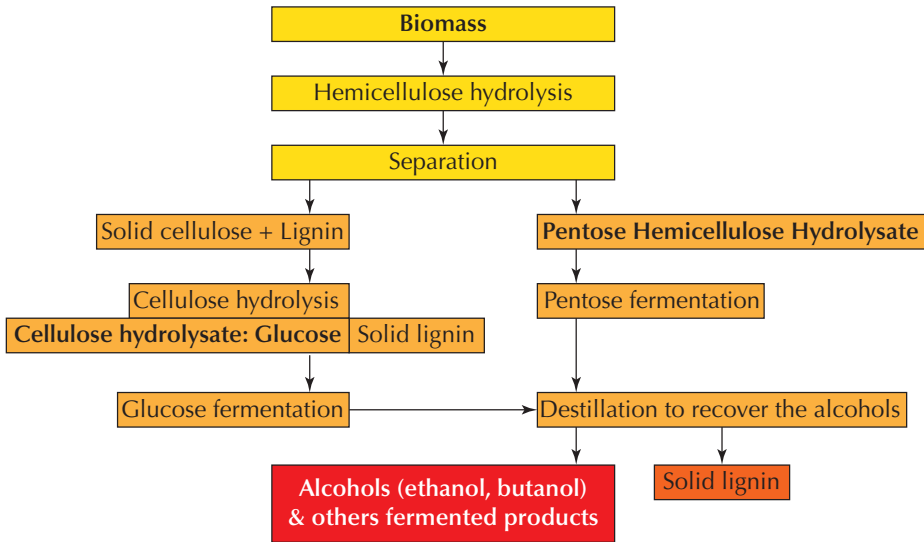


Figure 51 Flow chart for the production of two hydrolysates: hemicellulose pentose-rich hydrolysates and cellulose glucose-rich hydrolysate. Products are generated from both hydrolysates via fermentation or chemical pathways.

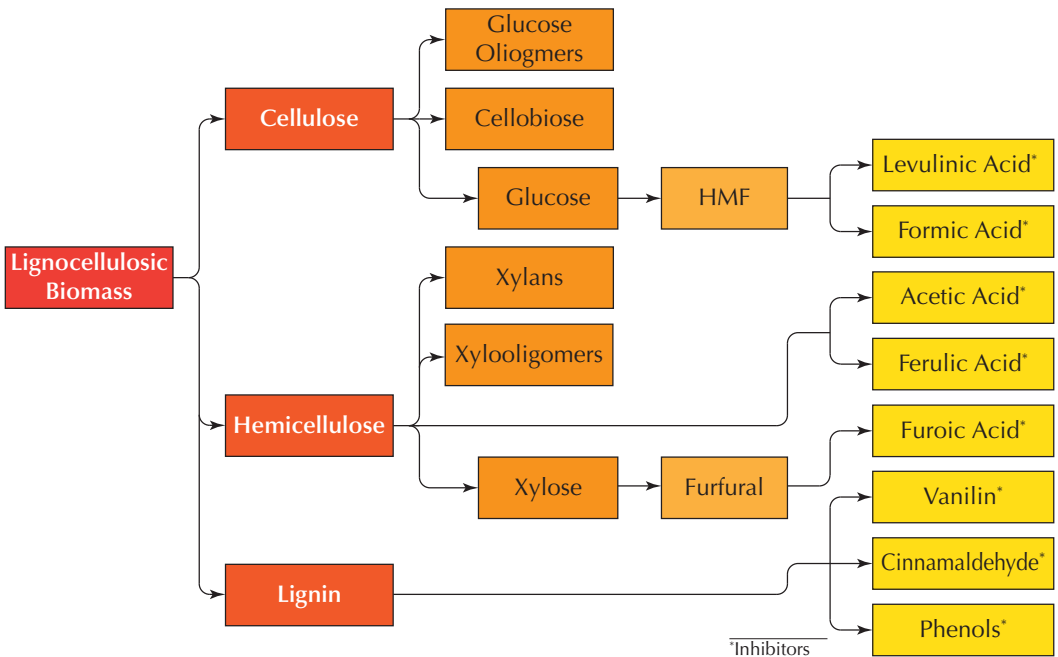


Figure 52 Product potential inhibitors to microbial growth from the cellulose, hemicellulose and lignin fractions of lignocellulosic biomass during pretreatment. Source: adapted from Modenbach; Nokes, 2012.

Enzyme hydrolysis technology is still being optimized and the price of the enzymes needs to be reduced further. There are some pilot and demonstration plants throughout the world, using different technological concepts aiming to increase the amount of solids in the reactors, to produce them in-house and to recycle enzymes or to do simultaneous saccharification/fermentation (SSF).

Industrial cellulases and xylanases are well-known commercial products, tailor-made according to the target commercial application. Very significant progress in the engineering of enzymes using advanced biotechnology techniques, like directed evolution and rational design studies have opened new markets, with enzymes being increasingly tailored for specific applications and higher activities. Protein engineering of lignocelluloses-degrading enzymes, including mutagenesis of potential active centre residues with subsequent kinetic analysis, has been used as a tool in the study of the catalytic mechanism and improvement of some properties of industrial enzymes. The “Improved low cost cellulase for biomass conversion” project, developed in the US in 2000–2003, aimed to reduce the cost of enzymatic hydrolysis, by reducing enzyme costs 10 fold. In-house enzyme production is also considered as an alternative to reduce the cost (KOVACS et al., 2009). A recent Brazilian project was developed from 2006 to 2007, aiming to produce in-house fungal enzymes, by submerge and by solid fermentation to reduce their costs (BON; FERRARA, 2007).

6.2.2.5 Fermentation to alcohols

The original feedstocks for this route are sugars and starches; however other alternatives include lignocellulosics, industrial waste gases and municipal solid wastes (MSW). Starches and sugars may be converted to alcohols through direct fermentation and industrial waste gases rich in CO can potentially be converted to alcohols by gas fermentation. Lignocellulosic biomass may be converted to alcohols after being hydrolyzed to simple sugars, followed by fermentation, or by gasification to produce synthesis gas ($\text{CO} + \text{H}_2$), followed by gas fermentation. A fraction of the organic MSW is fermented to carboxylic acids and further transformed into ketones and hydrogenated to secondary alcohols (KANITZ; KESSELRING, 2002).

These different wastes can potentially be used as feedstock for fermentation to alcohols or other chemical building blocks to be further converted to jet biofuel by a specific technology. Also the integration with conventional feedstocks should be considered to reduce the cost of the jet biofuel, when logistics for transport is designed.

1. **MSW:** The technology may be appropriate to produce liquid fuels by fermentation to organic acids, alcohols or other chemical building blocks. The technology will depend on the kind of waste separation and the kind of fraction considered.
2. **Industrial Residues:** There is no available inventory on residues from the Brazilian industry at the moment. The capabilities have been studied as feedstock for fermentation to alcohols or other chemical building blocks. The technology will depend on the kind of separation and purity considered.
3. **Gases:** The idea is to harvest carbon monoxide to feed microorganisms in a bio-reactor, which would be converted to alcohols to be further transformed into liquid fuels. Scaling-up has been planned in China (NIGRO, 2012).
4. **Sewage:** The strategic potential is considered very low and the technical risk is very high. The technology may be appropriate to produce liquid fuels by fermentation to alcohols or other chemical building blocks. No capabilities were detected.

6.2.2.6 Lipids from carbohydrates

Microbial lipids (microalgae, bacteria and yeasts): The feasibility of waste materials and energy-dedicated vegetables to be efficiently biologically converted into valuable chemicals or biofuels with higher added value or into building blocks for industrial needs depends on the capability of microorganisms to use pentoses besides of hexoses, and to stand the most common impurities originated from them. It is widely known that organic compounds produced by fermentation are alternatives for substitution of fossil derived chemicals, since substrates from nature, i.e. carbohydrates, can be converted into building blocks (organic acids, alcohols and others) which allow producing polymers, resins, and fuel. The monomers glucose, xylose and arabinose, main sugars from lignocelluloses, are abundant in nature, especially from agro-industry wastes (BLANCH, 2012).

Photosynthetic microorganisms (algae and cyanobacteria) and fungi produce materials with high-lipids content, have a shorter doubling time and allow continuous harvesting. Microalgae and cyanobacteria have recently called a lot of attention of the media, due to the lower quality requirements for land (lower demand of fertile land to produce, in theory, the same amount of lipids than oleaginous plants) (LAM et al., 2012). The literature describes the production of lipids from molds. In particular, oleaginous microorganisms also can be used to produce a great deal of lipid, up to 70% lipid of the total dry cell weight under certain conditions (BIGNAZZI et al., 2011). For this reason microbial feedstock is gaining attention and research investments from petrochemical industry.

Today, the dominant cost factor in microbial biofuel and commodities is the raw material; however several agricultural crops offer non-edible wastes, i.e. corn cobs, wheat and rice straw and sugarcane bagasse. Easy transport of short distances and good logistics allow the employment of suitable treated sugarcane bagasse to be used as feedstock (KOSKINEN; TANNER, 2012).

Since lignocellulosic biomass is the most abundant raw material from agricultural residues, it is very commonly left in the fields due to the original design of equipment for harvesting. Its utilization is an important option to be considered in industrial biotechnology and biorefining, to reduce the costs, to avoid competition with the food and feed industries and minimize environmental problems due to excessive volume of wastes to be disposed. Several authors have evaluated the viability of their use to produce chemicals and commodities (GOPINATH et al., 2012).

6.2.3 Technologies to produce jet biofuel

6.2.3.1 HEFA (hydroprocessed esters and fatty acids)

HEFA is sometimes also called HRJ (hydroprocessed renewable jet fuels) or HVO (hydrogenated vegetable oils), which are produced by “refining” lipid material, much like the way petroleum is refined today. The hydroprocessing of lipids, mainly the oils and fats (from plants, microbial or animal) involves converting them into hydrocarbons by the addition of hydrogen.

The first step converts the lipids to fully saturated hydrocarbons, or synthetic paraffins and propane, by saturating carbon double-bonds with hydrogen and removing oxygen as water. These paraffins are then selectively cracked and isomerized to produce primarily

diesel, jet fuel, gasoline and naphta. This process is a qualified process for renewable drop-in jet fuel in the market, and meets the required specifications (KAUL et al., 2012).

This process can be integrated into existing fossil fuel refining facilities and operated at similar costs of petroleum refining. It can also be added to the first generation biodiesel production facilities, or built from scratch in stand-alone refineries. HEFA fuels are ASTM certified for commercial use in up to a 50/50 blend with conventional jet fuel (RENEWABLE JET FUELS, 2013). Residues like used cooking oil, or the industrial sub-products tallow and yellow greases, can be used as feedstock. Hydrogen demand for different feedstock qualities varies, resulting in different conversion costs for diverse raw materials like palm oil, animal fats, camelina, jatropha, etc. (MILLER, 2010).

Investment cost for hydro-processing is considered to be lower than for the Fischer-Tropsch process, but the cost of the raw materials can represent more than 70% of total cost. Vegetable oil market prices are following petroleum price developments (OVALLES et al., 2011).

Other possibilities of feedstock for HEFA are microbial lipids, obtained by fermentation of fermentable sugars or from hydrolysates of lignocellulosic material. Some species of oleaginous yeasts, bacteria and heterotrophic microalgae can store up to 70% (w/w) of lipids in their cells (dry mass). The economic possibilities of these last alternatives are strongly dependent on the price ratio of sugar to ethanol to vegetable oils. The technology is known, however the improvement of the stability of the transgenic yeast/algae would be very much desirable to improve the performance of large bioreactors. These technologies are available to produce lipids directly from sugar, which then require hydro-cracking and are available in pilot plant stage. Commercial risks will be reduced when cellulose/lignocelluloses can be used as feedstock as they will benefit from second generation sugars.

HEFA technology is well developed, however expensive hydrogen is needed. When the process is done in a petro refinery plant, a hydrogen-rich stream is often available. The amount of hydrogen needed varies with different chemical structures of feedstock oils (MADSEN et al., 2011). This mixture produce hydrocarbons at different ratios, which can be fractionated (HUANG et al., 2011).

The percentages of the synthesized hydrocarbons (diesel, jet fuel, gasoline and naphta) vary much with the synthesis conditions, however they follow the Schultz-Flory distribution and no reliable values can be found in the literature.

Another process which converts lipids to liquid fuels is the thermal cracking of fatty materials, which gives good results, however much more development is needed to use it in a technical industrial scale. Used cooking oil is better used for thermal cracking since only filtration is necessary. This technology produces a mixture of hydrocarbons attending the requirements for diesel (about 10%), naphtha (10%) and 35% jet fuel, which are separated by distillation.

6.2.3.2 Alcohol to jet (ATJ)

ATJ is made via alcohol dehydration/oligomerization which involves linking short-chain alcohol molecules (e.g. methanol, ethanol and others) together to form jet-fuel range hydrocarbons. There are several chemical reactions that can be employed to oligomerize alcohols. In each of these processes, water and/or oxygen are removed from the alcohol molecules, and hydrogen

is added because the starting alcohol volume is reduced in order to produce a marginally more valuable hydrocarbon jet fuel (at current market prices), the economic rationale of these conversions must be critically examined on a company-by-company basis as shown in **Figure 53** (STREET et al., 2012).

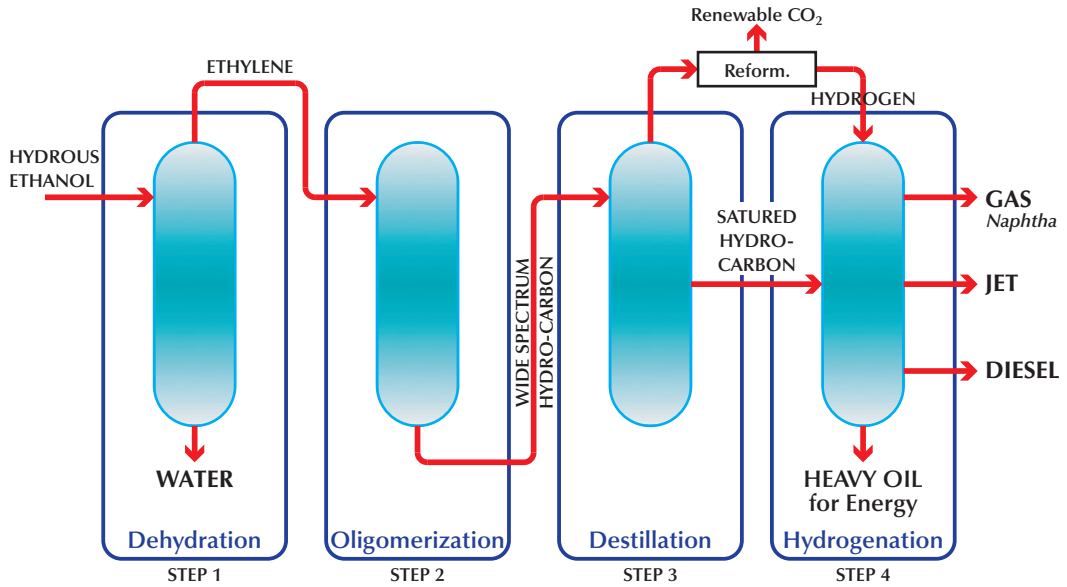


Figure 53 Steps of AJT process. Source: Weiss, 2012.

Different research groups have developed specific catalysts for the direct and high-yield conversion of bio-ethanol to fuel additives, rubbers and solvents. With increased availability and reduced cost of bio-ethanol, conversion of this particular bio-based feedstock to high valuable fuels and chemicals has been an especially important research goal. Currently, research on bio-ethanol conversion to value-added chemicals focuses mainly on ethanol dehydration to ethylene, or ethanol dehydrogenation to acetaldehyde and then to acetone via Aldol-condensations pathways (SUN et al., 2011).

The ATJ process, which is in the process of approval by ASTM, still needs subsidies/mandates, if sugar is employed as the feedstock, due to the high market price of sugar. However when cellulosic sugar or low cost alcohol from other sources such as industrial waste is available, the commercial risks can be reduced. The alcohol intermediates may be methanol, ethanol, butanol, isopropanol, other alcohols or a mixture of them (PARGHI et al., 2011). Large advantage in costs would be achieved with the minimization of the operation steps of this process.

The percentages of the synthesized hydrocarbons vary much with the synthesis conditions and are ruled by the Schultz-Flory distribution. According to Byogy, this technology produces a mixture of hydrocarbons attending the requirements for diesel (about 10%), naphtha (10%) and jet fuel (35%), which are separated by distillation.

Due to the large Brazilian experience in producing ethanol from sugarcane and the existence of a well-established agro-industrial sector dedicated to this subject, the natural

reference prices for liquid biofuels and lignocellulose concentrated biomass probably will be ethanol and sugarcane bagasse. Worth mentioning is that the ethanol production in Brazil in 2011 was approximately 18 billion liters, amount that, in energetic terms, is more than one and a half times the whole aviation fuel consumption in the same year.

6.2.3.3 Syngas/Fischer-Tropsch

The synthesis gas (CO and H₂) is converted into hydrocarbons by growing the carbon chains, catalyzed by metal supported catalysts (heterogeneous catalysis), according to reaction (1).



Fischer-Tropsch paraffinic kerosene can be produced from lignocellulosic biomass through gasification followed by gas cleaning and synthesis over appropriate catalysts (**Figure 51**). The process is approved for a 50% blend by ASTM. Although raw material cost in this field is very low, the transportation cost is important and limits the size of the processing plant, with large implications on investment costs (ALVES, 2011).

The product obtained by the Fischer-Tropsch synthesis is a mixture of hydrocarbons with chains of different sizes (**Figure 54**), from light gases to high molecular weight greases (LUQUE et al., 2012; KLERK, 2011). In order to achieve commercial specifications for fuels, the liquid mixture of hydrocarbons obtained must be appropriately separated and, as required by the market, also needs conversion steps for transforming molecules of high molecular weight into molecules of lower molecular weight hydrocarbons or adding other compounds (derived from traditional oil refining) to assist in adjusting the properties required for the specified fuel (Bartholic, 2000). The percentages of the synthesized hydrocarbons vary with the synthesis conditions and are ruled by the Schultz-Flory distribution.

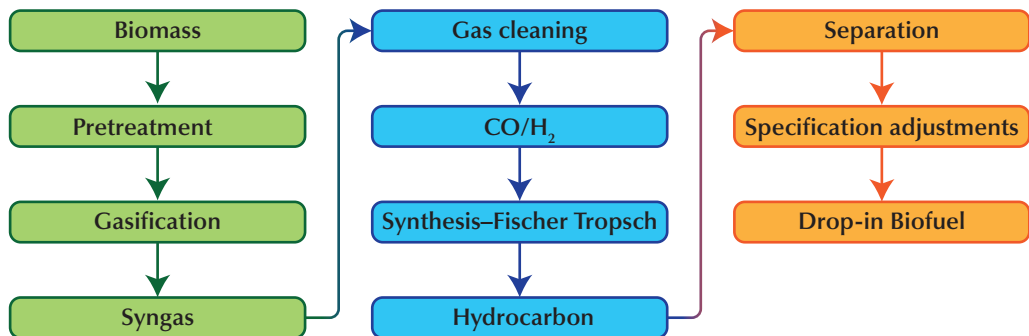


Figure 54 Operations required transforming biomass into drop-in jet biofuel by Fischer-Tropsch conversion.

Synthesis of methanol or dimethylether as a platform chemical to produce hydrocarbons is another route to jet biofuel (OLAH et al., 2012). **Figure 55** presents a the chemical platform to syngas.

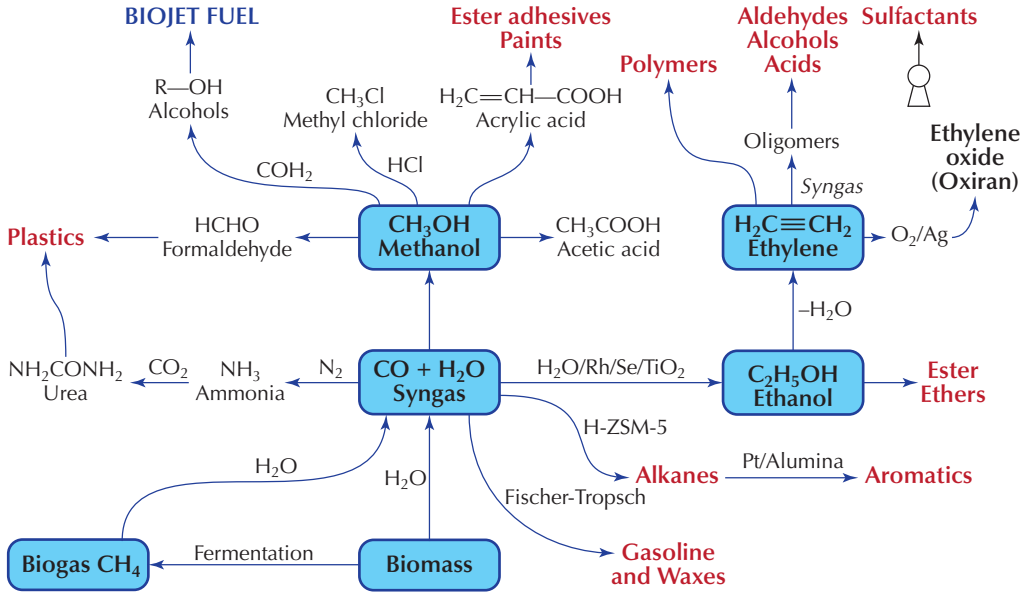


Figure 55 Fuels and chemicals from a biomass Syngas-Methanol platform.
Source: adapted and modified from Kamm et al., 2006.

6.2.3.4 Direct Sugar to Hydrocarbon (DSHC)⁹

A biotechnological approach was developed to directly bioconvert sugars by fermentation to farnesene (DOUGLAS et al., 2007), which can further be hydrogenated to farnesane (a branched paraffinic hydrocarbon containing 15 carbons (**Figure 56**) with desirable characteristics for jet fuel. This hydrocarbon has already been registered with the United States E.P.A. for widespread use in a 35% blend with petroleum diesel.

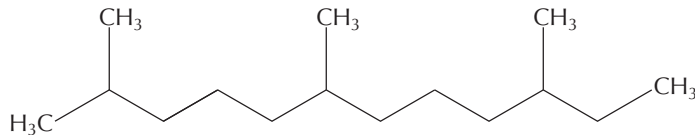


Figure 56 Farnesane molecule structure.

Farnesene is transformed into farnesane through a combination of hydroprocessing and fractionation operations (**Figure 57**). Hydrogenation of the farnesene feedstock with hydrogen in a catalytic bed is needed in order to reduce the double bonds. Fractionation consists in a gas/liquid separation (to remove hydrogen from the resulting hydrogenated compounds) and isolation of farnesane in order to reach jet fuel specification targets.

⁹ Now denominated Synthesized Iso-Paraffins (SIP) and approved by ASTM as Annex 3.

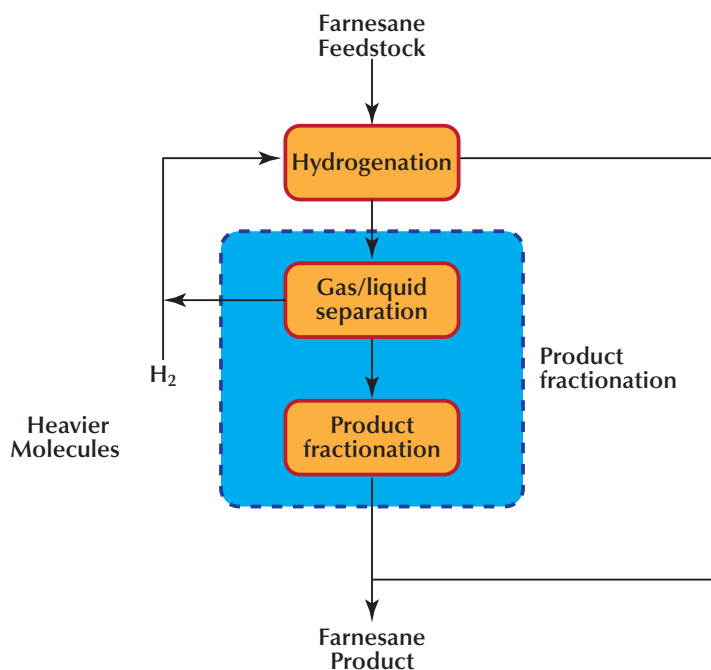


Figure 57 Simplified overview of the process to produce DSHC fuel.
Source: Amyris, 2012.

A demonstration flight using a blend of 20% farnesane DSHC, 30% C10 hydrocarbon and 50% jet fuel was performed in Brazil. The producer of the DSHC technology (Amyris) is seeking ASTM qualification for a low blend of farnesane into Jet A/A-1. The work group has completed the analyses of physical-chemical property and fuel specification data, according to ASTM D1655 and ASTM D7566, and is now undergoing Fit-for-Purpose testing at the Air Force Research Lab (AFRL). The resulting research report will be used to prepare a proposed ASTM DSHC fuel specification¹⁰.

In theory, it is expected that the efficiency for this pathway by aerobic fermentation is that 3 kg of sucrose are converted into 1 kg farnesene, considering both, 100% biological conversion and 100% purification with zero losses and 100% efficiency of the hydrogenation step (4 molecules of H₂ for each farnesene). However, lower conversion is presently achieved. The use of lignocellulose hydrolysates is being evaluated to replace sucrose.

6.2.3.5 Catalytic bio-oil upgrading

Different types of catalyst have already been investigated, both mesoporous and microporous. It seems that the ZSM-5 catalyst is a promising catalyst. Bio-oil upgrading has also been investigated using hydrodeoxygenation and catalytic cracking processes. For the deoxygenation, the research challenge is to design novel catalysts with enhanced activity and selectivity and, especially, better stability to deactivation. The partially deoxygenated

¹⁰ In fact already approved by ASTM (June/2014) as Synthesized Iso-Paraffins (SIP), permitted for blending of up to 10% with conventional jet fuel.

bio-oil is probably the best solution, since it can be further upgraded by co-processing with petroleum. For the catalytic cracking process the challenge is to design catalysts with less coke formation or to use bio-oil with less phenolic components (DE GRUYTER, 2012).

6.2.3.6 Hydrogen necessity of different conversion technologies

The hydrogen, necessary to convert the feedstocks into biofuels, may be produced within the conversion process or has to be added externally. Gasification of any biomass certainly produces enough hydrogen for the transformation of the synthesis gas into jet fuel (TIJMENSEN et al., 2002). Fast pyrolysis or liquefaction produces a bio-oil which has a relatively large percentage of formic and acetic acid, which can act as a hydrogen source for the transformation of the bio-oil into jet fuel (KARIMI et al., 2011). In these cases no expensive external hydrogen is needed. On the other hand, hydrogenation of farnesene (Amyris), hydroprocessing of fatty acids (Solazyme) or their esters (bio-diesel or algal oil) require expensive external hydrogen, which makes the jet fuel more expensive. Acid catalyzed dehydration of ethanol, obtained by fermentation, to jet fuel also requires external hydrogen; however the quantities are rather small.