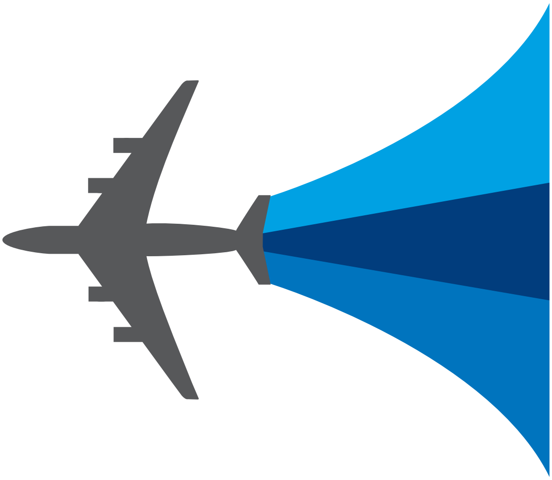


PART III

TECHNOLOGY DEVELOPMENT STRATEGY

10 TECHNOLOGY ALTERNATIVES

Augusto Barbosa Cortez [et al.]. "Technology alternatives", p.183-200. In: Luís Augusto Barbosa Cortez (Editor). **Roadmap for sustainable aviation biofuels for Brazil — A Flightpath to Aviation Biofuels in Brazil**, São Paulo: Editora Edgard Blücher, 2014.
http://dx.doi.org/10.5151/BlucherOA-Roadmap-010

10 TECHNOLOGY ALTERNATIVES

10.1 Feedstock

Feedstocks are a crucial element in the production of biofuel for aviation, affecting directly the final cost and environmental impacts. Nevertheless, the Brazilian conditions are particularly attractive for agricultural products in general, and among them, bioenergy. In fact, the variety of options is a challenge, more than the lack of alternatives to explore.

Brazil is a traditional agricultural goods producer and is among the world's leading producers and exporters of many agricultural products such as soybean, sugarcane, coffee, cotton, maize, tropical fruits, meats, etc. This relevant position was attained not only because of abundant land and good climate conditions, but also due to long-term investment in research and development and an entrepreneurial private sector. Thus, Brazil shows currently a favorable combination of availability of land for agriculture not occupied with native vegetation, notably pastures, with a dynamic agriculture sector presenting steady productivity growth, large amount of law protected native vegetation, strong conservation laws based on "control-command" enforcement and human health and safety regulations for rural activities equivalent to urban activities. This remarkable combination places the country, from a feedstock supply perspective, in a good position of developing an aviation biofuel program with compliance with responsibility principles and sustainability requirements.

The agricultural activities, including ranching, occupy 30.4% of the Brazilian territory, while 65% of the territory is covered with native vegetation (**Figure 24**). Law protected native vegetation (conservation units, indigenous reserves and private properties) represents 87% of the total remaining native vegetation. Annual and perennial crops, however, have a small share on the 30.4% of the total agricultural land: only 23% (7.1% of the Brazilian territory) (IBGE, 2013). The majority of the Brazilian agricultural land is occupied with pastures, used mainly for beef cattle production, and the introduction of better ranching practices can open a large area of arable land for agriculture.

The feedstock to be processed to produce aviation biofuels should be primarily a good carrier of solar energy converted in chemical energy. So, biomass material to be used for biofuels can be rich in sugar, starch, fat, oil, fiber and obtained directly or indirectly by cultivated crops, algae or residues, delimiting the conversion processes that can be adopted. Specifically for the production of biofuels for aviation, a large number of feedstocks can be used (and in fact have been proposed), however, important requirements such as capacity to improve yields, low direct and indirect greenhouse gases emissions, high efficiency in land use and positive social and economic impacts also need to be fulfilled. The possible feedstocks can be grouped according to their related chemical affinity:

1. Sucrose/starch rich plants (e.g. sugarcane (juice), sorghum, cassava)
2. Oil-bearing feedstocks (e.g. soybean, palm, jatropha, camelina, green algae, sunflower, peanut, other palm trees)
3. Lignocellulosic materials (e.g. forestry wood residues, sugarcane (bagasse), industrial forestry residues, agricultural residues)
4. Wastes (e.g. CO rich flue gas, municipal solid waste, used cooking oil, tallow, sewage sludge)

Feedstocks usually represent a significant percentage of biofuel production cost. In the case of Brazilian ethanol, sugarcane reaches 70% of overall costs and for biodiesel even 90% (NOGUEIRA, 2013). In the case of jet biofuel, this will depend on the processing costs, but assuming that the cost of new fuel will follow basically the same cost structure after the technologies have been mastered, then typically feedstocks will remain as the most critical cost item in the jet biofuel production. In this regards, is worth to stress that the jet biofuel will only be competitive with a low cost feedstock.

Possibly, the jet biofuel technology will follow a learning process similar to that experienced by the Brazilian ethanol, where a significant cost reduction was observed during the effective development of the market for this biofuel in Brazil, as a consequence of R&D activities and improvements in management and logistics (**Figure 75**). Other important aspects to take into account on feedstocks selection are productivity (e.g. allows to use less land and minimize other related impacts), complementarity (e.g. a certain feedstock may be a good solution for a particular region but there may be other good solutions for different regions) and commercial readiness (e.g. feedstock A may be fully commercial but feedstock B and C may need additional and substantial R&D investments).

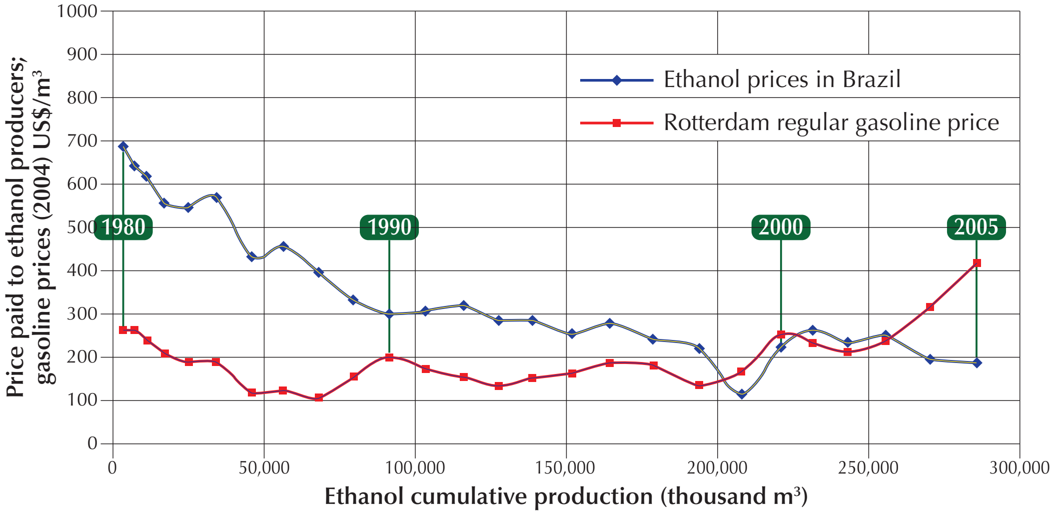


Figure 75 Sugarcane Ethanol Learning Curve. Source: Goldemberg, 2007.

A multi-criteria analysis conducted on 2nd Workshop (“Feedstock”) looked at feedstocks according to three broad categories: (i) strategic potential, (ii) technical risks and (iii) commercial risks. That analysis showed that all categories of feedstock alternatives have strategic potential to be compliant with the roadmap goals (**Figure 76**), but technical and commercial risks need mitigation and are somewhat specific to each feedstock being considered, as shown in section **Gaps and Barriers** (**Part II, Table 28 and Table 29**).

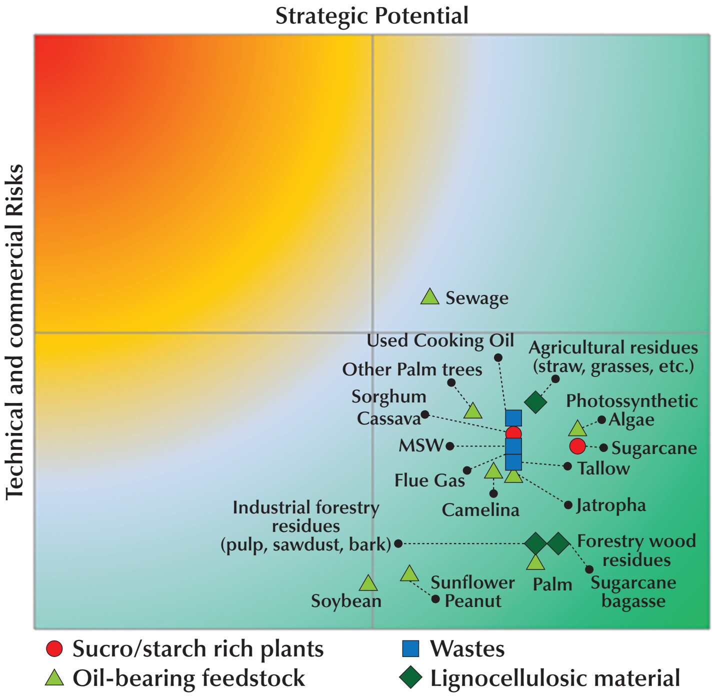


Figure 76 Multicriteria analysis of different feedstock alternatives.

This section is based on the compilation of results of the group discussions in that workshop. The participants were divided in four groups: oil-bearing feedstocks, sucrose/ starch, cellulosic feedstocks and wastes. The list of feedstocks analyzed covers a large number of products compared to those addressed in the individual presentations.

The participants scored the feedstocks according to three broad categories: strategic potential, technical risks and commercial risks. Each category was divided in several sub-categories (19) and the score process was based on four or five sets of options.

Table 32 summarizes the results and allows for the classification of the feedstocks according to its strategic potential and technical and commercial risks. Residues from widely produced feedstocks (forestry and sugarcane), from steel and chemical industries (CO rich flue gases) and wastes (Municipal Solid Wastes) were classified at the top of the ranking. Among them, with exception of sugarcane, all other feedstocks are by or co-products of different industries.

Oil-bearing crops, in general, received a lower score, especially because the participants perceive them with high commercial risks. This is coherent with the food security debate and with the fact that oil-bearing crops, in general, have lower energy yields. Sweet sorghum and cassava are in the middle probably because, either they are complementary to other crops (sorghum), or because they are a well-known crop (cassava).

Clearly the participants have scored the feedstocks assuming that by or co-products are better suited for producing biofuels, as well as high energy yield crops (sugarcane). The only exception was the agricultural residues, mainly because of the technical risks associated to collection and transportation.

These remarks should be considered taking into account that the participants in this scoring process were divided according their own experience and expertise, and therefore maybe presented some bias in their assessment, which explains the relative concentration of the scores in the positive region. Even so, the outcome is interesting should be taken by the relative value of each feedstock with regards to the other. Besides, forestry as a source of biomass was not included in this evaluation, but in many senses, it can be considered also an attractive feedstock, at same level of forestry residues, depending on the specie and yield considered, as will be discussed further in this chapter.

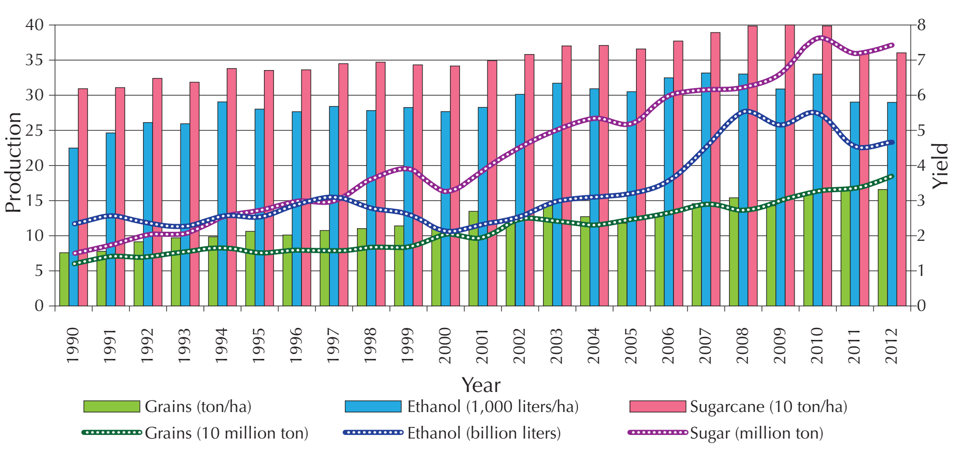
Table 32 Feedstocks classification: strategic potencial, technical risks and commercial risks.

FEEDSTOCK	STRATEGIC POTENTIAL	TECHNICAL RISKS	COMMERCIAL RISKS	TOTAL
Forestry wood residues	3.1	4.0	4.5	11.6
Sugarcane bagasse	3.1	4.0	4.5	11.6
Industrial forestry residues (pulp, sawdust, bark)	3.0	4.0	4.5	11.5
Sugarcane	3.3	4.2	2.7	10.1
Tallow	2.9	3.6	3.5	10.0
Flue Gas	2.9	3.4	3.7	9.9
MSW	2.9	3.2	3.7	9.7
Sorghum	2.9	4.0	2.7	9.5
Cassava	2.9	4.0	2.7	9.5
Used Cooking Oil	2.9	3.2	3.2	9.2
Agricultural residues (straw, grasses, etc.)	3.0	2.6	3.5	9.1
Palm	3.0	4.8	0.5	8.3
Jatropha	2.9	3.8	1.5	8.2
Photossynthetic Algae	3.3	3.2	1.5	8.0
Camelina	2.8	3.6	1.5	7.9
Sunflower	2.3	4.8	0.5	7.6
Rapeseed	2.3	4.8	0.5	7.6
Peanut	2.3	4.8	0.5	7.6
Soybean	2.0	4.8	0.5	7.3
Sewage	2.4	2.0	2.3	6.7
Other Palm trees	2.6	2.6	0.5	5.7
Other Oils	0.9	3.0	0.5	4.4

Box 3: Why indirect effects of biofuels feedstocks are low in Brazil

ILUC and food versus fuel are the two most relevant indirect effects raised as concerns in the biofuels debate. Several evidences indicate that the expansion of biofuels in Brazil have not undermined food production. The same evidences also show that the establishment of cause-effect straight relations between biofuels expansion and native land conversion has no support in the reality. The evidences are based in the following topics:

1. Brazilian agriculture is facing process of intensification and efficiency gains with increasing yields in crops and livestock;



2. There still is a lot of space for intensifying cattle production in Brazil. Technical yields such as slaughter age, calves' birth rate and meat produced per hectare are still low in Brazil.

3. Brazil has developed a double-cropping system allowing the integration of soybean and corn in the same year. The double cropping is already responsible for half of the total corn production in Brazil and since the year 2000 all corn production expansion has taken place as a second crop.

4. The expansion of sugarcane for ethanol, although very strong, has not undermined the expansion of other annual and perennial crops. Therefore, rather than food-versus-fuel, the reality in Brazil shows a food-and-fuel situation;

5. The cultivation of oilseeds in rotation with sugarcane is also generating food and fuel in the same systems.

6. Deforestation rates are being reduced since 2004. Deforestation levels in 2011 and early 2012 have been very encouraging, at around 75% lower than 2004 levels.

Partial conclusions

Brazil has several good options for plant feedstocks for aviation, associated to a large availability of land, water and favorable climate for crop production, however it seems still early to recommend the very best options. Scale of production is an important characteristic, affecting directly the product cost. Some crops are already widely produced because they are well adapted to local conditions, were object of much R&D investment in the past, have good market value and favorable price/cost ratio, and have the support of well-organized supply chains. Being proven for other purposes, these crops are also natural candidates as price-competitive feedstocks for aviation biofuel. Sugarcane and soybean are the main examples which are already used for the production of other biofuels.

Some aspects that may have been overlooked in the discussions and that affect cost, convenience and environmental impact are the capacity of the desired feedstock to be grown in high slope areas without causing excessive erosion (where competition with other food or non-food crops usually is less pronounced), to be able to be harvested in different seasons, and to be stored for long time without the need of immediate processing. Forest or woody species with long cycles are among the plants that meet these requirements. Brazil has large tracts of land with unfavorable slopes for row crops (food competition) but that are suitable for long cycle plants that can be harvested at long intervals, which may offset the problems and costs of operating in hilly landscapes.

Actually, the range of choices is wide. Therefore, the workshop did not focus only on the present success stories and the most obvious options as of today. A central objective of the workshop on feedstocks was to identify the main technological challenges each feedstock is currently facing and the critical variables that determine which technological alternatives should be selected for future developments. The strategy taken was to capture those elements using two approaches: individual presentations and group discussions.

Establishing technology drivers, however, was one of the concerns associated to the workshop. A second one was that a large group of feedstocks should be considered, not only because they have advantages and disadvantages, but also because several refining processes are flexible, accepting different types of feedstocks.

Another objective was to present to the participants the current situation of the feedstocks in terms of production status, alternative uses, level of competitiveness, potential of energy production, and limiting factors for large scale supply. It was expected also to understand the problems and challenges both on production and logistics, given that the localization of the refining facility is strongly affected by the distribution of the feedstocks.

The choice for evaluating several feedstocks was interesting because it made possible to gather a good set of information on several products. On the other hand, it became more difficult to harmonize and standardize the information for cross comparisons and to create classifications of the feedstocks analyzed. Not only the number of feedstocks was large, but also they were different in their nature and usage in the refining processes.

To establish balanced comparison between agricultural-based and non-agricultural feedstocks not necessarily leads to useful conclusions. While wastes such as CO rich flue gas and municipal solid wastes have in principle no problem of supply, they are not easily concentrate to create scale, but agricultural-based feedstocks uses land as main producing resource and might lead to food security concerns. On the other hand, widespread agricultural feedstocks have already available well organized supply chains, as observed in the soybean case, making its use to bioenergy purpose more straightforward.

Despite of the very different nature of the feedstocks analyzed, some consensus lines could be drawn from the ideas raised and discussed in the workshop. There was consensus that by and co-products from agricultural and forestry production are preferable because of the lower impacts on land use and food security, lower opportunity costs and high availability in current conditions. Oil-bearing crops, on the other hand, are available but have lower energy yields and raise concerns on food security. Some innovative oil-bearing crops that are not currently available for commercial production in Brazil, can be produced as a second crop or are able to be grown in degraded land, but the lower energy yields remain a disadvantage.

Crops that can be integrated to production systems taking advantage of the resources already being used were also positively considered. This is the case of sweet sorghum. This is also true for crops with large potential to increase yields such as cassava. Wastes (flue gas, MSW, used cooking oil and tallow) and agricultural residues (straw, trash, leaves) were also considered viable options but collection costs remain high.

At this stage of the aviation biofuel roadmap the recommendation is to consider a wide range of feedstocks instead of selecting a few, although recognizing that some feedstock present currently comparative advantages, such as sugarcane, forestry products and wastes. Depending on the results of research, other alternatives can be incorporated to this list.

10.2 Refining Technologies

Depending on the feedstock, there will be a group of technologies able to process it to the biofuel needed by the aviation industry. In other words, refining technologies are feedstock dependent and as such can be divided into basically in the same groups (**Table 33**).

Table 33 Refining Technologies groups.

Biofuels from sugars	• Alcohol to jet fuels
	• Direct fermentation of sugars to hydrocarbons[14]
Biofuels from oils	• Hydrotreatment/hydrocracking
	• Catalytic Hydrothermolysis
Biofuels from lignocellulosics	• Gasification
	• Solvent Liquefaction
	• Fast Pyrolysis
	• Acid Hydrolysis
	• Enzyme hydrolysis
Biofuels from wastes	• Fermentation to organic acids, to ketone to alcohol, (MSW)
	• Fermentation of CO/H_2 Gases to Alcohol
	• Hydrotreatment of Industrial Fatty Residues

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19 Presently approved and denominated by ASTM as Synthesized Iso-Paraffins (SIP).

Following a similar method used for feedstock assessment, a multicriteria analysis was conducted on 3rd Workshop ("Refining Technologies"), which also showed that all alternatives have strategic potential to be compliant with the roadmap goals (**Figure 77**), but, again, technical and commercial risks need mitigation and are somewhat specific to each alternative, as shown in section **Gaps and Barriers**.

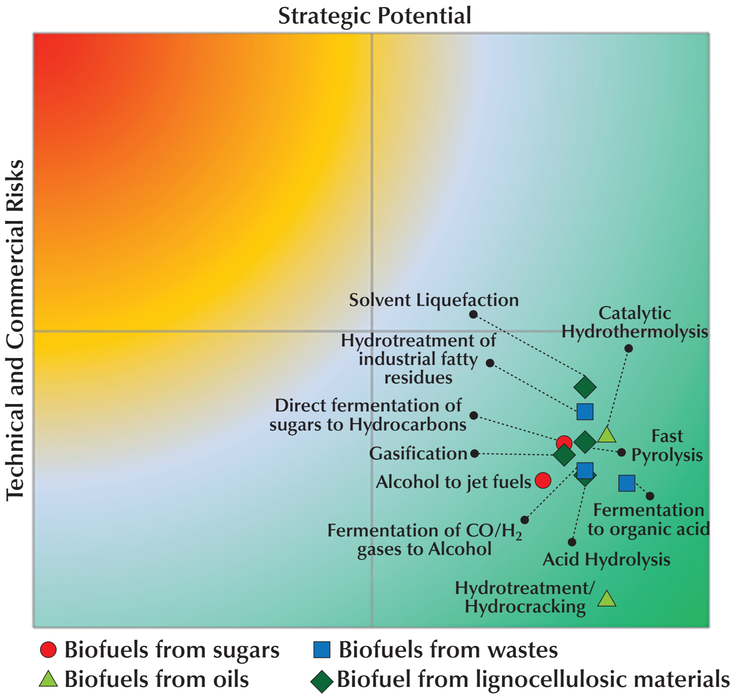

Figure 77 Multicriteria analysis of different refining technology alternatives.

One relevant differencing feature of a given refining technology is its level of development and the matureness. Considering the drop-in requirement and the certification procedure as established by ASTM, some processes for producing aviation biofuels are already available for feedstocks such as vegetable oils and lignocellulosic material (or solid biomass). Process using vegetable oils could be quickly installed as will be detailed in the next section. Another process approved by ASTM, using lignocelluloses to jet fuels needs much more time to be effectively developed. For gasification, pyrolysis and liquefaction, it is expected that at least 10 years are needed for further development. Process involving hydrolysis needs the development of pre-hydrolysis treatment, maybe possible in an industrial scale in more 5 years. However the alcohols produced from the fermented hydrolyzed biomass have to be transformed to jet fuels by chemical processes. Although the transformation of waste to jet fuel is promising, nothing is ready for implementation. In fact, for all technologies, improvements and scale up are still required in order to reduce capital and operation costs and increase reliability.

No preference should be given to any technological alternative. All of them are in principle valid to produce jet biofuel. However at the present conditions, none of the technologies can produce jet biofuels at market price. It is mandatory that the technology to be chosen can produce the cheapest jet fuel, which depends on the selected feedstock and its processing costs.

Conclusions

1. although with very different level of maturity, essentially all the presented technologies have potential for feasibility;
2. if in a short term a mandate for aviation biofuel were settled in Brazil, the quickest technology to be implemented would probably be based on vegetable oils to jet biofuel;
3. cellulosic residues and wastes are very cheap and their transformations by thermochemical or biochemical processes into jet biofuel are potentially very attractive. However, it is advisable to get more qualified data to have a more safe assessment;
4. it is expected that an efficient enzymatic hydrolysis of cellulose and a proper conversion of resultant sugar to jet biofuel can be a solution in a short to medium time period;
5. gasification of lignocellulose is also a very important alternative and jet biofuels could be obtained from synthesis gas for reasonable price within 5 to 10 years;
6. pyrolysis of celluloses is a third important option to make jet biofuel but more development is needed. Several patents have been filed to protect different aspects of process to obtain jet biofuels. It is difficult to analyze the level of conversion yields from the renewable feedstocks up to the final jet biofuel, since property rights usually protect these data
7. it is not easy to find data on the refining of the fractions of fuel that can be directly used or the necessary blending with conventional jet fuel or mixing with fossil additives, in order to accomplish the final specification;
8. each process, from the raw material to the aircraft filling, is composed of different operations, each of them need to be developed, adjusted, optimized and finally integrated to the others. Combinations of those will be needed to lead to the best technologies to produce renewable drop in jet biofuel;
9. a perfect scenario would be a combination of waste feedstock and well developed cheaper conversion process. However it, seems that in short term, only the sugar fermentation to ethanol and ethanol conversion, as well as hydrogenated esters and fatty acids will be suitable for jet biofuels production. For medium and long term, second generation technologies, processing cellulosic biomass may become economically more feasible.

10.3 Identified Pathways

After discussing the feedstocks and refining processes for producing renewable jet biofuel, multiple possible pathways were identified during the project. Certification requirements for regular use in commercial aviation are established internationally according to ASTM D7566 standard, which contains one specific annex for each approved alternative jet fuel production process. **Figure 78** presents an overview of all identified pathways pertinent to Brazil, including the denomination and status of the ASTM approval process. As depicted, two of the final alternative jet biofuel production processes are already approved (green boxes in **Figure**

78) and several others are still under evaluation in the D.02.J0.06 Emerging Turbine Fuels Committee[20].

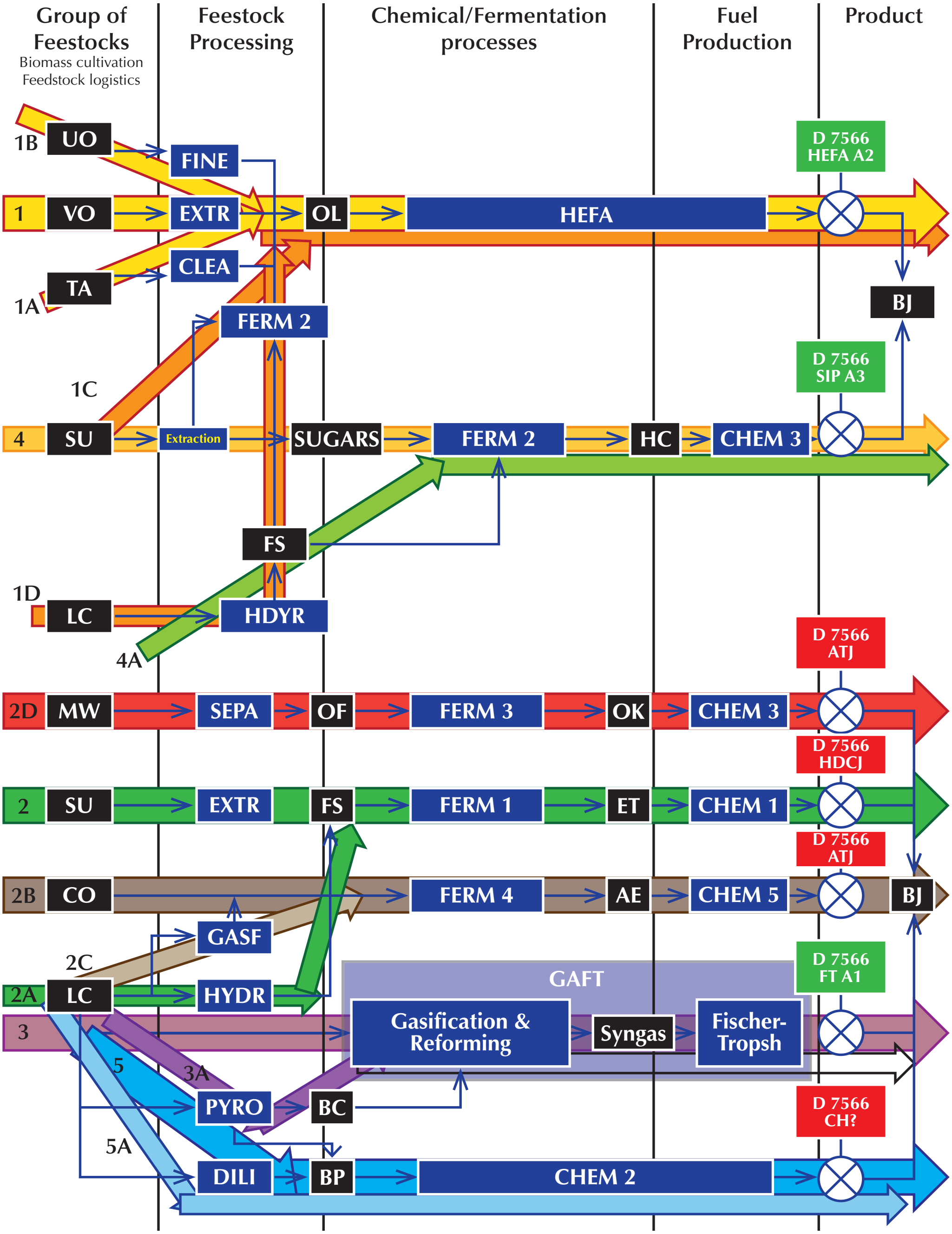

Figure 78 Identified pathways for the production of sustainable jet biofuel in Brazil.

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[20] Since June/2014, the route denominated here as DSHC was approved by ASTM as Annex 3 with the name Synthesized Iso-Paraffins (SIP), for up to 10% blend.

In general after pretreatment, the possible feedstocks are submitted to different conversion processes grouped in three categories: chemical processes for lipids, biochemical and thermochemical processes for other biomasses. The final jet biofuel production processes are usually oil-refinery-like processes to adjust the specification.

While lipids and thermochemical conversion processes have already some routes approved by ASTM, the various biochemical conversion routes still require approval. These processes are briefly discussed in the next paragraphs.

Correspondent Index is presented below (**Table 34**).

Table 34 Index of abbreviations used in the identified pathways.

1. Material streams	**2. Processes**
1.1 Precursors/Feedstock	**2.1 Preparation and Initial Processes**
LC = Lignocellulosic Biomass	HYDR = hydrolysis (acid and biochemical) of polysaccharides to simple sugars
MW = Municipal Solid Waste	PYRO = pyrolysis process of lignocellulosic biomass to bio-oil and bio-char
SU = Sucrose/Starchy Feedstock	DILI = direct liquefaction of cellulosic biomass to bio-oil
TA = Tallow/Yellow Grease	SEPA = separation process of organic fraction from municipal solid waste
UO = Used Cooking Oil	EXTR = extraction process of vegetable oils, of sugars or starches from agricultural products
VO = Oil-Bearing Feedstock	FINE = filtration and neutralization processes of used cooking oil
1.2 Intermediates	CLEA = cleaning, rendering and preparation of tallow
AE = Acetate and Ethanol from Process FERM5 (bellow)	**2.2 Intermediate Processing (conversion)**
	FERM1 = fermentation of sugars/starch to ethanol and other alcohols (conversion of primary feedstock to alcohol intermediates)
BP = Pyrolytic Bio Oil	FERM2 = fermentation of sugars to oils and lipids
BC = Pyrolytic Bio Char	FERM3 = fermentation of organic materials to organic acids
BO = Bio Oil from direct liquefaction of cellulosic materials	FERM4 = fermentation of CO rich flue gas in ethanol and other alcohols
	FERM5 = fermentation of sugars to hydrocarbons
CO = CO rich Flue Gas	GASF = gasification
ET = Ethanol and other Alcohols	**2.3. Final Processing/Refining**
FS = Fermentable sugars	CHEM1 = chemical processes to convert alcohols to jet fuel (dehydration, oligomerization and hydroprocessing)

Table 34 Index of abbreviations used in the identified pathways (continued).

OK = Organic Acids and Ketones	CHEM2 = chemical processes to convert pyrolytic bio-oil in jet fuel (hydroprocessing and fractionation)
OL = Oils, Lipids	CHEM3 = chemical processes to convert specific hydrocarbons in jet fuel
HC = Hydrocarbons	CHEM4 = chemical processes to convert organic acids through ketones and alcohols in jet fuel
OF = Organic Fraction of Municipal Solid Waste	CHEM5 = chemical processes to convert alcohols from FERM4 in jet fuel
1.3. Final product	**2.4. Integrated Processes**
BJ = Jet Biofuel (ASTM spec)	GAFT = gasification+Fischer Tropsch process (and similar)
	HEFA = hydrogenation of esters and fatty acids

10.3.1 HEFA (Hydroprocessed Esters and Fatty Acids)

Sometimes also called HRJ (hydroprocessed renewable jet) are produced by “refining” natural oils much like petroleum is refined today. Hydroprocessing natural oils (plant, microbial oils or animal fats) involve converting these oils from lipids to hydrocarbons through the addition of hydrogen (**Figure 79**, 1 and 1A). The first step converts the lipids to fully saturated hydrocarbons, or synthetic paraffins, by saturating oxygen bonds and double-carbon bonds with hydrogen. These hydrocarbons are then selectively cracked and isomerized to produce primarily diesel, jet fuel, and propane. This process can be integrated into existing fossil fuel refining facilities and operated at similar costs to petroleum refining. They can also be added on to first generation biodiesel production facilities, or built from scratch in stand-alone refineries. The sub-routes are the utilization of residues like used cooking oil (1B), or the industrial sub-products tallow and yellow greases (1A). Hydrogen demand for different feedstock qualities varies, resulting in different conversion cost for diverse raw materials like palm oil, animal fats, camelina, jatropha etc. After removal of oxygen and saturation with hydrogen, it is necessary to catalytic crack and branch the molecules with hydrogen.

Gaps

HEFA fuels are ASTM certified for commercial use in up to a 50/50 blend with conventional jet fuel. The existence of a Brazilian Biodiesel Program, well established in the market since 2005 and that is based upon the same type of feedstock, simplifies the economic comparison of feedstock pricing, because they are already competing for the same market. Consequently, the prices of feedstock, after the diverse necessary pre-processing can be consider equivalent, once taking into account the social benefit provisions of the Brazilian Biodiesel Program. In 2011, the country has produced circa 2.5 billion liters of biodiesel, quantity enough, in energetic terms, to more than one third of its jet fuel consumption (ANP, 2012). Investment cost for hydro-processing is considered to be low, but the cost of common raw materials can represent more than 70% of total cost (NOGUEIRA, 2011).

Other possibilities of feedstock are the microbial lipids, produced by fermentation of cianobacteria, algae or yeasts. They can be accumulated inside the cells after direct fermentation of sugars, i.e. sucrose and glucose (1C) or obtained by fermentation of the soluble sugars from lignocellulose hydrolysates (1D). The economical possibilities of these microbial pathways are strongly dependent on the price ratio of sugar or ethanol to vegetable oils. One relevant aspect is the stability of the transgenic yeast/algae, which has to be improved in large reactors. Commercial risks will be only reduced when cellulose can be used as feedstock. These technologies are available to produce lipids from direct sugar and pilot plant will benefit from second generation of sugars.

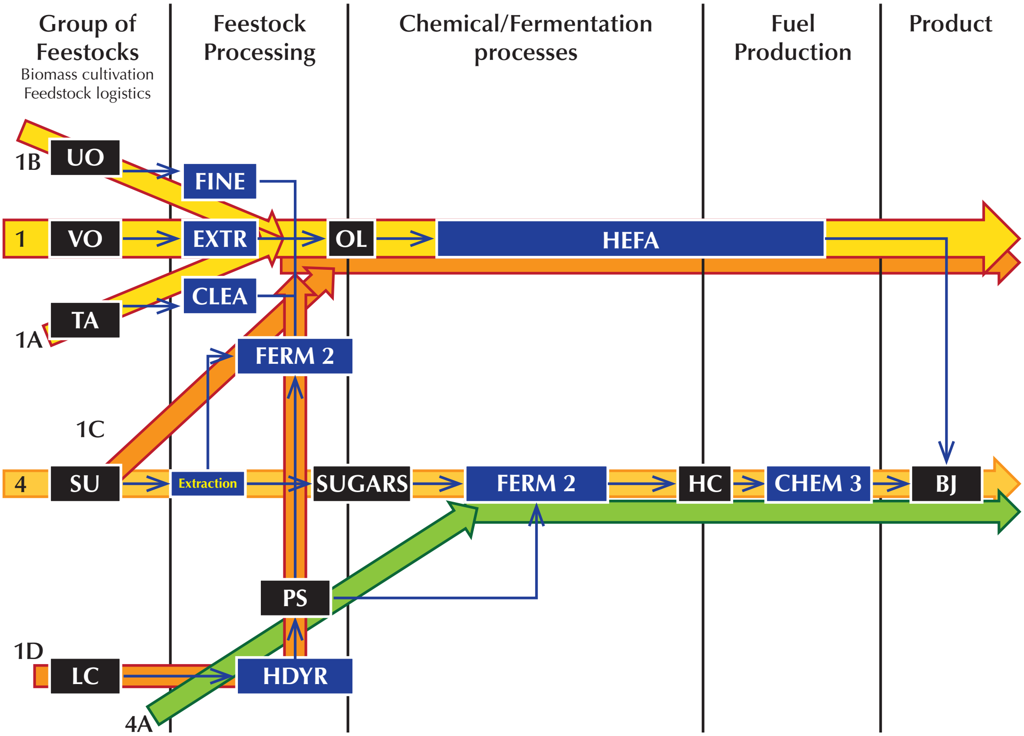

Figure 79 From biomass to HEFA jet biofuel or Solazyme (transgenic algae – lipids).

10.3.2 ATJ (Alcohol to jet)

ATJ (Alcohol to Jet) is made via alcohol oligomerization which involves linking short-chain alcohol molecules (e.g. ethanol or butanol) together to form jet-fuel range hydrocarbons. There are several chemical processes 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.

Research has been developed using catalysts for the direct and high-yield conversion of bio-ethanol to isobutene, a widely used intermediate chemical used for the production of fuel additives, rubber and solvents. The catalyst requires the presence of water, allowing producers to use dilute – i.e., less expensive – bio-ethanol rather than having to purify it first, potentially keeping costs lower and production times faster. Other methods also have been described by the literature. With increased availability and reduced cost of bio-ethanol, conversion of this particular bio-based feedstock to highly valuable fuels and chemicals has been an especially important research goal.

The original feedstocks for this route are starches or sugars (**Figure 80**). Other alternatives include lignocellulosic biomass, industrial waste gases and municipal solid waste. Starches and sugars may be converted to alcohols through direct fermentation (2). Industrial waste gases rich in CO can be converted to alcohols by gas fermentation (2B). Lignocellulosic biomass may be converted to alcohols by hydrolysis of polysaccharides to simple sugars, followed by fermentation (2A), or by gasification to produce gas (CO + H_2), that can be converted to alcohol by gas fermentation according (LANZATECH, 2012). After separation, the organic fraction of municipal solid waste can be fermented to carboxylic acids that are transformed in ketones that are hydrogenated to secondary alcohols (2D).

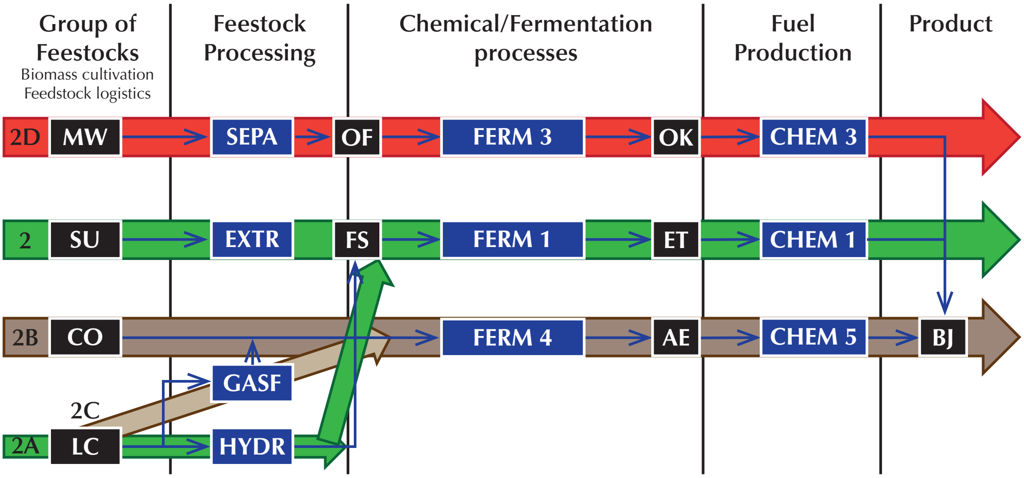

Figure 80 Conversion of sugars (SU), carbon monoxide (CO) and lignocellulose to jet biofuel.

Gaps

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). This route, which is in the process of approval by ASTM, requires two principal conversion steps: the conversion of feedstock to alcohols and; the conversion of alcohols to jet fuel. Although the ethanol production from sugarcane by the conventional process has been improved and presents economic competitiveness compared with automotive fossil fuels, the second step is still in development.

No important technical problems have been described for this technology. However, such oligomerization process still needs technical improvements to reduce the competitive gap with conventional jet fuel. Possibly when cellulosic sugar will be available, the commercial risks will be reduced. The alcohol intermediates may be ethanol, butanol, isopropanol, other alcohols, or mixed alcohols. Alcohols are then converted to jet fuel using standard chemical processes. However, the development of more selective catalysts which would convert the alcohols more efficiently to jet biofuels is needed. Due to the large Brazilian experience in producing ethanol from sugarcane and the existence of a well-established agro-industrial sector dedicated to the subject, the natural reference prices for liquid biofuels and lignocellulosic concentrated biomass probably will be ethanol and sugarcane bagasse. Worth mentioning that the ethanol consumption in Brazil in 2010 was approximately 25 billion liters, amount that, in energetic terms, is more than two times the whole aviation fuel consumption in the same year (ANP, 2012).

10.3.3 Syngas/Fischer-Tropsch technologies

The synthesis gas (CO and H_2) is converted into hydrocarbons by growing the carbon chains, usually catalyzed by metal supported catalysts (heterogeneous catalysis), according to reaction (1).

$$CO + 2H_2 \rightarrow CH_2 + H_2O \quad (1)$$

The product obtained by the Fischer-Tropsch reaction is a mixture of hydrocarbons with chains of different sizes, from light gases to high molecular weight greases (Luque et al., 2012; Klerk, 2011). The distribution of the products is a Gaussian type, allowing to be adjusted according to the desired product. 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 suffer conversion for cracking molecules of high molecular weight into lower molecular weight hydrocarbons or adding other compounds (derived from traditional oil refining) to assist in adjusting the properties required for the specified fuel. Fischer-Tropsch paraffinic kerosene can be produced from lignocellulosic biomass through gasification followed by gas cleaning and synthesis over appropriate catalysts. The process (**Figure 81**, 3) is approved by ASTM for blending up to 50%.

Gaps

Although the cost of the raw material in the field can be very low, the transportation cost is important and limits the size of the processing plant, with large implications on investment cost. Another possible route using lignocellulosic biomass is to start with pyrolysis, obtaining bio-oil and bio-char, intermediate products that could be transported economically through longer distances, to be then submitted to gasification and synthesis by the Fischer-Tropsch process (3A). The current capital cost for the FT alternative is given as high (1€/l for a 200 million liters/year production plant capacity) (MANIATIS et al., 2011). The organized industrial sector that is been considered as a possible supplier of the lignocellulosic biomass is the sugarcane sector, which would pyrolyse the bagasse to bio-oil and bio-char, which can then be transported to the much bigger gasification unit.

The cost of the process is still considered high due to the very special conditions required by the reactions (high temperature and pressure), low density of the biomass, logistic and transport. However, as shown in The Republic of South Africa, the cost of the reactor reduces considerably with increasing size of the reactor.

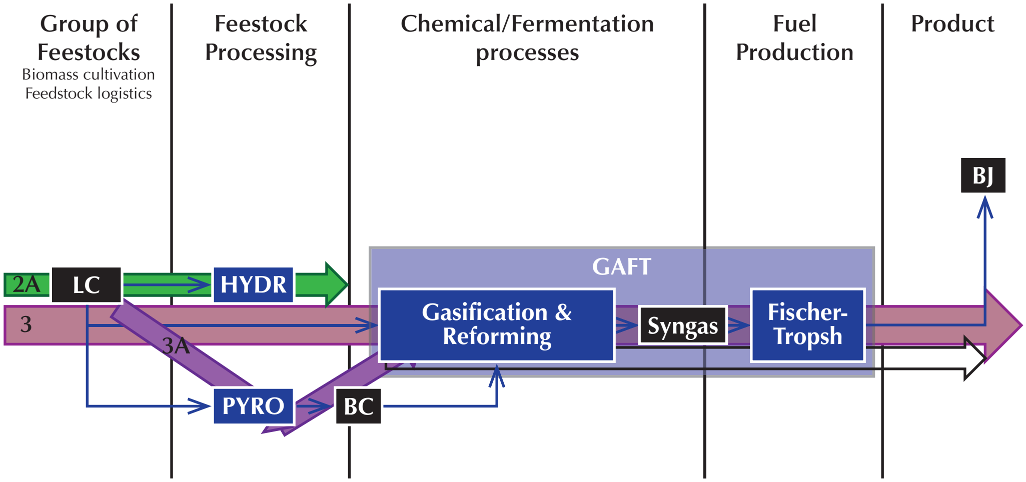

Figure 81 Production of liquid-fuels from biomass via Fischer-Tropsch.

Another possibility is using the synthesis gas for the production of dimethyl ether (what is being done in the demonstration plant at KIT, Karlsruhe, Germany) and then oligomerize and deoxygenate the dimethyl ether to hydrocarbons in the range of jet fuel.

10.3.4 DSHC (Direct fermentation of Sugars to Hydrocarbons)[21]

Some very interesting developments in the area of synthetic kerosene come from metabolic processes of genetically modified micro-organisms to generate hydrocarbon fuel. The principal feedstock for the micro-organisms has been sucrose (**Figure 78**), 4), even though an alternative is to start with lignocellulosic biomass submitted to hydrolysis to obtain fermentable sugars (4A). One of the characteristics of these metabolic intermediates is that they tend to have a very specific chemical identity, with very narrow distillation curves. So the certification challenge for this new route will be in the precise definition of how far one can stand from the broad distillation range of the actual jet fuel, in a way that the renewable fuel can be a ‘fit for purpose’ jet fuel.

The feasibility of materials and energy-dedicated vegetables to be efficiently biologically converted into biofuels with higher added value depends on the capability of microorganisms to use pentoses besides the hexoses, and to stand the most common impurities originated from them. Carbohydrates can be converted into biofuels, as the monosaccharides glucose, xylose and arabinose. Today, the dominant cost factor in 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, short distances and strong logistics allow the employment of suitable treated sugarcane bagasse as for feedstock. The direct sugars to hydrocarbons (DSHC) process, developed by Amyris is a high performing process, already in demonstration plants (5000 L) and planned to be scaled up to 200-600,000 L (AMYRIS, 2012). The sugar cane juice is evaporated and fermented in a closed and aerated bioreactor by a recombinant yeast. Then the excreted farnesene is separated from the broth

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[21] DSHC was approved by ASTM as Synthesized Iso-Paraffins (SIP).

and purified. Farnesene is hydrogenated to farnesane by introducing 4% of its mass in H. The industry is also developing another process in order to obtain a 10 carbon chain biofuel.

Gaps

The current yield is relatively low and should be improved; for the production of 1kg of farnesane, at least 5 kg of sugar is needed. This makes the Amyris Jet Fuel quite expensive at the present sugar price. Thus, the success of this path will also depend on production of cellulosic sugar at low cost.

10.3.5 HDCJ (Hydrotreated Depolymerized Cellulosic to Jet)

Hydrogenated pyrolysis oil kerosene is based on the pyrolysis oils from lignocellulosic biomass (**Figure 82**, 5). Pyrolysis oils can be hydrotreated either in dedicated facilities or co-processed with petroleum oils in refineries. Today pyrolysis oil is at the edge of research towards demonstration level. It is expected that the upgrading of pyrolysis oils will use existing refinery infrastructure, what would make it more competitive than FT. An alternative route to convert the cellulose and hemicellulose from biomass is an aqueous process to furan-derived bio-oil, relying on chemical reactions catalyzed in ionic liquids. The transformation of the bio-oil in jet biofuel is done by deoxygenation processes (5A).

Gaps

The deoxygenation of bio-oils needs drastic conditions. Specific catalysts and expensive hydrogen are needed. It is an area of extensive research, however, up to now no efficient process is available.

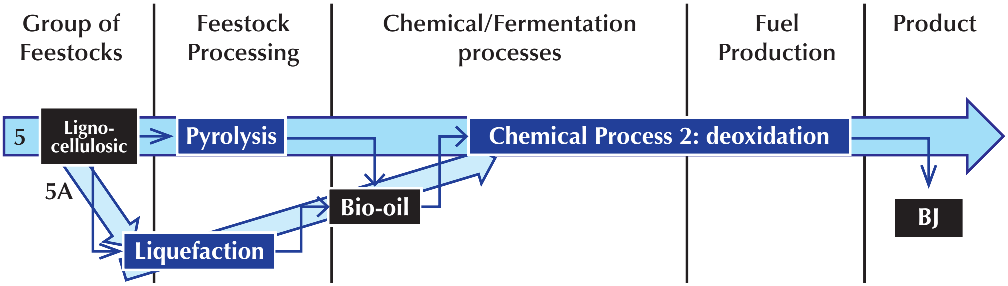

Figure 82 Production of liquid-fuels from biomass via fast pyrolysis or liquefaction.

10.3.6 Final comments on gaps

Due to existing Brazilian programs for promoting the use of renewable fuels for road transportation, the production of jet biofuel will have to compete for feedstocks presently utilized for biodiesel production or ethanol. As the processes to obtain a “drop-in” jet biofuel are more expensive than the processes for first generation ethanol or biodiesel, and because the energy price of jet fuel is usually not higher than gasoline or diesel energy prices, some kind of premium will have to be incorporated to make the production of jet biofuel economically viable. There is potential to expand the production of agriculture feedstocks in Brazil, but certainly their prices will tend to be connected to the prices of other agriculture commodities. Sugars will have to be produced from cellulose and lignocellulosics to make them available in larger amounts and at a compatible price. The conversion technologies of lignocellulosics (enzymatic hydrolysis, gasification and pyrolysis) are available, however there is no demonstration plant of these technologies at present in Brazil[22].

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[22] See 6.1.1.3 and II.5.2 for recent developments on the implementation of enzymatic hydrolysis in Brazil.