

BIOMASS THERMOCONVERSION USING BTL (BIOMASS TO LIQUID) TECHNOLOGY

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INTRODUCTION

Among the vegetable biomass with energetic purposes, sugarcane has a privilege position in Brazil. It is a consolidated culture with well developed logistics in terms of harvesting and transportation, giving an enormous competitive advantage in relation to other energetic cultures.

However, even with the exceptional level reached by the sugar-alcohol industry, energetic use as well as the current productive process is still low. This is because the ethanol production process used until now is based only the use of sucrose, which contains between 32% and 35% of the primary energy of sugarcane. The greatest part (between 65% and 68%) is concentrated in the lignocellulosic fraction made up by the bagasse and cane trash.

Ethanol production through the process of fermentation of sucrose is of about 86 liters per ton of sugarcane, representing approximately 26% of the primary energy of the full cane. Each ton of clean sugarcane (stem), the following dry matter is produced: 140 kg of cane trash, 140 kg of bagasse and 150 kg of sugars. According to LEAL (2007), for these quantities, the primary energy is distributed in the following manner: cane trash (2,500 MJ), bagasse (2,500 MJ) and sugars (2,400 MJ).

The thermochemical route presents itself as an option for the conversion of the sugarcane lignocellulosic material into biofuels, passing by obtaining synthesis gas, followed by catalytic synthesis, which makes achieving hydrocarbons, alcohols, hydrogen, ammonia, synthetic natural

gas etc., possible. The processes of the thermochemical route are known as BTL, biomass to liquid, or biomass for the production of liquid fuels.

Gasification is a route used to transform the components of biomass into synthesis gas (CO and H₂), used in the catalytic synthesis for the production of liquid fuels. The gasification technology is currently in an advanced phase of development. However, problems with feeding biomass in pressurized reactors, cleansing the gases and the need for high-scale production to reach economic feasibility, are factors which have barred its commercial exploitation.

Biofuels synthesis shows good economic feasibility indicators only when used in large scale. Some studies show values greater than 1,700 MW in energy from biomass, others refer to 5 million tons of biomass per year as the minimum economic size (LORA, 2008). This means that bubbling or fixed bed gasifiers, typical of small thermal capacities are not viable for industrial projects of synthesis gas production for biofuels. On top of that, the O₂ production plants have relative costs that are disproportionate for small capacities.

The dragged bed gasifiers, although easily scalable, require a very fine granulation in the biomass, which is technically difficult to achieve, due to the high power consumption in pretreatment. Pretreatment by roasting improves the granulation reduction process. For this reason, biomass fast pyrolysis for the production of slurry (mixture of bio-oil and fines charcoal from the process) and its later nebulized gasification, appears like an option for the operation of this type of gasifier, as

well as reducing costs related to transportation of biomass.

Fast pyrolysis is a technology which already proves to be economically viable in plants with capacity starting at 2 tons/hour of biomass. This process transforms the biomass in charcoal (20% to 30%), bio-oil (20% to 30%), pyroligneous acid (5% to 10%), and the remainder of hot gases with temperature between 400 °C and 600 °C. However, the production yield of bio-oil must be increased, since currently it is still low.

It is expected that gasification of bio-oil under pressure and in oxygen atmosphere should generate a much cleaner synthesis gas with quality for its use in the catalytic synthesis process. The use of pressurized reactors, fed with bio-oil, aims to reduce the investment costs and increase the production scale of synthesis gas. Although this may be true, there are many technology bottleneck points to be covered, in relation to feeding bio-oil, the quality of the gas, operational conditions of the reactor etc.

TECHNOLOGY NEEDS AND CAPABILITIES

Products or technologies targeted

Fast pyrolysis for the production of bio-oil for obtaining synthesis gas, within the proposed technologies, appears as an option for the use of sugarcane trash and bagasse in the production of synthetic biofuels through BTL, thus increasing the production of energy per hectare without the need to increase the planted area, by means of a more efficient use of the primary energy of sugarcane.

In this scenario, fast pyrolysis may be used as a pretreatment phase, improving the biomass characteristics for long-distance transportation, thus reducing the costs related to this phase, which currently weigh heavily on their cost.

Bio-oil may be considered a liquid biomass which presents density of 1,200 kg/m³, much greater than the gross density of polydisperse biomass which is in the range of 80 to 240 kg/m³.

Transporting biomass in its liquid state, that is, as a bio-oil, is more convenient than in the polydisperse solid form, due to its high energetic density,

lower humidity levels and ashes. It is possible to adapt the transportation logistics developed for other liquid fuels to bio-oil.

Furthermore, the use of bio-oil in gasifiers has advantages related to the feeding system and the production of a cleaner gas, of better quality, both for burning in combustion engines and turbines (energy generation), as for the use in catalytic synthesis for synthetic fuels, simplifying the purifications phases.

Gasification with pressurized oxygen instead of atmospheric air results in a high quality synthesis gas which is compatible with fuel synthesis catalytic systems and with the direct use in conventional gas moved turbines. Since it is a liquefied biomass, bio-oil may better adjust to the oxygen pressurized gasifiers such as the drag or fluidized beds.

Analyzing the possibilities for production of fuels via BTL using sugarcane trash and bagasse, we hereby propose the route going through pyrolysis and then gasification, where the bio-oil shall be used as raw material for the production of synthesis gas. In this case, the biofuel shall be obtained in fast pyrolysis plants in fluidized bed, in small scale. These plants may even be modular, so that they are located as close as possible to the biomass. The mixture of the entire production of bio-oil shall be transported to a large-sized plant for gasification and production of synthetic biofuels, fertilizers and other products through catalytic synthesis. This is the description of a bio-refinery based synthesis gas. Its structure should be in large scale since the catalysis plants are expensive and are only justified for great production volumes. Figure 1 shows a scheme to exemplify this scenario.

Calculations made considering the production average in the mills in the State of São Paulo (2006/2007 harvest), show that approximately 20 mills are necessary to provide sugarcane trash and bagasse to supply a gasification and synthesis plant. This is, considering the minimum feasible capacity of 5 million tons of biomass per year. This calculation considered use yield of 50% of the bagasse and 50% of cane trash (dry biomass).

Another possibility for feasible synthesis of biofuels would be the integration with oil refineries. The bio-oil produced could even be sent

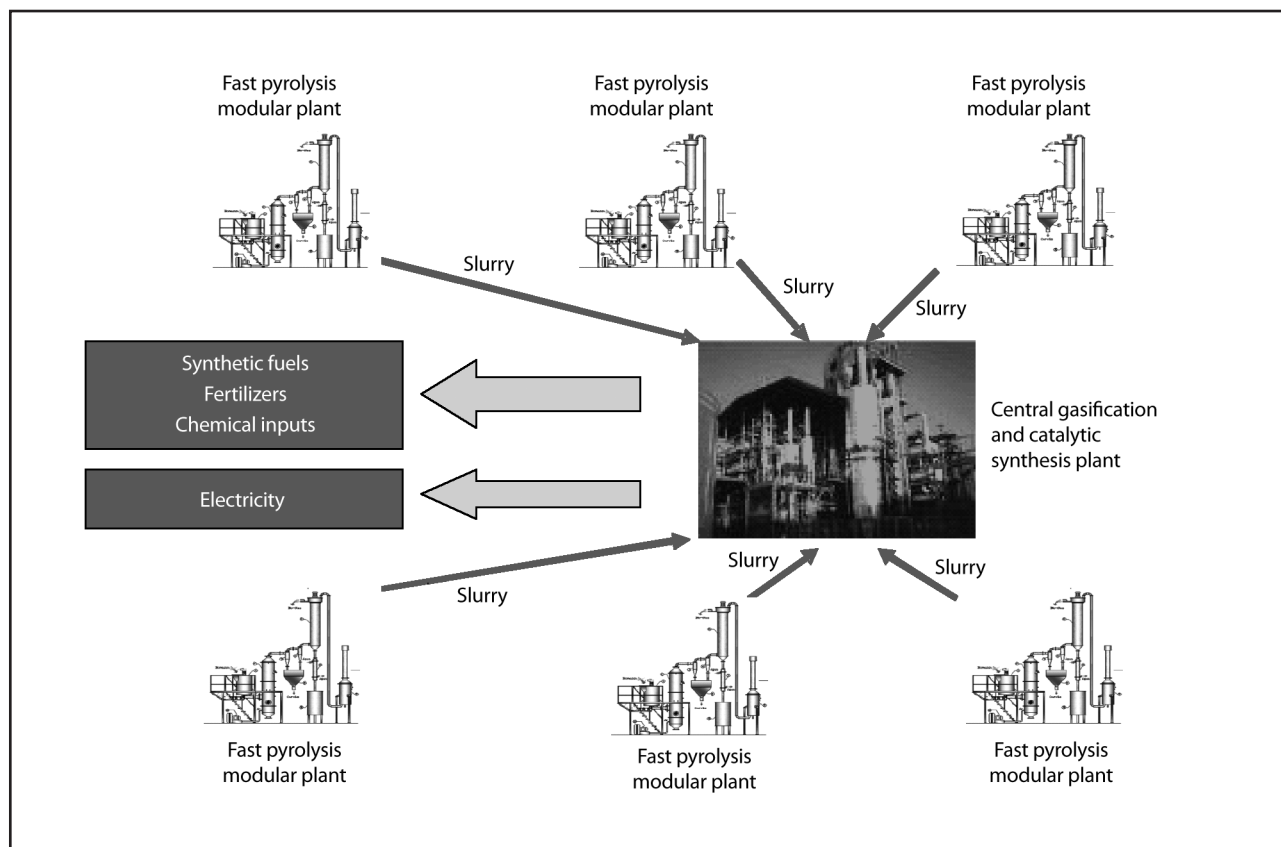


FIGURE 1 Scenario proposed for Pyrolysis/Gasification/Synthesis – BTL.

through oil ducts to the refineries, where it would be added to oil in the refining process. An example of this arrangement would be the Paulínia refineries, which could process bio-oil produced in the regions of Campinas and Piracicaba, which add up to 26 mills (UNICA, 2009; UDOP, 2009).

From the point of view of supplying raw material, it is also possible to have the integration of pyrolysis plants with hydrolysis plants, using the lignin resulting from the hydrolysis pretreatment process. The lignin is responsible for the formation of the phenolic components in bio-oil, as well as the implementation of fixed carbon in the solid fraction (LUENGO *et al.*, 2008). For the pyrolysis process, it would not be a problem to operate with lignin alone. This would even allow an increase in the processing capacity of a plant based on the conversion of lignocellulosic biomass, composed by lignin, cellulose and hemicellulose, as well as water and ashes.

At a first glance, the implementation of this scenario may seem simple, even for the fact that

the thermoconversion technologies are not new technologies, having been known for many decades. However, with the advent of oil, researches with these technologies have been abandoned, meaning that some bottlenecks have not been worked out, especially referring to the application of biomass.

Figure 2 shows a simplified block diagram of the proposed route, with the critical phases shown in red, where there are bottlenecks which need to be surpassed so that the proposed scenario may reach commercial maturity.

For a characteristic of the proposed fast pyrolysis process, first there is the extraction of fines charcoal and, then, of the bio-oil. This is due to the fact that the bio-oil separation system uses a gas cleanser to extract carboxylic acids, before extracting the bio-oil. The resulting mixture of fines charcoal to the bio-oil (slurry) for gasification, allows an increase in the product supply for this process, as well as increasing the global efficiency of the proposed route.

The phases identified as critical are the technology areas to which efforts should be directed in order to solve the related problems, problems which hinder the immediate commercial application of the proposed route. Some problems still involve basic research; however most of them are of technical-economical character, related to matters such as scale increase of the technologies involved.

Critical system requirements (CSR)

The aim of the proposed route is to increase general energy yield in relation to the use of primary energy from sugarcane, where, with the production of ethanol alone by the current process, this is of around 26%. The conversion of cane trash and bagasse, whether in the form of other biofuels which are not only ethanol or in the generation of electricity, shall allow an increase in the quantity

of energy produced from the same planted hectare of sugarcane.

The projections were made considering the scenarios for an increase in the production of sugarcane defined in Chapter 3 – TRM: Genetic Improvement. Tables 1 and 2 show the projections for the increase in energy produced per hectare of sugarcane due to the increase in sugarcane primary energy yield, with the use of cane trash and bagasse in the proposed route. Table 1 considers a scenario for sugarcane with higher level of sucrose (Scenario 1 of Genetic Improvement). Table 2 considers a scenario for sugarcane with higher fiber level (Scenario 2 of Genetic Improvement). In order to create a comparison parameter, these tables also show the equivalence in liters of ethanol.

For Tables 1 and 2, the following data was considered: production of 0.575 liters of ethanol/kg of sugar and use of 50% of cane trash and 50%

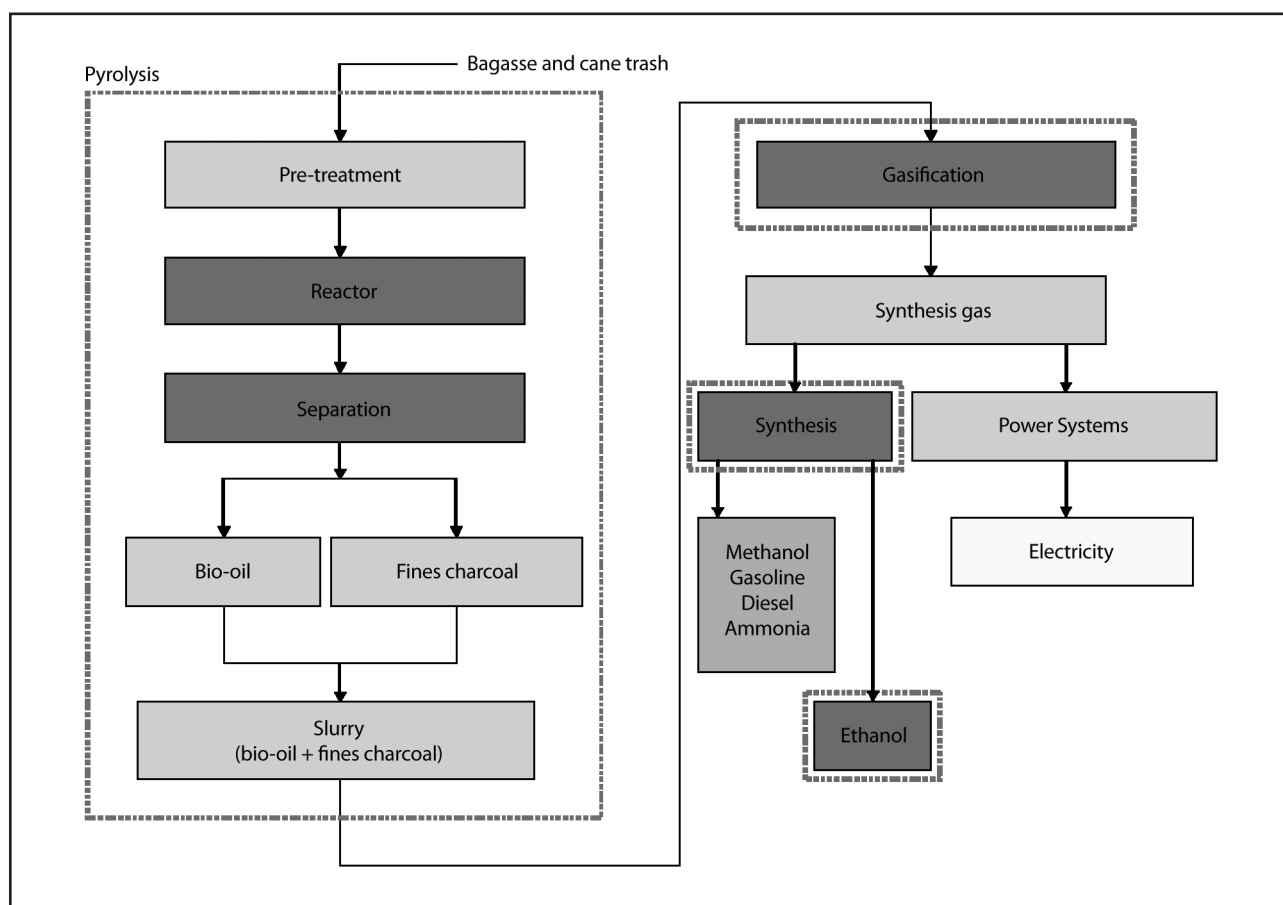


FIGURE 2 Block diagram of the thermo-chemical route for the production of synthetic biofuels and electric energy generation through pyrolysis and gasification.

TABLE 1 Projection of energy production per hectare and global efficiency of the conversion of primary energy from sugarcane, Scenario 1 of Genetic Improvement.

		Present	5 years	10 years	20 years
GJ/ha.year	1st generation Ethanol	145.4	152.7	169.2	198.3
	BTL Fuels	n.e.	39.7	62.9	89.2
	Total	145.4	192.4	232.1	287.5
Liters/ha.year	1st generation Ethanol	6,811	7,156	7,929	9,294
	BTL Fuels*	n.e.	1,859	2,947	4,182
	Total	6,811	9,015	10,876	13,476
Global efficiency (energy produced/ primary energy from sugarcane)		26%	31%	35%	40%

* Equivalence in liters of ethanol.

of bagasse in the thermoconversion processes. For ethanol an inferior calorific value was considered, of 21.34 MJ/liter (EPE, 2008). The data referring to the production of sugars, bagasse and cane trash and energetic equivalences, were the same shown in the Introduction, presented by CGEE (2004) and by LEAL (2007).

The current condition considered only the production of ethanol for the sucrose fermentation process (conventional route). This is because in Brazil, there still is not a production of synthetic biofuels by the proposed route. For the following

years (forecasts), the total production is the result of the sum of ethanol production from sucrose fermentation to the production of biofuels by the thermo-chemical route composed of Pyrolysis/Gasification/Catalytic Synthesis.

The projected increase is due to, as well as the increase in sugarcane production, the implementation of the thermo-chemical route and the gradual improvements in its processes (scale, cost, efficiency etc.), foreseen for the next 20 years. This data is presented in more detail in session Technology Drivers.

TABLE 2 Projection of energy production per hectare and global efficiency of the primary energy from sugarcane, Scenario 2 of Genetic Improvement.

		Present	5 years	10 years	20 years
GJ/ha.year	1st generation ethanol	145.4	156.8	177.4	191.4
	BTL Fuels	–	47	98.6	175.2
	Total	145.4	203.8	276	366.6
Liters/ha.year	1st generation ethanol	6,811	7,347	8,313	8,967
	BTL Fuels*	–	2,203	4,623	8,211
	Total	6,811	9,550	12,936	17,178
Global efficiency (energy produced/ primary energy from sugarcane)		26%	30%	34%	38%

* Equivalence in liters of ethanol.

Since in catalytic synthesis not all gas is converted into fuel, a parcel may be used in the generation of electricity. Recycling the gas allows a greater use for the conversion into fuel, however increases the consumption of energy used in the process. So, the option to produce more fuels or electricity shall depend on the future scenario, on factors such as demand and price. The popularization of hybrid and electric vehicles, as well as the increase of mass transportation based on electric energy, are factors which may lead to a greater consumption of electric energy.

To meet the projections shown in Tables 1 and 2 in relation to the proposed thermo-chemical route, there are the critical requirements: productivity, cost and environmental impact. Table 3 shows, for the next 20 years, the forecasts for these critical requirements.

Even with two different scenarios, the productivity requirements do not change, since the parameter is energy (electric or biofuels) per ton of biomass. That is, independent of the quantity of biomass per hectare, the yield is a characteristic of the process or processes, as we are discussing a route which involves pyrolysis, gasification and synthesis.

The environmental question does not appear as a critical point for the proposed route, since the use of water in the thermo-chemical processes is minimum, and the gases generated are or may be reused for heat generation in the processes themselves.

Even if there is not yet commercial scale production, the current cost of synthetic biofuels

production by the proposed route was estimated. This cost was estimated based on operation data of the fast pyrolysis pilot plant at FEAGRI-UNICAMP (PPR-200), with capacity of 200 kg/h of biomass. The current cost of gasification and synthesis was estimated based on bibliographical information, considering scale of pyrolysis plant PPR-200. This data is based on LORA (2008), SEABRA (2008) and data from the IPT (INOVAÇÃO TECNOLÓGICA, 2009).

The present cost of biomass (cane trash and bagasse) was taken for the same as the price paid for sugarcane trash used in tests at the pilot plant PPR-200, which is of R\$ 60.00 per ton. For future scenarios, a price reduction was considered, to R\$ 40.00 per ton in a period of 5 years and to R\$ 20.00 per ton in a period of 10 to 20 years. This would be due to technical improvements in cane trash recovery, such as reduced full harvesting, as well as an increase in the excess of bagasse due to optimization of the thermal processes in the mills.

The cost estimates for gasification and synthesis, for the 5, 10 and 20 year scenarios, were also based on data from LORA (2008), SEABRA (2008) and data by the IPT, quoted in INOVAÇÃO TECNOLÓGICA (2009).

Major technology areas

Pyrolysis

The observations in relation to the technical bottlenecks in pyrolysis were made based on results from tests with the pilot plant PPR-200 at Feagri-Unicamp.

TABLE 3 Critical system requirements of the proposed thermo-chemical route for the production of synthetic biofuels.

CSR		Present	5 years	10 years	20 years
Productivity	Liters/ton of biomass*	n.e.	172	260	341
	GJ/ton of biomass	n.e.	3.7	5.5	7.3
Cost	US\$/GJ	51.5	31.2	16.5	13.4
	US\$/liter*	1.09	0.67	0.35	0.28
Environmental Impact		Low	Low	Low	Low

Obs.: Exchange rate: R\$ 2.00/US\$ 1.00.

* Equivalence in liters of ethanol.

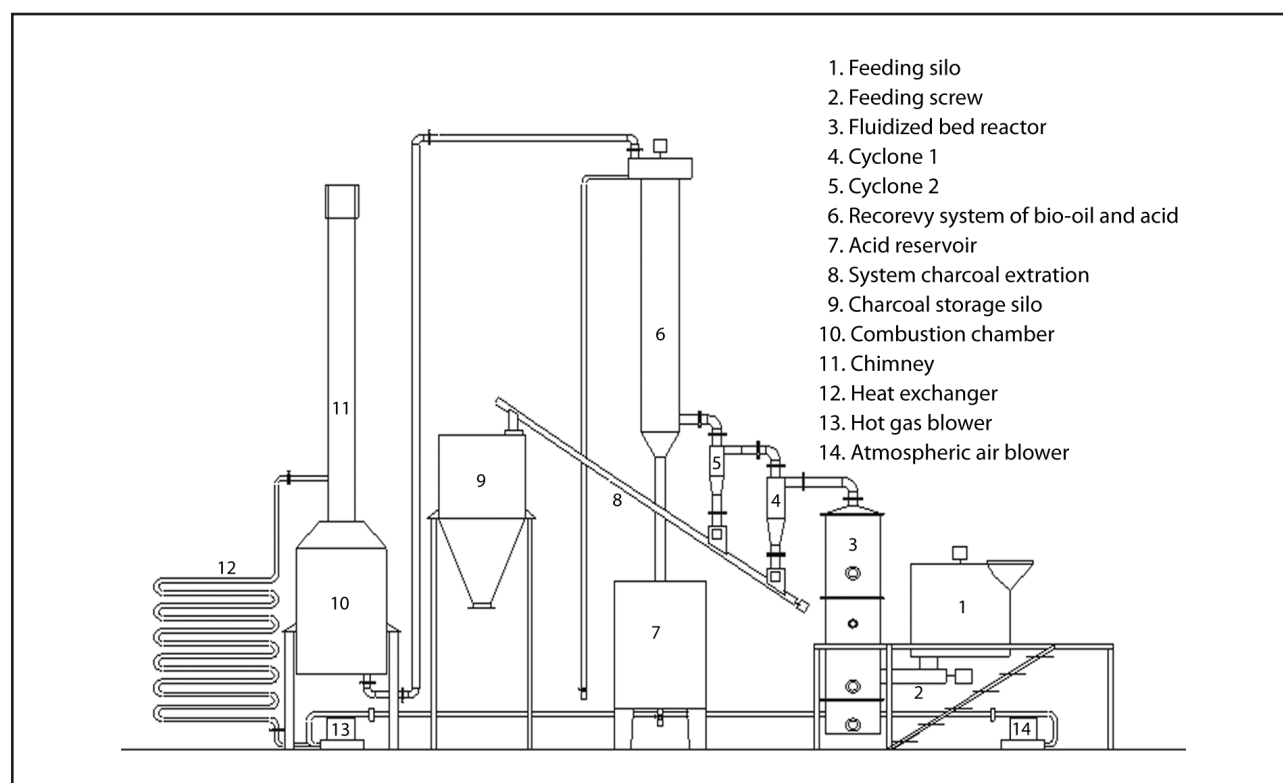


FIGURE 3 FEAGRI-UNICAMP (PPR-200) fast pyrolysis plant scheme.

Figure 3 shows a scheme with the main components of this plant. The operation of the plant happens in the following way: the biomass is fed into the silo (1), which has an infinite thread (2) which injects the biomass in the fast pyrolysis fluidized bed reactor (3). The biomass upon coming contact with the reactor bed at a temperature of about 450 °C to 500 °C is volatilized, transforming itself into a solid (fine charcoal), fumes (bio-oil and acid extract) and in gases.

The charcoal is separated in the cyclones (4 and 5) and stored in the silo (9), the acid extract and the bio-oil are separated in the recovery system (6) independently. In the reservoir (7) the acid extract is obtained and the bio-oil is removed through the superior side exit of the separation system through the rotation mechanical system. The remaining gases are burned in the combustion chamber (10). These gases could be used as fluidization agent in the bed using a heat exchanger (12) and a hot gas blower (13). However the tests held up to this point used atmospheric air from the existing blower (14).

Automation of the phases inside the pyrolysis plant

There are processes that take place in aqueous means, as is the case of the bio-technology processes: fermentation, biodigestion etc. However, for the thermal processes the biofuel should be dry or with compatible moisture content, varying between 8% to 15%, and for this energy must be used. Although in Brazil the sugarcane industry is specialized in direct burning of highly humid bagasse, other thermo-chemical conversion processes such as fast pyrolysis and gasification generally work with low moisture level biomass.

Appropriate stocking may help in the biomass initial moisture loss. Many processes normally have excessive thermal energy which may be used in drying, this is an advantage of plants located next to an existing manufacturing unit, such as mills for example, where the exhaust gases from the boiler could be used. Energetic integration of the process should be considered and practiced allowing for improved used of the raw material.



FIGURE 4 Pretreatment phases of sugarcane trash in a biomass fast pyrolysis plant pilot of FEAGRI-UNICAMP.

In the pretreatment phase, the biomass should be homogenized, involving the following operations: chopping, grinding, and screening. These unitary operations are used for the reduction and standardization of the size of particles. Some thermoconversion processes, such as fast pyrolysis, require homogeneity of the particles and control over size distribution is necessary and critical, ensuring a tight range of sizes.

Figure 4 shows the pretreatment phases of sugarcane trash when entering the fast pyrolysis plant PPR-200. Since this is an experimental plant, which does not operate continuously, these operations are all manual. However, considering an industrial scale, these operations should be automated.

Automation is an important point related to the issue of feeding the pyrolysis reactor. Maintaining the reactor operation temperature under control is very important and directly affects the yield in

bio-oil. Temperatures above 500 °C in the reactor bed are not favorable to the production of bio-oil. In the same way, high air venting, used as fluidization agent of the bed in self-thermal fluidized bed reactors, as is the case of the reactor at PPR-200.

In the case of PPR-200, reactor temperature control is made through manual control of biomass feeding and venting of the fluidizing agent, which is adjusted by valves, opened and closed manually. A monitoring system gives profile data on reactor pressure and temperature.

Automation of the reactor feeding system is important, in order to have a robust plant, capable of self-adjusting to the conditions and characteristics of the biomass and the process, aiming always at a higher yield of bio-oil.

With regard to pretreatment and feeding systems in Brazil, the availability of equipment for these operations in high e.g. industrial choppers and mills, stocking silos, transporting chains and

dryers of many kinds. These equipments must simply be adjusted to the needs of the pyrolysis plants, such as operation regime, capacity etc.

In automation, for operation efficiency a supervisory systems needs to be developed which is capable of receiving information from the plant, such as temperature, pressure etc. and take operation decisions, such as automatically increase or reduce biomass feeding. In the Brazilian market there is a wide variety of interfaces and programmable logic controllers (PLCs). Then there is only the matter of developing the control logic, based on the information which shall be made available.

Energy consumption in the pyrolysis process

Energy consumption in the fast pyrolysis plant is due to the need of supplying heat to the reactor and mechanical energy to move the air, biomass, cleansing water and separation of products. Figure 5 shows the energy flow balance at plant PPR-200 operating with sugarcane trash, made based on operation and yield data, considering the lower heating value of the cane trash, the bio-oil and fines charcoal, determined by analysis of these products. The energy flow value related to the gases and losses was determined by calculating the difference.

Electric energy represents the consumption of mechanical energy, which is not more than 1.6% of the energy produced in the form of bio-oil and fines charcoal. The thermal energy represents the plant's greatest consumption, of 36.5% of the energy generated in the form of fines charcoal and bio-oil. Because the reactor is self-thermal, this leads to a significant consumption of biomass, meaning that the yield of bio-oil in relation to gross biomass (mass yield) does not surpass 22%. The gross biomass is the total which goes into the plant, not discounting moisture, ashes and percentage which goes to combustion.

Use of the gases generated in the process would allow reduction of the biomass consumption for heat generation. There would be an initial consumption to start the reactor starts and then it would be retro-fed by these gases, which would serve as source of heat and fluidization agent in the bed.

This system has been designed for PPR-200, which is even commented in Figure 3, and needs financing for tests. It is necessary to evaluate the behavior of the reactor operating with the injection of these gases, in terms of quality and use of the products.

The biomass consumed to generate heat would be made available for the production of

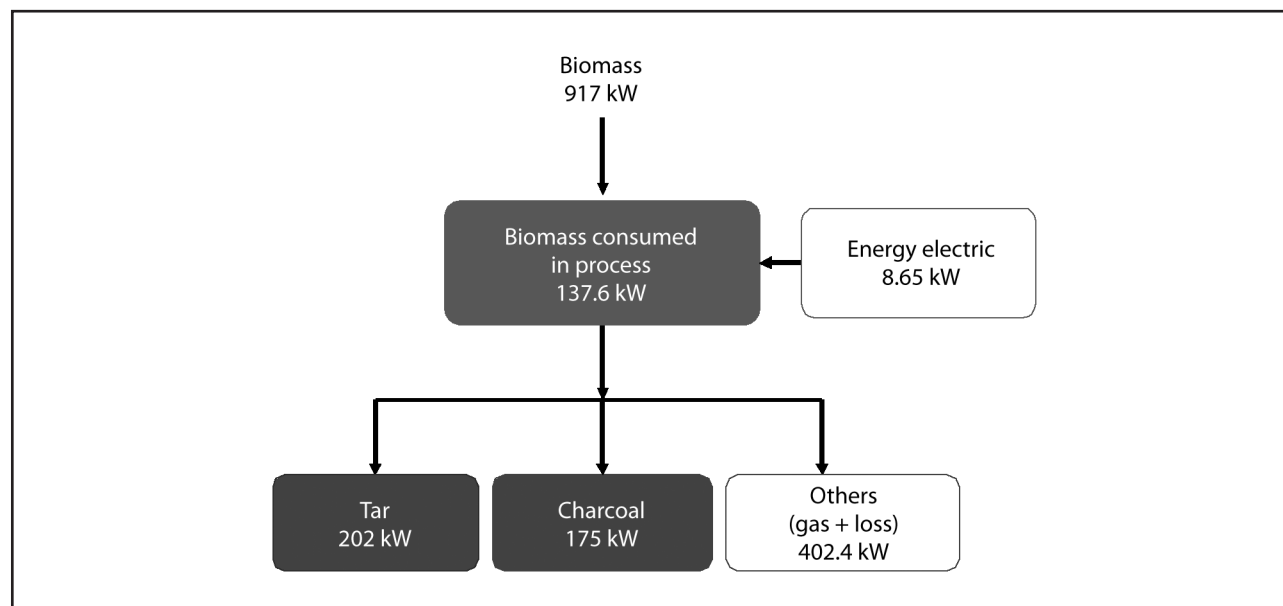


FIGURE 5 Energy flow balance at plant PPR-200.

TABLE 4 Typical yields of the products obtained from different forms of wood pyrolysis (dry base).

Process	Liquid	Charcoal	Gas
Fast pyrolysis	75%	12%	13%
Carbonization	30%	35%	35%
Gasification	5%	10%	85%

Source: OLIVAREZ GÓMEZ (2008).

fines charcoal and bio-oil. With this change, the conversion global efficiency of the plant based on the energy flow, fines charcoal and bio-oil, would go, considering current values, from 41% to 51.6%, which is still low. However there is also the question of increasing the yield of bio-oil.

Yield of bio-oil

The yield of fast pyrolysis products in laboratory scale using highly efficient bio-oil recovery equipment may reach 75% in mass (Table 4). This figure considers the total liquid mass recovered such as: water, acids, extracts and bio-oil.

In practice, as may be seen in Table 5, where the average yield of fast pyrolysis products at the pilot plant PPR-200 is shown, the bio-oil yield is not so high, in between 20% to 25% depending on the biomass composition, considering as calculation base the dry organic mass contained in the biomass fed into the reactor.

The organic mass (biomass liquid mass) is calculated subtracting the quantity of water and ashes in the biomass and discounting the percent-

TABLE 5 Average yields of fast pyrolysis products at plant PPR-200, installed at FEAGRI-UNICAMP.

Product	Yield in mass base (%)
Charcoal	25-30
Bio-oil	20-25
Acid extract	10-15
Hot gases (calculated by difference)	30-35

age of biomass which suffers combustion from the oxygen contained in the fluidization air to supply heat to the process. In case of PPR-200, between 10% and 15% of biomass is used to supply heat to the process, as the reactor is self-thermal.

As well as the question related to the consumption of biomass to supply heat to the pyrolysis process, there are other factors which affect the bio-oil yield, such as retention time (residence time) and the bio-oil separation system.

The total residence time at plant PPR-200, from entering the biomass particle in the reactor up to exiting the particle of bio-oil in the separator is still high, of about 8 seconds. Altering the reactor project and the separation column, it would be possible to reduce this time up to 2 seconds. This would reduce the possibility of the bio-oil particle suffering cracking, converting itself into gas.

The bio-oil separation system is another bottleneck in pyrolysis, as when it is cooled down it condenses in the form of a fog. The use of expensive however efficient equipments is not always viable when the question is biomass. For plant PPR-200 a technology of centrifuge separators was developed, which although it still operates with modest results, it is robust and cheap, and may be improved.

Scale of pyrolysis plants

In relation to scale, there are certain debates and controversies around the biomass fast pyrolysis plants. Some companies in the world use various technologies with great installed capacity, in the order of 100 to 200 tons of biomass per day. However these scales have not had much success due to the complexity of the plants and its relatively low performance.

In terms of values, as may be seen in Table 6, the cost/capacity relation is decreasing for fast pyrolysis plants. While the cost of a plant for 200kg/h is of R\$ 300,000.00, the cost of a plant for 2t/h is of R\$ 1.3 million, and the capacity is ten times greater.

In Brazil, studies have reached the scale of 200kg/h (PPR-200) and plants of 20 to 40 tons per day are capable of functioning satisfactorily. This

TABLE 6 Estimated costs of fast pyrolysis plants with fluidized bed reactors.

Capacity (kg/h)	Estimated cost (R\$)	Est. cost/Capacity (R\$/kg.h)
40	150,000.00	3,750.00
200	300,000.00	1,500.00
500	500,000.00	1,000.00
1.000	800,000.00	800.00
2.000	1,300,000.00	650.00
2.500	1,500,000.00	600.00

Source: BLOWARE (n.d.).

scale has already been projected, needing investments for its construction as a fundamental phase in scale increase.

The great technology difficulties in scale-up are related to the fact that the fluid-dynamic of the fluidized bed reactor is complex. Stable operations of the reactor (that is pressure and temperature profiles throughout the reactor in stationary regime) are only possible if the mixture between the material and the biomass is adequate. Problems of located temperature increases, sinterization, gas leakages, are common when the fluid dynamics of the bed is not dominated.

A scale-up, situation equivalent to an increase in the reactor diameter, has the inconvenience that the feeding point does not ensure a homogenous mixture of the biomass throughout the diameter perimeter of the bed. Distributing feeding points may help solve the problem, however economic and financial aspects of the implementation of these solutions must be evaluated carefully. The use of parallel reactors may be a less risky practice, however the economical aspects should be evaluated.

Stability of bio-oil

Moving from the question of process and approaching the question of products, there is the matter of high viscosity associated to the instability of bio-oil, which tends to increase with age, to the point where bio-oil resembles bitumen. This

could represent a problem in transportation and application in processes, when thinking of draining through ducts. Heating the bio-oil, rather than a solution, may be a problem, if temperature is not carefully controlled, as when heated to more than 70 °C bio-oil turns to coke. On the other hand, at 60 °C it has a pretty fluid behavior.

The study of catalysts to be injected in the reactor during the fast pyrolysis process, or additives to be mixed directly into the bio-oil is an option. In this sense there have been tests using ethanol as an additive to bio-oil. The use of ethanol as well as reducing the viscosity, gave chemical stability to bio-oil, as well as improved its combustion properties. Above 40 °C, with an ethanol concentration of 15% in mass, the bio-oil is totally fluid.

The high viscosity of bio-oil *in natura* is due to the use of air as a fluidization agent, which increases the concentration of pyrolytic lignin and the degradation of the bio-oil's lighter compounds. So, substituting fluidization air for the gases generated in the process may act in the sense of reducing the viscosity of bio-oil.

The stability problem of bio-oil may be overcome by reducing the time between production and processing.

Gasification

The gasification technology is old, having been used in Germany during World War II. But, while the Germans converted mineral coal into fuel, the current challenge is to do the same with biomass.

The conversion of biomass into fuel gas allows the use of engines and turbines in applications for generating energy, whether to move cargo or generate electricity, which constitutes a technical potential for increasing conversion efficiency. From gasified biomass, known as synthesis gas, it is also possible to obtain hydrocarbons with characteristics that are similar to the commercial liquid fuels, such as gasoline and diesel.

In case of generation of electric energy, gasification allows the use of biomass in gas turbines, in whose power thermal cycle the work fluids operate at much higher average temperatures (above 1,200 °C) than in the conventional vapor

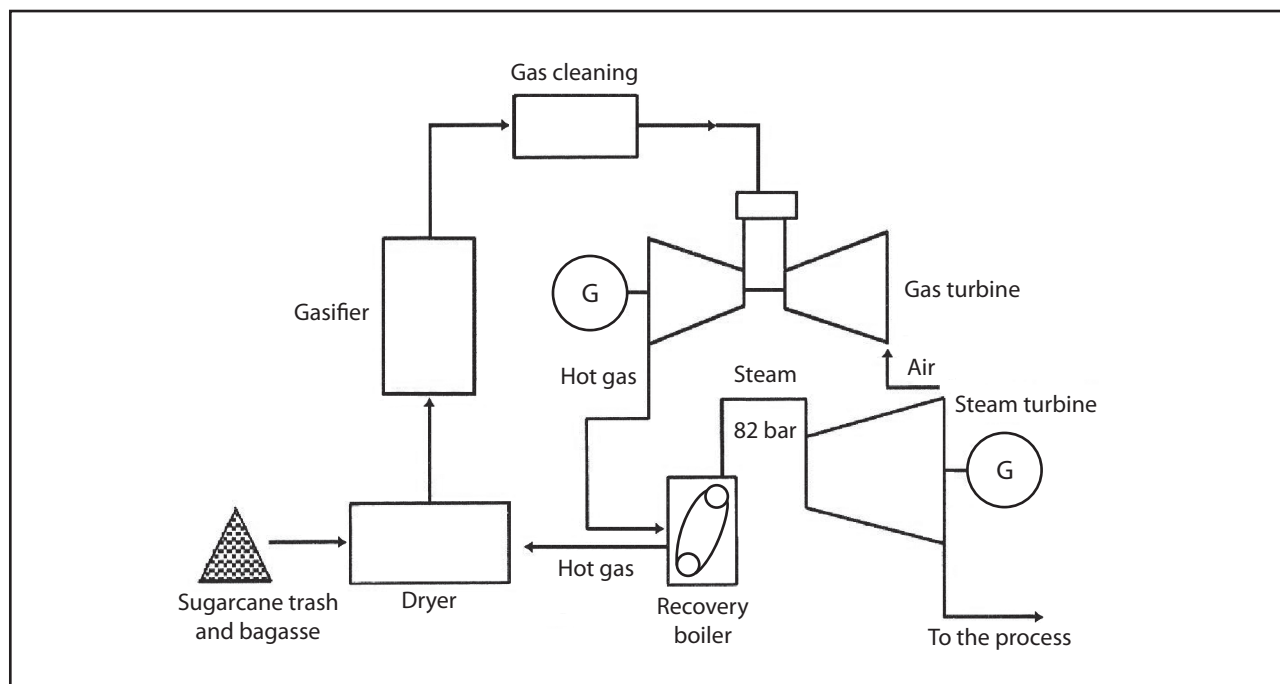


FIGURE 6 Simplified BIG-GT scheme.

cycles (below 600 °C), which reduces the thermodynamic losses and maximizes the performance.

In this sense, integration with gas turbines/vapor turbines combined cycles (biomass integrated gasification/gas turbine combined cycle BIG/GT-CC) may contribute to the increase in efficiency of conversion of biomass into electric energy. It is estimated that the BIG/GT-CC efficiency for the generation of electric energy may reach 45%, whereas in the vapor turbine cycles this efficiency is of about 15% to 35% (BNDES and CGEE, 2008). Figure 6 shows a simplified scheme of the BIG/GT-CC system, adapted from LEAL and LAMÔNICA (2003).

However, gasification of polydisperse solid biomass represents a challenge in terms of feeding reactors, as well as the question related to gas quality, as was previously commented. There are notorious cases of projects that were abandoned due to problems in feeding biomass.

Pelettization may be an alternative for the problem of feeding in pressurized gasification, as it increases the density of the biomass, improving its injection in the reactor.

On the other hand, the quality of gases is seriously compromised for its use in electric energy

generation when the solid biomass is gasified integrally. Table 7 shows the requisites for the use of synthesis gas as a fuel in some applications.

Another issue is related to the capacity of the gasifiers, which should be high, for economic matters and, also, to meet the production volumes of the sugarcane mills. The fixed bed gasifiers are normally used for the conversion of small quantities of biomass, generally employed in small capacity electric energy generation projects. The ascending flow models normally produce gas with high tar levels interfering in the operation of internal combustion engines. In the descending flow models, the difficulty in handling the high level of moisture and ashes is a common problem.

Fluidized bed gasifiers on the other hand are more adequate to the conversion of a larger quantity of biomass, and systems with capacity between 10 and 20 ton/h are already operational. However, there are problems with the quality of the gases. Due to the nature of the process itself, the quantity of particle material dragged tends to be greater; a second aspect is that the higher temperature of output gases means that the alkali come out in their gaseous phase, imposing additional difficulties to cleaning.

TABLE 7 Requirements for the use of synthesis gas in combustion engines, gas turbines and fuel cells.

Impurities	Units	Internal combustion engines	Gas turbines	Fuel cells
Particle level	mg/Nm ³	<50	<30	–
Size of particles	µm	<3	<5	–
Tar level	mg/Nm ³	<100	–	<1
Alkali level	mg/Nm ³	–	<0.25	–
NH ₃	mg/Nm ³	<55	–	<0.1
H ₂ S	mg/Nm ³	<1,150	–	<1
HCl	ppm	–	–	<1
SiO ₂	mg/Nm ³	–	–	<1

Source: KALTSCHMITT and HARTMANN (2001) quoted by LORA and VENTURINI (2008).

According to SEABRA (2008), the main bottlenecks in biomass gasification are:

- low density and polydisperse biomass feeding system in pressurized reactors;
- cleansing of gases;
- long lasting and reliable operation at commercial scale of oxygen pressurized gasifiers;
- need for large scale production to make it economically viable.

Catalytic synthesis

The fuels produced from lignocellulosic raw materials are known as second generation fuel. They may be produced by the thermo-chemical route, through gasification of biomass for the production of synthesis gas, which permits the

production of liquid fuels through various catalytic processes. The thermo-chemical route processes, also known as BTL processes are under development, which means there are still many challenges, especially related to the gasification phase itself.

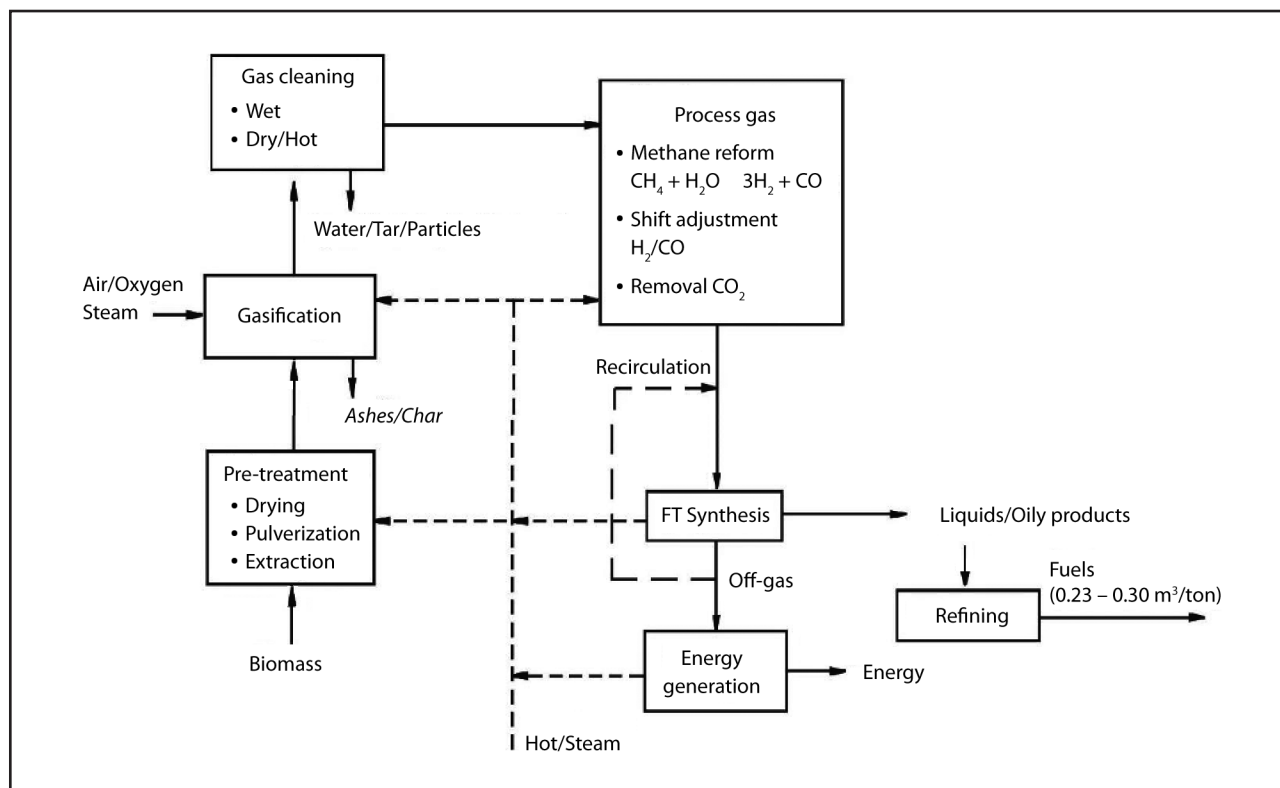
The fuel synthesis processes have a series of requirements in relation to pressure, temperature in the reactor, type of catalyst and H₂/CO relation in the synthesis gas (Table 8). The H₂/CO relation may be adjusted during gas conditioning using the shift reaction.

Another important factor is the quality of the gas, in relation to the levels of H₂S and other sulphurous compounds, particles, tar and alkali compounds. The required quality of the gas depends on which is the process which uses the synthesis gas as raw material. Table 9 shows these requirements in the case of methanol synthesis.

TABLE 8 Parameters and H₂/CO relation for different synthesis processes.

Process	Product	Pressure (bar)	Temperature (°C)	Catalyst	H ₂ /CO Relation
Methane	CH ₄	1 – 30	300 – 400	Ni	3/1
Methanol	CH ₃ OH	50 – 100	250 – 280	Cu/ZnO	2/1
F-T	– CH ₂ –	3 – 25	190 – 240	Co	2/1
F-T	– CH ₂ –	3 – 25	250 – 300	Fe	2/1

Source: ZUBERBULHER *et al.* (2006) quoted by LORA and VENTURINI (2008).



Source: Adapted from JENKINS (2007) quoted by LORA and VENTURINI (2008).

FIGURE 7 Phases in the process to obtain fuels through the thermo-chemical route.

Figure 7 shows an arrangement to obtain fuels through the thermo-chemical route, passing by direct gasification of biomass, obtaining synthesis gas and Fischer-Tropsch synthesis.

According to SEABRA (2008), the main obstacles in catalytic synthesis of biomass are:

- cleansing gas;
- catalysts (increase reactivity and reduce costs);
- scale of synthesis plants.

TABLE 9 Synthesis gas quality parameters (methanol synthesis).

Component	Permissible concentration (mg/Nm ³)
H ₂ S and other sulphurous compounds	< 0.1
Particles	<0.1
Tar	<1
Alkali compounds	<0.25

Source: ZUBERBULHER *et al.* (2006), quoted by LORA and VENTURINI (2008).

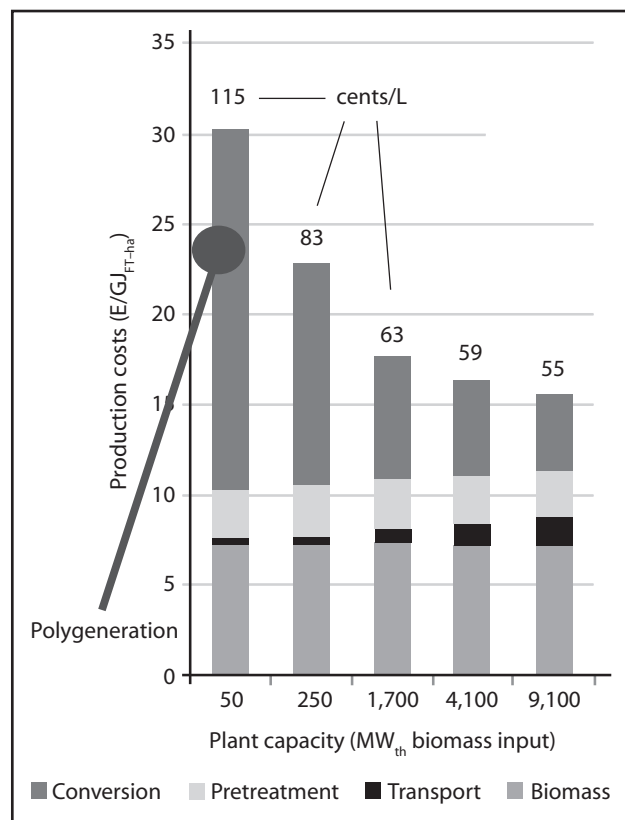
The BTL thermo-chemical route, which passes by pyrolysis production of bio-oil and gasification of the bio-oil, followed by the Fischer-Tropsch synthesis, has advantages in terms of feeding pressurized gasifiers and gas quality for use in catalytic synthesis.

Figure 8, taken from LORA (2008), shows the relation of the conversion cost with scaling of synthesis and gasification plants. The smaller the scale the greater is the cost, where there are included capital, operation and maintenance costs. It is verified that feasibility is achieved as of 1,700 MW of biomass entry.

TECHNOLOGY DRIVERS

Based on the needs of each technology area approached within the fast pyrolysis/gasification/catalytic synthesis route, technology drivers are created to meet the “Productivity” and “Cost” critical requirements.

Table 10 shows the technology drivers for each one of the technology areas in relation to the “Productivity” critical requirement.



Source: LORA (2008).

FIGURE 8 Relation between scale and cost in gasification and synthesis plants.

Automation of the pyrolysis process, reduction of biomass consumption in supplying heat to the reactor and improvement of the bio-oil recovery system will allow an increase in total product yield, from the current 55% to 71% in a period of 20 years. With this, conversion energetic efficiency of the pyrolysis process, which is now at 41%, shall increase to 70%. The current data is based in tests in a pilot plant. Bio-oil yield use as reference the organic mass available for pyrolysis (liquid mass), which ignores the humidity level and ashes, as well as the biomass consumed to supply heat to the reactor.

Table 11 shows the technology drivers for each technology area, aiming to meet the target referring to the “Cost” requirement, which foresees the reduction of the current cost, estimated in US\$ 1.09 per liter of synthetic fuel, to US\$ 0.28 in a period of 20 years. This reduction is the result of the increase in process efficiency, as well as reaching economies of scale for the production of synthetic biofuels.

The pyrolysis plant scale (ton of biomass/h) considers the gross mass fed into the reactor, with the moisture and ashes.

TABLE 10 Technology drivers for the increase in productivity aim of the fast pyrolysis/gasification/catalytic synthesis route for the production of synthetic biofuels.

		Present	5 years	10 years	20 years (Vision)
Productivity	Liters/ton of biomass*	n.e.	172	260	341
	GJ/ton of biomass	n.e.	3.7	5.5	7.3
Pyrolysis					
Residence time (s)		8	4	2	2
Bio-oil yield (% in mass base)**		25	35	50	56
Fines charcoal yield (% in mass base)**		30	20	15	15
Conversion energetic efficiency (%)		41	51	63	70
Gasification and catalytic synthesis					
Conversion energetic efficiency (%)		30	40	50	60
Relation H ₂ /CO		1/1	2/1	3/1	3/1
Production (Liters /ton of mud)*		n.e.	373	476	572

* Equivalence in liters of ethanol (PCI = 21.34 MJ/liter).

** Product mass/organic liquid mass free of moisture and ashes.

TABLE 11 Technology drivers for the cost reduction aim of the pyrolysis/gasification/catalytic synthesis route for the production of synthetic biofuels.

		Present	5 years	10 years	20 years (Vision)
Cost	US\$/liter*	1.09	0.67	0.35	0.28
	US\$/GJ	51.5	31.2	16.5	13.4
Pyrolysis					
Pyrolysis plant scale (ton of biomass/h)		0.2	5	7	10
Production per plant (ton of slurry/h)		0.09	2.31	3.82	5.96
Cost (US\$/ton of slurry)		150	80	50	42
Gasification and catalytic synthesis					
Gasification and synthesis plant scale (ton of slurry/h)		n.e.	44	145	358
Gasification and synthesis plants/pyrolysis plants		n.e.	1/19	1/38	1/60
Production scale (1000 liters of biofuel/h)		n.e.	16.41	72.36	179

* Equivalence in liters of ethanol (PCI = 21.34 MJ/liter).

Studies on gasification of bio-oil are currently under way in pilot units. It is thought that in 5 years it shall be possible to gasify also the charcoal mixed to the bio-oil in the form of slurry. The forecast above made for pyrolysis considers a pyrolysis module which may reach a biomass feeding scale of 10 ton/h.

Distribution of many pyrolysis modules for the production of mud shall enable reaching the economic scale for the production of synthetic fuels, which is of 5 million tons/year of biomass, approximately 600 ton/h of biomass, about 358 ton/h of mud, corresponding to 60 pyrolysis units with production capacity of 5.96 ton/h of slurry.

PRESENT SCIENTIFIC AND TECHNOLOGY CAPABILITIES

The state of São Paulo has many capable institutions. In the last 40 years, UNICAMP (FEQ, FEM, IFGW and FEAGRI mainly) has conducted studies in the field of biomass, gasification and pyrolysis, owning even a fast pyrolysis pilot plant. The IPT has done researches in the field of biomass conversion into fuel, through the route passing by gasification and catalytic synthesis.

Research directed to establishing the route being proposed may be conducted through the cooperation between universities and research centers (UNICAMP, UNIFEI, IPT and UFPA), manufacturers (Termoquip Energia Alternativa) and interested companies (Petrobrás, Oxiten, BRASKEM etc.). The implementation of joint projects in research centers abroad is also possible.

In the field of catalysts, the NEST/UNIFEI together with the Termoquip have tested a catalytic cleansing system (Ni base) attached to a crossed-flow gasifier. In Brazil, other universities also have high-level research groups in catalyst development. Among them, the CENPES-PETROBRAS, the Catalysis Group (DEQ/UFRN), the Studies Group in Kinetics and Catalysis (IQ/UFBA), the Group of Molecular Sieves (IQ/UNICAMP), among the others.

In the field of rapid pyrolysis, FEAGRI – UNICAMP, in cooperation with the company Bioware, is developing research related to pyrolysis of whole sugarcane and sugarcane trash. The purpose of these researches is the increase in bio-oil yield and the improvement of its physical and chemical characteristics, especially in relation to its stability. The question of scale increases in pyrolysis plants has been another point of focus.

GAPS AND BARRIERS

The cost of biomass has proved to be an important issue, needing to be worked, as it directly affects the products cost of all technologies proposed for using lignocellulosic biomass. As per studies held, considering an exchange rate of R\$ 2.00/US\$ 1.00, in the current scenario, an amount greater than US\$ 50 per ton would not permit the use of biomass in thermoconversion technologies. The cost of the ton of gathered sugarcane trash, transported up to a distance of 20 km, may reach up to US\$ 30, whereas one ton of sugarcane stem transported the same distance will not cost more than US\$ 20 per ton.

The current cost of bio-oil based on the production cost calculated in tests at the pilot plant, considering the value of the sugarcane straw at US\$ 30.00/ton with 15% moisture and 11% ashes, is of US\$ 150 per ton (0.508 tep), considering the sales of fines charcoal produced at US\$ 150 per ton. Yet the cost of one ton of ethanol (0.494 tep) is at around US\$ 309. Now the price of one ton of oil (6.3 barrels) is of about US\$ 441, considering US\$ 70 the barrel. The cost of 1 tep of bio-oil is of US\$ 295, where more than 70% of the production cost of bio-oil is due to the cost of the raw material (biomass).

A way of reducing these costs could be in the whole harvesting of sugarcane with the implementation of dry cleansing. The pyrolysis plants could be installations attached to the mills, benefitting

from the whole existing structure to reduce costs in the harvesting and conditioning phases.

FINAL CONSIDERATIONS

The thermo-chemical route proposed in this roadmap is an interesting option to increase efficiency in the use of primary energy of sugarcane, with the conversion of straw and pulp into fuels.

The thermoconversion technologies such as fast pyrolysis and gasification are already known. However, there is a need to tailor these technologies to the conversion of biomass. Research directed to solving operation problems with biomass and improving efficiency is necessary. Efficiency of these technologies with the use of biomass, based in pilot tests, is still low.

The catalytic synthesis technologies are already commercial and used in the conversion of natural gas into synthetic gasoline. For the application in the biomass conversion route, there is a need to improve the quality of the gas, in what concerns the purity and H₂ and CO concentration. The question of scale seems to be one of the main barriers, in relation to production cost.

A market for the products of fast pyrolysis needs to be created, so that scale production capable of covering the minimum demand necessary for the production of synthetic fuels is rendered feasible. For this research on the application of the products generated is necessary.

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