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VALORIZATION OF AGROINDUSTRIAL SOLID RESIDUES AND RESIDUES FROM BIOFUEL PRODUCTION CHAINS BY THERMOCHEMICAL CONVERSION: A REVIEW, CITING BRAZIL AS A CASE STUDY

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Abstract - Besides high industrial development, Brazil is also an agribusiness country. Each year about 330 million metrics tons (Mg) of biomass residues are generated, requiring tremendous effort to develop biomass systems in which production, conversion and utilization of bio-based products are carried out efficiently and under environmentally sustainable conditions. For the production of biofuels, organic chemicals and materials, it is envisaged to follow a biorefinery model which includes modern and proven green chemical technologies such as bioprocessing, pyrolysis, gasification, Fischer-Tropsch synthesis and other catalytic processes in order to make more complex molecules and materials on which a future sustainable society will be based. This paper presents promising options for valorization of Brazilian agroindustrial biomass sources and residues originating from the biofuel production chains as renewable energy sources and addresses the main aspects of the thermochemical technologies which have been applied.

Keywords: Biomass-to-energy; Residues; Biofuels; Pyrolysis; Gasification.

INTRODUCTION

According to the EIA's International Energy Outlook (U.S. EIA, 2011), world marketed energy consumption is expected to increase strongly, rising by nearly 50 percent from 2009 through 2035. Most of the growth occurs in emerging economies outside the Organization for Economic Cooperation and Development (OECD), especially in non-OECD Asia. Non-OECD nations account for 84 percent of growth in world energy use compared with a 14-percent increase in the developed OECD nations. Unless the world energy matrix is altered, fossil fuels will account for 90% of the increase.

The requirement to reduce carbon dioxide emissions has sparked interest in the use of many types of biomass as alternative energy sources. Since the biomass used in those processes is produced by the photosynthetic reduction of carbon dioxide, utilization of biofuels can essentially be carbon neutral with respect to the build-up of atmospheric greenhouse gases, increasing both the demand for the characterization of alternative fuels and the proliferation of scientific papers concerned with this

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*To whom correspondence should be addressed subject (Demirbas, 2004a, 2005; Obernberger *et al*., 2006; Werther *et al*., 2000).

Brazil has been a world leader in agroenergy for the last decades. The internal offer of energy in Brazil in 2011 was 272,380 million tons of petroleum equivalents. Renewable sources of energy were responsible for 44.1% of this amount, while 14.7% came from hydraulic and electricity, 9.7% from firewood and charcoal, 15.7% from sugarcane derived products and 4.0% from other renewable sources (Brasil, 2012).

Status of Biofuel Production

Since the mid-1970s several governments have implemented energy policies to increase the use of biofuels. The Brazilian Fuel Ethanol Program (Pró-Álcool) was a successful example to stimulate the use of ethanol as automotive fuel. Ethanol is consolidated in the Brazilian biofuel market, where gasoline contains 20–25% anhydrous alcohol by volume. Hydrated alcohol is consumed pure or mixed with any percentage of gasoline in flexible-fuel automobiles. The demand varies depending on the gasoline prices and on the motor vehicle fleet. Worldwide, fuel ethanol production is expected to hit 85.2 billion liters in 2012 according to the Global Annual Ethanol Production Forecast released by the Global Renewable Fuels Alliance in cooperation with F.O. Licht (RFA, 2012). Still according to this source, the United States and Brazil continue to be the largest producers of ethanol, with production continuing at a steady pace in 2012. Although production levels in Africa remain relatively low, this region will see the largest increase in production for 2012, which is expected to grow by 36%.

Another example of these policies is the National Program of Biodiesel Production and Use (PNPB), which was created in 2004. With the purpose of creating a market for biodiesel, since 2008 the blend of pure biodiesel in diesel oil has become mandatory through Law 11.097/2005. Between January and June 2008, the mix was 2%, between July 2008 and June 2009 it was 3%, between July and December 2009 it was 4%, and since January 2010, the B5 blend has been mandatory. According to the research report entitled “Biofuels Regain Momentum” conducted by the Worldwatch Institute’s Climate and Energy Program for the website Vital Signs Online (Shrank and Farahmand, 2011), global biodiesel production increased by 12 percent between 2009 and 2010, reaching an estimated production level of 19 billion liters. The EU remained the world’s largest biodiesel producing region in 2010, accounting for approximately 53 percent of global production, while the world’s top biodiesel producing countries were Germany and Brazil, with respective production levels of 2.9 billion liters and 2.3 billion liters. The U.S. biodiesel industry reached a key milestone by producing more than 1 billion gallons of fuel in 2011, according to year-end numbers released by the EPA in January 2012 (U.S. EPA, 2012).

Second Generation Biofuels and Other Products from Biomass

Besides ethanol and biodiesel programs, the production and use of charcoal is also a known example of Brazilian success in bioenergy, even though optimization of the conversion process and reduction of associated social and environmental impacts are still required. Most of the charcoal produced in Brazil is used in the iron and steel industry, the country being one of the world's largest producers of fused iron, steel and iron based products.

Research on second generation biofuels that can be produced from a variety of biomass residues and non-food crops through various process routes (e.g., chemical and biochemical hydrolysis, thermochemical) have been extensively carried out worldwide. Second-generation biofuels are not yet produced commercially, but a considerable number of pilot and demonstration plants have been announced or set up in recent years, with research activities taking place mainly in North America, Europe and a few emerging countries (e.g., Brazil, China, India and Thailand). Current IEA projections see a rapid increase in biofuel demand, in particular for second-generation biofuels, in an energy sector that aims at stabilizing the atmospheric CO_2 concentration at 450 parts per million (ppm) (IEA, 2010).

This sector has been developed in Brazil mainly driven by the potential of the sugarcane plant (Dias *et al*, 2011a, 2011b, 2012a, 2012b; Seabra *et al*., 2010; Seabra and Macedo, 2011; Walter and Ensinas, 2010). Currently, the focus of research and development efforts in Brazil has been on the production of ethanol (second generation ethanol) through hydrolysis of sugarcane bagasse and trash. This processing route has not yet become an industrial reality due to the lack of efficient and low cost technologies, which results in prohibitive investment and production costs as well as poor returns on investment. Difficulties in hydrolyzing the main components (cellulose, hemicellulose and lignin) of the plant cell wall and the consequent relatively low yield, low solids loading on hydrolysis and the lack of pentose fermentation to ethanol are the main issues (Cardona *et al*., 2010; Dias *et al*., 2011a, 2011b). The conversion process relies heavily on major technological innovations centered on effective and low cost enzymes, feedstock and efficient process design (Menon and Rao, 2012). Additionally, the search for more robust models for cellulose hydrolysis is a very important task. The related trends were extensively reviewed by Sousa Jr. *et al*. (2011) from the perspective of the application of kinetic models within a bioreactor engineering framework, where reactor design and process optimization are the ultimate goals, including scale-up, design and process optimization.

The production of liquid fuels through synthesis gas (produced through biomass gasification) is also an alternative. Ethanol production through hydrolysis and/or gasification using bagasse (and/or trash) as raw material can impact the potential of surplus electricity production. There is a tendency for enlarging electricity production from sugarcane residual biomass and investors believe that, in the short to mid-term, electricity could become a product as important as ethanol or sugar (the traditional products of this industrial branch) (Walter and Ensinas, 2010). With the development and commercialization of alternative biomass conversion technologies, there might be a tendency to drive the application of the available biomass sources to the most value added scenario. This is becoming a reality for sugarcane bagasse in Brazil, which does not constitute a costless material anymore. When no on site application is available, it has been sold as feedstock for electricity production. The decision regarding second generation ethanol production, for example, has considered the opportunity prices for the different biomass derived products (ethanol and other biofuels, bioelectricity and sugar, among others) (Dias *et al*., 2011b), which can promote competition for the use of lignocellulosic biomass.

For the future rearrangement of a sustainable economy based on biological raw materials, completely new approaches to research and development, production, and economy are necessary. Enhancement of biomass utilization requires tremendous efforts to develop new biomass systems in which production, conversion and utilization of bio-based products are carried out efficiently in near harmony with nature, thus constituting and implementing the biorefinery concept.

Agricultural energy comes from four biomass sources: carbohydrate- or starch-rich crops; vegetable oils or animal fat; wood; and agroindustrial residues. Brazil has comparative advantages worldwide in the production of all biomass sources and can create competitive advantages to lead the international renewable energy market. In addition, the size of the Brazilian market can guarantee the success of the biomass energy initiatives and a foreign market is beginning to emerge (Brasil, 2006). However, the use of biomass residues as an energy source has not had the same success as the ethanol and biodiesel programs, partly due to the lack of a dedicated and adequate governmental program, which demands immediate attention, and also because of the inherent difficulties in the use of these residues.

In 2006, the Brazilian Federal Government created the National Agroenergy Plan (PNA 2006–2011). The overall purpose of the National Agroenergy Plan was to ensure: the sustainability of the energy matrix; job and income generation; rational use of areas affected by anthropic actions; Brazilian leadership in biomarkets; energy autonomy at the community level; support to public policies; energy savings along agribusiness chains; and elimination of health risks. The Research, Development and Innovation (RD&I) program should unfold along the four principal areas of the main agroenergy production chains: ethanol and the co-generation of energy from sugarcane and other alternative biomass sources; biodiesel from animal and plant sources; forest biomass; and residues and wastes from agriculture and agroindustry.

Among the objectives of this plan was the creation of Embrapa Agroenergy (in 2006), a section of the Brazilian Agricultural Research Corporation (Embrapa), constituting a decentralized research unit focusing on agroenergy topics and support for the development of the country's agroenergy research system. In executing this plan, Embrapa joined multi-institutional and multidisciplinary RD&I networks, as well as started carrying out its own research, development and innovation activities in the field of agroenergy.

Biomass sources have become the basis of renewable energy and a valuable input for the chemical industry. The experts believe that energy from biomass will account for the better part of the revenues from international agricultural transactions beginning in 2050. However, the economic viability of bioenergy necessarily depends on an evaluation of its cost when compared to the price of petroleum, even though social (employment, income, migration flows) and environmental (climate changes, pollution) pressures can bring the timetables forward (Brasil, 2006).

In this context, the present paper aimed at identifying the potential biomass sources from the Brazilian agroindustrial sector and from the Brazilian biofuel (ethanol and biodiesel) production chains. The main aspects of the biorefinery concept and of the thermochemical technologies and processes which have been considered and applied to add value to residues have been addressed.

BIOMASS PROPERTIES

The fuel properties often form the basis for the selection of the most appropriate conversion technology. Depending on these properties, a biomass source may not be suitable for specific options, partially for technical and sometimes for environmental reasons. The characteristics of the biomass are influenced by its origin and also by the entire processing system preceding any conversion step.

Biomass is similar to other fuel types in the need for standardized analytical methods leading to accurate and consistent evaluations of fuel properties. Bahng *et al*. (2009) have presented detailed knowledge ranging from structural information of raw biomass, elemental composition, gas-phase reaction kinetics and mechanisms, and product distributions (both desired and undesired). Additionally, the various analytical methods of biomass pyrolysis/ gasification processing are discussed, including reactor types, analytical tools, and recent examples in the areas of compositional analysis, structural analysis, reaction mechanisms, and kinetic studies on biomass thermochemical processing, which are of great importance for technology development and scale up.

Summarized below are the major properties of biomass fuels frequently assessed and some examples of analytical tools and methodologies applied:

- Thermal behavior: isothermal and non-isothermal TGA analysis (e.g., Borrego *et al*., 2009);
- Proximate composition (moisture, ash, volatiles and fixed carbon): DIN 51718-20 (DIN, 1997, 2001, 2002);
- Ultimate elemental (carbon, hydrogen, nitrogen, oxygen and sulfur): ASTM 3176 (ASTM, 1997), oxygen by difference;
- Presence of sulfur and chlorine: selective ion electrodes and colorimetric methods, respectively;
- Higher Heating Value (HHV) and Lower Heating Value (LHV): ASTM D5865 (ASTM, 2004b) and DIN 51900 parts 1 and 3 (DIN, 2000, 2005);
- Ash elemental composition and ash fusibility: DIN 51729-10 (DIN, 1996) and ISO 540 (ISO, 1995) and ASTM D1857 (ASTM, 2004a);
- Presence of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF): according to DEV (1999), US EPA 8310 (U.S. EPA, 1986) and through high resolution gas chromatography mass spectrometry (GC-MS), such as described by Fytianos and Schröeder (1997), respectively;
- Trace elements: DIN 51719 (DIN, 1997);
- Reactivity: isothermal and non-isothermal TGA analysis (e.g., Cousins *et al*., 2006).

Biomass presents wide variation in physical and chemical properties. Demirbas (2004a, 2005), Jenkins *et al*. (1998), van Paasen *et al*. (2006) and Werther *et al*. (2000, 2007) related the biomass properties relevant to thermal conversion processes to their effects on the conversion process.

In a recent publication, the potential for application of various agroindustrial solid residues as alternative energy sources in thermochemical processes was assessed by characterizing their properties – including proximate and ultimate composition, energy content, thermal behavior, composition and fusibility of the ashes – and correlating them to the characteristics required for the optimal operation of pyrolysis, gasification and combustion processes (Virmond *et al*., 2012).

Existing conversion systems require modifications in order to accommodate the nature of the thermal behavior of biomass materials. Greater understanding of the physical and chemical processes occurring in the biomass during heating will aid the design and optimization of practical conversion systems.

The high moisture and ash contents generally found in biomass fuels can cause ignition and combustion problems and also influence the biomass pyrolysis behavior (the first step of gasification and combustion processes) and affects both the physical properties and the quality of the products (Demirbas, 2004b).

Wood and other plant biomass as well as crop residues are essentially a composite material constructed from oxygen-containing organic polymers. Due to the carbohydrate structure, biomass is highly oxygenated with respect to conventional fossil fuels including liquid hydrocarbons and coals. Typically, 30 wt.% to 40 wt.% of the biomass is oxygen (on a dry basis, db). The principal constituent of biomass is carbon, making up from 30 wt.% to 60 wt.% (db) depending on the ash content. Amongst the organic components, hydrogen is the third major constituent, comprising typically 5–6 wt.% (db). Nitrogen, sulfur, and chlorine can also be found in quantities usually lower than 1 wt.% (db), but occasionally well above this (Jenkins *et al*., 1998).

The sulfur in plants can be bound as inorganic sulfur or as organic sulfur. The roots of the plants assimilate S as SO_4^{2-}. The inorganic sulfate can be converted into amino acids for the production of protein. The sulfur content in biomass can range from 0.05 wt.% to more than 3 wt.%, depending on its origin. A rough distinction between (biologically) processed biomass like manure and sludge and unprocessed biomass can be made. The relatively high sulfur and nitrogen contents could be explained by the relatively high protein content in manure and sludge (van Paasen *et al*., 2006).

The chlorine in plants is mainly bound as inorganic salt in the form of potassium chloride (KCl) and quaternary ammonium chloride ($(NH_4)Cl$). Chloride ion is important in osmoregulation, the maintenance of electrochemical equilibrium in cells/ compartments and in the regulation of enzyme activity. The chlorine content in biomass can range from 0.01 wt.% to 2.4 wt.% on a dry and ash free basis (Phokawat, 2005).

These constituents are directly related to the gaseous emissions of compounds such as sulfur oxides (SO_x), hydrogen sulfide (H_2S), and carbonyl sulfide (COS); nitrogen oxides (NO_x); hydrochloric acid (HCl) and the occurrence of fouling and slagging in thermal conversion systems (Senneca, 2007).

The typically high reactivity of biomass is a consequence of its physical and chemical characteristics. The volatile content (80–90 wt.%) is at least twice that of mineral coals. The hydrogen/ carbon and oxygen/carbon molar ratios range between 1.3–1.5 and 0.5–0.6, respectively. These are higher values than those of mineral coals, which generally range between 0.8–0.9 and 0.1–0.3, respectively (Encimar *et al*., 2001).

The thermal processing of biomass containing different chemical and mineralogical compositions plays an important role in biomass reactivity and can create various problems that can affect the reactor operation. This can even make the conversion of biomass in conventional systems unprofitable depending on process conditions such as temperature and velocity distribution, reducing or oxidizing atmosphere and others (Jenkins *et al*., 1998; Masiá *et al*., 2007; Vamvuka and Zografos, 2004; Vamvuka and Kakaras, 2011).

The ash-forming constituents found in biomass fuels are quite diverse, depending on the type of biomass, type of soil and harvesting. The latter has special importance given that soil can be incorporated into the biomass and can potentially change the biomass ash composition and properties. One of the important features of biomass materials is the presence of significant amounts of alkali and alkaline earth metal species (mainly K, Na, Mg and Ca), which tend to volatilize during pyrolysis, gasification and combustion (Virmond *et al*., 2012). The alkali metals can be easily converted to new compounds during combustion, may interact with fuel gases (typically sulfur and chlorine) and with the reactive parts of the other materials inside the furnace. Thus, slagging, fouling and corrosion of surfaces are ash-related problems (Masiá *et al*., 2007; Vamvuka and Zografos, 2004; Vamvuka and Kakaras, 2011).

Llorente and García (2005) and Pronobis (2005, 2006) have presented ash fusibility correlations to evaluate the influence of biomass conversion on furnace fouling and wall slagging. Some control methods for mitigating these biomass ash-related problems have been tested (Vamvuka *et al*., 2008). Further studies on biomass ash composition concerning environmentally relevant heavy metals (especially Cd and Zn) (Obernberger *et al*., 1997; Singh *et al*., 2011d; Vamvuka and Kakaras, 2011) and on diverse possibilities for biomass ash application have also been conducted (Esteves *et al*., 2012; Kwong and Chao, 2010; Park *et al*., 2005; Pérez-Villarejo *et al*., 2012; Tan and Lagerkvist, 2011).

BIOMASS TYPES AND AVAILABILITY

The general definition of biomass was published in Directive 2009/28/EC of the European Parliament and of the Council, relative to the promotion of the energy exploitation from renewable sources (European Union, 2009). According to it, "Biomass: means the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste".

To produce second-generation biofuels and support the biorefinery sector, considerable amounts of biomass have to be provided, which will require an analysis of existing and potential biomass sources well before the start-up of large-scale production. Expert assessments in studies reviewed by the International Energy Agency (IEA, 2010) varied greatly. Hoogwijk *et al*. (2003) estimated 33 EJ per year in 2050 assuming that mainly agricultural and forestry residues are available for bioenergy production. In the most ambitious scenario (Smeets *et al.*, 2007), the bioenergy potential could reach roughly 1500 EJ per year in 2050. This scenario assumes the availability of 72% of current agricultural land for biofuel production, mainly through increased yields and more intensive animal farming. It has been reported that Brazil currently seems to be the only country amongst eight (Mexico, Brazil, China, India, South Africa, Cameroon, India, Tanzania and Thailand) with considerable potential to produce energy crops for second-generation biofuel production sustainably, mainly on underutilized pasture land.

Each year about 330 million metrics tons (Mg) of biomass residues (crop wastes and agroindustrial residues) are generated in Brazil (Felfli *et al.*, 2005a, 2005b, 2011; Suárez *et al.*, 2003). With an average heating value of 4324.45 $kcal.kg^{-1}$ on a dry basis (Virmond *et al.*, 2012), the annual fuel value is estimated at $1.427x10^9$ kcal.

The constraints related to the availability of additional land suggest that second-generation biofuel industries and biorefineries should focus on currently available feedstock sources in the initial phase of the industry. Agricultural and forestry residues form a readily available source of biomass and can provide feedstock from current agricultural and forestry activities without the need for additional land cultivation (IEA, 2010). However, there is an ongoing debate on the effective possibilities of crop residue removal from agricultural fields. According to Felfli *et al.* (2011), only a small fraction of this amount would be practically recoverable even under conditions of highly mechanized harvesting. On the other hand, the crop wastes have other important uses such as animal feed and bedding, as well as the soil fertility factor. Even a partial removal (30–40%) of crop residue from land can exacerbate the soil erosion hazard, deplete the soil organic carbon pool, accentuate emission of CO_2 and other greenhouse gases from soil to the atmosphere, and exacerbate the risks of global climate change (Lal, 2005, 2008).

All the possible benefits and disadvantages of crop residue collection for bioenergy use are still under discussion (Lal, 2008; Mann *et al.*, 2002; Wilhem *et al.*, 2004).

The crop wastes include the residues which remain in the field after harvesting, for instance, paddy straw, bean straw, soya straw, maize straw and wheat straw. The agroindustrial residues include rice husk, coffee husk, sugarcane and fruits bagasses, soybean husk and wood wastes, which are generated during the processing of the crops or logwood. Virtually all of these residues could be used for briquetting as they are homogeneous and present moisture contents below 15 wt.% (Felfli *et al.*, 2011).

Forest and wood residues are important sources. The Brazilian forest sector is one of the most developed and competitive in the world. According to the Brazilian Association of Planted Forest Producers (ABRAF), the country holds a relevant global planting share: 6.5 million hectares is the total area of forest plantations growing Eucalyptus (74.8%) and Pine (25.2%), (ABRAF, 2012). Firewood is an important source of thermal energy. Its importance in Brazil is perceived in industry, trade and rural housing. In 2011, Brazil produced 44.7 million cubic meters of firewood from planted forests. The Brazilian southern region consumed 69% of this total, as presented in Figure 1, corresponding to 35.2 million cubic meters of firewood. In the period between 2001 and 2011, the consumption of firewood grew at an average annual rate of 5%; the southern and southestern regions accounted for around 90% of the total volume consumed (ABRAF, 2012).

Forestry residues are generated by operations such as thinning of plantations, clearing for logging roads, extracting stem-wood for pulp and timber, and natural attrition. Wood processing also generates significant volumes of residues, usually in the form of sawdust, off-cuts, bark and woodchip rejects. This waste material is often not utilized and often left to rot on site, constituting a great opportunity as an energy source and as feedstock for high valued product production.

Sugarcane is one of the most important commercial crops in the world. Brazil is the leading producer, with more than 570 Mt produced in 2008/2009 and an increasing production trend (UNICA, 2012). With sugarcane ethanol production, large amounts of residual biomass (bagasse) are available at the mills nowadays at low cost and, in the years to come, the same could happen regarding trash (leaves and points of the sugarcane plant). In the region where the bulk of the production is concentrated (in the state of São Paulo), the complete phase-out of sugarcane burning should occur by 2017 (Walter and Ensinas, 2010), which may increase the amount of biomass available. The sugarcane trash is roughly equivalent to the bagasse in energy terms (about 2100 $MJ.ton^{-1}$ of sugarcane), biomass availability, and its quantity tends to increase remarkably with mechanized harvesting.

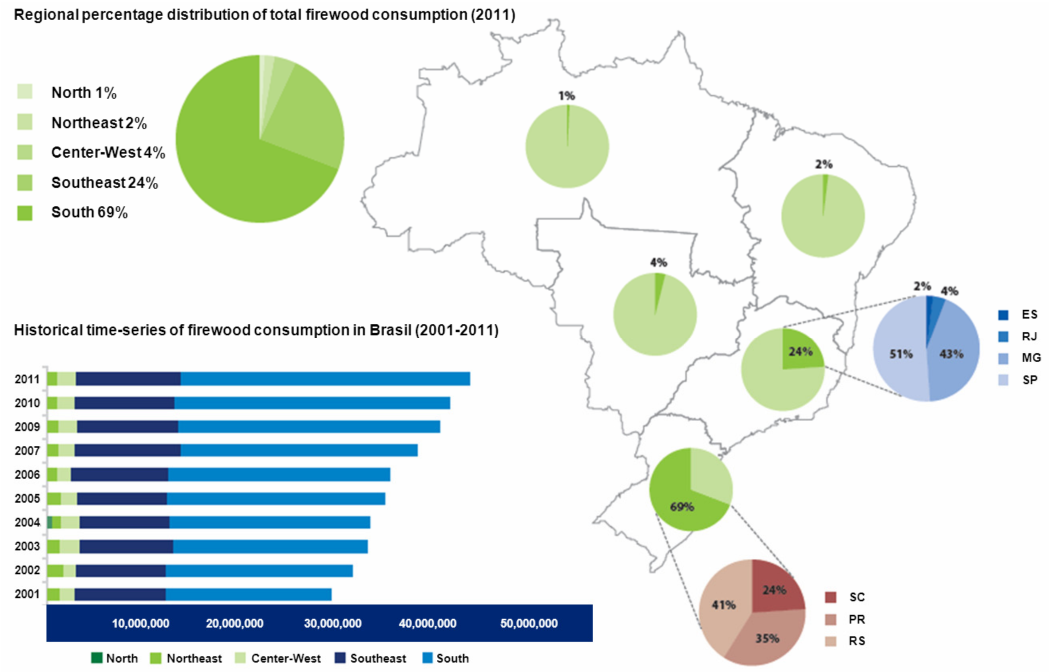


Figure 1: Distribution of regional firewood consumption in 2011 and total national consumption 2001-2011 (ABRAF, 2012)

Increasing volumes of byproducts from biofuel production require knowledge for sustainable utilization and for the development of new uses. Quantity, quality and concentration of wastes are factors that will impact the competitiveness of biofuels in the future.

Production of biodiesel is a promising application of biomass and its production is expected to grow rapidly in the future. Considering the many potential species with high edible and non-edible oil yield for biodiesel production in Brazil, a large variety and quantity of residues are to be generated.

Byproducts such as the press cake from seeds, fruit bodies, empty fruit bunches as well as the leaves of the plant (with low or no commercial value) offer additional opportunities for interesting product outlets (Kumar and Sharma, 2008; Manurung *et al*., 2009; Openshaw, 2000). Examples are the applications of the press cake proteins as a source of animal feed (after detoxification) (Haas and Mittelbach, 2000) and/or industrial applications like glues, coatings and films (Patel *et al*., 2008). The lignin as well as the fibers may be applied for making construction materials, while the carbohydrates could be applied as a source for bio-ethanol (Demirbas, 2007).

Crude glycerol is a major byproduct in biodiesel production from vegetable oils and animal fats through transesterification, with an average yield of about 10 wt.% (Adhikari *et al*., 2008; Lin *et al*., 2009). The tremendous growth of the biodiesel industry created a glycerol surplus that has caused some concerns. Nowadays, glycerol is often regarded as a waste stream with associated disposal costs. Hence, as more and more crude glycerol is generated by the biodiesel industry, it becomes important to develop an economical way for converting this low-grade byproduct to more useful products.

As presented by Yoon *et al*. (2010), crude glycerol derived from biodiesel production has generally been processed into more valuable components or burnt as a fuel owing to the low value of crude glycerol, the excess production of crude glycerol relative to commercial demand for purified glycerol, and the high cost to refine or purify it. The production of a variety of products derived from glycerol through different routes can be found in the literature (Chi *et al*., 2007; Garcia *et al*., 1995; Imandi *et al*., 2007; Karinen and Krause, 2006; Meesters *et al*., 1996; Narayan *et al*., 2005; Papanikolaou and Aggelis, 2002; Zheng *et al*., 2006). However, with fluctuating and increasing oil prices and limited energy resources, crude glycerol is being considered as a fuel source. It has been found that glycerol can be used as a substrate to produce hydrogen, methane and organic acid through the fermentation process (da Silva *et al*., 2009; Fountoulakis and Manios, 2009; Fountoulakis *et al*., 2010) or used as a bio-based reagent to improve the performance of liquefaction for liquid fuel production (Kržan and Zăgar, 2009). This byproduct originates from biomass and could be included in the renewable category and could also constitute a feedstock for the production of a variety of products through gasification and syngas processing.

Besides terrestrial crops and derived residues, extensive research has been conducted to investigate the utilization of algae as an energy feedstock, with applications being developed for the production of biodiesel, bioethanol, biohydrogen, other products and coproducts (Brennan and Owende, 2010; John *et al*., 2011; Levine *et al*., 2010; Mata *et al*., 2010; Melis and Happe, 2001; Singh and Olsen, 2011). On the basis of current scientific knowledge and technology projections, third-generation biofuels specifically derived from microorganisms and microalgae are considered to be a viable alternative energy resource that is devoid of the major drawbacks associated with first and second-generation biofuels (Nigam and Singh, 2011; Singh *et al*., 2011a, 2011b, 2011c). However, this subject has not been addressed in this review.

THE BIOREFINERY CONCEPT

Internationally, research, development and innovation programs are looking at ways to improve the use of different feedstocks and byproducts on pilot and industrial scales for the production of a wide range of products.

As presented by Lyko *et al*. (2009), in the currently propagated concept of the European Biorefinery it is planned to use seeds like wheat, rape, soya, lupines, rice, rye or peas, which are to be processed in industrial plants to obtain food oils, valuable food ingredients like gluten-free starch and pure gluten and derivatives for functional food, bioethanol, biogas and biodiesel. The shells of the cereals are to be processed to produce energy and even the incidental carbon dioxide is proposed to be used within the process chains as cover gas or to be sold. The European Biorefinery concept is supported by a pool of companies, which specialize in the engineering of biochemical conversion plants, in flour milling, bioethanol production, the production of food ingredients and the production of industrial gases. Currently no plant operating on this concept is known (Lyko *et al*., 2009).

As sugar, starch or oil containing raw materials are high value feedstock for the production of many valuable chemicals on the one hand, and the growing demand for fuels should be satisfied by non-food biomass on the other hand, the integrated (two-platform) biorefinery seems to be a very promising future model for processing different kinds of whole crops. Here fuels and building block chemicals are to be produced by thermochemical conversion of lignocellulose parts, while sugar, starch or oil containing kernels and fruits are reserved for biochemical/chemical conversion to valuable platform chemicals such as succinic acid or mono and diacylglycerols. Residues and waste from both conversion processes should be used to produce energy.

The two-platform refinery has not been realized at any large-scale production site yet (Lyko *et al*., 2009). However, integrated production sites can be realized in existing bioethanol or biodiesel plants, as well as in starch factories, paper mills or food processing industries.

The biorefinery concept incorporates the more efficient use of chemicals and materials at all stages in the supply chain, including growth and harvest, production and conversion, and final disposition of products. Biorefineries aim to use biomass for synthesis processes – for (co-)production of base chemicals, platform chemicals, transportation fuels, gaseous energy carriers – and energy production (heat, power, combined heat and power). By means of co-production of relatively (high) added value chemicals, the production costs of secondary energy carriers could potentially become market competitive (Zwart, 2006).

In essence, the biorefinery parallels the petroleum refinery: an abundant raw material consisting primarily of renewable polysaccharides and lignin enters the biorefinery and, through an array of processes, is fractionated and converted into a mixture of products, including transportation fuels, co-products, and direct energy. The biorefinery concept is supported by economies of scale and by efficient use of all incoming bioresources (Ragauskas *et al*., 2006).

Cherubini and Ulgati (2010) have presented the simplified system boundaries for the biorefinery and fossil reference systems in Figure 2. The biorefinery chain starts at the top of the diagram using agricultural residues made by carbon fixation from the atmosphere via photosynthesis. At the end, the biorefinery system supplies products and services. By contrast, the fossil reference system starts with consumption of nonrenewable sources (i.e., fossil oil and natural gas). Since production of the biomass feedstock requires a raw material previously dedicated to other purposes (i.e., left in the field to enhance soil fertility), the reference system also includes an alternative raw material use (residues ploughed back into the soil).

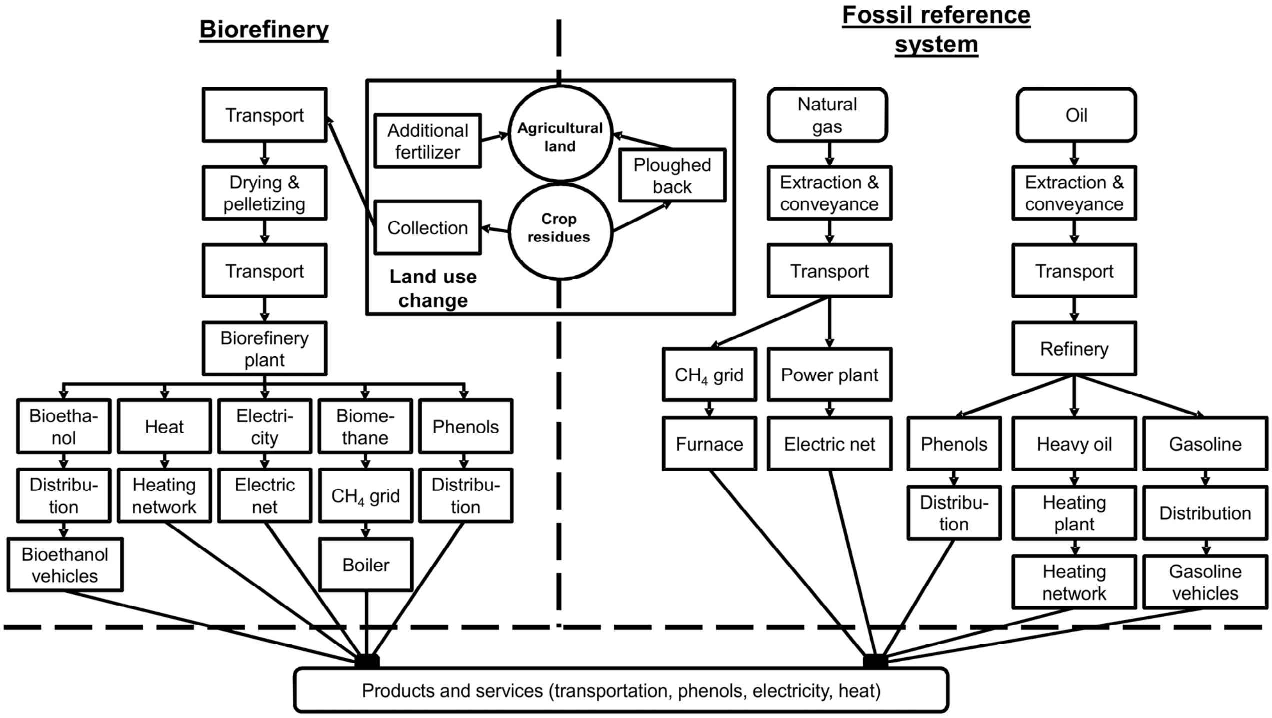


Figure 2: Comparison between the production chains of the biorefinery and the fossil reference system (Cherubini and Ulgati, 2010)

Where biorefineries operate at present, the product range is still limited to simple materials (i.e., cellulose, ethanol, biofuels and chemicals). Second generation biorefineries need to be built on the concept of sustainable chemical products through modern and proven green chemical technologies such as bioprocessing, thermochemical conversion including pyrolysis, Fischer-Tropsch, and other catalytic processes in order to make more complex molecules and materials on which a future sustainable society will be based (Naik *et al*., 2010).

Future biorefinery operations will first extract high-value chemicals already present in the biomass, such as fragrances, flavoring agents, food-related products, cosmetics related products, and high-value nutraceuticals. The availability of phenolic compounds with antioxidant activity from agricultural and industrial residues, for example, has been studied. Rodrigues *et al*. (2008) investigated phenolic compounds from coconut shell, which is similar to the woods used to store and age alcoholic beverages. During the ageing process phenolic compounds are extracted by lignin ethanolysis from the wooden casks. Sousa and Correia (2012) evaluated the phenolic content, the antioxidant activity and the antiamylolytic activity of extracts obtained from bioprocessed pineapple and guava wastes for producing biologically active products and enhance the value of fruit residues by providing a source of health relevant compounds. Phenolics are also used in the food industry as anti-microbial agents and food stabilizers (Martins *et al*., 2011).

In the last decades, there has been an increasing trend towards the utilization of the solid-state fermentation technique to produce these compounds. As a whole, the support material must present characteristics favorable for microorganism development and be of low cost. These characteristics are easily found in many residual natural materials derived from agricultural and agroindustrial activities. In addition, the use of these residues as carbon sources through solid-state fermentation provides an important way to reduce the fermentation cost and avoid environmental problems caused by their disposal, representing an economical and interesting solution for countries with an abundance of these materials. Several of these residues, including coffee pulp and husk, sugarcane and agave bagasses, fruit pulps and peels, corn cobs, among others, have been used as supports and/or substrates for the production of valuable compounds by solid-state fermentation, including enzymes (Guimarães *et al*., 2009; Mamma *et al*., 2008; Oliveira *et al*., 2006), organic acids (John *et al*., 2006; Sharma *et al*., 2008; Vandenberghe *et al*., 2000), antibiotics (Adinarayana *et al*., 2003; Ellaiah *et al*., 2004), flavor and aroma compounds (Medeiros *et al*., 2006; Rossi *et al*., 2009; Sarhy-Bagnon *et al*., 2000), and bioactive compounds (Hernández *et al*., 2008; Vattem and Shetty, 2003).

Once these relatively valuable chemicals are extracted, the biorefinery will focus on processing plant polysaccharides, lignin and residues from biochemical processes into feedstock for bio-based materials and fuels (Ragauskas *et al*., 2006).

There is increasing interest in the development of biodegradable plastics, biobased polymer products and plant derived composite materials, also referred to as “green” composites (Khalil *et al*., 2012; La Mantia and Morreale, 2011; Rosa *et al*., 2010; Spagnol *et al*., 2012), which may perfectly fit into the biorefinery scenario. The biorefinery concept has been applied to a variety of biomass sources, such as forest residue biorefinery (Mabee *et al*., 2005), wheat straw biorefinery (Deswarte *et al*., 2008), palm oil and oil palm biomass-based biorefinery (Chew and Bhatia, 2008), and corn biorefinery (Haung *et al*., 2008). Naik *et al*. (2010) presented part of a research program aimed at the integrated utilization of Jatropha in India and cereal crop residues in Canada, attempting to contribute to the first generation biofuels production (e.g., biodiesel) and parallel use of the residues for energy, second generation biofuels and related chemicals production from non-food crops. In addition, some biorefinery concepts based on different biomass feedstocks for second generation biofuels and their bioproducts were discussed.

Research institutions and industries in Brazil have been promoting and supporting the development of biorefineries as a great opportunity for expansion of the national bioenergy sector. The development of biorefineries is starting with sugarcane residues from sugar and ethanol production, which already represent a successful example of sustainable utilization of residues from biofuel production. The primary use of the fibrous byproduct (sugarcane bagasse) today is as an energy source in sugar/ethanol mills, providing the heat and electricity requirements for sugar and ethanol production and some electricity surplus to the national grid, electricity being currently consolidated as an additional product of the Brazilian sugarcane sector.

Since the feedstock is already available at the plant site (bagasse), or close to it (sugarcane trash), second generation biofuel production may share part of the infrastructure where first generation ethanol production takes place (Dias *et al*., 2012a). Electricity production has a great potential for expansion as mills adopt modern, commercial high pressure-temperature co-generation systems and integrated biomass gasification combined cycle systems (Botha and von Blottnitz, 2006; Lora and Andrade, 2009; Seabra *et al*., 2010), from which a range of new products can be produced through catalytic synthesis, besides electricity.

Thus, biorefineries should integrate thermochemical routes to the biochemical (ethanol from lignocellulosic biomass), chemical (transesterification for biodiesel production) and physical (briquetting and pelletization) processes, which may result in a much bigger and more diverse range of products compared to what is obtained nowadays from the same feedstock (Demirbas, 2009; Lyko *et al*., 2009; Menon and Rao, 2012; Seabra *et al*., 2010). This implies more efficient use of renewable sources.

Regardless of which process technologies are incorporated into a biorefinery, almost all will generate some waste products. These spent biomass residues will contain fragments from lignin, residual carbohydrates, and other organic matter, requiring treatments that are environmentally compatible, with the smallest ecological footprint. Such wastes and residues offer important energy sources within the biorefinery, given their chemical energy content, and are an ideal candidate for thermochemical conversion to syngas (Sricharoenchaikul *et al*., 2002) and derived products, which is further discussed in the following sections.

Logistics and Biomass Pretreatment for Thermochemical Processing

Portability, storage capacity and energy density are important attributes that help consolidate and broaden the share of an energy source in the energy matrix. Ethanol and biodiesel, for example, have portability, which facilitates their transportation to and storage in foreign countries, as opposed to electric power, which has transmission limitations. Biodiesel has the same characteristics as ethanol, but greater density, which reduces the relative transportation and storage costs (Brasil, 2006).

Crop wastes and agroindustrial residues frequently are not used as energy sources because they have poor energy characteristics (low density, low heating value, and high moisture content), causing high costs during transportation, handling, and storage. Some of these drawbacks could be overcome if physico-chemical technology was applied to improve physical and chemical properties of biomass residues.

Biomass feedstock logistics encompass all of the unit operations necessary to move biomass feedstock from the land to the energy plant and to ensure that the delivered feedstock meets the specifications of the conversion process. The packaged biomass can be transported directly from farm or from stacks next to the farm to the processing plant. Biomass may be minimally processed (i.e., ground) before being shipped to the plant, as in the case of biomass supply from the stacks. Generally the biomass is trucked directly from farm to biorefinery if no processing is involved. Another option is to transfer the biomass to a central location where the material is accumulated and subsequently dispatched to the energy conversion facility. While in the depot, the biomass could be preprocessed minimally (ground) or extensively (pelletized). The choice of any of the options depends on the economics and cultural practices (Zafar, 2012).

Physical pretreatments are the most commonly applied for thermochemical biomass conversion. Comminution of lignocellulosic materials is usually carried out through a combination of chipping, grinding, and/or milling. The size of the materials is usually 10–30 mm after chipping and 0.2–2 mm after milling or grinding.

The usual practice is that the harvested biomass is naturally dried before being transported by truck to a pretreatment plant. The first step of the pretreatment is size reduction and further active drying, after which the actual pretreatment conversion takes place. Other configurations need to be proposed for other biomass types (e.g., industrial residues). Biomass forms which are suitable for cost-effective transport over longer distances and allow transshipment with bulk handling processes are chips, pellets, bio-slurry, and torrefied pellets. To take advantage of the conversion of the biomass into an easily transportable form, the pretreatment plant should evidently be located preferentially near the production location of the biomass (Zwart *et al.*, 2006).

The final particle size and biomass characteristics determine the power requirement for mechanical comminution of agricultural materials. The energy consumption for size reduction of hardwoods and agricultural wastes as a function of final particle size and comminution ratio (size reduction) was quantified by Cadoche and Lopez *apud* Kumar *et al.* (2009). It was proposed that, if the final particle size is held to the range of 3–6 mm, the energy input for comminution can be kept below 30 kWh per ton of biomass.

Zwart *et al.* (2006) have presented biomass pretreatment as an important part of the Biomass-to-liquid (BTL) route, both to allow feeding of the biomass into the selected entrained-flow gasifier and to reduce transport costs by densification. To determine the technological and economic potential of BTL routes, integrated systems from overseas biomass to the Fischer-Tropsch product were assessed on the basis of different pretreatment options: chipping, pelletization, torrefaction, and pyrolysis.

Svoboda *et al.* (2009) have compared advantages and disadvantages of different methods for biomass (wood) thermal pretreatment (drying, torrefaction, flash pyrolysis and dissolution of wood in organic solvents) and grinding for feeding of the biomass-fuel to a pressurized entrained flow gasifier. The resulting fuels after pretreatment were compared in terms of heating value, grinding energy needed, overall efficiency of conversion (from raw biomass to fuel), auxiliary energy needed, fluidization properties, pneumatic feeding properties, pumping, viscosity and possible changes of properties of liquids/slurry, storage, microbial attack, emissions from thermal pretreatment and overall integration with pressurized entrained flow gasification. Advantages and disadvantages of individual methods for biomass pretreatment, grinding and feeding were summarized and important information relating to these biomass pretreatment processes are summarized in Table 1.

Biomass residues can be densified into pellets or briquettes in order to provide more energy per unit of volume, to improve transportation, storage and thermochemical processing (Felfli *et al.*, 2005a, 2005b, 2011; Suárez and Luengo, 2003).

In 2010, world pellet production reached 16 million tons. According to ABRAF (2012), Europe was responsible for approximately 67% of this production, followed by North America, which accounted for approximately 30% of the total volume produced. With regard to pellet consumption, Europe and North America are also the most important regions. Household consumption was the main destination: 8.5 million tons (54%), followed by industrial consumption with 5 million tons (31%) and commercial consumption with 2.4 million tons (15%).

Table 1: Characteristics of biomass pretreatment for thermochemical processing

Pretreatment	Process characteristics	Biomass form	Bulk density ($kg.m^{-3}$)	Advantages	Disadvantages
Size reduction (grinding, milling, pulverization)	Grinding. Power depends on biomass character (soft and hard wood, herbaceous biomass) content of moisture, extend of size reduction and way of disintegration	Chips (≥1 cm)	~350	Readily transportable and transshipped by bulk handling processes	Because of the relatively low bulk density, costs of transshipment, transport, and storage are relatively high
	Cutter mill. Estimated power consumption (related to thermal power or energy – heating value of wood) of 0.014 kW_e/kW_{th} (for 1 mm) and 0.055 kW_e/kW_{th} (for 0.2 mm) (Svoboda *et al*., 2009)	Particles, (1-0.2) mm	>350		Gasification: the milled wood still cannot be fed with conventional systems (typically applied to coal), as, because of the fibrous nature of the biomass, it does not fluidize and fluffs are formed that plug the piping (Zwart *et al*., 2006)
	Vibration mill. Estimated power consumption for final average sizes of ~0.100 mm is 7% of the energy value of the biomass (Zwart *et al*., 2006). Estimated power consumption (related to thermal power or energy – heating value of wood) of 0.03 kW_e/kW_{th} (for 0.2 mm) and 0.06 kW_e/kW_{th} (for 0.035 mm) (Svoboda *et al*., 2009)	Particles, (0.2-0.035) mm	>350		
Pelletization	n.a.	Pellets	~(450-650)	Increased biomass bulk density. Suitable for bulk handling (Zwart *et al*., 2006)	n.a.
Torrefaction	Typical conditions for dry torrefaction are: temperature range of 230-300 °C, near atmospheric pressure, absence of oxygen and relatively low particle heating rate (less than 50 $°C.min^{-1}$) during the process (Svoboda *et al*., 2009)	Torrefied biomass (wood chips, branches, leaves, needles, straw, etc)	<350	The main changes in biomass due to torrefaction involve decomposition of hemicellulose, partial depolymerization of lignin and cellulose (shortening of cellulose macrofibrils) (Svoboda *et al*., 2009). The product has higher content of carbon, lower mass and higher $LHV.kg^{-1}$. The material becomes dry, hydrophobic and brittle, can be transported as torrefied wood chips, which are suitable for bulk handling or can be easily milled, with lower electricity compared to the input biomass (Svoboda *et al*., 2009; Zwart *et al*., 2006). The combustible gas is typically used to provide the heat for the torrefaction process (Bergman *et al*., 2005a, 2005b), Bergman, 2005). Torrefied wood is suitable for storage and more stable against attacks of microorganisms than dried wood (Svoboda *et al*., 2009)	Torrefied branches, leaves, needles, straw, etc, carry too many fines during feeding (Zwart *et al*., 2006)

Continuation Table 1

Pretreatment	Process characteristics	Biomass form	Bulk density (kg.m^{-3})	Advantages	Disadvantages
	Suitable temperature for torrefaction (from the point of view of possible autothermal torrefaction process and low energy consumption in subsequent milling) is between 270–280 °C, sufficient holding (residence) time about 0.5 h (Svoboda *et al*., 2009)	Pellets of torrefied biomass (Bergman *et al*., 2005a)	~850	The energy consumption for milling of torrefied wood from cm pieces to size fraction below 0.4 mm is approximately 3 to 7 times lower (depending on temperature and time of torrefaction) than for untreated, partly dried wood with moisture content 12-16 wt.% (Svoboda *et al*., 2009). Pellets present increased energy and material density. This also happens in normal pellets; however, because of the resilient nature of fresh biomass, the increase in density is much smaller (Zwart *et al*., 2006)	Approximately 10-20% of the energy content of original dry wood is lost in production of torrefied wood. For straw and grass the energy loss is moderately higher (Svoboda *et al*., 2009)
Pyrolysis	Slow pyrolysis	Char	~(100-200)		Contains only approximately 50% of the energy of the biomass (Antal and Grønli, 2003). The remainder is contained in the (tar-rich) pyrolysis gas, which has to be used on site and is not available for Biomass-to-liquid production if the Fischer-Tropsch process is located elsewhere. Not considered to be a feasible general option because of the low efficiency (Zwart *et al*., 2006)
	Fast pyrolysis	Bio-oil, char and pyrolysis gas (70%, 20% and 10% of biomass energy, respectively) (Wang *et al*., 2005)	~1200 (bio-oil)	The gas can be used to generate the electricity for the plant, and about half of the char is required to produce the heat for the pyrolysis process. The other half is surplus. However, in most cases, it is burned inside the process as well (Zwart *et al*., 2006)	The efficiency of bio-oil production is considered low for large-scale BTL production; therefore, it is not considered to be a feasible option (Zwart *et al*., 2006)
		Bio-slurry (mixture of bio-oil and char). Content of char between 10-25 wt.%	~1200	It can be transported and handled as a liquid (comparable to heavy oil). Therefore, bio-slurry, unlike bio-oil, is considered to be a feasible candidate option (Zwart *et al*., 2006). It can be fed to a pressurized entrained flow gasifier by suitable pumping with possibility to avoid consumption of an auxiliary gas (Svoboda *et al*., 2009)	Health, safety, and environmental aspects of bio-slurry are not yet clear (Zwart *et al*., 2006). For better spraying in a pressurized entrained flow gasifier some auxiliary gas is often needed. The fast pyrolysis technology for bio-oil production is more sophisticated than the production of torrefied wood. Long term storage of bio-oil and corrosion properties (due to high content of organic acids) is problematic (Svoboda *et al*., 2009)

The use of pellets in the industrial sector is more common in countries where electricity production or central heating plants rely on the burning of biomass, as in the case of Sweden, Denmark, Holland, Belgium and the United Kingdom. Countries such as Germany, Italy and Austria, as well as countries in North America are more focused on residential heating. In both cases, fostering mechanisms have been important in the growth and driving of these demands. Brazil has twenty industrial pellet plants in operation, as well as new projects announced, most of them located in the South. Among the factors that lead to the consolidation of the pellet market in the national scenario, the reduced dependency on fossil fuels, the availability of waste generated by the wood sector, and growing demand stimulated by governmental incentive mechanisms have been highlighted. Brazilian production, consumption, import and export of pellets are still incipient; however, in the medium and long terms, the demand will tend to grow and stimulate production, domestic consumption and exports (ABRAF, 2012).

Biomass briquettes are not widely produced in Brazil yet. The expansion of this sector depends basically on three factors: residue availability for briquetting, adequate technologies and the market for briquettes, as presented in a study of the status of biomass briquetting and its perspectives in Brazil conducted by Felfli *et al*. (2011), which included determination of the availability and characteristics of the agroresidues for briquetting.

Brazil accounts for approximately one third of the charcoal production worldwide. Around ninety percent of that is destined to the Brazilian production of pig-iron, alloy iron, fused iron, steel and iron-based products, pure silicon, among others. Almost 75% of the charcoal is still produced through traditional processes (handcraft method) which have very low recovery of derivatives with a very negative environmental and social impact, given that powerful greenhouse gases like methane are released during charcoal production (Kammen and Lew, 2005; Rosillo-Calle *et al*., 1996).

The wood used for carbonization comes, in its majority, from reforested eucalyptus plantations. Reduced growth of reforested areas compared with the rate at which the demand increases, as well as the increase in the distances between charcoal production and final consumers are the main causes for an existing perception of lack of wood, popularly known as “forest shortage”. The development of a controlled, flexible, multi-product and integrated carbonization industry is a pressing need. Based on these premises, Peláez-Samaniego *et al*. (2008) explored several alternatives to improve the Brazilian carbonization industry in the context of the creation of a global biomass economy. The alternatives presented were based on the present charcoal needs and the potential advantage of other products derived from biomass carbonization.

Besides the use in the process of iron reduction, charcoal has many other uses which are poorly explored in Brazil, for example, in sugar refinement, as absorbent, in agriculture for soil amendment, etc. Charcoal is also an excellent feedstock for gasification. It can be gasified in conventional single step gasifiers to produce a synthesis gas with very low tar content. Different arrangements were proposed by Peláez-Samaniego *et al*. (2008), such as alternatives in which pyrolysis or carbonization units are located as part of the primary conversion or densification units in a biorefinery.

The production of pellets or briquettes of charcoal produced through modern pyrolysis technologies (fast pyrolysis) applied to forest residues would allow the obtention of bio-oil besides the charcoal and consequently reduce the atmospheric emissions usually associated with the traditional process, since heat would also be recovered from the gaseous product. A more detailed discussion of biomass pyrolysis as a pretreatment step in a biorefinery for bio-oil and char/bio-oil slurry production is presented below.

Integrating Thermochemical Processes Into the Biorefinery

Technologies for the thermochemical conversion of biomass to energy have recently received increased interest from the scientific community, governments, and industry. Biomass has the potential to displace petroleum-derived fuels and countries might be able to decrease their reliance on foreign petroleum significantly by deriving more energy from renewable feedstock. Thermochemical biofuels can often be produced locally, improving a country’s trade balance and its national security. Local agricultural industries can be supported and, since these approaches typically use the lignocellulosic materials contained in agricultural residues, forest byproducts or municipal waste, the impact on food production can be minimized.

The first step to implement the biorefinery concept is providing proper and dedicated logistics for the biomass supply. In this context, an extensive discussion on decentralized versus centralized processing plants has been conducted aiming at defining the most feasible options for biomass thermochemical conversion.

The integrated biorefinery concept has envisaged several decentralized pyrolysis plants implementing the logistics for collection, pretreatment (bio-oil production) and transportation of bio-oil to a centralized large-scale gasification and Fischer-Tropsch site, allowing the production of electricity, biofuels, fertilizers and chemicals at costs competitive with the ones obtained by the petroleum economy, as represented in Figure 3. Another option is to use the already installed oil infrastructure to process the bio-oil mixed with the fossil fuel equivalent.

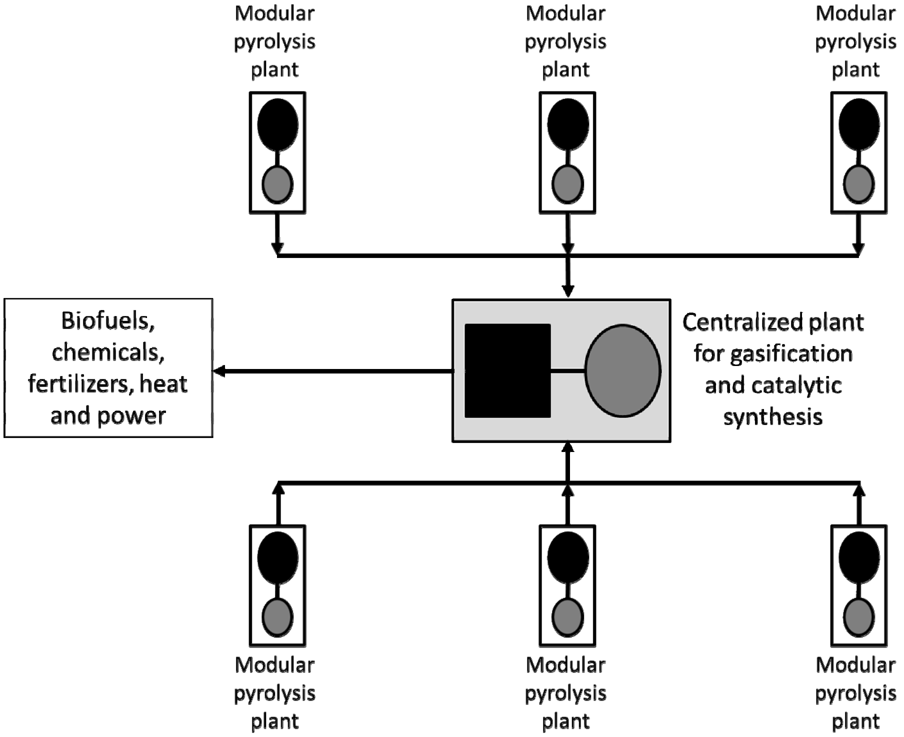


Figure 3: Proposed scenario for integrated biomass pyrolysis, bio-oil gasification and catalytic synthesis (Rocha, 2008, modified)

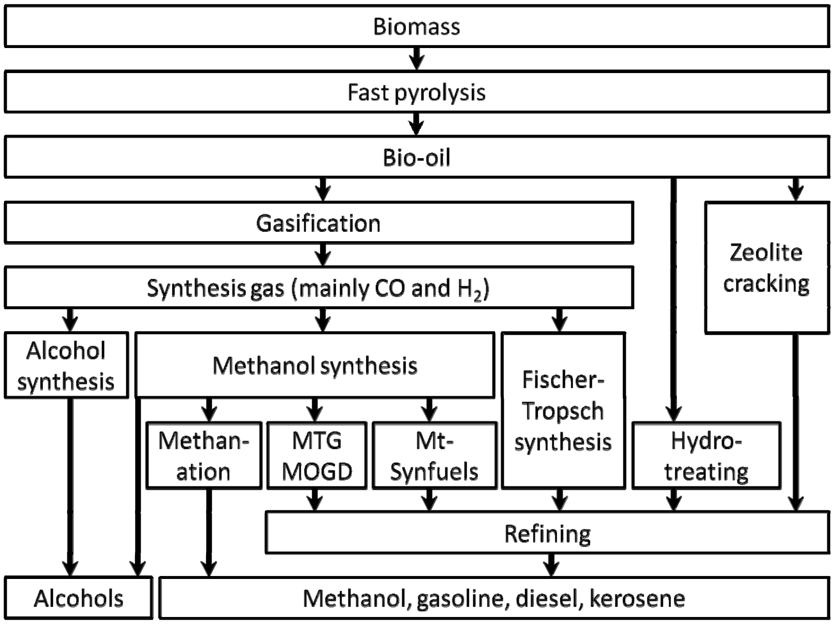
Among the thermochemical biomass conversion routes, combustion constitutes a well-established technology which has been applied to biomass residues for thermal energy generation (e.g., Floriani *et al*., 2010; Virmond *et al*., 2010, 2011), but biomass pyrolysis and gasification have attracted the highest interest as they can potentially offer higher efficiencies compared to combustion.

To truly understand and model these processes, detailed knowledge is required, ranging from structural information of raw biomass, elemental composition, gas-phase reaction kinetics and mechanisms, and product distributions (both desired and undesired). Considering the wide range of biomass sources, technology and products which can be obtained through biomass thermochemical conversion, it becomes important to integrate all these related aspects in order to optimize them and make them commercially available.

The thermochemical approach is largely based on existing technologies that have been in operation for a number of decades for conversion of coal-to-liquid (CTL) and gas-to-liquids (GTL) fuels and chemicals through the Fischer-Tropsch processes, which consist of technologies commercially available for obtaining a wide range of long chain hydrocarbon products such as gasoline, naphtha, diesel and wax. The long chain hydrocarbons produced are finally distilled, hydrocracked or upgraded before being used as a liquid transportation fuel (IEA, 2008; Laohalidanond *et al*., 2006; Zwart, 2006). These conversion routes have currently been applied to conversion of biomass-to-liquid (BTL).

The BTL approach combines elements of pyrolysis, gasification, and catalytic conversion. The potential product range can be increased if the entire platform is implemented in a biorefinery (IEA, 2008), as illustrated in Figure 4.

Integrating these processes to traditional industries such as the pulp and paper industry, based on forest biomass, and the sugar and ethanol industry, based on sugarcane has constituted the new arrangement of integrated biorefineries, which envisage technical, economic and environmental advantages.



MTG: Methanol To Gasoline.
MOGD: Methanol to Olefins, Gasoline and Diesel.
Mt-Synfuels: process developed by Lurgi to convert methanol to synthetic transportation fuels (gasoline, diesel) .

Figure 4: Upgrading of bio-oil to biofuels and chemicals (Bridgwater, 2012, modified)

Biomass Fast Pyrolysis and Bio-Oil Upgrading Routes

Fast pyrolysis of biomass with optimized yield of bio-oil is a possibility for biomass pretreatment. Essential features of a fast pyrolysis process are (Bridgwater and Peacocke, 2000; Zhang *et al.*, 2007):

- Very high heating and heat transfer rates, requiring feeding of relatively small biomass particles;
- Carefully controlled temperature, usually between 450 °C and 550 °C;
- Rapid cooling of the produced gases and vapors for bio-oil recovery.

As extensively reviewed by Bridgwater (1999b, 2012), Demirbas and Arin (2002) and Di Blasi (2009), pyrolysis of lignocellulosic materials can give rise to three product fractions: gases, vapors that give a pyrolytic liquid (bio-oil) and char. These products can result from both primary decomposition of the solid fuel and secondary reactions of volatile condensable organic products as they are transported through the particle and the reaction environment, also originating low-molecular weight gases and char.

This pyrolysis approach to biofuels is being pursued with biomass in general, with and without a catalyst. The main desirable product, bio-oil, is produced in yields typically between 60 wt.% and 80 wt.% (related to dry biomass feed). The byproducts are char (12–20 wt.%) and gas (10–20 wt.%) (Mohan *et al.*, 2006). The energy yield in bio-oil and char (heating value 24–32 MJ.kg^{-1}) together is about 90% (Bridgwater and Peacocke, 2000; Mohan *et al.*, 2006); for bio-oil derived from wood, it has been reported to be approximately 55–65% (Venderbosch and Prins, 2010). Some research results have shown that the oil yield is much less dependent on biomass particle size and vapor residence times than originally assumed (Wang *et al.*, 2005, 2006), although the oil composition is sensitive to these parameters (Venderbosch and Prins, 2010).

Apart from water, plant biomass sources are mainly composed of cellulose (mostly glucans), hemicellulose (mostly xylans), and lignin, consisting of highly branched, substituted, mononuclear aromatic polymers, often bound to adjacent cellulose and hemicellulose fibers to form a lignocellulosic complex. During pyrolysis, biomass is decomposed to a mixture of defragmented lignin and (hemi)cellulose and fractions derived from extractives (if present) (Venderbosch and Prins, 2010). Cellulose, hemicellulose, and lignin all have different thermal decomposition behaviors, which individually depend on heating rates and the presence of contaminants. Generally, the pyrolysis of any biomass can be considered as the superposition of these three main components (Orfao *et al*., 1999; Rao *et al*., 1998; Raveendran *et al*., 1996).

Hemicellulose is the first component to decompose, starting at about 220 °C, being complete around 400 °C. Cellulose appears to be stable up to approximately 310 °C, with almost all cellulose being converted to non-condensable gas and condensable organic vapors at 320–420 °C. Though lignin may begin to decompose already at 160 °C, it appears to be a slow, steady process extending up to 800–900 °C. At fast pyrolysis temperatures of around 500 °C, the conversion of lignin is probably limited to 40%. In general, a solid residue remains from fast pyrolysis, which is mainly derived from lignin and some hemicellulose fractions, respectively 40 wt.% and 20 wt.% of the original sample (Yang *et al*., 2007; Venderbosch and Prins, 2010). It can be concluded that the oil is derived mainly from cellulose, and only partially from hemicellulose (depending on the heating rate up to approximately 80% conversion to oil and gas) and lignin (roughly 50% conversion to oil and gas) due to differences in the inherent structures and chemical nature of the three components. Lignin and hemicellulose are linked through covalent bonds (ester and ether) and cannot be released that easily upon pyrolysis; cellulose and hemicellulose are linked by much weaker hydrogen bonds (Vaca-Garcia, 2008). Indirect evidence for this hypothesis is given by the composition of the pyrolysis-derived char, which has an elemental composition close to that of lignin (Venderbosch and Prins, 2010).

Crude pyrolysis liquid or bio-oil is a dark brown, free flowing liquid which approximates to biomass in elemental composition. It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product (ranging from about 15 wt.% to an upper limit of about 30–50 wt.% water, depending on the feed material, the process conditions and the way it was subsequently collected). Solid char may also be present (Bridgwater, 2012).

According to Bridgwater (2012), who presented the particular characteristics of bio-oil in detail, typical bio-oil can be considered to be a micro-emulsion in which the continuous phase is an aqueous solution containing a wide variety of low molecular weight oxygenated organic compounds (such as acetic acid, methanol, acetone), which stabilizes the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding. Aging or instability is believed to result from a breakdown in this emulsion. In some ways it can be considered to be analogous to the asphaltenes found in petroleum. The non-aqueous phase contains oxygenated compounds (such as aliphatic alcohols, carbonyls, acids, phenols, cresols, benzenediols, guaiacol and their alkylated derivatives), aromatic hydrocarbons (single ring aromatic compounds such as benzene, toluene, indene and alkylated derivatives) and polycyclic aromatic hydrocarbons (PAH, such as naphthalene, fluorene and phenanthrene, and alkylated derivatives) (Bridgwater, 1994, Williams and Nugranad, 2000).

Researchers at Aston University have discovered an innovative technique for suppressing the phase separation of bio-oils. The use of certain additives during pyrolysis of lignin-rich biomass results in a bio-oil which does not separate into distinct phases. The additives consist of high boiling point isoparaffinic liquid solvents acting as coolants, and an alcohol acting as a phase separation suppression agent.

While the liquid is widely referred to as “bio-oil”, it will not mix with any hydrocarbon liquids due to its highly oxygenated nature (35–40 wt.%), but it can be emulsified with diesel oil with the aid of surfactants (Bridgwater, 2012).

Upgrading bio-oil to a conventional transport fuel such as diesel, gasoline, kerosene, methane and liquefied petroleum gas requires full deoxygenation and conventional refining, which can be accomplished either by integrated catalytic pyrolysis or by a decoupled operation such as hydrotreating or hydrodeoxygenation to remove the oxygen as water under high pressures of hydrogen and in the presence of a catalyst (Bridgwater, 2012; Elliott, 2007; Mercader *et al*., 2010a, 2010b), catalytic vapor cracking using zeolites (Sharma and Bakhshi, 1993; Bridgwater, 2012), esterification and related processes, gasification to syngas followed by synthesis of hydrocarbons or alcohols (Bridgwater, 2012). There is also interest in partial upgrading to a product that is compatible with refinery streams in order to take advantage of the economy of scale and experience in a conventional refinery (Mercader *et al*., 2010a). Integration into refineries by upgrading through cracking and/or hydrotreating has been reviewed by Huber and Corma (2007) and

Bridgwater (2012).

The application of catalysis could be of major importance in controlling the oil quality and its chemical composition (Mihalcik *et al*., 2011; Mullen and Boateng, 2010; Mullen *et al*., 2011). Without any catalyst involvement, the bio-oil derived from fast pyrolysis is a mixture of hundreds of different, highly oxygenated chemical compounds. Catalysis could be applied for a number of reasons, and at a number of different positions in the process. Lower pyrolysis temperatures, a higher chemical and physical stability, high yields of target components, and an improved miscibility with refinery streams are all goals strived for. Bio-oils can be upgraded by either applying catalysts in the production process (catalytic pyrolysis), or by post-treatment of the bio-oil over a catalyst bed. This post-treatment may be the thermal cracking of re-evaporated bio-oil in a hot fluidized bed of Fluidized Catalytic Cracking (FCC) catalyst particles (bio-oil FCC), or the catalytic hydrodeoxygenation at elevated temperatures and hydrogen pressures (hydrotreatment) (Venderbosch and Prins, 2010).

The applicability of hydrodeoxygenation was studied by Mercader *et al*. (2010a) as a pyrolysis oil upgrading step to allow fluid catalytic cracking co-processing. The process proposed consists of co-processing upgraded pyrolysis oil from lignocellulosic biomass in standard refinery units, offering the following advantages: the use of decentralized pyrolysis plants near the biomass production site where only the oil is transported, reducing transportation costs due to the increase of the volumetric energy of the oil compared to the original biomass; after pyrolysis, most of the minerals from biomass are not transferred to the oil but remain as ash, thus resulting in a pyrolysis oil containing less inorganic material that could poison subsequent catalytic processes and in an ash that can be returned to the soil as fertilizer; because the upgrading plant would be next to (or inside) the refinery, all the necessary utilities would be already available and the product obtained after co-processing could use the existing distribution network.

These authors presented and discussed the results of the batchwise hydrodeoxygenation of pyrolysis oil produced from forest residues and the subsequent co-processing in a lab scale fluid catalytic cracking fluidized bed reactor. They showed that co-processing hydrodeoxygenated pyrolysis oils having an oxygen content up to 28 wt.% (on a dry basis) under standard lab scale fluid catalytic cracking conditions gave gasoline and light cycle oil range bio-hydrocarbons from a lignocellulosic feed source with similar product yields as were obtained from the base fluid catalytic cracking feed.

At the Technical University of Munich Lercher proposed a "one pot" approach based on aqueous-phase hydrodeoxygenation of phenolic monomers using bifunctional catalysis that couples precious metal catalyzed hydrogenation and acid-catalyzed hydrolysis and dehydration (Zhao *et al*., 2009). There is a significant hydrogen requirement in all hydrotreating processes to hydrogenate the organic constituents of bio-oil and remove the oxygen as water. The hydrogen could in principle be derived from processing an additional amount of biomass, for example by gasification. Alternatively, if only the organic fraction of bio-oil after phase separation is hydrotreated, the hydrogen required can be produced by steam reforming the aqueous phase (Huber and Dumesic, 2006). In all cases the upgraded product needs conventional refining to produce marketable products and this would be expected to take place in a conventional refinery (Bridgwater, 2012).

The first commercial production site for processing biomass to liquid was recently put into operation in Freiberg in Germany (capacity: 65,000 ton per year of biomass) by Choren Industries. It produces synthetic gasoline from lignocellulosic biomass by gasification and Fischer-Tropsch synthesis (Lyko *et al*., 2009).

Virtually no waste is generated in the biomass pyrolysis process as the bio-oil and solid char can both be used as fuel and the gas can be recycled back into the process as fuel for the generation of the required process heat, including feedstock drying (Bridgwater, 1999a; Bridgwater and Peacocke, 2000; Venderbosch and Prins, 2010). The byproducts left could also be applied otherwise. Active carbon, carbon black, or a pelletized fuel could be produced from the char. The char has also been proposed as a soil improver (biochar) (CSIRO, 2011; Kameyama *et al*., 2010; McHenry, 2009). For specific purposes, such as entrained flow gasification (syngas production, as described in sequence), recombination to the char/bio-oil slurry is considered, especially in the integrated biorefinery concept. The gaseous byproduct, essentially a mixture of CO and CO_2, can also be used for electricity production in an engine, if cleaned properly. Apart from possible flue gas emissions resulting from the char combustion, there are no waste streams. The ash in the original biomass will be largely concentrated in the char product and is separated when the char is combusted in the process for drying and heating the biomass feed stream. It allows recycling of the minerals as a natural fertilizer to the site where the biomass was grown originally (Venderbosch and Prins, 2010). The small particle size and high volatility of char, made in fast pyrolysis, cause it to be very flammable (auto ignition temperature between 200–250 °C), similar to powdered coal; hence, hot char must be properly handled. The ash content of the char is about 6–8 times greater than in the original feed and, as its alkali content is high, it may cause slagging, deposition and corrosion problems in combustion (Vamvuka, 2011).

For biomass types with high ash content, which is generally the case for the technologically interesting low-valued residues, the oil-yield can sometimes drop to values below 50 wt.%. Though extremely relevant for both the oil yield and oil quality, limited research has been carried out to understand the effects of ash on the pyrolysis reactions (Venderbosch and Prins, 2010).

Research on utilization of grape residues (redundant skins, stalks and seeds that remain once the juice has been extracted) for bio-oil production through flash pyrolysis was published by Xu *et al.* (2009). The authors presented the composition of the aqueous phase and an organic phase, showing that the organic phase is an attractive fuel with significant energy content, whereas the aqueous phase must undergo wastewater treatment. Therefore, the conversion of such residues to renewable energy would be attractive since it would solve pollution problems, reduce greenhouse gas emissions and provide a clean, low sulfur fuel. It is important to stress that the feedstock to be applied to thermochemical processes can be residues remaining from any processing type. In the case of grape residues, before subjecting the grape residue to pyrolysis, high value added products such as antioxidants can be initially extracted. It would definitely add value to the entire process and may be the key factor to make the entire process economically feasible.

Xiu *et al.* (2010) performed a series of laboratory scale experiments in a high-pressure batch reactor fed with mixtures of swine manure and crude glycerol (added as a co-substrate) at various ratios to produce bio-oil. The results indicated that co-hydrothermal pyrolysis of manure with crude glycerol or free fatty acid makes it possible to obtain a relatively high yield of bio-oil at a moderately high temperature. Even though laboratory scale research on pyrolysis of different biomass sources have been carried out, it is necessary to extrapolate them to the pilot scale so as to be able to technically and economically evaluate the feasibility for industrial application.

Biomass and Bio-Oil Gasification

Biomass gasification is generally a complex thermochemical process in which a solid fuel reacts with an oxidizing agent such as air, oxygen, steam, carbon dioxide, hydrogen or a mixture of these at temperatures in general above 700 °C, being converted into a gas mixture which contains carbon monoxide, carbon dioxide, hydrogen, methane, trace amounts of higher hydrocarbons such as ethane and ethene, water, nitrogen (if air is used as the oxidizing agent) and undesired impurities, such as tars, ammonia, sulfur-containing compounds, acidic species, and metals, depending on the biomass composition (Bridgwater, 2003).

As a renewable carbon source, biomass can be used as an alternative to fossil fuels for the production of “synthesis gas” (or syngas) – a mix of mainly CO and H_2 with some CO_2, methane and higher carbon compounds – by gasification with oxygen, CO_2 and/or steam.

The gaseous products composition is influenced by many factors such as the feed composition, water content, reaction temperature, and the extent of oxidation of the pyrolysis products (Bridgwater, 1995). A schematic process flow diagram for thermochemical conversion of sugarcane bagasse to ethanol, based on the 2007 NREL design report (Phillips *et al.*, 2007) for hardwood conversion to mixed alcohols using indirect steam gasification, developed by Seabra *et al.* (2010), is presented in Figure 5.

The gases generated are cleaned by removing the tars, and then filtered and the clean gas collected ready for use. Each syngas component (CO, CO_2, CH_4, H_2 etc.) could be recovered, separated and utilized. The volatile tar component, which can act as a technical barrier to large-scale production, has been exploited as a feedstock for value-added chemicals by companies such as Choren, Ensyn and Enerkem (Branca and Di Blasi, 2006).

Considering the residues from biofuel production, the usage of crude biodiesel byproduct (glycerol) as a fuel requires no refining or purification. Most previous research on crude glycerol as a fuel focused on catalytic steam reforming to produce hydrogen, owing to the relatively high content of hydrogen (Luo *et al.*, 2008; Slinn *et al.*, 2008; Valliyappan *et al.*, 2008). According to Yoon *et al.* (2010), application of the hydrogen produced is limited compared to syngas as costly metal catalysts such as nickel are used (Adhikari *et al.*, 2007, 2008). Additionally, the remaining catalyst (mainly alkaline) in the crude glycerol can cause problems with fouling of the catalyst surface and resistance to coke formation.

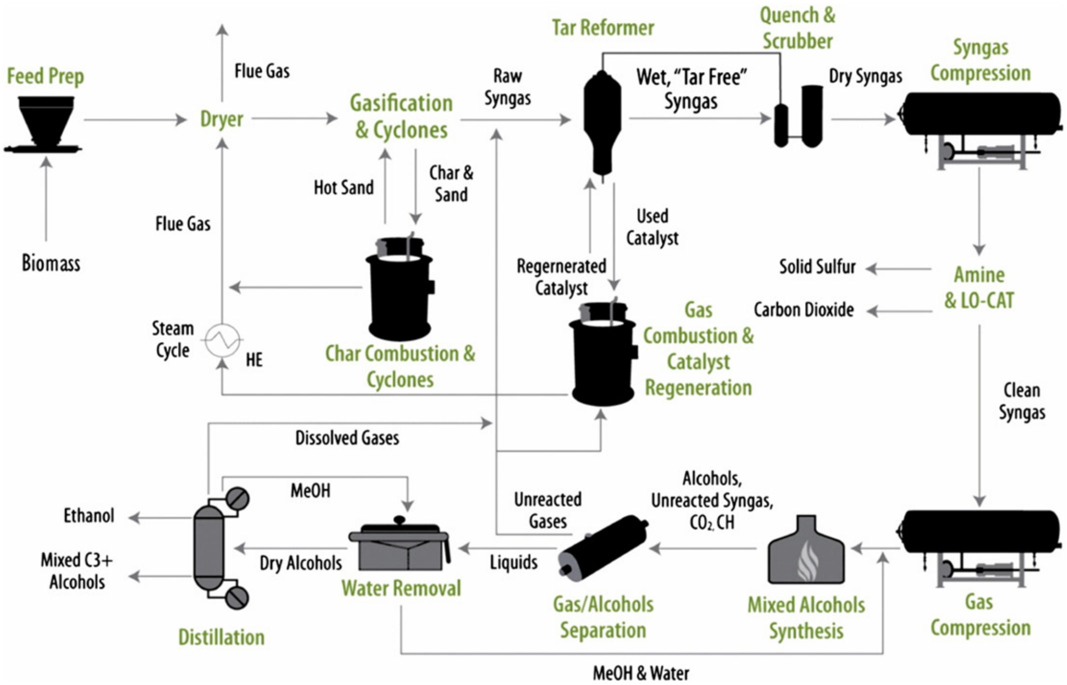


Figure 5: Schematic process flow diagram for thermochemical conversion of biomass to ethanol and higher alcohols (Seabra *et al*., 2010)

The syngas produced from crude glycerol can find a wide range of applications including use as feedstock for the production of a wide range of chemicals and as liquid fuels based on the Fischer-Tropsch processes, and in fuel cells and the electronics processing industries (Chmielniak and Sciazko, 2003; Higman and van der Burgt, 2008). Furthermore, in the gasification process, the alkaline catalyst, e.g., KOH, adopted for transesterification can be removed from syngas by scrubbing with water. After this, the aqueous solution can be neutralized with acid and the salt separated after crystallization.

van Rossum *et al*. (2009) studied the catalytic gasification of pyrolysis oil and catalytic gasification of glucose and glycerol in hot compressed water. They showed that the staged overall conversion of biomass to syngas is an example of a smart arrangement of the processes. In the primary conversion to pyrolysis oil, impurities, minerals and metals are concentrated in the char and, due to the mild process conditions (500 °C), a highly oxygenated reactive oil is produced. This oil can be effectively transported and, if desired, pressurized for the next conversion step. By reducing the cracking in the "re-evaporation" of the pyrolysis oil, the formed gas/vapor mixture can be readily reformed to syngas in a staged reactor system consisting of a fluid bed evaporator/atomizer and catalytic reformer in series. In contrast, a cracked methane and secondary/tertiary tar rich gas obtained under harsher evaporation conditions is more difficult to reform.

The studies addressed are only a few of many which have been carried out concerning the development and testing of gasification technologies that can be applied to a wide range of biomass materials. Thus, a great effort is still required in order to make the promising technologies industrially available and commercially competitive.

Pyrolysis and Gasification Technologies

This section gives some insight into pyrolysis and gasification technologies. It is not intended as a comprehensive review; for this, the reader is referred to recent publications in the field (e.g., Babu, 2008; Bahng *et al*., 2009; Bridgwater, 2003, 2012; Digman *et al*., 2009; Mohan *et al*., 2006; Qi *et al*., 2007; Vamvuka, 2011; Venderbosch and Prins, 2010). As presented by these authors, in recent years most of the research has centered on the development of important features of successful reactors dedicated to biomass conversion; these include very high heating rates, carefully controlled temperature, and rapid quenching of pyrolysis products. The main types of reactors were described by Venderbosch and Prins (2010) and are presented in Figure 6.

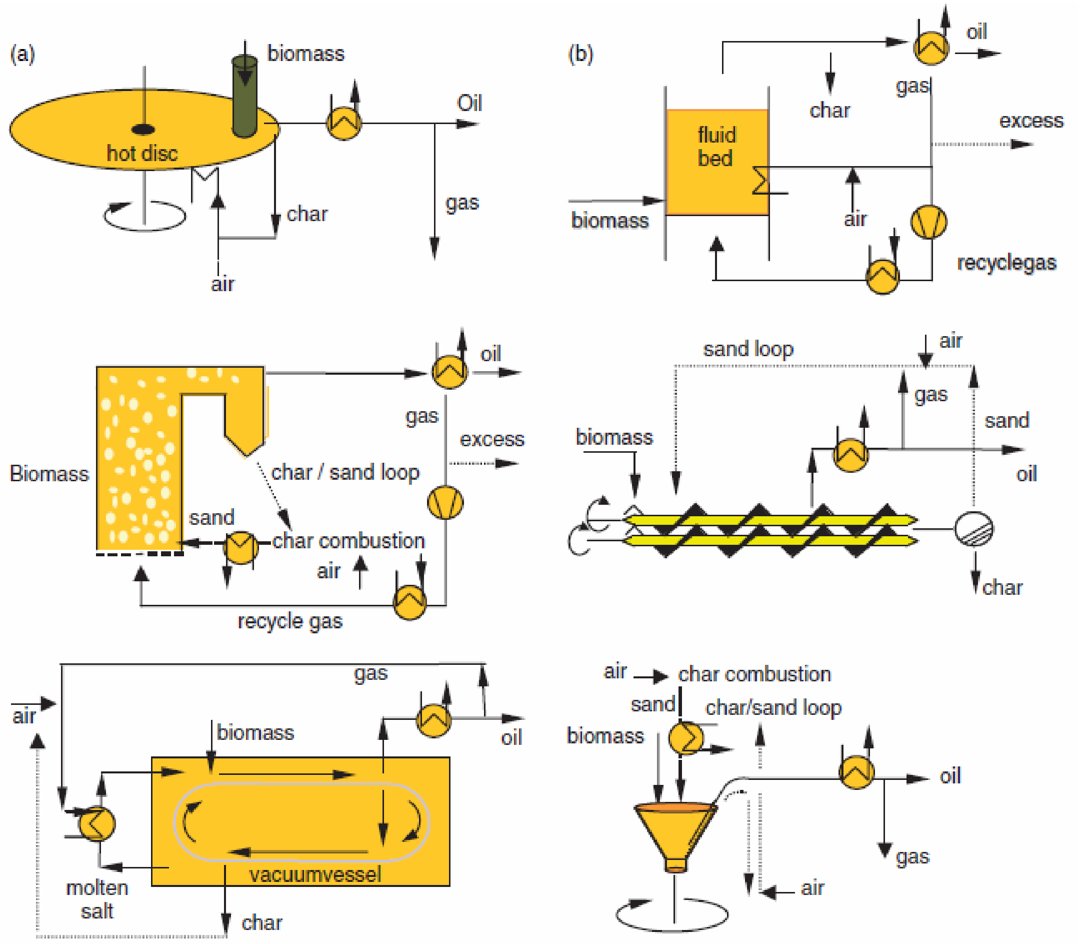


Figure 6: Main technologies applied to biomass pyrolysis. (a) Ablative, circulating fluidized bed and vacuum technologies. (b) Fluid bed, screw (auger) and rotating cone technologies (Venderbosch and Prins, 2010)

In pyrolysis, oxygen containing compounds (aldehydes, ketones, phenolics, and organic acids) make the oil too unstable and acidic for introduction into existing pipelines, tankers, and refineries (Bridgwater, 1999a). Thus, a primary research goal in biomass thermochemical conversion is directed towards the optimization of these processes to reduce the amount of unwanted byproducts if the oil is the preferred product.

The first facility using the fast pyrolysis principle in Brazil was described by Rocha *et al.* (2002). Bioware *Tecnologia* has grown and is scientifically supported by the University of Campinas, Brazil. Its main aim is to develop and produce high added-value products from forest and agro-industrial waste, using state-of-the-art and environmentally friendly technologies. Its research intends to develop biomass fast pyrolysis technology in a continuous atmospheric bubbling fluidized bed reactor in order to produce bio-oil and charcoal. The basic raw materials used are: elephant grass, cane trash and bagasse, which have already been processed with a measure of success. The bed temperature in the reactor fluctuates from 480 °C to 500 °C and the gas/feedstock mass ratio is 0.4 (dry basis). When the reactor operates under these conditions, the wet scrubber recovers an average of 40 wt.% bio-oil based on dry feed. The pilot facility, which is fully automated, has a nominal capacity of 300 kg.h^{-1} and was designed to produce bio-oil samples to be tested for laboratory and industrial applications. The bio-oil could be used as an emulsifying agent for heavy petroleum, an additive for cellular concrete, a substitute of phenol in PF resin formulations and fuel for the generation of energy. Moreover, the charcoal produced could be used as fuel in furnaces, as a pre-reducer for iron ore pellets, activated carbon and catalytic substrate. The supply of cheap raw materials to be used in the Bioware process is plentiful and practically limitless. Specifically, great support and interest have been shown by the Brazilian sugarcane industry regarding this technology. In addition, the pulp and paper sawmill and rice industries have expressed interest in becoming active partners. The company already cooperates with many national groups and companies (Rocha *et al*., 2002, 2004).

Wang *et al*. (2008) presented the configurations of the more common gasifier types and summarized the key features of each one. Even though different types of gasifier configurations have been developed, downdraft gasifiers are most often offered commercially, followed by fluid beds, updraft and other gasifier types (Bridgwater, 2003).

Fixed-bed, counter-current (updraft), and concurrent (downdraft) gasifiers are, in general, of very simple construction and operation. They also present high carbon conversion, long solid residence times, and low ash carryover. The updraft process is more thermally efficient than the downdraft process, but the tar content of the gas is very high (Di Blasi *et al*., 1999).

Performance of the air gasification depends on the initial air temperature supplied to the gasifier. In general we can distinguish gasification where cold or slightly preheated air is used, or the high-temperature air/steam gasification process (Blasiak *et al*., 2002; Lucas *et al*. 2004; Tsuji *et al*., 2002) in which high-temperature air or steam is used. The initial temperature of the feed gas determines the heating value of the dry fuel gas produced. In other words, the higher the air temperature the higher the heating value of the dry fuel gas that can be obtained.

Chars are formed as part of the biomass pyrolysis, and their formation involves the biomass drying, loss of volatiles and structural rearrangements in the solid phase. The char must then be converted efficiently to gas by a combination of gasification and combustion. In high-temperature (oxygen-blown, entrained flow and fixed bed) gasifiers this must occur during the short residence times, where the reactions are fast and efficient. In lower-temperature gasifiers (air-blown fluidized and fixed bed), complete conversion in one reactor is difficult to achieve given that the reactivity of the char diminishes rapidly. An additional reactor is then needed to burn the remaining carbonaceous material. In this type of gasifier, a greater understanding of the way the char reactivity changes with operating conditions can potentially be useful in maximizing the efficiency and economics of the overall system (Cousins *et al*., 2006).

In fixed-bed counter-current (updraft) and concurrent (downdraft) air gasifiers, different process are stratified along the bed height, such as biomass preheating, drying and pyrolysis, char gasification and char and volatile combustion. For updraft gasification, it is essentially the exothermic gasification of char which provides the heat for the exothermic gasification processes. For the downdraft configuration, homogeneous combustion of volatile pyrolysis products predominates over char combustion, which is still important for the stabilization of the reaction front. Given the large particle sizes required by these technologies, heating rates during the devolatization stage are much slower than those of fluid bed reactors (Di Blasi *et al*., 1999).

The recent technological progress on cyclonic gasifiers, a type of entrained flow reactor, may increase the application and the efficiency of biomass gasification processes in relation to conventional gasifiers, besides eliminating the necessity of complex gas cleaning systems (Gabra *et al*., 2001; Griffiths *et al*., 2000; Syred *et al*., 2004).

More recently, Wang *et al*. (2008) reviewed the recent advances in biomass gasification and syngas utilization and the critical technical issues and perspectives of biomass gasification were discussed. Production of syngas from coal, natural gas, and other carbonaceous sources is well established. Coal is normally gasified in entrained flow reactors at temperatures exceeding 1400 °C at 20–70 bar. Biomass is more reactive than coal and is usually gasified at temperatures between 800 °C and 1000 °C at 20–30 bar.

The greatest challenge in producing syngas from biomass in entrained flow pressurized gasifiers is biomass feeding. For relatively short residence times of fuel particles in the reactor, the biomass particles must be sufficiently small, relatively dry and they should be transported from atmospheric conditions to pressurized conditions in the entrained flow reactor. The pulverized fuel feeding system for coal feeding to this type of reactor can be applied to biomass (wood) under the assumption that the properties of biomass particles are similar. As described by Svoboda *et al*. (2009), a dense phase pneumatic transport, fluidized bed and lock hoppers with an inert gas could be considered. Pneumatic transport systems are not suitable for fibrous and needle-like biomass materials. Fluidization of pulverized wood (particle diameter <0.2 mm) is also difficult (Cui and Grace, 2007; van den Drift *et al*., 2004), because of high cohesion forces between the particles and channeling. In pneumatic feeding and lock hoppers only non-condensing inert gases and vapors can be considered (nitrogen, CO_2 and superheated steam) (Salman and Kjellström, 2000). Screw feeding of wood powder suffers from fluctuations of flow rates

(Joppich and Salman, 1999) and some corrections (e.g., vibration slabs) should be connected to them to smooth the feeding. Due to problems with high energy consumption and feeding of small wood particles, conceptions of feeding bigger wood particles (about 1 mm) have been suggested (van den Drift *et al*., 2004). Pressurizing of biomass fuels to high pressures (over approximately 2 MPa) is mediated by lock hoppers, pressurized usually by an inert gas (N_2 or CO_2). Another possibility for pressurizing to relatively lower pressures (less than approximately 1.8 MPa) is piston feeding (Svoboda *et al*., 2009).

Another challenge is the need to avoid poisoning the noble metal catalysts used in the subsequent downstream conversion to fuels and chemicals (Devi *et al*., 2003). Potential problematic products are the alkali metals, halides, sulfur gases, and especially the tars. A high quantity of tar is produced during the pyrolysis step as the organic components of biomass decompose. Evolution of tar from primary to tertiary species is rapid, but tertiary tar species are degraded slowly to CO and H_2 by water vapor or CO_2 at temperatures below 1100 °C. Catalytic conversion of tar in raw syngas to CO and H_2 is practiced, but the quantities of tar that must be converted are large, and robust catalysts that are insensitive to alkali metals, halides, sulfur, and nitrogen need to be developed (Ragauskas *et al*., 2006). Besides deactivating catalysts, the tars that are entrained with the vapor can plug transfer lines and damage compressors (Phillips, 2007).

Also presented by these authors, chloride, the predominant halide in biomass, is converted to HCl or sub-micrometer aerosols of potassium and sodium during gasification, which pose a corrosion issue. Most of the alkali metal chlorides are removed by filtering the cooled syngas. Sulfur gases can be removed by absorption. Remaining alkali metal chlorides and sulfur gases are removed by reaction with ZnO in a packed-bed filter.

Beside problems with slagging behavior of ash in high temperature biomass gasification (Coda *et al*., 2007), there are problems in feeding biomass to entrained flow pressurized gasifiers. Especially because of the fibrous nature of the biomass, it does not fluidize and fluffs are formed that plug the piping (Joppich and Salman, 1999; Zwart *et al*., 2006). Additionally, there are important requirements of disintegration of wood (biomass) and separation of the pressurized conditions in the gasifier from atmospheric conditions in the feeding line. In the context of integrating biomass pyrolysis to bio-oil gasification and catalytic synthesis, the feeding of bio-oil and the possibilities for production of slurries of bio-oil and char (such as previously presented in Tab. 1) and other slurries have been assessed.

Char from fast pyrolysis of biomass can be used either for heating the process of pyrolysis or can be ground and mixed with bio-oil. As proven experimentally by Henrich and Weirich (2004) and later on described by Svoboda *et al*. (2009), properly ground char particles (particle diameter <0.05 mm) in the form of a slurry with bio-oil (mass ratio char/bio-oil between 0.1–0.25) are pumpable and relatively stable. The viscosity of a char/bio-oil slurry is several times to 1 order higher than the viscosity of the pure bio-oil (depending on char content) and the slurry exhibits thixotropic behavior. For better pumping and spraying of the slurry in the entrained flow reactor, higher temperatures should be applied (50–80 °C). Due to the content of carbonaceous char in the slurry, the average content of oxygen in such a fuel is lower than in the original bio-oil and the carbon and oxygen demand in entrained flow gasification is higher. The lower heating value of such a char/bio-oil slurry is typically 20–22 $MJ.kg^{-1}$ and the LHV resembles the heating value of properly torrefied wood.

Other possibilities include mixing ground (pulverized) wood, torrefied wood or biochar with other bio-liquids, particularly waste liquids, to prepare pumpable slurries. Raw glycerol from production of biodiesel (Demirbas, 2007; Fernando *et al*., 2007), waste alcohols (ethanol, propanol etc.) or phenolic compounds (Maldas and Shiraishi, 1997) from biorefineries are examples of such waste bio-liquids (Svoboda *et al*., 2009).

Glycerol has a LHV similar to bio-oil (16 $MJ.kg^{-1}$) and a relatively high boiling point (290 °C). Its relatively high viscosity at lower temperatures can be reduced by heating to higher temperatures or by addition of alcohols. At higher temperatures (over 100 °C), glycerin partly dissolves wood, particularly under the hydrolytic and catalytic effects of acids (Kržan *et al*., 2005) or hydroxides and alkali carbonates (Kurimoto *et al*., 1999; Demirbas *et al*., 2000).

In spite of many years of research and commercial endeavors, cost effective and reliable methods of biomass gasification on the commercial scale remain elusive. Various gasification technologies have been developed and commercialized, but have been focused on gasification for power generation, where high calorific value gas is the target and impurities less of an issue than for Fischer-Tropsch synthesis (IEA, 2008). Although advances in syngas purification technologies are necessary for the catalytic conversion of syngas to other fuels or chemicals, they add further complications and increase the overall cost.

REMARKS AND CONCLUSION

Crop wastes, agroindustrial, forest and wood residues, byproducts from biofuel production such as the press cake from seeds, fruit bodies, empty fruit bunches as well as the leaves of the plant (with low or no commercial value) and crude glycerol, are amongst the many residues available in Brazil, offering great opportunities for interesting product outlets, representing a potential and highly available option to increase the bioenergy share in the country. A moving from residues towards alternative energy sources and high value products can also represent an option to improve the sustainability of the bioenergy chain, reducing negative environmental impacts related to inappropriate disposal.

These residues frequently are not used as energy sources due to their poor energy characteristics (low density, low heating value, and high moisture content), which can incur high costs during collection, transportation, handling, and storage. Additionally, the inappropriate removal of agricultural residues from fields may give rise to concerns of soil quality, decrease in soil organic carbon, soil erosion, crop yields and other environmental implications. Even though some research on these subjects can be found, it is important to increase the efforts on the development and implementation of the biorefinery concept, which requires multi-institutional and multidisciplinary networks in Brazil to carry out research, development and innovation activities in this field. Higher value-added products than fuels offer the most challenging opportunities.

The main issue to making the biorefinery concept a reality is the establishment of the logistics for biomass collection, pretreatment, transportation and storage, which should be modeled in order to integrate them into the current industrial infrastructure and serve as the basis for further developments.

Thermochemical processes are becoming more accepted as emerging technology with commercial potential and can be used to support the biorefinery development and improve the Brazilian bioenergy sector. Pyrolysis emerges as a great opportunity. The biochar is proposed as a soil improver and the bio-oil can be used as a source of renewable chemicals through various upgrading routes. For specific purposes, such as entrained flow gasification for syngas production, recombination to a char/bio-oil slurry is considered. This pyrolysis-gasification arrangement may provide a competitive way to convert diverse, highly distributed and low-value lignocellulosic biomass to syngas and, from this product, a wide range of value added products can be obtained through catalytic synthesis. The research opportunities appear in the entire bioenergy chain: biomass production; logistics for collection, transportation and storage; pretreatment and processing. Additionally, further research and development of the fundamental science is required for successful exploitation of the full biomass potential, thus providing the tools for the design engineers to achieve the requisite technological development and performance improvements.

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REFERENCES

ABRAF, Yearbook Statistical of the Brazilian Association of Forest Plantation Producers 2012, base year 2011. Brasília, p. 150 (2012).

Adhikari, S., Fernando, S. and Haryanto, A., Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts. Catalysis Today, 129, 355-364 (2007).

Adhikari, S., Fernando, S. and Haryanto, A., Hydrogen production from glycerin by steam reforming over nickel catalysts. Renewable Energy, 33, 1097-1100 (2008).

Adinarayana, K., Prabhakar, T., Srinivasulu, V., Rao, M. A., Lakshmi, P. J. and Ellaiah, P., Optimization of process parameters for cephalosporin C production under solid state fermentation from *Acremonium chrysogenum*. Process Biochem., 39, 171-177 (2003).

Antal, M. J. and Grønli, M., The Art, science, and technology of charcoal production. Ind. Eng. Chem. Res., 42, 1619-1640 (2003).

ASTM D1857, Standard test method for fusibility of coal and coke ash. July 1 (2004a).

ASTM D3176, Standard practice for ultimate analysis of coal and coke. September 29, (1989, reapproved 1997).

ASTM D5865, Standard test method for gross calorific value of coal and coke. April 1 (2004b).

Babu, B. V., Biomass pyrolysis - a state-of-the-art review. Biofuels, Bioproducts and Biorefining, 2, No. 5, 393-414 (2008).

Bahng, M.-K., Mukarakate, C., Robichaud, D. J. and Nimlos, M. R., Current technologies for analysis of biomass thermochemical processing: A review. Analytica Chimica Acta, 651, 117-138 (2009).

Bergman, P. C. A., Boersma, A. R., Kiel, J. H. A., Prins, M. J., Ptasinski, K. J. and Janssen, F. J. J. G., Torrefaction for entrained flow gasification of biomass, Report C--05-067. Energy Research Centre of the Netherlands (ECN): Petten, the Netherlands, p. 51, July (2005a).

Bergman, P. C. A. Combined torrefaction and pelletisation: The TOP process, Report C--05-073. Energy Research Centre of the Netherlands (ECN): Petten, the Netherlands, p. 29, July (2005).

Bergman, P. C. A., Boersma, A. R., Zwart, R. W. R. and Kiel, J. H. A., Torrefaction for biomass co-firing in existing coal-fired power stations "BIOCOAL", Report C--05-013. Energy Research Centre of the Netherlands (ECN): Petten, the Netherlands, p. 72, July (2005b).

Blasiak, W., Szewczyk, D., Lucas, C., Tsamba, A. J. and Rafidi, N., High temperature air/steam gasification technical report no. 1: High exergy rate gas aided low grade fuel utilization technology. Royal Institute of Technology, Stockholm, ISRN KTH/MSE - 02/16–SE ENERGY/TR, No. March (2002).

Borrego, A. G., Garavaglia, L. and Kalkreuth, W. D., Characteristics of high heating rate biomass chars prepared under N_2 and CO_2 atmospheres. International Journal of Coal Geology, 77, 409-415 (2009).

Botha, T. and von Blottnitz, H. A., comparison of the environmental benefits of bagasse-derived electricity and fuel ethanol on a life-cycle basis. Energy Policy, 34, 2654-2661 (2006).

Branca, C. and Di Blasi, C., Multistep mechanism for the devolatization of biomass fast pyrolysis oils. Ind. Eng. Chem. Res., 45, No. 17, 5891-5899 (2006).

Brasil - Brazilian Agroenergy Plan 2006-2011 / Ministry of Agriculture, Livestock and Food Supply, Secretariat for Production and Agroenergy - Brasília, DF: Embrapa Publishing House, p. 108 (2006). Available at: <http://www.embrapa.br/english/publications/agroenery_miolo.pdf>. (Accessed in: June 02, 2011).

Brasil - Brazilian Energy Balance 2012 Year 2011 / Empresa de Pesquisa Energética – Rio de Janeiro: EPE, p. 282 (2012). Available at: <https://ben.epe.gov.br/downloads/Relatorio_Final_BEN_2012.pdf>. (Accessed in: January 08, 2013).

Brennan, L. and Owende, P., Biofuels from microalgae – a review of technologies for production, processing, and extractions of biofuels and co-products. Renew. Sustain. Energy Rev., 14, 557-577 (2010).

Bridgwater, A. V., Catalysis in thermal biomass conversion. Appl. Catal., A, 116, 5-47 (1994).

Bridgwater, A. V., The technical and economic feasibility of biomass gasification for power generation. Fuel, 74, No. 5, 631-653 (1995).

Bridgwater, A. V., Fast Pyrolysis of Biomass: A Handbook. CPL Press, Newbury, UK (1999a).

Bridgwater, A. V., Principles and practice of biomass fast pyrolysis processes for liquids. Journal of Analytical and Applied Pyrolysis 51, 3-22 (1999b).

Bridgwater, A. V. and Peacocke, G. V. C., Fast pyrolysis processes for biomass. Renewable and Sustainable Energy Reviews, 4, 1-73 (2000).

Bridgwater, A. V., Renewable fuels and chemicals by thermal processing of biomass. Chemical Engineering Journal, 91, No. 2-3, 87-102 (2003).

Bridgwater, A. V., Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy, 38, 68-94 (2012).

Cardona, C. A., Quintero, J. A. and Paz, I. C., Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresource Technology, 101, 4754-4766 (2010).

Cadoche, L. and Lopez, G. D. (1989). In: Kumar, P., Barrett, D. M., Delwiche, M. J. and Stroeve, P., Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind. Eng. Chem. Res., 48, 3713-3729 (2009).

Cherubini, F. and Ulgiati, S., Crop residues as raw materials for biorefinery systems – A LCA case study. Applied Energy, 87, 47-57 (2010).

Chew, T. L. and Bhatia, S., Review: Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. Bioresource Technology, 99, 7911-7922 (2008).

Chi, Z., Pyle, D., Wen, Z., Frear, C. and Chen, S., A laboratory study of producing docosahexaenoic acid from biodiesel-waste glycerol by microalgal fermentation. Process Biochemistry, 42, 1537-1545 (2007).

Chmielniak, T. and Sciazko, M., Co-gasification of biomass and coal for methanol synthesis. Applied Energy, 74, 393-403 (2003).

Coda, B., Cieplik, M. K., De Wild, P. J. and Kiel, J. H. A., Slagging behavior of wood ash under entrained-flow gasification conditions. Energy Fuels, 21, 3644-3652 (2007).

Cousins, A., Paterson, N., Dugwell, D. R. and Kandiyoti, R., An investigation of the reactivity of chars formed in fluidized-bed gasifiers: The effect of reaction conditions and particle size on coal char reactivity. Energy and Fuels, 20, 2489-2497 (2006).

CSIRO, Sustainable Agriculture Flagship, Biochar for agronomic improvement and greenhouse gas mitigation, September 2010, Updated 14 October (2011). Available at: <http://www.csiro.au/Outcomes/Environment/Australian-Landscapes/Biochar-agronomic-improvement.aspx>. (Accessed in: June 13, 2012).

Cui, H. and Grace, J. R., Fluidization of biomass particles: A review of experimental multiphase flow aspects. Chem. Eng. Sci., 62, 45-55 (2007).

da Silva, G. P., Mack, M. and Contiero, J., Glycerol: A promising and abundant carbon source for industrial microbiology. Biotechnol Adv., 27, No. 1, 30-39 (2009).

Demirbas, A., Conversion of biomass using glycerin to liquid fuel for blending gasoline as alternative engine fuel. Energy Convers. Manag., 41, 1741-1748 (2000).

Demirbas, A. and Arin, G., An overview of biomass pyrolysis. Energy Sources, 24, No. 5, 471-482 (2002).

Demirbas, A., Combustion characteristics of different biomass fuels. Progress in Energy and Combustion Science, 30, No. 2, 219-230 (2004a).

Demirbas, A., Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis, 71, No. 2, 803-815 (2004b).

Demirbas, A., Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Progress in Energy and Combustion Science, 31, 171-192 (2005).

Demirbas, A., Progress and recent trends in biofuels. Prog. Energy Combust. Sci., 33, 1-18 (2007).

Demirbas, A., Biorefineries: Current activities and future developments. Energy Conversion and Management, 50, 2782-2801 (2009).

Deswarte, F. E. I., Clark, J. H., Hardy, J. J. E. and Rose, P. M., The fractionation of valuable wax products from wheat straw using CO_2. Green Chem., 8, 39-42 (2008).

DEV, Deutsche Einheitsverfahren, German standard methods for the examination of water, waste water and sludge. Jointly determinable substances (Group F) and determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (Group E). Berlin, Germany (1999).

Devi, L., Ptasinski, K. J. and Janssen, V., A review of the primary measures for tar elimination in biomass gasification processes. Biomass and Bioenergy, 24, No. 2, 125-140 (2003).

Dias, M. O. S., Cunha, M. P., Maciel Filho, R., Bonomi, A., Jesus, C. D. F. and Rossell, C. E. V., Simulation of integrated first and second generation bioethanol production from sugarcane: Comparison between different biomass pretreatment methods. Journal of Industrial Microbiology and Biotechnology, 38, No. 8, 955-966, (2011a).

Dias, M. O. S., Cunha, M. P., Jesus, C. D. F., Rocha, G. J. M., Pradella, J. G. C., Rossell, C. E. V., Maciel Filho, R. and Bonomi, A., Second generation ethanol in Brazil: Can it compete with electricity production? Bioresource Technology, 102, 8964-8971 (2011b).

Dias, M. O. S., Junqueira, T. L., Cavalett, O., Cunha, M. P., Jesus, C. D. F., Rossell, C. E. V., Maciel Filho, R. and Bonomi, A., Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash. Bioresource Technology, 103, 152-161 (2012a).

Dias, M. O. S., Junqueira, T. L., Cavalett, O., Jesus, C. D. F., Rossell, C. E. V., Maciel Filho, R. and Bonomi, A., Improving second generation ethanol production through optimization of first generation production process from sugarcane. Energy 43 246-252 (2012b).

Di Blasi, C., Signorelli, G. and Portoricco, G., Counter-current fixed-bed gasification of biomass at laboratory scale. Industrial and Engineering Chemistry Research, 38, 2571-2581 (1999).

Di Blasi, C., Combustion and gasification rates of lignocellulosic chars. Progress in Energy Combustion Sciences, 35, 121-140 (2009).

Digman, B., Joo, H. S. and Kim, D.-S., Recent progress in gasification/pyrolysis technologies for biomass conversion to energy. Environ. Prog. Sust. Energy, 28, No. 1, 47-51 (2009).

Elliott, D. C., Historical developments in hydroprocessing bio-oils. Energy and Fuels, 21, 1792-1815 (2007).

DIN 51718, Testing of solid fuels – Determination of the water content and the moisture of analysis sample. June 1 (2002).

DIN 51719, Testing of solid fuels – Solid mineral fuels – Determination of ash content. July 1 (1997).

DIN 51720, Testing of solid fuels – Determination of volatile matter content. March 1 (2001).

DIN 51729-10, Analysis of coal ash and coke ash by

X-ray fluorescence (XFA) (1996).

DIN 51900-1, Determining the gross calorific value of solid and liquid fuels using the bomb calorimeter, and calculation of net calorific value - Part 1: General information (2000).

DIN 51900-3, Testing of solid and liquid fuels – Determination of gross calorific value by the bomb calorimeter and calculation of net calorific value – Part 3: method using adiabatic jacket (2005).

Ellaiah, P., Srinivasulu, B. and Adinarayana, K., Optimisation studies on neomycin production by a mutant strain of *Streptomyces marinensis* in solid state fermentation. Process Biochem., 39, 529-534 (2004).

Encimar, J. M., González, J. F., Rodríguez, J. J. and Ramiro, M. J., Catalysed and uncatalysed steam gasification of eucalyptus char: Influence of variables and kinetic study. Fuel, 80, 2025-2036 (2001).

European Union, Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/ECL. Official Journal of the European Union, L 140/16-62. June 5 (2009).

Esteves, T. C., Rajamma, R., Soares, D., Silva, A. S., Ferreira, V. M. and Labrincha, J. A., Use of biomass fly ash for mitigation of alkali-silica reaction of cement mortars. Construction and Building Materials, 26, No. 1, 687-693 (2012).

Felfli, F. F., Luengo, C. A., Suárez, J. A. and Beatón, P. A., Wood briquettes torrefaction. Energy for Sustainable Development, 9, No. 3, 19-22 (2005a).

Felfli, F. F., Luengo, C. A. and Rocha, J. D., Torrefied briquettes: Technical and economic feasibility and perspectives in the Brazilian market. Energy for Sustainable Development, 9, No. 3, 23-29 (2005b).

Felfli, F. F., Mesa, J. M., Rocha, J. D., Filippetto, D., Luengo, C. A. and Pippo, W. A., Biomass briquetting and its perspectives in Brazil. Biomass and Bioenergy, 35, No. 1, 236-242 (2011).

Fernando, S., Adhikari, S., Kota, K. and Bandi, R., Glycerol based automotive fuels from future biorefineries. Fuel, 86, 2806-2809 (2007).

Floriani, S. L., Virmond, E., Luiz, D. B., Althoff, C. A., José, H. J. and Moreira, R. F. P. M., Potential of industrial solid wastes as an energy source and gaseous emissions evaluation in a pilot scale burner (ES2008-54355). Journal of Energy Resources Technology, 132, No. 1, 0011003-0011010 (2010).

Fountoulakis, M. S. and Manios, T., Enhanced methane and hydrogen production from municipal solid waste and agro-industrial by-products co-digested with crude glycerol. Bioresource Technology, 100, No. 12, 3043-3047 (2009).

Fountoulakis, M. S., Petousi, I. and Manios, T., Co-digestion of sewage sludge with glycerol to boost biogas production. Waste Management, 30, No. 10, 1849-1853 (2010).

Fytianos, K. and Schröder, H. Fr., Determination of polychlorinated dibenzodioxins and dibenzofurans in fly ash. Chromatographia, 46, 280-284 (1997).

Gabra, M., Pettersson, E., Backman, R. and Kjellström, B., Evaluation of cyclone gasifier performance for gasification of sugar cane residue - Part 1: Gasification of bagasse. Biomass and Bioenergy, 21, 351-369 (2001).

Garcia, R., Besson, M., Gallezot, P., Chemoselective catalytic oxidation of glycerol with air on platinum metals. Applied Catalysis A: General, 127, 165-176 (1995).

Griffiths, A. J., Syred, N. and Fick, W., A review of biomass and associated work at Cardiff relating to small scale heat and power systems. IFRF Combustion Journal, Article Number 200002, 1-40 (2000).

Guimarães, L. H. S., Somera, A. F., Terenzi, H. F., Polizeli, M. L. T. M. and Jorge, J. A., Production of β-fructofuranosidases by *Aspergillus niveus* using agroindustrial residues as carbon sources: Characterization of an intracellular enzyme accumulated in the presence of glucose. Process Biochem., 44, 237-241 (2009).

Haas, W. and Mittelbach, M., Detoxification experiments with the seed oil from *Jatropha Curcas* L. Ind. Crops Prod., 12, 111-118 (2000).

Haung, H. J., Ramaswamy, S., Tschirner, U. W. and Ramarao, B. V., A review of separation technologies in current and future biorefineries. Sep. Purif. Technol., 62, 1-21 (2008).

Henrich, E. and Weirich, F., Pressurized entrained flow gasifiers for biomass. Environ. Eng. Sci., 21, 53-64 (2004).

Hernández, J. S., Aguilera-Carbó, A. F., Herrera, R. R., Martínez, J. L., Aguilar, C. N., Kinetic production of the antioxidant ellagic acid by fungal solid state culture. Proceedings of the 10th International Chemical and Biological Engineering Conference. Portugal: CHEMPOR, 1849-1854, (2008).

Higman, C. and van der Burgt, M., Gasification. 2^{nd} Ed., Elsevier Science (2008).

Hoogwijk, M. M., Faaij, A., van den Broek, R., Berndes, G., Gielen, D. and Turkenburg, W., Exploration of the ranges of the global potential of biomass for energy. Biomass and Bioenergy, 25, 119-133 (2003).

Huber, G. W. and Dumesic, J. A., An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. Catal. Today, 111, 119-132 (2006).

Huber, G. W. and Corma, A., Synergies between bio- and oil refineries for the production of fuels from biomass. Angew. Chem. Int. Ed., No. 46, 38, 7184-7201 (2007).

IEA, International Energy Agency. Task 39 - From 1st to 2nd generation Biofuels - Full Report, Paris: OECD/IEA (2008). Available at: <http://www.iea.org/papers/2008/2nd_biofuel_gen.pdf>. (Accessed in: May 03, 2011).

IEA, International Energy Agency. Eisentraut, A., Sustainable production of second-generation biofuels – Potential and perspectives in major economies and developing countries. Extended Executive Summary, Paris: OECD/IEA (2010). Available at: <http://www.iea.org/papers/2009/biofuels_exec_summary.pdf>. (Accessed in: June 07, 2012).

Imandi, S. B., Bandaru, V. V. R., Somalanka, S. R. and Garapati, H. R., Optimization of medium constituents for the production of citric acid from byproduct glycerol using Doehlert experimental design. Enzyme and Microbial Technology, 40, 1367-1372 (2007).

ISO 540, Solid mineral fuels – Determination of fusibility of ash – High temperature tube method (1995).

Jenkins, B. M., Baxter, L. L., Miles Jr, T. R. and Miles, T. R., Combustion properties of biomass. Fuel Processing Technology, 54, 17-46 (1998).

John, R. P., Nampoothiri, K. M. and Pandey, A., Solid-state fermentation for L-lactic acid production from agro wastes using *Lactobacillus delbrueckii*. Process Biochem., 41, 759-763 (2006).

John, R. P., Anisha, G. S., Nampoothiri, K. M. and Pandey, A., Micro and macroalgal biomass: A renewable source for bioethanol. Bioresour. Technol., 102, 186-193 (2011).

Joppich, A. and Salman, H., Wood powder feeding difficulties and solutions. Biomass and Bioenergy, 16, 191-198 (1999).

Kameyama, K., Shinogi, Y., Miyamoto, T., and Agarie, K., Estimation of net carbon sequestration potential with farmland application of bagasse charcoal: Life cycle inventory analysis through a pilot sugarcane bagasse carbonization plant – Report. Australian Journal of Soil Research, 48, No. 6-7, Sept-Nov (2010).

Kammen, D. M. and Lew, D. J., Review of technologies for the production and use of charcoal. Renewable and Appropriate Energy Laboratory Report, Golden, CO: National Renewable Energy Laboratory (2005).

Karinen, R. S. and Krause, A. O. I., New biocomponents from glycerol. Applied Catalysis A: General, 306, 128-133 (2006).

Khalil, H. P. S. A., Bhat, A. H. and Yusra, A. F. I., Green composites from sustainable cellulose nanofibrils: A review. Carbohydrate Polymers, 87, 963-979 (2012).

Kržan, A. A., Kunaver, M. and Tišler, V., Wood liquefaction using dibasic organic acids and glycols. Acta Chim. Slov., 52, 253-258 (2005).

Kržan, A. and Zăgar, E., Microwave driven wood liquefaction with glycols. Bioresour. Technol., 100, 3143-3146 (2009).

Kumar, A. and Sharma, S., An evaluation of multipurpose oil seed crop for industrial uses (*Jatropha curcas* L.): A review. Ind. Crops Prod., 28, 1-10 (2008).

Kurimoto, Y., Doi, S. and Tamura, Y., Species effects on wood liquefaction in polyhydric alcohols. Holzforschung, 53, 617-622 (1999).

Kwong, C. W. and Chao, C. Y. H., Fly-ash products from biomass co-combustion for VOC control. Bioresource Technology, 101, No. 3, 1075-1081 (2010).

La Mantia, F. P. and Morreale, M., Green composites: A brief review. Composites: Part A, 42, 579-588 (2011).

Lal, R., World crop residues production and implications of its use as a biofuel. Environment International, 31, 575-584 (2005).

Lal, R., Crop residues as soil amendments and feedstock for bioethanol production. Waste Management, 28, 747-758 (2008).

Laohalidanond, K., Heil, J. and Wirtgen, C., The production of synthetic diesel from biomass. KMITL Sci. Tech. J., 6, No. 1, 35-45 (2006).

Levine, R. B., Pinnarat, T. and Savage, P. E., Biodiesel production from wet algal biomass through in situ lipid hydrolysis and supercritical transesterification. Energy Fuels, 24, 5235-5243 (2010).

Lin, L., Ying, D., Chaitep, S. and Vittayapadung, S., Biodiesel production from crude rice bran oil and properties as fuel. Applied Energy, 86, 681-688 (2009).

Llorente, M. J. F. and García, J. E. C., Comparing methods for predicting the sintering of biomass ash in combustion. Fuel, 84, 1893-1900 (2005).

Lora, E. S. and Andrade, R. V., Biomass as energy source in Brazil. Renewable and Sustainable Energy Reviews, 13, 777-788 (2009).

Lucas, C., Szewczyk, D., Blasiak, W. and Mochida, S., High-temperature air and steam gasification of densified biofuels. Biomass and Bioenergy, 27, 563-575 (2004).

Luo, N., Fu, X., Cao, F., Xiao, T. and Edwards, P. P., Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst – effect of catalyst composition and reaction conditions. Fuel, 87, 3483-3489 (2008).

Lyko, H., Deeberg, G. and Weidner, E., Coupled production in biorefineries - Combined use of biomass as a source of energy. Fuels and Materials. Journal of Biotechnology, 142, 78-86 (2009).

Mabee, W. E., Gregg, D. J. and Saddler, J. N., Assessing the emerging biorefinery sector in Canada. Appl Biochem. Biotechnol., 121-124, 765-778 (2005).

Maldas, D. and Shiraishi, N., Liquefaction of biomass in the presence of phenol and H_2O using alkalis and salts as the catalyst. Biomass and Bioenergy, 12, 273-279 (1997).

Mamma, D., Kourtoglou, E. and Christakopoulos, P., Fungal multienzyme production on industrial by-products of the citrus-processing industry. Bioresour. Technol., 99, 2373-2383 (2008).

Mann, L., Tolbert, V. and Cushman, J., Potential environmental effects of corn (*Zea mays* L.) stover removal with emphasis on soil organic matter and erosion. Agri. Ecosyst. Environ. 89, 149-166 (2002).

Manurung, R., Wever, D. A. Z., Wildschut, J., Venderboscha, R. H., Hidayat, H., van Dam, J. E. G., Leijenhorst, E. J., Broekhuisa, A. A. and Heeres, H. J., Valorisation of *Jatropha curcas* L. plant parts: Nut shell conversion to fast pyrolysis oil. Food and Bioproducts Processing, 8, No. 7, 187-196 (2009).

Martins, S., Mussatto, S. I., Martínez-Avila, G., Montañez-Saenz, J., Aguilar, C. N. and Teixeira, J. A., Bioactive phenolic compounds: Production and extraction by solid-state fermentation. A review. Biotechnology Advances, 29, 365-373 (2011).

Masiá. A. A. T., Buhre, B. J. P., Gupta, R. P. and Wall, T. F., Characterising ash of biomass and waste. Fuel Processing Technology, 88, 1071-1081 (2007).

Mata, T. M., Martins, A. A. and Caetano, N. S., Microalgae for biodiesel production and other applications: A review. Renew. Sustain. Energy Rev., 14, 217-232 (2010).

McHenry, M. P., Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk. Agriculture, Ecosystems and Environment, 129, 1-7 (2009).

Medeiros, A. B. P., Pandey, A., Vandenberghe, L. P. S., Pastore, G. M. and Soccol, C. R., Production and recovery of aroma compounds produced by solid-state fermentation using different adsorbents. Food Technol. Biotechnol., 44, 47-51 (2006).

Meesters, P., Huijberts, G. N. M. and Eggink, G., High cell density cultivation of the lipid accumulating yeast *Cryptococcus curvatus* using glycerol as a carbon source. Applied Microbiology and Biotechnology, 45, 575-579 (1996).

Melis, A. and Happe, T., Hydrogen production: green algae as a source of energy. Plant Physiol. Biochem., 127, 740-748 (2001).

Menon, V. and Rao, M., Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion Science, 38, No. 4, 522-550 (2012).

Mercader, F. M., Groeneveld, M. J., Kersten, S. R. A., Way, N. W. J., Schaverien, C. J. and Hogendoorn, J. A., Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. Applied Catalysis B: Environmental, 96, 57-66 (2010a).

Mercader, F. M., Kersten, S. R. A., Groeneveld, M. J., Venderbosch, R. H. and Hogendoorn, J. A., Pyrolysis oil upgrading by high pressure thermal treatment. Fuel, 89, No. 10, 2829-2837 (2010b).

Mihalcik, D. J., Mullen, C. A. and Boateng, A. A., Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components. Journal of Analytical and Applied Pyrolysis, 92, 224-232 (2011).

Mohan, D., Pittman, C. U. Jr. and Steele, P., Pyrolysis of wood/biomass for bio-oil: A critical review. Energy and Fuels, 20, 848-889 (2006).

Mullen, C. A. and Boateng, A. A., Catalytic pyrolysis-GC/MS of lignin from several sources. Fuel Processing Technology, 91, 1446-1458 (2010).

Mullen, C. A., Boateng, A. A., Mihalcik, D. J. and Goldberg, N. M., Catalytic fast pyrolysis of white oak wood in a bubbling fluidized bed. Energy and Fuels, 25, 5444-5451 (2011).

Naik, S. N., Vaibhav, V. G., Rout, P. K. and Dalai, A. K., Production of first and second generation biofuels: A comprehensive review. Renewable and Sustainable Energy Reviews, 14, 578-597 (2010).

Narayan, M. S., Manoj, G. P., Vatchravelu, K., Bhagyalakshmi, N. and Mahadevaswamy, M., Utilization of glycerol as carbon source on the growth, pigment and lipid production in *Spirulina platensis*. International Journal of Food Sciences and Nutrition, 56, 521-528 (2005).

Nigam, P. S. and Singh, A., Production of liquid biofuels from renewable resources. Progress in Energy and Combustion Science, 37, 52-68 (2011).

Obernberger, I., Biedermann, F., Widmann, W. and Riedl, R., Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. Biomass and Bioenergy, 12, No. 3, 211-224 (1997).

Obernberger, I., Brunner, T. and Bärnthaler G., Chemical properties of solid biofuels - significance and impact. Biomass and Bioenergy, 30, 973-982 (2006).

Oliveira, L. A., Porto, A. L. F. and Tambourgi, E. B., Production of xylanase and protease by *Penicillium janthinellum* CRC 87M-115 from different agricultural wastes. Bioresources Technology, 97, 862-867 (2006).

Openshaw, K., A review of *Jatropha curcas*: An oil plant of unfulfilled promise. Biomass Bioenergy, 19, 1-15 (2000).

Orfao, J., Antunes, F. and Figueiredo, J., Pyrolysis kinetics of lignocellulosic materials-three independent reaction model. Fuel, 78, No. 3, 49-58 (1999).

Papanikolaou, S. and Aggelis, G., Lipid production by *Yarrowia lipolytica* growing on industrial glycerol in a single-stage continuous culture. Bioresource Technology, 82, 43-49 (2002).

Park, B. B., Yanai, R. D., Sahn, J. M., Lee, D. K. and Abrahamson, L. P., Wood ash effects on plant and soil in a willow bioenergy plantation. Biomass and Bioenergy, 28, No. 4, 355-365 (2005).

Patel, V. C., Varughese, J., Krishnamoorthy, P. A., Jain, R. C., Singh, A. K. and Ramamoorty, M., Synthesis of alkyd resin from Jatropha and rapeseed oils and their applications in electrical insulation. J. Appl. Polym. Sci., 107, No. 3, 1724-2172 (2008).

Peláez-Samaniego, M. R., Garcia-Perez, M., Cortez, L. B., Rosillo-Calle, F. and Mesa, J., Improvements of Brazilian carbonization industry as part of the creation of a global biomass economy. Renewable and Sustainable Energy Reviews, 12, 1063-1086 (2008).

Pérez-Villarejo, L., Eliche-Quesada, D., Iglesias-Godino, F. J., Martínez-García, C. and Corpas-Iglesias, F. A., Recycling of ash from biomass incinerator in clay matrix to produce ceramic bricks. Journal of Environmental Management, 95, S349-S354 (2012).

Phillips, S. D., Technoeconomic analysis of a lignocellulosic biomass indirect gasification process to make ethanol via mixed alcohols synthesis. Industrial and Engineering Chemistry Research, 46, 8887-8897 (2007).

Phillips, S., Aden, A., Jechura, J., Dayton, D. and Eggeman, T., Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass. Golden, CO: National Renewable Energy Laboratory, Report No. TP-510-41168, April (2007).

Phokawat, N. P., Sulfur and chlorine removal for biomass gasification process – Appendices. TU Delft, IDP NR 028-05 (2005).

Pronobis, M., Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. Biomass and Bioenergy, 28, 375-383 (2005).

Pronobis, M., The influence of biomass co-combustion on boiler fouling and efficiency, Fuel, 85, No. 4, 474-480 (2006).

Qi, A., Jie, C., Tiejun, W. and Ying, X., Review of biomass pyrolysis oil properties and upgrading research. Energy Convers. Manage., 48, 87-92 (2007).

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick Jr., W. J., Hallett, J. P., Leak, D. J., Liotta, C. L, Mielenz, J. R., Murphy, R., Templer, R. and Tschaplinski, T., The path forward for biofuels and biomaterials. Science, 311, 484-489 (2006).

Rao, T. R. and Sharma, A., Pyrolysis rates of biomass materials. Energy, 23, 973-978 (1998).

Raveendran, K., Ganesh, A. and Khilar, K. C., Pyrolysis characteristics of biomass and biomass components. Fuel, 75, 987-998 (1996).

RFA – Renewable Fuels Association, Global Ethanol Production to Reach 85.2 Billion Litres in 2012 (2012), Available at: <http://www.ethanolrfa.org/news/entry/global-ethanol-production-to-reach-85.2-billion-litres-in-2012/.>. (Accessed in: June 27, 2012).

Rocha, J. D., Gómez, E. O., Pérez, J. M. M., Cortez, L. A. B., Seye, O. and González, L. E. B., The demonstration fast pyrolysis plant to biomass conversion in Brazil. World Renewable Energy Congress VII (WREC), 1-5 (2002). Available at: <http://www.bioware.com.br/arquivos/wrecvii.pdf>. (Accessed in: June 14, 2012).

Rocha, J. D., Olivares, Gómez, E., Mesa, Pérez, J. M. and Cortez, L. A. B., Bioware process – a fast pyrolysis technology for biomass developed in Brazil. PyNe, 17, No. 8 (2004).

Rocha, J. D., Workshop Tecnológico sobre BTL (Biomass to Liquids), Projeto Programa de Pesquisa em Políticas Públicas, Tema 1: Pré-tratamento da biomassa (2008), Available at (Portuguese only): <http://www.apta.sp.gov.br/cana/anexos/apresentacao_wks_btl_painel1_josedilcio.pdf>. (Accessed in: June 27, 2012).

Rodrigues, S., Pinto, G. A. S. and Fernandes, F. A. N., Optimization of ultrasound extraction of phenolic compounds from coconut (*Cocos nucifera*) shell powder by response surface methodology. Ultrasonics Sonochemistry, 15, 95-100 (2008).

Rosa, M. F., Medeiros, E. S., Malmonge, J. A., Gregorski, K. S., Wood, D. F., Mattoso, L. H. C., Glenn, G., Orts, W. J. and Imam, S. H., Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. Carbohydrate Polymers, 81, 83-92 (2010).

Rosillo-Calle, F., De Rezende, M. A. A., Furtado, P. and Hall, D. O., The charcoal dilemma: Finding a sustainable solution for Brazilian Industry. London: Intermediate Technology Publications (1996).

Rossi, S. C., Vandenberghe, L. P. S., Pereira, B. M. P., Gago, F. D., Rizzolo, J. A., Pandey, A., Soccol, C. R., Medeiros, A. B. P., Improving fruity aroma production by fungi in SSF using citric pulp. Food Res. Int., 42, No. 4, 484-486 (2009).

Salman, H. and Kjellström, B., Pneumatic conveying of wood by using a steam-jet ejector. Biomass and Bioenergy, 19, 103-117 (2000).

Sarhy-Bagnon, V., Lozano, P., Saucedo-Castañeda, G. and Roussos, S., Production of 6-pentyl-α-pyrone by *Trichoderma harzianum* in liquid and solid state cultures. Process Biochem., 36, 103-109 (2000).

Seabra, J. E. A., Tao, L., Chum, H. L. and Macedo, I. C., A techno-economic evaluation of the effects of centralized cellulosic ethanol and co-products refinery options with sugarcane mill clustering. Biomass and Bioenergy, 34, 1065-1078 (2010).

Seabra, J. E. A. and Macedo, I. C., Comparative analysis for power generation and ethanol production from sugarcane residual biomass in Brazil. Energy Policy, 39, 421-428 (2011).

Senneca, O., Kinectics of pyrolysis, combustion and gasification of three biomass fuels. Fuel Processing Technology, 88, 87-97 (2007).

Sharma, R. K. and Bakhshi, N. N., Catalytic upgrading of pyrolysis oil. Energy and Fuels, 7, 306-314 (1993).

Sharma, A., Vivekanand, V. and Singh, R. P., Solid-state fermentation for gluconic acid production from sugarcane molasses by *Aspergillus niger* ARNU-4 employing tea waste as the novel solid support, Bioresour. Technol., 99, 3444-3450 (2008).

Shrank, S. and Farahmand, F., Biofuels Regain Momentum (2011). Available at: <http://www.endseurope.com/docs/110831a.pdf>. (Accessed in: June 27, 2012).

Singh, A. and Olsen, S. I., A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels. Applied Energy, 88, 3548-3555 (2011).

Singh, A., Nigam, P. S. and Murphy, J. D., Mechanism and challenges in commercialisation of algal biofuels. Bioresource Technology, 102, 26-34 (2011a).

Singh, A., Nigam, P. S. and Murphy, J. D., Renewable fuels from algae: An answer to debatable land based fuels. Bioresource Technology, 102, 10-16 (2011b).

Singh, A., Olsen, S. I. and Nigam, P. S., A viable technology to generate third-generation biofuel. J. Chem. Technol. Biotechnol., 86, 1349-1353 (2011c).

Singh, S., Ram, L.C., Masto, R. E. and Verma, S. K., A comparative evaluation of minerals and trace elements in the ashes from lignite, coal refuse, and biomass fired power plants. International Journal of Coal Geology, 87, No. 2, 112-120 (2011d).

Slinn, M., Kendall, K., Mallon, C. and Andrews, J., Steam reforming of biodiesel byproduct to make renewable hydrogen. Bioresource Technology, 99, 5851-5858 (2008).

Smeets, E., Faaij, A., Lewandowski, I. and Turkenburg, W., A bottom-up assessment and review of global bioenergy potentials to 2050. Energy and Combustion Science, 33, 56-106 (2007).

Sousa, B. A. and Correia, R. T. P., Phenolic content, antioxidant activity and antiamylolytic activity of extracts obtained from bioprocessed pineapple and guava wastes. Braz. J. Chem. Eng., 29, No. 1, 25-30 (2012).

Sousa Jr., R., Carvalho, M. L., Giordano, R. L. C. and Giordano, R. C., Recent trends in the modeling of cellulose hydrolysis. Braz. J. Chem. Eng., 28, No. 4, 545-564 (2011).

Spagnol, C., Rodrigues, F. H. A., Neto, A. G. V. C., Pereira, A. G. B., Fajardo, A. R., Radovanovic, E., Rubira, A. F. and Muniz, E. C., Nanocomposites based on poly(acrylamide-co-acrylate) and cellulose nanowhiskers. European Polymer Journal, 48, 454-463 (2012).

Sricharoenchaikul, V., Frederick Jr., W. J. and Agrawal, P., Black liquor gasification characteristics. 1. Formation and conversion of carbon-containing product gases. Ind. Eng. Chem. Res., 41, No. 23, 5640-5649 (2002).

Suárez, J. A. and Luengo, C. A., Coffee husk briquettes: A new renewable energy source. Energy Sources Part A: Recovery, Utilization, and Environmental Effects, 25, No. 10, 961-967 (2003).

Svoboda, K., Pohořelý, M., Hartman, M. and Martinec, J., Pretreatment and feeding of biomass for pressurized entrained flow gasification. Fuel Processing Technology, 90, 629-635 (2009).

Syred, C., Fick, W., Griffiths, A. J. and Syred, N., Cyclone gasifier and cyclone combustor for the use of biomass derived gas in the operation of a small gas turbine in cogeneration plants. Fuel, 83, 2381-2392 (2004).

Tan, Z. and Lagerkvist, A., Phosphorus recovery from the biomass ash: A review. Renewable and Sustainable Energy Reviews, 15, No. 8, 3588-3602 (2011).

Tsuji, H., Gupta, A. K., Hasegawa, T., Katsuki, M., Kishimoto, K. and Morita, M., High temperature air combustion: From energy conservation to pollution reduction. Boca Raton: CRC Press (2002).

UNICA – Sugarcane Industry Association – Ethanol, Sugar, Energy, Brazil (2012). Available at: <http://english.unica.com.br/dadosCotacao/estatistica>. (Accessed in: June 05, 2012).

U.S. EPA - United States Environmental Protection Agency, Method 8310, Polynuclear Aromatic Hydrocarbons, Revision 0, September (1986). Available at: <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8310.pdf>. (Accessed in: June 05, 2012).

U.S. EIA - Energy Information Administration: Annual Energy Outlook 2011, with Projections to 2035, Office of Integrated and International Energy Analysis, U.S. Department of Energy, Washington, DC 20585, p. 246, April (2011). Available at: <http://www.eia.gov/forecasts/aeo/>. (Accessed in: June 01, 2012).

U.S. EPA - United States Environmental Protection Agency. 2011 EMTS Data (Updated on Thursday, June 18, 2012). Available at: <http://www.epa.gov/otaq/fuels/rfsdata/2011emts.htm>. (Accessed in: June 27, 2012).

Vaca-Garcia, C., Biomaterials. In: Introduction to Chemicals from Biomass. Edited by Clark, J. and Deswarte, F., John Wiley & Sons Ltd, Chichester (2008).

Valliyappan, T., Bakhshi, N. N. and Dalai, A. K., Pyrolysis of glycerol for the production of hydrogen or syngas. Bioresource Technology, 99, 4476-4483 (2008).

Vamvuka, D. and Zografos, D., Predicting the behaviour of ash from agricultural wastes during combustion. Fuel, 83, 2051-2057 (2004).

Vamvuka, D., Zografos, D. and Alevizos, G., Control methods for mitigating ash-related problems in fluidized beds. Bioresource Technology, 99, 3534-3544 (2008).

Vamvuka, D., Bio-oil, solid and gaseous biofuels from biomass pyrolysis - An overview. Int. J. Energy Res., 35, 835-862 (2011).

Vamvuka, D. and Kakaras, E., Ash properties and environmental impact of various biomass and coal fuels and their blends. Fuel Processing Technology, 92, 570-581 (2011).

Vandenberghe, L. P. S., Soccol, C. R., Pandey, A. and Lebeault, J-M., Solid-state fermentation for the synthesis of citric acid by *Aspergillus niger*. Bioresour. Technol., 74, 175-178 (2000).

van den Drift, A., Boerrigter, H., Coda, B., Cieplik, M. K. and Hemmes, K., Entrained flow gasification of biomass. Report ECN Petten, NL, ECN-C-04-039 (2004).

van Paasen, S. V. B., Cieplik, M. K. and Phokawat, N. P., Gasification of non-woody biomass - economic and technical perspectives of chlorine and sulfur removal from product gas (Non-confidential version), ECN-C-06-032 (2006). Available at: <http://www.ecn.nl/docs/library/report/2006/e06032.pdf>. (Accessed in: April 15, 2008).

van Rossum, G., Potic, B., Kersten, S. R. A. and van Swaaij, W. P. M., Catalytic gasification of dry and wet biomass. Catalysis Today, 145, 10-18 (2009).

Vattem, D. A. and Shetty, K., Ellagic acid production and phenolic antioxidant activity in cranberry pomace (*Vaccinium macrocarpon*) mediated by *Lentinus edodes* using a solid-state system. Process Biochem., 39, 367-379 (2003).

Venderbosch, R. H., Prins, W., Review: Fast pyrolysis technology development. Biofuels, Bioproducts and Biorefining, 4, 178-208 (2010).

Virmond, E., Schacker, R. L., Albrecht, W., Althoff, C. A., Souza, M., José, H. J., Moreira, R. F. P. M., Combustion of apple juice wastes in a cyclone combustor for thermal energy generation (ES2009-90152). Journal of Energy Resources Technology, 132, No. 4, 041401-041410 (2010).

Virmond, E., Schacker, R. L., Albrecht, W., Althoff, C. A., Souza, M., Moreira, R. F. P. M., José, H. J., Organic solid waste originating from the meat processing industry as an alternative energy source, Energy, 36, 3897-3906 (2011).

Virmond, E., de Sena, R. F., Albrecht, W., Althoff, C. A., Moreira, R. F. P. M., José, H. J., Characterisation of agroindustrial solid residues as biofuels and potential application in thermochemical processes. Waste Management 32, No. 10, 1952-1961 (2012).

Walter, A. and Ensinas, A. V., Combined production of second-generation biofuels and electricity from sugarcane residues. Energy, 35, 874-879 (2010).

Wang, X., Kersten, S. R. A., Prins, W. and van Swaaij, W. P. M., Biomass pyrolysis in a fluidized bed reactor. Part 2: Experimental validation of model results. Ind. Eng. Chem. Res., 44, No. 23, 8786-8795 (2005).

Wang, X., Biomass fast pyrolysis in a fluidized bed. Thesis, University of Twente, the Netherlands (2006).

Wang, L., Weller, C. L., Jones, D. D. and Hanna, M. A., Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. Biomass and Bioenergy, 32, 573-581 (2008).

Werther, J., Saenger, M., Hartge, E-U., Ogada, T. and Siagi, Z., Combustion of agricultural residues. Progress in Energy and Combustion Science, 26, 1-27 (2000).

Werther, J., Gaseous emissions from waste combustion. Journal of Hazardous Materials, 144, 604-613 (2007).

Wilhem, W. W., Johnson, J. M. F., Hatfield, J. L., Voorhees, W. B. and Linden, D. R., Crop and soil productivity response to corn residue removal: A literature review. Agron. J., 96, 1-17 (2004).

Williams, P. T. and Nugranad, N., Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy, 25, 493-513 (2000).

Xiu, S., Shahbazi, A., Shirley, V., Mims, M. R. and Wallace, C. W., Effectiveness and mechanisms of crude glycerol on the biofuel production from swine manure through hydrothermal pyrolysis. Journal of Analytical and Applied Pyrolysis, 87, 194-198 (2010).

Xu, R., Ferrante, L., Briens, C. and Berruti, F., Flash pyrolysis of grape residues into biofuel in a bubbling fluid bed. Journal of Analytical and Applied Pyrolysis, 86, 58-65 (2009).

Yang, H., Yan, R., Chen, H., Lee, D. H. and Zheng, C., Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel, 86, 1781-1788 (2007).

Yoon, S. J., Choi, Y-C., Son, Y-I., Lee, S-H. and Lee, J-G., Gasification of biodiesel by-product with air or oxygen to make syngas. Bioresource Technology, 101, 1227-1232 (2010).

Zafar, S., Biomass logistics (2012). Available at: <http://www.bioenergyconsult.com/biomass-logistics/>. (Accessed in: June 11, 2012).

Zhang, Q., Chang, J., Wang, T. and Xu, Y., Review of biomass pyrolysis oil properties and upgrading research. Energy Convers. Manag., 48, 87-92 (2007).

Zhao, C., Kou, Y., Lemonidou, A. A., Li, X. and Lercher, J. A., Highly selective catalytic conversion of phenolic bio-oil to alkanes. Angew. Chem. Int. Ed., 48, No. 22, 3987-3990 (2009).

Zheng, P., Wereath, K., Sun, J. B., van den Heuvel, J. and Zeng, A. P., Overexpression of genes of the dha regulon and its effects on cell growth, glycerol fermentation to 1,3-propanediol and plasmid stability in *Klebsiella pneumonia*. Process Biochemistry, 41, 2160-2169 (2006).

Zwart, R. W. R., Biorefinery - The worldwide status at the beginning of 2006, BioRef 0603, July (2006).

Zwart, R. W. R., Boerrigter, H. and van der Drift, A., The impact of biomass pretreatment on the feasibility of overseas biomass conversion to Fischer-Tropsch Products. Energy and Fuels, 20, 2192-2197 (2006).