

## Conceptual framework of bioethanol production from lignocellulose for agricultural profitability

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key words: agricultural market, biofuels, biorefinery, lignocellulose.

Received in April 2012. Published in August 2012.

### ABSTRACT

Among currently developed biofuel and green-power technologies, technological development of lignocellulose biomass-based production of ethanol will be particularly important in a short time perspective as those specific activities constitute an intermediary stage in the process of developing integrated processes of biomass conversion in the route to the universal energy carrier – hydrogen or electricity. Agricultural biorefinery or agri-refinery which converts agricultural biomass to a wide spectrum of biofuels and bioproducts is considered as

the key element of the future economy. The biorefinery which produces biofuels and generates bioenergy will constitute the so called agri-energy complex – a local power unit implemented in the system of dispersed energy generation. It is worth noticing that agri-refinery will integrate three fundamental drivers of sustainable development of rural areas – bioeconomics, environment and society. This paper aims at elaborating the conceptual framework of the agri-refinery in the aspect of conversion of agricultural lignocellulosic biomass into bioethanol and other bioproducts as well as the future economy and sustainable development.

### INTRODUCTION

The more the civilization develops, the higher living standards are and the higher demand for primary energy is. According to the forecast by 2030 the world's demand for energy will climb by 50%, and will double by 2050 (European Commission 2006). Over 75% of the energy demand growth will be posted by developing countries. China, India and South American countries will particularly represent highest energy consumption markets. The global energy consumption is estimated to rise by 25% only in European countries by 2030 and should we fail to diversify sources of energy to a great extent and successfully improve energy efficiency, the energy imports indicator will climb from the existing 50% up to 70%. All that causes the fuel and energy policy integrated with environment-friendly undertakings and climate-change combat to become the contemporary challenge – the policy that manifests itself in formal documents of the United Nations (UNEP 2008), European Union (3x20 by 2020

(Council of the European Union 2007), the programme that was amended in 2011) and the United States of America (the environmental programme proclaimed by Obama and Biden (2012)). Rational and sustainable use of all the available sources of energy, including renewables is the essential element of this policy.

Given the specific technological features of clean energy production, the following general division may be assumed: 1) biofuel, 2) electric and thermal energy obtained from renewable sources: biomass, wind, water, sun (sun collectors, PV cells) and geothermal energy, 3) fossil fuel-based pure energy technologies, including carbon dioxide reclaim and storage systems, 4) nuclear power. Within a longer time perspective, the use of the sea and ocean energy (tides, wave energy, water biomass) and advanced technology of generating heat energy from the Earth's heat may represent some percentage share in the energy consumption. The biomass of agricultural origin is prevailing and will prevail, which is a challenge and the opportunity for agriculture when the forest

\* Professor Janusz Gołaszewski was an invited speaker at The Third International Environmental Best Practices Conference, 13-16 September 2011, Offenburg, Germany

biomass cannot be renewed and used so fast (Gołaszewski 2009a). The percentage share of biomass in the renewable energy consumption is estimated to change globally from the existing 77% into 52% in 2040 but at the same time the biofuel production efficiency will rise (EREC 2004). The biomass accounting for approximately 10% in the mix of the primary energy sources now, will constitute approximately 30% in 2050 (Macqueen and Korhaliller 2011).

In the future the prospective biomass is indicated to be sourced out from woody crops of short, 2-4-year rotation (mainly willow and poplar), that is vegetative forest stand (SRC – Short Rotation Coppice, SRWC – Short Rotation Woody Crops), agricultural production and food industry lignocellulose waste as well as forestry (SRF – Short Rotation Forestry) that enjoy optimal fuel parameters upon the lapse of 8-15 years (e.g. Stolarski et al. 2009; Weih 2008). The tendency of assigning agricultural land to tree crops is strongly supported in Sweden, and also in Great Britain, Spain and the USA launched research programmes in that respect (Kumar 2009; Rowe et al. 2009). The subject of the research includes forest stand of relatively fast renewable potential, namely alder-tree, ash-tree, beech, birch, eucalyptus, poplar, willow, maple-tree (*Acer pseudoplatanus* L.), mulberry-tree (*Broussonetia papyrifera*), great maple, *Paulownia*, acacia, and others. According to Berndes and followers (2003) and the International Energy Agency (2004) in 2025 lignocellulose-based energy is estimated to account for as much as 2/3 of biomass energy production, and the effective conversion of lignocellulose into ethanol is going to be the essential technology for biofuel production. Thus, from the agricultural point of view, from among many currently developed biofuel and ecopower technologies, technological arrangements for lignocellulose biomass-based production of ethanol will be particularly important in a short time perspective as those specific technological arrangements constitute an intermediary stage in the process of developing integrated processes of converting biomass to an universal energy medium – hydrogen or electric current.

Development of the biofuel market according to the scenario exhibited in Figure 1 will boost continual research on mechanisms driving biological processes and knowledge transfer for the purpose of developing technologies for bioenergy production, biofuel production and other bioproducts production (bioeconomics). Agricultural biorefinery or agrirefinery processing agricultural resources, producing a wide spectrum of power products and non-power products may be the key element for the biofuel market. The biorefinery altogether with power generators will make up the so called agripower compound – a local power cell within the system of dispersed sources of energy consumed locally (Gołaszewski 2009b). It is plausible to state that the agrirefinery will locally integrate three fundamental factors of economic sustainable development in rural areas – bioeconomics, environment and society, and implementation of this system will directly contribute to sustainable development and energetic safety of the state.

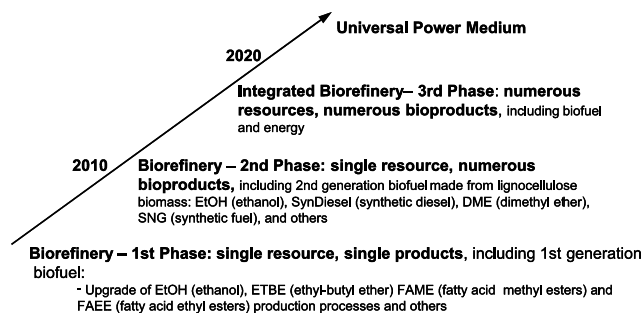


Figure 1. Biorefineries and biofuel generations development scenario.

**Biorefinery, 1<sup>st</sup> Phase – 1<sup>st</sup> generation biofuel** made from sugar crops, starch crops, and vegetable oil. In the past ten years:

- Upgrade of existing 1<sup>st</sup> generation biofuel production technologies.
- Research on improvement of technological efficiency for production of 2<sup>nd</sup> generation biofuel; biorefinery conceptual framework development; pilot installations for 2<sup>nd</sup> generation biofuel production were built – commercialization is in process.

**Biorefinery, 2<sup>nd</sup> Phase – 2<sup>nd</sup> generation biofuel:**

- 2<sup>nd</sup> generation biofuel production technology development.
- Universal character of commercial biorefinery, the basic product of which will be biofuel; research is continued on improvement of production efficiency for biofuel made from lignocellulose-based biofuel and integration of biorefining processes and power generation processes.
- Power crops development (new biological diversity of plants emerging from molecular biology engineering, new crops technologies) within the context of agricultural sustainable development.

**Integrated Biorefinery, 3<sup>rd</sup> Phase – integrated biorefining processes and power generation processes:**

- Power products (including universal biofuel – methanol) and non-power products, dispersed agripower compounds.

**Universal Energy Medium Market – (bio)hydrogen, electric current.**

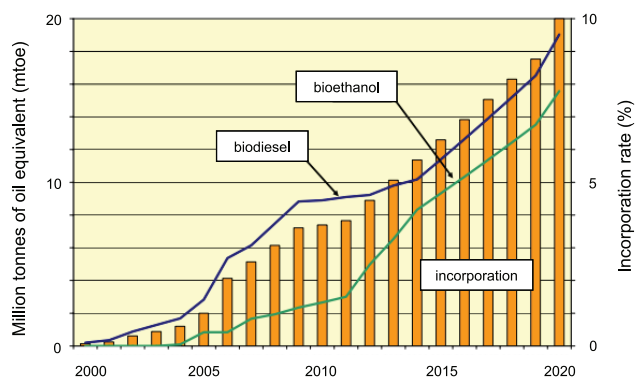
Given the current state-of-the-art of development of biofuel production technology and existing systems of biofuel production and distribution, improvement of production efficiency for bioethanol made from woody crops – the natural resource that is available in large quantities and is produced locally – is challenging today. Bioethanol, as a fuel for motor vehicles has been produced, for tens of years, from the natural resource such as crop that is rich in sugar (sugar cane, sugar beet) or starch (grains, potato crops), is 1<sup>st</sup> generation biofuel. Characteristic feature of 1<sup>st</sup> generation

biofuel includes natural competitiveness as compared to fodder or food production, relatively high production cost as compared to petrochemical fuel (low competitiveness) and low environment-friendly impact (Gołaszewski 2009c; Gołaszewski et al. 2008a). The aforementioned drawbacks are non-existent in the case of 2nd generation biofuel obtained from woody crops or agricultural waste or residues of high cellulose content called cellulose or lignin-cellulose or more often lignocellulose crops to highlight the substantial content of lignin – polymer that is hard to convert into simple chemical compounds, and which may serve, beside non-power opportunities, as the hard fuel for gasification processes and pyrolysis and further conversion into biofuel, and bioethanol too.

This paper aims at elaborating upon the conceptual framework of the biorefinery in the aspect of competitiveness of agricultural market and conferring upon conversion of lignocellulose biomass into bioethanol within the context of biorefining processes.

## BIOREFINERY AND AGRICULTURAL MARKET

Given the forecast biofuel incorporation index of 10% in the fuel market in the European Union by 2020, agriculture is assumed to take part in this policy and at the same time it will be one of the beneficiaries enjoying the implementation of the biofuel market development policy. Figure 2 presents the current and forecast interrelation between the fundamental biofuels, namely biodiesel and bioethanol (European Commission 2007). In the future the relation between these biofuels will probably not change as the use of biodiesel will prevail, including 2<sup>nd</sup> generation biodiesel made from synthesis gas (Fischer-Tropsch Synthesis) obtainable from biomass and fossil fuel (coal). However, the growth rate of bioethanol is estimated to be higher in the next coming three years. The market share of bioethanol will rise 2.5-fold from the existing 3 up to 8 million tonnes of oil equivalent (mtoe) in 2020.



**Figure 2.** Agricultural market of biodiesel and bioethanol and incorporation of biofuels in the fuel market in the European Union by 2020. Source: European Commission (2007).

Currently cellulose forestry-based biomass serves the purpose of producing 2<sup>nd</sup> generation bioethanol but the conversion processes for lignocellulose resource obtained from agricultural land (arable land and marginal land) are being developed. From the general point of view the assumptions for the technological process of producing ethanol from cellulose are recognized, nevertheless the production efficiency is unsatisfactory, which most of all results from high cost of biomass and cost-consuming degradation of cellulose into monosaccharides. According to Himmel and followers (2007), the biofuel industry and bioethanol production will be boosted by the progress in research performed to the extent of: (i) relatively slow kinetics of cellulose chemical hydrolysis into saccharides, (ii) low capacity of saccharides obtained from other polysaccharides (hemicellulose), and (iii) delignification. Biofuels represent just one out of prospective marketable products obtained from lignocellulose crops-based biomass but the industrial reclaim of organic chemical compounds and material from a variety of resources and further processing of the same is the essence of the research conducted today in the context of the future biorefinery processes, including Clark and Deswarte (2008):

- Structural metabolites: cellulose, hemicellulose and lignin being building material for stems, leaves, cell walls.
- Vestiges metabolites: oil, carbohydrates, proteins found in bulbs, roots, nuts, fruit, seeds.
- Secondary metabolites: phenols, organic nitrogen compounds (e.g. alkaloids), terpenes produced in stems, leaves, roots, seeds and fruit.
- Stem fibre and leave fibre.
- Flower pigments and aromatic oil, fruit, stem, leave and root pigments and aromatic oil.
- Wax, resin and rubber found in leaves, seed sprouts and fruit.
- Bio-oil obtained from whole plants, crops utensils-related residues.

In the past decade essential biotechnological progress was accomplished in result mostly of the genetic engineering applied to the food and fodder production and human health care. A new charter in white biotechnology development (facilitated by microorganisms and enzymes) and conventional chemical engineering focusing on applied research and development works over new semi-products and final products for industrial purposes, is drawn up by biorefinery (Laufenberg et al. 2003; Patel et al. 2006; Willke and Vorlop 2004). Biorefinery represents the installation for biomass conversion processes entailing simultaneous production of a variety of bioproducts, including biofuel, bioenergy, food ingredients, fodder, biomaterials and biochemicals. Biorefinery-based processes of fractioning biomass involve methods of physical, chemical, biochemical, biological (microbiological and enzymatic processes) and thermochemical conversion. Biorefinery-based processes are equivalent to crude oil refining processes, however there are essential and principal differences; natural resource processed in the biorefinery may be obtained locally and the

biorefinery that is erected locally may materialize and actualize the idea of presumption and boost local business initiative. Furthermore, similarly to the petrochemically refined products that are estimated to be more than two thousand in number, the potential of biorefinery products is assumed to be as large and prospective. Finally the economic effect of biorefinery-based production will always be the resultant of values of a variety of products produced by means of processing biomass, although the objective of the biorefinery and its operations will be to maximize biofuel production capacity. Succinic acid, fumaric acid and maleate acid, 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone acid, glycerol, sorbitol, xylitol/arabitol are referred to as the most valuable chemical precursors that determine the added value of the biorefinery and that result from very few products that are finely refined (ranked by the US Department of Energy 2004). Due to several functional groups capable of reacting on and on, each of the aforementioned chemical compounds is the input one for another range of semi-products (precursors) and new products that are successively developed.

Depending on the type of biomass, biorefinery-based processes result in a variety of biofuels. Production of ethanol and oil crops for the purpose of 1<sup>st</sup> generation fuel involves the major crop – grains, potato tubers, oil seeds, etc. The remaining part of biological crop (e.g. straw, chaff, haulm, etc.) is relatively inefficient for agricultural purposes (outdoor burning, ploughing, bedding, etc.) or when used as hard fuel burnt in biomass boilers. In the biorefinery the whole biological crop can be used up in the form of the highly lignified agricultural waste of any crop origin but most of all in the form of the biomass originating from dedicated lignocellulose crops that do not compete with crops grown for food, fodder production and industrial purposes. Globally the percentage share of lignocellulose biomass accounts for 90% of overall variety of biomass and from the production point of view approximately 8-20·10<sup>9</sup> (5-10%) tons of primary biomass representing the estimated potential of 200·10<sup>9</sup> tons of annual production will determine the potential of biomass to be used (Lin and Tanaka 2006).

Parallely with development of innovative technologies of biofuel production in the biorefinery (research and development area, industry), the agricultural sector will regularly adjust the development strategy by means of adapting itself to the changes in the biofuel market, that arise from the technological development, and taking into account the economic factors closely related to global conditionalities. The research conducted by Nonhebel (2005) proves that agricultural crops-based biomass has the potential to satisfy the requirement for natural resources for the purpose of motor vehicle fuel, food, fodder, and fibre under the condition that an essential progress is accomplished in biomass conversion technologies and the agricultural land use is rearranged with the net land area remaining unchanged. On the grounds of the environmental cost-benefit analysis of the biomass production for the purpose of

motor vehicle fuel, similar conclusions are represented by Hill (2007) who underlines that effective land use in accordance with social expectations will be particularly important in the face of the rising demand for food and energy in consecutive decades.

According to our own research (Gołaszewski and Stolarski, unpublished data), in Poland at least 15% of agricultural land of approximately 2 million hectares in area used respectively and proportionally for production of oil, sugar and starch and lignocelluloses can be allocated to the biorefinery purposes. If the energy crops area is regularly increased and 2<sup>nd</sup> generation biofuel production technology is developed and adapted, it would be only the agricultural sector solely that could fulfil the commitment thresholds of Poland by 2020 in respect of 7.5% share of biofuel in the fuel market, 20% share of energy from renewable sources and 20% reduction of CO<sub>2</sub> emission (85-90% by 2050 as compared to 1990). In many other countries parallel estimates are higher. In Great Britain the land use potential for power generation purposes is estimated to equal to 20% (Cookson 2007). In the USA the land use potential that is capable of sustainable biomass production for power generation purposes is estimated to be sufficient to replace 30% or more of the current consumption of petrochemical fuel (Perlak et al. 2008).

The major determinants for the agricultural biofuel market development should cover:

- The change in the relation between the costs of producing 1<sup>st</sup> and 2<sup>nd</sup> generation biofuels that are 30% higher for 2<sup>nd</sup> generation biofuel costs *inter alia* due to new biological diversity and effective biofuel production technologies as well as new support forms for 2<sup>nd</sup> generation fuel market.
- Higher use efficiency of production potential of agricultural land including dedicated lignocellulose crops, first of all on the excluded land (idle land, fallow) or marginal land of low crop potential, as well as maximizing use of biological crops.
- The change in the import policy and fiscal policy for biofuel including the policy opening the market for bioethanol, taking into consideration the relation between the biofuel prices and fossil fuel prices (the price for crude oil in excess of EUR 50 per barrel increases competitiveness of biofuel).

The need for development of the technology of producing biofuel from agricultural biomass is obvious but at the same time there are postulates posted against biofuel, which causes the related social perception to be pejorative to a great extent. One should not challenge scientific proof of possible adverse impact of biofuel production upon natural environment, respecting the need for rational action that addresses both positive aspects and consequences resulting from the future-oriented biomass used to a greater extent than nowadays (Gołaszewski 2009a). Table 1 presents more frequent postulates that challenge the rightfulness of developing biofuel technologies and objective arguments serving the grounds for purposefulness of biofuel production development.

**Table 1. Biofuel production postulates and facts.**

Postulates	Facts
Production of biofuel from resources that are traditionally used for food and fodder production is competitive in relation to fodder and food production	<p>Outstanding production potential in marginal or excluded land</p> <p>Outstanding biological and energetic potential of lignocellulose crops</p> <p>Waste that has low profile may be used as waste resource of low value: crop residues, dedicated crops, agricultural and food industry waste and industrial waste, paper waste, forest waste, herb waste and lignified waste of agricultural or horticultural origin</p>
Biofuels cause food prices to rise	<p>It is a fact that current prices of grains are 3-6% higher than the prices in 2005 but the following must be also taken into account:</p> <ul style="list-style-type: none"> <li>• Crude oil prices fluctuation</li> <li>• New dietary trends and higher living standards in the countries with high population growth rate (Asian countries and South America) – pressure and competition in the food production market</li> </ul>
Biofuels are not real option for petrochemical fuel	<p>The only rational way of gaining independence from crude oil now</p> <p>Fuel that is locally produced may guarantee continuity of production contributing to improvement of local energy safety, energy independence</p> <p>Diversification factor for fuel supply</p>
Biofuels contribute to reduction of greenhouse effect to a little extent	<p>High potential of reducing emission of greenhouse gases depends on energy resources and biofuel conversion technology</p> <p>Theoretically unlimited biomass resources that may be used for power generation purposes</p>
Biofuel production limits biological diversity	<p>Wider spectrum of crops</p> <p>Infertile land may be used</p> <p>Agriculture profitability may be increased</p>

Biomass production capital expenditures (crops, means of production), biomass transportation and the very biofuel production process and distribution are key issues in respect of prospective economic and environmental benefits arising from biofuel production. Within the energetic balance, the power capital expenditures for production purposes may be in excess of the calorific value of biofuel that is produced. Under the current market conditions, when the cost of biomass and its conversion into monosaccharides is high, the energy balance is generally negative in the case of production of 1<sup>st</sup> generation biofuel, having taken into account the environmental impact (bioethanol obtained from sugar cane is the exception). One of the indicators that enable us to compare the production of 1<sup>st</sup> and 2<sup>nd</sup> generation biofuel from the energy and economic point of view is FER – Fossil Energy (Replacement) Ratio that is the

quotient of biofuel energy units supplied to a final user in relation to fossil fuel energy units used for production of biofuel unit (Dale 2007; Sheehan et al. 2004). This means that the higher the FER is for biofuel production, the higher value of this biofuel as fossil fuel substitute is. For instance, for petrol FER=0.8, which means that production of fuel unit takes 1.25 of fossil fuel unit, bioethanol made from corn FER=1.4, wheat FER=1.2, potato FER=1, sugar cane FER=9, lignocellulose bioethanol FER represent values in the wide range of 5-10 depending on the type of resource (World Economic Outlook, October 2007). Harrow (2008), comparing the cost of fossil fuel (crude oil, coal, natural gas) when producing motor vehicle fuel, in terms of British Thermal Unit (BTU – 1.055kJ), reports that for petrol it stands at 1.23, for bioethanol made from corn 0.74, and bioethanol made from cellulose <0.2.

On the grounds of currently conducted research and development works it is plausible to state that research and development of biorefinery enters 3<sup>rd</sup> phase in which not only diversification of bioproducts is obtained but also diversification of resources and integration of technological processes and energy production take place. Depending on biomass to be processed, four categories of biorefineries may be distinguished: (1) lignocellulose, (2) whole plants, (3) green biomass, (4) double-platform (Clark and Deswarte 2008; Kamm and Kamm 2004; Kamm et al. 2010). Figure 3 presents general pictorial diagrams of the aforementioned biorefineries.

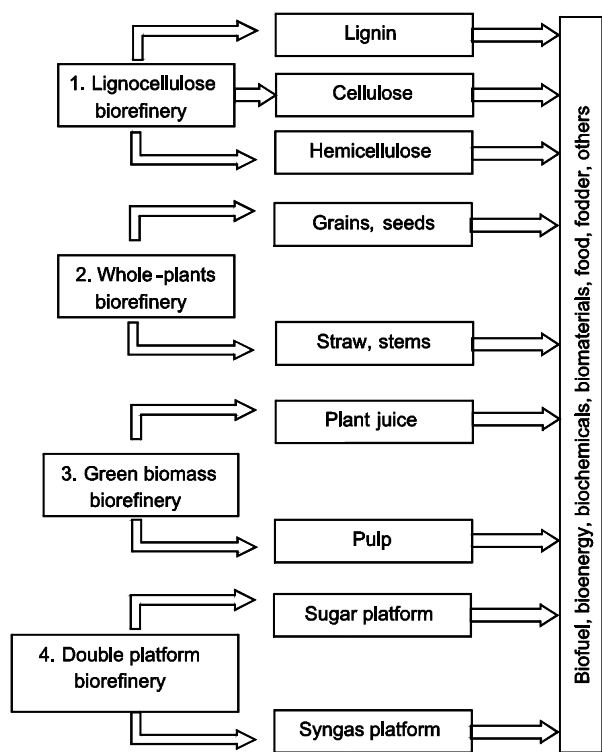


Figure 3. Types of biorefineries – 3<sup>rd</sup> developmental phase.

In the lignocellulose biorefinery (Figure 3.1) naturally dry lignocellulose biomass of various origin such as wood, hay, stems, straw, lupin, etc., is used to undergo successive processes until it is fractionated into three major components: lignin, cellulose and hemicellulose, and consequently into a variety of bioproducts. Among currently obtainable lignocellulose biorefinery bioproducts there are energy, bioethanol, carbon dioxide, methane, chemicals, wood pulp, cellulose derivatives, whereas among the products of the future there are respectively: nutraceuticals, methanol, polymers, emulgators, antioxidants, fertilizers, fodder additives, and others.

In the biorefinery in which whole plants are used (Figure 3.2), the processes of obtaining bioproducts from grains (seeds) and straw (stems) are run. For instance oil crop seeds are used to produce bio-oil and bi-oil and straw as well as post-process residues – pomaces and glycerine are used to produce a variety of bioproducts – biodiesel, soap, coating, glue, food, fodder, cosmetics, and others. A parallel pathway for a variety of biorefinery-based products is defined for root crops and grain crops.

Within the process of biorefining green mass (Figure 3.3) of unripe crops, that is naturally hydrated, first of all plant juice, that is rich in valuable components, is separated from pulp that is rich in fibre, and each of the components subsequently undergo processes in order to obtain a variety of bioproducts such as biofuels and energy as well as amino acids, several organic acids and vegetable juice pigments, insulation materials, construction panel components, and other pulp-based biocomposites (Kamm et al. 2009; Thomsen 2004).

The biorefinery integrating biofuel processes (Figure 3.4) produce products through two kinds of processes – biochemical process (the so called sugar platform) and thermal and chemical process (the so called syngas platform). The process of digesting sugar extracted from a variety of biomass serves the basis for the sugar platform of the biorefinery, whereas the syngas platform converts biomass – through the thermal gasification process or pyrolysis – into gaseous or liquid semi-products that may subsequently be used for producing several biofuels and other bioproducts (Wright and Brown 2007).

Summing up the biorefinery conceptual frameworks that are currently developed (3<sup>rd</sup> Phase), it is plausible to state that development of technological processes providing for a wide spectrum of bioproducts obtained from a variety of biomass is the supreme assumption of the research and development works (Kamm and Kamm 2004). Furthermore, among the aforementioned biorefinery conceptual frameworks, the results of the research currently conducted over bioconversion of lignocellulose into bioethanol and first effects of commercialization of installations of that type and subsequently the integration of processes of converting biomass of various origin and fuel and energy production processes (Figure 4) will have essential impact upon the future of the biofuel market.

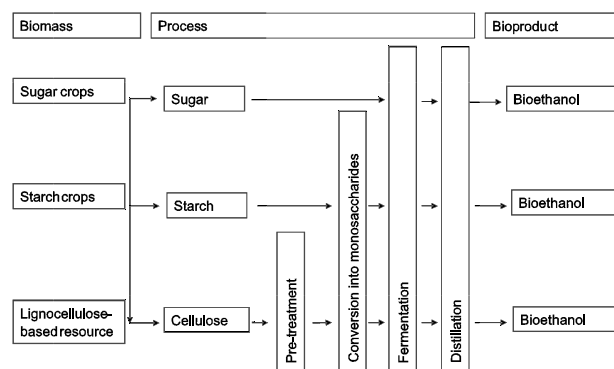
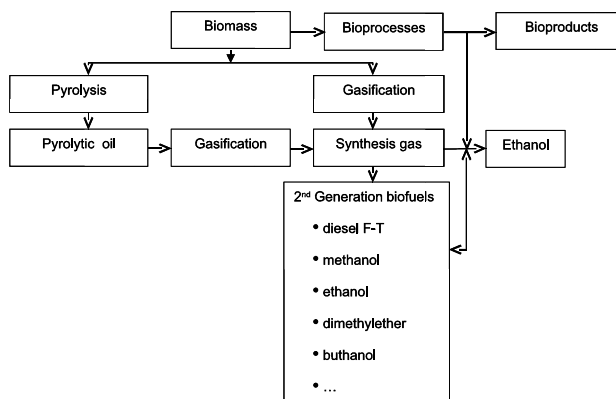


Figure 4. Diagram of integration of lignocellulose originating from a variety of crops, used for bioethanol production.

**RESEARCH POTENTIAL OF LIGNOCELLULOSE-BASED BIOFUEL PRODUCTION**

Continual improvement of reclaim and recycle processes and biomass conversion into bioenergy and biofuel in order to achieve higher efficiency of production, waste biomass use and processing is the supreme notion underlying the presently developed research, innovation and implementation. As it has been mentioned, lignocellulose biomass may be processed to obtain biofuel and energy in various manners, however in the biorefinery biological, biochemical, thermal and chemical and physical and chemical processes may be integrated and used according to needs and requirements (Figure 5), abiding by the supreme principle that second, third and subsequent energy products should be produced exclusively in conditions of ultimate disposal of waste (after repeated recycling) (Gołaszewski et al. 2011).



**Figure 5. Diagram of integrating energy and biofuel production processes.**

Some, essential research-based problems to the extent of biomass production and conversion modes that call for new arrangements, are presented in Table 2 (Gołaszewski 2009b).

**Table 2. Constraints and development potential of 2<sup>nd</sup> generation biofuel production.**

**Biochemical processes – hydrolysis, fermentation**

Lignocellulose biomass	25% higher dry matter production cost as compared to the existing technologies (genetic engineering, breeding, introduction of new genotypes)  High costs and low efficiency of lignocellulose degradation processes (enzymes aided by weak acids, new microorganisms like thermophiles <i>Acidothermus cellulolyticus</i> isolated from hot sources, fungi)  Low fermentation efficiency (enzymes) inter alia due to the lack or difficult conversion of 5-carbon saccharides – xylose and arabinose – breeding of new forms of yeast inducing fermentation of 6-carbon saccharides and 5-carbon saccharides into ethanol and other bioproducts (citric acid, milk acid)  High cost of enzymes per ethanol unit (enzyme biosynthesis)  Search for biocatalytic thermotolerant agents inducing the process of converting 5-and 6-carbon saccharides into final products – providing for simultaneous saccharification (decomposition of cellulose into glucose by means of cellulolytic enzyme) and co-fermentation (conversion of wood sugar to ethanol) – SSCF (simultaneous saccharification and co-fermentation)  Combining biochemical processes with thermal-and-chemical processes under syngas production, and subsequently methanol  Maximization of biomass value through increasing the scale of bioproducts (from solid biofuel to pharmaceuticals)
Starch biomass	Increasing production efficiency including reclaim of saccharides from post-fermentation fraction  Maximization of biomass value through increasing the scale of bioproducts (from liquid biofuel to pharmaceuticals)

**Thermal processes – gasification**

Non-forest biomass	Syngas purification and conditioning (reduction of pitch-like substance, ammonia decomposition, hydrogen sulfide) Membrane technologies – gas separation
Forest biomass	Energy reclaim and biofuel production (methanol, DME) from black liquor that contains over half of wood energetic potential used in paper industry – as a paper industry waste product contains lignin, hemicellulose, and other organic compounds residues
Hydrated biomass	Low-temperature catalytic hydrothermal gasification processes (LTCHG) that convert hydrated biomass to syngas

**Thermal and chemical processes – pyrolysis**

Biomass	Pyrolytic oil conditioning in refining process
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**Physical and chemical processes**

Oil plant biomass	Search for new crops of high oil capacity – ricinus, algae  Maximization of biomass value by means of glycerine phase (the need for development of conversion of glycerol to more valuable products)
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## LIGNOCELLULOSE BIOETHANOL

Ethanol production for food purposes and subsequently ethanol as lamp and lantern fuel component have been known since the beginning of 19th Century (Goettmoeller and Goettmoeller 2007). It was first used as fuel for Ford motor cars in 1930s (Kovarik et al. 1998). Furthermore, ethanol is commonly used as dissolvent and input substrate for production of various chemicals and their derivatives. For decades agricultural ethanol has not been an optional fuel for petrol due to a big difference in prices; neither has the lack of pro-environmental programmes contributed to that. Nowadays purposefulness of developing alternative fuel production processes, including bioethanol production, is supported by both economic and environmental concerns (Campbell and Laherrere 1998). Specific growth rate of bioethanol production was posted in the past three years of 2008, 2009 and 2010 when production of bioethanol regularly rose accounting for 132% and 157% and 177% of 2007 production volume, respectively, but the highest production volume growth rate was posted in the USA (Figure 6). Bioethanol is a significant element of the fuel portfolio in the United States (corn) and Brasil (sugar cane) accounting for approximately 88% (including 57% in the USA) of the world's production output of this fuel. The aforementioned countries allocated at least 4% and 1% of arable land to bioethanol production (Goettmoeller and Goettmoeller 2007).

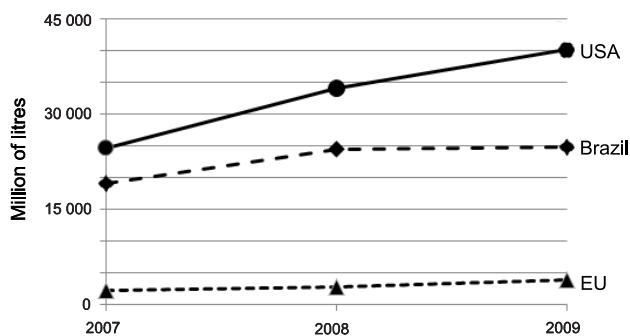


Figure 6. Bioethanol production in terms of millions of litres in the USA, Brasil and EU member states in the years 2007-2010. Source: Licht 2009, RFA 2008.

The increase in the use of crops as resources (vegetable oils, sugar crops and starch crops) for production of liquid biofuels has global dimension; on the one hand it encourages diversification of energy sources and contributes to improvement of energy safety and on the other hand it may result in shortages of strategic food resources in the world. Use of energy crops may cause difficulties in balancing the world's grain market, fodder crops and oil crops. For instance, in the United States in 2007/2008 season the higher demand for corn from the bioethanol industry caused the crops to change to the disadvantage of soyabean – the basic fodder crop, which in

turn caused the fodder prices to rise and consequently the food prices to rise. (FAO 2008; Gołaszewski et al. 2008b). Thus, obvious limitations to development of bioethanol production technology based on traditional saccharide and starch biomass – sugar cane, sugar beet, corn, wheat, rye, rice and potato, challenged contribution of this fuel to reduction of greenhouse gas emission (Farrell et al. 2006; Gołaszewski 2009b) as well as little price competitiveness in relation to petrol indicate purposefulness of searching for more effective resources that will not compete with man's consumer needs and requirements.

Forest is such a traditional, abundant source of energy crops. However, in the case of forest stock there are limitations of both economic and environmental nature that result from this long time that is indispensable to reconstitute forest stand and high industrial value of timber, which is why mainly waste or residues are used for energy purposes and due to environmental concerns, the supreme position of woodland must be stressed in the circulation of global carbon. This is why more and more research is done to use resources originating from dedicated crops including the crops on low-productive land. In the world's literature a variety of interdisciplinary research output has been accumulated on the issue of lignocellulose production resulting in solid fuel used for power purposes, and there are more and more papers elaborating on the subject of lignocellulose conversion into bioethanol. It may be assumed that knowledge that has been compiled, has not reached the critical mass yet, which could result in technology advancement. Presently in the world dozen or so pilot biorefineries operate to produce ethanol from lignocellulose (timber, straw), however none of them has reached any competitiveness in relation to petrochemical biorefinery; furthermore none of them is based on alternative resource – originating from dedicated crops. However, the outburst development of lignocellulose biofuel is forecast to take place in the years 2020-2030 when production of 1<sup>st</sup> generation biofuel is going to be strongly reduced (IEA 2008, 2009). Hamelinck and Faaij (2006) as well as van Vliet et al. (2009) have estimated that lignocellulose bioethanol will become competitive in relation to petrochemical fuel when the price falls below USD 0.50 per 1 litre.

As it has been mentioned, in lignocellulose biorefineries two ethanol conversion modes may be operated. The one is thermal-and-chemical through syngas into ethanol (that is out of this paper) and the other is biological or biochemical through hydrolysis, fermentation and distillation into bioethanol.

The agreed term „lignocellulose” defines the compound of three biopolymers: polysaccharides – cellulose and hemicellulose and polymer – lignin, that in conjunction with other chemical components (extracts, fats, proteins) are found in various proportions depending on species and crop habitats (Doolittle et al. 2006; Saha 2003; Sanders 2009; Sluiter et al. 2010). Table 3 exhibits typical biopolymer content in agricultural residues and lignocellulose crops.

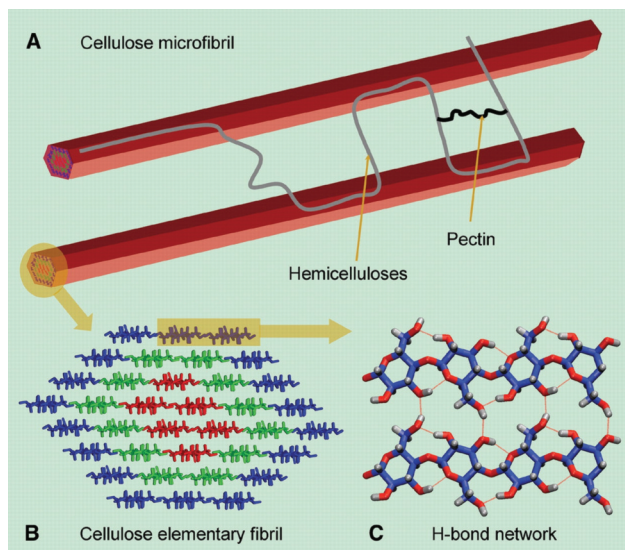


**Table 3. Chemical content of selected lignocellulose biomass sources.**

Lignocellulose biomass source	Chemical content (% dry mass)			Reference
	Cellulose	Hemicellulose	Lignin	
Corn cob	45	35	15	Saha (2003)
Corn stem	40	25	17	Saha (2003)
Rice straw	35	25	12	Saha (2003)
Wheat straw	30	50	20	Saha (2003)
Fibre residues from extracting sugar cane juice	40	24	25	Saha (2003)
Millet	45	30	12	Saha (2003)
Bermuda grass	25	35	6	Saha (2003)
Miscanthus	44	24	17	Blaschek and Ezeji (2007)
Pine tree ( <i>Pinus sylvestris</i> )	40	29	28	Sjöström (1993)
Spruce ( <i>Picea glauca</i> )	40	31	28	Sjöström (1993)
Eucalyptus ( <i>Eucalyptus camaldulensis</i> )	45	19	31	Sjöström (1993)
Birch ( <i>Betula vernocosa</i> )	41	32	22	Sjöström (1993)
Willow ( <i>Salix</i> sp.), 1-year cycle crops	45	13	14	Szczukowski et al. (2002)
Willow ( <i>Salix</i> sp.), 2-year cycle crops	48	12	13	Szczukowski et al. (2002)
Willow ( <i>Salix</i> sp.), 3-year cycle crops	56	14	14	Szczukowski et al. (2002)
Poplar	42-48	16-22	21-29	Sannigrahi et al. (2010)

Analysing numerous species of sugar crops, starch crops and lignocellulose crops Sanders (2009) indicated extensive volatile nature of chemical content. Within the chemical content balance, lignocellulose crops such as *Salix* or millet – apart from saccharides compound – they also contain 1-5% of protein, and other crops having lignocellulose residue potential (straw) such as grain crops, grass or oil crops may contain 3-30% of fats.

Lignocellulose-based biopolymers, particularly lignin, are hard to convert into simple compounds they are made from. The basic reason for that is essentially different sensitivity of those compounds to all and any thermal, biological and chemical processes. Thus cellulose and hemicelluloses content determine bioethanol capacity under biochemical process. In the case of cellulose, breaking glycoside bonds combining monosaccharides is a technological problem as the longer the saccharides chain is and the more branched it is, the more difficult the problem becomes. On the other hand in the case of hemicellulose, conversion into monosaccharides is easier, however those saccharides are more difficult to undergo fermentation. The specific nature of polysaccharides chemical bonding and mutual interactions are presented in Figure 7. Troublesome decomposition and extensive volatility of chemical content in the case of lignocellulose crops in relation to genotypes and crops habitats cause development of economically efficient preliminary processing and hydrolysis to be a great challenge.



**Figure 7. Lignocellulose-based polysaccharides structure and interactions.** (A) Simplified model of interactions among main polysaccharides in cell walls (no lignin whose interactions with cellulose and hemicelluloses are not well defined). In this model hemicelluloses are tightly connected with cellulose crystallites (micelle) building the network of microfibrils. Pectines are polysaccharides „splicing” cell wall components. (B) Structure of elementary cellulose microfibrils. (C) Intrachain and interchain hydrogen bonding. Source: Himmel et al. (2007).

Sluiter and followers (2010) reviewed 15 methods of analysing content/division of structural hydrocarbons and lignin through sulphuric acid-based hydrolysis. Beginning from 1922 until 1993 the analytical process of a variety of lignocellulose resource (timber, soft timber, wood residues, wood pulp, and others) of various refinement degree and various extraction modes was regularly developed. Development of cellulose chemical hydrolysis-based processes was also contributed by Polish inventors, including Troszkiewicz and Bogoczek who in 1954 patented „the mode of hydrolysis of timber or other materials containing cellulose, sophisticated due to that the hydrolysed material mixes cold with smoking nitrogen acid and immediately distills the acid under lower pressure.” In spite of many suggestions of specific arrangements, a number of contemporary research works have proven that for future arrangements the most promising will be inclusion of enzymatic hydrolysis but it bears noting that nowadays the cost of such a process has not become competitive yet (Ogier et al. 1999; Yu and Zhang 2004). Hahn-Hägerdal and followers (2006) analysing new technologies-related requirements and achievement of indispensable progress allowing for lignocellulose bioethanol to be commercially produced, have stated that optimization of the process engineering, fermentation technology, enzymes production and metabolic processes will be the real challenge for the next coming years.

For successful biological lignocellulose conversion into bioethanol, a set of principal processes is indispensable for a technological line: (1) defibration (delignification) entailing release of cellulose and hemicellulose out of lignin – preliminary process, (2) depolymerisation of polysaccharides into monosaccharides – mineral acid-based hydrolysis/enzymatic hydrolysis, (3) hexose and pentose fermentation into ethanol, (4) ethanol refining by means of distillation and refinement.

In the context of delignification process (stage 1), from among many various physical, chemical, biological and mixed methods (Table 4), the physical method „steam explosion” is referred to as a developing method, that entails treatment of disintegrated lignocellulose biomass with steam under a high pressure, and subsequent fast decompression causing the

cells to break up and inducing easier enzyme penetration. Bonini et al. (2008) analysing various physical parameters of the steam explosion in the presence of various chemical compounds, that is to treat disintegrated biomass of two resources: a pine and corn stems, have stated *inter alia* that the thermal-and-chemical method with temperature of 200°C applied for 5 minutes in the presence of 3% sulfuric acid results in the highest reclaim of lignin from corn stems, amounting to 65.08% of Klason lignin. Apart from the steam explosion, Zhu and Pan (2010) refer to two other technologies – Organosolv that entails lignin and hemicellulose organic solvents in the temperature of 140-220°C and SPORL – Sulfite Pretreatment to Overcome Lignocelluloses Recalcitrance. The Organosolv technology is used in the paper industry but purposefulness of its use for lignocellulose crops and residues has been quite frequently reported. Alcaide and followers (2003) have examined the impact of ethanol, acetone and water mixture upon the features of a pulp from wheat straw stating *inter alia* that the process entailing the said solvents should be run in the temperature of 180°C for 60 minutes in order to be effectively successful. The whole process covered three stages: 1 – Organosolv-based delignification reaction, 2 – lignin reclaim by means of pressurized dissolved air flotation, 3 – lignin used for polymer production.

Zhu et al. (2009), reported that the pulp, obtained from SPORL entailing treatment of raw soft timber chips with acid sulphite (8-10%) and sulphuric acid (1.8-3.7%), was particularly efficient in the context of enzymes efficiency. In consequence hemicellulose is almost completely separated, delignification is done partially and lignosulfonate is obtained, and upon the lapse of 48-hour enzymatic hydrolysis, cellulose is disintegrated in 90%.

In the process of cellulose and hemicellulose enzymatic hydrolysis, kindred enzymes produced by a numerous group of microorganisms (fungi, bacteria, protozoans, and others) are used, the fungi being the best recognized group of microorganisms.

Cellulases disintegrating cellulose are classified according to the nature of catalyzed reaction: hydrolytic cellulases, including endocellulases, exocellulases and beta-glucosidases (disintegrating internal bonding of cellulose crystalline

**Table 4. Lignocellulose biomass pretreatment methods. Source: Saha and Woodward (1997).**

Method/Treatment	Example
<b>Thermal-and-mechanical treatment</b>	Disintegration, grinding, coagulation, extruding
<b>Selfhydrolysis</b>	Steam pressure, steam explosion, supercritical carbon dioxide-based extraction
<b>Acids</b>	Dissolved or concentrated sulfuric acid or hydrochloric acid
<b>Alkalies</b>	Sodium hydroxide, ammonia, alkaline solution of hydrogen peroxide
<b>Organic Solvent-based Treatment</b>	Methanol, ethanol, butanol, phenol

structure into single cellulose chains, subsequently into disaccharides (cellobiose) and finally into monosaccharides), oxidase cellulases and cellulose phosphorylases responsible for phosphate-based cellulose polymer degradation (Reddy and D'Souza 1998).

Alcohol fermentation is a subsequent stage, that is performed by microorganisms, during which simpler compounds are released, such as monosaccharides fermented into ethanol and carbon dioxide. Particularly preferred is a type of yeast *Saccharomyces cerevisiae* accumulating the largest quantity of ethanol. Miyamoto (1997), Ingram and followers (1998) and Dien and colleagues (2003) refer to a number of types of bacteria, including pathogenic ones, for which the basis fermentation product is ethanol: *Clostridium sporogenes*, *Clostridium indoli*, *Clostridium sphenoides*, *Clostridium sordelli*, *Zymomonas mobilis*, *Spirochaeta aurantia*, *Spirochaeta stenostrepha*, *Spirochaeta litoralis*, *Erwinia amylovora*, *Escherichia coli*, *Leuconostoc mesenteroides*, *Streptococcus lactis*, *Klebsiella aerogenes*, *Mucor* sp., *Fusarium* sp.

Combining enzymatic hydrolysis (stage 2) and fermentation (stage 3) with the use of various types of yeast (Simultaneous Saccharification and Fermentation – SSF) was an innovative arrangement that was to improve efficiency of conversion of lignocellulose into ethanol, *inter alia* due to the enzyme cellulose produced by mutated strain of fungus *Trichoderma reesei* growing in the presence of hydrolysed glucose (normally glucose hampers this fungus from producing cellulose) (Kamm et al. 2010). The outcome problem with SSF technology arises from various optimal hydrolysis temperatures (45-50°C) and fermentation (28-35°C) and compatibility of microorganisms and enzymes (Lin and Tanaka 2006). Bothast and Saha (1997) have defined some economic minimum of the conversion of lignocellulose substrate into ethanol providing for high capacity of ethanol with approximately 3% of mass-volume concentration and substrate input above 10% as obtained in a relatively short time – shorter than 4 days. Under the research performed by Hari Krishna and Chowdary (2000) the minimum was satisfied by combining enzymatic hydrolysis and fermentation with the use of cellulose obtained from *Trichoderma reesei* QM-9414 cells and *Saccharomyces cerevisiae* NRRL-Y-132. Ferreira and followers (2010) analysing the processes of disintegrating the residues of sugar cane-based saccharides production, state that the majority of cellulose enzymes that are commercially available do not prove satisfactory activity under simultaneously performed processes of saccharification and fermentation. They also refer to a larger biotechnological saccharification and fermentation potential of recombinant strains of *S. cerevisiae* than in the case of *T. reesei* as far as the production of 2<sup>nd</sup> generation bioethanol is concerned. Modifications of SSF hitherto have aimed at optimization of environmental conditions for microorganisms responsible for both phases by means of running the processes in two reactors having various optimal temperatures – Non-isothermal SSF (Wu and Lee 1998) or biopolymer structure-oriented process – SSCF (Simultaneous

Saccharification and CoFermentation), performing hexose and pentose co-fermentation (Olofsson et al. 2010).

Effective production of bioethanol from lignocellulose is the subject of numerous research works and expected technological progress will be preconditioned by achievements in glucose conversion-oriented fermentation technology (out of cellulose) and xylose (out of hemicellulose) into ethanol, more effective production of hydrolysis and fermentation enzymes and intensified activity (costs reduction).

## CONCLUSION

The determinants for the agricultural biofuel market development are: (1) the change in the relation between the costs of producing 1<sup>st</sup> and 2<sup>nd</sup> generation biofuels by introducing new biological diversity and effective biofuel production technologies; (2) higher use efficiency of production potential of agricultural land including dedicated lignocellulose crops, first of all on the marginal land, as well as maximizing use of biological yield; and (3) the change in the import policy and fiscal policy for biofuel including the policy opening the market for bioethanol, taking into consideration the relation between the biofuel prices and fossil fuel prices.

On the grounds of currently conducted research and development works it is plausible to state that research and development of biorefinery enters 3<sup>rd</sup> phase in which diversification of resources and integration of technological processes and energy production take place. Depending on biomass to be processed, four categories of biorefineries may be distinguished: (1) lignocellulose, (2) whole plants, (3) green biomass, (4) double-platform.

Development of the biorefinery conceptual framework should result in the knowledge on the technology of obtaining larger and larger diversity of bioproducts, which apart from environment-friendly effects will allow for maximization of biomass capacity.

Biorefinery will affect the future energy biomass market and profitability of the whole agricultural sector.

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