Recent Findings and the Energetic Potential of Plant Biomass as a Renewable Source of Biofuels – A Review

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Nowadays the main sources of energy are petroleum, coal, and natural gas. However, these fossil sources are not reproduced in nature; on a human timescale their reserves are exhausted permanently and run down. Considerable attention in recent years has been given to plant biomass, which in contrast to the fossil sources is continuously renewed in nature. In this critical review the use of non-edible plant biomass for production of various kinds of biofuels is considered. To generate energy, plant biomass either can be burned directly or it can be used after its conversion into carbonized solid fuel (*e.g.* biochar), liquid fuels (bioethanol, biodiesel, bio-oil), or gases (biogas). Among various biofuels, production of bioethanol has potential to be the most attractive if recent technological advances become implemented, such that the co-production of ethanol and valuable byproducts can be combined together with recycling of solid and liquid wastes. A comparative analysis of energetic potential of biomass and various kinds of biofuels revealed that the most efficient way to produce energy is by direct burning of the plant biomass in a pelletized form, while the burning of such amount of the solid, liquid, or gaseous biofuel, which can be obtained from the plant material, gives a much smaller energetic effect. Novel types of pellets, as well as solid/liquid biofuels, having improved fuel characteristics are described.

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INTRODUCTION

Demands for Fuels

The existence and further development of the present civilization requires expanded consumption of energy, chemicals, and materials. Nowadays the main energy sources are fossil fuels, namely coal, petroleum, and natural gas. Over 80% (about 450 to 500 EJ per year) of the world's energy demands are met by the combustion of fossil fuels (Ioelovich 2010; Hossain 2012; IEA 2012; BP 2013). Coal gives about 28% of the world's consumed energy. Crude oil – petroleum, provides about 32% of the world's energy, while natural gas provides about 20% of the world's energy consumption.

The increased use of the fossil fuels is causing acute environmental problems, since the combustion of the fuels is accompanied by emission of carbon dioxide and water vapor, triggering the greenhouse effect and global warming of the Earth. Combustion of 1 ton of petroleum products (gasoline, kerosene, diesel fuel, *etc*.) or

natural gases (methane, propane, butane, *etc*.) is accompanied by the release of 3 to 3.2 tons of carbon dioxide, as well as 1.5 to 2 tons of water vapor. Combustion of 1 ton of coal generates higher volume of carbon dioxide, up to 3.7 tons. Furthermore, the combustion of coal and certain hydrocarbon fuels generates toxic sulfur and nitrogen oxides that contribute to the formation of acid rain, which pollutes the environment.

As is well known, fossil resources are not reproduced in nature within a human timescale; their reserves are exhausted and run down in an essentially permanent manner (Lee *et al.* 2007; Ioelovich 2013). Based on recent investigations, the proven reserves of coal in the world are about 900 to 1000 Gt; and known reserves of the crude oil are estimated as 2 to 3 trillion barrels. Proven resources of the natural gas (from gas fields and also accompanying gas from crude oil fields) are about 200 to 250 trillion cubic meters. In recent years huge volumes of shale gas and oil have been found in various countries, and such discoveries make possible the prolonged use of the fossil sources. Shale rocks containing a significant amount of the fossil sources have been discovered in various counties. But currently only the USA has innovative technologies, special equipment, and finance for extraction of the fossil feedstocks from shale rocks in commercial volumes. The result has been a considerable increase in accessible reserves of fossil sources in the USA. However, the shale sources have some shortcomings: their composition is complex; besides the extraction of these sources is more expensive than of the conventional fossil sources and harms the environment.

Non-Edible Biomass as a Potential Source of Energy

To eliminate the imbalance in the fossil sources, an increased utilization of alternative sources of energy and raw-materials is required. Considerable attention in recent years has been given to plant biomass, which in contrast to fossil sources is continuously renewed in nature. Total resources of plant biomass reach 1.5 trillion tons (Klemm *et al.* 2005), and increase by approximately 100 billion tons annually as a result of photosynthesis (Field *et al.* 1998). However, only a small portion of biomass can be utilized and used as a source of alternative energy and bioproducts. Currently, the share of the biomass-based energy is about 10 to 12% (55 to 58 EJ per year) of the world energy consumption (Hossain 2012; Lehtovaara *et al.* 2013). According to forecasts, the share of biomass in energy production will increase (Berndes *et al.* 2003; Haberl *et al.* 2011).

Currently implemented technologies for production of liquid biofuels are based on transformation of food-grade carbohydrates into bioethanol and vegetable oils into biodiesel fuel (Tokgoz and Elobeid 2006; Ioelovich 2010). The main sources of these carbohydrates are juices of sugarcane, sugar beet, and sweet sorghum, as well as starches of corn, wheat, potatoes, and some other agricultural plants. In Brazil, ethanol is produced completely from juice of sugar cane. In the USA, production of ethanol relies on corn starch. The typical representatives of the oil-crops are olive, rapeseed, sunflower, and some other plants. Since these carbohydrates and vegetable oils are required in the food industry, their use for the production of biofuels is limited. Moreover, further expansion of the production to higher volume of bioethanol and/or biodiesel will cause shortage of land areas, exhaustion of the soil, excessive consumption of water and energy, deficits of food and feed products, and increasing of their prices (Baier *et al.*

2009; Čuček *et al.* 2011). The Federal office for the environment in Germany also believes that there is not enough agricultural land in the world for cultivation of the energy crops that would be needed for production of biofuels sufficient to replace fossil fuels.

An alternative way to obtain biofuels without competing with the food industry is through the use of non-edible biomass (Pandey 2009; Bacovsky *et al.* 2010). This biomass type involves wood and some other plant species (*e.g.* miscanthus, switchgrass, Bermuda grass, *etc.*), forest residues (*e.g.* sawdust, twigs, shrubs, *etc.*), residues of agricultural plants (*e.g.* stalks, husks, cobs, *etc.*), residues of textile, pulp and paper, municipal paper waste, *etc.* Moreover, huge amounts of algae are not utilized yet and can be used as appropriate feedstock for production of energy or chemicals. The not-edible plant raw materials are related to abundant, renewable, and inexpensive biomass types. The total amount of such biomass that is accumulated annually in the world is estimated to be 10 billion tons at least. In the USA alone, the annual accumulation of the biomass is about 1 billion tons (Perlack *et al.* 2005; Zhang and Wang 2013). However, woody biomass is the main feedstock for wood and cellulose industries; therefore, only residues of this biomass can be used for other purposes. In Brazil, the main amount of sugarcane bagasse is already being used, such that only about 20% of this biomass is available. In the USA and some other countries, more than 20% of the agricultural biomass (corn stover, straw*, etc.*) is utilized as feed for cattle, organic fertilizer, feedstock for paper and cardboard, *etc.* (Kadam and McMillan 2003; Copeland and Turley 2008; Khan and Mubeen 2012). Besides, currently about 3 billion tons of plant biomass are burned to obtain heat. Thus, the current world resources of available non-edible biomass for biofuels and bioproducts can be estimated to range from 3 to 4 billion tons per year. In general, biomass can be used as feedstock for production of liquid biofuel for vehicles and as solid fuel for burning and/or gasification in order to generate heat, steam, and electricity, and also as feedstock for manufacturing of various bioproducts and biochemicals (McKendry 2002; Lucia *et al.* 2006).

Biomass Structure and Chemistry

As background for later discussion of biomass energetic potential, as well as its resistance to conversion to biofuels (*i.e.* its recalcitrance), the physical structure and chemistry of biomass will be summarized here based on current literature. Any plant biomass is an ensemble of multitude of plant fibers bonded with each other in the lateral direction by means of a lignin-hemicellulosic "glue". To isolate the individual fibers, the biomass can be subjected to biological or chemical maceration in combination with mechanical or ultrasound treatment. An individual cellulosic fiber is an elongated vegetable cell. The fibers can contain pores and structural defects. A hollow capillary space, the lumen, extends the length of the fiber. Fibers of biomass have different shapes and sizes (Sjöström 1993; Rowell 2005; Ioelovich 2013). The biomass of softwoods consists mainly of fibers called tracheids. Lengths of the tracheids are in the range 3 to 7 mm and the diameter is 20 to 40 μm, while width of the cell wall is 2 to 5 μm.

The biomass of hardwoods can consist of various types of fibers, mainly libriform (70 to 90%), as well as vessels and tracheids. Libriforms are short spindle-shaped fibers with lengths of 0.5 to 2 mm and average diameter of about 20 μm. Vessels have a wide

lumen with diameter of 50 to 90 μm. Twigs of the trees and shrubs have similar anatomic structure. The biomass of agricultural plants and grasses contain mainly libriform fibers and vessels (Khalil *et al.* 2006). Fibers of cotton and bast plants (flax, ramie, jute, *etc*.) are long (20 to 40 mm) and have specific shapes. Cotton fibers are twisted, while fibers of bast plants are straight and round.

The cell wall of any plant fiber is built from external primary P and inner secondary S walls (Sjöström 1993; Rowell 2005). The thin P-wall (about 100 to 200 nm) contains a loose net of cellulose fibrillar bundles. The S-wall has a thickness of 2 to 4 μm and is composed of three layers S1, S2, and S3. The layers S1 and S3 have nano-thickness. The dominating S2-layer is built of cellulose fibrillar bundles orientated mainly along the fiber axis (Ruel *et al.* 2006; Ioelovich 2014). The fibrillar bundles of the cell wall consist of elementary cellulose nanofibrils – thin filaments with diameter of 3 to 5 nm.

Any type of plant biomass consists of three basic polymer components: cellulose, hemicelluloses, and lignin. ***Cellulose*** is the most abundant organic matter on Earth (Klemm *et al.* 2005). This polysaccharide is present in all plants and algae; cellulose of the tunicin type forms a shell of certain marine creatures, and it is also synthesized by some microorganisms, *e.g*. *Gluconacetobacter xylinus*. The main sources of cellulose are plants. The content of cellulose in herbaceous plants is 30 to 40%, in woods 45 to 50%, in bast plants (flax, ramie, jute, *etc.*) 60 to 70%, and in cotton fibers upwards of 90% (Young and Rowell 1986; Hon 1996; Ioelovich 2013, 2014). The main commercial sources of cellulose are wood and to a lesser extent, cotton. To isolate the cellulose, the feedstock is heated within closed vessels under pressure in the presence of caustic soda (soda process), mixture of sodium hydroxide with sodium sulfide (kraft process), or sulfurous acid and salts thereof (sulfite process) (Nikitin 1962; Sjöström 1993; Biermann 1996). Organosolv, oxidative, and some other delignification methods are also used, but at a lower scale (Wildschut *et al.* 2013; Wyman 2013). As a result, lignin and hemicelluloses are removed, while cellulose is separated, washed, and dried. The production volume of wood pulp in the world is huge and reaches 300 to 350 million metric tons per year. Production of cotton cellulose is smaller, 20 to 25 million metric tons per year. The main part of the cotton fibers is intended for textile industry, and only short fibers (linter) and cotton wastes (nap) are used for the production of chemical grade cellulose, specialty paper kinds, microcrystalline cellulose, and cellulose derivatives.

Cellulose is a linear, stereoregular, semicrystalline polysaccharide composed of D-glucopyranosic units linked by chemical β-1,4-glycosidic bonds. The glucopyranosic units have a "chair" conformation. Macromolecules of natural cellulose from various origins may include 2,000 to 30,000 elementary units. During the process of cellulose isolation from plant materials and cellulose modification, a partial depolymerization of the macromolecules is observed. Each glucopyranosic unit of cellulose contains three hydroxyl functional groups: one primary and two secondary groups. The hydroxyl groups impart to cellulose materials a hydrophility and reactivity to various reagents.

The linear macromolecules joined by hydrogen bonds form supermolecular structure of cellulose that consists of thread-like elementary nanofibrils and their bundles called microfibrils. The lateral size of elementary nanofibrils of various cellulose samples is different and can vary from 3 to 5 nm for natural cellulose of herbaceous plants and

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woods to the range 10 to 15 nm for cellulose isolated from *Valonia* algae; length of the elementary fibrils reaches several microns (Klemm *et al.* 2005; Ioelovich 2014). The elementary nanofibrils usually are aggregated into microfibrillar bundles with lateral size of 20 to 40 nm, and such bundles can form the fibrillar network of nanofibrillated cellulose, lamellas, and layers of the cell wall of cellulose fibers.

Statistically alternating nano-scale crystallites along with non-crystalline domains are integral constituents of long and thin nanofibrils. Thus, a two-phase cellulose model containing crystalline and non-crystalline domains is currently used to describe the structural organization of cellulose (Krässig 1993). Further investigations have revealed the presence also of a paracrystalline fraction, which must be taken into consideration to describe structure and properties of cellulose (Ioelovich 2014). Recently, a detailed model of supermolecular structure of natural cellulose has been developed (Ioelovich *et al.* 2010; Ioelovich 2014). According to this model (Fig. 1), the elementary nanofibril of cellulose is built from orientated nano-scale crystallites and non-crystalline domains (NCD), and a thin paracrystalline layer (PCL) is located on the surface of the crystalline core (CRC). The crystalline cores can contain local defects (DEF), *e.g.* vacancies, caused by ends of the chains (Pakzad *et al.* 2012).

The nanocrystallites having three-dimensional order are strong and inaccessible structural elements. By contrast, the low-ordered non-crystalline nanodomains having twisted and curved segments are weak and accessible within the fibrils. Thereby, the cleavage of glycosidic bonds at hydrolysis occurs mainly in non-crystalline domains of cellulose nanofibrils, an action that facilitates release of the individual crystallites. The formed fragments have a level-off degree of polymerization (LODP) from 100 to 300, which approximately corresponding to average degree of polymerization of individual nanocrystallites. The nanocrystallites have the same lateral size as the elementary nanofibrils, but their length in plant materials of various origins can vary in the range from 50 to 150 nm, while the length of disordered non-crystalline domains can be 25 to 50 nm.
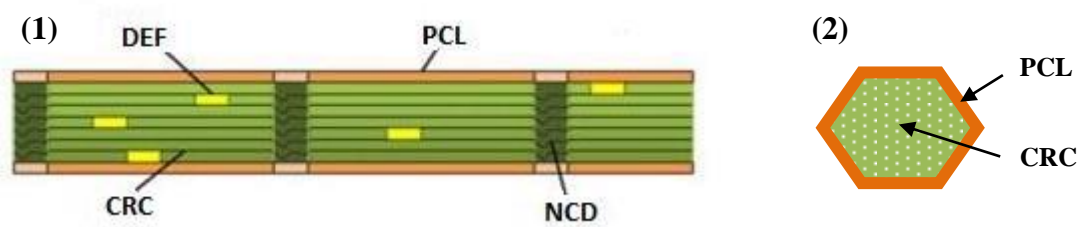
Fig. 1. Model of elementary nanofibril of natural cellulose: longitudinal section (1) and cross section (2)

The shape of crystallites of natural cellulose has been a subject of discussion. In several studies the cross-sectional shape of the crystallites has been depicted as a square or rectangle. However, recent studies have shown that the most likely cross-sectional shape of the crystallites of natural cellulose is a hexagon (Ding and Himmel 2006; Yang *et al.* 2011; Ioelovich 2014). Three groups of planes (100), (110), and (1-10) are located on the surface of CI$_\beta$ crystallites, allowing the co-crystallization process of adjacent crystallites in different lateral directions. The co-crystallization process taking place

during isolation or hydrolysis of cellulose causes the increase of lateral sizes of crystallites. Due to the relative high content of surface paracrystalline layers, the nanocrystallites are characterized by increased accessibility, solubility, and reactivity (Ioelovich 2014). The paracrystalline layers of nanocrystallites weaken the crystalline structure; as a result of the increase of paracrystallinity, the reduction of phase transition temperatures of nanocrystallites was observed.

Crystallinity degree ranges from 0.5 for herbaceous celluloses to 0.8 for bacterial and algal celluloses. Modification of cellulose leads to change in its crystalline structure. Structural investigations have shown that crystallites of natural celluloses have the allomorph type CI (Krässig 1993; O'Sullivan 1997). Furthermore it was found that the crystalline unit cell of CI can be in two distinct crystalline forms: triclinic I_α of P_1–space group and monoclinic I_β of $P2_1$-space group. The I_α form is characteristic for algae and bacterial celluloses, while the more stable I_β form is dominant in higher plants and tunicin (Sugiyama *et al.* 1991; Krässig1993; O'Sullivan 1997; Zugenmaier 2008). The specific gravity of I_β crystallites (1.62 g/cm^3) is slightly higher than I_α crystallites (1.60 g/cm^3). Three additional crystalline allomorphs: II, III, and IV, have been identified, which are attributed to modified celluloses.

The hydroxyl groups of cellulose can be reacted to form ethers and esters, carbonyl, carboxyl, and other derivatives (Fengel and Wegener 1984; Lewin and Pearce 1998; Hon and Shirashi 2000; Pantze 2006). Due to presence in non-crystalline domains of cellulose of labile glycosidic (semi-acetal) chemical bonds, this polysaccharide is depolymerized under the effect of oxidants, acids, and cellulolytic enzymes (Fengel and Wegener 1984). The product of partial hydrolysis of cellulose - microcrystalline cellulose (MCC) - has a great commercial importance. MCC is used as excipients for tablets, as a non-caloric food additive, and in some other areas (Battista and Smith 1962; Battista 1975; Kotelnikova *et al.* 1976). The nano-architecture of natural cellulose promotes the isolation of free nanofibrils and nanoparticles (Hubbe *et al.* 2008; Habibi *et al.* 2010; Ioelovich 2014).

The technology of cellulosic ethanol has received a lot of interest. The first stage of this technology is hydrolysis of cellulose into glucose. Such hydrolysis can be accomplished either by dilute acid at high temperatures or by cellulolytic enzymes. The enzymatic hydrolysis is preferable because this process is carried out at moderate temperatures and gives an increased sugar yield. The second stage is a yeast fermentation of glucose and production of ethanol. The theoretical yield of ethanol from 1 t of cellulose is 190 gal (Ioelovich 2013). However, the real yield is considerably lower due to limited conversion crystalline cellulose into glucose and incomplete glucose conversion into ethanol. The cellulosic bioethanol can be used as liquid fuel, organic solvent, antiseptic, component of alcoholic beverages, *etc.*

Hemicelluloses are attributed to non-cellulose polysaccharides. Their content in various plants can be in the range 20 to 40% (Hon 1996). Hemicelluloses are hydrophilic amorphous heteropolymers. In addition to physical bonding of cellulose, hemicelluloses also form ester bonds with lignin. Thus, in the cell walls of plant fibers, hemicelluloses fulfill the function of binder between hydrophilic cellulose fibrils and hydrophobic lignin. The chemical structure of hemicelluloses consists of chains of a variety of acetylated links of pentoses or hexoses and backbones (Sergeeva 1972; Horn *et al.* 2012). Various

plants and also its tissues contain different types of hemicelluloses. Agricultural and herbaceous plants, as well as hardwoods contain mainly the pentosan-type hemicellulose xylan, while softwoods are enriched with the hexosan-type hemicellulose mannan. Hemicelluloses are heteropolymers: xylan, for example, can be present in the form of glucuronoxylan (in hardwoods) or arabinoxylan (in grasses and grains), while mannan - in a form of glucomannan (in softwoods) or galactomannan (in carob tree).

Hemicelluloses can be hydrolyzed enzymatically by means of hemicellulases into monosaccharides, consisting of pentoses and hexoses (Horn *et al.* 2012). However, certain structural factors of hemicelluloses, namely branching and acetyl groups, impede the enzymatic digestibility. Moreover, enzymatic degradation of hemicelluloses yields a mixture of different sugars that may contain substantial amounts of pentoses that are difficult to ferment into ethanol by *Saccharomyces cerevisiae*. Another yeast *e.g. Pichia stipitis etc.*, is used for direct fermentation of pentoses into ethanol (McMillan 1993; Njoku *et al.* 2013). The pentose sugar – xylose, obtained by enzymatic hydrolysis, can be used as a feedstock for production of xylitol. Other significant application of pentoses is production of furfural, using dehydration process of the pentose in the presence of acidic catalyst.

Currently, isolated hemicelluloses are not produced on an industrial scale. Spent sulfite liquor remaining after the pulping process contains monomers and oligomers of hemicelluloses, which are used for production of ethanol and/or feed proteins (Takahashi *et al.* 2012; Tanifuji *et al.* 2013).

Lignin is a rigid, aromatic, amorphous, and hydrophobic polymer that is stable to some chemical reagents and cellulolytic enzymes (Horn *et al.* 2012; Ioelovich *et. al.* 2012). The content of lignin in plant biomass ranges from 10% for corn cob or rice straw to 48% for olive husk (Hon 1996; Abbasi and Abbasi 2010; Jahirul *et al.* 2012; Ioelovich 2013). Lignin is a complex polymer of phenylpropane units, which are cross-linked to each other with a variety of different chemical bonds. This polymer consists of three main phenylpropane units - guaiacyl (G), syringyl (S), and hydroxyphenyl (H). The relative ratios of these units can vary for different biomass sources. Lignin of softwoods is mainly of G-type, whereas lignin of hardwoods contains a mixture of G-and S-units. Lignin of herbaceous plants consists usually of all three types of the phenylpropane units (Chen and Dixon 2007).

In the lignified plant biomass, one portion of lignin is localized between the cells (fibers), while another portion of lignin is localized inside the cell (fiber) wall in the form of thin hydrophobic nano-layers. The cellulose elementary nanofibrils inside the plant cell wall are separated from each other by means of the thin layers of amorphous hemicelluloses, whereas fibrillar bundles consisting of the elementary nanofibrils of cellulose and hemicelluloses are surrounded with hydrophobic nano-layers of lignin, which protect the hydrophilic polysaccharides against biological and chemical attack (Kerr and Goring 1975; Larsen *et al.* 1995; Pan *et al.* 2005; Zhu 2005; Ioelovich 2013). In order to improve enzymatic hydrolysis of the lignocellulosic biomass, most of the lignin fraction should be damaged and/or removed. However, due to its relatively high resistance to chemicals, the damage or removal of lignin from the biomass requires harsh processing conditions, such as high-temperature treatment with alkali; sulfurous acid and

its salts; or treatment with hot nitric acid followed by extraction with boiling alkali (Nikitin 1962; Sergeeva 1972; Sjöström 1993; Biermann 1996).

Organosolv, oxidative, and some other methods are also used for delignification of the biomass (Draude *et al.* 2001; Mesa *et al.* 2011; Xu and Tschirner 2012; Wildschut et al. 2013; Wyman 2013). Limited amounts of lignin can be removed from the biomass by means of steam explosion, without or with addition of an acidic catalyst (Kaar *et al.* 1998; Cara *et al.* 2007; García-Cubero *et al.* 2010). On the other hand, addition of alkali facilitates the removal of lignin during steam explosion of the biomass. To remove residual lignin from pulp, various bleaching agents are used: chlorine, sodium chlorite, sodium or calcium hypochlorite, chlorine dioxide, hydrogen peroxide, oxygen, ozone, and permanganates, *etc*. (Rapson 1963).

The main industrial method of delignification is the kraft process, where lignin is fully utilized for regeneration of chemicals, and therefore it cannot be recovered and used as feedstock for bioproducts. Smaller amounts of lignin are produced in sulfite mills in a form of lignosulfonates, which can be used as surfactants and plasticizers in making of concrete.

The chemical composition of the plant biomass can be determined by conventional methods of chemical analysis (Fengel and Wegener 1984; Christian *et al.* 2002; Rowell 2005; Sun *et al.* 2005; Ioelovich *et al.* 2012). For example, the percentage of lignin can be determined by means of standard TAPPI procedure T222. The content of holocellulose in the biomass is measured after selective delignification of the sample with sodium chlorite (Browning 1963). The obtained holocellulose sample is hydrolyzed with boiling 1.5% hydrochloric acid for 2 h. The content of cellulose is calculated from the dry residue remaining after hydrolysis of the holocellulose, while the content of hemicelluloses is measured from weight loss of the hydrolyzed holocellulose sample. An NREL procedure includes the acidic hydrolysis of polysaccharides of the biomass with subsequent HPLC analysis of monosaccharides and simultaneous determination of lignin content (Hames *et al.* 2003; Sluiter *et al.* 2010).

Typical Biomass Composition

Table 1. Typical Chemical Composition of Dry Biomasses

Biomass	Cellulose, %	Hemicelluloses, %	Lignin, %
White cotton fibers	94-96	1-2	<1
Brown cotton fibers	85-88	2-3	5-7
Flax fibers	85-88	5-6	3-5
Softwood	46-50	20-23	27-28
Hardwood	44-46	25-27	22-25
Bagasse	37-39	23-25	19-21
Corn stalks	35-37	24-26	18-20
Corn cobs	34-36	36-38	9-11
Corn stover	35-37	28-30	18-20
Wheat straw	34-36	28-30	15-17
Rice straw	34-36	25-27	7-9
Switchgrass	36-38	26-28	17-19

The content of the basic polymer components - cellulose, hemicelluloses, and lignin - in some plant biomasses and in waste and residue of plant materials, is shown in Tables 1 and 2 (Hon 1996; Abbasi and Abbasi 2010; Ioelovich 2010, 2013; Jahirul *et al.* 2012; Young and Rowell 1986; *etc.*). The greatest amount of cellulose (94 to 98%) is observed in white cotton fibers and residues of the cotton and textile industry, while the highest amount of lignin (45 to 48%) is found in olive husk (Abbasi and Abbasi 2010; Jahirul *et al.* 2012). Some biomass samples, such as rice straw, used office and newsprint paper can contain increased amounts of mineral substances (15 to 30%).

Table 2. Typical Chemical Composition of Dry Waste and Residue of Biomasses

Biomass	Cellulose, %	Hemicelluloses, %	Lignin, %
Waste of textile	97-98	1-2	<1
Cotton linter	95-96	1-2	<1
Used office paper	60-62	4-6	1-2
Used newspaper	38-40	18-20	20-22
Used cardboard	58-60	14-15	10-12
Olive pomace	23-25	22-24	32-34
Olive husk	23-25	22-24	45-48

Continuing Advances in the Field of Biofuels

Many books, reviews, and articles have been published that are devoted to the use of biomass sources for production of biofuels and energy (Klass 1998; Kaltschmidt and Hartmann 2001; Berndes *et al.* 2003; Lee *et al.* 2006; Lucian *et al.* 2006; Lynd *et al.* 2009; Saxena *et al.* 2009; Abbasi and Abbasi 2010; Haberl *et al.* 2011; Stelte *et al.* 2012; Lehtovaara *et al.* 2013; Zhang *et al.* 2013; Yu *et al.* 2014; *etc.*). These papers contain reports about reserves of the biomass, forecast of its energy, known kinds of biofuels, methods of their production, cost and market potential, as well as about impact of the biomass and biofuels on the environment.

A distinctive feature of the present review is that it (1) contains the most recent data on transformation of non-edible plant biomass into different kinds of biofuel; (2) describes main features of various biofuels and evaluates their competitiveness compared to fossil fuels; (3) provides information on novel types of biofuels; (4) besides this review contains a critical analysis of energetic potential of various kinds of biofuels and non-edible biomass in order to disclose the most beneficial way for generating an alternative energy.

BIOFUELS FROM NON-EDIBLE BIOMASS

This section provides a review of the main approaches being considered for the conversion of raw biomass into other forms of fuel, which often can be advantageous in terms of transportation or use in various processes or engines. These approaches include pyrolysis, the preparation of biodiesel fuels, and enzyme-based approaches to the production of ethanol. The topic of bioethanol will be given greater emphasis in light of the high volume of continuing research and its prospects for achieving relatively high efficiency of conversion in terms of energy content.

Pyrolytic Biofuels

Pyrolysis is a thermochemical process for decomposition of the biomass in the absence or lack of oxidizing agents at high temperatures (Shafizadeh 1982; Zaror and Pyle 1982; Demirbas and Arin 2000; Di Blasi *et al.* 2001). Wastes and residues of various plant materials can be used for this purpose. The main products of the pyrolysis are charcoal, liquid bio-oil, and gases. The yield of various products is dependent on conditions of the pyrolysis process and biomass composition (Balat *et al.* 2009; Patwardhan 2010; Jahirul *et al.* 2012). The typical yield of products at slow pyrolysis is: charcoal 25 to 35%, liquid 20 to 40%, and gas 20 to 50%. For fast pyrolysis the corresponding numbers are charcoal 10 to 25%, liquid 50 to 70%, and gas 10 to 30%. Slow pyrolysis of the biomass with heating rate $< 60^\circ$/min up to temperatures of 300 to 500 °C and typical residence time of 10 to 20 min is used to produce the charcoal (biochar); this process is accompanied by the formation of bio-oil and gases. If the pyrolysis is carried out at temperatures of 550 to 650 °C, a sharp reduction in the yield of charcoal is observed. The high lignin content in the biomass contributes to higher yield of the charcoal after slow pyrolysis. Lignin can be regarded as the thermostable component of the biomass that decomposes at elevated temperatures, 400 to 500 °C, with the formation of about 40 wt. % of charcoal (Yang *et al.* 2007; Patwardhan 2010).

Thermal decomposition of cellulose occurs within the temperature range 300 to 400 °C (Lewin and Pearce 1998; Yang *et al.* 2007). It was found that pyrolysis of cellulose at a temperature of about 400 °C leads to forming about 20 wt.% of solid charcoal along with the liquid and gas fractions; but after pyrolysis above 400 °C, only the charcoal remains (Lewin and Pearce 1998). Hemicelluloses are less thermostable than cellulose; they decompose at temperatures between 200 and 300 °C (Yang *et al.* 2007; Patwardhan 2010).

Biochar (charcoal) is produced mainly from woody biomass in pyrolytic reactors with a yield of 30 to 35% (Jahirul *et al.* 2012). Hydrothermal pretreatment of biomass and subsequent pelletization can be used to improve the carbonization process of the biochar (Rizhikovs *et al.* 2012). Currently, the biochar is not used for energy generation in power plants. This solid biofuel is produced in limited quantities, mainly for household needs and some small factories. The calorific value of this biofuel is 25 to 30 MJ/kg. Combustion temperature of the charcoal can reach 2700 °C, which is above the melting point of iron. Due to its porosity, the charcoal is sensitive to the flow of air; therefore generated heat can be adjusted by the air flow to the fire. For this reason, the charcoal is an ideal fuel for forges and is still widely used by blacksmiths. However, combustion of the charcoal is accompanied by emission of a large volume of carbon dioxide, about 2000 m^3 per ton.

Since the late 20th century, the focus of researchers has shifted toward increasing the bio-oil yield using fast pyrolysis with a heating rate of about 200°/sec up to temperatures 400 to 600 °C and residence time for a few seconds. The flash pyrolysis method utilizes high temperatures of 700 to 900 °C, a heating rate about 1000°/sec, and a short residence time to produce a maximum yield of the bio-oil, 70-75 wt.% (Demirbas 2000; Bridgwater 2005; Jahirul *et al.* 2012). However, both fast and flash pyrolysis of the biomass has not been implemented in the industry, because the existing reactors could not heat several tons of the biomass for a few seconds up to high temperatures.

Bio-oil can be obtained with yield of 30 to 40 wt. % as a byproduct of the industrial slow pyrolysis of charcoal. The bio-oil is a dark and thick liquid containing complicated mixture of water and various organic substances (tar, hydrocarbons, derivatives of furan, aldehydes, ketones, phenols, organic acids, methanol, *etc*.). Due to acidic pH the bio-oil may cause corrosion of equipment (Balat *et al.* 2009). The calorific value of the bio-oil is 15 to 17 MJ/kg, which is significantly lower than of ethanol and hydrocarbon fuels (Evans and Milne 1987; Dobele *et al.* 2007; Jahirul *et al.* 2012). During storage, this liquid becomes more viscous due to condensation reactions and loss of volatiles; as a result too viscous bio-oil does not meet the characteristics of the viable fuel (Oasmaa *et al.* 2003, 2005; Jahirul *et al.* 2012). Studies of fuel characteristics showed that bio-oil exhibits poor combustion performances in boilers (Oasmaa *et al.* 2001). Burning of the bio-oil in diesel engines causes depositions of carbon, plugging of filters and injectors, failure of fuel pumps, excessive wear and corrosion of engines, high emission of carbon oxide, and other negative effects (Agarwal 2007).

Gasification of the biomass can be carried out at high temperatures, 700 to 1000 $^{\circ}$C (typically at 850 $^{\circ}$C) in the inert, steam or steam/oxygen environment, under normal or elevated pressure. As a result, the gaseous mixture is generated, which contains CO_2, CO, H_2, CH_4, and some other gases (Roy and Dutta 2013). Such biogas has a calorific value 8 to 12 MJ/Nm^3, *i.e.* 3-4 times lesser than the calorific value of natural gas (Goswami 1986; Surisetty *et al.* 2011; Gallmetzer *et al.* 2012; Hu *et al.* 2012). After cleaning of the biogas from carbon dioxide, residual oxygen and some other impurities, the purified H_2/CO mixture (syngas) can be used for synthesis of hydrocarbons by means of the Fischer-Tropsch process at 250 to 300 $^{\circ}$C and elevated pressure in the presence of catalysts (Khodakov *et al.* 2007),

$$(2n + 1)\, H_2 + n\, CO \rightarrow C_nH_{(2n+2)} + n\, H_2O \tag{1}$$
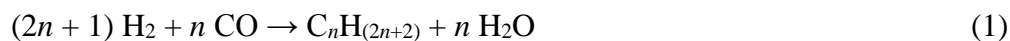
The syngas can be used also for catalytic synthesis of alcohols and some other products (Roy and Dutta 2013; Talmadge *et al.* 2013), *e.g.*

$$2H_2 + CO \rightarrow CH_3OH \tag{2}$$

$$4H_2 + 2CO \rightarrow C_2H_5OH + H_2O \tag{3}$$

However, methanol is toxic and has a low calorific value (20 MJ/kg or 16 MJ/L); therefore this alcohol is relatively unattractive as a biofuel. The yield of the synthetic hydrocarbons, ethanol, and some other products obtained from the biomass *via* gasification is low; moreover, these products are too expensive (Talmadge *et al.* 2013).

Thus, the literature data show that pyrolytic biofuels are not suitable as sources of alternative energy or engine fuels. Besides, currently the pyrolysis products of the plant biomass are unable to compete economically with fossil fuels (Jahirul *et al.* 2012).

Biodiesel Fuel

Generally, biodiesel fuel can be produced from animal fats and vegetable oils of various sources - soybean, rapeseed, olive, sunflower, palm, *etc*. (Coyle 2007; Schmidt 2007). However, these lipids are required in the food industry, and their use for the

production of biodiesel fuel is limited. Moreover, further production expansion of the biodiesel fuel will cause shortage of food-grade lipids and an increase of their prices (Baier *et al.* 2009).

Biodiesel fuel of second generation is based on the use of non-edible sources of lipids such as camelina, jatropha, pongamia legume tree, *Thlaspi arvense*, jojoba, castor, tung, hemp, flax, algae, tall oil - a byproduct of kraft cooking of wood, *etc.* (Borlaug *et al.* 1985; Lee *et al.* 2006; Scott *et al.* 2008). Residual oil of fallen olive fruits and pomace also can be utilized. Besides, used cooking and frying oils are considered as suitable feedstock for production of the biofuel (Lee *et al.* 2006).

Unfortunately, the technical oils already have applications in other areas. For example, jojoba oil is widely used in cosmetics; tung oil is used for preparation of protective coatings; castor and tall oils have numerous industrial applications. Tall oil, for example, is used as an emulsifier and as a feedstock for production of lubricants, soaps, adhesives, and some other products.

Among various non-edible feedstocks, algae have been considered as one of the most promising sources for biodiesel production because it can contain relatively high amounts of lipids, 40 to 50% based on dry matter (Chisti 2007; Mata *et al.* 2010). Additional positive features are that algae reproduce very fast; they can be fertilized with sewage and waste water and therefore algae do not compete with food crops for land or fresh water. Despite these advantages, industrial production of algae-based lipids is limited due to the following shortcomings:

(1). Algae mixtures contain 85 to 88% water; thus the real yield of lipids from wet raw materials is low, only 5 to 8%;

(2). Collection of big amounts of natural algae from seas and oceans is difficult to achieve;

(3). Creation of artificial ponds for the algae growing requires high areas and huge investments;

(4). Special conditions (temperature, light, nutrients, *etc.*) are needed for optimal growing of each type of algae.

(5). Appropriate industrial technology for separation lipids from algae has not been developed yet.

Though the vegetable oils, technical oils and other lipids have a high calorific value (35 to 40 MJ/kg), they are less suitable as a diesel fuel due to relative low cetane number, low volatility, high flash point, and increased viscosity. Use of unmodified vegetable or technical oils as a fuel can cause sharp problem to diesel engines (Bagly *et al.* 1987). To improve fuel characteristics, the lipids are subjected to transesterification. The essence of this process is the interaction of triglycerides (TGL) with alcohol, *e.g.* methanol (MET), in the presence of catalysts (Fukuda *et al.* 2001; Lee *et al.* 2006), for example:

$$C_3H_5(O_2CR)_3 + 3CH_3OH = 3RCO_2CH_3 + C_3H_5(OH)_3 \qquad (4)$$
$$\quad\text{TGL} \qquad\qquad \text{MET} \qquad\quad \text{BDF} \qquad\quad \text{GLY}$$

The obtained ester is used as a biodiesel fuel (BDF), and the byproduct, the glycerol (GLY), can be utilized for some other applications. The main volume of the global biodiesel production is concentrated in the European Union. The biodiesel fuel can

be a direct substitute for petroleum diesel fuel or blended in any amount with the diesel fuel, typically B20, for use in compression ignition engines (Lucia *et al.* 2006). An advantage of the biofuel is in reduced exhaust of carbon and nitrous oxides in comparison with the fossil fuel. Therefore, the production of biodiesel fuel is subsidized and has tax exemptions.

The current global production capacity of vegetable oils and animal fats is not sufficient to obtain such a large amount of biodiesel, which is required to replace the petroleum diesel fuels. Furthermore, high amounts of fertilizers, pesticides, water, energy, as well as land areas would be needed to produce the additional vegetable oils. The final conclusion is that available sources of non-edible lipids for the production of biodiesel fuel in the world are small and limited, about 10 to 15 million metric tons per year, which is insufficient to ensure the sustainable production of the biodiesel fuel.

Bioethanol

The main reasons for interest in bioethanol are that this alternative fuel can be used as a renewable energy additive to save non-renewable gasoline, improve octane number, and reduce emissions of carbon dioxide. Indeed, since bioethanol is produced from renewable natural sources, it can be assigned to the category of renewable fuels. It is also known that use of bioethanol instead of gasoline can reduce the emissions of carbon dioxide by an average of 34 vol.%. Disadvantages of this biofuel are high hydrophility and low value of combustion energy that is 1.5 times lower than of gasoline. Currently, industrial production of bioethanol is based on the enzymatic hydrolysis of sucrose or starch into monosaccharides followed by yeast fermentation (Gnansounou and Dauriat 2005; Onuki *et al.* 2008; Ioelovich 2010). The main sources of sucrose are the juices of sugarcane, sugar beet, and sweet sorghum, and starch sources are corn, wheat, potatoes, and some others agricultural plants. In Brazil, ethanol is made from juice of sugar cane, whereas in the USA the main part of ethanol is produced from corn starch (Tokgoz and Elobeid 2006). Brazilian bioethanol is cheap, with production cost less than $1 per gal. Production cost of corn ethanol is higher, $1.2 to 1.3 per gal. At present, the total annual production volume of fuel bioethanol in the world is about 23 billion gallons; moreover, the USA and Brazil account for about three-fourths of world biofuels production (Baier *et al.* 2009). The USA uses E10, E15, E30, as well as E85 ethanol/gasoline blends, which are subsidized or exempted from tax in order to compensate the price increase and make this fuel more attractive to consumers. Light-duty vehicles in the USA are adapted to operate normally with the E10 and E15 fuel. The E30 and E85 fuels are also available on the USA market today and can be used by flex-fuel vehicles. In Brazil the E25 fuel is used for cars, while motorcycles and flex-fuel vehicles can operate with a cheap biofuel, E100, which is 96% ethanol.

Non-food-based bioethanol

The use of sucrose and starch in the current bioethanol technology is a serious obstacle to increased production of this biofuel, because the further expansion of the production volumes of bioethanol from the food-grade carbohydrates can lead to shortage of land areas, increased consumption of water and energy, deficit of food products, and increasing of their prices (Baier *et al.* 2009; Čuček *et al.* 2011; Lagi *et al.* 2011). An

alternative way to produce bioethanol without competing with the food industry is the use of non-edible plant biomass, such as bagasse, corn stover, switchgrass, straw, waste paper, and some other lignocellulosic raw-materials.

Technology of bioethanol production from non-edible biomass comprises four main steps (Yu *et al.* 2014):

(1). Pretreatment of the initial biomass;
(2). Enzymatic hydrolysis (saccharification) of the pretreated biomass;
(3). Fermentation of the obtained sugar into dilute ethanol;
(4). Distillation and dehydration of ethanol.

Pretreatment

Due to dense structure of plant materials, barrier properties of lignin, and non-productive sorption of cellulolytic enzymes by non-cellulosic components, the initial biomass is generally highly recalcitrant to enzymatic hydrolysis (Chandra *et al.* 2007; Mesa *et al.* 2011; Xu *et al.* 2011; Wang *et al.* 2011; Horn *et al.* 2012; Kautto *et al.* 2014). Therefore, some kind of pretreatment is usually applied to make the biomass more accessible to enzymes. The main objectives of the pretreatment are to loosen the physical structure of the biomass and to eliminate the non-cellulosic components in order to increase accessibility and the percentage of cellulose fraction.

Hemicelluloses are unstable to chemical treatments and can be easily removed even under mild conditions. However, lignin is resistant to chemicals, and its extraction from the biomass demands harsher pretreatment conditions. Pretreatment methods and conditions determine the structure, chemical composition, and hydrolysis rate of the pretreated biomass. The effective pretreatment should be inexpensive and should provide more accessible and cellulose-rich biomass with high enzymatic digestibility.

Various pretreatment methods of lignocellulosic biomasses have been proposed, including organosolv, steam explosion, acidic treatment, alkaline extraction, ammonia treatment, oxidation, and some others (Draude *et al.* 2001; Chandra *et al.* 2007; Mesa *et al.* 2011; Xu *et al.* 2011; Wang *et al.* 2011; Ioelovich *et al.* 2012; Kautto *et al.* 2014). Organosolv pretreatment of the biomass with organic solvents is an expensive process (Kautto *et al.* 2014); furthermore, the use of flammable organic solvents is dangerous because it can cause fires and explosions.

The steam explosion (SE) method is widely used for lab and pilot pretreatment of the biomass. This pretreatment is carried out by pressurized steam at high temperatures (160 to 210 ºC) within a short time (1 to 5 min) without or with low addition of acid. Pretreatment of lignocellulosic biomass with diluted (0.5 to 1 wt.%) sulfuric acid at high temperatures (160 to 190 ºC) for 30 to 60 min has been realized in industry. However, both high-temperature SE and acidic pretreatments have some shortcomings. Hemicelluloses at the increased temperatures turn into aromatic aldehydes and organic acids that inhibit the enzymatic hydrolysis and yeast fermentation. Besides, as a result of condensation of furfural-based substances, so-called pseudolignin can be formed, increasing the total effective lignin content in the pretreated biomass (Sannigrahi *et al.* 2011). Besides, partial carbonization of the biomass at high temperatures is observed. To prevent the carbonization, formation of pseudolignin and inhibitors, the pretreatment temperature should be decreased; however this results in insufficient accessibility of

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substrate. Pretreatment of the biomass with ammonia is difficult to implement due to the danger of release of this harmful reagent. Oxidative pretreatment of plant materials with various oxidants (ozone, peracetic acid, peroxides, *etc*.) is efficient but highly expensive.

Among various methods, alkaline pretreatment of plant biomasses under mild conditions have been intensively studied due to their industrial feasibility, relatively low capital investment, as well as low consumption of chemicals and energy (Galbe and Zacchi 2007; Keshwani and Cheng 2009; Wang *et al*. 2011; Ioelovich *et al*. 2012; Xu and Tschirner 2012; Bali *et al*. 2014; Bufalino *et al*. 2015). This method is considered cheap and efficient, especially for herbaceous biomasses.

Along with one-step, also two-step pretreatments have been proposed using various combinations such as sulfuric acid/alkali (Weerasai *et al*. 2014), nitric acid/alkali (Ioelovich 2014a), formic acid/ammonium hydroxide (Zhang *et al.* 2010), and alkali /bleaching agent − peracetic acid, sodium chlorite or hypochlorite (Zhao *et al.* 2011; Ioelovich 2014a) in order to reduce the severity factors of the one-step process.

Enzymatic saccharification and fermentation

The saccharification of the pretreated biomass is performed by means of an enzyme complex that consists of three main enzyme types (Horn *et al.* 2012):

(1). Endo-1,4-β-glucanases cleave chemical glycoside bonds mainly in the amorphous domains of cellulose fibrils; as a result the fibrils are split with the formation of small particles with reduced degree of polymerization;
(2). Exo-1,4-β-glucanases attack the reducing or non-reducing ends of the depolymerized cellulose particles with forming oligomeric products containing di- and tetra-saccharides;
(3). β-glucosidases hydrolyze the oligosaccharides and convert these into glucose.

These three enzymes act synergistically because endo-acting enzymes generate new chain ends for the exo-acting enzymes, which release the oligosaccharides that are converted into glucose by β-glucosidases (Kostylev and Wilson 2012).

Cellulolytic enzymes can be synthesized by a number of microorganisms including filamentous fungi; mesophilic and thermophilic bacteria; and also actinomycetes (Mandels and Reese 1964; Lynd *et al.* 2002; Gautam *et al.* 2011). However, fungi (*e.g. Trichoderma, Aspergillus, etc*.) are the most widespread source of cellulolytic enzymes. Recently, the large companies have achieved great success in development of novel commercial enzyme preparations having high concentration of proteins (200 to 300 g/L), increased activity (300 to 500 FPU/mL), and decreased cost ($ 1.5-2 per L). Known types of such cellulolytic enzymes are Cellic CTec 2 and Cellic CTec 3 of Novozymes, as well as Accellerase-1500 and GC-220 of DuPont/Genencor, *etc.* This paves the way for the industrial production of fermentable sugars from the non-edible biomass. Optimal conditions of the enzymatic hydrolysis are the following: temperature 45 to 50 °C, pH = 4.5 to 5.0, dose of the enzyme 10 to 20 mg per 1 g of solid biomass. At the same conditions of enzymatic hydrolysis, the yield of obtained sugars is dependent on accessibility and chemical composition of the pretreated biomass (Ioelovich *et. al* 2012; 2013).

The distinctive feature of the acidic pretreatment consists of loosening of the biomass structure, removal of the main part of hemicelluloses, and forming cellolignin with increased content of cellulose and lignin. These peculiarities of the acid-pretreated biomass have an ambiguous effect on enzymatic hydrolysis: on the one hand, loosening of structure and increase of cellulose content could promote achieving higher enzymatic digestibility, but on the other hand increased content of lignin should hinder the enzymatic hydrolysis. The final result shows some improvement of the saccharification of the acid pretreated biomasses in comparison with non-treated sample; however, the yield of the obtained sugar – glucose – is relatively low.

In contrast to acidic pretreatment, alkaline pretreatment of the biomass reduces the content of both hemicelluloses and lignin, and it increases the proportion of cellulose in the remaining solids. As a result, the alkaline pretreatment improves the enzymatic digestibility of the pretreated biomass, while an additional bleaching, *e.g.* with sodium chlorite or hypochlorite, makes it possible to achieve a higher yield of the sugar (Ioelovich 2014a).

The overall effect of the pretreatment of biomass on enzymatic digestibility can depend on the chemical composition. As is well known, the lignin remaining in the pretreated biomass has negative effect, while cellulose has a positive effect on the enzymatic digestibility and yield of glucose (Selig *et al.* 2009; Sun *et al.* 2011). Study of various pretreated biomasses showed that the yield of glucose after enzymatic hydrolysis is directly proportional to the difference between contents of cellulose and lignin in the pretreated samples (Fig. 2) (Ioelovich 2014a). Thus, increasing of cellulose content and decreasing of lignin content in the pretreated biomass contributes to an enhancement of the glucose yield after enzymatic hydrolysis. To prepare cellulose-enriched biomass with a small content of residual lignin, a two-step pretreatment should be provided, such as combination of nitric acid treatment with alkaline extraction or a combination of mild alkaline pretreatment with an additional bleaching.

Conventional laboratory saccharification of the pretreated biomass samples is typically carried out at decreased loading of the biomass, *i.e.* ≤ 50 g/L. However, at the low biomass loading, the concentration of obtained glucose in the hydrolyzate is low, and this leads to low productivity and high cost of the sugar and products of its fermentation.
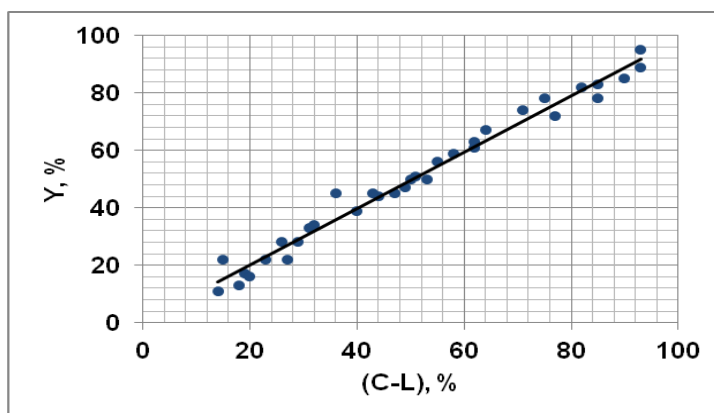
Fig. 2. Dependence of glucose yield (Y) on difference between contents of cellulose (C) and lignin (L) in the pretreated biomass samples

Enzymatic hydrolysis at the increased loading of pretreated biomass is a key to scale-up of this process to pilot and industrial production (Di Risio *et al.* 2011). Use of a high biomass loading throughout its conversion into fermentable sugars is important, foremost owing to techno-economical reasons (Modenbach and Nokes 2012). The approach just outlined makes it possible to achieve the high concentration of the glucose that can bring significant economic savings to the bioconversion process, such as reducing capital, decreasing operating cost for hydrolysis and fermentation, as well as minimizing energy consumption for distillation/evaporation and other downstream processes. It was shown, for example, that the energy required for distillation of the bioethanol can be significantly reduced if the fermentation broth contains higher than 40 g/L of ethanol (Zacchi and Axelsson 1989). To reach this ethanol level, a sugar concentration must be 80 g/L at least. Moreover, an initial loading of steam-exploded or acid-pretreated lignocellulosic biomass for enzymatic hydrolysis should be approximately 200 g/L (Larsen *et al.* 2008).

Unfortunately, enzymatic hydrolysis at the increased biomass consistency has shown a number of shortcomings. Since viscosity of the biomass system increases abruptly at enhanced loadings, the high-solids process causes limited mass transfer of the enzymes, and this can decrease the rate of the hydrolysis and the degree of conversion. It has been shown that the rise of the biomass loading at the enzymatic hydrolysis leads to a reduction in the conversion degree (Modenbach and Nokes 2012). Though the conversion was lower, the increased biomass loading contributed to obtaining higher sugar concentrations after enzymatic hydrolysis.

An additional problem connected with the enzymatic hydrolysis at the high-solids loading is diminution of the available volume of the sugar solution (hydrolyzate) owing to its absorption and retention by residual non-hydrolyzed biomass (Ioelovich *et al.* 2012a). The highly loaded biomass system has a solid-like behavior due to a lack of free liquid. During enzymatic hydrolysis, a gradual liquefaction of the solid system is observed; however, if the residual biomass absorbs most of the volume of the liquid hydrolyzate, the final available volume of the sugar solution becomes so low that its use for further fermentation will not be economically profitable; moreover, the use of the low volume of sugar solution for further fermentation decreases the volume of final bioethanol.

Thus, on the one hand, increasing of the biomass loading is favorable for obtaining a more concentrated sugar solution, but on the other hand it leads to decreased volume of the hydrolyzate. To optimize conditions of the high-solid enzymatic hydrolysis, the sugar amount (*P*, g per 1L of the initial liquid medium) has been used as an optimization function: $P = C \times V_a$, where *C* is the concentration of the sugar solution (g/L) and V_a is its relative available volume (L/L). It was found that with increasing of biomass loading (*BL*) the concentration (C) of hydrolyzate increases, while the available volume (V_a) declines; as a result the function $P=F(BL)$ has an extremum (Fig. 3) (Ioelovich 2013). Determination the maximal sugar amount entails finding the optimal saccharification conditions of the pretreated biomass sample: biomass loading (usually 150 g/L) and time (3 to 4 days), as well as characteristics of the maximal enzymatic digestibility, such as weight loss of the biomass, conversion degree of cellulose, concentration and yield of glucose, *etc*. For example, after enzymatic hydrolysis of the

pretreated switchgrass at optimal loading of 150 g/L for 4 days, the biomass had lost about 78% of its weight; as a result 77 vol. % of the glucose solution was obtained having concentration of 130 g/L (Ioelovich *et al.* 2012a).
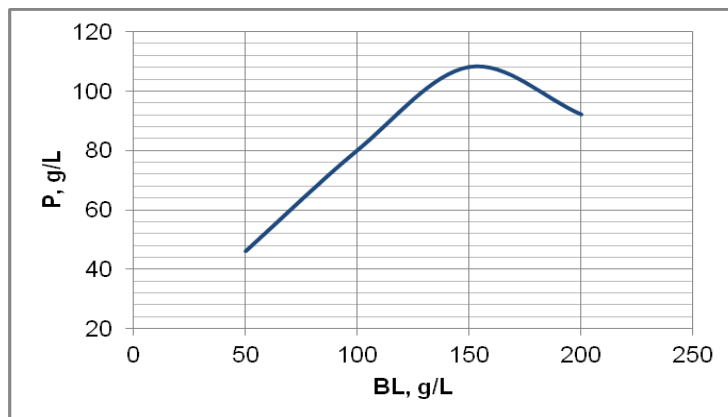
Fig. 3. Dependence of the glucose amount (P) on the initial biomass loading (BL) after enzymatic hydrolysis of the NA-pretreated switchgrass for 96 h

The fermentation of the sugar solution obtained after enzymatic hydrolysis of the pretreated biomass is carried out usually by the yeast of *Saccharomyces cerevisiae* at 30 °C, at pH=5 for 3 days. The concentration of the yeast is 10 g/L. Peptone and some other nutrients and salts are added to improve yeast growth (D'Amore *et al.*1989; Lin and Tanaka 2006). Various fermentation methods can be used: simultaneous saccharification and fermentation, simultaneous saccharification and co-fermentation, sequential fermentation, continuous fermentation, *etc*. (Wyman 1996; McMillan 1997; Gnansounou and Dauriat 2005).

The final concentration of ethanol after fermentation of the saccharified non-edible plant biomass usually does not exceed 50 to 60 g/L; therefore the dilute "beer" is distilled to obtain 95 to 96 wt.% ethanol. Since the fuel ethanol should not contain more than 1% water, the distilled ethanol is dehydrated to 99 wt.% using dewatering agents, *e.g.* zeolites. The theoretical yield of ethanol is 51 wt.% from mass of glucose, but the actual yield is slightly lower, usually 47 wt.% (Gnansounou and Dauriat 2005).

Vast studies in laboratories, at the pilot scale, and in demonstration plants have shown that elaboration of industrial technology for ethanol production from non-edible biomass is a difficult challenge. The main reasons are: complex and multistage production process; high consumption of chemicals and energy; high cost of enzymes; formation of inhibitors complicating the bioconversion; insufficient yield of glucose and ethanol; low productivity; the large amounts of solid and liquid wastes that must be regenerated, and some other factors. Due to mentioned factors, the production cost of lignocellulosic ethanol has been estimated to be $3 to $5 per gal, which is significantly higher than the production cost of bioethanol made from carbohydrates (Gnansounou and Dauriat 2010; Kazi *et al.* 2010; Kautto *et al.* 2014). Techno-economic analysis had shown that the final production value of bioethanol is most sensitive to costs for equipment, feedstock, and enzymes; besides, a significant portion of capital costs is related to the

pretreatment and disposal of residual wastes. The cost of biomass feedstock increases the final value by \$0.3-0.5 per gal EtOH; the price of enzymes and expenses for enzymatic hydrolysis contribute \$1 to 1.5 per gal; while pretreatment expenses introduce \$1 to \$2 per gal. Additional investments are required to cover the expenses needed for cleaning and distillation of ethanol, regeneration of chemicals, utilization of solid waste, treatment of sewage, depreciation of equipment, transport, wages, *etc.*

Various approaches have been proposed to reduce the production cost of lignocellulosic ethanol: one approach was to use the energy of a power plant or feedstock and infrastructure of a pulp mill for the ethanol production (Hahn-Hägerdal *et al.* 2006); another was co-production of bioethanol from corn and corn stover (Čuček *et al.* 2011). The implementation of these approaches may reduce the ethanol production cost by 20-30 percentage points; but that is not enough to make the production of this biofuel cost-effective. A more promising proposal to reduce the production value of lignocellulosic ethanol may be to manufacture the valuable byproducts along with the main product - ethanol (Ioelovich 2010; Kautto *et al.* 2014). For example, the estimated economic analysis revealed that the production of bioethanol from biomass pretreated by nitric acid/alkali method (Ioelovich 2014a) will be cost-effective, since after mutual neutralization of acidic and alkaline liquors, a valuable byproduct - nitrogen fertilizer, can be obtained, which significantly covers the cost of the bioethanol. As a result, the production cost of this biofuel can be reduced four times to \$1 per gallon, when the fertilizer is sold at a ~~low~~ price of \$25 per ton (Fig. 4).
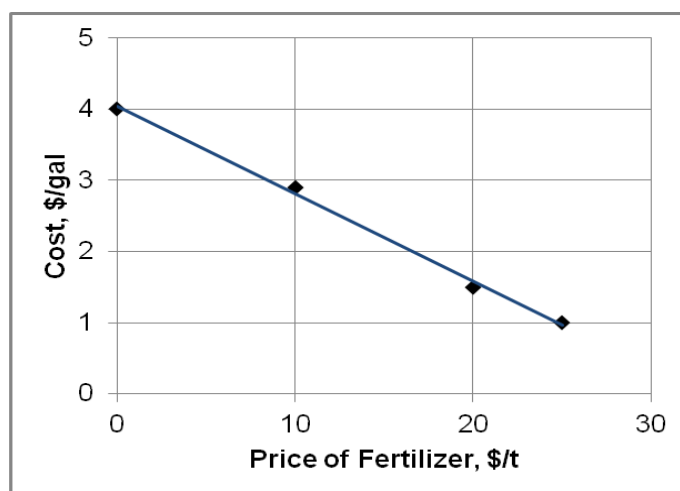

Fig. 4. Production cost of bioethanol as function of selling price of byproduct - fertilizer

An additional technological and environmental problem of lignocellulosic ethanol is accumulation of residual unhydrolyzed biomass as a solid waste in large quantities, of 200 to 500 kg per each ton of the feedstock (dry weight basis). The most rational way for disposal of this waste is by burning it. However, the direct combustion of the wet particles of residual biomass is a difficult and unprofitable process. More preferable is a preliminary transformation of the waste into dry briquettes or pellets to be used as a solid

fuel for productive generation of the thermal energy. The accumulated wastewater should be recycled and used in further production processes.

Thus, to create a competitive zero-discharge method for production of bioethanol from non-edible lignocellulosic biomass, state-of-the-art technology must be employed using cellulose-rich pretreated feedstock, co-production of the main product (ethanol) and byproduct (*e.g.* fertilizer), utilization of the solid biofuel (*e.g.* burning of pelletized residual biomass), as well as the recycling of chemicals and wastewater (Fig. 5).
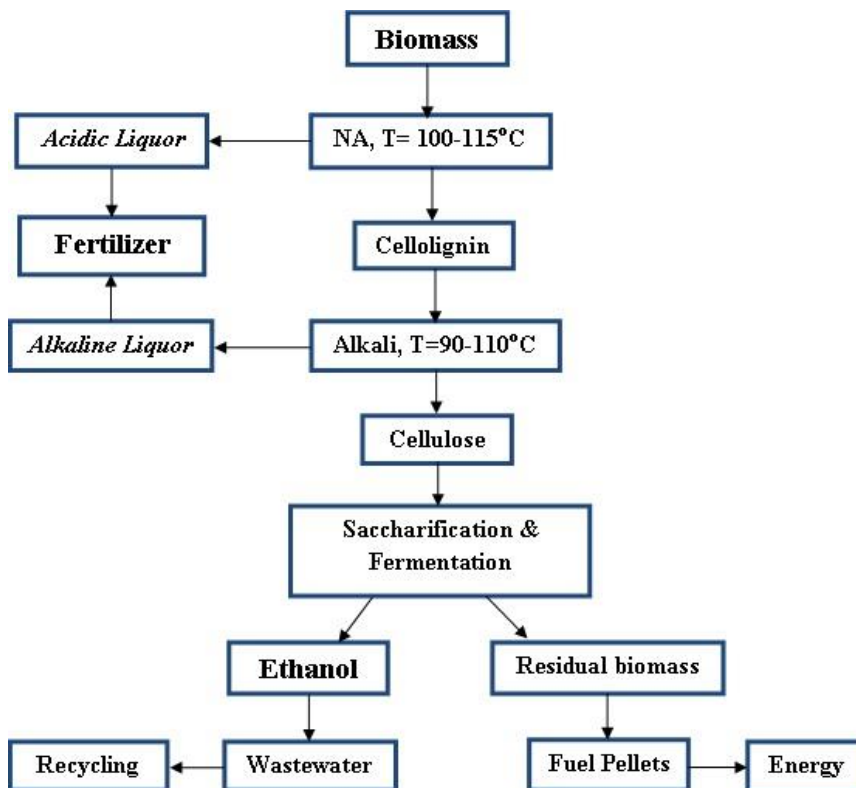
Fig. 5. Scheme of advanced zero-discharge bioethanol technology
(Note: NA is a dilute nitric acid used for first step pretreatment; see: Ioelovich 2014a)

ENERGETIC POTENTIAL OF PLANT BIOMASS

Having reviewed the state of technology for preparation of biofuels by use of different approaches, the present section will compare these different approaches in terms of the energy content of the respective fuels relative to the starting biomass.

Heating Values

As is known, some plant species and especially wastes of agriculture, forest, wood, textile, pulp, and paper industries can be used as a feedstock for production of solid, liquid, or gaseous biofuels (McKendry 2002; Pandey 2009; Bacovsky *et al.* 2010).

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To choose the most efficient way for production of bioenergy, it is necessary to know the energy potential of various biomass kinds and biofuels that can be obtained from these feedstocks.

The standard enthalpy or higher heating value (*HHV*) of dehydrated fuels is measured by means of a bomb calorimeter at 25 °C (Jessup 1970). The net calorific value (net combustion energy) or lower heating value (*LHV*) is calculated by the equation,

$$LHV = HHV - 0.225\ H \tag{5}$$

where *H* is the percentage of hydrogen in the fuel.

To predict the net combustion energy of various fuels, Mendeleev's equation can be used (Suris 2007; Gyulmaliev and Shpirt 2008),

$$LHV\ (\mathrm{MJ/kg}) = 0.339\ C + 1.029\ H + 0.109\ S - 0.109\ O \tag{6}$$

where *C*, *H*, *S*, and *O* are the percentages of the corresponding elements.

The study of non-edible biomasses revealed that the lowest net calorific value, 11 to 14 MJ/kg, is observed in the case of used printing and newsprint papers, rice straw, and some other samples having an enhanced content of mineral substances (Ioelovich 2013). The lipid-enriched samples (*e.g.* fallen olives), highly lignified samples (*e.g.* residue of hydrolysis), and the lignin itself exhibit the greatest net combustion energy, 23 to 26 MJ/kg, while *LHV* of the other investigated biomass samples varies in the range from 15 to 18 MJ/kg (McKendry 2002; Sheng and Azevedo 2005; Librenti *et al.* 2010; Moka 2012; Ioelovich 2013, 2013a; Protasio *et al.* 2013) (Table 3).

Table 3. Net Combustion Energy (LHV) of Dry Biomass Samples

Biomass	Ash, %	Lipids, %	Lignin, %	LHV, MJ/kg
Used printing paper	29	1	1	11.0
Used newspaper	18	1	22	12.9
Rice straw	16	3	8	12.3
Rice husk	15	2	20	14.6
Corn stover	6	3	19	15.0
Wheat straw	6	2	16	14.7
Switchgrass	5	3	18	14.8
Miscanthus	3	2	19	16.3
Used cardboard	7	1	11	15.0
Cotton linter	1	1	0	16.0
Cotton stalks	1	1	17	15.8
Waste of textile	1	1	0	16.2
Bagasse	5	3	20	17.4
Softwood residues	1	2	27	18.1
Residue of hydrolysis	1	0	76	23.0
Olive pomace	2	7	33	21.0
Fallen olives	4	35	22	26.1
Olive husk	2	5	46	21.2
Lignin Klason	1	0	100	25.0

Detailed study of the effect of some ingredients on the calorific value showed that lignin and lipids contribute to the increase of the net energy of the biomass, while mineral components (ash) and moisture reduce this energy (Fig. 6) (Ioelovich 2013). High-lignified and lipid-rich biomass will have an increased calorific value. This is a result of the higher specific combustion energy of lignin (25 MJ/kg) in comparison with polysaccharides (16 MJ/kg).

Net calorific value of extractive substances of the biomass – lipids, waxes, fats and resins, is about 37 MJ/kg, which is much higher than that of polymeric components of the biomass – lignin and polysaccharides. For example, fallen olives containing 35% lipids and 22% lignin are distinguished by the highest calorific value of 26 MJ/kg among the investigated biomass samples.
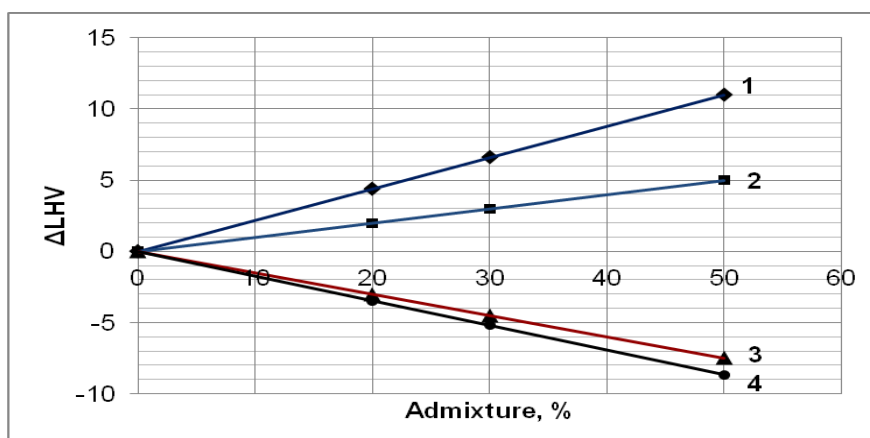

Fig. 6. Contribution of lipids (1), lignin (2), minerals (3) and moisture (4) to net combustion energy

The net calorific value of liquid biofuels and solid biochar usually exceeds the LHV of the plant materials (Table 4).

Table 4. Net Calorific Value of Biofuels

Biofuel	*LHV*, MJ/kg
Tall oil	37.0
Castor oil	37.1
Olive oil	37.3
Biodiesel fuel	37.6
Used cooking oils	37.4
Bioethanol	27.2
Bio-oil	17.0
Biogas	10.0
Biochar	28.0

Energy Penalties for Production of Solid or Liquid Biofuels

It is important to understand which way the biomass utilization might provide the greatest energy. One can ask the question, "Is more energy obtained by direct burning of the biomass or burning of solid or liquid biofuel that was obtained from this biomass?"

To obtain some concrete answers to this question, it is necessary to analyze some typical examples for production of the thermal energy (Ioelovich 2013, 2013a):

Example 1

Pathway 1: One ton of softwood chips was burned directly, resulting in the formation of 18.1 GJ of thermal energy;

Pathway 2: One ton of this biomass was pyrolyzed at 350 ºC to obtain the charcoal (yield 36%) that was burned, resulting in the formation of 10.0 GJ of thermal energy.

Example 2

Pathway 1: One ton of softwood chips was burned directly, resulting in the formation of 18.1 GJ of thermal energy;

Pathway 2: One ton of this biomass was pyrolyzed at 400 ºC to obtain the bio-oil (yield 35%) that was burned, resulting in the formation of 6.0 GJ of thermal energy.

Example 3

Pathway 1: One ton of softwood chips was burned directly, resulting in the formation of 18.1 GJ of thermal energy;

Pathway 2: One ton of this biomass was pyrolyzed at 850 ºC to obtain the biogas (yield 40%) that was burned, resulting in the formation of 4.3 GJ of thermal energy.

Example 4

Pathway 1: One ton of cotton linter was burned directly, resulting in the formation of 16.0 GJ of thermal energy;

Pathway 2: One ton of this biomass was enzymatically converted into glucose (yield 60%); the hydrolyzate was subjected to fermentation and distillation in order to produce the ethanol; and finally the obtained bioethanol was burned with the formation of 7.4 GJ of thermal energy.

Example 5

Pathway 1: One ton of switchgrass was burned directly, resulting in the formation of 14.8 GJ of thermal energy;

Pathway 2: One ton of this biomass was pretreated with alkali (yield 55%) and then enzymatically converted into glucose (yield 70%); the hydrolyzate was subjected to fermentation and distillation in order to produce the ethanol; and finally the obtained bioethanol was burned with the formation of 4.5 GJ of thermal energy.

Example 6

Pathway 1: One ton of fallen olive fruits (dry weight basis) containing 35% oil was burned directly, resulting in the formation of 26.1 GJ of thermal energy;

Pathway 2: One ton of this biomass was squashed to obtain 260 L of the vegetable oil, which was subjected to transesterification (yield of 87%), and the obtained liquid biodiesel fuel was burned with the formation of 7.4 GJ of thermal energy.

Analysis of these typical examples shows that in all cases the thermal energy of biofuels extracted from 1 t of the biomass is significantly lower than the energetic potential of 1 t of the starting biomass (Fig. 7). To generate the thermal energy, it is more profitable to burn 1 ton of woody biomass, than 360 kg of biochar (example 1), or 350 kg of bio-oil (example 2), or about 300 m^3 of biogas (example 3) produced from 1 t of this biomass by the pyrolysis method. The burning of 1 t of biomass generates 2 to 3 times

higher energy than the burning of bioethanol obtained from 1 t of starting biomass after its pretreatment, enzymatic saccharification and yeast fermentation (example 4 and 5). The thermal energy of about 220 L of biodiesel fuel extracted from 1 t of fallen olive fruits was also lower than the energetic potential of 1 t of this biomass (example 6).
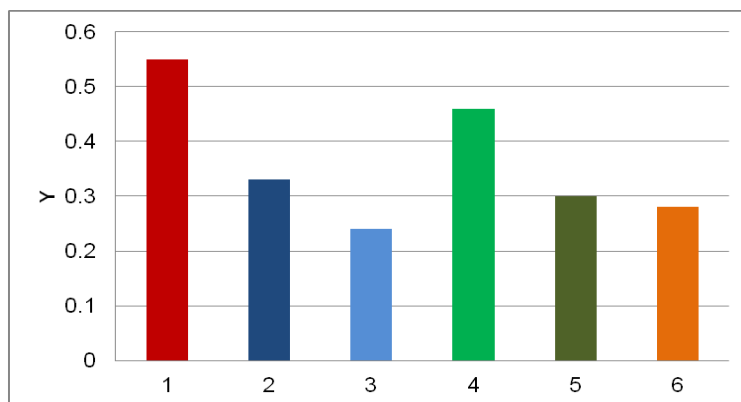
Fig. 7. Yield of heat energy (Y) of various biofuels extracted from 1 t of starting plant biomass, where Y is ratio of thermal energy of the resulting amount of the biofuel (E_f) to thermal energy of 1 t of the starting biomass (E_b): $Y = E_f/E_b$
(Note: numbers 1 to 6 are correspond to numbers of examples 1 to 6)

Despite the fact that the net calorific value of the biofuels is usually higher than of the starting biomass (Tables 3, 4), the total amount of the thermal energy generated by burning of these fuels is lesser due to their limited output from the plant materials. Thus, a most efficient way of the energy production is through the direct burning of the non-edible biomass, while the burning of such amount of the biofuel, which can be obtained from one ton of the starting plant material, gives a much smaller energetic effect.

Although Fig. 7 shows that there are substantial energy penalties, there still can be a preference for certain types of converted fuels, relative to the starting biomass, depending on what is needed. This is especially the case for liquid biofuels such as ethanol and biodiesel, which require only modest changes to conventional gasoline or diesel engines.

Plant Biomass as a Solid Biofuel

Currently, the main population of the world living in underdeveloped and developing countries, especially in rural areas, uses solid plant materials (firewood, wood chips, sawdust, twigs, bushes, straw, *etc*.) to meet their energy needs (Ahuja and Tatsutani 2009). In many countries, these resources account for over 90% of household energy consumption. The use of biomass plays a pivotal role also in the developed world in order to reduce the negative environmental impact caused by the burning of fossil fuels (McKendry 2002). Residues of pulp and wood are burned to generate steam and power energy for pulp and paper mills. Combined heat and power systems that use the biomass-based fuel are widespread in Europe and especially in the Scandinavian counties (Lucia *et al.* 2006; Lehtovaara *et al.* 2013). In some counties, the burning of refuse and solid municipal waste in specially designed incinerators is used to dispose of solid waste,

reduce pollution of the environment, and produce additional heat energy (BREF 2005; DEFRA 2013; Ionescu and Rada 2012). However, plant materials have shortcomings, namely, heterogeneity in sizes, shapes, and composition; increased content of mineral admixtures and moisture; low bulk density; and unsatisfactory fuel properties such as low calorific value, poor energetic density, and insufficient combustion efficiency (McKendry 2002; Surisetty *et al*. 2011; Moka 2012; Stelte *et al.* 2012). Freshly cut trees, bagasse, grasses, and other plant materials have moisture contents of 35 to 55%. Some biomass types, *e.g.* rice straw or husk, newspaper, office paper, *etc.* can contain 15 to 30% of mineral components. The bulk density of biomass varies from 40-80 kg/m^3 (grasses), to 150-200 kg/m^3 (wood chips), whereas the energetic density can range from 0.5 to 5 GJ/m^3. These negative features of plant materials hinder their application as a solid biofuel for the energy generation.

To overcome the low energetic density, the loose biomass feedstock should be compacted into dense pellets. The pelletization process requires many steps, namely, selection, reception, and intermediate storage of the feedstock; screening to remove foreign materials; shredding or pre-grinding; drying; additional fine milling; hot pressing; cutting; cooling; screening, and packaging (Dhamodaran and Afzal 2013; Warajanont and Soponpongpipat 2013). The pellets can be easily prepared from waste and residues of various plant materials, but especially from feedstocks having low moisture and ash content, as well as increased content of lignin and lipids. The wet biomass is dried to a moisture content of 10%, at most. The dried biomass is crushed in a hammer mill to obtain powder with average particle size of 1 to 3 mm; the powdered biomass is wetted to a moisture content of about 15 to 20%, and the binder (*e.g.* starch) is introduced as an option; the powder is compacted in a pelletizing press, *e.g.* in die press machine, where the roller pushes the powdered biomass under high pressure (*e.g.* 50 MPa) through the hole at a temperature of 80 to 90 ºC; after cooling, the formed rod having a diameter of 5 to 10 mm is cut into pieces with a length of 20 to 40 mm; the pellets are screened to separate the dust; finally, the pellets are moved into storage bags. The ability of the powdered biomass to undergo pelletizing is based on the softening of wet lignin and hemicelluloses at elevated temperatures, bonding of particles by softened ligno-carbohydrate adhesive, and hardening of this adhesive upon cooling (Stelte *et al.* 2012).

The prepared fuel pellets must have a bulk density of 600 to 700 kg/m^3, a net calorific value of 15 to 17 MJ/kg, and an energetic density of 10 to 12 GJ/m^3 (Gil *et al.* 2010; Ioelovich 2013; Liu, *et al.* 2013; Warajanont *et al.* 2013). This solid biofuel made from renewable biomass represents a promising source of "green" energy. Based on the principle of densification of particulate plant materials, the pellets offer improved burning properties and low emission of greenhouse gases; moreover, the densified solid biofuel is more economical to transport (Larsson *et al.* 2008; Stelte *et al.* 2012).

Global annual production of the fuel pellets in 2009 was about 15 million tons, whereas in 2011 it increased to 30 million tons (Stelte *et al.* 2012). A further growth of production capacity of this biofuel up to 50 million tons is expected by 2020. The selling price of the pellets in the USA is affected by transportation costs and can vary from $200 to $500 per ton. In the European Union, the pellets sold for 125 to 130 Euro per ton (Sikkema *et al.* 2011). Application of wood pellets can vary from household heating to

industrial and municipal combined heat and power generation. According to statistics, about 800,000 homes in the USA use wood pellets for heating.

Currently, fuel pellets are usually made from clean conifer sawdust and planer shavings. Production of pellets from hardwood is more difficult. If the feedstock is wet, a drying process is needed before grinding. Wood chips have a slower drying rate than sawdust, so a much larger drying capacity is needed.

An increase in demand of pellets and the limited availability of wood resources has resulted in efforts of broaden the feedstock for the pellets production using for this purpose the residues of agriculture and forest; as well as the residues of wood, pulp and paper industries, *etc.* Since these plant materials have a lower energetic potential than wood, attempts have been made to improve characteristics of the pellets by pretreatment of the starting biomass (Stelte *et al.* 2012). The steam explosion and hydrothermal pretreatments can promote pelletizing, but this only slightly improves the calorific value of the prepared pellets. Such pretreatment methods as torrefaction make it possible to reduce hydrophility, but the bonding ability and mechanical strength of the modified pellets are adversely affected. Furthermore, these pretreatments require additional expenses, thus increasing the cost to produce the pellets.

Even after pelletizing, the plant biomass generates approximately two to three times less heat energy compared to fossil fuels (Ioelovich 2013; Protasio *et al.* 2013). An additional problem is that these pellets are hydrophilic and their energetic potential decreases after storage. There are several ways to improve fuel characteristics of the pellets (Ioelovich 2014b). One way is the impregnation of the pellets with combustible liquids (*e.g.* used cooking oils) or melts (*e.g.* rosin). Another way can be by the introduction of some high-energy supplements (waste polyolefins, waxes, tar, rosin, *etc.*) in the biomass before pelletization. The third way is a combination of the previous two methods. As a result, the modified pellets acquire improved fuel parameters: a net combustion energy of 28 to 30 MJ/kg and an energetic density of 23 to 25 GJ/m^3. Thus, density and fuel parameters of modified pellets are significantly higher than common pellets; whereas, the characteristics of novel solid fuel and average-quality coal are close. Furthermore, unlike the coal, the modified pellets have reduced emission of particles, zero emission of sulfur oxides and neutral emission of carbon dioxide.

A solid/liquid type of biofuel, which is a dispersion of powdered biomass into liquid biofuel, has also been proposed (Ioelovich 2014b). An example of this fuel type can be the dispersion of sawdust in used cooking oil. Due to small particle sizes and the presence of thickening agents, the final dispersions were stable to phase separation. Moreover, introduction of the powdered biomass to combustible liquid reduces the price of the mixed fuel and decreases the emissions of carbon dioxide.

CONCLUSIONS

Considerable attention in recent years has been paid to plant biomass, which in contrast to the fossil sources is continuously renewed in nature. This paper has presented the most recently available data on structure, composition, and properties of the non-edible plant biomass of various origins. Moreover, some thermal, chemical, and biological methods of the biomass transformation into various kinds of biofuels have

been described. To generate energy, the plant biomass can be burned directly or after its conversion into carbonized solid fuel (*e.g.* biochar), liquid fuel (bioethanol, biodiesel, bio-oil), or gaseous fuel (*e.g.* biogas). Among various biofuels, the production of bioethanol can be the most attractive, but only if the state-of-art technology becomes implemented, which uses cellulose-rich pretreated feedstock, and combines the production of ethanol with production of a valuable byproduct (*e.g.* fertilizer) together with recycling of solid and liquid wastes.

The comparative analysis of energetic potential revealed that the most efficient way of the energy production is the direct burning of the plant biomass, while the burning of such amount of the solid, liquid, or gaseous biofuel, which can be obtained from the plant material, gives a much smaller energetic effect. Thus, non-edible plant biomass may be a promising feedstock for generation of heat energy. On the other hand, the initial plant biomass have shortcomings, including particularly high moisture, increased content of mineral admixtures, low bulk density, and reduced fuel properties, such as low calorific value, poor energetic density, and insufficient combustion efficiency. To improve the energetic characteristic, the initial biomass must be demineralized, dried, and compacted in order to obtain fuel pellets. Even after pelletizing, plant biomass generates two to three times less heat energy compared to fossil fuels. An additional problem is that these pellets are hydrophilic and their energetic potential decreases after storage. To overcome the negative features of common pellets, modified types of pellets having improved fuel characteristics and reduced emission of greenhouse gases have been developed.

REFERENCES CITED

Abbasi, T., and Abbasi, S. A. (2010). "Biomass energy and the environmental impacts associated with its production and utilization," *Renew. Sustain. Energy Rev.* 14, 919-937.

Agarwal, A. K. (2007). "Biofuels applications as fuels for internal combustion engines," *Prog. Energy Combust. Sci.* 33, 233-271.

Ahuja, D., and Tatsutani, M. (2009). "Sustainable energy for developing countries," *Sapiens* 2, 1-16.

Bacovsky, D., Dallos, M., and Wörgetter, M. (2010). "Status of 2nd generation biofuels demonstration facilities," *IEA Report* 39, 1-126.

Bagly, M. O., Freedman, B., and Schwab, A. W. (1987). "Preparation and properties diesel fuel from vegetable oils," *Fuels* 66(10), 1372-1378.

Baier, S., Clements, M., Griffiths, C., and Ihrig, J. (2009). "Biofuels impact on crop and food prices: using an interactive spreadsheet," *Int. Finance Discus. Pap.* 967, 1-32

Balat, M., Kirtay, E., and Balat, H. (2009). "Main routes for the thermo-conversion of biomass into fuels and chemicals - pyrolysis systems," *Energy Conv. Manag. 50*, 3147-3157.

Bali, G, Meng, X., Deneff, J. I., Sun, Q., and Ragauskas, A. J. (2014). "The effect of alkaline pretreatment methods on cellulose structure and accessibility," *ChemSusChem.* 11, 1-5

Battista, O. A., and Smith, P. A. (1962). "Microcrystalline cellulose," *Ind. Eng. Chem.* 54(9), 20-29.

Battista, J. A. (1975). *Microcrystal Polymer Science*, New York, McGraw-Hill Book.

Berndes, G., Hoogwijk, M., and Van den Broek, R. (2003). "The contribution of biomass in the future global energy supply: a review of 17 studies," *Biomass Bioenergy* 25 (1), 1-28.

Biermann, C. J. (1996). *Handbook of Pulping and Papermaking,* Acad. Press, London.

Borlaug, N., Baldwin, A. R., Estefan, R., Harris, M., and Plucknett, D. L. (1985). *Jojoba New Crop for Arid Lands, New Raw Material for Industry*, Washington, National Academy Press.

BP. (2013). *Statistical Review of World Energy.*

BREF (2005). *Reference Document on the Best Available Technology for Waste Incineration*, European IPPC Bureau, Seville, IPPC.

Bridgwater, A.V. (2005). *Fast Pyrolysis of Biomass: A Handbook,* Newbury, CRL Press.

Browning, B. L. (1963). *The chemistry of wood,* Warrenvile, Intersci. Publ.

Bufalino, L., Caixeta, L. A., Protásio, T. P., Scatolino, M. V., Mesquita, R. G. A., Mendes, L. M., Tonoli, G. H. D., and Marconcini, J. M. (2015). "Options for chemical modification of wastes from a Brazilian hardwood species and potential applications," *Key Eng. Mater.* 634, 321-328.

Cara, C., Moya, M., Ballesteros, I., Negro, M. J., González, A., and Ruiz, E. (2007). "Influence of solid loading on enzymatic hydrolysis of steam exploded or liquid hot water pretreated olive tree biomass," *Process Biochem.* 42, 1003-1009.

Chandra, R., Bura, R., Mabee, W., Berlin, A., Pan, X., and Saddler, J. (2007). "Substrate pretreatment: the key to effective enzymatic hydrolysis of lignocellulosics," *Adv. Biochem. Eng. Biotechnol*. 108, 67-93.

Chen, F., and Dixon, R. A. (2007). "Lignin modification improves fermentable sugar yields for biofuel production," *Natur. Biotechnol*. 25, 759-761.

Chisti, Y. (2007). "Biodiesel from microalgae," *Biotechnol. Adv.* 25, 294-306.

Christian, D. G., Riche, A. B., and Yates, N. E. (2002). "The yield and composition of switchgrass and coastal panic grass grown as a biofuel in Southern England," *Bioresour. Technol.* 83, 115-124.

Copeland, J., and Turley, D. (2008). *National and Regional Supply/Demand Balance for Agricultural Straw in Great Britain,* CSL, Sand Hutton.

Coyle, W. (2007). "The future of biofuels: a global perspective," *Amber Waves* 5 (5), 24-29.

Čuček, L., Martin, M., Grossmann, I. E., and Kravanja, Z. (2011). "Energy, water and process technologies integration for the simultaneous production of ethanol and food from the entire corn plant," *Comp. Chem. Eng.* 35(8), 1547-1557.

D'Amore, T., Russell, I., and Stewart, G. (1989). "Sugar utilization by yeast during fermentation," *J. Ind. Microbiol.* 4, 315-324.

DEFRA. (2013). *Incineration of Municipal Solid Waste*, DEFRA, London.

Demirbas, A. (2000). "Recent advances in biomass conversion technologies," *Energy Educ. Sci. Technol.* 6, 77-83.

Demirbas, A. and Arin, G. (2000). "An overview of biomass pyrolysis," *Energy Source, A* 24, 471-482.

Dhamodaran, A., and Afzal, M. (2013). "Modeling and characterization of reed canary grass pellet formation phenomenon," *Int. J. Renew. Sustain. Energy* 2(2), 63-73.

Ding, S. Y., and Himmel, M. F. (2006). "The maize primary cell wall microfibril: A new model derived from direct visualization," *J. Agric. Food Chem.* 54, 597-606.

Di Blasi, C., Branca, C., Santoro, A., and Hernandez, E. G. (2001). "Pyrolytic behavior and products of some wood varieties," *Combust. Flame* 124, 165-177.

Di Risio, S., Hu, C. S., Saville, B. A., Liao, D., and Lortie, J. (2011). "Large-scale, high-solids enzymatic hydrolysis of steam-exploded poplar," *Biofuel. Bioprod. Bioref.* 5, 609-620.

Dobele, G., Urbanovich, I., Volpert, A., Kampars, V., and Samulis, E. (2007). "Fast pyrolytic – Effect of wood drying on the yield and properties of bio-oil," *BioResources* 2(4), 699-706.

Draude, K. M., Kurniawan, C. B., and Duff, S. T. B. (2001). "Effect of oxygen delignification on the rate and extent of enzymatic hydrolysis of lignocellulosic material," *Bioresour. Technol.* 79, 113-120.

Evans, R., and Milne, T. (1987). "Molecular characterization of the pyrolysis of biomass," *Energy Fuel* 1, 123-137.

Fengel, D., and Wegener, G. (1984). *Wood Chemistry, Ultrastructure, Reactions,* Walter de Gruyter, Berlin/New York.

Field, C. B., Behrenfeld, M. J., Randerson, J. T., and Falkowski, P. (1998). "Primary production of the biosphere: Integrating terrestrial and oceanic components," *Science* 281, 237-240.

Fukuda, H., Kondo, A., and Noda, H. (2001). "Biodiesel fuel production by transesterification of oils," *J. Biosci. Bioeng.* 92, 405-416.

Galbe, M., and Zacchi, G. (2007). "Pretreatment of lignocellulosic materials for efficient bioethanol production," *Adv. Biochem. Eng. Biotechnol.* 108, 41-65.

Gallmetzer, G., Ackermann, P., Schweiger, A., Kienberger, T., Gröbl, T., Walter, H., Zankl, M., and Kröner, M. (2012). "The agnion Heatpipe-Reformer-operating experiences and evaluation of fuel conversion and syngas composition," *Biomass Convers. Biorefin.* 2(3), 207-215.

García-Cubero, M. T., Marcos, M., Bolado, S., and González-Benito, M. C. (2010). "Optimization of operating conditions in enzymatic hydrolysis of pretreated lignocellulosic materials," *Chem. Eng. Transact.* 21, 1285-1290.

Gautam, S. P., Bundela, P. S., Pandey, A. K., Khan, J., Awasthi, M. K., and Sarsaiya, S. (2011). "Optimization for the production of cellulase enzyme from municipal solid waste residue by two novel cellulolytic fungi," *Biotechnol. Res. Internat.* 2011, 1-8.

Gil, M. V., Oulego, P., Pevida, P., Pis, J. J. and Rubiera, F., (2010). "Mechanical durability and combustion characteristics of pellets from biomass blends," *Biomass Technol.* 101, 8859-8867.

Goswami, D. Y. (1986). *Alternative Energy in Agriculture,* Boca Raton, CRC Press.

Gnansounou, E., and Dauriat, A. (2005). "Ethanol fuel from biomass: a review," *J. Sci. Ind. Res*. 64, 809-821.

Gnansounou, E., and Dauriat, A. (2010). "Techno-economic analysis of lignocellulosic ethanol: A review," *Bioresour. Technol.* 101, 4980-4991.

Gyulmaliev, A. M., and Shpirt, M. Y. (2008). "Calculation of the enthalpy of formation of coal organic matter," *Solid Fuel Chem.* 42(5), 263-267.

Haberl, H., Erb, K-H., Krausmann, F., Bondeau, A., Lauk, C., Müller, C., Plutzar, C., and Steinberger, J. K. (2011). "Global bioenergy potentials from agricultural land in 2050: Sensitivity to climate change, diets and yields," *Biomass Bioenergy* 35 (12), 4753-4769.

Habibi, Y., Lucia, A. A., and Rojas, O. J. (2010). "Cellulose nanocrystals chemistry, self-assembly, and applications," *Chem. Rev.* 110, 3479-3500.

Hahn-Hägerdal, B., Galbe, M., Gorwa-Grauslund , M. F., Liden, G., and Zacchi, G. (2006). "Bioethanol the fuel of tomorrow from the residues of today," *Trends Biotechnol.* 24, 549-556.

Hames, B. R., Thomas, S. R., Sluiter, A. D., Roth, C. J., and Templeton, D. W. (2003). "Rapid biomass analysis; New tools for compositional analysis of corn stover feedstocks and process intermediates ethanol production," *Appl. Biochem. Biotech.* 105-108, 5-16.

Hon, D. (1996). *Chemical Modification of Lignocellulosic Materials*, Marcel Dekker Inc., New York.

Hon, D., and Shirashi, N. (2000). *Wood and Cellulose Chemistry*, New York, Marcel Dekker Inc.

Horn, S. J., Vaaje-Kolstad, G., Westereng, B., and Eijsink, V. G. (2012). "Novel enzymes for the degradation of cellulose," *Biotechn. Biofuel* 5, 45-57.

Hossain, K. A. (2012). "Global energy consumption pattern and GDP," *Int. J. Renewable Energy Technol. Res.*1, 23-29.

Hubbe, M. A., Rojas, O. J., Lucia, L. A., and Sain, M. (2008). "Cellulosic nanocomposites - A review," *BioResources* 3(3), 929-980.

Hu, J., Yu, F., and Lu, Y. (2012). "Application of Fischer-Tropsch synthesis in biomass to liquid conversion," *Catalysts* 2, 303-326.

IEA. (2012). *Key World Energy Statistics*, Report, OECD/IEA.

Ioelovich, M. (2010). "Biofuels - technology, problems and perspectives, a review," *SITA* 12, 106-126.

Ioelovich, M. (2013). *Plant Biomass as a Renewable Source of Biofuels and Biochemicals,* Saarbrücken, LAP.

Ioelovich, M. (2013a). "Energetic potential of plant biomass and its use," *Int. J. Renew. Sustain. Energy* 2, 26-29.

Ioelovich, M. (2014). *Cellulose: Nanostructured Natural Polymer,* Saarbrücken, LAP.

Ioelovich, M. (2014a). "Correlation analysis of enzymatic digestibility of plant biomass," *Biomass Convers. Biorefin*. 4(3), 269-275.

Ioelovich, M. (2014b). "Problems of solid biofuels made of plant biomass," *Adv. Energy* 2 (1), 15-20.

Ioelovich, M., Leykin, A., and Figovsky, O. (2010). "Study of cellulose paracrystallinity," *BioResources* 5(3), 1393-1407.

Ioelovich, M., and Morag, E. (2012). "Study of enzymatic hydrolysis of mild pretreated lignocellulosic biomasses," *BioResources* 7(1), 1040-1052.

Ioelovich, M., and Morag, E. (2012a). "Study of enzymatic hydrolysis of pretreated biomass at increased solids loading," *BioResources* 7(4), 4672-4682.

Ionescu, G., and Rada, E. C. (2012). "Material and energy recovery in a municipal solid waste system: Practical applicability*," Int. J. Env. Res.* 1(1), 26-30.

Jahirul, M. I., Rasul M. G., Chowdhury, A. A., and Ashwath, N. (2012). "Biofuels production through biomass pyrolysis," *Energies* 5, 4952-5001.

Jessup, R. S. (1970). *Precise Measurement of Heat Combustion with a Bomb Calorimeter*, Washington D.C., US Gov. Print. Office.

Kaar, W. E., Gutierrez, C. V., and Kinoshita, C. M. (1998). "Steam explosion of sugarcane bagasse as a pretreatment for conversion to ethanol," *Biomass Bioenergy* 14(3), 277-287.

Kadam, K. L., and McMillan, J. D. (2003). "Availability of corn stover as a sustainable feedstock for bioethanol production," *Bioresour. Technol.* 88, 17-25.

Kaltschmidt, M., and Hartmann, H. (2001). *Energy from Biomass: Basics, Techniques and Methods*. Berlin/Heidelberg/New York, Springer-Verlag.

Kazi, F. K., Fortman, J. A., Anex, R. P, Hsu, D. D., Aden, A, Dutta, A., and Kothandaraman, G. (2010). "Techno-economic comparison of process technologies for biochemical ethanol production from corn stover," *Fuel* 89, 20-28.

Kautto, J., Realff, M. J., Ragauskas, A. J., and Kässi, T. (2014). "Economic analysis of an organosolv process for bioethanol production," *BioResources* 9(4), 6041-6072**.**

Kerr, A. J., and Goring, D. A. I. (1975). "The ultrastructural arrangement of the wood cell wall," *Cellul. Chem. Technol*. 9(6), 563-573.

Keshwani, D. R., and Cheng, J. J. (2009). "Switchgrass for bioethanol and other value-added applications: A review," *Bioresour. Technol.* 100, 1515-1523.

Khalil, H. P. S., Alwani, M. S., and Omar, A. K. M. (2006). "Chemical composition, anatomy, lignin distribution and cell wall structure of Malaysian plant waste fibers," *BioResources* 1(2), 220-232.

Khan, T. S., and Mubeen, U. (2012). "Wheat straw: A pragmatic overview," *Current Res. J. Biol. Sci.* 4(6), 673-675.

Khodakov, A. Y., Chu, W., and Fongarland, P. (2007). "Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels," *Chem. Rev.* 107, 1692-1744.

Klass, D.L. (1998). *Biomass for Renewable Energy, Fuels and Chemicals*, San Diego/London, Acad. Press.

Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angew. Chem.* 44, 2-37.

Kostylev, M., and Wilson, D. B. (2012). "Synergistic interactions in cellulose hydrolysis," *Biofuels* 3, 61-70.

Kotelnikova, N. E., Petropavlovsky, G. A., Shevelev, V. A., Vasileva, G. G., and Volkova, L. A. (1976). "Interaction of microcrystalline cellulose with water," *Cellul. Chem. Technol.* 4(10), 391-399.

Krässig, H. (1993). *Cellulose: Structure, Accessibility and Reactivity*, Amsterdam, Gordon and Breach Publ.

Lagi, M., Bar-Yam, Y., Bertrand, K., and Bar-Yam, Y. (2011). "The food crises: A quantitative model of food prices including speculators and ethanol conversion," *ArXiv* 1109, 4859.

Larsen, M. J., Winandy, J. E., and Green, F. (1995). "A proposed model of the tracheid cell wall of southern yellow pine having an inherent radial structure in the S2 layer," *Mater. Organism.* 29, 197-210.

Larsen, J., Petersen, M. Ø., Thirup, L., Li, H. W., and Iversen, F. K. (2008). "The IBUS process - Lignocellulosic bioethanol close to a commercial reality," *Chem. Eng. Technol.* 31, 765-772.

Larsson, S. H., Thyrel, M., Geladi, P., and Lestander, T. A. (2008). "High quality biofuel pellet production from pre-compacted low density raw materials," *Bioresour.. Technol*. 99, 7176-7182.

Lee, S. Y., Hubbe, M. A., and Saka, H., (2006). "Prospects for biodiesel as a byproduct of wood pulping - A review," *BioResources* 1(1), 150-171.

Lee, S., Speight, J. G., and Loyalka, S. K. (2007). *Handbook of Alternative Fuel Technologies,* Boca Raton, CRC Press.

Lehtovaara, M, Karvonen, M., and Kässi, T. (2013). "The role of energy support schemes in renewable energy market penetration," *Int. J. Renew. Sustain. Energy* 2(2), 30-40.

Lewin, M., and Pearce, E. M. (1998). *Handbook of Fiber Chemistry,* New York, Marcel Dekker, Inc.

Librenti, E., Ceotto, E., and Candello, M. (2010). "Biomass characteristics and energy contents of dedicated lignocellulose crops," *Biomass & Waste* 3, 7-8.

Lin, Y., and Tanaka, S. (2006). "Ethanol fermentation from biomass resources: Current state and prospects," *Appl. Microbiol. Biotechnol*. 69, 627-642.

Liu, Z., Liu, X., Fei, B., Jiang, Z., Cai, Z., and Yu, Y. (2013). "The properties of pellets from mixing bamboo and rice straw," *Renew. Energy* 55, 1-5.

Lucia, L. A., Agryropoulus, D. S., Adamopoulus, L., and Gaspar, A. R. (2006). "Chemicals and energy from biomass," *Can. J. Chem.* 84, 960-970.

Lynd, L. R., Weimer, P. J., Van Zyl, W. H., and Pretorius, I. S. (2002). "Microbial cellulose utilization: Fundamentals and biotechnology," *Micro. Mol. Biol. Rev*. 66, 506-577.

Lynd, L. R., Larson, E., Greene, N., Laser, M., Sheehan, J., Dale, B. E., McLaughlin, S., and Wang, M. (2009). "The role of biomass in America's energy future: Framing the analysis," *Biofuels, Bioprod. Bioref*. 3, 113-123.

Mandels, M., and Reese, E. T. (1964). "Fungal cellulase and the microbial decomposition of cellulosic fabric," *Developm. Industr. Microbiol.* 5, 5-10.

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

McKendry, P. (2002). "Energy production from biomass: Overview of biomass," *Bioresour. Technol.* 83, 37-46.

McMillan, J. D. (1993). *Xylose Fermentation to Ethanol*, Springfield, NREL.

McMillan, J.D. (1997). "Bioethanol production: Status and prospects," *Renewable Energy* 10(2-3), 295-302.

Mesa, L., González, E., Cara, C, González, M., Castro, E., and Mussatto, S. I. (2011). "The effect of organosolv pretreatment variables on enzymatic hydrolysis of sugarcane bagasse," *Chem. Eng. J.* 168, 1157-1162.

Moka, V. K. (2012). *Estimation of Calorific Value of Biomass from its Elementary Components by Regression Analysis*, Rourkela. NIT.

Modenbach, A. A., and Nokes, S. E. (2012). "The use of high-solids loadings in biomass pretreatment - A review," *Biotechnol. Bioeng.* 109, 1-13.

Nikitin, N. I. (1962). *Wood and Cellulose Chemistry,* Moscow, Science.

Njoku, S. I., Iversen, J. A., Uellendahl, H., and Ahring, B. K. (2013). "Production of ethanol from hemicellulose fraction of cocksfoot grass using *Pichia stipitis*," *Sustain. Chem. Proc.* 1(13), 1-7.

Oasmaa, A., Kytö, M., and Sipilä, K. (2001). "Pyrolysis oil combustion tests in an industrial boiler," in: *Progress in Thermochemical Biomass Conversion*, Oxford Blackwell Science.

Oasmaa, A., and Kuoppala, E. (2003). "Fast pyrolysis of forestry residue: Storage stability of liquid fuel," *Energy Fuel* 17, 1075-1084.

Oasmaa, A., and Meier, D. (2005). "Norms and standards for fast pyrolysis liquids: Round robin test," *J. Anal. Appl. Pyrolysis* 73, 323-334.

Onuki, S., Koziel, J. A., Van Leeuwen, J., Jenks, W. S., Grewell, D., and Cai, L. (2008). "Ethanol production, purification, and analysis techniques: A review," *ASABE* Annual *Int. Meeting*. Providence, Rhode Island.

O'Sullivan, A. (1997). "Cellulose: The structure slowly unravels," *Cellulose* 4, 173-207.

Pakzad, A., Simonsen, J., Heiden, P.A., and Yassar, R.S. (2012). "Size effects on the nanomechanical properties of cellulose I nanocrystals," *J. Mater. Res.* 27, 528-536.

Pan, X., Xie, D., Gilkes, N., Gregg, D. J., and Saddler, J. N. (2005). "Strategies to enhance the enzymatic hydrolysis of pretreated softwood with high residual lignin content," *Appl. Biochem. Biotechnol.* 121/124, 1069-1079.

Pandey, A. (2009). *Handbook of Plant-based Biofuels*, New York, CRC.

Pantze, A. (2006). *Studies of Ester Formation on a Cellulose Matrix,* Skelleftea, LTU.

Patwardhan, P. R. (2010). *Understanding the Product Distribution from Biomass Fast Pyrolysis,* Ames, ISU.

Perlack, R. D., Wright, L. L., Turhollow, A. F., Graham, R. L., Stokes, B. J., and Erbach, D. C. (2005). "Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion ton annual supply," *DOE & USDA Report.*

Protasio, T., Bufalino, L., Tonoli, G., Junior, M., Trugilho, P., and Mendes, L. M. (2013). "Brazilian lignocellulosic wastes for bioenergy production: characterization and comparison with fossil fuels," *BioResources* 8(1), 1166-1185.

Rapson, W. H. (1963). *The Bleaching of Pulp,* Atlanta, TAPPI Press.

Rizhikovs, J., Zandersons, J., Spince, B., Dobele, G., and Jakab, E. (2012). "Preparation of granular activated carbon from hydrothermally treated and pelletized deciduous wood," *J. Anal. Appl. Pyrol.* 93, 68-76.

Rowell, R. M. (2005). *Handbook of Wood Chemistry and Wood Composites,* Madison, CRC Press.

Roy, P., and Dutta, A. (2013). "A review of life cycle of ethanol produced from biosyngas," *Bioethanol* 1(1), 9-19.

Ruel, K., Chevalier-Billosta, V., Guillemin, F., Berrio Sierra, J., and Joseleau, J.-P. (2006). "The wood cell wall at the ultrastructural scale – Formation and topochemical organization," *Ciencia y Tecnología* 8, 107-116.

Sannigrahi, P., Kim, D. H., Jung, S., and Ragauskas, A. (2011). "Pseudolignin and pretreatment chemistry," *Energy Environment. Sci.* 4, 1306-1310.

Saxena, R. C., Adhikari, D. K., and Goyal, H. B. (2009). "Biomass-based energy fuel through biochemical routes: A review," *Renew. Sustain. Energy Rev.* 13(1), 167-178.

Schmidt, C. W. (2007). "Biodiesel: Cultivating alternative fuels," *Environment. Health Perspectives* 115(2), 87-91.

Scott, P. T., Pregelj, L., Chen, N., Hadler, J. S., Djordjevic, M. J, and Gresshoff, P. M. (2008). "*Pongamia pinnata*: An untapped resource for the biofuels industry of the future," *Bioenergy Res.* 1, 2-11.

Selig, M. J., Vinzant, T. B., Himmel, M. E., and Decker, S. R. (2009). "The effect of lignin removal by alkaline peroxide pretreatment on the susceptibility of corn stover to purified cellulolytic and xylanolytic enzymes," *Appl. Biochem. Biotech.* 155 (1-3), 397-406.

Sergeeva, V. (1972). *Cell Wall of Wood and its Changes upon Chemical Treatment,* Riga, Science.

Shafizadeh, F. (1982). "Pyrolytic reactions and products of biomass," *J. Analyt. Appl. Pyrol.* 3, 283-305.

Sheng, C., and Azevedo, J. L.T. (2005). "Estimating higher heating values of biomass fuels from basic analysis data," *Biomass Bioenergy* 28, 499-507.

Sikkema, R., Steiner, M., Junginger, M., Hiegl, W., Hansen, M.T., and Faaij, A. (2011). "The European wood pellets markets: current status and prospects for 2020," *Biofuels Bioprod. Bioref.* 5(3), 250-278.

Sjöström, E. (1993). *Wood Chemistry - Fundamentals and Applications,* London, Acad. Press.

Sluiter, J. B., Ruiz, R. O., Scarlata, C. J., Sluiter, A. D., and Templeton, D. W. (2010). "Compositional analysis of lignocellulosic feedstocks 1: Review and description of methods," *J. Agricult. Food Chem.* 58, 9043-9053.

Stelte, W., Sanadi A.R., Shang, L., Holm, J. K., Ahrenfeldt, J., and Henriksen, U. B. (2012). "Recent developments in biomass pelletization - a review," *BioResourses* 7(3), 4451-4490.

Sugiyama, J., Vuong, R., and Chanzy, H. (1991). "Electron diffraction study on the two crystalline phases occurring in native cellulose from an algal cell wall," *Macromolecules* 24, 4168-4175.

Sun, X. F., Sun, R. C., Fowler, P., and Baird, M. S. (2005). "Extraction and characterization of original lignin and hemicelluloses from wheat straw," *J. Agricult. Food Chem.* 53, 860-870.

Sun, R., Song, X., Sun, R., and Jiung, J. (2011). "Effect of lignin content on enzymatic hydrolysis of furfural residues," *BioResources* 6(1), 317-328.

Suris, A. L. (2007). "Heat of combustion of liquid halogen-organic compounds," *Chem. Petrol. Eng*. 43(1-2), 20-22.

Surisetty, V. R., Kozinski, J., and Dalai, A. K. (2011). "Biomass, availability in Canada, and gasification: An overview," *Biomass Convers. Biorefin.* 2(1), 73-85.

Takahashi, S., Shiell, K., Fatehi, P., and Ni, P. (2012). "Ethanol production via in-situ detoxification of spent sulfite liquor," *J. Bioproc. Eng. Biorefin.* 1(1), 105-112.

Talmadge, M, Dutta, A., and Bain, R. (2013). *Techno-economic and Market Analysis of Pathways from Syngas to Fuels and Chemicals,* Chicago, NREL.

Tanifuji, K., Takahashi, S., Shiell, K., Jahan, S., Ni, P., and Ohi, H. (2013). "Improvement of ethanol fermentation from oligosaccharides in spent sulfite liquor with *Pichia stipitis* by combined calcium oxide and ion exchange resin treatments," *BioResources* 8(3), 3912-3923.

Tokgoz, S., and Elobeid, A. (2006). *An Analysis of the Link between Ethanol, Energy, and Crop Markets,* Ames, Iowa State University.

Wang, Y., Lindström, M. E., and Henriksson, G. (2011). "Mild alkaline treatment activates spruce wood for enzymatic processing: a possible stage in bio-refinery processes," *BioResources* 6(3), 2425-2434.

Warajanont, S., and Soponpongpipat, N. (2013). "Effect of particle size and moisture content on cassava root pellet fuel's qualities follow the acceptance of pellet fuel standard," *Int. J. Renew. Sustain. Energy* 2, 74-79.

Weerasai, K., Suriyachai, N., Poonsrisawat, A., Arnthong, J., Unrean, P., Laosiripojana, N., and Champreda, V. (2014). "Sequential acid and alkaline pretreatment of rice straw for bioethanol fermentation," *BioResources* 9(4), 5988-6001.

Wildschut, J., Smit, A. T., Reith, J. H., and Huijgen, W. (2013). "EtOH-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose," *Bioresour. Technol.* 135, 58-66.

Wyman, C. E. (1996). *Handbook on Bioethanol: Production and Utilization*, Taylor & Francis, Washington.

Wyman, C. E. (2013). *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley & Sons, Chichester.

Xu, L., Wang, J., Sharma-Shivappa, R. R., and Cheng, J. J. (2011). "Enzymatic hydrolysis of switchgrass and coastal Bermuda grass pretreated with different chemical methods," *BioResources* 6(3), 2990-3003.

Xu, L., and Tschirner, U. (2012). "Peracetic acid pretreatment of alfalfa stem and aspen biomass," *BioResources* 7(1), 203-216.

Yang, B., Dai, Z., Ding, S. Y., and Wyman, C. E. (2011). "Enzymatic hydrolysis of cellulosic biomass," *Biofuels* 2, 421-450.

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

Young, R. A., and Rowell, R. M. (1986). *Cellulose: Structure, Modification, and Hydrolysis*, Wiley, New York.

Yu, M., Hosseini, S.A., and Korokas, A. (2014). "Technology selection for bioethanol production: Supply chain perspective," *Bioethanol* 1(1), 28-47.

Zacchi, G., and Axelsson, A. (1989). "Economic evaluation of pre-concentration in production of ethanol from dilute sugar solutions," *Biotechnol. Bioeng.* 34, 223-233.

Zaror, C. A., and Pyle, D. L. (1982). "The pyrolysis of biomass: A general review," *Proc. Indian Acad. Sci.* 5, 269-285.

Zhang, B, and Wang, Y. (2013). *Lignocellulose: Biotechnology, Chemical Composition and Future Prospects,* New York, Nova Sci. Publ.

Zhang, M., Wang, F., Su, R., Qi, W., and Hw, Z. (2010). "Ethanol production from high dry matter corncob using fed-batch simultaneous saccharification and fermentation after combined pretreatment," *Bioresour. Technol.* 101(13), 4959-4964.

Zhao, X., Song, Y., and Liu, D. (2011). "Enzymatic hydrolysis and simultaneous saccharification and fermentation of alkali/peracetic acid pretreated sugarcane bagasse for ethanol and 2,3-butanediol production," *Enzym. Microbiol. Technol*. 49(4), 413-419.

Zhu, L. (2005). *Fundamental Study of Structural Features Affecting Enzymatic Hydrolysis of Lignocellulosic Biomass*, Texas, University Press.

Zugenmaier, P. (2008). *Crystalline Cellulose and Cellulose Derivatives: Characterization and Structures*, Springer-Verlag, Berlin/Heidelberg.