Application of Pulsed Electric Energy for Lignocellulosic Biorefinery

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Eugène Vorobiev and Nikolai Lebovka

Abstract

The biorefinery concept of conversion of lignocellulosic biomass is the hottest topic in the modern literature. Various physical, chemical, and biological techniques are tested in order to improve the efficiency of methods and their economic value. Recent applications of pulsed electric energy (PEE), both pulsed electric fields (PEF) and high voltage electrical discharges (HVED), in lignocellulosic biorefinery have demonstrated their high potential. The lignocellulosic biomass mainly consists of cellulose, hemicellulose, and lignin and contains small quantities of pectin, proteins, nonstructural sugars, chlorophylls, and ash. The existing schemes of lignocellulosic biomass biorefinery include thermo-chemical, physical, chemical, and biological (fermentation, digestion, and microbial processing) techniques. However, these techniques require a long processing time, large amounts of chemicals, solvents, and they are energy consuming. The PEF and HVED techniques can be effectively used for assistance of hydrolysis and fermentation, for production of biogas, and extraction of high added-chemicals and bioactive compounds. The range of tested biomass is rather limited so far and existing examples include wood and crop biomasses (sawdust, chips, barks, silage, and switch grass), sludges, and wastes. The recent findings evidenced

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the great potential of electroporation-assisted techniques for efficient utilization of agro-industrial waste, forestry wastes, and semisolid biological sludges. This chapter analyzes up-to-date information available on the PEE-assisted lignocellulosic biorefinery including the utilization of forest and agro-industrial residues, waste, and semisolid sludges.

Keywords

Pulsed electric energy (PEE) • Pulsed electric fields (PEF) • High voltage electrical discharge (HVED) • Lignocellulosic biorefinery • Biogas • High-valued chemicals

Contents

Introduction

Formally, biomass is defined as organic matter that can grow. It uses carbon dioxide (CO_2) for growth, and the same carbon dioxide can be generated after the biomass utilization. Therefore, biomass resources have the advantage of zero carbon dioxide emissions (Chen 2015). Biomass incorporates animals, microorganisms, plant products (crops, stalks, trees), and their wastes, including agro-industrial and forestry wastes and semisolid biological sludges. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin. Typically, conversion of this biomass to end products (bioenergy, biofuels, food and animal feed, biomaterials, and biochemicals) requires application of complex and costly techniques with high production costs. Nowadays, the biorefinery concept of conversion of lignocellulosic biomass becomes an increasingly hot topic. Recent monographs present different aspects of biorefinery applications to the pulp and paper industry (Bajpai 2013), processing of by-products (from wood bark, corn, cereals, soy, residues from sugarcane and citrus fruit processing, and pulp) (Bergeron et al. 2012), utilization of agro-residues (fruit, brewing, palm oil and wine industry by-products, cereal, straw, and bran residues), production of enzymes (cellulolytic, pectinolytic,

ligninolytic) (Nigam and Pandey 2009), production of biofuels (bioethanol, biohydrogen, and biobutanol) from lignocellulosic wastes (Karimi 2015), and application of biomass pretreatments for lignocellulosic biorefinery (Mussatto 2016).

For the recent two decades, electroporation-based techniques have been tested for biorefinery applications. Application of pulsed electric energy (PEE) may cause breakage/electroporation of membranes and effective disintegration of cells. Starting from the early 1990s, the PEE techniques have been tested for microbial killing, food preservation, assistance of extraction, drying, pressing, freezing, and many other processes and improvements of food processing have been demonstrated (Barba et al. 2015).

This chapter presents up-to-date information available on the PEE-assisted lignocellulosic biorefinery, including utilization of forest and agro-industrial residues, semisolid sludges, and wastes. The following text includes discussion on the structure and properties of lignocellulosic biomass, concept of lignocellulosic feedstock biorefinery (LCF biorefinery), and an overview of various pretreatment techniques with special attention to pulsed electric energy–assisted techniques. Applications of PEE techniques for biorefineries of wood and crop biomasses (sawdust, chips, barks, silage, and switch grass), sludges, and wastes are discussed in details.

Lignocellulosic Biomass

Lignocellulosic biomass is the most widespread substance on Earth, and it is available from different sources including straw and chaff from cereals, grasses, wood stems, leaves, paper and cellulosic municipal solid wastes, and many other raw materials. This biomass mainly consists of three primary chemical constituents: a cellulose (40–50%), a hemicellulose (25–35%), and a lignin (15–20%) and contains small quantities of pectin, proteins, nonstructural sugars, chlorophylls, and ash. A typical content of main constituents in a lignocellulosic biomass is presented in the Table 1.

More details on general structure and properties of cellulose, hemicellulose, and lignin in cell walls of plants are presented the Table 2.

Cellulose

A cellulose is a sugar (glucose) homopolymer consisting of $\beta(1 \rightarrow 4)$ and it differs from a starch, which consists of $\alpha(1 \rightarrow 4)$ bonds. The content of cellulose in wood stems (hard and soft) is 40–55%, and it is the highest in the cotton seed hairs and the papers and waste papers. This homopolymer is highly linear. The different molecules are linked together by a weak hydrogen and van der Waals bonds and form microfibrils and cellulose fibers. In biomass the cellulose polymers are organized in a crystalline (major%) and an amorphous forms.

Table 1 Cellulose, hemicellulose, and lignin contents (%) in lignocellulosic biomasses (Adapted from Kumar et al. (2009))

Material	Cellulose	Hemicellulose	Lignin
Wheat straw	30	50	15
Wood stems (hard and soft)	40–55	24–40	18–35
Leaves	15–20	80–85	0
Grasses	25–40	35–50	10–30
Nut shells	25–30	25–30	30–40
Cotton seed hairs	80–95	5–20	0
Paper	85–99	0	0–15
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–20	5–10
Primary wastewater solids 8–15	5–15	–	–

Table 2 Structure and properties of cellulose, hemicellulose, and lignin in cell walls of plants. The other details on chemical composition of subunits and chemical linkages between them can be found in (Maity 2015)

Characteristic	Cellulose	Hemicellulose	Lignin
Subunits	D-Pyran glucose units	D-Xylose, mannose, L-arabinose, galactose, glucuronic acid	Guaiacylpropane (G), syringylpropane (S), hydroxyphenylpropane (H)
Chemical linkages between the subunits	β-1,4-Glycosidic bonds	β-1,4-Glycosidic bonds in main chains; β-1.2-, β-1.3-, β-1.6-glycosidic bonds in side chains	Various ether bonds and carbon–carbon bonds, mainly β-O-4 ether bonds
Polymerization (Da)	800-17,000	150–200	>4000
Polymers	β-Glucan	Polyxylose, galactoglucomannan (Gal-Glu-Man), glucomannan (Glu-Man)	G lignin, GS lignin, GSH lignin
Crystallinity	3d linear molecule composed of the crystalline (major %) and amorphous regions	3d inhomogeneous molecule with a small crystalline region	Amorphous, inhomogeneous, nonlinear 3d polymer
Bonds between other components	Without chemical bonds	Contains chemical bonds with lignin	Contains chemical bonds with hemicellulose
Functions	Microfibrils play a structural role as support in the primary cell walls	Provides cross-linking of the cellulose microfibrils in the primary cell walls and limits the stretchiness of the cell walls	Provides stiffness, rigidity, and mechanical strength of plants. Supports a barrier function against attacks of insects and fungi

Hemicellulose

A hemicellulose is a sugar heteropolymer of pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, galactose, mannose), and sugar acids. The hemicelluloses can be divided into hardwood backbone (mainly xylans: xylose, arabinose, and glucuronic acid) and softwood side chains consisting of sugars (mainly glucomannans). The most important monomers of hemicellulose are the following: acetic acid, arabinose, galactose, glucose, glucuronic acid, mannose, and xylose. The hemicellulose is a highly branching macromolecule. Due to an amorphous structure the hemicellulose can be more readily hydrolyzed than the cellulose. A solubility of hemicellulose in water is influenced by the particular sugars and their positions. For example, the hemicellulose with acids in side chains is slightly charged and soluble in water. Other hemicelluloses are insoluble. A highest content of hemicellulose is in the leaves (80–85%). The hemicellulose can be extracted by alkali or hot water and hydrolyzed by diluted H_2SO_4.

Lignin

A lignin is one of the main constituent of the dry land plant cell walls. Its content is between 18% and 35% of dry weight in the trees and 10–30% in the grasses. The lignin is a very irregular and randomly cross-linked nonsugar polymer of phenylpropane units. It mainly consists of three hydrophobic hydroxycinnamyl alcohol monomers: p-coumaryl, coniferyl, and sinapyl alcohols. The lignin presents an amorphous structure and it provides stiffness, rigidity, and mechanical strength of such plants as trees. The lignin polymers are covalently bound to cell wall polysaccharides through lignin–carbohydrate complexes. Very important is also a barrier function of lignin against attacks of insects and fungi. The lignin is relatively hydrophobic and aromatic substance, and it allows preventing the absorption of water by polysaccharides in plant cell walls. It is important for the efficient transport of water in the vascular tissues. Moreover, the lignin shields plant cells against moisture loss and death due to drying. In production of high-quality bleached paper, the lignin is removed from wood pulp as the lignosulfonates. The lignosulfonates can be used as the dispersants in high performance cement applications, compositions for water treatment, as a renewable aromatic resource for the chemical industry, and for production of various chemicals (ethanol, DMSO, humic acid, etc.).

Lignocellulosic Feedstock Biorefinery (LCF Biorefinery)

The LCF biorefinery can be processed directly through the various routes, such as thermo-chemical (combustion, gasification, liquefaction, and fast pyrolysis), chemical (aqueous phase dehydration/hydrogenation), and biological (fermentation, digestion, and microbial processing) (Maity 2015). Figure 1 presents the schema of LCF biorefinery (Maity 2015). Combustion and gasification are the most

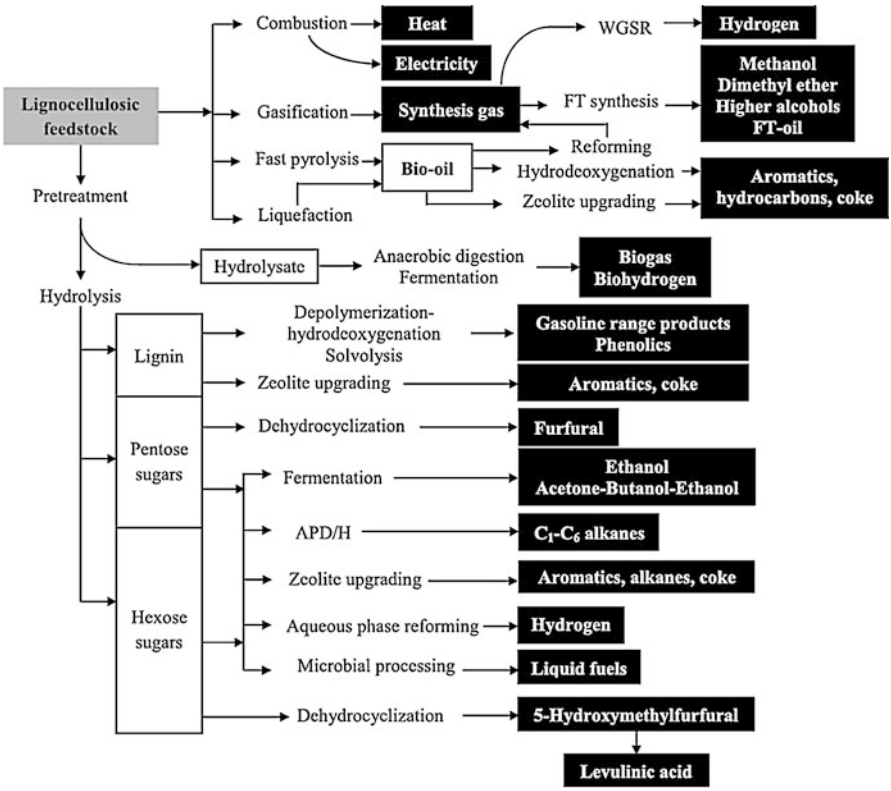

Fig. 1 Schema of the lignocellulosic feedstock biorefinery (LCF biorefinery) (From Maity (2015) with permission)

established technologies for production of heat, power, and valuable by-products from biomass. Fast pyrolysis and liquefaction are used for production of bio-oil and bio-crude. Aqueous phase dehydration/hydrogenation provides possibility for production of various chemicals. Fermentation and anaerobic digestion are widely used for production of alcoholic bio-fuels, biogas, and value-added organic chemicals. These processes are accompanied by production of lignin as a by-product. The lignin is also a promising source for conversion into bio-fuels and production of phenolic chemicals, carbon fiber, glues, and expanded polyurethane foams.

Various Pretreatment Techniques

Different pretreatment techniques for various lignocellulosic biomasses including municipal solid wastes, energy crops, forest residues, manure, and crop residues have been extensively investigated at lab and pilot scale. In cell walls the primary constituents of lignocellulosic biomass (cellulose, hemicellulose, and lignin) have

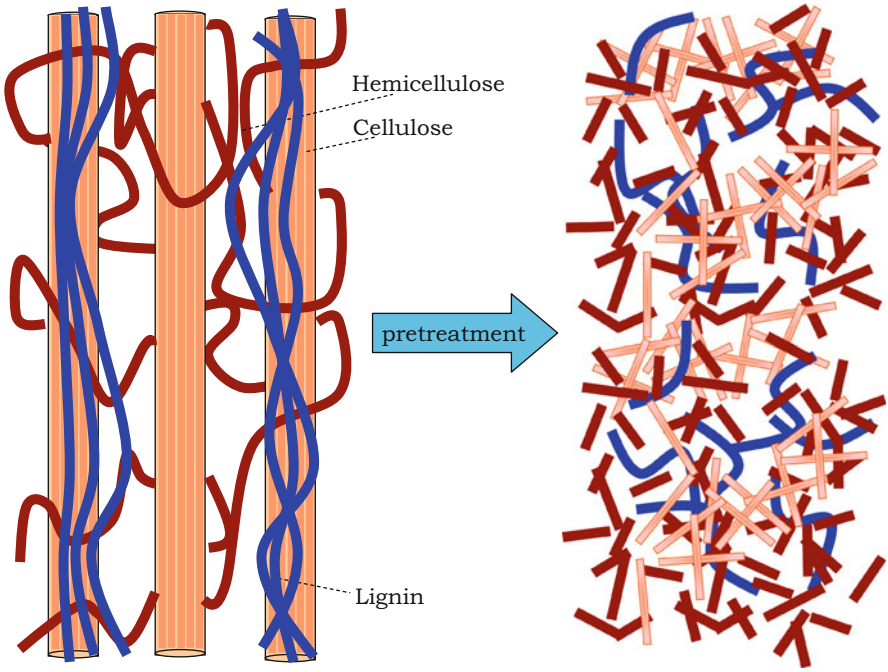

Fig. 2 Illustration of pretreatment of the lignocellulosic biomass

very strong interactions with each other forming three-dimensional networks in cell walls (Fig. 2). These networks are supported by strong hydrogen bonds between OH groups on the cellulose chains and by a complex mutual integration in plant cell wall of the crystalline cellulose microfibrils, hemicellulose, and lignin. Lignin and hemicellulose serve also for protection of the cellulose against microbial and chemical attacks.

To disrupt these strong cellulose–hemicellulose–lignin networks a preliminary pretreatment of lignocellulosic biomass for hydrolysis of the carbohydrate polymers into fermentable sugars is required. The preliminary pretreatment also aids a delignification of a feedstock and a damage of the lignin seals, cellulose aggregates, and hemicellulose chains. It allows an increase in biomass porosity and a decrease in a crystallinity of cellulose.

Common processing difficulties are related with poor digestibility of lignocellulose and low effectiveness of the enzymes for rapid hydrolysis and conversion of the carbohydrate polymers into fermentable sugars. Moreover, a lignocellulose is highly heterogeneous in nature and requires application of integrated pretreatment processes effective for different kinds of biomass. The conventional methods use heat, organic solvents, steam explosion, dilute acid, lime, and ammonia pretreatments and their combination of different severity. The high sugar yields ($\geq$90%) for woods, grasses, and corn obtained by using chemical and physicochemical pretreatment

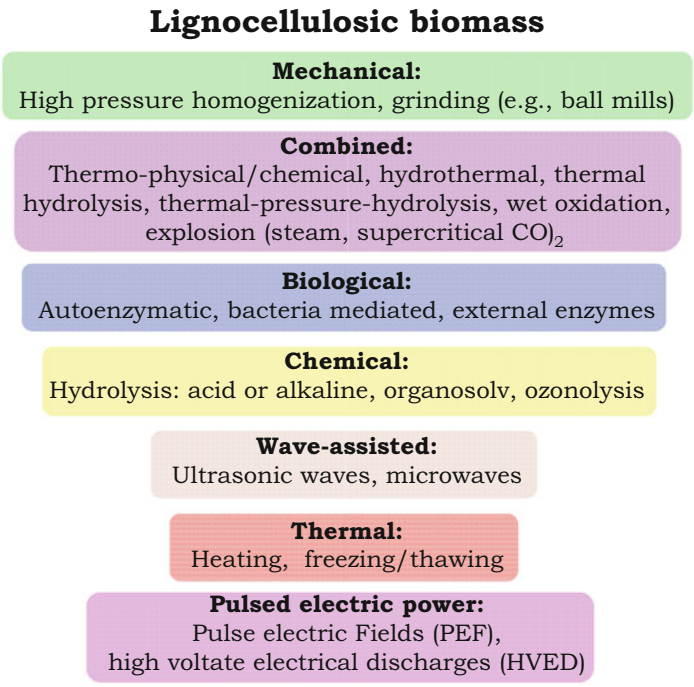

Fig. 3 Various techniques of the lignocellulosic biomass pretreatment

methods (e.g., alkali treatment, ammonia explosion, and others) have been demonstrated. Various unconventional physical techniques for increase of porosity of biomass, recovery of a cellulose from a wall matrix, damage of lignin seals, and decrease of a crystalline structure of a cellulose have been recently applied (Bundhoo et al. 2013; Kumar et al. 2009).

Figure 3 presents the physical, physicochemical, chemical, and biological pretreatment techniques that can be used for the lignocellulosic biomass biorefinery (Mussatto 2016). Mechanical pretreatment of lignocellulose feedstock requires special devices for high pressure homogenization, fine grinding, and mechanochemical processing of plant raw materials. Extrusion processing is continuous, can be done with short residence time and moderate temperatures, and does not require washing and conditioning. Combined methods include thermal, oxidation, and explosion (steam, wet, supercritical CO_2) techniques. Biological methods are mediated with microorganism that secrete ligninolytic enzymes and directly with enzymes. Chemical methods include lignocellulosic material chemical oxidation and pretreatment with acids, alkalines, alkaline peroxide, ammonia, ozone, metal salts, solvents (e.g., n-methylmorpholine n-oxide), hydrotropic pretreatment, and organosolv fractionation. Wave-assisted techniques are based on microwave and ultrasound irradiation. Hydrothermal treatment induced by microwave irradiation produces reactions in biomass compounds, and it can be used for effective

fractionation of lignocellulose and food-waste biomass, enhancement of enzymatic digestibility, and in solvothermal pretreatment. Ultrasound pretreatment can be used for assistance of chemical treatments (acids, alkalines organic solvents, ionic liquids), hydrolysis of lignocelluloses, and subsequent fermentation for bioethanol production. Thermal methods are based on utilization of heat-assisted processing. As an example, pyrolysis processing is widely used for transformation of lignocellulosic materials. In a pyrolysis reaction, the heat converts lignocellulosic material into a solid residue and volatiles under an inert atmosphere. The pyrolysis technology can be effectively used for production of energy and chemicals. Hydrothermal/liquid hot water pretreatment (auto hydrolysis) uses compressed hot water for biomass pretreatment and requires no chemicals to be added. For recovery of phenolic compounds the classical and well-established techniques such as conventional maceration and extraction under reflux can be applied.

However, commonly these techniques require a long processing time, large amounts of chemicals and solvents, and they are energy consuming. Conventional pretreatment of lignocellulosic feedstock has a high severity factor, *CS*, determined by the following equation (Wyman 2013):

$$CS = \log_{10}\left[t\exp\left(\frac{T-100}{14.75}\right)\right] \tag{1}$$

where t is the time (min), T is the process temperature (°C), and 14.75 (°C) is an empirical parameter related to activation energy and temperature.

In many cases, pretreatment techniques should be combined and applied as combination of physical, chemical, or biological methods in order to enhance recovery to the industry's expectation. Their effectiveness also depends on the types of lignocellulosic biomass and requires detailed optimization for valorization of various products. For further separation and purification of high-valued compounds the different extraction techniques can be applied, such as steam distillation, conventional solid–liquid extraction, ultrasound-assisted extraction, microwave-assisted extraction, PEE-assisted extraction, pressurized subcritical liquid extraction, supercritical fluid extraction, liquid–liquid extraction, membrane separation, and molecular distillation (Bergeron et al. 2012). Alternative physical methods also aim to decrease the severity of conventional pretreatment (Eq. 1).

Pulsed Electric Energy Assisted Techniques

In recent decades, the pulsed electric energy (PEE) has been applied by different groups for biomass pretreatment (Barba et al. 2015). Existing PEE techniques can be roughly divided on pulsed electric fields (PEF) and high voltage electrical discharges (HVED). The PEF and HVED techniques have different impact on the damage of cells, mechanical fragmentation of materials, temperature elevation, and other characteristics of treated materials.

The PEF technique is relatively nondestructive, nonthermal, and based on an electric field induced selective damage of biological membrane, i.e., phenomenon of electroporation. The electroporation occurs when the electrical potential induced on membrane u_m is above some threshold value, typically, 0.5–1.5 V. The effective electroporation of cells in plant tissues requires an electric field strength of $E =$ 500–1000 V/cm and a time of PEF treatment of $t_{PEF} = 10^{-4}$–10^{-1} s (t_{PEF} is a product of pulse duration and number of pulses). The electroporation of smaller cells (microbial cells, yeasts, microalgae) requires a higher electric field strength $E =$ 20–50 kV/cm and time of PEF treatment $t_{PEF} = 10^{-5}$–10^{-3} s. A rather short time of PEF treatment guarantees a nonsignificant elevation of temperature ($\Delta T \leq 10$ °C).

HVED technique can be more destructive with respect to the tissue constituents. HVED effects in liquid and solid medium have been intensively studied for many years. The activity in the field had been initiated by Russian scientist Lev A. Yutkin. He had applied HVED to liquid medium and discovered in 1938 the electrohydraulic effect. During a discharge an electrostatic energy is transformed into mechanical, thermal, and light energy. Transmission of electric energy to a sample can be achieved by a very short time discharging a capacitor bank through a gap between electrodes. The discharge in liquids results in formation of plasma channels and production of compression or shock waves followed by sound waves. The compression waves are formed during rapid expansion (only in a few microseconds) of the plasma channel with a very high temperature (≈ 1–$3 \cdot 10^4$ K), pressure ($\approx 10^8$ Pa), and charged particle concentration ($\approx 10^{20}$ cm^{-3}). The breakdown and propagation of a streamer accompanies by air bubble formation, cavitation effect, and light emission. In addition, HVED treatment of biomass suspension and waste sludges can produce a large quantity of radical species, ozone, and can provoke a fragmentation of solid particles suspended in treated systems. The effects of HVED treatment may include electroporation as well as additional thermal and mechanical stresses. HVED technique can be realized using the chambers with needle-plane or needle–needle electrode geometries.

The PEF and HVED applications were tested to assist decomposition, degradation, extraction, digestion, and dewatering of wood and crop biomasses, semisolid sludges, and wastes.

Wood and Crop Biomasses: Sawdust, Chips, Barks, Silage, and Switch Grass

Several studies have demonstrated a potential of PEE pretreatment for assistance of processing of wood and crop based lignocellulosic materials. It has been reported that the HVED-produced compression waves mechanically affects the structure of lignocellulosic particles (Mikula et al. 1997). The wood materials (beech sawdust and spruce needles) were mixed with water (25 g/L) and then obtained suspensions were treated by electrical discharges. In suspension of beech sawdust the discharge destruction was tested by the rate of acid hydrolysis in 3% H_2SO_4. The amounts of reducing saccharides and hydrolyzed polysaccharides increased with the number of

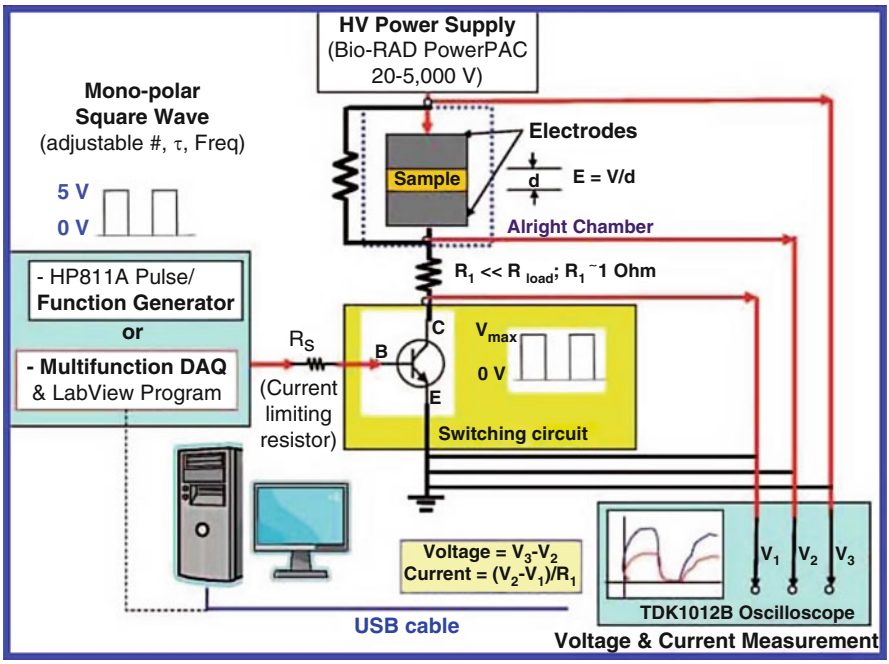

Fig. 4 Schematic of PEF system for pretreatment of biomass (From Kumar et al. (2011) with permission)

discharges. In suspension of the spruce needles an acceleration of microbiological processes in plasma treated samples was observed. The acceleration effect was documented by increase in protein content. The degassing and decomposition of suspended materials were found to be dominant effects of the pulse discharge.

The PEF treatment of wood chips (Southern pine) and switch grass has been studied (Kumar et al. 2011). The PEF apparatus consisted of a high-voltage power supply, a function generator, a switching circuit, a sample holder, and a measurement system (Fig. 4). To quantify the effect of PEF on internal diffusion in wood tissues, an uptake of a dye neutral red (NR) $C_{15}H_{17}ClN_4$ was studied. The samples were stirred in the NR aqueous solution and a concentration of NR was tested using a UV–VIS spectrophotometer. The samples were resistant to change in a structure at low field strengths. The samples treated at 2.5–5 kV/cm for both 2000 and 5000 pulses with pulse duration of 100 μs show MR uptake kinetic similar to those of untreated samples. However, an effective uptake of a colored NR for the PEF treatment at high electric field strength ($E \geq 8$ kV/cm) was observed. The PEF treated samples of switch grass showed faster dye uptake than fresh samples. Similar phenomena were observed for wood chip samples treated at $E = 10$ kV/cm. It can reflect an increase in porosity of the treated samples. After the dye uptake experiment, desorption of NR in pure deionized water was studied. For the PEF treated samples the faster desorption was observed. It was concluded that permeabilization

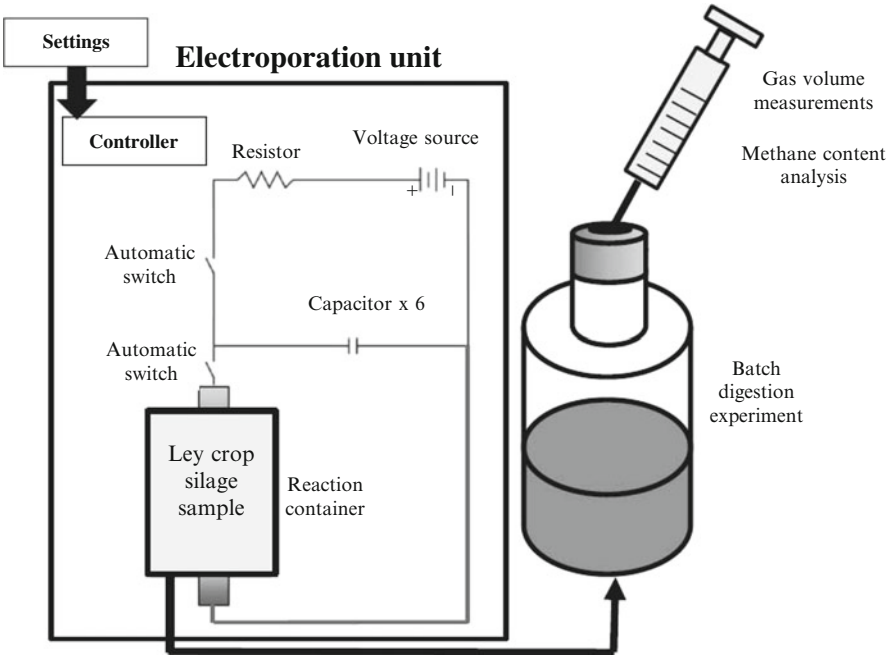

Fig. 5 An electroporation unit for a batch digestion experiment with ley crop silage. A reaction container (100-ml) has a vertical electrode configuration with one electrode mounted in bottom and the other mounted in a lid. The distance between the electrodes was 2.5–5 cm (From Lindmark et al. (2014) with permission)

of switch grass and wood chip species using the PEF can be utilized to improve the cellulose hydrolysis to sugar.

Electroporation of lignocellulosic biomass (ley crop silage) under the PEF treatment (at $E = 48$–96 kV/cm) has been investigated (Lindmark et al. 2014). Ley crop (a mixture that consists mainly of grass and clover) is commonly used in a crop rotation to fertilize a soil with nitrogen. Authors evaluated an effect of electroporation on a biogas yield. The PEF treatment was applied in batch-wise experiments (Fig. 5). The PEF treatment was applied before digestion and the results were evaluated in batch digestion experiments. Most of the biogas was produced within first 100 days of digestion. The noticeable increase of the biogas yield (up to 16%) was observed at $E = 96$ kV/cm with a total energy input W of 259 Wh/kg volatile solid. However, for the PEF treatment at $E = 48$ kV/cm and the same energy input, no effects of the treatment were observed. It was concluded that implementation of PEE pretreatment on agricultural crops and residues can be very promising to improve biogas production from the farmland used for substrate cultivation.

The PEF- and HVED-assisted aqueous extraction of polyphenols from the wood barks has been investigated (Bouras 2015). Results indicated enhancement of polyphenol extraction after the HVED and the effects were more pronounced for

treatments with a higher energy input. Data demonstrated that the polyphenols extraction was increased with the PEF and HVED application. The final extraction yields obtained with the PEF (4.94 ± 0.42 g GAE/100 g DM) and HVED (5.32 ± 0.41 g GAE/100 g DM) were close to that obtained for the ground product (6.04 ± 0.29 g GAE/100 g DM). The observed effects were attributed to cell electroporation as well as to the reduction of initial particle size after the HVED treatment (mechanical effect). The reported energy consumption of PEF (3.2 kJ/g) and of HVED (3.2 kJ/g) was lower than that of grinding (8.75 kJ/g).

The PEF-assisted aqueous extraction of polyphenols from Norway spruce *Picea Abies* at $E = 20$ kV/cm and pH 12 has been studied (Bouras et al. 2016). The PEF treatment was applied during diffusion (protocol 1) and after 1 h of diffusion (protocol 2). These protocols were applied at different initial humidity of bark samples (14% and 21%). The data for the PEF-treated and untreated samples (simple diffusion without PEF) were compared. The PEF treatment did not cause the physical degradation of bark tissue and did not affect the structure of wood. The positive effect of PEF on aqueous extraction of intracellular compounds was revealed. The kinetics of pH and electrical conductivity changes were explained by pH neutralization and electrolyte impregnation of wood tissue during extraction. The PEF treatment enhanced extraction of total phenolic compounds and antioxidant activity. For both PEF-assisted protocols the polyphenol extraction yield and antioxidant activity were increased in ≈ 8–10 times and in ≈ 30 times, respectively, as compared with untreated samples. It was concluded that the PEF treatment presents a good alternative to the energy-consuming high temperature and milling techniques.

The various physical treatments (ultrasounds (US), microwaves (MW), HVED, and PEF) have been applied to study their effects on enzymatic hydrolysis of rapeseed hulls (Brahim et al. 2016). Treated hulls were maintained in 0.3 mol/L of hydroxide sodium solution at 60 °C for 2 h. The results showed that application of physical treatments resulted in an increased yield of acid insoluble residue by 5% (PEF), 6% (MW), 8% (HVED), 12% (US), respectively, in comparison with a chemical treatment. Moreover, for the pulps isolated by physical-assisted techniques a higher enzymatic digestibility was obtained.

Sludges and Wastes

Sludges and wastes have significant potential as a substrate for biogas production. The PEE-assisted pretreatment step aims to improve the performance of digestion, dewatering, and the final sludge output quality. Different groups have run the PEE experiments with sludges and wastes in laboratory-scale and full-scale to make these biomasses more bioavailable.

The studies started in 1990s by application of pulsed electric currents to sludge stream in order to cause shock waves and induce cell lysis (Roxburgh et al. 2006). The tests for waste activated feed sludge (WAS) pretreatment prior to anaerobic digestion indicated a gas production increase by 12–20%. Later on the electrical pulsed arc pretreatment of anaerobically digested municipal wastewater plant

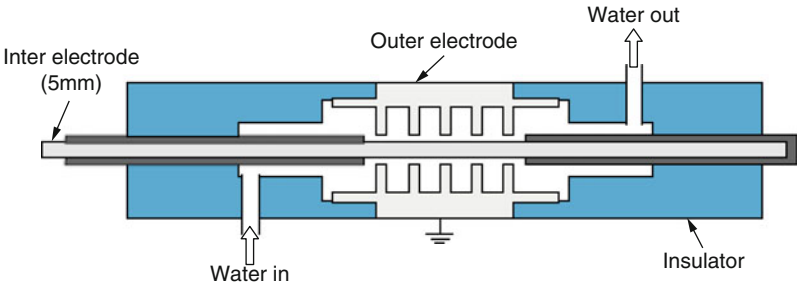

Fig. 6 Continuous pulsed-power reactor for treatment of waste activated sludge. The reactor produces an arc discharge in an electric gap (≈3 mm) between a coaxial electrode and 5-ring outer electrodes. The length of the inner electrode was 11 cm. The reactor and electrodes were made of stainless steel and the void volume of the reactor was about 20 mL. The sludge was introduced into the reactor by using a peristaltic pump (From Choi et al. (2006) with permission)

biosolids was applied for the purpose of dewaterability increasing (Abu-Orf et al. 2001). Such pretreatment can be used to reduce polymer requirements in typical dewatering procedure. The pulsed OpenCeL technology was developed for the treatment of an activated sludge and results appeared to be promising. Large scale trials were being implemented; they showed a significant enhancement of biogas yield for electrically treated biomass.

Impact of PEF on the properties of sludge, anaerobic degradation, sludge water reload, foaming of digesters, and biogas production has been investigated (Kopplow et al. 2004). Sludge cells disintegration has been achieved up to 20% and degradation rate of organic matter increased on about 9%. The PEE pretreatment (DC voltage of 20 kV, a pulsed power of 1.2 kW) has been applied to the WAS prior to anaerobic digestion (Choi et al. 2006). An electric pulsed-power reactor consisted of one coaxial electrode and multiple ring electrodes, and it produced an arc discharge in an electric gap between electrodes (Fig. 6). The sludge was treated by pulsed-power technology prior to anaerobic digestion. Comparison of SEM images of raw and pulsed-power sludge cells gave evidence for a distinct difference in cell appearance. The sludge cells were damaged by pulsed-power treatment that was attributed to the combined effects of shock waves, chemically active radicals, generated hydrogen peroxide molecules, and UV light. Polsed power treatment resulted in noticeably more rapid utilization of sludge cells by anaerobic microorganisms. The data demonstrated that the PEE pretreatment results in increase of SCOD/TCOD (SCOD is a soluble chemical oxygen demand and TCOD is a total chemical oxygen demand) and exocellular polymer (extracellular polymeric substance) content of WAS by 4.5 times and 6.5 times, respectively.

Focused pulsed (FP) technology for cell lysis has been applied for improving of biosolids digestion and conversion to methane (Rittmann et al. 2008) (Salerno et al. 2009). This technology utilized rapidly pulsing, high voltage electric fields (10–30 kV), and it is an adaptation of PEF technology for full-scale treatment of biomass slurries, such as WAS. The FP technology allows enhancing the

digestibility of sludge, reducing the digestion time, and increasing the biogas production. The full-scale FP technology was used for waste pre-treating in order to improve methane gas production and biosolids reduction in sludge digestion, without incurring problems of odors, toxicity, and high costs for chemical or energy consumption (Rittmann et al. 2008). The FP unit was installed between thickening centrifuges and anaerobic digesters. The energy consumption was 16 kWh/m^3. The FP pretreatment of a mixture of primary and secondary sludge increased the SCOD by 160%, dissolved organic carbon (DOC) by 120%, biogas production of the entire digester system by 40%, and permitted reduction in volume of digested biosolids by 30% over the control.

The efficiency of FP technology and sludge biodegradability were dependent on strength of electric field, pulse duration, pulse frequency, sludge conductivity, length of treatment chamber, sludge residence time in a treatment chamber, types of bacteria, and their concentration in a sludge (Salerno et al. 2009). For example, the FP treatment of manure with power consumption 4, 9.9, and 19.8 kWh/m^3 resulted in increase of treatment efficiency by factors of 9, 15, and 50, respectively. The full-scale FP technology application in the OpenCel^{TM} process has been tested for the sludge stream (Salerno et al. 2009). The nonarcing FP process operated at 15–100 kV/cm electric field strength, 2–15 μs pulse width, and 2–10 kHz pulse frequency. A 60% increase in biogas yield and a 40% reduction in biosolids, compared with untreated WAS, were obtained.

It has been demonstrated that the FP treatment increased the bacterial phylogenetical diversity and relative abundance of acetoclastic methanogens in a full-scale anaerobic digester (Zhang et al. 2009). Microbiological analysis of sludge revealed significant increases of organics in the presence of several methanogenic microbiological species. Bench-scale of FP pretreatment applied to secondary sludge had showed rapid denitrification kinetics because of the electron donor having high SCOD and ammonia concentrations (Lee et al. 2010). At a treatment intensity of 16 kWh/m^3 the semisoluble chemical oxygen demand (COD) had increased by 16 times.

The effects of FP pretreatment and solids retention time (SRT) on an anaerobic digestion of waste activated sludge have been investigated (Lee and Rittmann 2011). FP treatment increased the CH_4 production rate and TCOD removal efficiency by up to 33% and 18%, respectively, at a SRT of 20 days. The efficiency of FP pretreatment units was compared, and various compact continuous-flow reactors were developed.

Both bench- and pilot-scale setups have shown their high efficiency for disruption of the sludge flocs and cells and increasing of the biogas production. The payback period of setups was estimated as 3 years or less. Figure 7 compares the effects of FP pretreatment on sludge in bench- and pilot-scale studies (Zhang et al. 2016). The impact of FP treatment on a digester performance at the bench-scale was rather noticeable and gave 2.5 times increase of CH_4 production as compared with untreated WAS.

The combination of PEF pretreatment at a treatment intensity of 33 kWh/m^3 and a semi-continuous pre-fermentation of primary sludge has been applied to produce the volatile fatty acids (VFAs) (Ki et al. 2015). VFAs can serve as an electron donor for

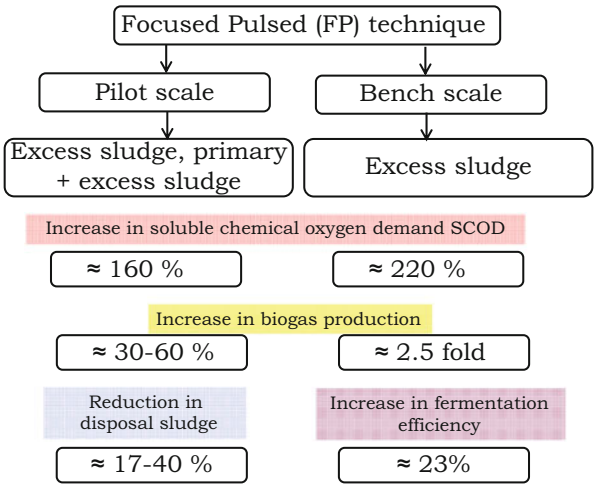

Fig. 7 The effects of FP treatment on sludge in a bench- and pilot-scale studies (Compiled from Zhang et al. (2016))

microbial electrolysis cells. The PEF treatment before fermentation did not alter production of VFAs and methane for a 3-day solids retention time. However, it yielded more (by 2.6-fold) of the most desirable fermentation product (acetate). The PEE batch treatment ($E = 24$ kV/cm, volume of chamber is ≈ 1 L) has been applied for enhancing the methane yield from municipal solid organic waste (Carlsson et al. 2008). Data indicated a 40% increase of the total biogas potential. The PEE treatment of three different substrates (sugar beets, source separated food waste and sludge from wastewater treatment nitrification) has been also studied. The effect of electroporation was tested by the digestion in continuous reactors. The experiments showed a marked improvement in gas production for sugar beets and waste. However, the response for the sludge was worse. The PEE treatment of municipal organic solid waste before digestion in a biogas plant has increased biogas production by up to 14% (Lagerkvist and Morgan-Sagastume 2012).

Conclusions

Pulsed electric energy (both PEF and HVED) is rather useful for application at different stages of lignocellulosic biorefinery. Recent results reported in literature have demonstrated the attractivity of PEE techniques for production of biogas, extraction of high-valued chemicals and bioactive compounds, and assistance of fermentation and hydrolysis. The range of tested biomass is rather limited so far and includes samples of wood and crop biomasses (sawdust, chips, barks, silage, and switch grass), sludges, and wastes. The existing results evidence the great potential of electroporation-assisted techniques for efficient utilization of agro-industrial, forestry wastes, and semisolid biological sludges. Laboratory- and pilot-scale studies confirm optimistic expectation for future industrial implementations of PEE techniques.

There still exist certain limitations and negative effects that delay the delivery of efficient PEE-assisted techniques for industrial-scale applications in lignocellulosic biorefinery. The most serious problem is related with corrosion of metal electrodes and migration of electrode materials inside treated media. This factor may be rather critical in extraction applications of PEE. The PEE technology can negatively affect and deteriorate the quality of extracted high-valued chemicals and bioactive compounds. The most intensive and rapid degradation of electrodes is typically observed for HVED treatment. The rapid degradation can be significantly reduced by using the special electrode materials and adaptation of PEE protocols. The electrodes effects may be not so critical in applications of PEE treatment to enhance biogas yield in anaerobic digestion. The typical biogas processes involve many steps (hydrolysis, main fermenter, and post fermenter steps). For intermediate treatment the PEE protocol has to be tuned in dependence on the location within the process. Optimization of PEE protocols is not an easy task, and it requires accounting for the many side effects such as shockwaves, ohmic heating, electrowetting, change in protein pattern of cells, generation of reactive electrode byproducts, and composition of a treated raw substrate (Pliquett 2015). Consequently, further investigations should be carried out for thorough adaptation of PEE protocols accounting for the target products, types of lignocellulosic biomass, and location of PEE within the biorecovery process.

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Cross-References

- ► Application of Pulsed Electric Energy for Grape Waste Biorefinery
- ► Application of Pulsed Electric Field Treatment for Food Waste Recovery Operations
- ► Application of Pulsed Electric Fields for Root and Tuber Crops Biorefinery
- ► High-Voltage Electrical Discharge-Assisted Extraction of Phenolic Compounds from Grape Seeds
- ► Polyphenol and Protein Extraction from Rapeseed Stems and Leaves Assisted by Pulsed Electric Fields
- ► Pulsed Electric Fields and High-Voltage Electrical Discharge-Assisted Extraction of Biocompounds from Vine Shoots
- ► Pulsed Electric Fields and High-Voltage Electrical Discharges-Assisted Extraction of Valuable Biocompounds and Biopolymers from Rapeseed By-Products
- ► Pulsed Electric Energy-Assisted Biorefinery of Oil Crops and Residues
- ► Pulsed Electric Fields-Assisted Extraction from Exotic Fruit Residues
- ► Selective Extraction of Biocompounds from Stevia rebaudiana Bertoni Leaves Using Electrotechnologies

► Selective Extraction of Molecules from Biomaterials by Pulsed Electric Field Treatment
► Techniques to Detect Electroporation in Food Tissues

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