


A comprehensive review of the application of cold plasma technology in lignocellulosic biomass pretreatment

Rasaq S. Abolore, Swarna Jaiswal, Amit K. Jaiswal,  Centre for Sustainable Packaging & Bioproducts (CSPB), School of Food Science and Environmental Health, Technological University Dublin–City Campus, Central Quad, Dublin, Ireland; Sustainability and Health Research Hub (SHRH), Technological University Dublin–City Campus, Dublin, Ireland

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Abstract: Lignocellulosic biomass (LCB) is a promising feedstock for the sustainable production of biofuels and other biobased products, owing to its abundance, low cost, and minimal competition with food crops for resources. It is mainly composed of cellulose, hemicellulose, and lignin, forming a complex biomass matrix. Its utilization is hindered by its complex structure and pretreatment is required to break down the chemical resistance caused by the strong association between the cellulose, hemicellulose, and lignin structures. Conventional methods such as acid and alkali pretreatment are used frequently but they require the use of high temperatures, high pressure, and corrosive chemicals. This has encouraged research into environmentally friendly pretreatments to overcome these challenges. Recently, cold plasma (CP) technology has emerged as a promising alternative to the aggressive conventional methods for producing value-added products, such as biofuels, and renewable chemicals from lignocellulosic biomass. Cold plasma technology uses electricity to generate a highly reactive, ionized gas in a variety of applications without producing any dangerous or polluting compounds. This review discusses the application of cold atmospheric pressure plasma in the biochemical conversion of biomass, with a focus on delignification, detoxification of biomass hydrolysate, surface modifications, and process intensification of cellulosic ethanol production. © 2024 The Author(s). *Biofuels*, *Bioproducts* and *Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

Key words: bioethanol; lignocellulosic biomass; cold plasma; cellulose; delignification; cellulosic ethanol

Correspondence to: Amit K. Jaiswal, Centre for Sustainable Packaging & Bioproducts (CSPB), School of Food Science and Environmental Health, Technological University Dublin–City Campus, Central Quad, Grangegorman, Dublin D07 ADY7, Ireland.
 E-mail: amit.jaiswal@tudublin.ie

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Introduction

Fossil resource depletion and environmental concerns over greenhouse gas emissions have driven research into alternative feedstocks to replace petroleum-based resources in the synthesis of fuel, energy, and chemicals.^{1,2} Bioethanol is a renewable biofuel with high oxygen content and the potential to lower vehicle emissions. It is one of the most promising alternatives to fossil fuels. First-generation (1G) bioethanol is mainly synthesized from food crops such as corn and sugarcane. Ethical concerns associated with 1G bioethanol because of direct competition with food resources have necessitated a search for an alternative nonfood feedstock for bioethanol production.³ Biomass sources other than those utilized as food must therefore be used to meet the growing demand for alternative fuel sources.⁴

Due to their renewability and abundance, biofuels derived from lignocellulosic biomass (LCB) are commonly regarded as a sustainable alternative to the controversies surrounding 1G biofuels. Lignocellulosic biomass is a plant biomass made up primarily of the carbohydrate polymers cellulose (40% to 60%), hemicellulose (20% to 40%), and aromatic polymer lignin (10% to 24%), as well as trace amounts of proteins and ash.⁵ The composition of LCB compounds varies based on source, origin, and climate conditions. Cellulose is the most prevalent LCB polymer accounting for 40% to 60% of LCB. It comprises β -D-glucopyranose units linked by β -(1,4) glycosidic linkages. Cellulose can be hydrolyzed into glucose and fermented by yeast under anaerobic conditions to produce ethanol and CO₂. Hemicellulose is the second most abundant polysaccharide present in LCB after cellulose and makes up between 20% and 40% of lignocellulosic biomass weight. Due to its amorphous form, particularly its heat sensitivity, hemicellulose is easily broken down during the hydrolysis process, so its removal does not pose significant challenges during pretreatment.⁶

Lignin is a complex polymer network, comprising a highly branched heterogeneous phenylpropanoid macromolecule consisting of random crosslinks between monomeric monolignols.⁷⁻⁹ Lignin serves as a barrier to cellulose and hemicellulose, contributing to LCB resistance to chemical deconstruction and enzymatic hydrolysis due to lignin linking with hemicelluloses and cellulose in the plant cell wall. The lignin concentration in LCB is therefore negatively linked with enzymatic digestibility in biomass and the removal of lignin is thus a crucial parameter for evaluating pretreatment efficiency.¹⁰

Pretreatment is the first step in lignocellulose biorefineries. Other processes include the hydrolysis of cellulose into fermentable sugars (such as glucose and xylose) and

fermentation, which generates cellulosic ethanol from the fermentable sugars.¹¹ Pretreatment of lignocellulose biomass solubilizes lignin, improves accessibility to cellulose and hemicellulose for hydrolysis, and enables the recovery of high-value platform chemicals from LCB. The effectiveness or otherwise of the pretreatment stage has downstream influences, for example on enzymatic hydrolysis rates, fermentation yield, enzyme loadings, product concentrations and purification, waste treatment, and energy consumption.¹² The pretreatment process allows enzymes to access the compact plant cell-wall structures. Without pretreatment, enzymatic hydrolysis activity can be as low as 20%. Various pretreatment methods to overcome biomass recalcitrance have been researched and developed. These pretreatment methods are classified broadly into the physical (milling, microwave, ultrasound, extrusion), chemical (acids, alkali, deep eutectic solvent, organosolvent, and salts), physicochemical (hydro-thermolysis, steam explosion, liquid hot water, and ammonium fiber explosion), biological (e.g. white-rot/brown-rot fungi, enzymes, and bacteria), and combinations of these pretreatment methods. However, many conventional pretreatment methods are limited by various constraints, such as lengthy processing times, use of hazardous chemicals, high energy requirements, and low sugar recovery, thereby making their deployment very challenging. It is therefore crucial to develop a sustainable and environmentally friendly pretreatment technique that will remove lignin efficiently, increase total sugar yields, and improve the substrate's accessibility to hydrolytic enzymes.¹³

Researchers have recently explored the application of emerging technologies in lignocellulosic biomass processing to overcome the limitations associated with conventional methods. These emerging methods include pulsed electric field, microwave, ultrasonication, and cold plasma (CP) pretreatment. Cold plasma, also known as nonthermal plasma, is the fourth state of matter. It is produced by exposing gas to an electric field, causing its atoms to ionize and become charged. However, the CP process does not alter the chemical composition of the gas; rather, it changes its physical state. Recently, CP has emerged as a promising technology in the pretreatment of lignocellulosic biomass due to its inherent advantages such as low-temperature operation, and quick processing times. Table 1 presents the benefits and limitations of CP compared with conventional pretreatment methods.

This review examines the application of CP generated at atmospheric pressure for lignocellulose biomass processing with a focus on delignification, detoxification of biomass hydrolysate, surface modifications, and process intensification during cellulosic ethanol production. The benefits and limitations of CP and other conventional methods of lignocellulosic biomass pretreatment are also presented.

Table 1. Benefits and limitations of cold plasma vs conventional pretreatment methods.

Method	Description	Advantages	Disadvantages	Reference
Cold plasma pretreatment	Employs ionized gas to modify the surface and internal structure of biomass	Environmentally friendly, low water usage. Selective modification of biomass components. Potential for in-line integration	Relatively new technology requires optimization. Limited commercial-scale application	14
Acid pretreatment	Uses dilute acids (sulfuric acid, hydrochloric acid) to hydrolyze hemicellulose and disrupt lignin structure	Well established technology Highly efficient and economical	Generates corrosive waste streams. Possible sugar degradation	15
Alkaline pretreatment	Use of Alkali such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) to solubilize lignin and partially deacetylate cellulose	Effective for lignin removal and improved enzymatic digestibility	High water consumption. Generates waste streams requiring neutralization	16
Steam pretreatment	Exposes biomass to high-pressure steam to disrupt physical structure and enhance accessibility	Simple and well understood technology. Cost effective	High energy consumption May cause sugar degradation. Formation of fermentation inhibitors	17
Biological pretreatment	Uses enzymes or fungi to degrade lignin selectively	Environmentally friendly approach High selectivity for lignin removal	Slower process than chemical methods Requires specific enzyme development for different biomass types	18

Plasma concept and classification

Plasma refers to partially or completely ionized gas and it is the fourth state of matter after solids, liquids, and gases.¹⁴

Plasma occurs as increasing energy input causes a transition in the state of matter: a solid transforms into a liquid, then gas, and when energy input exceeds a particular point, the gas molecules become ionized and produce the plasma state.¹⁵

Plasma is made up of varieties of active species, including atoms, photons, electrons, free radicals, negative and positive ions, and excited or unexcited molecules, which can be produced at either a high temperature or a low temperature.¹⁶

Plasma can be classified according to several parameters: pressure (atmospheric or low pressure), degree of ionization

and electron and ion temperature (high or low temperature), power supply frequency (DC, AC, radiofrequency, or microwave), and the electron affinity of the process gases (electropositive or electronegative).

However, the most common classification of plasma is based on the plasma's overall temperature (low temperature and high temperature) and the temperature distribution (thermal equilibrium and nonthermal equilibrium) among the different species (electrons, ions, and neutrals) within the plasma.¹⁷ Table 2 summarizes the characteristics and features of low-temperature and high-temperature plasma. In low-temperature plasmas, also known as CPs, the temperature of heavy species (neutral particles and ions) is close to room temperature (25–100 °C). However, the temperature of the

Table 2. Characteristics of low-temperature and high-temperature plasma.^{23,25}

	Low temperature plasma	High temperature plasma
Plasma temperature	Cold overall	Hot overall
Key parameters	Temperature of electrons is higher than the temperature of ions/neutrals	Electrons, ions, and neutrals have approximately the same temperature
Thermal Equilibrium	Non-equilibrium temperature	Equilibrium temperature
Electron density	Low electron density ($<10^{19} \text{ m}^{-3}$)	Higher electron density ($>10^{21} \text{--}10^{26} \text{ m}^{-3}$)
Electron temperature	1–10 eV	~1 eV
Key parameters	Electrons, ions, and neutral have approximately the same temperature	The temperature of electrons is over 10 000 K
Plasma pressure	$\leq 0 \text{ kPa}$	$\approx 101 \text{ kPa}$
Example	Neon sign	Fusion reactors, stars
Application	Corona, sterilization, glow discharges	Plasma arcs, welding, fusion experiments

electron is much higher (between 105 and 5000 °C). This is a state of thermal nonequilibrium as the temperature of electrons, ions, and neutrals are not uniform. The overall gas temperature (ions and neutrals) is low and close to room temperature irrespective of the higher electron temperature. Cold plasma can be generated using low-pressure gases such as nitrogen, oxygen, helium, and argon.

The most commonly used gases for industrial plasma applications are air, nitrogen, and carbon dioxide (CO₂) due to their accessibility and cheaper cost.¹⁸ Electron temperature is the kinetic energy of plasma electrons measured in kelvin and it is also expressed in terms of electron voltage (eV) whereas in high-temperature plasma, the plasma temperature is over 10 000 K (typically around 10 000 to 25 000 K) with high heat flux densities, and high electron and reactive species densities.¹⁹ High-temperature plasma is characterized by thermal equilibrium where the temperature of electrons is the same as the temperature of ions and neutrals. Applications of high-temperature plasma include arc welding, plasma cutting, plasma spraying, waste treatment, electric arc furnaces, nanoparticle synthesis, and particle spheroidization.

Cold plasma: sources and classification

Cold plasma can be generated using different types of energy sources such as alternating current (AC), direct current (DC), pulse direct current, radiofrequency (RF), and microwave energy (MW). However, AC is the most common energy source for CP generation when a continuous and stable plasma is required. Conversely, DC is associated with a more stable and less dynamic plasma. Pulsed DC is used for applications requiring controlled bursts of plasma, while RF and MW are used in various plasma processing applications.²⁰ The choice of an energy source depends on factors such as the type of plasma and application requirements. Each source has its benefits and limitations, and their selection depends on the desired plasma properties and overall system design.²⁰

The efficiency of CP treatment is influenced strongly by the working gas and the reactive gas species generated by the working gas. The various types of reactive gas species, ultraviolet radiation, energetic ions, and charged particles produced by CP influence significantly the physicochemical reactions in the material treated with CP. This is due to the different types of reactive species produced by the different working gases.²¹ For example, argon, helium, and nitrogen plasmas can generate excited argon species, helium atoms and reactive nitrogen species, respectively, whereas air can produce reactive oxygen species (ROS) and reactive nitrogen species (RNS) including ozone, hydrogen peroxide and atomic oxygen.²² Cold plasma can be generated at

atmospheric pressure and lower pressure ($P < 133$ mbar) at a temperature between 25 and 100 °C in reactors with varying configurations.²³ However, the generation of CP at low pressure requires a vacuum system, which makes the process more complex and expensive.²⁴ Atmospheric pressure generated CP is therefore more widely used due to its simplicity. Other factors influencing CP treatment include the treatment time, voltage, frequency, and electrodes. Cold plasma unit configuration typically consists of a power supply, electrode configuration, and working gas. Figure 1 provides a schematic illustration of the typical configuration of some common sources of low-temperature atmospheric pressure.

Cold plasma treatments typically involve voltages with amplitudes in the kilovolt (kV) range and frequencies in the kilohertz (kHz) range.²³ For instance, Okazaki *et al.*²⁵ generated a stable glow discharge in air, argon, oxygen, and nitrogen at atmospheric pressure using a 50 Hz plasma source.

Different plasma sources yield different effects, making it crucial to develop multiple sources for specific lignocellulosic biomass applications and to understand their fundamental mechanisms. In recent years, several plasma sources which can produce stable and comparatively homogeneous plasmas at or near atmospheric pressure have been developed. Some common examples of plasma in lignocellulose biomass processing includes dielectric barrier discharge (DBD), atmospheric plasma jets, corona discharges, radio frequency plasma, microwave discharge, and atmospheric pressure glow discharge plasma.

Application of CP in the lignocellulosic biomass processing

Cold plasma has emerged recently as a novel processing technology that can alter the structure of various plant materials. It has been employed in applications such as the reduction of microbial load in food,²⁶ bioactive substance concentration,²⁷ enzyme inactivation,²⁸ and enhancement of antioxidant activity in food.²⁹ This is due to the presence of reactive oxygen species (ROS) such as hydrogen peroxide, ozone, superoxide anion, singlet oxygen, atomic oxygen, hydroxyl radicals, hydroxyl ions, and reactive nitrogen species (RNS) including excited nitrogen (N₂), nitric oxide, and energetic ions.³⁰

Plasma-assisted biomass valorization processes have been employed as an alternative to conventional thermally driven methods. These processes offer feedstock flexibility due to the electricity-based heat source, creating a highly reactive environment.³¹ Plasma can enhance the formation of primary species and intermediates for downstream processing, facilitate direct biomass conversion to targeted products,

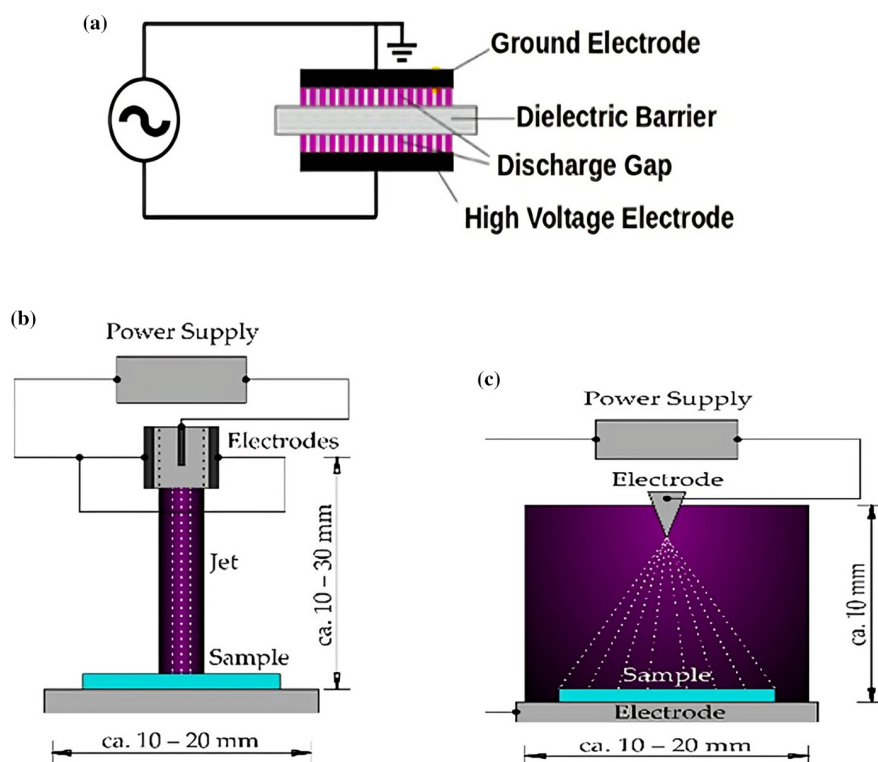


Figure 1. Schematic diagram of some plasma types. (a) Dielectric barrier discharges.⁷⁹ (b) Plasma jet.⁸⁰ (c) Corona discharge plasma.⁸⁰

and upgrade biomass processing side-streams. It can be used for the destruction of undesirable biomass residuals.³¹ The application of CP in the pretreatment of lignocellulosic biomass has been explored in relation to the species generated by CP, which can interact chemically with lignocellulosic materials and disintegrate its structures. These reactive species interact with water in a series of chain events that result in the formation of hydroxyl radicals and peroxides, which can speed up the breakdown of organic molecules.^{32,33}

Cold plasma also presents a sustainable technology for overcoming lignocellulosic biomass recalcitrance through plasma pretreatment of LCB in acid, neutral or alkaline conditions.³⁴ For example, ozone – one of the reactive species produced from CP – is a strong oxidant with an oxidation potential of 2.08 V, which can cleave the C–C and C–O and C–H bonds found in lignin due to its oxidative properties.³⁵

The efficiency of CP treatment of LCB is influenced by numerous process and biomass variables. These include biomass moisture content and composition, plasma frequency and power, working gas type, and duration of exposure. These factors can be optimized to achieve efficient delignification while maintaining cellulose and hemicellulose integrity. For example, at a higher moisture content, there

is greater formation of hydroxyl radicals, which facilitates effective lignin degradation. Also, the smaller the particle size of the biomass, the greater the surface area available for plasma interaction and more efficient delignification. Further, plasma power and frequency have a significant impact on delignification efficiency, higher power and optimal frequency improve the breakdown of lignin bonds. The type of gas used in the plasma affects the delignification process by producing a variety of reactive species that interact with the lignin. Exposure time is also important – longer times generally lead to more extensive delignification.

The application of CP in lignocellulosic biomass delignification

Cold plasma has emerged as a novel method for biomass delignification and offers an environmentally friendly alternative to chemical delignification processes. Delignification involves the application of various methods to solubilize lignin from lignocellulosic biomass matrix.³⁶ The dissolution of lignin from lignocellulosic biomass is a crucial step in its processing for biofuel production, pulp and paper manufacturing, and other applications. The degree of lignin

solubilization is one of the criteria for measuring the efficacy of a pretreatment process. The degradation of surrounding lignin increases the accessibility of carbohydrate polymers and enhances the effectiveness of the subsequent hydrolysis process.^{37,38}

The potential of cold atmospheric plasma to alter the structure of materials and induce oxidative degradation of unsaturated organic molecules in lignin causing structural disruption and exposing packed cellulose fibers to hydrolytic enzymes has been reported.³⁹ For example, Souza-Corrêa *et al.*⁴⁰ investigated the influence of biomass moisture content in the ozonation process of sugarcane bagasse samples that were pretreated with atmospheric oxygen pressure plasma based on DBD. The power source used for the experiment consisted of a sinusoidal wave function generator connected to an amplifier and a high-voltage transformer in series with a 20 k Ω resistor. The generator signal at a fixed voltage of 5 V was amplified to reach 13.0 kV over the DBD electrodes.

This DBD power supply (10.0 kHz) was connected to three DBD devices, each composed of coaxial electrodes separated by a dielectric ceramic tube. They noted that moisture content significantly influenced delignification and the subsequent saccharification, with 50% moisture content yielding the best delignification results. The lignin content reduced from 38.50% to 12% after 6 h pretreatment (65% cellulose converted into glucose). The authors concluded that moisture content between 40% and 50% in biomass is a good condition for obtaining high delignification performance, particularly for the ozonation process.

Different reactive species are generated from different plasma gases and the type of gas used in plasma generation influences the efficacy of plasma-mediated lignocellulosic biomass pretreatment. For example, Pereira *et al.*⁴¹ studied the influence of different plasma gases (pure air or air/argon), solids concentration (7.5%, 10% and 12.5%) and time on the delignification efficiency of CP on brewery by-products. The treatment conditions used were 15 min treatment time, 10% solid loading, and plasma power of 220 V. Using only pure air, the authors reported 43% lignin removal after 2.5 min of treatment and a maximum delignification of 50% was achieved after 5 min of cold plasma treatment with no further evidence of lignin removal reported after 5 min. The plasma gas type and treatment time were reported to influence the delignification outcome but the solid concentration had no significant effect on the delignification efficiency. The authors further reported that plasma generated by air/argon caused a reduction in the lignin but the treatment caused cellulose and hemicellulose degradation, which is undesirable. The authors concluded that pure air-generated CP is very economical and could facilitate the removal of lignin at a reduced cost. Pure

air-generated CP causes less sugar degradation, which can enhance future processes such as the enzymatic hydrolysis of the recovered solid.

Similarly, Miranda *et al.*⁴² employed an in-liquid DBD plasma reactor involving a noncontact electrode in the pretreatment of sugarcane bagasse to increase the rate of enzymatic hydrolysis of the residual sugarcane bagasse. The bagasse samples were pretreated with a solution containing sodium carbonate and sodium hydroxide followed by exposure to CP treatment using atmospheric air as the working gas for 2 h. The authors reported that CP treatment modified the biomass surface properties and enhanced their reactivity, aiding the enzymatic hydrolysis. After enzymatic hydrolysis, samples treated with Na₂CO₃ + NaOH at pH 12 combined with CP treatment gave the highest yield of glucose (51.3%) and xylose (38.5%). The authors concluded that CP is an effective pretreatment method for various lignocellulosic biomass such as bamboo, corn cob, and sugarcane bagasse. Further, for investigate the effect of CP treatment on brewery-spent grain for bioethanol production, Ravindran *et al.*³⁴ employed air as plasma gas in a submerged DBD ozonation system. The authors examined the effects of voltage variation (28, 25, and 22 kV), time (5, 10, and 15 min) and solvent type (water, acid and alkali) on the enzymatic hydrolysis of brewer spent grain. After hydrolysis, a 2.14-fold increase (162.90 mg g⁻¹ of BSG) in yield of the reducing sugar was achieved when compared with a control (75.94 mg g⁻¹ of BSG) following biomass treatment in water for 10 min at a voltage of 28 kV. A high ethanol titer of (25.062 g L⁻¹) was obtained after fermentation of the CP-treated hydrolysate. The authors concluded that subjecting lignocellulose to CP discharges can improve the efficiency of enzymatic hydrolysis by removing lignin from lignocellulosic biomass and increasing polysaccharide concentration.

Spyrou and Amorim⁴³ applied atmospheric pressure CP generated by a DBD cylindrical reactor using air and nitrogen as the working gases in the pretreatment of sugarcane bagasse. The objective was to evaluate the influence of CP on the structure of the natural fiber focusing on lignin degradation. The plasma reactor was operated by AC voltage with an amplitude of 1–40 kV and frequency of 3–40 kHz. According to the authors, plasma-treated sugarcane bagasse pellets showed a considerable degradation of the lignin macromolecule due to severe plasma degradation of the lignin linkages. Fourier transform infrared (FTIR) analysis showed stretching vibrations of OH and cleaving of the lignin's C = C and C = O bonds, which caused a significant modification of the lignin in both air and nitrogen plasmas after a relatively short treatment time of approximately 10 min. The authors concluded that CP could induce biomass

delignification, and that delignification was more effective in the filamentary regime of air-generated CP.

In another study, Wright *et al.*⁴⁴ employed a DBD-generated plasma microbubble reactor for the pretreatment of miscanthus grass for bioethanol production. The pretreatment was carried out using a 5% (w/w) miscanthus suspension for 3 h at a 10% duty cycle yielding 0.5% acid-soluble lignin and 26% sugar after hydrolysis. The authors submitted that the air-generated plasma induced lignin degradation, thereby increasing the access to polymeric sugar using a plasma microbubble reactor as dilute solutions or as a fluidized bed in dry form.

In addition to the type of plasma working gas, the effect of plasma sources on lignocellulosic biomass pretreatment has been evaluated. Ramamoorthy *et al.*⁴⁵ investigated the application of CP in the pretreatment of biomass to produce fuel-grade bioethanol for blending with diesel. The researchers employed a glow discharge plasma pretreatment to produce bioethanol from a mixture of used surgical cotton and cardboard. The plasma pretreatment for the biomass mixture achieved solubilization of 22.2% and 68.1% for hemicellulose and lignin respectively. *Saccharomyces cerevisiae* was employed for bioethanol fermentation from the pretreated biomass after cellulase saccharification, with a bioethanol yield of 143.48 g L⁻¹ obtained at a cellulose conversion rate of 56.5%. Using molecular sieves, 90% (v/v), 180 proof pure bioethanol was further dehydrated to 99.9% (v/v) yielding a 200 proof purity. The authors formulated E-10 and E-20 blends, which contained 10% (v/v) and 20% (v/v) bioethanol, respectively, in combination with diesel fuel.

Cold plasma detoxification of lignocellulosic biomass hydrolysate

In the biochemical conversion of lignocellulosic feedstocks into advanced biofuels and other products using a sugar-platform process, toxic chemicals and lignocellulose-derived byproducts are produced during the pretreatment and acid hydrolysis phases because of the structural breakdown of lignin, cellulose, and hemicellulose. Examples of these include furan derivatives like furfural and 5-hydroxymethylfurfural (HMF), phenolic compounds, weak organic acids (levulinic, formic, and acetic acids), raw material extractives (acidic resins, tannic acids, and terpene acids), and heavy metal ions (iron, nickel, aluminium, chromium, etc.).⁴⁶ These byproducts can be classified as inhibitors based on their sources. For example, furan derivatives such as furfural and HMF are produced from the hydrolysis of hemicellulose and cellulose whereas lignin hydrolysis produces phenolic. These toxic chemicals and lignocellulose-derived byproducts

prevent microbial, and enzymatic biocatalyst activities and reduce the fermentation process's effectiveness.³⁸

One of the most promising strategies to address inhibition challenges is the detoxification or conditioning of lignocellulosic hydrolysates and slurries, which enhances fermentation and increases ethanol production and yield.⁴⁵ Examples of common detoxification processes include heat treatment, ion-resin exchange, irradiation therapy, peroxidase treatment, adsorption, vacuum evaporation, and other biological methods.⁴⁷⁻⁴⁹ However, many of these approaches are ineffective for biomass detoxification due to the high rates of degradation of important components in biomass.

A variety of physicochemical and biological methods, including improved fermentative techniques, have been explored to overcome these fermentation inhibitors. Cold plasma-assisted detoxification of lignocellulosic biomass hydrolysate has been proposed recently as a novel and green alternative to conventional detoxification methods due to the efficacy of the reactive species in plasma in breaking down several organic compounds.^{50,51} In a study, Lin *et al.*⁵⁰ employed atmospheric cold plasma (ACP) using argon as the working gas to break down toxic substances in sulfuric acid-hydrolyzed sugarcane to obtain fermentable sugar for bioethanol production. Significant reductions in toxic substances (31% in formic acid, 45% in acetic acid, 80% in hydroxymethylfurfural, and 100% in furfural) were reported after ACP treatment. The authors submitted that minimal hydrolysate toxicity obtained from plasma treatment enhances bioethanol production using *Kluyveromyces marxianus*. The bioethanol productivity increased from 0.25 g L⁻¹ h⁻¹ to 0.65 g L⁻¹ h⁻¹ after treatment at 200 W ACP power for 25 min, indicating that ACP could break down toxins efficiently in the hydrolysate and consequently boost bioethanol production. Higher degradation of toxic components (7.4% of the formic acid, 79.7% of the furfural, and 23.6% of the HMF) was reported after 25 min of ACP treatment.

In another study to minimize the toxic compounds in hydrolyzed biomass, Santoso *et al.*⁵² employed rapid detoxification of pineapple peel waste hydrolysate (PPWH). Two different types of ACP reactor treatment were employed: ACP reactors-1 (R1) and ACP reactors-2 (R2). The ACP-reactor-1 (R1) used plasma power of 80–200 W with an argon (Ar) plasma source whereas ACP reactors-2 (R2) operated at a plasma power between 500 and 600 W using air plasma as the source. After ACP treatment in R1 for 15 min at 200 W, the formic acid, furfural, and HMF were reduced by 21.81%, 74.06%, and 51.38%, respectively, whereas ACP treatment in R2 at 600 W resulted in the reduction of furfural, HMF, and formic acid by 45.05%, 32.59%, and 60.41% respectively. The

authors' findings show that ACP treatment offers a cutting-edge detoxification method for reusing agricultural waste hydrolysate in fermentation.

In addition to generating toxic byproducts from cellulose and hemicellulose hydrolysis, some lignin hydrolysis byproducts inhibit fermentation. For example, during the industrial manufacture of bioethanol from lignocellulosic biomass, yeast cells are typically exposed to vanillin, a byproduct of lignin during the pretreatment of lignocellulosic biomass to produce fermentable sugar. Vanillin acts as a potent fermentation inhibitor that represses yeast growth and fermentative abilities. Concerns about hazardous issues with vanillin represent some of the biggest obstacles to cutting the production cost of cellulosic ethanol.

Cold plasma can be used in the removal of byproducts of lignin hydrolysis, such as vanillin. For example, Ito *et al.*⁵³ investigated the interactions of vanillin molecules with oxygen radicals produced by nonthermal atmospheric pressure plasma. After undergoing atmospheric pressure treatment, vanillin was transformed into vanillic acid, protocatechuic aldehyde, protocatechuic acid, methoxy hydroquinone, 3,4-dihydroxy-5-methoxybenzaldehyde, trihydroxy-5-methoxybenzene, and their respective ring-cleaved products. This resulted in decreased vanillin-specific toxicity to yeast during ethanol fermentation. After a further 16 h of incubation, the oxygen-radical-treated vanillin solution's ethanol concentration was seven times higher than that of the untreated solution. Comparable outcomes were seen when oxygen-radical treatment was applied to rice straw slurry that had previously been subjected to alkaline-pretreatment.

Cold plasma modification of lignocellulosic biomass structure and surfaces

The use of cellulose in composite production is limited by its high polarity and hydrophilic nature, which make it incompatible with most nonpolar matrices, such as polyolefins. This incompatibility leads to reduced mechanical properties due to moisture absorption.^{54,55} As a result, there is a need for specialized surface modification techniques to create an effective hydrophobic barrier, lower interfacial energy with nonpolar polymer matrices, and improve adhesion.⁵⁵ Cold plasma is an emerging, nonthermal, highly effective, and environmentally benign method used in transforming the surface of materials and particles.⁵⁶ Cold atmospheric plasma has direct chemical and physical interactions with biological components, including cells and tissues, and the potential application of cold atmospheric plasma to alter the structure of materials has been reported.⁵⁷ Plasma treatment can modify polymers by changing polymer

surface energy, causing surface crosslinking, and introducing reactive groups. This process strengthens the polymer surface and induces chemical modifications through a sputtering effect during plasma bombardment. Research has shown that plasma treatment can result in surface erosion of cotton fibers, leading to weight loss and an increase in carboxyl and carbonyl group content.

Plasma surface etching has been employed in the direct modification of the morphology and composition of polymer surface characteristics and chemical structures at a microscopic scale.²² This process involves etching the surface of a polymer with a reactive process gas, which removes material and increases the surface area.⁵⁸ Lignocellulose material surfaces can be modified directly using CP with significant improvement in the properties reported because of the modification. The surface modifications of cellulosic material, such as cellulose nanofibers, using CP technology have been reported. This process improved the polymer strength and grease barrier but reduced oxygen transmission rates and air permeability. Plasma polymerization has been used in the coating of cellulose with polymers like polylactic acid (PLA) and polyethylene terephthalate (PET) for various applications.⁵⁹

For example, Zanini *et al.*⁶⁰ evaluated the chemical alterations in wood fibers following treatment with argon (Ar) RF plasma. The fibers were treated in a cold Ar plasma reactor at low pressure, with an RF power input of 75 W, and exposure time ranging from 15 to 250 s. The Ar plasma treatments were performed at 0.4 mbar and 10 cm from the antenna. According to the author, lignin underwent a considerable change, which increased the concentration of phenoxy radicals, with the radicals first forming on lignin. The resultant radicals then interacted with added monomers to create C–C or C–O bonds causing a significant modification of lignin. By substituting chemical groups that are already present in the materials, plasma treatment was used to modify the surface properties of those materials.

Similarly, Cao *et al.*³⁶ investigated the plasma-induced modification of the chemical structure of lignin derived from corn cob and poplar using a DBD plasma source and air as the plasma gas. The plasma processing parameters used were 4.5 kW and 8 m min^{−1}. The width of the plasma generator is 20 cm, and the plasma treatment was administered for 1.5 s. According to the authors, atmospheric plasma demonstrated a powerful ability to cleave C–C covalent bonds in the aliphatic region of lignin, followed by oxidation. The authors reported that lignin was degraded and fragmented after the plasma treatment, with a considerable deconstruction of β -O-4 aryl ether. The β -O-4 aryl ether content was reduced

from the initial value of 65.1/100Ar to 58.7/100Ar for lignin from corncob and from the initial value of 72.5/100Ar to 63.8/100Ar for lignin from poplar after plasma treatment, respectively.

Futher, Silva *et al.*⁶¹ investigated the influence of plasma treatment on the physical and chemical properties of sisal fibers and its influence on methylene blue (MB) adsorption. The authors employed reactive microwave-assisted CP treatment as an alternative to conventional chemical treatments using a mixture of Argon and CO₂. The authors utilized plasma treatment at partial pressures of 4×10^{-1} and 2×10^{-1} Torr, resulting in a final pressure of 6×10^{-1} Torr over 1.5 min. The microwave plasma source power was 1000 W operating at 2.4 GHz. The gas flows were controlled by needle valves and the plasma chamber was continuously pumped by a rotary pump, model RV8. The treatment increased the fiber surface roughness and modified the structure of the material, while enhancing MB adsorption up to 96%. Kinetic and isotherm studies suggested favorable adsorption mechanisms for both untreated and plasma-treated fibers, with the plasma treatment maintaining the original properties of the fibers.

Similarly, Macedo *et al.*⁶² conducted a study to assess the impact of CP treatment for modifying kapok fibers. The study utilized 5 g of kapok fibers and controlled electric current from 0.09–0.12 A with voltage ranging from 400 to 500 V. The samples were exposed to oxygen gas for 30, 45, and 60 min at a temperature of 72 °C, a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$, and a work-distance of 4.0 cm. The pressure inside the reactor was maintained at 1.5 mbar, and the chamber was evacuated to 7×10^{-3} mbar before refilling with oxygen gas. The results from FTIR spectra showed changes in absorption bands, indicating chemical composition modification. Field-emission gun scanning electron microscope (FEG-SEM) observations revealed an increased surface roughness. The treatment affected water uptake significantly, improved oil absorption, suggesting a reaction mechanism. Thermogravimetric analysis (TGA) indicated slight alterations in thermal behavior and activation of the fiber surface. Overall, the findings suggest that CP treatment could be a viable method to enhance fiber-matrix adhesion for creating biodegradable polymer composites.

Cold plasma treatments have been employed to introduce chemically reactive functional groups, such as carboxyl or amine groups, onto polymer substrates. For example, Lim and Zulkifli,⁶³ investigated the effects of CP treatment on the surface reactivity, morphology, and oxygen-to-carbon ratio of pulverized empty fruit bunches (EFB) at various treatment durations. The authors reported a reduction in absorbance for syringyl-related CH and lignin-associated C=C bonds as the syringyl decomposed with increasing CP treatment durations.

The findings by the authors suggest that CP treatment can change the surface properties of pulverized (EFB) and boost conversion and processing efficiency by improving surface reactivity.

Application of CP in lignocellulosic biomass bioethanol process intensification

The economic inadequacy of the lignocellulose-based biorefinery process in comparison with the fossil-based biorefinery due to the naturally slow kinetics and lower yields of the fermentation process has hampered the development of bioderived products.⁶⁴ Poor bioethanol yield significantly affects the process's overall efficiency and economy, as well as the types of raw materials, which are important contributors to production costs. It is therefore important to investigate the process intensification strategy that can increase the yield of the fermentation process.⁶⁵

Bioprocess intensification refers to the techniques for increasing output per cell, in terms of time, volume, footprint, or cost in bioprocessing operations.⁶⁶ Bioprocess intensification is driven by the need to improve cost management and enhance process productivity.⁶⁶ Intensification is linked to a step shift in technology that leads to a major improvement in various environmental and economic parameters including energy consumption, carbon footprint, operational expenditure, capital expenditure, and a large gain in productivity.^{67,68} Process intensification is employed in improving various chemical processes including the enhancement of the fermentation process in lignocellulosic biomass biorefinery.⁶⁹

Recently, bioprocess intensification technology, based on the application of CP at atmospheric pressure to enhance lignocellulosic biomass processing has gained considerable interest. Cold plasma-assisted process intensification offers a promising technology for the future of lignocellulosic biomass biorefining by enhancing the various unit operations involved in the biochemical conversion of lignocellulosic biomass into bioethanol. This will promote efficient utilization of all process inputs and energy, improving the sustainable implementation of the lignocellulose biorefinery. Several technologies have been developed to improve the ethanol yield. These methods include strain modulation using physical, chemical, and/or biological methods, multiple stress evolution, process intensification by high pressure, ultrasonic irradiation, and so forth.⁷⁰ For instance, ultrasound was used for process intensification in the production of bioethanol from newspaper waste. The highest ethanol productivity of 14.1 g L^{-1} was obtained when fermentation

broth in a 12 h growth phase was exposed to ultrasound with a 25 kHz frequency, 160 W power, and 20% duty cycle.⁶⁵ The application of CP in the intensification for the enhancement of ethanol production by *Saccharomyces cerevisiae* has also been reported.⁷⁰

Recek *et al.*⁷¹ employed a CP jet in the treatment of yeast colonies to boost the conversion of glucose to ethanol during fermentation. An atmospheric pressure plasma jet with an overall electric power of 65 W, Argon (Ar) was employed as the feed gas at a gas flow rate of 5 standard liters. The authors found that plasma treatment could improve the metabolic activity of *S. cerevisiae* quickly, leading to faster conversion of glucose to ethanol and higher production of secondary metabolites. Different exposure times resulted in dose-dependent changes in metabolic pathways, with significant improvements in ethanol production and reduced levels of acetic acid and glycerol. The findings suggest that plasma pretreatment could be a promising approach to enhance industrial fermentations.

In addition to the acceleration of microbiological growth and fermentation, CP can speed up the pretreatment process, enhancing productivity, minimizing energy consumption, and reducing cost.⁶⁹ For example, Ibrahim *et al.*⁷² combined a CP ozone generator with ultrasound in the intensification of organosolvent pretreatment of corn cob and spelt husk. The authors reported a high lignin recovery of over 90% attributed to ozone pretreatment for raw corn cob and spelt husk. The authors confirmed that the yield obtained by CP application was greater than the yield of 85% obtained by the ethanol/organosolvent pretreatment alone. Ozone pretreatment was reported to cause a reduction in the crystallinity index values of maize cob and spelt husk from 45.5% to 36.8% and 30.2% to 28.3%, respectively, due to increased disorder and amorphization of the cellulose. After ozone pretreatment, the degree of polymerization of spelt husk remained unaltered but that of maize cob reduced by 17%. Before organosolvent pretreatment, ozone pretreatment improves the disruption and loosening of the biomass structure, enhancing the hydrolysis and breakdown of the links between the lignin and the carbohydrates. These linkages deteriorate following lignin's increased solubilization by ozone pretreatment at atmospheric pressure and mild temperatures, which results in a high percentage of recovered lignin, cellulose, and hemicellulose. On the other hand, higher extraction temperatures (120–180 °C) and pressures of around 2 MPa are required for organosolvent alone to promote the breakdown and solubilization of lignin-lignin bonds (ether bonds) as well as lignin-carbohydrate bonds (glycosidic bonds). The hemicellulose and cellulose fractions degrade more quickly

under these circumstances (high temperature and pressure), which reduces recovery.

Comparative analysis of conventional versus CP pretreatment method

Pretreatment is the most expensive stage in lignocellulosic biomass biorefinery and, in most circumstances, determines whether the process is economically viable or not.⁷³ Pretreatments are carried out on lignocellulosic biomass to reduce or remove LCB chemical resistance before saccharification to obtain fermentable sugars. The primary effect of these pretreatments on biomass is the solubilization and increasing the quantity of available polysaccharides. Another advantage of pretreatment is the degradation of hemicellulose into its monomeric form (D-xylose and D-arabinose).³⁷ Conventional pretreatment methods for lignocellulosic biomass involve either chemical or physical treatments. These processes often rely on elevated temperatures to break down the complex structure of lignocellulose.⁷⁴

Each of the pretreatment methods has its distinct features and mechanism of action. Table 3 presents some distinctions between CP and other conventional methods for lignocellulosic biomass pretreatment. For example, physical pretreatment methods are advantageous as they require fewer chemicals and low energy consumption. However, the disadvantages of physical pretreatment include equipment depreciation, high energy consumption, and minimal lignin removal.⁷⁵ Conversely, pretreatment using chemicals such as alkalis and acids is cost effective, breaks down hemicellulose and lignin in biomass, and increases the contact area for enzymatic hydrolysis. However, chemical pretreatment processes may contribute to pollution and the generation of toxic byproducts, which can pose environmental challenges. The elevated energy requirements for chemical processing can contribute to a larger carbon footprint, increasing costs due to the need for specialized equipment to sustain elevated temperatures.⁷³

Recently, the development of CP LCB pretreatment has offered low pollution by leveraging nonthermal ionized gas to enhance reactivity. The plasma species generated can modify lignocellulosic components selectively, resulting in a more efficient breakdown of biomass. This increased reactivity allows for targeted and controlled modifications, improving the overall efficiency of the pretreatment process. Cold plasma pretreatment generally has a lower environmental impact due to the minimal need for additional chemicals further reducing the risk of pollution. The major limitations of CP pretreatment include the generation of reactive species

Table 3. Distinction between the parameters for cold plasma and conventional methods for lignocellulosic biomass pretreatment.

	Cold plasma	Acid pretreatment	Alkaline pretreatment	Steam pretreatment	Biological pretreatment
Mechanism	Ionized gas (cold plasma) disrupts surface and internal structure through reactive species and physical etching	Dilute acids hydrolyze and disrupt the structure of lignin hemicellulose.	Strong alkalis such as NaOH/ KOH solubilize lignin and hemicellulose	High-pressure steam breaks down biomass structure	Enzymes or fungi selectively degrade lignin
Temperature	Relatively low (30–50 °C)	High (100–200 °C)	Moderate (60–100 °C)	High (160–200 °C)	Ambient temperature
Water consumption	Low	High	High	Moderate	Low
Use of chemicals	No	Yes (acids)	Yes (alkali)	No	Enzymes/fungi
Waste streams	Minimal	Corrosive acidic waste	Highly Alkaline liquid waste	Condensate requiring treatment	Spent enzymes/ fungal biomass
Selectivity	High biomass selectivity, depending on plasma parameters	Low	Moderate	Low	High
References	16	81	82	83	84

such as ozone, safety concerns associated with larger CP reactors, the complex nature of plasma equipment, and the high initial costs associated with plasma generation equipment, which may pose obstacles to successful scalability.⁷⁶

Challenges and bottlenecks towards optimizing and scaling up CP technology for LCB processing

Cold plasma technology has recently gained attention as an environmentally friendly method for the pretreatment of lignocellulosic biomass, especially in the production of biofuels and bioproducts.⁷⁷ The advantages of CP include minimal chemical usage, low energy consumption, and the ability to modify the surface properties of LCB.⁷⁷ However, various limitations and bottlenecks must be addressed to optimize and scale up this technology to enhance application in the lignocellulosic biomass biorefinery.⁷⁸ Cold plasma technology works by releasing a wide range of reactive species, including, UV photons, electrons, and ion radicals, which react with lignocellulosic biomass, making it versatile for biomass refining. However, due to the novelty of this technology, the specific mechanism by which these species alter cellulose, hemicellulose, and lignin remains elusive.^{16,77} This creates a bottleneck around long-duration investment in the optimization of the CP process to suit lignocellulosic biomass refining. Due to the limited understanding of plasma-biomass interactions, this further complicates the process.

The variability in the composition of lignocellulosic biomass and its heterogeneous nature pose significant challenges in the application of CP technology and the development of specific CP processing methods to suit LCB from various sources (e.g., energy crops, wood, agricultural waste). This variation further limits the standardization of CP pretreatment factors due to the requirement for substantial evaluations of CP technology to suit different LCBs. This further complicates the scale up and delays commercialization. The nonuniform exposure of biomass to plasma reactive species during large-scale biomass processing is another bottleneck presenting a challenge to the large-scale application of CP in LCB processing. Uneven exposure of biomass to CP treatment might lead to varying pretreatment results, increased energy consumption, and prolonging treatment durations to achieve the appropriate alteration of the entire biomass quantity. Present research involving CP pretreatment of lignocellulosic biomass is primarily performed in laboratories and small reactors built to handle small LCB quantities. The scaling up of the reactor design that can handle larger amounts of biomass while ensuring uniform plasma formation and efficient exposure to reactive species is a significant technical problem. Designing CP systems with the capacity to handle huge amounts of biomass while maintaining high throughput and without operating disruptions increases the complexity of the process design.

The type of gas used for generating the plasma for CP processing of LCB can produce reactive gases such as nitrogen oxides, ozone, and other byproducts that can present safety or environmental concerns. Minimizing the environmental footprint and ensuring safe handling

is crucial for the commercialization of CP applications in lignocellulose biomass processing. To overcome this, the cost of CP reactors requires specialized equipment, such as high-voltage power supplies, vacuum systems, and gas supply systems, leading to a high initial capital investment. Moreover, ongoing operational costs for power, gas supplies, and equipment maintenance add to the financial burden. To position CP as an attractive pretreatment method for the lignocellulosic biomass industry it must be compared favorably with existing lignocellulosic biomass refining process alternatives to enhance its efficiency and increase its benefits. For instance, if the economic and environmental implications of CP technology significantly outweigh the long-term benefits, it may be challenging to adopt CP processing for commercialization in the competitive lignocellulosic biomass industry.

To overcome these challenges, research into the application of CP in lignocellulose should be intensified to develop optimized protocols that will achieve the desired level of LCB modification. Combining CP with other energy-efficient pretreatment methods will help to reduce energy consumption while enhancing biomass modification. Modular reactor designs with enhanced biomass movement through the plasma field would promote efficiency to enhance the deployment of CP technology on a large scale. Collaboration with process engineers is necessary for integrating CP pretreatment systems into existing biorefineries with minimal disruption. The use of environmentally friendly gases and strategies for capturing and neutralizing byproducts will minimize environmental impacts and ensure safety. Overcoming the challenges mentioned above would enhance the commercial viability of CP technology in lignocellulosic biomass biorefining.

Conclusion

Cold plasma technology presents a promising and environmentally friendly alternative to conventional methods for lignocellulosic biomass biorefining. Its ability to operate at low temperatures while generating highly reactive species allows for the efficient breakdown of complex biomass structures, enhancing the accessibility of cellulose for subsequent biochemical processes. The selective modification capabilities of CP improve delignification and modify surface properties, thus facilitating higher yields in lignocellulosic bioethanol production and other biobased products. However, challenges remain such as scalability, high initial equipment costs, and safety concerns associated with larger reactors. Addressing these issues through further research and optimization could enhance the practical application and

economic viability of CP technology in industrial biomass conversion processes, making it a competitive and sustainable option for future biorefinery operations. Future research on CP technology should focus on optimizing operational parameters to enhance its efficiency and cost-effectiveness for large-scale applications. Investigating the integration of CP with other emerging technologies, such as microwave and ultrasound, would lead to synergistic effects that further improve biomass pretreatment outcomes.

Author contributions

Rasaq S. Abolore: conceptualization, data curation, investigation, methodology, writing – original draft, writing – review and editing. Swarna Jaiswal: supervision, validation, writing – review and editing. Amit K. Jaiswal: supervision, validation, writing – review and editing.

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Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could appear to influence the work reported in this paper.

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Rasaq S. Abolore is a researcher studying for a PhD at the Centre for Sustainable Packaging and Bioproducts, Technological University Dublin (TU Dublin), City Campus, Ireland. He holds an MSc in food safety management from TU Dublin.

Abolore's research focuses on developing an innovative biorefinery concept for the comprehensive valorization of lignocellulosic food waste with a particular emphasis on distillery and brewery spent grain. His work encompasses the pretreatment and downstream processing of lignocellulosic biomass to produce bioethanol and nanocellulose. He also specializes in the characterization of intermediate and final products and conducts process life-cycle assessments and economic feasibility studies.



Dr. Swarna Jaiswal is a Lecturer in Applied Microbiology and Packaging Technology at TU Dublin–City Campus, Ireland, and serves as the Director of the Centre for Sustainable Packaging and Bioproducts. She has authored over 100

publications, including journal articles and book chapters. With more than 10 years of experience in research and consultancy within food packaging and applied microbiology, Dr. Jaiswal is actively involved in multiple commercial and academic projects. Her work focuses on smart, active, biodegradable and compostable packaging films; antimicrobial coatings; biomaterials; and multifunctional coatings for biodegradable medical devices.



Dr. Amit K. Jaiswal currently is a Lecturer of Food Technology and Industrial Biotechnology in the School of Food Science and Environmental Health, TU Dublin–City Campus, Ireland. His research focuses on biorefinery strategies for converting

lignocellulosic biomass into biobased chemicals,

biofuels, and biomaterials such as nanocellulose and lignin, contributing to the circular economy. His work applies these sustainable materials in the development of innovative solutions, including food, packaging, coatings, energy storage devices, adhesives, and water purification systems. He integrates techno-economic analysis (TEA) and life cycle assessment (LCA) to evaluate the feasibility and environmental impacts of these innovations.