

Opinion

Biofuels and biochemicals from biomass

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Among various renewable energy sources, namely, biomass, solar, wind, hydrothermal and geothermal, biomass stand out as an environmentally benign, sustainable and an immediate substitute to fossil based fuels. This is due to the abundance of the carbon source in the form of cellulose in the biomass. Cellulose is the major chemical constituent of terrestrial biomass (40–50 wt.%, percentage by weight) with the other constituents being hemicellulose and lignin. However, owing to the extensive inter and intramolecular hydrogen bonding network existing in the cellulose structure, depolymerization of cellulose to monomeric carbohydrate glucose is nearly two orders of magnitude difficult than the hydrolysis of starch to glucose. The extensive inter and intramolecular hydrogen bonding network that hinders the access of acidic proton of the catalyst to attack the reaction site of β -1, 4 glycosidic bonds of cellulose (the linear homopolymer of glucose) is shown pictorially in Figure 1. The hydrogen bonding network within a single chain of glucose polymer in the cellulose structure is

called intramolecular hydrogen bonding while such bonding between two neighbouring linear chains of glucose polymers is called as intermolecular hydrogen bonding. The bond energy of such hydrogen bonding is 2 eV which is nearly 3–6 orders of magnitude higher than microwave energy ($1.24 \times 10^{-6} - 1.24 \times 10^{-3}$ eV) [1]. Yet, with the application of unconventional and novel methods of activation like microwave irradiation, the acid catalyzed hydrolysis of biomass (cellulose) to monosaccharides is accelerated by facilitating the access of the acidic proton of the chemical catalyst to the reaction site, namely, β -1, 4 glycosidic bonds. Such unusual activation of the cellulose structure making it conducive for the catalytic conversion selectively to glucose by microwave irradiation is possible owing to the peculiar phenomena called “threshold effect”.

This means, that beyond a particular value of microwave power, because of the non-thermal effects of microwave waves, the structure and dynamics of the tetrahedral structure of water with hydrogen bonding network is drastically

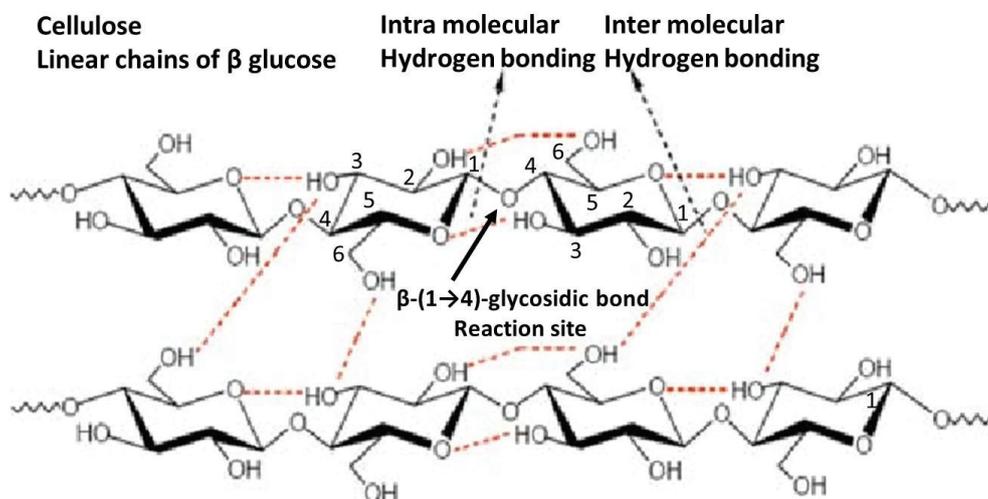


Figure 1: Extensive inter and intramolecular network prevailing in the cellulose structure.



altered and moreover the hydrogen bonding lifetime and number of hydrogen bonds are drastically reduced [2]. In fact, experimental evidence for such hydrogen bonding activating power of microwave irradiation in the cellulose structure (commercial Avicel PH 101, cellulose from cotton linters), is observed upon microwave irradiation of cellulose in water medium in the presence of HCl catalyst (7.5 wt.%, 2.38 M). The effect of microwave irradiation on the selective yield of glucose can be seen in Figure 2 [3]. Highest yield of 0.67 g glucose/g cellulose is obtained upon microwave irradiation for 7 minutes. The microwave irradiation of 1 g cellulose in 20 mL distilled water was carried out in a regular domestic microwave oven modified to have the provision for stirring and refluxing.

Such high and selective yield of glucose in short duration is achieved using microwave irradiation without any pretreatment of cellulose or the use of special solvents, like ionic liquids,

that enhance the performance of microwave heating. Cellulose hydrolysis is not the only reaction wherein the potential of microwave irradiation for selective glucose production is demonstrated. Microwave irradiation was proved to be promising for the acceleration of transesterification of lipids to biodiesel and for the pretreatment of biomass. Analogous to microwave irradiation, ultrasound irradiation was also proved to be a promising method for accelerating the biomass conversion processes like lipid extraction from microalgae, transesterification of triglycerides and fermentation of carbohydrates to bioethanol. However, unfortunately, these unconventional methods of activation are underutilized in biofuel production as see in Figure 3.

Even though the laboratory scale chemical reactions of biomass conversion are successful, the processes using these activation methods could not be scaled up to a pilot

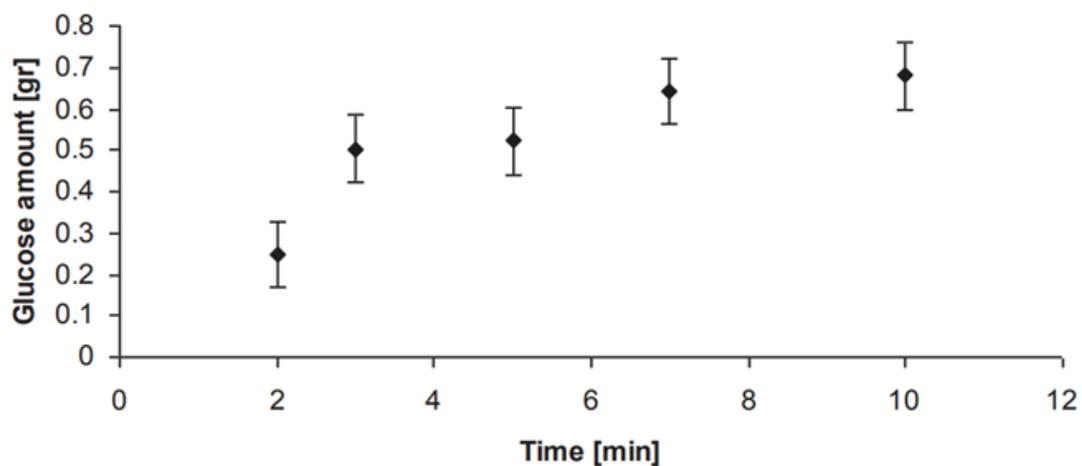


Figure 2: Effect of microwave irradiation time on the yield of glucose (Reaction conditions: 7.5 wt. % HCl; 1 g cellulose in 20 mL water; domestic microwave oven power: 1200 W; microwave frequency: 2.45 GHz). Adapted with permission from Elsevier [3].

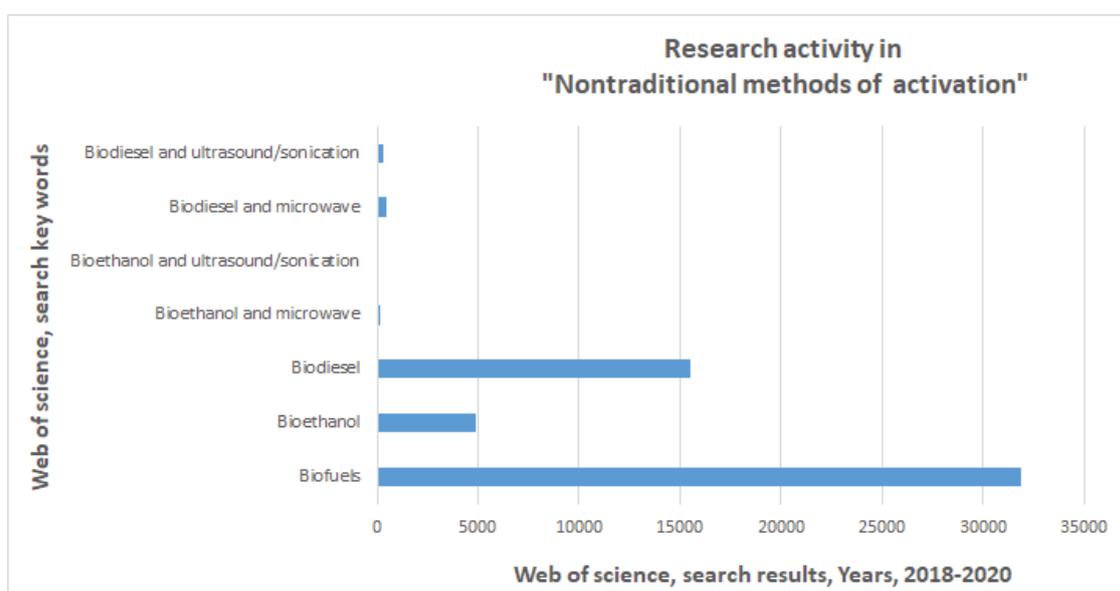


Figure 3: Research publications in the field of biofuels, biodiesel, bioethanol and the use of unconventional methods of activation, like microwave and ultrasound/sonochemical irradiation, in biofuels production.



plant level or industrial level operations. In addition to the ingenuity of chemists, innovation from engineers in designing large microwave and sonochemical devices is expected. The number of publications on the topics of biofuels, biodiesel and bioethanol in the years 2018–2020 are 31,909, 15,503, and 4,854 respectively indicating that the interest in this field is enormous. However the use of novel methods of activation like microwave and ultrasound/sonochemical irradiation is orders of magnitude lower in biodiesel and bioethanol production. Maturity in microwave technology especially, with respect to the scaling of the equipment suiting the chemical processes, like trans esterification of lipids and hydrolysis of lignocellulose biomass will result in a breakthrough in the field of biofuels production. The net contribution of biofuels to the total energy consumption is 0.8%, with a majority of the fraction being contributed by fossil fuels (79%) with the rest being contributed by other renewables (17.2%) and nuclear energy (3%). In the next 30 years, it is expected that 27% of the transportation energy comes from biofuels. It is possible, if microwave based transesterification and biomass hydrolysis methods are scaled up for large scale production [3–5]. Use of solar energy for biofuels should be encouraged [6].

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