

From first- to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity



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Implications

- Biofuels, in conjunction to their positive carbon balance with regards to fossil fuels, also represent a significant potential for sustainability and economic growth of industrialized countries because they can be generated from locally available renewable material.
- Biofuels are usually classified as follows:
 1. First-generation biofuels are directly related to a biomass that is generally edible.
 2. Second-generation biofuels are defined as fuels produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks to municipal solid wastes.
 3. Third-generation biofuels are, at this point, related to algal biomass but could to a certain extent be linked to utilization of CO₂ as feedstock.
- Scaling second- and third-generation biofuel processes thus requires solid economics that are directly dependent on optimized carbon utilization that relies on the production of fuels (commodities), as well as high value co-products.

Key words: biochar, biodiesel, biofuels, biomass, carbon balance, ethanol, feedstock, sustainability, syngas

Introduction

Biomass has always been a reliable source of energy, from the first man-made fire up to the utilization of pelletized wood as a feed for thermal plants. Although the use of lignocellulosic feedstock as a solid biofuel is a well-known concept, conversion of biomass into liquid fuel is a considerable challenge, and the more complex the biomass gets (in terms of chemical composition) the more complicated and generally expensive the conversion process becomes. Depletion of the oil stocks combined with the increasing worldwide energy demand have generated an increased interest toward biofuels in the last 10 to 20 years, although for most of the 20th century, research on biofuel closely followed the price of petroleum.

Another growing concern in the last 50 years is the environmental aspects of liquid fuel consumption. In Canada alone, over 8 billion liters of gasoline are used as transportation fuel yearly. With the growing concerns about the greenhouse gas emissions, the use of biofuels, although sometimes criticized, is often a more environmentally friendly option because the carbon balance of biofuel is close to neutral when compared with petroleum-derived fuels such as gasoline, diesel, or kerosene.

Biofuels by definition are fuels that are generated from biological material, a concept that has recently been narrowed down to renewable sources of carbon. Use of ethanol for lamp oil and cooking has been reported for decades (called spirit oil at the time) before Samuel Morey first tested it in an internal combustion engine in early 19th century. Ethanol then replaced whale oil before being replaced by petroleum distillate (starting with kerosene for lighting). By the end of the 19th century, ethanol was used in farm machinery and introduced in the automobile market. Oil-derived products replaced ethanol for most of the 20th century before being introduced again during the Arab oil embargo in the 1970s when the price of petroleum and its derivatives peaked.

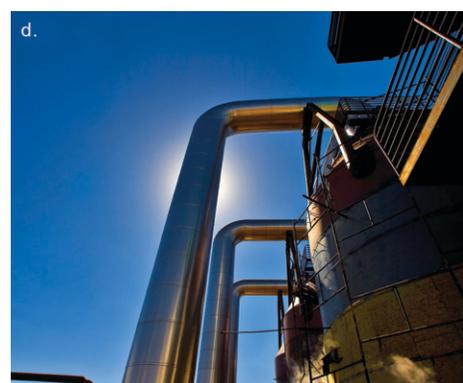
Ethanol is one of the best known biofuels in the Americas, although other biofuels, mostly biodiesel, are commonly used in other parts of the world such as Europe, Asia, and increasingly in Brazil. Both ethanol and biodiesel are considered as first-generation biofuels, although other types of biofuels like cellulosic ethanol and dimethyl ether (**bioDME**) are emerging, which could be characterized as second and third-generation biofuels.

First-generation Biofuels

First-generation biofuels include ethanol and biodiesel and are directly related to a biomass that is more than often edible. Ethanol is generally produced from the fermentation of C₆ sugars (mostly glucose) using classical or GMO yeast strains such as *Saccharomyces cerevisiae*. Only a few different feedstocks, mostly sugarcane or corn, are actually used for the production of first-generation bioethanol. Other more marginal feedstocks that are used or considered to produce first-generation bioethanol include but are not limited to whey, barley, potato wastes, and sugarbeets. Sugarcane is a common feedstock for biofuel production, Brazil being one of the leading countries for its use. The process that allows the production of



Sugarcane (a) is a common feedstock used for biofuel production. Once harvested (b), it can be crushed (c) and purified in a mill (d) to produce raw sugar or ethanol (photo credit, a: Parshotam Lal Tandon; b, c, and d: Sweeter Alternative).



ethanol out of sugarcane is rather simple. The sugarcane is crushed in water to remove sucrose, which is then purified either to produce raw sugar or ethanol. Although very advantageous for the producers, increases in the sugar price are a problem for the bioethanol business. In August 2012, the price of raw sugar was close to US\$0.20 per pound while the price for ethanol was US\$2.59 per gallon (US\$0.68/L). Production of 1 L of ethanol out of raw sugar should cost around US\$0.30 to US\$0.35, and therefore, the market favored production of raw sugar instead of ethanol. Corn is the other major source of carbohydrates for production of ethanol, although

unlike sugarcane, corn requires a preliminary hydrolysis of starch (Figure 1) to liberate the sugars that can then be fermented to ethanol. The enzyme generally used for hydrolysis of starch, α -amylase, is rather inexpensive at US\$0.04 per gallon of ethanol produced (McAloon et al., 2000). Corn market value in August 2012 was close to US\$338/t, leading to the production of 400 to 450 L of ethanol, depending on the process efficiency. Moreover, the value of the by-products, like post-distillation spent grain used for livestock feed, is a net asset for the whole economical balance of the process.

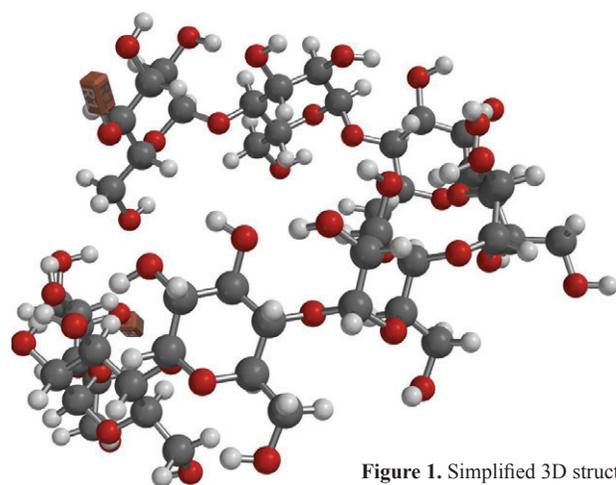


Figure 1. Simplified 3D structure of the starch macromolecule (structure made with Spartan 10).

Biodiesel is the only other biofuel produced on an industrial scale. The production process of this biofuel is very different from ethanol because it could be considered as a chemical process. Of course, it uses biomass (oily plants and seeds), but the process itself relies on extracting the oils and converting them into biodiesel by breaking the bonds linking the long chain fatty acids to glycerol, replacing it with methanol in a process called transesterification. A simplified version of the lipids used for the production of biodiesel is presented in Figure 2. Oil price on the international market varies among vegetable sources. As an example, in August 2012, soybean oil market value was US\$1,230/t while palm oil was US\$931/t. Canola oil, another common feedstock for the production of biodiesel, had a market value of US\$1,180/t. Based on the latter, it can be roughly estimated that each ton of oil will produce between 1,000 and 1,200 L of biodiesel with a market price estimated from diesel at US\$3.2077/gallon (US\$0.85/L). Production of biodiesel also requires methanol (typically between 125 and 150 L/t of oil converted) at an approximated market price of US\$0.35/L. The price for feedstock is the most crucial factor affecting biodiesel production. Therefore, use of other less expensive

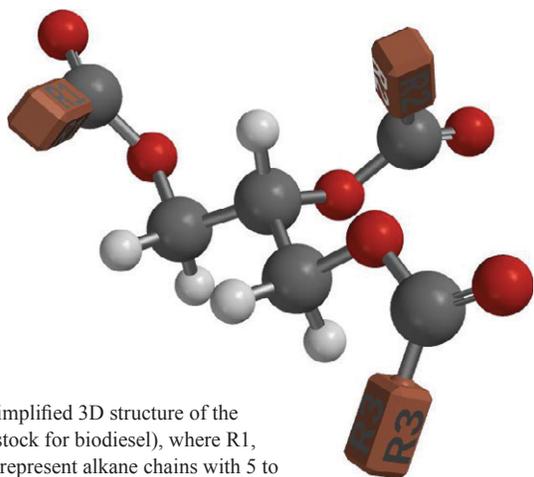


Figure 2. Simplified 3D structure of the lipids (feedstock for biodiesel), where R1, R2, and R3 represent alkane chains with 5 to 17 carbons (Bonhorst et al., 1948; structure made with Spartan 10).

sources such as used oils (US\$331/ton) and oil from non-edible plants like jatropha (estimated between US\$350 and US\$500/ton) is gaining interest. Algal biomass is also considered as a source of lipids for production of biodiesel, although it is generally related to third-generation biofuels. Production of ethanol from sugarcane or corn and biodiesel from edible oils depends on the prices dictated by the international market, whereas the prices of used cooking oil and jatropha are presently not influenced by such market, which is a good incentive for their use for biodiesel production. The availability of such oils is somehow less than the classical canola or soybean oil. Moreover, residual cooking oil requires additional processes for purification, whereas production of jatropha could be limited by its low market value which would not be appealing for production on good arable land, making it economically viable only on marginal land.

Second-generation Biofuels

Second-generation biofuels are defined as fuels produced from a wide array of different feedstocks, especially but not limited to non-edible lignocellulosic biomass. Biomass used for production of second-generation biofuels is usually separated in three main categories: homogeneous, such as white wood chips with a price value of US\$100 to US\$120/t; quasi-homogeneous, such as agricultural and forest residues pricing between US\$60 and US\$80/t; and non-homogeneous, including low value feedstock as municipal solid wastes (between US\$0 and US\$60/ton) as reported by Lavoie et al. (2011). The price for this biomass is significantly less than the price for vegetable oil, corn, and sugarcane, which is an incentive. On the other hand, such biomass is generally more complex to convert and its production is dependent on new technologies. Biofuel production is linked to the commodity market; consequently, the cost of converting the original feedstock to the final product must be as low as possible to maintain profitability. On the other hand, many biomasses (e.g., corn with the ethanol/livestock feed duality) allow the opportunity to generate a variety of products out of the same feedstock, thus adhering to the concept of a “biorefinery.” The conversion process for production of second-generation biofuels is usually done according to two different approaches, gener-

ally referred to as “thermo” or “bio” pathways. A simplified scheme of the second-generation biofuel production pathways is depicted in Figure 3.

The “thermo” pathway

The “thermo” approach covers specific processes where biomass is heated with a minimal amount of oxidizing agent, if any. All processes in that category lead to conversion of biomass into three fractions: one solid known as biochar, one liquid currently referred to as pyrolytic oil or bio oil, and one gas known as syngas, which is usually composed of carbon monoxide, hydrogen, short chain alkanes, and carbon dioxide. When processed at low temperatures (250 to 350°C) without oxygen, biomass undergoes a torrefaction process and the major conversion product is biochar. At greater temperatures (550 to 750°C), also without oxygen, the process is known as pyrolysis (either fast or slow depending on the heat exchange rate with the biomass) and the major product is bio oil. At greater temperatures (750 to 1,200°C) and with limited inputs of oxygen, gasification occurs producing mostly syngas with biochar and bio oils as by-products. Thermal processes are to a certain extent self-sufficient in terms of energy because the energy required to heat the biomass up to the requested temperatures can be supplied by the partial or total oxidation of carbon from the biomass, reactions that are usually very exothermic.

Biochar, considered as a solid biofuel, is gaining a lot of attention in the pelletizing business, especially in parts of the world where lignocellulosic biomass is rather inexpensive (Clarke and Preto, 2011). Nevertheless, for transportation fuel, production of pyrolytic oil or syngas is usually considered as more promising intermediaries. Pyrolytic oil is a liquid intermediary which, to a certain extent, looks similar to petroleum but is very different chemically. Therefore, to produce transportation fuel from this intermediary, a second transformation must be made, which is a rather difficult task because of the high water content as well as the corrosive nature of bio oil. Zhang et al. (2007) reviewed the four most promising processes for this transformation: 1) hydrodeoxygenation (reducing the amount of oxygen produces a mixture of alkanes similar to petroleum), 2) catalytic cracking, 3) steam reforming, and 4) the creation of an emulsion with diesel. Gasification, in contrast to pyrolysis, produces syngas, mostly composed of single carbon compounds and hydrogen. Nevertheless, although production of transportation fuels is possible out of syngas, it relies on the use of complex catalysts to induce the production of car-

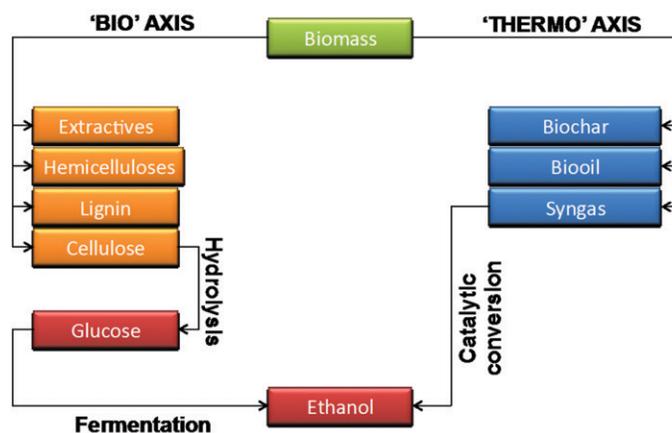


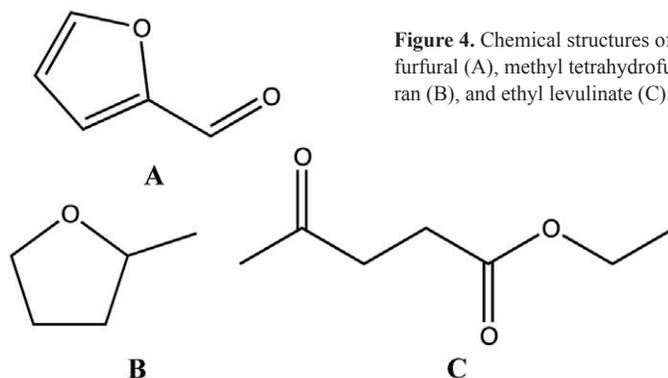
Figure 3. Simplified scheme for the “bio” and “thermo” pathways for conversion of lignocellulosic biomass into biofuels.

bon-carbon bonds. A typical example of such process is the Fisher-Tropsch process (Jun et al., 2004).

One of the simplest approaches for the industrial production of syngas is to produce methanol. Methanol can be produced from carbon monoxide and hydrogen directly under the action of a reducing catalyst. Recent reports have mentioned production rates varying from 500 to 560 L/ton of biomass using municipal solid wastes, a non-homogeneous type of biomass (Lavoie et al., 2012). Methanol is an end product of its own but it cannot be used as additive for fuel at this point. Therefore, further transformation is required. Relying on methanol as the starting material, many end products have been produced including alkanes via the methanol-to-gasoline (MTG) process, and ethanol via carbonylation processes (Lavoie et al., 2012). Methanol is also investigated for the production of a new generation of fuels such as bioDME, produced through etherification of two methanol molecules. It has been reported as an additive to diesel (Ribeiro et al., 2007) and has the distinctive advantage of being simple to produce under the action of an acid catalyst (Yoo et al., 2007). However, BioDME has specific properties that tend to limit its use in the transportation fuel market, specifically because of its low viscosity compared with diesel fuel causing excessive wear in fuel injection systems (Ribeiro et al., 2007).

Even if all carbon-based biomasses could in theory be converted to biofuels using any of the “thermo” processes, certain technical and economical restrictions apply. For example, gasification processes lead to the production of syngas and ultimately to transportation fuel (e.g., ethanol). The typical quantity of ethanol produced per ton of biomass is 360 L,

An aspen forest in Coconino National Forest, Arizona. One ton of biomass from a forest like this can potentially produce up to 313 L of ethanol (photo credit: USDA Forest Service, Coconino National Forest).



with the price of ethanol at US\$0.68/L and a production price close to US\$0.30/L. Therefore, the process is highly dependent on the feedstock price because the conversion from biomass to syngas, the purification of syngas, and the catalytic synthesis of ethanol represent significant technological challenges. Therefore, the most homogeneous and expensive biomasses would not be good candidates for such technology. Biomasses such as quasi-homogeneous or non-homogeneous would be more suitable (Marie-Rose et al., 2011).

The “bio” pathway

The “bio” pathway is somewhat comparable with a pulping process because, in most cases, cellulose is first isolated from the lignocellulosic biomass. Many processes have been considered, including classical pulping processes (Jin et al., 2010), steam explosion (Lavoie et al., 2010), and organosolv processes (Brosse et al., 2009). Isolation of cellulose is a technological challenge because it has to produce the highest purity of cellulose to remove most inhibitors without consuming too much energy or too many chemicals. Once purified, two approaches are generally used for saccharification of cellulose: either enzymatic (Sun and Cheng, 2002) or by chemical hydrolysis using acids (Chornet et al., 2010). In both cases, there are some limitations to the processes, mostly from an economical point of view as the price of the enzymes is forecasted to reach US\$0.12 to US\$0.20/L of ethanol produced in 2015 (Mielenz, 2001). On the other hand, chemical processes rely on rather inexpensive chemicals (e.g., sulfuric acid), although they have to be recuperated at a low cost to keep the process economically viable. Once isolated, the macromolecule (i.e., starch) requires hydrolysis to be fermented by yeasts.

Typical North American forest biomass weight (e.g., aspen) is composed of approximately 45% glucans (Lavoie et al., 2012), which leads to a potential production of 313 L of ethanol per ton of raw biomass. At a market price of US\$0.68/L, and a production price around US\$0.30/L, the value for cellulosic ethanol in this example would be US\$212/ton of biomass. Keeping in mind that the market value of such biomass varies between US\$60 and US\$80/ton and that saccharification of cellulose is a rather expensive process, there is a dire necessity to maximize the conversion of the biomass, such as using hemicellulose, lignin, and other extractives. Hemicelluloses are highly ramified carbohydrate-based polymers composed of both C5 and C6 sugars and account for 15 to 25% of the lignocellulosic biomass (dry weight). Usually, the ratio between xylans and glucans in hemicelluloses varies from 50 to 75% of the total carbohydrate content. The main advantage of hemicelluloses is that, due to their

highly ramified structure, they can be hydrolyzed easily using water at high temperatures or a very diluted aqueous mixture of acids. The key problem is that C5 sugars do not ferment with classical yeast strains and require genetically modified organisms to produce ethanol (Matsushika et al., 2009). Furthermore, acids (both acetic and formic) may inhibit the fermentation process, requiring an additional operation for detoxification. Another approach for valorization of C5 sugars could be via chemical pathways (Fuente-Hernandez et al., 2013). Many researchers have been working on this specific approach in which C5 sugars like xylose are dehydrated to furfural (4A), which acts as a platform chemical and an intermediary from which drop-in fuels such as methyl tetrahydrofuran (Figure 4B) and ethyl levulinate (Figure 4C) could be produced. Lignin, the second most abundant natural polymer found at 25 to 35% (dry weight) in lignocellulosic biomass (Lavoie et al., 2011), is mostly composed of phenyl propane units. The macromolecule is highly energetic and has been used for cogeneration (Dickinson et al., 1998) or as a fuel (Dayton and Frederick, 1996) by the pulp and paper industry. Although they could be used as fuel or as a source of hydrogen in a biorefinery process, the aromatic monomers from lignin could also be a very abundant source of high value chemical compounds that could be used in the plastic industry, as well as adhesives. In both cases, industrial-grade aromatics are actually obtained as side-products from petroleum. Consequently, the use of biomass to produce such monomers (or green chemicals) would lead to an interesting new market for bioadhesives and second-generation bioplastics. Recent work by our team has shown that it is possible to convert 10 to 20% weight of lignin into added value compounds such as guaiacol, catechol, and phenol (Beauchet et al., 2012). Reported work on lignin has also shown that it is possible to convert part of it into transportation fuels such as jet fuel (Shabtai et al., 1998).

Third-generation Biofuels

The most accepted definition for third-generation biofuels is fuels that would be produced from algal biomass, which has a very distinctive growth yield as compared with classical lignocellulosic biomass (Brennana and Owendea, 2010). Production of biofuels from algae usually relies on the lipid content of the microorganisms. Usually, species such as *Chlorella* are targeted because of their high lipid content (around 60 to 70%; Liang et al., 2009) and their high productivity (7.4 g/L/d for *Chlorella protothecoides*; Chen et al., 2011). There are many challenges associated with algal biomass, some geographical and some technical. Typically, algae will produce 1 to 7 g/L/d of biomass in ideal growth conditions (Chen et al., 2011). This implies large volumes of water are required for industrial scale, presenting a major problem for countries like Canada where the temperature is below 0 °C during a significant part of the year. The high water content is also a problem when lipids have to be extracted from the algal biomass, which requires dewatering, via either centrifugation or filtration before extracting lipids. Lipids obtained from algae can be processed via transesterification by the previously described biodiesel process or can be submitted to hydrogenolysis to produce kerosene grade alkane suitable for use as drop-in aviation fuels (Tran et al., 2010).

Conclusion

First-generation biofuels are well implemented around the world, although they may come with certain restrictions such as energy consump-



A researcher from Sandia National Laboratories views an algae sample as part of a project to cultivate green algae as a new biofuel supply. (photo credit: Sandia National Laboratories)

tion and utilization of arable lands, as well as the fuel versus food debate. Nevertheless, they remain a sure and economically viable approach for sustainability and reduction of fossil fuel consumption. Production of ethanol from sugarcane is in close competition with the sugar market, leading to a reduction in biofuel production in countries such as Brazil, one of the most important producers of ethanol/sugar in the world. Ethanol from corn is limited by a similar paradox with the increasing value of food on the world's market. The same reality applies for the biodiesel market, which is limited by the price of vegetable oils. In all cases, feedstock is getting increasingly expensive, leading to a growing interest toward second-generation biofuels. The latter is produced from a generally less expensive biomass such as forest, agricultural, animal, or municipal wastes. Numerous techniques are being investigated around the world for the production of second-generation biofuels, but overall they rely on two distinctive pathways: either "thermo" or "bio". The "thermo" pathway is based on a thermal treatment of biomass under a low or absent concentration of oxidizing agent (either CO₂, H₂O, water, air, or O₂). Under a range of temperature from 300 to 1,000 °C, the lower spectrum will lead mostly to the production of solid biofuel called biochar. In the middle spectrum, the most abundant product is pyrolytic oil, and at high temperatures, syngas. In case of pyrolytic oil and syngas, they could be considered as intermediaries, leading to the downstream production of biofuels (e.g., ethanol, diesel, gasoline). The "bio" pathway relies on use of microorganisms (usually yeasts) for the conversion of biomass into biofuels. The process requires pre-treatment for isolation of cellulose from the other macromolecules in the biomass. Although the process has been proven efficient, to be economical, the "bio" approach requires the complete utilization of the carbon content from the lignocellulosic biomass, thus transforming biomass into a "biorefinery" able to produce a wide array of biofuels and biocommodities. Third-generation biofuels are mostly related to algae. Therefore the major difference between the second and third-generations is the feedstock. Algae are known to produce biomass faster and on re-

duced land surface as compared with lignocellulosic biomass. Nevertheless, production of algal biomass presents technical challenges such as lipid extraction and dewatering, as well as geographical challenges in areas like Canada where temperatures are below freezing for a large part of the year. The future of biofuels may not rely solely on one generation, but may be a combination of the three generations to cope with increased worldwide demand as a result of depletion in the world's oil resources.

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About the Authors



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Dr. Jean-Michel Lavoie has a bachelor's degree in chemistry from Université Laval, followed by a M.Sc.A and a Ph.D. from Université Laval, after which he acted as a postdoctoral fellow under the supervision of Esteban Chornet, a world-renowned expert in the field of biofuels. In 2009, he started as the chairholder for the Industrial Research Chair on Cellulosic Ethanol at the Université de Sherbrooke. The chair has a strong relation with the industry, having developed an industrial-academic cooperation model where students interact

on both the academic and industrial levels. His team is now composed of more than 25 students and researchers, and their work is oriented for fast scale up. Lavoie is also an associate professor in the Department of Chemical and Biotechnological Engineering at the Université de Sherbrooke. His field of expertise includes gasification, pyrolysis, torrefaction, fractionation, reforming, and intermediates upgrading. He has published more than 20 peer-reviewed papers in the field and was invited as guest speaker to more than 10 international conferences. He is the author of seven patents. Finally, he acts as the East Platform leader for the BioFuelNet network that started in 2012.

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