The full citation of the published article is as follows:

Kusch, Sigrid: Cellulosic ethanol – Heading towards commercially viable advanced biofuels. SGEM2017 Conference Proceedings (17th International Multidisciplinary Scientific Geoconference SGEM 2017, 29 June - 5 July 2017), Vol. 17, Issue 42, 2017, pp. 111-118

DOI: 10.5593/sgem2017/42/S17.015

ISBN 978-619-7408-07-2 / ISSN 1314-2704

https://sgemworld.at/sgemlib/spip.php?article9971

CELLULOSIC ETHANOL – HEADING TOWARDS COMMERCIALLY VIABLE ADVANCED BIOFUELS

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ABSTRACT

Ethanol is the most common alternative transport fuel. The current standard market product bioethanol is criticised for limited environmental sustainability as it is largely based on utilisation of food crops. Cellulosic ethanol, derived from lignocellulosic biomass including organic wastes and residues, as well as biomass grown on marginal land, is considered clearly more sustainable under environmental criteria compared to first generation ethanol, and it makes use of highly abundant, low cost organic material. However, the production of cellulosic ethanol is more complex. Biochemical and thermochemical conversion pathways are both used. Cellulosic ethanol production procedures have been the subject of manifold research and development mainly during the last four decades. An assessment of market developments and a review of scientific literature both indicate that research and development in the field remain vibrant. Key bottlenecks that caused commercial uptake to proceed slower than had been expected around a decade ago, have now been overcome. Since few years, first commercial scale sites in Europe and the US produce cellulosic ethanol. The cellulosic ethanol industry is progressing towards full maturity.

Keywords: second generation bioethanol, advanced biofuel, lignocellulosic biomass, lignocellulose, transport fuel

INTRODUCTION

Bioethanol is increasingly used as a fuel, mainly in blends of five to twenty-five percent ethanol with gasoline (gasohol) [1-4]. Ethanol production has drastically increased during the last fifteen years (factor five between 2000 and 2015) [1]. Brazil, the USA and the European Union are the three main producers today [1-4]. The vast majority of bioethanol today is produced through so-called first generation processes, which use food crops rich in sugar and/or starch [1-7]. Therefore, first generation ethanol is linked to *food versus fuel* debates (competing interests for the same type of biomass) [4-8]. By bringing alternative fuels on research and policy agendas worldwide, first generation biofuels have facilitated occurrence of a fuel industry based on biogenic resources. However, there is growing consensus on the view that new biofuel production routes must be developed: a second generation of biofuel production pathways that seek to overcome the chief limitation of first generation feedstocks by avoiding the use of food crops and arable land for fuel production. Cellulosic ethanol, derived from lignocelluloses, is at the forefront of research and developments in the field of second generation fuels [4-12]. Feedstocks are globally abundant low cost resources which may include biogenic wastes and residues or energy crops grown on marginal land. A major bottleneck for cellulosic ethanol production is the natural recalcitrance of lignocellulosic biomass [5, 7-11].

Interest in bioethanol is further growing in the context of transitions from oil-based to bio-based industries. Along with higher needs for petroleum displacement, the coming decades will be characterised by increased demand for liquid fuels, and by implementation of rural development programmes in many countries. Non-liquid fuels such as electricity or gas-fuels can be expected to cover a share of the growing fuel demand, but the majority of vehicles in the coming decades will still use liquid fuels fully or in part. While other alcoholic fuels, mainly butanol, are further being considered [1, 4, 5, 7], bioethanol is expected to maintain and strengthen its prominent position, but at the same time to undergo a shift away from using food crops [1-6].

This publication provides an overview on state-of-the-art of cellulosic bioethanol production and explores market uptake of the technology. The work draws on literature and integrates an assessment of market developments.

BIOETHANOL PRODUCTION PATHWAYS

Bioethanol is mainly produced through the fermentation of sugar by making use of enzymes in the production chain [1, 4-8]. The process can be based on all biomasses that contain relevant amounts of sugar or of constituents that can be transformed into sugars (starch, cellulose) [5, 7], i.e. a large variety of biomass can be used, such as sugar crops, starch crops or cellulosic biomass. The clear majority of ethanol is today derived from converting food-grade sugar or starch (first generation ethanol) [1-7]. In the case of starch, the enzymatic hydrolysis to sugar is today a standard and effective process [5, 7]. Most common ethanol production feedstocks are maize in the USA, sugarcane in Brazil, and sugar beet and wheat in Europe [1-6]. Conversion of cellulose into ethanol (so-called cellulosic ethanol or second generation ethanol) has huge potential [1-9]. However, commercial uptake proceeded slower than had been expected in the first decade of the twenty-first century, which in consequence then rose some doubt about

the technology's perspective. During the last few years, commercial scale has now been reached (see below).

Cellulosic ethanol is produced from lignocellulose, the most abundant plant material. Cellulosic ethanol and first generation ethanol are chemically identical (CH_3CH_2OH). The main advantage associated with cellulosic ethanol is the fact that it can be produced from different types of raw material, including wastes and biomass grown on marginal land, resulting in significantly higher environmental benefits [1, 5-8], and the opportunity to make use of low cost biomass. Lignocellulosic biomass accounts for the majority of the total biomass present in the world, therefore the potential feedstock for cellulosic ethanol is huge [5-12]. Feedstock includes agricultural residues (straw, corn stalks), forest biomass (wood), biogenic wastes from industry or other sources, and energy grasses grown on marginal land. These biomasses would not compete with food supply, and their growth would not require additional irrigation, fertilisers and pesticides [4-12].

While cellulosic ethanol has a clearly more sustainable performance under environmental criteria, its production pathways are significantly more complex [5, 7]. Appropriate production procedures aiming to convert lignocellulosic biomass into ethanol have been subject to intense research and development since the 1970s, and significant investments have been and are still being made to achieve and secure full commercial scale [1, 3, 5]. Ethanol can be produced from lignocellulosic raw materials through two different pathways: biochemical conversion and thermochemical conversion [5, 7, 8, 11, 12], as illustrated in Figure 1. Most current projects focus on biochemical conversion based on fermentation of simple carbohydrates (sugars) released from the feedstock via pre-treatment and hydrolysis [8, 11]. The second main pathway (thermochemical route) is generation of ethanol (or other alcohols) from synthesis gas (syngas) via catalytic or biocatalytic routes after previous feedstock gasification into carbon monoxide (CO) and hydrogen (H2)-rich synthesis gas [5, 7, 12]. In Europe, the vast majority of demonstration projects utilise the biochemical route, while in North America biochemical fermentation and gasification/syngas conversion are both being pursued with comparable priorities [1, 3, 13, 14].

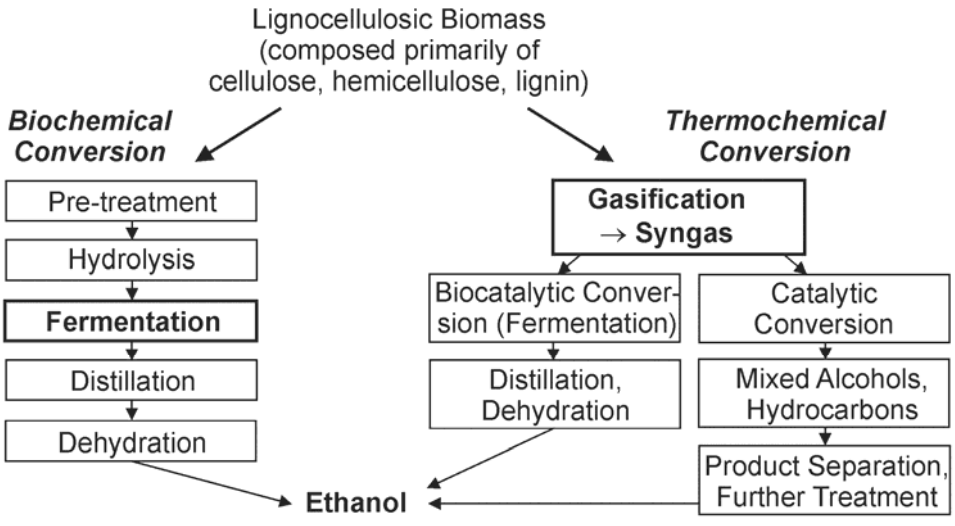

Figure 1: Cellulosic ethanol production routes

THERMOCHEMICAL CONVERSION

Currently, most mature gasification technology in commercial use is fossil-fuel-based (coal, petroleum). Alcohol production from synthesis gas is particularly well established for methanol (based on natural gas). However, utilisation of biomass as a feedstock is undergoing intensive research and development, as reflected by vibrant publication and patent activities during the last decade. A considerable variety of feasible ethanol production routes based on biomass gasification and synthesis gas conversion exists [5, 7, 12]. One key approach is the thermochemical Fischer-Tropsch (FT) process, where a metal catalyst is used to convert generated syngas to liquid fuels (hydrocarbon reformation into defined target products) [5, 7]. Biocatalytic routes with fermentation of synthesis gas are rather new approaches under research; technical feasibility has been demonstrated for ethanol production [12].

Several pilot and demonstration plants for biomass gasification and syngas conversion exist [1, 3, 13, 14]. At commercial scale (annual biofuel capacity of thirty-eight million litres), inaugurated in 2014 by *Enerkem*, gasification of municipal solid waste and catalytic refining of syngas (originally implemented for production of methanol, while ethanol is foreseen) is operated in *Edmonton* (Canada) [3, 13].

BIOCHEMICAL CONVERSION

Comparable to first generation ethanol, cellulosic ethanol can be derived through fermentation of simple sugars obtained from the raw material. In the case of lignocellulose, it requires significantly more complex procedures to gain access to fermentable compounds, i.e. the fermentable carbohydrates (cellulose components are protected by lignin) [5, 7, 8-11]. Once the carbohydrates have been extracted from the feedstock and polysaccharides have been broken down into free sugars, the basic principles in the further processing chain are the same for first and second generation ethanol production. They consist of fermentation of the sugars into ethanol, followed by recovery of ethanol via multi-stage distillation (obtaining around 95 percent pure alcohol) and dehydration to remove water (resulting into ethanol concentrations above 99.5 percent) [5, 7, 8-11]. From technology perspectives, biochemical first and second generation ethanol production processes therefore mainly differ in what concerns the usable types of feedstock and the procedures applied for extraction and preparation of fermentable carbohydrates.

Lignocellulose serves as structural material in plants and is composed primarily of cellulose, hemicellulose and lignin [5, 8-11]. To gain access to the fermentable components, the lignin barrier must first be broken, and the target components (carbohydrate polymers) must be released from the crystalline structure to make them accessible for hydrolysis (conversion of carbohydrate polymers into fermentable sugars) [1, 5, 7-11]. Cellulose ($(C_6H_{10}O_5)_n$), a polysaccharide consisting of a linear chain of glucose units and representing in general around fifty percent of the plant mass, is the main component for cellulosic ethanol production [5, 7, 8-11]. A number of factors, namely, cellulose crystallinity, accessible surface area, protection by lignin, and cellulose sheathing by hemicelluloses contribute to the resistance to hydrolysis [9, 11]. Effective pre-treatment is required, which in general comprises application of severe

conditions to disrupt the plant cell wall structures and to remove hemicellulose and lignin components so that cellulose becomes accessible to hydrolysis [5, 7-11]. Various physical or chemical pre-treatment technologies are known, including thermochemical or ultrasonic pre-treatment, use of different additives or steam pressure disruption [5, 7]. The choice of pre-treatment steps depends on economic viability, effectivity in cellulose liberation and minimisation of formation of components with unfavourable effects on subsequent steps [10]. Pre-treatment might generate enzyme inhibitors/deactivators and toxic substances that may subsequently affect enzymatic saccharification (production of sugars via hydrolysis) and fermentation processing [5, 7-11]. Further relevant factors are avoidance of destruction of hemicelluloses and cellulose, minimisation of energy demand, reduction of costs for pre-treatment equipment and reactors, minimisation of residues, consumption of little or no chemicals, minimisation of costs for chemicals [5, 7-11]. Materials with high lignin content, such as forest biomass, require adapted pre-treatment. Current research comprises further optimisation of pre-treatment processes, but also design of ideal biomass via plant genetic modification aiming at reducing the crystallinity of cellulose structures [8-11].

Pre-treatment is followed by cellulose hydrolysis (cellulolysis) to convert the polysaccharides into free sugar (glucose molecules). This can be achieved through acid hydrolysis or through enzymatic hydrolysis [1, 5, 7] Obstacles to acid processes are the formation of inhibitory by-products and the need to implement additional separation steps [1, 5, 7-11]. Enzymatic hydrolysis has undergone considerable improvements due to extensive research and development during the last decades, and is now generally the method of choice in production of cellulosic ethanol [1, 5, 7-11]. A range of formulated enzyme cocktails that match pre-treated substrates are available and are further being developed [1, 7]. Several enzyme companies have contributed to mass production of the specific enzymes (cellulases) [1, 2]. While some years ago, cellulolysis was considered a key obstacle to economic viability of cellulosic ethanol due to high enzyme costs, the costs have drastically declined during the last ten years, enabling competitive prices [1-3]. Subsequent fermentation of glucose to ethanol is a well-established technique.

Lignocellulosic biomass contains between fifteen to thirty-five percent hemicellulose [5, 7-12], which is considered an essential factor for the economic success of cellulosic ethanol production. Hemicellulose comprises a heterogeneous class of polymers and may contain varying proportions of pentoses (five-carbon sugar units: xylose, arabinose), hexoses (six-carbon sugar units: mannose, glucose, galactose) and other sugars [1, 5, 7, 10]. The 5- and 6-carbon monosaccharide units are released in the enzymatic hydrolysis step (making use of hemicellulase) [1, 5, 7-11]. Simultaneous fermentation of 5- and 6-carbon sugars into ethanol is considered a major breakthrough, as well as better adapted pre-treatments that allow for recuperation of both cellulose and hemicellulose [1-3, 5-11, 15]. Ongoing research aims at further simplifying ethanol production pathways by integrating pre-treatment, hydrolysis and fermentation as far as possible in one reactor, in the so-called consolidated bioprocessing (CBP) [1].

BIOREFINERY CONCEPTS AND INDUSTRIAL SYMBIOSIS

The biorefinery concept attempts to maximise the overall value obtained from the biomass by producing several products from the same feedstock (similarly to petroleum

refineries) [5, 7, 15], thus increasing economic viability and at the same time minimising occurrence of wastes. Products can cover liquid, gaseous or solid fuels, fibres, various chemicals. In cellulosic ethanol biorefineries (cellulosic ethanol as key target product), valorisation of lignin has a major role to play in achieving full competitiveness. Lignin is a phenolic polymer that cannot be used for fermentative ethanol production, it remains as residual material of the processing chain [1, 5, 7]. Possible lignin valorisation routes include use as solid fuel, conversion to oxygenated aromatics or esters, use as antioxidant, as binding material or for production of carbon fibres [1]. High-value energetic utilisation of residues, for example in the form of lignin pellets, can significantly increase energy efficiency of the cellulosic biorefinery itself or provide direct benefit to industrial partners. The case of the Kalundborg cellulosic ethanol plant (Denmark) [1, 15] demonstrates the benefits of implementation of industrial symbiosis: steam from the nearby power plant is used for biomass pre-treatment in the ethanol plant, while residual material is burned by the power plant. In addition to environmentally positive aspects, the partners have an economic advantage.

FROM PILOT SCALE TO COMMERCIAL SCALE

Despite the huge potential of cellulosic ethanol and its recognised high environmental credentials, the expectations for widespread commercial uptake had not been met during the first decade of the twenty-first century. The slow progress raised scepticism concerning the general viability of the technology and its potential performance. However, the breakthrough to commercial scale has now been reached with the progress achieved during the last few years, as described above:

- improved enzymatic hydrolysis of cellulose (and hemicellulose); mass production of specific enzymes (cellulases, hemicellulases) for cellulose (and hemicellulose) hydrolysis, resulting in drastic decline of enzyme costs
- improved pre-treatments that allow for efficient recuperation of fermentable components; in particular, adapted pre-treatments that enable recuperation of both cellulose and hemicellulose
- simultaneous fermentation of five- and six-carbon sugar units to ethanol
- simplification and integration of process steps

It is considered that the year 2013 marks a key milestone towards commercially proven large-scale cellulosic ethanol production based on the biochemical conversion route via enzymatic hydrolysis. In 2013, *Beta Renewables* commenced ethanol production at an annual capacity of seventy-five million litres in *Crescentino* (Italy), based on utilisation of agricultural residues [1, 3, 14]. The first commercial cellulosic ethanol plant in the US started production in 2014 at a comparable capacity (*'Project Liberty'* plant, operated by *POET-DSM Advanced Biofuels*) [1, 3]. Further companies are active in various countries, and the number of plants is growing [1-3, 13, 14]. Cellulosic ethanol industry is now consolidating and is advancing towards large-scale and global production.

Several dozens of demonstration and commercial scale plants are in operation or under construction in Europe, the USA, Brazil and other countries [1, 3, 13, 14]. Many companies active in the US cellulosic ethanol market are members of the *Advanced*

Biofuels Business Council, where information and data about market uptake can be obtained [3]. The *European Biofuels Technology Platform EBTP* (currently in transition to the *European Technology and Innovation Platform Bioenergy, ETIP Bioenergy*) provides an overview of flagship cellulosic ethanol facilities, demonstration plants, commercial scale plants and ongoing developments in research and industry [1]. Furthermore, a map and a database containing second generation biofuels production plants (operational, under construction, planned, non-operational) worldwide is available from the *IEA Bioenergy Task 39* initiative [14].

CONCLUSION

Cellulosic ethanol can be produced from a wide variety of biomass, including low cost lignocellulosic biomass such as wastes or biomass grown on marginal land. Therefore, cellulosic ethanol is more sustainable than first generation ethanol, however, it requires more complex production processes. Both biochemical and thermochemical pathways are possible. Most current projects focus on biochemical pathways, which is favoured in Europe, while in North America biochemical and thermochemical conversion are both focused.

Commercial breakthrough of cellulosic ethanol production was achieved in 2013, based on large-scale biochemical conversion of agricultural residues by *Beta Renewables* in *Crescentino* (Italy). Several commercial scale plants, built and operated by different companies and entities, are now in operation worldwide. Having overcome key process-related bottlenecks in the last few years, it can be expected that the cellulosic ethanol production industry will become fully mature within the next five years. However, further development will also depend on fuel prices, market dynamics and the general frameworks set by policy-makers. First generation biofuels will likely remain dominant during the first quarter of the twenty-first century, but it can be expected that second generation biofuels will then become the primary route to replacing fossil fuels by bio-based products.

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