SECONDARY PRODUCTS FROM THE BIOETHANOL PRODUCTION

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Abstract

In addition to the main product, the production of bioethanol by fermentation processes from common materials brings some by-products. These can reduce the quality and usability of bioethanol as biofuel, increase the amount of wastes and can cause environmental pollution. On the other hand, many of these secondary products represent an important raw material for other industries. The article describes the main processes of bioethanol production, its most frequent secondary products and possibilities of their utilisation.

Key words

Bioethanol, secondary products, by-products

Introduction

The use of bioethanol as an energy source has been known for quite a long time. In some countries, such as Brazil, bioethanol production is an important national economic activity. Also in Europe, in context of reducing the proportion of carbon dioxide emitted in individual countries, the importance of bioethanol (along with biodiesel) production keeps increasing. Directive 2003/30/EC on the promotion of biofuels for the transport sets a target of 5.75 % of all transport fuels by 2010. The recent European Commission energy roadmap had now increased this to 10 % by 2020. Production of bioethanol in the industrial way is a well-established technology, using the fermentation processes of sugar, starch or lignocellulosic biomass. The production of bioethanol is accompanied by formation of by-products (secondary) that must be eliminated or recycled. It is important to find the ways of dealing with them, to use all possible materials to reduce the input costs of production and also to ensure that their disposal, recovery and recycling have no negative impact on the environment.

Bioethanol production

The production of bioethanol in traditional means (or **1st Generation Biofuels)** is based upon fermentation procedures of starch crops like corn and wheat and from sugar crops like sugar cane or sugar beet. These technologies are advantageous in warmer areas, where it is possible to cultivate the plants with a high proportion of sugar (e.g. sugar cane or sugar beet) or starch components (e.g. wheat, maize, barley or rye). The **2nd Generation Biofuels** are typical for colder woody regions and they are based on lignocellulosic biomass. These technologies are also usable in our area with many lignocelluloses wastes (e.g. wood wastes, straw and residues from maize production).

- **Sugar beet** - After extraction of the sugar beet juice by the series of manufacturing processes, the clear sugar crystals and molasses are obtained. The molasses are separated from the crystals by centrifugation. Fermentation takes between 4-12 hours normally [1].
- **Cereal crops** - For starch (cereal) based crops, the procedure is similar to sugar crops, but with the added process of hydrolysis to break down the polymers into monomers which can then be broken down into simple C6 sugars. From the milling of the grain to release the starch, it is then diluted into water to adjust the volume of sugar in the mash. The mixture is cooked with yeast and all the water soluble starches dissolve into the water. And through either acid hydrolysis or enzymes, the starch is converted into sugars. The unrefined fermented liquid known as “beer” is produced and, through various evaporation and distillation stages, fuel grade ethanol can be produced [1].
- **Lignocellulosic Bioethanol -** The difference in process steps between starch and lignocellulosic feedstocks is that lignocellulosic biomass requires a more complicated hydrolysis stage. The reason for this is that cellulose in the wood contains carbohydrate polymers called cellulose. Cellulose is made up of long chains of glucose, and a more complex set of enzymes are required to break the long chains. Therefore, lignocellulosic bioethanol is technically more demanding and thus more expensive. Work at the moment is ongoing to enhance the pre-treatment methods such as steam explosion, ammonia steam explosion, acid processing and synthesising more efficient enzymes. Another area for development is fractionation technology where one can use more variable biomass, such as agriculture and forest crop residues and urban waste. The chemical structure of the crop and forest residues are highly variable which creates added complexity compared to the homogeneity of starch or sugar crops [1].

Secondary products from bioethanol production

Such as many biotechnological processes, the production of bioethanol in practice also brings many by-products, e.g. higher alcohols, distillation residues, residues from hydrolysis of corn and lignocellulosic materials or greenhouse gas - carbon dioxide.

- Refining of raw ethanol generated three different fractions **-"heads", "hearts"** and **"tails".** During distillation, the heads boil off first. They can usually be recognized by their solvent or lacquer aromas. This fraction is generally unsuitable for consumption and should be discarded. It should be separated carefully. During the middle distillation run (the "hearts"), the principal alcohol in all spirits, ethyl alcohol (ethanol), is distilled. This part of the distilling run, where the content of volatiles other than ethanol is lowest and the purest fruit aromas are found is always collected. The "tails" of the distillation include acetic acid and fusel oils, which are often identified by unpleasant vinegary and vegetal aromas. They are also discarded, but they may be re-distilled because some ethanol is invariably included with the tails. It is a mixture of higher alcohols and it is white or light-yellow liquid with characteristic strong odour. They have an oily consistency and contain heavy fractions of refining witch are isopentyl-, isobutyl-, propylalcohol and residue of bioethanol. The main component of tails is optically active pentanol (2-methyl-1-butanol). They can be used to produce chemical compounds, detergents, solvents or can be used for combustion [2, 3].

- **Distillation residues** – also known as stillage, distillery wastewater, distillery pot, distillery slops, distillery spent wash, dunder, mosto, vinasse, and thin stillage, are the main aqueous by-products from the distillation of ethanol following fermentation of carbohydrates. They are one of the most significant waste productions of bioethanol. This is not only for their quantity, but also for relatively high content of organic and inorganic substances, which are included [4-7]. The dry matter content is between 5 to 8 wt. %, there is low pH values as well and show a high chemical oxygen demand (COD) [7]. The evaluation of quality of stillage reported the higher amounts of suspended solids, total COD, total biological oxygen demand (BOD), digestible N compounds (proteins, dextrin, amino acids), nutritionally important components, fats, pulp, total phosphorus and potassium, the sulphate amount, total magnesium, dissolved organic salt, temperature of stillage and ash as well [5, 8]. Up to 20 litres of stillage may be generated for each litre of ethanol produced and the pollution potential of stillage can exceed the chemical oxygen demand (COD) of 100 g/L. The production and characteristics of stillage are highly variable and dependent on feedstocks and various aspects of the ethanol production process. Wash water used to clean the fermenters, cooling water blow down, and boiler water blow down may all be combined with the stillage and contribute to its variability. However, while the volume and COD concentration of stillage may vary considerably, the total amount of COD produced can be expected to be more consistent with the amounts of feedstock processed and ethanol produced [9].
- **Hydrolysis residues –** Lignocellulosic materials are composed of carbohydrate polymers (cellulose and hemicellulose), lignin and a remaining smaller part comprising extractives and minerals in an intricate structure, that is recalcitrant to deconstruction. For their decomposition to fermentable sacharides, chemical (e.g. acid hydrolysis, alkaline hydrolysis, ozonolysis), physic-chemical (e.g. autohydrolysis, expansive effect of CO_2, NH_3) or enzymatic processes are used. Depending on the process and conditions used during pre-treatment, hemicellulose sugars may be degraded to weak acids and furan derivatives which potentially act as microbial inhibitors during the fermentation step to ethanol. [10] Also lignin derived products can be formed and further interfere along the process. Some of hydrolysis products are described in Fig. 1.

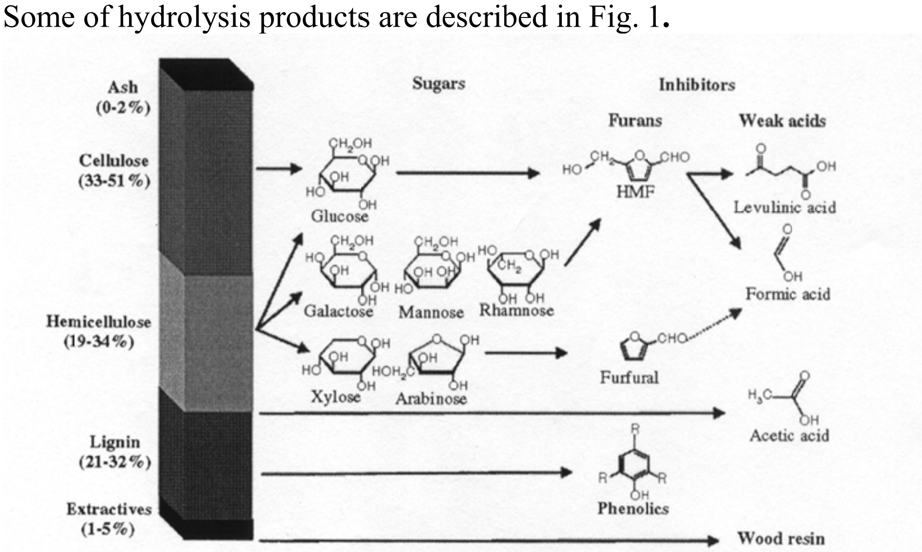

Fig. 1 *Average composition of lignocellulosic biomass and main derived hydrolysis products* [11]

- Ethanol is produced through fermentation of various grains (i.e. corn, sorghum, barley, and wheat) and sugar crops (i.e. sugar cane, sugar beets and sweet sorghum) also with **carbon dioxide** (CO_2) as a by-product. The CO_2 produced from fermentation processes is a saturated gas, at low to atmospheric pressure. Fermentation CO_2 from an ethanol plant is highly-concentrated and nearly pure. Therefore, the only required purification processes are dehydration and compression. During dehydration, the residual moisture is removed from the gas in order to prevent corrosion in CO_2 pipelines. This is followed with compression of the CO_2 gas to typical pipeline pressures. The few impurities are in the forms of organic compounds, such as ethanol, methanol and sulphur compounds including H_2S and dimethyl sulphide (DMS). DMS taints CO_2 off-gas stream odour, which presents a serious problem for food and beverage applications. However, this high-concentration source of CO_2 is still a good candidate for merchant markets for capture and purification. It is worthy to note that the current scale of ethanol fermentations CO_2 is a limited stream and is a negligible component in terms of total global CO_2 emissions [12].

Utilization of secondary products from bioethanol production

The composition **of stillage** is uneven and their subsequent use (like as combustion, biogas production, feed production, or use as fertilizer) depends on several parameters such as sort, quality and type of pretreatment of starting material, methods of work in processing raw materials, conditions of fermentation, the degree of spent wort and way of managing the process of distillation. These production parameters have affects to the amount of produced stillage per unit weight of raw material processed. The stillage quality also depends of the manner and speed of processing [5, 13].

- In the past, the most common way to dispose of stillage was **direct feeding**, witch using their relatively decent nutritional value [2, 5]. Also, they can be used **as fertilizer**, because they contain all the nutrients and substances are returned to the land where agricultural activity has been withdrawn [2, 14]. Such fertilizer is odourless and the use of the fields does not threaten groundwater or surface water [14]. However, is necessary to remember the high acidity stillage, which is solvable in combination with an appropriate waste disposal "alkali" substrates or pH adjustment. Comparing with the direct application of **soil composting** plant has an advantage in relieving acidity and combinability of different substrates (e.g. for better use of N-substances) [5].
- **Direct combustion** - because stillage is a natural material, i.e. which do not contain any hazardous constituents (pollutants), burning of them produce undesirable emissions. Thermal analysis (determination of combustion heat and calorific value of wheat stillage) were significantly below-specified values for all critical components of air pollution (particulate matter - dust, SO_2 and NO_x) [5, 15, 16]. By the standard method was determined calorific value of solid dried wheat stillage (42.4 MJ kg^{-1}), which is comparable to the quality of fuels, for example fuel oil. Briquettes made of this material are strength and fragility similar to those made of coarse wood chips [5].
- **Biogas production –** fermentation of stillage is possible by dry (dry matter content less then 12 %) or wet processes (dry matter content between 20-60 %) appropriate for the sparse stillage.The production of bioethanol, mainly the distillation process, requires a high consumption of thermal energy and cooling. This energy difficiency can be covered by biogas cogeneration [17].

The **hydrolysis yields** other secondary products which can be adjusted to the desired material (pure lignin, 92 % furfural, levulinic acid, acetic acid and formic acid) and then used [18, 19].

- **Furfural** (fural, 2-furaldehyd) is an important industrial raw material. It is used as selective extractant in the petrochemical industry, in the production of solvents, thermoset and other kinds of plastic polymers. It can also be used to protect plants and the productions of biologically active compounds [20] or can be used in civil engineering, chemical and pharmaceutical industries [18].
- **Levulinic acid** is a compound that has got application in synthetic chemistry. By hydrogenation it can be converted to maleic anhydride, methylethyl ketone and the other compounds as well. In this way and some other subsequent reactions are obtained pentadiol, 1,4-pentadiol and 1,3-pentadiene. Some levulinic acid derivatives can also produce antifreeze additives.
- The main by-product of bioethanol production is **lignin**. The lignin recovery in the fibers after pretreatment is affected by several parameters, such as degradation and solubility of sugars (and also mineral, protein and wax content of the straw) leading to a concentration of lignin in the fibre fraction. However, some of the lignin in the straw is also degraded and dissolved in the liquid fraction during pretreatment e.g. as free phenols [21]. Residual lignin and cellulose can be used to generate electricity and / or heat [22]. Lignin is not soluble in water, is resistant to chemical reactions and has a high surface area and these properties show that lignin has the potential to be used as suitable biosorption material in removing heavy metals (Cr^{+VI}) [23] and various organic substances (2,4,6-trinitrotoluene - using modified lignin) from waste water [24].

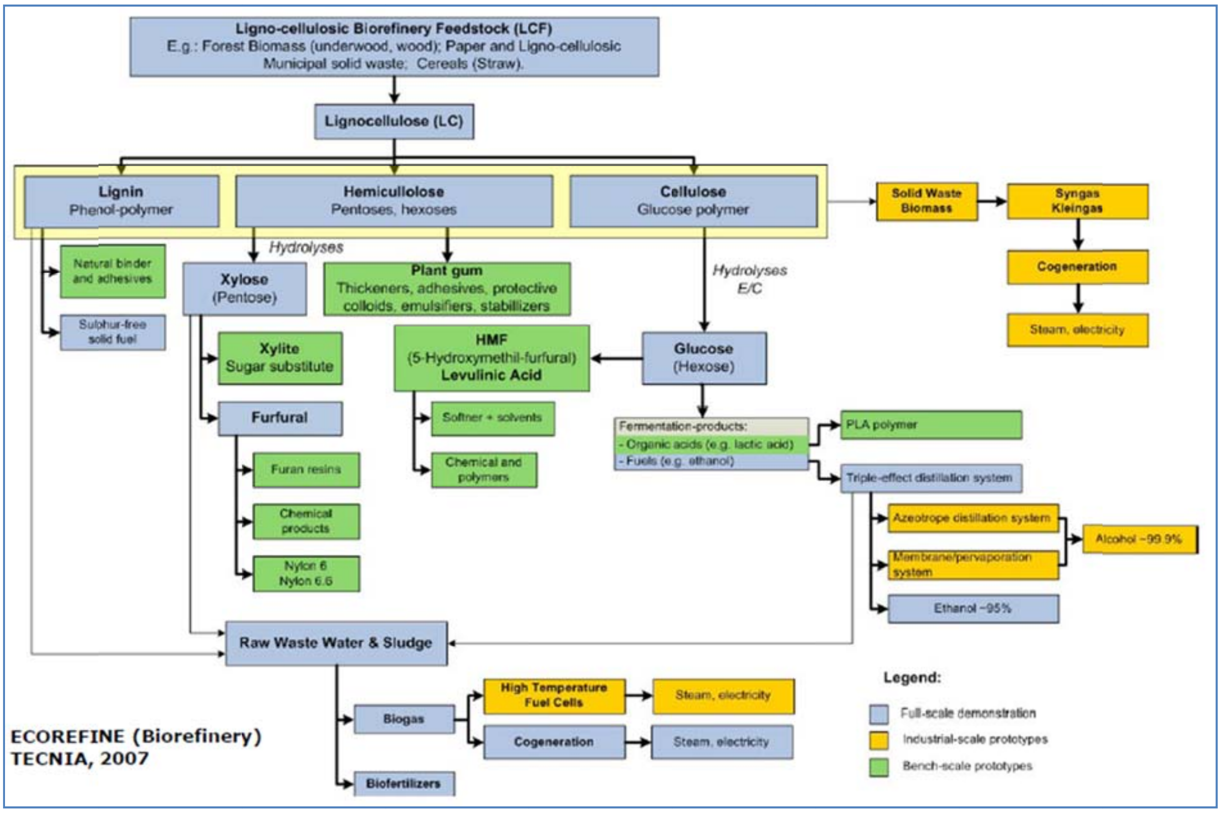

***Fig. 2** Typical products from biorefinery* [11]

Conclusions

The massive utilisation of fuel bioethanol in the world requires that its production technology be cost-effective and environmentally sustainable. Environmental sustainability is related mainly to monitoring, liquidation or utilization of bioethanol by-products.

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