Case Report

Nanocellulose and chemicals from by-products and waste

Abstract

A new concept for processing post-harvest biomass from plant production and industrial lignocellulosic by-products to marketable products is presented. In treating by-products of agricultural or industrial plant material, the primary separation is an alkaline extraction at a low temperature. Cellulosic fraction is separated and refined. Hemicellulose in black liquor is enzymatically or acid hydrolyzed to oligosaccharide and monosaccharide stages, and lignin precipitated by acid is received in native state. Remaining acidic liquor is neutralized, concentrated and fermented to biogas, preferentially using rapid anaerobic filter technique. Precursors of nanocellulose are separated from selected parts of agricultural crops or small-sized industrial lignocellulosic wastes, directly without previous separation of cellulose, by dielectric heating or by treatment with water-soluble organic solvents. Potential applications and down stream processings are presented. Economical advantages over conventional technologies are highlighted.

Keywords: biomass, post-harvest, by-products, cellulose, lignin, nanocellulose, biogas

Volume 4 Issue 1 - 2017

Yrjö Mälkki
Cerefi Ltd, Finland

Correspondence: Yrjö Mälkki, Cerefi Ltd and Nanorefix Oy, Livornonkatu 2 D 167, FI-00220Helsinki, Finland, Tel +358 40 5813943, Email yrjo.malkki@kolumbus.fi

Received: November 24, 2016 | **Published:** January 05, 2017

Introduction

In the ongoing public discussion on reducing climatic changes and carbon imprint, one of the key solutions has been replacing fossile fuels by those prepared from biomass from agriculture and forestry. The point of gravity of industrial investments implemented or planned has been in the production of liquid fuels especially from wood-based materials. The potential of the biomass of by-products from agriculture and connected industry is acknowledged, but exploiting it has been hampered in logistic costs involved. Furthermore, efforts to exploit have been mainly directed to production of ethanol or biogas. Market prices of these can cover only a minor part of production and investment costs, incomes from by-products are small, and thus such investments and production have been possible only by massive subsidies from public sources.

Separation of nanocellulose was for the first time presented and patented for 34years ago, and efforts to its implementation were reactivated in the late 1990's. Tens of important applications have now been presented, but industrial implementation is still in small scale. The global market of it has been forecasted to be in 2020's annually ca 35 million tons, the targeted market being in part in production of bulk products such as paper, packagings, composites and cement, another part various electronic and medical applications. The price level is expected to be 4 to 11dollars/kg.[1,2] However, the production capacity is still limited to pre-commercial units. The largest production capacity published, now under construction by Borregaard in Norway, will be 1000tons per year. The gap between production and expected demand is due to the high costs of both investment and processing using the presently available technologies.

Case presentation

The purpose of the concept described in this paper is to enable exploiting the massive biomaterial resources existing and now abandoned by focusing on the potential for profitable production, by obtaining incomes from all of the main components of these materials, cellulose, hemicellulose and lignin, and yet contributing to the green energy production.

Cellulose

The earlier production of cellulose from cereal straw by using the so called soda method has now been for environmental reasons forbidden in most of the industrialized countries. In China it was earlier produced on ca. 1000plants. Due to the river pollution it caused, already more than a half of these have been closed, and the remaining have to be closed within 5years. Although the river pollution has been diminished, in the proximity of the closed factories farmers now burn the straw on the fields, which causes serious air pollution and results traffic jams. Search for replacing by non-polluting technology has not so far succeeded.

In the technology the group of the author has developed, feedstock material can be post-harvest residues of cereal or oilseed plant production, or lignocellulosic by-products of food, feed or cellulose industries. The dissolving chemical used is similarly sodium hydroxide, but the extraction is performed at lower temperatures. The separated pulp fraction is refined to the degree required for the marketing. Hemicellulose present in the black liquor is enzymatically or acid hydrolyzed to mono and oligomer stages, and lignin is separated by acid precipitation.[3,4] Liquor remaining after the precipitation is neutralized, concentrated and fermented to biogas, whereby alternatives are the conventional biogas units bypassing the rotting stages, or the rapid anaerobic filter technique known as such but seldomly implemented.

In countries with limited forest resources, cellulose obtained can in part replace imported cellulose for paper and cardboard manufacture. In industrialized countries this cellulose is competitive mainly for preparation of thin paper qualities, and due to its thin diameter, as reinforcing fibre for composites, for reducing vehicle weight in the car industry, and for various electronic and medical applications. For purposes where mechanical strength is important, the most favourable quality can be obtained e.g. from maize stalks, which have thin and long fibres and fibrils giving large contact surface to the matrix and high tensile strength.

Nanocellulose

In the process developed by the author,[5] advantage is made of the precursors of nanocellulose which are submicroscopical in size and exist in the cellular walls of plant fibres and fibrils. They are in hydrated state and encapsulated in minute water droplets. By focusing intensive heat such as dielectric energy on these sites, the water pressure created breaks down the capsules and the precursor particles are released. Similarly water soluble organic solvents such as ethanol can penetrate and disintegrate the walls of the capsules and release nanocellulose precursors rapidly. After being released, the minute particles move intensively in Brownian movement and combine with each other to chains, aggregates or aerogels forming nanofibrils and further microfibrils, thin macrofibrils and their networks. It is thus possible to separate nanocellulose without separating and purifying cellulose and costs for using plenty of energy for breaking it down. Applications of it can be both in bulk products, where the present price level has been a preventive factor, and for the numerous high technology purposes

Lignin

In the separation process described above, the main advantage as compared to other cellulose processes is preserving the native structure of lignin due to the low temperature used. This enables separation of various industrial chemicals in the downstream processing. As an example of a potential application, it has been possible to separate from this native lignin with a good yield a fraction which has higher radical trapping effect than the commercial antioxidant butylated hydroxy toluene (BHT) at an equivalent concentration. An ample demand for antioxidants exists in plastic, rubber, medical, food and cosmetic industries. Another potential downstream line is ingredients for polyurethanes and phenolic resins. Presently the main part of lignin obtained from industrial processes is burned for energy production.

Hemicellulose and extractives

In the separation process described, hemicellulose is hydrolyzed enzymatically or by acid to monosaccharide and oligosaccharide stages. The liquor remaining after the precipitation of lignin also contains substantial amounts of small molecular extractive compounds such as fatty and hydroxy acids. This composition offers possibilities for separation of special chemicals such as different monosaccharides, but for most of them, the volumes of the market are small and competitive. Another pathway, where the market is larger, is to ferment it to butanol(s), whereby both the hexose and pentose based carbohydrates of this liquor can be utilized. This has to compete with petrochemical production of butanols, but plant capacity is said to exist already for awaiting sufficient elevation of crude oil prices to start production of butanol by fermentation.

The most advantageous way to exploit this fraction is probably to neutralize, concentrate and ferment it to biogas, whereby both its carbohydrates and other extractives can be converted to an easily marketable product. Since cellulose and other macromolecules are at the earlier stages removed from the liquor, the fermentation can now be implemented without the traditional rotting chamber stage and proceed rapidly. The reduced hydraulic retention time reduces both investments and energy needed for maintaining proper temperatures at the process. When bypassing the rotting chambers or using the anaerobic filter or column technology, the retention time can be hours or a few days instead of several weeks in the conventional biogas processes.

Environmental impacts

Using the processes described environmental loads can be reduced by several means. By increased collecting of post-harvest residues of crop production the amount of greenhouse gases emitted from the fields is reduced. Residues of leaches from the process are controllable. The only by-product which might be problematic is the salinity of the liquor after neutralization, since it is necessary to reduce it before fermentation. The chemical for the neutralization should be selected in view of possibilities to market the salt resulting, either sodium sulfate or calcium sulfate, and the economy at that stage or possibilities for its disposal.

Discussion

In the laboratory, bench and small scale pilot studies on the separation and nanocellulose production no technological risks for implementation have been found. For the primary separation process, the total cash flow per ton biomass processed is fivefold as compared to the market price of fuel ethanol from ton biomass. Production costs for nanocellulose depend largely on the plant material selected for processing and on the purity of the product to be marketed, but are clearly lower than in the processes now available. Implementing of these processes awaits results from pilot studies presently ongoing.

Acknowledgements

None.

Conflict of interest

The author declares no conflict of interest.

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