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Second Generation Biofuels and Biorefinery Concepts Focusing on Central Europe

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Utilization of the agricultural residues as lignocellulosic biomass should involve economical processes. Accordingly, it is not enough to produce biofuel from the agricultural residues but one should develop chemical/biochemical processes which produce valuable platform chemicals, as well. This paper gives a brief survey on the possible future processes focusing on the Central Europe. Such kind of technological processes should be developed in the next future in this region in order to make the utilization of lignocellulosic biomass profitable.

1. Introduction

Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for production of transportation biofuels, and chemical intermediates such as alcohols or acids, and platform chemicals like e.g. levulinic acid, furfural, lactic acid or phenolic compounds, etc. The EU countries are mandated to meet by 2020 a target of 20 % renewable resources in the energy supply and 10 % renewable resources in energy in transport sector (Bensten and Felby, 2012). From this 10 %, 6 % should be utilized lignocellulose. Accordingly the biomass consuming should be increased up to 10.0 EJ by 2020. Ethanol production from lignocellulosic wastes has the potential to significantly improve sustainability of biofuels by avoiding land-use competition with food crops and reducing impacts related to agricultural inputs. However, high production costs remain the bottleneck for large-scale utilization. In that sense, a huge potential exists in upgrading fuel and energy producing pathways into biorefineries in order to improve its financial performance and long-term sustainability. A biorefinery is a process, based in intensive fractionation scheme of fossil fuel refineries, in which biomass conversion leads to a multifunctional system producing fuels and value added chemicals (Villeages and Gnansounou 2008). Biorefineries are integrated bio-based industries using a variety of technologies to make products such as chemicals, biofuels, food and feed ingredients, biomaterials aiming at maximizing the added value. There are lots of biorefinery concepts depending on the raw biomass material as: the whole-crop, cereal, green, forest based and lignocellulosic, oilseed, waste oil biorefineries (Soetaert, 2009). The bioenergy potential in EU is reviewed by Bentsen and Felby (2012). A forest and agricultural areas are summarized in Central Europe by Ericson and Nilsson (2006). Biomass production potentials in Central and Eastern Europe are analyzed by Dam et al. (2007). The biodiesel separation and purification was reviewed by Atadashi et al. (2011) while the upgrading of second generation biofuels by Graca et al. (2013). Classification of the biorefinery concepts are e.g. C6 sugar, syngas and C5 platform biorefineries. An overview of current platforms, product, feedstocks and conversion processes is given by IEA Bioenergy Task (2008).

In this paper a brief survey is given for second generation biofuel processes, biofuel upgrading processes as well as on the platform chemicals focusing on possibilities in Central Europe.

2. Biomass production potential in Central Europe

For the near future, increasing biomass use, mainly lignocellulosic biomass, is considered to be essential in meeting the targets set out by the EU. Biomass sources are wastes, energy crops, agricultural residues

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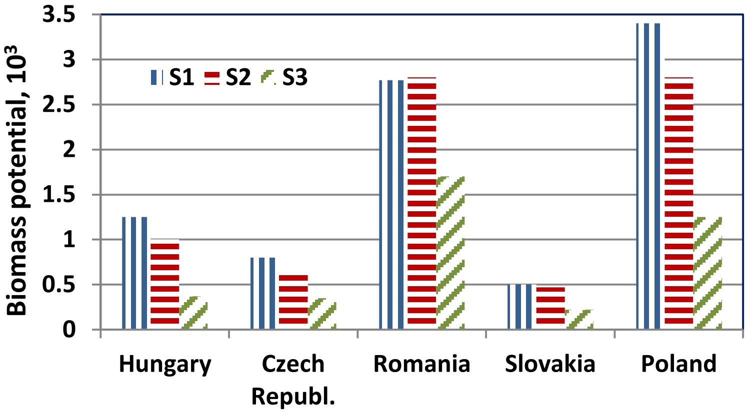

Figure 1: Biomass potential in the Central European countries at three different scenarios (1 PJ=1x1015 J): S1: liberalized trade; S2: no internal trade barriers within Europe; S3: priority for sustainable development (data from Dam et al., 2007)

or residues from forest. The utilization of energy crops in the next future is uncertain, but in the longer term potentially it will be the largest contributor to bio-energy production (Dam et al., 2007). Biomass resources are mostly agricultural and forest residues and wood from surplus forest and biomass from energy crops. This depends strongly on the Agricultural Policy of the EU countries. Biomass potential from energy crops, agricultural residues, forest residues and surplus forest are discussed and predicted for time of 2030 at different scenarios by Dam et al. (2007) depicted in Figure 1. Three scenarios are plotted here from the five ones analyzed by Dam et al. (2007). S1 scenario means that no market barrier exists between EU and the word market for agricultural products. There are no international trade barriers within EU and it protects strongly its own international market assuming by S2. EU has priority for sustainable development and nature conservation marked by S3 in Figure 1. As can be seen the biomass potential strongly depends on the market conditions of the agricultural products in the European countries. The energy potential of forest (assuming the sum of the forest residues and forest industry by-products) and agricultural (the sum of the straw and maize residues end energy crops) waste are plotted in Figure 2., which were estimated, taking into account the yearly increment in 2000, for a short, 10-20 y, time period by Ericsson and Nilsson (2006), There is an significant difference between countries depending on their territory and the weather conditions for agricultural production and forest industry.

3. Lignocellulosic biofuel production

The biomass potential and the energy content of forest and agricultural residues, discussed in section 2, orient us on the possibilities for biofuel production in Central Europe. The main question is its economy comparing the production cost to that of the fossil fuels. The conventional biochemical (the other route is thermochemical) process for producing ethanol from lignocellulosic biomass includes four main steps: pretreatment, enzymatic hydrolysis, fermentation and concentration (distillation. rectification-dehydration). Numerous research and development projects, throughout the word, are seeking economic, commercializable operations. The key obstacle to be overcome is the pretreatment selection. The pretreatment operations include mainly physical (e.g. biomass size-reduction) and thermochemical processes that involve the disruption of the recalcitrant material of biomass. Main pretreatment methods are: dilute acid (H_2SO_4, HCl [0-5-5 %]), hot water, lime, ammonia fiber expansion, ammonia recycle percloration, steam explosion with catalyst, organosolv, sulfite, ozone, alkaline wet oxidation, fungal bioconversion (Limayem and Ricke, 2012). We have pretreated the agricultural wastes, e.g. corn-stalk, wheat straw, by dilute acid and organosolv method using 43 wt% alcohol-water mixtures to it. It was obtained that the removal of C6 sugars reaches, after hydrolysis, close to 100 % of the polysaccharide content of the corn-stalk, at 200 °C and 0.5 h time period of treatment.

3.1 Separation and purification of ethanol

Several papers discussed the energy demand of the distillation (Nagy and Boldyryev, 2013) for ethanol separation and energy saving by application of pervaporation (Nagy et al., 2012). Pervaporation is a promising process in order to reduce the energy demand of the ethanol separation. However, membranes.

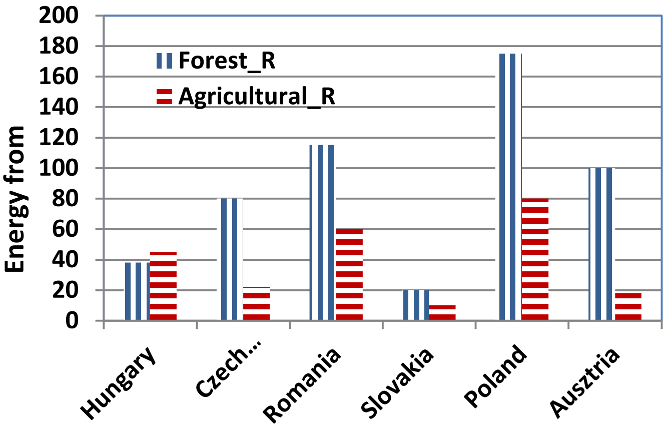

Figure 2. Energy potential from forest and agricultural wastes (Ericsson and Nilsson, 2006)

with rather high separation properties are needed to fulfill it. Results of pervaporation experiments, applying hydrophobic, PDMS ceramic membrane for low concentration ethanol separation, are depicted in Figure 3. The permeate flux and the selectivity denoted by α are plotted as a function of the ethanol feed concentration. Hydrophobic membrane should be used to remove the ethanol from the feed phase. The separation coefficient was calculated by eq. (1) as a ratio of the concentration's ratio of the two phases. The value of the separation coefficient, α was calculated by expression (C denotes concentration):

$$\alpha = \left(\frac{C_{EtOH}}{C_W}\right)_{perm} \Big/ \left(\frac{C_{EtOH}}{C_W}\right)_{feed} \tag{1}$$

The selectivity factor, α changes between about 3-5 in the concentration regime investigated. It was proved by Nagy and Boldyryev (2013) that the separation factor strongly affects the energy demand. The pervaporation will be more economic only, comparing to distillation, when the value of α is larger than 50. Let us look at how the separation varies at larger concentration range, namely when ethanol concentration is larger than 50 wt%. Figure 4 illustrates the results obtained by hydrophilic (Hybsi) ceramic membrane. Here the separation factor, 1/α, is essentially higher, it changes between 40 and 70 depending on the feed concentration. Its value lowers as a function of ethanol concentration. The permeate flux strongly decreases with the increase of the feed ethanol concentration. The lignocellulosic fermentation broth has rather low ethanol concentration (3-5 wt%), thus its concentration up to fuel grade quality (higher than 99.5 wt%) needs both hydrophobic and hydrophilic membranes. Ethanol has not enough hydrophobic character, thus it is a difficult task to create membrane with high separation factor for ethanol-water binary mixture. In any case, membrane with high selectivity, more than few hundred, has been prepared in lab scale, Thus, it can be expected that technologically suitable membrane will be available for industrial purposes in the next future. According these results it can be stated that the pervaporation will probably be a real alternate process of the distillation or the combination of these two processes, as hybrid process, for reduction of the energy demand for production of bioethanol of fuel grade quality. The methodology used by Nagy et al. (2012) makes easy to predict the energy demand of separation in case of a given pervaporation membrane.

4. Biorefinery concepts

Biorefinery is similar to petroleum refinery except that it utilizes biomass instead of crude oil to produce transportation fuels, heat power, chemicals, and materials. Several projects investigated the biomass elaboration methods in order to work out the biorefinery concepts applying different feedstock in both the USA and European Union (e.g. EU Biorefinery Euroview, BioCore, SupraBio, Bioref-Integ, Star-Colibri, BioPol, IEA-Bioenergy.Task-42-biorefineries) in the last 15 y. Many definitions for biorefinery are currently being used (Diep et al., 2012) from that the next two ones seems to be important to be given:

- Biorefineries are integrated bio-based industries, using variety of technologies to produce chemicals, biofuels, food and feed ingredients, biomaterials (including fibers) and power from raw biomass materials (EU Biorefinery Euroview, 2007);.

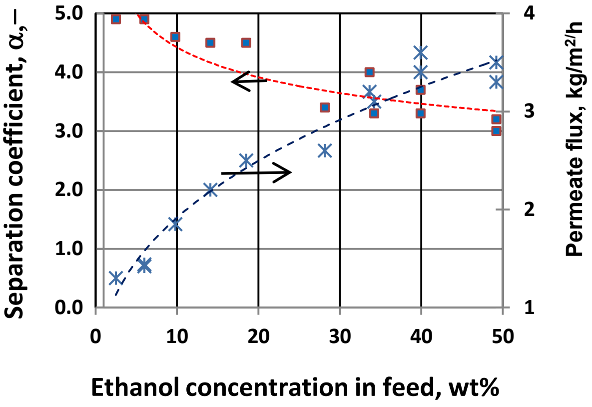

Figure 3. Pervaporation of ethanol-water mixture in low ethanol concentration range applying commercially available PDMS membrane at 60. °C (dotted line: permeate flux; solid line: separation factor)

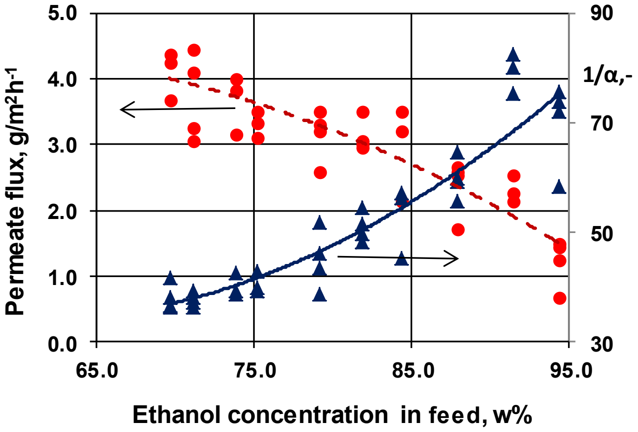

Figure 4. Separation of ethanol by pervaporation at higher ethanol concentration regime applying hydrophilic (Hybsi type) membrane at 60 °C

- Biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy (IEA Bioenergy Task 42)

It can clearly see that biorefinery concept involves sustainability, economics environmental aspects, market and products (food, feed, chemicals, materials). Different biorefinery concepts have been presented, depending on the raw materials (Kamm et al., 2012):

- Sugar and starch biorefineries,
- Green biorefineries,
- Lignocellulosic biorefineries,
- Thermo-chemical biorefineries,
- Plant oil and algae biorefineries,
- Biogas biorefineries,

Syngas biorefineries IEA Bioenergy Task 42's approach to biorefinery classification considers four main features, which are able to identify and describe the different biorefinery systems: platform, products, feedstocks and conversion processes (Figure 5). The platforms (e.g. C5/C6 sugars, syngas, biogas, lignin, oil, pyrolytic liquid, H2) are intermediates which are able to connect different biorefinery systems and their processes. Two main product groups are energy products (e.g. bioethanol, biodiesel, and synthetic biofuels) and material products (e.g. chemicals and building blocks, materials, food and feed). Feedstocks are grouped as energy crops from agriculture or biomass residues from agriculture, foresty, trade and industry, waste streams from biomass processing (organic residues, grasses, starch crops, sugar crops, lignocellulosic crops, lignocellulosic residues, oil crops, marine biomass, oil based residues). Concerning

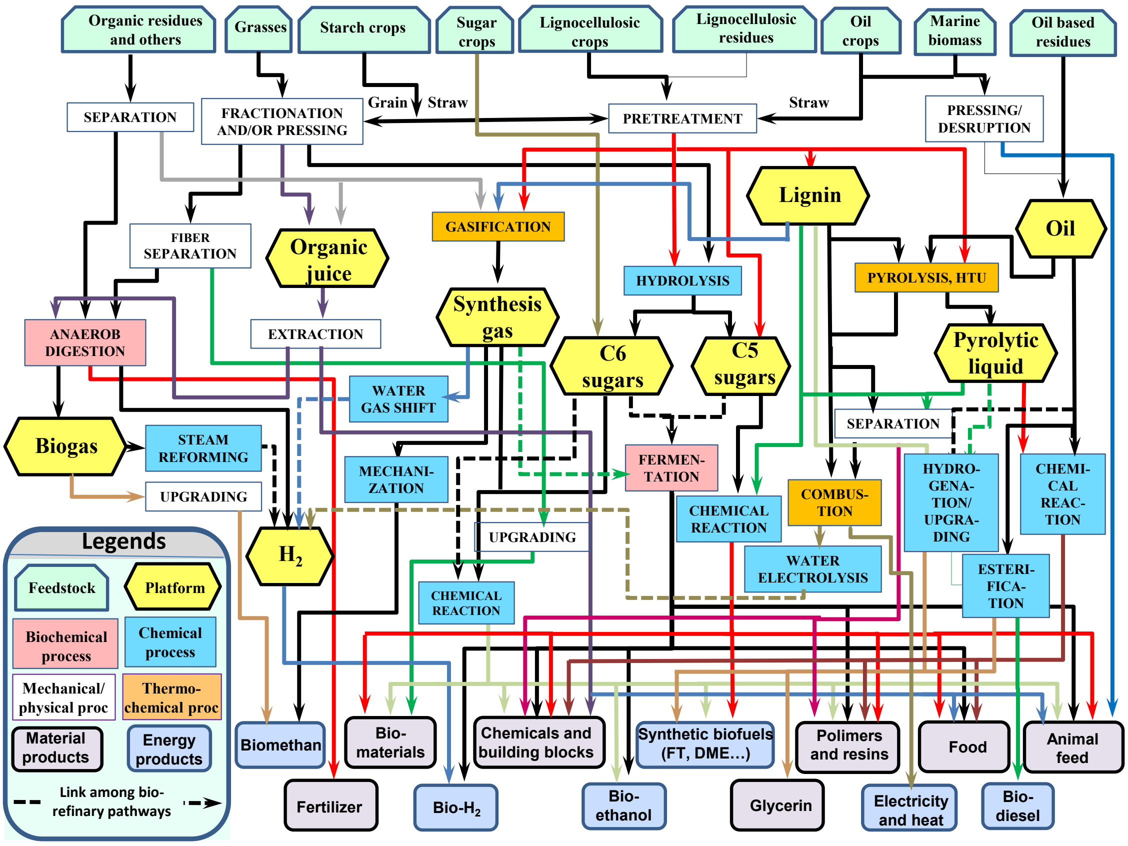

Figure 5. Overview of the biorefinery classification system (IEA Bioenergy Task 42, 2008, Diep et al., 2012)

conversion processes, it identifies four main groups, including, biochemical (e.g. fermentation, enzymatic conversion), thermo-chemical (e.g. gasification, pyrolysis), chemical (e.g. acid hydrolysis, synthesis, esterification) and mechanical processes (e.g. fractionation processing, size reduction).

4.1 Conversion of lignocellulosic biomass into chemicals

Technically viable and economic conversion of lignocellulosic biomass into chemicals is an important challenge that requires integrated processing and the effective utilization of both hemicelluloses and cellulose, consisting primarily C5 and C6 sugars, respectively. A report sponsored by US Department of Energy summarizes the top 12 (as well as 30) value added chemicals from biomass (Figure 5) and pathways how these compounds can be prepared. (Werpy and Petersen, 2004). Later Wettstein et al. (2012) analysis the reaction pathways of C5 and C6 sugars for chemicals from lignocellulosic biomass. The screening criteria for this included the raw material and estimated processing costs, estimated selling price, the technical complexity associated with the best available processing pathway and the market potential for each of the candidate building blocks. By integrating the production of higher value bioproducts into the biorefinery's fuel and power output, the overall profitability makes it more attractive for new biobased companies to contribute to the fuel supply by reinvesting in new biorefineries. Increased productivity and efficiency can be achieved through operations with lower overall energy intensity of the biorefinery's unit maximizing the use of all feedstock components, byproducts and waste streams.

Table 1: Top candidate building blocks from the first screen (Werpy and Petersen, 2004)

C3	Glicerol		
	3-hydroxy propionic acid	C6	Itaconic acid
C4	1,4 succinic, fumaric and malic acids		Xylitol/arabinitol
	Aspartic acid		Sorbitol
	3-hydroxybutirolactone		Glucaric acid
C5	Levulinic acid		2,5 furan dicarboxylic acid
	Glutamic acid		

4.2 Commercialization activity for lignocellulose utilization in Central Europe

The lignocellulosic biomass utilization in Central Europe, including the six countries,shown in Figures 1. and 2., is rather modest (Balan et al., 2013). First of all there is intensive activity in this respect in Austria where there are commercial pilot- or demo-plants in Guessing, Hallein, Utzenaich, Lenzing. Besides those, there is a commercial plant only in Poland, Coswinowice.

5. Conclusions

The widespread commercialization of the utilization of lignocellulosic biomass is still missing. New technological processes should be developed in the next future, which should involve production of valuable platform chemicals, in order to get economical technologies for the utilization the lignocellulosic, agricultural residues. Huge research efforts are still needed, especially in Central Europe, to develop most effective operations, chemical and/or biochemical technologies for it.

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