PHYSICAL AND TECHNICAL ENERGY PROBLEMS

BIOREFINERY TECHNOLOGIES FOR BIOMASS CONVERSION INTO CHEMICALS AND FUELS TOWARDS ZERO EMISSIONS (Review)

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Exhausting of world resources, increasing pollution, and climate change are compelling the shift of the world economy from continuous growth to a kind of economy based on integration of technologies into zero emissions production systems. Transition from non-renewable fossil resources to renewable resources provided by solar radiation and the current processes in biosphere is seen in the bio-refinery approach – replacing crude oil refineries by biomass refineries. Biotechnology and nano-technologies are getting accepted as important players along with conventional biomass refinery technologies. Systems design is a significant element in the integration of bio-refinery technologies in clusters. A number of case-studies, steam explosion auto-hydrolysis (SEA) in particular, are reviewed to demonstrate conversion of biomass into value-added chemicals and fuels. Analysis of energy flows is made as part of modelling the SEA processes, the eMerger (energy memory) approach and sustainability indices being applied to assess environmental impacts.

Keywords: zero emissions, biomass, bio-energy, bio-refinery, systems design

1. INTRODUCTION

The world economy still based on exploitation of the remaining deposits of fossil resources for many reasons is unsustainable. In general, sustainable well-being of people depends on transfer of the economic system from fossil to renewable resources. A possible way of making the shift from fossil to renewable feedstock through integration of bio-refinery technologies towards zero emissions is in the focus of the present paper.

People whose happiness depends on unlimited consumption of material goods in the reality of a finite world are less happy than those who enjoy finding ways to comply the material needs with the amounts of available resources for satisfaction. It is interesting that two conditional phases [1] can be distinguished in well-being perceived by individuals vs. economic development (GNP per capita) – the phase of “economic gain” and the phase of “lifestyle” (Fig.1). Undoubtedly, the
“footprint” of the global population would irreversibly drive the civilisation into a collapse if the countries of “economic gain” started living by the standards of consumption of the present “lifestyle” societies and using the same amount of resources per capita.

Since developed countries are the main polluters, the exploitation of the systems of industrial production needs new concepts and principles.

2. ZERO EMISSIONS CONCEPT

The UN University/Institute of Advanced Studies (UNU/IAS) Zero Emissions concept [2-6]:

- emphasises the shift from the traditional linear industrial model in which wastes are inevitable to systems of integrated technologies where everything is used;
- introduces sustainable cycles as found in nature;
- industries are reorganised into clusters such that each industry’s wastes/by-products comply with input requirements of another industry, and the integrated whole produces no waste of any kind.
3. THE BIO-REFINERY CONCEPT

According to Biomass Eco-Efficient Conversion Laboratory of the Latvian State Institute of Wood Chemistry (LSIWC/BE-ECL) [7], bio-refinery is a cluster of technologies integrating biomass conversion into transportation fuels, power, chemicals, and advanced materials within the framework of zero emissions and is based on two platforms: energy and chemicals & materials (Fig.2).

The bio-refinery concept is the analogue of today’s petroleum refineries producing multiple fuels and products from petroleum. By a combination of chemistry, biotechnology, engineering and systems approach, bio-refineries could produce food, feed, fertilisers, industrial chemicals, fuels, and power from biomass. Crucial for the bio-refinery concept development is the assumption that our planet cannot act as a reservoir of infinite fossil resources or a sink for an infinite flow of waste. For that reason bio-refinery should go in the direction of Zero Emissions integrated technology clusters.

Many of the bio-refinery ideas overlap with the ideas and approaches of green chemistry [8].

As accented by Kamm [9], „Bio-refineries combine the necessary technologies between biological raw materials and industrial intermediates and final products”. The principal goal in the development of bio-refineries is defined as (biomass) feedstock-mix + process-mix → product-mix”. 

Fig. 2. Platforms according to the LSIWC/BE-ECL bio-refinery concept.
4. GENERAL STUDIES

4.1. Biomass conversion flow-chart

Figure 3 demonstrates a bio-refinery network as flow-chart of bio-based products [10]. The general sequence from the source to the final product includes seven stages: Biomass → Precursors → Platforms → Building Blocks → Secondary Chemicals → Intermediates → Products/Uses. New markets of bio-refinery products could be added to the picture. A variety of chemical and biotechnology processes can be applied to convert the bio-based materials to chemicals and fuels.

![Flow chart of biomass conversion](image)

Fig. 3. A bio-based flow-chart model of biomass feedstock [10].

4.2. Pyrolysis and gasification

Proportions of the pyrolysis products – char, oil, and gas – depend on the temperature and time of reaction. Temperatures and the relevant time spans may go from ~ 300°C and hours to 400-500 °C and minutes or seconds, to over 700 °C and fractions of a second. The basic chemistry of pyrolysis focusing on the conversion of carbohydrate components is shown in Fig. 4 (Lange J-P., 2007).

Gasification of biomass by incomplete combustion produces a mix of combustible gases: carbon monoxide (CO), hydrogen (H2) and traces of methane (CH4). This mixture is called producer gas or syn[thesis] gas the endothermic formation of which proceeds at high temperature above 1000 °C, consuming the energy of about 25% of the starting material. Syn gas can be converted to methanol and/or dimethyl ether. By the Fischer-Tropsch synthesis it is converted into a
mixture of hydrocarbons – the excellent transportation fuel. Syn gas is also a source of hydrogen in the hydrogen-based economy.

4.3. Hydrolysis of polysaccharides and fermentation of sugars

Hydrolysis of polysaccharides is catalysed by acids or bases (Fig. 5) and results in formation of individual sugars, sugar isomers and oligomers [11].

In a series of consecutive reactions, furan compounds (furfural and hydroxymethyl furfural) are formed – the by-products inhibiting fermentation of sugars being easily condensed to tars or converted to levulinic acid and formic acid.
Different yeasts stop the metabolism at the stage of ethanol (complete fermentation turns sugars into water and carbon dioxide). Conversion of glucose to ethanol (Fig. 6) proceeds by way to pyruvic acid and acetaldehyde [11], wherefrom further continues by different metabolic pathways. The pyruvic acid intermediate can be re-hydrogenated to lactic acid – the building block of polylactate polymer [12]. The acetaldehyde intermediates by methanogenic microorganisms are oxidised to acetic acid and CO$_2$/CH$_4$ – the biogas.

Fig. 6. Fermentation of sugars [11].

5. CASE STUDIES

5.1. Steam explosion pre-treatment. First-, second- and third-generation feedstocks for biofuels

The main idea of Zero Emissions approach is clustering industries for zero wastes. Steam explosion auto-hydrolysis (SEA) can serve as a seed for dispersed integrated clusters comprised of fine chemical industry, paper industry, building industry, food industry, pharmaceutical industry, fuel industry, biotechnology, and farming components [13-15].

Efficient pre-treatment technologies and new uses of the lignocellulosic biomass are needed for future bio-refineries, the SEA pre-treatment being one of the most prospective technologies. Such kind of pre-treatment facilitates separating components of the lignocellulosic biomass and in a single course of action providing biofuels, chemicals, and nano-materials.

SEA (also referred to as steam explosion, steam explosion pulping, or steam cracking) principally is a simple technique [13]. The biomass (wood or non-wood forest material, agricultural waste or waste from forestry and plantation management) is treated with saturated steam, usually at pressures up to 40 atmospheres. The treatment time varies from some seconds to some minutes.

After the treatment, within a split second, the biomass is decompressed (exploded) to the pressure of the ambient atmosphere. Empirically, severity of the
treatment is estimated by a single parameter expressed in terms of treatment time (minutes) and temperature (T (ºC)) [16]:

\[ R_o = t \cdot \exp \left(\frac{(T-100)}{14.75}\right), \]  

(1)

with respect to the base temperature \( T_{\text{base}} = 100 ^\circ\text{C} \). Similar SEA results may be achieved by different combinations of \( t \) and \( T \). However, there is certainly a contribution from other factors such as moisture content of the sample, particle size, etc.

The two most important chemical and physical processes at SEA treatment are:

- formation of acid molecules from split-off functional groups (for example, acetic acid from acetic groups in hemicellulloses) acting as catalysts of hydrolysis of the treated material (auto-hydrolysis);
- defibration of wood or other plant biomass as a result of blasting the material by the pressure difference in the tissues of the material and surrounding atmosphere after abrupt release of the pressure at the end of the SEA process.

Since the lignocellulosic material, under conditions of steam explosion, can provide “self-sufficient” chemical and physical transformation, both the processes – hydrolysis and defibration – are achieved just by the “tools” inherent in the system itself, without any additional reagents (except steam). Further fractionation [5] of the biomass products after SEA is rather simple (Fig.7).

![Fractionation of steam exploded biomass](image)

Fig. 7. Fractionation of steam exploded biomass [5].

The main problem, of course, is that of how to optimise fractionation technologies including vacuum evaporation, microfiltration, ultrafiltration, reverse osmosis, etc., after SEA treatment.

All the SEA products have various applications [17]. Hemicelluloses during SEA can be hydrolysed (for example, acetic groups in hemicelluloses provide formation of the acetic acid) and used as molasses, the substrate for fodder yeast or bioethanol. The xylose sugar can be hydrogenated to xylitol (sweetener) and can also be dehydrogenated to furfural being an excellent feedstock for chemical processing.
SEA lignin [17] can be used as an adhesive for plywood, self-binding fibre and particle boards. Lignin is also applied as a component in coatings and foams. Besides, lignin and its modifications serve as dispersants, slow-release fertilizers, sorbents, insecticides and plant hormones. Many of the lignin derivatives have good properties, but their commercial potential is still unclear. The sulphur-containing lignin from conventional technologies is often burned for heat. The SEA lignin is chemically reactive and does not contain sulphur. During the SEA treatment, lignin coalesces on the surface of cellulose fibres as spheres of a diameter of some micrometres [14] the cellulose being exposed to enzymatic attack.

Cellulose can be hydrolysed to glucose and oligosugars [17]. The enzymatic isomerisation of glucose to fructose is well established. Glucose can be fermented to acids, alcohols, polyols, and ketones. Cellulose can also find use as a source for different derivatives. They serve as animal fodder, substrate for microorganisms and mushrooms, super-swelling gels, liquid crystals etc. Microcrystalline cellulose is used in the paper industry and also in the food and pharmaceutical industries. SEA produces cellulose micro-fibrils. Homogeneous dispersion of the cellulose fibrils within a polymer matrix looks promising for nano-composite structures (the nano-technology). Finally, cellulose fibres are a fundamental source for the paper industry.

In addition, SEA technology is flexible in the meaning of the demand on tree-free pulping (“tree-free paper”). To mitigate extensive deforestation requires that fibre materials are obtained from baggase, bamboo, straw, kenaf, and other fast-growing plants but wood.

Rudolf Diesel and Henry Ford first demonstrated the use of biofuels from a variety of crops. Now only biodiesel and bioethanol are industrial products. However, feedstock for so-called first-generation biofuel production is food crops. The main criticism against first-generation biofuels industry is the use of agricultural land, rising food prices, and rather a small effect of reducing emissions of greenhouse gases (GHG) (“food versus fuel”).

The target is the shift from first-generation biofuels to second-generation biofuels, the feedstock of which is lignocellulosic non-food materials such as straw and waste wood. Separating lignin from lignocellulosic carbohydrate polymers is the main problem to derive ethanol from cellulose and hemicelluloses, and different pre-treatment methods serve to solve it. SEA being an excellent technology in the number is to play an important part in material science and energy sector along with the recent idea of third-generation biofuels. In the consolidated bioprocessing (CBP) system [18] the production of cellulose, substrate hydrolysis and fermentation are accomplished in a single step by cellulolytic microorganisms. CBP offers potential for lowering the costs of biofuel production due to a simpler feedstock processing, lower energy inputs, and higher conversion efficiencies compared with separate processes of hydrolysis and fermentation being an economically attractive goal of the production of third-generation biofuel in the near future. The SEA pre-treatment technology for separation of lignin is also seen as an important part in production of third-generation biofuels.
5. 2. Modelling the energy flow

A simple model of the SEA system applied to calculate the energy costs and environmental impacts [19, 20] is illustrated in Fig. 8.

The energy consumed in the process has been found to depend on the moisture content of the raw material. A critical amount of moisture $H_c$ at which the energy for heating the waterless part of biomass and the absorbed water are equal is found as the ratio:

\[ H_c = \frac{C_b \Delta T}{C_b \Delta T + \Delta h}, \]

where $C_b$ is the specific heat of dry biomass;
$\Delta T$ is the difference between the operation temperature and the initial temperature;
$\Delta h$ is the difference between the enthalpy of water and steam.

In Eq. (2) the heat of absorption of water molecules is neglected, and all water is assumed to be evaporated. Experimental studies are necessary to refine the model calculations with account for the actual energy required by the biomass to reach the operation temperature.

![Fig. 8. A model of the steam explosion system](image)

The critical moisture content being close to that of air-dry wood, the optimisation of energy consumption by SEA pre-treatment requires that energy spent on drying up the biomass has to be taken into account. Apart from that, as experimental observations show, there is some smallest or threshold amount of moisture content needed to initiate hydrolysis.

Attempts have also been made to assess environmental impacts of the SEA technology related to the energy consumption and sustainability. The latter is considered in two aspects: environmental accounting for the impacts of a technology on the global system (and particularly on the biosphere), and physical accounting for sustainability of the technological process itself mainly dependent on availability of the necessary resources.
A comprehensive account of sustainability requires that calculations are made on a general basis common for environment, resources, and other components of the system under consideration. One of possible solutions – the emergy (energy memory) approach offered by H. Odum [21] based on the energy of solar radiation as the primary source of all other resources and products – has been applied to evaluate biomass pre-treatment by the SEA technology [19, 20]. The model calculations included the basic energy flow and the source material under assumptions that 20% of the energy used in the process is supplied by hydroelectric power plants and 80% – by thermoelectric power plants, and the biomass resource is naturally grown wood (any energy or other costs of planting, growing, felling, chipping, transporting, etc., for simplicity being neglected). Under condition that wood consumption is sustainable – the rate of consumption does not exceed the rate of regeneration – the biomass and hydroelectric power in the calculations have been regarded as renewable resources.

Under assumptions presented above, sustainability $S$ of the process is defined by the ratio of renewable emergy $R$ – the sum of emergies of the biomass and hydroelectricity – to the total of renewable and non-renewable (NR), i.e. thermoelectricity:

$$S = R / (R + NR)$$ (3)

The value of $S$ is zero if $R = 0$, meaning that only non-renewable resources are used and the process is not sustainable. If $NR = 0$, then $S = 1$ (or 100%), indicating condition of a completely sustainable process.

In the case considered within a simplified model discussed here, sustainability $S$ equally refers to the environment and to the SEA process itself, since the major impact on the environment is due to release of carbon dioxide by thermoelectric power plants. A more sophisticated model may require a somewhat different and more comprehensive approach to the assessment of environmental impacts.

Assuming that the total energy consumed for pre-treatment is 1 kWh per 1 kg of dry wood biomass and taking transformities – the solar energy equivalents of hydroelectricity, biomass and thermoelectricity from M. T. Brown and S. Ulgiati [22] – the value of $S$ is found to be 0.15, approaching 0.1 at 3 kWh per kg biomass and 0.3 at less than 0.5 kWh per kg biomass.

It has to be noticed that the SEA process can be made completely self-sufficient, since the energy necessary to generate steam and sustain the temperature of the reactor can be provided from burning biomass. The model calculations show that over 80% of available wood can be processed if 50% efficiency of utilisation of the combustion energy of air-dry wood is achieved.

6. WOOD CELL WALL STRUCTURE – OPPORTUNITY TO MAKE BIOFUELS, ADHESIVES, AND SELF-BINDING BOARDS TAKING ADVANTAGE OF STEAM EXPLOSION

Natural wood is a complex and multifunctional composite material used by humans for a vast variety of their needs – from the source of energy to the stuff for arts, competing successfully with other substances and modern synthetics. During millennia humans have learned to improve and modify the natural properties of wood for special needs by special treatment and selection [23].
The cell wall structure of plants is a composition of three groups of biopolymers on the supramolecular-nano level. The cellulose makes a fibrous reinforcement of the matrix of lignin and hemicelluloses. The matrix has a network structure, formed by the superposition of four separate semi-interpenetrating virtual networks realised by self-assembling through mainly intermolecular hydrogen bonds, physical chain intertanglements, covalent lignin-carbohydrate bonds and the weakly cross-linked network of lignin [24].

Nanotechnology as the study of wood cell structures with dimensions of 1-100 nm or larger (microstructures) is a promising field for research and industrial application. Cellulose consists of micro-fibrillated nanostructures (whiskers) of high stiffness and strength. Less clear is the state of lignin nanostructures. The Riga group has formulated the fractal hypothesis of the primary nanostructures of lignin [25].

The small-angle X-ray scattering (SAXS) has been used to study nm-size structures since the beginning of the 20th century. In the 1970s, the X-ray studies of soft materials dramatically increased due to synchrotron facilities enabling determination of the particle shape in dilute solutions. For example, the shape of proteins and, more recently, also the shape of lignin and other polymers that cannot be characterised by an exact molecular formula have been determined by synchrotron X-ray measurements [26]. The morphology of a kraft lignin particle in solution is exemplified in Fig. 9. In addition to SAXS the small-angle neutron scattering (SANS) can also be used. Although the flux in neutron experiments is much smaller compared with modern synchrotron facilities, the possibility to vary the contrast in different parts of the particle using, e.g., deuteriation is often appreciated.

![Fig. 9. Dimensions of a kraft lignin particle in 5 g/l solution of 0.1 M NaCl determined using ultra-small angle X-ray scattering and small-angle X-ray scattering [26]. The radius of gyration $R_g$ of the particle is 2.3 nm. The balls in the model are dummy atoms and do not represent real atomic positions.](image)

The scattering methods have facilitated the understanding of the fundamental phenomenological properties of plant lignocellulosics at nano-scale and can be used in evaluation of cell wall structures and their use in new composite materials and biofuels.

7. EFFICIENCY OF DIFFERENT BIOFUELS

In the process of biofuel production the main problem is the land-use efficiency. Efficiency of production of biofuels from the same reference area differs for different crops. A leaflet [27] impressively illustrates the statement (Fig. 10). Bio-methane and biomass-to-liquid (BtL) are very efficient fuel
technologies. The efficiency of rapeseed oil, biodiesel, and bioethanol is much lower. However, efficiency of the latter could be improved utilising their by-products. Bio-methane and bioethanol are used in petrol engines while vegetable oil, biodiesel and BtL are suitable for diesel engines.

8. THE WORTH AND LIMITS OF BIOENERGY

As mentioned by Spangenberg [28] “Bioenergy is no silver bullet – it may play a part in an integrated system of future energy supply. Given the current consumption levels, bioenergy will not be able to deliver any meaningful contribution unless the reduction of total primary energy use of up to 4/5 becomes reality”. He also added that the bio-fuelled world is a *fata morgana*. The authors agree with Spangenberg. Bioenergy in Latvia – a country rich of forest resources – is an important factor decreasing dependence on imported fossil resources. The question is who will pay the additional cost for bioenergy. For obvious reasons, unbiased judgement would convince everybody that a 100% substitution of fossil energy sources with bio-based energy at the current rates of consumption is illusion. Moreover, since only a very small quantity of the total energy the planet receives from the Sun is accumulated in the biomass, there is little sense in counting on biomass as a sustainable source of renewable energy to replace depleted fossil resources unless efficiency of photosynthesis is increased by order or two. Meanwhile, bioenergy should be a concern of rational use of land and the biomass harvested from it, with account for the energy necessary to convert biomass into fuels. Improving the uses of biomass as a traditional source of energy and supporting innovative uses of bioenergy is the appropriate way for Latvia.

![Fig.10: Biofuels in comparison (adapted from [27]). The assumed fuel consumption: 7.4l/100 km for petrol engine and 6.1 l/100 km for diesel engine. White sectors of rapeseed, biodiesel, and bioethanol show possible increase in biofuel production from utilisation of their by-products. Reference area - 1 hectare.](image)

9. CONCLUSIONS

Bio-refinery is the future of bio-based economy requiring integration of diverse technologies into zero emissions production systems. Bioenergy is one of bio-refinery products the main part of which is chemicals, new composites, and
nano-materials. At the presently achieved technological development and rate of consumption the total replacement of fossil-based energy by bio-energy is impossible. However, advancement of bioenergy is important from different aspects.

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REFERENCES


Aplūkojot virkni konkrētu tehnoloģisko risinājumu, TSA – biomasas autohidrolīzī tvaika sprādzienā tā skaitā, iztirzātas ar biomasas konversiju, izmantošanu un augstas pievienotās vērtības produkta pamata līmeņa nozīmi kā ekologijs, enerģeikiznes un enerģētiskās atmiņas, izmantošanu un citos aspektos. Latvijas enerģētikas nozīme ir tradicionālo bioenerģijas resursu izmantošanas efektivitātes celšanai un inovatīvo bioenerģijas tehnoloģiju valstiskam atbalstam.