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Biorefinery for production of chemicals, energy and fuels

A brief overview of state and trends in utilisation of renewable raw materials to produce fuels and especially chemicals which can serve as platforms for further syntheses in chemical industry. Stress will be given to biotechnological production routs of organic acids and their separation and application of ionic liquids in separations.

Keywords: biorefinery, biomass, biofuels, organic acids, ionic liquids, separation

1. INTRODUCTION

In preindustrial era until the 19th century, renewable raw materials were the major source of energy and material use. During the Industrial Revolution, the use of coal increased sharply and coal quickly becomes a key raw material in the chemical industry and energy production. In the 20th century, there has been a changeover in fossil fuel sources from coal to crude oil and natural gas due to lower prices, simpler logistics and the versatility in usage of oil and gas. In connection with the limited availability and increasing price of crude oil and natural gas, the question now arises how to face this situation and what raw material base will develop in the future? Biomass as a renewable raw material could be answer [1-3]. There is a historical line of dominant resources used from local renewable resources to coal, coal gas and tar industries to crude oil and natural gas in petroleum refineries and petrochemical industry and recently switch to biomass in biorefineries and other renewable resources is of increased importance.

Transformation of raw material platform to biomass will not be quick and simple. It requires concerted cooperation of several scientific disciplines as agriculture, forestry, biology, biotechnology, chemistry, chemical engineering, environmental sciences, but also industrialists, strong economical and political impulse, etc. Renewable raw materials will be increasingly used in the future. The speed of change however, will most probably be determined by the future development of the oil and gas prices. New processes have to be developed to transform biomass to fuels, energy and chemicals in economically competitive way.

This paper will present brief overview of state and trends in utilisation of renewable raw materials to produce fuels and especially chemicals which can serve as platforms in chemical industry. Stress will be given to biotechnological production routs of organic acids and their separation.

2. BIOREFINERIES

What is biorefinery? The members of IEA Bioenergy have agreed on the following definition for biorefinery [4]: “Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, and chemicals) and energy (fuels, power, and heat)”. This means that biorefinery can be a concept, a facility, a process, a plant, or even a cluster of facilities. There are several types of biorefinery. The first generation of biorefineries are based only on one feed and produce one main product, e. g. ethanol from corn. More advanced newer biorefineries produce more products from one feed. For example processes developed within BioHub programme based on cereal grain (www.biohub.fr) [1]. Overview of European and some others biorefineries is presented in report [5].

The most developed phase III biorefineries [1] are able to produce variety of energy and chemicals from various types of biomass. This will allow greater flexibility of the refinery on the market. They are developing four biorefinery systems based on mixed lignocellulosic feedstock, whole crop (grain and straw), green biorefinery and two platform biorefinery (combine sugar platform with thermochemical syngas platform). Green biorefinery process wet green biomass (green grass, lucerne, algae, etc.) which is separated green juice and fiber rich press cake [1, 6]. These are further utilized to many products as aminoacids, organic acids, dyes, press cake to fodder, insulation materials, and for combustion to produce energy [7-8].

Despite its high volume, fuel is a low value product. As a result, the return on investment in biofuel-only operations presents a significant barrier to realizing the biorefinery’s economic goal [9]. Biorefinery integrating biofuels and chemicals offers a much higher return on investment and meets its energy and economic goals simultaneously.

3. BIOMASS TYPES

There are several types of biomass which have to be treated in specific way to produce materials, chemicals and energy. Many biomass feedstocks are seasonal products, wood lignocelluloses could be an exception. Green biomass cannot be stored. Main biomass types with individual examples and selected references on their utilisation are presented in Table 1.

Table 1. Biomass types

Biomass type	Examples	References
Lignocellulose	Wood	[10-15]
	Plant lignocelulose	[11, 16]
Oilseed crops	Soybean, rapeseed	[17-18]
Sugar crops	Sugar beet, sugar cane	[19-21]
Starch crops	Corn, wheat	[22-24]
Green biomass	Grass, lucerne, clover, etc.	[6, 25-27]
Aquatic cultures	Algae, water weed, water hyacinth, etc.	[28-30]
	Marine algae	[31-32]
Biowastes	Agricultural wastes and by-products	[10, 33-35]
	Straw, stover	[34, 36-37]
	Urban and domestic wastes	[38]
	Bio-sludge	[39-42]
	Waste waters with organics	[43-45]
	Used plant oils and animal fats	[46-47]

Besides classical biomass types should be stressed importance of biomass based on aquatic cultures and biowastes. The advantages of using microalgae to produce biofuels are their continuous production, simple cell division cycle, acquisition of organic compounds through photosynthesis, tolerance to varying environmental conditions, use of waste or brackish water, use of land not used for agriculture and, when subjected to physical and chemical stress, they can be induced to produce high concentrations of specific compounds [29]. In addition, the application of microalgae for biofuels helps reduce carbon dioxide, the main greenhouse gas, thus reducing climate change. Biowastes are available in huge amounts and their utilisation will help in their disposal and at the same time useful fuels and chemicals can be produced.

4. BIOMASS CONVERSION PROCESSES

A great variety of processes for conversion of biomass have been developed which are presented in Table 2. Direct combustion is the oldest way of using biomass. Biomass thermochemical conversion technologies such as pyrolysis and gasification are certainly not the most important options at present; combustion is responsible for over 97% of the world's bioenergy production. Direct combustion and co-firing with coal for electricity production from biomass has been found to be a promising method for the near future.

Table 2. Biomass conversion processes [1, 3]

		References
Thermochemical	Combustion	[3, 43]
	Pyrolysis	[48-52]
	Gasification	[15, 53-54]
	Liquefaction	[55-57]
	Torrefication	[54, 58]
Biochemical	Fermentation	[59-64]
	Enzymatic treatment of biomass	[16, 65-66]
Electrochemical		[44-45, 67-68]

The pyrolysis and direct liquefaction processes are sometimes confused with each other. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products [18]. In the case of liquefaction, feedstock macro-molecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights. With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase. The differences in operating conditions for liquefaction and pyrolysis are mainly in water content. Liquefaction works with feed containing water (no drying of feed is required) at lower temperature (525-600°C) and higher pressure (5-20 MPa) while pyrolysis requires lower water content in the feed higher temperature (650-800°C) and lower pressure (0.1-0.5 MPa) [18].

Liquefaction processes result in liquid product, which can be easily stored and transported and require lower process temperatures. Due to these advantages, it is becoming increasingly evident that liquid products offer more potential for the production of biobased products than gas products and this is reflected in the rapid development of these processes and the large amount of research in this area [56-57, 69-70].

Levulinic acid (LA) is a valuable platform chemical due to its particular chemistry – it has two highly reactive functional groups that allow a great number of synthetic transformations [9]. Advanced Biofine process [10] for production of LA will be described as an example. Lignocellulose feedstock of size 0.5 to 1 cm is mixed with recycled dilute sulphuric acid (1.5-3%, depending on feedstock). The Biofine Process consists of two distinct acid-catalysed stages that are operated to give optimal yields with a minimum of degradation products and tar formation. The first reactor is targeted towards the dominant, first order, acid hydrolysis of the carbohydrate polysaccharides to their soluble intermediates (e.g. hydroxymethylfurfural). This reaction is favoured by the use of a plug flow reactor, a temperature of 210-220 °C, and a pressure of 2.5 MPa. The rapid nature of the hydrolysis reaction means that a residence time of only 12 seconds is required.

The completely mixed conditions of the second reactor favour the first order reaction sequence leading to LA rather than higher-order tar-forming condensation reactions. Operating conditions are less severe of 190-200 °C and 1.4 MPa. A residence time in this reactor is approximately 20 minutes. furfural and other volatile products tend to be removed at this stage while the tarry mixture of LA and residues are passed to a gravity separator. From here, the insoluble mixture goes to a dehydration unit where the water and volatiles are boiled off. The heating of the mixture to boil off LA is carried out under reduced pressure and results in the tarry material being “cracked”, to give a bone-dry powdery substance (‘char’). The crude 75% levulinic acid product can be purified up to a purity of 98%. Sulfuric acid is recovered in the final recycle stage, allowing it to be reused in the system. The Biofine Process is entirely chemical and does not rely on the use of any form of micro-organism, as is the case in enzymatic hydrolysis and in conventional dilute/concentrated acid hydrolysis technologies.

5. BIOFUELS

First-generation biofuels refer to biofuels as ethanol and biodiesel made from sugar, starch, vegetable oils, or animal fats using conventional technology. They are produced from food crops such as grains, sugar beet and oilseeds are limited in their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth.

Second-generation biofuels produced from larger feedstocks from lignocellulosic materials include cereal straw, forest residues, bagasse, and purpose grown energy crops such as vegetative grasses and short-rotation forests. Low-cost crop and forest, wood process wastes, and the organic fraction of municipal solid wastes can all be used as lignocellulosic feedstocks. Biodiesel can be further upgraded by catalytical hydrodesulphurisation and hydrodeoxygenation in mixture with gas oil [71].

Third-generation biofuels are based on algae and aquatic cultures. Algal biodiesel has potential to become important biofuel [28].

Recent works have shown that butanol is a potential gasoline replacement that can also be blended in significant quantities with conventional diesel fuel [72]. These efforts have transitioned to research focused on the development of viable methods for the production of an array of oxygenated and fully saturated jet and diesel fuels from butanol.

6. CHEMICALS FROM BIOMASS

Nowadays, carbon-based products in the chemical industry are largely produced on the basis of crude oil. The change in raw materials in the chemical industry signifies not only a conversion from oil to renewable raw materials but also to natural gas and coal. For example, from raw materials used in German chemical industry presently 76 % is based on oil, gas and renewable raw materials are evenly balanced at about 11 % each and only 2 % is based on coal [2]. Present routs of production of organic chemicals and materials starts mostly at hydrocarbons. Quite different will be situation when biomass will be source of carbon. Platform bulk chemicals will be produced via fermentations, gasification, and pyrolysis or by direct liquefaction.

A biorefinery that supplements its manufacture of low value biofuels with high value biobased chemicals can enable efforts to reduce non-renewable fuel consumption while simultaneously providing the necessary financial incentive to stimulate expansion of the biorefining industry.

However, the choice of appropriate products for addition to the biorefinery's portfolio is challenged by a lack of broad-based conversion technology coupled with a great number of potential platform chemicals. In 2004, the US Department of Energy (DOE) addressed these challenges by describing a selection process for chemical products that combined identification of a small group of compounds derived from biorefinery carbohydrates with the research and technology needs required for their production [73].

The intent of the report was to catalyze research efforts to synthesize multiple members of this group, or, ideally, structures not yet on the list. There were selected 15 candidates for platform chemicals which can be used as intermediates for further syntheses. Out of these 15 chemicals 10 were organic acids. In the six years since DOE's original report, considerable progress has been made in the use of carbohydrates as starting materials for chemical production by fermentation. Bozell and Petersen [9] updated evaluation of potential target structures using similar selection methodology, and an overview of the technology developments that led to the inclusion of a given compound. Selected platform chemicals are listed in Table 3. This list provides a dynamic guide to technology development that could realize commercial success through the proper integration of biofuels with biobased products. Some other chemicals may increase their importance. For example butanol platform could be attractive as well [72]. Potential of individual platform chemicals as a primary biorefinery building blocks is discussed, e. g. in works [9, 73].

Table 3. Potential platform chemicals [9].

Ethanol
Furfural
Hydroxymethylfurfural (HMF)
Furandicarboxylic acid (FDCA)
Glycerol
Isoprene
Biohydrocarbons
Lactic acid
Succinic acid
Hydroxypropionic acid (HPA)
Levulinic acid
Sorbitol
Xylitol

A large number of white biotech products are already economically viable compared with their petrochemical equivalents, and it is believed that organic acids constitute a class of molecules with a great future [74-75]. Mixed carboxylate platform generated from organic wastes could be attractive for production of bioproducts [64]. Concentration of product in fermentation broth is not high and is usually in multicomponent mixture. Isolation and concentration of product is an important issue. In most mature chemical processes, about 60–80% of the process costs are due to separation steps.

Organic acids constitute a significant fraction of those compounds available in a minimum number of steps from biorefinery carbohydrate streams, and as such have received much attention as platform chemicals. Papers on fermentation production of selected organic acids and their separation are presented in Table 4.

7. SEPARATION PROCESSES FOR BIOREFINERY

Separation processes in current and future biorefinery are discusses by Huang et al. [128]. This paper presents a critical review of separation methods and technologies related to biorefining including pre-extraction of hemicellulose and other value-added chemicals, detoxification of fermentation hydrolyzates, and ethanol product separation and dehydration. Potential separation processes for future ethanol producing biorefineries were identified; extractive distillation with ionic liquids and hyperbranched polymers, adsorption with molecular sieve and bio-based adsorbents, nanofiltration, extractive fermentation, membrane pervaporation in bioreactors, and vacuum membrane distillation. They hold great promise for further investigation, development and application.

Biorefinery producing organic acids by fermentation route will require their separation. Overview of extractive separations of organic acids is presented in review papers [88, 129-132]. Further papers on separation of individual organic acids are shown in Table 4. New reactive extractants and solvents for organic acids and other compounds based on ionic liquids have great potential and will be discussed below.

Table 4. Fermentation production of selected organic acids and their separation. MBSE – membrane based solvent extraction, SIR – solvent impregnated resin

Acid	References	
	Fermentation	Separation
Lactic acid	[39, 60, 76-84]	Extraction: [85-88] Extraction by SIR: [89] Pertraction: [90-91] MBSE: [92] Adsorption: [8, 76, 93-96] Electrodialysis: [97-98]
Succinic acid	[23, 62, 99-103]	Extraction: [104] Adsorption: [104-105] Crystallization: [106]
Levulinic acid	[31, 103]	Extraction: [107-110] Adsorption: [111-112]
Butyric acid	[59, 61, 113-118]	Extraction: [113, 119-122] Extraction by SIR: [123] Pertraction: [113, 124-125] MBSE: [115, 126] Adsorption: [127]

Separation of solutions on molecular or colloidal level by membrane separations will be of importance. Removal of microorganisms from broth before separation is one option [133]. The use of nanofiltration to fractionate hot-water extracts of wood and wood hydrolysate was tested in paper [134]. Recirculation of water in biorefinery is important task which can be supported by membrane separations depending on character of pollutant. Palm oil mill effluent treatment by ultrafiltration was studied in paper [135] and recovery of high value protein from a corn ethanol process by ultrafiltration in paper [136].

Ionic liquids in separations

Ionic liquids (ILs) are composed of organic cations and either organic or inorganic anions that remain in liquid state over a wide temperature range, including room temperature. ILs are a new group of designer solvents of great interest which have recently been studied widely as potential “green solvents”, especially in chemical and biochemical syntheses [137-139]. A great advantage of ILs is their vapour pressure practically equal to zero as compared with widely used volatile organic solvents. Less information is available on solvent properties of ILs in extractive separations. The majority of works deals with ILs with imidazolium cations. A new promising group of ILs based on phosphonium cations was developed.

Potential of application of ionic liquids (ILs) in the biorefinery is discussed in papers [140-141]. ILs could be used in biorefinery in several ways. The discovery that ionic liquids can be used as non-derivatising cellulose solvents has lead to a huge body of work. Four general processing applications in lignocellulose processing arise from this. ILs can be used in cellulose regeneration, chemical modification, enzymatic hydrolysis, and chemical depolymerisation which is discussed in these references.

Extractive separations by ILs

Potential of application of ionic liquids (ILs) in extractive separations is great [131-132, 142]. ILs, especially phosphonium ones, extracts more effectively organic acids than classical extractants, e.g. trioctylamine as shown in papers [86-87, 121] and in Fig. 1. Structure of cation and especially of anion influences much extractive properties of ILs [86, 132]. Three processes with application of ILs will be discussed.

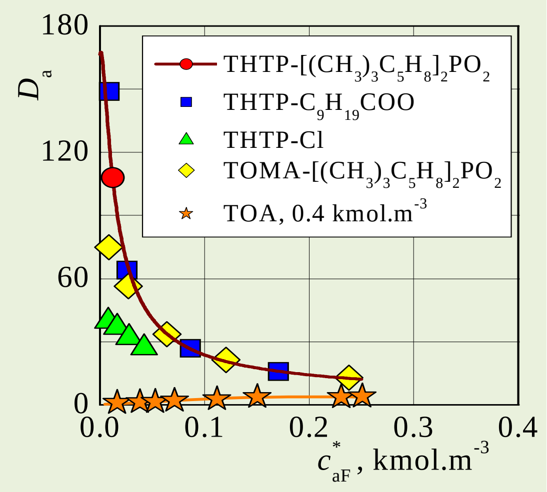

Fig. 1. Concentration dependence of the distribution coefficient of butyric acid for different extractants. THTP – ILs with trihexylhexadecylphosphonium cation and different anions, TOMA – IL with trioctylmethylammonium cation, TOA –trioctylamine

Extraction of butyric acid to SIR

The first process, extraction of butyric acid (BA) into solvent impregnated resins (SIR) with new ammonium IL [123]. Kinetics of extraction has been found fast and polymeric support did not influenced extraction mechanism and capacity. SIR impregnated with IL solution in dodecane exhibit faster extraction kinetics with lower saturation times compared to SIR with pure IL, what can be attributed to lower viscosity of the solvent with diluent. The kinetics of extraction of BA into SIRs with a mean particle diameter of 660 μm was fast and 95 % of their equilibrium saturation was achieved in less than 350 s which is one order of magnitude faster than achieved in adsorption into ion-exchange resins. This shows potential for application of SIRs in classical fixed bed column separations but also in hybrid systems.

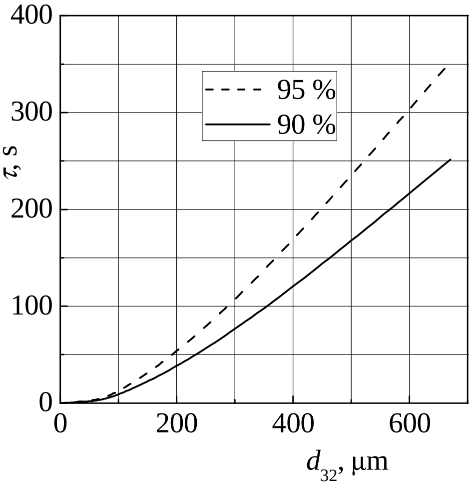

Fig. 2. Time needed to achieve 90% and 95% approach to equilibrium in extraction of BA to SIR impregnated by pure ammonium IL vs. the mean particle size. Lines are estimated from effective diffusion coefficient evaluated from experimental data on extraction kinetics.

Extraction of butanol

Tricyanomethide-based ionic liquids are used to extract 1-butanol from the fermentation broth after separating and recycling the microorganisms [143]. The 1-butanol-depleted aqueous phase is re-fed into the fermentation vessel, while 1-butanol is removed from the ionic liquid phase by distillation. The ionic liquids claimed for the process exhibit distribution coefficients D_{BuOH} between 3.4 and 4.7 and selectivity between 28 and 240, hence improving the performance when compared to both the hexafluorophosphate system discussed above and the often used oleyl alcohol (D_{BuOH} = 3.5 and α = 230). Extraction of butanol by phosphonium and ammonium ILs was studied in paper [144].

Extractive distillation of ethanol.

For fuel applications, ethanol essentially free of water has to be produced. Considering the low concentration achieved during fermentation, a huge separation effort has to be expected. In addition, an azeotrope is formed in this system, which cannot be further separated by simple distillation. Entrainers, which are fed in counter-current into the separation column, are hence chosen to interact selectively with the high-boiling component, in this case water, thus reducing its activity and increasing the relative volatility of ethanol. A high capacity is also important to keep the column diameter to a minimum. Entrainers enhance the separation factor, and the ionic liquid [C2mim][BF4] is more efficient than ethanediol if similar concentrations are used. The use of an ionic liquid entrainer reduces thus the number of plates and/or the recirculation ratio, leading to overall reduced separation costs [145]. As shown for the two examples of alcohol purification, ionic liquids may provide higher energy efficiency than other methods.

8. HYBRID PROCESSES IN BIOREFINERIES

Hybrid process where two processes, e.g., reaction and separation are carried out simultaneously *in one equipment* or in closely cooperating *parallel equipment* connected by a *circulation loop of an active component*, e.g., binding agent, extractant or catalyst which is typical for membrane reactors or bioreactors. Hybrid processes combining production and separation parts of technology in interactive way can provide synergistic improvements for reaction/separations processes. Moreover, also hybrid separations combining two separation processes could be advantageous. Hybrid processes with membranes proved to be a useful approach in designing more effective processes and systems. Some of them have been applied in the industry (membrane bioreactors in water treatment). It is a potential for a further progress in the development of new hybrid reaction-separation systems and some other configurations. Development and application of new binding agents as microparticulate adsorbents as well as solvents or binding agents based on ionic liquids can help in formulation of new hybrid processes with membranes. Some examples of hybrid systems studied are listed in Table 5.

Application of hybrid process utilizing microparticles of SIR impregnated with ammonium IL is possibly limited to recovery of micro-components as follows from simulation [146]. On other hand fast kinetics of extraction to SIRs with ammonium IL (Fig. 2) as shown above can allow design of hybrid system with extraction to SIR in packed column with particle size of about 200 to 300 μm with still excellent kinetics (Fig. 2).

Phosphonium IL Cyphos IL-104 (diluted in dodecane to decrease viscosity) is a good extractant of BA. A new promising process for regeneration of the solvents with IL by molecular distillation (MD) has been proposed. A simulation of a hybrid process combining fermentation, membrane based solvent extraction (MBSE) of butyric acid (BA) and on-line stripping of the loaded solvent by MD (Fig. 3) has been studied [149-150]. Main advantage of this process compared to classical stripping with alkali solution is that the product is obtained as free acid, not its salt. In simulation, own data on two stage regeneration by MD at 130 and 160°C and pressures of 13 and 2 kPa, and L/L equilibrium data in system BA-water-dodecane and BA-water-dodecane-IL have been used [149]. Results of the simulation have confirmed a great potential of the process with MD. Regeneration of ILs containing volatile components by MD could be generally useful approach not only in extractive separations but also in designing of the reactor systems.

Table 5. Hybrid processes considered in production or recovery of organic acids.
MBSS – membrane based solvent stripping, HF – hollow fiber.

Acid	Process	References
Lactic acid	Fermentation with adsorption lactate to particles of anion-exchanger	[96], in Situ [94]
	Fermentation combined with in Situ extraction to SIR particles	[89]
Butyric acid	Fermentation with in situ extraction coupled with stripping	[113]
	MBSE coupled with MBSS to recover BA from model fermentation broth	[126]
	Recovery of BA from fermentation broth by pertraction in HF contactor with ionic liquid	[125]
	Recovery of BA from fermentation broth by extraction to SIR microparticles with ionic liquid coupled with microfiltration and SIR regeneration	[146]
5-Methyl-2-pyrazine-carboxylic acid (MPCA)	MBSE coupled with MBSS in HF contactors to recover MPCA from biotechnology process	[130]
2,5-Furandicarboxylic acid (FDCA)	Chemical reactor where from fructose 5-hydroxymethylfurfural is formed extracted to the solvent and oxidized to FDCA.	[147]
Phenol	Removal of phenol from fermentation broth by extraction to SIR particles with ionic liquid	[89, 148]

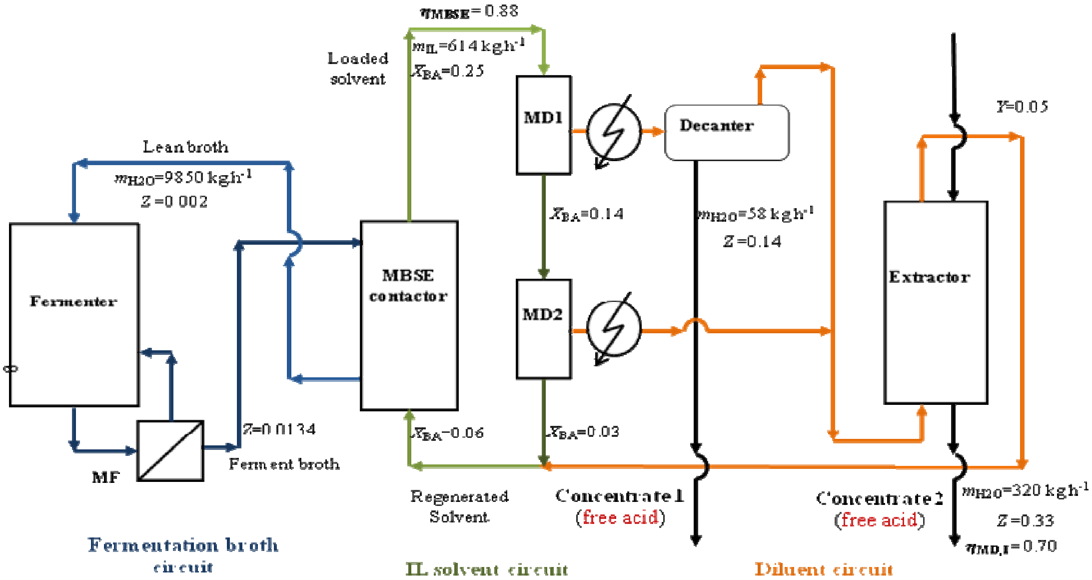

Fig. 3. Flowsheet of the hybrid process combining fermentation, MBSE and regeneration of the solvent by two stage MD.

9. BIOELECTROCHEMICAL SYSTEMS AND FUEL CELLS

Different bio-electrochemical systems (BES) are being examined to make wastewater treatment facilities net energy producers by capturing electrical energy directly from the wastewater. BES such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are engineered to capture electrical current produced by exoelectrogenic microbes that oxidize soluble organic matter present in wastewater [44, 67, 151]. These systems contain anodes where microbes grow and release electrons, and a cathode, where electrons are consumed to form different products. Exoelectrogenic bacteria transfer electrons to the anode of a BES either through direct contact (via highly conductive nanowires or membrane associated proteins) or by using soluble electron shuttles. Electrons flow from the anode through an external circuit and reduce O2 to H2O in an MFC, and protons to hydrogen in an MEC [152]. The open circuit potential of a BES anode is typically -300 mV at standard conditions, which is not sufficient to overcome the minimum potential for hydrogen evolution (-414 mV). As a result, hydrogen production from an MEC requires supplemental voltage from an external power source [152]. MFCs have been used to generate electricity from a variety of wastewaters including brewery, chocolate, food processing, meat packing, and paper recycling wastewaters, etc. as discussed in papers [44-45]. Hydrogen production using the effluent from cellulose fermentation in a well buffered medium with a high solution conductivity was 0.96 - 0.16 L/L-day, with an overall energy recovery of 220±30 % based on the energy value of the hydrogen compared to the electrical energy input [153].

Improving biofuel and chemicals yields and water reuse are two important issues in the further development of biorefineries [68]. The potential advantages of this alternative scheme in a biorefinery include minimization of heat loss and generation of a higher-value product: electricity (in MFC) or hydrogen (MEC). The need for 5–15 litres of water per litre of ethanol can be reduced significantly via recycling of water after MEC treatment. Removal of inhibitory byproducts such as furans, phenolics, and acetate in MFC/MECs to generate energy, thus, has dual advantages: improvements in energy efficiency and ability to recycle water. Conversion of the sugar and lignin degradation products to hydrogen is synergistic with biorefinery hydrogen requirements for upgrading Fischer-Tropsch liquids and other byproducts to high-octane fuels and/or high-value products. Potential process alternatives utilizing MECs in biorefineries are capable of improving energy efficiency by up to 30% [68].

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