Biorefinery

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1. Theme description

Many efforts have been made to move from today's fossil based economy to a more sustainable economy based on biomass. The reasons can be summarized as follow:

- the need to develop an environmentally, economically and socially sustainable global economy,
- the anticipation that oil, gas, coal and phosphorus will reach peak production in the not too distant future and that prices will climb,
- the desire of many countries to reduce an over dependency on fossil fuel imports, so the need for countries to diversify their energy sources,
- the global issue of climate change and the need to reduce atmospheric greenhouse gases (GHG) emissions.

Current global bio-based chemical and polymer production (excluding biofuels) is estimated to be around 50 million tonnes [1]. Examples of bio-based chemicals include non-food starch, cellulose fibres and cellulose derivatives, tall oils, fatty acids and fermentation products such as ethanol and citric acid. However, the majority of organic chemicals and polymers are still derived from fossil based feedstocks, predominantly oil and gas.

Recently, the consumer demand for environmentally friendly products, the population growth and limited supplies of nonrenewable resources have opened new opportunities for biobased chemicals and polymers.

Bio-based goods can be produced in single product processes or in an integrated biorefinery processes producing both biobased products and secondary energy carriers (fuels, power, heat), in analogy with oil refineries [2], [3].

Actually, the main driver for the development and implementation of biorefinery processes is the transportation sector. Significant amounts of renewable fuels are necessary in the short and midterm to meet policy regulations both inand outside Europe.

A very promising approach to reduce biofuel production costs is to use so called biofuel-driven biorefineries for the coproduction of both value-added products (chemicals, materials, food, feed) and biofuels from biomass resources in a very efficient integrated approach.

From an overall point of view, a key factor in the realisation of a successful bio-based economy will be the development of biorefinery systems that are well integrated into the existing infrastructure.

At the global scale, the production of bio-based chemicals could generate US\$ 10-15 billion of revenue for the global chemical industry [3].



Figure 1 - Biorefinery system scheme [2]

Biorefineries can be classified mainly on the feedstocks used to produce bio-based goods (see figure 1). Major feedstocks are perennial grasses, starch crops (e.g. wheat and maize), sugar crops (e.g. beet and cane), lignocellulosic crops (e.g. managed forest, short rotation coppice, switchgrass), lignocellulosic residues (e.g. stover and straw), oil crops (e.g. palm and oilseed rape), aquatic biomass (e.g. algae and seaweeds), and organic residues (e.g. industrial, commercial and post consumer waste). These feedstocks can be processed in different unit of a biorefinery, called platforms. The platforms include single carbon molecules such as biogas and syngas, 5 and 6 carbon carbohydrates from starch, sucrose or cellulose; a mixed 5 and 6 carbon carbohydrates stream derived from hemicelluloses, lignin, oils (plant-based or algal), organic solutions from grasses, pyrolytic liquids. These primary platforms can be converted to wide range of marketable products using combinations of thermal, biological and chemical processes.

2. Biobased Platforms

2.1 Biogas Platform

Actually, biogas production is mainly based on the anaerobic digestion (see figure 2) of "high moisture content biomass" such as manure, waste streams from food processing plants or waste from municipal effluent treatment systems. Biogas production from energy crops will also increase and will have to be based on a wide range of crops that are grown in versatile, sustainable crop rotations. Biogas production can be part of sustainable biofuels-based biorefineries as it can derive value from wet streams. This value can be increased by optimizing methane yield and economic efficiency of biogas production [4] and deriving nutrient value from the digestate streams [5].



2.2 Sugar Platform

Sugar platforms can implements processes to degrade sucrose in glucose or to hydrolyse starch or cellulose in glucose. Glucose serves as feedstock for fermentation processes to give a variety of important chemical building blocks.

The hydrolysis of hemicelluloses and then the fermentation of these resulted carbohydrate streams can in theory produce the same products as six carbon sugar streams; however, technical, biological and economic barriers need to be overcome before these opportunities can be exploited. Chemical manipulation of these streams can provide a range of useful molecules (see figure 3).

Indeed, by selective dehydration, hydrogenation and oxidation reactions it is possible to obtain useful products, such as: sorbitol, furfural, glucaric acid, hydroxymethylfurfural (HMF), and levulinic acid. Over 1 million tonnes of sorbitol is produced per year as a food ingredient, personal care ingredient (e.g. toothpaste), and for industrial use [6], [7].



Figure 3 – Sugar platform scheme [2]

2.3 Vegetable Oil Platform

Global oil production in 2009 amounted to 7.7 million tones of fatty acids and 2.0 million tonnes of fatty alcohols [8]. The majority of fatty acid derivatives are used as surface active agents in soaps, detergents and personal care products [9].

Major sources for these oils are coconut, palm and palm kernel oil, which are rich in C12–C18 saturated and monounsaturated fatty acids. Rapeseed oil, high in oleic acid, is a favoured source for biolubricants. Commercialized bifunctional building blocks for bio-based plastics include sebacic acid and 11aminoundecanoic acid, both from castor oil, and azelaic acid derived from oleic acid. Dimerized fatty acids are primarily used for polyamide resins and polyamide hot melt adhesives. Biodiesel production has increased significantly in recent years with a large percentage being derived from palm, rapeseed and soy oils. In 2009 biodiesel production was around 14 million tonnes; this quantity of biodiesel co-produces around 1.4 million tonnes of glycerol.

Glycerol is an important co-product of fatty acid/alcohol production. The glycerol market demand in 2009 was 1.8 million tonnes [8]. Glycerol is also an important co-product of fatty acid methyl ester (FAME) biodiesel production. It can be purified and sold for a variety of uses [5].

2.4 Algae Oil Platform

Algae biomass can be a sustainable renewable resource for chemicals and energy. The major advantages of using microalgae as renewable resource are:

- Compared to plants algae have a higher productivity. This is mostly due to the fact that the entire biomass can be used in contrast to plants which have roots, stems and leafs. For example, the oil productivity per land surface can be up to 10 times higher than palm oil.
- Microalgae can be cultivated in seawater or brackish water on non-arable land, and do not compete for resources with conventional agriculture.
- The essential elements for growth are sunlight, water, CO₂ (a greenhouse gas), and inorganic nutrients such as nitrogen and phosphorous which can be found in residual streams.
- The biomass can be harvested during all seasons and is homogenous and free of lignocellulose.

Microalgae can contain a high protein content, with all 20 amino acids present. Carbohydrates are also present and some species are rich in storage and functional lipids. Other valuable compounds include: pigments, antioxidants, fatty acids, vitamins, anti-fungal, -microbial, -viral toxins, and sterols.

2.5 Lignin Platform

Until now, the lignin platforms are mainly based on lignosulfonates (see figure 4). These sulfonates are separated from acid sulfite pulping and are used in a wide range of lower value applications. Major end-use markets include construction, mining, animal feeds and agriculture uses.



Figure 4 – Lignin platform scheme [2]

Besides lignosulfonates, Kraft lignin is produced as commercial product at about 60kton/y. New extraction technologies, will lead to an increase in Kraft lignin production at the mill side for use as external energy source and for the production of value added applications [10].

The production of bioethanol from lignocellulosic feedstocks could result in new forms of higher quality lignin becoming available for chemical applications. The production of more value added chemicals from lignin (e.g. resins, composites and polymers, aromatic compounds, carbon fibres) is viewed as a medium to long term opportunity which depends on the quality and functionality of the lignin that can be obtained [11].

3. Opportunities

The opportunities for chemical and polymer production from biomass has been comprehensively assessed in several reports and papers [12], [13], [14], [15], [16], [17].



Figure 5 – Plastics Europe anticipated biopolymer production capacity (in tonnes/year) by 2015

Bio-PE:Biorenewable Polyethylene; **Bio-PET**: Biorenewable Polyethylene Thereftalate; **PLA**: Polylactic Acid; **PHA**:

Polyhydroxy Alchanoates; **BP**: Biodegradable Polyesters; **BSB**: Biodegradable Starch Blends; **Bio-PVC**: Biorenewable Polyvinyl chloride ; **RC**: Regenerated Cellulose; **PLA-B**: Polylactic Acid Blends; **Bio-PP**: Biorenewable Polypropylene; **Bio-PC**: Biorenewable Polycarbonate.

An international study¹⁴ found that with favourable market conditions the production of bulk chemicals from renewable resources could reach 113 million tonnes by 2050, representing 38% of all organic chemical production. Under more conservative market conditions the market could still be a significant 26 million tonnes representing 17.5% of organic chemical production (see figure 5).

Currently, commercialised bio-polymers (i.e. PLA, PHA, thermoplastic starch) are demonstrating strong market growth. Market analysis shows growth per annum to be in the 10-30% range [18], [19], [20].

Bio-based polymer markets are dominated by biodegradable food packaging and food service applications. It can be rationalised that the production of more stable, stronger and longer lasting biopolymers will lead to CO_2 being sequestered for longer periods and leads to recycling rather than composting where the carbon is released very quickly without any energy benefits⁵.

Between the most important players in biorefining, there are Novamont (Italy) leader on biodegradable bags based on Mater-Bi (bioplastic derived from thermoplastic starch); NatureWorks (U.S.A) leader in the PolyLacticAcid production (a biobased plastic used also for the production of biodegradable bottles) and Biochemtex belongs to M&G Chemicals Group (Italy) specialized in the production of bioethanol of second generation. [1] Higson, A 2011. NNFCC. Estimate of chemicals and polymers from renewable resources. 2010. NNFCC. Estimate of fermentation products. 2010. Personal communication

[2] Kamm, B., P. Gruber, M. Kamm [ed.]. Biorefineries – Industrial Processes and Products. Weinheim : Wiley-VCH, 2006. ISBN-13 978-3-527-31027-2.

[3] World Economic Forum. The Future of Industrial Biorefineries. s.l. : World Economic Forum, 2010.

[4] Bauer A., Hrbek a, B. Amon, V. Kryvoruchko, V. Bodiroza, H.Wagentristl, W. Zollitsch, B. Liebmanne, M. Pfeffere, A. Friedle, T. Amon. 2007. Potential of biogas production in sustainable biorefinery concepts. (<u>http://www.nas.boku.ac.at/uploads/media/0D7.1_Berlin.pdf</u>).

[5] De Jong E., Higson A., Walsh P., Wellisch M., 2011, Biobased Chemicals Value Added Products from Biorefineries, IEA Bioenergy, Task 42 Biorefinery.

[6] Vlachos, D.G. J. G. Chen,R. J. Gorte, G.W. Huber, M. Tsapatsis. Catalysis Center for Energy Innovation for Biomass Processing: Research Strategies and Goals. Catal Lett (2010) 140:77–84

[7] ERRMA. EU-Public/PrivateInnovation Partnership "Building the Bio-economy by 2020". 2011.

[8] ICIS Chemical Business. Soaps & Detergents Oleochemicals. ICIS Chemical Business. 2010, January 25-February 7.

[9] Taylor D.C., Smith M.A., Fobert P, Mietkiewska E, Weselake R.J. 2011 Plant systems – Metabolic engineering of higher plants to produce bio-industrial oils. In: Murray Moo-Young (ed.), Comprehensive Biotechnology, Second Edition, volume 4, pp. 67–85. Elsevier.

[10] Öhman, F., Theliander, H., Tomani, P., Axegard, P. 2009. A method for separating lignin from black liquor, a lignin product, and use of a lignin product for the production of fuels or materials. W0104995 [11] Zakzeski, J., P.C.A. Bruijnincx, A.L. Jongerius, and B.M. Weckhuysen. The catalytic valorization of lignin for the production of renewable chemicals. Chemical Reviews 110 (6), 3552-3599.

[12] Shen, L., Haufe, J., Patel, M.K. Product overview and market projection of emerging bio-based plastics. s.l. : Utrecht Univeristy, 2009.

[13] U.S. Department of Agriculture. U.S. Biobased Products, Market Potential and Projections Through 2025. s.l. : U.S. Department of Agriculture, 2008.

[14] Patel, M., Crank, M., Dornburg, V., Hermann, B., Roes, L., Hüsing, B., van Overbeek, L., Terragni, F., Recchia, E. 2006. Medium and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources – The BREW Project. (http://www.projects.science.uu.nl/brew/programme.html)

[15] Bozell, J.J., G.R. Petersen. 2010.Technology development for the production of biobased products from biorefinery carbohydrates – the US Department of Energy's "Top 10" revisited. Green Chemistry.12, 539-554.

[16] Werpy, T, G. Petersen. 2004. Top Value Added Chemicals from Biomass, Volume 1 Results of Screening for Potential Candidates from Sugars and Synthesis Gas. (http://www1.eere.energy.gov/biomass/pdfs/35523.pdf)

[17] Nexant ChemSystems. Biochemical Opportunities in the Uniten Kingdom. York : NNFCC, 2008.

[18] Pira. The Future of Bioplastics for Packaging to 2020. s.l. : Pira, 2010.

[19]SRI Consulting. Biodegradable Polymers. [Online][Cited:17Januaryhttp://www.sriconsulting.com/CEH/Public/Reports/580.0280.

[20] Helmut Kaiser Consultancy. Bioplastics Market Worldwide 2007-2025. [Online] 2009. [Cited: 17 January 2011.] http://www.hkc22.com/bioplastics.html.