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Integrative Biorefinery Technologies for Efficient Converting of Lignocellulosic Biomasses to Biofuels, Valorized Chemicals and Materials

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Abstract: On the basis of Thailand as an agricultural-based country, several types and numerous amounts of agricultural feedstocks (i.e. lignocellulosic biomass, oily plants) are available. The efficient conversion of these feedstocks to high value-added products including biofuels and expensive chemicals (i.e. biomaterial, acid, furan, aromatic and phenolic compounds) would strengthen the national energy security as well as promote the capability of local industrial section. The concept for converting these agricultural resources to biofuels, chemicals and biomaterials is technically known as "biorefinery" process, which is expected to be the platform technology for global sustainable development in the near future. This article provides the technological overview of biorefinery process with an aim to maximize the benefit from biomass conversion to value-added products.

Keywords: Biomass; Biorefinery; Cellulose; Hemicelluloses; Lignin.

1. Introduction

The need for sustainable energy sources, the strong rise and fluctuation in oil price, and increasing public environmental concerns lead to an increasing interest in biorefineries during the past decade. A number of process designs have been investigated for improvement in economic feasibility of different biorefineries models by valorisation of process by-products for co-production of "fuels, chemicals, and materials" [1]. In conventional petroleum refinery, where most of the feedstock is used for production of bulk fuels and low value products, only a small feedstock stream is used for production of a range of co-products which can provide significantly large revenues for profitability of the whole refinery process [2]. In analogy to refinery, R&D in biorefinery has been increasingly focused on integrated process design for maximized valorization of fractionated biomass streams for fuels and spectrum of co-products in response to specific demands from local industries (Fig. 1). Fractionation of lignocelluloses for separation of cellulose, hemicelluloses, and lignin is thus a key issue for current R&D. Various model processes have been assessed as a strategy for maximized utilisation of separated lignocellulosic components for specific purposes [3]. Such integrated biorefineries can produce biofuels, syngas, feed, and a spectrum of commodity and specialty chemicals in addition to possible energy products and lignin derivatives as functionalized biomaterials [4]. Diversity of products and processing technologies can provide various combinations so as to suit different needs to geographical location, economy of scale, and national priorities. This leads to improved economics from co-products with environmental benefits from the overall zero-waste process in a well-designed integrated biorefinery process.

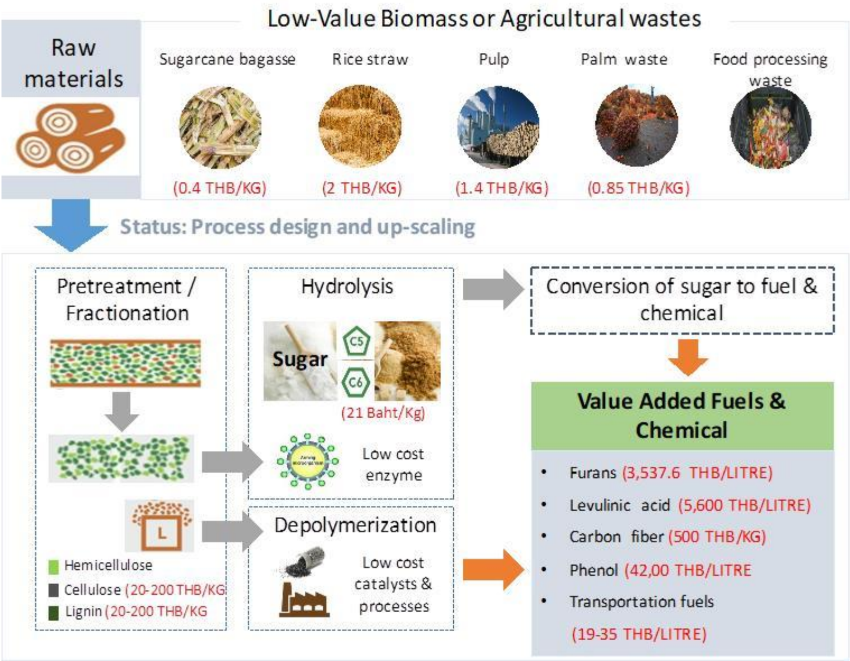

Figure 1. Potential value-added products from local low-cost biomasses.

Table 1. Effects of the different pretreatments on the physical/chemical composition and structure of lignocelluloses [8].

	Increase accessable surface area	**Decrystalization cellulose**	**Solubilisation hemicellulose**	**Solubilisation lignin**	**Formation furfural**	**Alteration lignin structure**
Mechanical	+	+				
ST/SE	+		+	-	+	+
LHW (batch)	+	ND	+	-	-	-
LHW (flowthrough)	+	ND	+	+/-	-	-
Acid	+		+	-	+	+
Alkali	+		-	+/-	-	+
Oxidative	+	ND		+/-	-	+
Thermal + acid	+	ND	+	+/-	+	+
Thermal + alkali (lime)	+	ND	-	+/-	-	+
Thermal + oxidative	+	ND	-	+/-	-	+
Thermal + alkali + oxidative	+	ND	-	+/-	-	+
Ammonia (AFEX)	+	+	-	+	-	+
CO_2 explosion	+		+			

+ = major effect; - = minor effect; ND = not determined

2. Lignocellulose structure and composition

Lignocellulosic biomass is the non-starch, fibrous part of plant material with key advantages from its renewability and abundance. Lignocellulosic materials consist of mainly three different types of polymers *i.e.* cellulose, hemicelluloses, and lignin, which are associated with each other in addition to low amounts of acids, salts, and minerals. The percentage compositions of these constituents vary but cellulose is commonly the largest fraction, comprising of 30–50% while hemicellulose contributes 20–40% and lignin presents 15–25% of the total dry matter.

Cellulose

Cellulose is generally the largest fraction in lignocellulosic biomass. Cellulose is a crystalline glucose polymer arranged in long straight chains, consisting of β-1,4 linkages of D-glucopyranose monomers, with an average molecular weight of around 100,000 [5]. The length of a cellulose chain is given by the degree of polymerization (DP). Hydrogen bonds in structure help maintain and support the flat, linear conformation of the chain. The top and bottom of the cellulose chains are hydrophobic whereas the sides of the cellulose chains are hydrophilic [6]. Unlike cellulose, starches are amorphous glucose polymers (also called glucan) that have α-1,4-glycoside linkages (amylose and amylopectin form) and also have a large amount of α-1,6 glycoside linkages (amylopectin form). Starches are commonly found in the vegetable kingdom (e.g. corn, rice, wheat, beans, and potatoes). Human and animal enzyme systems can easily digest starches. In starch hydrolysis, alpha-amylase and gluco-amylase enzymes are mainly used. In nature, cellulose is much more abundant than starch. Furthermore, cellulosic feedstocks tend to be more productive and require less energy to produce than starch crops. However, technologies for the hydrolysis of the cellulosic feedstocks are currently not commercially developed at a scale approaching for starch.

Hemicellulose

The hemicellulose fraction of lignocellulosic biomass is a complex amorphous polymer, which consist of branched structures and vary with biomasses. Within the plant, hemicellulose is connected to lignin by covalent links and is fixed in the fiber structure. The backbone chain generally consists of pentoses (e.g. xylan), or other units of mannose and glucose (mannans or glucomannans) or galactose units (galactans) [5]. Hemicellulose is bound to lignin, and cellulose strands are interlaced with hemicellulose. Hemicellulose is relatively easy to hydrolyze because of its branched and amorphous nature. Its hydrolysis starts at a temperature lower than that of cellulose, which renders it soluble at elevated temperatures [7]. The presence of acid highly improves the solubility of hemicellulose in water.

Lignin

Lignin, a large polyaromatic compound, is another major component of biomass composed of methoxylated phenylpropane structures, such as coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol. Lignin surrounds the hemicellulose and cellulose fractions. Lignin can be removed from biomass to isolate the carbohydrate fraction through depolymerization/solubilization in alkaline-alcohol solutions. This is known as the Kraft process in paper pulping [6]. Lignin can be used as a feedstock in the production of valuable chemicals such as phenolic resins.

3. Biomass conversion technologies via integrative biorefinery concept

Lignocellulose pretreatment/fractionation

In sugar platform biorefinery, pretreatment refers to a step on modification of lignocellulosic biomass structure for increasing its digestibility in the subsequent enzymatic hydrolysis step into sugars for further conversion. The factors that have been identified to affect the hydrolysis of cellulose include porosity (accessible surface area) of the materials, cellulose fiber crystallinity, lignin and cellulose contents, and degree of polymerisation. The presence of lignin and hemicellulose makes the access of cellulase enzymes to cellulose difficult, thus reducing the efficiency of hydrolysis. Lignin can also interfere with the hydrolysis by irreversibly binding to hydrolytic enzymes. The purpose of the pretreatment step is thus to remove lignin and hemicellulose, reduce crystallinity and increase the porosity of the materials. In general, the pretreatment must meet the following requirements: (1) improve the formation of sugars or the ability to subsequently form sugars by the downstream enzymatic hydrolysis; (2) avoid the degradation or loss of carbohydrate; (3) avoid the formation of by-products inhibitory to the subsequent enzymatic or conversion processes; and (4) be cost-effective to make the process viable. Implementation of optimal pretreatment step will result in improved total yield of monomeric sugars in the hydrolysis step and the production of target fermentation products. Physical, chemical, thermal, and biological approaches have been studied for efficient pretreatment of lignocellulosic biomass. Each pretreatment technology has different advantages and disadvantages in terms of efficiency and economics, and is suitable for different biomass. They also possess different effects on the cellulose, hemicelluloses and lignin, the three main components of lignocellulosic biomass. Among various of pretreatment technologies, steam pretreatment, lime pretreatment, liquid hot water, and ammonia based pretreatments are the promising ones according to the economic effectiveness and the effects of the pretreatments [8] (Table 1).

In the current context of the lignocellulosic biorefinery, pretreatment refers almost exclusively to processes that provide disruption of lignocellulose's biopolymeric matrix sufficient to improve access to polysaccharides and simplifying their subsequent enzymatic hydrolysis. High selectivity (i.e., complete separation of cellulose, hemicellulose and lignin) is not a prerequisite, and most pretreatment technologies considered commercially viable within the strict economic constraints of ethanol production [9]. However, biorefineries focusing only on ethanol or related biofuel production have limited opportunities for profitability. Next generation biorefineries will follow the model of the petrochemical industry by integrating low value fuel with the production of high value chemicals derived from each of the primary components of lignocellulose (Fig. 2). Accordingly, pretreatment processes will require a significantly greater emphasis on the yield and purity of the resulting individual biorefinery process streams used for the production of chemicals. While more selective processes may result in higher costs, the ability to incorporate high value chemical products in an integrated operation will provide a revenue stream able to pay for increased selectivity at the front end [10]. Compared to the basic pretreatment, fractionation processes optimized for an integrated biorefinery will exhibit selective separation of each component of a biomass feedstock, offer easy access to and isolation of the components after separation, allow recovery of each component in high yield, give process components ready for conversion to chemicals with minimal purification and will demonstrate economic viability. This process can be performed using various strategies based on different pretreatment technologies for a specific biomass with the focus on selectivity, accessibility, recoverability, and utility as well as process economics as the main criteria. Extensive research on fractionation of various lignocelulosic feedstocks is thus considered as an important platform for development of an economically viable integrated biorefinery process.

Valorization of lignocellulosic components

Cellulose conversion and valorization

Cellulosic fraction is considered the major streams from lignocellulose fractionation process and serves as the most abundant feedstock in biorefineries. Glucose is the major product from degradation of cellulose, which is commonly used for production of biofuel i.e. ethanol as the main bulk product and can also be considered as a feedstock for conversion to a range of commodity and specialty chemicals, fuels, and polymers by fermentation, enzymatic, and catalytic processes.

Hemicellulose valorization

Hemicelluloses are heterogeneous polysaccharides which typically account for up to 30% of the lignocellulosic biomass materials. Most biomass hemicelluloses consist of either xylan or glucomannan backbones with acetyl group, arabinose, galactose, and methyl glucuronic acid on the side chains. Compared to cellulose and lignin, hemicelluloses are generally much less stable and are prone to degradation during chemical or thermal treatments. For this reason, hemicellulose has been presented as an underutilized biomass component in most biomass conversion processes. Sugars, particularly pentoses from hemicelluloses, can be converted through fermentation and chemical processes to a range of co-products including ethanol, butanol, butanediol, xylooligosaccharides, xylitol, furans, levulinic acid, and surface active agents (alkylpolyxylosides). One interesting conversion pathway is to produce acrylic acid from hemicelluloses sugar via lactic acid, which can be produced by fermentation or the recently reported catalytic conversion, which is a competitive synthesis route for lactic acid from biomass pentoses and glucose. Further conversion of lactic acid to diverse chemical products has been studied, including dehydration to acrylc acid and acrylate, which are primary materials for industrial polymers. Hemicelluloses can also be isolated in oligomeric form from the pre-hydrolysis liquor using ethanol precipitation. The isolated hemicelluloses are used for production of cationic hemicelluloses used as paper making additives, which could substitute for starch or other petrochemical-based cationic polymers and semi-bleached hemicelluloses used as wet end additives to increase the basis weight of paper products. Preparation of hemicelluloses particles by supercritical processing for medical and cosmetic applications has also been reported [11]. These works thus provide a wide range of potential value-added co-products for application in chemical, material, and food industries which can be obtained from the fractionated hemicelluloses stream in pulp processing.

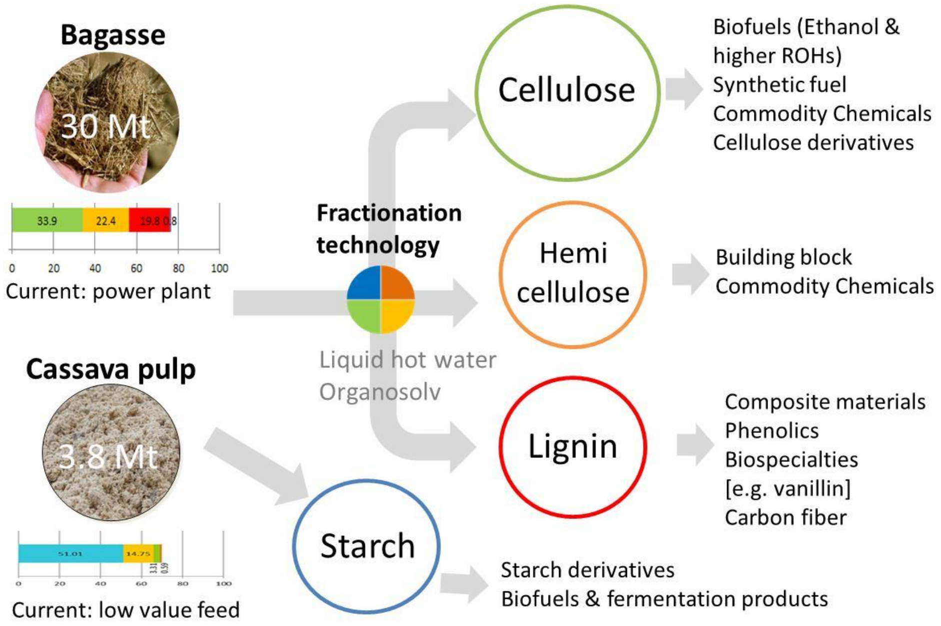

Figure 2. Bioresources as renewable starting materials.

Fractionation technology and biomass sources have a major impact on the composition of hemicelluloses prehydrolysate fraction, which in turn governs their potential on product development. Xylose and xylooligomers are the main sugar compounds. Furfurals are produced from xylose dehydration and acetic acid is mainly derived from acetyl groups on the xylan backbone, in addition to some phenolic compounds dissolved in the prehydrolysate. The potential products that can be derived from these compounds have been extensively discussed [12].

Lignin valorization

Lignin is a ubiquitous component in almost all plant biomass. Large quantities of lignin are produced annually as a waste product from chemical pulping processes. The bulk of the industrial lignin is currently produced from kraft pulping process as kraft lignin while some of the lignin is derived from sulfite pulping process as lignosulphonates. Most of the industrial lignin is burned as a low cost fuel in the chemical recovery boiler, providing energy in the manufacturing process. Developing specialty and commodity products from lignin has been an important R&D topic in biorefineries.

A number of thermochemical conversion methods have been proposed to depolymerise lignin to low molecular weight compounds. Among them, base-catalysed depolymerisation, pyrolysis (lignin to liquid, LtL), and Lewis acid-catalysed solvolysis have received a considerable amount of attention. Phenolic compounds derived from depolymerisation of lignin can be readily used for replacing phenol from petroleum in phenolic resin manufacturing. Oxidative ring degradations lead to aromatic ring cleavage reactions and produce carboxylic acids as the final products, of which muconic acid and its derivatives are the predominant products. Muconic acid is a precursor of adipic acid, a key intermediate for production of nylon, which has attracted an increasing interest for alternative production from renewable biomass by catalysis. Peroxyacid-based reactions are also considered a potential method for converting biomass lignin to phenolic compound in high yield. These alternative applications for production of aromatics and aliphatic chemicals from lignin or utilization of lignin in crude or oligomeric forms can significantly improve the economics and environmental sustainability of biorefinery process in overall.

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