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Overview of Biomass Conversion Processes and Separation and Purification Technologies in Biorefineries

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1.1 Introduction

There has been an increasing interest in conversion of biomass to biofuels, energy and chemicals due to increase in global demand, price and decrease in potential availability of crude oil, the need for energy independence and energy security, and the need for reduction in greenhouse gases emission from fossil fuel contributing to global climate change, and so forth.

Biomass feedstock suitable for producing biofuels, energy and co-products can be starchy biomass (e.g., corn/wheat kernel, cassava), sugarcane and sugar beet, ligocellulosic biomass including agricultural residues (e.g., corn stover, crop residues such as wheat straw and barley straw, and sugar cane bagasse), forest wastes, fast-growing trees such as hybrid poplar and willow, fast-growing herbaceous crops such as switchgrass and alfalfa, oily plants such as soybean and rapeseed, microalgae, waste cooking oil, animal manure, as well as municipal solid waste. The total amount of biomass feedstock available is huge. In the United States, based on the estimation by U.S. Department of Energy (U.S. Department of Energy 2011), total potential biomass resource is about 258 (baseline)–340 (high-yield scenario) million dry tons in 2012. Potential supplies at a forest roadside or farmgate price of \$60 per dry ton range from 602 to 1009 million dry tons by 2022 and from about 767 to 1305 million dry tons by 2030, depending on the assumptions for energy crop productivity (1% to 4% annual increase over current yields). This estimate excludes resources that are currently being used, such as corn grain and woody biomass used in the forest products industry. Worldwide, the biomass availability is also significantly high of the order of 5.0 billion tons per year (Bauen *et al*. 2009; U.S. Department of Energy 2011).

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Biofuels made from starchy crops, sugar plants as well as vegetable oils are usually called first-generation biofuels; for example, bioethanol produced from maize, starch, or sugar via fermentation, biodiesel from soybean oil, rapeseed oil, palm oil, or other plant oil by transesterification. Biogas from anaerobic digestion of waste streams also belongs to the first-generation biofuels. As the first-generation biofuels produced from food crops competes with food production and supply, and biogas can only be produced in small quantities, the first-generation biofuels alone generally cannot meet our energy requirements. Biofuels such as cellulosic ethanol made from lignocellulosic biomass such as woody crops, fast-growing trees and herbaceous crops, agricultural residues and forestry waste are referred to as the second-generation biofuels. The focus for second-generation biofuels was primarily ethanol. Unlike the first-generation biofuels, the second-generation biofuels are based on non-food crops and other lignocellulosic biomass; it can also bring about significant reduction in greenhouse gas emissions as well as reduction in fossil fuel use. The third-generation biofuels are made from genetically modified energy crops that may be carbon-neutral, biofuels from algae, or biofuels directly produced from microorganisms or using advances in biochemistry. Fourth-generation biofuels have also been suggested, which are carbon negative—they consume more carbon than they generate during their entire life cycle. Examples of this could be carbon-fixing plants such as low input high-diversity perennial grasses (Tilman, Hill, and Lehman 2006).

A biorefinery is a facility to convert biomass to bioproducts including bioenergy (fuels, heat and power) and diverse array of co-products (including materials and chemicals) (Huang *et al*. 2008; Huang and Ramaswamy 2012). The biorefinery concept is similar to today's petroleum refinery, which produces multiple fuels and products from petroleum (http://www.nrel.gov/biomass/biorefinery.html). Biorefinery can be divided into two basic conversion platforms: biochemical conversions, and thermo-chemical conversions. A biorefinery can also be a combination of both biochemical and thermo-chemical conversion approaches. Biochemical conversions of biomass using enzymes and microorganisms (yeast and bacteria) are often referred to as "sugar-platform" conversions, where biomass is firstly pretreated and hydrolyzed to mono-sugars: glucose, xylose, arabinose, galactose, and mannose, and so forth. The mono-sugars are then fermented or digested to biofuels such as bioethanol and biobutanol, or chemicals such as lactic acid and succinic acid, depending on the biocatalysts used. Thermo-chemical conversion of biomass includes biomass combustion for heat and power, pyrolysis for bio-oil and biochar, hydrothermal liquefaction to bio-oils as major product, and biomass gasification to syngas. Syngas (mainly CO and H_2) from biomass gasification can be further synthesized into a wide range of different fuels and chemicals under different catalysts and operating conditions; biomass gasification or "syngas platform" represents the major thermo-chemical platform. In addition to these basic thermo-chemical conversions, there are a variety of other chemical conversion processes such as conversion of oil-containing biomass such as soybean and microalgae for biodiesel, and the conversion of building block chemicals such as lactic acid to its corresponding commodities, chemicals, polymers and materials.

This chapter provides an overview of the separation and purification technologies in biorefineries for producing bioproducts including biofuels, bioenergy, biochemicals and materials, with more emphasis on lignocelluose biorefineries.

1.2 Biochemical conversion biorefineries

In the biochemical conversion biorefineries or "sugar platforms," biomass is subjected to hydrolysis and saccharification and then the resulting sugars, including hexoses (glucose, mannose, and galactose) and pentoses (xylose, arabinose) are converted to biofuels such as ethanol and butanol, chemicals, and materials.

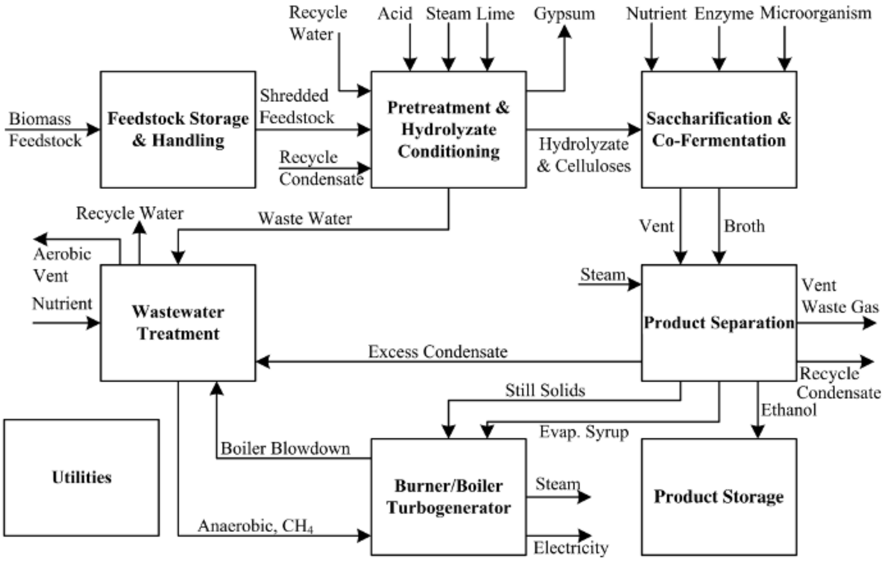

Figure 1.1 *Simplified process block diagram of basic lignocellulose to ethanol biorefinery (Aden et al. 2002; Huang et al. 2008)*

As an example, the basic process for conversion of cellulosic biomass to fuel ethanol is shown in Figure 1.1, which mainly consists of the following eight major process areas (Aden *et al*. 2002):

1. Feedstock handling including biomass storage and size reduction (shredding).
2. Pretreatment and hydrolyzate conditioning or detoxification. Here, the shredded biomass is pretreated with dilute sulfuric acid at a high temperature (using steam), and thus most of the hemicellulose is hydrolyzed to fermentable monosugars (mainly xylose, mannose, arabinose, and galactose) while glucan in the hemicellulose and a small fraction of the cellulose are converted to glucose. In addition, the hydrolysis reaction produces acetic acid liberated from acetate in biomass, furfural and hydroxymethyl furfural (HMF) from degradation of pentose and hexose sugars respectively. These compounds are inhibitory to the subsequent fermentation so, following the pretreatment, the prehydrolysys slurry is flashed to remove a portion of the acetic acid, and most of the furfural and HMF. The hydrolyzate, after being separated from the solids, is then overlimed to pH 10 by adding lime to remove the remaining inhibitors, followed by neutralization and precipitation of gypsum. After filtering out the gypsum, the detoxified hydrolyzate and the solids (cellulose) are sent to the saccharification and co-fermentation area. This step also solubilizes some of the lignin in the feedstock and make the cellulose accessible to subsequent enzymatic hydrolysis.
3. Saccharification and co-fermentation. The cellulose is biochemically hydrolyzed or saccharified to glucose by cellulase enzyme in the continuous hydrolysis tanks. The co-fermentation of the detoxified hydrolyzate slurry is carried out in anaerobic fermentation tanks in series using the microorganism *Zymomonas mobilis*. With several days of separate and combined saccharification and cofermentation, most of the cellulose and xylose are converted to ethanol.
4. Product separation and purification. Beer is firstly preconcentrated by distillation, followed by vapor-phase molecular sieve separation for ethanol dehydration. The postdistillation slurry from the

distillation bottom is separated into the solids and liquid. The liquid is then evaporated and separated into the concentrated syrup, and the condensed water is recycled in the process. The solids and the syrup obtained are sent to the combustor.

5. Wastewater treatment. Part of the evaporator condensate, together with the wastewater from pretreatment area, is treated by anaerobic digestion. The biogas (rich in methane) from anaerobic digestion is sent to the combustor for energy recovery. The treated water is recycled for use in the process.
6. Product storage.
7. Combustion of solids (lignin) for heat (steam) and power. The solids from distillation, the concentrated syrup from the evaporator, and biogas from anaerobic and aerobic digestion are combusted in a fluidized bed combustor to produce high-pressure steam for electricity production and process heat. Generally, the process produces excess steam that is converted to electricity by steam turbines for use in the plant and for sale to the grid.
8. Utilities.

This process involves a number of separation tasks as follows:

- removal of inhibitors from hydrolyzate prior to fermentation;
- liquid–solid separation such as separation of prehydrolyzate slurry and postdistillation slurry;
- ethanol recovery from beer by distillation and its dehydration using molecular sieve adsorption;
- water scrubbing of fermentation vents for recovering of the ethanol;
- water recovery by multiple effect evaporation;
- gas-solid (particles) separation from combustion flue gas.

The capital and operating costs of all the above separation processes account for a large fraction of the total capital and operation costs of the whole process.

The lignocellulose bioethanol process described above is only one case of “sugar-platform” biorefineries. Other bioconversion processes have similar steps in preparation of fermentable mono-sugars from biomass feedstock. In other words, in addition to bioethanol the biomass-derived mono-sugars including pentose and hexose can be fermented to other biofuels such as butanol, and biochemicals such as carboxylic acids (including succinic, fumaric, malic, itaconic, glutamic, lactic, 3-hydroxypropionic, citric, and butyric acids) (Yang *et al*. 2006), other chemicals (e.g., 1,3-propanediol), and materials, depending on the microorganism used. Among the carboxylic acids, succinic, fumaric, malic, itaconic, glutamic acids, and 3-hydroxypropionic acids are the major building block chemicals that can subsequently be converted to a number of high-value bio-based chemicals and materials. Building-block chemicals are molecules with multiple functional groups that have the potential to be transformed into new families of useful molecules. Biological transformations account for the majority of routes from plant feedstocks to building blocks, but chemical transformations predominate in the conversion of building blocks to molecular derivatives and intermediates (U.S. Department of Energy 2004). In addition, xylitol, and arabinitol are also important building-block chemicals. They can be employed to produce commodity and specialty chemicals such as xylaric acid, glycerol, propylene glycol, ethylene glycol, and lactic acid. Xylitol and arabinitol can be produced by hydrogenation of sugars or extraction from biomass pretreatment (U.S. Department of Energy 2004). In the following section, some important biofuel and building block chemicals including biobutanol, succinic acid, itaconic acid, 3-Hydroxypropionic acid, 1,3-propanediol, and lactic acid will be briefly introduced.

Biobutanol (C_4H_9OH) can be used as a chemical solvent in the food and pharmaceutical industries, and as a fuel. Biobutanol as a fuel is superior to ethanol in that it has higher energy content, lower vapor pressure, lower hygroscopy and hence causes less corrosion to pipelines and equipment. It has a higher octane rating, and is more safe. Butanol can be produced by ABE (Acetic acid, Butanol and Ethanol) fermentation of biomass carbohydrates using *C. acetobutylicum*, *C. beijerinckii*, or *C. saccharobutylicum*. The ABE fermentation broth is very dilute, with total ABE concentration of less than 20 g/L (A:B:E = 3:6:1 (molar)), and the butanol yield is low. This makes product separation a big challenge (Green 2011).

Succinic acid ($HOOCCH_2CH_2COOH$), also called amber acid or butanedioic acid, is primarily used as a sweetener in the food industry. In addition, it is a key building block for deriving both commodity and specialty chemicals such as 1,4-butanediol (BDO), tetrahydrofuran (THF), γ-butyrolactone (GBL), pyrrolidinones, and N-Methylpyrrolidone (NMP) (U.S. Department of Energy 2004; Cukalovic and Stevens 2008). Succinic acid is produced by fermentation of glucose using an engineered form of the organism *A. succiniciproducens* and, most recently, via an engineered *Eschericia coli* strain. Currently, highly efficient microorganism for production of succinic acid are *A. succinogenes*, *A. succiniciproducens*, and *M. succiniciproducens* (Cheng *et al*. 2012). The process also has the benefit of carbon dioxide fixation, as seen in its reaction formula (Zeikus, Jain and Elankovan 1999):

$$C_6H_{12}O_6 + CO_2 = HOOCCH_2CH_2COOH + CH_3COOH + HCOOH$$

In addition to glucose, glycerol can also be the carbon source for succinic acid fermentation. This provides a good opportunity to produce a value-added chemical from glycerol, the relatively cheap co-product of biodiesel production.

Itaconic acid, or methylsuccinic acid ($HO_2CCH_2CH(CH_3)CO_2H$), is used in polymers, paints, coatings, medicines, and cosmetics (Bressler and Braun 1999). As a value-added building block chemical, itaconic acid has the potential to be used for deriving both commodity and specialty chemicals such as 2-methyl-1,4-BDO, 3-methyl THF, 3-&4-methyl-GBL, 2-methyl-1,4-butanediamine, and other value-added chemicals (U.S. Department of Energy 2004). It is produced commercially by the fungal fermentation of carbohydrates. The most commonly used organism for itaconic acid production is *Aspergillus terreus*, grown under phosphate-limited conditions (Willke and Vorlop 2001).

3-Hydroxypropionic acid (3-HPA), as an important C3 building block, has the potential to derive several commodity and specialty chemicals such as 1,3-propanediol (1,3-PDO), acrylic acid, methyl acrylate, acrylamide, and other valuable chemicals (U.S. Department of Energy 2004). 3-HPA can be produced from glycerol using a recombinant strain *E. coli* (Raj *et al*. 2008), *Klebsiella pneumoniae* (Luo *et al*. 2010a; Huang *et al*. 2012), or from glucose using a recombinant strain *E. coli* (Rathnasingh *et al*. 2010). When cultivated aerobically on a glycerol medium containing yeast extract, the recombinant *E. coli* SH254 produced 3-HPA at a maximum of 6.5 mmol l^{-1} (0.58 g l^{-1}). The highest specific rate and yield of 3-HPA production were estimated as 6.6 mmol g^{-1} cdw h^{-1} and 0.48 mol mol^{-1} glycerol, respectively (Raj *et al*. 2008). The engineered *K. pneumoniae* can effectively produce 3-HPA and 1,3-PDO from glycerol under anaerobic conditions (Huang *et al*. 2012).

1,3-propanediol (1,3-PDO) is used in manufacturing polymers, medicines, cosmetics, food, and lubricants (Drożdżyńska, Leja and Czaczyk 2011). It can be produced from glycerol using pathogenic microorganisms such as *Klebsiella pneumoniae* and non-pathogenic microorganisms such as *Clostridium butyricum*, *Clostridium acetobutylicum*, and *Lactobacillus diolivorans*. *C. butyricum* has been reported to produce 1,3-PDO with a titer of 94 g/l when using glycerol as the carbon source (Wilkens *et al*. 2012). A recombinant strain of *C. acetobutylicum* produces up to 84 g/l in fed-batch cultivation (González-Pajuelo *et al*. 2005). The 1,3-PDO concentration obtained was 73.7 g/l in a fed-batch co-feeding glucose and glycerol with a molar ratio of 0.1. *L. diolivorans* proves to be a top candidate microorganism for industrial production of 1,3-PDO from glycerol. The wild-type strain produces up to 0.85 g 1,3-PDO/l h and product concentrations up to 85.4 g/l (Pflügl *et al*. 2012). 1,3-PDO can also be produced from glucose and molasses in a two-step process using two recombinant microorganisms. The first step is the conversion of glucose or other sugar into glycerol by the metabolic engineered *S. cerevisiae* strain HC42 adapted to high ($>200\,g\,l^{-1}$)

glucose concentrations. The second step is to convert glycerol to 1,3-PDO in the same bioreactor using the engineered strain *C. acetobutylicum* DG1 (pSPD5). The best results were obtained with an initial glucose concentration of 103 $g\,l^{-1}$, leading to a final 1,3-PDO concentration of 25.5 $g\,l^{-1}$, a productivity of 0.16 $g\,l^{-1}\,h^{-1}$ and 1,3-PDO yields of 0.56 $g\,g^{-1}$ glycerol and 0.24 $g\,g^{-1}$ sugar (Mendes *et al*. 2011). Recently, 1,3-PDO production by microorganisms were reviewed (Saxena *et al*. 2009; Drożdżyńska, Leja, and Czaczyk 2011).

Lactic acid is widely used in the food industry (Zhang, Jin, and Kelly 2007), and as a building-block chemical (Lee *et al*. 2011). It can be used for the production of biodegradable and biocompatible polymers such as polylactic acid (PLA), lactate esters, propylene glycol, acrylic acid and esters (Adsul *et al*. 2011). The current status of the production of potentially valuable chemicals from lactic acid via biotechnological routes has been reviewed recently (Gao, Ma and Xu 2011). Lactic acid can be produced from lignocellulose-derived sugars using microorganisms such as recombinant *Escherichia coli* (Dien, Nichols and Bothast 2001), *Bacillus coagulans* (Maas *et al*. 2008), *Lactobacillus sp*. (Wee and Ryu 2009), and *Lactococcus lactis* (Laopaiboon *et al*. 2010). There has been a recent overview of the lactic acid production (Vijayakumar, Aravindan, and Viruthagiri 2008; Abdel-Rahman, Tashiro, and Sonomoto 2011).

Biofuels (ethanol and butanol) and valued-added building-block chemicals (e.g., succinic acid, 3-HPA, and 1,3-PDO) derived from lignocellulosic carbohydates by biochemical conversion as described earlier, are often very dilute in their fermentation broths. This usually causes high production costs. In addition to improving microbial biocatalysts to increase substrate and hence product concentrations, yields, and productivities, development of efficient separation and purification processes with low costs are much needed.

1.3 Thermo-chemical and other chemical conversion biorefineries

1.3.1 Thermo-chemical conversion biorefineries

The major thermo-chemical conversion biorefineries involve combustion, hydrothermal liquefaction, pyrolysis, and gasification of biomass into heat (steam) and power, biofuels and chemicals.

Biomass combustion, the complete oxidation process, is a simple way to recover energy from biomass. As the steam turbine used in the process for generating power is not efficient, combustion of biomass, especially the whole biomass, is not the best option. Owing to the simplicity and the maturity of the combustion technology, combustion of the whole biomass, including non-fermentable residues, is commercially common. Combustion of biomass solid residues from distillation for steam and power for process use, as part of Figure 1.1, is a typical example. The carbon dioxide produced from biomass combustion was originally absorbed by the biomass plant during growth from environment via photosynthesis; so it is assumed to be carbon-neutral. In terms of separation, postcombustion capturing and sequestration of CO_2 from flue gases produced by the biomass combustion is very important and interesting.

Biomass pyrolysis is a thermal conversion process converting biomass to liquid (bio-oil), solid (char) and gas in the absence of oxygen. Based on different reaction rates and product distributions, pyrolysis can be classified as four categories: torrefaction, carbonization, intermediate pyrolysis, and fast pyrolysis. Table 1.1 shows the typical product yields for pyrolysis of wood using different modes and conditions.

The pyrolysis bio-oil can be used as feedstock of gasification for producing syngas, which can then be synthesized into fuels and chemicals. In addition, bio-oil can be used to produce transportation fuels. Fast pyrolysis liquid has a higher heating value of about 17 MJ/kg as produced with about 25 wt.% water that cannot easily be separated. Besides, pyrolysis bio-oil has a high oxygen content of around 35–40 wt% (Bridgwater 2012), leading to instability and relatively low heating value. Thus, pyrolysis bio-oil needs to be catalytically upgraded to transportation fuels and fuel additives by hydrotreating, cracking and decarboxylation, or esterification of bio-oil with alcohols followed by water separation to reduce their oxygen content and improve their thermal stability (Bulushev and Ross 2011). Bio-oil upgrading technologies have

Table 1.1 *Typical product weight yields (dry wood basis) for different pyrolysis of wood. Adapted from Bridgwater, A. V., © 2012 with permission from Elsevier*

Pyrolysis mode	Temperature (°C)	Residence time	Yields (%)		
			Liquid	*Solid*	*Gas*
Torrefaction (slow)	~290	~10–60 min	0	80	20
Carbonization (slow)	~400	hours to days	30	35 (char)	35
Intermediate	~500	~10–30 s	50	25 (char)	25
Fast	~500	~1 s	75	12 (char)	13

been recently reviewed (Huber and Corma 2007; Bulushev and Ross 2011; Bridgwater 2012). Furthermore, the separation of some chemicals such as acids and phenolics from bio-oil is another alternative option. Bio-oil is a complex mixture of several hundreds of organic compounds including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, phenolics (phenols, guaiacols, catechols, syringols, isoeugenol) and other oligomeric lignin derivatives, along with around 25% water. About 35–50% of the bio-oil constituents are non-volatile (Czernik and Bridgewater 2004). Separation of value-added compounds from bio-oil becomes significantly important.

Hydrothermal liquefaction (HTL) is the process where the reaction of biomass is carried out in water media at high temperature and pressure with or without added catalyst. Its products include a bio-oil fraction, a water fraction containing some polar organic compounds, a gaseous fraction and a solid residue fraction (Biller and Ross 2011). Generally, HTL operates at 280–370 °C and 10–25 MPa (Behrendt *et al*. 2008). As HTL operates in water media, it can process directly the wet biomass feedstock such as wet microalgae (Wu, DeLuca and Payne 2010; Zou *et al*. 2010; Anastasakis and Ross 2011; Vardon *et al*. 2011; Vardon *et al*. 2012), animal manure (Yin *et al*. 2010; Vardon *et al*. 2011; Theegala and Midgett 2012), and digested anaerobic sludge (Vardon *et al*. 2011) without the need for predrying the biomass. Thus, the HTL process has energy-saving potential and it is a promising conversion process. There has been a recent overview of HTL of biomass for bio-oil (Akhtar and Amin 2011; Toor, Rosendahl and Rudolf 2011). The Hydro Thermal Upgrading (HTU®) process is one example of HTL. The HTU process, carried out at 300–350 °C, 100–180 bar and a residence time of 5–20 min, produces bio-oil (or biocrude) having a heating value of 30–35 MJ/kg (Goudriaan and Naber 2008; Toor *et al*. 2011). Due to the low oxygen content (10–18%wt), this bio-oil can be upgraded by hydrodeoxygenation (HDO) to premium quality diesel fuel. The thermal efficiency of the HTU process is 70–90% (Goudriaan and Naber 2008).

Biomass gasification is a partial oxidation process operating at a temperature in the range of 700–850 °C and a pressure of 0.1–3 MPa using steam, air or oxygen as oxidant. For gasification of black liquor from pulp mills can be conducted at conditions of 900–1200 °C and 2–3 MPa. It is one of the prominent thermochemical conversion methods to produce renewable fuels, energy, chemicals and materials. In addition to producing heat and power, synthesis gas from biomass gasification can be subsequently converted into liquid transportation fuels such as diesel and gasoline, alternative fuels such as methanol, dimethyl ether (DME) and ethanol, and other chemicals under different catalysts and operating conditions (Huang and Ramaswamy 2009). Synthetic diesel can be produced by the Fischer–Tropsch (FT) synthesis of syngas over iron or cobalt-based or hybrid (composite) catalysts (Khodakov, Chu, and Fongarland 2007). Methanol, which is also a material for fuel cell in addition to being an alternative fuel, can be synthesized from syngas over the Cu/ZnO catalyst (Zhang *et al*. 2009). Dimethyl ether can be produced by dehydration of methanol. It can also be manufactured directly from syngas by a single-step process using the hybrid catalyst composed of CuO, ZnO, Al_2O_3, and/or Cr_2O_3) for methanol synthesis and an acid function catalyst (such as γ-Al_2O_3, H-ZSM-5 or HY zeolites) for conversion of methanol into DME (Bae *et al*. 2008). In addition, mixed alcohols can be synthesized from syngas. Mixed alcohols synthesis from syngas is an important process for the production of oxygenated fuels, fuel additives, and other intermediates for value-added chemical feedstock for applications in medicine, cosmetics, as lubricants, as detergents, and for polyester (Fang *et al*. 2009). The potential catalysts for mixed alcohols synthesis from syngas include Cu-based catalysts and Mo-based catalysts. The synthesis of mixed alcohols from syngas over Cu-Fe based catalyst consists of alcohol formation (major reaction), hydrocarbon formation, and water–gas shift reaction are the side reactions (Fang *et al*. 2009). Methanol can also be synthesized to gasoline over zeolites. Hydrogen can be produced from syngas for fuel cell or power generation, or synthesis of ammonia for fertilizer. Table 1.2 shows the reactions of these important biofuels.

1.3.1.1 Example: Biomass to gasoline process

Biomass can be converted to gasoline via methanol synthesis and methanol-to-gasoline (MTG) technologies, as illustrated in Figure 1.2. In this process, biomass feedstock, after shredding and drying, is sent

Table 1.2 *Reactions of common syngas-based fuel synthesis*

Product	Reactants	Main reactions	Catalyst	Ref.
Methanol	$CO + H_2$	$CO + 2H_2 \rightarrow CH_3OH$ $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $CO + H_2O \rightarrow CO_2 + H_2$	Cu-ZnO-Al2O3 hybrid	(Zhang, Xiao and Shen 2009)
Diesel and waxes	$CO + H_2$	$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ $nCO + (2n + 1) H_2 \rightarrow C_nH_{2n+2} + nH_2O$	iron or cobalt	(Khodakov, Chu and Fongarland 2007)
Mixed alcohols	$CO + H_2$	alcohol formation: $nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$; hydrocarbon formation: $nCO + 2nH_2 = C_nH_{2n} + nH_2O$; $nCO + (2n + 1)H_2 = C_nH_{2n+2} + nH_2O$ water–gas-shift reaction equilibrium: $CO + H_2O = CO_2 + H_2$	Cu-Fe	(Fang *et al.* 2009)
DME	Methanol	$2CH_3OH = CH_3OCH_3 + H_2O$	γ-Al_2O_3 or modified ZSM-5 zeolite	(Fu *et al.* 2005; Kim *et al.* 2006)
	$CO + H_2$	Two overall reaction routes: (1) $3CO + 3H_2 = CH_3OCH_3 + CO_2$ (2) $2CO + 4H_2 = CH_3OCH_3 + H_2O$		(Ogawa *et al.* 2003)
Gasoline	Methanol	$nCH_3OH \Leftrightarrow \frac{n}{2}CH_3OCH_3 + \frac{n}{2}H_2O \xrightarrow{-nH_2O} C_nH_{2n} \rightarrow n[CH_2]$	zeolite ZSM-5	(Chang 1992)

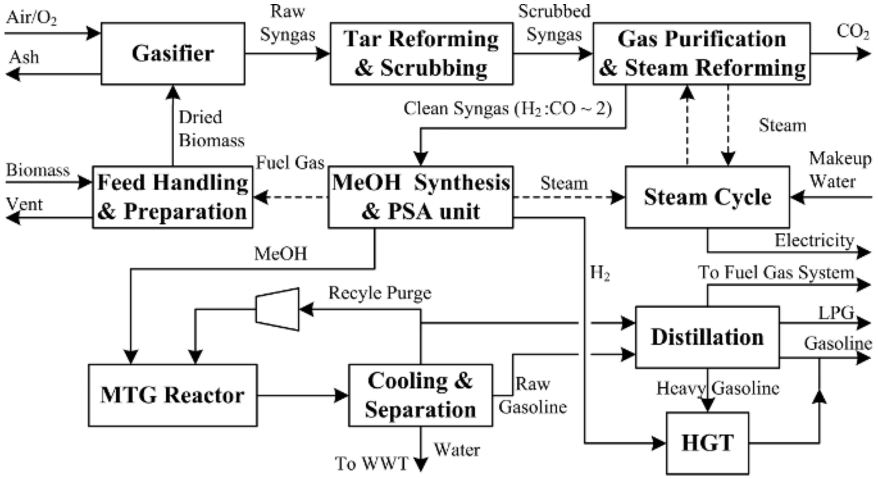

Figure 1.2 *Block diagram of biomass-to-gasoline process (Jones and Zhu 2009)*

to the gasifier for producing syngas. The raw syngas is sent to a tar reformer, a particulate scrubber, and finally a sulfur removal unit. Then the syngas enters a steam reformer where CH_4 is converted to H_2 and CO and the H_2/CO ratio is adjusted to that required by methanol synthesis. Excess CO_2 is removed by amine absorption. The clean syngas is then compressed and sent to the methanol synthesis. Part of the purge gas from methanol synthesis is used to produce hydrogen by a pressure swing adsorption (PSA) unit; the remaining purge gas is used as fuel for drying the feedstock. Raw methanol is converted to hydrocarbons and water in the MTG reactors. The raw gasoline isolated from water by phase separation, is distilled to produce fuel gas, liquefied petroleum gas (LPG), light gasoline, and heavy gasoline. The heavy gasoline is hydrotreated with hydrogen from the PSA to meet the final gasoline specifications. Steam generated in the process is collected and sent to the steam cycle for power generation. Some steam is used in steam reforming and other processes (Jones and Zhu 2009).

1.3.2 Other chemical conversion biorefineries

In addition to the major thermo-chemical conversion approaches mentioned above, biorefineries may also involve various other chemical conversion processes. For instance, production of value-added building block chemicals such as levulinic acid and sorbitol, the conversion of oil-containing biomass for biodiesel, and conversion of those building block chemicals described above to commodity, chemicals and materials. Next, some important value-added building block chemicals including levulinic acid, glycerol, sorbitol, and xylitol/arabinitol are briefly introduced, followed by an example of chemical conversion process.

1.3.2.1 Levulinic acid

Levulinic acid is an important platform molecule that can be used to produce a wide range of compounds such as $\gamma-$valerolactone (GVL), 2-methyltetrahydrofuran, δ-aminolevulinic acid, β-acetylacrylic acid, diphenolic acid, and 1,4-pentanediol (U.S. Department of Energy 2004). Levulinic acid can be catalytically converted to fuel additives through intermediates such as γ-valerolactone and valeric acid, and this has been recently highlighted (Lange *et al*. 2010; Bond *et al*. 2010; Bozell 2010). Also, 2-methyltetrahydrofuran and various levulinate esters derived from levulinic acid can be used as gasoline and biodiesel additives, respectively (U.S. Department of Energy 2004). Different from biofuels production via fermentation of biomass-derived sugars, levulinic acid is produced by acid catalyzed hydrolysis of biomass-derived sugars, a conventional chemical processing approach. This presents another promising route for biofuels.

1.3.2.2 Glycerol

Glycerol can be used as raw material for the cosmetics, pharmaceutical, and food industries (Leoneti, Aragão-Leoneti, and de Oliveira 2012). It is the major co-product of biodiesel production by transesterification of oils, with a weight ratio of 1/10 (glycerol/biodiesel). Glycerol can be considered a renewable building block for producing value-added products obtained by chemical (syn-gas, acrolein, and 1,2-propanediol) or bio-chemical (ethanol, 1,3-propanediol, D-lactic acid, succinic acid, propionic acid, and poly-3-hydroxybutyrate) routes (Posada *et al*. 2012). The wide use of glycerol in producing so many chemical building blocks plus its low price due to the fast growth of biodiesel industry and the surplus of glycerol makes it an excellent renewable feedstock and important building block for producing multiple products in biorefineries. Moreover, glycerol can be utilized to produce triacetin (or 1,2,3-triacetoxypropane), a biofuel additive, by esterification of glycerol with acetic acid. However, the glycerol from biodiesel production as a by-product must be purified before it is used in these industries (Leoneti, Aragão-Leoneti and de Oliveira 2012). Distillation, solvent extraction, ionic exchange, electrodialysis, and simulated moving bed (SMB) can be used for separation and purification of glycerol.

1.3.2.3 Sorbitol

Sorbitol is a potential key chemical intermediate from biomass resources for deriving a number of intermediates and chemicals such as propylene glycol, ethylene glycol, glycerol, lactic acid, and isosorbide (U.S. Department of Energy 2004). Sorbitol is commercially produced by the hydrogenation of glucose.

1.3.2.4 Xylitol/Arabinitol

Xylitol and arabinitol, the sugar alcohols, can be produced by hydrogenation of 5-carbon sugars xylose and arabinose from biomass. There is no major technical barrier associated with the production of xylitol and arabinitol (U.S. Department of Energy 2004). Separation and purification of the pentoses, xylose and arabinose, is important for production of xylitol and arabinitol. In addition, xylitol, and arabinitol can be produced by direct extraction from biomass pretreatment processes. Efficient separation and purification approaches such as ion exchange and nanofiltration are also necessary for this route.

1.3.2.5 Example: Conversion of oil-containing biomass for biodiesel

As an example, the conventional process of the plant oil to biodiesel conversion is shown in Figure 1.3. In this process, fatty acid methyl ester (FAME, biodiesel) is synthesized by esterification of oil with methanol over an alkali catalyst (NaOH). The resultant liquid mixture enters the methanol distillation column where methanol is removed and recycled for use as the reactant. The bottom liquid out of the distillation column is then washed and separated into the oil phase (raw FAME) and the aqueous phase (mainly glycerol). The raw FAME is purified by distillation, while the aqueous solution is neutralized with H_3PO_4, followed by filtering out the solid Na_3PO_4, and the distillation for glycerol concentration.

This homogeneous process using liquid catalyst (NaOH) has many disadvantages: requirement of alkali and acid chemicals and their handling, large separation burden and hence high separation capital and

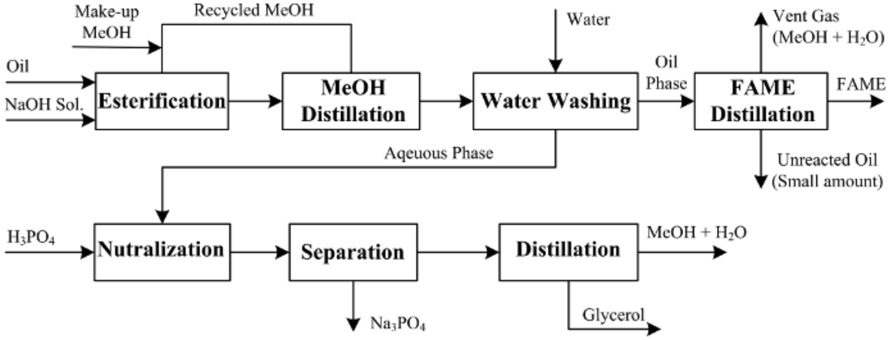

Figure 1.3 *Simplified block diagram of conventional biodiesel production process (Zhang, Dube and McLean 2003)*

operation costs. In addition, dehydrated vegetable oil with less than 0.5 wt.% free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems, and thus the low-cost waste cooking oil is not suitable as feedstock for this process; otherwise, soap occurs during the biodiesel production and this requires additional soap related separation, making the system more costly (Zhang, Dube, and McLean 2003). To overcome these disadvantages of the conventional biodiesel process, heterogeneous biodiesel process using solid catalyst can be applied. Figure 1.4 shows the simplified block diagram of the Esterfip–H biodiesel process (Axens-IFP Group Technologies).

In this continuous system, oil reacts with methanol in two fixed-bed reactors packed with a non-noble metal solid catalyst supplied by Axens. Excess methanol is removed after each of the two reactors by a partial flash vaporization. Esters and glycerol are then separated in a settler. Glycerol phases from each reactor, after being separated from settlers, are combined and the last traces of methanol are removed by vaporization. Biodiesel is produced after final recovery of methanol by full vaporization under vacuum (Bacovsky *et al*. 2007). This process has many advantages: high biodiesel yield (close to theoretical); high purity glyderol without the need for further purification; no soap formation and no low-value fatty acids; no handling of hazardous acid and base chemicals; much lower catalytic cost as compared to other processes (Bacovsky *et al*. 2007).

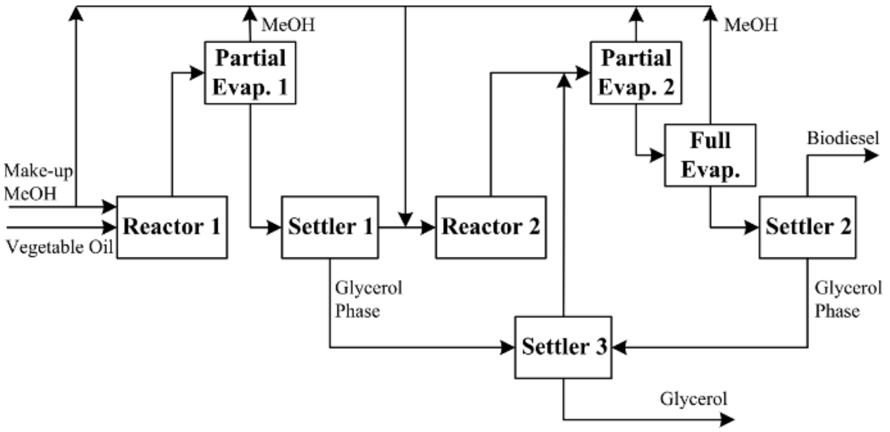

Figure 1.4 *Simplified block diagram of Esterfip–H biodiesel process (Bacovsky et al. 2007)*

1.4 Integrated lignocellulose biorefineries

Integrated lignocellulose biorefineries (ILCB) or integrated forest biorefineries (IFBR) are comprehensive approaches that make full use of all the components of biomass feedstock to produce heat (steam) and power, biofuels, cellulose fibers for pulp and paper, and multiple products (chemicals, polymers or materials). Figure 1.5 below is the general ILCB, modified from the diagram of the advanced pulp mill-based integrated forest biorefinery (IFBR) (Huang *et al*. 2010). The ILCB include not only the pulping process for pulp and paper, but also the following processes that could make value-added coproducts:

- separation of phytochemicals from woody biomass at mild conditions (optional);
- extraction of hemicellulose prior to pulping for biofuels and chemicals;
- extraction of lignin and chemicals (e.g., acetic acid) from spent pulping liquors;
- gasification of biomass including spent pulping liquor and forest residues and agricultural residues, for heat and power, syngas production, and syngas synthesis into fuels an chemicals such as methanol, DME, diesel, gasoline, and mixed alcohols;
- the extracted hemicellulose, combined with isolated short fiber, is hydrolyzed to monosugars, which are then fermented to sugar-based biofuels (e.g., ethanol, butanol), building blocks (e.g., lactic acid, succinic), and chemicals, depending on the microorganism used.

For changing a current pulp mill to an ILCB, the additional incremental costs for realizing a commercial biorefinery can be minimized by fully utilizing the existing infrastructure. Modification of the modern day pulp mills into ILCB presents an excellent opportunity to produce, in addition to valuable cellulose fiber, co-products include fuel grade ethanol/butanol and additional energy, thus resulting in increased revenue streams and profitability and potentially lower the greenhouse gas emissions (Huang *et al*. 2010).

Separation and purification technologies also play a significant role in the ILCB. Pre-extraction of value-added chemicals such as phytochemicals and extraction of hemicellulose prior to pulping,

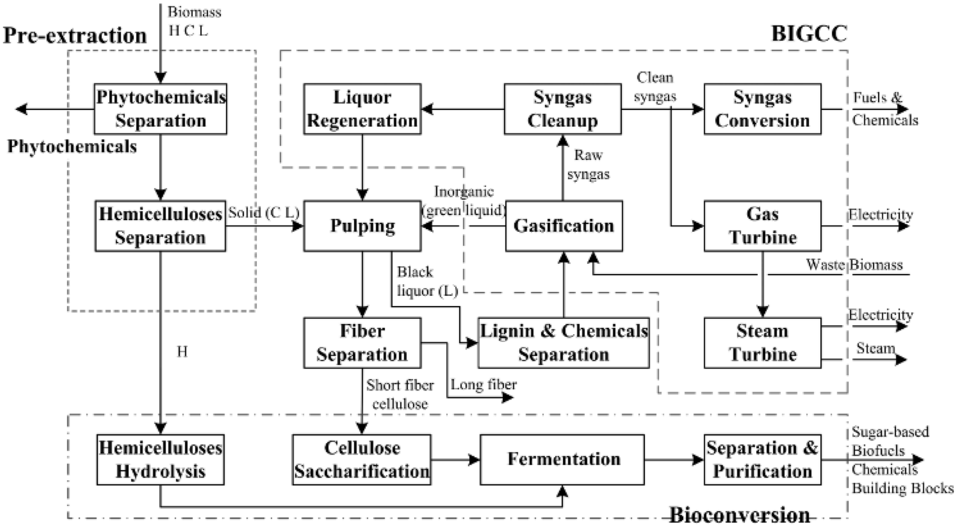

Figure 1.5 Block diagram of the general ILCB

separation of valuable chemicals from biomass prehydrolysis liquor, syngas cleanup, purification of reactants, for example purification of glycerol from biodiesel production for production of intermediates such as succinic acid, and separation and purification of products (ethanol, butanol, lactic acids etc.) are only some of the examples. Generally, the capital and operating costs of separation and purification processes usually account for a large fraction (about 20–50%) of the total capital and operating costs of biorefineries. Significant improvement in of separation and purification technologies can significantly reduce the overall production costs.

1.5 Separation and purification processes

As discussed earlier, in each of the multitude of lignocellulose based biorefinery applications, in addition to the biomass conversion processes, separation and purification of the biomass components and the products streams and their full integration with the overall process is of utmost importance. In many instances this can be the single biggest factor influencing the overall success and commercialization of biorefineries. Given the significance and importance of this area, separation and purifications technologies and their applications in biorefineries is the focus of this book.

The following section presents a brief introduction and outlines the challenges and opportunities in many of the plausible separation and purification technologies in biorefineries. Each of the separation and purification technologies is then the focus of the remainder of the book and they are dealt in greater detail in each of the following chapters.

1.5.1 Equilibrium-based separation processes

1.5.1.1 Absorption

Absorption is often used for separation of particles or desired gas components from a gas mixture into a liquid solvent phase. In biorefineries, absorption is commonly used for removal of acid gases such as H_2S and CO_2 from syngas prior to synthesis of syngas into methanol and diesel, and so forth. There are two major type of absorption: physical and chemical absorption. Physical absorption is commercially used to remove acid gas such as CO_2 and H_2S from syngas in the production of hydrogen, ammonia and methanol. The most well-known physical absorption processes are the Selexol process using the dimethyl ethers of polyethylene glycol at relatively high pressure (2.07–13.8 MPa) and the Rectisol process using cold methanol at $-40\,^{\circ}\mathrm{C}$ and 2.76–6.89 MPa for separating H_2S and CO_2 (Kohl and Nielsen 1997). Other major absorption processes include the Purisol process using N-methyl-2-pyrollidone, and the FLUOR process using propylene carbonate (Olajire 2010).

Currently, both the chemical absorption based on aqueous methyldiethanolamine (MDEA) and the Selexol process are selected in commercial IGCC (Integrated Gasification Combined Cycle) facilities for removal of acid gases. While physical absorption processes can meet the stringent sulfur cleanup required by catalytic synthesis of syngas, they are more expensive than the MDEA-based chemical absorption. On the other hand, although the Selexol process by itself is more expensive than an MDEA process, the total acid gas removal (AGR), sulfur recovery process, and tailgas treating process system, based on Selexol, could be more cost effective than the system based on MDEA, especially if the syngas pressure is high and deep sulfur removal (e.g., to 10–20 ppmv) is required. The Rectisol process is capable of deep sulfur removal, but it is the most expensive AGR process. Hence, Rectisol is generally used for chemical synthesis of syngas where very pure syngas is required (Korens, Simbeck and Wilhelm 2002). An overview of CO_2 separation has recently been presented elsewhere (Olajire 2010).

1.5.1.2 Distillation

Distillation is a commonly used separation method in chemical and biochemical industries. There are different distillation processes for liquid mixture separation: ordinary distillation, azeotropic distillation, extractive distillation. For separation and dehydration of ethanol from fermentation broth, it is impossible to separate ethanol–water in a single distillation column because ethanol forms an azeotropic mixture or azeotrope, at 95.6% by weight with water at a temperature of 78.15 °C. The separation and dehydration of ethanol usually consists of two steps: the ordinary distillation is firstly used to obtain approximately 92.4 wt% ethanol from the dilute broth, azeotropic distillation, extractive distillation, liquid–liquid extraction, and adsorption and so forth are then applied for further dehydration. The major distillation processes including ordinary distillation, azeotropic distillation, and extractive distillation potentially used in biorefineries has been reviewed taking ethanol separation and dehydration as example (Huang *et al*. 2008).

Molecular distillation (MD) is a special distillation process that is carried out under high-vacuum conditions and is suitable for the fractionation and separation of chemicals from pyrolysis bio-oils (Wang *et al*. 2009; Guo *et al*. 2009, 2010). Under these conditions the mean free path length of the molecules to be separated is generally longer than the distance between the evaporation surface and the condenser surface. It can also be used for purification of biodiesel obtained by esterification of cooking oil with methanol (Wang *et al*. 2010), and isolating heat sensitive phytochemicals from biomass or biomass extract (Huang and Ramaswamy 2012). As described before, the properties of pyrolysis liquid can be improved by hydrogenation and/or HDO. On the other hand, pyrolysis bio-oil is a valuable source for the production of chemicals, such as alcohols, aldehydes, ketones, acids, phenolics and sugars. Separation of these chemicals, for example the acid compounds for refining pyrolysis oil (Guo *et al*. 2009) and phenolic fraction for production of pharmaceuticals, adhesives, and specialty polymers (Žilnik and Jazbinšek 2011) from bio-oil, is an alternative option. Wang *et al*. (2010) explored the purification of crude biodiesel with molecular distillation and showed that it resulted in the high yield of FAME (up to 98.32%). In order to enhance the condensation efficiency of molecular distillation, traditional vacuum distillation was firstly used to remove most of the water in the crude bio-oil. The resulting bio-oil was then fractionated by molecular distillation. Results indicated that the distilled fractions were rich in low molecular weight carboxylic acids and ketones; the residual fraction hardly contains water and it has improved heating values of 21.29 MJ/kg and 22.34 MJ/kg for two operating conditions (80 °C, 1600 Pa and 80 °C, 340 Pa), respectively.

Steam distillation is a conventional commercially utilized process for isolating volatile organic compounds such as essential oils that are sensitive to high heat from plant material. Different from the earlier separation methods, steam distillation is used for direct separation of the desirable components from solid biomass feedstock, not liquid mixture. In this method, steam is introduced by heating water, and passed through the oil-containing plant material. With the addition of steam, the oil–water mixture boils at a lower temperature (<100 °C at 1 atm) allowing heat-sensitive compounds to be separated with less decomposition. Steam distillation is suitable for extracting light components whose vapour pressures are relatively high (≥ 1.33 kPa at 100 °C). For components whose vapour pressures at 100 °C are between 0.67 kPa and 1.33 kPa, superheated steam is used for the distillation. Steam distillation can be used to separate light components of essential oils and bioactive compounds from biomass (Huang and Ramaswamy 2012), and this could bring value-added co-products for biorefineries.

Chapter 2 by Lei *et al*. provides additional details on distillation and its applications in biorefineries.

1.5.1.3 Liquid-liquid extraction

Liquid-liquid extraction (LLE), or solvent extraction, is a conventional separation process where one or more mixed solvents are used to extract desirable component from the feed liquid phase to the solvent phase. Liquid-liquid extraction can be used for separating biofuels and chemicals from dilute liquid mixtures—for example, extracting bioalcohols (Simoni *et al*. 2010) and carboxylic acids (Bressler and Braun 1999; Aşçi and İnci 2012; Oliveira *et al*. 2012) from their fermentation broths, extracting inhibitors (compounds toxic to microorganisms used for fermentation) from biomass hydrolyzates (Grzenia, Schell, and Wickramasinghe 2011), and removing impurities (soap, methanol, and glycerol) in biodiesel from used cooking oils (Berrios *et al*. 2011). For example, Chapeaux *et al*. (2008) and Simoni *et al*. (2010) studied the LLE of 1-butanol from water using ionic liquids (ILs) as solvents. Experimental results show that some ILs have high distribution coefficients and selectivities of 30 to 300. 1-hexyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate shows especially good extraction capability with the distribution coefficient of 5 and the selectivity of 300 for 5 wt% 1-butanol aqueous mixture.

Organic acids such as succinic, maleic, lactic, and itaconic acids can be extracted from their fermentation broths by amine extractants, which is based on reactive extraction. For instance, extraction of itaconic acid from aqueous solutions has been studied by six different solutions of trioctylamine (TOA)–tridodecylamine (TDA) mixtures and one of the following diluents: dimethyl phthalate (DMP), methyl isobutyl ketone (MIBK), 2-octanone, 1-octanol, cyclohexyleacetate (CHA), and 1-decanol. The maximum itaconic acid recovery was 98.39% with DMP and $3.14\,\mathrm{mol\,L^{-1}}$ initial concentration of the TOA–TDA mixture (Aşçi and İnci 2012). In addition, organic acids, particularly acetic acid, are reported from the aqueous fraction of the pyrolysis liquid using a long chain aliphatic tertiary amine. The best results were obtained with TOA in 2-ethyl-hexanol (40 wt%, as diluent) with 84% acetic acid recovery at equilibrium conditions (room temperature). Formic acid and glycolic acid present in the feed were also co-extracted with 92% and 69% extraction efficiencies respectively, as well as relatively non-polar compounds such as substituted phenolics and ketones (Rasrendra *et al*. 2011). Furthermore, the extraction of succinic acids, l-lactic, and l-malic from fermentation broths and dilute waste water using ionic liquid as extractant was investigated, and the results show that phosphonium-based ILs can be better extractants than the organic solvents traditionally used (Oliveira *et al*. 2012).

Extraction of acetic acid from biomass hydrolysates using mixed solvent consisting of 85% octanol and 15% Alamine 336 (w/w) for the purpose of inhibitor removal or detoxification, extraction of 5-hydroxymethylfurfural (HMF) from an aqueous reaction solution obtained by acid dehydration of six carbon sugars for production of HMF, using MIBK as extractant, and the extraction of glycerol from 2-butanol into an aqueous phase during the manufacture of biodiesel have also been studied (Grzenia *et al*. 2011).

Liquid-liquid extraction of the key chemicals from bio-oils have been investigated (Vitasari, Meindersma, and de Haan 2011; Žilnik and Jazbinšek 2011). For instance, different aqueous extractions and extraction with combined use of a hydrophobic-polar solvent and antisolvent for extraction of fast pyrolysis bio-oils were studied. Results show that alkali solution was more efficient than water or aqueous NaHSO3 solution; MIBK was shown to be the most efficient solvent for extraction of phenolics from bio-oil in combination with 0.1 M or 0.5 M aqueous NaOH solution, followed by butyl acetate (Žilnik and Jazbinšek 2011).

Chapter 3 by Hu *et al*. provides additional details on liquid-liquid extraction and its applications in biorefineries.

1.5.1.4 Supercritical fluid extraction

In the supercritical fluid extraction (SFE) process, a supercritical fluid is used to extract the valuable solutes from a solid matrix or a liquid mixture at its supercritical condition. $\mathrm{ScCO_2}$ is the most commonly used supercritical fluid in the food, pharmaceutical, and chemical industries. Being non-polar, or hydrophobic, $\mathrm{ScCO_2}$ is very suitable for extracting hydrophobic constituents from biomass (Huang and Ramaswamy 2012). For example, some value-added phytochemicals such as pigments, phenolics, and carotenoids can be recovered from microalgae with $\mathrm{ScCO_2}$ extraction. Phytochemicals from plants including other plants such as switchgrass and alfalfa have the potential to be used in pharmaceuticals, cosmetics, nutritional, and consumer products. Extraction of phytochemicals at mild conditions prior to biomass pretreatment could bring value-added co-products in addition to using biomass for producing biofuels, chemicals, and materials. This could help lower the overall production cost of the major products of biorefineries. In addition, lipid in microalgae can be extracted via ScCO2 extraction for biodiesel production (Halim *et al*. 2011; Soh and Zimmerman 2011). The extracted lipid in this case had a suitable fatty acid composition for biodiesel (Halim *et al*. 2011). Besides, the $ScCO_2$ extraction has a comparable efficiency in extracting lipids compared to the conventional solvent extraction such as hexane extraction, indicating potential energy benefits by avoiding conventional algal mass dehydration prior to extraction. In other words, $ScCO_2$ extraction is a promising procedure for extracting algae oil for biodiesel production (Soh and Zimmerman 2011). A brief review on $ScCO_2$ of phytochemials from biomass has been recently published (Huang and Ramaswamy 2012).

Chapter 4 by Mantell *et al*. provides additional details on super critical fluid extraction and its applications in biorefineries.

1.5.2 Affinity-based separation

Adsorption, ion exchange, and chromatography are the three conventional sorption processes where certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in liquid in a vessel or packed in a column.

Both adsorption and ion exchange can be used for efficient removal of inhibitors from biomass hydrolysate. For illustration, the detoxification of sugarcane bagasse hydrolyzate to improve ethanol production by *Candida shehatae* NCIM 3501 was studied and comparisons were made between five detoxification methods: neutralization, overliming, activated charcoal, ion-exchange resins (IER), and enzymatic detoxification using laccase. Results show that ion exchange was most efficient in removing furans (63.4%), total phenolics (75.8%), and acetic acid (85.2%); activated carbon is the second best with 38.7, 57 and 46.8% removal of furans, phenolics and acetic acid, respectively (Chandel *et al*. 2007). In addition, adsorption and ion exchange can be used for product separation and purification. The adsorption for ethanol-water separation was previously reviewed (Huang *et al*. 2008). Obviously adsorption with different adsorbents can also be applied for separation and purification of other biofuels and chemicals, for example the dehydration of biobutanol with molecular sieve, which is similar to ethanol dehydration. Here are some examples of the application of adsorption and ion exchange in separation and purification of biofuels and chemicals. The raw biodiesel from esterification of used cooking oils contains several impurities: free glycerol, methanol, free fatty acids (FFA), soap, catalyst, metals, water and glycerides (Berrios and Skelton 2008). These impurities should be removed to improve the biodiesel quality to its standard specification. Biodiesel is traditionally purified by water washing, which introduces additional water leading to increased cost and production time. One alternative commercial process uses adsorption with magnesium silicate as adsorbent (Magnesol®). Using the Magnesol process, methanol can be efficiently removed (Berrios and Skelton 2008). Other research showed that adsorption (magnesium silicate and bentonite) can remove soap, methanol, and glycerol effectively (Berrios *et al*. 2011). Glycerol and free fatty acids (FFA) can also be removed efficiently from biodiesel with the adsorption process using silica gel as adsorbent (Yori *et al*. 2007; Manuale *et al*. 2011). Like adsorption, ion-exchange resin is a commercial process that can be used for purification of biodiesel (Berrios and Skelton 2008; Berrios *et al*. 2011), separation of carboxylic acids such as succinic acid (Zeikus *et al*. 1999), as well as purification of xylose from biomass prehydrolyzates (Vegas *et al*. 2005). Using the ion exchange process, glycerol and free fatty acids (FFA) can be efficiently removed from biodiesel (Berrios and Skelton 2008). Ion-exchange resin (Lewatit® GF202) was also applied for purification of used cooking oil biodiesel. Soap, methanol and glycerol removal were 52.2%, 98.8% and 20.2%, respectively. This resin has the advantage in that

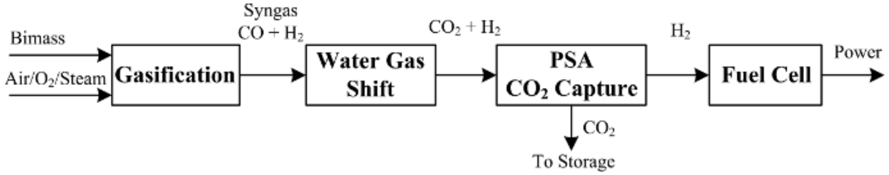

Figure 1.6 *Hydrogen production for fuel cell*

it can be regenerated for reuse, while other resins can be used only once (Berrios *et al*. 2011). Another application of ion exchange in lignocellulosic biorefineries is the purification of succinic acid where the ion exchangers are used for simultaneous acidification and crystallization (Zeikus *et al*. 1999).

Chapter 5 by Venkatesan provides additional details on adsorption and its applications in biorefineries. Chapter 6 by Berrios *et al*. provides additional details on ion exchange and its applications in biorefineries.

Pressure swing adsorption (PSA) can be used for hydrogen purification (Majlan *et al*. 2009; Lopes, Grande and Rodrigues 2011) and for capturing CO_2 (Ribeiro, Santos and Rodrigues 2010). One of the primary applications of PSA is for removal of CO_2 as the final step in the production and purification of hydrogen for use in biorefineries and in the production of ammonia, or the separation of CO_2 from biogas to increase the methane content. Figure 1.6 shows the block diagram of hydrogen production for fuel cell where PSA is used to capture CO_2 and purify H_2 for fuel cell.

Chapter 19 by Simo provides additional details on pressure swing adsorption and its applications in biorefineries especially using dehydration of ethanol as a case study.

1.5.2.1 Simulated moving-bed chromatography

Simulated moving-bed (SMB) chromatography is a continuous separation and purification technique that has better performance (higher throughput and less solvent requirement) than traditional batch chromatography. In the SMB process, a flow of liquid (mobile phase) moves countercurrent to a constant flow of solid (stationary phase), resulting in more efficient separation. SMB technology has been commercially used in pharmaceutical and specialty chemical manufacturing. It can also be applied for biofuels and chemicals separation in biorefineries. For instance, SMB can be used for purification of glycerol from biodiesel production. The sequential SMB chromatography, using the Ambersep BD50 resin, can extract glycerol with 99.5% purity in the extract stream. The raffinate stream contains the salts and other organic impurities including free fatty acids (Lancrenon and Fedders 2008). Similarly, a commercial SMB process using gel-type acidic ion-exchange resin beads was introduced to separate fatty acid salts and inorganic salts from the crude glycerol byproduct of the biodiesel production (Rezkallah 2010). Besides, the SMB chromatography has been proposed for purification of oligosaccharides made up of xylose and arabinose units (Ohsaki, Tamura and Yamaura 2003). In addition, a four-zone SMB chromatography was studied for isolating lactic acid from acetic acid, a major impurity in the fermentation broth of *L. rhamnosus* resulting in 99.9% purity and over 93% yield of lactic acid (Lee *et al*. 2004). More recently, the four-zone SMB system was investigated to separate sugars (glucose and xylose) and 1-ethyl-3-methylimidazolium acetate (EmimAc) from the biomass hydrolyzate where EmimAc, an ionic liquid, was used as the biomass pretreating agent for biomass hydrolysis. Glucose, xylose, and EmimAc were recovered at the yields of 71.38, 99.37 and 98.92% respectively (Mai *et al*. 2012). In summary, SMB chromatography could be efficiently applied for separation and purification of chemicals in biorefineries.

Chapter 7 by Wang *et al*. provides additional details on simulated moving bed and its applications in biorefineries.

1.5.3 Membrane separation

Membrane separation technologies have been widely researched for biofuel separation in biorefineries (Huang *et al*. 2008; He *et al*. 2012).

Electrodialysis (ED) is a process used to extract ions selectively from one solution through ion-exchange membranes to another solution based on electric potential difference. It can remove low molecular weight ionic components efficiently from a liquid mixture. Its applications include seawater desalination and salt production, drinking water production, desalting of glycol, glycerol purification, and organic acid production, and so forth.

Electrodialysis is commonly used for the separation of organic acids or carboxylic acids such as acetic acid and oxalic acid (Wang *et al*. 2011), citric acid (Wang, Wen and Zhou 2000; Wang *et al*. 2011), gluconic acid (Wang, Huang and Xu 2011), and succinic acid (Groot 2011) from their fermentation broths. An overview on the application of electrodialysis for production of organic acids has been presented (Huang *et al*. 2007). As an example, lactic acid can be produced by continuous fermentation with an integrated product recovery process based on bipolar membrane electrodialysis, as illustrated in Figure 1.7. In this process, conventional electrodialysis is used to concentrate the lactate salt, and then bipolar membrane electrodialysis is applied for the conversion of the lactate into lactic acid and base. The resulting lactic acid is purified by ion exchange, while the resulting base is recycled to the fermenter to control the pH-value (Strathmann 2010). This system requires a much smaller amount of ion-exchange resin in a final purification step compared to the conventional lactic acid production in a batch process where the lactic acid is isolated and purified mainly by ion-exchange resulting in a large volume of waste water with regeneration salts (Strathmann 2010).

Other potential similar applications of bipolar membrane electrodialysis include the recovery of gluconic acid from sodium gluconate, ascorbic acid from sodium ascorbate, and succinic acid from sodium succinate.

Recently, membrane technologies have been widely studied for biorefineries. Microfiltration (0.050–10 µm), ultrafiltration (1–100 nm), or nanofiltration (<2 nm) can be selected for separation of biofuels and chemicals, depending on the molecules to be separated.

Membrane can be used for removal of inhibitors such as acetic acid. The bioconversion of lignocellulosic biomass usually involves conversion (hydrolysis) of cellulose and hemicellulose to monosugars, followed by fermentation of the monosugars into the desired products. Acetic acid is liberated from acetate in biomass during biomass pretreatment or hemicellulose hydrolysis. As acetic acid is an inhibitor to the subsequent fermentation, it must be removed from the hydrolyzate prior to fermentation. Wickramasinghe and Grzenia (2008) showed that anion exchange membrane can efficiently remove acetic acid from biomass

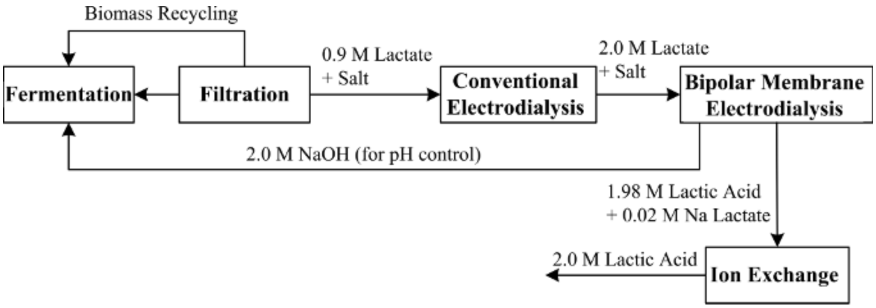

Figure 1.7 *Block flow diagram of the lactic acid production process with integrated bipolar membrane electrodialysis (Strathmann 2010)*

hydrolysates, and it exhibited better separation performance in terms of throughput and product loss compared to anion-exchange resin.

Membrane technologies can be applied for algal biomass harvesting. Algal biomass harvesting is a key step and a big challenge for microalgae biodiesel production because the cells are small (3–30 µm) and fragile, their density is close to water leading to difficulty in separation by gravity, and it is a highly diluted aqueous slurry (Ríos *et al*. 2012). Microfiltration and ultrafiltration can be applied for harvesting algal biomass, offering several advantages such as mild operating conditions without using additional chemicals (Rossignol *et al*. 1999; Rossi *et al*. 2004; Rossi *et al*. 2005). Ríos *et al*. (2012) used a pH-induced flocculation-sedimentation as preconcentration for antifouling, followed by dynamic microfiltration. The preconcentration step concentrated about ten times at a relatively low cost and enlarged the particle size for dynamic microfiltration. The pilot experiments at optimized conditions resulted in concentration factor up to 200 and permeability up to 600 L/h/m^2/bar (Ríos *et al*. 2012).

Chapter 21 by Cooney provides additional details on oil extraction from algae as a case study in biorefinery applications.

Membrane processes can be used for separating hemicelluloses from biomass hydrolyzates or process water of pulp mills. For example, nanofiltration (NF) is suitable for separating hemicelluloses of small molecular weights from hydrolyzates. Biomass pretreatments such as alkaline process usually produce hemicelluloses with smaller molecular weights, compared to other pretreatments such as hot water pretreatment. In this case, nonfiltration, is much better than ultrafiltration for separating hemicelluloses from hydrolyzates (Schlesinger *et al*. 2006). For isolating hemicelluloses from alkaline process liquors containing 200 g/l NaOH, for instance, the hemicelluloses of molar mass over 1000 g/mol are almost retained. In addition, two of the membranes with the nominal molecular weight cutoff (MWCO) of 200–300 and 200–250 g/mol, respectively can retain up to 90% of hemicelluloses, while the tight ultrafiltration membrane with MWCO of 2000 g/mol retain less than 70% hemicelluloses (Schlesinger *et al*. 2006). Ali *et al*. patented an alkaline treatment system for recovering hemicelluloses where prefiltration units with a screen size of 400–650 mesh, followed by one NF membrane was able to retain compounds with a molecular weight of about 200 and higher (Ali *et al*. 2005). Besides, ultrafiltration (UF) can be used for isolating the hemicelluloses or the hemicellulose galactoglucomannan from process water from a thermomechanical pulp mill (Persson, Jönsson, and Zacchi 2005; Persson and Jönsson 2010). Different hydrophobic and hydrophilic UF membranes with 1–5 kDa cutoff were studied and compared for separating hemicelluloses from the process water of the thermo-mechanical pulping of spruce. Results show that the hydrophilic membrane C005F, from Microdyn Nadir GmbH with cut-off 5 kDa, had the highest flux and the most efficient separation of product and contaminants (salts and monosugars). The flux was $140\,\mathrm{L\,m^{-2}\cdot h^{-1}}$ at 0.8 MPa and 40 °C. The retention of hemicelluloses and monosugars were 90% and 3% respectively (Persson, Jönsson and Zacchi 2005). In addition, hydrophobic membranes were fouled by hydrophobic molecules such as lignin and resins, while hydrophilic membranes had no fouling (Persson, Jönsson, and Zacchi 2005).

Membrane can be applied for lignin recovery from pulp mill waste liquors (Jönsson, Nordin and Wallberg 2008; Jönsson and Wallberg 2009) *and biomass prehydrolysis liquor* (Alriols *et al*. 2010). Lignin constitutes up to 30% of biomass. Effective use of lignin is critically important for biorefineries. There are three categories of opportunities for lignin use. First, power—fuel—syngas, i.e., for power by combustion, and for fuel and syngas via gasification (near term); Second, macromolecules such as carbon fiber, polymer modifiers, adhesives and resins (medium-term opportunities), and, third, aromatic chemicals such as BTX chemicals (benzene, toluene, and xylene), phenol, lignin monomer molecules, and oxidized lignin monomers including vanillin and vaillic acid (long term) (Holladay *et al*. 2007). Lignin recovery is necessary for the second and the third categories of lignin use. Lignosulphonates have long been separated by UF from spent liquor in sulfite pulp mills. The isolation of lignin from kraft black liquor has often been extracted by precipitation. This requires changing the pH or the liquor temperature, which could be less cost effective. For this reason, the membrane method has been studied for lignin recovery (Jönsson, Nordin, and Wallberg 2008; Jönsson and Wallberg 2009). For instance, a hybrid UF/NF process was used for separating lignin from the black liquor withdrawn before the evaporation unit. UF was firstly used to retain most hemicelluloses and large molecules. The resulting permeate having 100 g/l lignin with lean or poor hemicelluloses was then concentrated by NF, leading to the product stream (retentate) of 165 g/l lignin (Jönsson, Nordin and Wallberg 2008). In addition, the ethanol organosolv pre-treatment coupled with membrane UF was utilized for fractionation and separation of lignin and other fractions from non-woody biomass, *Miscanthus sinensis*. The organosolv process allowed fractionation of the biomass feedstock into different fractions of products: cellulose hemicellulose-derived sugars and lignin. Ultrafiltration using tubular ceramic membranes with different cutoffs (5, 10 and 15 kDa) was used to obtain specific molecular weight lignin fractions (Alriols *et al*. 2010). Ultrafiltration with similar membranes was applied for recovering lignin from black liquor from the alkaline pulping of the *Miscanthus sinensis* (7.5% NaOH, 90 min and 90 °C) (Toledano *et al*. 2010a). In comparison with selective precipitation, UF has the advantages in that its lignin has higher purity (contains less contaminants such as hemicelluloses), and the UF process allowed controlling the molecular weight of the obtained fractions by selecting the right cutoff of the membrane (Toledano *et al*. 2010b).

Chapter 18 by Zacchi *et al*. provides additional details on cellulosic bioethanol production as a case study in biorefineries.

Chapter 20 by van Walsum provides additional details on separation and purification processes pertaining to lignocellulose hydrolyzates and their applications in biorefineries.

Membrane techniques can be utilized for biodiesel separation and purification. Conventional technologies used for biodiesel separation, such as gravitational settling, decantation, filtration, and biodiesel purification such as water washing, acid washing, and washing with ether and absorbents, have proven to be inefficient and less cost effective. The membrane technology shows great promise for the separation and purification of biodiesel (Atadashi, Aroua, and Aziz 2011).

Membrane techniques can be used for separation of liquid mixtures, for example, carboxylic acids from dilute solutions. Lactic acid is widely used in food and chemical industries. It can be manufactured by either chemical synthesis or carbohydrate fermentation. The high cost of the traditional lactic acid production by lactose fermentation is associated with the separation steps required for food-grade lactic acid. In order to reduce costs, different separation techniques such as reactive extraction, membrane technology, ion exchange, electrodialysis and distillation have been studied for lactic acid separation (Gonzalez *et al*. 2008; Pal *et al*. 2009). Some researches have shown that NF can be used to remove lactic acid from the fermentation broths for improving the fermentation yield (Gonzalez *et al*. 2008; Umpuch *et al*. 2010). Nanofiltration and reverse osmosis membranes can also be applied for separation of carboxylic acids from aqueous fraction of fast pyrolysis bio-oils (Teella 2011). Another example is the application of membrane in separation and purification of ionic liquid solvents by NF (Abels *et al*. 2012).

Chapter 22 by Kamble *et al*. provides additional details on separation and purification technologies in biopolymer production processes.

Membrane technologies can be used for gas separation and purification. Separation of hydrogen, a clean energy carrier, is a good example. Hydrogen can be combusted in fuel cells and gas turbines with zero or near-zero emissions at a high efficiency (Berchtold *et al*. 2012). H_2 is also widely used in chemical industry, for example, for upgrading bio-oil via hydrotreating, and for ammonia synthesis for fertilizer. Hydrogen can be separated from syngas produced by biomass gasification (National Academy of Science 2004; U.S. Department of Energy 2007; Huang and Ramaswamy 2011) or biogas produced by dark fermentation of biomass carbohydrate using anaerobic bacteria in the dark (National Academy of Science 2004; Kovacs *et al*. 2006). Membrane gas separation technology are widely used to separate hydrogen from syngas or the biogas produced, to provide a high purity H_2 product (Ji, Feng and Chen 2009; Sánchez, Barreiro, and

Maroño 2011). For instance, a robust industrially viable polybenzimidazole (PBI)/stainless steel composite membrane was developed and evaluated for H_2 separation at elevated temperatures. The PBI composite membrane demonstrated exceptional long-term thermo-chemical stability and excellent separation performance for H_2 over the other syngas components. The H_2 permeance and H_2/CO_2 selectivity of the composite membrane for simulated dry syngas were 7 GPU (~88 barrer) and 47, respectively (Berchtold *et al*. 2012). Among the microporous membranes, the X-ray amorphous metal oxide membranes, mainly silica, and zeolite membranes, especially the MFI-type membranes (silicalite-1 and ZSM-5), are the most common ones (Caro and Noack 2010). In addition, membrane technology can also be utilized for CO_2 separation from synthesis gas, natural gas or biogas (Zhao *et al*. 2008; Park *et al*. 2010; Sandström, Sjöberg, and Hedlund 2011).

Chapter 8 by Jonsson *et al*. provides additional details on membrane separation processes of microfiltration, ultrafiltration, and diafiltration and their applications in biorefineries.

Chapter 9 by Nisstrom *et al*. provides additional details on membrane separation processes of nanofiltration and its applications in biorefineries.

Membrane pervaporation is one of the most promising technologies for molecular-scale liquid/liquid separations in biorefinery, petrochemical, pharmaceutical industries, and so forth. It is highly selective, economical, safe and ecofriendly (Jiang *et al*. 2009). It has been widely studied for removal of inhibitory products from fermentation broth (Huang *et al*. 2008). For instance, a continuous cultivation of *Clostridium acetobutylicum* ATCC 824 is described using a two-stage design to mimic the two phases of batch culture growth of the organism. A hydrophobic pervaporation unit was coupled to the second fermentor containing the highest solvent titers. This *in situ* product recovery technology efficiently decreased butanol toxicity in the fermentor while the permeate was enriched to 57–195 $g\,L^{-1}$ total solvents depending on the solvent concentrations in the fermentor. By the alleviation of product inhibition, the glucose concentration could be increased from 60 to 126 $g\,L^{-1}$ while the productivity increased concomitantly from 0.13 to 0.30 $g\,L^{-1}\,h^{-1}$. The continuous fermentation was conducted for 1172 h during which the pervaporation was coupled to the second fermentor for 475 h with an average flux of 367 $g\,m^{-2}\,h^{-1}$. The energy consumption was calculated for a 2 wt.% *n*-butanol fermentation broth and compared with the conventional process (Hecke *et al*. 2012).

Chapter 10 by Chung *et al*. provides additional details on membrane pervaporation and its applications in biorefineries.

1.5.4 Solid–liquid separation

1.5.4.1 Conventional filtration

Conventional filtration is a mature, commercially available solid–liquid separation technology. It has been widely used in chemical and biochemical industries. With the solid biomass as starting feedstock for producing biofuels, chemicals and materials, the biorefineries involves a numberof solid–liquid separation tasks, such as separation of prehydrolyzate slurry and post-distillation slurry. Therefore, selection and/or design of efficient, cost-efffective filtration processes are equally important for improving the overall process performance.

Chapter 12 by Ramarao *et al*. provides additional details on conventional filtration and its applications in biorefineries.

1.5.4.2 Solid–liquid extraction

Solid–liquid extraction (SLE) is the process where a solvent or solvent mixture is used to extract valuable compounds from the solid matrix of feedstock. The SLE technologies mainly include conventional solid–liquid extraction, ultrasound-assisted extraction, microwave-assisted extraction, and pressurized subcritical liquid extraction. Biomass feedstock, such as woody and perennial plant materials, and microalgae, usually contains significant phytochemicals such as phenolics, terpenes, sterols, enzymes, polysaccharides, alkaloids, toxins, and pigments, depending on the biomass species. These phytochemicals are value-added co-products, which can be used in neutraceutical and pharmaceutical industries. In order to reduce the overall production cost of biofuels and chemicals from biomass, it is necessary to extract and separate bioactive compounds or phytochemicals as value-added co-products prior to or during biomass conversion (Huang and Ramaswamy 2012). Phytochemicals from plants are usually present in very dilute concentrations. The heat-sensitive properties of phytochemicals and the increased difficulty of SLE over LLE bring a great challenge for efficient separation of phytochemicals from such a dilute biomass matrix. Based on the recent review on the phytochemicals separation (Huang and Ramaswamy 2012), the SLE technologies can be effectively applied for selective isolation of phytochemicals from biomass feedstock.

Chapter 13 by Abidin *et al*. provides additional details on solid–liquid extraction and its applications in biorefineries.

1.5.4.3 Precipitation and crystallization

Pre-extraction of hemicelluloses from wood chips prior to pulping for production of value-added products has gained interests in development of integrated forest biorefinery (Huang *et al*. 2008; Al-Dajani and Tschirner 2008; Mao, Genco and Yoon 2008). Ethanol precipitation can be used for recovery of hemicelluloses (polysaccharides) from the pretreated hydrolyzates (pre-hydrolysis liquor) (Liu *et al*. 2011b) and the spent liquors from pulp mills (Liu *et al*. 2011a). Precipitation by acidification using carbon dioxide, or sulfuric acid can be applied for extracting lignin from kraft black liquor (Öhman *et al*. 2007a; Öhman *et al*. 2007b; Öhman *et al*. 2007c; Wallmo *et al*. 2009; Minu *et al*. 2012). For the separation of hemicelluloses and lignin from pre-hydrolysis liquor (PHL), lignin was firstly removed by acidification of PHL to a pH of 2, resulting in 47% lignin precipitation. The lignin precipitation could be further improved by adding polyethylene oxide and poly aluminum chloride, or ethyl acetate. The hemicelluloses was then precipitated and isolated by adding ethanol to the acidified PHL, at a volumetric ratio (ethanol/PHL) of 4 to 1 (Liu *et al*. 2011a).

Precipitation and crystallization can also be used for separation and purification of succinic acid from its fermentation broth. As an example, the broth liquor in a fed batch bioreactor using *Actinobacillus succinogenes* BE-1 as biocatalyst has the concentrations of succinic acid, formic acid, lactic acid and acetic acid of 97.8 g/L, 23.5 g/L, 5.1 g/L and 17.4 g/L respectively. By controlling the fermentation broth at 4 °C and pH <2, succinic acid was easily and selectively crystallized and isolated with 70% yield and 90% purity, while the by-products lactic acid, acetic acid and formic acids were miscible in the solution. In comparison, succinic acid isolated by the traditional calcium precipitation coupled with ion exchange adsorption, had 52% yield and 92% purity (Li *et al*. 2010). Huh *et al*. studied the production of the highly purified succinic acid from the fermentation broth by recombinant microorganism, *Mannheimia succiniciproducens*. In their proposed method, the preseparation process such as reactive extraction and vacuum distillation was firstly used to effectively remove acid byproducts. The crystallization was then applied without adding any salts to produce highly purified succinic acid, with 99.8% purity and 73.1% yield (Huh *et al*. 2006).

1.5.5 Reaction-separation systems for process intensification

For reversible reactions such as esterification of plant oil with methanol for biodiesel production, the conversion rate and the product yield are limited by the reaction equilibrium. Integration of a reversible reaction with separation into a reaction-separation unit allows removing the byproduct (water) simultaneously with reaction, shifting the reaction equilibrium toward the key product (ester). Thus, the reaction performance increases. For many fermentation processes the products themselves also inhibit the fermentation processes. Thus, the product concentration and yield, as well as the substrate concentration, are limited to the low levels, leading to low fermentation performance. To get higher product concentration and yield and allow using higher concentration of the substrate, the fermentation can be integrated with separation into a system so that the product can be removed simultaneously with fermentation. This can eliminate or reduce significantly the product inhibition and hence increase the product yield and concentration.

The common reaction-separation systems include hybrid reaction-membrane separation (membrane filtration, membrane electrodialysis, membrane pervaporation, or membrane distillation), fermentation-extraction (extractive fermentation), reactive distillation, and absorptive distillation systems.

1.5.5.1 Reaction–membrane separation systems

Reaction–membrane separation systems include membrane bioreactors, (chemical) membrane reactors, bioreactor-membrane pervaporation, bioreactor-membrane distillation, and so forth. Membrane bioreactors can be used for biodiesel production. For example, Dube *et al*. (2007) developed a membrane reactor that removed unreacted vegetable oil from the FAMEs product after transesterification, yielding high-purity biodiesel. A related review has been presented by Atadashi, Aroua and Aziz (2011).

In addition, fermentation-membrane pervaporation system has been widely investigated. Taking a hybrid reaction–membrane pervaporation system for butanol production such as two stage continuous cultivation of *C. acetobutylicum* ATCC 824 coupled with a hydrophobic pervaporation unit using PDMS composite membranes was employed for ABE production. With this *in situ* product-recovery technology, the product (butanol) inhibition decreased significantly in the fermentor. Correspondingly, the glucose concentration increased from 60 to $126\,\mathrm{g\,L^{-1}}$, the productivity increased from 0.13 to $0.30\,\mathrm{g\,L^{-1}\,h^{-1}}$, and the permeate was enriched to $57–195\,\mathrm{g\,L^{-1}}$ total solvents depending on the solvent concentrations in the fermentor (Hecke *et al*. 2012).

The fermentation–bipolar membrane electrodialysis system for succinic acid production is another case of a reaction–membrane separation system. In this process, the fermentation is neutralized with sodium hydroxide, forming soluble sodium succinate during the fermentation. The whole broth is filtered with a microfiltration unit to separate the cells and large insoluble particles from the succinate broth. The filtered sodium succinate is fed to a batch desalting electrodialysis unit, where the ionic species are separated from the non-ionic ones (sugars) and molecules with large molecular masses. The sodium succinate solution is then fed to a batch bipolar membrane electrodialysis unit where the ionic species are converted to their equivalent acid and base forms and separated. Sodium ions are transported across the cation membrane and associate with the hydroxyl ions to form sodium hydroxide, which is reused for fermenter neutralization. After succinic acid is purified (99.5%), a further distillation is required to purify acetic acid to 99.9% (Luo *et al*. 2010b).

Chapter 11 by Izquierdo-Gil provides additional details on membrane distillation and their applications in biorefineries.

Chapter 14 by Cabral *et al*. provides additional details on membrane bioreactors and their applications in biorefineries.

1.5.5.2 Extractive fermentation (Reaction–LLE systems)

Extractive fermentation, a combination of fermentation and liquid-liquid extraction, has been widely investigated. As an example, five non-ionic surfactants (Triton X 114, L64, L62, L62LF, and L61) were examined as extractants for extracting butanol from the fermentation broth in extractive acetone-butanol (AB) fermentation using *Clostridium pasteurianum*. Biocompatibility tests using 3% (vol.) surfactants showed that

L62, L62LF, and L61 did not show inhibition to AB production in 72-h fermentation using *C. pasteurianum*, while L64 reduced the AB yield and Triton X 114 inhibited the AB production. The results showed that L62 is a good extractant for isolating butanol from the fermentation broth, with the partition coefficient of 3–4 for butanol, and it significantly enhanced the butanol production with a butanol yield of 225% higher than the control using 6% (vol.) L62 (Dhamole *et al*. 2012).

However, extractive fermentation with *in situ* product removal, most previously researched of this kind, may not be suitable for large-scale production due to slow mass transfer into solvent phase, formation of emulsions through agitation, cell inhibition by solvent (interface toxicity), loss of cells at interfaces, difficult process control, and so forth (Kraemer *et al*. 2011). For this reason, fermentation integrated with external product removal in an extraction column with a recycle of product-lean broth was proposed (Figure 1.8), and mesitylene was identified as novel solvent with excellent properties for ABE extraction from the fermentation broth by using the computer-aided molecular design (Kraemer *et al*. 2011). This hybrid process allows using the toxic-to-cells solvents having a very low solubility in water and high extraction performance.

Membrane-assisted solvent extraction (membrane extraction, or perstraction), can also be utilized for recovery and separation of organic acids (Schlosser, Kertész, and Marták 2005), biofuels, and other chemicals. Coupling membrane-assisted extraction with fermentation is an efficient process-intensification approach. Non-dispersive membrane extraction has been used to detoxify corn stover biomass hydrolysates pretreated using dilute acetic acid. Ethanol yields for hydrolysates detoxified using an organic phase consisting of 15% Alamine 336 in oleyl alcohol are about 10% higher than hydrolysates detoxified using ammonium hydroxide treatment. The results of this study indicate that membrane extraction could be a feasible unit operation for detoxification of biomass hydrolysates. Unlike many current detoxification processes, acetic acid is also removed. Since membrane based processes are modular, scale-up is straightforward. The commercial viability of membrane extraction will depend on selection of an optimal organic phase diluent (Grzenia, Schell, and Wickramasinghe 2012). Besides, membrane-assisted extractive (MAE) fermentation of acetone–butanol–ethanol (ABE) by *Clostridium saccharoperbutylacetonicum* N1-4 using a polytetrafluoroethylene (PTFE) membrane and 1-dodecanol was studied. The membrane separates the aqueous phase from the organic phase allowing the use of the toxic extractant 1-dodecanol with high distribution coefficients in extraction of butanol without contact and toxifying the microorganism. Compared to conventional batch fermentation, MAE–ABE fermentation with 1-dodecanol as a extractant decreased butanol inhibition and increased glucose consumption from 59.4 to 86.0 g/L, and total butanol production increased from 16.0 to 20.1 g/L. The maximum butanol production rate increased from 0.817 to 0.979 g/L/h. The butanol productivity per membrane area was remarkably high with this system—78.6 g/L/h/m^2 (Tanaka *et al*. 2012).

Chapter 15 by Yang *et al*. provides additional details on extractive fermentation and its applications in biorefineries.

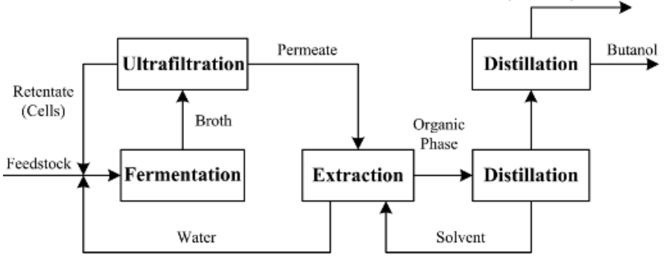

Figure 1.8 *Simplified block diagram of hybrid fermentation-external LLE process*

1.5.5.3 Reactive distillation

Reactive distillation, a combination of reaction and distillation in one unit, is a process intensification technique that can be applied successfully to produce biodiesel (Kiss, Dimian, and Rothenberg 2008), succinate ester (Orjuela *et al*. 2011), and upgrade the flash pyrolosys oil (Mahfud *et al*. 2007). By combining reaction and separation into a single unit, one can shift the reaction equilibrium toward the key product (ester) by continuous removal of byproduct (water), instead of using an excess of reactant. Rigorous process simulations show that combining metal oxide catalysts with reactive distillation technology is a feasible and advantageous solution for biodiesel production (Kiss, Dimian, and Rothenberg 2008). Orjuela *et al*. investigated the esterification of mixtures of succinic acid and acetic acid from fermentation of biomass carbohydrates with ethanol in a continuous reactive distillation system. The experimental results show that the conversions of both succinic acid and acetic acid were close to 100%; succinate ester (diethyl succinate) was separated as bottom products with 98% purity, and ethyl acetate was recovered in the distillate (Orjuela *et al*. 2011). Mahfud *et al*. studied the upgrading of flash pyrolysis oil in a reactive distillation using a high boiling alcohol such as n-butanol and a solid acid catalyst at 323–353 K under reduced pressure (<10 kPa). Results demonstrate that the water content of the pyrolysis oil reduced significantly. Using n-butanol and the solid acid Nafion SAC13, the product properties of the upgraded pyrolysis oils, particularly the heating value and the acidity were considerably improved (Mahfud, Melian-Cabrera, and Manurung 2007). Besides, reactive distillation can also be used for glycerol esterification with acetic acid for production of triacetin, which can be used as a biofuel additive (Hasabnis and Mahajani 2010).

Chapter 16 by Miller *et al*. provides additional details on reactive distillation and its applications in biorefineries.

1.5.5.4 Reactive absorption

Reactive absorption (RB), the combination of reaction and absorption in one unit, is another technology for process integration and intensification. RB can also be applied in the biodiesel production. An innovative technology based on RB using solid acid catalysts has been recently studied for biodiesel production. It was found that RB has many advantages over reactive distillation such as lower capital investment and operating costs due, higher conversion and selectivity, and no thermal degradation of products (Kiss and Bildea 2011). Also, this process eliminates all conventional catalyst-related operations, simplifying the production process (Kiss 2009). Details on the RB technology will be presented in a separate chapter of this book.

Chapter 17 by Kiss *et al*. provides additional details on reactive absorption and its applications in biorefineries.

1.6 Summary

This chapter attempted to provide an introduction and overview of the important biomass conversion processes including biochemical and thermochemical conversions and the potential separation and purification technologies in biorefineries. A number of representative value-added chemical building blocks and different biorefinery scenarios were introduced. Separation and purification technologies in current and future biorefineries were then reviewed. These included equilibrium-based processes such as absorption, distillation, liquid-liquid extraction, and supercritical fluid extraction; affinity-based separation such as adsorption, ion exchange, and simulated moving bed; membrane separation, solid–liquid extraction, as well as hybrid reaction-separation systems.

Separation and purification processes are one of the most important components of biorefineries. Generally, the costs of separation and purification processes account for 20–50% of the total costs of the biorefineries. Many biorefineries, especially the biochemical and biological approaches, have tremendous challenges in separation and purification due to number of factors including low feed concentration, product inhibition, and low product yield. There are number of significant challenges and opportunities in separation and purification in biorefineries including separation of phytochemicals from biomass, separation of biomass components including cellulose, hemicellulose, lignin and extractives, separation of fermentation inhibitors in hydrolyzates, separation and purification of different chemical species in the feed streams after initial pretreatment and hydrolysis, concentrating each of the species for varying end products and applications, separation of lignin and chemicals in spent pulping liquor, simultaneous removal of products which are also inhibitors during fermentation, integration of separation and purification technologies with bioprocessing, as well as downstream product separation and purification. These are just a few examples of challenges and opportunities that need to be addressed and solutions need to be developed and implemented for successful commercialization of biroefineries. They offer tremendous opportunities for research and development and it is imperative that both government and private industry continue to support research in this important area.

There are also significant opportunities for developing totally new approaches to separation and purification, especially suitable for biorefineries and their full integration in the overall biorefineries. Here are some examples of exciting potential approaches and opportunities. Ion exchange is the preferred approach for detoxification and will be still used in the future biorefinery because of its high detoxification efficiency, easy (continuous) operation and flexible combination of different anion and cation exchangers. Adsorption with a molecular sieve is efficient in breaking the ethanol–water or butanol-water azeotrope for biofuel dehydration (Huang *et al*. 2008). Membrane separation, especially ultrafiltration and nanofiltration represents a promising separation procedure for recovery of hemicelluloses from hydrolyzates and lignin from spent liquor. Hybrid separation systems such as extractive-fermentation and fermentation-membrane pervaporation are promising in removal of product inhibition, and hence are able to increase process performance. Fermentation, bipolar membrane electrodialysis, reactive distillation, and reactive absorption are suitable for separation of products obtained by esterification such as biodiesel production. Integrated bioprocessing, consolidated bioprocessing integrating pre-treatment, bioprocessing and separation and purification offer tremendously exciting new opportunities in future biorefineries.

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