Korean J. Chem. Eng., **29**(7), 831-850 (2012)
DOI: 10.1007/s11814-012-0080-6

INVITED REVIEW PAPER

Bioprocessing aspects of fuels and chemicals from biomass

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(*Received 17 April 2012 • accepted 25 May 2012*)

Abstract–This review deals with a recent development of biofuels and chemicals from biomass. Some of the grain-based biofuels and chemicals have already been in commercial operation, including fuel ethanol, biodiesel, 1.3-propanediol, polylactic acid (PLA) and polyhydroxy butyric acid/alkanoates (PHB/PHA). The next generation bioproducts will be based on lignocellulosics due to their abundance and to stabilize rising food prices. However, the technologies of handling biomass are yet in their infancy and suffer from low yield, low product titer, and low productivity. This review focuses on bioprocessing technologies for biofuels production: organic raw biomaterials available in Korea; volatile fatty acids platform, multi-stage continuous high cell density culture (MSC-HCDC), enrichment of fermentation broth by forward osmosis; various purification methods of pervaporation of ethanol, solvent extraction on succinic, lactic acids and reactive separation methods.

Key words: Biorefinery, Productivity, Product Titer, High Cell Density Culture, Products Enrichment, Separation

INTRODUCTION

The Big Bang theory tells us that the universe was once in an extremely hot and dense state, which expanded rapidly and caused the young universe to cool, resulting in its present state of expansion. The Big Bang occurred 13.7 billion years ago [1]. Life on planet Earth is transient and limited as shown in Fig. 1 [2]. "Stromatolites," the first life on earth appeared in the form of cyanobacteria 3.8 billion years ago, 800 million years after the birth of the earth [3]. 1.8 billion years ago, oxygenated atmosphere appeared as photosynthesis proceeded. The initial atmospheric composition consisted of NH_3, CH_4, and H_2, CO/CO_2, in a more reducing state than now [4]. Plants and animals began to appear 500 million years ago from present day and have about 500 million years left to live along with humans. (Taxonomically *Homo sapiens*, Latin for "wise man" or "knowing man") are the only living species in the *Homo* genus. Anatomically modern humans originated in Africa about 200,000 years ago, reaching full behavioral modernity around 50,000 years ago [5].

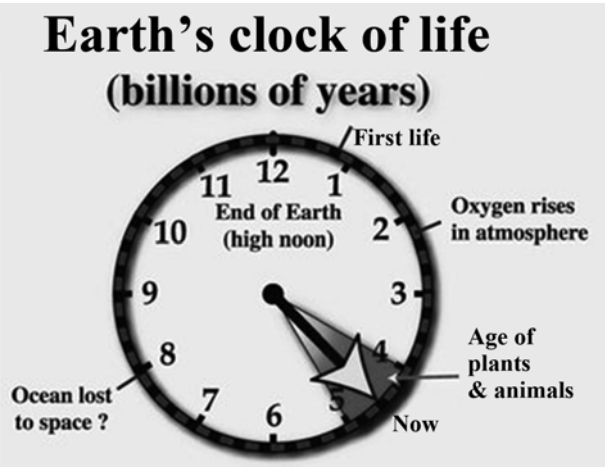

Fig. 1. Earth's Clock of Life. First life (+0.8b, –3.47b), Oxygen rise in atmosphere (2.2b, –2.35b), age of Plants and Animals (4.0~5.0b, –0.55~+0.45), Microbial & lower living things age (5.0~8.0b, +0.55~3.55b), Ocean lost (8.0b~, 3.55b~), Sun and Earth become One planet (10~12b, 5.55~7.55b). First number in the parenthesis refers to the time counted from the birth of earth, second number counted from present backward (–) and forward (+) [2].

It is calculated that the expanding sun will engulf Mercury, Venus, and Earth in about 6-8 billion years from now.

Humans need at least two resources, energy and materials, for their survival on earth. Currently, the most economical source is atomic energy based on fission of uranium 235. Nuclear fusion based atomic energy will be more beneficial, but it may take another 100 years to reap its benefit, where obtaining electric energy would be the least of our worries. Of course, we may use renewable energies such as wind power, solar energy and bioenergy. As far as materials are concerned, inorganic materials are limited in amount so that new mining sites may be needed or a dependency on intensive recycling practice. The ocean can serve as future inorganic sources of lithium and uranium. Biomass is also renewable through photosynthesis, and it is the most reliable resource for organic raw material that makes transportation fuels and other needed organic chemicals. We can also produce fuels from coal, oil, natural gas and methane hydrates, Fig. 2 illustrates a change of fuel sources starting with biomass, to coal, oil, and returning back to biomass.

The two Koreas (South and North) have no grains and plant oils

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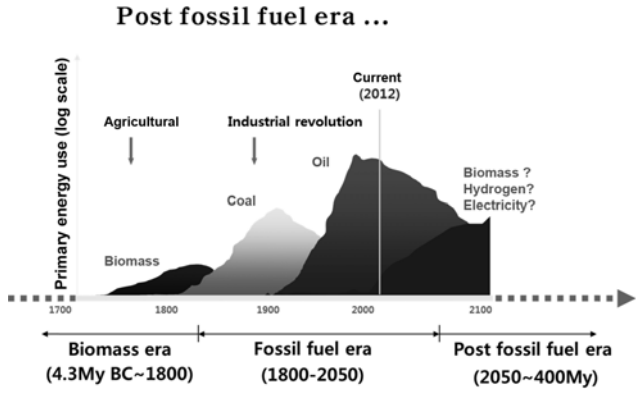


Fig. 2. Energy Era for Humans. Agricultural~ biomass; Industrial revolution ~ fossil fuel (coal, oil), Post fossil fuel (solar energy, wind, atomic (fission followed by fusion), biomass.

to produce fuel ethanol and biodiesel. Rather than depending on foreign resources and doing research on uneconomical fuel manufacturing process in Korea, we focused our research on making an economical and indigenous biofuel in South Korea. In biofuels, raw materials account for 70-80% of the manufacturing cost. Unlike crude oil, biomass resources are not suitable for long distance delivery because of low energy density. Thus, looking for low cost raw materials in Korea was the next option. Two biomass-conversion platforms of thermochemical syngas and enzymatic glucose have been studied in countries like the US, Japan and European countries. There are many steps to a successful commercialization of fuels and chemicals from biomass: supply chain of feedstock (amount and cost), biomass conversion (less costly than grain-based), bioenergy distribution, and bioenergy end use [6]. Currently, none of these requirements are met in many countries. But with waste organics, at least the first supply chain of feedstock is met better than any other lignocellulosic biomass. Wastes are generated in substantial amounts every day, year round and collected by municipal governments. Once we select a suitable conversion platform, we expect to build test-pilot and production plants in a near future that may be economical biofuels production in Korea. We selected the volatile fatty acid platform because we have a considerable experience in producing volatile fatty acids (VFA) as a way of treating food wastes to be used as electron donor for denitrification of municipal wastewater in Korea. Professor Holtzapple of Texas A&M University has been studying VFAs for mixed alcohol biofuel production using waste newspapers and published many works on volatile fatty acids based mixed alcohol [7].

We estimate a maximum production of bioethanol in Korea from three different resources: 300,000 tons/year of bioethanol from 800,000 dry-tons (4 million wet tons, 20% solid content); 3,000,000 tons from all the waste organics; and roughly 30 million tons from 100,000,000 tons of woody biomass. The VFA platform is very different from thermochemical syngas and enzyme-glucose platform because it uses a natural process of anaerobic digestion by mixed culture. The product is a mixture of acetic, propionic and butyric acids rather than CO and H_2 or glucose and xylose. The conversion costs can be much smaller than with the two existing platforms. One of the advantages over conversion platform lies in raw material cost, which can be near zero or even negative. The purpose of this review is to inform biofuel researchers of our new development of multi-stage continuous high cell density culture (MSC-HCDC) system [8]. It can yield a titer equivalent to that of fed-batch with higher productivities in each fermentation application. Enrichment of a low product titer to several times higher titer is possible by forward osmosis with much a lower energy cost [9]. Biomass-based conversion process or any new chemical development for succinic acid, lactic acid and butanol purification research will be covered here as well. New research efforts of MSC-HCDC and enrichment of fermentation broth will become useful in the utilization of volatile fatty acids from lignocellulosic biomass in a future. VFAs can be easily obtained from food wastes even without any pretreatment and enzymes. Although VFA-platform has many advantages over thermochemical or sugar platforms, it is not easy to extend this technology to woody lignocellulosic biomass, which should be dealt better with thermochemical or sugar platform. However, three major obstacles already have some early solutions in a laboratory scale: selection of biodegradable organic wastes for economical biofuels; for a higher productivity by MSC-HCDC and low product titer enrichment by forward osmosis.

FUELS AND CHEMICALS FROM BIOMASS

1. Availability of Biomass on Earth

Global warming, increasing CO_2 level, declining fossil fuel resources and increasing grain commodity prices are current problems to be dealt with urgently. We are entering a post-fossil era in which oil is in very short supply or does not play an important role anymore (Fig. 2). A peak oil production means a point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline [10]. The United States will reach its peak anywhere between now and 2020. Some optimists say the global peak will be 2020.

Yearly biomass production can be estimated in terms of land productivity dependent on climate regions [Table 1]. Its total amount on earth is 1.841×10^9 ton of biomass, and its annual production rate is estimated to be 172.5×10^9 ton. This amounts to five times the global energy consumption per year and ten times the global transportation fuel [11]. South Korea, having an area of 100,000 km^2, produces 100 million tons of biomass each year [12]. Table 1(a) was available in WIKIPEDIA.org website until a few years ago, but now you can find this table only in many biomass textbooks in print, and Table 1(b) has a similar content [13,14].

Summarizing terrestrial and marine biomass:

The total terrestrial and marine biomass production amounts to 65 TW and 25 TW, respectively. 76 TW out of 90 TW is decomposed each year.

(1) Land biomass lasts 10 years but marine biomass decomposes in a month.

(2) The current photosynthetic efficiency is 0.13% (3.00 TW, current total fuel energy replacement of 7.7%) and the maximum replacement can be 26.7 TW with 3% efficiency, which can replace 178% of current fuel total energy. The chemical energy is 12-20 MJ/kg.

(3) This biomass is located in regions between north/south latitude of 30%: North and South America, Southeast Asia and central Africa. Utilization of unused farm lands and land in fallows can suffice in biomass needed for biofuels production.

Table 1. Total biomass on earth and its productivity

(a)

Climate	Area (10^6) Km^2	Current amount (dry)		Net production (dry)	
		Average (ton/ha)	Total (10^9 ton)	Average (ton/ha/y)	Total (10^9 ton/y)
Tropical rain	17.0	450	765	22	37.4
Tropical seasonal (subtropical)	7.5	350	260	16	12.0
Temperate ever-green	5.0	350	175	13	6.5
Temperate deciduous tree	7.0	300	210	12	8.4
Tundras (subartic)	12.0	200	240	8	9.6
Subtotal	48.5	50	1,650	14	69.5
Desert	82.0	27	222	2.8	12.9
Agriculture	14.0	11	14	6.5	9.1
Marsh	2.0	150	30	30	22.9
Land water	2.5	0.2	0.05	5	9.1
Land total	**149.0**	**123**	**1,836**	**7.8**	**6.1**
Ocean total	**361.0**	**0.01**	**3.9**	**1.6**	**1.3**
Total (land and ocean)	(510)	3.61	(1,841)	3.4	(172.5)

(b)

Producer	Biomass productivity ($gC/m^2/yr$)	Total area (million km^2)	Total production (billion ton C/yr)
Swamps and marshes	2,500		
Tropical rainforests	2,000	8	16
Coral reefs	2,000	0.28	0.56
Algal beds	2,000		
River estuaries	1,800		
Temperate forests	1,250	19	24
Cultivated lands	650	17	11
Tundras	140		
Open ocean	125	311	39
Deserts	3	50	0.15

Comparison of biomass productivities: rain forest (A: 22, B: 48), tundras (A: 8, B: 3.36), total land (A: 116.2 billion, B: 135.3 billion). There are some differences in rain forest and tundras of Table 1(a), 1(b), but the total land productivities of A and B have similar values. In addition to the plant biomass (unit: m-tons), human, 100; bacteria, 35,000-550,000; cattle, 156; sheep and goats, 31.5, chicken, 14.4; fresh ants, 900-9,000; termites, 455; blue whales, 36; marine fish, 800-2,000; antartic krill, 379; zoo plankton, 3 times human biomass; cyanobacteria, 1000
(a) Biomass productivities on earth with climate regions, previously at Wikipedia.org but now, unavailable. Rain forest has a productivity of 22 ton/ha·y; Tundras 8 tons/ha·y; Total land productivity=7.8×149 $km^2\times10^6=7.8\times149\times100$ $ha\times10^6=1162\times10^8$ ton/y=116.2×10^9 tons/y
(b) Biomass productivities in terms of carbon-g/m^2/y [15,16]. Net primary production is the rate at which new biomass is generated, mainly due to photosynthesis. Global primary production can be estimated from satellite observations. This results in 56.4 billion tons C/yr (53.8%), for terrestrial primary production, and 48.5 billion tons C/yr for oceanic primary production. Rain forest: 2 kg C/(m^2·y)=20 ton C/ha·y=48 ton biomass/ha·y, Tundras 0.14 kg·C/ha·y=1.4 tonC/ha·y=3.36 ton biomass; total biomass 56.4×10^9 ton C=$56.4\times2.4\times10^9$ ton biomass=135.3×10^9 tons/y. A factor of 2.4 comes from the ratio of $C_{12}H_{22}O_2$ (342)/12C (144)=2.4

(4) The current global energy consumption is 15 TW. Fossil fuel covers 11.8 TW (coal 3.6 TW, natural gas 3.2 TW and oil 5.0 TW). Current transportation fuel uses 3.6 TW.

Biofuel production is liable to feedstock prices and supply of raw materials. It is desirable to have a long-term view on supply and demand of the future energy.

2. Energy Outlook

Exxon Mobil released "Exxon Mobil Energy Outlook 2007" on primary energy, renewables and wind, solar and biofuels in MBDOE (million barrels per day of oil equivalent) [Fig. 3]. The growth rate in primary energy sector will be 1.3%; 1.5% in all renewables; and 8.7% in wind (10.5%), solar energy (9.9%) and biofuels (8.7%). The important thing is that fossil fuels (natural gas-1.7%, petroleum-1.2% and coal-0.9%) have a positive growth rate. Oil is known to have reached peak production, but it has a positive growth rate that can be due to a potential resource of oil such as sand oil in Canada and oil shale in USA or elsewhere in the world [19]. The wind and solar energy generates electricity, while biofuels can be a good substitute for current transportation fuel.

3. Biomass Conversion Technology and Commercialization

There is a possibility of making substantial amount of fuels and chemicals from biomass utilizing appropriate biomass conversion technology. Fig. 4(a) shows three major biomass platforms: thermochemical-syngas, enzyme-glucose/xylose, and volatile fatty acids.

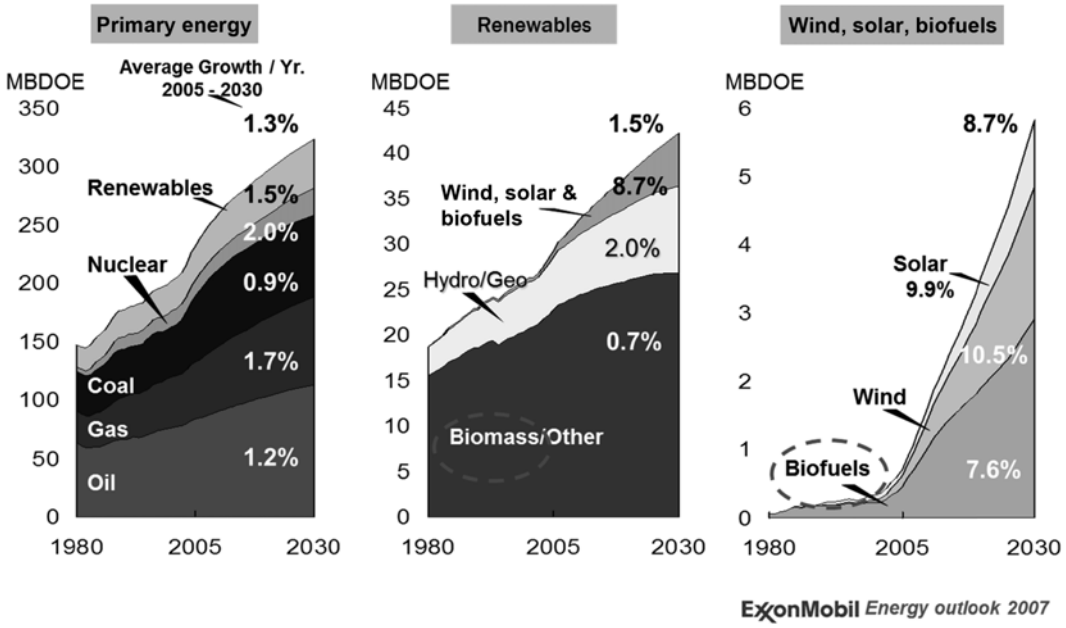


Fig. 3. Energy Outlook by Exxon-Mobil. Current share and its growth rate (%) of primary energy (oil, gas, coal, nuclear, renewables); renewables (biomass/other, hydro/geo, wind, solar & biofuels); wind, solar and biofuels (share, growth rate) [17,18].

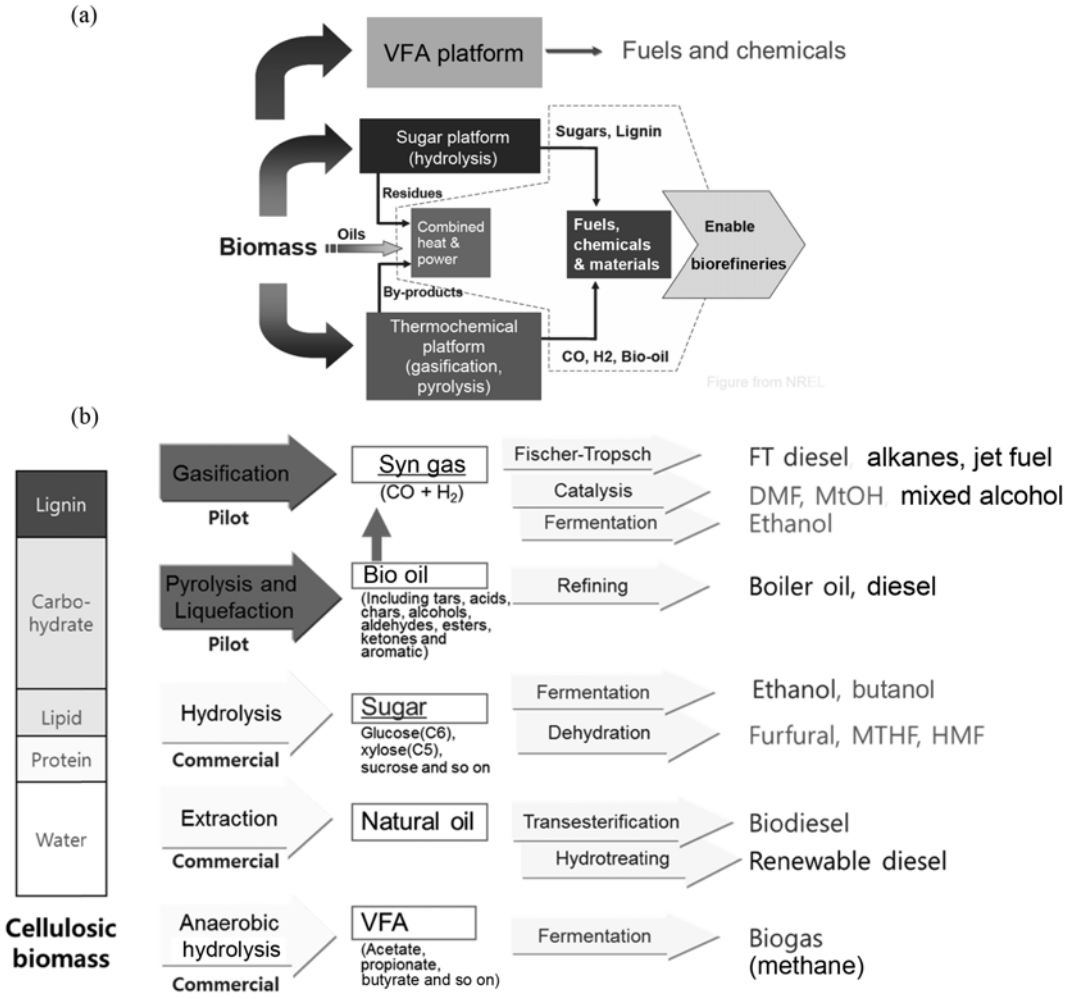


Fig. 4. (a) Major conversion platforms of biomass. Fuels (heat and power), chemicals and materials are produced [11, modified]. (b) Cellulosic biomass conversion technologies to fuels.

The leftover of the conversion technologies, lignin as byproduct, can be used for power generation. A biorefinery can substitute for the current fossil fuel based refinery in the near future. Practically, there can be many kinds of refineries, depending on different raw materials.

Solid biomass has energy content of 12-20 (MJ/kg), solid coal is 15-30, liquid-petroleum is 42, and natural gas is 50. Biomass contains a large amount of water and its real energy content can be much lower than the other fossil fuels. The most convenient form of energy source is liquid with high energy density such as oil. However, a long distance transport of biomass, such as oil, is very difficult and expensive. Fig. 4(b) shows several conversion platforms of lignocellulosic biomass. A general biomass can be converted to syngas, through $CO+H_2$ with various chemicals that can be made with Fischer-Tropsch catalysis. Gas transportation to long distances is rather difficult, and thus the conversion plant should be located on-site or within a proximity to biomass source. The second option can be conversion to bio oils by thermal heating, which can be transported to a biorefinery located at a distant location. The three bioconversion processes have advantages and disadvantages. A coal-based syngas method is in operation in the Republic of South Africa, but biomass based F-T conversion is in pilot operation in Germany and

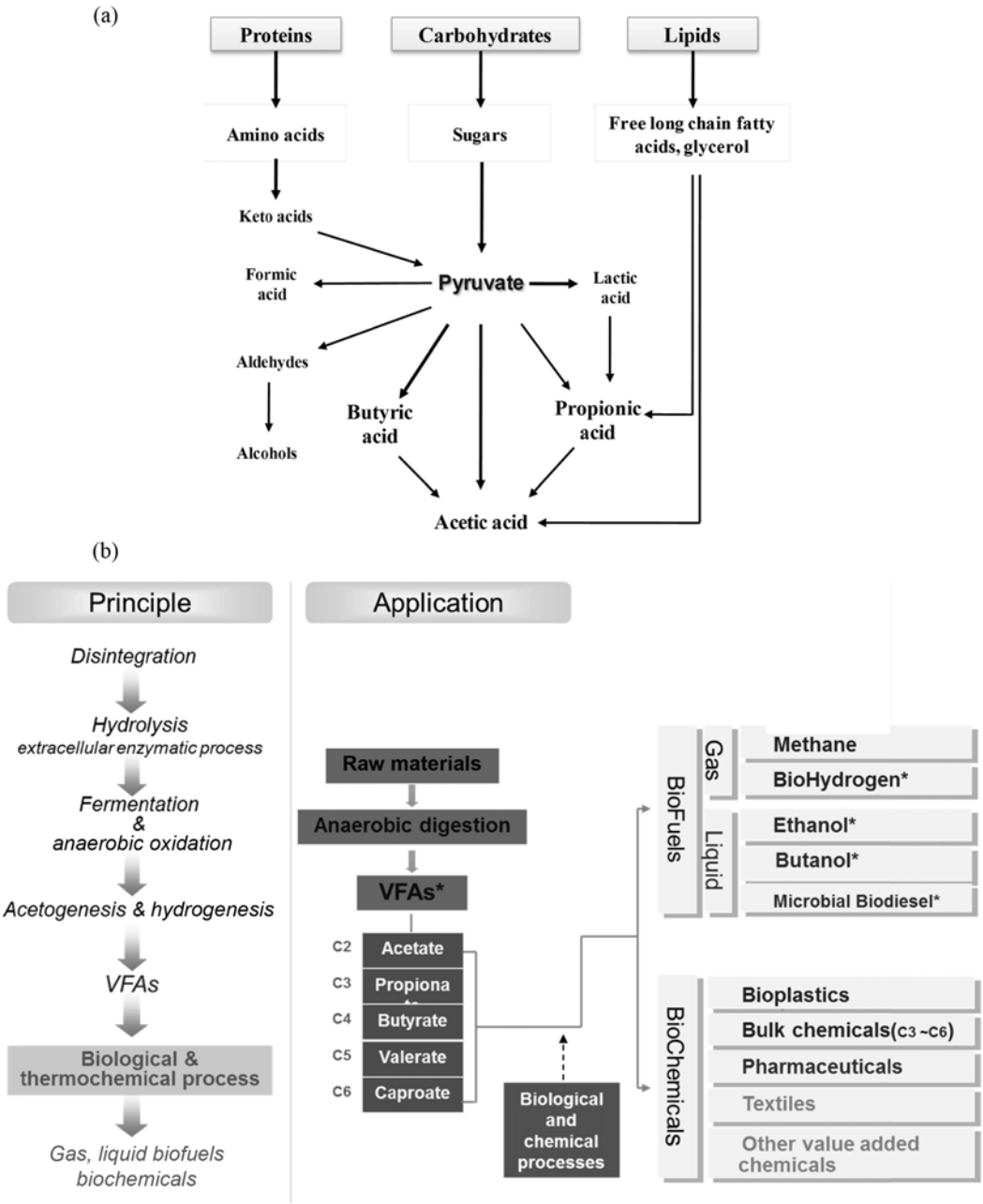


Fig. 5. (a) Volatile fatty acids pathways of carbohydrate, proteins and Lipids. Major products of anaerobic digestion by mixed bacteria are VFAs, CO_2, NH_3 and H_2S form protein decomposition. Further processing of VFAs ends up with CH_4 and CO_2 gases. (b) VFA platform for fuels and chemicals from biomass. Fuels (gas: CH_4, H_2, liquid: ethanol, butanol, microbial diesel). Many kinds of biochemicals can be made from acetic, propionic and butyric acid platform.

Korea (small-scale), which is considered not economical. The enzyme-sugar platform can produce bioethanol, but its commercialization is delayed because the process is not yet economical in comparison with grain-based bioethanol in its quantity and price.

Fig. 5(a) introduces a new platform based on volatile fatty acids, which can be made by stopping methane-forming step in a series of the following reaction process: biomass→conversion to glucose →amino acids, glucose, free long chain fatty acids and glycerol→ VFA acids→biogas. The last methane-forming step eliminates liquid phase soluble organics into gas phase carbon dioxide and methane gas. Since CO_2 does not have any energy content, all the energy will be concentrated in methane gas. The accumulation of volatile fatty acid is possible by inhibiting the last step to methane gas formation. It is a biological process governed by mixed culture rather than pure culture. However, it is a very slow process. It is slow because the rate-limiting step is solubilization of solid particles, and also the

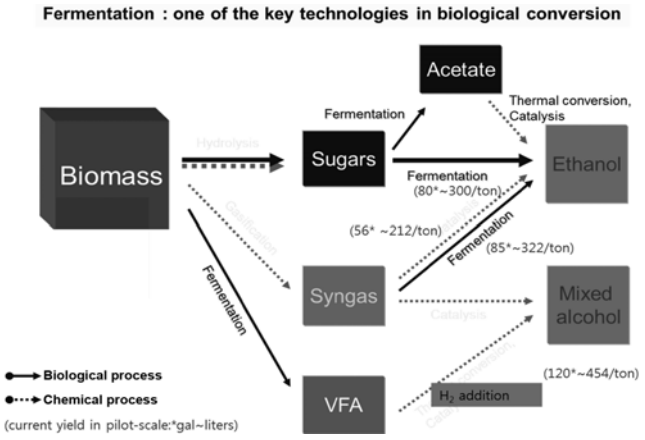


Fig. 6. Yields of bioethanol or its equivalent in various conversion platforms.

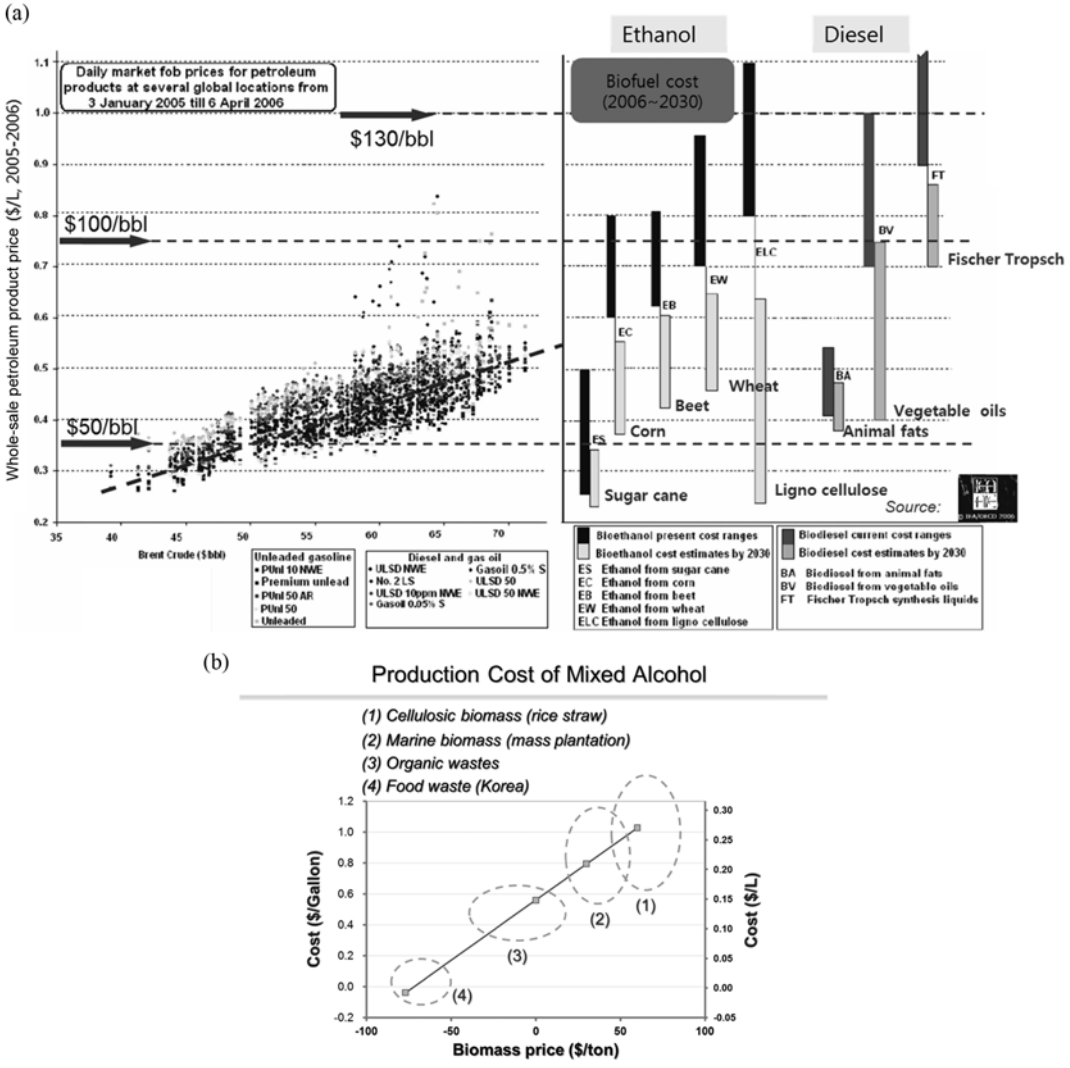
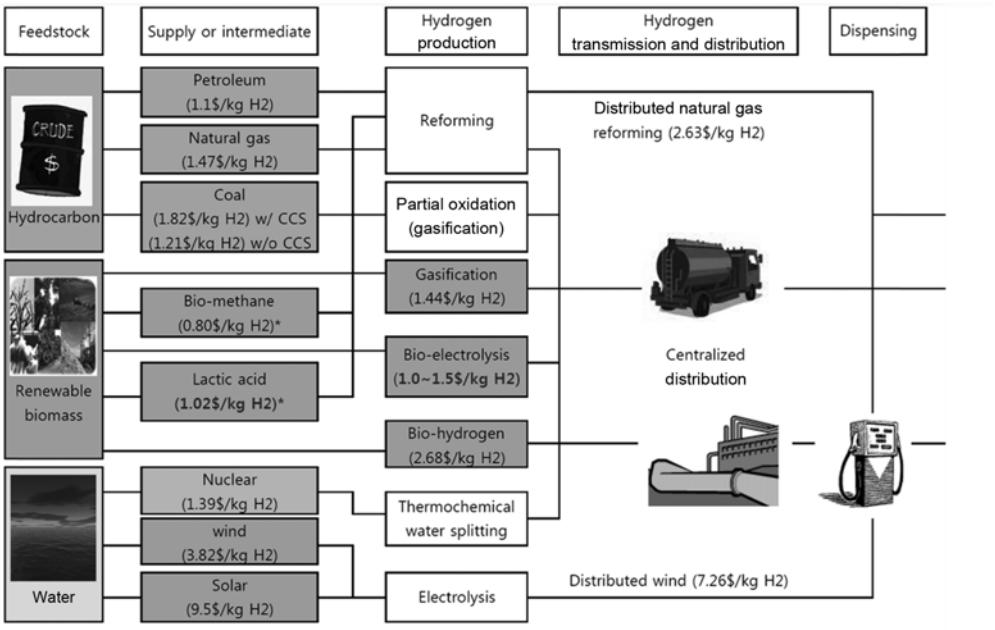


Fig. 7. (a) Various grain-based biofuels against oil price. Left side: Wholesale petroleum product price ($/L) in a 2005-2006 period is proportional to brent crude price ($/bbl, X-axis). Right side: Price range (current-black, 2030-gray) shows competitiveness of biofuels from various feedstocks (ethanol~ sugar cane, corn, beet, wheat, lignocellulose; diesel~animal fats, vegetable oils, Fisher Tropsch); Ethanol from sugar cane and biodiesel from animal fats are most competitive (©IEA/OECD 2006) [20]. (b) Mixed alcohol with various kinds of Lignocellulosics. The cost of lignocellulosics can vary depending on sources. Foodwastes in Korea is most competitive but its amount is limited. Rice straw can be most expensive.



[US Energy information administration (2008) Hydrogen Use, Petroleum Consumption and Carbon Dioxide Emission, Assumes biomass steam reforming yield of 60% and additional processing costs of 30% CCS: Carbon Capture and Sequestration] http://www.eia.gov/oiaf/servicerpt/hydro/hydrogen.html

Fig. 8. Simplified Overview of the Estimated Hydrogen Economy. H_2 can be made from fossil fuel sources, renewable resources and by water splitting with high temperature or electrolysis. Electrolytic method is most expensive; nuclear, natural gas coal without CCS is the next; reforming of bio-CH_4 and lactic acid renewable sources are most economical [21].

cell density is very low. MSC-HCDC (multi-stage continuous high cell density process) is a high productivity process because it uses 10 times higher cell mass. Also, this process is a new process that needs many revolutionary bioprocessing technologies.

A mixture of ethanol, propanol, and butanol can be produced with VFA platform. This platform makes acetic, propionic butyric acids and its derivatives (Fig. 5(b)). VFAs can be precipitated as calcium salts. Thermal decomposition of calcium salts yields ketone from which adding hydrogen generates alcohols having C_7-C_{10} hydrocarbons.

Fig. 6 compares ethanol yields by the three platforms. A sugar platform can yield 300 L ethanol if xylose is fully utilized; otherwise 200 L ethanol is possible. Syngas platform may give a maximum of 150-200 L, and VFA-platform can produce C_2-C_4 with $2H_2$, and C_3-C_7 alcohol with $1H_2$ hydrogen molecules. The amount for C_2-C_4 alcohols can be 500 L/ton. Fig. 7(a) shows current grain-based ethanol competitiveness against crude oil price per barrel (bbl): sugarcane~50$/bbl, corn, beet~90$/bbl, wheat~100$/bbl, lignocellulosics~130$/bbl. In biodiesel, animal fats are competitive with 70$/bbl, and plant oils with 120$/bbl.

Fig. 7(b) shows that food waste (Korea) with sugar or VFA platforms is very competitive even now and other organic wastes such as cattle manure, sludge are competitive while agricultural wastes is less competitive since its raw material cost is small compared to that of grains, due to very low product yield. Marine biomass is an excellent raw material for VFA-platform, while it is a very poor raw material for sugar platform. Cellulosic biomass can be a suitable raw material for sugar and syngas platforms, but its suitability for VFA-platform is unknown and needs more investigation. The economical production of hydrogen needed for a biorefinery depends on its raw materials [Fig. 7(b)]. H_2 can be produced from three sources: hydrocarbon refinery in terms of $/kg hydrogen (petroleum 1.15, natural gas 1.47 and coal 1.825; biomethane 0.80, lactic acid 1.025, gasification 1.44, bioelectrolysis 1.0-1.3, biohydrogen 2.68; nuclear 1.39, wind 3.82 and solar energy 9.5 [Fig. 8].

4. Bioethanol and Biodiesel and Chemicals by Grains and Plant Oils

4-1. Grain-and Plant Oil Based Biofuels

Fuel ethanol is commercially produced from sugarcane in Brazil, corn in the USA, and cassava in Southeast Asia [22]. Ethanol production amount/year in 2011 is 22.9 bgy (billion gallons per year), among which USA produces 57.6%, 13.2 bgy. The USA enacted the Energy Independence and Security Act (EISA) in 2007 and plans to produce 36 bgy by 2022. In Korea, there is no fuel ethanol production yet, but there is ethanol production for liquor using imported grains. However, there are Korean companies that produce fuel ethanol in Southeast Asia.

Biodiesel is commercially produced using waste oil, animal fats, plant oils from palm, soybean, sunflower and rapeseeds. Its production capacity in 2008 amounts to 32.6 million ton, MT ton/year (1 MT=264.2 gallons). Among them only 11.1 million tons are used for production. The USA uses 650 mgy out of 3300 mgy (million gallons per year,) and Europe's demand is about 80% of the total while the rest of the world is only 20%. The details are found in "Biodiesel 2020" published by emerging market [23,24]. Global ethanol biofuel 2008 amounts to 17.3 bgy and biodiesel is 11.1×

264/1000=2.93 bgy. The ratio of ethanol/diesel is 17.3 bgy/2.93 bgy=5.93. The US fuel consumption in 2008 was 133 bgy for gasoline, 42 bgy for diesel, and 15 bgy for airplanes. The transportation total is 190 bgy [25]. The ratio of transportation total/diesel is 190/42=4.52. Bioethanol is 9 bgy, which accounts for 6.76% of gasoline. The use of bioethanol may go up to 13.2/133=9.9% in 2010 and in 2022 will be 36 bgy, going up to 25%.

4-2. PLA and PHB

Poly (lactic acid) or **polylactide** (**PLA**) is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States), tapioca products (roots, chips or starch mostly in Asia) or sugarcanes (in the rest of world). PLA is polymerized chemically from lactide monomer made thermally from two lactic acid molecules. Lactic acid is a fermented product from glucose. PLA can biodegrade under aerobic conditions naturally, but recycled PLA can be decomposed thermally to lactide monomer again. [26]. PLA has wide applications such as woven shirts (ironability), microwave trays, casing of mobile phones, hot-fill application and engineering plastics, biodegradable bags, biomedical polymers.

Natureworks (USA), Purac biomaterials (Netherlands), and several Chinese manufacturers and Futerro (Belgium) are currently producing PLAs, but the amount is rather small. According to CNN.com report (2009-11-23), Korea's science and engineering university, KAIST (Korea advanced Institute of Science and Technology) has found a way to produce PLA using bio-engineered *Escherichia coli* [27,28].

Polyhydroxybutyrate (**PHB**) is a polyhydroxyalkanoate (PHA), a polyester polymer first isolated and characterized in 1925 by Indian microbiologist Abhilash Singh. PHB is produced by microorganisms (like *Ralstonia eutrophus* or *Bacillus megaterium*), apparently in response to conditions of physiological stress [29,30].

Many polymers of this class include poly-4-hydroxybutyrate (P4HB), polyhydroxyvalerate (PHV), polyhydroxyhexanoate (PHH), polyhydroxyoctanoate (PHO) and their copolymers.

ICI had developed the material to pilot plant stage in the 1980s, but interest faded because of high raw material cost and poor properties in comparison with its petrochemical counterpart, polypropylene. Monsanto once owned all the rights on PHB manufacturing from ICI/Zenetra, but its commercial effort failed, and sold its right to Metabolix. Now Metabolix is developing a cost-effective method for manufacturing PHAs in general including PHB. Another group of researchers at Micromidas Inc. has begun to produce PHB from the bacteria in municipal wastewater. This approach shows a promise for the future of human waste disposal and biodegradable plastic production. Brazil PHB Industrial is producing PHBs using waste organic stream and sugar cane. Its market share of PHB is 0.8% (4-5 million US$) of all the plastic markets in Brazil and quite comparable to the PLA imported from USA (0.9%) [31]. Three kg of sugar cane is needed to make 1kg PHB [32].

Biopol is currently used in the medical industry for internal suture. It is nontoxic and biodegradable, so it does not have to be removed after recovery. PHB can be blended easily with polycaprolactone (PCL), a biodegradable polyester with a low melting point of around 60 °C and a glass transition temperature of about 60 °C.

4-3. Propanediol [33]

Previously 1,3-Propanediol was chemically synthesized by the hydration of acrolein. The second chemical method is to use the hydroformylation of ethylene oxide to produce 3-hydroxypropionaldehyde, which is hydrogenated to give 1,3-propanediol.

Now we have two other routes involving fermentation by certain micro-organisms:

(1) Conversion from corn syrup effected by a genetically modified strain of *E. coli* by DuPont Tate & Lyle BioProducts. 120,000 tons were produced in 2007 according to DuPont; the Bio-PDO process uses 40% less energy than conventional processes, and reduces greenhouse gas emissions by 20% [34]. Conversion from glycerol (a by-product of biodiesel production) occurs by using *Clostridium diolis* bacteria and *Enterobacteriaceae* [35].

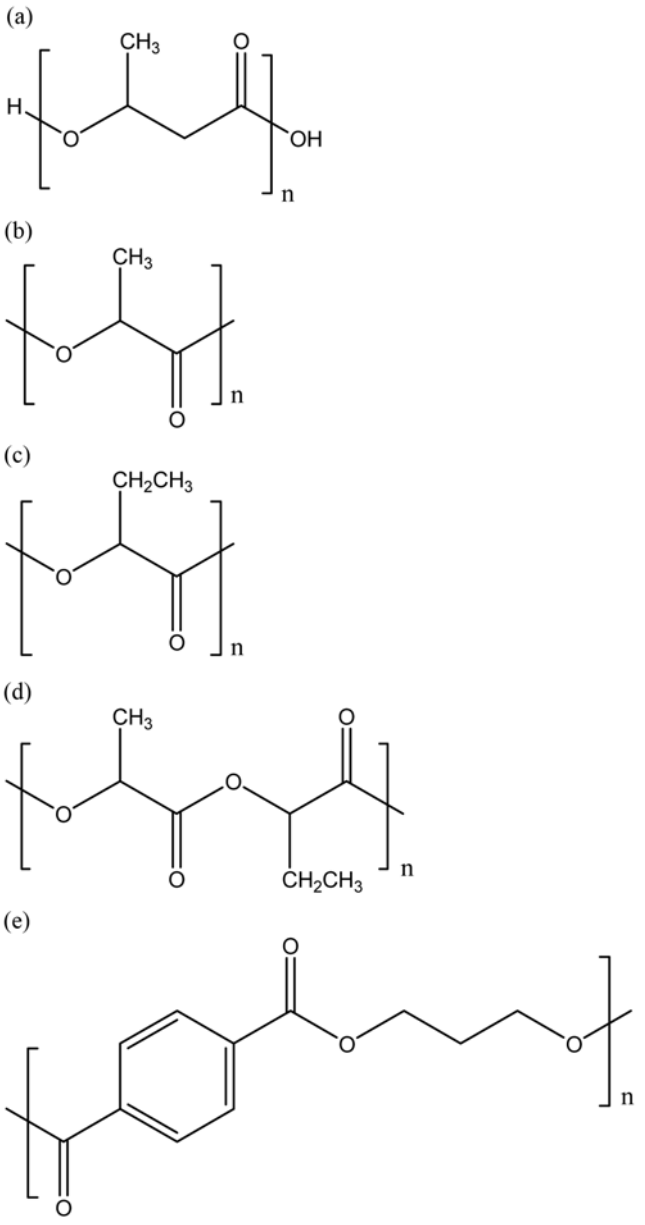


Fig. 9. Chemical structures: (a) Polyhydroxybutyrate (PHB). (b) Poly-3-hydroxybutyrate (P3HB). (c) Polyhydroxyvalerate (PHV). (d) Poly-3-hydroxybutyrate-co-3-hydroxyvanderate (PHBV). (e) SORONA (PTT: polytrimethylene terephthalate).

Purification of 1.3 propanediol involves filtration, ion exchange, flash evaporation and distillation [36]. In addition to the production of polymers such as polytrimethylene terephthalate, 1,3-Propanediol can be formulated into a variety of industrial products including composites, adhesives, laminates, coatings, moldings, aliphatic polyesters, copolyesters. It is also a solvent and used as an antifreeze and wood paint.

SORONA is a polymer created by DuPont based on 1,3-propanediol (PDO). It was named and commercialized in 2000. The fibers are claimed to be both soft and extremely stain resistant with high strength and stiffness. SORONA (also called PTT or 3GT) is poly(trimethylene terephthalate), a co-polymer of *Bio-PDO* (fermentation-derived 1,3-propanediol), and petroleum derived terephthalic acid (TPA) or dimethyl terephthalate (DMT). Related polymers in this series include polyethylene terephthalate (2GT) and polybutylene terephthalate (polytetramethylene terephthalate) (4GT) [37].

BIOPROCESSING OF NEW BIOFUELS AND CHEMICALS FROM BIOMASS

1. Lignocellulosic Ethanol

Each year the US Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy issues biomass multi-year program plan (biomass MYPP, 2011) regarding technology progress and its realization program, and "Biomass-to-Bioenergy Supply Chain" is shown below [6].

The Office of Energy Efficiency and Renewable Energy (EERE) aims at improving energy efficiency of current operating systems and renewable energies, thereby using less fossil fuels. The MYPP consists of feedstock supply, biomass conversion, bioenergy distribution and bioenergy end use. The USA has a full supply chain except feedstock supply, while Korea does not have any of the above supply chain. Korea has a good feedstock supply chain for food waste raw materials while the remaining three chains are not ready yet. The US DOE/EFRE program covers only biochemical (sugar-platform) and thermochemical (syngas) program. More information on various renewable energies can be found further at the US National Renewable Energy Laboratory [38].

2. Microalgae and Microbial Biodiesel

Biodiesel production based on plant oils competes with food supply and may not cover all the petroleum diesel needs. As an alternative to plant oils, diesel production by Fisher-Tropsch method is also considered [39,40]; biologically autotrophic microalgae using solar energy and CO_2 [41,42]; heterotrophic microbial diesel production using glucose and volatile fatty acids are under consideration [43-46]. Diesel algae are grown in shallow lagoon or raceway pond (Sapphire energy, Aurora biofuels, Live fuels) and closed pond (Green Star). Plastic tubes (BioFuel Systems SL), Thin film (e.g., Green-Fuel Technologies), Open/Closed systems (e.g., Petro Algae, HR Biopetroleum). In controlled systems algae productivity increased about 7 times but with increased capital/operating costs.

3. Platform Chemicals for Organic Synthesis

There can be many platform chemicals from which many precious fine chemicals can be derived. In biotechnology succinic acid, furfural, and 5-hydroxymethyl furfural (HMF) are called important platform chemicals. Their characteristics and applications are given in the references [47-51]. Succinic acid is made by fermentation from glucose and xylose. Furfural is made from xylose by thermal treatment in acidic conditions, while 5-hydroxymethyl furfural comes from glucose by a thermal treatment similar to furfural. Butanol is a good candidate for fuel ethanol in a near future and is made by fermentation. Citric acid is produced by fermentation in large quantities.

3-1. Succinic Acid

Fermentation on succinic acid was studied in collaboration with Professor SY Lee at KAIST for almost 10 more years. Initial studies were done with an existing strain of *A.succiniciproducens*. To find optimal conditions on this microbe we had to change mediums from glucose to wood hydrolyzate, whey and corn steep liquor [52-55]. Later we found a new strain of *Mannheimia succiniproducens* MBE55E [56]. We tried to do a continuous high cell density culture of succinic acid using external membrane cell recycle reactor, which failed owing to the contamination of presumably lactic acid bacteria [57].

3-2. Lactic Acid

Lactic acid was a target material for the study of MSC-HCDC, but lactic acid itself was a very important key raw material for high molecular weight polylactic acid (PLA) polymers. To improve lactic acid productivity in fermentation we added vitamin [58] and we used microencapsulation technique, which did not give a high productivity [59]. Realizing immobilization of cells does not solve basic problems of high cell density culture turned us to work on suspension cultures with high cell densities. We carried out two-stage high cell density culture to obtain a higher product titer together with high productivity [60]. This result encouraged us to propose a multistage continuous high cell density work in general fermentations (MSC-HCDC) [8]. The Polymer synthesis group of Woo and Park worked together with us for chemical synthesis of high molecular weight PLA [61,62].

3-3. Citric Acid

Citric acid is a commodity chemical, and more than a million tons are produced every year by fermentation. It is used mainly as an acidifier, as a flavoring, and as a chelating agent. We immobilized *A. niger* in the polyurethane sponge [63] or tried to produce citric acid in dual hollow fiber bioreactor (DHFBR) [64]. The latter attempt gave us a very high productivity, but the reactor was distorted by the expansion of immobilized fungal cells.

4. MSC-HCDC (Multistage Continuous High Cell Density Culture)

A benefit of high cell density culture is to obtain high productivity, which may be proportional to cell mass (X). For higher bioreactor productivity, the residence time of fluids (HRT) needs to be very short, which may result in incomplete substrate conversion. Retaining cells in a bioreactor needs a separation of HRT from those of cells (solid retention time, SRT). High titer can be obtained with a supply of high substrate concentration, which may cause substrate

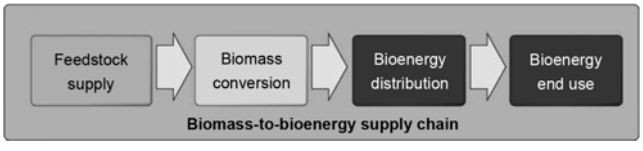
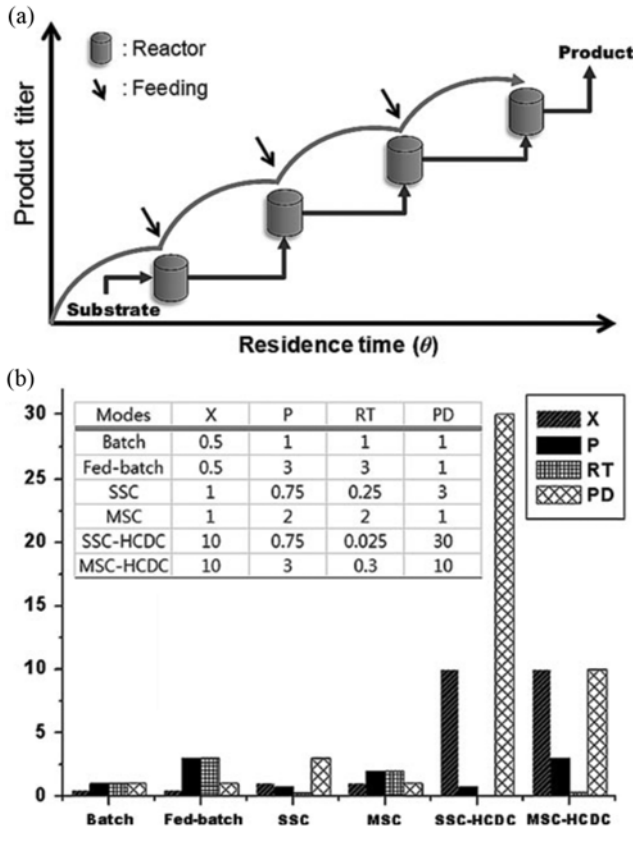


Fig. 10. Multi-year production plan (MYPP, 2011). Biomass supply chain.

inhibition. That is why we need fed-batch method, which may yield high product titer but with lower productivity because of low cell concentration. Bioreactor productivity is expressed as specific cell productivity (qp/x). times cell density (X), where bioreactor titer is given by Yp/s (So) assuming 100% substrate conversion. Many biochemical engineers who used to work on fermentation and purification now work on a new field of metabolic engineering in order to make faster, higher product yielding strains [65]. Chang and his associates showed that MSC-HCDC system can replace commercial fed-batch system with much high productivity by maintaining fermentation titer equivalent to that of fed-batch system [8]. Fig. 11(a) shows a replica of the fed-batch system. The only difference is that fed-batch is a batch system with a low cell density, while MSC-HCDC is a truly continuous system with high cell density. A continuous system gives three times biomass productivity of the batch system, while MSC-HCDC can give ten times high cell density of the batch or fed-batch system. Fig. 11(b) shows that single stage HCDC gives a 30 times productivity of batch/fed-batch system but with lower titer, while MSC-HCDC gives a little reduced productivity of 10 times of the batch/fed-batch productivity.

Studies on the reuse of enzymes with ultrafiltration membrane retaining hollow fibers were started in early 1970s in the United States. Application to microbial production of ethanol and lactic acid started in late 1970s and early 1980s. Unlike enzymes, microbial cell hollow fiber reactors experienced difficulties of plugging due to over-growth in the continuous running of bioreactors. The interest faded very quickly after people realized that industrial substrates cannot be used in this type of reactor. Immobilized packed cell reactors had similar problems of instability and diffusion limitation in the particle matrix [66].



Modes	X	P	RT	PD
Batch	0.5	1	1	1
Fed-batch	0.5	3	3	1
SSC	1	0.75	0.25	3
MSC	1	2	2	1
SSC-HCDC	10	0.75	0.025	30
MSC-HCDC	10	3	0.3	10

Fig. 11. (a) Analogy of MSC-HCDC with fed-batch. The differences between the two are in whether the system is *high cell density* (MSC-HCDC) or low cell density (fed-batch); *continuous* or batch. (b) Comparison with various fermentation methods. MSC-HCDC achieves the same titer with 10 times fed-batch productivity. Single stage HCDC gives a 3 fold higher productivity but the titer is lower than in fed-batch [8].

Chang and his associates realized that high cell density culture is needed, but it should be based on suspension culture rather than immobilized cells [67]. Lee and Chang [68] raised the cell concentration to 210 g/L in ethanol production with glucose using external hollow fiber bioreactor and proposed kinetics on high cell density culture for the first time. This membrane cell recycle system makes it possible to obtain high cell density culture. The role of membrane is to separate solid (cell) retention time (SRT) and from hydraulic retention time. If we adjust all the effluent to pass through the membrane, the cell density will keep increasing without loss. However, 210 g/L was too viscous to run the bioreactor, and hollow fiber plugging was a problem to solve for long-term running. During about 10 day's operation the cell density was 100-150 g/L, ethanol concentration was 65 g/L and the productivity was 85 g (/L.h) with a 14% glucose substrate [68]. A new internal stainless filter cell recycle was used for continuous ethanol fermentation [69]. The maximum yeast cell concentration of 157 g/L was obtained to be successfully operated for 10 days. In membrane recycle bioreactor for solvent extraction, glucose conversion increased from 45% to 91% at a concentration of 270 g/L with dibutyl phthalate solvent [70]. This internal membrane bioreactor was used in production of ethanol from wood hydrolyzates and tapioca [71,72].

Chang and his associates introduced depth filter perfusion system where hybridoma cells producing monoclonal antibodies were successfully immobilized [73-76]. Unlike a conventional hollow fiber system with a pore size less than yeasts 0.2 μm, the depth filter perfusion system has a pore-size larger than the size of animal cells. This means that the retention of cells is less than 100%. An upflow packed-bed was used for separating cells from the broth in ethanol production [77]. Its rejection against cells is much lower than 100%, depending on particle size with respect to cells. Now we have a hollow fiber system having a 100% cell rejection, and depth filter perfusion and packed bed filtration system yielding a less than 100% rejection with which we can run high cell density fermentation. The packed bed system can be very useful in separating larger particles of cm or several millimeter sizes. In comparison with sedimentation we can obtain much faster rate of separation than hollow fibers or depth filter perfusion system. We have an experience of one year's plugging free packed-bed operation for separating small particles from kitchen disposer ground wastewater stream [78].

Chang and his group performed 2-stage high cell density culture system to see whether a multistage high cell density culture system could increase product titer as compared with the single stage HCDC system. Indeed the 2-stage HCDC system did increase the product titer with less higher productivity than the single stage HCDC system.

Chang and his associates have accumulated many years' experience of single stage high cell density culture system and successful experimental results with two-stage high cell density culture system, which made it possible to propose multistage continuous high

cell density culture (MSC-HCDC) system [8].

4-1. Membrane Module Studies

Researches on membrane module were carried out in late 1970s because of our interest in efficiency of membrane modules and mass transfer in electrodialysis [79]. This interest was extended to ultrafiltration membranes in solving mass transfer limitation owing to diffusion limitation. Convection in the form of pressure and ultrafiltration pulsing were introduced between two membrane chambers of enzyme bioreactor to facilitate mass transfer between lumen and shell side [80,81]. Three types of membrane modules are used: plate and frame module, spiral wound, and tubular types. In late 1970s and 1980s we carried out a numerical analysis on spacer and turbulence promoter to understand what affects mass transfer efficiency in membrane permeation of plate-and-frame, spiral wound modules [82,83]. A flow distribution on hollow fiber module was done numerically and experimentally [84]. Our finding was that flow distributions are not uniform, but overall reaction efficiency of hollow fiber module did not change much. Sometimes residence time in blood oxygenator module can affect blood coagulation because non-uniform residence time distribution can cause blood coagulation in some hollow fibers.

MSC-HCDC needs cell recycling devices such as hollow fiber, depth filter, packed-bed and even settling. Usually, the density of a cell is 1.03 g/cm^3, slightly heavier than water and the cells will precipitate but very slowly. Thus a hollow fiber can be a good choice, but it has plugging and fouling problems. If we choose a hollow fiber device, we have to think of regeneration or cleaning. Any cleaning method should not harm cells. Other choice will be to use many systems and one of the many will be in cleaning service all the time.

A hollow fiber system has 100% rejection, but a depth filter has a fouling and plugging problem, too with less than 100% rejection. Packed-bed separation works very well for large particle substrates. The typical rejection % can be much less than 100%, but we do not have to worry much about plugging problems. Even if plugging occurs, backwashing is much easier than in the other two systems.

4-2. Microencapsulation of Immobilized Cell and Enzymes

At an early stage of animal cell cultivation, microencapsulation of animal cells with biocompatible membrane was considered [85]. Chang and his associates immobilized microbial cells in the microcapsules to use it as immobilized whole cell enzyme. The cells were completely enclosed by semi-permeable membranes and were kept alive depending medium supplied from outside [86-91]. This method is not useful for aerobic cell application because of short oxygen penetration depth [92]. There can be many applications if semi-permeable membrane with chemical and mechanical resistance is used [93].

4-3. Applications to Extracellular Products

We have to consider the following four items for the operating cost evaluation of bioproducts: (1) raw materials and product yield, (2) utility (electricity, steam), (3) labor, and (4) depreciation (capital cost).

The highest impact of research can be to find a new raw material with low cost since it accounts for 70-80% of the manufacturing cost. The next will be to reduce utility cost needed for product enrichment and purification. The third sector of labor is not much important, but high R&D cost may add up to the manufacturing cost and delay of product launching. Finally, a low productivity in reaction and separation may increase capital cost. Our focusing on the bioprocessing of fuels and chemicals from biomass lies in finding and using economical raw materials such as organic wastes for volatile fatty acids, high reactor productivity, and low energy enrichment process. Our current processing technologies are MSC-HCDC for higher reactor productivity, and a low enrichment process is based on membrane separation rather than conventional distillation and extraction.

4-3-1. Ethanol, Lactic Acid, Succinic Acid

Ethanol is a typical high volume low cost. Since the current commercial process is batch (high titer, low productivity), we focused efforts on developing high productivity fed-batch substitute process and the result is to develop MSC-HCDC to a commercially successful process [8]. A number of studies were carried out for high cell density culture [67,68], an upflow packed bed [77], wood hydrolyzate [71], tapioca [72] and detoxification of hydrolyzates [94]. Chang and his associates did a number of important studies on annual herbaceous plants to get 56 g/L (SSF) and 69.3 g/L (SHF) and marine biomass *Laminaria japonica* to obtain 23.0-29 g/L of ethanol [95,96].

Lactic acid: The goal is the same as ethanol. We carried out 2-stage MSC-HCDC [60]. *Lactobacillus casei* cells immobilized in liquid-core alginate capsules were tested and vitamin B effect on lactic acid production were studied [58,59].

Succinic acid: A number of studies for the production of succinic acid fermentation were already described in this manuscript. Recently we tried to run a single stage high cell density culture of succinic acid production, but failed because of contamination by *Lactobacillus* sp. [57].

4-3-2. Volatile Fatty Acids: Many Applications

Volatile fatty acids (VFA) are mixtures of acetic, propionic, butyric, valeric, caproic acids derived by anaerobic fermentation of carbohydrates, lipids and proteins. The degradation process of any organic waste (biodegradable) goes anaerobically through a process of monomers by hydrolysis, volatile fatty acids, carbon dioxide and methane gas. Stopping the last step to CO_2 and CH_4 will accumulate volatile fatty acids. Sulfur and nitrogen compounds in protein will become H_2S and NH_3. Anaerobic digestion of glucose will yield 50% CO_2 and 50% CH_4 if none of glucose is used for cell synthesis. If a substrate contains more lipids, then CH_4 content will go up to 70%.

Fig. 5(a) shows the details of VFA production from biodegradable organic substrates. Lim et al. (2008) studied volatile fatty acid production from Korean food wastes by changing, temperature, hydraulic residence time and organic loading rate in a once-a-day feeding and drawing-off bioreactor [97]. The VFAs can be used in the denitrification of municipal wastewater treatment as electron donor [98,99]. Recently, the VFAs were used in fuel cell applications [100, 101]. In this review paper we propose the VFA-platform for fuels and chemicals from biomass [102]. Various carbon number alcohols can be made with hydrogen addition reaction or can be fed to oleaginous microbial cells for biodiesel lipids application [43,44]. There is a question concerning a supply of hydrogen for synthesis of alcohol from VFAs. VFAs can be converted to hydrogen by catalytic reforming [103], which needs more and longer research efforts for industrial application. In the mean time we may use hydrogen from natural gas reforming, which is a fully established commercial process.

4-3-3. Monoclonal Antibodies

High cell density culture of animal cells for monoclonal antibod-

ies was performed by entrapping cells in polymer supports, spin filter, and various other methods were used, but not successfully. The current consensus is that it should be in suspension form rather than in immobilized cells. Continuous culture is accepted in the form of hollow fiber culture where cells are in suspension state. A depth filter perfusion system (DFPS) does not reject animal cells by 100%, but the rejection rate is 70-80%. Cells are not immobilized but are suspended in small pores larger than the animal cells of the DFPS. Chang and his associates carried out very successful experiments of two-stage continuous for short term, single stage continuous for long-term cultures, and MSC-HCDC (multistage continuous high cell density) simulation studies [8,75]. The reactor productivity was around 30-10 times batch depending on the pore sizes. Some adherent cells attached to the pore surfaces caused plugging of pores and prevented long-term running of single stage HCDC reactor. The treatment of trypsin on these cells made possible long-term running of 81 days [76]. Kim et al. (2007, 2008) carried out high cell continuous culture using cell centrifuges [104,105].

4-4. Applications to Intracellular Products

4-4-1. Intracellular Recombinant Proteins

Lee and Chang (1990) obtained 145 g/L of *E. coli* dry cells containing recombinant penicillin acylase using hollow fiber membrane recycle system (external) [106]. The oxygen content in the air was controlled at 50-60% of the air saturation and high purity oxygen. This is the first production of intracellular products in continuous (single-stage) high cell density culture. Intracellular products need oxygen for product synthesis. As a result, high oxygen transfer rate is needed in high cell density culture system. *Bacillus thringiensis* cells were cultured in 2-stage high cell density culture [107]. Later, this system was applied to toxin production, bioadhesive and nar-promoter utilization [108-110]. Although many of intracellular products are produced by fed-batch, this can be done with MSC-HCDC technology, too.

4-4-2. Polyhydroxybutyric Acids (PHB)

Kim et al. (1994) obtained 164 g/L of cell mass containing polyhydorxy butyrate (PHB) and 121 g/L of PHB (content 73.8%) with a productivity of 2.42 g/(L.h) [111]. The PHB gene was cloned in *E. coli* to produce PHB [112]. Han et al. (1994) purified PHB with various methods [113]. Ryu et al. (1997) obtained 281 g/L cell mass and 232 g/L PHB (content 82.5%) with phosphate limitation in 60 L fermentor [114]. PHB productivity was 3.14 g/L/h. Chang et al. (2003) studied the effect of CO_2 in the final cell mass and its PHB content [115]. Poly-beta-hydroxybutyrate biosynthesis was studied in *Alcaligenes eutrophus* under various nutrient-limiting conditions. When the cells were cultivated in nitrogen-limited media, both the levels of NAP(P)H/NADP were higher than those under nitrogen-sufficient conditions [116]. Recombinant *E. coli* harboring PHB can produce PHA [117].

4-4-3. Microbial Lipids

As an alternative to biodiesel from plant oils and animal fats, microalgae and microbial lipids are considered for biodiesel production. Microalgae can be grown in autotrophic culture with solar energy and CO_2 [41,42]. It is faster than palms or soybeans but still slower than microorganisms. Another disadvantage for microalgae is that they need subtropical or tropical climate regions, and much more area or space than microbial cells. We are developing a microbial lipid production based on MSC-HCDC system. For microbial lipids to become economical we need a very cheap substrate (0.1-0.2$/kg), such as volatile fatty acids from organic wastes or glucose or xylose from lignocellulosic biomass. We may make biolipds at a cost of a dollar. Since biomass grows everywhere in the world, this production plant does not have any area or space limitation wherever/whenever any kinds of biomass (animal or plant, or its waste) are available. The current projection of algae fuel cost ranges from lowest 1$/L to highest 3$/L. We did research on biolipid production using *Cryptococcus albus* yeast, which yields 0.167 g/g of *C. albus*, which corresponds well with its theoretical yields [42]. In a two-stage continuous membrane cell recycle culture, the cell concentration, lipid concentration, lipid content was 26.4 g/L, 14.5 g/L and 55.1%, respectively [44]. Our MSC-HCDC based simulation on microbial diesel production predicts a bioreactor productivity over 5 g-lipid/L.h, about 10 times 0.54 g/(L.h) by Li et al. (2007) [118]. The raw material cost estimation with glucose, wood hydrolyzates and VFAs varies from 0.25-1.53$/kg-lipid [119]. For the biodiesel cost we have to add processing (fermentation, purification) and capital depreciation costs, and conversion to diesel cost. Here, we did not consider any benefit of improving the yeast strains. This new MSC-HCDC based technology needs to be competitive against palm lipids (currently, 1$/L).

Summarizing MSC-HCDC technology, we started high cell density culture from external membrane module and moved to using internal membrane module. The cell separation module changed from hollow fiber to a system with depth filter and packed-bed system, including hollow fibers located inside the bioreactor. The further study will develop the MSC-HCDC system which can deal with particulate substrates, too.

ENRICHMENT AND SEPARATION

Fermentation products of biofuel (ethanol, butanol or isopropanol) and platform chemicals (succinic, lactic acids), from the broth, need to be separated and purified to the final marketable forms. Succinic acid and lactic acid are platform chemicals that can be used in the synthesis of plastics and intermediate compounds needed for the synthesis of other chemicals. Their importance was recognized long before the 1980s, after which interest arose, as an effort to decrease global warming gas and industrial importance has become very significant. Also, succinic acid can serve as sinking agent by using gaseous CO_2 during the fermentation process.

Fermentation broth contains a variety of impurities that need to be removed. This cost accounts for a substantial portion of the manufacturing costs. In most cases, the separation and purification step follows the fermentation process, which needs to be a continuous process, especially when product quantities are large. In most cases the fermentation products are produced in the form of a low concentration (titer) aqueous solution. Effective and economical means of extracting desired products from the broth are necessary for successful commercialization of new products of fuels and chemicals from biomass.

1. Enrichment of Fermentation Broth by Forward Osmosis

van't Hoff of the Netherlands published his thoughts on the osmotic pressure of organic solutes in water in 1887, and its translated version, entitled "The role of osmotic pressure in the analogy between solutions and gases," was reprinted in the Journal of Mem-

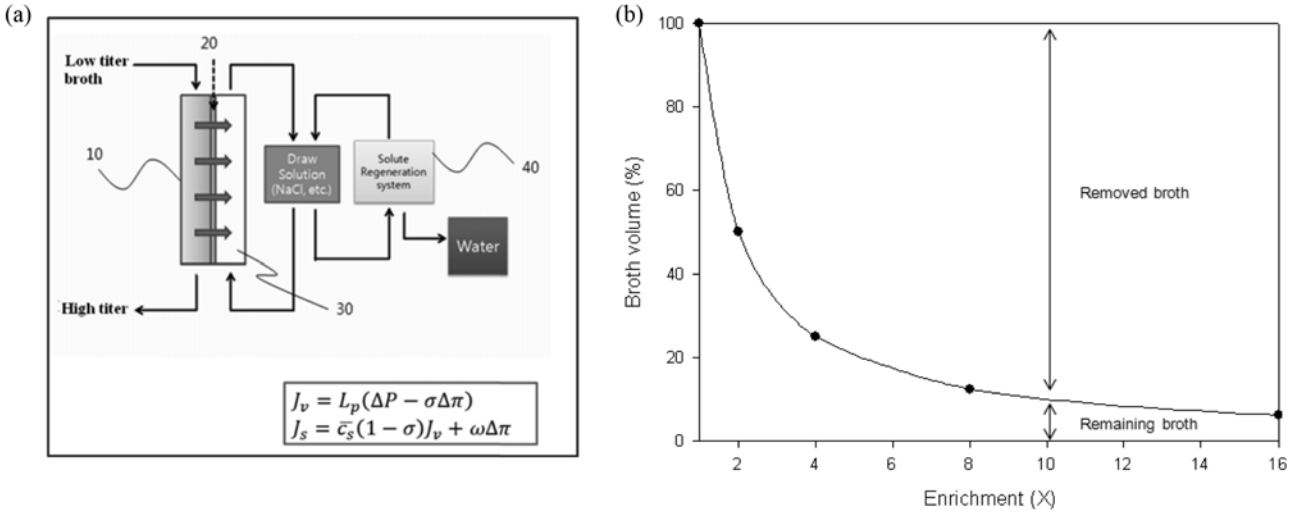


Fig. 12. (a) Enrichment of fermentation broth by forward osmosis (FO). Enrichment of the broth differs from desalination in which the draw compartment is a product stream while in the broth enrichment is feed solution is the product stream. Low titer stream→ the feed compartment (water removal by forward osmosis)→high titer stream. (b) Enrichment Factor vs % broth removal. 2× (two-fold enrichment) needs 50% water removal, and 4× needs 75%. Higher fold enrichment needs more water removal.

brane Science in 1995 [120,121]. However, almost 90 years after van't Hoff, Loeb and Sourirajan of UCLA made asymmetric cellulose acetate membrane in 1962, which made possible current commercial reverse osmosis process [122].

The concept of forward osmosis was introduced by Loeb in 1976 [123-125], and in 2009 pressure retarded osmosis was used to generate 4 kw electricity from the salinity difference between river and seawater in Norway [125-127]. McCutcheon et al. (2005) published a paper on desalination of sea water using forward osmosis [128, 129]. Reverse osmosis uses high pressure from a feed side as the driving force for filtration of water through the membrane, while forward osmosis uses high osmotic pressure on the chamber of the product side. Draw solution loses its osmotic pressure as water moves from the feed side to the product side.

Enrichment of fermentation broth differs from desalination: the product in the broth enrichment is the feed stream, while the desalination product is the draw solution; the economics of the process is different [Fig. 12(a)]. Suppose the feed solution contains 3.5% VFA corresponding to 35 g/1,000 g-solution, the rest of the 965 g will be water. If we remove 500 g water by forward osmosis, the feed solution contains 35 g/500 g (7 wt%) and the additional removal of 250 g water will result in a solution having 35 g-solute (VFA) and 215 g water (14 wt%, 4-fold enrichment). The enrichment cost was evaluated recently by Chang and associates (Vietnam, AFOB) based on the energy in the forward osmosis being only 0.75 kwh, and 215 g water removal by MSF (multi-stage flash evaporation) needs 5.32 kwh [130]. A simple evaporation all the way from 3.5% to 100% VFA needs 19.5 kwh/kg-VFA, 3.5→100% VFA(MSF)~0.73 kwh/

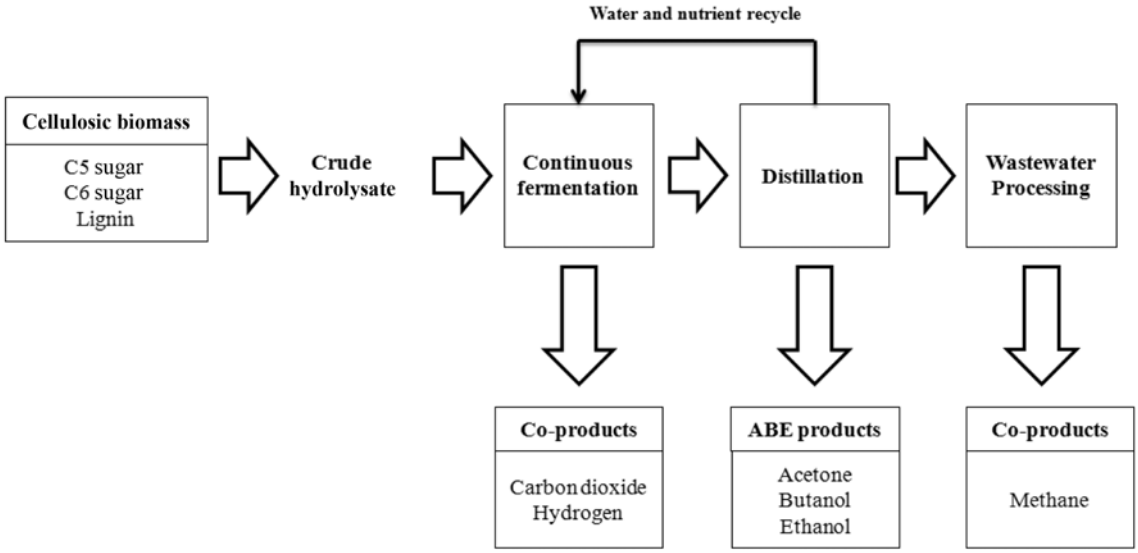


Fig. 13. Continuous bioprocessing of fuels and chemicals from biomass. Biorefinery requires high productivity fermentation, separation and even waste processes because of its nature of low cost high volume. CO_2 and CH_4 can be considered as coproducts [138].

kg-VFA and 3.5%→14% by FO→100% VFA (MSF) will need only 0.19 kwh/kg-VFA [130]. Fig. 12(b) shows the degree of enrichment versus the remaining solution. Enrichment of a dilute fermentation titer needs more water removal and it means low bioreactor productivity. Recently, reversal of electrodialysis was used for power generation like pressure retarded forward osmosis [132,133].

2. Pervaporation of Alcoholic Fuel

Distillation is commonly used for recovery of ethanol from the fermentation broth. Grain-based broth contains about 10 wt% ethanol concentration, while lignocellulose based broth contains less than 5 wt% ethanol. Fig. 6(a) shows complete removal of water from the broth by dehydration process to final products such as acetone, butanol and ethanol. The dehydration step consists of a primary dehydration step (up to their azeotrope points) and the secondary dehydration step that carries out a complete removal of water. The need for a secondary step requires more intensive energy and makes the process more complex. The second dehydration step includes azeotropic distillation, pervaporation, molecular sieve adsorption and reactive distillation [134-137].

Pervaporation refers to a membrane-based separation method for liquid mixtures by partial vaporization through a non-porous or porous membrane. Membrane materials may have hydrophilic or organophilic character. The former membrane is used to remove water from the mixture such as azeotropic mixture of water and ethanol, while organophilic membrane is used to extract organic compounds from the broth.

Hydrophilic membranes, in general, include cellulose or polyvinylalcohol (PVA), polyacrylic-acid (PAA), polyacrylonitrile (PAN). The property of the membrane is characterized by its side group. Selectivity of PVA membrane is controlled by adjusting its crystallinity from the hydroxyl group of the precursor hydrolysis. A target chemical interacts with a polar side group of membrane during the permeation, which determines the flux and rejection of pervaporation [140]. Use of a membrane has the advantage of a continuous process and low processing energy. Sometimes it causes swelling in aqueous environment to change its structure very easily. Crosslinking or crystallization with PAA as crosslinking agent improved the physical property of membranes [141]. Use of crosslinking agent eliminates the polymer side group capable of increasing or decreasing hydrophilicity, which may influence selectivity of membrane. Recently, biopolymers such as chitosan or sodium alginate polymers were also used instead of PVA [142-146]. Such a carbohydrate-based polymer has a bulky structure with high free volume that facilitates water transport. Also, the presence of many hydroxyl groups increases water selectivity from H_2O-alcohol mixture [147]. Fig. 14(b) shows membrane permeation flux versus weight fraction of water by varying degrees of hydrolysis. The maximum flux is achieved at weight fraction about 50% and degree of hydrolysis is about 99% [148,149]. However, too high a hydrophilicity of membrane can cause the stability of membranes to decrease its selectivity, for which problems remain to be solved in the future.

3. Reactive Extraction

In general, we use liquid-liquid extraction and recrystallization methods to recover acids as platform chemicals. The former method separates the target chemical by moving it into an organic phase using the solubility difference between the two phases. A low solubility of target chemical in the organic phase needs a large amount of

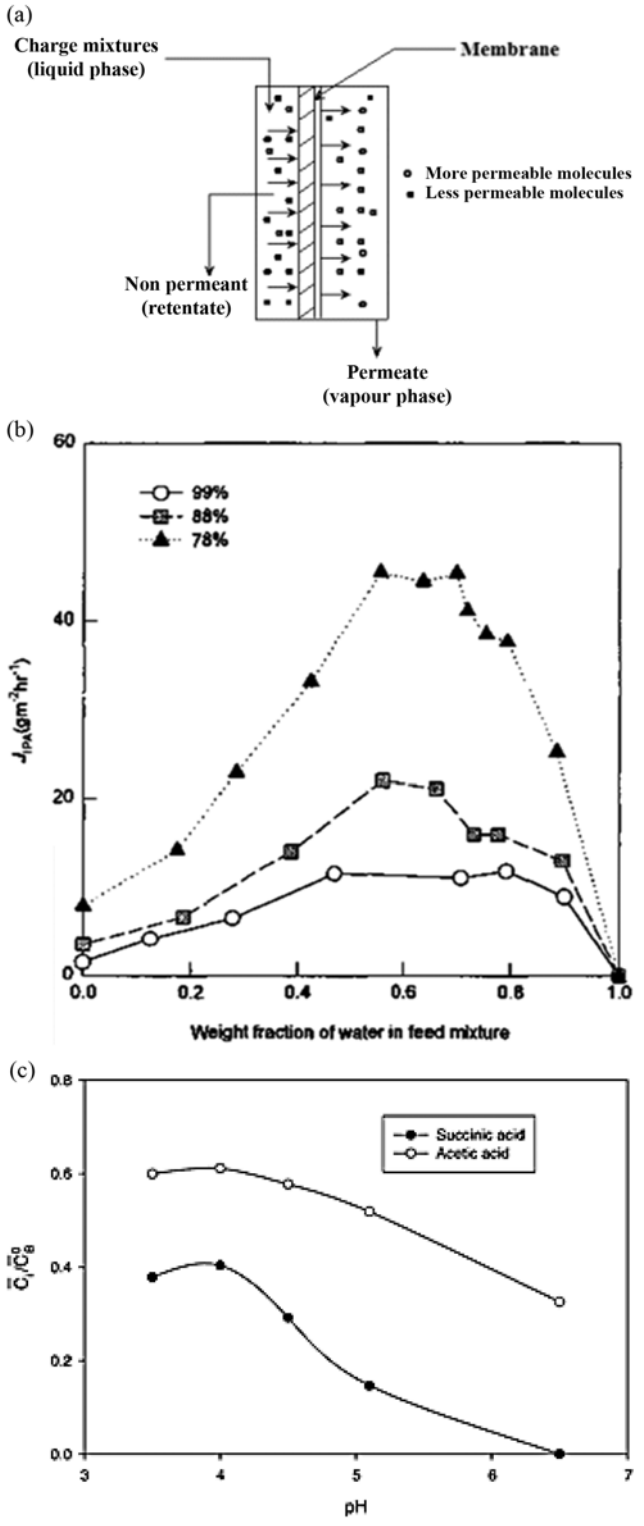


Fig. 14. (a) Schematics of pervaporation for alcohols by the differences of water vapor versus other solute products [139]. (b) Membrane permeation flux (J) versus % feed weight fraction of water. The symbols in the figure denote different degrees of hydrolysis at the membrane. The maximum flux is achieved at a 50% feed weight fraction and degree of hydrolysis 99% [148,149]. (c) Separation of carboxylic acids with tri-amine extractant. The solution pH decides the degree of ionization for solutes to change solubilities of solutes in solvents (octanol+triamine) [160].

solvents, which may require large energy for its regeneration. Recrystallization uses insoluble calcium salts and carboxyl group of succinic acids. The crystals are filtered and sulfuric or hydrochloric acids are added to liberate succinic acid. A large amount of solid slurry and calcium sulfates are generated as waste or byproducts.

To overcome these difficulties, electrolysis, adsorption with porous adsorbents, and nano-filtration are employed [150-152]. As an alternative we consider reactive extraction on the recovery of succinic acid and lactic acid, where extractant and target chemical react, and the complex is dissolved. A succinic acid complex can be formed by the interaction. In the carboxylic acids, phosphorous bonded oxygen donor extractant, such as TBP (tributylphosphate), TOA (tri-n-octylamine), is favored since it has a higher extraction capacity over high molecular weight aliphatic amines and salts extractant. The capacity of extraction, in addition to alkalinity of extractant, is affected by polarity of diluent, aqueous phase pH and many others [153-156]. Amine extractants form salts by reaction of amine (+) group and carboxyl group (−) of acids [157]. Since the reaction rate of carboxyl group and amine group is a rate-limiting step, it is important to choose extractant with high capacity [158,159].

There exist many kinds of organic acids in a fermentation broth, which make it necessary to purify a desired compound selectively. Compounds of salts, acetic acid and pyruvic acid decrease efficiency of succinic acid and lactic acids [160]. This problem can be solved by using amine extractant TOA extracting un-ionized acids [Fig. 14(c)]. The degree of ionization can be adjusted by controlling pH of organic acids [161-163]. These extraction methods can be applied to various kinds of high molecular weight to low molecular fatty acids.

4. Extraction Process for Biodiesel Lipids

An effective separation method of extracting lipids from wet microalgae and wet microbial cells is essential for the successful and economical bioprocessing lipids to biodiesel. So far hexane, chloroform and toluene have been used, but nontoxic and environmentally friendly extraction methods such as ionic solvents, supercritical extraction and milking need to be investigated. Fig. 15 shows a schematic of lipid bioprocessing of microbial biodiesel [46].

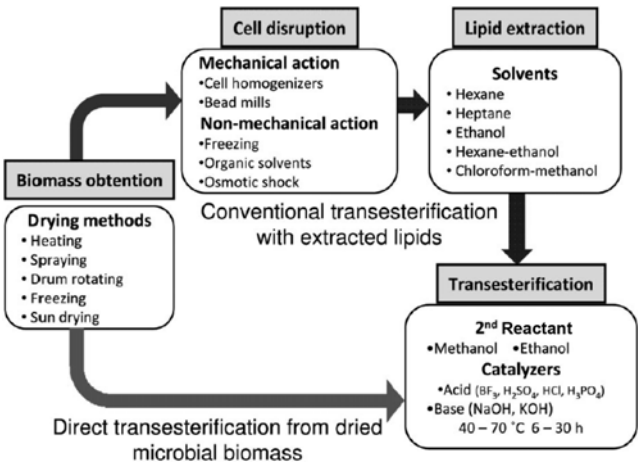


Fig. 15. Extraction of lipids and transesterification to biodiesel. Single-step isolation and subsequent transesterification can reduce bioprocessing cost a lot if it were done in a high yield [44].

ECONOMICS OF BIOFUEL FROM ORGANIC WASTES IN KOREA

1. Organic Waste and Biofuel Production Potential

South Korea is located within latitudes of N33-N39 and has land area of 100,000 km^2 surrounded by sea on three sides [164]. Its population is 50 million as of 2012. South Korea generates 100 million dry tons of biomass each year in its land area [12]. Four million wet tons (800,000 dry ton) of food waste is generated each year. Food waste, sludge from municipal waste water, fallen leaves (city), and cattle wastewater with manure are collected by municipal governments and treated. Six million tons of rice straw are produced each year, but these are used mostly for animal feed (cost 100$/ton). From the above resources we may get 300,000 tons of ethanol from food waste, 3,000,000 tons of ethanol from total organic wastes, including rice straw, and 30 million tons of ethanol from all the biomass each year [12].

1-1. Korea's Fuel Statistics

According to the Yearbook of Energy Statistics (2011) by Korea Energy Economic Institute [165], diesel production in 2010 amounted to 268,392 k-bbl (=42.9 m-kL: m=million) while gasoline was 111,811 k-bbl (17.8 m-kL). However, about of half of them were exported (diesel 130,761, gasoline 39,338) and the net domestic consumptions were 134,648 k-bbl (21.5 m-kL) for diesel and 68,931 k-bbl (11.0 m-kL) for gasoline. The needed biodiesel with a 2% blend policy by Korea Government will be 0.430 m-kL.

2. Recent Biofuel Researches using Organic Biowaste in Korea Usefulness of Up-flow Packed [165]

According to Chang et al. (2010), South Korea has 100 million tons of new biomass every year and 4 million tons of food waste that can be used to make 300,000 kL of ethanol from food waste, and 3 million tons of ethanol from all the organic wastes with VFA platform [12]. Treating the waste or waste water containing high strength BOD is troublesome and very costly. One way of getting out of this trouble is to remove organic components in the form of energy or valuable materials. Chang and associates separated disposer-ground food wastes successfully that was delivered from collective residences to the basement of the apartments, using an upflow packed separator which ran for a year without any trouble [166]. This separation process with upflow packed-bed is more effective than with a centrifuge or settling in terms of speed or reliability.

Chang et al. (2011) proposed that 1,000 L ethanol is possible with VFA-platform from 1 dry-ton of Korean food waste that contains carbohydrates, proteins and lipids [167]. Actually, Chang and his associates obtained, from 1 kg (dry) of food waste, 0.495 kg VFAs having 5-AA,1-PA, 5-BA mixture. With hydrogenation this mixture can produce a 500 L mixed alcohol equivalent to 600 L ethanol in terms of energy. Here AA, PA and BA refer to acetic acid, propionic and butyric acids, respectively. According to the energy electron theory under development, 1 mole AA contains 8ee, PA-14ee and BA-20ee. A VFA mixture with 5AA : 1PA : 5BA ratio will have 100% PA energy content [167]. Jeon et al. (2011) studied ethanol production using waste drink from fast food restaurants [168] and Yu et al. (2011) obtained FAME (fatty acid methyl ester, biodiesel) from high strength food waste water containing lipids [169]. Finally, Han et al. (2011) studied ethanol production from waste cassava stem, a leftover material in their fuel ethanol plant in Southeast Asia [170].

In addition to the above, investigations on the biofuels were carried out in Korea and Asia: synthetic regulatory tools for microbial engineering by Seo et al. [171]; immobilization of cellobiose dehydrogenase on silica gel and cellobiose hydrolysis by acid-functionalized nanoparticles [172,173]; fermentation of seaweed sugars by Lactobacillus [174], cultivation of *Spirulina palatensis* in open race way pond [175], alginate lyase [176], cellulose production from the corn stover [177], bioconversion composition of Korean herbal medicine by *Lactobacillus fermentum* [178], organic solvent tolerant alkaline lipase [179], kinetics of enzymatic saccharification of lignocellulose by fractal kinetic analysis [180] and anaerobic codigestion of swine manure with energy crop residues [181].

3. Bioethanol [182]

Biomass as well as grains, current and future raw materials of fuel ethanol are located within south and north latitudes of 30 °C of earth. Many countries located in temperature climate zones lacking in fuel resources should depend on biofuels produced in resource-rich countries. However, unlike fossil fuels, temperate region countries have some amount of their own biomass and organic wastes, proportional to land area and their own populations, respectively. Korea has the potential of producing 300,000 m^3-ethanol/year from its food waste, 3 million m^3 of ethanol from all the organic waste, and 30 millions of ethanol from its total biomass.

Economics of bioethanol from organic waste (food waste) can be as follows. Korean regional city governments spends 70,000 Won (1$=1100₩, won) per ton (wet) of food waste having a 20% solid content [183].

We performed an economic assessment using the following assumptions and variables: population-4 million, raw material (=rm) cost (1 rm-700₩, 2 rm-0, 3 rm-200₩ for rice-straw), capital cost (1 cc-100% self-financing, 2 cc-60%-government+40% self-financing), plant capacity=30,000 m^3/y: VFA-platform, 1 ton=0.5 ton VFA= 500 L mixed alcohol (45%, ethanol, 10% propanol, 45% butanol= energy density 100% propanol equivalent).

Scenario 1 (=SN1): 53₩/L [1 rm; 1 cc: chemicals 100₩, hydrogen 150₩; utilities 200₩; labor 50₩; depreciation 133₩, profit 120₩]

SN2: 728₩/L[2 rm, all the other conditions are identical with those of SN1

SN3: 636₩/L[2 rm: cc2, SN4:1073₩/L with 3 rm and cc1; SN5: 981₩/L, 3 rm, cc2

The most appropriate scenario will be SN1A having 1 rm and 2 cc. In this case we will have even a smaller manufacturing cost than SN1. If we use sugar platform, we will have even less manufacturing cost because it will need more food waste per liter of ethanol manufacturing, but the total sales volume and profit will be smaller than those of VFA-platform.

4. Biodiesel

4-1. Economic Assessment of Biodiesel [184]

The Korean Government introduced a biodiesel blend policy in 2002 with a production of 1588 kL, which reached 0.21 m-kL (m= million, 1% of the total) in 2008. According to a feasibility study for introducing biodiesel in Korea, biodiesel production is competitive to petro diesel only with tax-exempt condition. The tax amounts to nearly 100% of the manufacturing cost, 1,342 won (2009) consisting of 157 won (processing 192, methanol (48), stabilizer (7), labor (137), byproduct-glycerol 35)+raw material 1185. Because of the freezing point during the winter in Korea, only soybean oil is mostly imported. Local supply of rapeseed oil failed owing to high product price and low agricultural productivity in Korean soil. A-0.30 m-kL production out of 0.90 m-kL capacity accounts for 1.3% of the total diesel consumption and the full capacity production would be 3.9%. Korea has to rely on imports for its biodiesel raw materials, where even a domestic production of 0.10 m-kL biodiesel would have a very significant meaning. The agricultural production is not ready and may not be economical, likewise biodiesel supply by algae. A current report says the algae-based biodiesel would be $3.00/L, much higher than petro-diesel $1.00/L or plant oil based biodiesel of $1.31/L.

4-2. Microbial Biodiesel

We have introduced a feasibility study of microbial biodiesel in Korea [119]. This research is not yet finished nor verified experimentally. We used two kinds of substrates: S1 having a low C/N ratio for cell mass growth such as glucose, woodhydrolyzate, and S2 having a high C/N ratio for lipid accumulation. The economics of VFA-based biolipid production depends very much on costs of S1 and S2, yield, % accumulation of lipid in *C. albus* yeasts. With a calculated unit cost of lipid we add 0.18$/L for fermentation cost of lipid production and 0.30$/L for biodiesel production. The use of glucose for S1 and S2 (0.400$/kg) would give costs of cell mass/kg, lipid/kg and biodiesel/L of $1.53, $1.55, $1.79~scenario-1(SN1), respectively. We assumed that the cell yield and lipid yield are 0.5 kg/kg-S1 and 0.30 kg/kg-S2; lipid content (X2=0.8). Changing S2 from glucose to VFA (0.1$/kg, lipid yield=0.4 kg/kg) would give $.36,0.45,0.86 [SN2]; Changing S1→woodhydrolyzate (Wh1) 0.1$/kg [0.24,0.30,0.74 [SN3]; S1 (Wh2=0.2$/kg); S1=wh2 (0.2$/kg) [0.28, 0.35, 0.76, SN4]; X2=>0.7 [0.30, 0.42, 0.84, SN5]; X2=0.6 [0.31, 0.52, 0.92, SN6]; X2=0.5 [0.33, 0.65, 1.03, SN7]; X2=0.4 [0.34, 0.85, 1.20, SN8]; X2=0.3 [0.53, 1.76, 1.97, SN9].

Based on the current technological advances in our laboratory SN5 or SN6 would be feasible. Furthermore, waste-based biofuel can expect various incentives from central and local governments in terms of waste treatment cost, 60% of production plant loans, too. Biodiesel cost is evaluated as lipid cost ($/L)x 0.85+0.18 for processing+0.30 for biodiesel conversion.

The fermentation and biodiesel conversion cost can be reduced by advanced fermentation technology, such as high purity oxygen [185], advanced extraction lipid extraction from microbial cells and lipid to diesel conversion methods [46].

We hope that the competitiveness of microbial biodiesel may be against petro-diesel rather than agricultural plant oil based biodiesel. The assumptions used in the above cost estimation need to be proved by desk-top, bench-scale and pilot plants. About 15 years ago we achieved 82.5% PHB accumulation (X2=0.825), and 225 g/L cell mass and 280 g/L cell mass in 60-L pilot plant. Also, a preliminary study on the application of MSC-HCDC to the biolipid production showed that 5 g/L/h lipid productivity is possible, which can build a very cost-effective production plant. Also improving and optimizing the capability of our current strain *C. albus* would give a better projection on the economic assessment of microbial biodiesel production.

5. Biofuel Summary

We have summarized the possibility of bioethanol and biodiesel production in Korea where no indigenous grain-based and plant-

oils are produced at all. The demands for bioethanol and biodiesel would be 1.1 m-kL (kL=m^3, 10%, blend) and 0.43 m-kL (2% blend), respectively, which would require 2.2 m-ton waste biomass (VFA-based, 1 ton=0.6 m-kL) for ethanol), and 2.15 m-ton biomass (VFA-based, 1 ton=0.2 m-kL) for biodiesel. Currently, South Korea has 800 dry k-ton biomass (400 wet m-ton) and 10 m-ton organic waste (equivalent to 3 m-kL, ethanol) and 100 m-ton biomass each year (30 m-kL ethanol-equivalent). 5 m-ton biomass would be needed to cover all of 10% ethanol blend gasoline and 2% blend diesel, which corresponds to eight times the food waste, 50% total organic waste and 5% of Korea's national biomass in total. Organic waste-based biofuel are economically competitive to petro-additive (MTBE) gasoline-additives and petro-biodiesel even without tax incentives.

CONCLUSIONS

1. It is important to have knowledge on how our universe, solar system, earth were born and their fates. As our knowledge about the earth advances, our strategy on energy, materials, and living environment may change.

2. The advantage of liquid fuels of gasoline and diesel, and the alternatives, bioethanol and biodiesels, should never be overlooked because of electric cars and hydrogen fuel cars. The alternative biofuels will be derived from vast amount of biomass on earth and sufficient quantities will be supplied as the most reliable source of transportation fuels.

3. Global warming and grain price hikes can be avoided by switching biofuel raw materials from grain and plant-oil sources to biodegradable waste organics at the beginning, and extending VFA-platform technology gradually to ordinary woody lignocellulosic biomass or energy crops in the future.

4. Biomass conversion technologies need to include volatile fatty acid (VFA-platform) in addition to the current thermochemical-syngas and enzyme-sugar platform. The VFA-platform appears to have an advantage over the syngas and sugar platform in the economics of waste-organic based biofuel platform.

5. The amount of biofuels that can be produced from waste bio-organics is great enough to meet South Korea's 10% ethanol blend policy and 2% blend policy demand.

6. The conventional bioprocessing technologies that are now being used for grain-based ethanol and plant-oil based biofuels are suitable for VFA-based platforms. Completely new and innovative technologies need to be developed to solve raw material selections, low productivities, and low titer, separation and purification problems.

7. Biofuels of ethanol and diesel have been well accepted as transportation fuels in the EU and US. Thus, any new biofuel candidates under development can replace them easily because a new biofuel supply chain needs to be built again for a new biofuel.

8. In addition to raw materials of waste bio-organics, MSC-HCDC (multi-stage continuous high cell density culture) for high bioreactor productivity, enrichment of low fermentation titer appear to be amenable to solution of many obstacles that hinder commercialization of lignocellulosic biomass.

9. Many acidic and alcohol forms of bioproducts were successfully separated from the fermentation broth to its pure components by applying hydrophilic membranes, reactive distillation and amine extractions. The advancement of separation processes for biomass-based bioproducts will speed up early introduction biochemicals from biomass.

ACKNOWLEDGEMENT

This work was supported by the Brain Korea (BK21) Program, the Advanced Biomass R&D Center (ABC-2011-0031354 and N01110680) of Global Frontier Project funded by the Ministry of Education, Science, and Technology of Korea. The authors are also indebted to the financial support by the Korean Ministry for Food, Agriculture, Forestry and Fisheries, and the support by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (N01110180).

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