

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Biorefinery

2.1.1 Biorefinery Concept

Among the several definitions of biorefinery, the perfect definition was defined by the International Energy Agency Biorefinery: “Biorefining is the processing of biomass into a spectrum of marketable products and energy”. Biorefinery is facility that integrates biomass conversion processes and equipments to convert biomass resources (e.g., sugarcane, wood, palm, etc.) into basic products like starch, oil, and cellulose, which can be transform to value added products, biofuels, chemicals, materials, and energy. This concept is analogous to today’s petroleum refinery that produces multiple fuels, chemicals, materials, and energy (Cherubini, 2010, Cherubini *et al.*, 2010). Figure 2.1 shows the biorefinery concept (Clark *et al.*, 2012).

The purpose of biorefinery is to obtain high-cost products from low-cost feedstocks due to the potential use of resources and minimize wastes, consequently maximizing benefits and profitability (King *et al.*, 2010). The major challenge for biorefinery development seems to be the efficient and cost effective production of transportation biofuels. However, with the co-produced biomaterials and biochemicals, additional economic and environmental benefits can be gained. Thus, the two important concepts are (1) to take maximum advantage of intermediate and by-products to produce additional chemicals and materials and (2) to balance high-value/low-volume bio-based chemicals and materials with high-volume/low-value biofuels (Cherubini, 2010, King *et al.*, 2010).

Demirbas (2009) and King *et al.* (2010) indicated that a biorefinery might produce one or some low-volume, but high-value, chemical products and a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use at the same time and perhaps enough for the sale of electricity. The high-value products enhance profitability, the high-volume fuel helps

meet national energy needs, and the power production reduces costs and avoids GHG emissions (Demirbas, 2009, King *et al.*, 2010).

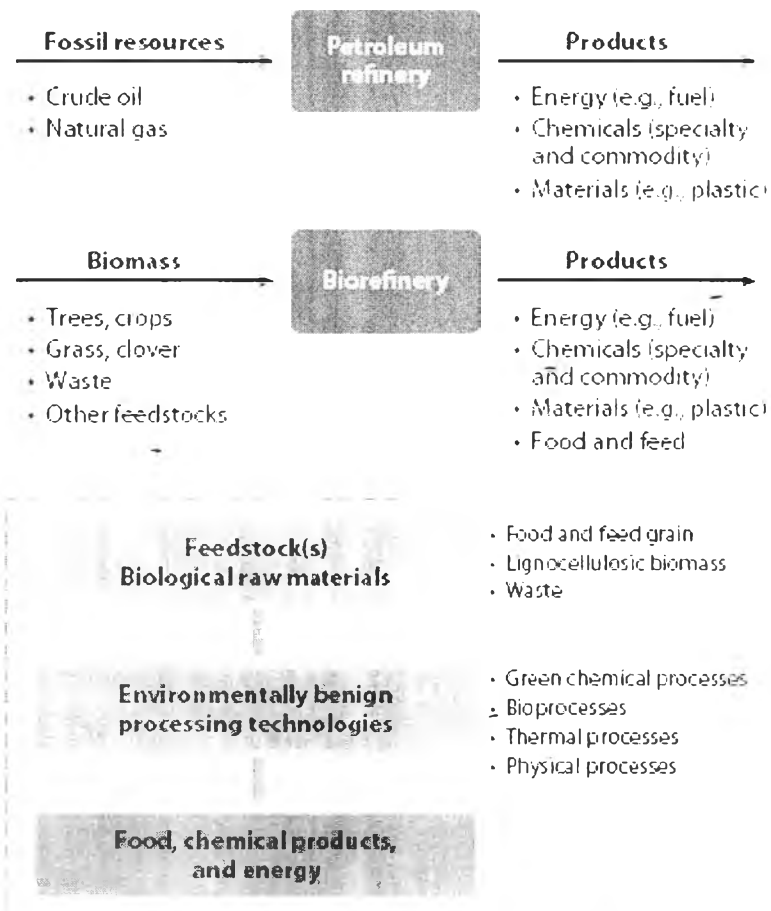


Figure 2.1 The biorefinery concept: from biomass to valuable products via low-environmental-impact valorization practices (Clark *et al.*, 2012).

Around a dozen additional chemicals apart from syngas and fuels may currently be produced per refinery but, ultimately, the local market value for the final products will determine which products will be produced.

2.1.2 Biomass Feedstocks

Biomass feedstock refers to renewable carbon-based raw materials used in biorefinery. The biomass is synthesized by plants via the photosynthetic process that can convert atmospheric carbon dioxide and water into sugars. The sugar

is used by plants to synthesize the complex materials that are generically named biomass. Two categories of biomass feedstock dominate research are first and second generation. First generation products are produced from edible biomass such as starch-rich or oily plants. Second generation products are made from residual non-food parts of current crops or other non-food sources, such as perennial grasses or algae (Cherubini, 2010, King *et al.*, 2010). Figure 2.2 shows the whole plant valorization in biorefinery based on the function of plant components used as raw material (Octave *et al.*, 2009).

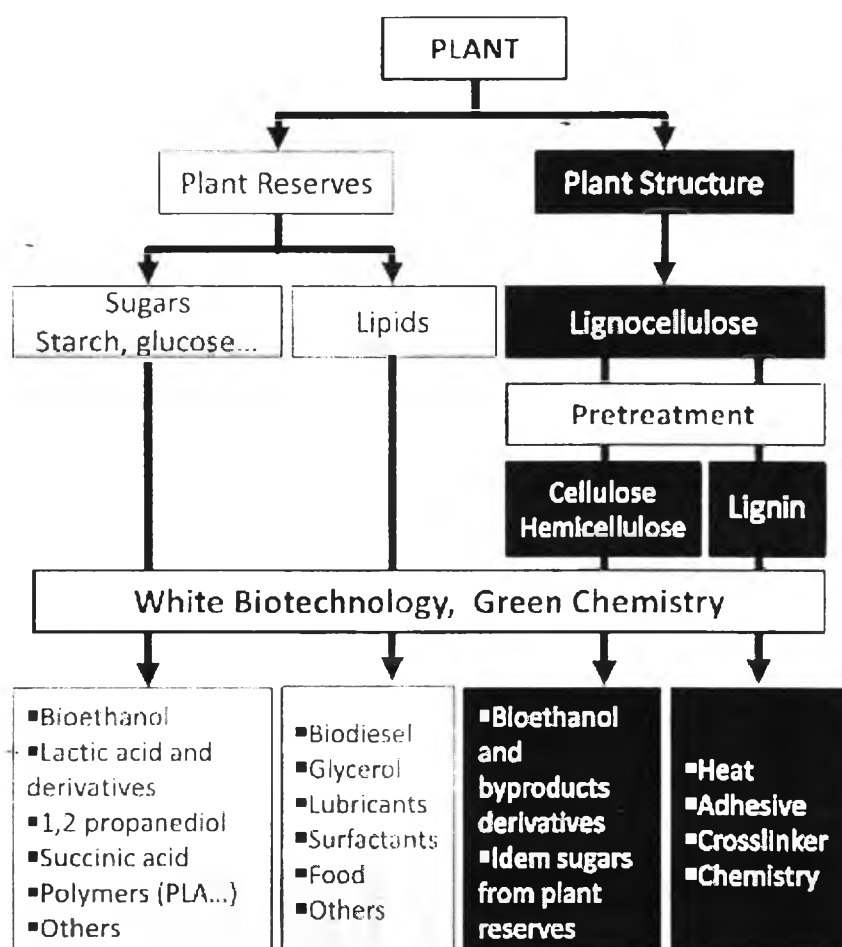


Figure 2.2 Whole plant valorization in biorefinery based on the function of plant components used as raw material (Octave *et al.*, 2009).

Biomass feedstock for biorefinery are provided from four different segments: (1) agriculture (dedicated crops and residues), (2) forestry, (3) industries

(process residues and remnant) and households (municipal solid waste and wastewaters), and (4) aquaculture (algae and seaweeds) (Cherubini, 2010).

The main biomass feedstock can be grouped in 3 wide categories: (1) carbohydrates and lignin, (2) triglycerides (lipids), and (3) mixed organic residues (Cherubini, 2010).

2.1.2.1 *Carbohydrates and Lignin*

Carbohydrates that produced from starch, cellulose, and hemicelluloses are the most common biomass component found in plant feedstocks. Carbohydrates must be hydrolyzed to form sugar that is feedstocks of fermentation stage to produce ethanol (Cherubini, 2010).

Starch is a very large polymer molecule consisted of many hundreds or thousands of glucose molecules (polysaccharides). The most widespread starch crops are wheat and corn. Starch must be broken down into one or two molecule pieces. followed by the microbial fermentation stage to produce bioethanol. The two most important sugar crops are sugarcane and sugar beet. Sugar crops can be directly fermented to produce ethanol (Cherubini, 2010, King *et al.*, 2010).

Lignocellulose is the most abundant biomass representing near of 70% of the total plant biomass. Lignocellulose has three major components contains microfibrils of cellulose (30–50% of total lignocellulosic dry matter), hemicelluloses (20–40% of total lignocellulosic dry matter) and lignin (15–25% of total lignocellulosic dry matter). Lignocellulosic biomass can be provided either as a crop or as a residue.- Large amounts of cellulosic biomass can be produced via dedicated crops like perennial herbaceous plant species, or short rotation woody crops. Other sources of lignocellulosic biomass are waste and residues such as straw from agriculture. wood waste from the pulp and paper industry and forestry residues. Lignocellulose has been selected during the evolution to be the key element of plant structure and consequently to be resistant to biotic and abiotic stresses. This characteristic involved some bottleneck in the industrial processing of biomass. Starch can be easily hydrolyzed by enzymes or acid attack to the single sugar monomers, while cellulose is much more difficult to hydrolyze and set free individual glucose monomers. Hemicellulose is a relatively amorphous component that is easier to break down with chemicals or heat than cellulose. Lignin is the

largest non-carbohydrate fraction of lignocelluloses, but can be used as fuel to produce heat. Moreover, lignin can be incorporated in resins to substitute phenols or acting as a cross linker in epoxy-resins (Octave *et al.*, 2009, Cherubini, 2010).

2.1.2.2 Triglycerides (Lipids)

Oils and fats are triglycerides which generally consist of glycerin and saturated and unsaturated fatty acids. The sources of oils and fats are a variety of vegetable and animal raw materials. Oilseeds are commonly used to produce fatty acids and protein-rich cakes used to feed animals. Oilseeds provide a unique opportunity for the production of biofuel and high-value fatty acids that can replace petrol sources of specialty chemicals and other applications like lubricants, or detergents. Nowadays, oils from Sunflower, rape, soybean or palm are the mostly used to make biodiesel by transesterification process. Triglycerides are reacted with primary alcohol (mainly methanol) to get fatty acid methyl ester (FAME) used as biofuel and receive glycerol as a by-product. The glycerol can be synthesized to be valuable products such as coatings, adhesives, plasticizers and other chemicals. Other sources of vegetable oil for biofuel conversion can be found in waste streams of food industry, where waste edible oil is mainly generated from commercial services and food processing plants such as restaurants, fast food chains and households. Waste vegetable oil can also be converted into biodiesel, but requires refinement (Octave *et al.*, 2009, Cherubini, 2010, King *et al.*, 2010).

2.1.2.3 Mixes Organic Residues

Organic fraction of the Municipal Solid Waste (MSW), manure, wild fruits and crops, proteins and residues from fresh fruit and vegetable industries are biomass sources excluded from above categories. The physical and chemical characteristics of this wide spectrum of biomass resources vary largely. Some streams such as sewage sludge, manure from dairy and swine farms and residues from food processing are very wet, with moisture contents over 70%. Therefore, these feedstocks are more suited for an anaerobic digestion process to generate biogas, rather than other fuels or chemicals. Other streams, such as organic MSW, may be more or less contaminated with heavy metals or other elements, but represents a high potential for energy recovery (Cherubini *et al.*, 2008). Obviously,

the different properties and characteristic of the biomass waste require the application of different conversion technologies (Cherubini, 2010).

2.1.3 Technological Processes in Biorefinery

The sustainability of a biorefinery depends on the comprehensive utilization of the biomass feedstock in order to provide a wide range of products. This would only be possible with an optimal mix of processes (Ghatak, 2011). The processes used are based on the feedstock and the desired output (King *et al.*, 2010).

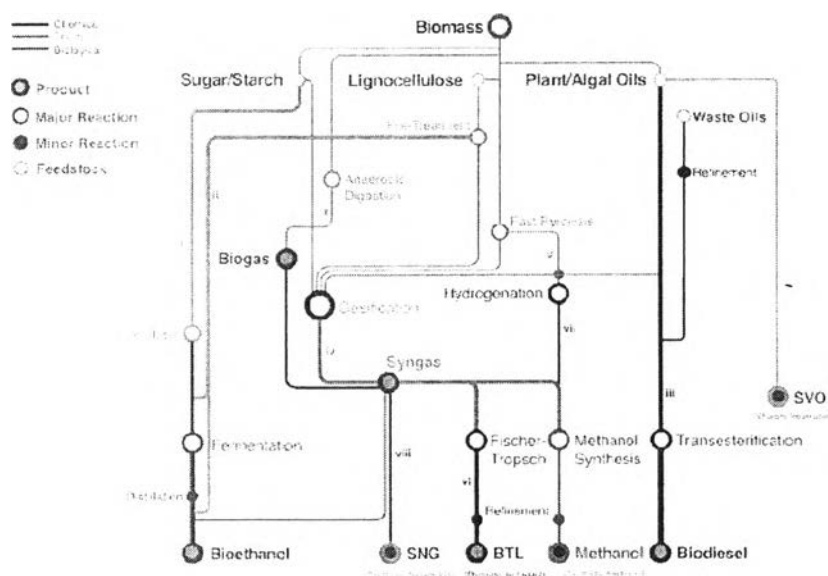


Figure 2.3 The multiple synthetic conversion routes of major biofuels produced from first and second-generation biomass feedstock (King *et al.*, 2010).

Biorefinery processes can be thermochemical, biochemical, chemical, or a combination of them. A full realization of the utilization potential of any biomass resource often requires a complex set of operations. Besides the actual chemical transformation steps, a variety of physical processes are involved in the raw material pretreatment as well as in the separation of intermediates and products (Ghatak, 2011). Figure 2.3 shows the multiple synthetic conversion routes of major biofuels produced from first and second-generation biomass feedstock (King *et al.*, 2010).

2.1.3.1 Thermochemical Processes

- Gasification: Formation of Syngas

Gasification of biomass allows the breakdown of carbonaceous materials into their synthesis gas compounds that is to say H₂ and CO are known as syngas. Gasification can be completed by thermal decomposition in the presence of a limited amount of oxygen. The resultant mixture of hydrogen and carbon monoxide is then converted by partial oxidation at elevated temperature or via a Fischer-Tropsch reaction into the molecules of choice (Bridgwater, 1995).

- Fast Pyrolysis

Similar to the formation of syngas, pyrolysis is the thermal decomposition of the biomass into a liquid bio-oil containing various hydrocarbons and an oxygen content of 35-40%, which can be converted via hydrogenation or via gasification into the target hydrocarbon. The use of pyrolysis and the properties of the bio-oil produced are still in development, but it is thought that it can reduce the costs of gasification compared with feeding solid biomass directly into the gasifier (Bridgwater, 1995).

2.1.3.2 Biochemical Processes

- Fermentation of Sugar/Starch Crops

The fermentation of sugar solutions originating from either starch crops or lignocellulosic material requires pretreatment of the feedstock to release the sugars from the plant material. Starch is usually hydrolyzed enzymatically to deliver sugar solutions, followed by the microbial fermentation stage to produce bioethanol. Sugar crops such as sugar cane can be directly fermented to produce ethanol (Corra *et al.*, 2007).

- Fermentation of Lignocellulosic Biomass

When using lignocellulosic biomass, feedstock processing needs to separate the cellulosic and hemicellulosic material from the non-fermentable lignin, which is strongly bonded by covalent cross-links (King *et al.*, 2010). This is usually done mechanically, followed by acid, alkali, and/or steam treatment. While the lignin is currently mostly combusted to deliver energy, the cellulosic and hemicellulosic components are hydrolyzed enzymatically to deliver

sugar solutions, followed by fermentation. As opposed to the fermentation of pure C6 sugars (as in starch or saccharose), fermentation of broken-down hemicellulose also requires special fermentation organisms capable of converting C5 sugars such as xylose (Olsson *et al.*, 1996). At present, there is a need for more efficient and robust microorganisms that can withstand higher temperatures and pressures to deliver the fermentation product for both of the above biomass feedstocks.

- *Anaerobic Digestion*

SNG production can also involve the conversion of biodegradable waste or energy crops into a gaseous fuel called biogas, made up largely of 50%+ methane and carbon dioxide. Commercial conversion processes typically run via anaerobic digestion or fermentation by anaerobes. This biological process is used as a renewable substitute for commercial natural gas and is estimated to have a conversion efficiency of 70% (Drift, 2008).

2.1.3.3 Mechanical Processes

Mechanical processes are processes which do not change the state or the composition of biomass, but only perform a size reduction or a separation of feedstock components. In a biorefinery pathway, they are usually applied first, because the following biomass utilization requires reduction of the material size within specific ranges, depending on feedstock specie, handling and further conversion processes. Biomass size reduction is a mechanical treatment that refers to either cutting or comminuting processes that significantly change the particles size, shape, and bulk density of biomass. Separation processes involve the separation of the substrate into its components, while with extraction methods valuable compounds are extracted and concentrated from a bulk and inhomogeneous substrate (Huang *et al.*, 2008). Lignocellulosic pre-treatment methods (e.g. the split of lignocellulosic biomass into cellulose, hemicelluloses, and lignin) fall within this category, even if some of hemicelluloses are also hydrolyzed to single sugars (Cherubini, 2010).

2.1.3.4 Chemical Processes

- *Transesterification of Triglycerides*

Transesterification of plant or algal oil is a standardized process by which triglycerides are reacted with methanol in the presence of a catalyst to deliver fatty acid methyl esters (FAME) and glycerol. Waste vegetable oil can also

be converted, but requires refinement. Both acid and alkali catalysts can be used, although the alkali catalyzed reaction proceeds 4,000 times faster than the same reaction with acid. The main problems associated with using triglycerides as a diesel replacement tend to be high viscosity, low volatility, and polyunsaturated character. Transesterification is a method of reducing the viscosity of the triglycerides and enhancing the physical properties of the fuel. As a result, FAME biodiesel is the most common form of biodiesel used today (Fukuda *et al.*, 2001).

- Hydrogenation

A more energy-efficient alternative of producing synthetic biofuel, involving hydro treatment of bio-oils to produce hydro treated renewable jet fuels (HRJ). Hydrogenation removes oxygen and other impurities from organic oils. These oils can be extracted directly from feedstocks with high oil content, such as jatropha, camelina or algae, or produced through pyrolysis. Hydrotreating bio-oils with hydrogen at medium to high temperatures convert bio-oils to hydrocarbon fuels, such as HRJ. The resultant fuels are pure hydrocarbon and have indistinguishable physical properties from fossil-based fuels. HRJ fuels tend to have better combustion performance and higher energy content, similar to Fischer-Tropsch fuels and, most importantly, have good low-temperature stability, making them ideal as a renewable source of jet fuel. In December 2009, the first aviation test flight powered by biofuel sourced from jatropha oil was undertaken by Air New Zealand (King *et al.*, 2010).

- Fisher-Tropsch Synthesis

The conversion of syngas via the Fischer-Tropsch process into synthetic fuel involves the catalytic conversion of syngas into liquid hydrocarbons ranging from C1 to C50. A selective distribution of products is achievable with control over temperature, pressure, and the type of catalyst (King *et al.*, 2010). Although this process is widely recognized, there is a possibility of catalyst shortages in large-scale productions if catalyst regeneration is not improved. This technology is commonly found in the commercial generation of electricity and synthetic fuels from conventional fossil fuels. However, the same principles can be applied to biomass and biofuels production; it is therefore commonly referred to as biomass-to-liquid (BTL). Gasification of biomass has had little commercial impact

owing to competition from other conversion techniques. There has been renewed interest in this process. Economically viable examples are rare (Bridgwater, 1995)

- Conversion of Syngas to Methane

Methane can be produced from syngas as a result of thermal gasification and a variation of the Fischer-Tropsch reaction. It can also be found as a by-product of Fischer-Tropsch biofuel synthesis. Synthetic natural gas (SNG) is a substitute for natural gas that can be fed directly into the national grid, and used as a transport fuel if liquefied (King *et al.*, 2010).

2.1.4 Biorefinery Products

The products of biorefinery systems can be grouped in two broad categories: (1) material products and (2) energy products which are shown in Table 2.1 (Ghatak, 2011). Energy products are those products which are used because of their energy content, providing electricity, heat or transportation service. On the other hand, material products are not used for an energy generation purpose but for their chemical or physical properties. In some cases, a further distinction for the characterization of products is needed because some products like biohydrogen or

Table 2.1 Biorefinery products (Ghatak, 2011)

Biorefinery products		Remarks	
Energy products	Biochemical	Methanol	<ul style="list-style-type: none"> • Alcohols and heat are additional products from biomass • Biomass derived energy often suited to decentralized applications • Electricity from waste biomass may be economically competitive with that from fossils • Products like DME, FT diesel, SNG, and hydrogen still to find wide acceptance
		Ethanol	
		Higher alcohols	
	Chemical	Biogas	
		Biodiesel	
		DME	
		FT diesel	
	Thermochemical	Biocrude	
		Heat	
		Electricity	
Biomaterials	Cellulose based	Syngas	
		SNG	
	Hemicellulose based lignin based	Hydrogen	
		Methane	
		Paper and paperboard	<ul style="list-style-type: none"> • Cellulose based products have well established markets • Development and utilization of lignin based products outside of energy realm is still not so widespread
		Rayon	
		Cellophane	
		Adsorbents	
	Furfural		
	Adhesives		
Dispersants			
Miscellaneous	Emulsifiers		
	Adsorbents		
	Vanillin		
	Soil conditioners		
	Particle board		
	Carbon products		
	Animal feed		

bioethanol might be used either as fuels or as chemical compound in chemical synthesis. In these cases, it is necessary to identify the addressed markets, for instance the transportation sector for H₂ and bioethanol. The products of a biorefinery must be able to replace fossil based fuel products coming from oil refinery, both chemicals and energy carriers (Cherubini, 2010).

2.1.4.1 Energy Products

The most important energy products which can be produced in biorefineries are biofuels. Concerning the fuels, a biorefinery must replace conventional fossil fuels (mainly gasoline, diesel, heavy oil, coal, and natural gas) with biofuels coming from biomass upgrading (Cherubini, 2010). The term biofuel is referred to as solid, liquid, or gaseous fuels that are predominantly produced from biorenewable feedstocks. There are two global biorenewable liquid transportation fuels that might replace gasoline and diesel fuel. These are bioethanol and biodiesel. Bioethanol is good alternate fuel that is produced almost entirely from food crops. Biodiesel has become more attractive recently because of its environmental benefits. Biofuels can be classified based on their production technologies: first generation biofuels (FGBs); second generation biofuels (SGBs); third generation biofuels (TGBs); and fourth generation biofuels.

First generation biofuels (FGBs) refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. FGBs produced from food crops such as grains, sugar beet, and oil seeds are limited in their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth. A possible exception that appears to meet many of the acceptable criteria is bioethanol produced from sugarcane. The basic feedstocks for the production of first generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that, can be used in biodiesel. The production of FGBs such as sugarcane ethanol in Brazil, corn ethanol in US, oilseed rape biodiesel in Germany, and palm oil biodiesel in Malaysia is characterized by mature commercial markets and well understood technologies. Future targets and investment plans suggest strong growth will continue in the near future.

Second generation biofuels (SGBs) produced from lignocellulosic materials include cereal straw, forest residues, bagasse, and purpose-grown energy crops such as vegetative grasses and short rotation forests. The SGBs could avoid many of the concerns facing FGBs and potentially offer greater cost reduction potential in the longer term. Many of problems associated with FGBs can be addressed by the production of biofuels manufactured from agricultural and forest residues and from non-food crop feedstocks. Low-cost crop and forest, wood process wastes, and the organic fraction of municipal solid wastes can all be used as lignocellulosic feedstocks. Second and third generation biofuels are also called advanced biofuels. Third generation biofuel, is a biofuel from algae. On the other hand, an appearing fourth generation is based in the conversion of vegoil and biodiesel into biogasoline using most advanced technology (Demirbas, 2009).

2.1.4.2 Chemical and Material Products

Biorefinery can provide an array of chemicals like adhesives, cleaning compounds, detergents, dielectric fluids, dyes, hydraulic fluids, inks, lubricants, packaging materials, paints and coatings, paper and box board, plastic fillers, polymers, solvents, and sorbents. Concerning the chemicals, this objective can be met by producing the same chemical species from biomass instead of from fossils (e.g. phenols), or producing a molecule having a different structure but an equivalent function (Cherubini, 2010).

2.2 Potential Feedstocks for Biorefinery in Thailand

Thailand is known as an agro-industrial based country. In 2007, the agricultural areas in Thailand were about 20.85 million hectares contributing 40% of the total area of Thailand (51.31 million hectares). The three major groups in the agricultural sector are rice, farming plants (such as cassava, sugarcane) and fruits, and standing timber consist of 48%, 21% and 22% of the total agricultural area, respectively. The agricultural production statistics of important crops of Thailand is shown in Table 2.2 (Jongskul, 2013). These crops can be used as biomass feedstocks for biorefinery as shown in Table 2.3 (DEDE, 2009). The biorefinery model under study use sugarcane and cassava as feedstocks.

Table 2.2 The agricultural production statistics of important crops of Thailand (Jongskul, 2013).

Year	Production (1,000 tons)					
	Sugarcane	Rice	Maize	Oil Palm	Cassava	Para Rubber
2003	-	29,823	4,249	4,903	-	2,860
2004	64,996	28,873	4,341	5,182	21,440	3,007
2005	49,586	30,649	4,094	5,003	16,938	2,980
2006	47,658	29,994	3,918	6,715	22,584	3,071
2007	64,365	32,482	3,890	6,390	26,916	3,022
2008	73,502	32,020	4,249	9,271	25,156	3,167
2009	66,816	32,396	4,616	8,163	30,088	3,090
2010	58,808	36,004	4,861	8,223	22,006	3,052
2011	95,950	38,091	5,022	10,777	21,912	3,349
2012	98,400	36,854	4,965	11,327	29,410	3,625
2013	99,597	-	-	-	27,135	-

Table 2.3 Energy potential of agricultural residues in Thailand, 2009 (DEDE, 2009).

Products	Production (Tons)	Residue	Available unused residue for energy	Heating value	Energy potential	
			(Tons)	(MJ/kg)	(TJ)	(ktoe)
Sugarcane	66,816,446	Bagasse	4,190,794.31	14.4	60,347.44	1,428.54
		Top & trash	13,439,727.21	17.39	233,716.86	5,532.52
Paddy	31,508,364	Husk	3,510,598.90	14.27	50,096.25	1,185.87
		Straw	25,646,547.96	10.24	262,620.65	6,216.73
Soybean	190,480	Stalk, leaves, shell	170,383.17	19.44	3,312.35	78.41
Maize	4,616,119	Corn cob	584,539.15	18.04	10,545.09	249.62
		Stalk	2,758,777.36	18.04	49,768.34	1,178.11
Oil palm	8,162,379	Empty bunches	1,024,868.34	17.86	18,304.15	433.29
		Fiber	162,970.06	17.62	2,871.53	67.97
		Shell	38,959.04	18.46	719.18	17.02
		Shaft	2,203,740	9.83	21,824.24	516.62
Cassava	30,088,025	Stalk	2,439,236.19	18.42	44,930.73	1,063.60
		Rhizome	1,834,466.88	18.42	33,790.88	799.89
Coconut	1,380,980	Shaft	628990.82	15.4	9686.46	229.3
		Spathe	464250.95	16.23	7534.79	178.36
		Shell	128936.58	17.93	2311.83	54.73
Hevea wood	3,090,280	Branch/Shaft	312,118.28	14.98	4,675.53	110.68
Total	145,853,073		59,539,905.20		504,339.40	11,938.60

2.2.1 Sugarcane

Sugarcane is one of the most important feedstock for bioethanol production because cane juice contains sucrose, a fermentable sugar that can be directly fermented by yeast to produce ethanol. The typical conversion factor ranges between 12.5-14.3 kg sugarcane/L ethanol. Thailand ranked as the world's second leading sugar exporter after Brazil which is the outstanding sugarcane producer. This sugar is mainly produced from sugarcane which grows well in the tropical and subtropical climate. The crop is usually planted either before or after the rainy season and can be harvested around 10-12 months after cultivation. The harvest season of sugarcane is typically short: only 4-5 months each year (December-March). Sugarcane plantations in Thailand occupy an area of about one million hectares mainly concentrated over 47 provinces in the Northeastern, Central and Northern regions of Thailand contributing 38%, 35%, and 27% of the total planted areas, respectively. The growth is spurred by several factors including rising in both domestic and international demand, the attractiveness of sugarcane prices, and the recent creation of new bioethanol sector (Silalertruksa *et al.*, 2010). The annual average yield from 2011/12 to 2013/14 is shown in Table 2.4 (Bongsunun, 2013).

Table 2.4 Forecasting result of sugarcane by whole kingdom year 2013 (Bongsunun, 2013).

Crop year	Planted area (M ha)	Productions (M ton)	Production/Area (t/ha)
2011/12	1.33	102.09	76.81
2012/13	1.34	103.37	76.98
2013/14	1.35	105.37	77.98

2.2.2 Cassava

The cassava plant is cultivated in most equatorial regions and is known by many names as shown in Table 2.5. The plant grows to a height of 1 – 3 m and several roots may be found on each plant. Manioc prefers a fertile sandy-clay soil. It pounds well. A typical composition of the root is presented in Table 2.6.

Table 2.5 Various names of cassava in different region.

Region	Name
Indonesia	Ubi kettella, Kasper
South America	Manioca, Yucca, Mandioca, Aipim
Africa	Manioc, Cassava
India	Tapioca
Thailand	Cassava

Table 2.6 Composition of cassava.

Content	% weight
Moisture	70
Starch	24
Fiber	2
Protein	1
Other	3

*Starch content may be as high as 32%.

Cassava, a starch-accumulating crop, is classified into “sweet” and “bitter” varieties. Sweet cassava can be directly eaten because it has a low level of hydrocyanic acid as-compared to the bitter type. However, the sweet cassava has no large-scale plantation in Thailand because the market is limited. It is commonly grown and used for household and sold in limited quantities in local markets. It is the opposite to the bitter type, also called industrial cassava that is widely grown. Bitter cassava is unsuitable for directly eating because of toxicity from a high level of hydrocyanic acid but it also contains a high level of starch that can be converted to fermentable sugar i.e. glucose by the enzyme or acid process. In the past, cassava was very well utilized in several industries i.e. starch and starch derivatives such as modified starch and sweeteners and chip/pellet industry. However, today, cassava is being promoted as a feedstock for ethanol production in Thailand due to its several advantages i.e. cassava is able to grow with minimal inputs, possibility for all year round plantation and harvest, high root productivity and high-quantity of carbohydrate. Although both cassava fresh roots and dried chips can be put in the ethanol conversion process, dried chips are recommended. The advantages of using

dried chips over fresh roots are chips can be produced by farmers during the peak of harvesting season (when root price is at the lowest) and stored for use when roots are not harvested. The chips can be used to produce ethanol by advanced processes such as simultaneous saccharification and fermentation (SSF) and used with grains to minimize production cost. The typical conversion ratio ranges between 5.5-6 kg of cassava roots (based on 25% starch content) per liter of ethanol. Thailand is known as one of the world's largest cassava producer and exporter contributing about 70% world market share. In 2008, the cultivated area of cassava was 1.24 million hectares, yielding 25.6 million tons fresh roots (yields = 3.5 ton roots/rai) (Silalertruksa *et al.*, 2010). In 2012, cassava yield is 24.78 million tons fresh roots. The annual average yield from 2011/12 to 2013/14 is shown in Table 2.7.

Table 2.7 Forecasting result of cassava by whole kingdom year 2013 (Bongsunun, 2013).

Crop year	Planted area (M ha)	Productions (M ton)	Yield (t/ha)
2011/12	1.27	26.60	21.01
2012/13	1.26	27.55	21.78
2013/14	1.26	29.06	23.13

- Cassava Rhizome

Cassava Rhizome is an attractive lignocellulosic material for ethanol production, most of which comes from agricultural residues. The rhizome is also non-edible. Cassava production in Thailand is about 29 million tons per year, Thailand was ranked first as producer of cassava in Southeast Asia and third in world. Every kilogram of cassava produces 0.06-0.09 kg of rhizomes, around 1.5-2.6 million tons of rhizomes is expected to be produced per year, and most of it will be used as firewood, while the rest go to waste. Rhizome has many characteristics that make it a staple in high demand for production of ethanol. It has a high cellulose and hemicellulose content that can be easily hydrolyzed into sugars that can be digested. But it also has roots high lignin content, which is a drawback in its use for the production of ethanol (Mangnimit *et al.*, 2013).

- Fresh Cassava Pulp

Fresh cassava pulp is generated approximately 5.2 Mt annually from the production of cassava starch in Thailand (Panichnumsin *et al.*, 2010). Every tonne of cassava starch produces 460 kg of cassava pulp (Chinnawornrungrsee *et al.*, 2013). Cassava pulp containing high starch is regarded as a nice potential substrate for biogas (Rattanachomsri *et al.*, 2009). Furthermore, to utilize the cassava pulp, an approach can also convert its components to ethanol (Kosugi *et al.*, 2009).

According to Dr. Tico Cohen, environmental biotechnologist in New Zealand, future projects will, in addition to the wastewater, also incorporate the anaerobic digestion of cassava pulp. Pilot scale research done by Waste Solutions has indicated that this material has a very high potential for biogas generation (Rajgor, 2004). The Project will accept 1,500 tons of cassava pulp and with specialized pretreatment and digestion, convert into valuable biogas energy. 100% of the biogas energy thus produced will be converted to electrical energy. The proposed biogas energy plant will digest more than 450,000 tons of pulp annually generating 43,000,000 m³ biogas energy annually, which will be converted to 94,000,000 kWh (if 300 days) of electrical energy annually as shown in Figure 2.4 (Godson, 2012).

The bioenergy technology converting cassava pulp into biogas from Asia Biogas Management Co., Ltd was described as following procedures.

Cassava pulp is diluted in slurry pond by waste water from biogas system. Then waste water from biogas system starts up in anaerobic baffled reactor (ABR). Normally, basic chemical such as lime is added to adjust pH in mixing pond and adjusting amount depends on pH of each condition. Electricity consumption is from any pumps in this system such as in mixing pond. Biogas generated depends on cassava pulp used. Generally, cassava pulp 1 ton daily produces biogas about 60-69 m³ based on 300 days plant capacity; methane concentration is about 55-60%. Excess sludge is normally dried on yard to produce fertilizer. It can be degraded up to 90%. However, some data is not disclosed due to confidentiality agreement and some data is not necessary due to neutral environmental impact.

- Sugar

Sugar is one of the main products in Thailand. Furthermore, Thailand is the 4th sugar exporter of the world in 2013 (MacLeod, 2013). According to bioplastics value chain industries as shown in Figure 2.5, sugar from both sugarcane and cassava can be converted into bioplastics (NIA, 2013). Also glucose can be converted to succinic acid through enzymatic hydrolysis (Leung *et al.*, 2012). However there is no any processes directly converting sugar to succinic acid since PTTMCC BioChem Company Limited is establishing the factories as the first one in the world (Thouphan, 2011). Using sugar from sugarcane as the raw material and a new large-scale lactide plant became on stream at Purac's site in Thailand in 2011. The biopolymer PLA is made from lactic acid that can be produced from sugars by fermentation. In addition, according to PTTMCC BioChem Company Limited, products produced polybutylene succinate (PBS), one of famous bioplastic, are from two types of material i.e. SA and 1,4 Butanediol (BDO). Both materials can be produced from precursor is raw sugar (Thouphan, 2011).

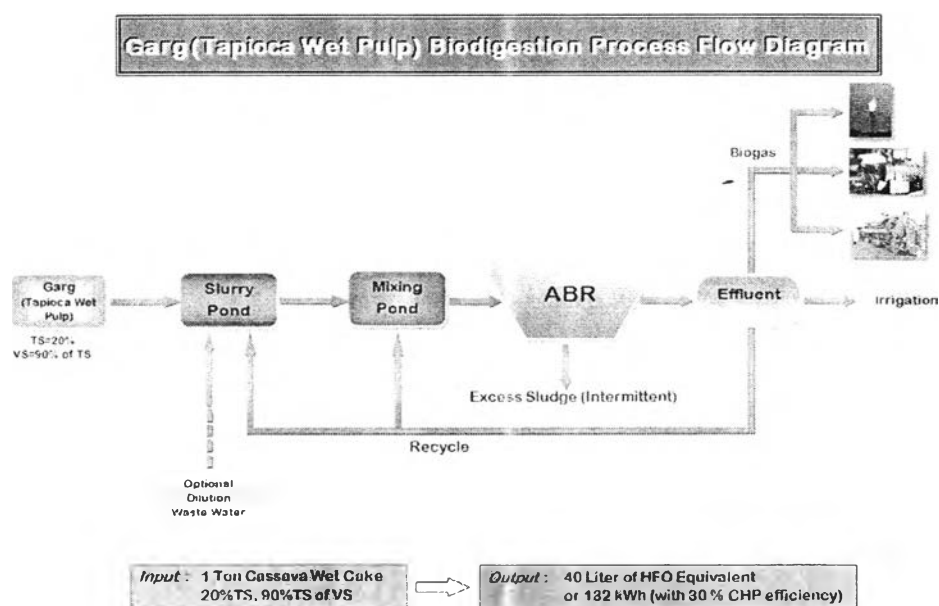


Figure 2.4 Flow chart of cassava pulp biodigestion process (Godson, 2012).

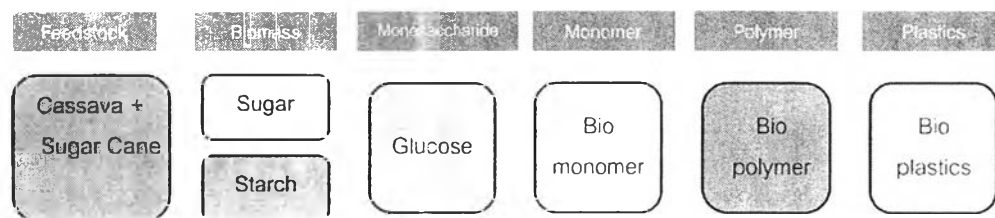


Figure 2.5 Bioplastics value chain industries (NIA, 2013).

2.3 Current Status of Bioethanol Productions and Uses in Thailand

The use of gasohol in Thailand is not compulsory and premium gasoline (octane 95 gasoline) and regular gasoline (octane 91 gasoline) are still available at a price 10–15% and 22–26% lower respectively than E10 (10% ethanol blend with octane 91 gasoline). Hence, it is anticipated some consumers may not find the prices attractive enough to shift to E10, particularly those running on premium gasoline. The biofuel promotion policy is meeting a certain amount of success in Thailand, shown by the increasing trend of gasohol consumption which is illustrated in Table 2.8 (EnergyStatistics, 2012). Also the government is providing a series of incentives to stimulate ethanol production and consumption, including, excise tax exemption for ethanol producers selling ethanol in Thailand, subsidies using the State Oil Fund to reduce the selling price of gasohol at the pump which enables refineries to lower the retail price of gasohol, and more advantageous excise tax reduction for car manufactures of vehicles running on E85 (Gheewala *et al.*, 2011).

Currently, molasses, cassava and sugarcane juice are the major feedstocks being promoted for the commercial ethanol plants due to their surplus availability and their economic and technical feasibility (Silalertruksa *et al.*, 2011). In 2009, ethanol production amounted to 400.7 million liters or 1.1 million liters/day. There are currently 19 ethanol plants in operation which are shown in Table 2.9 with a production capacity of 2.9 million tons per day. About 50% of the plants are flexible feedstock based ethanol plants; 60–70% of ethanol production is molasses-based since 70% of the ethanol plants have sugar mills as their core business (Sutabutr,

2010). Schematic of the molasses based ethanol production from a biorefinery complex is shown in Figure 2.6. To satisfy the government target of three million liters per day by 2011, the number of ethanol plants in Thailand will increase to 23 plants in 2011 with a total production capacity of 4.6 million liters per day. Table 2.10 shows ethanol plants which were planned to produce in 2012 (Sutabutr, 2012).

Table 2.8 Gasohol consumption in Thailand (including E10 octane 91, E10 octane 95, E20, and E85) (EnergyStatistics, 2012).

Year	Million Liter	Million Liter per Day	% Change of Consumption per Day
2008	3,392	9.29	-
2009	4,470	12.25	31.78
2010	4,382	12.01	-1.97
2011	4,213	11.54	-3.86
2012 ^{primary}	4,609	12.63	9.40

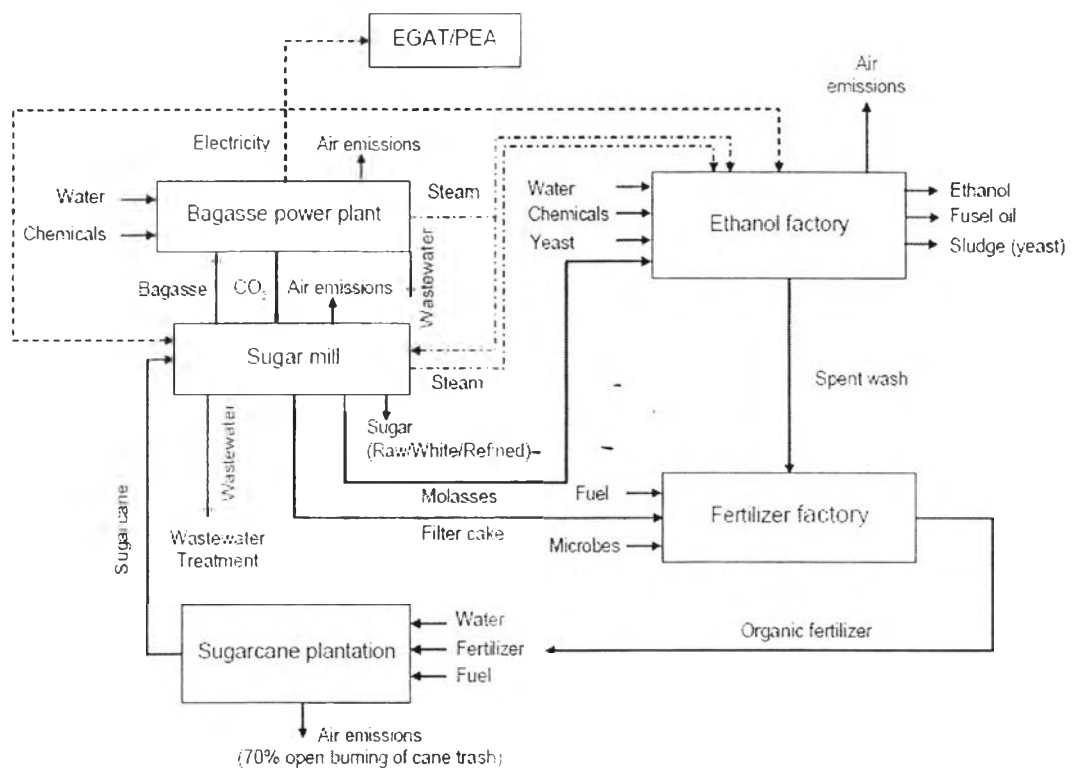


Figure 2.6 Schematic of the molasses based ethanol production from a biorefinery complex (Gheewala *et al.*, 2011)

Table 2.9 Current ethanol plants in Thailand (Sutabutr, 2010).

No	Plant	Site	Capacity (l/d)	Feedstock
1	Pornwilai International Group Trading	Ayutthaya	25,000	Molasses Cassava root
2	Thai Agro Energy Co., Ltd.	Suphanburi	150,000	Molasses
3	Thai Alcohol Public Co., Ltd.	Nakhon Pathom	200,000	Molasses
74	Khonkaen Alcohol Co., Ltd.	Khonkaen	150,000	Molasses Starch
5	Thai Nguan Ethanol Co., Ltd.	Khonkaen	130,000	Cassava root Cassava chip
6	Thai Sugar Mill Co., Ltd.	Kanjanaburi	100,000	Molasses
7	KI Ethanol Co., Ltd.	Nakhon Ratchasima	100,000	Molasses
8	Petro Green Co., Ltd. (Kalasin)	Kalasin	200,000	Molasses Sugarcane
9	Petro Green Co., Ltd. (Chaiyaphum)	Chaiyaphum	200,000	Molasses Sugarcane
10	Eakarattattana Co., Ltd.	Nakhon Sawan	200,000	Molasses
11	Thai Roong Ruang Sugar Group Co., Ltd.	Saraburi	120,000	Molasses Bagasse
12	Rachaburi Ethanol Co., Ltd.	Rachaburi	150,000	Cassava chip Molasses
13	ES Power Co., Ltd.	Sakaeo	150,000	Molasses Cassava chip
14	Mae Sod Clean Energy Co., Ltd.	Tak	200,000	Sugarcane
15	Sapthip Co., Ltd.	Lopburi	200,000	Cassava chip
16	Thi Phing Ethanol	Sakaeo	150,000	Cassava root Cassava chip
17	PSC Starch Production	Chonburi	150,000	Cassava root Cassava chip
18	Petro Green Co., Ltd. (Danchang)	Suphanburi	200,000	Molasses Sugarcane
19	Khonkaen Alcohol Co., Ltd. (Bo-Ploy)	Kanjanaburi	150,000	Molasses Sugarcane

Table 2.10 Ethanol Plants as On-going Process in 2012 (Sutabutr, 2012).

No	Plant	Site	Capacity (l/d)	Feedstock
1	PTK Ethanol -Phase 1	Nakorn Ratchasima	340,000	Cassava Chips
	PTK Ethanol -Phase 2,3	Nakorn Ratchasima	680,000	Cassava Chips
2	Thai Agro Energy (Dan Chang) Phase 2	Suphanburi	200,000	Cassava Chips
3	Double A Ethanol	Pracheenburi	250,000	Starch
4	Sima Inter Products	ChaShoengSao	150,000	Fresh Cassava Tubers
5	Impress Technology	ChaShoengSao	200,000	Fresh Cassava Tubers/ Cassava Chips/Molasses
6	Ubon Bio Ethanol	Ubon Ratchathani	400,000	Cassava: Fresh Tubers/Chip

2.3.1 Sugarcane Based Ethanol Production

As sugarcane based ethanol plant is not exist in Thailand, sugarcane ethanol conversion data from Brazil was studied (Ometto *et al.*, 2009). A simple process diagram is shown in Figure 2.7.

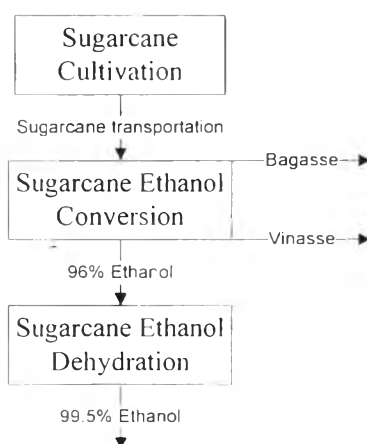


Figure 2.7 A simple process diagram of sugarcane based ethanol production (Ometto *et al.*, 2009).

2.3.1.1 Sugarcane Cultivation

Sugarcane, the essential raw material for sugar industry in Thailand, is found abundantly in the central region accounting for the highest percentage of the national sugarcane production. The process procedure of sugarcane cultivation include, land preparation and planting, fertilizing and weeding, and harvesting is shown in Figure 2.8 (Nguyen *et al.*, 2008).

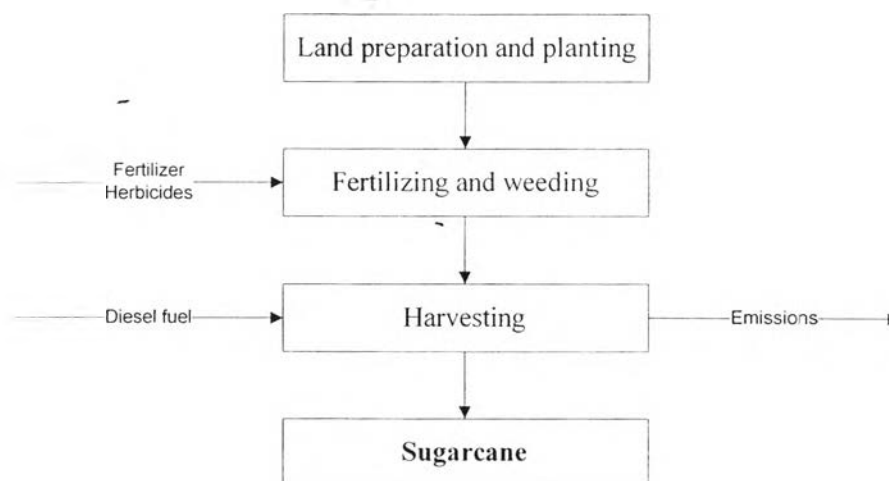


Figure 2.8 Process procedure of sugarcane cultivation (Nguyen *et al.*, 2008).

2.3.1.2 Sugarcane Ethanol Conversion

The industrial transformation into hydrated ethanol begins with the washing of sugarcane. The washed sugarcane is transported by conveyor belts to the millings, where the sugarcane juice is extracted. The products of the sugarcane milling are juice and bagasse. The juice is used to produce alcohol and the bagasse is burned to generate steam and electricity in cogeneration plants. The extracted juice enters decanters, where solid materials are separated from the juice. Then, the juice is inoculated by yeast (*Saccharomyces*), which converts saccharose ($C_{12}H_{22}O_{11}$) into ethanol (C_2H_5OH) and carbon dioxide (CO_2) by fermentation cubs. The fermentation product is transported to distillation columns to elevate the alcohol concentration. The products of distillations are hydrated ethanol (96% ethanol) and vinasse. Relevant information on sugarcane ethanol conversion process was extracted from literature (Ometto *et al.*, 2009).

2.3.2 Molasses Based Ethanol Production

Molasses based ethanol production process include sugarcane cultivation, sugarcane milling, and molasses ethanol conversion process is illustrated in Figure 2.9. This model uses bagasse and biogas as fuels to produce steam and electricity.

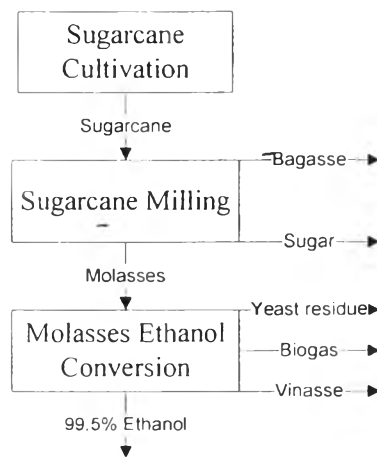


Figure 2.9 A simple process diagram of molasses based ethanol production.

2.3.2.1 Sugarcane Milling

According to section 2.3.1.1, sugarcane was cultivated and then transported to sugarcane milling which is a process to produce sugar for sugarcane based PLA resin production process and to produce molasses for molasses ethanol conversion process. Raw sugar production process is divided into 5 steps as shown in Figure 2.10 (MTEC, 2010).

1) Juice Extraction: sugarcane pass through a series of five crushing mill to extract as much sugar juice as possible. Most of the crushing mills are driven by steam turbines.

2) Juice Purification: The sugarcane juice which is delivered from the milling train contains some soil and other undesirable impurities. To remove these, juice is heated and lime is added to settle the unwanted material. The impurities settle out in the clarifier and then go to the rotary vacuum filters, which

filter out any remaining juice. The filter mud from the vacuum filters is rich in nutrients and is recycled back to cane fields.

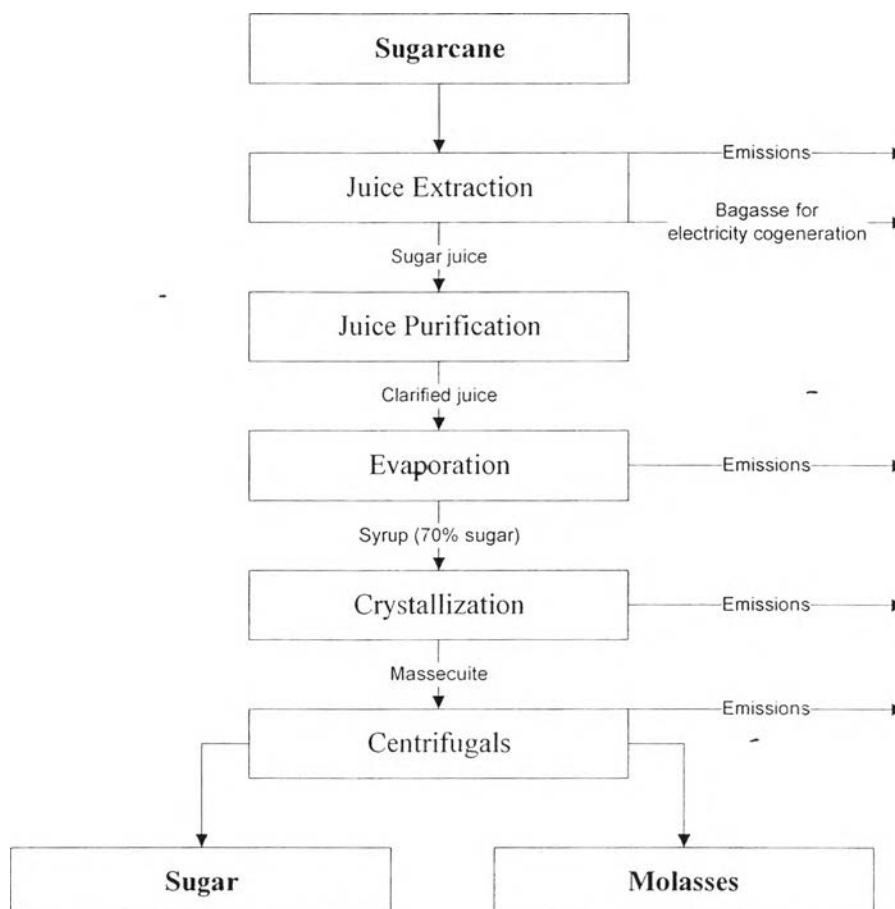


Figure 2.10 Process procedure of sugar milling.

3) Evaporation: The clarified juice is concentrated to thick syrup by boiling off water in the evaporators. The juice passes continuously from vessel to vessel until it is concentrated to syrup containing approximately 70% sugar.

4) Crystallization: At this stage the syrup from the evaporators is converted to crystal sugar. A charge of syrup is taken into a vacuum pan and again boiled under a vacuum. A quantity of very fine “seed” crystal is introduced. As water is evaporated fresh syrup is added and sugar is deposited on the seed crystal. This process continues until the crystals have reached the desired size

(approx. 1 mm square). The resulting semi liquid mass of sugar crystals and molasses is called massecuite.

5) Centrifugation: Sugar crystals are separated from the syrup in the centrifugals. The centrifugals are perforated metal baskets spun at high speed by an electric motor. While the sugar is spinning in the baskets it is given a short burst of hot water to help wash the sticky molasses off the sugar crystals.

Based on Figure 2.10, residue of this process (bagasse) can be used as fuel to generate electricity and steam.

2.3.2.2 *Electrical Energy Cogeneration*

Cogeneration system is the system which can produce electricity and steam. It is used in industrial plants in Thailand more than 30 years such as sugar milling plant and palm oil plant because this kind of industry has biomass residue from production process like bagasse, empty fruit branch, etc. (Tossanaitada *et al.*, 2009). Nowadays, most of cogeneration system in Thailand has low efficiency due to low inlet steam pressure of turbine were in range of 18 to 22 Bar_a. In order to improve the efficiency, the low pressure steam is replaced by higher pressure steam at 68 Bar_a which is used in Europe countries. The data of cogeneration system was collected by thesis of Suranaree University of Technology (Witayapairot, 2010). Moreover, according to Department of Industrial Promotion, Ministry of Industry (2009), biogas 1 m³ can produce electricity 1.2 kWh, CO₂ emission from biogas combustion, being of biogenic origin, are considered net zero as also bagasse combustion.

2.3.2.3 *Molasses Ethanol Conversion*

After molasses from sugar milling was produced, it was transported to the process making molasses based ethanol consists of yeast preparation, fermentation, distillation and dehydration, as shown in Figure 2.11 (KAPI, 2007).

2.3.3 Cassava Based Ethanol Production

Cassava based ethanol production process include cassava cultivation, cassava chips production, and cassava ethanol conversion process is shown in Figure 2.12, this model has biogas which is fuel to produce electricity for

the biorefinery model. Moreover, dried distiller grain with soluble (DDGS) was produced in cassava ethanol conversion process.

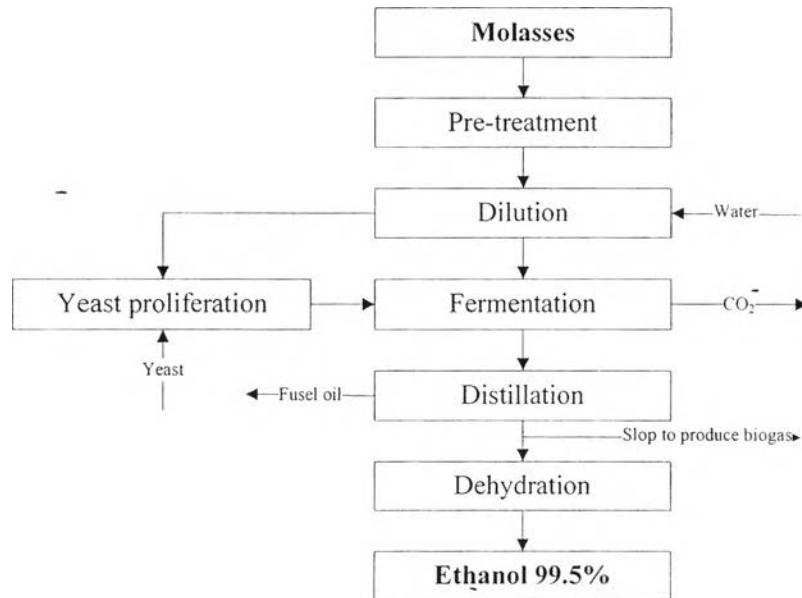


Figure 2.11 Flow chart for molasses ethanol conversion process (KAPI, 2007).

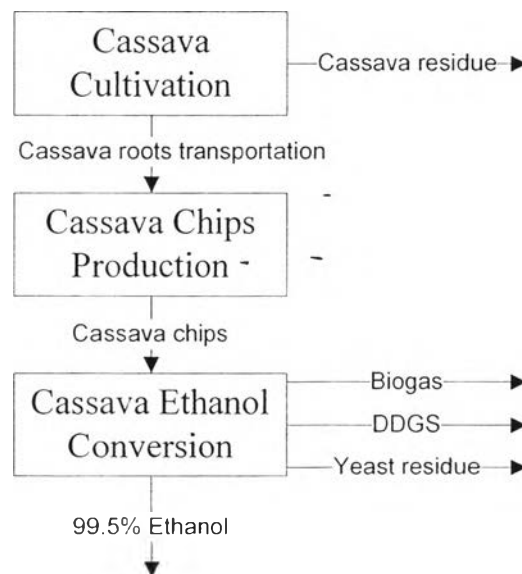


Figure 2.12 A simple process diagram of cassava based ethanol production.

2.3.3.1 Cassava Cultivation

The cassava production can be illustrated as shown in Figure 2.13. In cassava production includes 4 sub-processes (Khongsiri, 2009):

1) Land preparation before planting by soil tillage to eliminate the weed and create the trench for cultivation.

2) Preparation of breeding and cultivation, cassava strains were selected and chopped to appropriate size for cultivation. Then place them in the trench.

3) The maintenance: Consists of important events such as eliminate the weeds by tillage and use chemicals. Including put the fertilizer. Farmers tend to use both manure and chemical fertilizers

4) Harvesting can be done by using machine harvesting or workers.

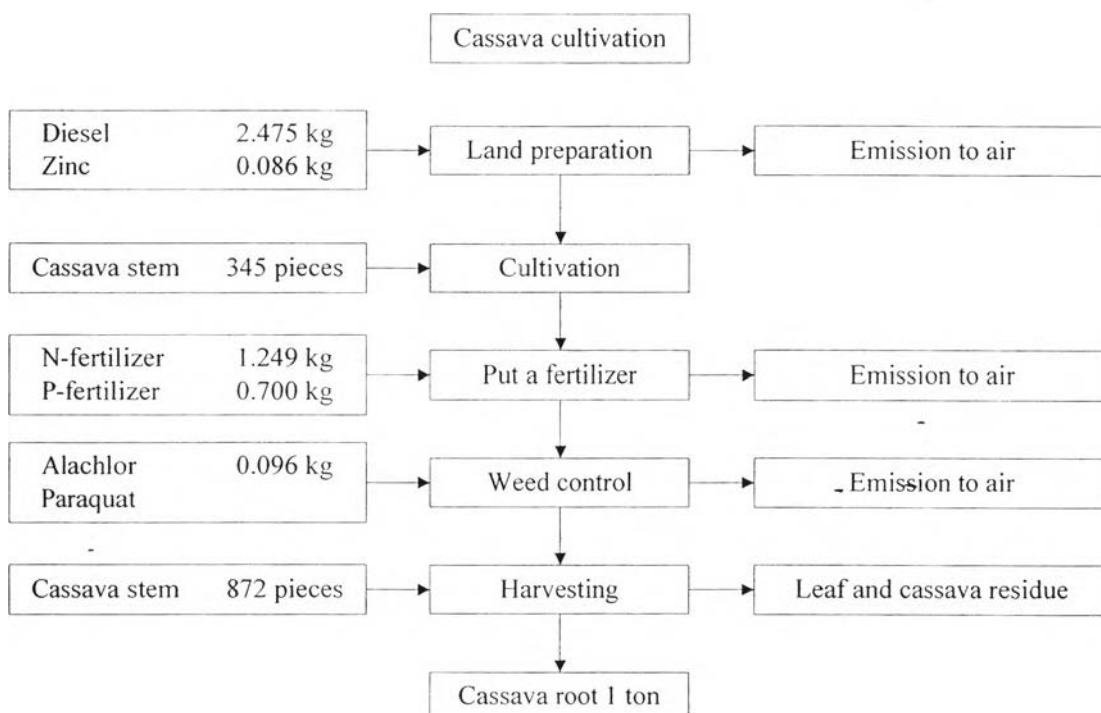


Figure 2.13 The process procedure of cassava cultivation in rainy season with water (Khongsiri, 2009).

2.3.3.2 Cassava Ethanol Conversion

The cassava ethanol plant includes four main sub-processes i.e., milling and mixing, liquefaction, fermentation, distillation, and molecular sieve dehydration, as shown in Figure 2.14. Biogas is a by-product that used as fuel for electricity generation (KAPI, 2007). Due to feedstock of this process is cassava chips, it need to add cassava chips production process between cassava cultivation and cassava ethanol process (Silalertruksa *et al.*, 2011).

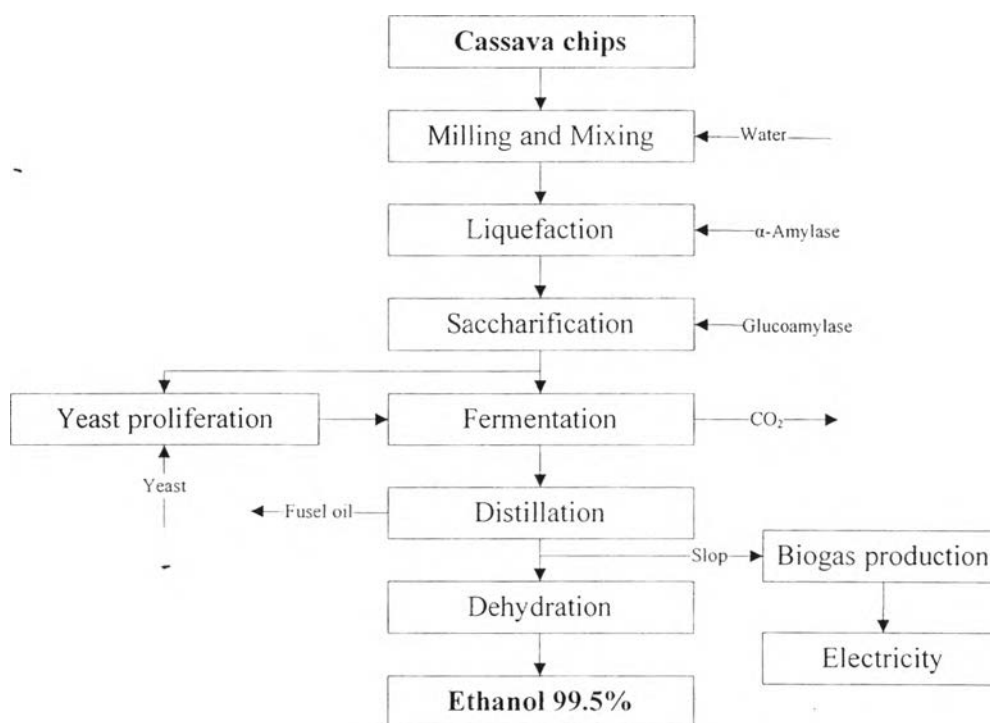


Figure 2.14 Flow chart for cassava ethanol conversion process (KAPI, 2007, Silalertruksa *et al.*, 2011).

2.3.4 Cassava Rhizome Based Ethanol Production

Actually there is no any factory to produce ethanol from cassava rhizome in Thailand. According to Mangnimit *et al.* (2013), study shows results from a systematic model based analysis in order to produce bioethanol from potential lignocellulosic materials in Thailand generally and cassava rhizome particularly.

The sources of cassava rhizome are by-product from harvest at field, cassava chip production and cassava starch production. However, the main source is from cassava residue after harvest.

S. Mangnimit et al. had simulated bioethanol production from cassava rhizome as shown in Fig 2.15. Cassava rhizome is milled and sent to pre-treatment zone. Then concentrated sulfuric acid is added to the reactor to hydrolyze cellulose and hemicellulose into C6 and C5 sugars. The hydrolyzate is sent to detoxification to eliminate the contaminants such as furfural and HMF. After that detoxified hydrolyzate is 10% separated for yeast (seed) production and the rest is sent to fermentation. Eventually, the output from fermenter is sent to recovery section to obtain 99.5 % ethanol.

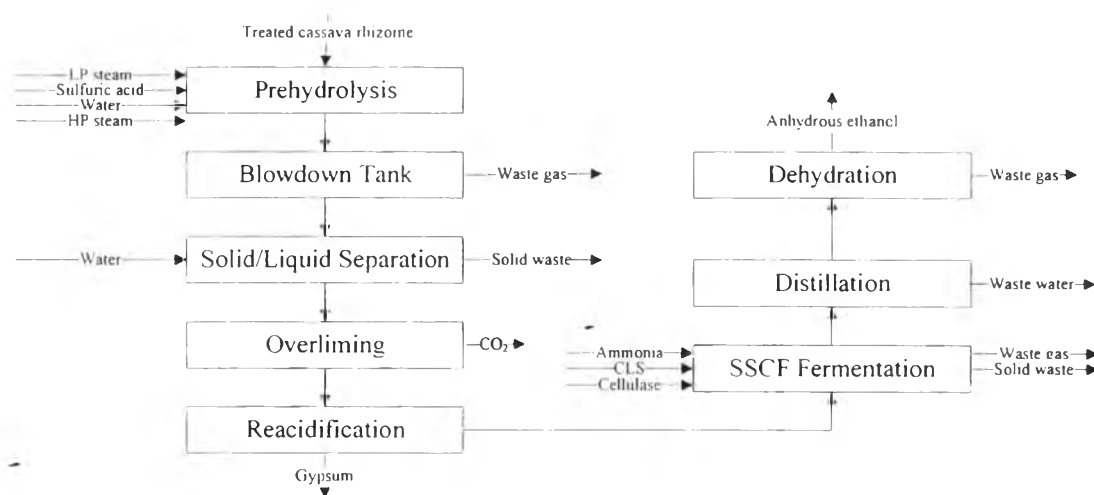


Figure 2.15 Flow chart for cassava rhizome ethanol conversion process (Mangnimit *et al.*, 2013).

2.3.5 Cassava Pulp Based Ethanol Production

New Energy and Industrial Technology Development Organization (NEDO) of Japan has signed a memorandum of understanding with the National Innovation Agency (NIA) of Thailand to support budget 276 million baht under the demonstration project to produce ethanol from cassava pulp. Eiamburapa Ethanol Company Limited is a private company of Thailand has been transferred of

technology during 2013-2016. Target is to transfer of research from the University of Japan and expand globally (Saengchan, 2012).

However, this process was not chosen for studying due to the deficiency of LCI data.

2.4 Current Status of Biosuccinic Acid (BSA) Productions and Uses in Thailand

Succinic acid (SA), known as amber acid or butanedioic acid, can be used as a chemical precursor in many important industries including adipic acid, 1,4-butanediol, tetrahydrofuran, N-methyl pyrrolidinone, 2-pyrrolidinone, succinate salts, and gamma-butyrolactone as shown in Figure 2.16 (Song *et al.*, 2006).

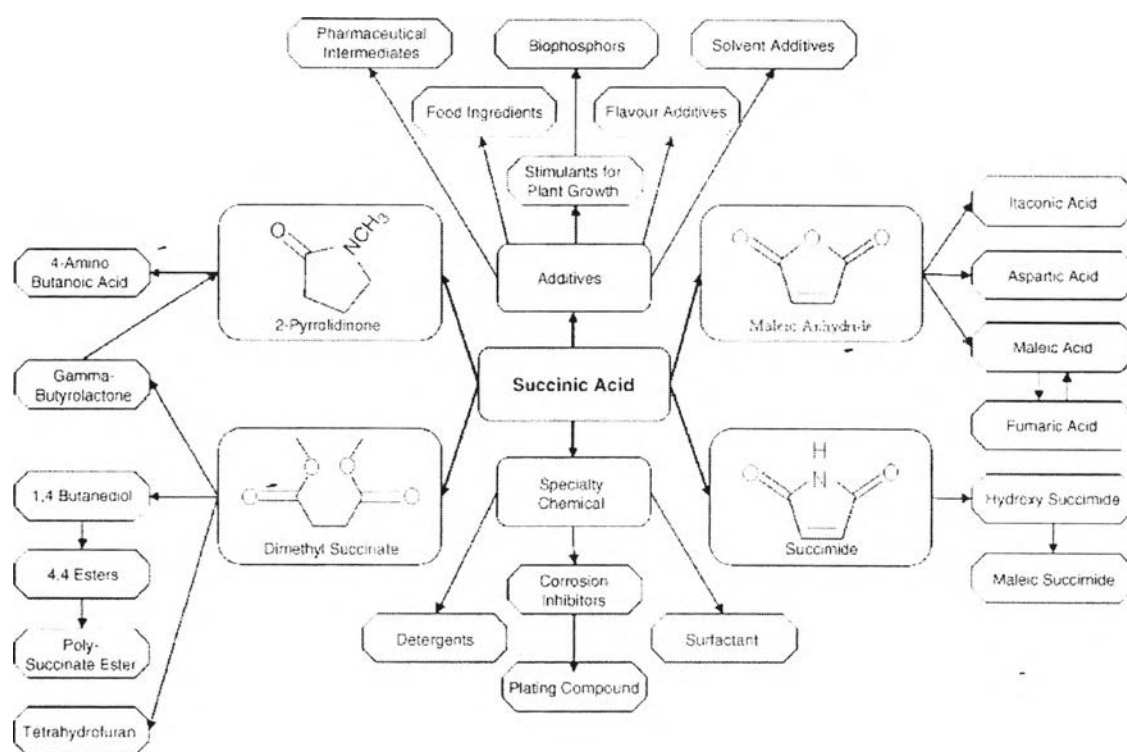


Figure 2.16 Various chemicals and products that can be synthesized from succinic acid (Song *et al.*, 2006).

In the year 2010, SA global demand was found to be 43,000 tons and would have grown up to 145,000 tons by the year 2025, representing a growth rate of 8

percent per year. Bio-based SA has the advantage over petroleum-based SA since produced from biological processes and production costs can be competitive. Applications of both bio-based and petroleum-based SA are equivalent (Thouphan, 2011).

On 30th March 2011, PTT Public Company Limited (PTT) and Mitsubishi Chemical Corporation (MCC) were registered as a PTTMCC BioChem Company Limited to establish manufacturing facilities of biosuccinic acid (BSA) 36,000 tons and PBS 20,000 tons annually from sugar as the first one in the world as shown in Figure 2.17. By trading on both domestic and international markets with a focus on Europe and America. The two high-tech factories of MCC is expected to submit a commercial operation in late 2014. As a source of raw materials, agricultural potential such as sugarcane and cassava, Thailand is also located near the strategic importance of the plastic market, including China, Korea, Japan. Hence, the cost of transportation and trade has the advantage over other countries (Thouphan, 2011).

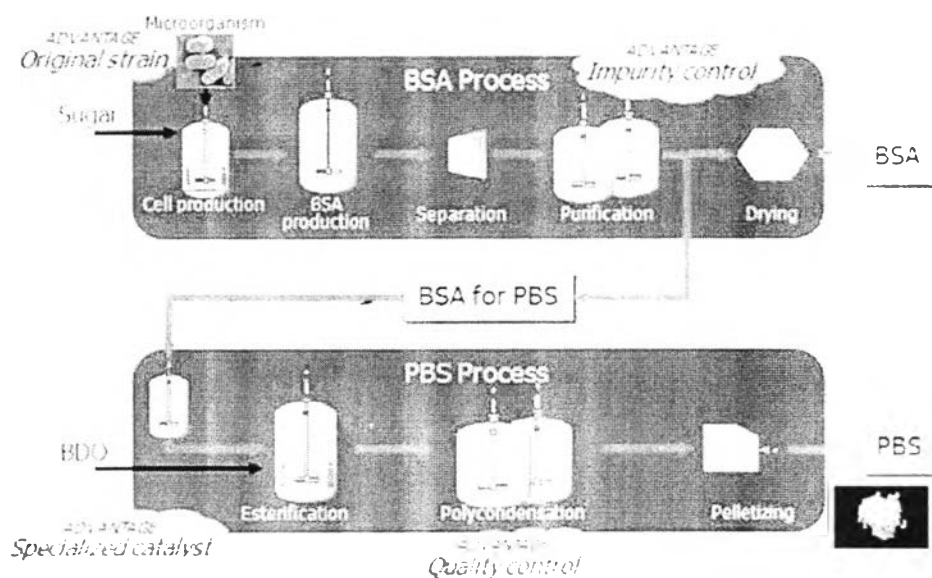


Figure 2.17 Schematic of reactants bio-succinic acid (BSA) and biopolymer polybutylene succinate (PBS) (Thouphan, 2011).

2.4.1 BSA Production

A simple process diagram of sugarcane based BSA and cassava based BSA production is shown in Figure 2.18.

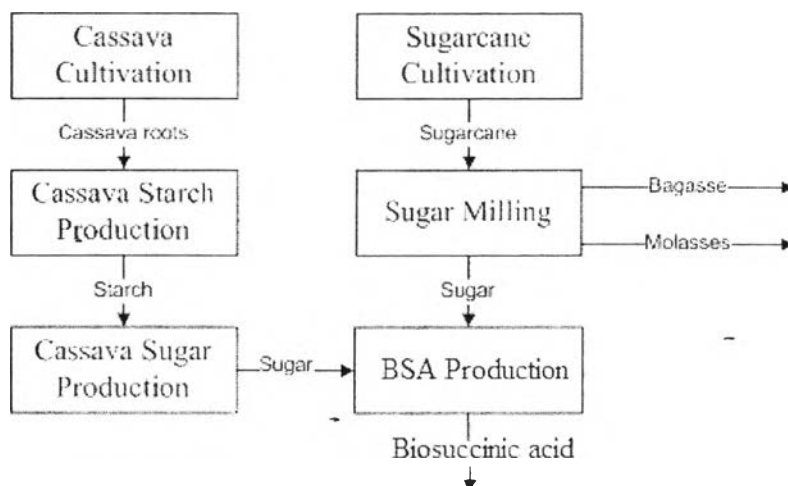


Figure 2.18 A simple process diagram of sugarcane based BSA and cassava based BSA production.

2.4.1.1 *Cassava Starch Production*

At plant, cassava production process mainly use dewatering centrifugal method which consist of main step as follows

After cassava roots were cultivated as described in section 2.3.3.1, they were delivered to a sand removal drum. Then, they are transferred to a rinsing gutter for cleansing and peel separation. After washing, the clean cassava roots are sent to a chopper to chop into small pieces (approximately 20-25 mm) and then taken to a rasper. During rasping, water is added to facilitate the process. The resulting slurry, consisting of starch, water, fiber, and impurities, is then pumped into the centrifuges for extraction of the starch from the fibrous residue (cellulose). The extraction system consists of three or four centrifuges in series. There are two types of extractors: a coarse extractor with a perforated basket and a fine extractor with a filter cloth. Suitable amount of water and sulfur-containing water are constantly applied to the centrifuges for dilution and bleaching of the starch.

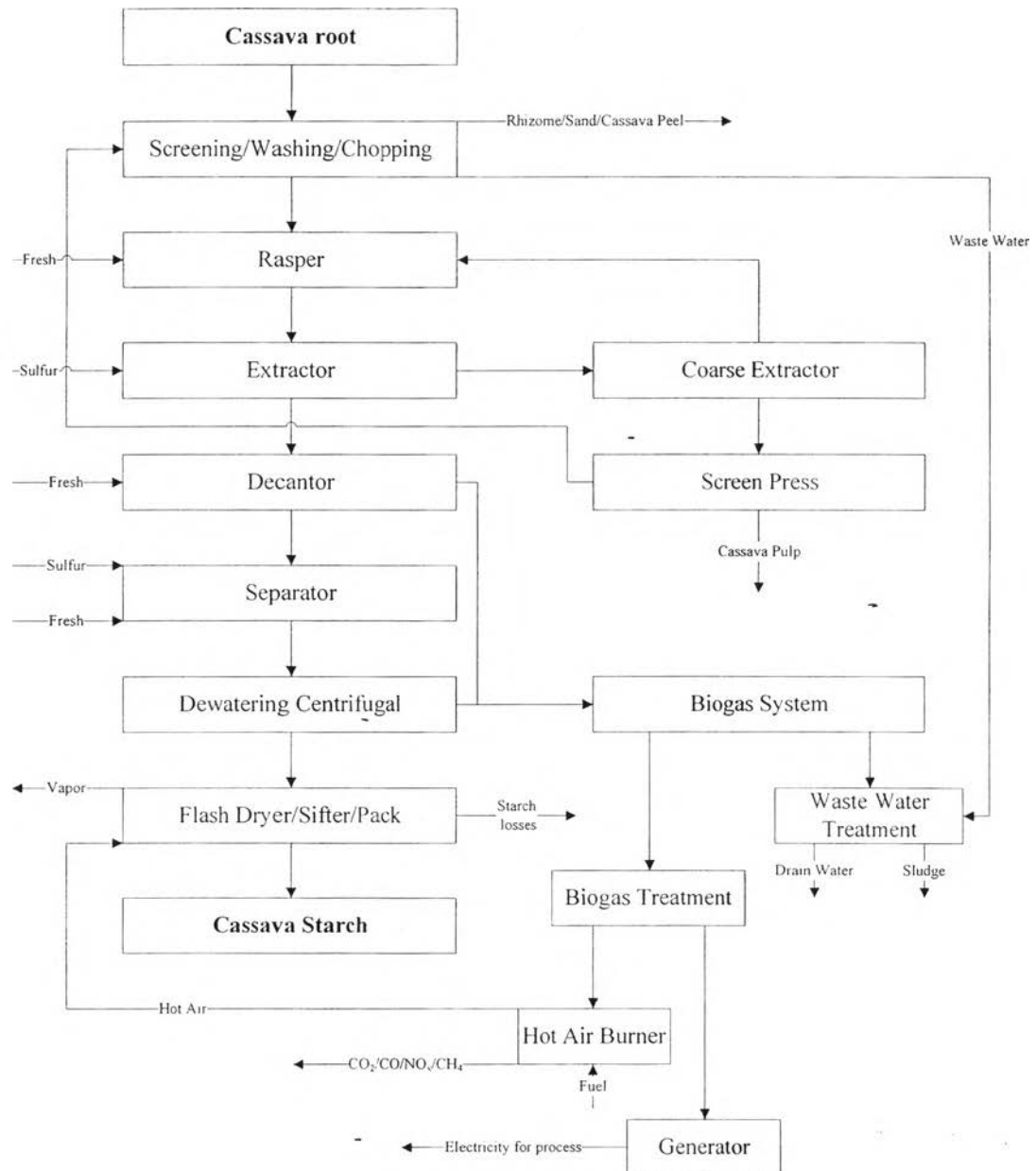


Figure 2.19 Flow chart for cassava starch production with biogas production line (Khongsiri, 2009).

The starch slurry is then separated into starch milk and fibrous residue. The coarse and fine pulp is passed to a pulp extractor to recover the remaining starch and the extracted pulp is then delivered to a screw press for dewatering. The dewatered fibrous residue is sold to a feedstock mill. The starch milk from the fine extractor is pumped into a two-stage separator for impurity

removal from the protein. After passing to a second dewatering machine, the starch milk has the starch content up to 18-20 Baume' (Chavalparit *et al.*, 2009). Then, the concentrated starch milk is pumped into dehydration horizontal centrifuges (DHC) to remove water before drying. The DHC consists of filter cloth placed inside, rotating at about 1000 rpm to remove water from the starch milk. The resulting starch cake has a moisture content of 35-40%. The starch cake is taken to a drying oven consisting of a firing tunnel and drier stack. Drying is effected by hot air produced by oil burners. During the drying process, the starch is blown from the bottom to the top of the drier stack and then fallen into a series of two cyclones in order to cool down the starch. The dried starch with a moisture content of less than 12% is conveyed through a sifter for size separation and finally packaging (Khongsiri, 2009). A simple process diagram of cassava starch production with biogas is shown in Figure 2.19.

2.4.1.2 Cassava Sugar Production

Glucose syrup production from cassava can be subdivided into the following process areas of liquefaction, saccharification, and purification.

Native starch consists of microscopic granules having a complex internal structure. At room temperature, these granules are insoluble in water. However, if starch slurry is heated above 60 °C, the granules will swell and eventually rupture. This results in a dramatic increase in viscosity. At this point, the starch has been "gelatinized". The gelatinized starch is now susceptible to attack by amylase enzymes. In practice, cassava starch is gelatinized and partially hydrolyzed very rapidly in one step (see flow chart) by heat-stable amylase. This step is called liquefaction. The partially degraded starch chains called dextrins are suitable starting materials for the later steps in syrup production (MTEC, 2010).

- Liquefaction

Starch slurry is made with 30-35% dry solids and its pH is adjusted to 6.0-6.4. Calcium is added using calcium hydroxide or calcium chloride. Calcium ions stabilize the enzyme. A heat-stable α -amylase (Novo's Termamyl 120 L) is mixed into the slurry, and then the slurry is instantaneously heated to 100 °C and held at this temperature for 10 min before it is cooled to 90 °C. This temperature is maintained for 1-3 h to further hydrolyze the starch. At the end of this step, the starch has been converted to dextrins with a dextrose equivalent (DE) between 8 and

15. (The physical properties of the syrup vary with the DE and the method of manufacture.) DE is the total reducing sugar in the syrup expressed as dextrose on a dry weight basis.

- **Saccharification**

After liquefaction, the pH is reduced to between 4.2 and 4.5 and the solution is cooled to 60 °C. A glucomylase (Novo's AMG 300L) is added immediately. The reaction time for saccharification is usually between 24-48 h depending on enzyme dose. Glucoamylase releases single glucose units from the ends of dextrin molecule. Syrups of 95% glucose or higher are manufactured. e.g., a typical 98 DE syrup could have the sugar profile as shown in Figure 2.20.

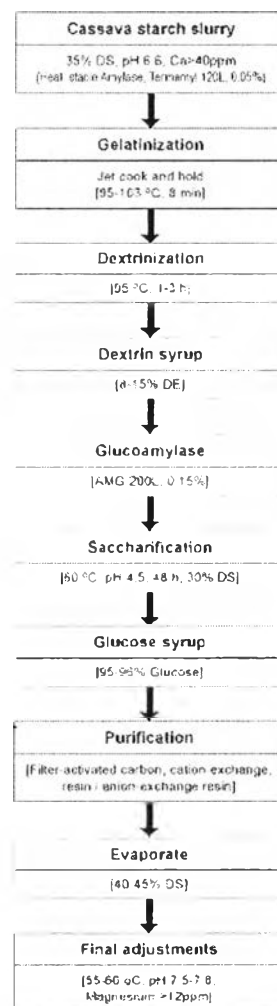


Figure 2.20 Flow chart for glucose syrup production from cassava (ICP, 2004).

2.4.1.3 BSA Production

The schematic of the BSA production is shown in Figure 2.20. From this data, sugar from sugarcane (section 2.3.2.1) and sugar from cassava (section 2.4.1.2) could be used in the same process and the same condition but it should be separate process into two parts for SuBSA and CaBSA because it might be risk for reaction of each other.

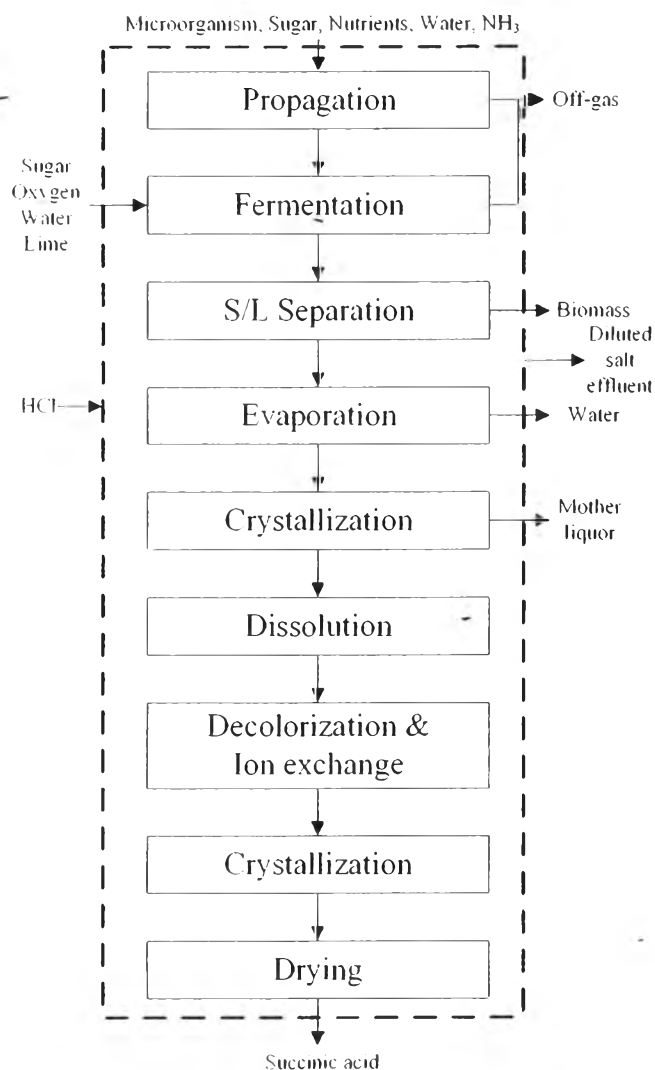


Figure 2.21 Flow chart for BSA production process (Cok *et al.*, 2013).

There are several productions of biosuccinic acid from Cok *et al.* (2013), journal referred. However, the low pH yeast fermentation followed by

direct crystallization process was chosen due to the best environmental performance. Unfortunately, BSA process is quite modern so life cycle inventory cannot be completely disclosed owing to confidentiality agreement. The amounts of sugar and titrants consumed have to be calculated corresponding to the related references, i.e., DSM's journal (Tsiropoulos *et al.*, 2013) and DSM's patent (US 20120238722A1) (Van De Graaf *et al.*, 2012).

In this process, microorganisms used can produce BSA at low pH. Therefore, lime controlling pH is little used. Yeast is propagated by adding sugar, nutrients NH_3 and water. To produce BSA, sugar, oxygen, water and lime are added into aerobic fermenter. HCl is applied for mild acidification and softening. For the evaporation process, mechanical vapor recompression (MVR) is used to concentrate dissolved product stream. For the crystallization process, BSA crystals are split from mother liquor. Biogas can be produced by mother liquor containing 7% wt. BSA. Finally, high-grade BSA is purified by polish treatment, recrystallization and drying as illustrated in Figure 2.21.

More data corresponding to direct crystallization are needed in order to calculate LCI. Downstream process with acidification at pH less than 2.0 can easily crystallize BSA at temperature 4°C (Li *et al.*, 2010, Lin *et al.*, 2010).

2.5 Current Status of Lactic Acid (LA) Productions and Uses in Thailand

Lactic acid is an intermediate used in a wide range of food processing and industrial applications. Lactic acid has a potential to become the very large volume, commodity-chemical intermediate produced from carbohydrates for used as raw materials for biodegradable polymers, oxygenated chemicals, plant growth regulators, environmentally friendly 'green' solvents, and specialty chemical intermediates (Datta *et al.*, 1995).

Demand for lactic acid has increased significantly due to a variety of lactic acid applications especially to be the raw material for the production of biopolymer polylactic acid (PLA). It can be produced either by chemical synthesis or by microbial fermentation. Currently, almost all of lactic acid produced worldwide is manufactured by the fermentation route (Abdel-Rahman *et al.*, 2011).

At present, Thailand has lactic acid (LA) production plant which belongs to Purac of the Netherland. Purac has started up a modern low-cost lactic acid plant near Rayong in Thailand. Using sugar from sugarcane as the raw material and a new large-scale lactide plant became on stream at Purac's site in Thailand in 2011. Although LA can be used in various application, Purac focused on production of bioplastic PLA as shown in Table 2.11.

According to Thailand's National Bioplastics Roadmap, the maximum investment of bioplastics in Thailand is PLA as shown in Figure 2.22 (NIA, 2013). The major company is PTTGC/Nature Work. The joint venture will allow the company to have the technology and the increase in revenue since PLA NatureWorks LLC has production of 1.5 tons/year in the United States and plans to expand its plant in the two regions in Southeast Asia as well. Thailand has the advantage of raw material is sugar and cassava which are the raw materials for the production of bioplastics (iBizChannel, 2011).

The biopolymer PLA is made from lactic acid that can be produced from sugars by fermentation. Lactic acid has a carboxylic and hydroxyl group and through esterification PLA chains of lactic acid moieties, may be formed. The Schematic of the production chain from agriculture to LA is illustrated in Figure 2.23 (Groot *et al.*, 2010).

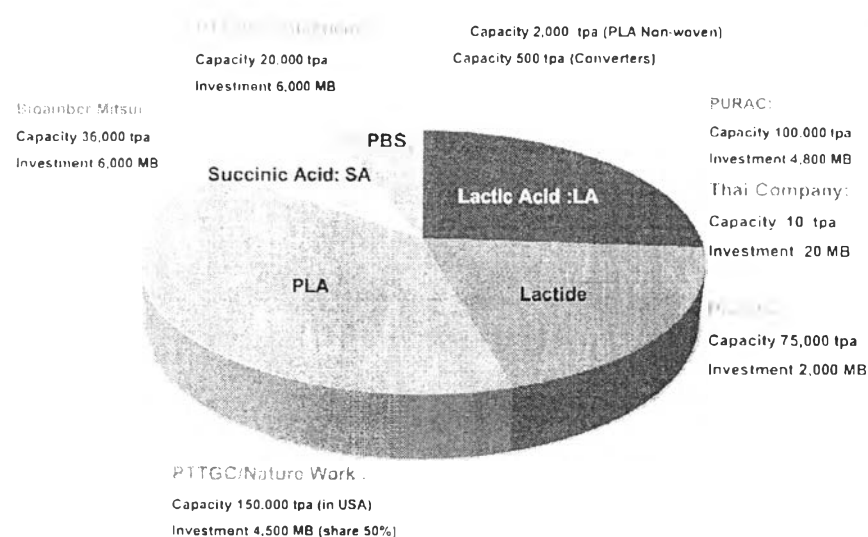


Figure 2.22 Current bioplastics investment in Thailand (NIA, 2013).

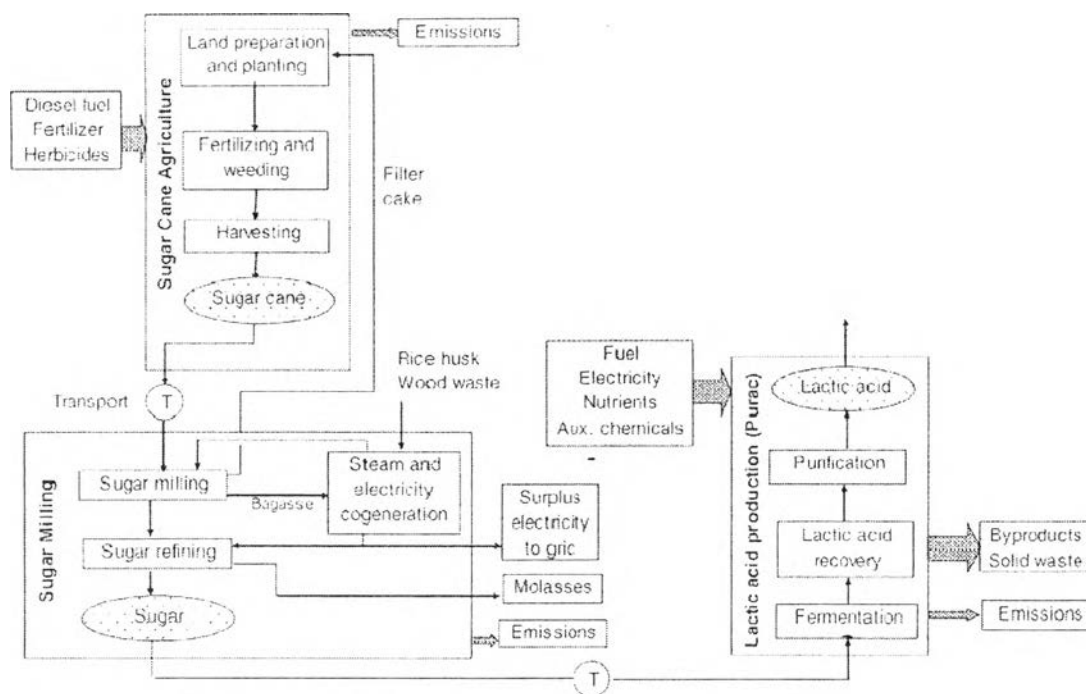


Figure 2.23 Schematic of the production chain from agriculture to LA (Groot *et al.*, 2010).

Table 2.11 Companies which are doing business with biopolymers in Thailand (NIA, 2008).

	Company's name	Location	Product	Technology
1	Advance Packing Co.,Ltd. (Special Tech Group)	Ayutthaya	Plastic bag	- Made from corn starch. - Import polymer from USA.
2	M.S.V. Trading Ltd., Part	Bangkok	Food container	
3	Saha Kim Co.,Ltd. (Bio Mat)	Bangkok	Bag, cup, straw	- Add plasticizer with conventional plastic in order to make bioplastic.
4	Bio Green World Co., Ltd. (BGW)	Samut-Prakarn	Food container	- Made from PLA. - Import PLA from Taiwan.
5	BIOFOAM Jazzy Creation Co., Ltd	Bangkok	Food container	- Made from cassava starch.
6	Biodegradable Packaging for Environment Co.,Ltd. (BPE)	Bangkok	Food container	- Made from bagasse.
7	KU-GREEN: Biodegradable Package	Bangkok	Food container	- Made from cassava starch.
8	Thantawan Industry Public Co.,Ltd.	Bangkok	Plastic bag and plastic film	- Import polymer from USA and compounded polymer from Japan.
9	PURAC Thailand	Rayong	Lactic acid	- Made from sugar and cassava.

2.5.1 LA Production

A simple process diagram of sugarcane based LA and cassava based LA production is shown in Figure 2.24.

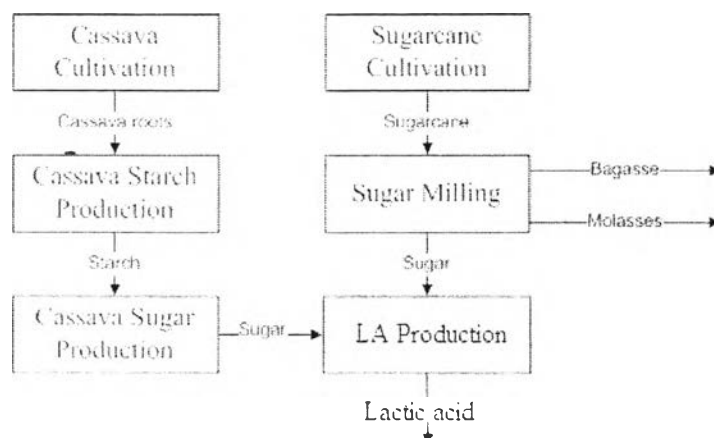


Figure 2.24 A simple process diagram of sugarcane based LA and cassava based LA production.

2.5.1.1 LA Production

The schematic of the LA production is shown in Figure 2.24. From this data, sugar from sugarcane (section 2.3.2.1) and sugar from cassava (section 2.4.1.2) could be used in the same process and the same condition but it should be separate process into two parts for SuLA and CaLA because it might be risk for reaction of each other.

For lactic acid production from H. Andreanne (2010), the batch fermentation is applied by temperature 45°C, pH 6, time 72 hours; yield obtained 90%. There are four major steps: media preparation, media pre-heating, lactic acid fermentation, and lactic acid purification as shown in Figure 2.25.

1) Media preparation corresponds to mixing the substrate before fermentation such as CSL, chemicals, nutrients etc.

2) Media pre-heating is heating the media to the fermentation temperature.

3) Fermentation includes adding calcium hydroxide to control pH.

4) Purification consists of biomass filtration, the calcium lactate dissociation by sulfuric acid, the filtration of gypsum and concentration of lactic acid to 88% wt.

To remove soluble impurities, ultrafiltration or carbon treatment can be performed. The environmental impacts of those processes can be neglected since they are very low.

From this data sugar from sugarcane and sugar from cassava can be used in the same process and the same condition but process should be separated into two parts for SuLA and CaLA because it might be risk for reaction of each other.

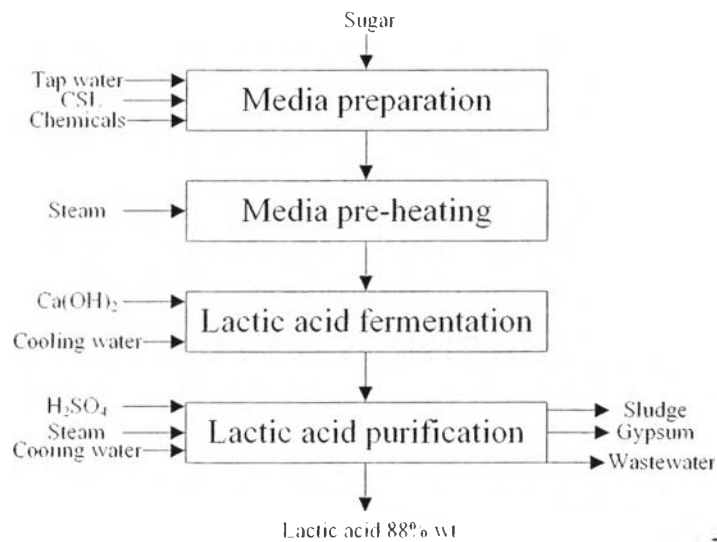


Figure 2.25 Flow chart for LA production process (Andreanne, 2010).

2.6 Life Cycle Assessment (LCA)

2.6.1 Overview

The history of LCA goes back almost 40 years and started with energy and material budgets to which complementary pollution aspects were progressively

added. With the two oil crises in the 1970s, interest in LCA was boosted, but mostly for the energy efficiency part. With the growing solid-waste issues at the end of the 1980s, the development of the methodology accelerated and in 1992 the first formal framework for the impact assessment phase was proposed. The purpose of this phase, based on scientific knowledge and models, is to convert inventory data into potential impacts on ecosystems and human health. The refining of this phase remains one of the key scientific challenges of the methodology for many research teams around the world (Mens *et al.*, 2007).

2.6.2 Definition of LCA

Life Cycle Assessment is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and materials used and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing, extracting and processing raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling, and final disposal. The general categories of environmental impacts needing consideration include resource use, human health, and ecological consequences (SETAC, 1993).

Life Cycle Assessment (LCA) is used as a tool to assess the environmental impacts of a product, process or activity throughout its life cycle; from the extraction of raw materials through to processing, transport, use and disposal. In its early days it was primarily used for product comparisons, for example to compare the environmental impacts of disposable and reusable products. Today its applications include government policy, strategic planning, marketing, consumer education, process improvement and product design. It is also used as the basis of eco-labeling and consumer education programs throughout the world.

2.6.3 Methodology

A framework for LCA has been standardized by the International Organization for Standardization (ISO) in the ISO 14040 series. It consists of 4 elements: Goal and Scope Definition, Inventory Analysis, Impact Assessment, and Interpretation as illustrated in Figure 2.26.

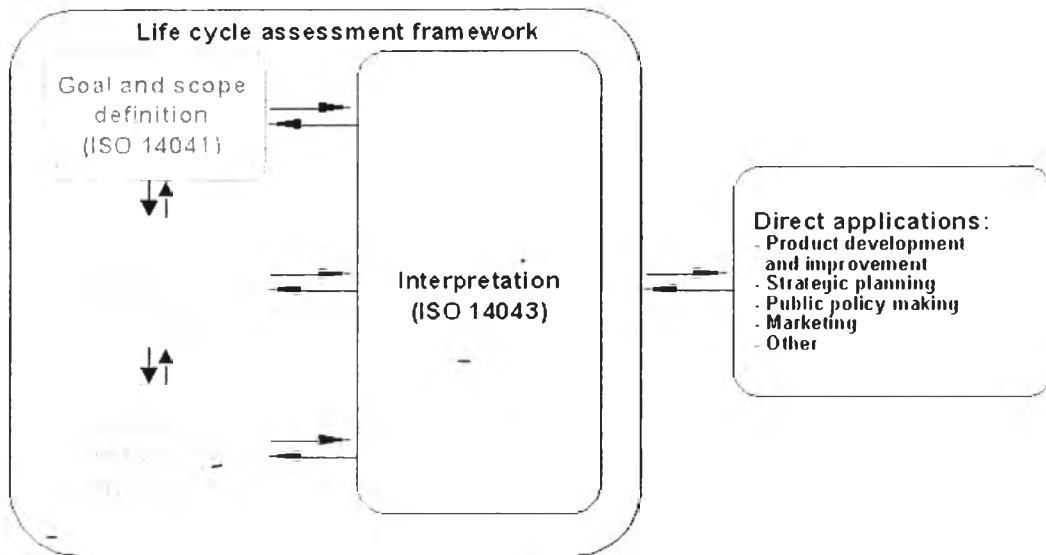


Figure 2.26 Life-cycle assessment framework as laid down in ISO 14040:1997 (Mens *et al.*, 2007).

2.6.3.1 Goal and Scope Definition

Goal and scope definition is the first phase in a life cycle assessment containing the following main issues (Jensen *et al.*, 1997):

- Goal

The goal of an LCA study shall unambiguously state the intended application, including the reasons for carrying out the study and the intended audience, i.e. to whom the results of the study are intended to be communicated.

- Scope

The scope describes the breadth, the depth and the detail of the study. It is important to define a functional unit and the system boundaries. The data quality requirements should be carefully specified.

- Functional Unit

One of the main purposes for a functional unit is to provide a reference to which the input and output data are normalized. A functional

unit of the system shall be clearly defined and measurable. The result of the measurement of the performance is the reference flow.

- System Boundaries

The initial system boundary defines the unit processes which will be included in the system to be modeled. Ideally, the product system should be modeled in such a manner that the inputs and outputs at its boundary are elementary flows. However, as a practical matter, there typically will not be sufficient time, data, or resources to conduct such a comprehensive study. Decisions must be made regarding which unit processes will be modeled by the study and the level of detail to which these unit processes will be studied.

Any omission of life cycle stages, processes or data needs should be clearly stated and justified. Ultimately, the sole criterion used in setting the system boundaries is the degree of confidence that the results of the study have not been compromised and that the goal of a given study has been met.

- Data Quality

The quality of the data used in the life cycle inventory is naturally reflected in the quality of the final LCA. The data quality can be described and assessed in different ways. It is important that the data quality is described and assessed in a systematic way that allows others to understand and control for the actual data quality.

2.6.3.2 Inventory Analysis

Life Cycle Inventory (LCI) is the phase of the LCA involving the compilation and quantification of inputs and outputs; it comprises data collection and data calculation. Data collection consists of the identification and quantification of the relevant input and output flows for the whole life cycle of a product.

Basically three types of flows can be differentiated: elementary flows (emissions, resources) that are emitted into the environment or extracted from it, product flows (goods, services), that come from or go to the techno sphere, and waste flows (a sub-type of product flows). The use of resources and the use of land, raw materials, fabricated products, auxiliary materials, energy carriers and electricity are recorded as inputs. Emissions to air, water, and land as well as wastes and by-products are outputs in an inventory analysis. In the later stage of the

impact assessment, the quantitative information on the product system's elementary flows (and in some methods the waste flows) is used to analyze the product's impacts.

The most important steps of life cycle inventory work are determination of the reference quantity (e.g. functional unit, reference flow), description of system in flow diagrams, identification of unit processes to be modeled separately in LCI model, qualitative determination of inputs and outputs, quantitative determination of inputs and outputs, documentation of the type of data survey, inventory data collection, inventory data collection of transport, and Calculation of the inventory, including allocations and covering the inventories of the background data sets (Jensen *et al.*, 1997).

2.6.3.3 Impact Assessment

The impact assessment is carried out on the basis of the inventory analysis data. It is the third phase in a life cycle assessment containing the following main issues (Bianchi, 2008):

- Category Definition

The impact assessment categories should link the potential impacts and effects on what is referred to as the "areas of protection" of the LCA, i.e. the entities that we want to protect by performing and using the LCA. Today, there is acceptance that the protection areas of life-cycle assessment are:

- natural resources
- natural environment
- human health
- and often also: man-made environment

- Classification

In the classification step the inventory data are assigned to categories according to their impact. For instance, carbon dioxide emissions contribute to the greenhouse effect and are hence assigned to the impact category Climate change. If a substance contributes to several impact categories, it has to be taken into account in all of these categories. Such a case is, for example, nitrogen oxide that causes both eutrophication and acidification.

- Characterization

Classification is followed closely by characterization. Every substance is assigned a potential impact in the impact category under study. The potential impact of a substance is given relative to a dominant factor in the category, e.g. for the Climate change potential this is typically 1 kg of carbon dioxide emissions. These relative impacts (the characterization factors of a substance) are then multiplied with the amount of each emission and the resulting impact values are summed for the respective impact category.

Life Cycle Impact Assessment uses generally the following categories:

- Greenhouse effect (or global warming potential)

Global warming is called the greenhouse effect because the gases that are gathering above the earth make the planet comparable to a greenhouse. By trapping heat near the surface of the earth, the greenhouse effect is warming the planet and threatening the environment. The climate changes that will result from global warming are extremely difficult to predict. If temperatures do indeed rise significantly, the most important result would be that some portion of the polar icecaps would melt, raising global sea levels. The Global Warming Potential (GWP) is the potential contribution of a substance to the greenhouse effect. This value has been calculated for a number of substances over periods of 20, 100 and 500 years because it is clear that certain substance gradually decompose and will become inactive in the long run.

- Acidification

The Acidification Potential (AP) is expressed relative to the acidifying effect of SO_2 . Other known acidifying substances are nitrogen oxides (NO_x), sulfuric acid (H_2SO_4), and hydrogen chloride (HCl).

- Eutrophication

Eutrophication is an increase in the concentration of chemical nutrients (nitrogen (N) and phosphorus (P)) in water bodies, often leading to changes in animal and plant populations and degradation of water and habitat quality. The Nutriphication Potential (NP) is expressed as kg phosphate (PO_4^{3-})

equivalents. Other emissions also influence eutrophication, notably nitrogen oxides and ammonium.

2.6.3.4 Interpretation

Within the framework of an evaluation, the results from the impact assessment and the inventory analysis are analyzed and conclusions and recommendations are established. A further aspect is the transparent presentation of the LCA results. The ISO standards comprise three interpretation elements (Bianchi, 2008):

- Significant Issues

In order to determine the significant issues the main contributions of each impact category have to be identified (which emissions and/or which processes are dominant within each category). The relevant inventory data which cannot be recorded through impact categories must also be integrated into the study. Following the scope definition, the main contributions can be grouped by the individual process step, individual life phases and the entire life cycle. Together with these results, the significant issues can now be established, since it is now also clear which processes or life phases are dominant.

- Results Evaluation

To evaluate the results according to the ISO standard, a completeness check, a sensitivity check, and a consistency check of the identified processes or life phases must be carried out. Completeness is checked by e.g. a mass and energy data analysis - and considering experts' know-how of the modeled processes. Sensitivity is determined by calculating scenarios for different processes or different parameters (e.g. varying yield of processes and emission factors). The effects of the different assumptions on the total result show the sensitivity. It must be ensured that all necessary information and data relevant to the interpretation are available and complete; for confidentially needs or process operators the ISO standards foresee to establish respective agreements. It is also important to check to what extent uncertainties, for example through the estimation of data due to data gaps, may influence the result. The consistency check should ensure that the procedure is consistent with the goal and scope definition and that the methodology

and other rules have been accurately and consistently applied for the whole product system.

- **Conclusions and Recommendations**

The aim of this third step of the interpretation is to reach conclusions and recommendations for the report of the LCA study or life cycle inventory study. This step is important to improve the reporting and the transparency of the study. Both are essential for the readers of the LCA report. The results of the critical review of the study shall also be included when presenting the conclusions and recommendations.

2.6.4 Applications of LCA

The applications of LCA can be included into decision making in various fields. examples are (Bianchi, 2008):

- product development and improvement
- process and service operation
- strategic planning
- technological impact assessment
- public policy making
- marketing

Concerning the scientific literature about the application of LCA methodology to biorefinery systems, it is nowadays limited, and very few case studies exist. Since climate change mitigation and energy security are the two most important driving forces for biorefinery development. Thus, LCA of biorefinery has a special focus on GHG and energy balances.-Other environmental impact categories are investigated according to the Centrum voor Milieukunde Leiden (CML) method (Cherubini *et al.*, 2010).

2.7 LCA and Related Studies on Biorefineries

In 2010, Cherubini and Ulgiati studied a biorefinery concept which produces bioethanol, bioenergy and biochemicals from two types of agricultural residues, corn stover and wheat straw. These biorefinery systems was investigated

using a Life Cycle Assessment (LCA) approach, which takes into account all the input and output flows occurring along the production chain.

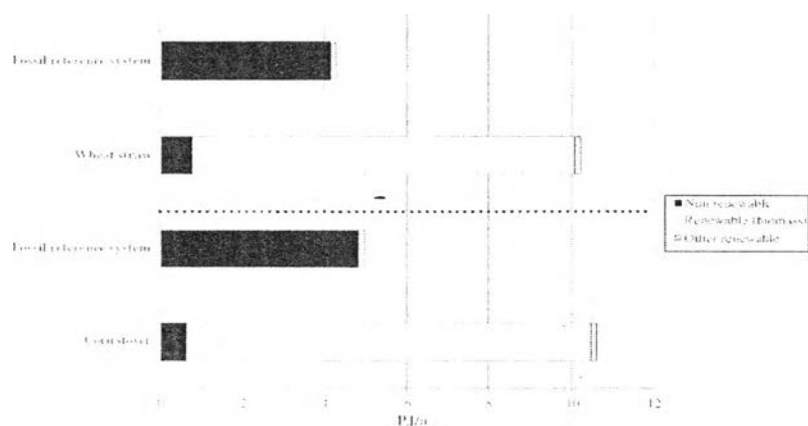


Figure 2.27 Cumulative primary energy demand of the biorefinery and fossil reference systems (Cherubini *et al.*, 2010).

In this analysis, elaborated on land use change aspects, i.e. the effects of crop residue removal (like decrease in grain yields, change in soil N₂O emissions and decrease of soil organic carbon). Moreover, they were comparing between the biorefinery systems and the respective fossil reference systems producing the same amount of products/services from fossils instead of biomass. The assessment focuses on greenhouse gas (GHG) emissions and cumulative primary energy demand. Results show that the use of crop residues in a biorefinery saves GHG emissions and reduces fossil energy demand. For instance, GHG emissions are reduced by about 50% and more than 80% of nonrenewable energy is saved as seen in Figure 2.27. Land use change effects have a strong influence in the final GHG balance (about 50%).

In 2009, Ometto and Hauschild presented the life cycle assessment (LCA) of fuel ethanol, as 100% of the vehicle fuel, from sugarcane in Brazil. The functional unit is 10,000 km run in an urban area by a car with a 1,600 cm³ engine running on fuel hydrated ethanol, and the resulting reference flow is 1,000 kg of ethanol. The product system includes agricultural and industrial activities, distribution, cogeneration of electricity and steam, ethanol use during car driving, and industrial

by-products recycling to irrigate sugarcane fields. The use of sugarcane by the ethanol agribusiness is one of the foremost financial resources for the economy of the Brazilian rural area, which occupies extensive areas and provides far reaching potentials for renewable fuel production. But, there are environmental impacts during the fuel ethanol life cycle. The aforementioned impact potentials have been normalized by the EDIP method, using world and European normalization references, which represent the annual average impact from an average citizen a person equivalent, PE. The normalization references for the global impacts are based on an average global citizen and for the regional impacts are based on an average European citizen given that EDIP normalization references have not yet been especially the rural activities of the sugarcane cultivation, is highly mechanized, with intensive use of pesticides, nutrients and diesel. The inputs of renewable resources are high mainly because of the water consumption in the industrial phases, due to the sugarcane washing. During the lifecycle of alcohol, there is a surplus of electricity due to the cogeneration activity. Another focus point is the quantity of air emissions and the diversity of the substances emitted, especially during the harvesting, because of the sugarcane burning and the high consumption of diesel. The L.CIA conclusions are that the fuel ethanol lifecycle contributes to all the impacts analyzed: global warming, ozone formation, acidification, nutrient enrichment, ecotoxicity, and human toxicity. The main cause for the biggest impact potential indicated by the normalization is the nutrient application, the burning in harvesting, and the use of diesel. Normalized impact potentials for fuel ethanol lifecycle are given in Figure 2.28.

In 2008, Nguyen and Gheewala investigated the life cycle assessment of fuel ethanol from cassava in Thailand. In this paper divided the process into four main unit processes of the cassava based E10/E85 fuel system for the life cycle inventory (LCI) are cassava production, ethanol conversion, transportation and fuel combustion in vehicles as given in Figure 2.29.

Cassava production is also notable for its contribution to acidification, nutrient enrichment and POCP. Acidification originates principally from SO_2 emission from the manufacturing of P fertilizer and NO_x emission (direct and indirect)

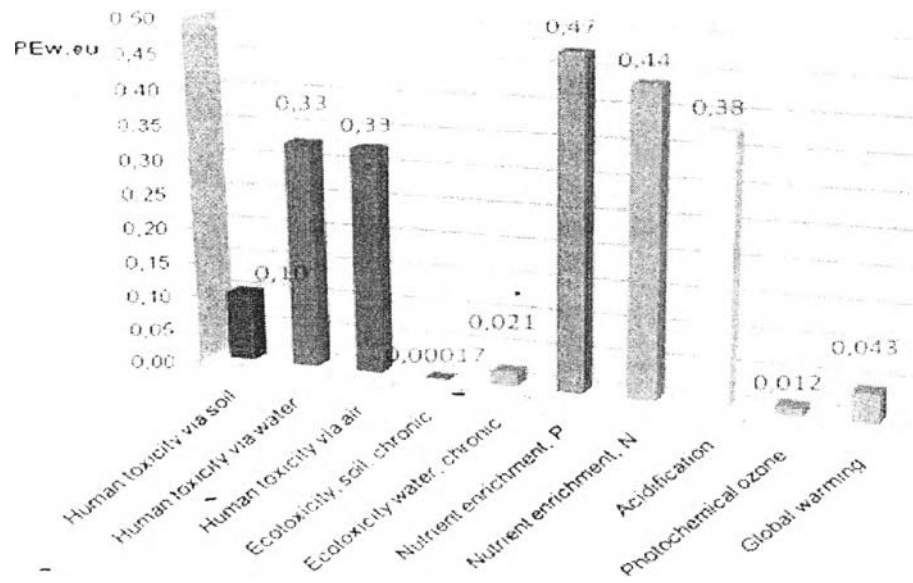


Figure 2.28 Normalized impact potentials for fuel ethanol lifecycle (Ometto *et al.*, 2009).

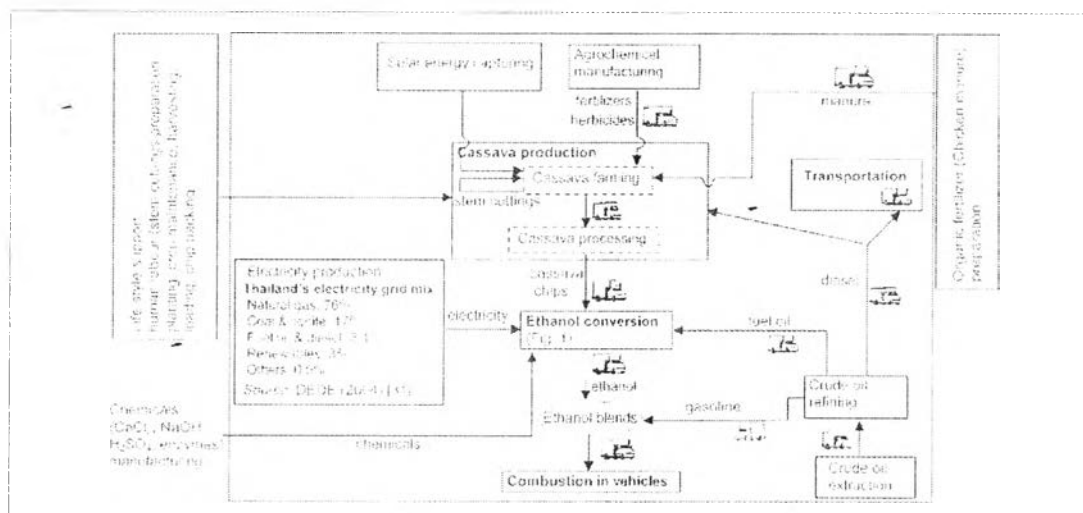


Figure 2.29 System boundary of the cassava-based E10/E85 fuel life cycle (Nguyen *et al.*, 2008).

from diesel used to power farm tractors. This amount of NO_x also contributes to nutrient enrichment. However, the largest contributor to nutrient enrichment from cassava production is N_2O soil emissions from N fertilizer application, as seen in Figure 2.30.

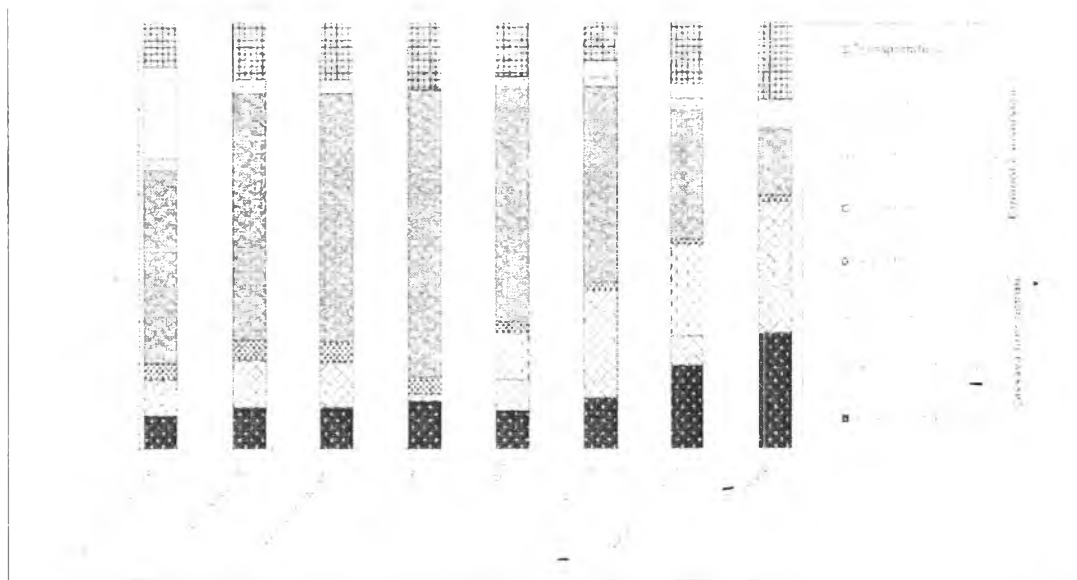


Figure 2.30 Characterization results – Contributions to the environmental impacts from ethanol production cycle.

In 2010, Vink et al. demonstrated the eco-profile for current Ingeo[®] polylactide production. This paper gave the latest life cycle inventory data based on new lactic acid production technology that was implemented in December 2008. Although the objective of this paper is to provide detailed inventory data sufficient for use by LCA practitioners interested in the use of Ingeo resin for specific products, process illustrated in Figure 2.31 can be used as the lactic acid production section in this thesis (Vink *et al.*, 2010).

The eco-profile of current and near-future NatureWorks[®] polylactide (PLA) production reported by Vink et al. (2007). They provide the cradle-to-polymer-factory-gate life cycle inventory data (eco-profiles) for the 2006 and the near-future PLA production system and explain the use of RECs (renewable energy certification). The cradle-to-factory-gate PLA production system is divided into five major steps (Vink *et al.*, 2007):

- Corn production and transport of corn to the corn processing wet mill
- Corn processing and the conversion of starch into dextrose
- Conversion of dextrose into lactic acid
- Conversion of lactic acid into lactide

- Polymerization of lactic into polylactide polymer pellets

Lactic acid is produced by fermentation of dextrose received from the corn wet mill. The process combines dextrose and other media, adds a microbial inoculum, and produces crude lactic acid whose pH is controlled by the addition of calcium hydroxide. The lactic acid broth is then acidified by adding sulfuric acid, resulting in the formation and precipitation of gypsum. Gypsum is removed by filtration, and the lactic acid is concentrated by evaporation. After final purification, the lactic acid enters the lactide/PLA process.

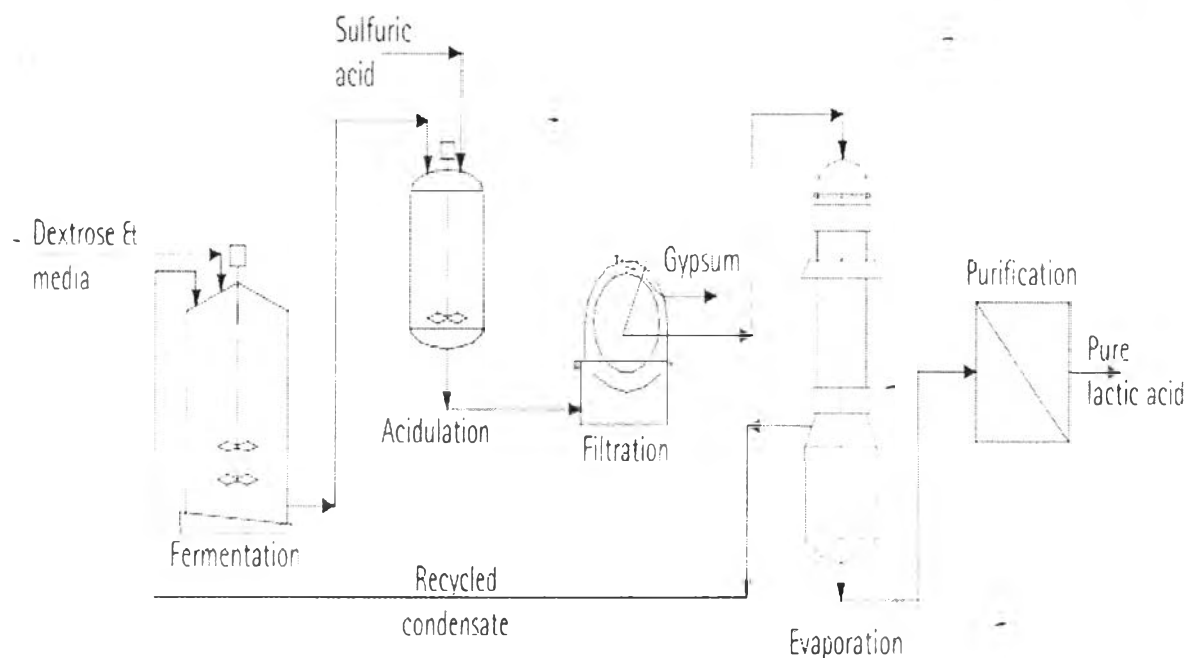


Figure 2.31 NatureWorks lactic acid production process (Vink *et al.*, 2010).

In 2013, S. Mangnimit *et al.* studied on the design of sustainable processes to produce ethanol from cassava rhizome included process simulation, sustainability analysis, economic evaluation and life cycle assessment (LCA).

- A steady state process simulation is performed to generated base case to produce ethanol using cassava as feedstock as illustrated in Figure 2.32.

- Sustainability analysis is performed to analyze relevant indicators in sustainability metrics.
- Economic analysis is performed to analyze profitability and sustainability.
- LCA is performed to assess environmental impacts.

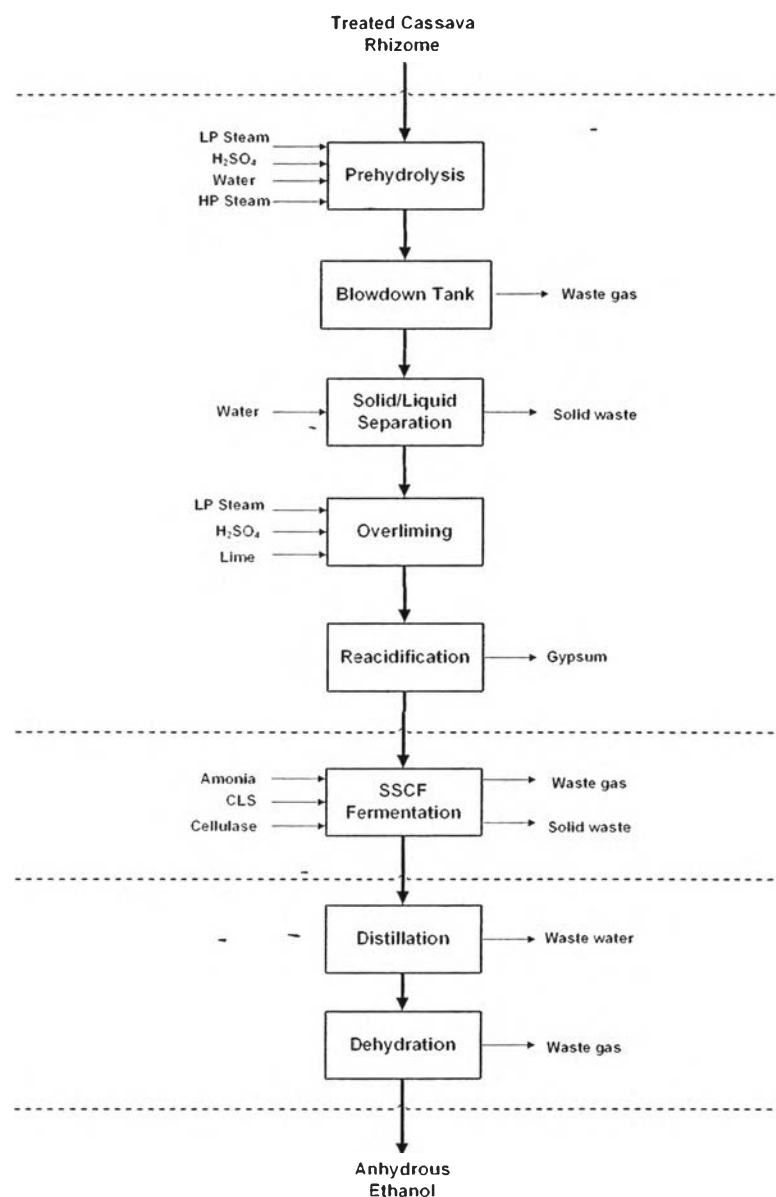


Figure 2.32 Flow chart for bioethanol production process from cassava rhizome (Mangnimit *et al.*, 2013).

The choices of candidate were compared to the base case in terms of economics, LCA, energy consumption, and environmental impact in order to identify the most sustainable design for the production of ethanol. The ability to produce ethanol is 150,000 liters/day, which is about 1.3% of the total demand of ethanol in Thailand. LCA in base case pointed to the amount of CO₂ emissions and CO (from the combustion engine transportation) biowaste and waste water is released from the distillation column, which affects terrestrial ecotoxicity. Analysis of sustainable development in the base case points to the large waste water and lignin, which are then targets for potential improvement.

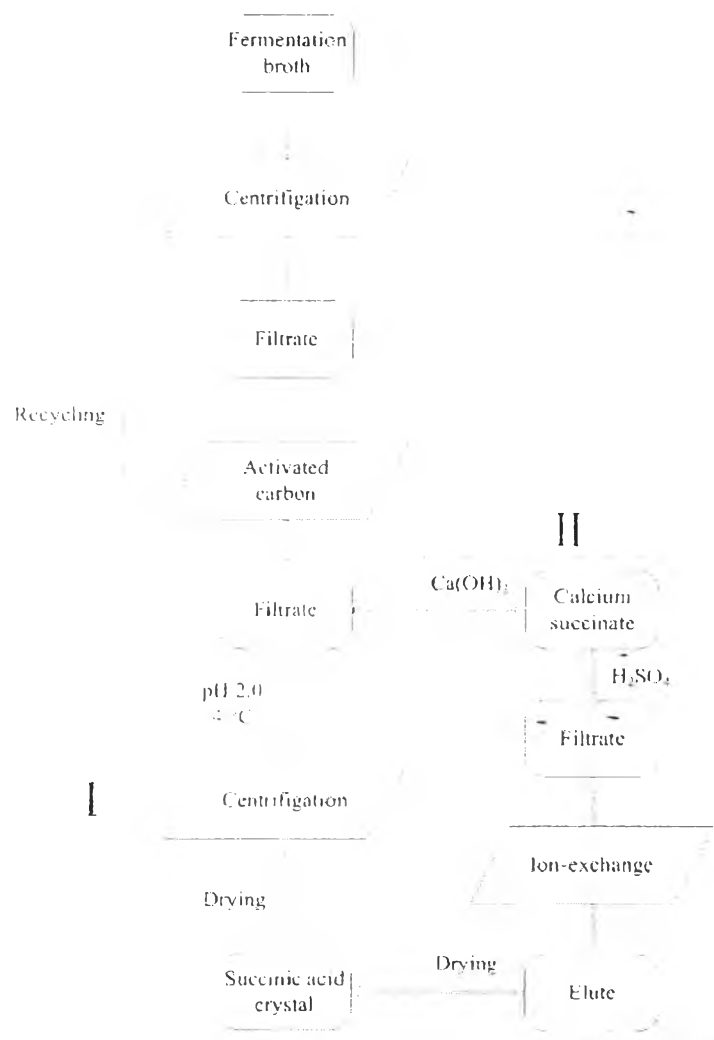


Figure 2.33 Schematic diagrams of two recovery processes of succinic acid, (I) direct crystallization, (II) modified calcium precipitation (Li *et al.*, 2010).

In 2010, Li et al. studied one step recovery of the desired product succinic acid crystal from the fermentation broths as the first time. Since downstream recovery process is estimated to account for over 60% of the overall production cost. The existing separation methods are usually not easily operated to separate target acid from the carboxylic acid mixture in the fermentation broths. Traditionally, $\text{Ca}(\text{OH})_2$ is usually added to neutralize the fermentation broth and precipitate succinate. Calcium succinate is recovered by filtration, and free acid is released from the precipitate by adding sulfuric acid. However, large amount of CaSO_4 and some Calcium lactate could be accumulated. The reactive extraction with amine-based extractant is needed. Figure 2.33 shows 2 different recovery methods.

The result showed that when the pH value of the fermentation broth was controlled less than 2.0, crystallization of succinic acid could be carried out at 4 °C easily, while major acid by-products such as lactic acid, acetic acid and formic acids were miscible in solution. By this one step recovery method, succinic acid yield was 70% and the purity was 90%. In comparison, for traditional calcium precipitation coupled ion-exchange adsorption, the yield and purity were 52% and 92%, respectively.