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 and Jungmeier, 2009; Cherubini, 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.

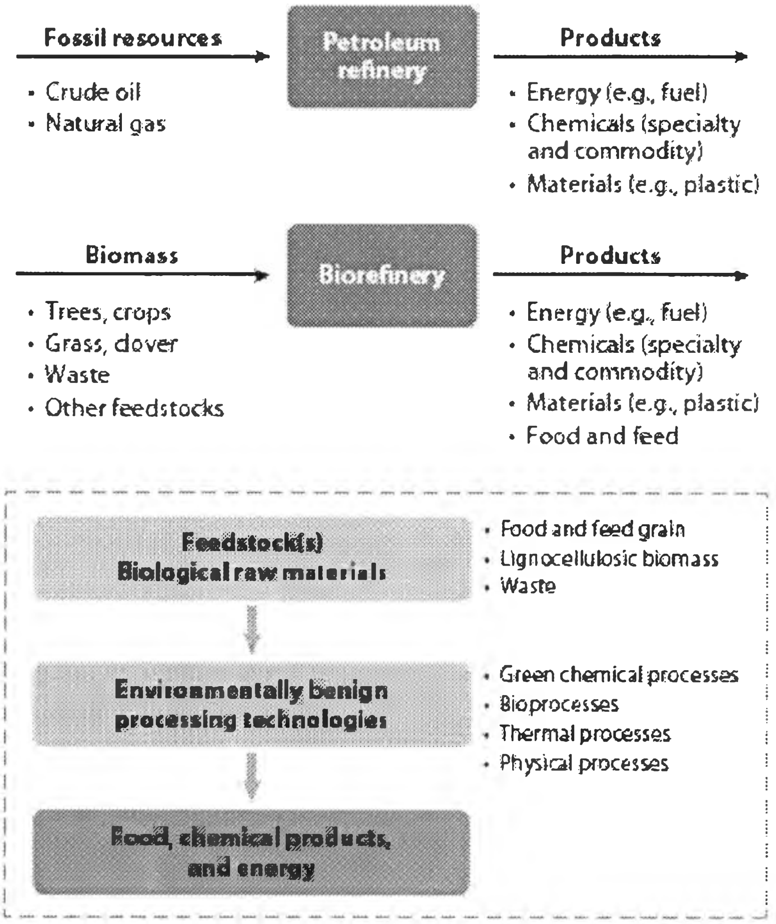


Figure 2.1 The biorefinery concept: from biomass to valuable products via low-environmental-impact valorization practices (Clark *et al.*, 2012).

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 and Thomas, 2009).

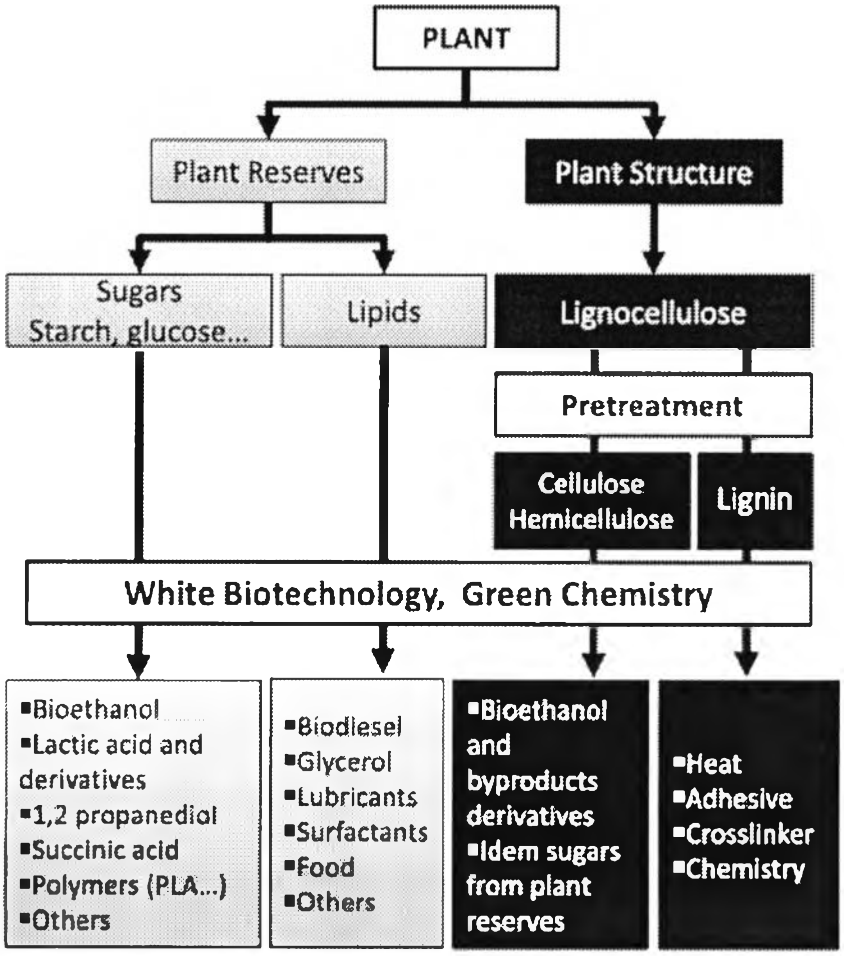


Figure 2.2 Whole plant valorization in biorefinery based on the function of plant components used as raw material (Octave and Thomas, 2009).

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 and Thomas, 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 and Thomas, 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).

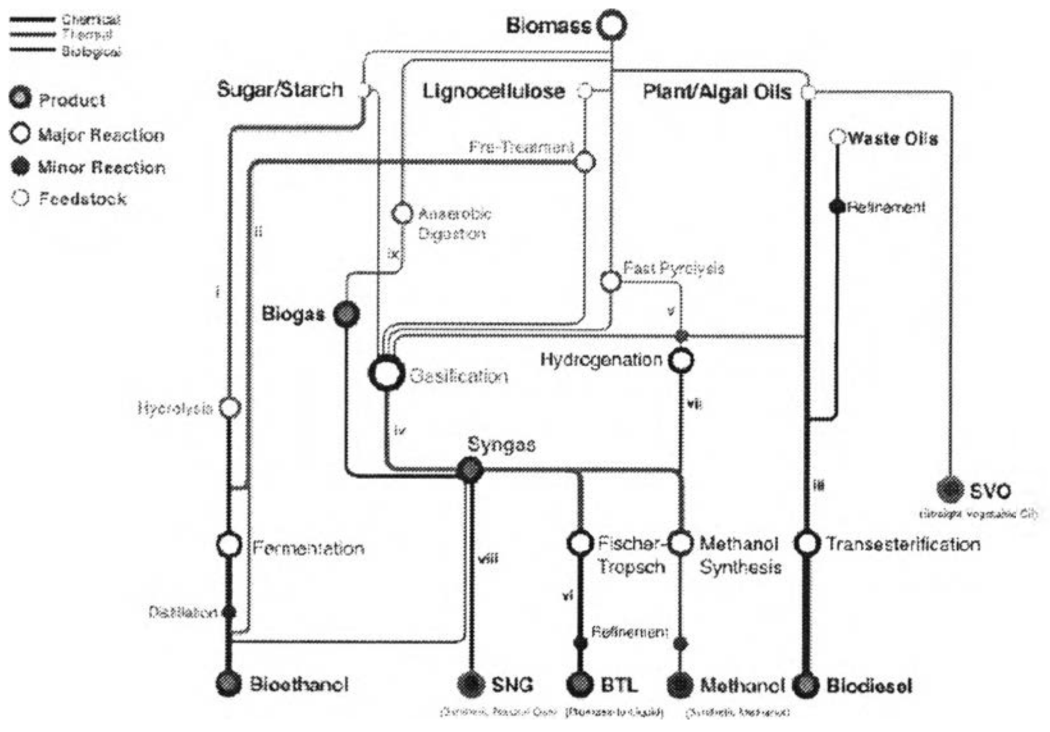


Figure 2.3 The multiple synthetic conversion routes of major biofuels produced from first and second-generation biomass feedstock (King et al., 2010).

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 H_2 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 (Corma 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, 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% (Van der 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 commuting 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).

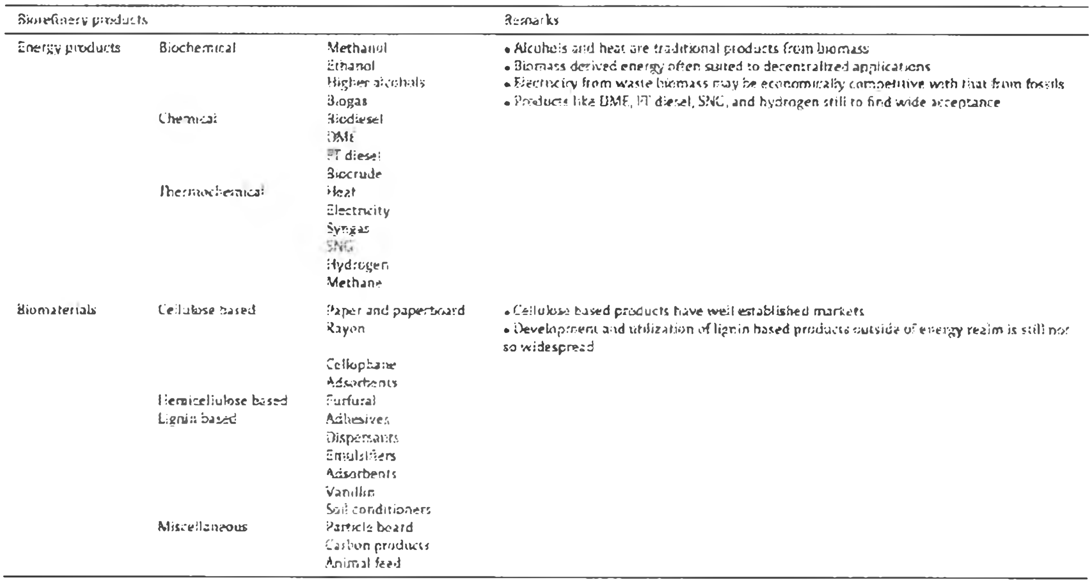
- Conversion of Syngas to Methane

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 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 H_2 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).

Table 2.1 Biorefinery products (Ghatak, 2011)



Biorefinery products			Remarks
Energy products	Biochemical	Methanol	• Alcohols and heat are traditional products from biomass
		Ethanol	• Biomass derived energy often suited to decentralized applications
		Higher alcohols	• Electricity from waste biomass may be economically competitive with that from fossils
		Biogas	• Products like DME, FT diesel, SNG, and hydrogen still to find wide acceptance
	Chemical	Biodiesel	
		DME	
		FT diesel	
		Biocrude	
	Thermochemical	Heat	
		Electricity	
		Syngas	
		SNG	
		Hydrogen	
		Methane	
Biomaterials	Cellulose based	Paper and paperboard	• Cellulose based products have well established markets
		Rayon	• Development and utilization of lignin based products outside of energy realm is still not so widespread
		Cellophane	
		Adsorbents	
	Hemicellulose based	Furfural	
	Lignin based	Adhesives	
		Dispersants	
		Emulsifiers	
		Adsorbents	
		Vanillin	
		Soil conditioners	
	Miscellaneous	Particle board	
		Carbon products	
		Animal feed	

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. These crops can be used as biomass feedstocks for biorefinery. The biorefinery model under study use sugarcane and cassava as feedstocks.

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 and Gheewala, 2010). The annual average yield from 2006/07 to 2011/12 is shown in Table 2.2 (Bank of Thailand, 2012).

Table 2.2 Sugarcane productivity in Thailand

Year	Planting area (M ha)	Sugarcane product/Area (t/ha)	Sugarcane product (M t)
2006/07	1.00	63.80	63.80
2007/08	0.99	73.81	73.31
2008/09	1.03	64.63	66.46
2009/10	1.09	63.50	68.48
2010/11	1.30	73.38	95.36
2011/12	1.43	69.25	97.97

2.2.2 Cassava

The cassava plant is cultivated in most equatorial regions and is known by many names as shown in Table 2.3. 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 2.4.

Table 2.3 Various names of cassava in different region

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

Table 2.4 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 and Gheewala, 2010). In 2012, cassava yield is 24.78 million tons fresh roots.

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 2.5. 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 and Gheewala, 2010). 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 2.6 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. Schematic of the molasses based ethanol production from a biorefinery complex is shown in Figure 2.4. 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 2.7 shows ethanol plants which plan to produce in 2010-2011.

Table 2.5 Gasohol consumption in Thailand (including E10 octane 91, E10 octane 95, E20, and E85).

Year	Million Liter	Million Liter per Day	% Change of Consumption per Day
2004	59.5	0.16	
2005	690.23	1.89	1,081.25 %
2006	1,279.30	3.5	85.20 %
2007	1,762.76	4.83	38.00 %
2008	3,393.98	9.29	90.90 %
2009	4,456.44	12.21	31.43 %
2010	4,382.34	12.01	-1.64 %
Mar 11	1,112.56	12.51	4.16 %

(Source: http://www.dede.go.th)

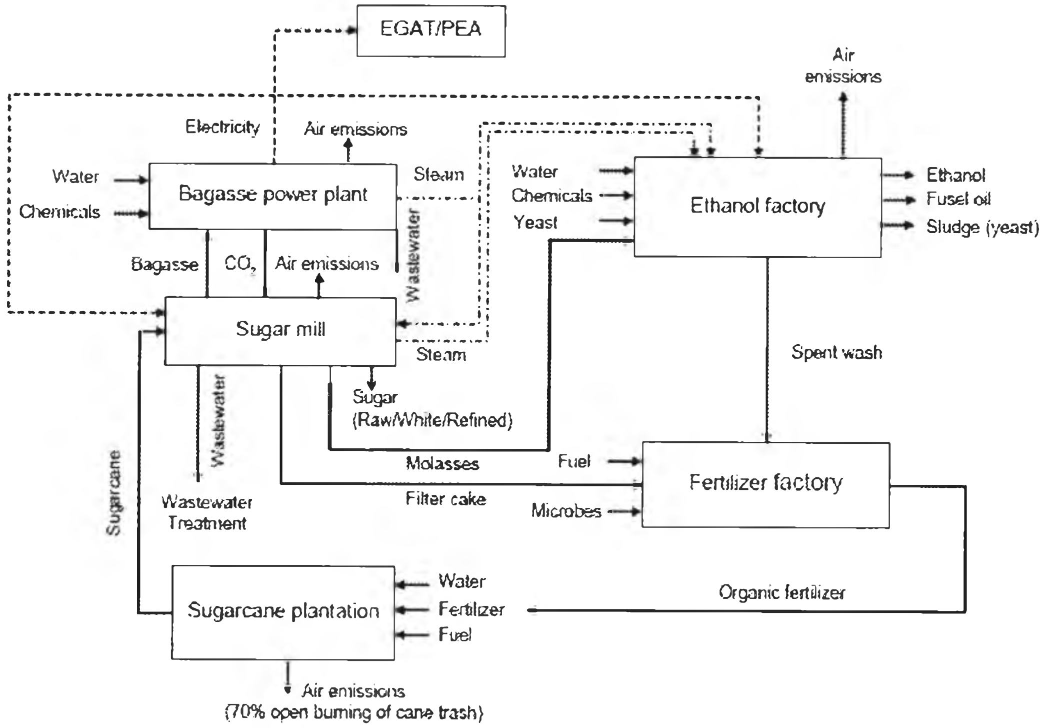


Figure 2.4 Schematic of the molasses based ethanol production from a biorefinery complex (Gheewala *et al.*, 2011).

Table 2.6 Current ethanol plants in Thailand

	Company's name	**Location**	**Raw material**	**Capacity (L/d)**
1	Pornwilai International Group Trading	Ayutthaya	Molasses Cassava root	25,000
2	Thai Agro Energy Co., Ltd.	Suphanburi	Molasses	150,000
3	Thai Alcohol Public Co., Ltd.	Nakhon Pathom	Molasses	200,000
4	Khonkaen Alcohol Co., Ltd.	Khonkaen	Molasses Starch	150,000
5	Thai Nguan Ethanol Co., Ltd.	Khonkaen	Cassava root Cassava chip	130,000
6	Thai Sugar Mill Co., Ltd.	Kanjanaburi	Molasses	100,000
7	KI Ethanol Co., Ltd.	Nakhon Ratchasima	Molasses	100,000
8	Petro Green Co., Ltd. (Kalasin)	Kalasin	Molasses Sugarcane	200,000
9	Petro Green Co., Ltd. (Chaiyaphum)	Chaiyaphum	Molasses Sugarcane	200,000
10	Eakaratpattana Co., Ltd.	Nakhon Sawan	Molasses	200,000
11	Thai Roong Ruang Sugar Group Co., Ltd.	Saraburi	Molasses Bagasse	120,000
12	Rachaburi Ethanol Co., Ltd.	Rachaburi	Cassava chip Molasses	150,000
13	ES Power Co., Ltd.	Sakaeo	Molasses Cassava chip	150,000
14	Mae Sod Clean Energy Co., Ltd.	Tak	Sugarcane	200,000
15	Sapthip Co., Ltd.	Lopburi	Cassava chip	200,000
16	Thi Phing Ethanol	Sakaeo	Cassava root Cassava chip	150,000
17	PSC Starch Production	Chonburi	Cassava root Cassava chip	150,000
18	Petro Green Co., Ltd. (Danchang)	Suphanburi	Molasses Sugarcane	200,000
19	Khonkaen Alcohol Co., Ltd. (Bo-Ploy)	Kanjanaburi	Molasses Sugarcane	150,000

(Source: http://www.dede.go.th)

Table 2.7 Ethanol plants which plan to produce in 2010-2011

	Company's name	**Location**	**Raw material**	**Capacity (liter/day)**
1	TPK Ethanol Co., Ltd. (Phase 1)	Nakhon Ratchasima	Cassava chip	340,000
	TPK Ethanol Co., Ltd. (Phase 2,3)	Nakhon Ratchasima	Cassava chip	680,000
2	Double A Ethanol Co., Ltd.	Prajeenburi	Starch	250,000
3	Sima Inter Product Co., Ltd.	Cha Choeng Sao	Cassava root	150,000
4	Impress Technology Co., Ltd.	Cha Choeng Sao	Cassava root	200,000

(Source: http://www.dede.go.th)

2.3.1 Sugarcane based Ethanol Production

As sugarcane based ethanol plant is not exist in Thailand, Sugarcane ethanol conversion data from Brazil (Ometto et al., 2010) was studied. A simple process diagram is shown in Figure 2.5

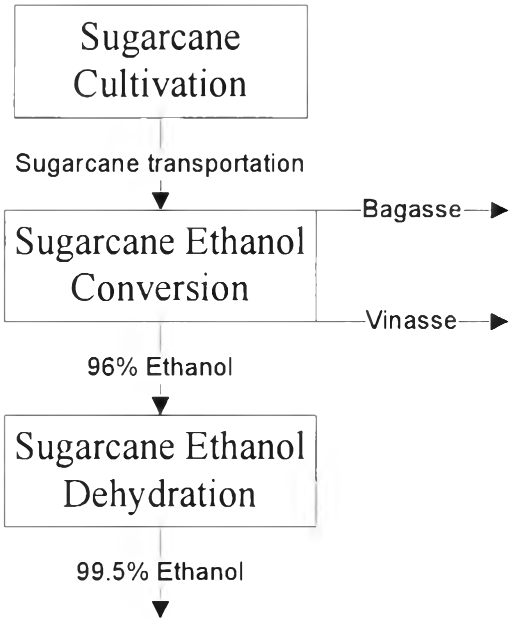


Figure 2.5 A simple process diagram of sugarcane based ethanol production.

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 2.6 (Nguyen and Gheewala, 2008).

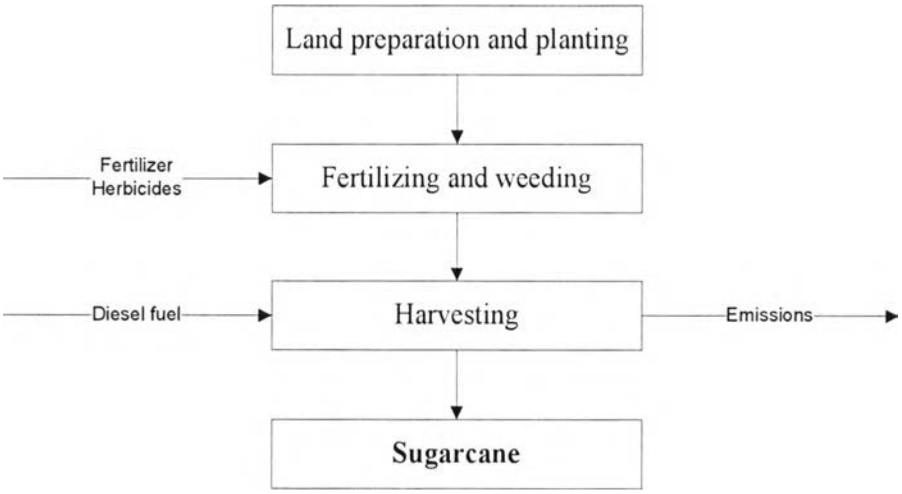


Figure 2.6 Process procedure of sugarcane cultivation.

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 sacharose ($C_{12}H_{22}O_{11}$) 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 2.7. This model has bagasse and biogas which are fuel to produce steam and electricity.

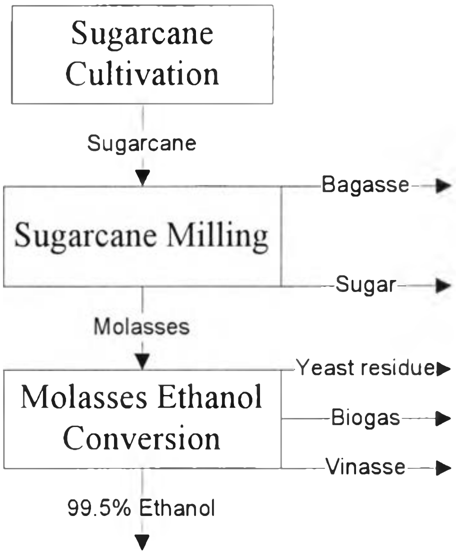


Figure 2.7 A simple process diagram of molasses based ethanol production.

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 2.8 (MTEC, 2008).

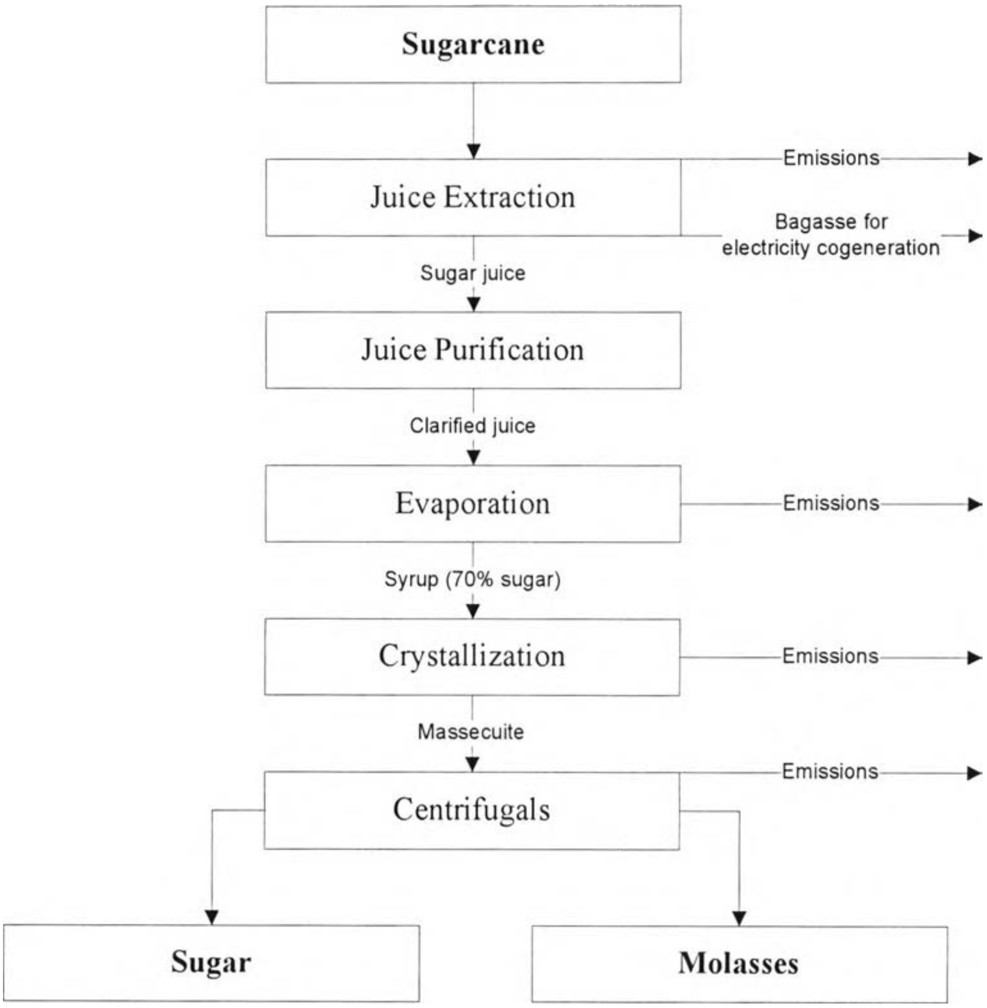


Figure 2.8 Process procedure of sugar milling.

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.

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) Centrifugals: 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 2.8, 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 industrials 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 and Tia, 2008). Moreover, according to Department of Industrial Promotion, Ministry of Industry (2009), biogas 1 m^3 can produce electricity 1.2 kWh, CO_2 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 2.9 (KAPI, 2008).

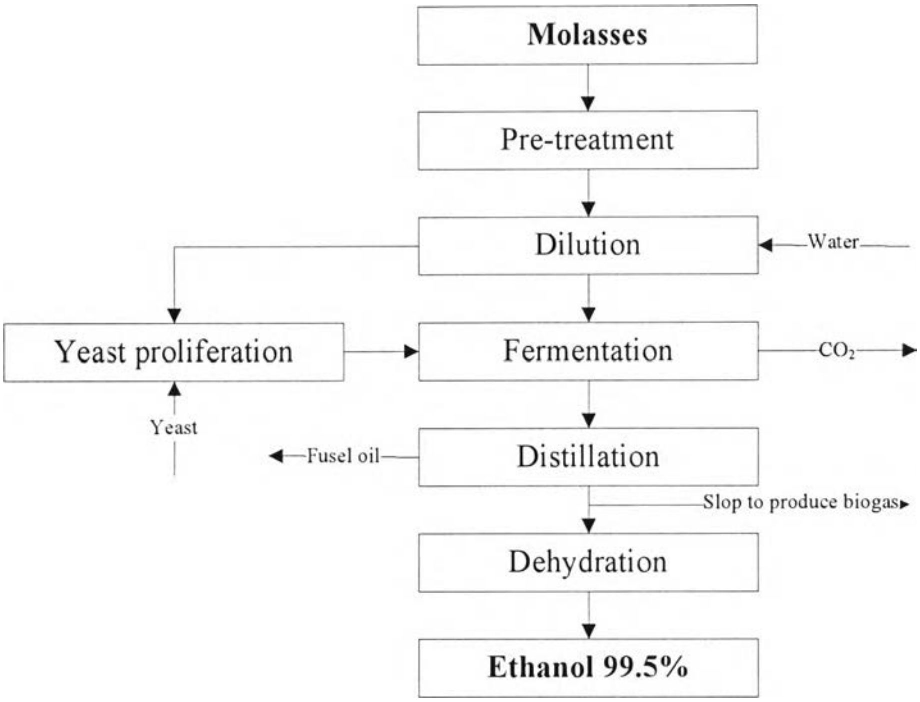


Figure 2.9 Flow chart for molasses ethanol conversion process.

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 2.10, 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.

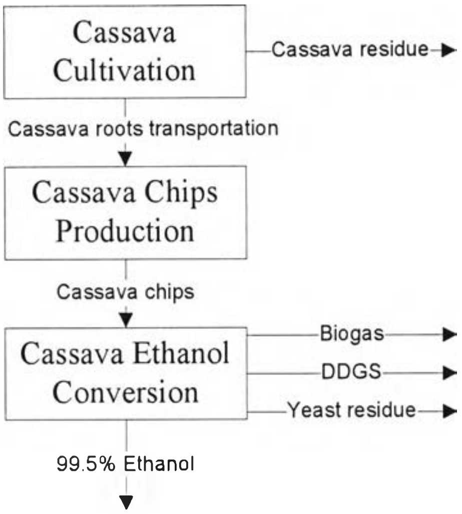


Figure 2.10 A simple process diagram of cassva based ethanol production.

2.3.3.1 Cassava Cultivation

The cassava production can be illustrated as shown in Figure 2.11. 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.

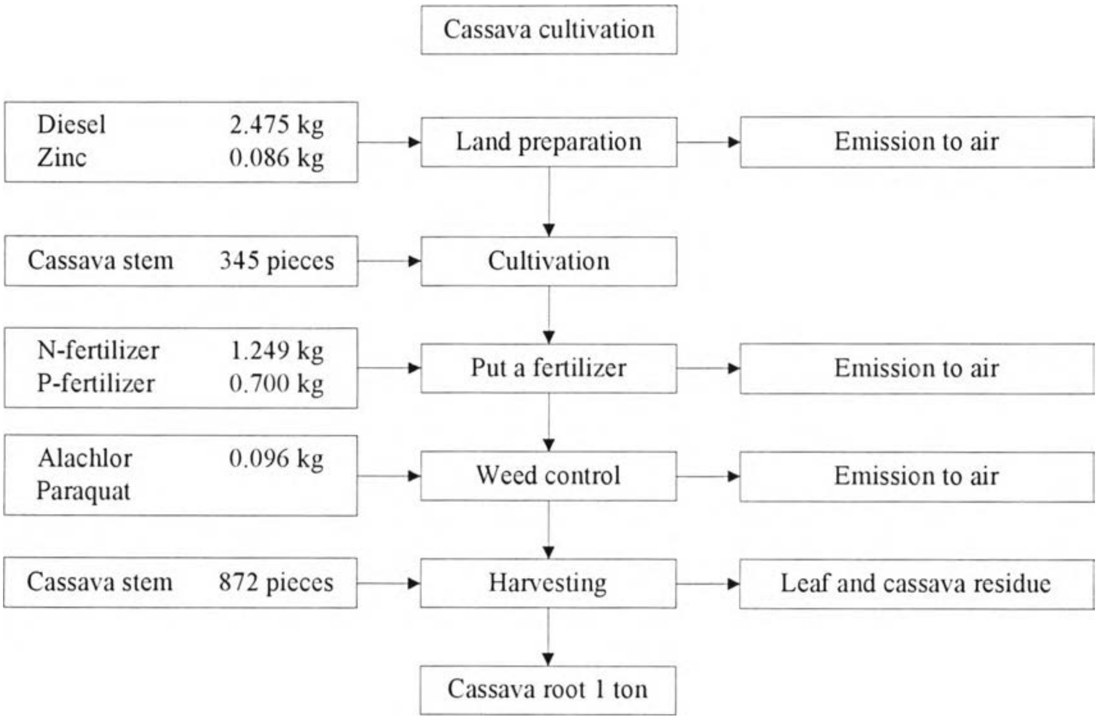


Figure 2.11 The process procedure of cassava cultivation in rainy season with water (Khongsiri, 2009).

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 2.12. Biogas is a by-product that used as fuel for electricity generation (KAPI, 2008). 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 and Gheewala, 2011).

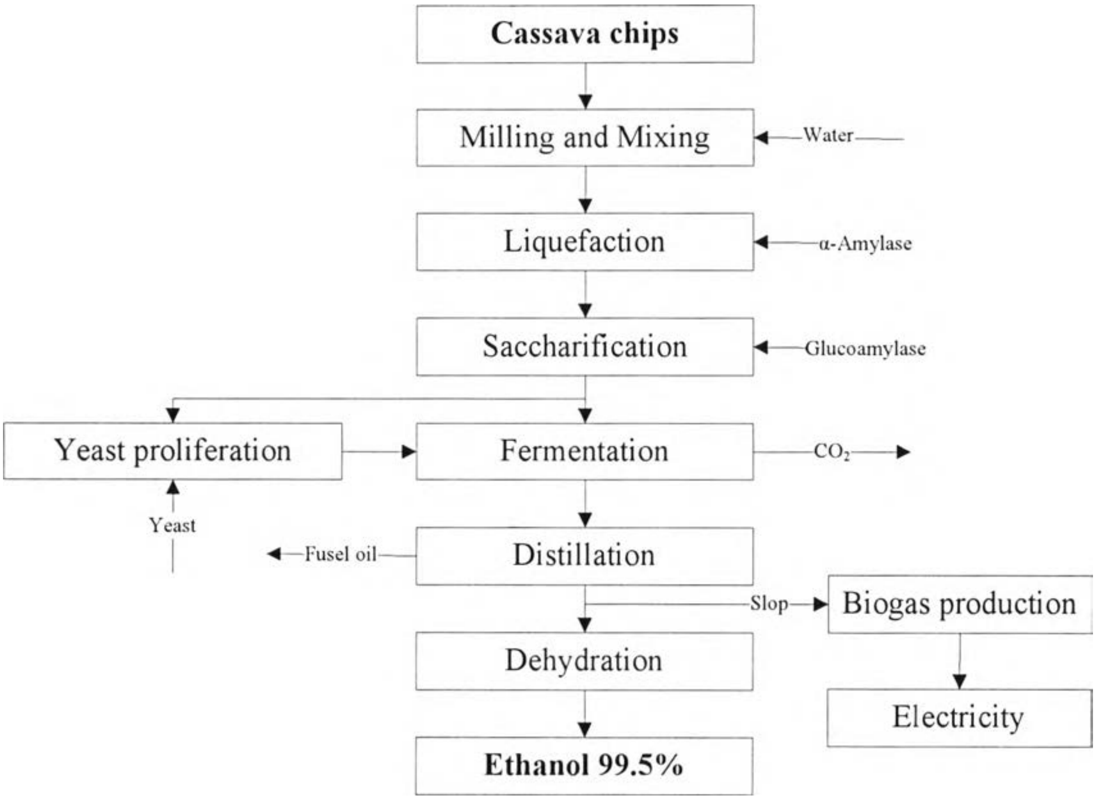


Figure 2.12 Flow chart for cassava ethanol conversion process.

2.4 Current Status of Polylactic acid (PLA) Productions and Uses in Thailand

Biopolymers are receiving much attention in the emerging topic of green chemistry since they can be made from renewable resources or will degrade easily later in nature or under industrial conditions. 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 will become 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. Lactic acid has a carboxylic and hydroxyl group and through esterification PLA, chains of lactic acid moieties, may be formed. In practice, PLA is normally made through ring opening polymerisation of lactide, a ring structure formed by selfesterification of two lactic acid molecules. The Schematic of the production chain from agriculture to PLA is illustrated in Figure 2.13 (Groot and Borén, 2010). However, Thailand lacks PLA production plant (PLA is polymerized from LA). This company has realized awareness of Thailand, especially our biomass resources (e.g., sugarcane and cassava). This includes NatureWorks Company which is interested to build PLA production plant in suitable area such as Thailand, Malaysia, and China. Thailand also has policy to expand bioplastic market in Japan which is the major importer of plastic pellets and plastic products. Japan imports goods and plastic products from Thailand at the value of 513.07 million dollar (6.48 percent) so it is possible to expand market to Japan. Thailand has to accelerate the development of bioplastic industry to reach the needs of customers, both domestic and international, and to have measures and policies of environmental management to support the use of products which are environmental friendly.

Since there are currently no bioplastics factories in Thailand, many companies have started importing bioplastics compounds to use the existing plastics processing machinery to produce finished bioplastics products as pilot production for both domestic and export markets. Moreover, some companies have started developing their business to produce bioplastics products as shown in Table 2.8.

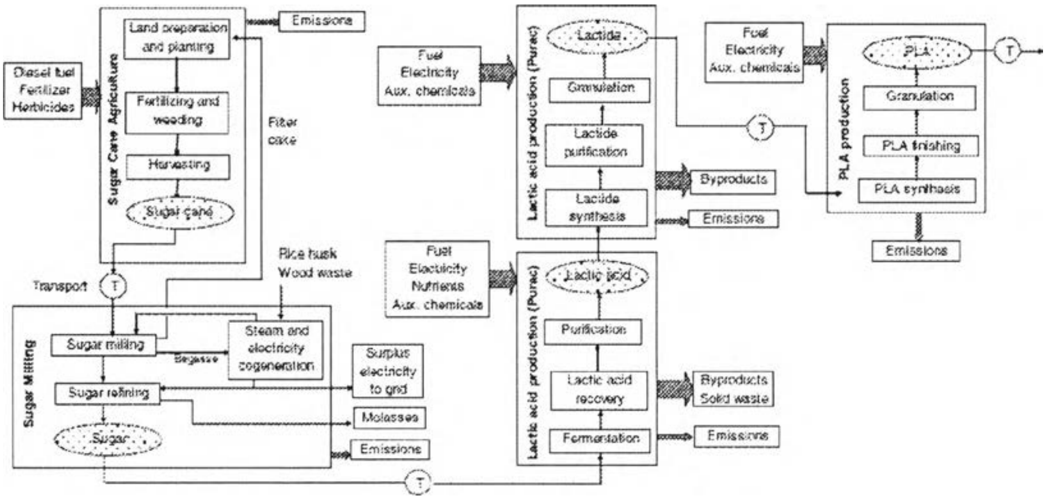


Figure 2.13 Schematic of the production chain from agriculture to PLA (Groot and Borén, 2010).

Table 2.8 Companies which doing business with biopolymers in Thailand

	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.

(Source: http://www.nia.or.th)

2.4.1 PLA Resin Production

A simple process diagram of sugarcane based PLA resin and cassava based PLA resin production is shown in Figure 2.14.

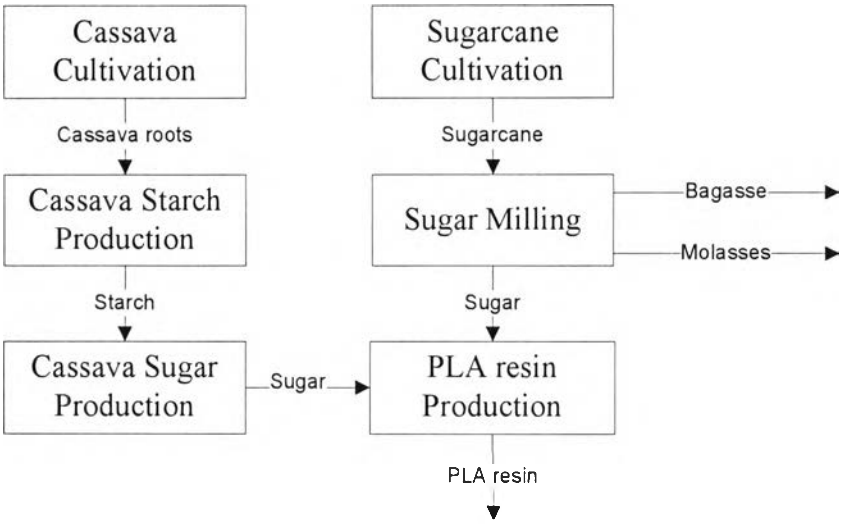


Figure 2.14 A simple process diagram of sugarcane based PLA resin and cassava based PLA resin production.

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.

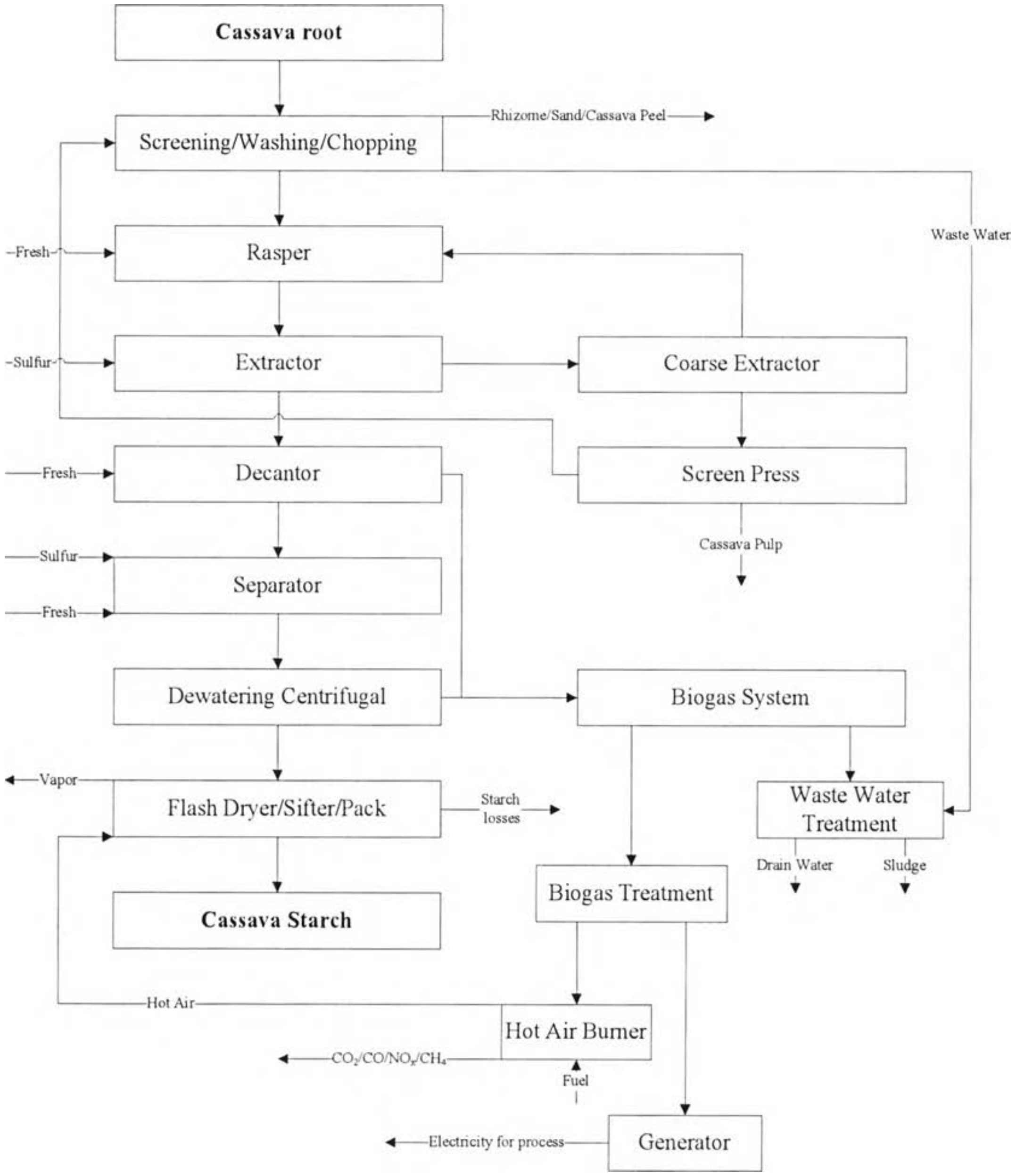


Figure 2.15 The process procedure of cassava starch production with biogas production line (Khongsiri, 2009).

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′ (Orathai and Maneerat, 2008). 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 2.15.

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 in 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, 2012).

- 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 a-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 2.16.

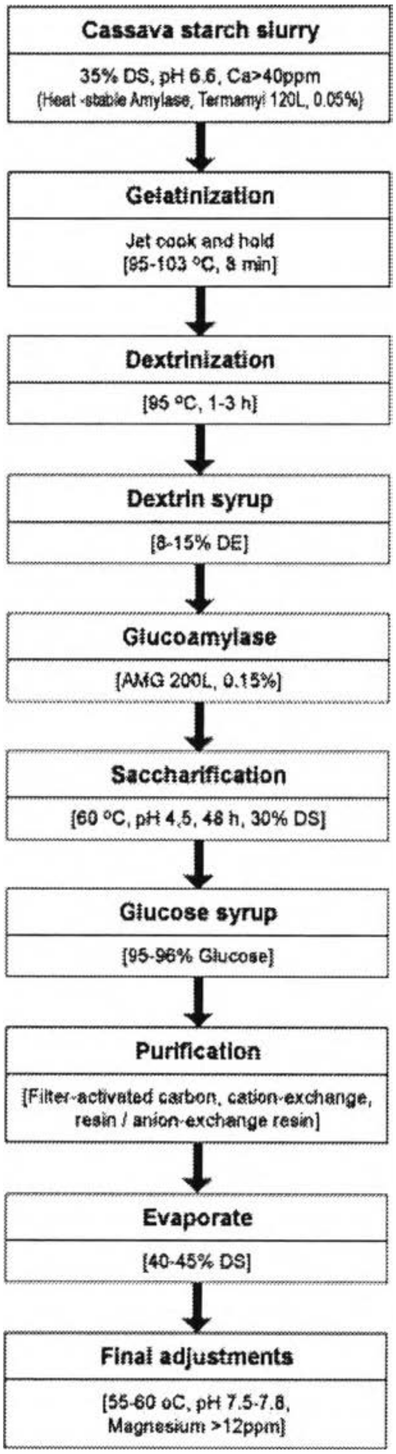


Figure 2.16 Flow chart for glucose syrup production from cassava (Source: http://www.cassavabiz.org/postharvest/gsyrup01.htm).

2.4.1.3 PLA Resin Production

The schematic of the PLA resin production is shown in Figure 2.17. 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 SuPLA and CaPLA because it might be risk for reaction of each other.

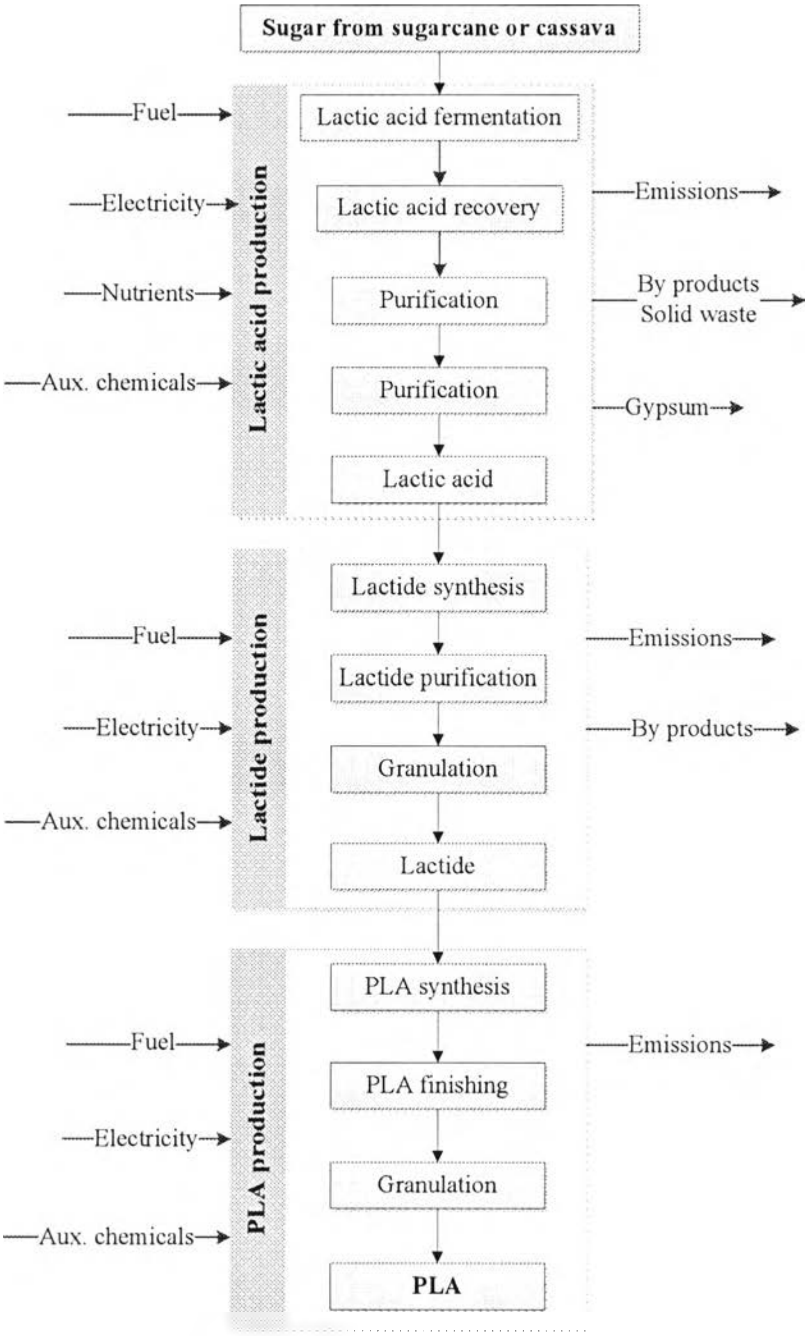


Figure 2.17 Schematic of the PLA resin production (Groot and Boren, 2010).

2.5 Life Cycle Assessment (LCA)

2.5.1 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, 2007).

2.5.2 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.

2.5.3 Methodology

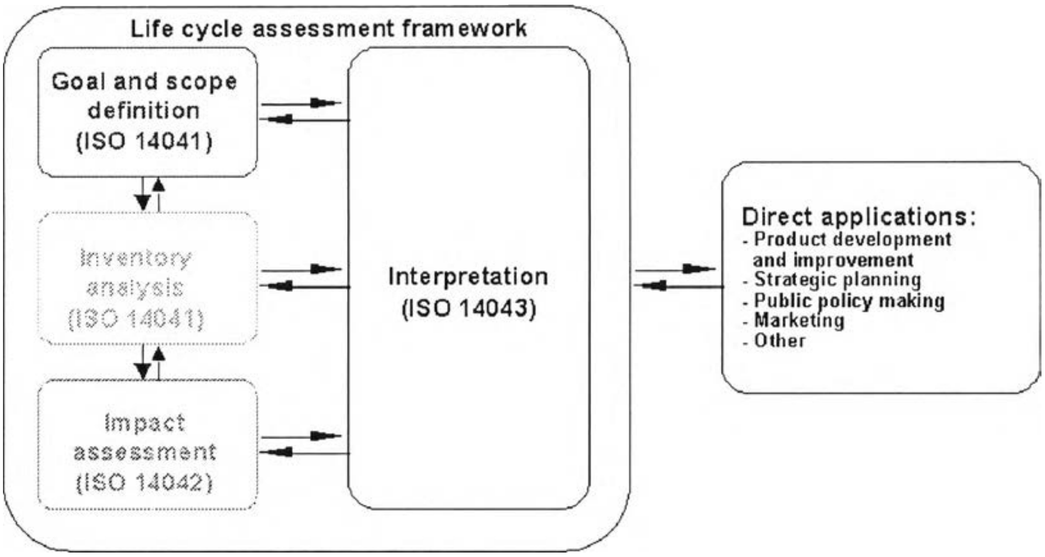


Figure 2.18 Life-cycle assessment framework as laid down in ISO 14040:1997 (Source: http://www.boustead-consulting.co.uk).

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 2.18.

2.5.3.1 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.

2.5.3.2 *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).

2.5.3.3 *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 than 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 rela-tive to the acidifying effect of SO2. Other known acidifying substances are nitrogen oxides (NOx), sulfuric acid (H2SO4), and hydrogen chloride (HCl).

- Eutrophication

Eutrophication is an increase in the concentration of chemical nutrients (nitrogen (N) and phosphorus (P)) in water bodies, often lead-ing to changes in animal and plant populations and degradation of water and habitat quality. The Nutriphication Potential (NP) is expressed as kg phosphate (PO4) equivalents. Other emissions also influence eutrophication, notably nitrogen oxides and ammonium.

2.5.3.4 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.

2.5.4 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 Millieukunde Leiden (CML) method (Cherubini and Jungmeier, 2009).

2.6 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.

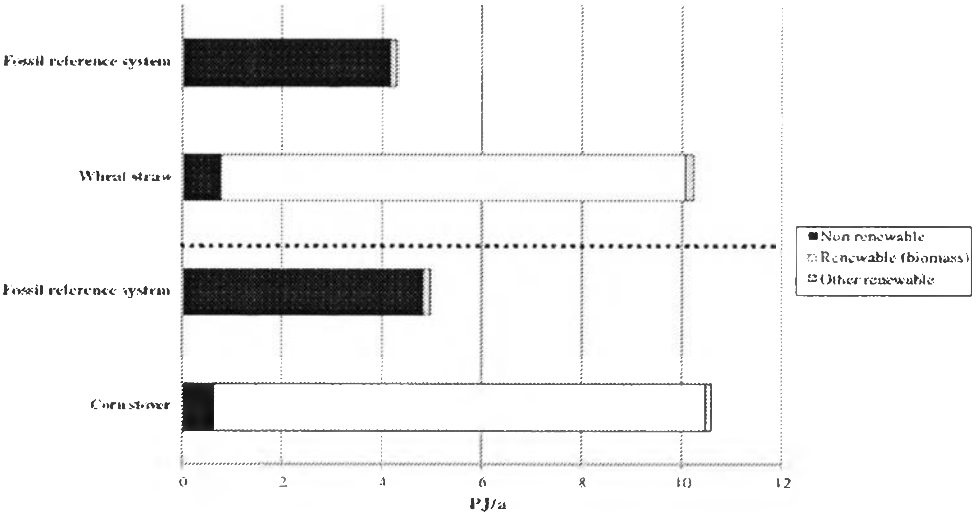


Figure 2.19 Cumulative primary energy demand of the biorefinery and fossil reference systems.

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 N_2O 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 2.19. Land use change effects have a strong influence in the final GHG balance (about 50%).

In 2011, Garcia and co worker proposed the life-cycle greenhouse gas emissions and energy balances of sugarcane ethanol production in Mexico. The purpose of their work was to estimate GHG emissions and energy balances for the future expansion of sugarcane ethanol fuel production in Mexico with one current and four possible future modalities.

- EMF – ethanol from ‘‘C’’ molasses using bagasse and fuel oil.
- EMBF – ethanol from ’’B’’ molasses using bagasse and fuel oil.
- EMB – ethanol from ‘‘C’’ molasses using bagasse.
- EDJ – ethanol from direct juice using bagasse and without surplus electricity.
- EDJE – ethanol from direct juice using bagasse and generating surplus electricity.

They used the life cycle methodology that is recommended by the European Renewable Energy Directive (RED), which distinguished the following five system phases: direct Land Use Change (LUC); crop production; biomass transport to industry; industrial processing; and ethanol transport to admixture plants. The industrial processes of ethanol production using sugarcane are shown in Figure 2.20.

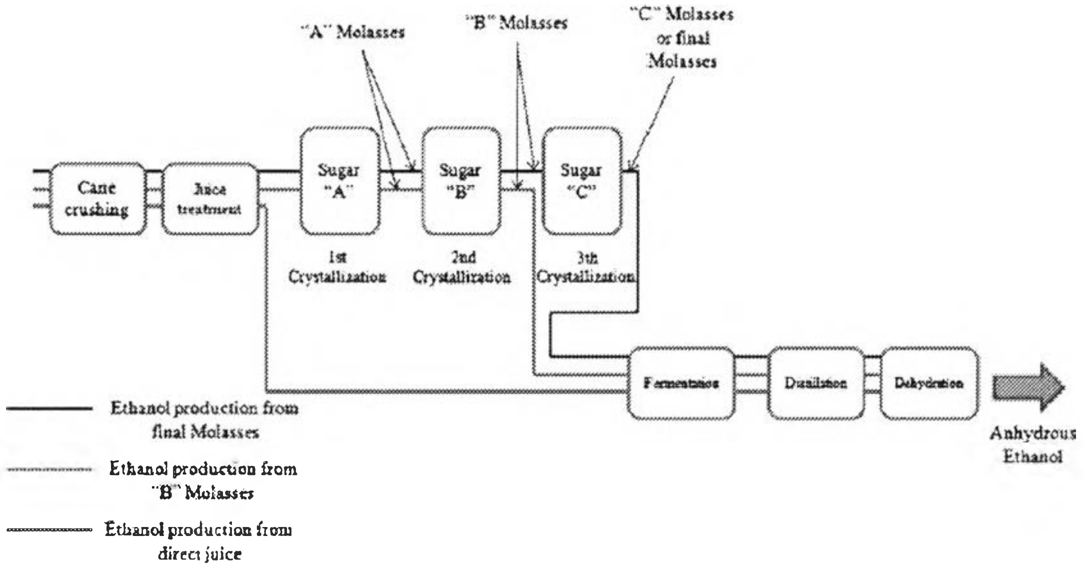


Figure 2.20 Industrial processes of ethanol production using sugarcane.

They discovered the key variables affecting total GHG emissions and fossil energy used in ethanol production were LUC emissions, crop fertilization rates, the proportion of sugarcane areas that are burned to facilitate harvest, fossil fuels used in the industrial phase, and the method for allocation of emissions to co-products. They also found that the lower emissions and higher energy ratios were observed in the present Brazilian case were mainly due to the lesser amount of fertilizers applied also were due to the shorter distance of sugarcane transport, and to the smaller proportion of sugarcane areas that were burned to facilitate manual harvest. In this studied, the resulting modality with the lowest emissions of equivalent carbon dioxide (CO_2e) was ethanol produced from direct juice and generating surplus electricity with 36.8 kg CO_2e/GJ ethanol as given in Figure 2.21. This was achieved using bagasse as the only fuel source to satisfy industrial phase needs for electricity and steam. Mexican emissions were higher than those calculated for Brazil (27.5 kg CO_2e/GJ ethanol) among all modalities. The Mexican modality with the highest ratio of renewable/fossil energy was also ethanol from sugarcane juice generating surplus electricity with 4.8 GJ ethanol/GJ fossils.

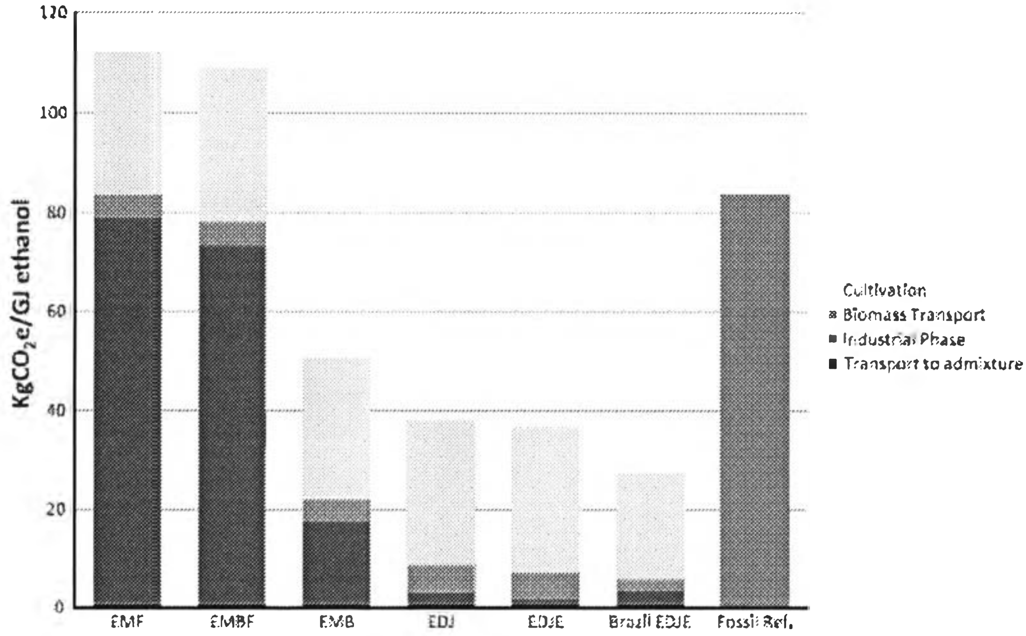


Figure 2.21 Green house gas emissions.

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 cm^3 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 LCIA 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 is given in Figure 2.22.

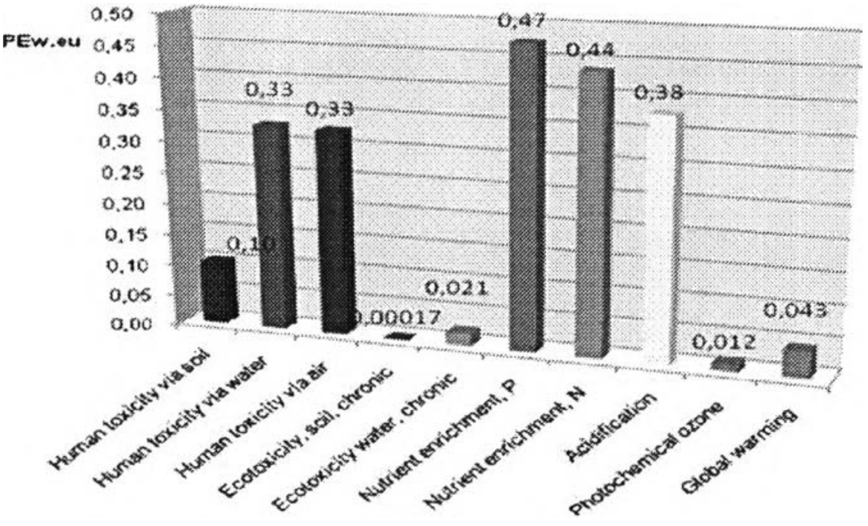
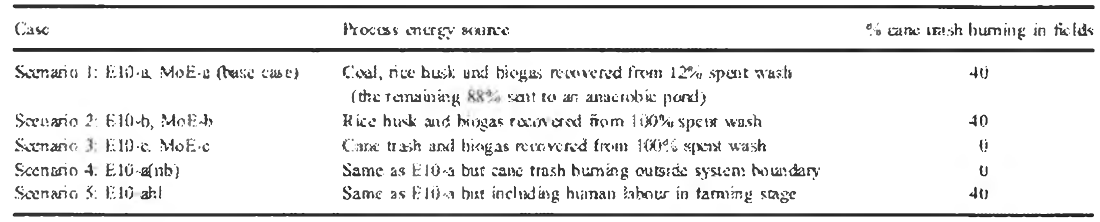


Figure 2.22 Normalized impact potentials for fuel ethanol lifecycle.

In 2008, Nguyen and Gheewala studied the life cycle assessment of fuel ethanol from cane molasses in Thailand. This study aims to evaluate the environmental impacts of substituting conventional gasoline (CG) with molasses-based gasohol in Thailand. The life cycle assessment (LCA) procedure carried out follows three interrelated phases: inventory analysis, characterization and interpretation. The functional unit for the comparison is 1 L gasoline equivalent consumed by a new passenger car to travel a specific distance. Ethanol is more environmentally friendly if less fossil fuel is consumed to produce it. Since sugar cane production is one unit process in molasses ethanol production cycle, cane trash burning essentially plays a role in the environmental performance of the fuel. Accordingly, four main scenarios concerned with process energy sources in ethanol conversion and cane trash burning have been examined as shown in Table 2.9.

Table 2.9 Scenarios of molasses-based ethanol case study



Case	Process energy source	% cane trash burning in fields
Scenario 1: E10-a, MoE-a (base case)	Coal, rice husk and biogas recovered from 12% spent wash (the remaining 88% sent to an anaerobic pond)	40
Scenario 2: E10-b, MoE-b	Rice husk and biogas recovered from 100% spent wash	40
Scenario 3: E10-c, MoE-c	Cane trash and biogas recovered from 100% spent wash	0
Scenario 4: E10-a(nb)	Same as E10-a but cane trash burning outside system boundary	0
Scenario 5: E10-ahl	Same as E10-a but including human labour in farming stage	40

The results of the study show that molasses-based ethanol (MoE) in the form of 10% blend with gasoline (E10), along its whole life cycle, consumes less fossil energy (5.3%), less petroleum (8.1%) and provides a similar impact on acidification compared to CG. The fuel, however, has inferior performance in other categories (e.g. global warming potential, nutrient enrichment and photochemical ozone creation potential) indicated by increased impacts over CG as seen in Figure 2.23.

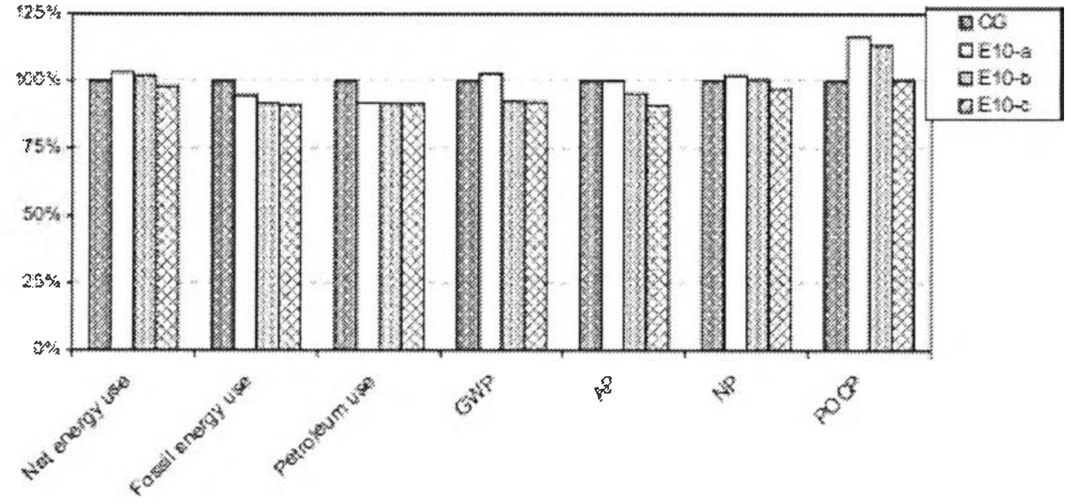


Figure 2.23 Comparison of life cycle energy and environmental performance of E10 and gasoline.

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 2.24.

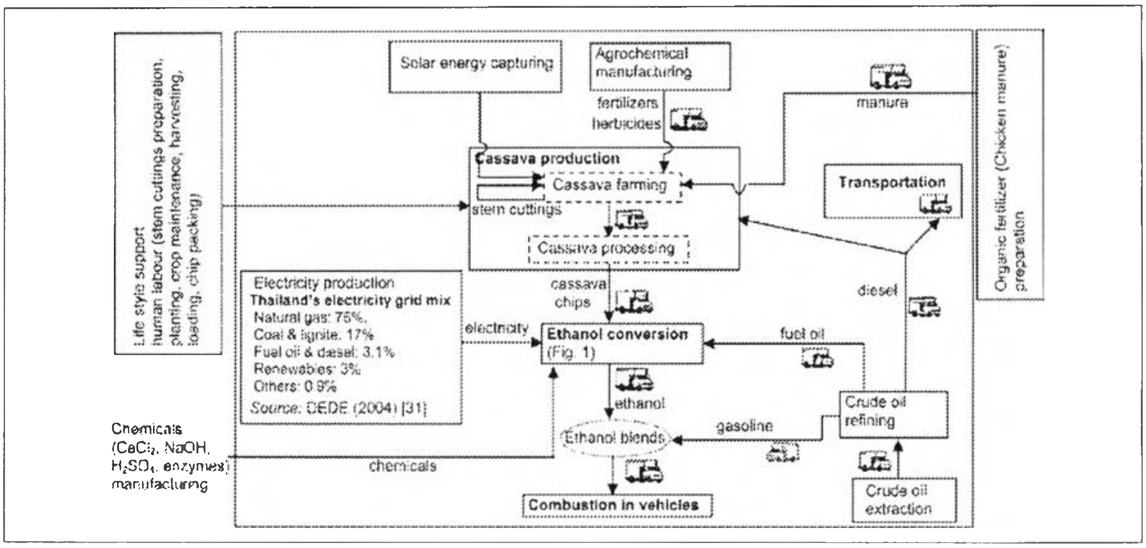


Figure 2.24 System boundary of the cassava-based E10/E85 fuel life cycle.

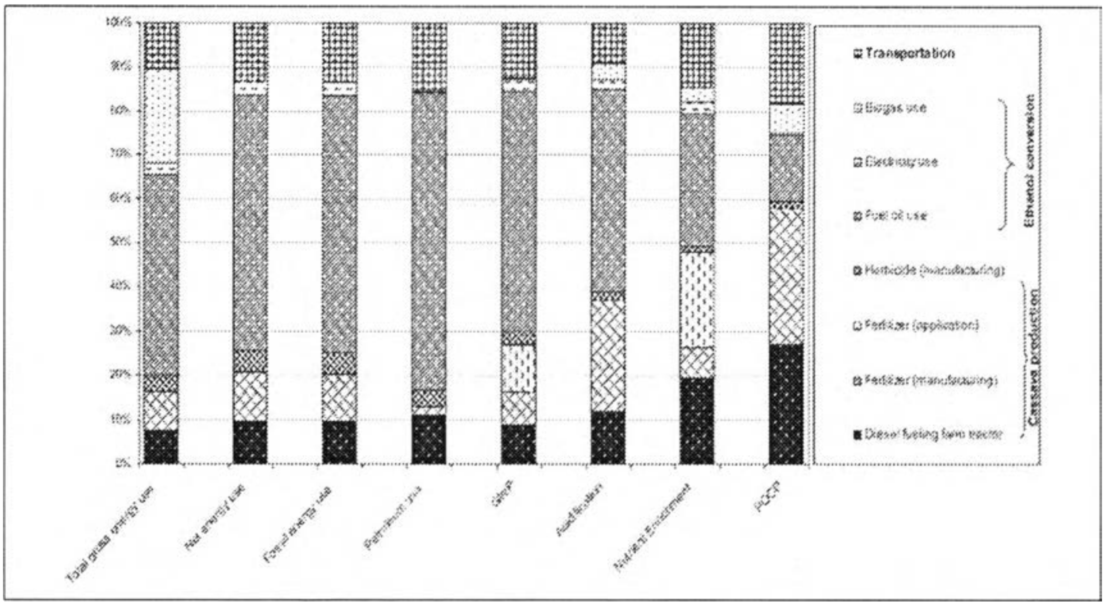


Figure 2.25 Characterization results – Contributions to the environmental impacts from ethanol production cycle.

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) 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 2.25.

In 2008, Noksa-nga and co worker investigated the comparison of life cycle assessment for cassava-based and molasses-based ethanol fuel production in Thailand. Their research aimed to compare the environmental impacts over the entire life cycle of bio-ethanol fuel produced from cassava and molasses. The inventory data collected at sites and factories included raw materials usage, energy consumptions and emissions covering from farming and harvesting, transportation, processing and conversion to bioethanol. The life cycle inventory (LCI) were compiled and analyzed for the life cycle impact assessment (LCIA) for one liter of 99.5% bio-ethanol using SimaPro 7.1 program with Eco-indicator 95 method. The relevant environmental impact categories of interest are global warming, acidification, eutrophication, smog formation and energy resource. The LCA results show that cassava-based ethanol has higher environmental impact than molasses-based ethanol in most categories, except euthrophication and acidification. Moreover, the greenhouse gas (GHG) balances also show that the cassava based ethanol has about 3 times higher global warming potential than molasses-based ethanol, as shown in Figure 2.26. They explained that the resulting mainly from the extensive use of fossil-based fuel (coal) in the conversion phase of the cassava-based ethanol production. On the other hand, the molasses-based system shows higher environmental impacts during farming and harvesting phase, particularly in GHG emission, which came from fertilizer application in sugarcane cultivation. Based on the results obtained in this study, it is shown that the molasses-based ethanol has a better environmental efficiency than cassava-based ethanol which results from an efficient renewable energy usage.

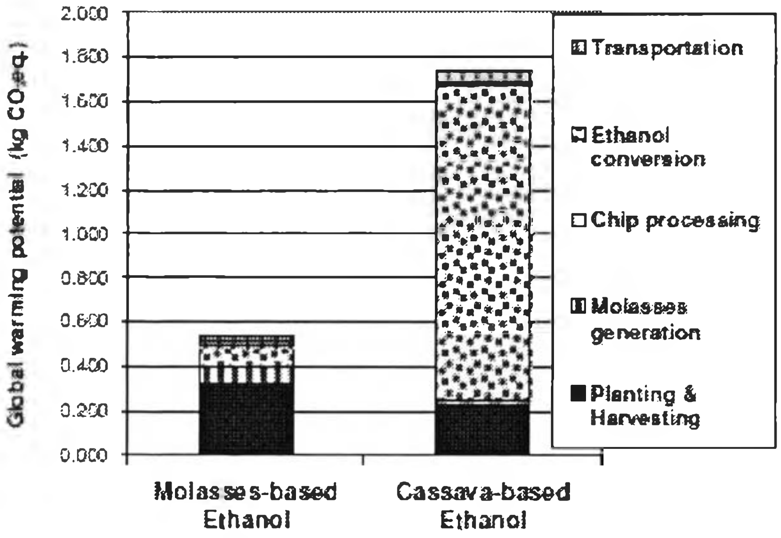


Figure 2.26 GWP of 1 liter anhydrous ethanol production.

In 2010, Groot and Borén studied the Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. The LCA of this paper was carried out for L-lactide, D-lactide, PLLA, and two PLLA/PDLA blends made from sugarcane in Thailand. They were compared with that of fossil-based polymers. The LCA complies with ISO standards, and is a cradle-to-gate analysis including sugarcane cultivation, sugarcane milling, auxiliary chemicals production, transport, and production of lactide and PLAs. Process data were taken from the designs of full-scale plants for the production of lactic acid, lactides, and PLA. The data were combined with eco-profiles of chemicals and utilities and recalculated to the following environmental impacts: primary renewable and non-renewable energy, non-renewable abiotic resource usage, farm land use, global warming, acidification, photochemical ozone creation, human toxicity, and eutrophication. A schematic of the production chain from agriculture to lactide and PLA is shown in Figure 2.27.

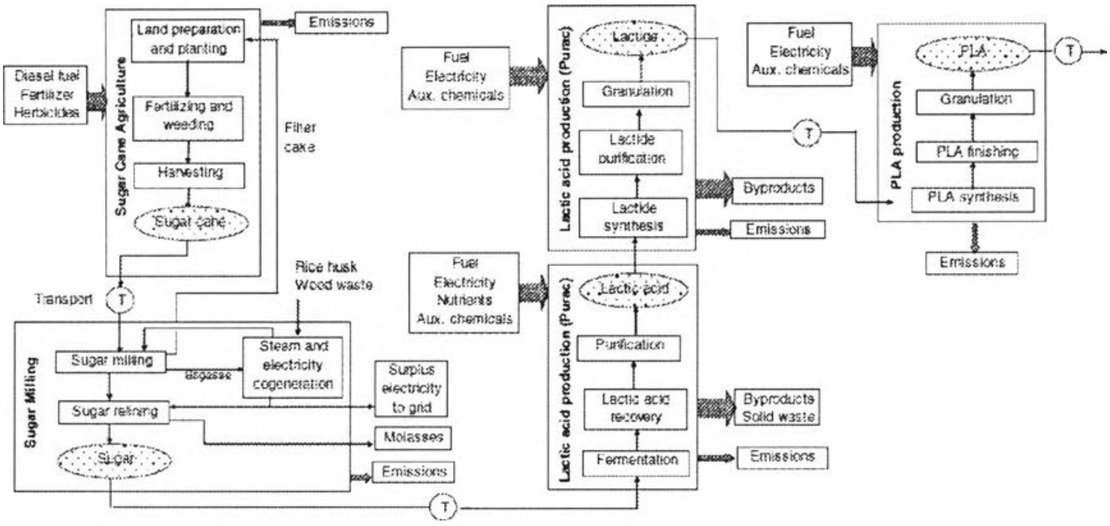


Figure 2.27 Schematic of the production chain from agriculture to PLA.

From their study, it was shown that on a weight-by-weight basis, PLLA results in significantly lower emissions of greenhouse gasses, and less use of material resources and nonrenewable energy, compared to fossil-based polymers. With the present calculations, the Global Warming Potential (GWP) in L-lactide production is 300–600 kg CO_2 eq./t and for PLLA 500–800 kg CO_2 eq./t. The range indicates the sensitivity of the GWP to the energy credit for electricity production from bagasse in the sugar mill. The GWP of PLLA/PDLA blends with increased heat resistance is also lower compared to fossil based polymers with similar durable character. Being based on an agricultural system the bio-based PLA gives rise to higher contributions to acidification, photochemical ozone creation, eutrophication, and farm land use compared to the fossil polymers. Figure 2.28 shows that the global warming potential of PLLA is much lower than for fossil based polymers, and this is one of the main drivers today for producing biopolymers.

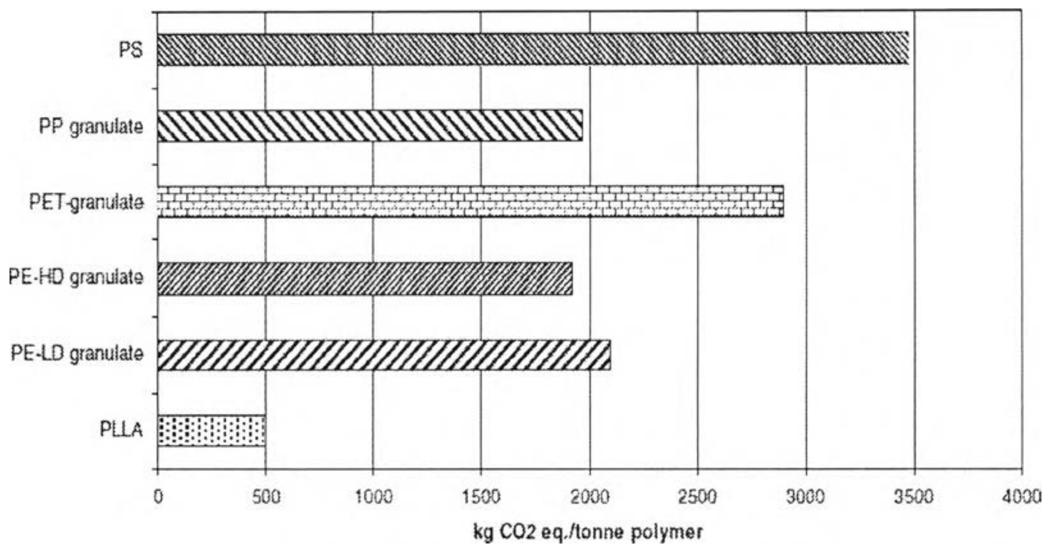


Figure 2.28 GWP involved with the production of PLLA and other polymers.

Another way of comparing the eco-profile of biopolymers and fossil-based polymers is to address the gross energy demands. The energy demand is the combination of the energy used in the process and the feedstock related energy; for PLA the feedstock is the sugar plant, and for fossil-based polymers it is oil. The feedstock-related energy represents the energy of fuel-type materials that are fed in the system, but used as carbon based building blocks rather than fuels. Figure 2.29 shows the comparison on the gross energy demand for PLLA and fossil-based polymers. A further division into renewable and non-renewable energy now splits the total into four parts.

- The feedstock related renewable energy. This number reflects the average energy content of the sugar substrate.
- The process related renewable energy. This number is high for PLLA as it represents the energy in the bagasse (excludes energy equivalents for coproduced power fed to the grid). For fossil-based polymers, this number is very small and represents, e.g., the use of wood in addition to natural gas or oil in national energy based economy.

- The process related non-renewable energy used to make the polymer (recovery of crude oil, transportation, refining for steam, and electricity production to make the polymer)
- The feedstock related non-renewable energy. This number is zero for biopolymers. In case of fossil based polymers, this number reflects the average energy content of the feedstock.

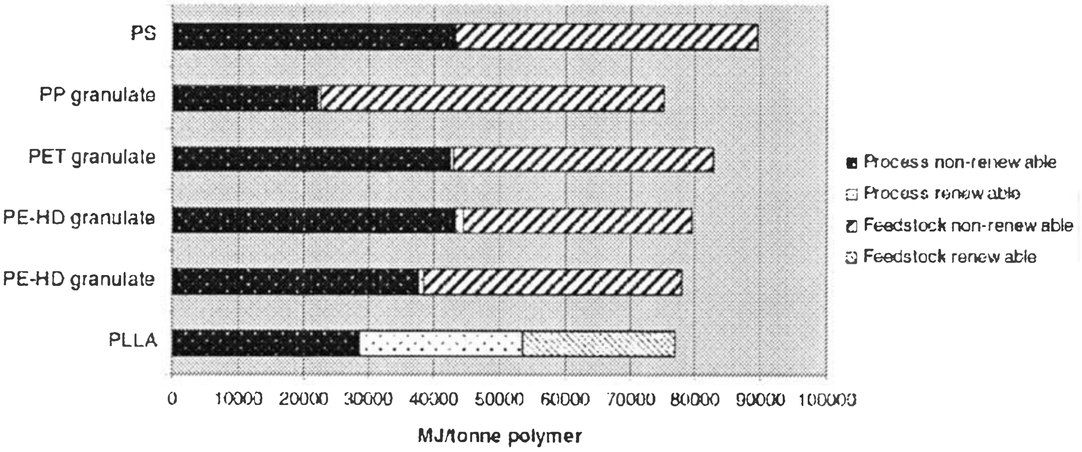


Figure 2.29 Primary energy demand involved with the production of PLLA and other polymers.

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 implement in December 2008. Further, the use of Renewable Energy Certificate was no longer included in the reported eco-profile. 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. Figures 2.30 and 2.31 show non-renewable energy use and greenhouse gas emissions which are less than Ingeo since 2005 reported by Vink *et al.* (2010). They also illustrate Ingeo target in the near-future of both energy use and greenhouse gas emission.

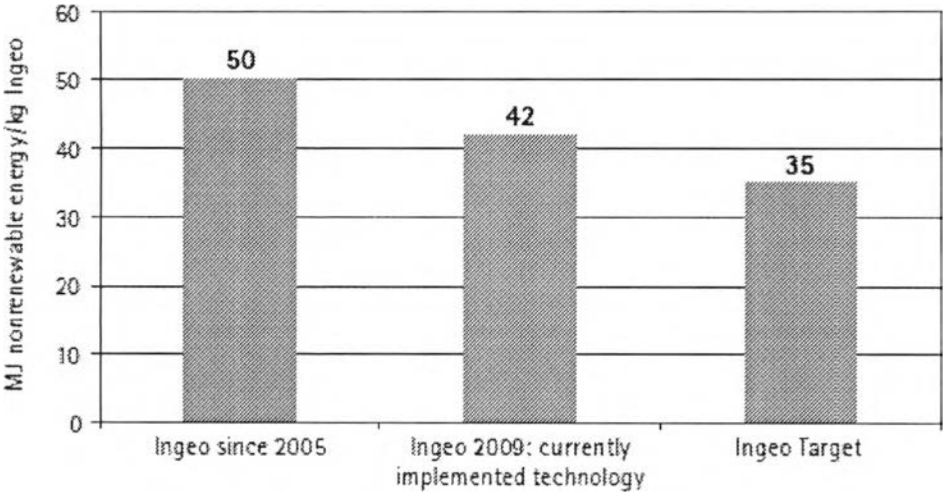


Figure 2.30 Cradle to polymer factory gate nonrenewable energy use for the various Ingeo production systems.

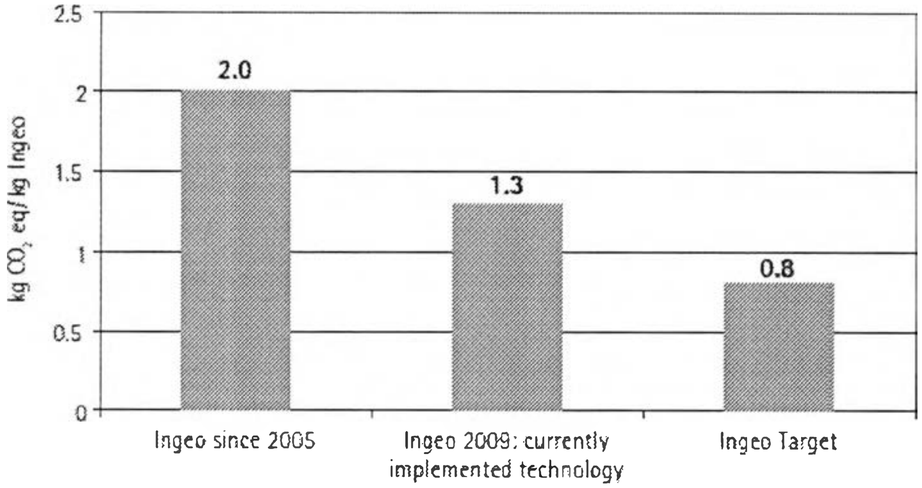


Figure 2.31 Cradle to polymer factory gate greenhouse gas emissions for the various Ingeo production systems.

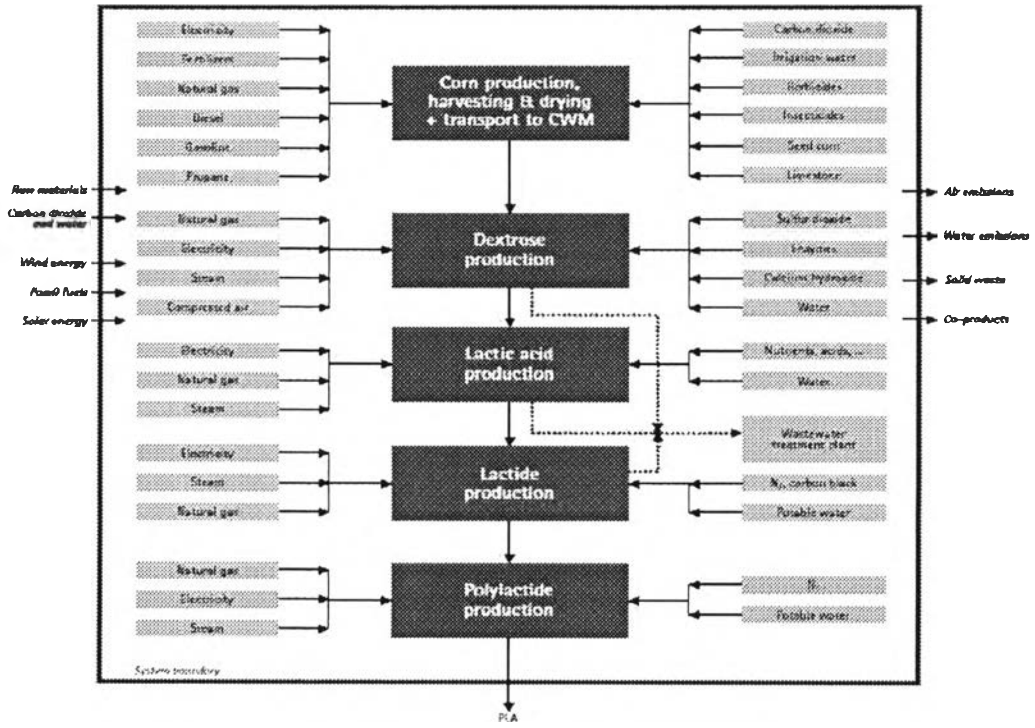


Figure 2.32 Simplified flow diagram and system boundary for the NatureWorks PLA production system.

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). Figure 2.32 shows the simplified flow diagram and system boundary for NatureWorks PLA production system. The cradle–to–factory–gate PLA production system is divided into five major steps:

- 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

From their study, it was shown that PLA production in 2006 emitted 0.27 kg CO_2 eq./kg PLA, 7.7 g NO_x/kg PLA, 2.5 g SO_x/kg PLA, and used 27.2 MJ/kg PLA of fossil energy.

Applications of life cycle assessment to NatureWorks^{TM} polylactide (PLA) production by Vink *et al.* (2002). They explained the role of life cycle assessment (LCA), a tool used for measuring environmental sustainability and identifying environmental performance-improvement objectives. This paper gives an overview of applications of LCA to PLA production and provides insight into how they are utilized. The first application reviews the contributions to the gross fossil energy requirement for PLA (54 MJ/kg). In the second one PLA is compared with petrochemical-based polymers using fossil energy use, global warming and water use as the three impact indicators as shown in Figure 2.33, 2.34, and 2.35, respectively.

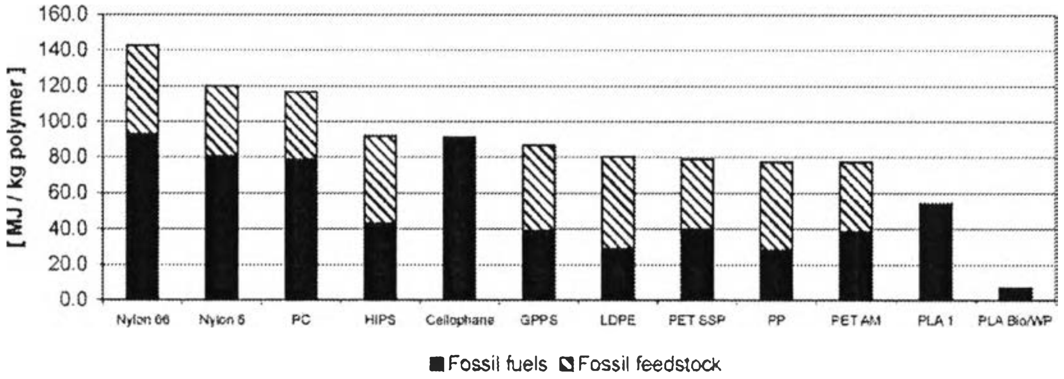


Figure 2.33 Fossil energy requirement for some petroleum based polymers and polylactide.

The last application gives more details about the potential reductions in energy use and greenhouse gasses. Cargill Dow's 5 – 8 year objective is to decrease the fossil energy use from 54 MJ/kg PLA down to about 7 MJ/kg PLA. The objective for greenhouse gasses is a reduction from +1.8 down to -1.7 kg CO_2 equivalents/kg PLA. Polymers from renewable resources can be significantly lower in greenhouse gas emissions and fossil energy use today as compared with conventional petrochemical-based polymers. Over the longer term, LCA demonstrates that PLA production processes can become both fossil-energy free and a source of carbon credits. This bright future will come only with significant investment of time, effort and money. A final, important benefit of LCA is that it can serve as a tool for monitoring return on these investments over time.

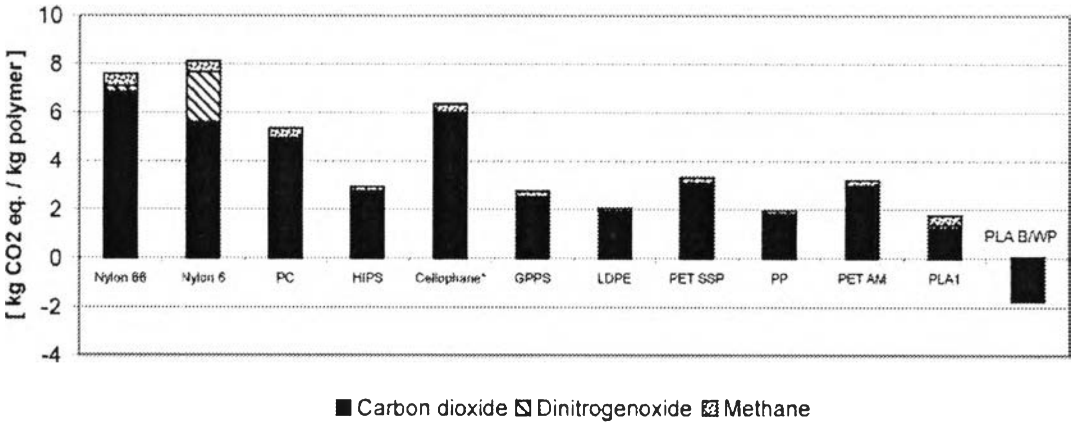


Figure 2.34 Contributions to global climate change for some petrochemical polymers and the two polylactide polymers.

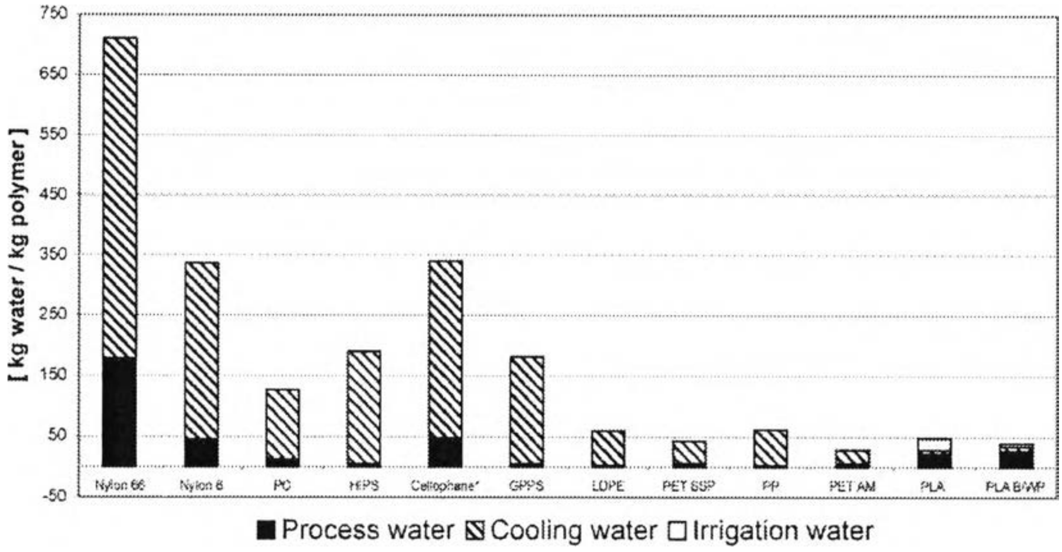


Figure 2.35 Gross water use by petrochemical polymers and the two PLA cases.

In 2008, Leng *et al.* investigated the entire life cycle of cassava-based ethanol fuel from cassava plantation, ethanol conversion, transport, fuel ethanol blending and distribution to its end use. Product system of cassava-based ethanol fuel is described and it is divided into six unit processes. The functional unit of their system is to produce 100,000 ton ethanol and cassava dry chip conversion rate of fresh cassava: 3:1. Figure 2.36 shows the unit process of cassava cultivation and treatment.

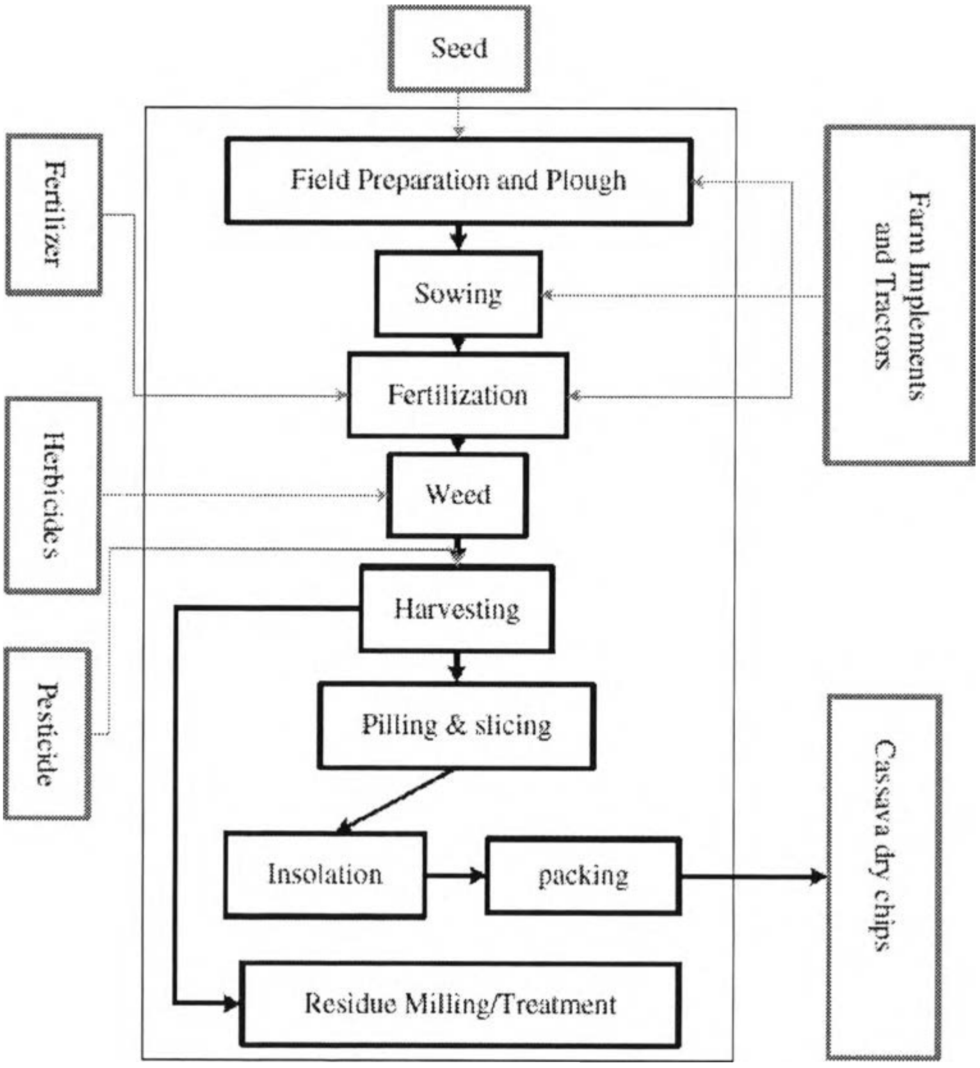


Figure 2.36 Unit of cassava cultivation and treatment.

This study also showed emission for cassava cultivation and treatment (g/ton chips) as shown in Table 2.10.

Table 2.10 Emission for cassava cultivation and treatment (g/t chips)

	Item	VOC	CO	NO_x	PM_{10}	SO_x	CH_4	N_2O	CO_2	Solid
1	Chemical production	16	102	277	25	252	363	3	201,082	/
1.1	N	3	32	45	4	38	128	1	52,399	/
1.2	P_2O_5	3	22	83	7	93	76	0	50,573	/
1.3	K_2O	2	5	19	2	19	17	0	11,250	/
1.4	Multiple nutrient	2	13	27	2	27	50	0	23,860	/
1.5	Herbicide	6	32	102	9	75	91	1	63,000	/
2	Cassava plantation	40	144	440	24	29	58	200	−188.614[a]	/
3	Transport	0	0	2	0	0	1	0	357	/
3.1	Chemical transport	0	0	1	0	0	0	0	170	/
3.2	Stem transport	0	0	0	0	0	0	0	26	/
3.3	Fresh cassava transport	0	0	0	0	0	0	0	80	/
3.4	Haulm	0	0	0	0	0	0	0	81	/
4	Haulm burning	/	180,000	363,000	/	/	15,000	21,000	/	/
5	Cassava pre-treatment	0	0	0	0	0	0	0	97	5
	Total	56	180,246	363,717	49	281	15.421	21,203	12.565	5

[a] CO_2 is taken out of the atmosphere during growth of the cassava.