CHAPTER II
LITERATURE REVIEW

2.1 Biofuel

Environmental concerns may help make biomass an economically competitive fuel. Because biomass fuels are generally less dense, lower in energy content, and more difficult to handle than fossil fuels, they usually do not compare favorably to fossil fuels on an economic basis. However, biomass fuels have several important environmental advantages. Biomass fuels are renewable, and sustainable use is greenhouse gas neutral (biomass combustion releases no more carbon dioxide than absorbed during the plant's growth). Biomass fuels contain little sulfur compared to coal (reduced sulfur dioxide emissions) and have lower combustion temperatures (reduced nitrogen oxide emissions). However, unless biomass is efficiently and cleanly converted to a secondary energy form, the environmental benefits are only partially realized, if at all. For this reason, efficient, modern biomass utilization must be favored over traditional applications (NEPO, 2000).

2.1.1 Definition

Fuel produced from renewable biomass material, commonly used as an alternative, cleaner fuel source (http://www.clean-energy-ideas.com).

2.1.2 Uses of Biofuel

National biofuel target of Thailand will increase renewable energy use from 0.5 % in 2002 to 8.0 % in 2011 which consists of 1 % of power generation, 4 % of heat process and 3 % of biofuel in transportation. Biofuels currently in use are:

- Bioethanol
- Biobutanol
- Biodiesel
- Biogas
- Vegetable Oil

From the biofuels listed above, this work focuses on bioethanol.

Ethanol or ethyl alcohol (C_2H_5OH) is a clear colorless liquid, biodegradable, low in toxicity and causes little environmental pollution if spilt. Ethanol burns to produce carbon dioxide and water. Ethanol is a high octane fuel and has replaced lead as an octane enhancer in petrol. By blending ethanol with gasoline we can also oxygenate the fuel mixture so it burns more completely and reduces polluting emissions. Ethanol fuel blends are widely sold in the United States. The most common blend is 10 % ethanol and 90 % petrol (E10). Vehicle engines require no modifications to run on E10 and vehicle warranties are unaffected also. Only flexible fuel vehicles can run on up to 85 % ethanol and 15 % petrol blends (E85).

Bioethanol fuel is mainly produced from sugar fermentation process by yeast showing the chemical equation below. Although, it can also be manufactured by the chemical process of reacting ethylene with steam (http://www.strath.ac.uk). The reaction is shown in Equation 1 below:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2 \qquad (1)$$

A) Raw Material

Bioethanol can be produced from many sources including sugar substances (such as sugarcane juice and molasses), starchy materials (such as wheat, corn barley, potato and cassava), and lignocellulosic materials (such as forest residuals, straws and other agricultural by-products). The dominating sugars available or produced from these popular raw materials are:

- Glucose, fructose, and sucrose in sugar substances;
- Glucose in starchy materials;
- Glucose from cellulose and either mannose or xylose from hemicelluloses of lignocellulosic materials.

B) Process Overview

Some sugars can be converted directly to bioethanol, whereas starch and cellulose must first be hydrolyzed to sugar before conversion to bioethanol. Most of the polymeric raw materials are available at prices lower than refined sugars. However, transportation costs of the raw materials make it necessary to use locally available raw material.

The fermentation method generally uses three steps: (a) the formation of a solution of fermentable sugars (milling dry/wet); (b) the fermentation of these sugars to bioethanol (ethanol process); and (c) the separation and purification of the ethanol (product recovery), usually by distillation as shown in Figure 2.8.

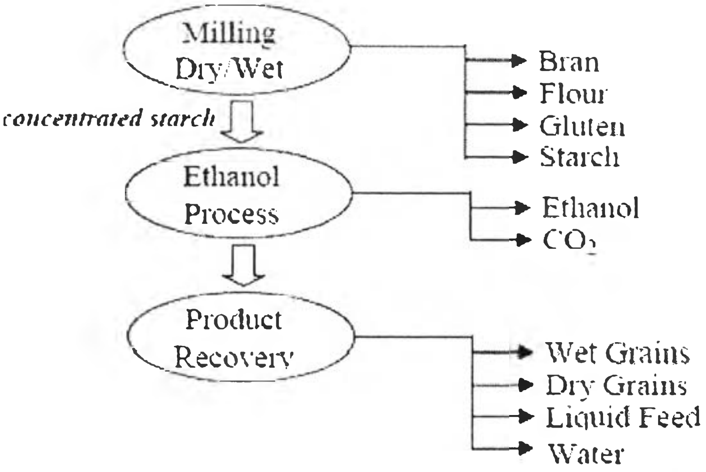

Figure 2.1 Overview of the Ethanol Production Process (CBIN, 2007).

C) Benefits of Using Ethanol

a) Ethanol is Good for The Environment

Overall, ethanol is considered to be better for the environment than gasoline. Ethanol-fueled vehicles produce lower carbon monoxide and carbon dioxide emissions, and the same or lower levels of hydrocarbon and oxides of nitrogen emissions. E85, a blend of 85 percent ethanol and 15 percent gasoline, also has fewer volatile components than gasoline, which means fewer emissions from evaporation. Adding ethanol to gasoline in lower percentages, such as 10 % ethanol and 90 % gasoline (E10), reduces carbon monoxide emissions from the gasoline and improves fuel octane.

b) Ethanol is Widely Available and Easy to Use

Flexible fuel vehicles that can use E85 are widely available and come in many different styles from most major auto manufacturers. E85 is also widely available at a growing number of stations throughout the United States. Flexible fuel vehicles have the advantage of being able to use E85, gasoline, or a combination of the two, giving drivers the flexibility to choose the fuel that is most readily available and best suited to their needs.

c) Ethanol is Good for The Economy

Ethanol production supports farmers and creates domestic jobs. And because ethanol is produced domestically, from domestically grown crops, it reduces U.S. dependence on foreign oil and increases the nation's energy independence (http://environment.about.com, 2010).

2.1.3 Gasohol in Thailand

2.1.3.1 Overview

According to previous data, this work focuses on bioethanol. So, this work interested in gasohol issue. Gasohol is a blending of gasoline and ethanol, which is a pure alcohol produced from domestic crops, such as cane, cassava and other grains for ex: sorghum, rice, corn, etc The government through an Energy Ministry has promoted an increasing use of gasohol by gasohol 95 lower than gasoline 95 price equal to 3.30 baht and gasohol 91 lower than gasoline 91 price equal to 2.80 baht. Gasohol types are presently available in gasohol 95 for gasoline 95 substitutions, and in gasohol 91 for replacing of gasoline 91.

Therefore, filling of gasohol can help to reduce the national fuel import and raise prices of agricultural crops. In addition, gasohol is clean energy, so exhaust pollution releases less than common gasoline. Therefore, using of gasohol is good for our own health and reduces environmental damage to the country. The most important is "we can produce your own using our local raw materials"

2.1.3.2 Background of Gasohol Usage in Thailand

Gasohol production in Thailand had originated by the Royal Project of King Bhumibol in 1985, in the Study Project on Gasohol Production for an Alternative Energy by producing ethanol from cane. Later on, awakening of promising ethanol occurred towards the public and private sectors to participate in development and tests with engines.

In 2000, PTT carried out the tests of using gasohol in cars and found that it helps reducing of pollution, saves energy and no effect to the car performance. Alcohol production from fresh cassava bulb has been conducted by

Science and Technology Research Institute of Thailand, which then would delivery to Bangchak Oil Refinery for gasohol production. An experiment for distribution in 2001 was for 5 BangChag gas stations in Bangkok Gasohol price was slightly lower than of the unleaded gasoline 95. thus getting satisfied achievement from the people acceptances.

2.1.3.3 Types of Gasohol

Currently, the Ministry of Energy allows producing gasohol in three types:

A) Gasohol E10

It is divided into two types—Gasohol octane 91 and Gasohol octane 95. The mixture of ethanol contain up 10 % and no less than 9–90 % of gasoline by volume. It can replace or switch to gasoline 95 and 91 normally, without engine modification.

B) Gasohol E20

It contains ethanol up to 20 % and not less than 19 % and 80 % gasoline by volume basis.

C) Gasohol E85

It contains ethanol 85 % gasoline and 15 % by volume based or ethanol, at least 75 %. (DEDE, 2010).

2.1.3.4 Gasohol Consumption in Thailand

The current blends of ethanol with gasoline in the Thai market are E10 (10 % ethanol with 90 % gasoline) in Octane 91 and Octane 95, E20 (20 % ethanol with 80 % of gasoline) in Octane 95, and E85 in Octane 95 (85 % of ethanol with 15 % of gasoline). Sales of gasohol in Thailand have been increasing continually since the start in 2004 (see Table 2.2). The most recent available data of gasohol sales in Thailand was for the month of January 2009 at 390.01 million liter or 12.581 million liter per day (as compared to the sales of gasohol in January 2008 at 220.84 million liters or 7.124 million liter per day).

Table 2.1 Gasohol sales in Thailand (including E10 octane 91, E10 octane 95, E20, and E85) (Bloyd, 2009)

	Million Liter	**Million Liter per Day**	**% Change of Sales per Day**
2004	59.50	0.16	
2005	690.23	1.89	(1081 %)
2006	1,279.30	3.50	(85.2 %)
2007	1,762.76	4.83	(38.0 %)
2008	3,391.73	9.221	(90.9 %)
January 2009	390.01	12.581	(36.4 %)

Production and sales of E10 increased drastically in 2008 as compared to 2007. The production of E20 began in 2007, and of E85 in 2008. (see Table 2.3).

Table 2.2 Production and Sales of Gasohol in 2007 and 2008 (http://www.doeb.go.th)

	Production		**Sales**	
	2007	**2008**	**2007**	**2008**
E10 octane 91	248.160	928.730	244.256	923.501
E10 octane 95	1,516.133	2,435.466	1,518.507	2,439.182
E20	0.047	29.395	–	29.028
E85	–	0.037	–	0.021
Total	1,764.34	3,393.628	1,762.763	3,391.732

2.1.3.5 Problems and Obstacles in Production and Distribution of Gasohol in Thailand

After several months of distribution, PTT and Bangchak Plc. Didthe survey on customer's opinion about gasohol usage. Price gap and trial and following the trend are two main reasons that customers use gasohol in their cars (Bhandhubanyong, 2010).

There are still several problems for the country-wide distribution of gasohol which are listed below:

- Customer's confident in the quality of gasohol. Although the government requested for the full cooperation from automobile manufacturers in Thailand, there is still no full guarantee issued from the company.
- Price differentiation. The price gap was set at 0.0125 c/l in the initial stage, then it was increased to 0.40 c/l in the beginning of 2005. The price gap can be wider with the secure supply of raw materials such as cassava and sugar cane.
- Instability in ethanol supply. The ethanol prices are still varied due to the raw materials price fluctuation. The RTG set the ceiling price for ethanol at 30 c/l which is enough for the initial stage. But as sugar cane, molasses, and cassava price increased due to the lack of supply the ethanol producers are requested for the upward adjustment of the ceiling price to 40c/l.
- Blending and distribution equipment are not ready for general gasoline distributors. This problem will be solved with the ban of MTBE in the year 2007.

2.2 Biomass-based Bioethanol

2.2.1 Biomass

2.2.1.1 What is Biomass?

Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material.

2.2.1.2 The Difference between Biomass and Fossil Fuels

The vital difference between biomass and fossil fuels is one of time scale. Biomass takes carbon out of the atmosphere while it is growing, and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. This is either during woodland or arboricultural management or coppicing or as part of a continuous program of replanting with the new growth taking up CO_2 from the atmosphere at the same time as it is released by combustion of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels.

2.2.1 3 Categories of Biomass Materials

Within this definition, biomass for energy can include a wide range of materials. The realities of the economics mean that high value material for which there is an alternative market, such as good quality, large timber, are very unlikely to become available for energy applications. However there are huge resources of residues, co-products and waste that exist in the UK which could potentially become available, in quantity, at relatively low cost, or even negative cost where there is currently a requirement to pay for disposal.

There are five basic categories of material:

- *Virgin wood*: from forestry, arboricultural activities or from wood processing
- *Energy crops*: high yield crops grown specifically for energy applications
- *Agricultural residues*: residues from agriculture harvesting or processing
- *Food waste*: from food and drink manufacture, preparation and processing, and post-consumer waste
- *Industrial waste and co-products*: from manufacturing and industrial processes(www.biomassenergycentre.org.uk).

2.2.2 Outlook of Raw Materials for Ethanol Industry in Thailand

Ethanol or ethyl alcohol, capable of being blended with gasoline to produce an alternative fuel namely gasohol, can be produced from diversified carbohydrate-containing materials. Those important ones are agricultural materials and industrial wastes such as crop biomass, sawdust and agricultural residues. In Thailand, the main economic crops potentially being used as the raw material for ethanol production are sugar cane and cassava.

2.2.2.1 Sugar Cane

Sugar cane is one of the most predominant raw materials for fuel ethanol production in the world. The cane juice contains sucrose, a fermentable sugar that can be directly fermented by yeast to produce ethanol. As a result, sugar crops are considered as the most promising feedstock for fuel ethanol production.

2.2.2.1.1 Current Production of Sugar Cane in Thailand

The annual productivity of sugar cane in Thailand is approximately 75 million tons (2004/2005). This crop is cultivated mainly in the northeastern and central parts of Thailand, which are mostly the nonirrigated area and less farm management. The crop is usually planted either before or after the rainy season and can be harvested around 10 to 12 months after cultivation. Therefore, the harvest season of sugar cane is typically short and lasts only 4 to 5 months each year (December to March).

2.2.2.1.2 Current Industrialization of Sugar Cane in Thailand

All sugar canes produced in Thailand are supplied to sugar factories. At present, the total production capacity of all 46 sugar factories in Thailand are more or less 75 million tons of cane. After harvested, the canes are directly supplied only to the factory with contract - farming. The trading of sugar cane is based on the CCS (Commercial Cane Sugar calculated from Pol, Brix and Fiber in cane) value and the profit sharing between the factory and farmers are regulated by law, i.e. The Sugar and Cane Act. Currently, the total sugar production is about 7.3 million tons (including Refined, White and Raw sugar) with the domestic consumption of only 2.0 million tons.

2.2.2.2 Molasses

In sugar industry, molasses, a by-product of sugar industry, is a potential raw material for ethanol production.

2.2.2.2.1 Current Production of Molasses in Thailand

With the total production of 75 million tons of cane per year, around 3.75 million tons of molasses are produced annually (accounting for 5% of sugar cane). The sugar content reported as total sugar (TS) in molasses from the sugar factories is around 50%. This can be a very good feedstock for yeast fermentation to produce ethanol.

2.2.2.2.2 Current Industrialization of Molasses in Thailand

Around 50 %of molasses are locally utilized in many industries including food, feed and distillery, and the rest are supplied to export market. This surplus portion to export market can be arranged for producing, daily, up to 1 million liters of ethanol for a year (a conversion ratio is 4 kg of molasses / 1 liter of ethanol). To produce ethanol by using molasses, this plant should be annexed to the sugar factory to share the same energy facilities to yield the lowest production cost.

2.2.2.3 Cassava

Cassava is a starch-accumulating crop, which is very well utilized in various industries producing starch and starch derivatives such as modified starch and sweeteners. To produce ethanol, starch is initially converted to fermentable sugars namely glucose by the enzyme or acid process. The sugars are then fermented to ethanol by yeast similar to fermentation of cane sugar.

2.2.2.3.1 Current Production of Cassava in Thailand

Cassava is able to grow with minimal inputs for a reasonable returning yield on infertile land where the cultivation of other crops is difficult unless considerable inputs are applied. Therefore, the planting area of cassava is maintained more or less 1.07 million hectare (6.7 million Rai). With the production efficiency around 19 tons of fresh root per hectare (3.0 ton per Rai), the annual root productivity is about 18 to 20 million ton fresh roots. Cassava is mainly cultivated in the northeastern and eastern parts of Thailand. The plants are typically cultivated before the rainy period and the roots can be harvested at 8 to 12 months after planting, depending on the root price. Given the significance to the productivity of this commercial crop, Thailand has developed and released new varieties of higher starch yield and also has an efficient extension service to ensure the dissemination of new varieties to entire farmers, in order to replace the traditional local variety. As a result of improved variety and production technology, the production efficiency of cassava roots targets to be increased (the root productivity of 3.7 ton per Rai or 23 ton per hectare).

2.2.2.3.2 Current Industrialization of Cassava Roots in Thailand

In general, cassava roots are mainly consumed by two major industries namely starch and chip/pellet industry. The starch industry typically requires 8 million tons of fresh roots (at 25% starch content) for a production of 2 million tons of starch. Another quantity of 8 million tons of fresh roots is processed to chips and pellets, mainly for export markets. The remainder of 4 million ton fresh roots has been then promoted for more domestic consumption such as feed industry. These surplus can be absorbed by the ethanol industry and is estimated to be sufficient to supply the ethanol production, at 85% production efficiency, of 2 million liters per day for a year (a conversion ratio is 6 kg of cassava roots at 25% starch content / 1 liter of ethanol). In order to effectively utilize for ethanol production, dried cassava chips are recommended as the most suitable raw material because of these following reasons:

(1) Chips can be produced by farmers during the peak of harvesting season (when root price is at the lowest).
(2) Chips can be stored and used when roots are not harvested.
(3) Chips can effectively transported to the ethanol plant.
(4) Chips can be used to produce ethanol by advance processes such as Simultaneous Saccharification and Fermentation (SSF) as used with grains to minimize production cost.

Thailand has confronted with the oil crisis as well as many parts in the world and is seeking for other challenging energy source. Ethanol, an environmentally friendly fuel, which can be produced from various renewable agricultural materials, can be a solution for an agricultural country as Thailand. (http://www.cassava.org)

2.2.3 Ethanol Production in Thailand

Thailand has continued to promote domestic biofuel utilization. Production and consumption of bioethanol in Thailand have continued to increase at a fast rate due to aggressive policies of the Thai government in reducing foreign oil import and increasing domestic renewable energy utilization.

As of June 2009, there are a total of fifteen commercial ethanol plants, with total installed capacity of 2.275 million liters per day (see Table 2.4). This is 0.7 million liters per day more than last reported in August 2008 as four more ethanol plants started their operation in 2009. Eight additional ethanol plants (mainly using cassava as a feedstock) are being constructed with an additional capacity of 3.42 million liters per day (see Table 2.5). As of April 2009, 47 more ethanol plants received construction permits with total production capacity of 12.295 million liters per day.

Table 2.3 Existing Ethanol Plants in Thailand (June 2009) (Bloyd, 2009)

Company	**Installed Capacity (L/day)**	**Feedstock**	**Province**	**Commencing Date**
1. Pornwilai International	25,000	Molasses	Ayuddhaya	Oct 03
2. Thai Alcohol	200,000	Molasses	Nakhon-Pathom	Aug 04
3. Thai Agro Energy	150.000	Molasses	Suphanburi	Jan 05
4. Thai Nguan Ethanol	130,000	Cassava	Khon Khan	Aug 05
5. Khon Khan Alcohol	150,000	Sugarcane /Molasses	Khon Khan	Jan 06
6. PetroGreen	200,000	Sugarcane /Molasses	Chaiyaphoom	Dec 06
7. Thai Sugar Ethanol	100,000	Sugarcane /Molasses	Kanchanaburi	Apr 07
8. KI Ethanol	100,000	Sugarcane /Molasses	Nakhon Ratchasima	Jun 07
9. PetroGreen	200,000	Sugarcane /Molasses	Kalaseen	Jan 08
10. Ekarat Pattana	200,000	Molasses	Nakhonsawan	Mar 08
11. Thai Rung Ruang Energy	120.000	Sugarcane /Molasses	Saraburi	Mar 08
12. Ratchaburi Ethanol	150,000	Cassava/ Molasses	Ratchaburi	Jan 09
13. ES Power	150,000	Molasses/ Cassava	Sakaew	Jan 09
14. Maesawd Clean Energy	200,000	Sugarcane	Tak	May 09
15. SupThip	200,000	Cassava	Lopburi	May 09
Total	2,275,000			

Table 2.4 Ethanol Plants under Construction (Bloyd, 2009)

Company	**Installed Capacity (L/day)**	**Feedstock**	**Province**	**Commencing Date**
1. TaiPing Ethanol	150,000	Fresh Cassava/(Cassava)	SaKaew	Jun-09
2. PSC Starch Production	150,000	Fresh Cassava/(Cassava)	Chonburi	Oct-09
3. PTK Ethanol-Phase 1 PTK Ethanol -Phase 2	340,000 680,000	Cassava Cassava	Nakorn Ratchasima	Jan-Mar 2010 Jun-Jul 2010
4. Petro Green (Suphanburi)	200,000	Molasses/(sugarcane juice)	Suphanburi	Dec-09
5. Double A Ethanol	500,000	Fresh Cassava/Cassava	Pracheenburi	Mar-10
6. Impress Technology	200,000	Fresh Cassava/(Cassava)	ChaShoeng-Sao	May-10
7. Sima Inter Products	150,000	Fresh Cassava/(Cassava)	ChaShoeng-Sao	To Be Operated next
8. BoonAnake	1,050,000	Fresh Cassava/(Cassava)	NakornRatchsima	To Be Operated next
Total Capacity	3,420,000			

The actual production of ethanol (January 2009) is at 1.33 million liters per day—an increase of 51 % over the average production of 0.88 million liter per day in 2008 (see Table 2.6). The Energy Ministry has targeted the use of ethanol at 9 million liters per day in 2023.

As seen in the Table 2.4, molasses is the main supply feeding ethanol plants in Thailand. So this work will use molasses as feed stock to observe in economic term which is minimizing waste and maximizing profit.

Table 2.5 Ethanol production in Thailand 2006–2009 (Bloyd, 2009)

	Million Liter	**Million Liter/Day**
2006	135.35	0.37
2007	191.75	0.53
2008	322.19	0.88
January 2009	41.30	1.33

2.2.4 Study on Biomass-based Ethanol Process

Morales *et al.* (2008) worked on using computer aided tools for sustainable design and analysis of bioethanol production by considering the production of 99.95 % pure ethanol from lignocellulosic materials where the hydrolytic enzyme is purchased. Hardwood chips were used as the feedstock and PRO/II simulator was used as simulation program. The base case process was based on NREL process (Wooley *et al.*, 1999). The main operations of the process are shown as PRO/II flowsheets in Figure 2.9. The process can be described as follow:

a) First the hardwood chips feedstock is delivered to feed handling area where it is treated for size reduction and storage.

b) Afterwards the biomass is conveyed to the pretreatment area of the process. At this point the feedstock is treated with high temperature dilute sulfuric acid for a short period of time, in order to liberate hemicellulose sugars and other compounds.

c) In the blowdown tank (or flash) several inhibitors are removed together with water. After the blowdown tank the process stream is separated in solid and liquid fraction so that the stream that is fed to the ion exchange does not have excess of insoluble solids that could affect its well functioning. Thus the liquid fraction is sent to the ion exchange, while the solid fraction is sent to the Simultaneous Saccharification & Co-Fermentator (SSCF).

d) The ion exchange, overliming and gypsum filter have the same purpose, which is to further remove inhibitors. This means compounds liberated in the pretreatment that are toxic to the fermentation microorganisms. In the pH adjustment step (overliming and gypsum filter), the pH is increased to appropriate levels for introducing in the SSCF by removing sulphuric acid.

e) The previously separated stream with the insoluble solids is then again mixed with the detoxified hydrolizate slurry and fed to the SSCF. In the SSCF fermentor, two different operations are occurring: saccharification of the remaining cellulose to glucose using the enzymes of cellulase, and also the fermentation of the resulting glucose and other sugars (from the dilute acid pretreatment of hemicellulose) to ethanol. The fermentation is carried out in a series of continuous anaerobic fermentation trains. The necessary organism for fermentation Zymomonas mobilis is grown in consecutively larger batch anaerobic fermentations. To the first fermentor is added the inoculum, together with the cellulase enzyme and other nutrients. Several days of saccharification and fermentation will follow so that almost all the cellulose and xylose are converted to ethanol, being the resulted beer sent to the product recovery and separation area. According to the NREL report, 7 % of the sugars available for fermentation are lost due to contamination reactions.

f) Product recovery consists of two consecutive distillation columns to distil the process stream until a mixture of nearly azeotropic water and ethanol is obtained. The ethanol mixture is then further purified using vapor-phase molecular sieves in order to obtain bioethanol within the specifications.

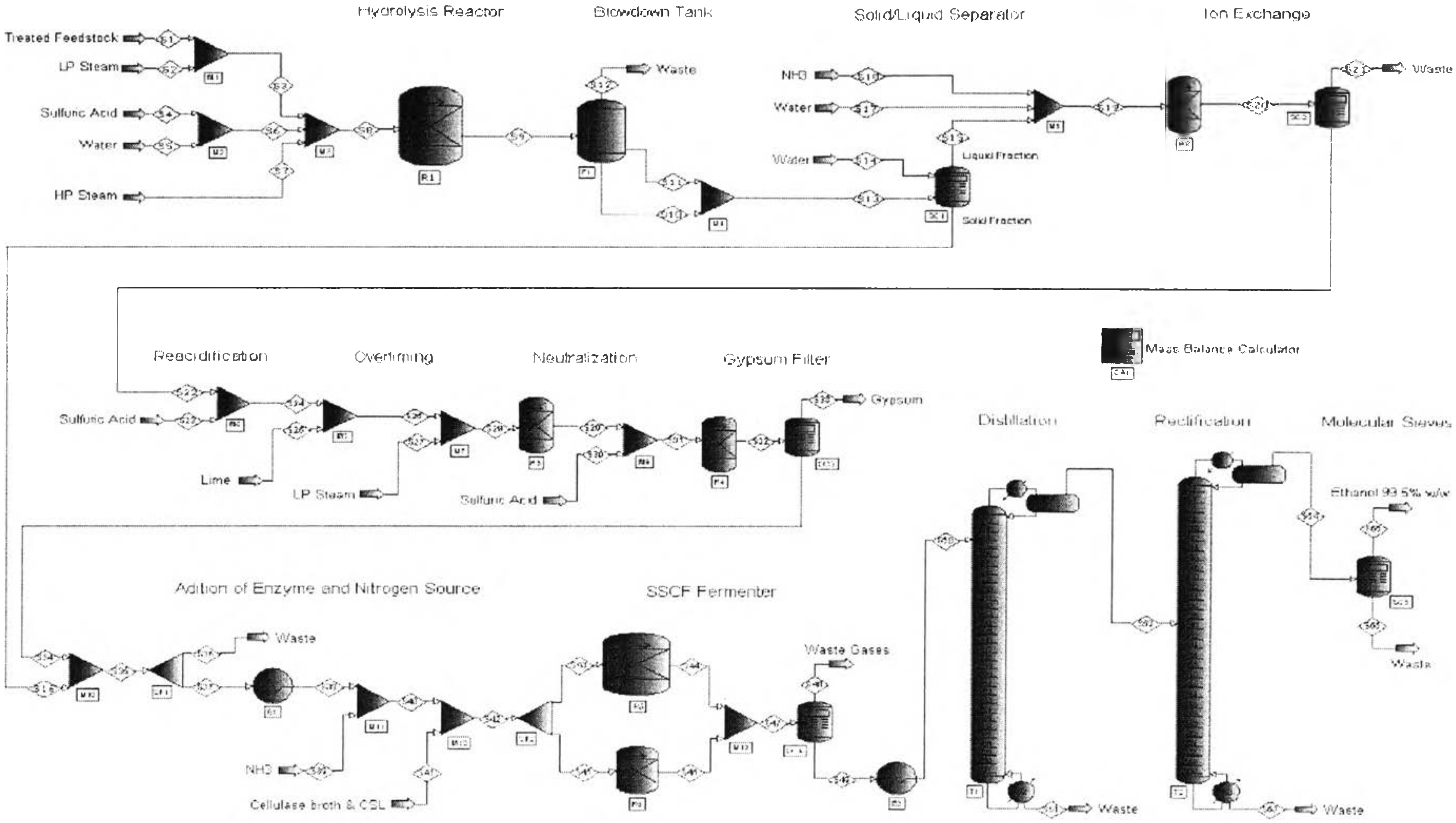

Figure 2.2 The main operations of the bio-ethanol process from lignocellulosic biomass (Morales *et al.*, 2008).

Dias *et al.* (2009) worked on production of bioethanol and other bio-based materials from sugarcane bagasse : integration to conventional bioethanol production process. Ethanol may be produced using sugarcane bagasse as raw material through the Organosolv process with dilute acid hydrolysis, thus increasing ethanol production with the same cultivated sugarcane area. In this work simulations of bioethanol production from sugarcane juice and bagasse are carried out using software UniSim Design. A typical large scale production plant is considered: 1000m3/day of ethanol is produced using sugarcane juice as rawmaterial. A three-step hydrolysis process (pre-hydrolysis of hemicellulose, Organosolv delignification and cellulose hydrolysis) of surplus sugarcane bagasse is considered. Pinch analysis is used to determine the minimum hot utility obtained with thermal integration of the plant, in order to find out the maximum availability of bagasse that can be used in the hydrolysis process, taking into consideration the use of 50% of generated sugarcane trash as fuel for electricity and steam production. Two different cases were analyzed for the product purification step: conventional and doubleeffect distillation systems. It was found that the double-effect distillation system allows 90% of generated bagasse to be used as raw material in the hydrolysis plant, which accounts for an increase of 26% in ioethanol production, considering exclusively the fermentation of hexoses obtained from the cellulosic fraction.

2.3 Sustainability Analysis

2.3.1 Sustainable Development

Sustainable development is a pattern of resource use that aims to meet human needs while preserving the environment so that these needs can be met not only in the present, but in the indefinite future. In other words, development that meets the needs of current generation without compromising the needs of future generations is termed as sustainable development. Thus, when development is viewed in terms of "quality of life" and not mere "numbers", the complementarity between environment and development comes to the fore. The scheme of sustainable development is shown in Figure 2.10 (Delhigreens, 2009).

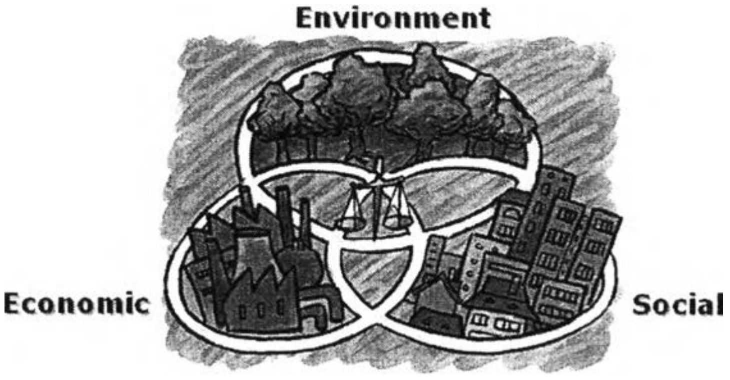

Figure 2.3 Sustainable development concept.

2.3.2 SustainPro

The discussion about sustainability has increased significantly in the past few years, and most importantly comes the analysis if for instance a process is more sustainable than other. Recently has increased the search for methods and tools to make processes more sustainable.

SustainPro is a sustainability analysis tool on Excel platform developed by Carvalho and her coworkers. It is the first tool to perform sustainability analysis of a process. It also provides targets for improvement in order to make the process safer and more sustainable, both in environmental and economical terms. The systematic mothod in SustainPro is divided into 6 steps as shown in Figure 2.11 (Carvalho *et al.*, 2008, 2009).

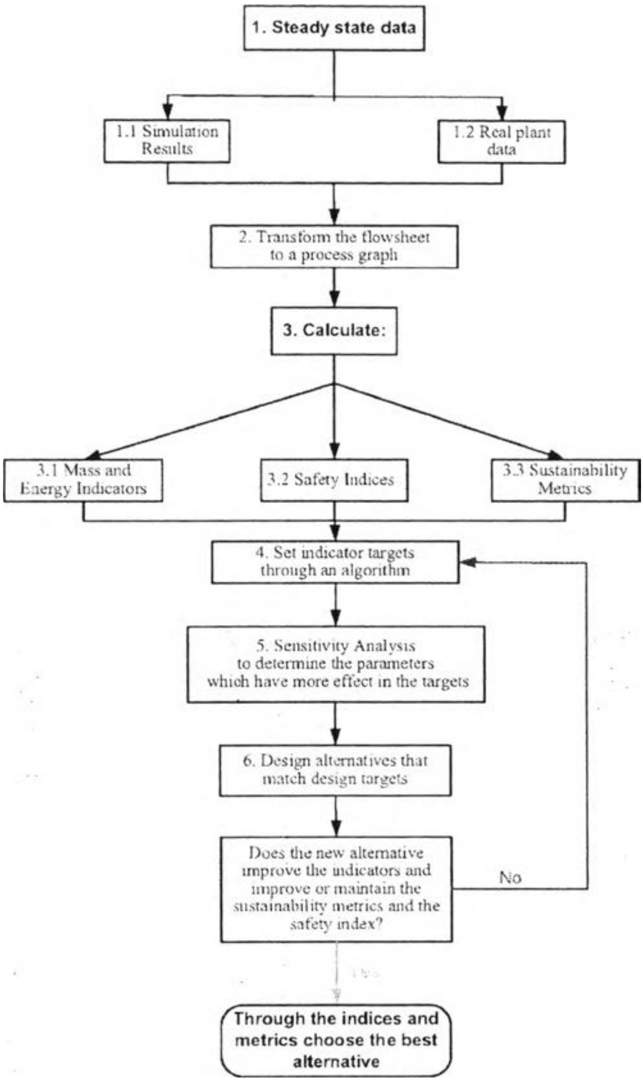

Figure 2.4 The systematic methodology in SustainPro (Terra, 2008).

2.3.2.1 Collection Steady-state Data

This step is to collect mass and energy balance from either plant data or steady-state simulation result (PRO/II or Aspen).

2.3.2.2 Flowsheet Decomposition

This step is to identify all the mass and energy flow-paths in the process by decomposing into open-paths and close-paths for each compound in the process. The closed-paths are the process recycles with respect to each compound in the process. An open-path consists of an entrance and an exit of a specific compound in the process.

2.3.2.3 Calculation of Indicators, Sustainability Metrics and Safety Indices

A) Calculate Mass and Energy Indicators

a) Material-value Added (MVA)

For a given open path it is desirable to calculate the value generated from start to end point. This is done by calculating the difference between the value of the component path flows outside the process boundaries and the costs in raw material consumption or feed cost. Negative values for MVA indicates value losses and show that there are potentials for improving the economic efficiency. MVA is calculated in cost units per year.

$$\mathbf{MVA = (mass)\ (sales\ price - raw\ material\ cost)}$$

b) Energy and Waste Cost (EWC)

The EWC indicator consists of two parts: EC considers the energy costs and WC the process waste costs associated with a given path, by allocating the utility consumption and waste treatment costs. The results will indicate the maximum theoretical saving potential for a given path. High EWC values indicate high energy consumption and waste costs that could be reduced by decreasing the path flow or the duties. EWC is calculated in cost units per year.

$$\mathbf{EWC = EC + WC}$$

$$\mathbf{EC = (duty)\ (cost)\ \frac{Component\ mass \times characteristic\ physical\ property}{sum\ of\ all\ component\ (mass \times characteristic\ physical\ property)}}$$

$$\mathbf{WC = (mass)\ (waste\ treatment\ cost)}$$

c) Reaction Quality (RQ)

This indicator measures the effect a component path flow may have on the reactions that occurs in its path. If the RQ value is positive, the path flow has a positive effect on the overall plant productivity. Negative values indicate an undesirably located component path flow in the process.

$$\mathbf{RQ} = \frac{\text{extent of reaction} \times \text{reaction parameter}}{\text{sum of desired products}}$$

d) Accumulation Factor (AF)

AF is a way of measuring the accumulative behavior of individual components in recycles. Note that the term ''accumulation'' is not used to mean inventory in this method. It indicates the amount of material being recycle relative to its input to the process and/or output from the process.

$$\mathbf{AF} = \frac{\text{mass of component in recycle}}{\text{sum of component mass leaving recycle}}$$

e) Total Value Added (TVA)

This indicator describes the economic influence a component path flow may have on the variable process costs. Negative TVA values indicate improvement potentials in the process. Still, if a path flow has a high EWC value that is compensated by a high MVA value and gives a positive TVA value it can still be possible to reduce the energy cost. TVA is calculated in cost units per year.

$$\mathbf{TVA = MVA - EWC}$$

f) Energy Accumulation Factor (EAF)

The energy accumulation factor (EAF), calculates the accumulative behaviour of energy in an energy cycle path flow. Since it is of interest to recycle or recover energy, these factors should be as large as possible in order to save energy. The energy accumulation factor can be calculated as:

$$\mathbf{EAF} = \frac{\text{energy recycled}}{\text{enery leaving the recycle}}$$

g) Total Demand Cost (TDC)

This indicator is applied only to open-paths and traces the energy flows across the process. For each demand in the process the sum of all DC, which pass through it, are calculated. DC can be calculated using the following equation:

$$\mathbf{DC_{Su,d} = PE_{Su}\ EOP_{Su,d}}$$

Where PE is the utility cost, in units of price/energy. The total cost for all the paths is expressed by:

$$\mathbf{TDC_d} = \sum_{Su=1}^{SS} \mathbf{DC_{Su,d}}$$

Where SS is the total numbers of supplies that energy contributes are significant to the demand, d. High values of this indicator identify the demands that consume the largest values of energy, so these are the process parts, which are more adapted to heat integration.

B) Calculate Safety Indices

The safety of the process is another important parameter that should be taken into account. In order to achieve the inherently safety index the value for some sub-indices need to be calculated. These sub-indices can be divided into two groups, one group, which takes into account the chemical inherent safety, and the other group that is dependent on the process inherent safety. A scale of scores for each sub-index has been defined. These scales are based on the values of some safety parameters, such as the explosiveness, the toxicity, the pressure of the process and so on as shown in Table 2.7.

Table 2.6 List of safety indices and their sources (Carvalho *et al.*, 2008)

	Score
Total inherent safety index (ISI)	
Chemical inherent safety index, I_{ci}	
Sub-indices for reactions hazards	
Heat of the main reaction, I_{rm}	0-4
Heat of the side reactions, I_{rs}	0-4
Chemical interactions, I_{int}	0-4
Sub-indices for hazards substances	
Flammability, I_{fl}	0-4
Explosiveness, I_{ex}	0-4
Toxicity, I_{tox}	0-6
Corrosivity, I_{cor}	0-2
Maximum, I_{ci} score	28
Process inherent safety index, I_{pi}	
Sub-indices for process conditions	
Inventory, I_I	0-5
Temperature, I_T	0-4
Pressure, I_P	0-4
Sub-indices for process conditions	
Equipment, I_{eq}	
I_{ISBL}	0-4
I_{OSBL}	0-3
Process structure, I_{st}	0-5
Maximum, I_{pi} score	25
Maximum, I_{Si} score	53

The sum of all the sub-indices scores is the inherent safety index value; this parameter has the maximum value of 53. Note that the higher is the inherent safety index value the more unsafely is the process, so the aim in all the design alternatives is to try to reduce its value as much as possible. In Table 2.7 the entire set of sub-indices, as well as the respective scales, are specified.

C) Calculate Sustainability Metrics

The sustainability metrics that are implemented in SustainPro were defined by the institution of Chemical Engineer (IChem^{E}) by Azapagic (2002). The 49 metrics has been defined and divided into three main areas: environmental, social and economical. The sub-areas related to these metrics are highlighted in Figure 2.12, for each sub-area, more than one metric is calculated. The use of the sustainability metrics follows the simple rule that the lower the value of the metric the more effective the process. A lower value of the metric indicates that either the impact of the process is less or the output of the process is more.

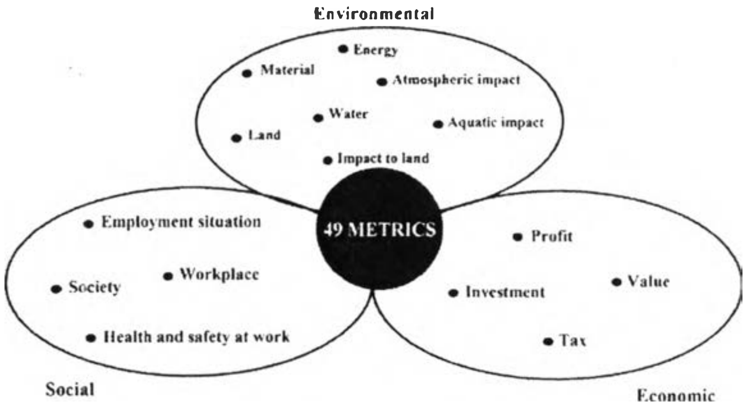

Figure 2.5 Example of the sustainability metrics (Carvalho *et al.*, 2008).

Out of the 49 defined metrics, SustainPro has used 23 of them, because the limitation of the information requested by the program. The metric calculated in this analysis are shown in Table 2.8, divided by the group of metrics.

Table 2.7 The sustainability metrics considered in SustainPro

Group	**Metrics**
Energy	Total Net Primary Energy Usage rate (GJ/y)
	% Total Net Primary Energy sourced from renewables
	Total Net Primary Energy Usage per Kg product (kJ/kg)
	Total Net Primary Energy Usage per unit value added (kJ/$)
Material	Total raw materials used per kg product (kg/kg)
	Total raw materials used per unit value added
	Fraction of raw materials recycled within company
	Fraction of raw materials recycled from consumers
	Hazardous raw material per kg product
Water	Net water consumed per unit mass of product (kg/kg)
	Net water consumed per unit value added
Economic	Value added ($/yr)

For the environmental impact related metrics, the waste reduction (WAR) algorithm has been proposed in order to calculate the environmental impacts from a chemical process. The Environmental impact factors and their meaning determined in WAR algorithm are shown in Table 2.9. The lower the PEI of a process, the more environmental friendly it is. This method is based on a Potential Environmental Impact (PEI) balance.

Table 2.8 The environmental impact factor is WAR algorithm

Impact Factor	**Meaning**
HTPI	Human Toxicity Potential by Ingestion
HTPE	Human Toxicity Potential by Exposure both Dermal and Inhalation
TTP	Terrestrial Toxicity Potential
ATP	Aquatic Toxicity Potential
GWP	Global Warming Potential
ODP	Ozone Depletion Potential
PCOP	Photochemical Oxidation Potential
AP	Acidification Potential

However, the WAR algorithm is not implemented in SustainPro, therefore, it is calculated using CAPEC software, the Intregreted Computer Aided System (ICAS).

To calculate these metrics, the flowrates for each compound coming into the process and leaving the process are needed as known information.

Summarizing, the indicators are applied to the entire set of open and closed paths. With their values the critical points of the process as well as the areas that should be improved in the process are determined. The sustainability metrics and the safety index are calculated using the steady-state data for the global process and they are used to measure the impact of the process in its surroundings. They will be used as performance criteria in the evaluation of the new suggested design alternatives.

2.3.2.4 Indicator Sensitivity Analysis (ISA) Algorithm

This step is to determine the parameters which have more effect in the targets. To apply this algorithm the indicators having the highest potential for improvements are identified first. Then an objective function such as the gross-profit or the process total cost is specified. For positive values of indicator, the high value, the high potential for improvement. Others are the opposite, therefore if it is more negative, it is more potential for improvement. However, the same logic applies to all indicators as the closet to zero in their value which is shown in Figure 2.13.

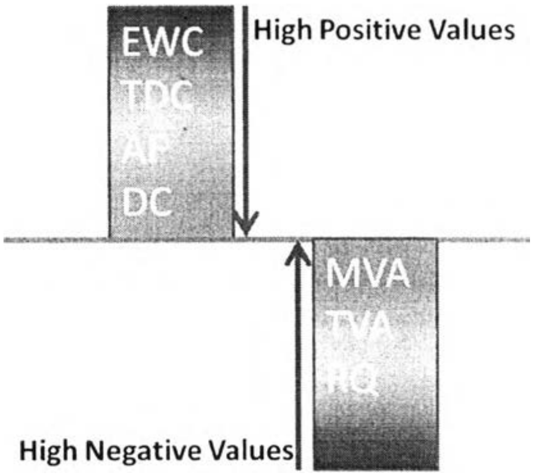

Figure 2.6 The target improvement for the indicators.

A sensitivity analysis is then performed to determine the indicators that allow the largest positive (for profit) or negative (for cost) change in the objective function. The most sensitive indicators are selected as targets for improvements.

2.3.2.5 Operational Sensitivity Analysis

A sensitivity analysis with respect to the operational (parameters) variables, which influence the target indicators, is performed. The analysis identifies the operational variables that need to be changed to improve the process in the desired direction.

2.3.2.6 Generation of New Design Alternatives

This step is to generate the new sustainable design alternative, the first step, is to verify in which operation type, the operational parameter (determined in Step 5) can be included. That is, identify if the operational parameter is involved in a separation, or involved in a reaction, or in flowrate reduction in a closed-path, or in a flowrate reduction in an open-path. Next, an appropriate process synthesis algorithm is employed to generate the new sustainable alternatives that are able to change the operational parameters.

Finally, a validation and a comparison to the new alternatives that match the design targets in terms of their improvements in the performance criteria, is done.

2.4 Life Cycle Assessment (LCA)

2.4.1 Overview

The concept of the life cycle of a product or a process is a relatively recent one which emerged in response to increased environmental awareness on the part of the general public, industry and governments. The precursors of life cycle analysis and assessment (LCAs) were the global modeling studies and energy audits of the late 1960s and early 1970s. These attempted to assess the resource cost and environmental implications of different patterns of human behavior.

A number of different terms have been coined to describe the processes. One of the first terms used was Life Cycle Analysis, but more recently two terms have come to largely replace that one: Life Cycle Inventory (LCI) and Life Cycle Assessment (LCA). These better reflect the different stages of the process. Other terms such as Cradle to Grave Analysis, Eco-balancing, and Material Flow Analysis are also used. Whichever name is used to describe it, LCA is a potentially powerful tool which can assist regulators to formulate environmental legislation, help manufacturers analyses their processes and improve their products, and perhaps enable consumers to make more informed choices. Like most tools, it must be correctly used according to Figure 2.14. However, a tendency for LCAs to be used to 'prove' the superiority of one product over another has brought the concept into disrepute in some areas (World Resource Foundation, 2010).

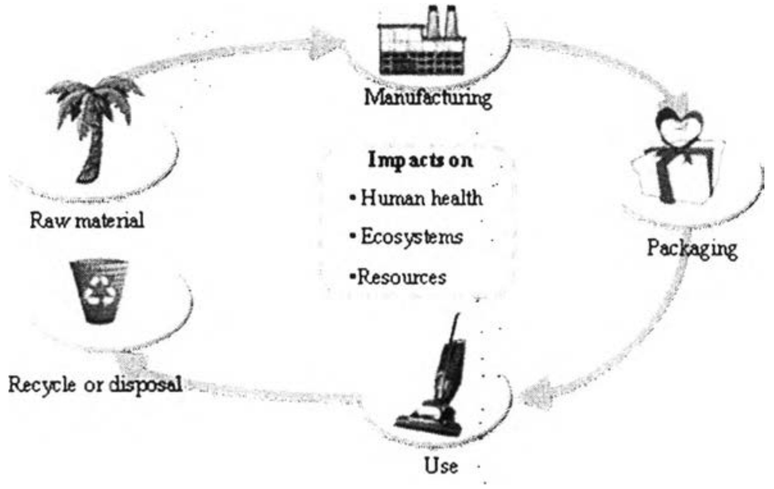

Figure 2.7 Structure of the life cycle assessment (http://www.scienceinthebox.com).

2.4.2 Why Perform LCAs?

LCAs might be conducted by an industry sector to enable it to identify areas where improvements can be made, in environmental terms. Alternatively the LCA may be inten-ded to provide environmental data for the public or for government. In recent years, a number of major companies have cited LCAs in their marketing and advertising, to support claims that their products are 'environmentally friendly' or even 'environmentally superior' to those of their rivals. Many of these claims have been successfully challenged by environmental groups.

All products have some impact on the environment. Since some products use more resources, cause more pollution or generate more waste than others, the aim is to identify those which are most harmful.

Even for those products whose environmental burdens are relatively low, the LCA should help to identify those stages in production processes and in use which cause or have the potential to cause pollution, and those which have a heavy material or energy demand.

Breaking down the manufacturing process into such fine detail can also be an aid to identifying the use of scarce resources, showing where a more sustainable product could be substituted (World Resource Foundation, 2010).

2.4.3 LCA`s Definition

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 (SETAC, 1993).

2.4.4 LCA's Methodology

According to the ISO 14040 and 14044 standards, a Life Cycle Assessment is carried out in four distinct phases consisting of:

a) Goal and Scope Definition

Identify the LCA's purpose and the expected products of the study, and determine the boundaries (what is and is not included in the study) and assumptions based upon the goal definition.

In this phase, we have to formulate and specify the goal and scope of study in relation to the intended application. The object of study is described in terms of a so-called "functional unit". For the example of comparing glass vs. plastic bottles, the functional unit could be "1 liter bottle container for refrigerated juices".

Comparing 1 kg of plastic bottles directly with 1 kg of glass bottles, disregarding the packed volume, would not be an appropriate functional unit for the desired functionality of bottles.

Apart from describing the functional unit, the goal and scope should address the overall approach used to establish the system boundaries. The system boundary determines which unit processes are included in the LCA and must reflect the goal of the study.

Finally, we will obtain the goal and scope including a description of the method applied for assessing potential environmental impacts and which impact categories those are included.

b) Inventory Analysis

Quantify the energy and raw material inputs and environmental releases associated with each stage of production.

In this phase, "Inventory" involves data collection and modeling of the product system, as well as description and verification of data. This encompasses all data related to environmental (e.g. CO_2) and technical (e.g. intermediate chemicals) quantities for all relevant and within study boundaries unit processes that compose the product system. Example of inputs and outputs quantities include: (1) inputs of materials, energy, chemicals and other; and (2) outputs in the form of air emissions, water emissions or solid waste. Other types of exchanges or interventions such as radiation or land use can also be included.

The data must be related to the functional unit defined in the goal and scope definition. Data can be presented in tables and some interpretations can be made already at this phase.

Finally, we will obtain the results of the inventory called "LCI" which provides information about all inputs and outputs in the form of elementary flow to and from the environment from all the unit processes involved in the study.

c) Impact Assessment

Analyze and compare the impacts on human health and the environment burdens associated with raw material and energy inputs and environmental releases quantified by the inventory.

In this phase, "Life Cycle Impact Assessment" (LCIA) is aimed at evaluating the contribution to impact categories such as global warming, acidification, ozone depletion and etc.

The first step of LCIA is termed "characterization". Here, impact potentials are calculated based on the LCI results. The next steps are "normalization" and "weighting", but these are both voluntary according the ISO standard. Normalization provides a basis for comparing different types of environmental impact categories (all impacts get the same unit). Weighting implies assigning a weighting factor to each impact category depending on the relative importance.

d) Interpretation

Evaluate opportunities to reduce energy, material inputs, or environmental impacts at each stage of the product life-cycle.

In this phase, "Interpretation" is the most important one. An analysis of major contributions, sensitivity analysis and uncertainty analysis leads to the conclusion whether the ambitions from the goal and scope can be met.

All conclusions are drafted during this phase. Sometimes an independent critical review is necessary, especially when comparisons are made that are used in the public domain.

Finally, we can also analyze an improvement, in which recommendations are made based on the results of the inventory and impact stages. These may include modifying a production process, using different raw materials, or choosing one product over another (ISO 14040 and 14044, 2006).

To understand easily, the framework within which life cycle assessment is carried out is shown in Figure 2.15. Two main activities—inventory analysis and impact assessment—are preceded by a vitally important planning phase and followed by extended interpretation, which will normally involve checking the results both against the initial goals and for self-consistency.

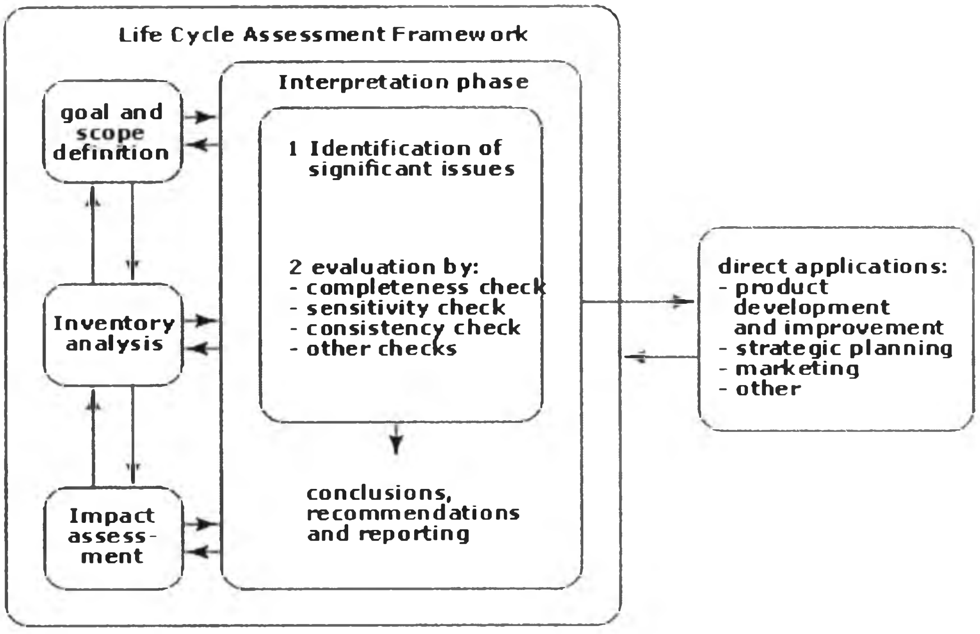

Figure 2.8 Life cycle assessment framework (http://www.ami.ac.uk).

2.4.5 LCA Studies on Bioethanol

Bioethanol has become the new challenge on the reduction of fossil resource use and global warming concern. After that, many research teams have conducted the LCA on bioethanol in various materials including sugar, starchy, and lignocellulosic materials.

In 2003, Fu *et al.* worked on the life cycle assessment of Bio-ethanol Derived from cellulose. His study presents first conclusion that ethanol fuel as a blend in gasoline may help to reduce overall life-cycle greenhouse gas emissions only if the energy required to generate the process steam derives from biomass (e.g. lignin or bio-fuel) rather than fossil fuel for pretreatment of the feedstock. Second, replacing traditional gasoline by E10 fuel may save energy, lead to less summer smog and ozone depleting substances, and lower discharges of heavy metals. It may, however, result in increased eutrophication, acidification and winter smog, and generate more solid wastes. Third, for bio-ethanol production, enzyme manufacturing, energy consumption for breaking down feedstock and haulage are the main sources of impact. It is in these areas that research can best be focussed to improve overall life cycle environmental performance. Finally, feedstock cultivation contributes significantly to environmental impact in almost all categories, but particularly to acidification, eutrophication, heavy metals and carcinogenic substances. It can also be expected to give rise to biodiversity, landscape modification and land-use impacts. Use of biomass waste as a feedstock avoids these impacts.

In 2007, Nguyen and coworkers worked on the life cycle assessment of cassava utilization for fuel ethanol in Thailand. His study showed the positive impacts of using cassava-based ethanol on fossil energy use and green house gas (GHG) emission. The majority of emissions came from the energy used in ethanol conversion process. He also compared the GHG emission between gasoline and ethanol from cassava in Thailand, and ethanol from other feedstocks. The comparison is shown in Table 2.10.

Table 2.9 Green house gas emission comparison (Nguyen *et al*, 2007)

Feedstock	**Gross emission less emissions displaced by co-products (gCO_2 eq/L EtOH)**	**% Reduction**
Cassava in China	1538	23.3
Corn in the US	1506	48.4
Cassava in Thailand	964	62.9
Sugarcane in Brazil	256	90.9
Herbaceous biomass in the US	245	91.6

The table showed that herbaceous which is a lignocellulosic material, emiting the lowest CO_2 with 91.6 % reduction from gasoline. Following by sugar base material (sugarcane) and starchy material (cassava).

Searcy *et al.* (2008) compared the LCA emission renewable energy routes that convert straw/corn stover into usable energy were examined. The conversion options studied were ethanol by fermentation, syndiesel by oxygen gasification followed by Fischer Tropsch synthesis, and electricity by either direct combustion or biomass integrated gasification and combined cycle (BIGCC). The greenhouse gas (GHG) emissions were 830 g CO_2 e/kWh for direct combustion, 839 g CO_2 e/kWh for BIGCC, 2,060 g CO_2 e/L for ethanol production, and 2,440 g CO_2 e/L for FT synthesis of syndiesel. The comparison in unit per mega joules is shown in Table 2.11.

Table 2.10 Comparison of GHG emission from difference sources

Method	**Emission (g CO_2/MJ)**
Direct Combustion	230.56
BIGCC	233.06
Fermented Ethanol	97.31
FT Syndiesel	67.40

The result showed that bioethnol choice gave more attractive than those from electricity choices. However, syndiesel emitted the lowest emission with 67.40 g CO_2 per mega joules. By this, it means that the use of lignocellulosic materials in conversion process to be ethanol is better than use it to generate electricity.

Nguyen *et al.* (2008) work on life cycle assessment of fuel ethanol from cane molasses in Thailand. 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 which are shown in Table 2.12. 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. In most cases, higher impacts from the upstream of molasses-based ethanol tend to govern its net life cycle impacts relative to CG. This makes the fuel blend less environmentally friendly than CG for the specific conditions considered. However, as discussed later, this situation can be improved by appropriate changes in energy carriers. Conclusions, the LCA procedure helps identify the key areas in the MoE production cycle where changes are required to improve environmental performance. Specifically, they are: (1) use of coal as energy source for ethanol conversion, (2) discharge of distillery spent wash into an anaerobic pond, and (3) open burning of cane trash in sugar cane production.

Table 2.11 LCA characterization results for 8 impact categories (displayed per functional unit) (Nguyen *et al.*, 2008)

Impact category	CG	E10-a		E10-a(nb)	
		% change relative to CG		% change relative to gasoline	
Net energy use (MJ)	38.70	39.95	+3.2	39.95	+3.2
Fossil energy use (MJ)	38.59	36.55	−5.3	36.55	−5.3
Petroleum use (MJ)	34.83	32.00	−8.1	32.00	−8.1
GWP (kg CO2 eq.)	2.99	3.07	+2.8	3.07	+2.7
AP (g SO2 eq.)	3.29	3.29	+0.1	3.16	−3.9
NP (g NO_3 eq.)	5.00	5.10	+2.1	4.94	−1.2
POCP (g C2H4 eq.)	1.53	1.79	+17.0	1.59	+3.9
Land use (m2.year)	–	0.18			

In 2009, Luo and co-workers worked on lifecycle assessment and life cycle costing of bioethanol from sugarcane two cases in Brazil. The two cases engaged were: base case—bioethanol production from sucrose, and heat and electricity generation from bagasses using the current technology (1); future case—bioethanol production from both sucrose and bagasses (2), and heat and electricity generation from wastes. His study performed LCA and compared gasoline with E10, E85 and Ethanol as well. The result is shown in Figure 2.16.

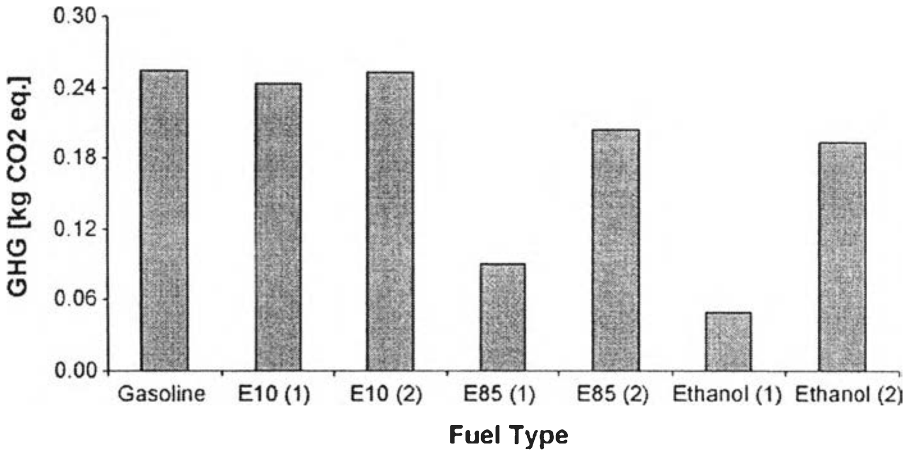

Figure 2.9 Green house gas emission of ethanol from sugarcane (Luo *et al.*, 2009).

When GHG emissions were concerned, burning bagasse for electricity generation (base case) was a much better option than converting bagasse to ethanol (future case). They also performed life cycle costing, the result indicated that driving with ethanol fuels was more economical than gasoline, and the future case was economically more attractive than the base case, which have been the driving force for the promotion of advanced technologies converting bagasse to ethanol.

Garcı´a *et al.* (2009) study on Life cycle assessment of flax shives derived second generation ethanol fueled automobiles in Spain. This study shows the results of a LCA performed upon flax shives based fuel ethanol and its use in FFV whether blended or not with gasoline. In this study, flax shives are agricultural co-products from pulp fibre production (the main product of this kind of crop). Shive production, processing and transport to refinery gate, ethanol conversion and transport to blending refinery, ethanol blending with gasoline in two ethanol fuel applications (E10 and E85) and, E10, E85 and E100 burning in FFV were evaluated and compared with the use of conventional gasoline. According to the results, the allocation methodology can greatly alter the environmental effects when different alternatives are being compared. This illustrates the importance of avoiding allocation when possible, as the selection of a coefficient potentially affects the conclusions of the study. Cellulosic fuel ethanol as a blend with gasoline (or not) may help to reduce the greenhouse gases emissions only when a large allocation factor is assumed for the flax shives (in this case, mass allocation). However, using ethanol based fuels would increase the contributions to other impact categories, such as eutrophication and photochemical oxidants formation and should reduce the fossil fuel consumption in spite of the allocation factor selected. On the contrary, the contributions to other impact categories such as acidification, human toxicity and ecotoxicity could be reduced when a small allocation factor is assumed due to the shorter contributions from the feedstock cultivation stage. Ethanol fuel used in form of blends in gasoline can help increase the security in the energy supply regardless the allocation coefficient chosen. Agricultural activities related to feedstock production were identified as notable contributors to the environmental performance. Thus, high yielding varieties, reduction of tillage activities and decline in fertilization should help to reduce these impacts.