# CHAPTER II
# LITERATURE REVIEW

## 2.1 Petroleum Outlook in Thailand

### 2.1.1 Crude Oil Market

Petroleum, also called crude oil is the most important natural resources. It is used mostly, by volume for producing fuel for transportation sector. It can be converted to be gasoline, jet fuel, and diesel fuel to run cars, trucks, aircraft, ships, and other vehicles. It has played a vital role in the world economy. Unfortunately, this fossil fuel is a non-renewable energy source that takes millions of years to form and therefore once existing and any new reserves are depleted there is no way to obtain more. The world's prove reserve at the end of 2007 is 1237.9 thousand million barrels which it will be exhausted within 41.6 years (BP, 2008). In 2008, the price of crude oil skyrocketed to new record highs above $147 per barrel affecting the prices of gasoline and diesel in Thailand reached 43.35 and 43.68 baht a liter, respectively (EPPO, 2008). Thailand is heavily dependent on crude oil which accounts for approximately 42% of the total primary energy supply in 2006 (MOEN, 2008). The total primary energy supply in Thailand is shown in Figure 2.1.

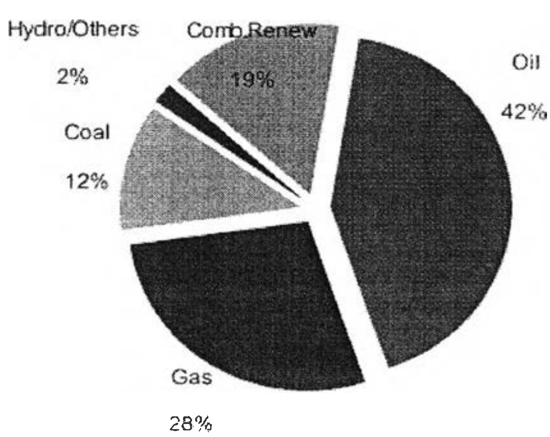



**Figure 2.1** Total primary energy supply in Thailand (source: www.energy.go.th).

2.1.2 Oil Potentials, Supply, Demand, and Consumption

In 2007, Thailand held proven oil reserves about 176 million barrels and produced roughly 135 thousand barrels per day of crude oil and about 79 thousand barrels per day of condensate (MOEN, 2008). The oil demand in Thailand is shown in Figure 2.2.

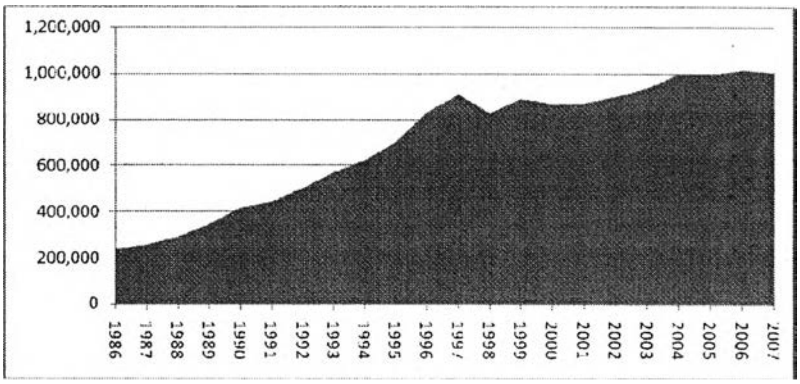



**Figure 2.2** Thailand's oil demand in barrel per day (source: www.energy.go.th).

Despite the fact that Thailand can produce crude oil locally, the country needs very high demand to propel the economic. The demand in Thailand is approximately 1 million barrels per day but the country can meet just 13.5% of the demand. Thailand imported around 809 thousand barrels per day of crude oil in 2008. The majority of crude oil (83%) was imported from the Middle East (UAE, Saudi and Oman) (MOEN, 2008). The crude oil import sources are shown in Figure 2.3.

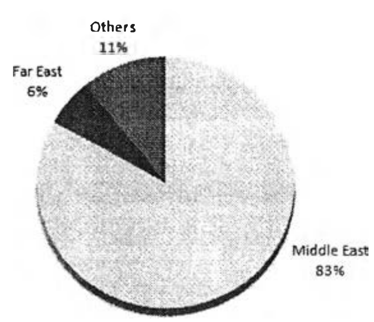



**Figure 2.3** Crude oil import sources.

2.1.3 Petroleum Products

In order to use crude oil as energy, burning crude oil itself is of limited use. To extract the maximum value from crude, it first needs to be refined into petroleum products. The crude oil products and processes of Thaioil, the biggest refinery in Thailand, is illustrated in Figure 2.4.

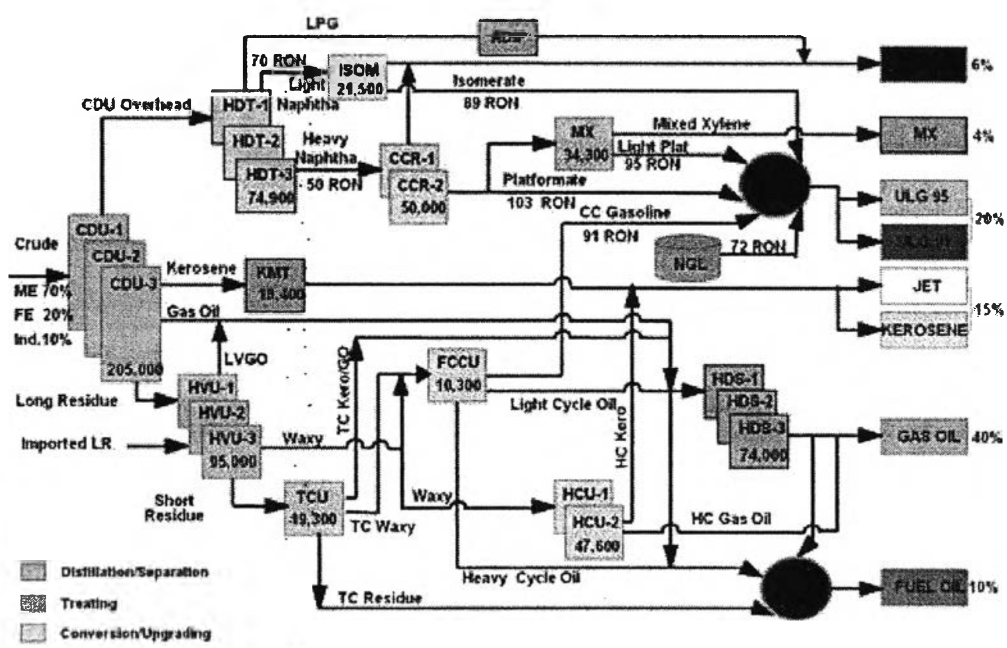



**Figure 2.4** Thaioil refining process and products (source: www.thaioil.co.th).

The figure illustrates that products from their complex refinery can be divided into three categories. Light distillates, which account for 30 % of their products and comprise LPG, and 91- and 95-octane unleaded gasoline. Middle distillates, which represent 60 % and comprise jet fuel, kerosene, and diesel. Residues or fuel oil, which constitutes the remaining 10 % (TOP, 2009).

In 2008, the majority of petroleum products in Thailand is diesel with the production 56.9 M liters per day, followed by LPG (23.5), gasoline (23.1), fuel oil (18.8), jet fuel (16.4) and kerosene (0.5) (EPPO, 2009). While Thaioil shared around 25% of the total production of petroleum products in Thailand (MOEN, 2008).

2.1.4 Uses of Petroleum Products

Products produced from crude oil were mainly consumed in transport sector shared 72.3%, followed by agricultural sector, manufacturing sector, residential sector, commercial sector, construction sector and mining sector, shared 11.0%, 8.3%, 5.0%, 2.9% and 0.5% respectively. The main proportion of petroleum products consumption was diesel (including palm diesel) shared 48.6%, followed by gasoline (including gasohol), LPG, jet fuel, fuel oil, and kerosene, shared 16.9, 13.4%, 12.3%, 8.8%, and 0.04% respectively (MOEN, 2008). The petroleum products uses in Thailand are shown in Figure 2.5.

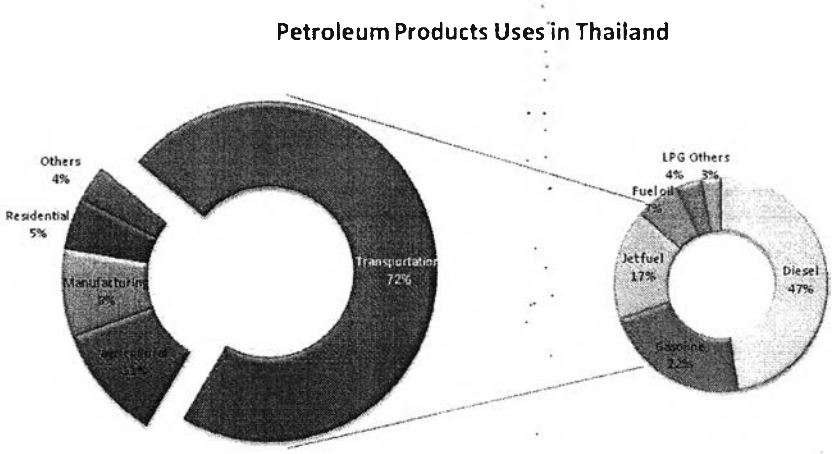



**Figure 2.5** Petroleum products uses in Thailand.

Focusing on transportation sector, most of the energy consumed in this sector were crude oil products, comprising diesel (including palm diesel) 47.4%, gasoline (including gasohol) 22.4%, jet fuel 16.5%, fuel oil 6.8%, and LPG 3.9% (MOEN, 2008).

## 2.2 The Use of Ethanol as Fuel

As seen from Figure 2.5, the consumption of gasoline in Thailand ranks the second (22%) in transportation sector. This number also includes gasohol which contains ethanol from bio based resources or bioethanol.

2.2.1 Ethanol as a Transportation Fuel and Additive

Ethanol can be used in gasoline as a gasoline additive to enhance octane number and also as a gasoline substitute. Nowadays, it is focused as a fuel. However gasoline has a major drawback. The comparison between ethanol and the typical hydrocarbon components of refined oils in term of internal combustion engines burn fuels is shown in Table 2.1. Ethanol is more oxygenated, and its combustion in oxygen generates less energy compared either a pure hydrocarbon or a typical gasoline. However, ethanol has high octane number (leading to high engine efficiencies) and also generates an increased volume of combustion products (gases) per energy unit burned; these factors in optimized ethanol engines significantly eroded the differential advantages of gasoline. Similar arguments could not be extended to a comparison between ethanol and diesel fuel, and ethanol had only 58 to 59% of the energy (net heat of combustion) of the latter (Mousdale, 2008).

**Table 2.1** Energy parameters for ethanol, isooctane, gasoline, and diesel (Mousdale, 2008)

| | Ethanol | Isooctane | Gasoline | Diesel |
|---|---|---|---|---|
| Density, lb/gal | 6.6 | 5.8 | 6.25 | 7.05 |
| Net heat of combustion, Btu ($\times 10^3$)/gal | 75.7-76 | 110.5-119.1 | 109-119 | 128.7-130 |
| MON | 104.5 | - | - | - |
| RON | 106 | 110 | - | - |

The high miscibility of ethanol and refined oil products allow a more conservative option that is the use of low ethanol additions to standard gasoline (such as E10) and requires no modifications to standard gasoline burning vehicles.

The top 8 countries ethanol producers are shown in Table 2.2. In 2008, the world's giant ethanol fuel producer were the United States and Brazil with produced 9.0 and 6.4 billion US gallons respectively, accounting for 89 percent of world production of 17.33 billion US gallons. While Thailand was ranked at the 6$^{th}$ with 89.8 million gallons.

**Table 2.2** World's ethanol producers

| **Annual Fuel Ethanol Production by Country 2008<br>Top 8 countries** | | | |
|---|---|---|---|
| World rank | Country/Region | Production[1]<br>(M US gallons) | Main feedstock |
| 1 | United States | 9,000.0 | Corn[2] |
| 2 | Brazil | 6,472.2 | Sugarcane[2] |
| 3 | European Union | 733.6 | Sugar beet, wheat[3] |
| 4 | China | 501.9 | Corn, cassava, sweet sorghum, potato sweet[2] |
| 5 | Canada | 237.7 | Corn[2] |
| 6 | Thailand | 89.8 | Sugar cane molasses, Cassava[2] |
| 7 | Colombia | 79.3 | Sugarcane[4] |
| 8 | India | 66.0 | Sugarcane[5] |
| | World Total | 17,335.29 | |

Sources: [1] RFA [2] APEC
[3] Baka *et al.* (2009) [4] www.ers.usda.gov/Publications/WRS0901
[5] http://www.ethanolindia.net/sugarind.html

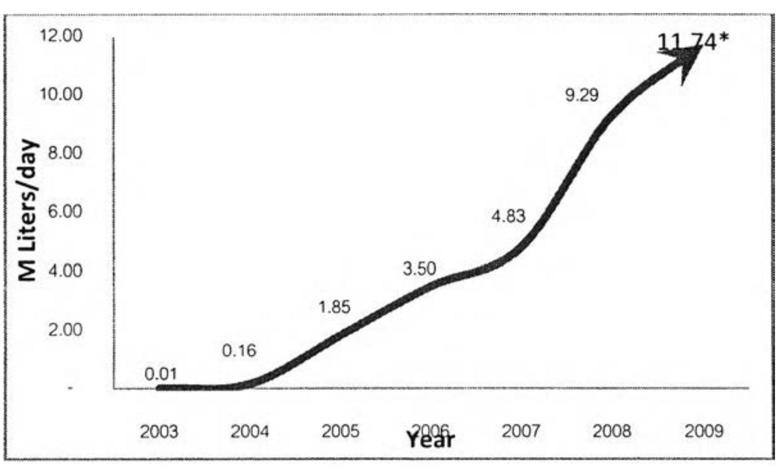
Ethanol 99.5% purity, fuel grade, can mix with gasoline. The mixture of ethanol and gasoline has "E" numbers which describe the percentage of ethanol in the mixture by volume, for example, E10 is 10% ethanol and 90% gasoline. Low ethanol blends (5-25%) are also known as gasohol, though internationally the most common use of the term gasohol refers to the E10 blend.

2.2.2 Ethanol as Fuel 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, the national oil company 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. It is released to the country in 2001. In 2008 PTT and Bangchak Petroleum started supplying E20 in January, after that, PTT lunched E85 to the country in August.

Figure 2.6 illustrates that the gasoline consumption is dramatically increasing. In the 1st quarter 2009, the consumption rate has been raised to 11.74 million liters per day, 73 times higher than 2004 (EPPO, 2009).




*1st Quarter, 2009

**Figure 2.6** Gasohol consumption in Thailand.

## 2.3 Bioethanol

Generally, ethanol is produced from both as a petrochemical, through the hydration of ethylene which is synthesis from fossil fuel, and biologically, by the fermentation of sugar which is called "Bioethanol".

Bioethanol is being considered as the new hope to serve the world's fuel consumption. The conversion by yeast can be summarized as chemical equation below.

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2.$$

### 2.3.1 Raw Materials

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

### 2.3.2 Process Overview

The process of ethanol production depends on materials used. A general process scheme for ethanol production is shown in Figure 2.7.

This scheme is noted that if sugar substances, such as molasses and sugarcane juice, are used as raw materials, then milling, pretreatment, hydrolysis, and detoxification are not necessary. For the production of fermentable sugar from starchy materials, milling, liquefaction, and saccharification processes are usually necessary. In the same way, milling, pretreatment, and hydrolysis are typically used for the process from lignocellulosic materials. In addition, a detoxification unit is not always considered, unless a toxic substrate is fed to the bioreactor.

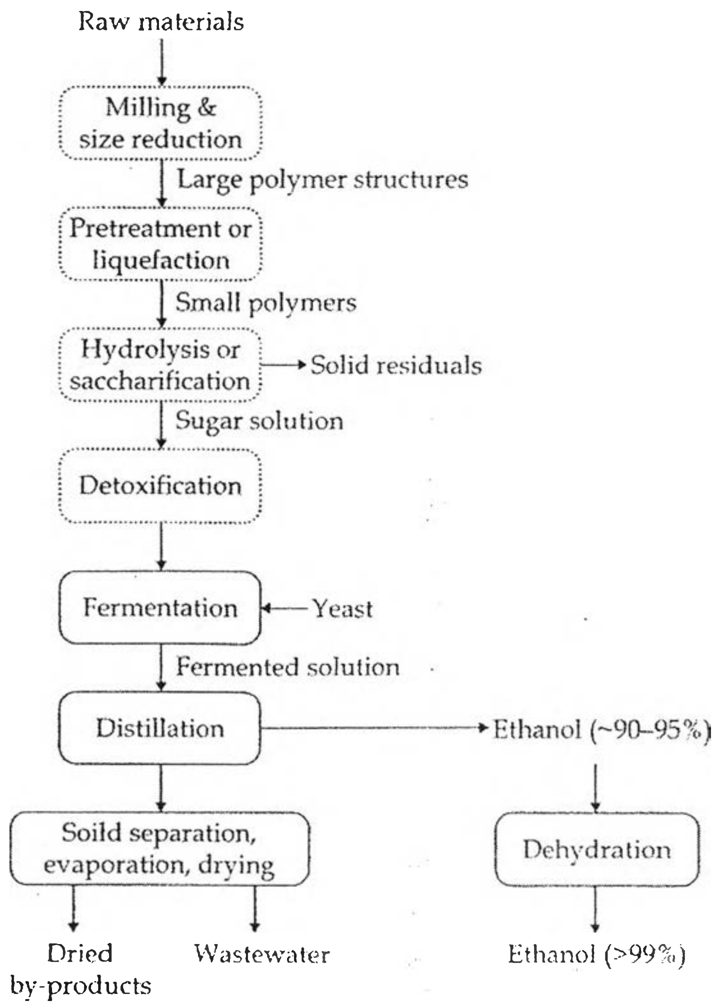



**Figure 2.7** General process scheme for ethanol production (Nag, 2008).

## 2.4 Lignocellulosic-based Derive Ethanol

### 2.4.1 Lignocellulosic Biomass

Lignocellulosic biomass is the least expensive, most abundant renewable feedstock on earth, with around 200 billion tons produced annually (Zhang, 2008). It requires less input (such as water and fertilizer) per unit of biomass produced when compare with grain and crop. It is composed of three major components: cellulose, hemicelluloses, and lignin as shown in Figure 2.8.

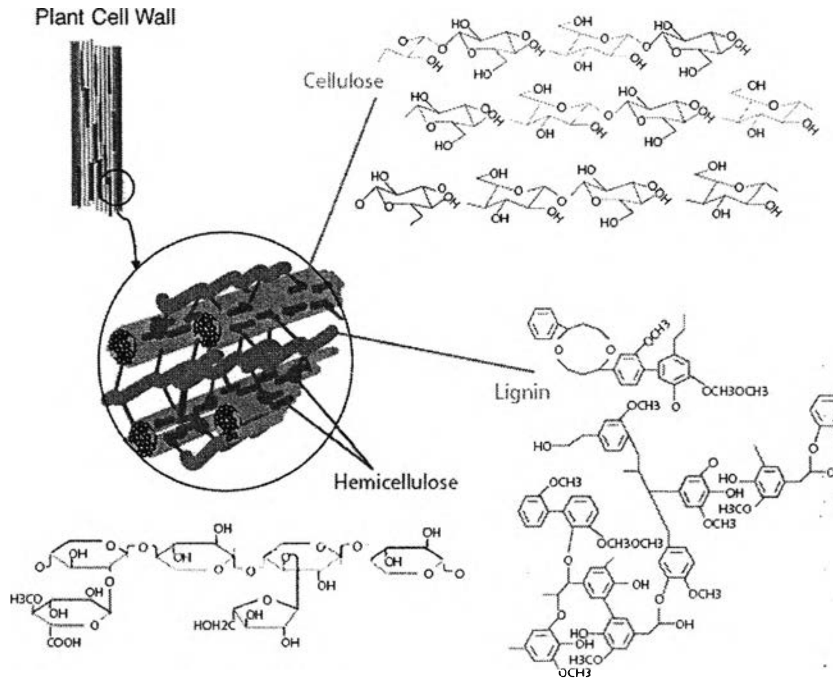



**Figure 2.8** Composition of lignocellulosic materials (Sierra *et al.*, 2008).

Cellulose is the main component of most lignocellulosic materials. It is a linear polymer of up to 27000 glucosyl residues linked by β-1,4 bonds. It is similar to starch, which is a polymer of glucose linked by α-1,4 bonds. The seemingly minor difference in linkages makes a major difference in reactivity. For the same enzyme loading, amylase hydrolyzes starch about 100 times faster than cellulase hydrolyzes cellulose. This is because the hydrogen bonds between adjacent cellulose polymers form crystalline structures that give plants structural strength, but make them particularly difficult to digest.

Hemicellulose is a highly branched and heterogeneous polymer composed primarily of pentose (xylose and arabinose), hexose (manose, glucose, and galactose), and sugar acid. It is chemically bonded to lignin and serves as an interface between the lignin and cellulose. Hemicellulose is randomly acetylated, which reduces its enzymatic reactivity.

Lignin, a polymer of phenyl propane units linked in three-dimensional structure, acts as "glue." It is a very complex molecule. A plant can be compared to fiberglass, where the cellulose is analogous to the glass fibers and the lignin serves as the epoxy resin. Chemical bonds have been reported between lignin and both cellulose, and hemicelluloses. Lignins are extremely resistant to chemical and enzymatic degradation. Biological degradation can be achieved mainly by certain fungi. The contents of cellulose, hemicelluloses, and lignin in common lignocellulosic materials are shown in Table 2.3 (Nag, 2008).

**Table 2.3** Contents of cellulose, hemicellulose, and lignin in common lignocellulosic materials

| Lignocellulosic materials | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|
| Hardwood stems | 40-75 | 10-40 | 15-25 |
| Softwood stems | 30-50 | 25-40 | 25-35 |
| Corn cobs | 45 | 35 | 15 |
| Wheat straw | 30 | 50 | 15 |
| Rice straw | 32-47 | 19-27 | 5-24 |
| Sugarcane bagasses | 40 | 24 | 25 |
| Leaves | 15-20 | 80-85 | 0 |
| Paper | 85-99 | 0 | 0-15 |
| Newspaper | 40-55 | 25-40 | 18-30 |
| Waste paper from chemical pulps | 60-70 | 10-20 | 5-10 |
| Grasses | 25-40 | 25-30 | 10-30 |

The common lignocellulosic materials are wood chips, grasses, and agricultural residues. In the US, lignocellulosic ethanol is the only viable scenario to replace 30% of US petroleum use as shown in Figure 2.9.

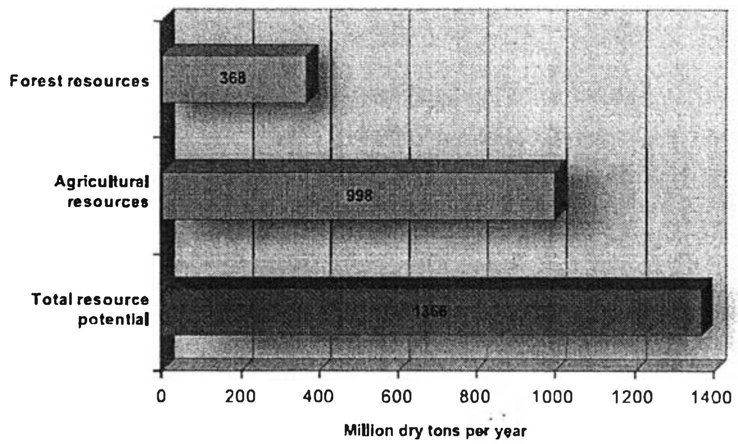



**Figure 2.9** The US annual biomass resource potential (USDE, 2005).

It can be seen that about 368 million dry tons of sustainably removable biomass could be produced on forestlands, and about 998 million dry tons could come from agricultural lands. That all of 1.3 billion tons of biomass could be produced exclusively for energy production in the United States each year. Even though, in term of heating value, it can redeem more than 50% of the crude oil consumption. However, with today best's available conversion technology, this quantity of biomass can replace about 30% as shown in Figure 2.10.

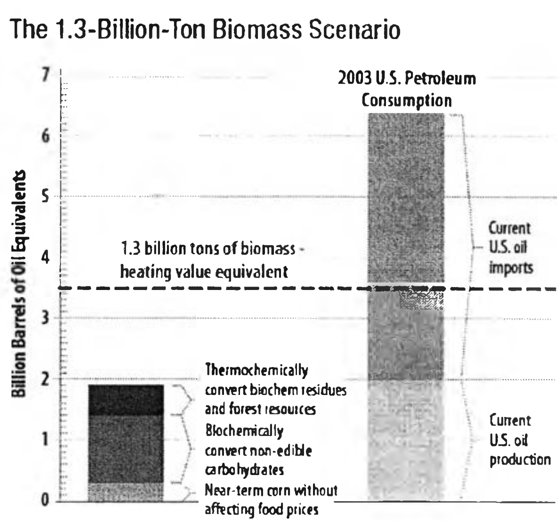



**Figure 2.10** The US biomass scenario (NREL, 2006).

### 2.4.2 Potential of Cellulosic Materials in Thailand

Thailand is agricultural country and has a lot potential of agricultural goods and also the country is one of the leading producers and exporters in the world market. The potential of lignocellulosic materials in Thailand are both forest and agricultural residues. Nowadays, more than 30% of whole Thai area is forest. However, the forest area in Thailand has decrease from 53% in last 50 years (RFD, 2009). Focusing on agricultural residues, it is a big challenge for change that residues to ethanol especially from rice, sugarcane, and cassava. All of them is the major crops and release a lot of residues. Thailand is the biggest rice exporter of the world since 1981. More than 10 million tons Thai rice export account around 35% of the world's rice market. The country is also the world's number one cassava products (chips, pellets and starch), account around 70% of the world's cassava market. Furthermore, Thailand is the second sugar exporter (10%) which comes after the giant, Brazil. Other agricultural plants, oil palm, corn, also have potentials (OAE, 2009). The potential of lignocellulosics materials in Thailand is shown in Table 2.4.

**Table 2.4** Potential of lignocellulosic materials in Thailand

| Major crops | Crop output[1] (M tons) | Type of residue | Conversion factor[2] | | Residue amount (M tons) | Available unused residue (M tons) |
|---|---|---|---|---|---|---|
| | | | CRR* | SAF** | | |
| Sugar cane | 73 | Bagasses | 0.3 | 0 | 21.9 | 0 |
| | | Trash | 0.2 | 0.8 | 14.6 | 11.68 |
| Rice | 31 | Rice straw | 1.19 | 0.5 | 36.89 | 18.45 |
| | | Rice husk | 0.23 | 0.25 | 7.13 | 1.78 |
| Oil palm | 9 | Fronds | 0.27 | 0 | 2.43 | 0 |
| | | EFB | 0.22 | 0.45 | 1.98 | 0.89 |
| | | Fiber | 0.15 | 0 | 1.35 | 0 |
| | | Shells | 0.13 | 0.25 | 1.17 | 0.29 |
| Cassava | 25 | Rhisome | 0.09 | 1 | 2.25 | 2.25 |
| | | Stalk | 0.12 | 0.3 | 3 | 0.9 |
| Corn | 4 | Corncob | 0.19 | 0.3 | 0.76 | 0.23 |

*CRR = Crops to Residue Ratio Sources: [1] OAE

**SAF = Surplus Available Factor [2] TISTR

From Table 2.4, it is clear that rice straw is the highest potential from agricultural residues with 18 M tons, followed by sugarcane trash, cassava rhizome, rice husk. The contents of cellulose, hemicellulose, and lignin from lignocellulosic materials in Thailand are shown in Table 2.5.

**Table 2.5** Contents of cellulose, hemicellulose, and lignin in Thai-based- lignocellulosic materials

| Lignocellulosic materials | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|
| Rice straw[Inoue *et al*, 2009] | 26 | 16 | 4 |
| Cassava rhizome[Pattiya *et al*, 2007] | 28 | 40 | 22 |
| Cassava stalk[Kingsuwannarat, 2002] | 32 | 14 | 27 |
| Sugarcane bagasse[TRE, 2009] | 44 | 29 | 27 |
| Sugarcane trash[Singh *et al*, 2007] | 40 | 25 | 18-20 |
| Jatropha [Gunaseelan *et al*, 2009] | 33 | *NA* | *NA* |
| Oil palm fronds[Wanrosli *et a*, 2007] | 47 | 35 | 15 |
| Oil palm EFB[Alriols *et a*, 2009] | 37 | 24 | 24 |

2.4.3 Ethanol Plant in Thailand

There are 17 ethanol plants operating in commercial scale in Thailand as shown in Table 2.6 (DEDE, 2009). The total production capacity is 2,575,000 liters per day. They use sugarcane molasses and cassava as raw materials. There is only one plant using lignocellulosic materials. Thai Roong Ruang Energy or TRE locates in Saraburi. The co-production of ethanol from sugarcane molasses and sugarcane bagasse produces ethanol 120,000 liters per day.

**Table 2.6** List of ethanol plants in Thailand

| No. | Plant | Site | Raw materials | Production Capacity (l/d) |
|---|---|---|---|---|
| 1 | PawnWilai International Group Trading Co.ltd | Ayuddhaya | Molasses/ Cassava | 25,000 |
| 2 | Thai Alcohol Plc | Nakorn Pathom | Molasses | 200,000 |
| 3 | Thai Agro Energy Plc | Suphanburi | Molasses | 150,000 |
| 4 | Thai Nguan Ethanol Plc | KhonKhen | Cassava | 130,000 |
| 5 | KhonKhen Alcohol Co.ltd | KhonKhen | Molasses | 150,000 |
| 6 | Petro Green Co.ltd (Chaiyaphoom) | Chaiyaphoom | Molasses/ Sugarcane Juice | 200,000 |
| 7 | Thai Sugar Ethanol Co.ltd | Kanchanaburi | Molasses | 100,000 |
| 8 | KI Ethanol Co.ltd | Nakorn Ratchasima | Molasses | 100,000 |
| 9 | Petro Green Co.ltd (Kalaseen) | Kanlaseen | Molasses/ Sugarcane Juice | 200,000 |
| 10 | Ekaratpathana Co.ltd | Nakorn Swan | Molasses | 200,000 |
| 11 | Thai Roong Ruang Energy Co.ltd (TRE) | Saraburi | Molasses/ Bagasse | 120,000 |
| 12 | Ratchburi Ethanol Co.ltd | Ratchburi | Molasses/ Cassava | 150,000 |
| 13 | ES Power Co.ltd | Sakaew | Molasses/ Cassava | 150,000 |
| 14 | MaeSawd Clean Energy Co.ltd | Tak | Sugarcane Juice | 200,000 |
| 15 | SupThip Co.ltd | Lopburii | Cassava | 200,000 |
| 16 | ThayPing Ethanol Co.ltd | Sakaew | Cassava | 150,000 |
| 17 | PSC Starch Production Plc | Chonburi | Cassava | 150,000 |
| | Total Capacity | | | 2,575,000 |

*2.4.3.1 TRE Ethanol Production*

TRE ethanol plant is called "The Model Project for Ethanol Production from Molasses and Bagasse in the Sugar Factory in Thailand" operated under the collaboration of New Energy and Industrial Energy Development Organization (NEDO), Japan and Office of Cane and Sugar Board (OCSB), Thailand. This model project aims to introduce technology for producing ethanol as a transport fuel from sugarcane bagasse (plant residue from the sugarcane refining process) and sugarcane molasses (syrup produced during the sugar refining process). These resources have not been effectively used in the past by Thailand's sugar refining industry, a key industry in the country. The main operations of TRE plant are shown in Figure 2.11.

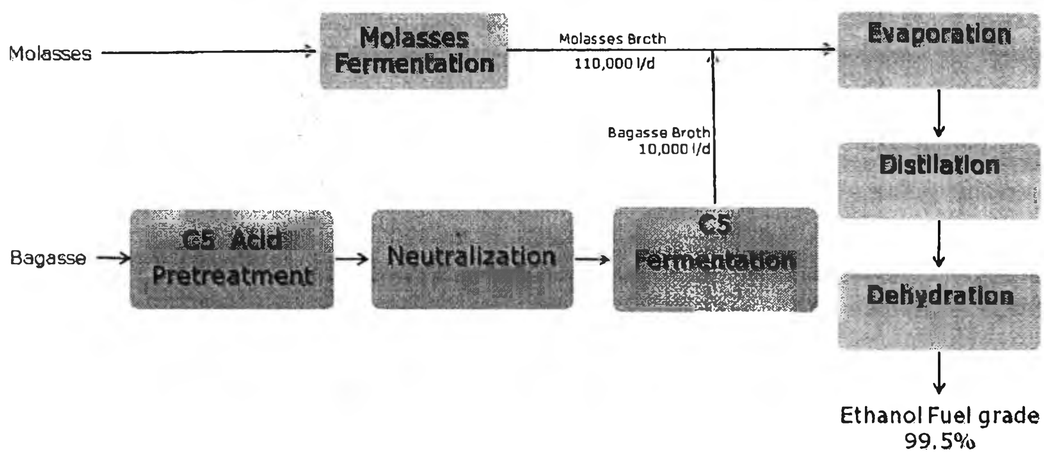



**Figure 2.11** The main operations of TRE plant.

Sugarcane molasses go to molasses fermentation by yeast directly while sugarcane bagasse passes though C5 acid pretreatment, neutralization, and C5 fermentation by micro organism. And then those two broths are inline mixed. After that, the mixed broth is passed though ethanol recovery section, which are evaporation, distillation, and dehydration (OCSB, 2009).

## 2.5 Sustainability Analysis

### 2.5.1 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 2.12 (Delhigreens, 2009).

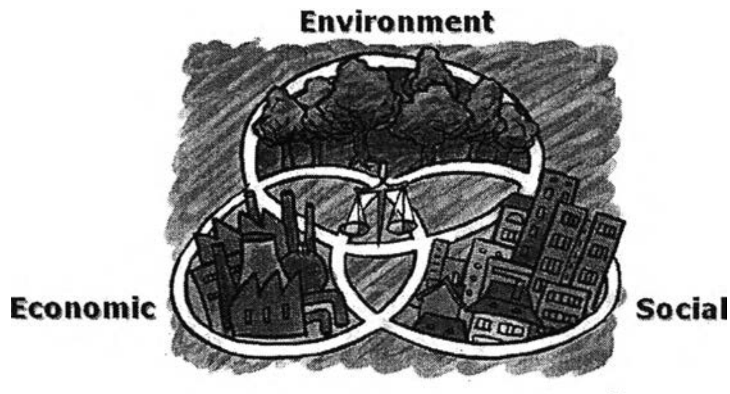



**Figure 2.12** Sustainable development concept.

2.5.2 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 2.13 (Carvalho *et al.*, 2008, 2009).

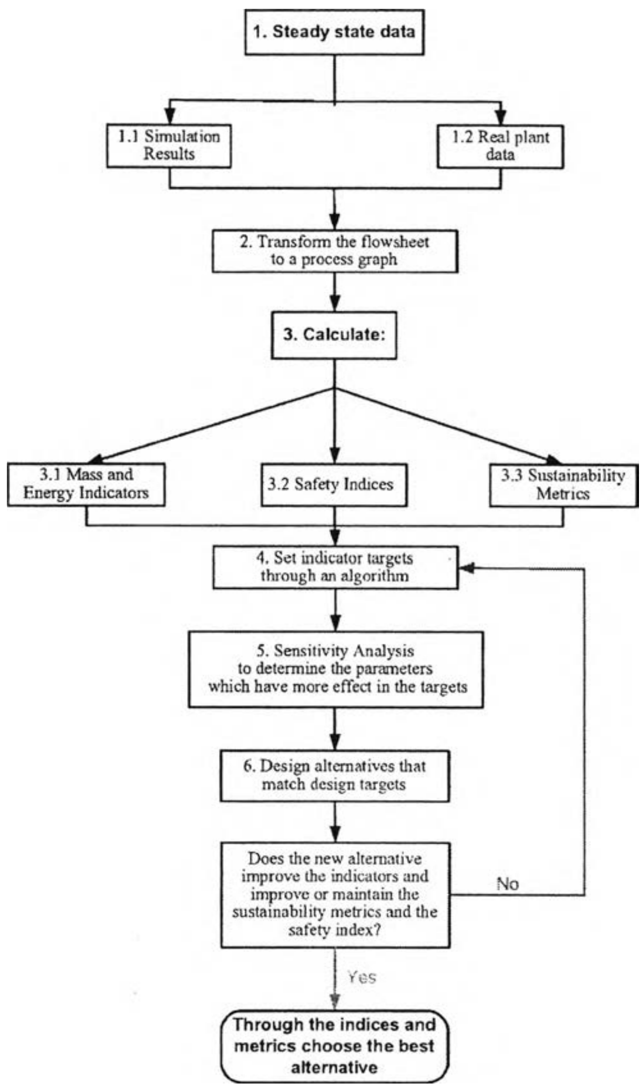



**Figure 2.13** The systematic methodology in SustainPro (Terra, 2008).

*2.5.2.1 Collect 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).

*2.5.2.2 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.

*2.5.2.3 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.

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

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.

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

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:

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

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:

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

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.

**Table 2.7** 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 2.14, 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.

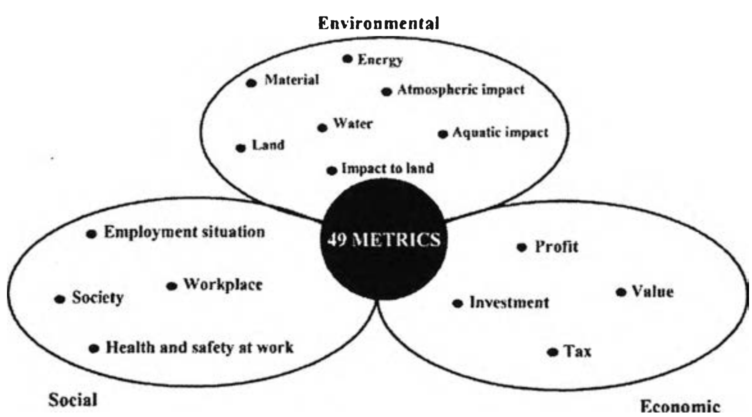



**Figure 2.14** Example of the sustainability metrics (Carvalho *et al.*, 2008).

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 2.8** 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 2.9** 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.

*2.5.2.4 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, the better as shown in Figure 2.15.

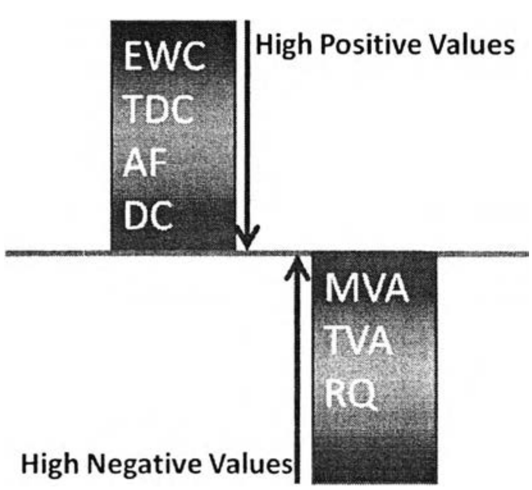



**Figure 2.15** The target improvement for the indicators.

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.

*2.5.2.5 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.

*2.5.2.6 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.

2.5.3 Sustainability Analysis Study on Bioethanol

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 and SustainPro was used to perform the sustainability analysis.

*2.5.3.1 Process Simulation*

The base case process was based on NREL process (Wooley *et al.*, 1999). The main operations of the process are shown in PRO/II flowsheets in Figure 2.16.

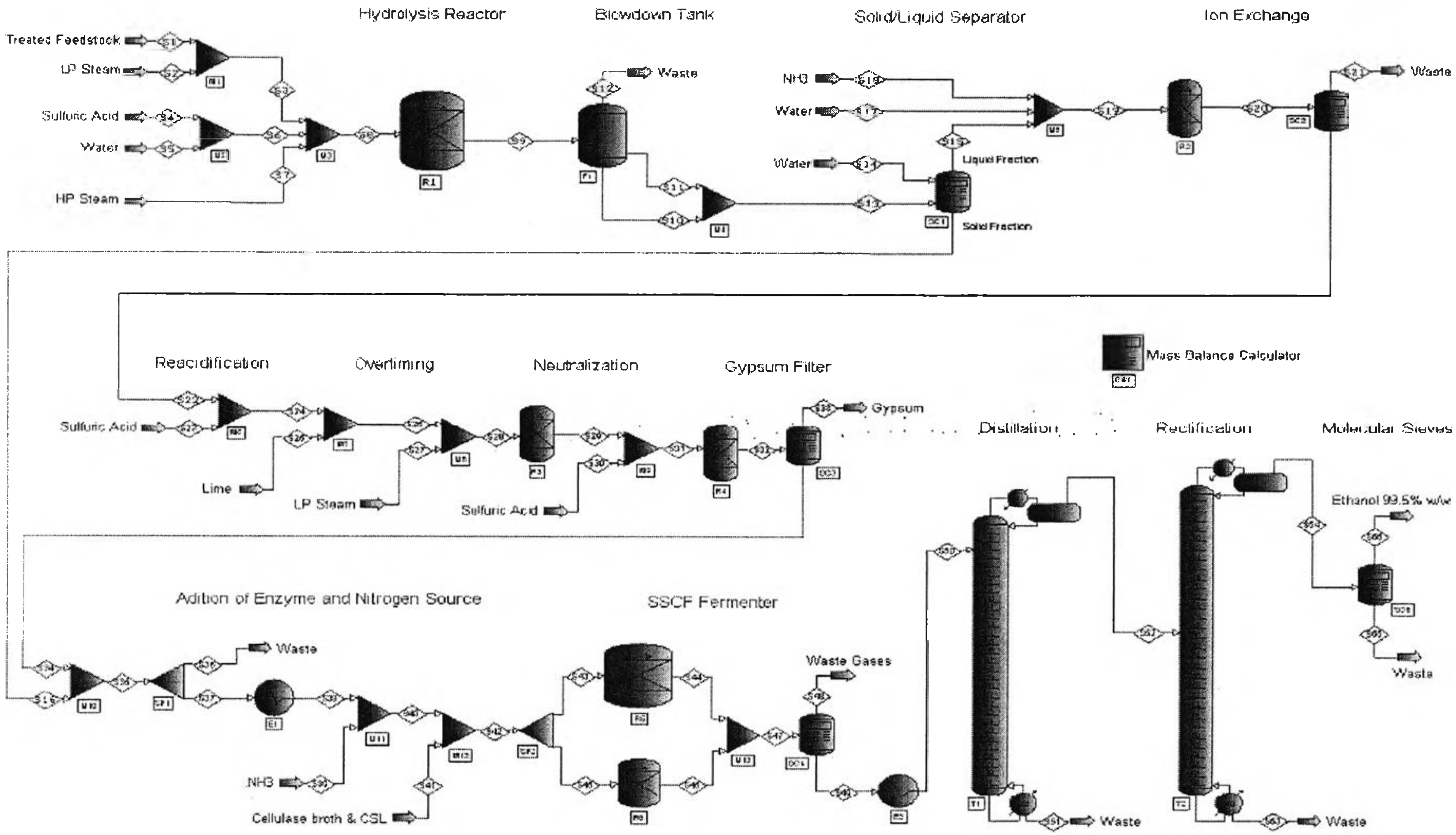



**Figure 2.16** Lignocellulosic-based bioethanol process flow sheet (Mareles *et al.*, 2008).

### 2.5.3.2 *Sustainability Analysis*

SustainPro was used to perform sustainability analysis on base case process. The new design alternative was generated based on SustainPro's results. The comparison of indicators between base case design and new design is shown in Table 2.10.

**Table 2.10** The comparison of indicators between base case design and new design (Morales *et al.*, 2008)

| Path | MVA | Prob. | Path | EWC | Prob. | Path | TVA | Prob. |
|---|---|---|---|---|---|---|---|---|
| OP 1297-new $H_2O$-61-58 | -6.1 | High | OP 1297 $H_2O$-61-58 | 288.5 | High | OP 1297 $H_2O$-61-58 | -294.6 | High |
| OP 1807-base $H_2O$-14-51 | -107.2 | High | OP 1807 $H_2O$-14-51 | 8084.3 | High | OP 1807 $H_2O$-14-51 | -8191.6 | High |

The new value the OPs for the MVA, TVA and EWC indicators was reduced after the recycle of water back to the system. The less negative of MVA and TVA, the less money they pay for material. The less positive of EWC, the less money they pay for energy.

## 2.6 Life Cycle Assessment (LCA)

### 2.6.1 Overview

Life cycle assessment (LCA) is a method for determining the environmental impact of a product (good or service) during its entire life cycle—from extraction of raw materials through manufacturing, logistics and use to scrapping and recycling. In LCA substantially broader environmental aspects can be covered, ranging from GHG emissions and fossil resource depletion to acidification and toxicity aspects, hence it is a good tool for quantifying environmental impacts of a defined product system. However, LCA as it stands has its limitations such as the difficulties in data acquisition and validation, and the misleading results due to the choice of methodology especially on allocation issues. Figure 2.17 illustrates the life cycle of biofuels involving $CO_2$ emission.

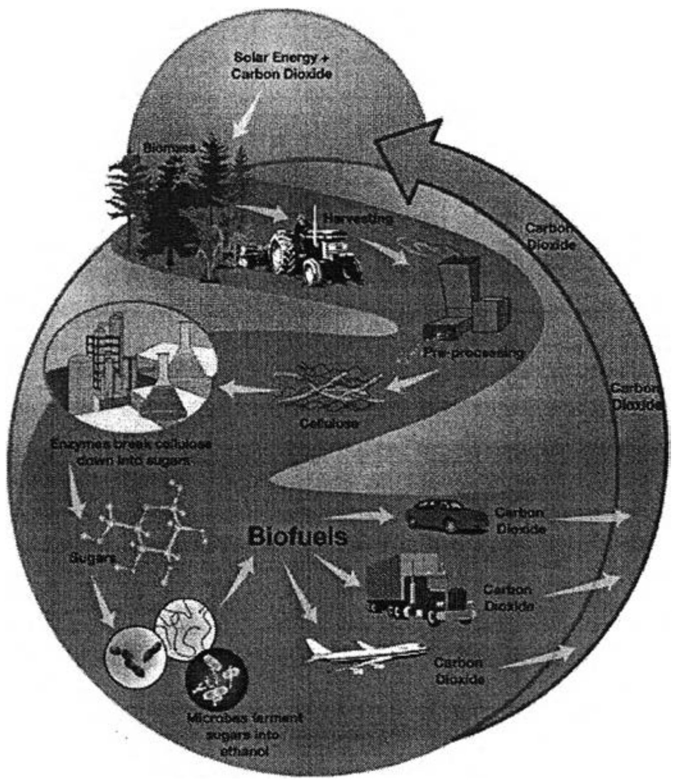



**Figure 2.17** Life cycle of biofuels (source: www.alternative-energy-news.info/images/technical/biofuel-conversion.jpg).

In the case of petroleum-derived fuels, this means LCA includes everything from the time the oil is extracted from the ground, transported to the refinery, made into fuel and distributed to your local gas station. This is also known as a Well-to-Wheels Study because it starts at the oil well and ends at the wheels - or more specifically the tailpipe of your car or truck.

For a crop like corn ethanol, the LCA is much more complex. Tracking of the energy and emissions it takes to plant the corn, and make the fuels, fertilizers, and pesticides to grow the corn. Estimating whether growing the corn increases or decreases carbon in the soil. Appraising how much fuel it takes to get the corn to the ethanol refinery and how much energy is consumed and the amount of emissions that are generated in the bioethanol plant. Corn ethanol refineries typically make a co-product called distillers grain, which is a high-protein feed for cattle. This production is counted as a credit in our accounting spreadsheet. It also includes the impact of getting ethanol to the service station by rail and truck.

2.6.2 Definition of LCA

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

2.6.3 Methodology

The LCA framework was standardized by the International Organization for Standardization (ISO), and it is constituted by four elements:

*2.6.3.1 Goal and Scope*

The first step is where the intention of the use of LCA is defined, and where the setting of the boundaries for the product system takes place. Through these are also defined the technological and temporal scope, as well as the assessment parameters. The system is quantified in the functional unit which is the function or service that determines the reference flow of products. For instance a packaging study might choose to define the functional unit as —packaging of 1000 liters of milk in containers of 1 litre. Taking this, the relevant significant comparison can be between 1000 carton boxes and 40 returnable polycarbonate bottles, which can be used in average 25 times. Usually what LCA does is compare different ways of obtaining the same function. Therefore in order to guarantee fairness and relevance it is crucial to be comparing between product systems that actually provide the same function, being this assured through carefully defining the functional unit. This step follows ISO 14040.

*2.6.3.2 Inventory Analysis*

This step is where all the necessary input and output data for the processes regarding the product system is gathered. These gathered data are related with the reference flow given by the functional unit. Typically the data for the different processes is combined over the life cycle and presented as the total emissions of a substance or total use of a resource. This step follows ISO 14041.

*2.6.3.3 LCIA*

The third step was referred previously means life cycle impact assessment (LCIA), has the purpose of translating the inventory data on input (materials and resources) and output (waste and emissions) into information regarding the impacts the product system has on the environment, human health, and resources. This step follows ISO 14042.

*2.6.3.4 Interpretation*

The last step is where the results from the previous step will be related with the goal of the study. In order to quantify the results sensitivity and uncertainty are also analyzed in this step. This step follows ISO 14043.

The relationships of these elements are illustrated in Figure 2.18.

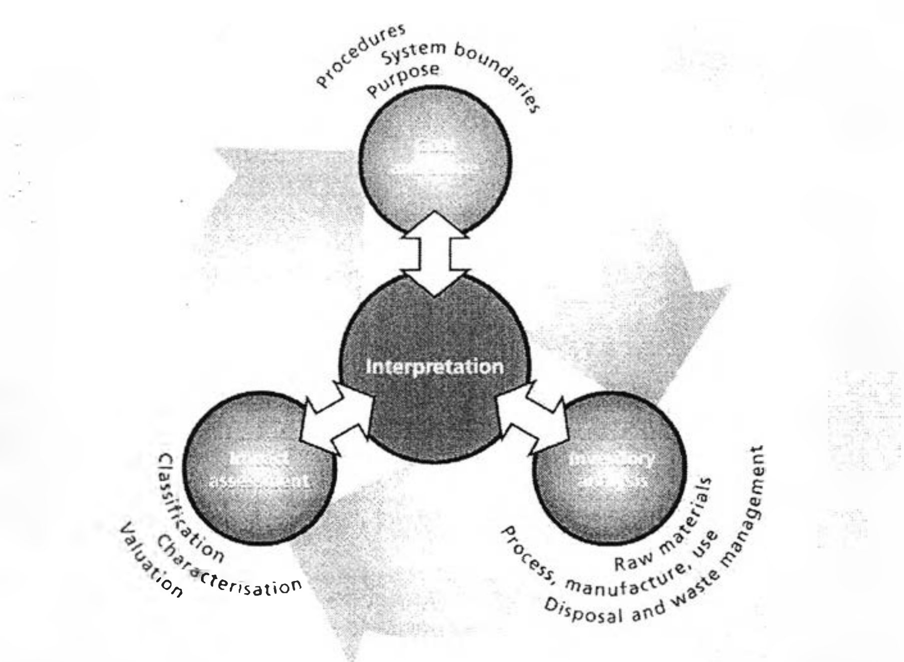



**Figure 2.18** Life cycle assessment framework
(source: http://www.tangram.co.uk/TI-LCA_Introduction.html).

2.6.4 LCA Studies on Bioethanol

Since bioethanol has become the new challenge on the reduction of fossil resource use and greenhouse effect. Many research teams have conducted the LCA on bioethanol in various materials including sugar, starchy, and lignocellulosic materials.

In 2007, Nguyen *et al.* worked on the life cycle assessment of cassava utilization for fuel ethanol in Thailand. His study shows the positive impacts of using cassava-based ethanol on fossil energy use and greenhouse 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 2.11.

**Table 2.11** Greenhouse 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 is shown 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).

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 2.19.

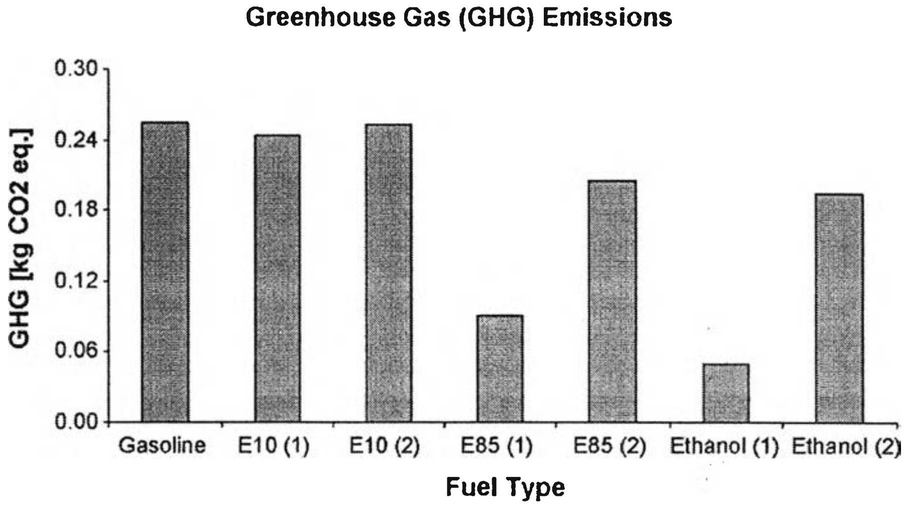



**Figure 2.19** Greenhouse gas emission per one kilometer driving (Luo *et al.*, 2009).

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.

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 2.12.

**Table 2.12** The 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 results show 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.

In 2009, González-García and coworkers studied on the Life cycle assessment of flax shives in Spain. They compare the emission in difference allocation method, economic and mass. Three scenarios (EA1, EA2 and EA3) based on economic allocation were evaluated according to the large difference in the market prices (from 15 to 36 €/ton regardless of their final destination). Mass allocation (scenario MA) was also assumed in order to estimate the effect of allocation. The comparison of global warming potential in difference allocation methods are shown in Figure 2.20.

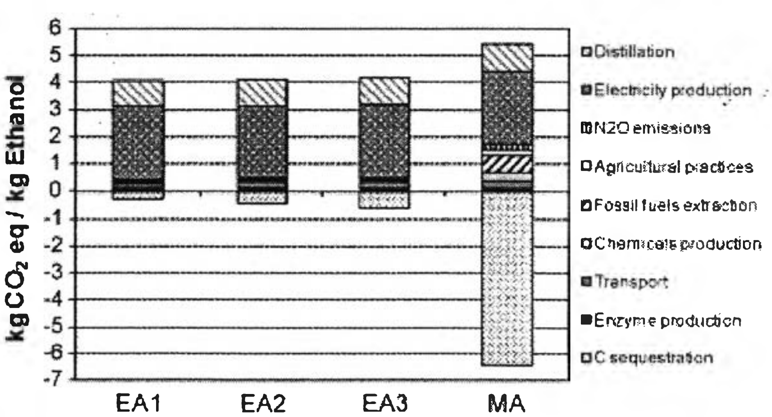



**Figure 2.20** The comparison (between allocation factor) of $CO_2$ equivalent emission for ethanol production and main process involved (González-García *et al.*, 2009).

Activities related to the ethanol conversion plant, such as distillation and electricity production, are the main hot spots in this impact category. In addition, when mass allocation is assumed, there is a remarkable contribution from fossil fuel extraction due to a higher amount of diesel from agricultural machineries being allocated to the flax shives. Moreover, it is important to remark the positive effect of the carbon sequestered during crop growth (9.9 ton $CO_2$/ha), which contributes to offset the GHG emissions. This effect is more outstanding in the mass allocation (highest allocation factor) since more $CO_2$ taken up during the crop growing is allocated to flax shives.