



## **CHAPTER II**

### **THEORETICAL BACKGROUND AND LITERATURE REVIEW**

#### **2.1 History of Life Cycle Assessment (LCA)**

LCA first took off in 1990, although the first LCA was carried out in the late 1960's on a Coke Cola can. Originally these were called Resource and Environmental Profile Analysis (REPA) studies. REPA looked at resource use and environmental releases of a product. In the late 80's a few were carried out, by 1993 this had risen to 180 studies carried out by 16 research groups. A typical analysis takes about 4-5 man months, mainly due to lack of availability of basic input data, (rather a case of reinventing the wheel).

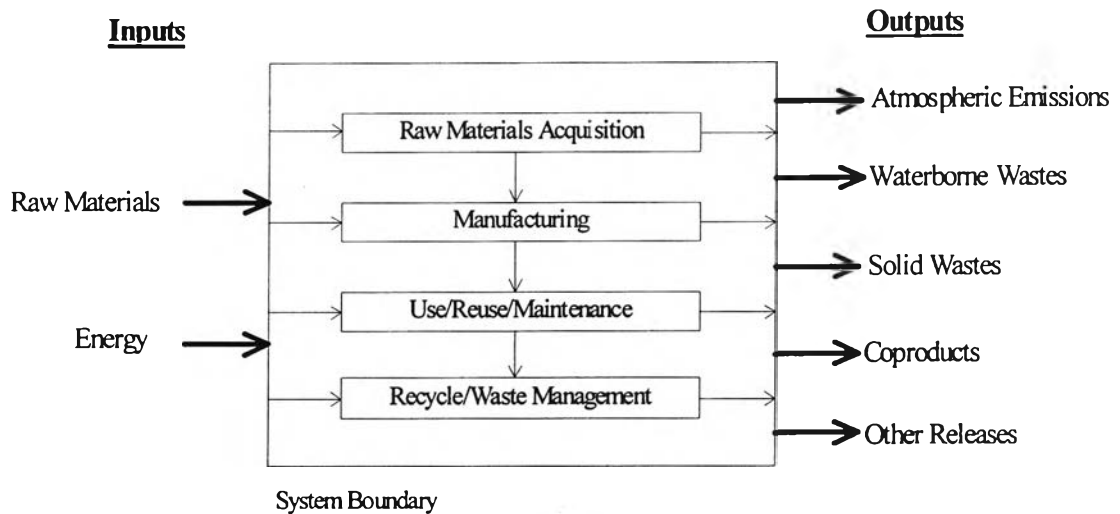
The Society of Environmental Toxicology and Chemistry (SETAC) works to develop broad consensus on the conduct of LCA which was initiated in 1990. A Society for the Promotion of Life Cycle Development (SPOLD) has been set up, SPOLD- members include Dow Chemical, Norsk Hydro, Proctor and Gamble and Unilever. It aims to promote the development of LCA as a scientific tool and to use the results for inputs into discussions concerning legislation such as eco-labeling.

#### **2.2 Life Cycle Assessment (LCA) Definition**

Life cycle assessment (LCA) is a method for assessing the environmental aspects and potential impacts associated with a product. LCA studies the environment aspects and potential impacts throughout a product's life (i.e. cradle-to-grave) from raw material acquisition through production, use, and disposal (ISO).

LCA is a technique for assessing all the inputs and outputs of a product, process, or service (Life Cycle Inventory); assessing the associated wastes, human health and ecological burdens (Impact Assessment); and interpreting and communicating the results of the assessment (Life Cycle Interpretation) throughout the life cycle of the products or processes under review. The term "life cycle" refers to the major activities in the course of the product's life-span from its manufacture, use, maintenance, and final disposal; including the raw material acquisition required

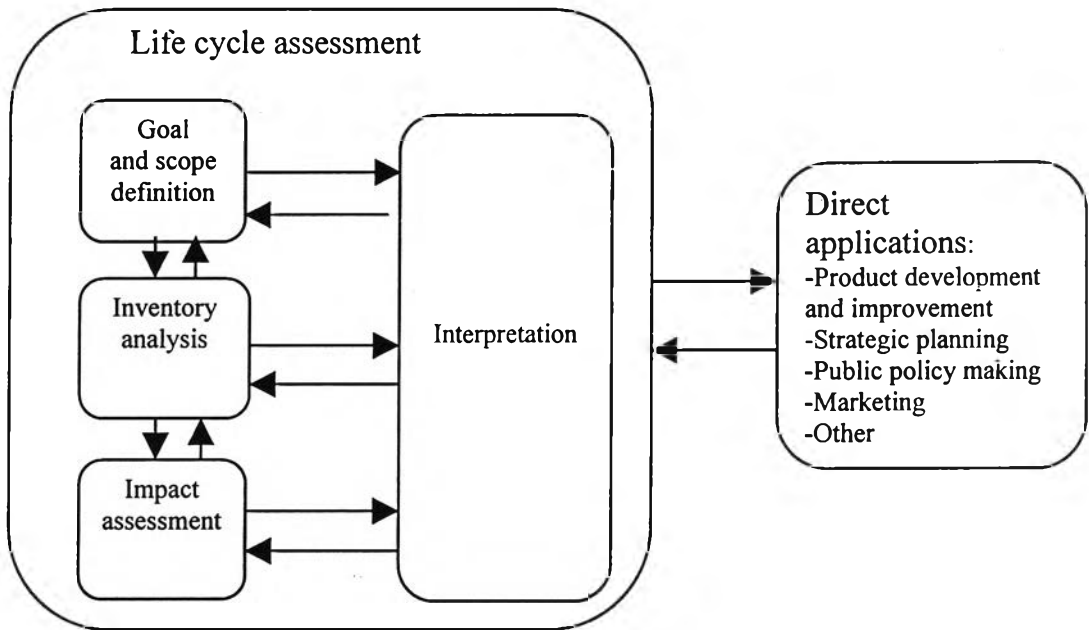
to manufacture the product. Figure 2.1 illustrates the possible life cycle stages that can be considered in an LCA and the typical inputs/outputs measured.



**Figure 2.1** LCA frameworks (US. EPA, 1993).

### 2.3 LCA Method

The method of LCA is now being standardized as ISO 140040 series. According to ISO 14040, LCA framework consists of 4 elements: Goal and Scope Definition, Inventory Analysis, Impact Assessment, and Interpretation as illustrated in Figure 2.2.



**Figure 2.2** Phases of a LCA (ISO, 1997).

### 1. Goal and Scope definition

Goal and Scope definition is the phase of the LCA process that defines and describes the product, process or activity. Establish the context in which the assessment is to be made and identify the boundaries and environmental effects to be reviewed for the assessment.

### 2. Inventory Analysis

Inventory Analysis is the phase for identify and quantify energy, water and materials usage and environmental releases (e.g., air emissions, solid waste disposal, wastewater discharge). It can be used in various ways. It can assist an organization in comparing products or processes and considering environmental factors<sup>8</sup> in material selection. In addition, inventory analyses can be used in policy-making, by helping the government develop regulations regarding resource use and environmental emissions.

### 3. Impact Assessment

The impact assessment can be expressed as a “quantitative and/or qualitative process to characterize and assess the effects of the environmental interventions identified in the inventory table” (Heijungs & Hofstetter, 1996). Impact

Assessment is the phase evaluate of potential human health and environmental impacts of the environmental resources and releases identified during the life cycle inventory (LCI). A life cycle impact assessment attempts to establish a linkage between the product or process and its potential environmental impacts. The impact assessment component consists in principle of the following three or four elements: classification, characterization, normalization, and valuation; normalization, and valuation are sometimes merged. Valuation is proposed changed to weighting by ISO (ISO, 1997c) and this terminology has been adapted by the SETAC-Europe working group (Udo de Haes, 1996a).

The life cycle impact assessment involves as a first element the definition of the impact categories to be considered (ISO, 1997c). This is a follow-up of the decisions made in the goal and scoping phase. Based on the type of information collected in the inventory phase the boundaries defined in the goal and scoping may be redefined. The examples of impact categories considered are:

- Global warming
- Acidification
- Stratospheric ozone depletion
- Photochemical oxidant formation
- Ecotoxicological impacts
- Eutrophication
- Etc.

The life cycle impact assessment includes as a second element classification of the inventory input and output data (ISO, 1997c). The classification element aims to assign inventory input and output data to categories. The third element of life cycle impact assessment includes characterization of the inventory data. Characterization is mainly a quantitative step based on scientific analysis of the relevant environmental processes. The characterization has to assign the relative contribution of each input and output to the selected impact categories. The potential contribution of each input and output to the environmental impacts has to be estimated. For some of the environmental impact categories there is consensus about equivalency factors to be used in the estimation of the total impact (e.g. global warming potentials, ozone depletion potentials etc.) whereas equivalence factors for

other environmental impacts are not available at consensus level (e.g. biotic resources, land use etc.). This is called characterization factor. Characterization factor (exposure factor, effect factor, exposure-effect factor, equivalence factor) is a factor which expresses the contribution of a unit environmental intervention (such as the atmospheric emission of 1 kg CFC-11) to the chosen impact categories (such as global warming and ozone depletion). The examples of Equivalence factors for relevant inputs and outputs to the impact categories will be presented in Tables 2.1 to 2.3.

Global warming - or the “greenhouse effect” - is the effect of increasing temperature in the lower atmosphere. The potential global warming or greenhouse effect is normally quantified by using global warming potentials (GWP) for substances having the same effect as CO<sub>2</sub> in reflection of heat radiation. GWP for greenhouse gases are expressed as CO<sub>2</sub>-equivalents i.e. their effects are expressed relatively to the effect of CO<sub>2</sub>. Global warming potentials are developed by the “Intergovernmental Panel on Climatic Change” (IPCC) for a number of substances (Albritton et al., 1996). GWPs are normally based on modeling and are quantified for time horizons of 20, 100 or 500 years for a number of known greenhouse gasses (e.g. CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CFCs, HCFCs, HFCs and several halogenated hydrocarbons etc.) as shown in Table 2.1.

Acidification is caused by releases of protons in the terrestrial or aquatic ecosystems. The potential effects are strongly dependent on the nature of the receiving ecosystem e.g. nitrogen oxides (NO<sub>x</sub>) can be fixed in the ecosystem due to uptake in plants. This problem can be managed by using two scenarios as suggested by Lindfors *et al.* (1995a). In the two scenarios the acidification potential from NO<sub>x</sub> and NH<sub>3</sub> are calculated as zero and as the theoretical maximum value respectively. Lindfors *et al.* (1995c) recommend that the following substances should be considered: SO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub> and HCl but also other substances having a proton releasing effect have to be considered (i.e. other sulfur compounds and other acids). The acidification potential (AP) can be estimated as SO<sub>2</sub> equivalents or as mole hydrogen (H<sup>+</sup>). The acidification potentials for acidifying substances are given in Table 2.2.

Decomposition of the stratospheric ozone layer will cause increased incoming UV radiation leading to impacts on humans such as increased levels of e.g. skin cancer, cataracts and decreased immune defense, but also impacts on natural organisms and ecosystems e.g. plankton in the South Pole region, where the decomposition of the ozone layer is already significant. The decomposition of ozone is enhanced by the stratospheric input of anthropogenic halogenated compounds (e.g. CFCs, HCFCs, halons etc.). Ozone depletion potentials (ODP) have been presented by the World Meteorological Organization (WMO) for a number of halogenated compounds (Solomon & Wuebbles, 1995; Pyle *et al.*, 1991). The ODPs are given as CFC-11 equivalents. ODPs are presented in Table 2.3 for CFCs, HCFCs and halons.

**Table 2.1** Global warming potentials (GWP) given in kg CO<sub>2</sub>-eq./kg gas (Albritton *et al.*, 1996)

Substance	Formula	GWP, 20 years	GWP, 100 years	GWP, 500 years	Life time, years
Carbon dioxide	CO <sub>2</sub>	1	1	1	150
Methane	CH <sub>4</sub>	62	25	7.5	10
Nitrogen dioxide	NO <sub>2</sub>	290	320	180	120
Tetrachloromethane	CCl <sub>4</sub>	2,000	1,400	500	42
Trichloromethane	CHCl <sub>3</sub>	15	5	1	0.55
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	28	9	3	0.41
Chloromethane	CH <sub>3</sub> Cl	92	25	9	0.7
1,1,1-Trichloroethane	CH <sub>3</sub> CCl <sub>3</sub>	360	110	35	5.4
Tetrafluoromethane	CF <sub>4</sub>	4,100	6,300	9,800	50,000
Hexafluoroethane	C <sub>2</sub> F <sub>6</sub>	8,200	12,500	19,100	10,000
CFC-11	CFCl <sub>3</sub>	5,000	4,000	1,400	50
CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	7,900	8,500	4,200	102
CFC-13	CF <sub>3</sub> Cl	8,100	11,700	13,600	640
CFC-113	CF <sub>2</sub> ClCFCl <sub>2</sub>	5,000	5,000	2,300	85

**Table 2.1** Global warming potentials (GWP) given in kg CO<sub>2</sub>-eq./kg gas (Albritton *et al.*, 1996) (Continued)

Substance	Formula	GWP, 20 years	GWP, 100 years	GWP, 500 years	Life time, years
CFC-114	CF <sub>2</sub> ClCF <sub>2</sub> Cl	6,900	9,300	8,300	300
CFC-115	CF <sub>2</sub> ClCF <sub>3</sub>	6,200	9,300	13,000	1,700
HCFC-22	CHF <sub>2</sub> Cl	4,300	1,700	520	13
HCFC-123	CF <sub>3</sub> CHCl <sub>2</sub>	300	93	29	1.4
HCFC-124	CF <sub>3</sub> CHFCl	1,500	480	150	5.9
HCFC-141b	CFCl <sub>2</sub> CH <sub>3</sub>	1,800	630	200	9.4
HCFC-142b	CF <sub>2</sub> ClCH <sub>3</sub>	4,200	2,000	630	19.5
HCFC-225ca	C <sub>3</sub> F <sub>5</sub> HCl <sub>2</sub>	550	170	52	2.5
HCFC-225cb	C <sub>3</sub> F <sub>5</sub> HCl <sub>2</sub>	1,700	530	170	6.6
HFC-23	CHF <sub>3</sub>	9,200	12,100	9,900	250
HFC-32	CH <sub>2</sub> F <sub>2</sub>	1,800	580	180	6
HFC-43-10me	C <sub>5</sub> H <sub>2</sub> F <sub>10</sub>	3,300	1,600	520	21
HFC-125	CF <sub>3</sub> CHF <sub>2</sub>	4,800	3,200	1,100	36
HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	3,100	1,200	370	12
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	3,300	1,300	420	14
HFC-143	CHF <sub>2</sub> CH <sub>2</sub> F	950	290	90	3.5
HFC-143	CF <sub>3</sub> CH <sub>3</sub>	5,200	4,400	1,600	55
HFC-152a	CHF <sub>2</sub> CH <sub>3</sub>	460	140	44	1.5
HFC-227ea	C <sub>3</sub> HF <sub>7</sub>	4,500	3,300	1,100	41
HFC-236fa	C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	6,100	8,000	6,600	250
HFC-245ca	C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	1,900	610	190	7
Halon 1301	CF <sub>3</sub> Br	6,200	5,600	2,200	65

**Table 2.1** Global warming potentials (GWP) given in kg CO<sub>2</sub>-eq./kg gas (Albritton *et al.*, 1996) (Continued)

Substance	Formula	GWP, 20 years	GWP, 100 years	GWP, 500 years	Life time, years
Sulfur hexafluoride	SF <sub>6</sub>	16,500	24,900	36,500	3,200
Carbon monoxide	CO	-	-	-	months
non-Methane VOC	-	-	-	-	days-months
Nitrogen oxides	NOx	-	-	-	days

**Table 2.2** Acidification potentials for acidifying substances (Hauschild & Wenzel, 1997d)

Substance	Formula	Reaction	Molar g/mole	weight AP kg SO <sub>2</sub> /kg
Sulfur dioxide	SO <sub>2</sub>	SO <sub>2</sub> +H <sub>2</sub> O⇌H <sub>2</sub> SO <sub>3</sub> ⇌2H <sup>+</sup> +SO <sub>3</sub> <sup>2-</sup>	64.06	1
Sulfur trioxide	SO <sub>3</sub>	SO <sub>3</sub> +H <sub>2</sub> O⇌H <sub>2</sub> SO <sub>4</sub> ⇌2H <sup>+</sup> +SO <sub>4</sub> <sup>2-</sup>	80.06	0.80
Nitrogen dioxide	NO <sub>2</sub>	NO <sub>2</sub> +½H <sub>2</sub> O+1/4O <sub>2</sub> ⇌H <sup>+</sup> +NO <sub>3</sub> H <sup>-</sup>	46.01	0.70
Nitrogen oxide	NO	NO+O <sub>3</sub> +½H <sub>2</sub> O⇌H <sup>+</sup> +NO <sub>3</sub> <sup>-</sup> +3/4O <sub>2</sub>	30.01	1.07
Hydrogen chloride	HCl	HCl⇌H <sup>+</sup> +Cl <sup>-</sup>	36.46	0.88
Hydrogen nitrate	HNO <sub>3</sub>	HNO <sub>3</sub> ⇌H <sup>+</sup> +NO <sub>3</sub> <sup>-</sup>	63.01	0.51
Hydrogen sulfate	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub> ⇌2H <sup>+</sup> +SO <sub>4</sub> <sup>2+</sup>	98.07	0.65
Hydrogen phosphate	H <sub>3</sub> PO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub> ⇌3H <sup>+</sup> +PO <sub>4</sub> <sup>3-</sup>	98.00	0.98
Hydrogen fluoride	HF	HF⇌H <sup>+</sup> +F <sup>-</sup>	20.01	1.60
Hydrogen sulfide	H <sub>2</sub> S	H <sub>2</sub> S+3/2O <sub>2</sub> +H <sub>2</sub> O⇌2H <sup>+</sup> +SO <sub>3</sub> <sup>2-</sup>	34.03	1.88
Ammonium	NH <sub>3</sub>	NH <sub>3</sub> +2O <sub>2</sub> ⇌H <sup>+</sup> +NO <sub>3</sub> <sup>-</sup> +H <sub>2</sub> O	17.03	1.88



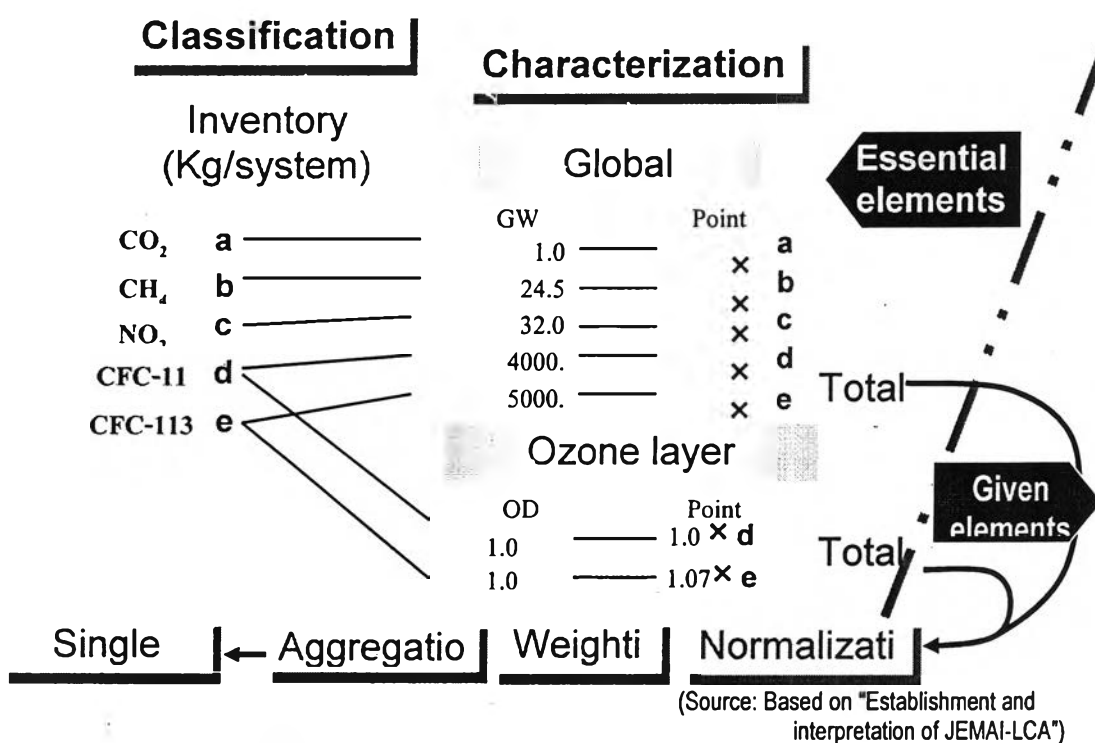
**Table 2.3** Ozone depletion potentials (ODP) given in kg CFC-11 equivalents/kg gas (Solomon & Wuebbles, 1995; Pyle *et al.*, 1991; Solomon & Albritton, 1992)

Substance	Formula	Life time,	Total ODP
CFC-11	CFCl <sub>3</sub>	50±5	1.00
CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	102	0.82
CFC-113	C CF <sub>2</sub> ClCFCl <sub>2</sub>	85	0.90
FC-114	CF <sub>2</sub> ClCF <sub>2</sub> Cl	300	0.85
CFC-115	CF <sub>2</sub> ClCF <sub>3</sub>	1,700	0.40
Tetrachloromethane	CCl <sub>4</sub>	42	1.20
HCFC-22	CHF <sub>2</sub> Cl	13.3	0.04
HCFC-123	CF <sub>3</sub> CHCl <sub>2</sub>	1.4	0.014
HCFC-124	CF <sub>3</sub> CHFCl	5.9	0.03
HCFC-141b	CFCl <sub>2</sub> CH <sub>3</sub>	9.4	0.10
HCFC-142b	CF <sub>2</sub> ClCH <sub>3</sub>	19.5	0.05
HCFC-225ca	C <sub>3</sub> F <sub>5</sub> HCl <sub>2</sub>	2.5	0.02
HCFC-225cb	C <sub>3</sub> F <sub>5</sub> HCl <sub>2</sub>	6.6	0.02
1,1,1-Trichlorethan	CH <sub>3</sub> CCl <sub>3</sub>	5.4±0.4	0.12
Halon 1301	CF <sub>3</sub> Br	65	12
Halon 1211	CF <sub>2</sub> ClBr	20	5.1
Halon 1202	CF <sub>2</sub> Br <sub>2</sub>		~1.25
Halon 2402	CF <sub>2</sub> BrCF <sub>2</sub> Br	25	~7
HBFC 1201	CF <sub>2</sub> HBr		~1.4
HBFC 2401	CF <sub>3</sub> CHBr		~0.25
HBFC 2311	CF <sub>3</sub> CHClBr		~0.14
Methyl bromide	CH <sub>3</sub> Br	1.3	0.64

The previous element, characterization, results in a quantitative statement on different impact categories e.g. global warming, stratospheric ozone depletion and acidification effects. Comparison of these categories is not immediately possible. Therefore, the life cycle impact assessment includes as a fourth element a

valuation/weighting of the impact categories against each other (ISO, 1997c). Weighting is a qualitative or quantitative step not necessarily based on natural science but often on political or ethical values. Weighting has previously been referred to as valuation. Weighting methods have been developed by different institutions based on different principles (Lindeijer, 1996). The valuation can result in an environmental index.

The step of doing life cycle impact assessment is shown in Figure 2.3.



**Figure 2.3** Procedure of life cycle impact assessment.

#### 4. Interpretation

Interpretation is a systematic technique to identify, quantify, check, and evaluate information from the results of the life cycle inventory (LCI) and the life cycle impact assessment (LCIA), and communicate them effectively. Life cycle interpretation is the last phase of the LCA process.

The International Organization for Standardization (ISO) has defined the following two objectives of life cycle interpretation:

4.1. Analyze results, reach conclusions, explain limitations and provide recommendations based on the findings of the preceding phases of the LCA and to report the results of the life cycle interpretation in a transparent manner.

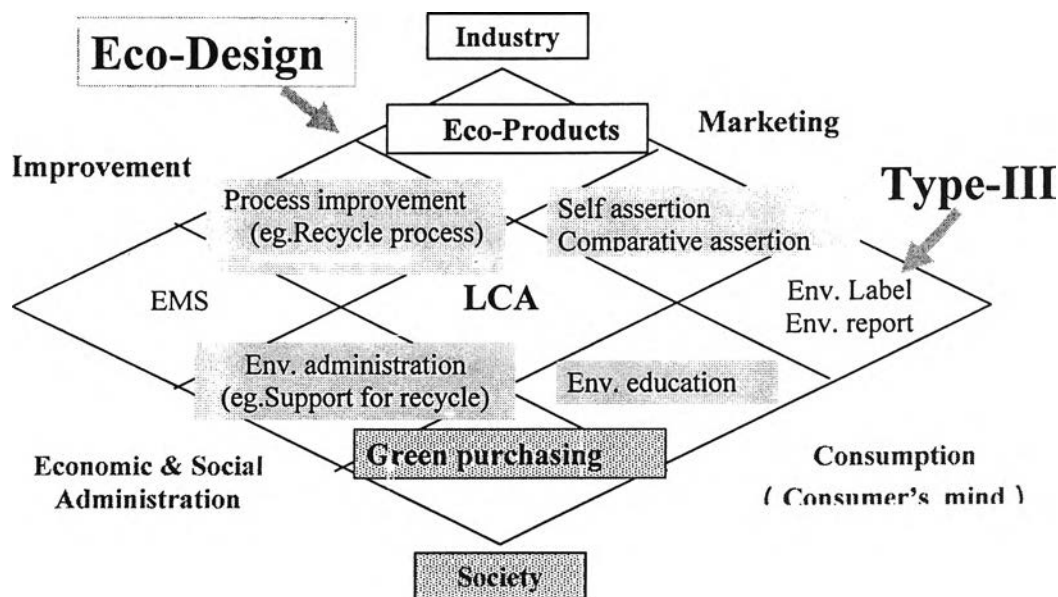
4.2. Provide a readily understandable, complete, and consistent presentation of the results of an LCA study, in accordance with the goal and scope of the study. (ISO 1998b).

## **2.4 Applications of LCA**

LCA can be considered as a useful tool for many applications, ranging from product development, through eco-labeling, to environmental policy and priority setting and to comparative environmental assessment. LCA methodologies were originally developed to create decision support tools for distinguishing between products, product systems, or services on environmental grounds. LCA application as illustrated in Figure 2.4.

During the evolution of LCA, a number of related applications have emerged, these examples are as shown below:

- Internal industrial use in product development and improvement,
- Internal strategic planning and policy decision support in industry,
- External industrial use for marketing purposes, and
- Governmental policy making in the areas of ecolabelling, green procurement and waste management opportunities.



Dr.Inaba (July 2003)

Figure 2.4 Applications of LCA (Inaba, 2003).

## 2.5 Plastics and Their Classifications

### 1. Definition

Plastics are polymers which are defined as long chain, high molecular weight chemical materials. A polymer formed into a shape by molding, extrusion, foaming, etc. is called plastic (Witcoff, 1996). Plastics provide the most important application for polymers. The molecules resulting from a chemical reaction which leads to polymers can be:

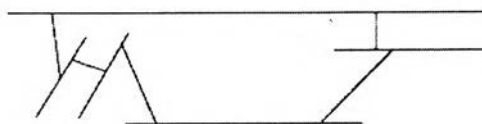
Linear



Branched



### Crosslinked



## 2. Classifications

The classification is very important regarding the chemistry and the scientific research of polymers. From the technical point of view and more related to the applications, it is necessary to divide the polymer materials in the way given in the following list in Table 2.4.

From Table 2.4, there are 2 classifications of polymer:

### 1. Thermoplastic

These polymer molecules consist of long chains which have only weak bonds between the chains. The bonds between the chains are so weak that they can be broken when the plastic is heated. The chains can then move around to form a different shape. The weak bonds reform when it is cooled and the thermoplastic material keeps its new shape.

### 2. Thermosetting

These polymer molecules consist of long chains which have many strong chemical bonds between the chains. The bonds between the chains are so strong that they cannot be broken when the plastic is heated. This means that the thermosetting material always keeps its shape.

**Table 2.4** Classification and properties of plastics (Taksina, 2003)

<b>Class</b>	<b>Structure</b>	<b>Physical Appearance</b>	<b>Behavior on Heating</b>	<b>Behavior on Solvent Treatment</b>
Thermo-plastics	linear or branched macromolecules	<u>partially crystalline</u> : flexible to horn-like; hazy, milky or opaque; only thin films transparent	material softens, fuses and becomes clear on melting; often fibers can be drawn from melt; heat sealable	may swell; difficult to dissolve in cold solvents, but readily dissolved on heating in solvent
		<u>amorphous</u> : clear and transparent without additives (except heterophasic systems); hard to rubbery (on adding plasticizer)	material softens, fuses and becomes clear on melting; often fibers can be drawn from melt; heat sealable	soluble in certain organic solvents, after initial swelling
Thermo-sets (after processing)	densely crosslinked macromolecules	amorphous; hard; opaque with fillers; transparent without fillers	remain hard, almost dimensionally stable until chemical decomposition sets in	insoluble, do not swell or only slightly

### 3. Application of Plastics

Plastics are used in such a wide range of applications because they are uniquely capable of offering many different properties that offer consumer benefits unsurpassed by other materials. From daily tasks to our most unusual needs, plastics have increasingly provided the performance characteristics that fulfill consumer needs at all levels. They are also unique in that their properties may be customized for each individual application as shown in Table 2.5.

**Table 2.5** Plastics application (Chem Systems, 1987)

Polymer Type	Application
High density polyethylene (HDPE)	Bottles for milk and washing-up liquids, dustbins, bottles, pipes
Low density polyethylene (LDPE)	Carrier bags and sacks, bin liners, squeezable detergent bottles, wire and cable applications, and film applications.
Polypropylene (PP)	Margarine tubs, microwaveable meal trays, ketchup bottles, yogurt containers, medicine bottles, pancake syrup bottles, and automobile battery casings.
Polystyrene (PS)	Yoghurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys, household chemicals, computers, and video and audio cassettes.

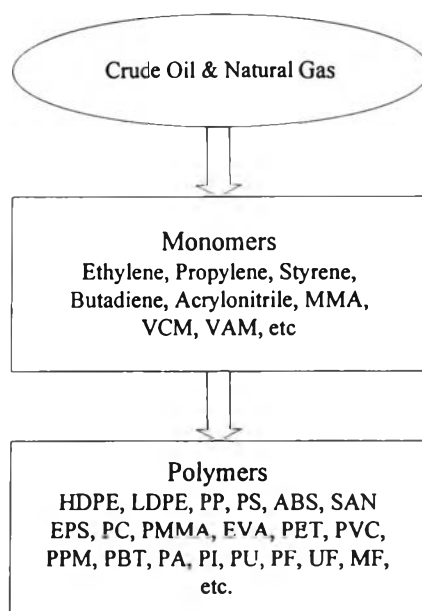
**Table 2.5** Plastics application (Chem Systems, 1987) *(Continued)*

Polymer Type	Application
Polyvinyl chloride (PVC)	Blood bags, credit cards, pipe and fittings, siding, carpet backing and windows, wire and cable sheathing, insulation, film and sheet, floor coverings, synthetic leather products, coatings, and medical tubing.
Polyethylene terephthalate (PET)	Electrical/electronic components, automotive electrical components, consumer products, office furniture components, fizzy drinks bottles, oven- proof trays, and anorak and duvet filling
Polyurethane	Upholstery, sports shoe soles, roller skate wheel, and electrical/electronic components
Polyacrylate	Glazing, electrical/electronic components, automotive fog lamps, and microwave oven components
Nylon	Wire and cable, barrier packaging film, electrical connectors, windshield wiper parts, radiator and tanks, brake fluid reservoirs, gears, impellers, and housewares
Polycarbonates	Electrical/electronic components, housings, switches, aerodynamically styled headlights, glazing, appliances, medical apparatus, compact (audio) discs, baby bottles, car headlights, and firemen's helmets
Other plastics	Any other plastics that do not fall into any of the above categories. - An example is melamine, which is often used in plastic plates and cups



#### 4. Synthesis and Production of Plastics

The general process for polymer production is shown in Figure 2.5.



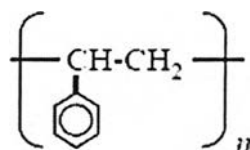
**Figure 2.5** Polymer resin integration (Taksina, 2003).

In this study, polystyrene and polyurethane are the main products of interest for LCA study. Their backgrounds are reviewed in the following sections.

#### 2.6 Polystyrene

Polystyrene is a versatile polymer resin used in a wide range of applications especially in the packaging industry. It is sold in three main forms: crystal or general purpose polystyrene (GPPS), high impact polystyrene (HIPS) and expandable polystyrene (EPS).

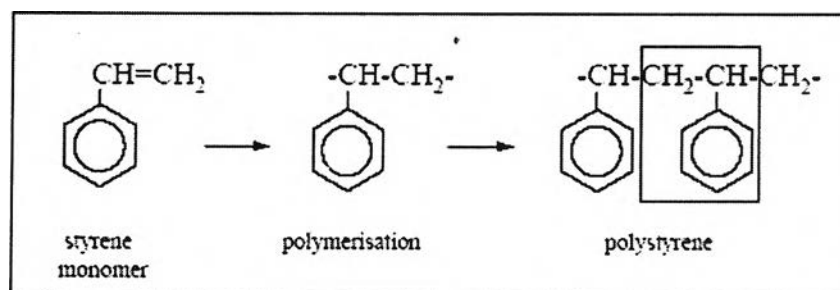
The rarely used systematic IUPAC name for polystyrene is poly-(1 - phenylethylene) and the chemical structure of polystyrene is



In 1930 BASF, then part of IG Farben, installed a plant for producing 100 tonnes of polystyrene per annum and in 1933 the first injection moulded articles were produced. In the US semi-plant-scale work at the Dow Chemical Company showed promise of commercial success in 1934. As a consequence they became available shortly before World War II. After the war, there was a large surplus capacity of plant for the manufacture of styrene and polystyrene together with a great deal of knowledge and experience that had been collected over the war years. In the late 1990s a crystalline form of polystyrene, *syndiotactic polystyrene* became commercially available.

The production of styrene monomer can be thought of as replacing one of the hydrogen atoms in ethylene by a benzene ring ( $C_6H_6$ ) as shown in Figure 2.6. The monomer is then polymerized in a manner similar to polyethylene; that is, the double bonds in the monomer molecules are opened and neighboring molecules link together to form a chain. The repeat unit, shown inside the shaded box in Figure 2.6, has the same chemical composition as the styrene monomer.

The bulk of commercial styrene is prepared by the Dow process or some similar system. The method involves the reaction of benzene and ethylene from crude oil refinery as known as naphtha to ethylbenzene, its dehydrogenation to styrene and a final finishing stage. It is therefore useful to consider this process in each of the four stages. The process to produce polystyrene of Dow Chemical Company as illustrated in Figure 2.7. STYRON and STYRON A-TECH are Dow's trademark for polystyrene. STYRON process is shown in Figure 2.8.



**Figure 2.6** The reaction scheme for producing polystyrene from styrene monomer (Adams *et al.*, 1993).

From Crude Oil to Polystyrene

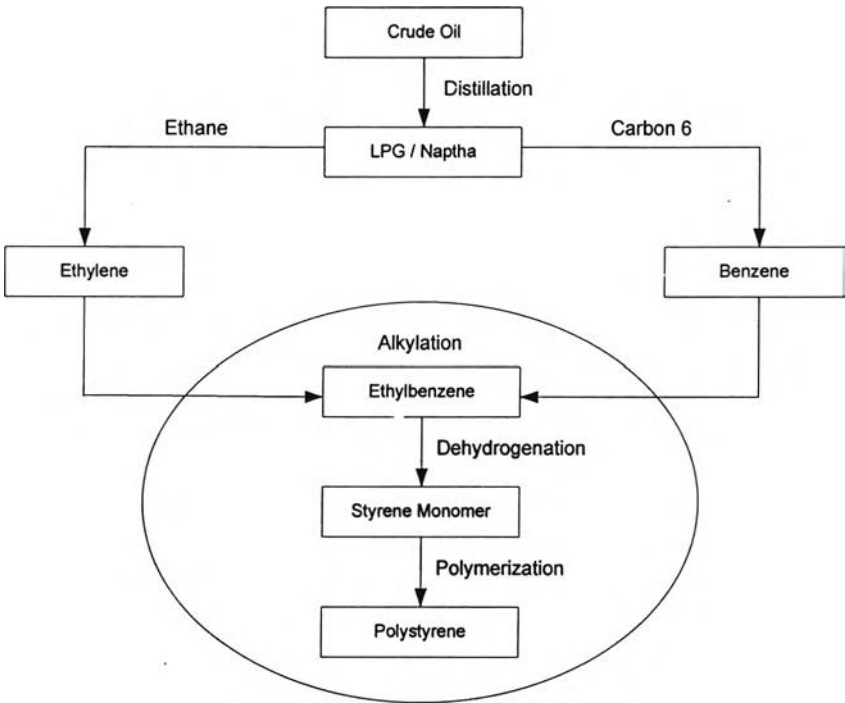


Figure 2.7 Polystyrene production (Dow, 2003).

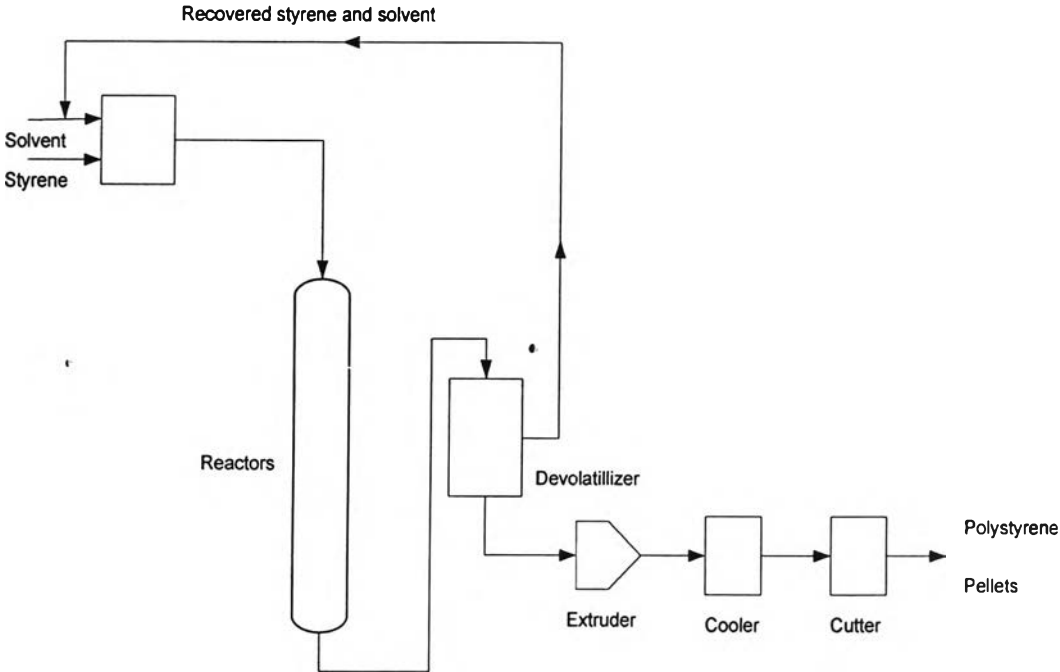
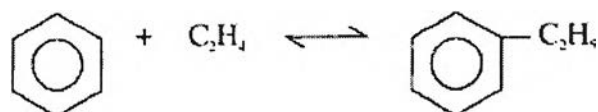


Figure 2.8 STYRON production process (Dow, 2003).

The 4 stages of polystyrene preparation are:

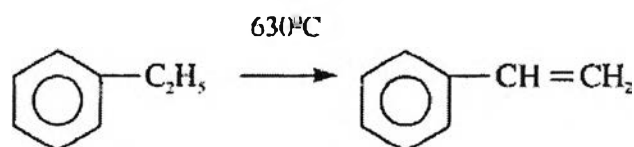
### 1. Preparation of ethylbenzene

Ethylbenzene is prepared by reaction of ethylene and benzene in the presence of a Friedel-Crafts catalyst such as aluminium chloride at about 95°C. This stage is shown below:



### 2. Dehydrogenation

Styrene is produced from the ethylbenzene by a process of dehydrogenation. This is an endothermic reaction in which a volume increase accompanies dehydrogenation. The reaction is therefore favored by operation at reduced pressure. In practice steam is passed through with the ethylbenzene in order to reduce the partial pressure of the latter rather than carrying out a high temperature reaction under partial vacuum. By the use of selected catalysts such as magnesium oxide, and iron oxide this reaction is shown below:



### 3. Styrene purification

The dehydrogenation reaction produces 'crude styrene' which consists of approximately 31.0% styrene, 61% ethylbenzene and about 2% of aromatic hydrocarbon such as benzene and toluene with some tarry matter. The purification of the styrene is made by specially designed distillation columns.

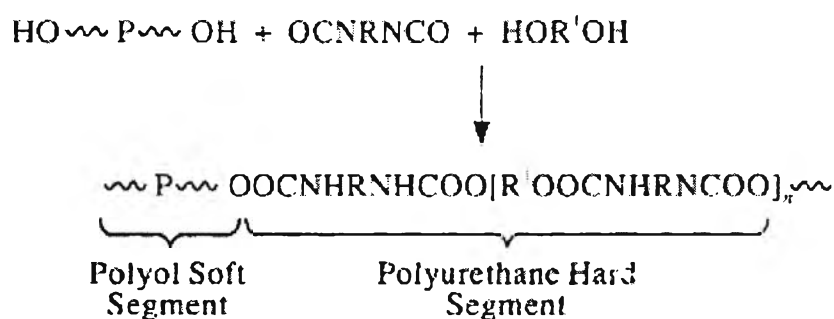
### 4. Polymerization

The polymer may be prepared by mass, suspension, solution, and emulsion methods, the first two being the most important mass polymerization has the advantage of apparent simplicity and gives a polymer of high clarity and very good electrical insulation characteristics. Suspension polymerization is suspended monomer in droplets 1/32-1/64 in. in diameter in a fluid, usually water.

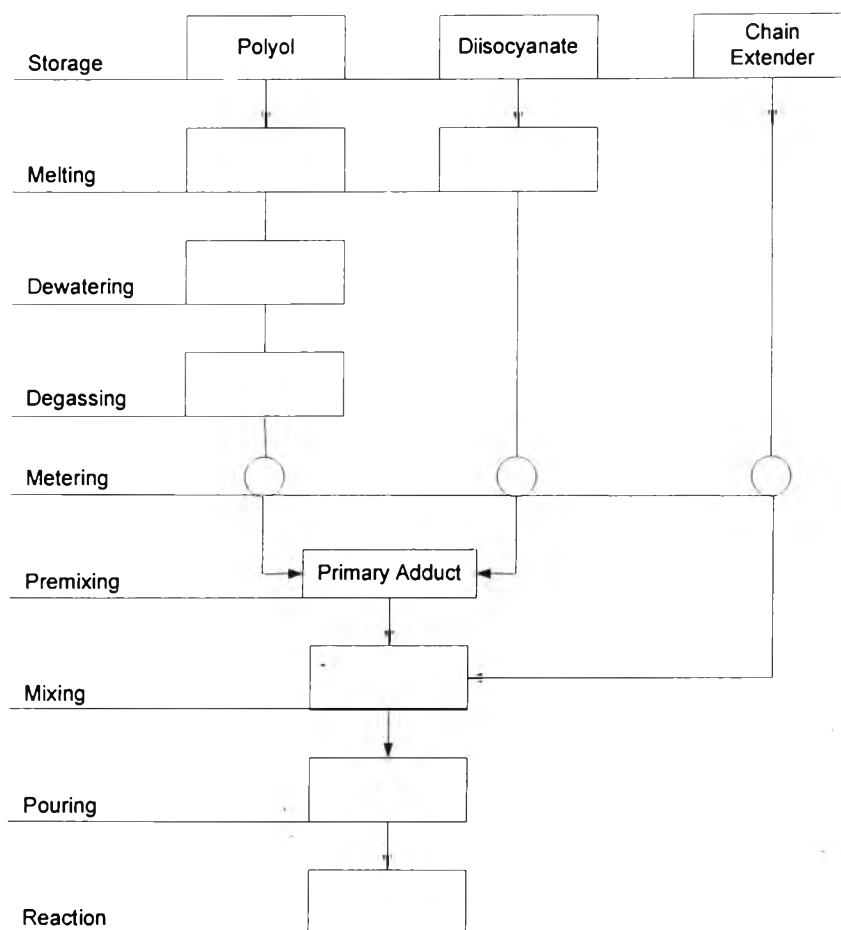
Polymerization in solution reduces the exotherm but may lead to problems of solvent recovery and solvent hazards. Emulsion polymerization techniques are seldom used with polystyrene since the large quantities of soap used seriously affects clarity and electrical insulation characteristics. This process is therefore used only for the production of polystyrene latex.

## 2.7 Polyurethane

Polyurethanes (PUR) were first produced in 1937 by Otto Bayer and his co-workers in Germany and represent a family of polymers rather than a single polymer. Urethane polymers can be produced with a wide variety of properties, ranging from soft flexible foams through to hard solids and so can be used in a diverse range of applications. Polyurethanes are formed by reacting a Polyether-polyols (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives.

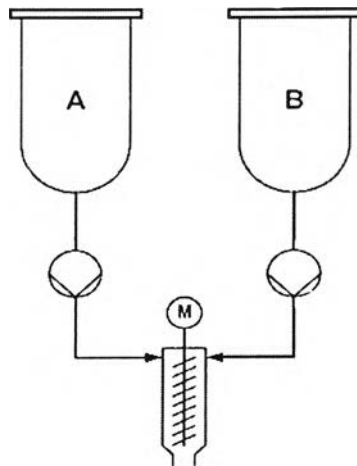


Most polyurethanes are thermoset materials; they cannot be melted and reshaped as thermoplastic materials can be. Polyurethanes exist in a variety of forms including flexible foams, rigid foams, chemical-resistant coatings, specialty adhesives and sealants, and elastomers. The polyurethane process is shown in Figure 2.9. When polyols, di-isocyanates, and glycols are reacted together; polyurethane segment will show high intersegment attraction as shown in basic equation below. This may include hydrogen bonding. Furthermore the segments may be able to crystallize.

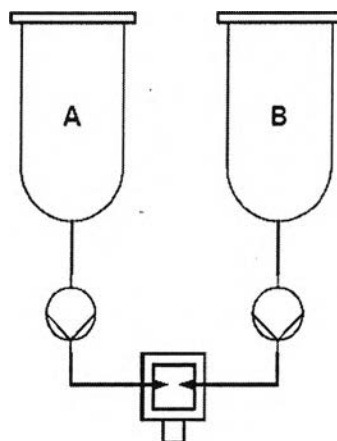


**Figure 2.9** Block diagram of a processing plant for polyurethane elastomers (Oertel, 1985).

There are basically two processes that are used to mix the polyurethane raw materials. The low pressure mixing method employs mechanical stirrers or stationary mixing elements as shown in Figure 2.9. High pressure mixing works according to the impingement injection principle or the parallel stream injection principle where highly pressurized (>120 bar) reaction components are injected into a mixing chamber as shown in Figures 2.10 and 2.11.



**Figure 2.10** Principle of low-pressure mixing (Thomas *et al.*, 1992).

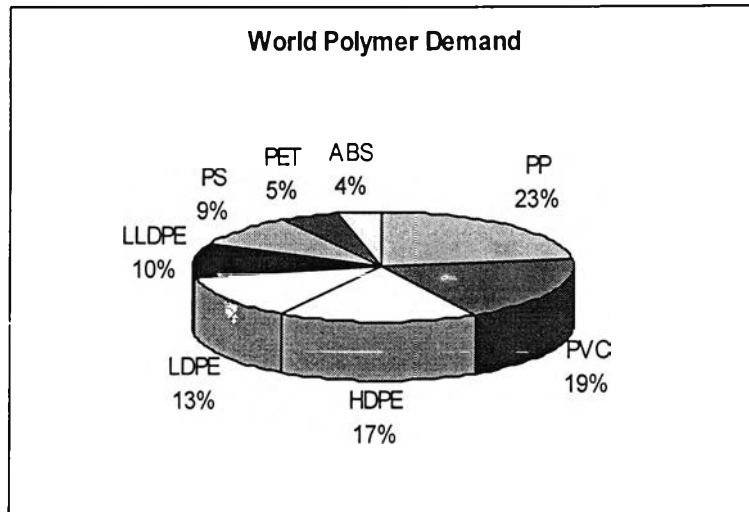


**Figure 2.11** Principle of high pressure mixing (Thomas *et al.*, 1992).

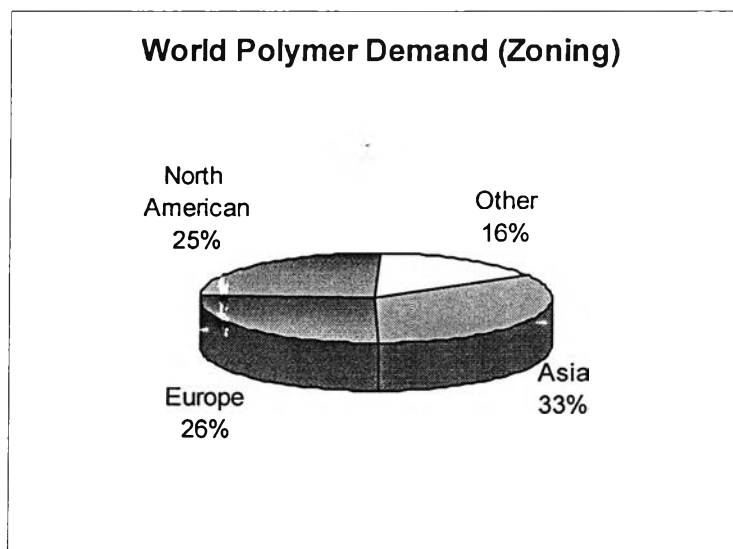
## 2.8 Demand – Supply of Plastics

### 1. Demand – Supply of Plastics

In present, there are many kinds of polymer in the world which are used in the industries. Figure 2.12 shows demand of each kind of polymer in the world, Figure 2.13 shows zone of world polymer demand, and Figures 2.14 and 2.15 show demand and supply of plastics in Thailand.



**Figure 2.12** World polymer demand (Taksina, 2003).

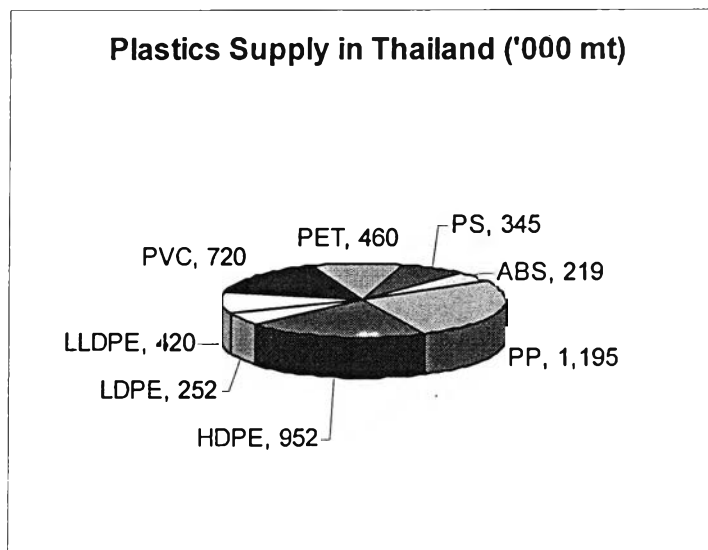


**Figure 2.13** Zoning of world polymer demand (Taksina, 2003).





**Figure 2.14** Plastic demands in Thailand (Taksina, 2003).



**Figure 2.15** Plastics supply in Thailand (Taksina, 2003).

## 2. Demand – Supply of Polystyrene

In Thailand, there are 2 favorite types of polystyrene commonly used in the industry; GPPS (General Purpose Polystyrene) and HIPS (High Impact Polystyrene). The uses of these 2 polymers in the market are shown in Figures 2.16 and 2.17.

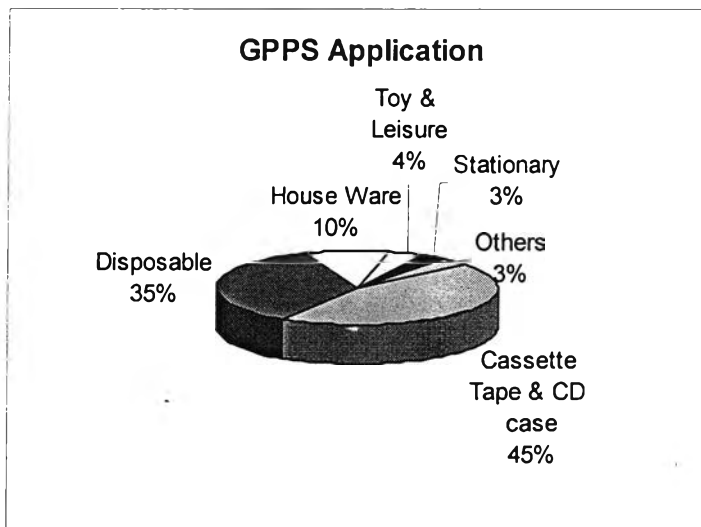


Figure 2.16 GPPS application in Thailand (Taksina, 2003).

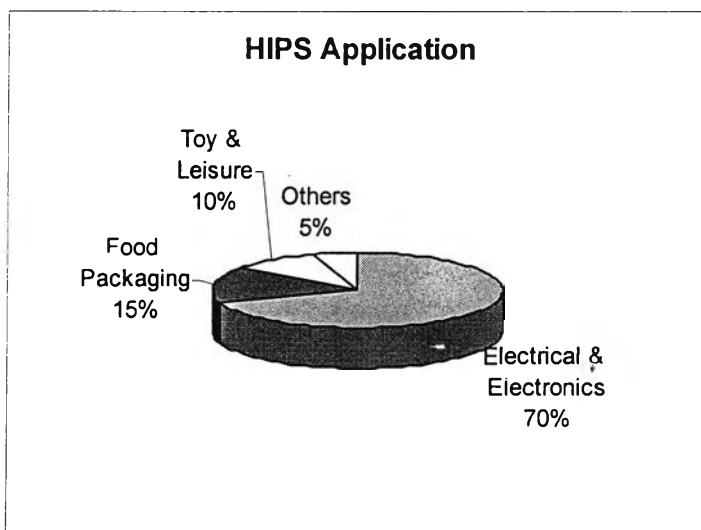
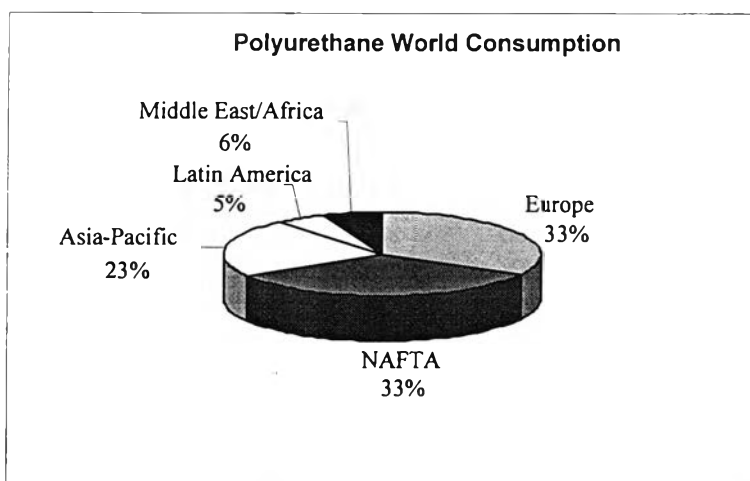


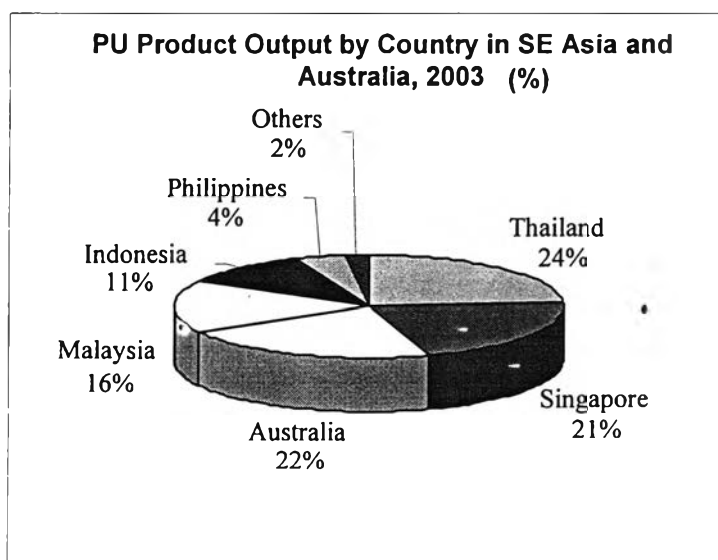
Figure 2.17 HIPS application in Thailand (Taksina, 2003).

### 3. Demand – Supply of Polyurethane

Figure 2.18 shows polyurethane world consumption by region. Asia-Pacific, Europe and the NAFTA countries are the biggest polyurethane markets. Nearly 90% of all polyurethanes are consumed there. Output of polyurethane products in Southeast Asia and Australia totaled 343,090 tonnes in 2003 with Thailand and Australia accounting for almost half, as shown in Figure 2.19.

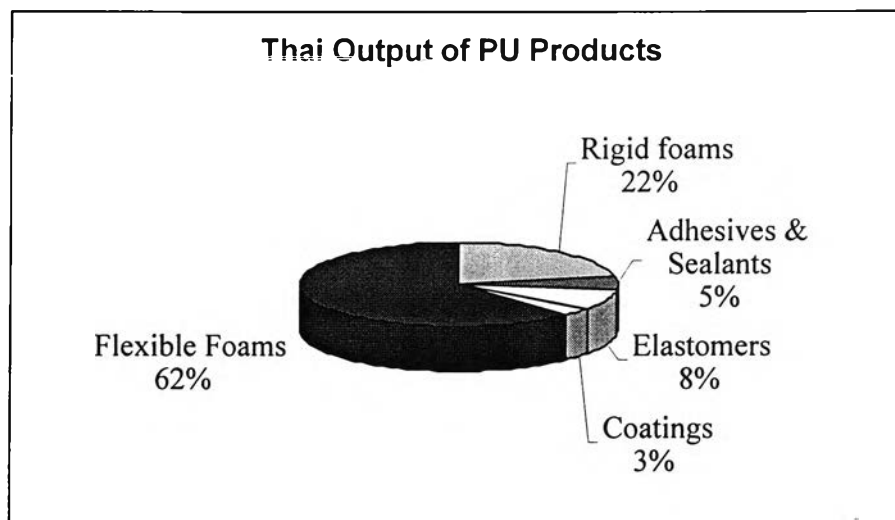


**Figure 2.18** Polyurethane world consumption (Kramer, 2000).



**Figure 2.19** Polyurethane product output by country in Southeast Asia and Australia, 2003 (%) (IAL Consultants, 2003).

Thailand is the leading producer of polyurethanes in each PU sector except for coatings, where Australia dominates. Thailand's output of polyurethane products amounted to 82,090 tonnes in 2003, which breaks down as shown in Figure 2.20.



**Figure 2.20** Thai output of polyurethane products, 2003 (IAL Consultants, 2003).

## 2.9 Plastic Disposal

Currently 80% of post-consumer plastic waste is sent to landfill, 8% is incinerated and only 7% is recycled (Wastewatch, 2003). There are 6 ways to disposal plastics:

### 1. Landfill

The primary purpose of solid waste management processes is to remove wastes from living and work areas in ways that protect human health and the environment. Fortunately, new landfill technologies, stabilization techniques and site-monitoring systems are ensuring the protection of our present and future environment. Many landfills include thick plastic liners, required by the EPA, that help protect groundwater from contamination as well as several foot-thick linings of clay and an imperious synthetic fabric to prevent rain and other liquids from draining into the ground. Pipes collect water that accumulates above the liner and it is pumped

into holding tanks for treatment. Systems are also in place that monitors methane gas, a volatile byproduct of rotting garbage.

## 2. Incineration

In many countries, incineration is a traditional and available method in reducing the different plastic wastes. In view of both reduction and destruction, incineration is a valuable means of waste disposal with the advantage of being highly effective in reducing the volume of waste. Thus, the method or technology regarding incineration is becoming a more widespread concern. During the incineration process, air pollutants such as CO, NO<sub>x</sub>, SO<sub>x</sub>, particles, and polycyclic aromatic hydrocarbons (PAHs) are exhausted. Understanding the characteristics of both formation and emission of PAHs is necessary because it is proved that some PAHs are carcinogenic. PAHs and their derivatives are widespread harmful compounds generated by incomplete combustion of organic material arising, in part, from natural combustion such as forest fires and volcanic eruptions, but for the most important part, from human activities, such as industrial production, transportation, waste incineration, and so on.

## 3. Energy Production

Plastics have high calorific value which often equal to heating oil – generates valuable energy for heat and electricity. A number of countries already make use of this. For example, Sweden recovers energy from around half of its domestic waste to meet the needs of approximately 15 per cent of its district heating. Fuel pellets produced from mixed plastics and plastics/paper fractions separated from household waste can be used as a fuel replacing coal. There are many such power stations across Europe using large amounts of pulverized coal that has the potential to be substituted by fuels based on pre-treated mixed plastics waste.

## 4. Biodegradable

In some areas of the country, alternate disposal methods such as composting are available as a solid waste disposal option for readily degradable materials. But it is important to remember that compost facilities and landfills are very different things. Modern landfills are designed to limit degradation, so degradable materials of any type are not likely to affect the amount of landfill space available. Most people

do not realize that plastics act similarly to other materials in a modern landfill, since the conditions necessary for rapid degradation are not present - or even desirable.

#### 5. Photodegradation

This method is able to be broken down by exposure to ultraviolet rays, i.e.: from the sun; having the ability to absorb the high-energy radiation in the UV portion of the light spectrum, which activates the (plastic) electrons to higher activity and causes oxidation, cleavage, and other degradative reactions.

#### 6. Recycling and Reuse

The most important strategy for environmental protection in the plastics products industry is the use of recycled and recyclable plastic. Many kinds of plastic are easily recycled within the production process, so there is very little scrap. Most of the environmental concerns in such companies are about air emissions. Changes in plastic formulation and improvements in air emissions controls are the main environmental protection solutions for air pollution. Energy efficiency is particularly important for this sector because almost all processing uses heat. When scrap plastic cannot be recycled within the production process, it often can be ground up and used as filler in other products.

Reusing plastic is preferable to recycling as it uses less energy and fewer resources. Long life, multi-trip plastics packaging has become more widespread in recent years, replacing less durable and single-trip alternatives, so reducing waste.

### **2.10 Environmental Impacts of Plastics in Life Cycle Concept**

The production and use of plastics has a range of environmental impacts. Firstly, plastics production requires significant quantities of resources, primarily fossil fuels, both as a raw material and to deliver energy for the manufacturing process. In addition, plastics manufacture requires other resources such as land and water and produces waste and emissions. The overall environmental impact varies according to the type of plastic and the production method employed.

Plastics production also involves the use of potentially harmful chemicals, which are added as stabilizers or colorants. Many of these have not undergone

environmental risk assessment and their impact on human health and the environment is currently uncertain.

The disposal of plastics products also contributes significantly to their environmental impact. Because most plastics are non-degradable, they take a long time to break down, often several hundred years, when they are landfilled. With more and more plastics products, particularly plastics packaging, being disposed of soon after their purchase, the landfill space required by plastics waste is a growing concern.