DOKUZ EYLUL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED

SCIENCES

LIFE CYCLE ASSESSMENT OF PET BOTTLE

by

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İZMİR

LIFE CYCLE ASSESSMENT OF PET BOTTLE

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"LIFE CYCLE ASSESSTMENT OF PET BOTTLE"** completed by **SECIL KIRSEN DOGAN** under supervision of **ASST. PROF. DR. ENVER YASER KUCUKGUL** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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LIFE CYCLE ASSESSMENT OF PET BOTTLE

ABSTRACT

Human being is recently in petroleum period after living the stoneage and mine age with taking place in history. Petroleum and its derivatives are used nearly all in our daily life and becoming indispensable of our lifes day by day. Crude oil, which is formed by plant and animal residues that putrefied over millions of years, pass through many processes from winning to becoming ready to be delivered to the consumer. Because of petroleum and petroleum products' indispensable role in our lifes, technology which cares about environment must be chosen, wastes of production process must be lowered end disposed with appropriate methods. In this study, PET, which is used for placing on the market our life resource;water, will be evaluated together with its LCA (life cycle assessment). Manufacturing chain of PET (polyethylene terepthalate) bottle started quickly and dense after patented in 1973. The chain consists of crude oil winning, taking naphtha by refining crude oil, getting terephthalic acid and ethylene glycol from naphtha, polymerization terephthalic acid and ethylene glycol, all the stages of PET production and the usage and disposal phases. Types of wastes, environmental fate due to manufacturing process and methods of production wastes' dispose have been evaluated and also feedback mechanisms after the usage of productions are examined and the necessity of feedback is investigated in this study. The aim is to evaluate LCA of PET numerically with material-energy-waste- environmental impact circle.

Keywords: LCA, Petroleum and Environment, PET production processes, Waste Production,

PET ŞİŞENİN YAŞAM DÖNGÜ ANALİZİ

ÖZ

Petrol ve türevleri günlük hayatımızın neredeyse tamamında kullanılmakta ve gün geçtikçe hayatımızın vazgeçilmezi olmaktadır. Denizlerdeki bitki ve hayvan kalıntılarının milyonlarca yıl boyunca çürümesi sonucu oluşan ham petrol, yeryüzüne çıkarılmasından günlük hayatımızda kullanılan malzeme haline gelinceye kadar birçok süreçten geçmektedir. Bu çalışma petrol türevlerinden biri olan, sürekli olarak kullandığımız ve yaşam kaynağımız olan suyun ambalajlanarak piyasaya sürülmesinde kullanılan PET; yaşam döngüsüyle LCA (life cycle assessment) incelenmiştir. Polietilen tereftalat (PET) şişenin; 1973 yılında patentlenmesiyle başlayan hızlı ve yoğun üretimi, ham petrolün çıkarılması ile başlayıp, ham petrolün rafinasyonu ile nafta elde edilmesine, naftadan tereftalik asit ve etilen glikol üretilmesine, tereftalik asit ve etilen glikolün polimerleştirilmesi ile PET şişe üretimine kadar olan üretim adımlarını ve PET şişenin kullanımı sonrasında oluşan atıkların geri dönüşüm işlemlerini kapsamaktadır. Tüm bu üretim zincirinde oluşan atık türleri, üretim proseslerinin yarattığı çevresel etkiler ve üretim atıklarının bertaraf yöntemleri değerlendirilmiş, ürünlerin kullanımı sonrası oluşan atıkların geri dönüşüm uygulamaları irdelenmiş ve geri dönüşümün gerekliliği ele alınmıştır. PET için oluşturmaya çalıştığımız LCA, madde-enerji-atık-çevresel etki döngüsü sayısallaştırılarak değerlendirilmiştir. Petrol ve petrol ürünleri hayatımızda vazgeçilmezlerimiz arasındaki yerini aldığına göre yapılması gerekenler, üretim süreçlerinde çevreyi dikkate alan teknolojileri seçmek, üretim safhasında oluşan atıkların azaltmak ve uygun yöntemlerle bertarafını sağlamaktır. Diğer polimerik plastiklerle kıyaslandığında tamamen geri dönüşebilir olan PET şişelerin kullanımı sonucu oluşan atıkların geri kazanımı arttırılmalıdır.

Anahtar kelimeler: LCA, Petrol ve Çevre, PET Üretim Süreçleri ve Atık Oluşumu

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 General Introduction

Human being is recently in petroleum period after living the Stone Age and mine age with taking place in history. Petroleum and its derivatives are used nearly all in our daily life and becoming indispensable of our lifes day by day. Crude oil, which is formed by plant and animal residues that putrefied over millions of years, pass through many processes from winning to becoming ready to be delivered to the consumer. Because of petroleum and petroleum products' indispensable role in our lifes, technology which cares about environment must be chosen, wastes of production process must be lowered end disposed with appropriate methods.

1.2 Goal Of This Thesis

Our study's aim is the analyzing the pet bottle with life cycle assessment which is the one the derivatives of petroleum, is used very occasionally and used in the process of the selling the food and beverage products with packaging.

PET, which is used for placing on the market our life resource; water, will be evaluated together with its LCA. Manufacturing chain of PET (polyethylene terepthalate) bottle started quickly and dense after patented in 1973 by chemist Nathaniel Wyeth. The chain consists of crude oil winning, taking naphtha by refining crude oil, getting terephthalic acid and ethylene glycol from naphtha, polymerization terephthalic acid and ethylene glycol, all the stages of PET production and the usage and disposal phases. Types of wastes, environmental fate due to manufacturing process and methods of production wastes' dispose have been evaluated and also feedback mechanisms after the usage of productions are examined and the necessity of feedback is investigated in this study. The aim is to evaluate LCA of PET numerically with material-energy-waste- environmental impact circle.

CHAPTER TWO
LIFE CYCLE ASSESSMENT

The concept of life cycle assessment (LCA) originated in the late 1960's when it became clear that the only sensible way to examine industrial systems was to examine their performance, starting with the extraction of raw materials from the earth and tracing all operations until the final disposal of these materials as wastes back into the earth (cradle to grave).

Life cycle assessment is a "cradle-to-grave" approach for assessing industrial systems . "Cradle-to-grave" begins with the gathering of raw materials from the earth to create the product and ends at the point when all materials are returned to the earth. LCA evaluates all stages of a product's life from the perspective that they are interdependent, meaning that one operation leads to the next. LCA enables the estimation of the cumulative environmental impacts resulting from all stages in the product life cycle, often including impacts not considered in more traditional analyses (e.g., raw material extraction, material transportation, ultimate product disposal, etc.). By including the impacts throughout the product life cycle, LCA provides a comprehensive view of the environmental aspects of the product or process and a more accurate picture of the true environmental trade-offs in product and process selection.

There were two reasons for this approach. First, individual component operations could apparently be made cleaner and more efficient by simply displacing the pollution elsewhere, thus the benefits occurring in one location were offset by the problems generated elsewhere so that there was no overall real improvement. A current example is the proposal to introduce electric cars into towns: this reduces the pollution in the towns but displaces it to the pollution arising elsewhere from the power stations needed to provide the fuel (electricity). The second reason was that traditionally engineers had concentrated their efforts into making individual unit operations more efficient, but nobody was looking at the way in which these unit operations were put together to form an overall production and use sequence.

Sometimes, by rearranging the building blocks, overall systems can be made more efficient (Boustead, 2007).

2.1 Introduction to Product Life Cycle Concepts

Products, services, and processes all have a life cycle. For products, the life cycle begins when raw materials are extracted or harvested. Raw materials then go through a number of manufacturing steps until the product is delivered to a customer. The product is used, then disposed of or recycled. These product life cycle stages are illustrated in Figure 2.1 , along the horizontal axis. As shown in the Figure, energy is consumed and wastes and emissions are generated in all of these life cycle stages.

Processes also have a life cycle. The life cycle begins with planning, research and development. The products and processes are then designed and constructed. A process will have an active lifetime, then will be decommissioned and, if necessary, remediation and restoration may occur. Figure 2.1, along its vertical axis, illustrates the main elements of this process life cycle. Again, energy consumption, wastes and emissions are associated with each step in the life cycle.

Traditionally, product designers have been concerned primarily with product life cycles up to and including the manufacturing step. Chemical process designers have been primarily concerned with process life cycles up to and including the manufacturing step. That focus is changing. Increasingly, chemical product designers must consider how their products will be recycled. They must consider how their customers will use their products and what environmental hazards might arise. Process designers must avoid contamination of the sites at which their processes are located. Simply stated, engineers must become stewards for their products and processes throughout their life cycles. These increased responsibilities for products and processes throughout their life cycles have been recognized by a number of professional organizations.
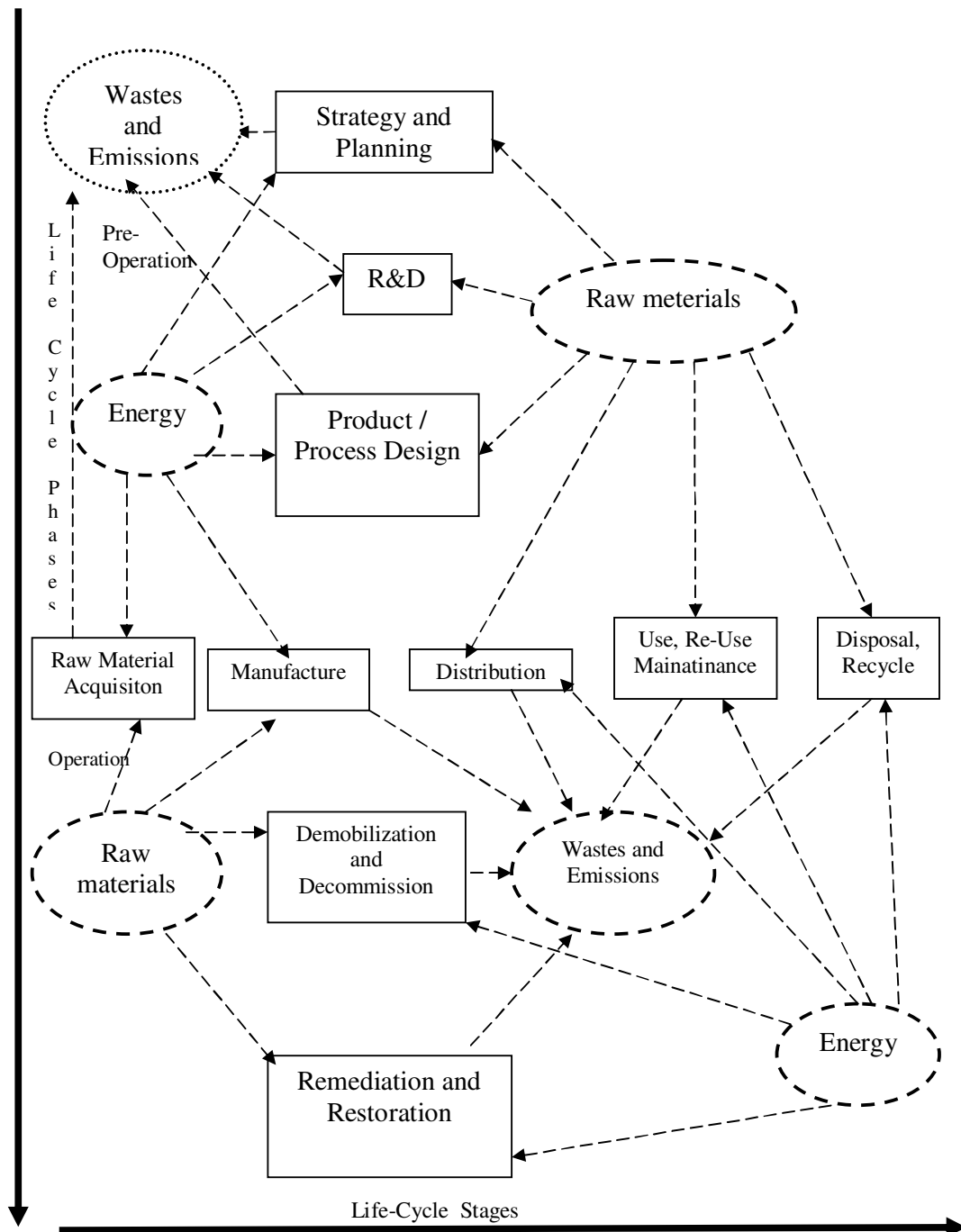
Figure 2.1 Product Life Cycle

Figure 2.1 Product life cycles include raw material extraction, material processing, use and disposal steps, and are illustrated along the horizontal axis. Process life cycles include planning, research, design, operation and decommissionning steps and are shown along the vertical axis. In both product and

process life cycles, energy and materials are used at each stage of the life cycle and emissions and wastes are created .

2.2 Life-Cycle Assessment

Life-cycle studies range from highly detailed and quantitative assessments that characterize, and sometimes assess the environmental impacts of energy use, raw material use, wastes and emissions over all life stages, to assessments that qualitatively identify and prioritize the types of impacts that might occur over a life cycle. As shown in this chapter, different levels of detail and effort are appropriate for the different uses to which life-cycle information is put. In this section, the steps involved in conducting detailed, highly quantitative life-cycle assessments are described.

Step 1 The first step in an LCA is to determine the scope and boundaries of the assessment. In this step, the reasons for conducting the LCA are identified; the product, process, or service to be studied is defined; a functional unit for that product is chosen; and choices regarding system boundaries, including temporal and spatial boundaries, are made.

Step 2 The second step in a life-cycle assessment is to inventory the outputs that occur, such as products, by products, wastes and emissions, and the inputs, such as raw materials and energy, that are used during the life-cycle. This step, shown conceptually in Figure 2.2, is called a life-cycle inventory, and is often the most time consuming and data intensive portion of a life cycle assessment.

Inputs

Raw Materials

Energy

Outputs

Atmoshperic Emissions

Waterborne Wastes

Solid Wastes

Coproducts

Other Releases

Raw Materials Acquiation

Manufacturing

Use/Resuse/Maintenance

Recyle/Waste Management

System Boundary
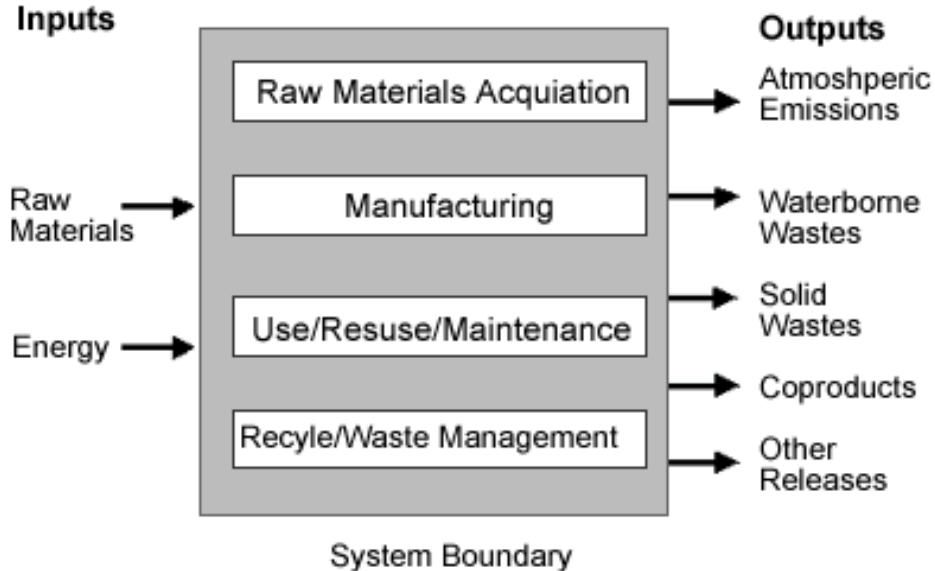
Figure 2.2 Life Cycle Stages

Step 3 The output from a life cycle inventory is an extensive compilation of specific materials used and emitted. Converting these inventory elements into an assessment of environmental performance requires that the emissions and material use be transformed into estimates of environmental impacts. Thus, the third step in a life cycle assessment is to assess the environmental impacts of the inputs and outputs compiled in the inventory. This step is called a life-cycle impact assessment.

Step 4 The fourth step in a life cycle assessment is to interpret the results of the impact assessment, suggesting improvements whenever possible. When life-cycle assessments are conducted to compare products, for example, this step might consist of recommending the most environmentally desirable product. Alternatively, if a single product were analyzed, specific design modifications that could improve environmental performance might be suggested. This step is called an improvement analysis or an interpretation step.

2.2.1 Life-Cycle Inventories

A life-cycle inventory is a set of data and material and energy flow calculations that quantifies the inputs and outputs of a product life-cycle. Some of the values that are sought during the inventory process are objective quantities derived using tools such as material and energy balances. As is shown later in this section, other values are more subjective and depend on choices and assumptions made during the assessment.

Before describing, in detail, the data elements associated with a life cycle inventory, take a moment to review the stages of a product life cycle. The first stage in a product life cycle, as shown along the horizontal axis of Figure 2.1, is raw material acquisition. Examples of raw material acquisition are timber harvesting, crude oil extraction, and mining of iron ore. After raw material acquisition is the material manufacture stage, where raw materials are processed into the basic materials of product manufacture. Felled trees are processed into lumber and paper, for example. Crude oil is processed into fuels, solvents, and the building blocks of plastics. These materials move to the product manufacture stage where they are used to make the final product. In this stage, paper and plastic may be made into cups, steel turned into car bodies, or solvents and pigments turned into paints. The next stage of the life-cycle stage is use. Some products, such as automobiles, generate significant emissions and wastes during use, while other products, such as grocery sacks have negligible material and energy flows associated with the use of the product. The final life-cycle stage consists of disposal or recycling.

Recycling can occur in several ways. A product might be reused, which is what happens when a ceramic cup is washed and reused instead of being thrown away. The product could be remanufactured, where the materials it contains are used to make another product. A newspaper, for example, might be made into another newspaper or might be shredded and used for animal bedding. Finally, products might be recycled to more basic materials, through processes such as plastics

depolymerization or automobile disassembly which yield commodity materials such as monomers and steel.

Tracking material flows, over all of the stages of a life cycle, is required for a comprehensive lifecycle inventory. Even for a simple product made from a single raw material in one or two manufacturing steps, the data collection effort can be substantial.

Other complexities in life-cycle inventories arise when processes have co-products. To illustrate the concept of co-product allocation, consider the allocation of inputs and outputs for the processes. If a life cycle inventory is being performed on one of the two products, then the input and emissions must be allocated between the two products. Another area of life-cycle inventories where subjective decisions are made is in allocation of inputs and outputs for products that are recycled or that are made from recycled goods. Some life-cycle practitioners treat products made from recycled materials as if they had no raw material requirements, while others allocate a portion of the raw material requirements from the original product to the product made from recycled materials.

Perhaps the most important uncertainty in life-cycle inventories, however, is due to the quality of data available on the processes being inventoried and the level of aggregation of the data. Overall data quality issues, such as whether data are direct measured values or are based on engineering estimation methods, are fairly straightforward to identify and deal with. Data aggregation issues can be more subtle.

In summary, this section has described the basic elements of a life cycle inventory. In performing the inventory, a number of assumptions are made concerning functional units, system boundaries, coproduct allocation, data aggregation methods and other parameters. These assumptions, as illustrated in the thesis, and as illustrated by a number of problems at the end of the thesis, can have a significant impact on the findings of a life cycle inventory.

2.2.2   Life-Cycle Impact Assessments

Life-cycle inventories do not by themselves characterize the environmental performance of a product, process, or service. This is because overall quantities of wastes and emissions, and raw material and energy requirements must be considered in conjunction with their potency of effect on the environment. Simply stated, a pound of lead emitted to the atmosphere has a different environmental impact than a pound of iron emitted to surface waters. To develop an overall characterization of the environmental performance of a product or process, throughout its life cycle, requires that life cycle inventory data be converted into estimates of environmental impact. The process of producing life-cycle impact assessments is generally divided into three major steps. They are:

- ✓ *classification,* where inputs and outputs determined during the inventory process are classified into environmental impact categories; for example, methane, carbon dioxide and CFCs would be classified as global warming gases.
- ✓ *characterization*, where the potency of effect of the inputs and outputs on their environmental impact categories is determined; for example, the relative greenhouse warming potentials of methane, carbon dioxide and CFCs would be identified in this step.
- ✓ *valuation,* where the relative importance of each environmental impact category is assessed, so that a single index indicating environmental performance can be calculated.

2.2.3   Interpretation of Life Cycle Data and Practical limits to Life-Cycle Assessments

While the process of a life-cycle assessment might seem simple enough in principle, in practice it is subject to a number of practical limitations. In performing the inventory, system boundaries must be chosen so that completion of the inventory is possible, given the resources that are available. Even if sufficient resources are

available, the time required to perform a comprehensive life cycle inventory may be limiting. Then, even if the necessary time and resources are available, life-cycle data are subject to uncertainty for the reasons cited earlier in this section.

The limitations of life-cycle inventories are then carried forward into the impact assessment stage of life-cycle studies, and the impact assessment methodologies add their own uncertainties. For example, potency factors are not available for all compounds in all impact categories. Issues of temporal and spatial aggregation, as described in this section arise. Finally, valuation adds an element of subjectivity into the analyses.

This is not to say that life-cycle assessments are without value. Rather, despite the uncertainties involved, these assessments provide invaluable information for decision-making and product stewardship. They allow environmental issues to be evaluated strategically, throughout the entire product life cycle. The challenge is to take advantage of these valuable features of life cycle assessments while bearing in mind the difficulties and uncertainties (Allen & Shonnard, 2001).

CHAPTER THREE
PET PRODUCTION

Plastics are becoming increasingly more popular and important in today's society. There is a wide range of uses for this synthetic polymer. Polyethylene terephthalate (PET) is a plastic material which has found increasing applications within the packaging field. It is a simple long-chain polymer. PET is an acronym for polyethylene terephthalate, which is a long-chain polymer belonging to the generic family of polyesters. PET is formed from the intermediates, terephthalic acid (PTA) and ethylene glycol (EG), which are both derived from oil feedstock. There are other polyesters based on different intermediates but all are formed by a polymerization reaction between an acid and an alcohol. PET, in its purest form, is an amorphous glass-like material. Under the influence of direct modifying additives it develops crystallinity. Also, crystallinity can be developed by heat treatment of the polymer melt. Soft drink and water bottles are made from this resin as are many plastic jars and clamshell packages (like cookie containers or trays). PET is the type of plastic labeled with the #1 code on or near 10 ottom of bottles and containers and is commonly used to package soft drinks, water, juice, peanut butter, salad dressings and oil, cosmetics and household cleaners. PET is a popular package for food and non-food products. Manufacturers use PET plastic to package products because of its strength, thermo-stability and transparency. Customers choose PET because it is lightweight, resalable, shatter-resistant and recyclable.

In the late 1950s PET was developed as a film. It was first used for video, photographic and X-ray films in addition to uses in flexible packaging. Later PET was modified for use in injection moulded and extruded articles, primarily reinforced with glass fibre. In the early 1970s PET was stretched by blow moulding techniques which produced the first oriented three dimensional structures initiating the rapid exploitation of PET as lightweight, tough, unbreakable bottles.

3.1   Processes Scheme
We can see the production stages of pet bottle briefly in the Figure 3.1.

Figure 3.1 PET Bottle Production Scheme
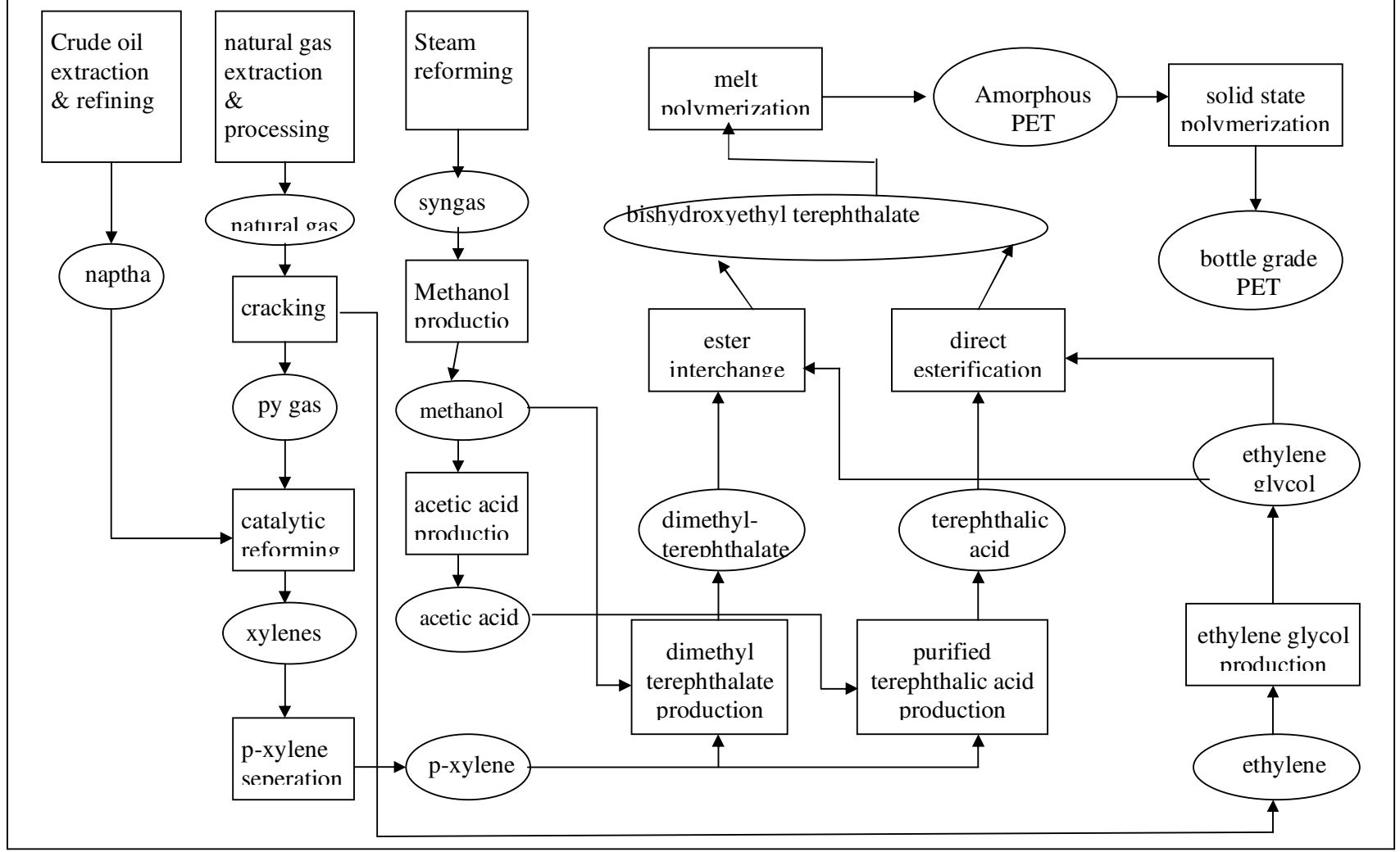
3.2 Crude Oil Exploration And Drilling

Liquid natural hydrocarbons are defined as crude oil, while gaseous hydrocarbons are defined as natural gas and both crude oil and natural gas together is named as "petroleum". Generally, the definition of petroleum is that; it is something formed by very small organics' (like planktons) chemical and biological transformations under absolute heat and pressure because of tectonic and geological movements through millions of years. However, there are some other factors and situations that form petroleum.

From drilling ability aspect, the basic elements petroleum needs are;

      i)   An appropriate main rock

      ii)   Geological structure's porosity and permeability where accumulation would be (Yanmaz, 2004).

"Oil reservoir" is the place where oil occurs underground. But contrary to known, there isn't an oil lake, a cave or whole that is full of petroleum. Different quantities of production possibilities exist which are affected by porosity and permeability of structure and pressure of reservoir as an average 15% of petroleum in a reserve can be produced with existing techniques. In other words, 15 % of petrol reserves are being produced in the world. Technological improvements are increasing this proportion but progress is not fast enough.

After an oil deposit is detected through exploratory drilling and determined whether it is an economical reserve, the area is opened for production. Drilling can take place both on land and offshore. Detecting lasts in 6 months averagely while production may continue more than 30 years. Oil reservoirs may be under 200 m or 6000 m.

"Rotary exploration systems" are used for detection and drilling in recent times. These are designed as different systems for land and offshore oil areas. The principal is to turn round pipe with mounted drill together. Pieces are brought to surface, drill is cooled and down hole pressure is controlled by a special fluid "drilling mud" that is pumped down through pipe. After the hole is drilled, a steel pipe (casing) slightly

smaller than the hole is placed in the hole, and secured with cement. The well is continued to be drilled deeper with a smaller bit. If enough care isn't taken petroleum can gush out and may cause fire hazard. To prevent this and to keep pressure on top of the bit "drilling fluid" is used. Also the top is usually outfitted with a collection of valves. These valves regulate pressures and control flows. If the pressure isn't high enough to expose petroleum to the surface, it is drilled by pumping or pulling down high pressure gas.

After an oil deposit is detected and some tests are performed, the real drilling may take place. Crude oil may differ in composition depending on where it is won. The average composition of crude oil is given in table 3.1 (Hannisdal, 2006).

Table 3.1 Composition of Crude Oil

Element	Wt % composition
Carbon	83.0-87.0
Hydrogen	11.0-14.0
Sulphur	0.05-6.0
Oxygen	0.05-1.5
Nitrogen	0.1-2.0
Metals (Ni, V)	< 0.1

3.3   Production Of Naphtha

After delivering the crude oil to the refinery it first will be subjected to a pre-treating process (desalting) in order to remove water, inorganic salts, suspended solids, and water-soluble trace metals. These contaminants can cause corrosion, plugging, and fouling of equipment or poison the catalysts in downstream processing units. After pretreatment, the crude oil will be distilled into a series of fractions. Although each fraction is still a complex mixture, the components now exhibit a smaller range of molecular masses. The fractions that are separated within different boiling ranges (often referred to as *cuts*) are given names. One of these cuts, called the naphtha - fraction, is the one used in providing petrochemical feedstock.

3.3.1 Desalting

Crude oil and heavy residues can contain varying quantities of inorganic compounds such as water soluble salts, sand, silt, rust and other solids, together characterized as bottoms sediment. The salt in the crude is primarily in the form of dissolved or suspended salt crystals in water emulsified with the crude. Those impurities, especially salts, could lead to fouling and corrosion of heat exchangers (crude preheaters) and especially the crude distillation unit overhead system. Salts are detrimental to the activity of many of the catalysts used in the downstream conversion processes and sodium salts stimulate coke formation (e.g. in furnaces). Some inorganic impurities are chemically bound, such as vanadium and nickel, often referred to as oil-soluble salts. These cannot be eliminated in a desalter. Moreover, water should preferably be removed if the water content of the crude is relatively high. Therefore desalting of the incoming crude oil is generally applied before separation into fractions. The principle of desalting is to wash the crude oil or heavy residues with water at high temperature and pressure to dissolve, separate and remove the salts and solids.

After preheating to 115 - 150 °C, the oily feedstock is mixed with water (fresh and pre-used water) in order to dissolve and wash out the salts. Intimate mixing takes place by contacting the wash water in a globe valve mixer, a static mixer or a combination of both. The water must then be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The separation efficiency depends on pH, density and viscosity of the crude oil, as well as the volume of wash water used per volume of crude. Either AC or DC fields may be used or potentials from 15 to 35 kV are used to promote coalescence. Many refineries have more than one desalter. Multiple stage desalters also exist. The wash water containing dissolved hydrocarbons, free oil, dissolved salts and suspended solids is further treated in an effluent treatment plant. Where bottoms sediments are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids.

Figure 3.2 shows a simplified process flow diagram of a modern design crude desalter (European Commission, 2003).
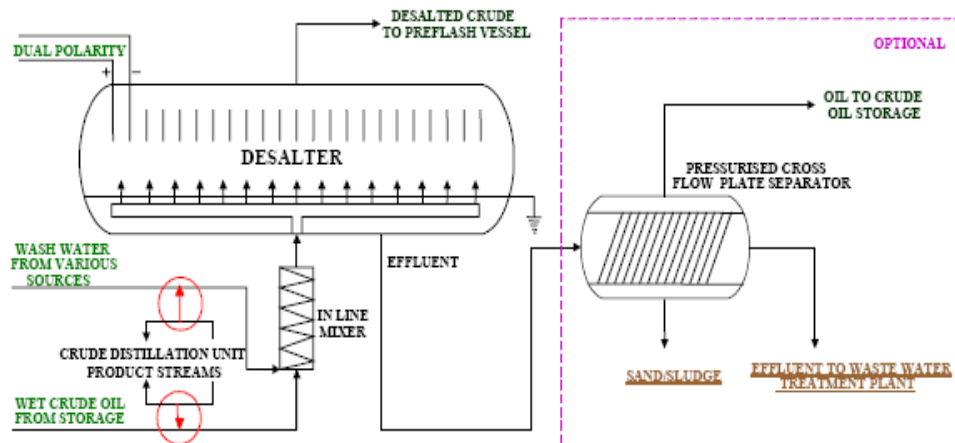
Figure 3.2 Process description crude oil desalting process

The water used in desalting the crude oil is water which of untreated or treated of other processes of refinery. The washing water is used % 3-10 according the volume of the crude oil. Electricity consumption is 0,075-0,15 kWh for desalting the crude oil.

3.3.2 Atmospheric Crude Oil Distillation Unit

The Atmospheric Crude Oil Distillation Unit (CDU) is the first important processing step in a refinery. Crude oil is heated to elevated temperatures and then generally subjected to distillation under atmospheric pressure (or slightly higher) separating the various fractions according to their boiling range. Heavier fractions from the bottom of the CDU, which do not vaporize in this column, can be further separated later by vacuum distillation.

Distillation involves the heating, vaporization, fractionation, condensation, and cooling of feedstock's. The desalted crude oil is heated to about 300 - 400 ºC and fed to a vertical distillation column at atmospheric pressure where most of the feed is vaporized and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The

lighter fractions condense and are collected towards the top of the column. The overhead hydrocarbon vapours are condensed and accumulated in the overhead reflux drum of the main fractionators. In this drum sour water, light fractions (about 0.5 % on crude charge) and stripping steam (1.5 % on crude), are separated from the hydrocarbon liquid. The overhead hydrocarbon liquid, the so-called naphtha minus stream, is commonly fed directly to the downstream naphtha treater. Within each atmospheric distillation tower, a number of side-streams of low-boiling point components are removed from different trays in the tower. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side-streams are each sent to a different small stripping tower containing four to ten trays with steam injected under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side-stream draw tray. Most of these fractions generated in the atmospheric distillation column can be sold as finished products after a hydro treatment, or blended with products from downstream processes. In Figure 3.3 a simplified process flow diagram of a crude distillation unit is shown. Many refineries have more than one atmospheric distillation unit (European Commission, 2003).
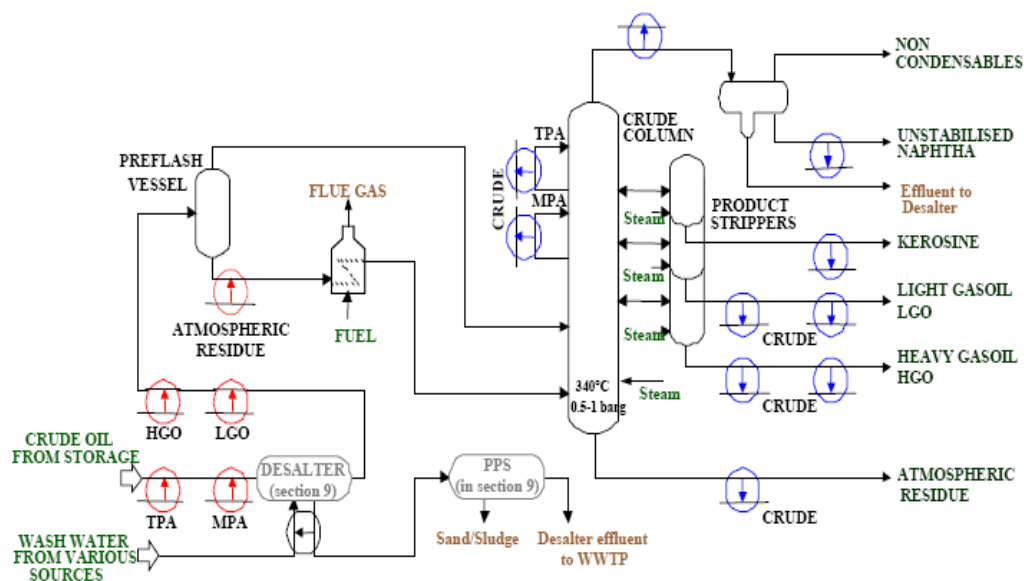
Figure 3.3 Process flow diagrams for crude oil distillation units

In this process the raw material is desalted crude oil. Products are naphtha, light products, light gas oil, and heavy gas oil. In the distillation of 1 tone of crude oil is used 2-6 kWh electricity, 4 m^3 cooling water, 112-190 kWh energy.

3.4 Petrochemical Processes

Petrochemicals are organic compounds derived from petroleum raw materials (called naphtha) or natural gas or a derivative produced from such a substance by chemical reaction, e.g., ammonia, carbon black and thousands of organic chemicals. Petrochemicals are commonly referred to a plastics or synthetic resins. We can use crops as substitutes for petrochemicals.

This industry comprises establishments primarily engaged in converting feedstocks derived from petroleum, or from petroleum and natural gas liquids, into petrochemicals.

Some important processes used in petrochemical manufacturing include steam cracking and steam reforming. For the purpose of defining this industry, petrochemicals consist of acyclic (aliphatic) hydrocarbons and cyclic aromatic hydrocarbons.

3.4.1 Ethylene Production

Almost the entire world demand for ethylene and butadiene, and the majority of propylene, is produced using the steam cracking process. In this process, suitable hydrocarbons are heated to very high temperatures, in the presence of steam, to split or 'crack' the molecules into the desired lower olefin products. Unlike much of the chemical industry, a small number of international technology contractors license the equipment employed on crackers. These specialist contractors utilize similar generic designs, but with modifications that optimize the plant performance to local conditions (especially with respect to integrated energy efficiency). Most proprietary designs concern the furnace, but there may also be variations in the pressure and

temperature of the fractionation columns; refrigeration systems (open versus closed loop); and the use of turbo expanders. Manufacturers are not tied to one particular technology contractor, and it is normal to find a cracker retro-fitted with equipment from rival contractors. Regardless of contractor or feedstock, a cracker can be broken down into three separate sections: pyrolysis; primary fractionation / compression; and product fractionation;

The hydrocarbon feedstock is preheated in heat exchangers and then vaporized with superheated steam before passing into tubes arranged in a cracking furnace. The tubes are long (50 - 200 meters) and of narrow bore (25 - 125 mm), and normally made of chromium nickel. The tubes are externally heated to 750 - 875 °C by oil or gas fired burners. By controlling the residence time, temperature profile and partial pressure, the hydrocarbon feedstock is cracked into smaller molecules (mainly ethylene, propylene, other mono-olefins and di-olefins). The conversion of saturated hydrocarbons to unsaturated compounds is highly endothermic and therefore requires a high-energy input. Steam is injected to reduce the partial pressure of the hydrocarbon mixture and also to minimize coke formation. Very small amounts of dimethyldisulphide (DMDS), or other sulphur containing additives, may also be added to minimize the formation of coke and carbon monoxide. The transfer line exchangers (TLEs) are used to quickly quench the product gases to 550 - 650 ºC (to prevent degradation by secondary reactions) and to generate high-pressure steam for plant re-use.

The primary fractionation and compression section consists of the primary fractionators (naphtha and gas oil feed only), quench tower, gas compressor and gas cleanup facilities. The latter may include an amine unit or caustic unit and drying facilities. The primary fractionator is used to condense out and fractionate fuel oil streams produced from naphtha and gas oil fed crackers. The gases are de-superheated in the quench tower by a circulating oil or water stream. The circulating oil or water stream is used as a medium level heat source for the rest of the plant. Some plants have no quench water tower and use direct cooling of the cracked gas with air coolers and/or cooling water. Tarry bottoms are removed from the system as product, which mostly fuels non-steam cracking furnaces and boilers. Most of the

dilution steam is condensed. Dilution steam is generally recovered and recycled back to the front end of the plant. During the start-up of the recovery and fractionation areas gases may be flared whilst the correct operating conditions are established and gas recycles may be used to reduce the need for flaring.

Gas compression product gases from the quench tower are condensed by four or five stages of gas compression. The gas is cooled after each stage and passed through a liquid knock-out drum. Large centrifugal compressors are used and are usually driven by high-pressure condensing steam turbines, or occasionally by electric motors. Gas Cleanup. Some naphtha and gas-oil feeds may contain up to 10000 ppm (1 %) of sulphur although most have typical levels of 100 ppm or less. Gas feedstock has a general requirement for acid gas removal upstream of the cracker and is therefore virtually sulphur-free as cracker feed. Sulphur is, however, a well known inhibitor of catalytic coke formation, and most operators inject sulphur, either in the dilution steam or hydrocarbon feed steam, to give a sulphur level in the furnace feed of around 50 - 100 ppm. There is a need to remove acid gases and carbon dioxide (produced at levels of a few hundred parts per million in the cracking process) from the cracked gas (ethylene and propylene products). Carbon dioxide may form solid deposits in the cryogenic sections of the plant and is an unacceptable impurity in the final ethylene product. The acid gas removal systems are designed to reduce the concentration of carbon dioxide and sulphur compounds in the cracked gas to less than one ppm. Acid gas removal involves a caustic unit (sometimes in combination with amines) and this generates an effluent that requires treatment. Gasoline may also be injected into the caustic scrubber to reduce polymer formation and to dissolve any that is present. Carbon dioxide can be removed by absorption in monoethanolamine (MEA). Drying, typically in molecular sieves, is also required after the final compression stage because the cryogenic temperatures in the downstream fractionation equipment would cause ice formation.

The chilling train usually consists of four or five successive stages of chilling, incorporating ethylene and propylene refrigeration, as well as an elaborate self-refrigeration system. This produces hydrogen that is used for downstream hydrogenation, hydrotreating of the heavier products (e.g. fuel oil) and as a saleable

product. In some processes, C_2 acetylene is hydrogenated in the cracked gas, prior to de-methanation. The methane stream from the chilling unit is used as fuel gas, mostly internally in the plant's furnaces and boilers. The exact process flow sequence varies according to the feedstock and the design arrangement, but various fractionation towers are used to separate the desired products. This may include a sequence of de-methaniser (to further remove methane), followed by a de-ethaniser (to remove ethane, ethylene and a small quantity of acetylene). Bottoms from the de-ethaniser are directed to the de-propaniser and then to a de-butaniser. The lighter the feedstock, the less need for the later separation systems. After separation, the ethylene still contains undesirable acetylene and ethane. Acetylene is either removed by selective catalytic hydrogenation or by extractive distillation. The separation of ethylene and ethane requires a particularly effective column due to the close proximity of their boiling points. The ethane component may be recycled back to the cracker for re-working. Similarly, the C_3 fraction still contains methyl acetylene and propadiene after separation. Selective hydrogenation is used to convert this into propylene and propane prior to separation in a C_3 splitter (European Commission, 2003).

In the process that being used naphtha as a raw material in the ethylene production; Approximately 3.2-3.4 tonnes naphtha, 44-54 kWh electricity, 370-470 m^3 cooling water are used for production 1 tonne ethylene (DPT, 2001).

3.4.2 Ethylene Glycol Production

Ethylene glycols are produced by reacting ethylene oxide (EO) with water. Ethylene oxide is formed by reacting gaseous ethylene and oxygen over a solid, silver containing catalyst. The reaction between ethylene and oxygen is carried out in a multi-tubular, fixed bed type reactor, with a silver oxide catalyst in the tubes and a coolant on the shell side. The heat generated by the exothermic reactions is removed by the coolant, and is recovered by producing steam. The steam is used as a heating medium in various sections of the plant. A large gas flow is circulated continuously through the EO reactors. Reaction products (EO, carbon dioxide and water) are

removed from the circulating gas while unconverted oxygen and ethylene are recycled back to the reactor. A small amount of an organic chlorinated compound (typically ethyl chloride or dichloroethane) is added to the recycle gas for catalyst performance control, and the chloride will end up in various product and effluent streams, partly as inorganic chloride. A vent stream is taken from the recycle gas in order to reduce the build-up of inserts like ethane, argon and nitrogen, impurities present in the ethylene and oxygen feedstock. The inserts vent is typically used as fuel gas and burned (e.g. in a cracker furnace or steam boiler). Make-up ethylene, oxygen and diluents are added to the recycle gas loop.

EO is recovered from the gaseous reactor effluent by absorption in water. The aqueous EO solution from the absorber is concentrated in a stripper. The top stream of the stripper is a concentrated EO/water mixture that is routed to a section for non-condensable removal and EO purification. The bottom stream of the stripper is an EO free water stream that is cooled and returned to the EO absorber.

Part of the recycle gas that leaves the EO absorber is routed through a column in which carbon dioxide is removed by absorption in a hot potassium carbonate solution. The carbon dioxide is subsequently removed from the carbonate solution in a stripper. The carbon dioxide vent from the top of the stripper is either routed to atmosphere or recovered for further use (e.g. carbonated drinks). The regenerated carbonate solution from the stripper bottom is cooled and recycled to the carbon dioxide absorber. The carbon dioxide depleted overheads stream from the absorber is recombined with the recycle gas stream and routed to the EO reactor(s).

Glycols are manufactured by feeding a mixture of EO and water to a reactor that is operated at an elevated temperature of typically 150 - 250 °C. Under these conditions reaction rates are fast and no catalyst is required. Sufficient residence time is provided to react all EO to full conversion. A reactor pressure of 30 - 40 bars is typically applied to avoid vaporization of the EO. The reactor feed contains an excess of water in order to limit the adiabatic temperature rise and to enhance the selectivity to MEG. Typically the glycol products consist of 70 - 95 %w/w MEG,

with the remainder being DEG and some TEG. All (100 %) of the EO feed is converted into glycols although some of the heavy glycols may be subsequently incinerated. The product stream from the glycols reactor contains the various glycol products and the excess of water. The excess water is removed by multiple effect evaporation with subsequent vacuum distillation and, after heat exchange, is recycled back to the glycols reactor. A bleed is taken from the water recycle to reduce the build-up of impurities. Low-pressure steam generated in this section is used as heating medium at various locations in the plant. The water depleted crude glycol stream is fractionated in a number of vacuum columns to recover the individual glycol products at high purity level. The glycol products are cooled and routed to storage. The bottom stream from the last vacuum column contains the heavier glycols and can be sold for further glycols recovery or sent for disposal (e.g. incineration) (European Commission, 2003).

In the production of ethylene glycol, approximately 0.6 tonnes ethylene, 0.6 tonnes oxygen, 468 kWh electricity, 314 m^3 cooling water are used for production 1 tonne ethylene glycol (DPT, 2001).

3.4.3   Para-xylene Production

Most of the xylene produced annually is derived from petroleum fractions. However, the concentration of light aromatics [*e.g.*, benzene, toluene, and xylene (BTX)] in petroleum rarely exceeds one percent. Through processing, petroleum, specifically crude oil, can be converted to BTX streams. Several petroleum fractions are used in aromatic conversion processing. The fraction most important to the para-xylene production process is "straight-run light naphtha" which includes all of the crude oil components heavier than pentanes and up to a final boiling point between 105°C and 170°C. A second refinery stream, also used as a feedstock in xylene production, is the naphtha that results from the pyrolysis or "steam cracking" of heavier distillate fractions. Although the primary goal of cracking naphtha is to manufacture ethylene and propylene, secondary reactions also produce considerable amounts of "pyrolysis gasoline" rich in aromatics. Additional xylene production

methods include separation from coal tars and disproportionate or transalkylation of toluene.

Hydro treating is the process by which the quality of liquid hydrocarbon streams is improved by subjecting them to mild or severe conditions of hydrogen pressure in the presence of a catalyst. Both pyrolysis gasoline and straight-run light naphtha (*e.g.*, catalytic reformer feeds) undergo hydro treating prior to subsequent processing and xylene recovery. The liquid petroleum feed is preheated, heated in a furnace, and combined with recycled hydrogen gas. The combined feed is passed through a reactor containing a catalyst bed where the hydrogenation reaction takes place. Upon leaving the reactor, the stream is cooled and moved to a separator vessel where recycle or net hydrogen is removed. The liquid then moves to a stabilizer or stripper which removes hydrogen, hydrogen sulfide, ammonia, water, organic compounds of arsenic and palladium, and light hydrocarbons dissolved in the separator liquid. The stripped, hydro treated fraction is then routed to the next processing step, secondary hydrogenation (for pyrolysis gasoline).

Pyrolysis gasoline, a by-product of ethylene and propylene manufacture, accounts for four percent of domestic xylene production capacity feedstock materials. Because pyrolysis gasoline contains reactive compounds (*e.g.*, diolefins and styrene's) which will polymerize if subjected to reactor conditions severe enough to saturate olefins and remove sulfur compounds, it must undergo an initial hydrogenation step to reduce the reactive to olefins prior to storage or further processing. The resulting product can be used as a high octane gasoline blending component or treated further for aromatic (*e.g.*, benzene, toluene, and xylenes) extraction.

Isomerization of xylene isomers requires an acidic catalyst, whereas isomerization of ethyl benzene additionally requires a hydrogenation catalyst, usually platinum. Removal of ethyl benzene increases the efficiency of p-xylene separation and the isomerization of the remaining C9 aromatics. Ortho-xylene is often produced along with p-xylene in the isomerization process and is recovered separately. Therefore, prior to p-xylene isomerization or recovery, o-xylene and ethyl benzene are usually isolated. Recovery of p-xylene is then performed via crystallization or adsorption,

and the remaining liquor or raffinate is isomerized to convert m- xylene to o- and p-xylene. The isomerization unit feed is sometimes mixed with hydrogen, heated to the reaction temperature, and passed over the catalyst. Vapor-phase and high-temperature isomerization processes are commonly used. The octafining process uses a combination of silica-alumina and platinized alumina catalysts to isomerize xylenes, however, most companies use the zeolite-based isomerization processes introduced in the 1970s. It is claimed that these processes can isomerizes xylenes, selectively disproportionate the remaining ethyl benzene, and improve the overall p-xylene yield.

A high-purity p-xylene stream can be isolated by using a two-stage, low-temperature crystallization process. The first crystallization, the coldest stage, yields slurry of crude p-xylene and a filtrate containing other isomers. Melting of the resulting slurry with a subsequent higher temperature recrystallization yields high-purity p-xylene. In the Parex process (licensed by UOP, Inc.) and the Aromax process (licensed by Toray Industries, Inc.), p-xylene is continuously and selectively retained on a zeolite adsorbent in the liquid phase. Zeolite permits entry of the main feed components into the pore structure and selectively adsorbs p-xylene. These continuous processes operate with a fixed bed, which appears to move in the direction opposite to the liquid streams. The p-xylene retained on the adsorbent is removed by a desorbent such as toluene or p-diethyl benzene; with p-xylene separated from the desorbent hydrocarbon by distillation. The typical p-xylene product from this process is around 99.5 percent pure and contains about 0.3 percent ethyl benzene, 0.17 percent m-xylene, and 0.1 percent o-xylene (EPA, 1994).

In the production of p-xylene, approximately 4.3 tonnes heavy naphtha, 31 kWh electricity, 258 m^3 cooling water are used for production of 1 tonne p-xylene.

3.4.4 Pure Terephthalic Acid Production

There are a variety of processes for producing both terephthalic acid (TPA) and dimethyl terephthalate (DMT). Different processes are used to produce technical and

polymer grades of terephthalic acid and dimethyl terephthalate. This discussion will concentrate on the polymer grade production methods used. Polymer grade terephthalic acid /dimethyl terephthalate is required for a majority of the derivatives manufactured from terephthalic acid /dimethyl terephthalate.

Amoco produces polymer grade terephthalic acid based on the liquid phase oxidation of p-xylene in the presence of a catalyst to produce crude terephthalic acid. Acetic acid and p-xylene are fed to a reactor with a cobalt acetate catalyst. The reactor is fed with compressed air to supply oxygen for the reaction. Reactor pressure and temperature are maintained at 1,500 kPa - 3,000 kPa (220 psi - 435 psi) and 175°C - 230°C respectively. Products from the reactor are pumped to a centrifuge to separate the crude terephthalic acid. The crude terephthalic acid produced is purified using the Amoco purification process. This process consists of processing aqueous slurry of the crude terephthalic acid through a dissolver which operates at greater than or equal to 250°C. The solution from the dissolver is pumped to a hydrogenation reactor which contains a noble metal catalyst. Hydrogen is fed to the reactor and impurities, such as 4-formylbenzoic acid, are converted to soluble compounds which remain in the mother liquor during the recrystallization process for the polymer grade terephthalic acid (EPA, 1994).

In the production of terephthalic acid, 0.665 tonnes p-xylene, 450 kWh electricity, 213 m^3 cooling water are used for production of 1 tonne terephthalic acid (DPT, 2001).

3.5 PET Bottle Production

The manufacturing process of the PET bottle for the prior art can be separated to three main steps:
- ✓ Melted state polycondensation operation
- ✓ Solid state polycondensation operation
- ✓ Blow molded manufacturing operation

3.5.1 *Melted State Polycondensation Operation*

In the continuous melted state polycondensation operation process, the terephthalic acid (PTA) and the ethylene glycol (EG) are blended to form thick liquid; the isophthalic acid (IPA) 0~10 mol % is added thereafter and blended together and then transmitted to esterification tank so as to perform direct esterification. The operation temperature of esterification is between 220~265°C. The operation pressure of esterification is between normal pressure and 2.0 kg/cm$^{2.}$ The produced water and alcohols during said process should be distilled out. While the esterification has completed 95~98% of esterification conversion ratio, the esterification has been stopped and the polycondensation is initiated. A catalyst should be added before polycondensation in order to expedite the rate of polycondensation so as to shorten the polycondensation time. Antimony acetate or antimony trioxide or germanium dioxide or titanium, or their mixture can normally be used as catalyst to expedite the completion of polycondensation. In addition, the stabilizer such as phosphoric acid, phosphorous acid, trimethyl phosphate, triphenyl phosphate, triethyl phosphate is added.

The polycondensation of PET and its copolymer includes pre-polymerization and main-polymerization. The operating temperature for pre-polymerization is between 270~280°C., and the operating vacuum intensity for pre-polymerization is between 250~15 mmHg. The operating temperature for main-polymerization is between 275~285°C., and the operating pressure for main-polymerization are below 1 mmHg. The intrinsic viscosity of PET polymer is raised to 0.5~0.7 dl/g at the end of PET melted state polycondensation. Then, the polymer is unloaded to cooling water for quick cooling-down and further is cut to PET chip with column shape. The residual of acetaldehyde in PET chip at this stage is approximately higher than 50 ppm, which makes the PET chip unsuitable to be directly processed by the blow molder to manufacture PET bottles. The mixture then reacts further, distils out excess ethylene glycol and forms the PET (Figure 3.4).

$$HOOC\langle O \rangle COOH + HOCH_2CH_2OH \rightarrow HO\left[OC\langle O \rangle COOCH_2CH_2O\right]_n OH + 2H_2O$$

| PTA | EG | Oligomer[n=2 to 5] | water |

1.Catalyst 285°C vacuum
2. Solid phase polymerization -220°C

$$\mathbf{HO\left[OC\langle O \rangle COOCH_2CH_2O\right]_n OH}$$

Polyethylene Terephthalate[n=130–150]
Molecular weight ca 25,000
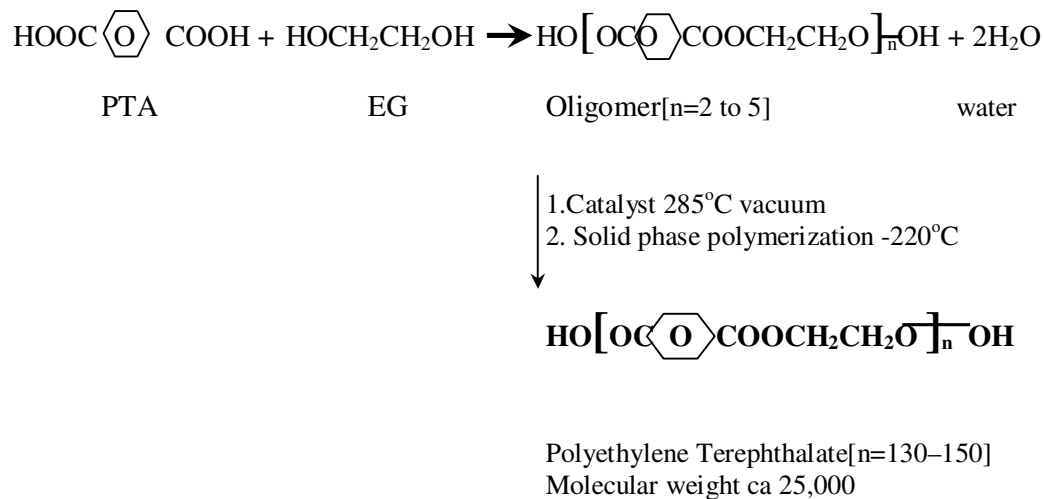
Figure 3.4 Chemistry of Formation of PET

The DMT process is the older than PTA processes. Polymerization grade PTA has been available only since 1963. The production of methanol in the DMT process creates the need for methanol recovery and purification operations. In addition, this methanol can produce major VOC emissions. To avoid the need to recover and purify the methanol and to eliminate the potential VOC emissions, newer plants tend to use the TPA process (Patentstorm, 2002).

3.5.2 Solid State Polycondensation Operation

The intrinsic viscosity of the PET chip made from "Melted state polycondensation operation" is somewhere between 0.5~0.7 dl/g; however, the molecular weight of the PET chip is too low for "Blow molded manufacturing operation". Besides, its strength is below enough. Moreover, the residual acetaldehyde in the PET chip is too high to manufacture PET bottles. Consequently, "solid state polycondensation" is a necessity to raise the intrinsic viscosity of PET chip up to somewhere between 0.72~1.2 dl/g so as to obtain enough molecular weight needed by the succeeding blow molding process and to reduce the residual acetaldehyde in PET chip to below 1 ppm. One of the solid state polycondensation processes is the batch process, where the PET chip is heated in a vacuum revolving tank. The other one is the continuous process, where the PET chip is treated by crystallization and dryness, then an inert gas (such as nitrogen gas) is led into the solid state polycondensation tank in order to

raise the intrinsic viscosity and to reduce the residual acetaldehyde in PET chip to below 1 ppm.

The solid state polycondensation is operated in an inert gas stream or vacuum environment, the operating temperature of which is between 180~240°C.; in general, the operating temperature is below the melting point of PET and its copolymer to prevent stocking from taking place. In normal circumstance, the PET chip solid state polycondensation for continuous process is operated at the exist of inert gas stream. The inert gas includes nitrogen, carbon dioxide, helium, argon, krypton, xenon gases or their mixture. The helium gas is commonly used as inert gas. The continuous solid state polycondensation reactor includes fluidized bed and moving bed. In most cases, a column shape polycondensation reactor is better to be utilized, wherein the PET chip is transmitted through the reactor in a speed which fits the needed reaction time. The column shape reactor should be high enough to allow the PET chip be transmitted by gravity from the top to the bottom of the reactor in a speed that fits the needed reaction retention time to obtain the required final intrinsic viscosity. The reaction retention time can be controlled by adjusting the effluent at the bottom of the reactor. The inert gas flows upward by counter current through the reactor with a speed better lower than turbulent point so as not to make the PET chip to flow. The PET chip remains the same physical form throughout the overall course of solid polycondensation process (Patentstorm, 2002).

In the production of PET, 0.32-0.355 tonnes ethylene glycol, 0.825-0.87 tonnes terephthalic acid, 584-1260 kWh electricity, 0.4-10 m^3 cooling water are used for production of 1 tonne PET.

3.5.3 Blow Molded Manufacturing Operation

Stretch blow molding is best known for producing PET bottles commonly used for water, juice and a variety of other products. Stretch blow molding has been used since the early 1970's especially for packaging detergent, and has grown in existence with the primary use for making carbonated beverage bottles.

One of the major advantages of stretch blow molding is the ability to stretch the preform in both the hoop direction and the axial direction. This biaxial stretching of material increases the tensile strength, barrier properties, drop impact, clarity, and top load in the container. With these increases it is usually possible to reduce the overall weight in a container by 10 to 15 percent less then when producing a container in another way.

The PET chip with high intrinsic viscosity, which has been processed by solid state polycondensation, required by blow molding is further processed by the ejector and blow molder to produce transparent PET bottles. The operating temperature of the ejector is somewhere between 260~285℃., where the acetaldehyde content of PET chips is quickly increased by the function of this high temperature and mechanical shear force (Patentstorm, 2002).

Stretch blow molding is divided into two different categories single-stage and two-stage;

Single-stage uses the extruder to inject parison into a preform mold where the plastic is rapidly cooled to form the preform. The preform is then reheated and placed in the bottle mold. Then softened parison stretches to about twice its original length. Compressed air is then blown into the stretched parison to expand to the bottles mold. Once the bottle is cooled the mold is opened and the finished bottle is emptied from the mold cavity. This technique is most effective in specialty applications, such as wide mouthed jars, where very high production rates are not a requirement.

Two-stage stretch blow molding is the same as single-stage, except the preforms are already made. The single-stage process is usually done using one machine, where the two-stage process uses preforms that have already been made and cooled. This allows companies to either make or buy their own preforms. Because of the relatively high cost of molding and RHB equipment, this is the best technique for

producing high volume items such as carbonated beverage bottles. In this process, the machinery involved injection molds a preform, which is then transferred within the machine to another station where it is blown and then ejected from the machine. This type of machinery is generally called injection stretch blow molding and usually requires large runs to justify the very large expense for the injection molds to create the preform and then the blow molds to finish the blowing of the container. This process is used for extremely high volume runs of items such as wide mouth peanut butter jars, narrow mouth water bottles, liquor bottles etc (Syam Plastic, 2008).

1 PET resin is melted to produce the mid-stage product Preform	2 Preform is reheated to the desired temperature	3 Preform is put inside a blow-Mold
4 Stratching and first Blowing with low air pressure	5 Final formation using intense pressure to form the desired bottle shape	6 Final product is cooled and removed from metal pattern
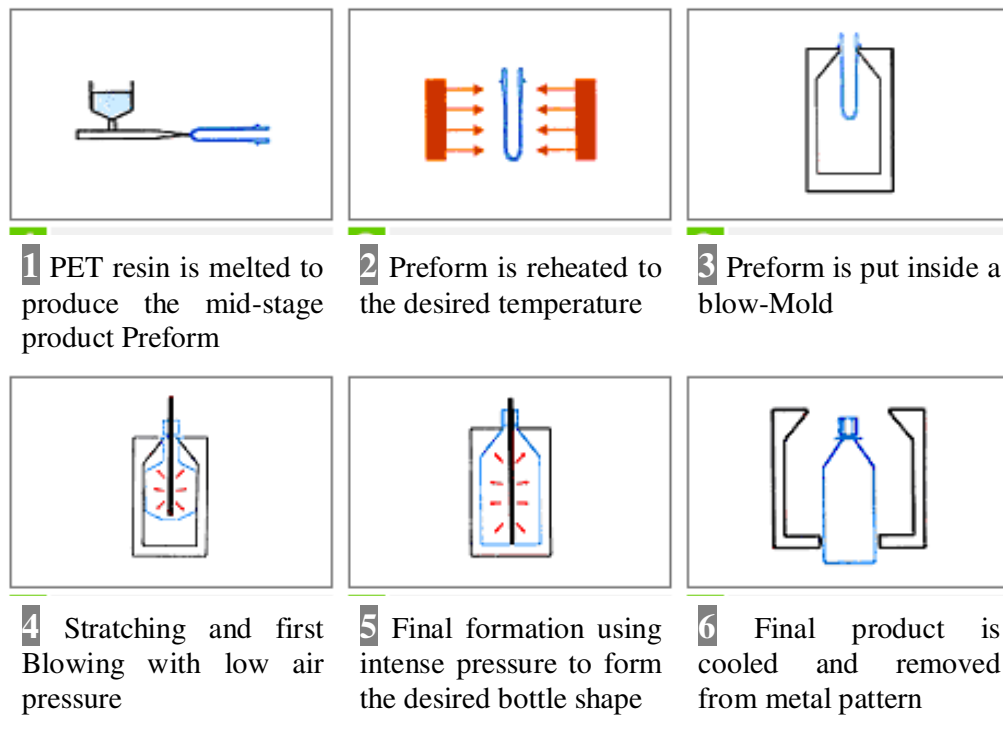
Figure 3.5 Stretch blow molding scheme

CHAPTER FOUR
MASS BALANCE OF THE PET BOTTLE PRODUCTION

The amount of water and energy consumption which are used to calculate PET bottle production mass balance and raw materials required for producing PET bottle are like that;

- ✓ 800 L production water is occurred for production of 1 L crude oil. This production water is not calculated in the consumption of natural spring because of the fact that the production water is deepenjected to underground again after the treatment (Nagy, 2002).

- ✓ Between 0.075 – 0.15 kWh electricity are comsupted to desalting of 1 tonne crude oil. The water which is used in the crude oil desalting is the water of not treated of other refinery process or partly treated. Between %3-10 washing water is needed according to density of crude oil (European Commission, 2003).

- ✓ In the distillation of 1 tonne desalting crude oil 2-6 kWh electricity, 4 m^3 cooling water, 112-190 kWh energy are used (European Commission, 2003).

- ✓ In the refinery, there are produced approximately % 8 light naphtha, %8 heavy naphtha with desalting and distillation of 1 tone crude oil. These product amounts are taken as a approximate amounts because of the fact that these amounts change according to the quality of the oil and process (Tüpraş, phone call).

- ✓ In the process where is used naphtha as a raw material in the production of 1 tonne ethylene, approximately 3.2-3.4 tonnes light naphtha, 44-54 kWh electricity, 370-470 m^3 cooling water are used.

- ✓ Approximately 0.6 tonnes ethylene, 0.6 tonnes oxygen, 468 kWh electricity, 314 m^3 cooling water are used for production of 1 tone ethylene glycol (DPT, 2001).

- ✓ 4.3 tonnes heavy naphtha, 31 kWh electricity, 258 m^3 water are used for production of 1 tonne p-xylene.

- ✓ 0.665 tonne p-xylene, 450 kWh electricity, 213 m^3 cooling water are used for production of 1 tonne pure terephthalic acid (DPT, 2001).

- ✓ 0.32-0.355 tonnes ethylene glycol, 0.825-0.87 tonnes terephthalic acid, 5138 kWh electricity, 0.4-10 m^3 cooling water are used for production of 1 tonne PET.
- ✓ 251-264 kWh electricity, 0.2-15 m^3 water is used for solidification process of 1 tonne PET (Shyam Plastic, 2008).
- ✓ 31 gr PET perform are needed for production a PET bottle of 1,5 L (European Commission, 2007).

In the Table 4.1 there are given the unit consumptions production of PET bottle. The amounts in the table are consumptions of electricity and water and the amount of raw material used as a product of 1 tonne.

Table 4.1 Unit Consumptions for 1 tonne Product

Product	Raw Material	Raw Material Consumption for 1 tonne Product (tonne/tonne)	Electricity Consumpt. (kWh/tonne)	Water Consumpt. (m^3/tonne)
Crude Oil	Desalting Crude Oil	-	0.075-0.15	0.03 - 0.1
Refinery Products	Distillation Crude Oil	-	2-6	4
Heavy Naphtha	Crude Oil	0.08	-	-
Light Naphtha	Crude Oil	0.08	-	-
Ethylene	Light Naphtha	3.2 - 3.4	44 -54	370 - 470
Ethylene glycol	Ethylene	0.6	468	314
P-xylene	Heavy Naphtha	4.3	31	258
Pure terephthalic acid	P-xylene	0.665	450	213
PET resin	Ethylene glycol	0.32 - 0.355	5138	0.4-10
	Pure terephthalic acid	0.825 - 0.87		
PET cips	PET resin	-	251-264	0.2 -15
TOTAL			**6,384- 6,411**	**1,156-1,280**

From the point of the fact that 31 gr preform are used for one PET bottle, raw materials needed for PET resin are calculated according to this amount. With this method all raw materials, water and electricity consumptions are calculated and these

amounts are shown in the figure 4.1 (PET bottle production mass balance). In the figure 4.1 there is mass balance required for producing a PET bottle of 1.5 L. The amount of water and energy consumption which are used to calculate this mass balance and raw materials required for producing PET bottle.
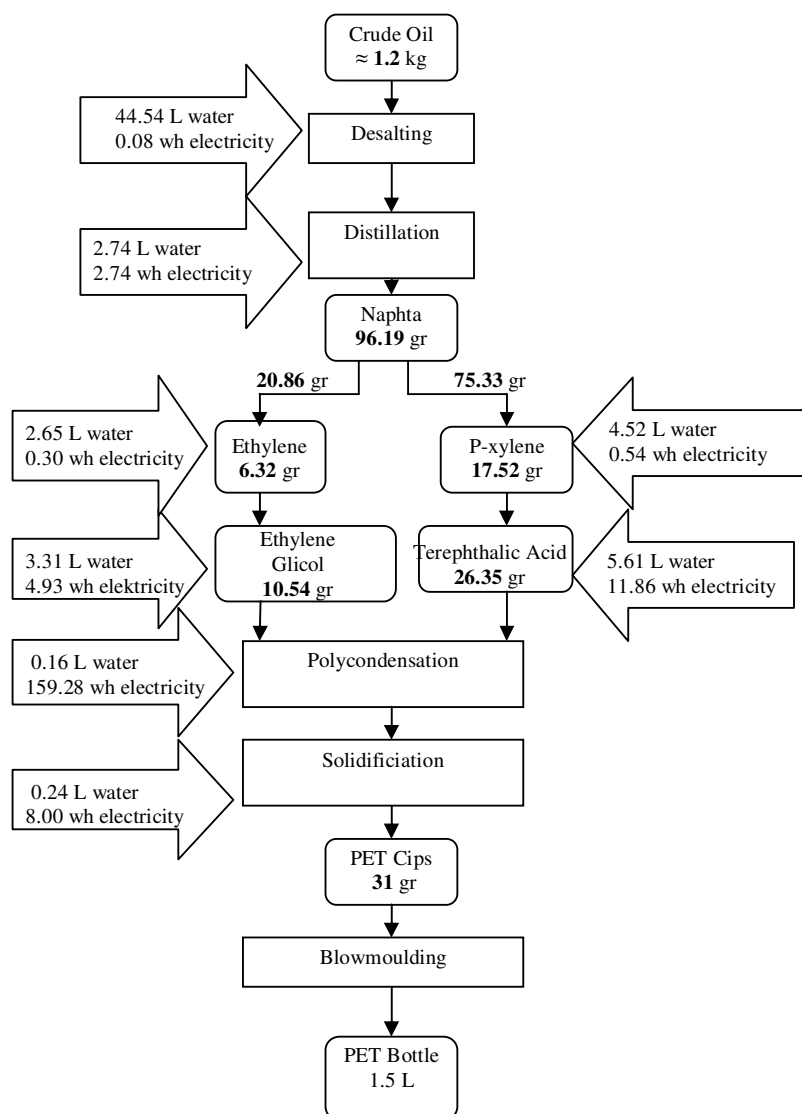
Figure 4.1 PET bottle production mass balance

CHAPTER FIVE
ENVIRONMENTAL EFFECTS OF PET PRODUCTION PROCESSES

5.1   Environmental Effects Of Crude Oil Exploration And Drilling

Oil drilling has different environmental impacts on land and offshore. The most important waste that occurs during oil drilling is "process water" by forming 95 % portion of all wastes. A mass quantity of water is produced with hydrocarbons in oil drilling areas all around the world. Quantities increase by production more and more. Produced water is seen as principal product with petroleum products and needs to be managed effectively. Due to consisting of chemicals, it may cause technical, economical and environmental problems. So, its chemical characteristics must be well known to be able to control it. Produced water brought up to the surface is processed to remove the crude oil product. Treatment of produced water makes use of vessels such as free water knock-out tanks, heater-treater tanks, and water treatment plants. Prior to disposal, produced water is typically contained in large storage tanks. Produced water samples were taken from holding tanks intended for disposal into sewers, holding tanks for Class II injection wells, and from pipelines leading to an irrigation canal, intended for agricultural use. The practicality of the method depends largely on the regional characteristics. For example, percolation ponds would not be likely in an urban setting.

Soil and rock cuttings are lifted to the surface by the fluid circulated through the drilling pipe and collected into a nearby earthen pit, called drilling pit. The composition of the drilling wastes reflects the characteristics of the formation being drilled, and the composition of the drilling fluid utilized. Drilling waste often appears as sludge, with an aqueous layer floating on the surface. The composition of the drilling fluid itself might vary, depending on the circumstances of drilling. Typically a mixture of water and clay, drilling fluids may contain other additives. A common additive is barite, a weighting agent, used to improve the viscosity of the fluid and its ability to counterbalance the formation pressure and to float soil material to the surface. Oil-based and synthetic fluids are used in special circumstances, such as

drilling to great depth or through high-pressure formations. Based on information supplied by industry representatives, the most common method of disposal for drilling wastes is on-site burial of drilling pit contents after aggregation of the aqueous component with cement. This method has regional limitations and may not be appropriate where drilling fluids other than water based fluids are used. An alternate method of disposal is shipment to a commercial disposal facility that accepts E&P wastes (EPA, 2002).

Water based mud (WBM) wherever possible throughout its operations because of the known reduced environmental effects associated with WBM compared to other mud types. Over 90% of the WBM that is used during drilling will be discharged, with the remainder estimated to be lost down-hole through filtration or lost circulation or left behind casing.

The drilling wastes are mainly collected in tanks near the drilling rig and sometimes, after some initial treatment, are dumped or buried. One of the worldwide most popular method of drilling waste treatment is solidification and stabilization. If pollution is below the allowed limit, drilling waste can be solidified. Cement and silica are the most popular agents. In this way we can get two targets: better mechanical properties by the solidification and the stabilization by the pollution encapsulation. The stabilization minimizes the solubility and mobility of the pollution. The solidification changes the suspension or detached rock into the solid rock. A modification of this method is cementing in the CO_2 atmosphere. In the regular cementing large blocks arise, but in CO_2 a granulated product can be achieved. The injection of cuttings into injection layers or salt caverns is a very often used method. It is successful as well in onshore as in offshore operations. The thermal method is very useful for cleaning the cuttings. It can be done by burning, the low temperature thermal desorption , the thermal phase separation, the rotary kiln and the cement kiln A more sustainable solution is to use natural forces and processes. Bioremediation can be done in five ways: composting, bioreactors, vermiculture and land farming. But the true sustainability can be meeting by a combination of some of the above methods and a new design of proecological

drilling process. As a result, we can get a new sustainable model of drilling waste management (Knez&Gonet, 2006).

The main sources of atmospheric emissions during offshore drilling will result from diesel burnt for power generation for the drill rig and standby vessel and also from flaring associated with possible well testing (BG Group, 2005).

Table 5.1 Atmospheric emissions from the Channon Well

Gas	Drill Rig (tones)	Standby Vessel [2] (tones)	Total (tones)
Carbon dioxide	1,843.20	774.14	2,617.34
Carbon monoxide	6.05	2.54	8.59
Oxides of nitrogen	22.86	9.60	32.46
Sulphur dioxide	3.46	1.45	4.91
Methane	0.06	0.03	0.09
Volatile organic chemicals	0.752	0.32	1.072
TOTAL	1,876.38	788.08	2,664.46

   Note 1: Emission factors used from UKOOA 2002a based on methodology proposed by OGP (former E&P Forum, 1994)
   Note 2: Rig is estimated to consume @ 12 tones fuel/day and safety standby vessel @ 5 tones fuel/day for 48 days duration of drilling program.

The main waste product from offshore drilling operations is rock cuttings and fine solids from the centrifuges. Other waste products include the discharge of cement during the cementing process. It is estimated that the drilling of the well will generate a maximum total of 1235 tones of cuttings. During the drilling, between 1155 and 1235 tones of drill cuttings will be discharged directly onto the seabed and assuming there was no effects from currents cuttings will accumulate in the immediate vicinity of the well. Once the marine riser is in place, the cuttings are returned to the rig and collected for return to shore and licensed disposal. Water generated from rig wash-down may contain trace amounts of mud, lubricants and residual chemicals resulting from small leaks or spills and rainfall from open deck areas. The volume of these discharges depends on the frequency of wash-down and amount of rainfall. Liquid storage tanks and areas that might be contaminated with oil are segregated from other deck areas to ensure that any contaminated drainage water can be treated prior to

discharge and accidental spills contained. Drainage water from these areas and 'machinery spaces' is collected, treated to remove hydrocarbons (less than 15 parts per million hydrocarbons in water) as required under the MARPOL Convention and the cleaned water then discharged to sea. Black (sewage) and grey water is also collected, treated to meet the requirements of the MARPOL Convention and discharged to sea. These are all relatively low volume discharges containing small residual quantities of contaminants. The MARPOL convention prohibits discharge of any garbage or solid wastes into the sea. Periodically these will be transported to shore and the waste recycled or disposed of in a controlled manner through authorized waste contractors. Careful consideration is given to minimizing the amount of waste generated and controlling its eventual disposal. Typically, 24 tones of waste are generated per month from a single well drilling programmed (BG Group, 2005).

5.2   Environmental Effects Of Desalting

The quantity of inorganic impurities in the crude oil depends very much on both the crude origin and the crude handling during transport from the crude well to the refinery.

Air Emissions: No major emissions to the air are produced during the desalting processes. Air emissions from the heating processes are expected and fugitive emissions hydrocarbons may be expected.

Waste Water: The desalter is a big contributor of process waste water (30 - 100 liters / tone feedstock desalted). The desalting process creates an oily desalter sludge and a high-temperature salt water waste stream (possible the most polluted in the refinery) which is typically added to refinery waste water treatment facilities. The waste water generated is highly contaminated. Table 5.2 shows the ranges to be expected from waste waters from desalters.

Table 5.2 Composition of the waste water generated in the desalting process

Water pollutants	Typical concentration (mg/L)
Temperature (°C)	115 - 150
Suspended solids	50 - 100
Oil/oil emulsions	high
Dissolved hydrocarbons	50 - 300
Phenols	5 - 30
Benzene	30 - 100
BOD	high
COD	500 - 2000
Ammonia	50 - 100
Nitrogen compounds (N-Kj)	15 -20
Sulphides (as H_2S) 10	10

Solid Wastes Generated: The quantities of desalter sludge generated depend on the solid content of the crude, the separation efficiency and the applied dislodging mode and frequency. Normally a desalter clean-out is done twice a year, yielding from 60 - 1500 t/yr oily sludge, dependent on the throughput and efficiency of the process to capture solids. The sludge generated can contain iron rust, clay, sand, water (5 - 10 %), emulsified oil and wax (20 - 50 % w/w) and metals (European Commission, 2003).

5.3   Environmental Effects Of Atmospheric Crude Oil Distillation

Air Emissions

Potential releases into air are from:

✓ Flue gases arising from the combustion of fuels in the furnaces to heat the crude oil.

✓ Pressure relief valves on column overheads; relief from overhead accumulator are piped to flare as well as the vent points.

✓ Poor containment in overhead systems, including barometric sumps and vents.

✓ Glands and seals on pumps, compressors and valves.

✓ De-coking vents from process heaters. During furnace decoking (once or twice a year) some emission of soot can occur if operation is not properly controlled in terms of temperature or steam/air injection.

✓ Venting during clean-out procedures.

✓ Fugitive emissions from atmospheric and vacuum distillation units account for 5 - 190 t/yr for a refinery .

Table 5.3 Examples of air emissions generated by crude oil distillation units

Factory	Fuel Consump. (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	PM
OMV Schwechat	1536,9	8200000 Crude oil	mg/m^3 t/yr kg/t	46 71 0,009	107 165 0,02	6 9,3 0,001	298149 36	1 1,5 0
Mider	1138,8	8500000	mg/m^3 t/yr kg/t	35 35,2 0,004	100 100,4 0,012	100 100,4 0,012	220927 26	5 5 0,001

Waste Water: Process waste water generated in the atmospheric distillation units is 0.08 - 0.75 m^3 per tone of crude oil processed. It contains oil, H_2S, suspended solids, chlorides, mercaptans, phenol, an elevated pH, and ammonia and caustic soda used in column overhead corrosion protection. It is generated in the overhead condensers, in the fractionators and can also become contaminated from spillages and leaks. The overheads reflux drum (gas oil dryer condensator) generates 0.5 % water on crude + 1.5 % steam on feed with a composition of H_2S 10 - 200 mg/l and NH_3 10 - 300 mg/l. Sour water is normally sent to water stripper/treatment.

Residual Wastes Generated: Sludges can be generated from the cleaning-out of the columns. The amount depends mode of desludging and the base solid and water content of the crude processed. The solid waste generation from a crude unit of 8.7 Mt/yr ranges from 6.3 - 20 t/day (European Commission, 2003).

5.4 Environmental Effects Of Ethylene Production

Total emissions in the ethylene production consist of cracking, point resources, decocing operations, flyer etc.

NO_x	1.0-2.8 kg/ t ethylene
SO_2	0.01-3.3 kg/ t ethylene
CO	0.2-1.0 kg/ t ethylene
VOC	0.03-6.0 kg/ t ethylene
PM	0.05-1.5 kg/ t ethylene
CO_2	1.5-2.1 t/t ethylene

Air Emissions: A European Chemical Industry Council(CEFIC) survey has elicited responses from 39 Lower Olefin producers, covering 42 crackers (more than 80 % of steam cracker population) and 441 furnaces. Data on emissions of carbon monoxide and nitrogen oxides are given in Table 5.4.

Table 5.4 CEFIC survey response on CO and NOx emissions

	CO (mg/Nm^3)		NO_x (mg/Nm^3)	
	Number	Range	Number	Range
Full range	35	0.2-620	39	61-250
1st tier	12	0.2-12	13	61-110
2nd tier	12	12-30	13	110-143
3rd tier	11	30-620*	13	145-250

* Includes 2 figures, reported as > 250 mg/Nm3, which are believed to have been incorrectly reported. Reference conditions were not collected in the CEFIC survey but the concentration data can be interpreted as 30 - 60 minute averages at normal temperature and pressure, 3 % oxygen, dry gas.

22 respondents to the CEFIC survey reported levels of SO_2 emissions in the range 0.1 - 100 mg/Nm^3 (as 30 - 60 minute averages at normal temperature and pressure, 3 % oxygen, and dry gas). All but 3 are less than 20 mg/Nm^3, which corresponds to the expected figure with normal sweet residue gas (methane/hydrogen). For this reason SO_2 emissions are not normally considered to be significant for steam crackers. 15 respondents to the CEFIC survey reported particulate emissions in the range 0.2 - 25 mg/Nm^3.

All crackers are provided with flare gas systems to allow safe disposal of any hydrocarbons or hydrogen that cannot be recovered in the process. This is particularly the case during unplanned shutdowns, and during start-ups, when the intermediate streams have not reached the compositions required to enable the production of full-specification products.

During normal operation there are very few VOC emissions from the cracking process because they are recycled into the process, used as a fuel or routed to associated processes on an integrated site. Hydrocarbons are mostly emitted due to leakage and flaring of the residual gases. In the Netherlands, VOC emissions were attributed to 72 % from leakage losses from appendages, pumps, etc., 18 % from flaring and disruption, 1 % from losses due to storage and handling, 5 % from combustion and 4 % from other process emissions.

Water Emissions: There are three effluent streams that are specific to the steam cracking process, namely: process water, spent caustic and decoke drum spray water. All aqueous streams, from whatever source, pass through some or all of the treatment facilities, and the contribution of each cannot be easily isolated for reporting purposes. Accordingly, the total aqueous effluent flow rate (per tone of ethylene) can vary greatly, depending on the individual water management requirements at the location. With no dilution steam generation, the contribution of the process water stream to the total waste water flow from the plant is therefore also between 1 and 4 m^3/t ethylene. Dilution steam generation systems are typically designed to recycle around 90 % of the process water, which would therefore reduce the contribution to aqueous effluent from this source to 0.1 to 0.4 m^3/t ethylene. Table 5.5 shows the effluent quantity and quality both before treatment (the stream leaving the core unit, upstream of final treatment) and after treatment. The data are based on 39 survey responses representing 42 crackers on 34 sites.

Table 5.5 CEFIC survey results for total aqueous effluent pre/post treatment

Range	Volume (m³/t ethylene)		TOC(g/t ethylene) [5]			TOC(mg/l) [5]		
	Pre treatment (1)	Post treatment (1)	N° off	Pre treatment (2)	Post treatment (6)	N° off	Pre treatment (3)	Post treatment (4,6,7)
Full	0.02-8.5	0.02-8.5	36	13-2700	2-800	26	30-1650	1.8-330
1st tier	0.02-1.5	0.02-1.5	9	13-210	2-23	9	30-100	1.8-13
2nd tier	1.5-2.5	1.5-2.5	9	220-400	30-60	9	120-200	15-33
3rd tier	2.5-8.5	2.5-8.5	8	430-2700	65-800	8	200-1650	46-330

1. The lowest figure (0.02) is probably an outlier and the next lowest is 0.3. The range excludes data from plants using a once through cooling water system, but it includes data from plants that do not have facilities for dilution steam recovery from primary fractionator / quench column spent water.
2. The highest value (2700) is maybe an outlier and the next highest figure is 1400.
3. Only 2 figures exceeded 400.
4. When expressed as COD, the full range is 5 - 800 ppm.
5. Responses made in units of COD have been converted to TOC using a factor of 2.5 (COD/TOC=2.5). Some organic load is made up of oxygen-containing hydrocarbons including methanol (about 10 ppm), acetaldehyde
(about 15 ppm) and traces of acetone and acetic acid
6. The range includes data from plants without biological oxidation systems.
7. There is evidence to suggest that lower figures may be due to differences in analytical technique and / or assumptions in determining the contribution of lower olefin effluent to a central waste water treatment facility.

Solid Wastes: Relatively little solid waste is generated in the steam cracking process when running on gas or naphtha, although there is more significant production on a gas-oil feedstock. The bulk of steam cracker solid waste is organic sludges and coke, but there are also specific arisings of spent catalyst, spent adsorbents and solvent purges. Catalysts have an economic lifetime of roughly 5 years. Once efficiency declines to an unacceptable level spent catalysts are generally returned to the catalyst supplier for recovery of the noble metal. Drying adsorbents have a typical economic lifetime of 3 - 4 years. They are generally land filled after regeneration/deactivation (European Commission, 2003).

5.5 Environmental Effects Of Ethylene Oxide/ Ethylene Glycol Production

In the oxygen-based process, the overhead stream of the carbon dioxide stripper contains carbon dioxide and small amounts of ethylene, methane and EO. It is treated

by physical treatment (enrichment for recycling of valuable substances), or by thermal or catalytic oxidation. The resulting stream is essentially pure carbon dioxide (and water) containing traces of hydrocarbons (methane and/or ethylene), and where possible is sold to a customer. More often the treated stream is vented to atmosphere. Effluent and emission levels are given in Table 5.6.

Table 5.6 Carbon dioxide removal vent pre treatment and post treatment

Parameter	Effluent stream pre treatment		Emissions post treatment	
	All units	Lowest 50 % of units	All units	Lowest 50 % of units
Ethylene (kg/t EO ex reactor)	0.1-2	-	-	-
Methane (kg/t EO ex reactor)	0-1	-	-	-
Ethylene + methane (kg/t EO exreactor)	0.4-3	0.4-1	0*-3.1	0*-0.2

* In the case of treatment by oxidation the emissions are considered to be zero

In some plants, the water used to absorb EO is cooled down in a cooling tower. As this water contains some traces of organics, the air from the cooling tower contains VOCs (between 0.015 to 0.6 kg VOC/t EO ex-reactor. There is no direct treatment of the gas stream leaving the cooling tower and cooling tower vapours are vented to atmosphere.

Water Emissions: In many cases, the aqueous effluent streams are treated in central facilities together with other streams, and this makes it difficult to establish the true contribution to the overall emission. CEFIC have assumed that, on the basis of the high biodegradability of glycols, then biotreatment will reduce the organic load by at least 90 %.

Solid Wastes: The EO catalyst looses its efficiency over the time and it is periodically changed (typically every 1 to 4 years). The rate of generation is 0.12 - 0.8 kg/t EO (0.12 - 0.3 kg/t EO for the lowest 50 % of units). The catalyst is sent to reclaimers for recovery of the metallic silver content. The inert, inorganic support for

the catalyst requires land filling once the silver has been recovered (European Commission, 2003).

5.6   Environmental Effects Of P-xylene Production

Air Emissions: There are not usually continuous VOC emission sources on aromatics plants, although some plants may use vacuum systems that have a continuous air emission. Most VOC emissions are normally from fugitives (e.g. valve, flange and pump seal leaks) and from non-routine operations (maintenance, inspection). However, due to lower operating temperatures and pressures, the fugitive emissions from some aromatics processes are considerably less than in other LVOC processes where higher temperatures and pressures are employed. The quantification of fugitives is dependent on the calculation method, but CEFIC experts consider that a release of 50 t/year of hydrocarbons is a plausible order of magnitude for non-routine emissions from a typical aromatics installation (CEFIC). VOCs may arise from small leaks in the cooling unit as ethylene, propylene and/or propane can be used as coolant fluids in the p-xylene crystallization unit. VOCs may also arise from storage tank breathing losses and displacement of tanks for raw materials, intermediate products and final products (European Commission, 2003). Table 5.7 gives performance data for two plants in the Netherlands.

Table 5.7 Emissions to air Aromatic Processes

Plant	Emission source	Emission type	Pollutant	Emission factor (kg/tone of BTX product)
Dutch Process A (BTX from aromatic mixture)	Flare release/ fluegases/ gas motors	Point source	SO_2 NO_x	0.53 0.86 [1]
	Tanks	Point source	VOC	0.05 [2]
	Various	Fugitive	VOC Metan	0.15 [3] 0.09
Dutch Process B (benzene from pygas)	Desulphurising	Point source	SO_2	0
	Furnaces	Combustion	NO_x CO VOC	0.013 0 0.0008
	Processes	Point source	VOC	0
		Fugitive	Benzene Toluene Pentanes VOC saturated C_1-C_4 VOC aliphatic C_2-C_{10} Total Aromatics Total VOC	0.01 0.004 0.004 0.0005 0.0018 0.017 0.03

Water Emissions: In aromatics processes there is generally little or no continuous waste water stream, but the exact quantity depends on the plant configuration. The main waste water source is process water recovered from condensates of the steam jet vacuum pumps and overhead accumulators of certain distillation towers (due to the water content of the feedstock or water added to improve extraction efficiency). These streams contain small quantities of dissolved hydrocarbons and are generally

drained to a central treatment facility. Waste water containing sulphide and COD may also arise from any caustic scrubbers. The only other arisings are unintentional spillages, purge of cooling water, rainwater, equipment wash-water, which may contain extraction solvents and aromatics. Water generated by tank drainage and process upsets may contain aromatics. Waste water containing hydrocarbons may be collected separately, settled and steam stripped prior to biological treatment. CEFIC report that effluents typically contain 1 ppm benzene after treatment by such methods(CEFIC). Table 5.8 gives actual performance data for two processes in The Netherlands. In the case of Process A, a central WWTP reduces the benzene level by an estimated 99.8 %. In Process B, the central WWTP reduces aromatics by >99 % (to 0.2 μg/l) and COD by 60 % (to 20 mg/L).

Table 5.8 Emissions to water from Dutch aromatics processes

Source	Destination	Pollutant	Emission factor (kg / tonne of product)	Waste water flow (m^3 / tonne of product)
Waste water from process drains/ polluted and non polluted areas	Central WWTP (externally)	Benzene Toluene COD N-Kjeldahl	0.003 0.001 0.087 0.0009	0.5

Solid Wastes: The different types of solid wastes are usually treated and disposed of by third parties away from the aromatics complex. There is no production of hazardous waste during normal operation and virtually all the feedstock is recovered into valuable products, or as fuel gas. The major solid waste categories are:

Catalysts - from the liquid or gas phase hydrogenation of olefins/diolefins and sulphur. Typical lifetime is 2 to 5 years. Spent catalysts are typically processed by a reclaimer, often the catalyst supplier himself, to separate the valuable metal for re-use from an inert support usually disposed of via landfill. Catalysts used in Toluene Disproportionate or Xylene isomerisation can have lifetimes up to 10 years.

Clay - from olefins removal and typically having a lifetime 6 months to 2 years. Clay is typically processed via landfill or incineration for disposal.

Adsorbents - from xylenes separations and typically consisting of alumina or molecular sieves which can have a lifetime as low as 3 to 4 years, but typically more like 10 years. Adsorbents are typically disposed of via landfill.

Sludge / solid polymerization material - recovered from process equipment during maintenance activities. It is typically incinerated offsite but can be used on-site as a fuel source. Solvent regeneration is typically used in many aromatics complexes to remove a more concentrated stream of sludge from the process. This reduces solvent losses to the environment.

Oil contaminated materials and oily sludges **-** (from solvents, bio-treatment and water filtration) are incinerated under carefully controlled conditions, with associated heat recovery (European Commission, 2003).

5.7 Environmental Effects Of Terephthalic Acid Production

Air Emissions: Off-gases which is formed in the proceses of oxidation, consists of CO, acetic acid, methyl acetate, p-xylene and methyl bromate. Solvent recycle column vents (CO, acetic acid, methyl acetate and p-xylene). Atmospheric absorbing vent (acetic acid, methyl acetate). Distillation department consists of terephthalic acid and acetic acid. Off gase drying vent consist of methyl acetate, acetic acid and p-xylene.

Water Emissions: There are acetic acid, formaldehyde, methyl acetate, p-xylene and methanol in the condensation waters which are occurred in the departmet of solvent recycle and wastewater which comes out acetic acid dehydration column. There are p-toluic acid, terephthalic acid, benzoic acid, other organic acids and manganez/ cobalt salts in the wastewater which comes out in the distillation of crude teraftalic.

Solid Waste: Waste cake occurred after recycling

5.8 Environmental Effects Of Continuous Polycondensation Process

Table 5.9 gives that emissions and waste per tonne of PET at polycondensation process. In this process VOC emissions depend on the viscosity of the end-product. The values for COD always refer to waste water prior to entering a waste water treatment plant (European Commission, 2007).

Table 5.9 PET Polycondensation emissions table

Consumption Data	TPA Process
Emissions to air	
Acetaldehyde (g/t)	up to 60
EG (g/t)	up to 10
VOC (g/t)	up to 1200 5 using catalytic oxidation (only point sources)
Generation of waste	
Polymer waste (g/t)	140 - 18000
Hazardous waste (g/t)	up to 0.45
Other waste (g/t)	2000 - 5000
Waste water	
COD (g/t)	2000 - 16000

5.9 Total Emissions to PET Bottle Production

The manufacture of PET plastic also creates air emissions. Table 5.10 demonstrates that 2.45 kg of air emissions are created per kg of PET produced (Wastereduction, 2002).

Table 5.10 Air Emissions to Produce 1 Kg PET Plastic

Air Emissions	Unit	Average
Dust	mg	3,800
Carbon Monoxide	mg	18,000
Carbon Dioxide	mg	2,330,000
Nitrogen oxides	mg	20,200
Sulphur oxides	mg	25,000
Hydrogen Chloride	mg	110
Hydrocarbons	mg	40,000
Organics	mg	9,400
Metals	mg	10
Total Air Emissions	**kg**	**2.45**

In the process of manufacturing PET plastic, several water pollutants are emitted in industry effluents. Table 5.11 demonstrates that 21.461 gr of water emissions are created from the production of 1 kg of PET plastic (Wastereduction, 2002).

Table 5.11 Water emissions to produce 1 Kg PET plastic

Water Emissions	Unit	Average
COD	mg	3300
BOD	mg	1000
Sodium ions	mg	1500
Acid as H+	mg	180
Metals	mg	120
Chloride Ions	mg	710
Dissolved Organics	mg	13000
Suspended Solids	mg	600
Detergent/oil	mg	20
Hydrocarbons	mg	400
Dissolved Solids	mg	580
Phosphate as P_2O_5	mg	10
Sulphate ions	mg	40
Other Nitrogen	mg	1
Total Water Emissions	**gr**	**21.461**

One by-product of manufacturing PET plastic is solid waste. Table 5.12 demonstrates that 45.13 gr of solid waste is created in the production of 1 kg of PET plastic (Wastereduction, 2002).

Table 5.12 Solid Waste to Produce 1 Kg PET Plastic

Solid Waste	Unit	Average
Mineral Waste	mg	30000
Stags and Ash	mg	9600
Mixed Industrial	mg	3500
Regulated Chemicals	mg	130
Inert Chemicals	mg	1900
Total Solid Waste	**gr**	**45.13**

CHAPTER SIX
PET BOTTLE RECYCLING
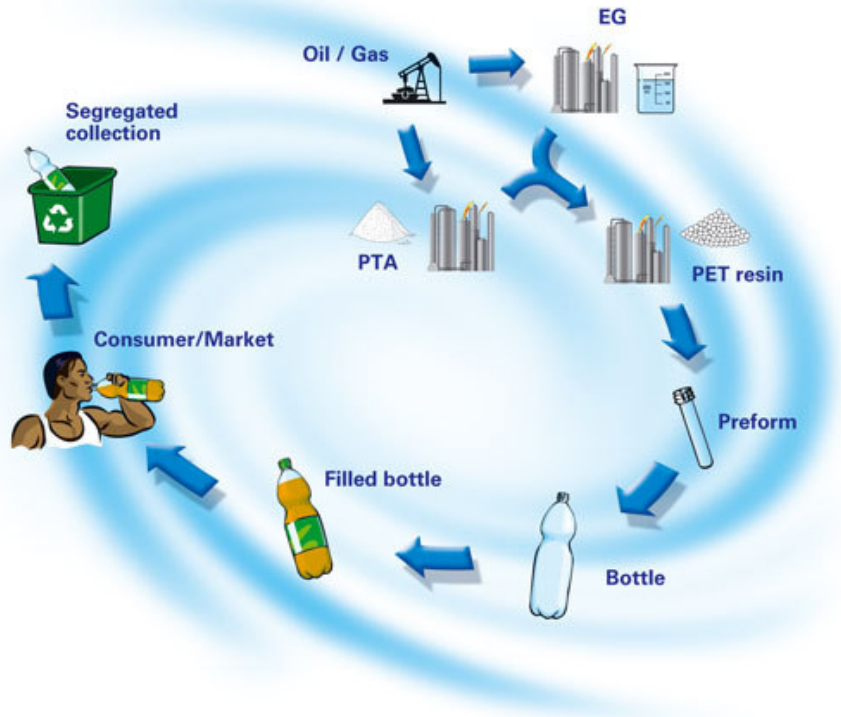
In the time period it is needed to reduce the environmental effect that is caused by human being in the world. The environmental effects of plastic wastes attracks more attention by day by. Package materials that can be recycle achieved to draw attention. Plastics are being source of the very big environment problem when they throw as a waste to environment. When plastics are thrown to garbage, they stay in the nature very long time without decay, oxidation and not spoiled as a biologycal. Some of the plastics can stay in the nature 700 years without spoiled and cause to become dirty of water and soil. Plastics that thrown to nature also cause to alives in the water and even the death.

Polyethylene terephthalat (PET) is one of the plastic that used mostly. This plastic is used to preserve of drinking water in the different dimension, fruit waters, alcoholic drink, food package, cleaning products and other foods.

First PET recycling project is been started in the 1976 by the firm which name is St. Jude Polymers. Using the plastics again without determine the quality and without separate according the quality can cause the secondary product problems. The environment and energy cost of the production of plastic again can be very high. The procedures of decomposition in the using of using plastic again, can cause the materials like toxic and carcinogenic to diffuse environment. Responsibility and knowledge of customers is needed for recycyling of plastics in healty way. Grouping and separeting the collected plastic, producing the plastic that does not extend with synthetic, melted polymer, obtaining new products from melted plastic are very important in the recycling of plastic.

Using areas of can that produced with PET and can be filled again are increasingly extended. PET is suitable for using again because of the fact that it is resistive to CO_2 transition. The most important point is that plastic materials can interact with chemicals or not. The possibility of become dirty with harmful contents of Cans that can be filled is important for restriction of re production of can. In each European Union country, there are laws that regulate the using recycling plastics that contact with food. In countries like Belgium and France, it is needed to approval of recycling process beforehand for using recycling materials in the plastics that contact with food. Using recycling materials in the plastics that contact with food is forbidden at least in two Europe country (Spain and Italy). Using materials again after consumption in the Coca-Cola bottles is accepted by FDA (Food and Drug Administration) in January 1991. For evaluate recycling of all PET bottles used in the food package, it is needed to guess maximum contamination of concentration waited in polymer. Activation from non food contamination in food can that produced recycling PET is been argued and it is have been suggested to develop tests that explain the relation by FDA for produce suitable cans that can be used for food (Korhek, 2007).

Recycling of PET bottle has been provided with three ways; as chemical, thermal and metarial. Thermal recycling depends on producing electricity with burning Pet bottles and especially burning heat is higher than other home waste. Because of this,

ıf the PET bottle is completely composed the efficiency of production electricity will be higher. But it is not being thought as alternative of recycling because of the problem of CO_2 emission. PET sawdustes are produced with dirtiness removing, breaking and washing in the method of metarial recycling. In this method consumption of energy is low but PET sawdust is not used again for the bottle production because of the fact that polymer structure of the PET can be fail. PET sawdustes are used the sectors like fiber, rope etc. Chemical recycling is the method of getting monomer again with depolimerizing of PET. Because of the fact that, obtained monomer has the same quality with its originional although electricity production, monomer can be used in the production of metarial. Chemical proces is needed more energy than the mechanic proces and when it is considered according the environmental point, metarial recycling can be selected as a most efficiency method (Hirao, 2005).
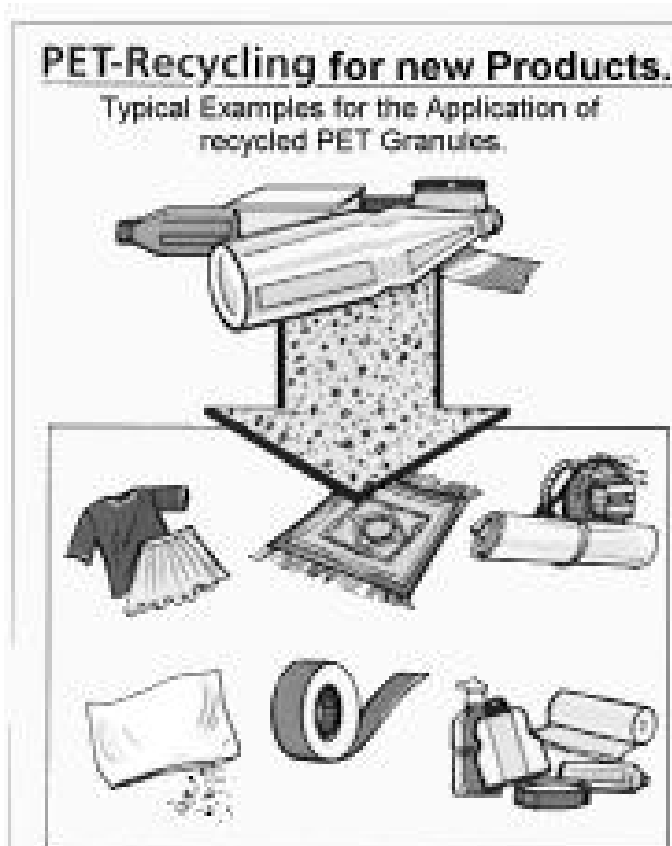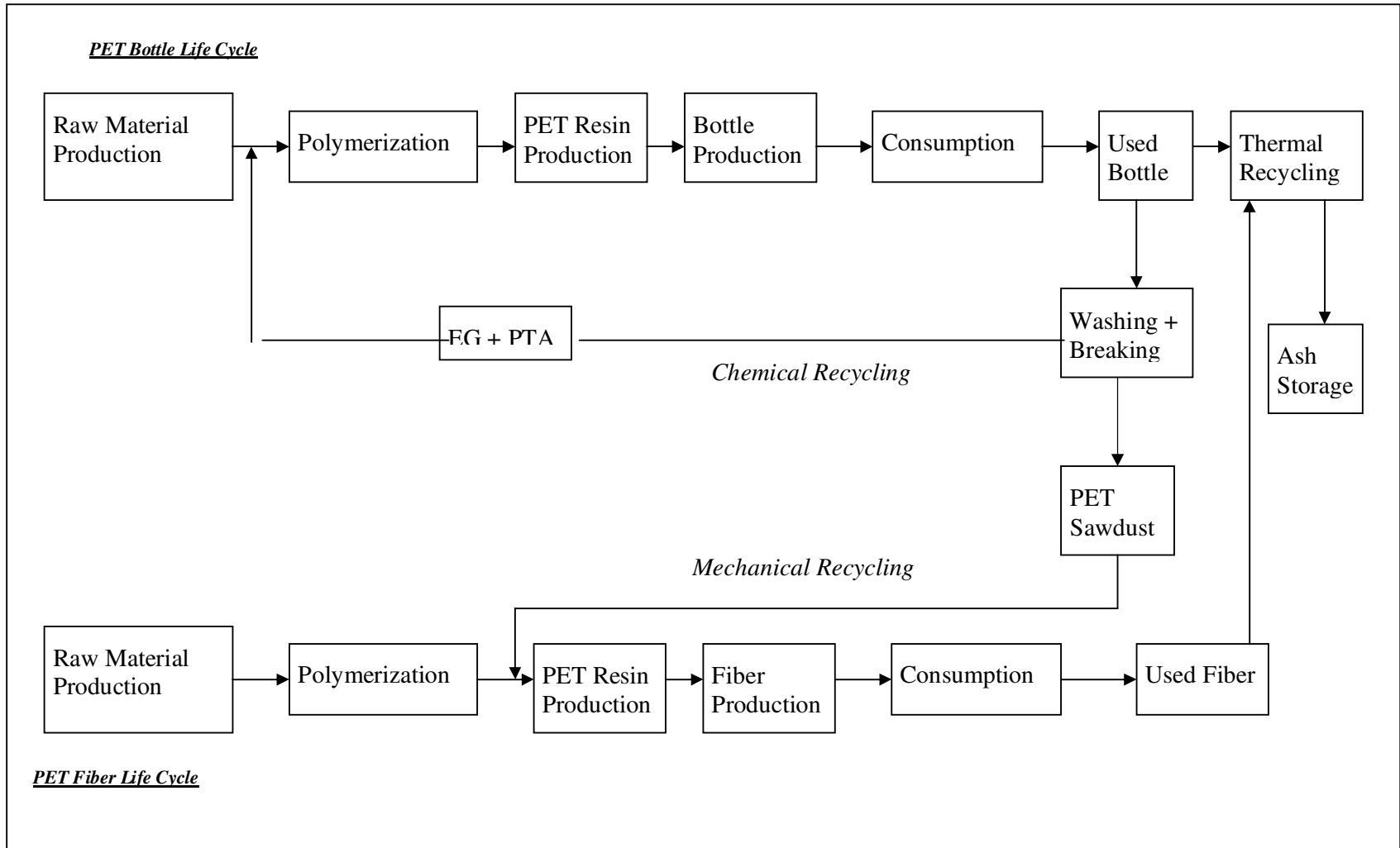
Figure 6.1 Recycling of PET Bottle

PET Bottle Life Cycle

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┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────┐     ┌──────────────┐
│ Raw Material │ ──▶ │Polymerization│ ──▶ │ PET Resin    │ ──▶ │ Bottle       │ ──▶ │ Consumption  │ ──▶ │ Used     │ ──▶ │ Thermal      │
│ Production   │     │              │     │ Production   │     │ Production   │     │              │     │ Bottle   │     │ Recycling    │
└──────────────┘     └──────────────┘     └──────────────┘     └──────────────┘     └──────────────┘     └──────────┘     └──────────────┘
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                     ┌──────────┐                                                                          ┌──────────────┐
                     │ EG + PTA │  ◀─────────────── Chemical Recycling ──────────────────────────────────│ Washing +    │
                     └──────────┘                                                                          │ Breaking     │
                                                                                                          └──────────────┘

                                                                                                          ┌──────────┐
                                                                                                          │ PET      │
                                                                                                          │ Sawdust  │
                                                                                                          └──────────┘
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Chemical Recycling

Mechanical Recycling

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┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────┐
│ Raw Material │ ──▶ │Polymerization│ ──▶ │ PET Resin    │ ──▶ │ Fiber        │ ──▶ │ Consumption  │ ──▶ │ Used Fiber   │
│ Production   │     │              │     │ Production   │     │ Production   │     │              │     │              │
└──────────────┘     └──────────────┘     └──────────────┘     └──────────────┘     └──────────────┘     └──────────────┘
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┌──────────┐
│ Ash   │
│ Storage │
└──────────┘

PET Fiber Life Cycle

Package Wastes Control Regulation is published in Official Gazette No 26562 dated 24.06.2007 by Ministry of Environment and Foresty. After this regulation was published the studies of recycling of storage waste was begun and business enterprises that sell their products in the storage are compulsory to collect storage wastes. In this scope re-gaining ratios for collecting storage wastes that are given in the implementing regulation, are given in Table 6.1.

Table 6.1 Recycling ratios of package waste

	Recycling Annual Targets According to Materail (%)			
Years	Glass	Plastic	Metal	Paper / Cardboard
2005	32	32	30	20
2006	33	35	33	30
2007	35	35	35	35
2008	35	35	35	35
2009	36	36	36	36
2010	37	37	37	37
2011	38	38	38	38
2012	40	40	40	40
2013	42	42	42	42
2014	44	44	44	44
2015	48	48	48	48
2016	52	52	52	52
2017	54	54	54	54
2018	56	56	56	56
2019	58	58	58	58
2020	60	60	60	60

CHAPTER SEVEN
RESULTS AND DISCUSSION

In our study we discussed PET material which is one of the plastics used commonly in food sector lately with stressed the description, target and evaluation of life cycle analysis. Thus we formed the mass balance of one litre PET bottle and depending on this we evaluated the life cycle analysis.

In this scope in the third chapter of our study, production proseses that starts with having crude oil process and going on process of production PET with using teraphthalic acid- p-xylene and consumption of raw materials have been stressed briefly. Mass balance in the fourth chapter has been shaped with the way of unit consuptions in the firs chapter. When it is analyzed the mass balance in figure 2, we reach that for production of one PET bottle, approximately 1,2 kg crude oil, 65 litre water and 200 wh electricity are used. These values are consumptions in production process and consupmtions in transfer, carrying, refining waste water and waste aside are not considered.

In chapter four important subjects are crude oil amount, water consumption amount, amount of waste and their characteristics, electricity amount while having crude oil. And these amounts are deal with the characteristic of well. In the same time the amount of naturel source consumption and also amount of waste and aside methods can change according the well in the land or sea. For this reason the stage of having crude oil has not been considered in our study.

In chapter five one by one environmental effects of the processes needed for producing PET bottle are given. In 5.9 title total emissions that are given to air and water for producing 1 kg PET and amount of solid waste have been given. From the point of these amouns and 31 gr PET is used in the production of one bottle production we can reach the result that total 76 gr air emissions, 0,66 gr water emissions and 1,4 gr solid waste are occured after the production one PET bottle production.

In the study ın chapter 6 that we discussed recycle of PET bottle, we reached the result that, 1 kg PET sawdust is obtained from 1,246 kg PET bottle bale with the mechanic recycle method of PET bottle, 1 kg PET polymer is obtained from 1.133 kg PET bottle bale with chemical recycle method (Hirao, 2005). Carpet floor, sleeping bag, quilt, pillow, isolation material in clothes, car pieces, paint brushes, lifeguard pillows, pockets, post boxes, picnic tables, fences, walking shoes, buckets with two division, lasic tonern cartridge, slide and other materials like that are produced with PET which gained with recycle. Thus naturel resources which is used to produce these materials (especially crude oil) are not consumed again and there will no environmental dirtiness as a result of recycle of wastes. As known in our country regular storage areas are compulsory and in these areas the price of aside solid waste is high so the regaining of plastics is increased. Howewer plastics are light materials and they occupy big places as a volumetric, they make shorten the life of storage areas. In last years in some countries the taxation of storage areas or aside price for unit tone accelerate regaining.

Because of all these reasons, consumers and package producers that working in the subject of producing package with the scope of Package Waste Control Regulation takes part in chapter six, are compulsory to provide the targeted regaining ratios. However it is very important that consumers should give countenance to projects of collection of wastes difference.

CHAPTER EIGHTH
CONCLUSION

PET market gone very big forward within twenty years. Because of the fact that PET is light and has impermeability to oxygen and carbon dioxide, it penetrated firstly to carbon dioxide soft drink market. PET bottles started to participate the big share in the water bottle market recently because of the fact that it is durable and unbreakable and does not cause any changing the transparenty and taste of water. PET can find the practice areas in many market as sport beverage and fruit water bottles.

If we summarize for the last time our study in the scope of PET bottle production in Türkiye we may get more clear results. Pet bottle production is 176,000 tonnes in Türkiye in 2006. When we calculate the natural source consumption at this production level, 6,800,000 tonnes crude oil, 370,000,000,000 L water and 1,135,000,000 kWh electricity have been consumpted. When the emissions that occured with this production have been calculated, we will see that 431,000 tonnes air pollution, 3,800 tonnes waste water and 8,000 tonnes solid waste have been appeared. These numbers are very terrifing at the present time that global warming and its effects are getting increased.

Well then, what must be done? Plastic is fixture in our life and in our life areas that we have to accept this reality. It can not be thought the quitting PET. In that case what must be done? When we discuss the life-cycle analysis that is in our study, natural source consumption in the production proceseses must be reduced at the very least, emissions and wastes must be prevented by controlling, after using the products they must be attend again to waste life-cycyle by recycling or using again. Besides preferring big demijohn instead of small dimension PET may be another solution to prevent more waste

Finally like in our study, life-cycle studies are uniquely useful tool for assessing the impact of human activities. These impacts can only be fully understood by assessing them over a life cycle, from raw material acquisition to manufacture,

use, and final disposal. Life-cycle techniques have been adopted in industry and the public sector to serve a variety of purposes, including product comparison, strategic planning, environmental labeling, and product design and improvement.

REFERENCES

Allen, D.T. & Shonnard, D.R. (2001). *Green Engineering: Environmentally Conscious Design of Chemical Processes.* New Jersey: Prentice.

Awaja, F. & Pavel, D. (May 2005). *Injection stretch blow moulding process of reactive extruded recycled PET and virgin PET blends,* European Polymer Journal 41. Retrieved June 20, 2007, from Science Direct.

BG Group Limited, (July 2005). *Channon Exploration Well Environental Impact Assessment.* London.

Boustead, I. & Dove, W. (September 2007). *What is LCA?.* Retrieved April, 2008, from
http://www.boustead-consulting.co.uk/introduc.htm

Chun Jen, Z. (2002). *Manufacturing method of copolyester for low acetaldehyde content of PET bottles.* Retrieved March , 2007 from
http://www.patentstorm.us/patents/6489434-description.html

Devlet Planlama Teşkilatı, (2001). *Sekizinci Beş Yıllık Kalkınma Planı, Petrokimya Sanayi Özel İhtisas Komisyonu Raporu*. Ankara.

Drive, R. B. (May 2006). *Life Cycle Assessment: Principles and Practice*. National Risk Management Research Laboratory Office of Research and Development U.S Environmental Protection Agency. Cincinnati, Ohio.

EPA, (1994). *Locating And Estimating Air Emissions from Sources Of Xylene,* Emission Inventory Branch Technical Support Division Office Of Air Quality Planning And Standard. North Carolina.

EPA, (1991). *Organic Chemical Process Industry* AP 42. (Fifth Edition) Volume I Chapter 6. Introduction to Plastics

European Commission (February 2003). *Integrated Pollution Prevention and Control Reference Document BREFs,* Mineral Oil and Gas Refineries. Retrieved February, 2008 from
http://eippcb.jrc.ec.europa.eu/pages/FActivities.htm

European Commission (February 2003). *Integrated Pollution Prevention and Control Reference Document BREFs,* Large Volume Organic Chemical Industry. Retrieved May, 2007 from
http://eippcb.jrc.ec.europa.eu/pages/FActivities.htm

European Commission, (August 2007). *Integrated Pollution Prevention and Control Reference Document BREFs,* Polymers. Retrieved March , 2008 from
http://eippcb.jrc.ec.europa.eu/pages/FActivities.htm

Garcia, D. & Kapila, M.(2006).*Calculation of energy requirements and air emissions for drill cuttings management.* 13th International Petroleum Environmental Conference. San Antonio, Texas

Gibbons, J.H. (March 1992). *Managing Industrial Solid Wastes from Manufacturing,* Mining, Oil and Gas Production, and Utility Coal Combustion. (67-85). Washington, DC

Hannisdal, A. (May 2006). *Particle stabilized emulsions and heavy crude oils.* Norway

Hirao, M. (2005). *LCA as a component of configuration engine for KIH*

International Life Sciences Institute, (July 2000). *Packaging Materials*, 1.Polyethylene Terephthalate (PET) for Food Packaging Applications. Brussels, Belgium.

Knez D., & Gonet A., & Fijał J., & Czekaj L.(2006). *Trends in the Drilling Waste Management.*

Magremis, M.(2002).*The environmental impacts of a solid waste reduction program.* Retrieved April, 2008, from http://www.wastereduction.org/Baxter/Bax5.htm

Mulder, K. F.(September 1997). *Sustainable Consumption and Production of Plastics?*

Narayan, R.& Patel, M.(2003) *Review and Analysis of Bio-based Product LCA's.* Proceedings of the International Workshop Assessing the Sustainability of Bio-based Products, Institute for Science & Public Policy, Oklahoma, USA.

Nagy, C. N. (May 2002). *Oil Exploration and Production Wastes Initiative*. Department of Toxic Substances Control Hazardous Waste Management Program Statewide Compliance Division. California

Neff, J.M. (January 2005). *Composition, environmental fates, and biological effects of water based drilling muds and cuttings discharged to the marine environment.* A synthesis and annotated bibliography. Duxbury, MA

Okandan E. (2006). *Türkiyenin Petrol Arama ve Üretim Potansiyeli*, ODTÜ, Petrol ve Doğal Gaz Mühendisliği Bölümü ve Petrol Araştırma Merkezi

Pacific Northwest Pollution Prevention Research Center.(1993). *Pollution prevention opportunities in oil and gas production, drilling, and exploration*. Seattle

Sevencan F. & Vaizoğlu S.A. (2007). *PET ve Geri Dönüşümü.* Retrieved August, 2008, from
http://www.korhek.org/khb/khb_006_04-307.pdf

Shyam Plastic Machinery (n.d). *Type of PET Blow Moulding.* Retrieved February, 2008 from
http://www.petmachine.in/type_of_blow_moulding.htm

Teknopet, (2007). *PET Preforms.* . Retrieved April , 2008 from
http://www.teknopet.com/english/preformlar.htm

World Bank Group, (1998). *Oil and Gas Development, Pollution Prevention and Abatement Handbook* (359-362).

Van der Haar, S. (October 2005). *A comparison of calamity risk versus standard operational risk for PET film production.*

Veil, J.A.(November 1998). *Data Summary of Offshore Drilling Waste Disposal Practices.* Argonne National Laboratory. Washington, DC

Yanmaz, Ş. (2004). Türkiye'nin Petrol Macerası. *Panoroma Dergisi* (Sayı 1). Retrieved April 16, 2007.