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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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PRODUCTION OF PETROCHEMICALS
USING CLEAN TECHNOLOGIES

- July 1992 -

CONTENTS

These guidelines were prepared by Gheorghe Ivanus, M.Sc., Ph.D., UNIDO consultant, based on knowledge available in many countries with advanced technologies in this field and can be very useful for developing countries and especially for Eastern European countries.

1. INTRODUCTION

1.1. Objectives of the guidelines

The principal goals of the overall compendium is:

- to examine the extent to which low polluting technologies have been at present introduced in the production of petrochemicals in response to pollution control;

- to note the contribution of low polluting technologies to reduce emissions and wastes, as well as energy and raw material consumptions in the industry;

- to identify the main factors influencing the selection of processes in petrochemical production and to point out potential possible conflicts with regard to the adoption of low polluting technologies;

- to assess the scope for introducing low polluting technologies in future petrochemical processes.

Some representative petrochemical technologies have been selected taking into consideration the differences in size, nature and the feedstocks involved, together with other key factors including the economics of this particular industry.

The compendium on low-waste petrochemical technology is focussed on the following aspects:

- to reduce materials and energy consumption by increasing the overall efficiency of processes and internal recycling of residues;

- to enable the different residual materials and energy coming out from individual plants to be used as valuable inputs by adjacent plants;

- to increase recovery of residues having in view their subsequent reutilization;

- to reduce the materials and energy requirements, extend the lifetime of equipments and catalysts and facilitate the recovery and recycling of valuable materials after their utilization in the process.

The guidelines on low-waste petrochemical technology can be considered as a basis for collection and dissemination of up-dated information on the available alternative technology. We are also confident that the dissemination of such information may facilitate concluding commercial agreements and other arrangements such as licensing and joint ventures, useful for developing countries and Eastern European countries.

The guidelines cover three main sections, namely:

a) Selection of principal petrochemical technologies examined in point of environmental protection.

This part of the compendium gives a critical discussion of the evolution of the principal petrochemical technologies in the fields of monomers, elastomers, polyolefins, fibres, tires, rubber goods.

For each individual substance there is a brief presentation of: evolution of technological processes, brief process description, the reason for switching from one process to another as well as the approximate quantity and quality of the gaseous, liquid and solid pollutants resulted from the process.

Comments are also given on the ways of using the wastes and of reducing the pollutants by up-dating processes rather than destroying pollutants.

b) Critical analysis of the methods, ways and procedures applied on industrial scale for the recovery and incineration of solid residues, treatment of water contaminated with inorganic substances, biological treatment of water contaminated with biodegradable organic substances, recovery of residual fuel gases and systems for burning noxious gases to flare.

c) Economic effects of the selection of low polluting petrochemical processes.

The compendium is also accompanied by a list of literature publications pertaining to environmental protection.

1.2. Definition of low polluting technologies in the petrochemical industries

Petrochemicals, sometimes called petroleum-chemicals, are defined in this study as any chemicals deriving from crude oil, natural gas or other petroleum sources.

Raw materials used in the production of petrochemicals include crude oil, natural gas, refinery gas, natural gas condensate, light tops or naphtha, heavy fractions such as fuel oil, as well as coal and biomass.

Primary, intermediate and third generation products are produced by exposure of feedstocks to specific conditions, which dictate the chemistry of the transformation.

More than 500 different processing sequences are used in the petrochemical industry. The wide variety of process sequences coupled with the wide variety of products produced by the petrochemical industry leads to a complex waste problem. A list of the main petrochemical processes and the wastes which may be expected to come out as a result of their use is presented in Table 1.

The information presented in Table 1 reveals that many air and water pollutants along with solid wastes are generated during the production of petrochemicals.

Petrochemical wastes may produce a variety of adverse effects on public health and the environment. Biodegradable organic matters discharged to the receiving waters may produce anaerobic conditions in the receiving rivers. These conditions will kill or drive off any aerobic organisms including fish and even more developed animals. Anaerobic decomposition may also produce odor and colour problems.

Thermal pollution from petrochemical discharges will also affect receiving waters, including death or decreased productivity of many aquatic species. Increased water temperature also decreases oxygen solubility, enhances atmospheric oxygen transfer and may produce an increased biological activity.

Petrochemical processing plants can also be significant sources of air pollution. A list of the air pollutants emitted by petrochemical processing plants and the major sources of these emissions is found in Table 2. Air pollution from petrochemical plants is produced by the combustion of fuel and by various emissions of processing equipment.

Carbon monoxide, sulfur oxides and nitrogen oxides emissions are mainly a result of the combustion of fuels.

Table 1

Waste sources from petrochemical processes

Process	Source	Pollutants
1	2	3
1. Ethylbenzene	Waste water	Tar, hydrochloric acid, caustic soda, fuel oil
2. Styrene from ethylbenzene	Catalysts	Spent catalysts (iron, magnesium, potassium, copper, zinc and chromium); heavy tars
	Condensates from spray tower	Aromatic hydrocarbons, including styrene, ethylbenzene and toluene, tars
3. Butadiene from n-butane and butylene	Quench waters, solvent and caustic wash	Residual gas, tars, oils, soluble hydrocarbons, caustic soda, sulfuric acid
4. Ketone production	Distillation slops	Hydrocarbon polymers, chlorinated hydrocarbons, glycerol, sodium chloride
5. Desulfurization	Waste gases	Hydrogen sulphide, mercaptans
6. Isobutylene extraction and purification	Acid and caustic wastes	Sulfuric acid, C_4 hydrocarbon, caustic soda
7. Butadiene absorbtion	Solvent	Cuprous ammonium acetate, C_4 hydrocarbons, oils
8. Butadiene extractive distillation	Solvent	Furfural, C_4 hydrocarbons
9. Halogenation		
- Addition to olefins	Separator	Spent caustic soda
- Substitution	HCl absorber, scrubber	Chlorine, hydrogen chloride, spent caustic soda, hydrocarbon isomers and chlorinated product oils
- Dehydrohalogenation	Separator	Dilluted salt solution
- Hypochlorination	Hydrolysis	Calcium chloride, soluble organics, tars
- Hydrochlorination	Surge tank	Tars, spent catalyst, alkyl halides
- Hydrocarboxylation (OXO process)	Still slops	Soluble hydrocarbons, aldehydes

1	2	3
10. Hydrocyanation (for acrylonitrile, adipic acid, etc.)	Process effluents	Cyanides, organic and Inorganic substances
11. Isomerization	Process wastes	Hydrocarbons, aliphatic, aromatic and derivative tars
12. Nitration		
- Paraffins		By-product aldehydes, ketones, acids, alcohols, olefins, carbon dioxide
- Aromatics		Sulfuric acid, nitric acid, aromatics
13. Oxidation		
- Ethylene oxide and glycol manufacture	Process slops	Calcium chloride, spent lime hydrocarbon polymers, ethylene oxide, glycols, dichloride
- Aldehydes, alcohols and acids from hydrocarbons	Process slops	Acetone, formaldehyde, acetaldehyde, methanol, higher alcohols, organic acids
- Acids and anhydrides from aromatic oxidation	Condensates, still slops	Anhydrides, aromatic acids, pitch
- Phenol and acetone from Aromatic oxidation	Decanter	Formic acid, hydrocarbons
- Carbon black	Cooling, quenching	Carbon black, dissolved solids
14. Polymerization		
- Acid catalysts	Catalysts	Spent acid catalysts (phosphoric acid), aluminium chloride
- Polyethylene	Catalysts	Chromium, nickel, cobalt, molybdenum, titanium
- Butyl rubber	Process wastes	Scrap butyl rubber, oil, light hydrocarbons
- Copolymer rubber	Process wastes	Butadiene, styrene serum, softener sludge
- Nylon 66	Process wastes	Cyclohexane oxidation products, succinic acid, adipic acid, glutaric acid, hexamethylene-diamine, adiponitrile, acetone, methyl ethyl ketone
15. Sulfonation of olefins	Waste waters	Alcohols, polymerized hydrocarbons, sodium sulphate, ethers
16. Sulfonation of aromatics	Caustic wash	Spent caustic soda

1	2	3
17. Thermal Cracking for Olefin Production	Furnace effluent and caustic treating	Acids, hydrogen sulfide, mercaptans, soluble hydrocarbons, polymerization products, spent caustic soda, phenolic compounds, residual gases, tars and heavy oils
18. Utilities	Boiler blow-down	Phosphates, lignins, heat, total dissolved solids, tannins
	Cooling system blow-down	Chromates, phosphates, algicides, heat
	Water treatment	Calcium and magnesium chlorides, sulfates, carbonates
19. Nitrobenzene	Waste water and solid wastes	Crude nitrated, aromatics
20. Epichlorhydrin	Waste water	Epichlorhydrin, dichlorhydrin, chloroethers, trichloropropane, tars
21. Toluene diisocyanate and methylene diphenyl diisocyanate	Waste water	Polyurethane, isocyanates, amines, tars
22. Vinyl chloride monomer	Distillation columns	Dichloroethanes, trichloroethanes, tetrachloroethanes, tars
23. Methyl Methacrylate	Reaction system	Hydroquinone, polymeric residues
24. Acrylonitrile	Waste water	Acrylonitrile, higher nitriles
25. Maleic anhydride	Waste water	Maleic anhydride, fumaric acid, aromatic compounds, tars
26. Ethanolamines	Waste water	Triethanolamines, tars
27. Furfural	Stripped hulls	Fines particulates
28. Polystyrene, ABS resins	Separation system	Styrene, acrylonitrile, polybutadiene
29. Acrylic Fibres	Process water	Acrylonitrile, vinylchloride, comonomer
30. Acrylic resins	Process water	Methylmethacrylate, cyanide
31. Polyester Fibres	Process residue	Terephthalic acid, dimethyl terephthalate

Table 2

Air Pollutants from Petrochemical Plants

Plant	Process	Pollutants
1	2	3
1. Acetaldehyde	From ethylene	Hydrocarbons -
2. Acetic Acid	From ethanol	-
	From methanol	Oxides of nitrogen
	From butane	Hydrocarbons
	From acetaldehyde	Carbon monoxide, hydrocarbons
3. Acetic Anhydride	From acetic acid	Hydrocarbons, carbon monoxide
4. Acrylonitrile	From propylene	Hydrocarbons, oxides of nitrogen, carbon monoxide
5. Adipic acid	-	Particulates, oxides of nitrogen, carbon monoxide
6. Adiponitrile	From butadiene	Hydrocarbons, particulates, oxides of nitrogen, carbon monoxide
	From adipic acid	Particulates, oxides of nitrogen
7. Carbon black	Aromatics hydrocarbons	Hydrocarbon, particulates, oxides of nitrogen, sulfur oxides, carbon monoxide
8. Cyclohexanone	via Benzene	Hydrocarbons, carbon monoxide
9. Dimethyl Terephthalate + Terephthalic acid	via pXylene	Hydrocarbons, particulates, oxides of nitrogen, sulfur oxides, carbon monoxide
1o. Steam craking	Low pressure steam craking of naphta	Hydrocarbons, particulates, oxides of nitrogen, sulfur oxides, carbon monoxide
11. Vinyl chloride	From oxichlorination	Hydrocarbons, particulates, carbon monoxide
	Direct chlorination	Hydrocarbons
12. Ethylene oxide	Direct oxidation	Hydrocarbons, oxides of nitrogen, sulfur oxides
13. Formaldehyde	Silver catalyst	Hydrocarbons, carbon monoxide
	Iron catalyst	HYdrocarbons, carbon monoxide
14. Glycerol	From epichlorhydrin	Hydrocarbons
15. Hydrogen cyamide	Direct process	Cyanic compounds
16. Isocyanates	Process with phosgen	Hydrocarbons, particulates, sulfur oxides, carbon oxides
17. Maleic Anhydride	From benzene	Hydrocarbons, carbon monoxide
	From butane	Hydrocarbons, carbon monoxide

1	2	3
18. Phthalic Anhydride	From oxylene	Hydrocarbons, carbon monoxide, particulates, oxides of nitrogen, sulfur oxides
	From naphthalene	Particulates
19. Nylon 6, Nylon 66	Polyamide	Particulates
20. OXO Process	From propylene	Hydrocarbons, particulates, oxides of nitrogen, carbon monoxide
21. Phenol	From I.P.B.	Hydrocarbons
22. High Density Polyethylene	From ethylene, low pressure	Hydrocarbons, particulates
23. Low Density Polyethylene	From ethylene, high pressure	Hydrocarbons, particulates
24. Polypropylene	Suspension process	Hydrocarbons, particulates
25. Polystyrene	Suspension process	Hydrocarbon, particulates, sulfur oxides
26. Polyvinyl chloride	Suspension process	Hydrocarbon, particulates
27. Styrene	Ethyl benzene dehydrogenation	Hydrocarbon, particulates, oxides of nitrogen
28. Styrene-butadiene rubber	Emulstion process	Hydrocarbons, particulates, sulfur oxides
29. Vinyl acetate	via Acetylene via Ethylene	Hydrocarbons Hydrocarbons
30. Vinyl chloride	Oxychlorination process	Hydrocarbons, particulates

However, other processes in the plant may cause emissions of these pollutants. Hydrocarbon emissions may occur due to fuel combustion or various process losses, including leaking valves, flanges, pumps and compressors, evaporation from process drains, waste water treatment processes, cooling water and blow-down systems, and losses from relief valves on operating and storage vessels. Hydrocarbon emissions may be as great as 0.6% by weight of total production, for petrochemical plants.

Hydrogen sulfide and mercaptans, produced by some processes and emitted as process losses, may create significant odor problems.

These air pollutants have significant bad health effects. Air pollutants may adversely affect plants life, reducing crop yields and plant growth rate and, in some cases, causing the death of susceptible plants. Air pollution may also have corrosive effects on metals, building materials and textiles.

Four possible solutions may be considered for avoiding pollution problem in the petrochemical industry depending on the waste produced:

- first, some wastes may be recovered as salable coproducts;
- second, waste streams can be recycled after some process modification for conversion to prime product or for their re-use in the process as a reagent or an intermediate product;
- third, the waste may be usable as a fuel;
- fourth, and least desirable, wastes may be treated in waste treatment processes when they are converted to less harmful products and/or dispersed in small quantities which may be assimilated by the environment.

Low-waste technology can be defined as "the practical application of knowledge, methods and means so as - within the needs of man - to provide the most rational use of natural resources and energy, and to protect the environment". In essence, low-waste technology is the planning and management of human activity in order to minimize waste of materials and energy.

Low-waste technology is a method of production under which all raw materials and energy resources are used in a most rational and integrated way in a cycle: raw materials - production - consumption - secondary raw materials, so that any impact on the environment do not disturb its normal functions.

Low-waste technology should be regarded as both: a goal or target and a policy so that its development is consequently a short and long term endeavour of great importance, whose achievement will bring about positive changes in all sectors of industry.

In the absence of so-called "ideal processes", in which all inputs are fully converted to desired and valuable outputs, all production processes will generate a certain amount of "residual products" (see fig. 1, 2, 3).

The amount of such "residues" generated by any particular process depends primarily on the technical characteristics of the process in question.

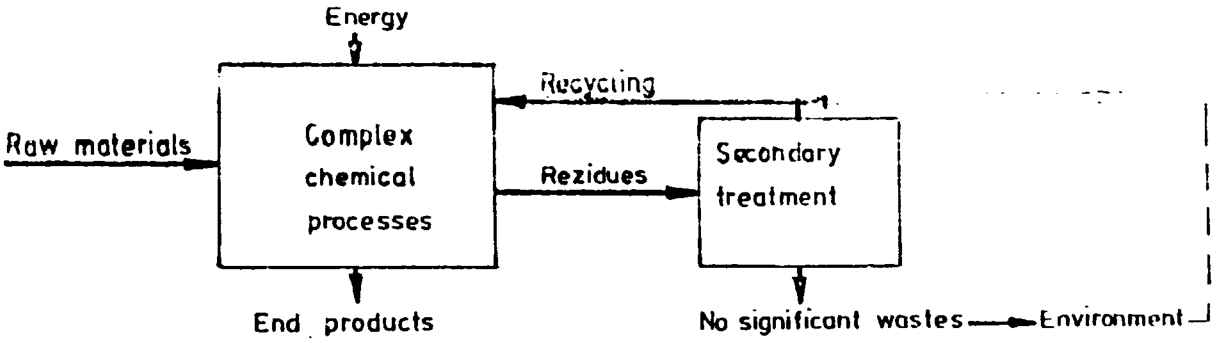


Fig. 1 Ideal case.
(Non pollutant technology)

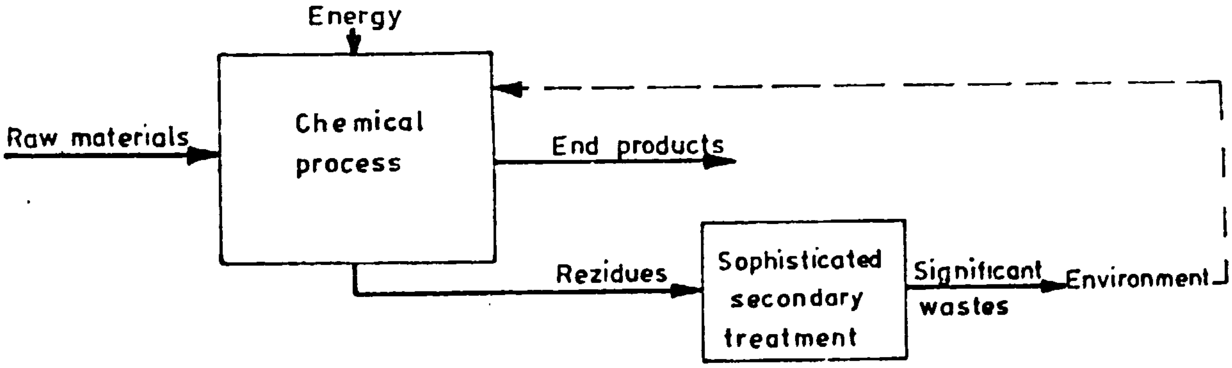


Fig. 2. Conventionaly case.
(Pollutant technology)

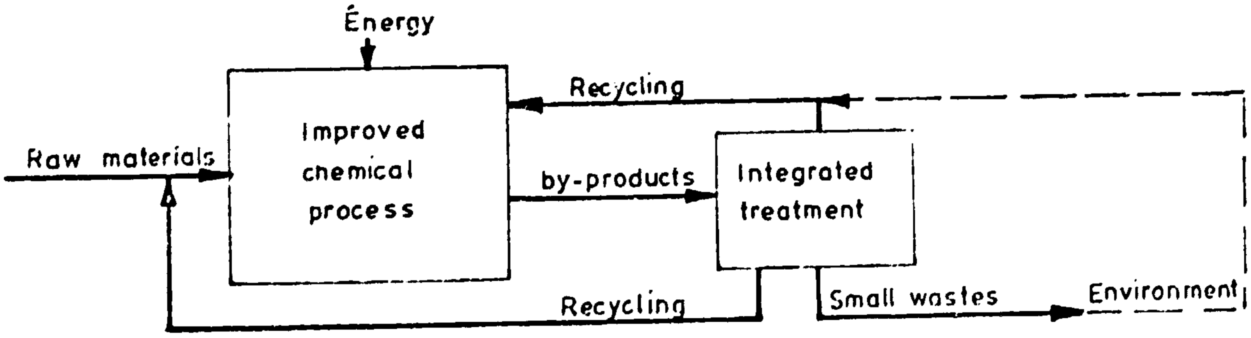


Fig. 3. Improved case.
(Low pollutant technology)

Depending on the composition of the residual products and the existing process inputs, part of these residues can be recovered and re-utilized. The remainder, which at the prevailing level of prices has no economic value, is defined as "waste".

In the past, the major tendency of environmental policy with regard to pollution control of industrial processes and waste reduction was towards the installation of add-on control devices treatment facilities rather than focussing on process changes aiming at eliminating pollution sources or reducing their emission/discharges or polluting substances. Priority is now being given to the promotion of low- and non-waste technology.

A special feature of the concept of low- and non-waste technology is its emphasis on the minimization of materials and energy inputs "upstream" in the production process as a way of reducing "downstream" residual products and waste generation.

Of course, the ideal case does not exist until now, in spite of huge efforts made in the chemistry and engineering fields.

It should be noted that this new concept of low-waste technology in its broad terms must be implemented in a socio-economic sphere. and enters into a particular technological environment, into specific legal and administrative settings, into association with typical use consumption patterns, discharge attitudes and related infrastructure and different environmental exigencies.

However, the concept of cleaner technologies is in reality not always readily apparent. For example, one process may have less overall wastes/by-products associated with it, higher yield, but may produce a more toxic waste stream than the existing or new alternative.

The compendium will only identify a cleaner technology where one process has a clear overall advantage in terms of emissions/wastes, judged by its potential impact or by the measures necessary to improve any consequent impact.

Clearly, there is room for argument in assigning the label of cleaner technologies. What, of course, must be emphasized, is that the actual impact of emissions/wastes from particular process will depend upon the receiving environment. In other words, the identification of cleaner technology should not necessarily imply that other process technologies are "dirty" or unacceptable.

A more interesting conflict in selection of a cleaner technology arises when one bulk chemical process has significantly lower associated emissions/wastes but a higher energy consumption per unit of product.

The concept of low-waste technology as recognized by ECE countries in its broad terms does not only refer to industrial production processes, which save materials/energy and which generate low levels or no waste at all, but also promotes:

a) waste collection programmes which permit the recovery of usable product components and their recycling as raw materials into new products;

b) increased durability of products, as the longer the consummer can use them, the less need there is for replacing them and thus less resources, including energy, are needed for manufacturing them;

c) substitution of product materials which is drawn from scarce resources by materials with abundant availability and of product material of bio-accumulative, persistant, toxic nature by those which do not impair the environment once released as wastes or accidental releases;

d) remanufacturing and reconditioning oriented design to render product already in their design a planning stage fit for being easily dissociated and parts thereof or entirely reused in the same or new products, this process being an economy both for the producer and for the customer.

2. MAIN TECHNOLOGIES CONSIDERED FROM THE VIEW POINT OF ENVIRONMENTAL PROTECTION

2.1. Petroleum refining

Crude oils are complex mixtures of thousands of chemical compounds ranging from methane and ethane, which are dissolved gases, to compounds which are solids at room temperature. Chemists have identified more than 3,000 different compounds in crude oil, and these are only a small part of the total. Although crude oils contain thousands of different compounds, the compounds (other than water and trace contaminants) are all composed mostly of carbon and hydrogen and are called hydrocarbons.

The purpose of refining is to separate a crude oil into its saleable components, shift the original component ratio and properties to meet the customer's demand, and to remove impurities detrimental to product quality.

2.1.1. Refinery classification

The processes by which crude oil is manufactured into a multitude of products are numerous and complex. Crude oils from different sources vary significantly, and refineries are often designed to process crude from a particular source.

In order to classify refineries for the purpose of setting standards for limitations on effluents that may be discharged, refineries may be subcategorized by processes employed. This approach is practical because raw waste load and emission characteristics are related to process complexity rather than capacity.

A general description of the subcategories of refineries is given in Table 3.

The initial refining process separates crude oil into different fractions based on their boiling ranges. Some of the lighter and intermediate fractions are blended into products. Heavier fractions may be further processed by cracking the large hydrocarbon molecules into smaller ones. The structures of some of these molecules are re-arranged or they are joined in different combinations to provide the desired components for blending into finished products. This takes place in a number of refinery process units, each with a specific purpose, integrated into a processing sequence.

Table 3

Subcategorization of Petroleum Refineries

Subcategory	Basic Refinery Operations
A. Topping	Topping and catalytic reforming. It may include other processes but not thermal processes (coking, visbreaking etc.) or catalytic cracking.
B. Cracking	Topping and cracking. It may include other processes except petrochemical operations and lube oil manufacture.
C. Petrochemical	Topping, cracking and petrochemical operations. It may include other processes but not lube oil manufacturing.
D. Lubricating Oil	Topping, cracking and lube oil manufacturing. It may include other processes except petrochemical operations.
E. Integrated	Topping, cracking, lube oil manufacturing and petrochemical operations. It may include other processes in addition to these.

Although many different individual processes may be used to refine crude oil, the operation of a refinery can be divided into seven process areas:

- Separation of Crude Oil. The most widely used methods for separating crude oil are atmospheric and vacuum distillations. Pre-treatment of the crude oil in a desalter is typically included as a part of the separation processes.

- Conversion of Hydrocarbon Molecules. Conversion processes, which change the size of structure of the hydrocarbon molecule, convert some of the crude oil fractions into higher value products. The most common conversion processes are cracking (thermal, catalytic, viscosity breaking, hydrocracking and coking), combining (alkylation and polymerization), and re-arranging (catalytic reforming and isomerization).

- Treating Crude Oil Fractions. Some of the original sulphur compounds are converted to hydrogen sulphide (H_2S), which can be separated and converted to elemental sulphur by treating processes such as hydrodesulphurizing and chemical treating. Other compounds which may be removed include nitrogen, olefins, metals, asphaltenes, naphthenic acids and phenols.

- Blending Hydrocarbon Products. Most petroleum products are a blend of hydrocarbon fractions or components produced by various refinery processes.

- <u>Auxiliary Operating Facilities.</u> A number of refinery units are used to maintain normal operating conditions. Included among the functions of auxiliary operating facilities are hydrogen production, light ends recovery, acid gas treating, sour water stripping, sulphur recovery, tail gas treating, and wastewater treatment.

- <u>Refinery Offsite Facilities</u>. Refinery offsite facilities are equipment and systems used to support refinery operations. These facilities include storage tanks, electricity, steam generating systems, flare and blow-down systems, cooling water systems, receiving and distribution systems, and refinery fire control systems.

- <u>Emission and Effluent Control.</u> Refineries generate air emissions, wastewater, solid waste, and noise which must be controlled for efficient processing and environmental protection.

The general flow of the crude oil and petroleum products through a complex refinery and the processes involved are shown in figure 4. Brief description of the individual processes which may be used in refineries are given further on (20)

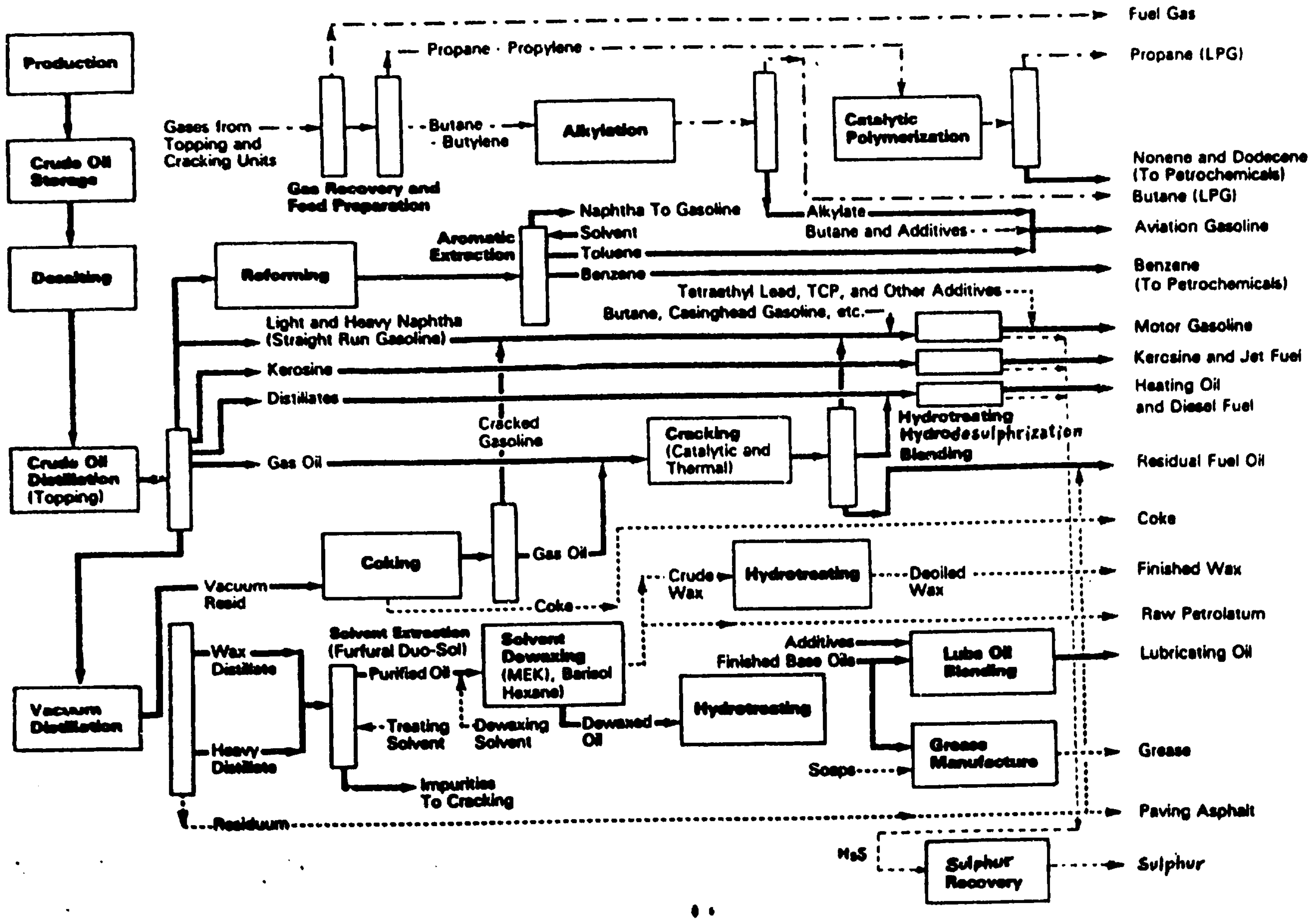
2.1.2. Refinery environmental concerns

Refineries and terminals seek to avoid the release of any substance in such a quantity that it will be harmful to human health or the environment. In order to achieve this it is necessary at the outset to distinguish between accidental releases and releases which are part of routine operation. Accidental releases may have a serious or a minor impact on the environment, but whatever the impact the environmental considerations are only part of many considerations implicit in accidental prevention and mitigation. Safety management is the mechanism through which refining and terminal managements seek to avoid harm including environmental harm from accidents.

The release of a substance as part of routine operation is in a different category. These releases and their potential impact represent the outcome of decisions taken with regard to design construction, operating procedures, feedstocks, product requirements, inspection, maintenance etc. considerations and in this context are a normal part of handling and processing feedstocks and products.

Figure 4

Simplified Flow Chart of a Complex Refinery



The areas of primary operating concern in environmental management are air, water, groundwater, solid wastes and noise. Several steps have been taken during the last decade to address these concerns, predominantly through improved refining processes and environmental control devices and more responsive operating and maintenance procedures. These steps have resulted in fewer contaminants and/or reduced concentrations being discharged, leading to an improvement in the environment.

The operating guidelines included below are intended to highlight typical steps which can be taken to reduce the generation and disposal of contaminants and minimize their release to the environment. Inspection, maintenance, training and co-operation of employees at all levels are integral parts of successful implementation of the operating guidelines.

2.1.2.1. Air Pollution Control

Air emissions vary significantly, both in quantity and type, among refineries and their effect on the environment will vary. Among the factors that affect the amount and type of refinery air emissions are: crude feedstocks, processes, types of equipment, air pollution control measures, housekeeping, maintenance practices and the age and category of refinery. Air emissions occur from a multitude of specific sources and are usually handled separately. Thus, air pollution control systems, when used, are associated with specific process units and are usually designed to remove or modify specific contaminants.

The major types of air contaminants associated with refining are shown in Table 4 along with the major sources.

Hydrocarbons

Hydrocarbons emissions are potentially the largest type of emission from a refinery and considerable attention is given to reducing these emissions.

Potential sources include process stacks (primarily the process heaters), storage tanks, the product loading terminals and fugitive sources such as valve stems, pump and compressor seals, drains and oil/water separators. Specific sources of hydrocarbons are discussed below.

Table 4

Potential Sources of Specific Emissions from Oil Refineries

Sulphur oxides	Boilers, process heaters, catalytic cracking unit, regenerators, treating units, H_2S flares, decoking operations.
Hydrocarbons	Loading facilities, turn-arounds, sampling, storage tanks, wastewater separators, blowdown systems, catalyst regenerators, pumps, valves, blind changing, cooling towers, vacuum jets, barometric condensers, air-blowing, high pressure equipment, handling volatile hydrocarbons, process heaters, boilers, compressor engines, distillation towers, separators.
Nitrogen oxides	Process heaters, boilers, compressor engines, catalyst regenerators, flares.
Particulate matter	Catalyst regenerators, boilers, process heaters, decoking operations, incinerators, flares.
Aldehydes	Catalyst regenerators.
Ammonia	Catalyst regenerators.
Odours	Treating units (air-blowing, steam-blowing), drains, tank vents, barometric condenser, pumps, wastewater separators, process vessels.
Carbon monoxide	Catalyst regeneration, decoking, compressor engine, incinerators, boilers, flares

Sulphur Oxides (SOx)

Sulphur dioxide (SO_2), one of the most common air pollutants, is most often produced when a sulphur-containing fuel is burned. In refineries the major part of the SO_2 emissions arise from the combustion of refinery fuels to provide energy for the various processes and to raise steam. The major sources of SO_2 emissions are the boilers, process heaters, catalytic-cracking unit, regenerators, treating units, coking operations and where used H_2S flares.

Refinery fuel combustion emissions can be controlled either by restricting the sulphur level in refinery fuel or by scrubbing the stack gases prior to discharge into the atmosphere. Methods of reducing the sulphur level in refinery fuels may include maximization of the use of natural gas as a fuel, using petroleum fuels and by-product fuels that have been desulphurized, and blending heavier high-sulphur internal fuels with desulphurized distillates.

The sulphur recovery unit (typically a Claus unit) emissions are controlled both by increasing the level of sulphur recovery and by stack gas scrubbing. The Claus process, which is the most widely used system, uses both thermal and catalytic conversion reactions

Nitrogen Oxides (NOx)

The major sources of NOx emissions are from combustion processes including process heaters, boilers, compressor engines, catalyst regenerators and gas stabilisers.

Oxides of nitrogen (NO_x) formed in combustion processes are usually due either to thermal fixation of atmospheric nitrogen in the combustion air, leading to "thermal NO_x", or to the conversion of chemically bound nitrogen in the fuel, leading to "fuel NO_x". It is generally accepted that thermal NO_x is formed at temperatures in excess of 1800°C in the presence of excess air. Fuel NO_x is due to oxidation of a portion of the nitrogen combined with the fuel. The bound nitrogen is emitted preferentially as molecular nitrogen and only partly as NO_x emissions.

NO_x control techniques for stationary sources operate either through suppression of NO_x formation through combustion modification in the process or through physical or chemical removal of NO_x from the stack gases.

Carbon monoxide (CO)

The fluidized catalytic cracker (FCC) generator, steam boilers, process heaters, compressor engines and the ags turbines are the major sources of CO. Control can be accomplished either by proper design and operation of the equipment, or, as is usually the case, with the catalyst regenerators, by providing a separate means for completing the conversion of carbon monoxide to carbon dioxide.

In the case of the FCC regenerator, the best demonstrated control technology for carbon monoxide is considered to be the carbon monoxide incinerator-waste heat boiler. An alternative to the CO boiler is the use of the new fluid catalytic crackers that use improved catalyst and high-temperature regeneration to limit CO generation.

CO emissions from the process heaters and boilers are minimized by monitoring the combustion parameters, especially oxygen, to ensure good combustion. Gas turbine and compressor emissions are treated in a like manner.

Particulates

The primary sources of particulates are process heaters, boilers, FCC regenerators, gas turbine, and solid-waste incinerators. Particulates can be controlled by the use of wet scrubbers and high-efficiency mechanical collectors (cyclones, bag house); high efficient cyclones or electrostatic precipitators on catalyst regenerators and power plant stacks; controlled combustion to reduce smoke; controlled stack and flame temperatures; improved burner and incinerator design; and use of smokeless flares.

The emissions from boilers and process heaters are largely a function of the quality of the fuel used. If a fuel has a high ash content, a large portion of that ash will appear as fly ash in the fuel gases. The technology for the removal of particulates resulting from the combustion of coal or oil is typically high-efficiency mechanical cyclones and electrostatic precipitators. Also, particulates can be controlled by proper operating parameters and adjustments of the air-to-fuel ratio.

The principal refinery process unit subject to control of particulates is the fluid bed catalytic cracker. Particulates from the FCC are controlled by electrostatic precipitators, high-efficiency cyclones, dry scrubbers, wet scrubbers or baghouses. The most commonly used equipment is the electrostatic precipitator.

Odours

The nose is an extremely sensitive detector of odours and can be matched by only the most sensitive instrumental technique. The main offenders have been shown to be sulphur compounds, such as H_2S, mercaptans, and disulphides, which are known to be present in crude oil fractions and have been detected in refinery atmospheres. Because of their offensive smell and low olfactory levels, these compounds give rise to the majority of complaints.

Most refinery odour problems are due to leakages or mal-operations which are intermittent in nature and which may usually be prevented by good housekeeping and maintenance.

Table 5 summarizes some typical refinery smells, their possible source, and the most probable compounds contributing to the odour. A listing of the most common odour-causing compounds found in the refinery emissions is shown in Table 6.

Table 5

Refinery odours and sources

Type of smell	Source	Odours compounds
Bad eggs	Crude storage distillation of gases sulphur removal flare stacks (extinguished)	H_2S +trace of disulphides
Sewer smell	effluent water biological treatment plants LPG odourizing, spent caustic loading and transfer	dimethyl sulphide, ethyl and amyl mercaptans
Burnt oil	catalytic cracking unit coking asphalt blowing asphalt storage	unsaturated hydrocarbons
Gasoline	product storage CPI & API separators	hydrocarbons
Aromatics (Benzene)	aromatic plants naphtha reformers	benzene, toluene
Hot Tar	asphalt storage	hydrocarbons, mercaptans, H_2S

Table 6

Odours of compounds which may be found in refinery emissions

Chemical	Odour threshhold(ppb)[x]	Odour description
Acetic acid	1,000	Sour
Acetone	100,000	Chemical, sweet
Amine, monomethyl	21	Fishy, pungent
Amine, dimethyl	47	Fishy
Amine, trimethyl	0.2	Fishy, pungent
Ammonia	46,800	Pungent
Benzene	4,700	Solvent
Benzyl sulphide	2	Sulphidy
Carbon disulphide	210	Vegetable-like, sulphidy
Chlorine	314	Bleach, pungent
Chlorophenol	0.03	Medicinal
Dimethyl sulphide	1-2	Vegetable-like, sulphidy
Diethyl sulphide	6	Garlic-like, foul
Diphenyl sulphide	5	Burnt, rubbery
Hydrogen sulphide	5	Rotten eggs
Methyl ethyl ketone	10,000	Sweet
Mercaptan, methyl	1-2	Sulphidy, decayed cabbage
Mercaptan, ethyl	0.4-1	Sulphidy, decayed cabbage
Mercaptan, n-propyl	0.7	Sulphidy
Mercaptan, n-butyl	0.7	Strong, sulphidy
Paracresol	1	Tarry, pungent
Paraxylene	470	Sweet
Phenol	47	Medicinal
Phosphine	21	Oniony, mustard
Sulphur dioxide	470	Sharp, pungent
Toluene	2,000-4,700	Solvent, moth balls
Butane	6,000	
Heptane	18,000	
Amylenes and pentenes	170-2,100	

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x) Units in parts per billion by volume.

Operating Guidelines for Controlling Air Emissions

The guidelines for operating a refinery or refinery associated terminal can be divided into four general areas which relate to each other. These areas are design and operating procedures, inspection, maintenance and housekeeping. Training to ensure that the goals for each of these areas are met is necessary. The extent of detail in the guidelines is a matter for local discretion dependent on local conditions.

The following are some design and operation procedures which are generally beneficial with regard to controlling air emissions. The list is by no means exhaustive.

- The practices of open stirring, venting and flaring should be avoided;

- Tank gauging and sampling which require opening the tank to the atmosphere should be carried out to the extent it is possible, at the time of day when the tank temperature and, therefore, pressure is at a minimum, so the vapour loss will be minimized. Consideration should be given to the use of automatic gauges and side sample connections, Operating practices should minimize spillage and ensure that vapour collection and recovery equipment will control vapour loss to the atmosphere from product transfer operations including loading of tank trucks, tank cars, and drums;

- Masking agents or odour counteractants may be used to cover up odours if the problem is exclusively one of odour suppression and does not impact on safety and leak detection. Spilled materials should be picked up by a vacuum truck and the material reprocessed, if possible;

- Pressure settings on fixed roof storage tank should be set based on the vapour pressure of the stored material to limit the release of hydrocarbon vapours;

- Wastewater streams containing odorous materials should be kept separate, if practical, from the total effluent system and treated separately;

- The biological wastewater treatment unit should be maintained in an aerobic state to minimize odour;

- Malodorous compounds, such as spent caustics, can sometimes be sold for recovery of chemicals;
- Odours from incineration processes may be minimized by raising the combustion temperature;
- If it becomes necessary to flare H_2S, the fuel gas feed to the flare should be increased, and the steam flow decreased, thereby improving the combustion of H_2S and minimizing the odour emissions.

Regular or periodic inspection is necessary to ensure that all process and pollution control equipment is operating properly and to detect any faulty equipment that results in leakage of hydrocarbons or any other meterial. Maintenance of all equipment that is inspected and found to be faulty should be conducted as soon as practical, both to minimize emissions and to prevent a major failure of the equipment.

2.1.2.2. Water Pollution Control

The volume and characteristics of the wastewaters produced and discharged by petroleum refineries are dependent upon parameters such as the properties of the crude oil, types of processing units, final product mix, and method of treatment and disposal. Therefore, the characteristics of the wastewaters produced and discharged will reflect individual site conditions, and a "typical" wastewater cannot be defined.

Treatment Processes

Two systems are employed in the treatment of refinery wastewaters: the in-plant sour water stripping unit and the wastewater treatment units. The sour water stripping unit is employed in the refinery process units for pre-treatment of waters containing H_2S. The wastewater treatment units treat all contaminated waters prior to discharge mostly, but not necessarily, on a site basis.

Sour Water Stripping Unit

Water containing sulphides is termed sour water or sour condensate. Refinery operations produce sour water from processes such as hydrotreating, catalytic cracking, and coking and whenever steam is condensed in the presence of gases containing hydrogen sulphide. In addition, sour water normally contains ammonia and small amounts of phenol and other hydrocarbons. These contaminants are odorous and may cause wastewater treatment plant upsets and wastewater discharge violations if they were discharged without treatment. Sour water stripping is used by refineries to reduce the level of the contaminants in sour condensate to allow further use of this condensate.

Sour water stripping can remove hydrogen sulphide, ammonia and some phenolics from the water. Sour water stripping will also remove varying amounts of phenols, mercaptans and other contaminants present in the feedwater. The actual amount of these materials removed is dependent upon the unit operating conditions and feedwater characteristics. The sour gas from the stripper is removed to the sulphur recovery unit and the stripper bottoms are fed to the crude oil desalters or discharged directly to the wastewater treatment system.

Wastewater Treatment Units

The purpose of wastewater treating is to upgrade the quality of effluent water so that it can be safely disposed of or recirculated to the refinery. Refinery wastewaters typically contain oil, phenols, sulphides, ammonia, and/or dissolved and suspended solids. Some refinery wastewaters contain other organic and inorganic chemicals. The types of treatment processes utilized vary with the types of concentrations of contaminant and with the effluent quality requirements.

A typical refinery wastewater system consists of: drainage and collection system; gravity-type oil-water separators and auxiliaries required to remove oil and sediment; treatment units or disposal facilities to handle segregated chemical solutions and other process wastes, and to control the effects of pollutants which have toxic properties, cause taste and odour and so forth; and some form of secondary treatment following gravity separation, where required.

Five stages of wastewater treatment may be used in a refinery based on the type of wastewaters being treated and the quality and type of receiving waters. These stages are: in-plant pre-treatment (including sour water stripping, neutralization, etc.),primary treatment (oil/water separation and removal of settleable solids), intermediate treatment (holding basins), secondary treatment (biological oxidation), and tertiary treatment (activated carbon absorption and filtration).

Wastewater Characteristics and Classification

The water contaminant parameters determined in refinery wastewater include biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), oil, total suspended solids (TSS), ammonia (NH_3), phenolics, hydrogen sulphide (H_2S), trace organics and some heavy metals. Table 7 shows the major sources of each of the contaminants. Process wastewaters contribute to a portion of virtually all, while other sources have more specific contaminants discharges.

The characteristics of the wastewater will determine both the degree and type of treatment required and the effect of the wastewater treatment plant effluent on the receiving waters. The specific characteristics of wastewater of importance for refinery effluents include pH, salinity, acidity, alkalinity, dissolved oxygen, oxygen demand, hardness, osmotic effects, toxicity, taste and odour, colour, turbidity, suspended matter, oil and temperature.

Table 7

Wastewater Pollutant Sources

Pollutant	Sources
BOD_5, COD, Oil	Process wastewater Cooling tower blow-down (if hydrocarbons leak into cooling water system) Ballast water Tank flow drainage and run-off
Total suspended solids	Process wastewater Cooling tower blow-down Ballast water Tank flow drainage and run-off
Phenolics	Process wastewater (particularly from fluid catalytic cracking unit)
NH_3, H_2S, trace organics	Process wastewater (particularly from fluid catalytic cracking unit and coker)
Heavy metals	Process wastewater, tankage Wastewaters discharges Cooling tower blow-down (if chromate type colling water treatment chemicals are used).

Table 8 indicates the type of pollutant typically expected in the wastewaters from the various refinery processes.

Table 8

Wastewater contaminants from refinery unit processes

Processes	Pollutants typically expected in wastewater
Crude oil desalting	Inorganic chlorides HC, (H_2S, phenols) SS
Atmospheric distillation	HC, H_2S (NH_3, phenols)
Vacuum distillation	HC, H_2S (NH_3, phenols)
Fluid catalytic cracking	HC, H_2S, NH_3, CN, phenols
Coking (delayed or fluid)	HC, H_2S, NH_3, CN, phenols
Visbreaking	HC, H_2S, NH_3, CN, phenols
Steam cracking (gas oils)	HC, H_2S, NH_3, CN, phenols
Catalytic hydrocracking	H_2S, NH_3, (HC), phenols
Catalytic reforming	H_2S, HCl
Naphtha hydrodesulphurization	H_2S, NH_3, HC, (phenols)
Distillate hydrodesulphurization	H_2S, NH_3, HC, (phenols)
Heavy oil hydrodesulphurization	H_2S, NH_3, HC, (phenols)
Gas recovery plants:	
- Unsaturates	H_2S, NH_3, RSH, CN, amine, (HC, phenols)
- Saturates	H_2S, NH_3, RSH, amine, (HC)
Merox treaters	NaSH, NaSR, Sodium phenolates. (HC)
Alkylation	Sulphuric or hydrofluoric acid or acid salts, SS
Isomerization	Caustic stream containing organic chlorides
Hydrogen synthesis	(CO_2, CN, NH_3, amine)
Aromatic extraction	(solvents, aromatic HC)
Petrochemicals	(various)
Lubricating oil	Solvents and various others
Asphalt	HC, (phenols)
Sulphur recovery	

Abbreviations:

HC - hydrocarbon liquids or oils;
H_2S - hydrogen sulphide;
NH_3 - ammonia;
CN - cyanides and thiocyanates;
HCl - hydrogen chloride;

RSH - mercaptans;
NaSR - sodium mercaptides;
NaSH - sodium hydrosulphide;
CO_2 - carbon dioxide;
SS - suspended solids.

The pollutants enclosed in () indicate those which may not be present in all cases.

Operating Guidelines for Effluent Water Pollution Control

The same four general areas identified for controlling air emissions, namely design and operating procedures, inspection, maintenance and housekeeping, together with training, are applicable to controlling water pollution. The thrust of the operating practices is to operate in a manner which will permit meeting the goals of the facility design such as environmental protection, maximum water re-use and recycle, water conservation, and adequate waste water treatment. Examples of design and operation procedures which are generally beneficial are as follows:

- Recovery of oil spills and hydrocarbons with vacuum trucks to reduce emissions and water effluents;
- Separation of oily wastes, concentrated wastes, and other process wastes from general effluents for more effective treatment;
- Reduction of shock pollutant loads on treatment facilities through the periodic flushing of process sewers to prevent contaminant build-up and by the use of flow and load equalization prior to treatment;
- A specialized programme for handling oily wastes, sludges, wash waters and other effluents;
- Maximization of air fan cooling and employ cooling water only for those services in which low process temperatures make air fan cooling impractical or uneconomic;
- Recovery of waste chemicals for re use or sale;
- Routing various wastewater streams to the appropriate type of sewer and/or treatment;
- Washing tanks with petroleum products to minimize volume of oil contaminated water requiring treatment;
- Use of alternate chemicals or mixes of chemicals that reduce wastewater contamination;
- Limiting the amount of water used for process unit washdowns;
- Converting four water strippers to reboiler strippers to reduce foul water and recover condensate;
- Installing equipment (such as valves or pumps) which will leak minimum amounts of petroleum products;
- Removing colling water from pumps;
- Using blocked operation of foul water strippers;
- Using caustic injection into desalted crude to reduce [illegible] [illegible] to control corrosion in the crude unit overhead system.

2.1.2.3. Groundwater Pollution Control

Escape of liquid petroleum products from storage and transport facilities under the surface of the earth and from above-ground spills into the soil have become an important area of concern. The acute aspects of the problem - raw product in drinking water wells, gasoline fumes in basements, fires and explosions - create immediate danger to life and property. The more chronic effects include sub-toxic but unpalatable levels of contamination in drinking water, unsightly seepage at springs and along streams, etc. and should stimulate the same sense of urgency.

The two basic sources of spilled liquid petroleum products are equipment failure and operator error. Equipment failure includes corrosion and leaking or both above and below-ground piping and tanks, valves failure, refinery unit upsets and sewer and drain leaks. Many of these failures may be avoided through proper inspection and maintenance procedures. Operator error includes overfilling tanks and improper alignment of valves and piping. These and other operator errors can best be corrected through developing proven operating procedures, regular training and testing of personnel, and systematic follow-up to assure that procedures are followed.

The material in this section applies to both refineries and terminals (refinery-associated and crude or product transportation and storageterminals).

Preventive Measures

Preventive actions are designed to minimize the effect of any future events which may result in pollution; these actions restrict the effects of pollution to a limited and controlled zone. For any preventive measure, the method must be properly engineered. It must be stressed that the preventing measures discussed are likely to be practical only at new oil industry installations. For many existing installations, some of the proposals would be either extremely expensive or not feasible.

The preventive measures to be installed during the construction of a permanent structure should consider the following:

- The type of construction (refinery, storage tank, pipeline etc.)
- The volume and the nature of the oil likely to pollute the site;
- The geology and hydrogeological environments; nature of the terrain, depth, activity and quality of the aquifer;
- The economic environment; proximity to and capacity of water wells and intakes for domestic purposes, risk of pollution of a river etc.;
- The preventive system involves four areas: corrosion protection, surface preventive measures, subsurface preventive measures, and monitoring devices to detect and warn of un-suspected pollution not visible from the surface or of a dangerous change in groundwater levels.

2.1.2.4. Solid and Semi-solid Wastes Control

Petroleum refineries also generate a wide variety of solid and semi-solid wastes (hereafter referred to as solid wastes), some of which may contain materials currently considered to be hazardous (i.e. heavy metals such as chromium and zinc and polynuclear aromatics) which are potentially hazardous to health and the environment.

Typical solid wastes generated at a refinery include process sludges, spent catalysts, wastewater and raw water treating sludge, and various sediments. The volume of waste generated, as well as the economics of material recovery, are determined to a large degree by the type, age, and condition of process units and the market for product "mix". Pollution control methods are further affected by geographic conditions, transportation distances, disposal site hydrogeological characteristics and regulatory requirements.

Refinery process solid wastes can be divided into two types: intermittent and continuous. Intermittent process wastes are those which generally result from the cleaning of refinery facilities and which require disposal at intervals greater than two weeks.

Intermittent wastes are a function of refinery size and refinery diligence in maintenance and housekeeping practices.

2.1.2.5. Noise Control

A noise is any unwanted, undesidered, or valueless sound and can cause both physiological and psychological damage to human beings. Noise may produce mental stress, fatigue, dizziness and loss of balance and may have an adverse effect on human activities such as work, recreation, sleep, communication and rest.

There are two major categories of noise: continuous and intermittent. Continuous noises usually have a rather stable level. Intermittent noises are any fluctuating, repetitive sounds.

Noise problems in process plants can be categorized as either community or in-plant problems. Solutions to in-plant problems should be aimed at preventing hearing loss, avoiding speech interference and minimizing adverse effect on workers. Compliance with any workplace noise regulations should be emphasized in the facility design.

The noise levels in a community near a process facility are function of manu parameters, including: distance to the nearest unit or units, size of the facility, noise control treatments and other noise sources (other industrial sources, traffic etc.). Community noise problems are solved through the elimination or prevention of annoyance to neighbours and/or the reduction of the noise levels to within a legal limit.

Noise sources that characteristically generate low frequency noise, such as furnaces and air coolers, tend to contribute significantly to community noise levels. Also, noise sources that are used in large numbers, such as electric motors and air coolers, can contribute significantly to the community noise level.

Excessive noise in existing plants can be controled or abated to an acceptable level by engineering controls. Operating requirements and operator and plant safety may preclude the use of the most efficient and economical methods. In general, control of existing sources is less effective and more expensive in dollars per decibel of noise reduction than including noise limitations in the original design.

Inspection and maintenance of all potential noise sources and operator training are the major management practices to ensure that all the noise abatement practices incorporated in the design are effective. Final means of noise abatement are planning of construction activities and the use of extremely noisy equipment and scheduling vehicular traffic to periods of time when the surrounding community will best tolerate noise approaching or even exceeding the level of annoyance.

2.2. Monomers and basic petrochemicals process

Bulk petrochemical manufacture is almost by definition the initial or early stages of the production process in the petrochemical industry.

However, sometimes, as is particularly the case with certain inorganics and polymers, bulk chemicals can be the finished products of the industry sold for application in other industrial processes. Most bulk chemicals experienced enormous growth from the 1950s to the early mid-1970s. The consequences of this growth were:

- The economic incentive for minimizing production costs resulted in considerable research and development effort being devoted to imrpoving process technology, search for new feedstocks etc. This was an innovative era for the development and introduction of new process technologies;
- Average plant capacities increased many times in size and became large unit consumers of raw materials and energy;
- A high proportion of petrochemical, bulk organic and polymer production processes became continuous (often in the gas phase), utilizing selective catalysts;
- Changed feedstock availabilities/cost has had a considerable influence on process technology development, most markedly with the development of petroleum based ethylene chemistry away from coal based acetylene chemistry;
- Even before the 1974 and 1979 rise in energy production prices, energy costs have contributed with a large share to total production costs; the bulk chemical industry has devoted considerable process research effort to improve energy efficiency.

A radical change in the economic situation and outlook for the bulk chemical industry has occurred since the mid-1970s, which has been principally induced, either directly or indirectly, by the oil/energy crisis. Another contributing factor may be the fact that large volume substitution opportunities for bulk chemical synthetic materials/fibres had also been considerably exploited by this time. The result for the bulk chemical industry in the European Community was:

- excess production capacity in many sectors of the industry since 1975-1978;

- market growth rates much reduced and growth sometimes eliminated altogether;

- low or negative profit margins;

- less R & D funds being devoted to the development of new process technology for bulk chemicals production.

Given the nature of bulk chemical manufacturing, the following observations may be made with respect to their associated emissions and wastes and their treatment:

- While certain sectors of the industry produce emissions of high toxicity, including "black" and "grey" list substances, environmental problems mainly arise from the large effluent load for which adequate dispersal in certain environments may be difficult;

- Emissions/wastes from continuous processes are likely to be more amenable to economic pollution control treatment than those from small scale usually batch processes. Large plants by definition can offer the opportunity for realising economies of scale in gaseous emission scrubbers or effluent treatment plant;

- A particular environmental problem of certain bulk chemical manufactures is the production of large quantities or rather inert solid inorganic wastes/by-products;

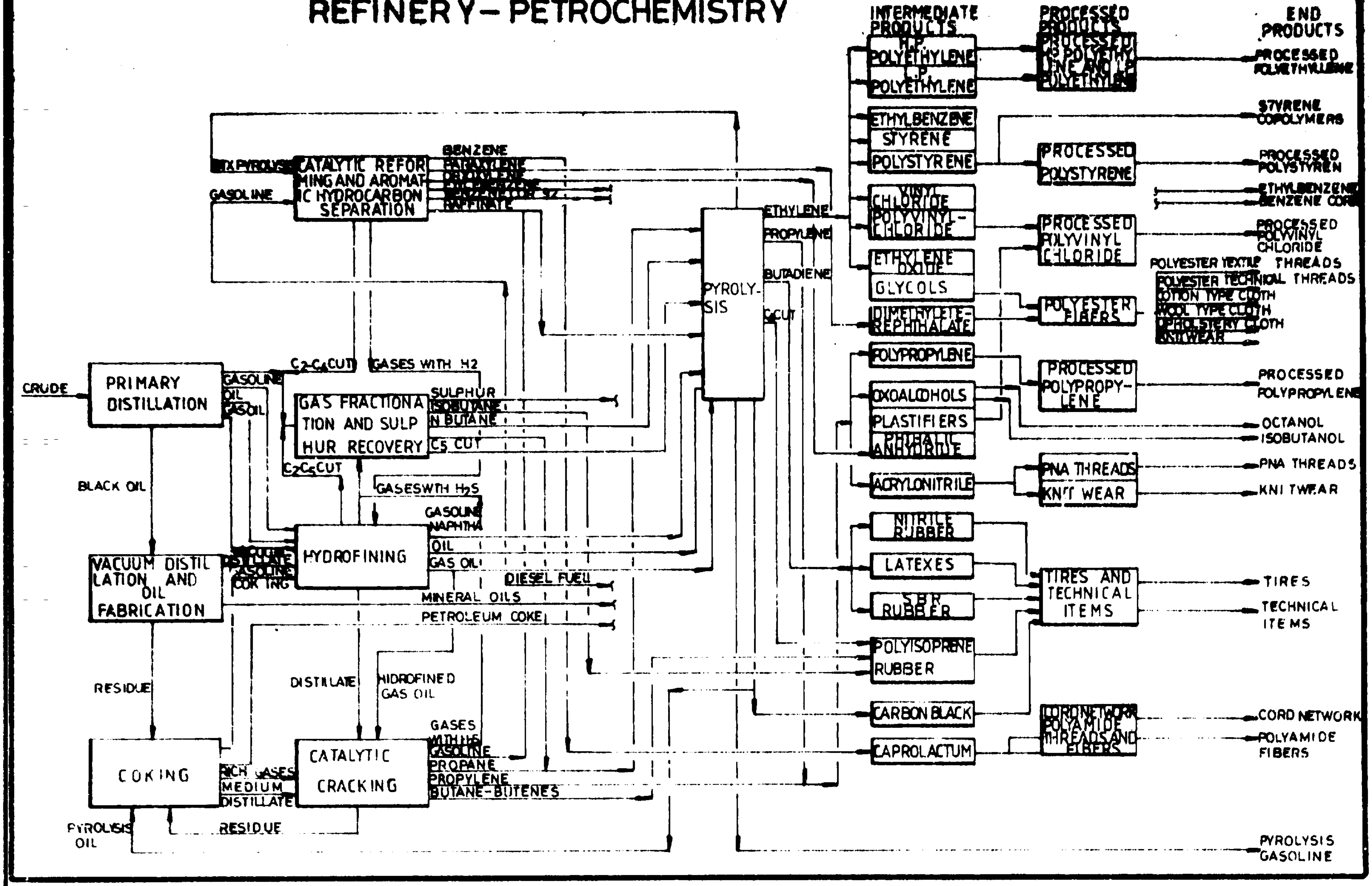
- Large quantities of aqueous weak acid effluent can also be associated with certain bulk chemical production processes.

In the following sub-sections we determine the extent to which cleaner process technologies, so far indentified, have been adopted in the natural evolution and expansion of the petrochemical industry. In later sub-sections, we consider the incidence of other forms of cleaner technologies, such as recycling/reuse of waste streams, recovery of by-products etc. However, the concept of cleaner technologies is in reality not always readily apparent.

This chapter deals with the evolution in time of the technological processes regarding synthesis monomers and some basic petrochemical substances. The evolution of them is examined from the viewpoint of the reason for switching from one process to the other considering principal characteristics of the processes and the consequences thereof on the environment.

The processes selected are those which have an important share in point of their industrial production, as well as their environmental consequences, the conditions and composition of noxious substances which can contaminate air, water or soil.

Fig. 5. FLOW DIAGRAM OF AN INTEGRATED COMPLEX REFINERY – PETROCHEMISTRY



The literature data published did not allow in all cases a quantitative evaluation of the gaseous, liquid and solid effluents resulted from some less known or rather recent processes in which cases the estimations were based on similitudes with other known processes.

Concerning the composition of gaseous, liquid and solid effluents, the paper mentions only the main pollutants expressed in concentrations per liter, cubic meter or percentage by weight.

Herein further is given the list of synthesis monomers and basic petrochemical products making the object of this chapter: 1. Ethylene; 2. Propylene; 3. Butadiene; 4. Isoprene; 5. Ethylbenzene; 6. Styrene; 7. Phenol-acetone; 8. Ethylene oxide; 9. Dimethylterephthalate; 1o. Maleic anhydride; 11. Phthalic anhydride; 12. Acrylonitrile; 13. Acrylic acid; 14. Methyl methacrylate; 15. Acetylene; 16. Formaldehyde; 17. Vinyl acetate; 18. Vinyl chloride; 19. Methyl chloride; 2o. Chloroform; 21. Carbon tetrachloride; 22. Perchlorethylene; 23. Epichlorhydrin; 24. Toluenediisocyanate (TDI); 25. Methylene diphenyldiisocyanate (MDI); 26. Glycerine.

The tables list the main technological processes applied on commercial scale in order to produce the above mentioned products, tables being elaborated on the basis of published literature data as described in the bibliographical chapter of this paper, as well as on the basis of the data known from personal design and operation experience acquired in similar plants.

ETHYLENE MANUFACTURING

Ref. no. 0	Process 1	Period introduced 2	Principal characteristics 3	Environmental aspects 4	Reason for adoption 5
1.	Separation from crude coke-oven gas	1920	Gases with 1.8-2% ethylene content resulted as by-product from coke-oven gases treated with sulphuric acid to yield ethyl alcohol	Environmental pollution with acid liquid residues	Ethyl alcohol used to produce anti-freeze solution. Difficulties in separation,low recovering efficiency. The process is abandoned.
2.	Ethyl alcohol dehydration	1930	Ethyl alcohol dehydration over alumina or phosphoric acid catalyst on coke carrier yielding an ethylene having a concentration between 97-99.5% wt.	Chemically contaminated water with hydrocarbons,organic acids, catalysts slurry	Increased demand of ethylene for the production of polyethylene by high pressure polymerization

0	1	2	3	4	5
3.	Acetylene hydrogenation	1940 - 1945	Acetylene hydrogenation via carbide	Gas effluents with fire and explosion risk, water contamination due to acetylene production via carbide	Applied in Germany for military reasons during the II-nd World War. The process is not profitable and is now abandoned
4.	Steam cracking	1950	Thermal cracking at low pressure 2-3 atm and temperatures between 800-900°C of gas and liquid fractions coming from crude processing. The yield in ethylene is 23-32% from naphta	Spent lye 0.4 m^3/t containing 4% NaOH and 5% Na_2CO_3. Chemically contaminated water 0.2 m^3/t containing: 100 mg/l phenols and pH = 5-6	Since 1950 it is the most widely spread process yielding over 98% of world production of ethylene
5.	Steam cracking	1980	Thermal cracking occurs in tubular coils whose length and geometry improved in time and from one licenser to another	Spent lye 0.1 m^3/t chemical contaminated water 0.1 m^3/t containing phenol and hydrocarbons	Kellog,Stone-Webster Linde, Mitsubishi, Lurgi, developed new process with higher yield of ethylene

0	1	2	3	4	5
6.	Milisecond process	1985	Thermal cracking occurs in tubular coils whose diameter is very small	Chemical contaminated water	Kellog, Idemitsu

PROPYLENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Separation from thermal cracking gases	1920	Sulphuric acid absorption of gases coming from the thermal cracking at high pressure of crude cuts yielding isopropyl alcohol	High acid polluting of the environment	The process was introduced by Standard Oil in USA in 1920 to produce isopropyl alcohols by using refinery gases.The process is abandoned due to its low efficiency
2.	Fisher-Tropsh synthesis in view of obtaining synthetic gasoline	1940	Synthesis gas at 10 atm and 225°C over iron catalysts yields simultaneously synthetic gasoline and 9% propylene in the gases separated from the process	Atmospheric air pollution	The process was introduced in Germany during the II-nd World War by I.G.Farben-industrie. The process is updated starting from synthesis gas obtained from renewable sources (biomass, wood) or coal

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0	1	2	3	4	5
3.	Hydrocarbons pyrolysis	1950	Thermal cracking at low pressure of crude cuts yields propylene	Spent lye: 0.4 m^3/t containing 4% NaOH and 5% Na_2CO_3. Chemically contaminated water 0.2 m^3/t	The most widely used process nowadays. Over 60% of world production is obtained by this process. The balance of propylene is obtained by fractionation and separation of refinery gases

BUTADIENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Butadiene production by n-butylene dehydrogenation (DOW)	1946- USA 1960 - Soviet Union 1962- Romania	The process consists in n-butylene dehydrogenation on specific catalysts (endothermal dehydrogenation) - conversion 18% vol. - selectivity 80% vol.	0.165 t/t fuel gas 10 t/t waste water with organic substances traces 0.035 t/t heavy hydrocarbons (fuel)	Increasing demand for synthetic rubber
2.	Butadiene production by n-butylene oxidehydrogenation (Petro-Tex)	1965 - USA 1981 - Romania	Oxidative dehydrogenation of n-butenes over specific catalysts (Ferite type) - 65% mol. conv. - selectivity 93% mol.	2.44 t/t waste gases 4.08 t/t waste water 0.061 t/t liquid fuel	Higher performances as compared to the classical dehydrogenation (endothermal) lower raw material consumption. Low energy consumption (steam, fuel)

ISOPRENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Synthesis isoprene production from isobutylene and formaldehyde in two steps (Soviet Union)	1968 - USSR 1975- Romania	The process consists in formaldehyde condensation with isobutylene and decomposition of resulted dimethyldioxane to isoprene and formaldehyde Isobutylene consumption 1.2 t/t Methanol consumption 1.05 t/t	0.64 t/t by-products are fully used as floating agents, solvents, fuels 0.1 t/t waste water	Existance of raw material and development of rubber consumers
2.	Synthesis isoprene production from isobutylene and formaldehyde in one step	1985 - Soviet Union	The process consists in formaldehyde condensing with isobutylene (liquid-liquid or gas-solid catalysis) isobutylene consumption 1.18 t/t methanol consumption 0.8 t/t	0.35 t/t by products are fully used as fuels 3 t/t organically contaminated water	Higher yield and lower energetic consumptions

0	1	2	3	4	5
3.	Isoprene production from isopentane by dehydrogenation in two steps (Soviet Union)	1968 - USSR	Isopentane dehydrogenation in two steps I-st step - yield 31% wt. - selectivity 72% wt. II-nd step - yield 32% wt. - selectivity 77.4% wt. Isopentane consumption 2.0 t/t	0.44 t/t fuel gases 0.24 t/t gases from regeneration of catalysts contaminated with dust (within allowed limits) 0.18 t/t C_5 cut from separation 0.036 t/t C_6 cut (solvent) 0.164 t/t dimers and oxigenated compounds (fuel) 0.0416 t/t organically contaminated water Specific break-up catalysts	The process presents high consumption of raw materials (2 t/t) and energy. The reason for adoption was the available raw material in USSR

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0	1	2	3	4	5
4.	Isoprene production from isopentane by dehydrogenation in one step (Houndry -US)	1962 - USA 1965 - Romania (under research on pilot scale not applied on commercial scale)	The process consists in isopentane dehydrogenation in one step Isopentane consumption 2.0 t/t	0.284 t/t fuel gas, 0.68 t/t pentane, pentadiene and cyclopentadiene cut 0.026 t/t heavy acetylene cut with isoprene	The process is not adopted dueto the high consumption of raw material and the complex character of the plant and therefor on commercial scale

ETHYLBENZENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Liquid phase alkylation	1950	Ethylene and benzene alkylation in liquid phase at temperatures between 80-100°C and pressures of 1.2 bars over aluminium chloride catalysts	- Acid water: 0.025 t/t EB containing 25% Cl_3Al 0.2% benzene and $Al(OH)_3$ traces - Polyalkylbenzene 0.02 t/t EB containing: 56% diphenyl ethane , 40% hexamethyl benzene and 4% tetraethyl benzene - Chemically contaminated water 1.2 t/t EB containing: benzene 10 mg/l $Al(OH)_3$ 0.05%	Increase demand for ethylbenzene for styrene fabrication. The process is highly corrosive for the equipment due to the presence of aluminium chloride in liquid phase and water contamination Badger, Union Carbide Monsanto, CdF Chemie Technip, Mitsubishi

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0	1	2	3	4	5
2.	Alkylation in gaseous phase	1955	Ethylene and benzene alkylation in gaseous phase over phosphoric acid catalysts settled on Kiselgur at 200-250°C and 14 atm. According to Alkar (UOP) the catalyst is aluminium oxide activated with borine trifloride at 150°C and 150 atm.	Low amounts of waste water which does not require special purifications. Negligeable amounts of by-products	Non corrosive reaction conditions thus making possible to use carbon steel carbon. the process does not require concentrated ethylene, being also possible to use diluted ethylene over 10% wt. such as results from catalytic cracking gases or from coke-oven gas UOP, Mobil-Badger
3.	Separation from aromatic C_8 cut (xylene)	1955	Ethylbenzene separation by superfractionation of C_8 cut coming from catalytic reforming . Separation is economically convenient in case xylene cut contains over 20% ethylbenzene	Minor environmental pollution risk	The process implies difficulties of technical nature. The process cannot be widely used due to limited C_8 cut resources

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0	1	2	3	4	5
4.	Alkylation in gaseous phase	1975	Ethylene and benzene alkylation in gaseous phase over zeolite catalysts, in fixed bed reactor, at 420°C and 20 ata	Low amounts of waste water which does not require any purification	Non corrosive reaction conditions, higher yields of ethylbenzene

STYRENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Ethylbenzene dehydrogenation	1937	Ethylbenzene dehydrogenation reaction to styrene is endothermal and can be conducted in adiabatic type reactors (Dow chemical) or isothermal (BASF) Reaction temperature varies between 550-650°C and the pressure between 1.3-2.0 atm over iron oxides catalysts The yields obtained are 88-91 % for conversions between 50-60%	Chemically contaminated water: 7.5 t/t EB containing: styrene 50 mg/l, ethylbenzene 30 mg/l sulphur traces	The need to develop an industrial production of styrene was determined by an increased demand for SBR and polystyrene. The isothermal dehydrogenation process has the advantage of a lower steam consumption and lower temperatures in reactor. The adiabatic process offers higher conversions, 60%, compared to the isothermal process, only 40% Dow chemical, BASF, Mitsubishi, Monsanto, Union Carbide

0	1	2	3	4	5
2.	Ethylbenzene hydroperoxidation (oxirane process)	1965 - USA	Halcon oxidation process is based on ethylbenzene oxidation to ethyl-benzene hydroperoxide followed by propylene epoxidation yielding propeneoxide and phenyl-1-carbinol which is further dehydrated to styrene	Chemically contaminated water with hydrocarbons, phenol, organic acid metal salts	Hydroperoxidation process is preferable when apart of styrene propaneoxide is also required. The process has high styrene yields 95% compared to 88-91% at dehydrogenation process Halcon Co, Scientific Design

PHENOL MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Alkaline sulphonatation and melting	1925-1930	Alkaline melting of benzene sodium sulphonate is achieved in agitation reactors at 310°C in the presence of 70% NaOH solution. Benzene sulphonation can be conducted either in liquid or vapour phase (more economically convenient)	Significant amount of waste water with high phenol content. Residue coming from splitting sulphur bioxide and sodium sulphite	Increasing demand for phenol Abandoned process
2.	Phenyl-chloride hydrolysis	1927	Anhydrous benzene reacts with gaseous chlorine at 80°C and 1.12 at. in the presence of $FeCl_3$ yielding phenyl chloride. Phenyl chloride hydrolyses is achieved at 400°C and high pressure with NaOH solution Phenol is released with HCl solution	Strongly contaminated water with phenol, chlorinated products, hydrochloric acid	Increasing demand for phenol Abandoned process

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0	1	2	3	4	5
3.	Benzene oxichlorination (Rashing)	1938	Phenol production from benzene and air through an intermediate phase of phenyl chloride	Strongly contaminated waste water with phenol and chlorinated products	Availability of benzene
4.	Cumene process (i.p.b.)	1950	Isopropyl benzene production by benzene alkylation with propene over orthophosphoric acid catalyst followed by cumene decomposition in acid medium, in phenol and acetone	Phenol water 4 t/t containing 1.5-3.5 g/l phenol Phenol residue 0.15 t/t Polyalkyl benzene 0.15 t/t	Over 90% of world production of phenol comes by this process. Phenol and acetone are also simultaneously obtained Low polluting process

ETHYLENE OXIDE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Envrionmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Chlorhydrin process	1915	Chlorine and lime react with ethylene in an aqueous medium Ethylene chlorohydrin is an intermediate	Large aqueous effluent containing salts and chlorinated organic by-products	Good yield (over 90%)
2.	Air oxidation of ethylene	1940	Ethylene and air are passed over a silver-based catalyst at 200-300°C	Less aqueous effluent. Large volumes of impure nitrogen evolved.	Much more economic for large scale production. Only about 75% yield on ethylene
3.	Oxidation of ethylene using oxygen	1960	Ethylene and oxygen are passed over a silver based catalyst at about 250°C	Minimal gaseous and liquid effluents. Somewhat cleaner process	Marginally better yields. Availability of cheap oxygen

VINYL CHLORIDE MONOMER MANUFACTURING

Principal characteristics 3	Environmental aspects 4	Reason for adoption 5
Purified HCl gas in excess and acetylene passed over a catalyst, e.g. mercuric chloride, at 150-250°C	Clean reaction from acetylene. Carbide production is dusty	Easy process when acetylene is available. Up to 99% yield on acetylene carbide for acetylene need very large energy input
Addition of chlorine to ethylene at 50° and cracking of the resultant ethylene dichloride at 500°C and recycling of uncracked EDC	Large quantities of co-product HCl neutralised for discharge as salt or preferably sold as hydrochloric acid	High costof acetylene.Falling cost and increasing availability of ethylene to meet growing demand for PVC.Suitable for large production capacities Up to 95% over all yield of vinyl chloride

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DIMETHYLTEREPHTHALATE MANUFACTUR

Ref. no. 0	Process 1	Period introduced 2	Principal characteristics 3
1.	Paraxylene oxidation	1960	P-xylene and air mixture is subjected to oxidation in the presence of cobalt catalysts at 150°C and 6 bars
2.	Terephthalic acid process by esterification	1970	Catalytic oxidation of p-xylene with air in acetic acid medium in the presence of cobalt and mangan salts and broming salts used as promotors. Oxidation occurs at temperatures between 210-240°C and pressures of 20-24 bars.

3	4	5
of the EDC is produced sing byproduct HCl ir with ethylene at over a copper cata-	By-product HCl from other manufacturers can be fully employed. Large volumes of waste gases carry traces of EDC into the atmosphere	Chlorine scarce and costly. Able to use the chlorine content of byproduct HCl. Highly exothermic. High yields on ethylene
bove but using oxy- nstead of air	Volume of waste gases very much smaller; discharge of EDC is thus minimised	High cost of incineration to destroy chlorinated hydrocarbons in waste gas streams
ancing production a combination of ses 1 and 2 elimi- byproduct HCl	As for 1 and 2 above with advantage of elimination of HCl	Suitable for exploiting HCl from process 2 in small scale units

MALEIC ANHYDRIDE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	
0	1	2	3	
1.	Benzene oxidation	1960	Benzene and air vapours below hazardous limits (0.9 - 1.5% vol. benzene) at 2.5 bar and 450°C are converted to maleic anhydride at a conversion rate of 60% over vanadium catalysts	Chemica water, maleic acid
2.	Butane-butene cut oxidation	1975	The air mixed butane-butene cut below the lower explosion limit, at a temperature of 450°C	Chemica water 1 maleic propion

HLOROMETHANES 1 MANUFACTURING

Principal characteristics	Environmental aspects	Reason for adoption
3	4	5
ing of methanol at with a dissolved hloride catalyst l	Requires use of NaOH to remove HCl from product gases and oleum to remove water. Aqueous effluent stream	Process is a useful sink to absorb HCl byproduct from other chlorination reactions. 98% yield on methanol
on of chlorine thane at 400°C	HCl by product and higher chloromethanes production	Saleable HCl can be produced
lar quantities of nol and HCl passed ed vapour at 350°C catalyst, typically na, zinc chloride or carbon	Same as liquid phase. Only 0.5 m^3 aqueous effluent per ton CH_3Cl	Lends itself to continuous operation. Improved control and new principal process. 98% yield of CH_3OH

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PHTHALIC ANHYDRIDE MANUFACTURIN

Ref. no.	Process	Period introduced	Principal characteristics
0	1	2	3
1.	Oxidation of naphthalene by oleum	1896	Mercuric sulphate catalyst Sulphur dioxide by product Liquid phase
2.	Vapour phase oxidation of naphthalene	1920's	Air oxidation over vanadium pentoxide catalyst. Highly exothermic.
3.	Oxidation of o-xylene	1950's	Liquid or gas phase, air oxidation of o-xylene over vanadium pentoxide based catalysts.

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0	1	2	3	4	5
4.	Low air oxidation o-xylene	1970's	Same as 3 but lower air-to-o-xylene ratio. Molten salt reaction temp. heating system	Large aqueous effluent remains but reduces gaseous emissions.	Cleaner process Electricity consumption cut by 55%

ACRYLONITRILE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Ethylene Cyanohydrin route	1940 - USA	Process starts from ethylene oxide and HCN which is then dehydrated to acrylonitrile	Significant aqueous organic impurities containing cyanides, hydrogen cyanide	Market demande increasing
2.	Acetylene/ HCN route	1940's Europe	Aqueous phase in presence of cuprous chloride	Wide range of acetylenic by-products	Cheaper more convenient feed-stocks. Purer by-product 80% yield
3.	Ammoxideation process a. Sohio b. BP/Ugine c. Montedison	1950's/60's	Propylene, air and ammonia are passed over catalyst (several patents), sometimes in presence of water	Significant quantities of by-products, mainly - hydrogen cyanide - acetonitrile - ammonium sulphate Not easily recoverable	More economic process to match strong demand Yield 50% on propylene

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0	1	2	3	4	5
4.	Improved ammoxidation - Sohio process	1976	More selective catalyst Sohio used fluidised bed	Reduced by-product yields especially acetonitrile and ammonium sulphate	Reduction of ammonium sulphate and acetonitrile by products. Improved overall Acrylontirile yield to around 80% (Sohio)

ACRYLIC ACID MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Acetylene process (Reppe synthesis)		Synthesis of acrylic derivatives from acetylene, carbon monoxide and water or alcohols carried out in the presence of catalysts: metal and metallic compounds which can make carbonyls. For acrylic acid the reaction temperature is 210-330°C and the pressure 15 atm.	Chemically contaminated water containing acrylic acid, alcohols, residues from decomposition of catalytic complex	The need to obtain acryl derivatives with multiple industrial and technical applications
2.	Propylene process		Indirect catalytic oxidation of propylene by means of acroleine or direct oxidation yielding acrylic acid. The direct oxidation process of propylene occurs at 280-450°C in the presence of Mo, Bi, Fe, and P oxides and a pressure of 11 atm	Waste water 0.9 t/t containing organic acids, aldehydes and acroleine 2%. Liquid residue 0.012 t/t containing polymers, hydrochinone and acrylic acid. Off gases 0.9 t/t containing CO, CO_2, propane-propylene, aldehydes, organic acids	The increasing demand for acrylic acid and the propylene available from petrochemical sources imposed the direct oxidation process for propylene. The process using propylene leads to higher techno-economic indices

METHYL METHACRYLATE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Acetone cyanhydrin process	1930's	Acetone and HCN combine to form acetone cyanhydrin. This is hydrolysed by dilute sulphuric acid and then esterified with methanol	Ammonium sulphate and weak sulphuric acid by-products (3 tonnes of waste acid per tonne product)	Reasonable yield 85%. Some companies use the $(NH_4)_2SO_4$ as a fertiliser and pyrolise the weak H_2SO_4 to produce SO_2
2.	Isobutylene process	1960's	Isobutylene is passed with steam and air over a catalyst at 350°C to produce methacrylic acid. Esterification with methanol gives methyl methacrylate	Effluent gases must be scrubbed or incinerated to remove organic by-products. Avoids hazardous and scarce HCN	Availability of raw material and specific long life catalysts. 55-65% yield of methacrylic acid on isobutylene Esterification yield better than 95%

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0	1	2	3	4	5
3.	DOW-BASF Reppe synthesis	1960's	Direct carboxylation of ethylene in the presence of methanol. Catalytic, gaseous phase reaction	Control of gaseous emissions to ensure oxidation of CO. Direct and apparently cleaner process	Better yield
4.	Isobutane based technologies (oxirane)	1970	One step oxidation of isobutane to methacrylic acid. Selectivity are 50% to methacrylic acid and 20% to potentially recyclable methacrolein	Cleaner process than acetoncyanhydrin route	The use of isobutane would be more attractive in the U.S. and Europe since it is more widely available and much cheaper than isobutylene

ACETYLENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Partial methane oxidation	1967	The process consists of the following main phases: - partial oxidation of methane - preliminary purification and compression of pyrolysis gas - pyrolysis gas washing - decarbonization - acetylene absorption - desorption - ammonia distillation and off gas washing	- high acetylenes and ammonia: 0.19 t/t - gas oil and polymers 0.08 t/t - water with carbon black (about 1.4%): 2.93 t/t - CO_2: 0.8 t/t - water with gas oil: 24.0 t/t - water with carbon black (about 0.53-4.0 t/t)	Methane gas complex chemical processing; 1 t C_2H_2 yields 10,000 Nm^3 synthesis gas of which about 4 t CH_3OH can result Other applications: - oxosynthesis - CO and H_2 separation

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0	1	2	3	4	5
2.	Carbide hydration	1920	The process consists of the following main phases: - raw material preparation - charging + feeding - acetylene generation - cooling, washing - acetylene purification	By products: - calcium hydroxide $Ca(OH)_2$ - 4.4 t/t	- Easy to procure raw materials (coals and limestone) - unsophisticated process - 99.6% concentration C_2H_2 can be obtained

FORMALDEHYDE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Partial oxidation and dehydrogenation of methanol	1925	Partial oxidation and dehydrogenation of methanol mixed with air over silver catalyst at temperatures ranging between 680-720°C. Methanol conversion is 97-98%	No chemically contaminated waste water results. Off gases 0.65 t/t containing : nitrogen,hydrogen, CO, CO_2	After methanol fabrication by synthetical way,formaldehyde production is extended due to its application for the production of resins and other chemical synthesis BASF,Mitsubishi, BAYER, Nichimen ,ICI

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0	1	2	3	4	5
2.	Methanol oxidation with excess air	1945	Methanol oxidation with excess air over iron oxide and molybdenum at temperatures ranging between 270-380°C Methanol conversion 95-98%	Waste gases containing nitrogen, hydrogen, CO, CO_2	With regard to formaldehyde use in the production of urea-formaldehyde resins, methanol oxidation process over metal oxides catalyst is preferable

VINYL ACETATE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
1.	Acetic acid addition to acetylene	1925	The process consists in excess acetylene bubbling over acetic acid at temperatures between 72-80°C in the presence of mercury based catalyst	Alkaline water 0.8 t/t containing 4% sodium hydroxide. Used-up catalyst 0.015 t/t containing active carbon soaked with mercury. Purged acetylene 3.2 t/t containing 99% acetylene	The process is abandoned due to the high cost of acetylene and great environmental pollution problems
2.	The process from ethylene	1970	Bubbling of ethylene and oxygen mixture in a solution or a suspension of palladium chloride, in redox system	Chemically contaminated water with hydrocarbons remains of used-up catalyst	As the production of ethylene from petrochemical sources increases the process becomes profitable and gets a prevailing price within industry development. National Distillers

0	1	2	3	4	5
4.	Same as 2 but avoids use of $NaOH/H_2SO_4$	1970's	Hi pressure (14 ata and 120°C) process. By-product hydrocarbon separated and recycled	Produces weak acid effluent	Cleaner process. Avoids salt contaminated aqueous effluents

CHLOROMETHANES 3 CHLOROFORM MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Liquid phase chlorination of alcohols or ketones	19-th century	Acetone or ethyl alcohol warmed to 62°C in an aqueous suspension of bleaching powder	Considerable aqueous effluent stream	Medical application
2.	Chlorination of methane	1950	Chlorine methane and recycled carbon tetrachloride passed through a fluidised catalyst at 700°C	Only 0.5% of non-volatile residue. Larger quantity of by-product HCl than in 3	Availability of methanol as raw material. Minimal CCl_4 production
3.	High temperature chlorination of CH_3Cl	1965	Methylchloride reacted with excess chlorine at 500°C	HCl and a large proportion of CCl_4 by-product (50%)	Local condition, availability of CH_3Cl

CHLOROMETHANES 4 CARBON TETRACHLORIDE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Chlorination of carbon disulphide	1890	Reaction of chlorine with CS_2 in the presence of $SbCl_5$ or $AlCl_3$	Toxic waste streams	Approx. 90% yield
2.	Chlorination of methane	1950	Reaction of chlorine with methane at 650°C, or at 300° on a fluidised filler's earth catalyst	Only 0.5% of residue	Use of HCl as by-product
3.	Pyrolitic chlorination of higher hydrocarbons	1950	High temperature chlorination of ethane, propane	The main byproducts are perchlorethylene and HCl	Continuous operation Integration with production of other chlorinated hydrocarbons
4.	Pyrolitic chlorination of chlorinated residues	1960	Typically, pyrolitic chlorination of chlorinated organic residues produces an unusable residue less than 20% of the original weight	Clean process Uses other waste streams of chlorinated aliphatics	Better yields

PERCHLORETHYLENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Acetylene chlorination	1900	Chlorination and dehydrochlorination of acetylene to trichlorethylene and then chlorination	Chlorinated by products	Easy process when acetylene is available
2.	Pyrolytic chlorination of aliphatic hydrocarbons	1950	Chlorination of individual or mixed aliphatic hydrocarbons at 550-700°C	Carbon tetrachloride is the major co-product and can be recycled to minimise its production rate	High cost of acetylene. Abundance of other hydrocarbons and by-product chlorohydrocarbons
3.	Oxychlorination of ethylene dichloride, or lower chlorinated aliphatic hydrocarbons	1950	Ethylene passed through a fluid bed catalyst (e.g. $KCl, CuCl_2$ mixture) at 425°C mixed with chlorine, oxygen, steam and recycled chlorinated hydrocarbons. Well known in the USA but not in Europe	Trichlorethylene is a major by-product and is recycled to minimise its overall production	Availability of ethylene. Demand for trichlorethylene. Also clean process

EPICHLORHYDRIN MANUFACTURING

Ref. no. 0	Process 1	Period introduced 2	Principal charac teristics 3	Environmental aspects 4	Reason for adoption 5
1.	Glycerine hydrochlorination	1930	Glycerine hydrochlorination into dichlorhydrine glycerine which is subsequently converted to epychlorhydrin by well-known ways	Chemically contaminated water containing glycerine,epychlorhydrin and chlorinated products Fuel solid residues	The process was introduced at the begining of epichlorhydrin fabrication and is abandoned at present
2.	Allyl chloride hipochlorination	1950	Hipochlorination of allyl chloride leads to formation of glycerine-dichlorhydrin which further treated with lime milk yields epichlorhydrin	Chemically contaminated waste water,70 t/t containing epichlorhydrin 0.04% dichlorhydrin 0.03%,trichlorpropane 0.06%, calcium hydroxide, Chlorinated products residues 0.12 t/t	The process was developed due to the increase propylene availability being widely on industrial scale

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0	1	2	3	4	5
3.	Allyl chloride epoxidation	1955	Allyl chloride epoxidation with perborate peracids or terbutyl hydroperoxide in the presence of vanadium catalysts leads to formation of epichlorhydrin	Chemically contaminated waste water containing epichlorhydrin, chlorinated products	The process has few technological phases but requires vanadium tungsten and molibdenum catalysts and severe working conditions due to peracids
4.	Acroleine chlorination	1965	Chlorination of acroleine in anhydrous state with carbon tetrachloride leads to formation of dichlorpropion aldehyde,which,by decomposition with sulphuric acid yields glycerin dichlorhydrin which hydrolysis to give epichlorhydrin	Chemically contaminated waste water containing acrolein,epichlorhydrin organic compounds with chlorine	High epichlorhydrine yields 96% and glycerine dichlorhydrine resulted as intermediate product. More severe working condition as compared to other processes.

TOLUYLENEDIISOCYANATES (TDI) MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Dinitrotoluene (DNT) hydrogenation to toluylenediamine (TDA) followed by its phosgenation to TDI in a Venturi type (Rhone-Poulenc) reactor	1950	Hydrogenation: $T=100-200^{\circ}C$ $P=20-30$ at Fluid,water Phosgenation: $T=100-200^{\circ}C$ $P=20$ at Fluid, toluene	- Amine water to incineation: amines 0,04% wt. NH_3 0.08% wt. organic compounds 0.15% wt. - Water to biological treatment Polyisocyanates: to incineration	Growth in polyurethane products Process better yield than older
2.	DNT hydrogenation to TDA followed by amine phosgenation to TDI in a reaction loop (Mitsui)	1962	Hydrogenation: $T=120^{\circ}C$ $P=12$ at Fluid - water Phosgenation: $T=200^{\circ}C$ $P=2-3$ at Fluid: orthodichlorbenzene	-Amine water to incineration NaCl .... 3.4% wt. Na_2CO_3 ... 6.4% wt. NaOH ..... 12.1% wt. amines : not specified - Water to biological treatment Polyisocyanates to incineration	Growth in polyurethane products

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0	1	2	3	4	5
3.	DNT hydrogenation to TDA followed by amine phosgenation to TDI in a tube reactor - Neftehim -	1980	Hydrogenation T = 100°C P =25-26 at Fluid - ethyl alcohol Phosgenation T =180-240°C P =50-80 at Fluid - monochlorbenezene	Amine water to incineration NaCl ..... 5-15% wt. Na_2CO_3 .... 1.5% wt. $NaNO_3$ ..... 1.5% wt. NaOH ...... 1.5% wt. amines 300 mg/l monochlorbenzene: 300 mg/l - water to biological treatment ash results after incineration of solid residues of polyisocyanates	

METHYLENEDIPHENYLDIISOCYANATE (MDI) MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Aniline condensation with formaldehyde in the presence of hydrochloric acid yielding methylenediphenyl diamine (MDA) followed by its phosgenation to MDI Condensation in 3 reactors with agitation. Phosgenation in a reaction loop (Mitsui)	1970	Condensation: $T=50-110^{\circ}C$ $P=1$ at Phosgenation: $T=160^{\circ}C$ $P=1-3$ at Fluid: orthodichlorbenzene	- Amine water to incineration NaCl .... 12.5% wt. NaOH .... 5.2% wt. amines ... 0.04% wt. - Water to biological treatment	Growth in polyurethane products
2.	Aniline condensation with formaldehyde in the presence of hydrochloric acid yielding MDA in a tube reactor followed by phosgenation yielding MDI in tube reactors (Up-John)	1966	Condensation $T=150-160^{\circ}C$ $P=7-10.6$ at Phosgenation $T=200^{\circ}C$ $P=50$ at Fluid: orthodichlorbenzene	Amine water to incineration NaCl ...... 1.4% wt. NaOH ...... 1 % wt. amine - 0.04 % wt. water to biological treatment	Growth in polyurethane products

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0	1	2	3	4	5
3.	Aniline condensation with formaldehyde in the presence of hydrochloric acid in autoclave type reactors with agitation batchwise process - yielding MDA followed by amine phosgenation to MDI in tube reactor - Neftehim -	1980	Condensation T =100°C P =1 at Phosgenation T=180-240°C P=50-80 at Fluid: monochlorbenzene	- Amine water to incineration NaCl .... .. 5-15% wt. Na_2CO_3 ..... 1.5 % wt. NaOH .... 1.5% wt. amines ..... 300 mg/l monochlorbenzene 300 mg/l - Water to biological treatment	Growth in polyurethane products

GLYCERINE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Fats splitting	Prevailing process until 1949	Animal and vegetable fats hydrolise by alkalies treatment at 250°C and 50 atm.	Chemically contaminated water containing: glycerine alkalies, organic acids	The need to meet the glycerine demands for plastifiers: explosives industry etc. The Process developed due to the excess of fats
2.	Synthesis processes from propylene	1950	Propene chlorination into allyl chloride followed by dichlorohydrine hydrolises yielding glycerine. Allyl chloride can be converted to glycerine via epichlorohydrine too.	Chemically contamined water containing glycerine, organic compounds with chlorine, hydrochloric acid	Propylene availabilities from petrochemical sources and decrease of fats resources

Based on the data mentioned in above tables, hereinunder follows a study of the progress and more significant changes occured in the evolution of the technological processes in the basic petrochemistry correlated to the reduction of environmental pollution.

It is worth noting that the process improvements were in most cases particularly focussed on the reduction of the raw materials and energy consumptions and less on the reduction of the environmental pollution which in certain cases is a concurrent component of the main goal in view, namely: the increase of the economic competitivity of products.

Nevertheless, in those cases where the petrochemical processes by their nature, are highly polluting, efforts were made to improve the processes meant to reduce noxious and pollutants release in the form of gases - liquid or solids.

Ethylene and propylene

Low pressure steam cracking of naphtha and gas oil particularly is the most widely used process at present to produce low olefines. The process knows great improvements particularly with regard to pyrolysis furnaces zone meant to increase the ethylene and propylene yield (23% to 34%) and to decrease energy consumptions by process engineering methods.

The principal air pollutants resulting from the pyrolysis plants are: C_1-C_4 hydrocarbons, sulphide hydrogen, nitrogen oxides, sulphur oxides, carbon oxide and solid particles as soot (carbon black). The highest pollution is attributed to: sulphur oxides 78% wt. C_1-C_4 hydrocarbns and hydrogen sulphide 20% wt, the ballance of pollutants representing 2% wt.

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Reductions of air pollution were obtained by improving the flare facilities and particularly by recovering flare gases in specially designed plants. At the same time with the decrease of air pollution, flare gas recovery is also a way to decrease the energy consumptions of the pyrolysis plants.

Chemically contaminated water comes-from soda washing, about 0.4 m^3/t ethylene and from liquid phase separations and leaks, about 0.2 m^3/t ethylene being contaminated with NaOH, SNa_2, Na_2CO_3, phenols and heavy hydrocarbons.

No solids residues are obtained from pyrolysis plants except the emergency cases and the periods for cleaning organic deposits on the inner faces of heat exchangers, vessels and distillation columns.

Butadiene

Butadiene synthesis fabricaton processes greatly developed after 1965, passing from -nbutenes dehydrogenation through an endothermal process (Dow Chemical 1946- USA) to the exothermal process whereby n-butenes are oxidehydrogenated to butadiene (Petrotex - USA). The new process is widely spread due to its higher technological performance compared to Dow-Chemical process. Butenes oxidehydrogenation has in addition the advantage of getting much lower amounts of liquid gaseous pollutants as compared to the classical process.

The gaseous effluent is mainly constituted of nitrogen (84% wt.) and comes from the air used for reaction process containing O_2, H_2, CO, CO_2, argon and oil traces.

The waste water contains lower traces of formaldehyde and acroleine compared to butene dehydrogenation (Dow).

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Isoprene

The main processes applied on industrial scale for isoprene fabrication are in chronological order: isoprentane dehydrogenation in two stages (Soviet Union), isobutane and formaldehyde condensation (Soviet Union, Romania) isoamelenes dehydrogenation (Shell) and isoprene separation from pyrolysis gasoline (Romania, Japan) . Isoprene fabrication process from propylene (Scientific Design) was abandoned while isopentane dehydrogenation in one stage to isoprene (Houdry) is not yet in commercial operation.

From the view point of environmental protection,the least polluting process is the one producing isoprene from pyrolysis gasoline followed by isobutene condensation with formaldehyde whereas isopentane dehydrogenation in two stages represents the process with the most polluting sources.

Ethyl benzene

The main processes applied on commercial scale to yield ethylbenzene are: benzene alkylation with ethylene in liquid phase, in gaseous phase and separation from xylene cut.

Benzene alkylation process with ethylene in gaseous phase is less polluting than the liquid phase process being in addition less corrosive, making it possible to use nonalloyed carbon steel equipment.

Ethylbenzene separation from C_8-xylene cut showing minor environmental pollution risk cannot meet the increasing demand of ethylbenzene for styrene fabrication.

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Styrene

The styrene fabrication processes did not develop greatly in point of environmental protection as this process does not release major polluting substances.

The gaseous effluents obtained from ethylbenzene dehydrogenation contain: hydrocarbons 99% wt. and traces of nitrogen oxides and solid particles.

Waste water, about 7 t/t styrene contains: styrene 50 mg/l, ethylbenzene 30 mg/l, benzene 20 mg/l and traces of sulphur and catalysts decomposition products (Fe_2O_3, Cr_2O_3).

Phenol-acetone

The industrial processes used for phenol fabrication represent major pollution sources particularly due to the waste water with phenol content. Thus about 4 t/t phenol waste water is obtained with a phenol content of 1.5-3.5 g/l requiring phenol separation and biological treatment operations. the discharges of gas from the safety valves contain mainly C_2-C_4 hydrocarbons.

The specific problems raised by phenol separation and the biological treatment are widely dealt with in chapter 3.3.2.

Ethylene oxide

Ethylene oxide production by chlorhydrin process was abandoned among other reasons, due to the large amounts of waste water having a high content of salts, chlorinated organic compounds and unusable by-products.

The up-to-date processes of ethylene oxidation with air or oxygen over silver catalyst made their way due to the minimum amounts of gas and liquid effluents and the elimination of chlorine use in the process.

The gas effluents coming from ethylene oxidation processes with air or oxygen,contain: waste nitrogen, unreacted oxygen, hydrocarbons, nitrogen oxides, sulphur oxides.

The waste water resulting from the process does not raise special problems as far as the content of pollutants is concerned.

Dimethylterephthalate

The modern processes for the fabrication of dimethylterephthalate (terephthalic acid) starting from p-xylene have been applied on industrial scale for many years.

The gas effluents resulting by these processes contain: C_1-C_4 hydrocarbons 70% wt, carbon monoxide 28% wt. and nitrogen oxides, sulphur oxides and solid particles 2%.

Acid waste water is also obtained from oxidation, esterification and distillation: 1.25 t/t DMT containing 0.3% xylene, 3% acetic acid, 1% formic acid 0.2% formaldehyde and 3% methanol.

Waste water contaminated with petroleum products can also result 5 t/t DMT containig 1-2% xylene, esters and acetates.

Witten process for DMT production also yields liquid waste fuel, about 100 kg/t DMT which can be either burnt or used as ingredients for asphalt, bitumen, etc.

Maleic anhydride

The industrial process having the biggest share in the world production of maleic anhydride is the one starting from benzene although due to the lack felt on world scale in the aromatic hydrocarbons production, the process starting from C_4 cut acquires an increasing importance.

The process using benzene yields about 0.8 t/t MA waste water contaminated with maleic acid, fumaric acid at a concentration of approx. 4% wt.

The process using C_4 cut yields about 3 t/t AM waste water containing: maleic acid and fumaric acid 1.5 mg/l, acetic acid 50 mg/l and propionic acid 5 mg/l.

Phthalic anhydride

Phthalic anhydride processes greatly developed between 1896, when it was first produced and 1970 as a consequence of the increase of world consumption for chemical synthesis equipment.

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Air oxidation of o-xylene is the process which imposed to greatest extent leading to yields of 38% wt. phthalic anhydride compared to o-xylene injected in the reaction and a lower environmental pollution compared to the naphthalene oxidation processes.

The low air oxidation process leads to smaller amounts of gases containing volatile substances.

Acrylonitrile

Acrylonitrile imposed itself within the industrial production in 1940 in the United States by ethylene cyanohydrin process and almost simultaneously in Europe by BASF acetylene and cyanohydrin process.

After 1950 and then after 1970 the acrylonitrile production by amonoxidation of propylene (Sohio, B.P./Ugine and Montedison) developed and got priority within world production.

The gas effluent contains about 40% wt. light hydrocarbons, 50% wt. carbon oxide and 8-10% wt. nitrogen oxides.

The waste water resulting from the process contains cyan ions, reason for which its destruction can be achieved by their burning only, with fuel consumption from outside.

Significant amounts of hydrocyanic acid, acetonitrile and ammonium sulphate also result from the process. The catalysts improved after 1970 by Sohyo (phosphomolybdate/bismuth) lead to the production of lower amounts of acetonitrile and ammonium sulphate and to acrylonitrile yields of about 80%.

Acrylic acid

The process which is most widely used at present starts from propylene

The process yields off gases, about 0.7 t/t Ac.A. containing propane-propylene 2% wt. acrylic acid and acetic acid 0.2% wt, acetic aldehyde formic aldehyde, acrolein 0.3% wt, carbon monoxide and carbon dioxide 4%, oxygen 7%, water 2%, and the balance 84% nitrogen coming from the remanent air used for oxidation.

Waste water, about 1.2 t/t Ac.A. contains acrylic acid, acetic acid and maleic acid max. 1% wt. and aldehydes and acrolein 1% wt.

The process also yields liquid organic residue containing hydroquinone, polymers and acrylic acid.

Methyl methacrylate

The processes applied on commercial scale start from: acetone cyanohydrin (1930) isobutene (1960) and direct carboxylation of ethylene Dow-BASF - by Reppe synthesis (1970).

The process using acetone cyanohydrin is the most polluting one as it yields diluted waste acid, 3 t/t MM which does not easily find utilization as well as great amounts of ammonium sulphate which due to its contamination with organic substances, cannot be used as chemical fertilizer without purification.

The process using isobutene requires burning of off gases to remove cyanhydric acid and other organic substances.

Reppe synthesis using ethylene seems the most promising process in point of environmental protection but the process is not yet proved on industrial scale.

Acetylene

Acetylene fabrication process from carbide is the oldest one applied on commercial scale due to the case in procuring the raw material (coals and limestone) being a rather straight forward process yielding an acetylene with a concentration of 99.6% w It has nevertheless the disadvantage it cannot be used to get big amounts of acetylene while releasing large amounts of solid residues, 4.4 t/t A $Ca(OH)_2$.

The partial oxidation of methane especially applied afte 1960 leads to higher techno-economic indices as compared to the process using carbide. This process too pollutes the environment as it releases: off gases, high acetylenes and ammonia waste water contaminated with organic substances and carbon black.

The least polluting process seems to be acetylene production by electrocracking, which nevertheless due to some high energy consumptions, is not widespread.

Formaldehyde

The main processes applied on commercial scale for formaldehyde production make use of methane oxidation over silver or iron oxides catalysts.

The off gases obtained by both processes contain C_1-C_4 hydrocarbons and carbon monoxide. Quantitatively the gaseous effluent obtained by the process with iron oxide is about three times lower than that obtained by the process using silver catalyst (0.60 t/t formaldehyde sol. 37%).

No chemically contaminated waste water results by either process, except the emergency cases and after equipment cleaning.

Vinyl acetate

Vinyl acetate process from acetylene yields the following by-products:

- purged acetylene 3.2 t/t V.A. to be sent to acetylene unit for purification and then back to the process
- acetaldehyde and vinyl acetate: 0.01 t/t V.A. which goes to acetaldehyde recovery
- solid residues (ethylenediacetate): 0.015 t/t V.A. which goes to dump for future distruction
- alkaline water: 0.8 t/t V.A. which neutralizes with acid water 0.035 t/t V.A. resulted from the same process.

Vinyl chloride

Among the processes applied on industrial scale for vinyl chloride fabrication, ethylene oxichlorination process with oxygen has great advantages against other processes in point of environmental protection.

The volume of off gases is much lower than in the other processes while dichlorethane entrainment by off gases is correspondingly lower.

Nevertheless the process has the disadvantage of a high cost of incineration of chlorinated organic products from off gases.

Methyl chloride, chloroform, carbon tetrachloride, perchlorethylene

The chlorinated products belonging to this category are produced starting mainly from: methane, methanol, acetylene or ethylene.

Methyl chloride production starting from methanol represents a less polluting way than the processes starting from methane, avoiding the use of $NaOH/H_2SO_4$.

Chloroform production from methyl chloride yields the lowest amounts of waste products.

Carbon tetrachloride obtained by chlorination of higher hydrocarbons at high temperatures is a clean process and allows the use of other aliphatic chlorinated residues.

Perchlorethylene production by ethylene oxichlorination imposed due to ethylene availabilities, having at the same time a less polluting character as compared to the processes starting from acetylene.

Epichlorhydrin

Epichlorhydrin manufacturing from propylene leads to significant amounts of waste water, 70 cu.m/t EC contaminated with calcium chloride, calcium hydroxide, di-and tri-chlorhydrin as well as epichlorhydrin.

Solid residues also have a big share, i.e. chlorinated solid wastes - 0.12 t/t EC, tars 0.16 t/t EC and solid organic wastes 0.07 t/t EC which are usually distroyed by incineration with fuel consumption.

Toluenediisocyanate (TDI) and methylenediphenyldiisocyanate (MDI)

The most widely spread processes consist in the phosgenation of corresponding amines: toluene diamine and methylene diphenyl diamine being at the same time highly environmental polluting processes.

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The protection measures for the operation personnel, neighbouring polluted areas as well as emissaries whereto waste water discharges are very severe due to the fact that the substance handled are particularly toxic, i.e. : phosgene, hydrochloric acid and isocyanates themselves.

The gas discharges contain mainly carbon oxide 98% wt, sulphur oxides, hydrocarbons and solid particles.

The waste water contains: amines, isocyanates, ammonia, monochlorbenzene and polyisocyanates which cannot be purified by chemical methods, being necessary their incineration with fuel consumption.

Solid residues - polyisocyanates - also result from the process, and are distroyed by burning.

Isocyanates process from carbon monoxide without phosgene seems to be less polluting but it is not yet commercially applied.

Glycerin

Glycerin processes improved from fatts splitting to the synthesis processes using propylene via epichlorhydrin.

Glycerin fabrication from epichlorhydrin yields gaseous effluents formed particularly from C_1-C_4 hydrocarbons and waste water containing epichlorhydrin, glycerin, chlorinated products and hydrochloric acid.

2.3. Elastomers, polyolefines and copolymers processes

As in the preceding chapter, the object of this chapter is the evolution in time of the technological process for the manufacturing of elastomers, polymers and copolymers, evolution commented upon critically in point of the reason for switching from one process to the other and of environmental protection.

Then have been selected such processes which have a big share with regard to world production capacities and their future possibility to be kept in operation and their technological development.

Hereinunder is the list of the examined processes:

1. Low density polyethylene (LDPE)
2. High density polyethylene (HDPE)
3. Polypropylene (PP)
4. Polyvinyl chloride (PVC)
5. Polystyrene and acrylonitrile butadiene styrene copolymer (PS + ABS)
6. Styrene butadiene rubber (SBR)
7. Polyisoprene rubber (PIR)
8. Polybutadiene rubber (PBR)
9. Terpolymers - ethylene + propylene (EPR)
10. Thermoplastic rubber (TPR)
11. Butyl rubber (BR)
12. Polychloroprene rubber (PCR)
13. Nitrile rubber (NR)
14. Polyethers (PEt)
15. Polycarbonates (PC)

Following tables show the principal technological processes applied on industrial scale forthe production of the above said products, tables worked out on the basis of published literature data given under bibiliography chapter of this paper as well as on the basis of the data known by designing and operating similar plants.

LOW DENSITY POLYETHYLENE (LDPE) MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
A.	L.D.P.E. HOMOPOLYMER - HIGH PRESSURE REACTION (1000-3500 bar) - FREE RADICAL INITIATOR - AUTOCLAVE REACTOR				
1.	Imperial chemical industries limited	1939	Bulk polymerization of ethylene at high pressure of 1100-1500 bar and temperature of 160-270°C in presence of organic peroxides catalyst and propane or propylene as chain transfer agent,obtaining of 16-20% per pass	No waste water Small quantities of ethylene in atmosphere in emergency cases	Large range of polymers for usual fields of aplication Improvements of autoclave reactor type of catalysts
2.	C.D.F. Chemie	1954	Bulk polymerization of ethylene at high pressure of 1200-2000 bar and temperature of 150-300°C in presence of organic peroxides and propane or propylene as chain transfer agent, obtaining a conversion of 18-20% per pass	No waste water Small quantities of ethylene in atmosphere in emergency cases	Large range of polymers for usual fields of application. Improvements of autoclave reactor,type of catalysts.Flexibility in operation due to line capacity

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B.LD.P.E. HOMOPOLYMER - HIGH PRESSURE REACTION (1000-3500 bar) OXIGEN OR/AND FREE RADICAL INITIATOR - TUBULAR REACTOR

0	1	2	3	4	5
3.	ATO Chemie France	1960	Bulk polymerization of ethylene at high pressure of 2000-2500 bar and temp.of 200-300°C using oxygen as reaction initiator and propane or propylene as chain transfer agent obtaining a conversion of 21-23% per pass	No waste water. Very small quantities of ethylene in atmosphere in emergency cases	Lower maintenance and investment costs due to utilisation of the tubular reactor (Static type) and oxygen as initiator. Large line capacity
4.	ANIC - Italy	1964	Bulk polymerization of ethylene at high pressure of 2000-2450 bar and temp. of 250-320°C using oxygen and an organic peroxide as initiator and propane or propylene as chain transfer agent obtaining a conversion of 26% per pass	No waste water . Very small quantities of ethylene in emergency cases	Lower maintenance costs due to utilisation of the tubular reactor. High conversion by using of oxygen and organic peroxides

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0	1	2	3	4	5
5.	STAMICARBON Holland	1965	Bulk polymerisation of ethylene at high pressure of 2500-2700 bar and temp. of 240-310°C using organic peroxides catalysts and propane or propylene as chain transfer agent obtaining a conversion of 28-30% per pass	No waste water . Very small quantities of ethylene in emergency cases	High conversion by using of adequate type of peroxides. Lower maintenance costs due to utilization of the tubular reactor

LINEAR LOW DENSITY POLYETHYLENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
C.	LLDPE - ETHYLENE OLEFINE COPOLYMER - LOW PRESSURE 20-35 bar GAS PHASE, TRANSITION METAL CATALYST, FLUIDIZED BED REACTOR				
1.	Union Carbide UNIPOL	1972	Copolymerization of ethylene with butene 1 or hexene at pressure of 15-30 bar and temp. of 80-100°C in presence of a high efficiency catalyst (transition metal catalyst) in a fluidized bed reactor obtaining a conversion of ethylene of 2%	Absence of polluting effluents (air, water and solid wastes)	Lower investment and operating costs due to simplicity of the plant. Lower energetic consumptions. Polymers with improved mechanical properties which causes reduced consumption of polymer at Client

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0	1	2	3	4	5
		D. LLDPE - ETHYLENE OLEFINE COPOLYMER - LOW PRESSURE 20-35 bar GAS PHASE, TRANSITION METAL CATALYST, STIRRED BED REACTOR			
2.	AMOCO	1975	Copolymerization of ethylene and propylene or butene 1 using a diluant butane or izopentan at low pressure in presence of a superactive catalyst in a stirred bed reactor	No waste water. Small quantities of ethylene in emergency cases	Lower investment costs.
		E. LLDE ETHYLENE - OLEFINE COPOLYMER - LOW PRESSURE (28-32 bar) LIQUID PHASE SLURRY PROCESS, TRANSITION METAL CATALYST			
3.	Phillips Petroleum	1972	Copolymerizaton of ethylene with butene 1 and hexene at pressure of 30-40 bar and temperature of 70-80°C in presence of high activity catalysts in a loop reactor	Small quantities water with solvents	Very high heat transfer due to reactor type, high yield of catalysts. Low investment costs. Due to large range of polymers this process held 50% of LLDPE polyethylne from USA

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0	1	2	3	4	5
		F. LLDPE - ETHYLENE - OLEFINE COPOLYMER, LOW PRESSURE (28-42 bar) LIQUID PHASE SOLUTION PROCESS, TRANSITION METAL CATALYST			
4.	Du Pont	1974	Copolymerization of ethylene with butene 2 at pressure of 28-42 bar and temp. of 80-120°C in presence of high activity catalysts. Process involve deashing of catalysts	Waste water with solvents and aluminium compounds	Lower investment costs
		G. LLDPE - ETHYLENE - BUTENE 1 COPOLYMER, HIGH PRESSURE 800-1400 bar TRANSITION CATALYST, RETROFITTING OF TUBULAR REACTOR PLANT			
5.	ENICHEM Italy		Retrofitting of a standard tubular reactor plant by using the following process: copolymerization of ethylene with butene 1 (or hexene 1) in presence of high efficiency Ziegler Nata catalysts (instead of oxygen and organic peroxides) at pressure of 800-1200 bar and temp. of 170-280°C	No waste water. Small quantity of ethylene in emergency cases	High quality polymers with improved mechanical properties. Lower operating costs.

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H. LLDPE - ETHYLENE - BUTENE 1 COPOLYMER, HIGH PRESSURE 800-1400 bar TRANSITION METAL CATALYST, RETROFITTING OF AUTOCLAVE PLANT

0	1	2	3	4	5
6.	SOFRAPO-ENIMONT (CDF CHEMIE)		Retrofitting of a standard autoclave reactor plant by using the following process: Copolymerization of ethylene with butene 1 (or hexene 1, octene) in presence of high efficiency Ziegler Natta catalysts (instead of organic peroxides) at pressure of 800-1000 bar and temperature of 200-300°C	No waste water. Small quantity of ethylene in emergency cases	High quantity polymer with improved mechanical properties Lower operating costs

HIGH DENSITY POLYETHYLENE (HDPE) MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
			A. SUSPENSION POLYMERIZATION WITH CLASSICAL CATALYST OF ZIEGLER NATTA TYPE LOW PRESSURE		
1.	Mitsui Petrochemical JAPAN	1962	Polymerization of ethylene in presence of a catalyst complex at pressure of 6-10 bar and temp. of 80°C achieving . Process needs deashing	Waste water with solvents and aluminium compounds Solid wastes (at active polymer)	
			B. SUSPENSION POLYMERIZATION WITH HIGH EFFICIENCY ZIEGLER NATTA CATALYST TYPE LOW PRESSURE		
2.	Phillips Petroleum	1965	Polymerization of ethylene in presence of high efficiency catalyst at pressure of 7-35 bar and temp. of 70-110°C, achieving conversions of 20-25%.	Small quantity of waste water	High efficiency catalyst. No deashing Lower investment costs

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0	1	2	3	4	5
		c. SOLUTION POLYMERIZATION WITH HIGH EFFICIENCY ZIEGLER NATTA CATALYST TYPE LOW PRESSURE			
3.	Du Pont - USA	1962	Polymerization of ethylene in presence of high efficiency catalyst at high temp. of 150-200°C and at pressure of 30-50 bar, achieving a high conversion of 95%	Small quantity of waste water	No catalyst preparation section, due to solubility in solvent. Small reactors and low residance time
		D. LOW PRESSURE GAS PHASE - FLUIDIZED BED WITH HIGH EFFICIENCY ZIEGLER CATALYST TYPE LOW PRESSURE			
4.	Union Carbide U.S.A.	1968	Copolymerization of ethylene with butene 1 or hexene, octene at pressure of 15-30 bar and temp. of 80-100°C in presence of high efficiency catalyst in a fluidized bed reactor obtaining a conversion of ethylene 2%	Absence of polluting effluents (air, water and solid wastes)	Lower investment costs due to simplicity of plant. Lower energetic consumptions. Polymer with improved mechanical properties which causes reduced consumption of polymer at client

POLYPROPYLENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	El Paso Chemical Co.	1972	Polymerization of propylene in presence of high efficiency Ziegler Natta supported catalysts at 130-180°F and 28-42 bar in an agitated reactor. Ethylene-propylene random copolymers are also produced	Small quantities of waste water. Small quantity of purge gas	Reducing production cost due to the elimination of the deashing step, increase in monomer yield, higher onstream factor increase in production rates and lower maintenance costs. Steam usage is reduced by 89% and electricity by 12% when compared with conventional liquid pool process Removal of catalyst residue and atactic polymer (deashing is no longer necessary). Polymer yield 5000-7000 kg/kg of solid catalyst

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0	1	2	3	4	5
2.	Mitsui Petrochemical Industries - MONTEDISON SpA	1970	Polymerization of propylene and/or copolymerization with ethylene using high yield-high stereospecificity catalyst (HY-HS Catalyst) in a hydrocarbon solvent at temp. in range of 60 to 80°C and pressures of 5 to 15 bars in stirred reactor yield of at least 1000 kg polymer/g tc an isotactic index of 98-99	Chemically contaminated water: solvent,oil and catalyst	Elimination of deashing and simplified solvent recovery makes it possible to save approx. 20% of plant investment cost. Considerable savings in operation costs obtained due to reducing of: monomer consumption costs for catalyst removal and effluent treatment costs for solvent recovery and atactic removal section,labor costs and maintenance costs
3.	MONTEDISON SpA		Spheripol process enables production of propylene homopolymers and copolymers by high yield-high stereospecificity - spherical form catalyst at 60-80°C and 30-40 bar in a tubular loop reactor	Chemically contaminated water	Investments costs for a plant based on Spheripol process are 40% of those required for conventional low yield,slurry process due to elimination of catalyst separation,monomer recovery and purification atactic polymer separation,pellotization.

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0	1	2	3	4	5
			All grades of homopolymers black and random copolymers with top level quality can be produced. Polymer yields of 20.000 kg/kg of supported catalyst, and new catalyst has in isotactic index of 96-99%		Considerable savings in operating costs are obtained (monomer,electric power, steam, labor and maintenance costs)

PROPYLENE - OLEFINE COPOLYMER - LOW PRESSURE - GAS PHASE - TRANSITION METAL CATALYST FLUIDIZED BED RACTOR

0	1	2	3	4	5
4.	Union Carbide		Copolymerization of propylene with elefine at pressure of 28-35 bar in presence of high efficiency catalysts in a fluidized bed reactor	Absence of polluting effluents (air, water and solid wastes)	Lower investment and operating costs due to simplicity of the plant. Lower energetic consumptions . Large range of polymers: homopolymer,random and impact copolymer

POLYSTYRENE MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Suspension polymerization of styrene	1930 I.G. Farben-industrie Germany (BASF at present)	Styrene polymerization in suspension medium, water in the presence of benzoyl peroxide initiator in autoclave type reactors with agitation, batchwise system	- 3.33 t/t ps chemically contaminated water, containing: polymers 0.1% g oligomers 50 ppm $CaCl_2$, NaOH, HCl, pH=4 - 0.02 t/t ps solid wastes as crust	Thermoplastic substance with various applications in industry, house building, household object ARCO, BASF, Petrocarbon
2.	Styrene block polymerization	After 1960	Block polymerization of styrene in tubular reactors with full displacement or in autoclave type reactors with agitation	1 t/t ps organically contaminated water 0.01 t/t ps solid wastes	Polymerization is conducted continuously, lower plant complexity. Lower specific investments and high quality polystyrene as compared to suspension process. MITSUI Toatsu, Cosden Badger, Gulf Oil Chemicals Process

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0	1	2	3	4	5
3.	Mass-press polymerization of styrene	After 1965	The mass-press polymerization process is a batch process. Styrene prepolymerization is performed in agitation reactors up to conversion of 30% of styrene. Polymerization is accomplished in plate frame press reactor in the presence of chain modifying catalysts	1.5 t/t ps organically contaminated water 0.01 t/t ps solid wastes	As the process is batchwise it also has the disadvantages specific to the system. Unsophisticated plant with lower specific consumptions of raw materials and utilities.
4.	Emulsion polymerization of styrene	1970	In the firest step, by mixing butadiene, catalyst and an emulsifier a hot polybutadiene rubber is obtained. This feed mixture is introduced into the grafting reactor at 65°C to meet styrene monomer acrylonitrile, catalyst and emulsifier in addition	5 t/t ABS chemically contamined water containing: 0.1% wt polymer 50 ppm oligomers, traces of acrylonitrile pH = 9 0.02 t/t solid wastes as crust	Emulsion polymerization as a method for industrial processes was adopted only for some special purpose. It used to produce latexes for paints and other surface coatings and ABS copolymers

0	1	2	3	4	5
5.	Solution polymerization of styrene	1975	Styrene is fed continuously into the three stage stirred polymerization train, where approx. 90% conversion is attained	Organically contaminated water	The solution polymerization process in commercial production of polystyrene ramains to be the least popular manufacturing process

STYRENE-BUTADIENE RUBBER (SBR) MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Cold emulsion polymerization by free radicals	1930 - 1940	Butadiene and styrene copolymerization in agitation reactors at 5°C and 1-4 atm to maintain butadiene inliquid state. Emulsifiable phase consisting of water, fatty acids and other surface agents	Waste water 10 t/t_{SBR} containing: styrene 300 mg/l, colophony soap, 800 mg/l, chlorides 800 mg/l, rubber particles 20 mg/l and pH = 6.5 - 8	90% of SBR rubber production is obtained by cold emulsion copolymerization
2.	Ionic solution polymerization	1960 - 1965	Butadiene and styrene copolymerization occurs in hydrocarbons solution in the presence of polymerization promotors based on lithium	Waste water contaminated with solvents, hydrocarbons and rubber particles	10% of world production of SBR is obtained by solution polymerization. More flexible process yielding in the same plant polybutadiene rubber No waste water with hydrocarbons is released

POLYISOPRENE RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Solution polymerization with Ziegler Titan Aluminium catalyst	1963	Isoprene polymerization at 50°C, 1 bar, in hexane solvent, in agitation autoclave	10 m^3/t methanol water having the following content: - methanol 500 mg/l - isopantane 150 mg/l - NaCl 1500 mg/l 30 kg/t p.i. liquid fuel residues	80% conversion per pass, polymerization time: 2 h Reaction heat is discharged through reactor shell and by heat exchange with monomer and solvent mixture. Goodyear,Godrich and Snam Progetti
2.	Solution polymerization with Butyl-lithium catalysts	1965	Isoprene polymerization at 55°C, 1.5 bars in isopentane so solvent,in polymerization autoclaves with agitation	8 m^3/t p.i. hydrocarbons and methanol contaminated water 20 kg/t p.i. liquid fuel residues	75% conversion per pass, polymerization time 2 h. Reaction heat is discharged by evaporation of part of isopentane solvent.Shell

POLYBUTADIENE RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Solution polymerization with Ziegler cobalt catalyst	1960	Butadiene polymerization with agitation reactors at +5°C, 0.3 bars and in solvent (benzene)	20 m^3/t p.b. chemically contaminated water containing: - hydrocarbons 100 mg/l - methylcellulose 150 mg/l - antioxidant 300 mg/l 80 kg/t pb.liquid fuel	80% conversion per pass and polymerization time 5 h. High consumption of catalyst and chemicals Shell,Goodrich Gulf, Huls, Montecatini
2.	Solution polymerization with Ziegler catalyst	1961-65	Butadiene polymerization takes place in agitation reactors at 0°C, pressure of 3.5 bars in toluene solvent	22 m^3/t pb. chemically contaminated water 70 kg/t pb. liquid fuel	Total polymeirzation time: lower by 2 h. Lower cnsumptions of catalyst, chemicals and solvent. Philips, Bayer, Goodyear, Esso, Goodrich Gulf and Polimer Corp.

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0	1	2	3	4	5
3.	Solution polymerization with nickel catalyst	1961 1965	Butadiene polymerization at temperatures higher than 40°C and pressures of 3.5 bars in toluene solvent	20 m^3/t p.h. chemically contaminated water 60 kg/t p.b. liquid fuel	High conversion: 87% per pass and low polymerization time 2 h Bridgestone Tire Co. and Japan Synthetic Rubber Co. from Japan
4.	Solution polymerization with butyl-lithium catalysts	1961 1965	Butadiene polymerizattion occurs at temperatures higher than 50°C pressures of 3.5 bars, hexane solvent	15 m^3/t pb. chemically contaminated water 50 kg/t pb. liquid fuel	High conversion: 97% per pass for a polymerization time of 4 h. Firestone Tire Rubber Co.

ETHYLENE-PROPYLENE RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Solution polymerization process	1961-1962	Ethylene and propylene copolymerization takes place in liquid phase at +40°C and 15 bars in the presence of $VOCl_3$, $(C_2H_5)Al_2Cl_3$ catalysts in hexane solvent	6 t/t ep. chemically contaminated water containing 0.5-1% solvent 1 t/t ep. recoverable fuel gases	Conversion per pass is 50% for ethylene and 10% for propylene and 80% for diene (for terpolymer E.P.D.M.) Esso Research and Exxon Engineering Co
2.	Suspension polymerization process	1963	Ethylene and propylene copolymerization takes place in suspension fluid containing liquid propylene in the presence of catalysts based on vanadium and aluminium alkyl and in toluene solvent	5 t/t ep. chemically contaminated water containing solvent 1 t/t ep. recoverable fuel gases	Increase of concentration of solid particles of polymer from 10% (by solution process) to 30% (by suspension process) thus an efficient use of specific reaction volume

THERMOPLASTIC RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Styrene-butadiene styrene copolymers, or styrene isoprene-styrene copolymers	1965	Anionic polymerization in homogeneous phase initiated with lithium based catalyst at reaction temperatures between 60-80°C and residance time in polymerization autoclaves of 1-2 h	20 cu.m/t organically contaminated water from solvent separation having the following content: - methylcellulose 230 mg/l - topanol 500 mg/l - rubber particles 500 mg/l - 2-4% off spec. product	Specific properties due to the simultaneous presence of rigid (resulted from styrene) and elastic (coming from butadiene or isoprene) substances
2.	Thermoplastic copolymers based on polyurethanes	1970	Thermoplastic elastomers consisting of a rigid block made up of an isocyanate (1.4-butane diol and MDI-methylendiphenyl diisocyanate) and an elastic block consisting of a polyester or polyether polyol	- 10 cu.m/t organically contaminated water - 2% off spec. product	High strength due to hydrogen bonds coming from the functional groups of methanes

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0	1	2	3	4	5
3.	Esters-ethers copolymers (Hytrel)	1972	Produced from terephthalic polytetramethylene acid, ether glycol and 1.4 butane diol	Organically contaminated water	Polymer is made up of rigid crystalline structures (sequents) and of elastic amorphous sequents. Du Pont de Nemours

BUTYL RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
1.	Solution polymerization	1942	Isoprene and isobutene copolymerization at low temperature -100°C in the presence of Cl_3Al as catalyst in polymerization reactors with agitation	Waste water with organic hydrochloric acid, aluminium chloride contamination	The polymer contains 97-98.5% isobutene and 3-1.5% isoprene. Low isoprene content makes isoprene virtually saturated and less sensitive to external factors such as: heat, light, oxygen, ozone and aggressive substances (acids, alkali, solvents) Esso Standard Oil (Exxon)

POLYCHLOROPRENE RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Chloroprene process obtained from acetylene	1932	Acetylene dimerization over CuCl catalyst at 25-80°C and 5 bars yielding monovinyl acetylene. Monovinyl acetylene conversion to chloroprene by HCl addition in the presence of CuCl	Waste water contaminated with organic substances, copper compound HCl	Availability of raw materials acetylene and the need for chloroprene rubber due to its high resistance at the activation of ozone,oxygen, oils. DuPont de Nemours
2.	Chloroprene based process starting from butadiene	1960	Butadiene chlorination in vapour phase at 330°C yielding dichlorbutene; isomerization of dichlorbutenes and dehydrochlorination of dichlor 3,4 butene-1 at 100°C in alkaline medium	Waste water contaminated with organic substances,chlorinated compounds	With the development of petrochemistry,chloroprene process starting from butadiene developed due to certain advantages of technical and economic order. British Petroleum Distillers

0	1	2	3	4	5
3.	Chloroprene polymerization	1932 1960	Emulsion polymerization of chloroprene at 40°C, atmospheric pressure in the presence of potassium persulphate in polymerization reactors with agitation	Organically contaminated waste water	Specific applications for machine industry, adhesives, cables coatings, electrical threads

NITRILE RUBBER MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Hot emulsion polymerization	1940	Butadiene copolymerization with acrylonitrile (abt. 32% wt) in polymerization reactors with agitation of temperatures between 20-$30^{\circ}C$ and reaction time ranging between 10-24 h	Waste water 8 t/t_{NR} containing traces of acrylonitrile, butadiene,emulsifier, chlorides	Excellent resistance to activation of oils,fats various chemical agents. Application: machine building industry,aeronautics,textile industry etc. Perbunan-Buna N.
2.	Cold emulsion polymerization	1975	Butadiene copolymerization with acrylonitrile in agitation reactors at about 10-$20^{\circ}C$	Waste water 6 t/t_{NR} with traces of butadiene,crylonitrile, chlorides	Lower consumptions of raw materials,chemicals, energy. Polysar,Goodrich,Goodyear, Uniroyal, Bayer

POLYETHERS MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Propyleneoxide and ethyleneoxide polyaddition in the presence of a chain initiator of polyol type and a basic catalyst	1960	The process consists of the following main phases: - potassium glycerolate synthesis - prepolyethers synthesis - intermediates polyethers synthesis - oxethylated oplyether synthesis - polyether neutralization - polyether anhydrizing - polyether filtering - polyether stabilizing and storing	Waste water 1.07 t/t water with about 10% propyleneoxides, 0.14% t/t water with about 5% ethyleneoxide By-product: cake from filtering with about 27% polyether, 0.12 t/t	The process is performed at low temperatures and pressure

POLYCARBONATES MANUFACTURING

Ref. no. 0	Process 1	Period introduced 2	Principal characteristics 3	Environmental aspects 4	Reason for adoption 5
1.	Melt transesterification and polycondensation	1950	Noncatalytic reaction between sodium phenolate and phosgene at 20°C and atmospheric pressure yielding diphenyl carbonate. Transesterification of biphenol A with diphenylcarbonate at temperatures between 180-305°C, under vacuum (between 40-0.5 mm Hg remanent pressure)	Organically contaminated waste water 0.04 t/t pc containing 1500 ppm phenol 50 g/l .Anorganically contaminated waste water 0.02 t/t pc containing ClNa, Na_2CO_3. Low amounts of degraded polymers. Off gases with phosgene traces.	Special polymer applications in electrotechnic aeronautical industry
2.	Interfacial polycondensation	Introduced in 1956 by Buyer and General Electric	In aqueous solution of Na bisphenolate phosgene is bubbled yielding polycarbonate to be dissolved in methyl chloride present in the system	Waste water contaminated with organic and inorganic substances	High electrotechnical characteristics

Based on the data given in above tables hereinunder is given an examination of more significant progresses recorded in the evolution of the technological processes in the field of elastomers and plastics synthesis correlated with the reduction in the environmental pollution.

Low Density Polyethylene (L.D.P.E.)

Low density polyethylene (high pressure) manufacturing with autoclave type reactor or tubular reactor represents non-aggressive processes which do not pollute the environment.

Gaseous effluent is especially made of purge ethylene which goes back to pyrolysis unit for purification.

The process also yields low amounts of waste water containing biodegradable organic substances.

High Density Polyethylene (H.D.P.E.)

The high density polyethyelne processes with autoclave type reactors in solvent slurry or solution as well as those in gaseous phase are not aggressive for the environment. The gaseous effluent is mostly made of ethylene and solvent vapours, effluent sent to ethylene recovery.

Small amounts of waste water contaminated with biodegradable organic substances result from the process.

Polypropylene (PP)

Polypropylene fabrication with Ziegler Natta catalyst leads to the production of gaseous effuents containing particularly light hydrocarbons, hexane and methanol vapours. The waste water resulting in the process contain aluminium and titanium hydroxides oil and solid suspensions.

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The atactic polymer, about 8% of the polypropylene production is not a ballast as it has multiple applications.

Propylene polymerization processes with superreactive catalysts do not yield significant amounts of attactic polymer.

Polyvinyl Chloride (PVC)

Polyvinyl chloride manufacturing is harmful to human body as it was proved in 1965 - the linking of acroosteolysis and 1974 liver angio sarcoma with VCM. For this reason the removal of unreacted monomer from polymer is thoroughly studied by researchmen in the field of improving polyvinyl chloride manufacturing process. The international norms provide vinyl chloride removal from the polymer in proportion of 99.8 % wt.

In the enclosed working areas belonging to polyvinyl chloride fabrication unit, vinyl chloride concentration is limited to max. 1 ppm.

Polystyrene and acrylo-nitrile Butadiene Styrene Copolymers (PS + ABS)

Suspension polystyrene fabrication processes lead to the discharge of some gaseous effluents especially containing hydrocarbons and solid particles of polymers and waste water, 3.33 t/t_{PS} contaminated with: polymers 0.1% wt, oligomers 50 ppm and $CaCl_2$, NaOH, HCl with pH = 4.

Block styrene polymerization processes are less polluting leading to the discharge of only 1 t/t_{PS} waste water contaminated with organic substances.

Acrylo-nitrile butadiene styrene (ABS) process in emulsion also yields significant amounts of waste water, 5 t/t_{ABS} contaminated with polymers, oligomers and traces of acrylonitrile.

Butadiene Styrene Rubber (SBR)

Emulsion polymerization of butadiene with styrene or with alphamethylstyrene yields waste water from the process and from equipment washing containing: styrene max. 300 mg/l, chlorides 800 mg/l, colophony soap 800 mg/l and rubber particles 20 mg/l.

The continuous discharges to atmosphere through the safety valves system contain hydrocarbons, sulphur oxides and solid particles.

Polyisoprene Rubber (P.I.R.)

Solution isoprene polymerization with butyl-lithium catalysts leads to the release of somehow smaller amounts of waste water (8 cu.m/t p.i) compared to the solution polymerization process over Ziegler catalyst: titanium - aluminium (10 m^3/t pi).

Waste water contains methanol, solvent, hydrocarbons, metal salts.

Polybutadiene Rubber (P.B.R.)

Solution polymerization process of butadiene over cobalt or titanium catalyst leads to the discharge of gaseous effluents and waste water almost equal in point of quantity and quality. The resulted waste water, about 20-22 m^3/t_{PB} is contaminated with hydrocarbons, methylcellulose, antioxidant and rubber particles.

Ethylene-Propylene Rubber (E.P.R.)

From the point of view of the steps taken for environmental protection, the two processes applied on commercial scale for the fabrication of ethylene-propylene and amine rubber in suspension and solution are rather similar.

About 5-6 m^3/t_{EPR} waste water results from the process contaminated with hydrochartons and solvent.

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Thermoplastic Rubber (T.P.R.)

The process for the manufacturing of thermoplastic rubbers meant for certain applications started being run after 1970 based on polyurethanes and esters-ethers, being less polluting compared to the classical, styrene-butadiene-styrene process.

Butyl, Nitryl and Chloroprene Rubber

The environmental pollution problems raised by butyl rubber manufacturing are minor while the problems raised by nitryl rubber process are similar to those caused by butadiene styrene process. As a matter of fact, nitryl rubber can be obtained in consecutive runs in SBR plants with little changes.

Chloroprene rubber process is nevertheless more aggressive due to the presence of chlorine and organic compounds with chlorine.

Polyethers

Polyethers fabrication process by polyaddition of propylene-oxide and ethylene oxide yields waste water, about 1 t/t_{PET}, contaminated with basic reagents.

Polycarbonates

The waste water resulting from the process is contaminated with: phenol 1500 ppm, sodium chloride 50 g/l Na_2CO_3, 150 mg/l being biologically treated.

2.4. Chemical Fibres Processes

The analysis of the evolution in time of the main processes for the manufacturing of chemical fibres as well as their impact over the environment covers the following products:

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1. Adipic acid
2. Caprolactum
3. Polyamide
4. Acryl fibres
5. Polyester fibres
6. Nylon 66 - polyhexamethylendiamine adipate)
7. Nylon 6 - polymerised caprolactum

Following tables present the evolution of synthetic fibres manufacturing processes as well as their influence on the environment .

ADIPIC ACID MANUFACTURING

Ref. no. 0	Process 1	Period introduced 2	Principal characteristics 3	Environmental aspects 4	Reason for adoption 5
1.	Catalytic oxidation with nitric acid	1945 - 1950	Continuous process with high degree of automation. Minimum economically convenient capacity of 1 line: 4,000 t/y Competitive specific consumptions of raw materials and utilities. High grade end products	a) Reaction gas with nitrogen oxides 400 kg/t b) Chemically contaminated water with acid nature: 2 t/t	Favourable techno-economic indices. It provides 80% of world output
2.	Catalytic air oxidation in two stages	1945 - 1950	Continuous process with high automation degree. Minimum economically convenient capacity of one line 5000 t/y	a) Reaction gas b) Chemically contaminated water Lower pollution level than the one achieved by oxidation process with nitric acid	Techno-economic indices lower than those achieved by the oxidation process with nitric acid

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0	1	2	3	4	5
3.	Air-nitric acid catalytic oxidation in two stages	1945-1950	Continuous process with high automation degree. Minimum economically convenient capacity of one line 5000 t/y	a) Reaction gas b) Chemically contaminated water Lower pollution level than the one achieved by oxidation process with nitric acid	Techno-economic indices lower than those achieved by the oxidation process with nitric acid
4.	Butadiene chlorination and hydrocyanic acid addition to the intermediary product	1980 1982	Continuous process with high automation degree. Minimum economically convenient capacity of one line 5000 t/y. Lower costs of raw materials, utilities,specific consumption. The process is under improvement applied under licence. High grade end product	a) Reaction gas: polluting b) Chemically contaminated water	Highly profitable process

CAPROLACTAM MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
A.	Process with hydroxylamine		Caprolactam synthesis by classical processes is achieved by cyclohexanone oxidation with hydroxylamine salts, the two basic intermediates being obtained by the following processes: - cyclohexanone - from benzene - from phenol - hydroxylamine - Raschig - catalytic - phosphate		
1.	Cyclohexanone from benzene	1960	Catalytic hydrogenation of benzene into cyclohexanone, catalytic oxidation with air into cyclohexanol and cyclohexanone, catalytic separation, dehydrogenation of cyclohexanol to cycloheanone, purification	Saponificated oxidation tars 0.1 t/t product	Cheap and easy to procure raw materials

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0	1	2	3	4	5
2.	Cyclohexanone from phenol by selective hydrogenation	1970	Direct catalytical hydrogenation of phenol to cyclohexanone	Waste water, small quantities of residues	Safety operation - high quality of caprolactam - lower energy consumptions
3.	Hydroxylamine Raschig	1940	Nitrogen oxide absorption in ammonium carbonate solution with formation of ammonium nitrate where SO_2 gases are absorbed with formation of hydroxylamine disulphonate which by hydrolysis goes to hydroxylamine sulphate. Acid solutions are neutralized with ammonia yielding ammonium sulphate recovered by evaporation crystallization	- gases with SO_2 0.005 t/tp - gases with NO 0.003 t/tp - ammonium sulphate 4.5-5.2 t/t product	- Unsophisticated process without special technical conditions - Ammonium sulphate is used as fertilizer for certain agricultural soils The process is used to obtain about 40% of world caprolactam production

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0	1	2	3	4	5
4.	Catalytic hydroxylamine	1965	Catalytic hydrogenation of nitrogen oxide in heterogeneous system by means of platinum catalyst suspension over graphite carrier in sulphuric acid. It results hydroxylamine sulphate with 0.5 mol.H_2SO_4 thus reducing the quantity of ammonium sulphate from oximation stage	Ammonium sulphate 2.3 - 2.9 t/t contaminated water with hydrocarbons	- Reduced environmental pollution - Reduced amount of ammonium sulphate, by-product - Low energy costs The process is applied to obtain 25-30% from world output
5.	Hydroxylamine by phosphate-oxime	1975	Catalytic hydrogenation with paladium catalyst in suspension of nitrated ion in phosphoric acid ammonium acid phosphate medium with formation of hydroxylamine phosphate used at oximation without formation of ammonium sulphate	Ammonium sulphate 1.8 - 2.1 t/t contaminated waste water	Low amount of secondary ammonium sulphate - low corrosion and pollution The process is used to obtain 15% of world output

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0	1	2	3	4	5
I.	Process without hydroxylamine				
1.	Photochemical chlornitrization of cyclohexane	1960	Cyclohexane chloronitrization with nitrosyl in the presence of U.V. radiations yielding directly cyclohexynone chlorhydrate followed by Beckman transposition	- ammonium sulphate 1.8-2.1 t/t - chlorcyclohexyl 0.065 t/t - ammonium sulphate 1.8-2.1 t/t - tetrahydrobenzene 1 t/t	The process is used only for 4% of world capacity (Japan,SU) characterized by a high corrosion degree and high energy costs
2.	Toluene based process (SNIA-Italy)	1975	Toluene oxidation to benzoic acid,hydrogenation to cyclohexanecarbonyl acid which decomposed in the presence of nitrosyl sulphonic acid directly to caprolactam and O_2. By extraction with an alkylphenol no ammonium sulphate is formed		High corrosion High energy consumption.8% of world production is achieved by this process. Complex process with high corrosion degree

ACRYLIC FIBRES MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Suspension polymerization, wet spinning	1960	a) comonomers - acrylonitrile - ∿ methyl styrene - vinyl acetate b) solvent - ethylene carbonate c) main phases - suspension polymerization in redox system at 60°C - polymer filtering and drying - solving in ethylene carbonate - wet spinning	Liquid: - chemically contaminated water Q = 25 cu.m/t.p. pH = 4-5 - ACN = max. 150 mg/l - PACN = max. 100 mg/l Salts = max. 100 mg/l (Na_2SO_4, NaCl, CH_3COONa) Gas: Wet air, t = 60-65°C Q = 45 thou.mm/t.p. with max. 30 mg/cu.m	- Low environmental pollution - Nontoxic, non flammable, non-corrosive solvent

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0	1	2	3	4	5
2.	Suspension polymerization, wet spinning		a) comonomers - acrylonitrile with sodium allyl sulphonate or itaconic acid or methyl acrylate or methylvinyl pyridine b) solvent - dimethylformamide, or - dimethylacetamide, or - nitric acid 70%, or - sodium rhodonate c) main phases - suspension polymerization - polymer filtering, drying - polymer solving - wet spinning	a) Liquid Chemically contaminated water, acid water with ACN , PACN, salts b) Gas Vapour release of toxic and flammable solvent (dimethyl formamide,dimethylacetamide)	- spinning solutions with higher polymer concentrations lead to low recovering cost - some better fibres grades

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0	1	2	3	4	5
3.	Solution polymerization and dry spinning		a) comonomers - acrylonitrile - sodium vinyl sulphonate b) solvent dimethylformamide c) main phases - solution polymerization - spinning solution purification - dry spinning	a) Liquid: unsignificant b) Gas: vapours release of toxic and flammable solvent (dimethylformamide)	- shorter process flow (without filtering,drying solving) - lower energy consumptions

POLYESTER FIBRES AND YARNS MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Continuous process by polyethyleneterephthalate (Torray-Japan)	about 1970	DMT and ethyleneglycol are continuously proportioned at reaction temperature of 180°C in transesterification reactor whereto a catalyst is added: cobalt acetate, calcium acetate. Polymerization is performed in the presence of Sb_2O_3 and trimethylphosphate catalyst	Water with 0.5-1% methanol 0.1 t/t PE fibres Liquid fuel residue 0.05 t/t PE fibres	Capital cost lower by 50% as compared to the batchwise process
2.	Continuous process from terephthaltic acid (Dupont USA)	1972	Instead of DMT, terephthalic acid is used under similar conditions of reaction and catalyst	Water with 0.5% ethylene oxide: 0.2 t/t PE fibres. No methanol water results	Electric energy consumption is reduced by about 15% and by 20% the investment capital as compared to the DMT via process
3.	Melt spine process (Chemtex USA)	1973	Direct melt-spine at 290°C and drawing speed 250 m/sec.	Fibres wastes 0.150 t/t PE fibres	The energy consumption is reduced

(POLYHEXAMETHYLENEDIAMINE ADIPTATE) NYLON 66-$NH(CH_2)_6NH \cdot CO(CH_2)_4CONH(CH_2)_6NH$-
MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Envrionemntal aspects	Reason for adoption
0	1	2	3	4	5
1.	From phenol via adipic acid	1930's U.S.A.	Phenol is hydrogenated to cyclohexanol and by nitric acid oxidation to adipic acid. Half this acid is ammoniated to adipamide and reduced to hexamethylene diamen. Mixing produces nylon salt and the polymer is produced by heating the salt in autoclaves	Nitrous fumes evolved during nitric acid oxidation	Market demande
2.	From cyclohexane via adipic acid	1950's	Air oxidation gives a mixture of cyclohexanol and - one. This is oxidised to adipic acid as in process 1	Nitrous fumes evolved during oxidation. Avoids use of toxic feedstock phenol. However more flammable	Availability of petrochemical cyclohexane
3.	HMD from butadiene	1950's	The HMD half of the nylon is produced by reaction of HCN with butadiene to adiponitrile and hydrogenation of this to HMD	Large amounts of toxic liquid and solid wastes produced	Plentiful supply of butadiene available

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0	1	2	3	4	5
4.	HMD from acrylonitrile	1970	Adiponitrile is formed by electrolytic dimerisation of acrylonitrile and is then hydrogenated to HMD	Usable nitriles and unusable heavy ends produced	Availability of acrylonitrile Relatively clean process

(POLYMERISED CAPROLACTAM) NYLON 6 - $NH(CH_2)_5CO \cdot NH(CH_2)_5CO$ - MANUFACTURING

Ref. no. 0	Process 1	Period introduced 2	Principal characteristics 3	Envrionmental aspects 4	Reason for adoption 5
1.	Phenol process	1940's Germany	Caprolactam is traditionally made via Leckmann rearrangement of cyclohexanone oxime and is then polymerised in autoclaves at 200°C. Starting from phenol, hydrogenation and oxidation gives cyclohexanone which is reacted with hydroxylamine in situ to give the oxime	Large amount of by-product ammonium sulphate	Feedstock availability Market demands
2.	Cyclohexane process	1950's U.S.A.	The same as above except that the cyclohexanone is obtained by oxidation of cyclohexane	Large amount of by-product ammonium sulphate	Feestock availability
3.	Nitration process	1960's	Cyclohexane nitrated to nitrocyclohexane and this reduced to cyclohexanone oxime	Much reduced ammonium sulphate by-product involved	Environment reason

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0	1	2	3	4	5
4.	Photo	1960's Japan	Action of chlorine, nitric oxide and light produces cyclohexanone oxime directly	Much reduced ammonium sulphate by-product involved	Low cost route "cleaner route" assuming $(NH_4)_2SO_4$ recovery not economic
5.	Benzoic acid process	1970 Italy	Benzoic acid is hydrogenated to cyclohexane carboxylic acid which is converted directly to caprolactam by nitrosyl sulphuric acid	No ammonium sulphate by-product. Oleum required to absorb nitrogen oxides. Alkyl phenol solvent extraction in process	Avoids ammonium sulphate

Based on the data given above tables hereinfurther are examined the more important progresses recorded in the evolution of the processes for main chemical fibres fabrication.

Adipic acid

Adipic acid fabrication by air oxidation in two stages leads to waste water having a lower contamination degree as compared to the process using nitric acid.

The gaseous effluent contains: nitrogen oxides over 98% the balance consisting of carbon monoxide and solid particles.

Caprolactam

Caprolactam fabrication processes from cyclohexanone via benzene or phenol are less polluting as compared to the processes starting from amine hydroxyl.

Polyamide

Lactam plymerization in column or vacuum columns does not lead to the production of polluted effluents harmful for the environment.

Acrylic fibres

Solution polymerization processes are less polluting than the suspension polymerization ones.

Polyester fibres

Polyester fibres processes using terephthalic acid or dimethylterephthalate yield low amounts of waste water: 0.1 t/t fibre PEst contaminated with methanol 0.5-1 %.

Nylon 6 and Nylon 66

The processes starting from benzoic acid and acrylonitrile respectively are less polluting compared to other processes.

2.5. Down-streams petrochemicals

The class of products covered by the conventional name of down-streams petrochemicals is varied enough while a demarcation line between this class and certain petrochemical goods cannot be very clearly cut.

For this reason and especially because the products falling in the incidence of this category do not display obvious phenomena with regard to environmental protection, only the most significant processes were chosen, namely:

1. Tyres manufacturing
2. Rubber goods manufacturing
3. Plastics manufacturing

It is worth mentioning that these processes do not raise major problems concerning the environment, belonging to the class of processes with low pollution degree except tyres fabrication where carbon black pollution can be considerable.

In the modern processes, rubber concentrate with carbon black is obtained in the synthesis unit of SBR so that carbon black pollution of the environment by tyre plants is greatly reduced.

TYRES, RUBBER GOODS AND PLASTICS MANUFACTURING

Ref. no.	Process	Period introduced	Principal characteristics	Environmental aspects	Reason for adoption
0	1	2	3	4	5
1.	Diagonal and radial tyres fabrication	1945-1975	Preparation of rubber mixtures assembling of components obtained by extrusion,calendering etc. curing in presses autoclaves	Rubber wastes,cord, gum,and some tires about 2% reject	Development of transportation industry Cured rubber wastes are regenerated and reused mostly back in the process
2.	Fabrication of technical rubber goods (conveyor,belts, V-belts,gaskets)	1950-1970	- proportioning - mixing - manufacturing - curing	Cured rubber wastes about 3%	Development of technical rubber goods industry. Wastes of cured rubber are regenerated and reused to great extent in the process
3.	Fabrication of various plastics articles	1956	Depending on raw material - for PVC: proportioning of components,mixing,moulding, - for polyurethanes: preparation,pouring,ageing - for thermoplastic polymers injection,extrusion,moulding	Wastes, particulates	Development of consuming industry and increase of staple products requirement Wastes are recovered and reused

3. ENVIRONMENTAL ASPECT OF HAZARDOUS WASTES MANAGEMENT

During the brief period of about a decade, management of hazardous wastes has become one of the most critical environmental problems facing mankind. The increase in the varieties and total quantities of such wastes generated in recent years, and the enhancement of our knowledge and understanding of the adverse impacts of hazardous wastes on human health and on environment has led to the progress of hazardous waste management towards the top of any environmental agenda of the present time.

Among the options that are currently available for waste management the following should be considered:

1. Minimization of wastes generated by improving or changing the industrial processes;

2. Reprocessing of the wastes produced in order to recover materials and energy;

3. Transfer of the wastes to another industry which can use them as inputs;

4. Separation of hazardous from non hazardous wastes at the source, thus reducing the total volume to be disposed of in an environmentally safe manner with a corresponding reduction in the overall costs of handling, transportation and disposal;

5. Process of the wastes physically or biologically in order to render them less hazardous or non-hazardous;

6. Incineration of hazardous wastes;

7. Waste disposal in a properly managed land-field.

Minimization of wastes generated can be achieved by applying low-and non-waste technologies which provide a technical solution to the elimination of waste at their source. There are two main approaches to low- and non-waste processes: the recycling of wastes generated and the development of new technologies which produce less or no wastes.

UNIDO has already made an useful contribution in the area of hazardous waste management and industrial safety and undoubtedly will have a major role in the future. At present there are many areas where UNIDO can make a contribution to developing countries such as:

training, establishment of a network for technology transfer, operational guidelines to carry out environmental protection, to respond immediately to any request for assistance.

With major advances in science and technology in recent decades, many substances are now being manufactured, which may be either hazardous if used improperly or may produce hazardous wastes during the production processes. While these are significant benefits from the products manufactured, careless use of pesticides and other toxic products and improper disposal of by-products and wastes which are hazardous imply fundamental dangers to human, animal and plant life and the general environment.

Wastes are generated by almost all branches of modern industry, but a few major groups are most likely to produce hazardous toxic wastes which require special treatment, suc as: petroleum refining, petrochemical industry, organic and inorganic chemicals, iron and steel, non-ferrous metals, leather tanning, paint and coatings, electroplating and metal finishing.

In general, a hazardous waste is a waste that has physical, chemical or biological characteristics which require special storage procedures to avoid risk to health and other environmental effects.

There is no single univerally acceptable definition of hazardous wastes, which could vary from one country to another, and sometimes may even vary between different institutions within the same country.

Generally speaking, however, a waste can be considered hazardous if meets with one or more of the following criteria:

- ignition: wastes that imply a fire hazard during routine handling. Fire presents not only immediat dangers of heat and smoke, but also can spread harmful particles over wide areas;

- toxicity: when improperly handled, wastes may release toxic substances in sufficient quantities to become a substantial hazard to human health or the environment;

- reactivity: wastes that tend to react spontaneously with air or water, to be unstable to shock or heat, to generate gases or to explode;

- corrosivity: wastes requiring special containers because of their ability to dissolve contaminants.

A hazardous waste can present either a short-term acute hazard or a long-term environmental hazard.

Many wastes that offer no significant short-term hazard may cause severe long-term hazards due to their physical or chemical properties. For example, the short-term hazard of certain halogenated hydrocarbon solvents is low because they are non-flammable and at low level of acute toxicity. They can, however, cause problems in landfills because their slow rate of breakdown may consequently bring the risk of surface run-off or damage to ground water.

3.1. Solid residue incineration

Solid wastes in the petrochemical industry may occur as real solids, such as waste plastics, paper or metal; as semi-solids, such as tars and resins, and as suspended and dissolved solids, such as waste polymers and inorganic salts. These wastes include water treatment sludges, cafeteria and lunch-room wastes, plant trash, incinerator residues, plastics, metals, waste catalysts, organic chemicals, inorganic chemicals and wastewater treatment solids. The materials may be characterized as combustible or non-combustible, organic or inorganic, inert or biodegradable, dry or mixed with either aqueous or non-aqueous liquids.

The solid wastes generated by the petrochemical process may be handled by many different methods which are dependent on the existing conditions such as: (i) characteristics of the wastes (volume, weight, density, rate of production, toxicity, biodegradability etc.); (ii) potential value of salvaged materials; (iii) adaptability of the disposal method to the waste of interest, and (iv) availability of land and expected land use patterns. Almost every petrochemical plant has some form of solid waste handling and/or disposal facilities on the plant premises. A recent survey of the petrochemical industry revealed that 90 percent of the solid wastes generated at petrochemical processing plants was disposed of on plant site.

The plastics encountered in the petrochemical industry such as: polyethylene, polypropylene, polystyrene and polyvinylchloride produce a lot of polymer wastes, some of them are presented in the table 3.1. below:

Table 3.1.

Form of polymers wastes

- in % -

	Primary resin producers	Processors and fabricators
Pellets	18	14
Dropped or shreded	2	3
Dust or powder	21	3
Random, large (> 100 lb)	10	28
Random, small (< 100 lb)	14	16
Other, off-specification product and contaminated product	35	36
TOTAL	100	100

Plastics particles may range in size from powder and pellets to chunks weighing more than 50 kg. Waste plastics are generated by off-specification production, spills, product contamination, clean out, emergency dumps, and miscellaneous other sources during plastics manufacturing. Plastics are generally biologically inert substances.

Water treatment facilities may be found at many petrochemical processing plants. Solids composet of slit, sand and lime, or alum-based flocculant material are produced during the water treatment process and require treatment and/or disposal.

During waste water treatment processes, suspended or dissolved solids are separated from waste-streams by physical-chemical unit processes producing sludges which must be disposed. Biological unit operations used in waste water treatment processes such as activated sludge, trickling filters, extended aeration, waste water.

Stabilization process and anaerobic digestion also produce sludge which require disposal.

Spent catalysts may be liquid, semi-solid or solid. Catalysts possess a wide range of chemical characteristics. These catalysts may be toxic and thus would require special handling.

A wide variety of other organic and inorganic chemicals may enter the waste stream as a result of production processes.

Solid and semi-solid waste materials generated in the petrochemical industry may be disposed of by several techniques, including: incineration, open dump burning, no-burning dump, salvaging, landfill, land furming, lagooning and ocean dumping.

Open dump burning os normally an unacceptable disposal alternative and may be illegal in many countries.

Non-burn dumping involves the dumping of waste material on the ground or into pits. This method used for non-combustible materials, requires large areas of land which may be rendered unsaleable for future development.

Disposal by this technique also produces the potential for ground water and surface water contamination.

Incineration is a controlled combustion process for burning solid, liquid or gaseous combustible wastes to gases and residues containing little or no combustible material.

Incineration as we know it today began slightly more than one hundred years ago when the first municipal waste destructor was installed in Nottingham, England. Incineration use grew rapidly also in United States of America, Europe and other regions of the world.

Incineration practice

Incineration is an engineered process that employs thermal decomposition via thermal oxidation at high temperature, usually 900°C or greater, to destroy the organic fraction of waste and to reduce volume.

Generally, combustible waste or wastes with significant organic content are considered most appropriate for incineration. However, technically speaking, any waste with a hardous organic fraction, no matter how small, is at least a functional candidate for incineration. For instance, significant amounts of contaminated water coming from acrylonitrile processes are currently incinerated and contaminated soils are also being incinerated with increasing frequency.

Different incineration technologies have been developed for handling the various types and physical forms of hazardous wastes. The major sub-systems which may be incorporated into a hazardous waste incineration system are: (a) waste preparation and feeding; (b) combustion chambers; (c) air pollution control; (d) residue or ash handling.

The normal orientations of these sub-systems is shown in figure 3.1. along with typical process component options.

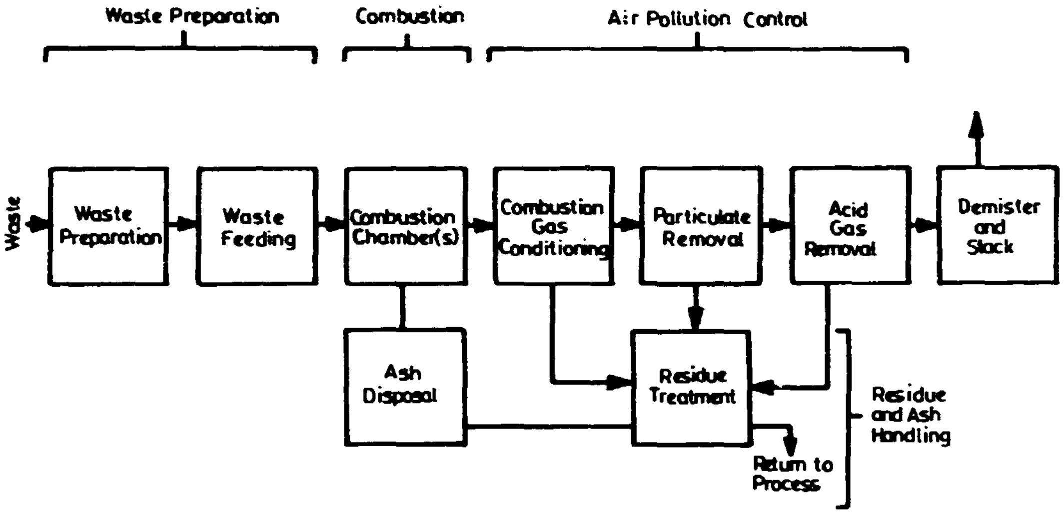


Figure 3.1. General orientation of incineration subsystems and typical process component options

Fig. 3.1 - General orientation of incineration sub-systems and typical process component options

(a) Waste preparation and feeding

Liquids are blended,then pumped into the combustion chambers through nozzles or via specially designed atomizing burners. Wastes containing suspended particles may need to be screened to avoid clogging of small nozzle or atomizer openings. While sustained combustion is possible with waste heat content as low as 9,900 Kcal/Kg liquid wastes are typically blended to a net heat content of 18,600 Kcal/Kg or greater. Blending is also used to control the chlorine content of the waste fed to the incinerator. Wastes with chlorine content of 70 percent and higher have been incinerated; however, most operators limit chlorine content to 30 percent or less.

Blending to these levels provides best combustion control and limits the potential for formation of hazardous free chlorine gas in combustion gases.

Sludges are typically fed using progressive cavity pumps and water cooled lances. Bulk solid wastes may require shredding for control of particle size. They may be fed to the combustion chamber via rams, gravity feed, air lock feeders, vibratory or screw feeders, or belt feeders. Containerized waste is typically gravity or ram bed.

(b) Combustion chambers

The physical form of the waste and its ash content determine the types of combustion chambers.

Liquid injection incinerators or combustion chambers are applicable almost exclusively for pumpable liquid waste. These units (figure 3.2) are usually simple, refractory lined cylinders (either horizontally or vertically aligned)equipped with one or more waste burners. Liquid wastes are injected through the burners, atomized to fine droplets and burned in suspension. Burners as well as separate waste injection nozzles may be oriented for axial, radial or tangential firing. Improved utilization of combustion space and higher heat release rates, however, can be achieved with the utilisation of swirl or vortex burners or designs involving tangential entry.

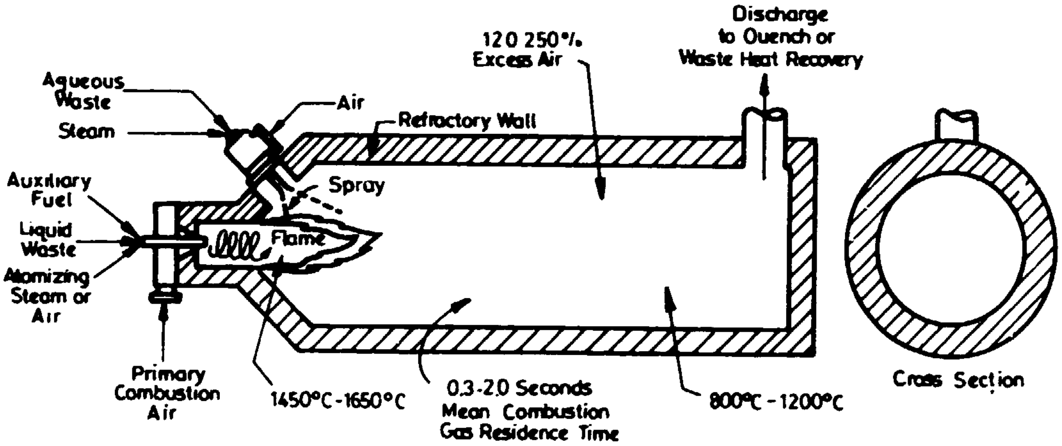


Figure 3.2. Typical liquid injection combustion chamber

Fig. 3.2. - Typical liquid injection combustion chamber

Rotary kiln incinerators (figure 3.3.) are more versatile incinerators in the sense that they are applicable to the destruction of solid wastes, slurries, and containerized waste as well as liquids. These units are most frequently incorporated into commercial off-site incineration facility design. The rotary kiln is a cylindrical refractory lined shell that is mounted on a slight incline. Rotation of the shell provides for transportation of waste through the kiln as well as for enhancement of waste mixing. The residence time of waste solids in the kiln is generally 1 to 1.5 hours. This

is controlled by the kiln rotation speed (1-5 revolutions per minute), the waste feed rate and in some instances, the inclusion of internal dams to retard the rate of waste movement through the kiln. The feed rate is generally adjusted to also limit the amount of waste being processed in the kiln to atmost 20 percent of the kiln volume.

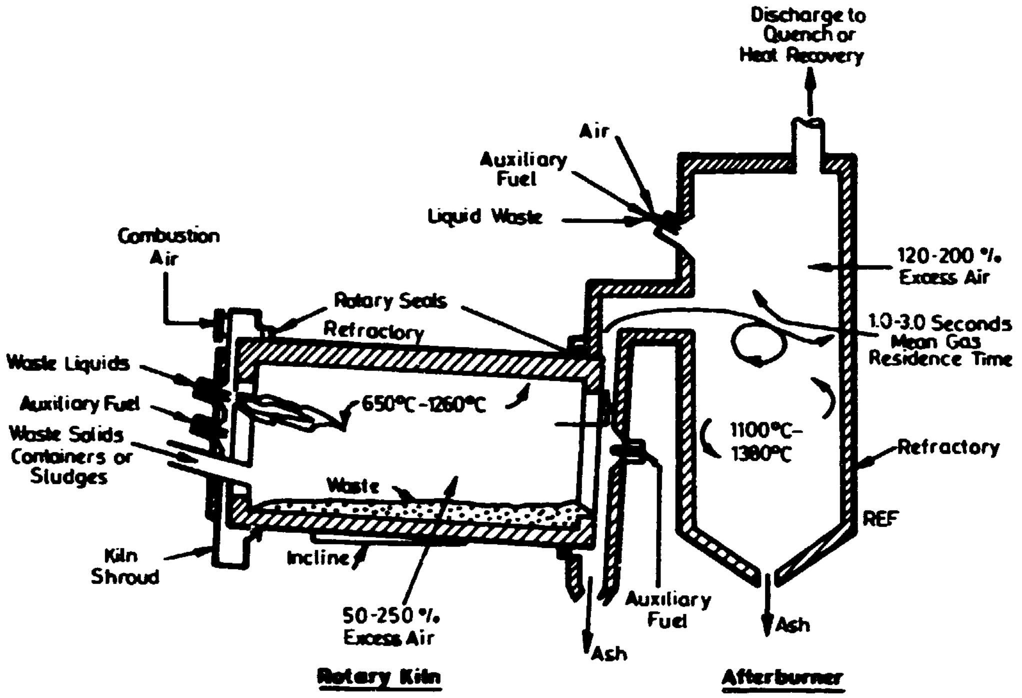


Figure3.3 Typical rotary kiln/afterburner combustion chamber

Figure 3.3. - Typical rotary kiln/afterburner combustion chamber

Fixed hearth incinerators, also called controlled air, starved air, or pyrolytic incinerators, are the third major technology in use for hazardous waste incineration today.

These units employ a two-stage combustion process, much like rotary kilns (figure 3.4.). Waste is ram fed into the first stage or primary chamber, and burned at roughly 50 to 80 percent of stoichiometric air requirements. This starved air condition causes most of the volatile fraction to be destroyed pyrolytically, with the required endothermic heath provided by the oxidation of the fixed carbon fraction. The resultant smoke and pyrolytic products, consisting rpimarily of volatile hydrocarbons and carbon monoxide, along

with products of combustion, pass to the second stage or secondary chamber. Here, additional air is injected to complete the combustion, which can occur either spontaneously or through the addition of supplementary fuels. The primary chamber combustion reactions and turbulent velocities are maintained at low levels by the starved-air conditions to minimize particulate entrainment and carry-over; with the addition of secondary air, total excess air for fixed hearth incinerators is in the 100 to 200 percent range.

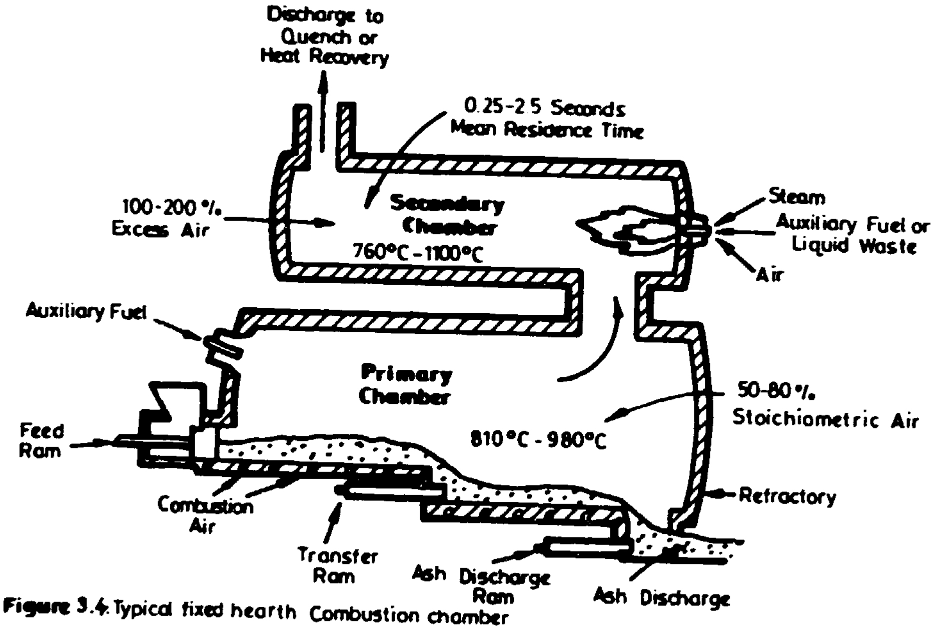


Figure 3.4 Typical fixed hearth Combustion chamber

Figure 3.4 - Typical fixed hearth combustion chamber

Fluidized beds incinerators have long served the chemical processing industry as a unit operation. This type of combustion system has only recently begun to see application in hazardous waste incineration. Fluidized bed incinerators may be either circulating or bubbling bed designs. Both types consist of a single refractory-lined combustion vessel partially filled with particles of sand, alumina, sodium carbonate or other materials. Combustion air is supplied through a distributor plate at the botton of the combustor (figure 3.5) at a rate sufficient to fluidize (bubbling bed) or entrain the bed material (circulating bed). In the circulating bed design air velocities are higher and the solids are blown overhead, separated in a cyclone and returned to the combustion chamber. Operating temperatures are normally maintained in the 760 to 780°C range and excess air requirements range from 100 to 150 percent.

Fluidized bed incinerators are primarily used for sludges or shredee solid materials. To allow for good distribution of waste materials within the bed and removal of solid residues from the bed. all solid generally require pre-screening or crushing to a size less than 2 inches in diameter. Fluidized bed incinerators offer high gas to solid ratios, high heat transfer efficiencies, high turbulence in both gas and solid phases, uniform temperatures throughout the bed, and the potential for in situ acid gas neutralization by lime or calcium carbonate addition. However, fluid beds also have potential for solids agglomeration in the bed if salts are present in waste feeds and may have a low residence time for fine particulates.

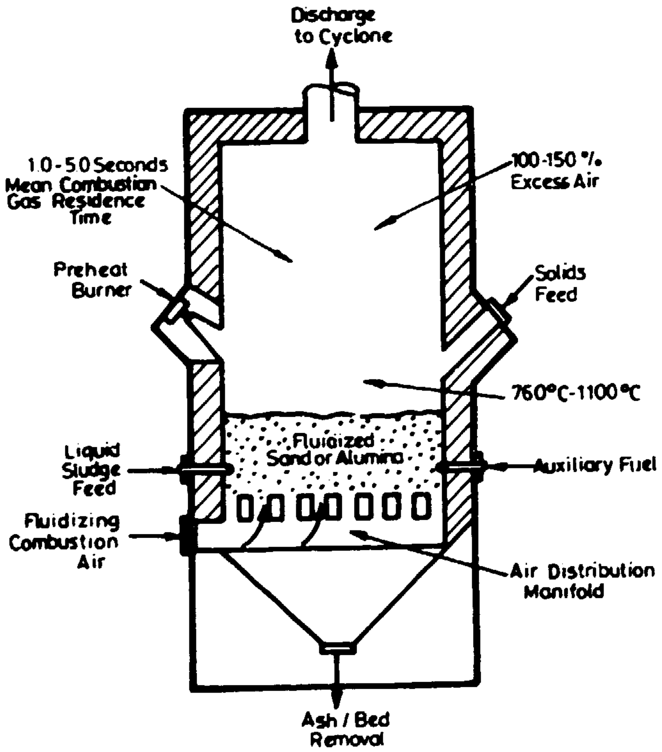


Figure 15. Typical fluidized bed combustion chamber

Figure 3.5 - Typical fluidized bed combustion chamber

(c) Air pollution control

Following incineration of hazardous wastes, combustion gases may need to be further treated in an air pollution control system. The presence of chlorine or other halogens in the waste will generally signals a need for a scrubbing or absorption step for combustion gases to remove HCl and other halo-acides. Ash in the waste is not destroyed in the combustion process. Depending on its composition, ash will either exit as bottom ash, at the discharge end of a kiln or hearth, for example, or as particulate matter suspended in the combustion gas stream (fly ash). Particulate emissions from most hazardous waste combustion systems generally have particle diameters less than one micron and require high efficiency collection devices. In addition, gas cleaning systems provide some limited aditional buffer against accidental releases of incompletely destroyed waste products. Such systems however are not a substitute for good combustion and operating practices.

(d) Residue and ash handling

The inorganic components of hazardous wastes are not destroyed by incineration. These materials exit the incineration system either as bottom ash from the combustion chamber, as contaminants in scrubber waters and other air pollution control residues, and in small amounts in air emissions from the stack.

Ash is commonly either air-cooled or quenched with water after discharge from the combustion chamber. From this point ash is frequently accumulated on site in storage lagoons or in drums prior to disposal in a permitted hazardous waste land disposal facility. Dewatering or chemical fixation/stabilization may also be applied prior to disposal.

Air pollution control residues are generated from the combustion gas quenching, particulate removal and acid gas absorption steps in an incineration system. These residues are typically aqueous streams containing entrained particulate matter, absorbed acid gases (usually as HCl) and small amounts of organic contaminants.

These streams are often collected in sumps or recirculation tanks where the acids are neutralized with caustic and returned to the process. Eventually a portion or all of these waters must be discharged for treatment and disposal (generally when the total dissolved solids level exceeds 3 percent). Manu facilities discharge neutralized waters to settling lagoons or a chemical precipitation step to allow for suspended contaminants to be concentrated and ultimately sent to land disposal. Depending upon the nature of the dissolved contaminants and their concentration after treatment, waters may either be returned to the process or discharged to sewers.

Measuring process performance for incinerators

Proper and accurate measurement of the emissions from incineration systems is a critical issue. Fortunately, significant progress has been made in adopting measurement methods to the rigors of specific compound indentification and the level of detection and accuracy.

Performance measurement may have any of the following three purposes:

- to establish compliance with performance standards (e.g. trial burns);
- to monitor process performance and direct process control (e.g. continuous monitoring);
- to conduct performance measurements for research and equipment development purposes.

Methods employed in assessing regulatory compliance are generally official methods which have been standardized and published. Routine performance monitoring for process control often involves the use of continuous monitors for emissions and facility-specific engineering parameters (e.g. temperature, pH, kiln rotation). Research and equipment assessment investigations may involve any of the above techniques in combination with standard and often non-standard sampling and analysis techniques designed for rapid screening of performance or for ultra-low detection of specific materials.

Figure 3.6 illustrates sampling points which may be involved in assessing incinerator performance. In the case of trial burns activities, the main focus of sampling activities is on collection of waste feed and stack emission samples. Ash and air pollution

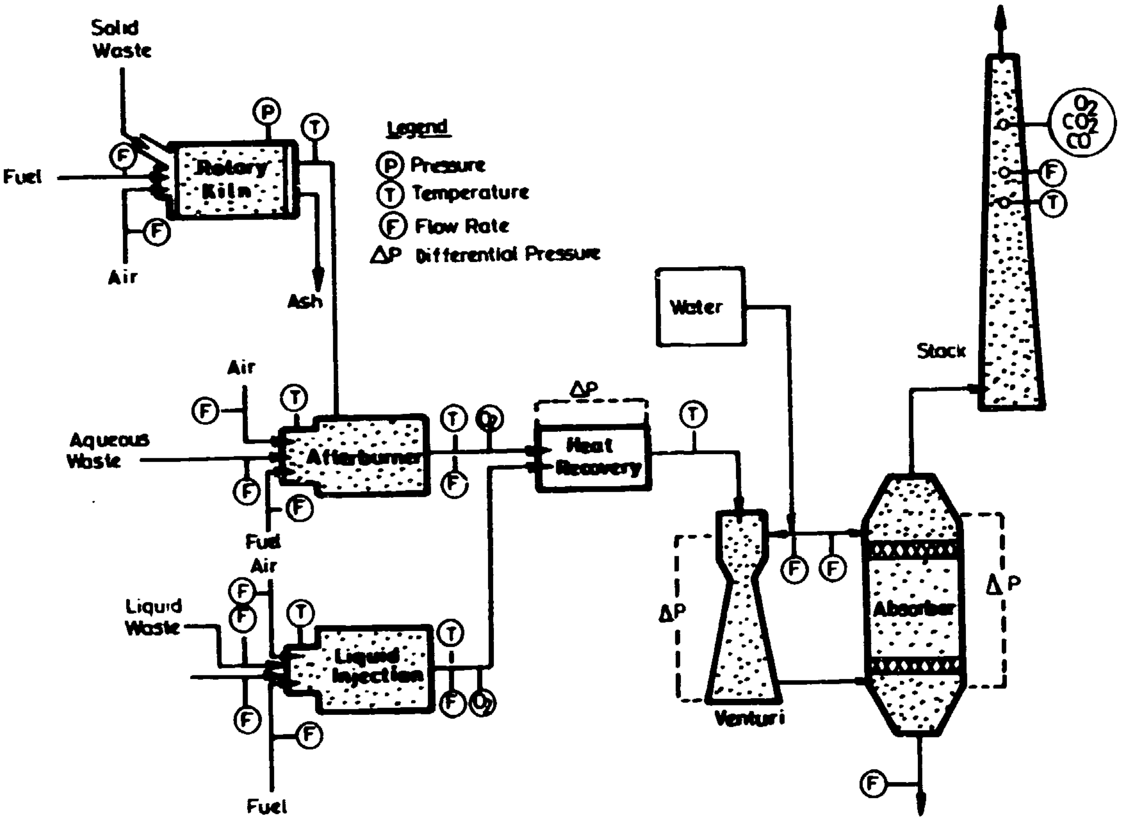


Figure 3.6. Potential sampling points assessing incinerator performance

Figure 3.6 - Potential sampling points assessing incinerator performance

control system residues are also sampled and analyzed. Sampling of input/output streams around individual system components (e.g. scrubbers) may also be conducted in research testing or equipment evaluation studies.

The main focus of analytical activities is on principal organic hazardous constituents POHCs. Stack gases analysis also includes determination of HCl and particulate emissions, and may be extended to a determination of other organic chemical compound emissions as well as metals of concern. In the case of particulate emissions, the size distribution of stack particles may also be of interest.

The size of emitted particulate affects its transportation and fate in the atmosphere and influences the likehood of inhalation, an important factor in health effects assessment. Few hazardous waste incinerator tests have actually collected particle size data, primarily due to time and funding limitations.

Measurement of a wide variety of incinerator operating parameters may be necessary to maintain thermal destruction conditions which are equivalent to those observed during a successful trial burn. These measures are used as indicators of the performance of incineration system and serve as input to automatic and manual process control strategies. There are nearly two dozen potential measurements, including such parameters as: combustion temperature, waste feed rate, oxygen and carbon monoxide concentration in the stack, gas flow rate at strategic points, and scrubber solution pH. These parameters and their use are described in detail in a number of resource documents (27).

Continuous emission monitors (CEM) are often used or required in measuring combustion gas components such as carbon monoxide (CO), oxygen (O_2), nitrogen oxides (NO_x) and total unburned hydrocarbons (TUHC). If properly interpreted, combustion gas components may be indicators of the completeness of the thermal destruction reaction. These methods typically require extraction of gas samples from the gas stream of interest and measurement with a remote instrument. Some parameters such as CO and O_2 may be measured in situ (in the stack). Table 3.2 summarizes monitor types and available concentration measurement ranges.

Ideally, the primary products from combustion are carbon dioxide, water vapour and inert ash. In reality, what appears outwardly to be straightforward, simple process is actually an extremely complex one, involving thousands of physical and chemical reactions, reaction kinetics, catalysis, combustion aerodynamics and heat transfer. This complexity is further aggravated by the complex and fluctuating nature of the waste feed to the process. While combustion and incineration devices are designed to optimize the chances for completion of these reactions, they never completely attain the ideal. Rather, small quantities of a multitude of other products may be formed, depending on the chemical composition of the waste and the combustion conditions encountered. These products along with potentially unreacted components of the waste become the emissions from the incinerator.

Table 3.2

Summary of continuous emission monitors

Pollutant	Monitor type	Expected concentrated range	Available range
O_2	Paramagnetic Electrocatalytic (e.g.zirconium oxide)	5-14%	o-25%
CO_2	NDIR (non-dispersion infrared)	2-12%	0-21%
CO	NDIR	o-1oo ppm	o-5ooo ppm
NO_x	Chemiluminiscent	o-4ooo ppm	o-1oooo ppm
SO_2	Flame photometry Pulsed fluorescence NDUV (non-dispersion ultraviolet)	o-4ooo ppm	o-5ooo ppm
SO_3	Colorimetric	o-1oo ppm	o-5o ppm
Organic compounds	Gas chromatography FID (Flame ionization detector)	o-5o ppm	o-1oo ppm

3.2. Waste water treatment

Wastewater streams in the petrochemical industry may be categorized into five principal source components:

(i) wastes discharged directly from production units during normal operation;

(ii) utility operations such as blowdown from energy production and cooling systems;

(iii) ballast water discharged from tankers during product handling);

(iv) contaminated storm run-off from process areas;

(v) miscellaneous discharges from spills, turn-arounds, sanitary sewage, from administrative areas, locker rooms, shower and food handling areas.

Petrochemical wastes may include various chemicals derived from petroleum derivatives and natural gas, toxic substances, lubricants, gas oil, fuel oil, wax, asphalt and petroleum coke. The hydrocarbons found in these wastewater stream generally originate from leaks, spills, and product dumps. Steam condensate from reflux systems may contain hydrogen sulphide and mercaptans. Caustics, when used to purify hydrocarbon streams, produce alkaline wastestreams which are potentially toxic.

Ammonia may be added to product streams for corrosion control, and by the breakdown of nitrogenous compounds present in the feedstock. Other components of petrochemical wastestream which may be of concern are corrosion inhibitors, particularly heavy metals.

The data shown in table 3.3 illustrate the variability of waste characteristics in the petrochemical industry. The pH values of petrochemical wastewaters are generally greater than 7, and the wastestreams typically contain large amounts of total solids and low concentrations of suspended solids, indicating that most solids in these wastewaters are in the dissolved form. The variability in the data found in table 3.3 suggests that each petrochemical wastestream must be analysed separately to predict its characteristics. The variability can be attributed to the large number of choices of processes that may be selected fo form a petrochemical plant.

The most commonly used method for predicting the quality and quantity of petrochemical production wastewaters is to study each individual unit process and relate the quantity and quality of the wastestreams produced to production units.

Treatment methods

The design of wastewater treatment facilities for petrochemical production facilities will not be reliable unless wastewaters have been fully characterized and the performance characteristics of alternative treatment processes have been evaluated by treatability studies and pilot plant operations. Treatability studies should establish the effects of operational parameters such as hydraulic detention time, sludge age and temperature on organic removal rates, oxygen requirements, sludge production, sludge characteristics and process stability.

Table 3.3

Petrochemical plants effluent analyses (before treatment)

Plant products	Mixed chemicals incl. ethylene oxide, propylene oxide, glycols, amines and ethers	Refinery, detergent alkylate	Chlorophenols	Refinery butadiene butyl rubber	Phenols cresols
Alkalinity (mg/L)	4,000	365	-	164	192
BOD_5 (mg/L)	1,950	345	16,800	225	550-850
Chlorides (mg/L)	430-800	1,980	120,000	825	230
COD (mg/L)	7,970-8,540	855	25,000	610	100-2000
Oils (mg/L)	547	73	-	-	traces
pH	9.4-9.8	9.2	-	7.5	4.6-7.2
Phenols (mg/L)	-	160	-	17	280-550
Sulphates (mg/L)	655	280	-	-	-
Suspended solids (mg/L)	27-60	121	500	110	15-90
Total nitrogen (mg/L)	1,160-1,253	89	45	48	-
Total solids (mg/L)	2,191-3,029	3,770	150,000	2,810	1,800-2,300

Treatability studies can identify wastestreams which should be treated separately to enhance process performance. Wastewater survey, wastewater characteristics, in-plant consideration, treatability study and incorporation of result.

The unit processes which can provide treatment of petrochemical manufacturing plant wastewaters are as varied as the unit processes used in the manufacturing plants themselves. Studies have shown, however, that there are seldom cost effective alternatives to biological treatment coupled with physical-chemical pre-treatment and/or polishing where needed. Biological treatment coupled with post-filtration has been considered as the "best practicable technology" currently available for treating petrochemical processing wastewaters.

In order to produce a high quality effluent, it is probable that the most petrochemical wastewater systems will include all or some of the processes listed in table 3.4 and shown in figure 3.7.

A central biological treatment plant is the preferred method of treating the aqueous effluents of the petrochemical industry because: 1) they are geared to BOD removal, which was generally required by the responsible authorities; 2) biological process costs to achieve BOD removal are low compared to other treatment processes and 3) when effluents limitations are in terms of COD, biological processes will remove a significant amount of COD with less expense than a non-biological process designed to remove the same amount of COD.

Effluents from biological treatment systems may still contain dissolved organics and suspended solids which may be removed by further treatment such as aerated lagoons and polishing ponds, sand or multimedia filtration or other physical-chemical processes such as reverse osmosis, ultrafiltration, extraction and chemical oxidation. Activated carbon adsorption preceded by filtration for solid removal was generally found to be the best economically available technology for reduction of the residual COD of biologically treated effluents.

Table 3.4

Petrochemical wastewater treatment systems

Pre-treatment	Intermediate treatment	Secondary treatment
API separators	Dissolved air flotation	Biological oxidation
Tilted plate separators	Coagulation-precipitation	Chemical oxidation
Filtration for oil removal pH control	Equalization	Filtration
Stripping processes	Detoxification for biological treatment	Adsorption
Monitoring system to detect breakdown and spills		

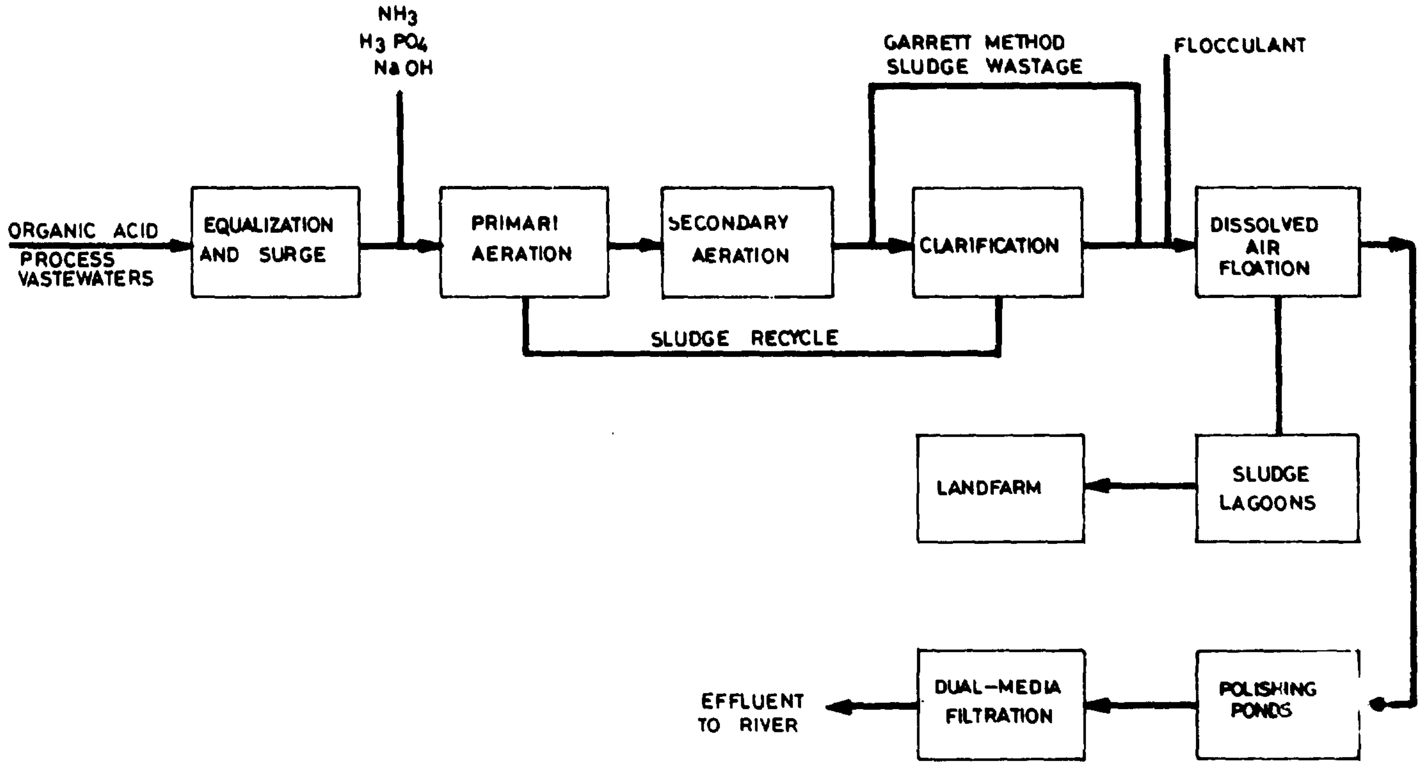


Figure 3.7. WASTE TREATMENT FLOW DIAGRAM

The utility of anaerobic lagoon pre-treatment of petrochemical waste was investigated by Hovious and others (1, 5). A design procedure for the selection of lagoon volume based on organic loading and temperature was presented. Using this design procedure it was estimated that a lagoon with a hydraulic detention time of about ten days and a temperature of 20°C would achieve a 40 percent COD removal and a 50 percent BOD removal when the effluent contained 3,000 mg/L of COD. Examination of chromatographically identifiable organic compounds in the waste used during this research indicated that all compounds except metabolic intermediates were removed to a significant extent in the anaerobic lagoon. The effects of temperature on the biological treatment of petrochemical wastewaters were observed to be more drastic than temperature effects on municipal wastewater treatment systems.

Recent advances in the field of bio-engineering have led to the development of microbial cultures which have the ability to break down molecules resistant to biological degradation. A specially adapted strain of bacterial inoculum applied to the biological treatment process at a petrochemical processing plant significantly improved effluent quality. The addition of these selectively adapted microbes reduced effluent total oxygen demand and biochemical oxygen demand, improved system stability, eliminated an existing foam problem and resulted in the elimination of at least one compound (tertiary butyl alcohol) from the effluent not previously degraded. These results, combined with recent advances and interest in genetic engineering, suggest that biological treatment processes may be improved by these techniques; however, further research is required.

Physical-chemical processes plan an important role in petrochemical wastewater treatment. Many physical-chemical treatment processes are used to pre-treat petrochemical wastewater in preparation for biological treatment. API separators are used to remove materials less dense than water, such as free oil, and suspended matter that is more dense than water. Tilted plate separators are also used to remove materials less dense than water. Several types of filtration devices are also used to remove free oil and solids from wastewater streams prior to biological treatment.

Neutralization is commonly used and required in the treatment of petrochemical wastewaters. Acid streams may be neutralized by fluidized mixing with slurries, dolomitic lime slurries, caustic or soda ash. Alkaline streams may be neutralized with sulphuric or hydrochloric acid or with boiler flue gas (carbon oxide). Neutralization can often be accomplished by mixing internal wastewater streams. Volatile organic compounds, hydrogen sulphide and ammonia are often removed from wastewater streams by stripping processes.

Dissolved Air Flotation (DAF) is commonly used in petrochemical waste treatment plants to enhance oil and suspended solids removal. DAF units, while not economical as API separators and tilted plate separators, produce a better quality effluent which is often required to meet effluent oil limitations. If a significant portion of the oil is emulsified, chemical addition with flocculation chambers may be a part of the flotation unit. Coagulation-flocculation processes are effective in removing suspended solids, some nutrients and heavy metals from petrochemical wastestreams.

Activated carbon adsorption systems may be used to remove residual organic compounds from petrochemical wastewaters. A review of the literature on activated carbon adsorption as a treatment concept for petrochemical wastewaters was presented by Matthews.(2[illegible]) Compounds in the alcohol, aldehyde, amine, pyridine and morpholine, aromatic, ester, ether, glycol and glycol ether, ketone, organic acid, oxide and halogenated organic groups were found to be amenable for carbon adsorption.

Petrochemical wastewater was treated in a treatment system consisting of oil removal, biological oxidation, chemical treatment, filtration and activated carbon adsorption. The COD was reduced from 3,2000 mg/L to 30 mg/L. The activated carbon columns were found to remove dissolved organics not amenable for biological treatment along with colour.

3.3. Flare and flare gases recovery

3.3.1. Flare

The off-gases resulting in several cases from refineries and petrochemical plants cannot for various reasons be discharged into the air.

Depending on the nature and composition of off-gases there are various processing methods to convert the off-gases into less noxious compounds which can be discharged into the air.

One of the oldest and easiest ways to process noxious off-gases is their incineration in certain devices called flares. In such devices one can burn fuel and flammable gases with a not too high content of inert gases (CO_2, N_2), as well as noxious and flammable gases in which case measures shall be taken to disperse the products resulted by burning.

The demand of the modern industry on energy savings and environment protection gains more and more importance. One modality of responding to this task is to recover the flare gas and use it as energy in the fuel gas system.

Two kinds of streams are directed to the flare:

(a) A permanent gas stream, resulting from:

- leakage of safety valves;
- valve by-passes or vent lines;
- waste gas from compressor seal oil systems;
- overhead product accumulators;
- LPG tanks.

(b) Emergency gas streams released by one or more safety valves in case of technical failures which cause overpressure in plant equipment.

With the flare gas recovery system those gases can be compressed and sent to the fuel gas network of the complex.

Such a system is not intended for large emergency flows or medium size flows that may last for a few hours or a day. In these cases recovery equipment would be largely oversized and used only during a short time that it cannot be economically justified. There is also no safe and reliable place for user to send the recovered material during an emergency.

The permanent flare gas stream is the indicated one to be recovered and the energy saved by using it as fuel gas.

Depending on the capacity of the units, the design, construction, type of piping and valves, etc., the recovered gas stream is typically between 1000 and 5000 m^3/h.

The flares are facilities meant torun in view of increasing the safety degree of the process unit itself and consist of the following sub-assemblies: demister, hydraulic seal, flare stack, flare head including pilot flare and main burner, flare piping and automatic ignition system of flame.

Flares are fed with off-gases collected from safety valves discharges installed on pipes and on process equipment.

The molecular weight of gases varies between 11.3 and 42.45, while the hydrogen content varies between 7% volume and 65% volume. For a discharge frequency of 65% of safety valves the flow rates of the gases discharged into the flare system can vary between 0 and 2,700 kg/h.

From gas collector, the gasses further go through demister (see fig. 3.8) wherein liquid drips entrained with diameters over 400 μ are separated. Drips separation is necessary due to the incomplete incineration thereof, producing soot.

From demister, the gases go through a hydraulic seal which does not allow the gases to come from the flare stack back into the pipe system. From the hydraulic seal the gases enter the flare stack which directs the gases to flare head raising at the same time the flare flame to a certain height to diminish the radient effect of flame on the environment. Before entering the flare head the gases go through a device called "molecular seal" which prevents the flame from entering the flare stack. This device is closed by a gas having a low molecular mass: air, methane.

The flare head is the most important part consisting of a metallic cylinder with a cone ring called flare head nozzle. The nozzle is provided with a steam distribution pipe necessary to measure the turbulence as well as to improve gas burning and burning of the incandescent carbon particles, according to the reaction:

$$C + H_2O = CO + H_2$$

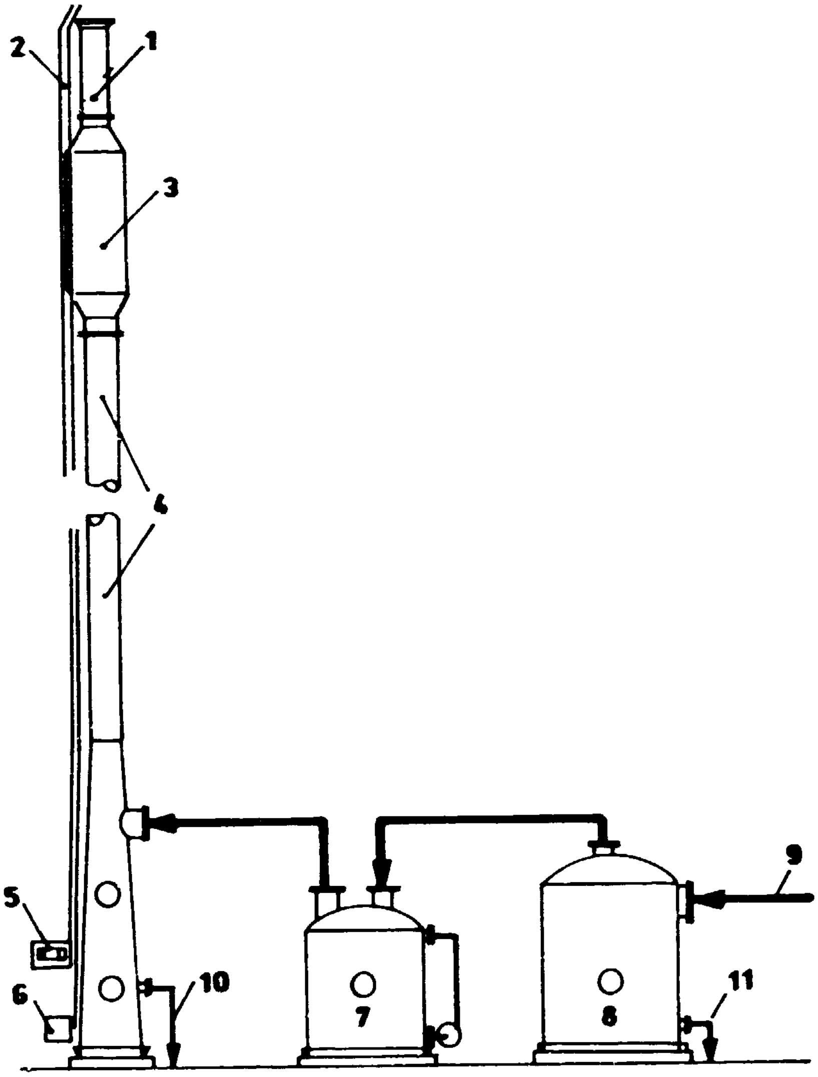


FIG.3A FLARE UNIT

1-MAIN BURNER 2-PILOT BURNER 3-MOLECULAR SEAL
4-FLARE STACKE 5-IGNITION DEVICE 6-PILOT BURNER CONTROL
7-HYDRAULIC SEAL 8-DEMISTER 9-GATHERING LINE
10-11-DISCHARGES

To prevent flame extinction the flare head is provided with a pilot burner whose ignition is achieved electronically by means of electrodes while the pilot flame running is controlled by a thermocouple.

During the design stage of the flares, the following main questions are to be solved:

(a) the reduction of the noise level generated by gas circulation through the flare stack and by gas burning in flare stack head;

(b) the reduction of the effect of the thermal radiation of flame;

(c) the reduction of environmental pollution.

(a) In order to reduce the noise level the optimum diameter of flare stack is chosen as per relation:

$$D = \sqrt{\frac{4G}{W}} \qquad \text{where}$$

D = diameter of flare stack - m

G = flow rate of gas circulating through stack, kg/s

W = gas velocity in stack, m/s

ρ = gas density calculated at stack temperature and atmospheric pressure, kg/m^3.

Gas flow rates is calculated by the following relation:

$$G = \sum_{1}^{n} G_{c.i} + \sum_{1}^{n} G_{s.i} \qquad \text{where}$$

$\sum_{1}^{n} G_{c.i}$ = flow rates for continuous discharges - kg/s

$\sum_{1}^{n} G_{s.i}$ = flow rates resulted from safety valves discharges - kg/s.

Since the frequency of safety valves discharges cannot be established accurately, it is considered that about 60% of the safety valves discharges simultaneously.

Gas velocity in the flare stack is given by the relations:

$$W = Ws \cdot M \quad \text{or} \quad W = (0.2\text{-}0.3)Ws \qquad \text{where}$$

M = Mach number

Ws = sound velocity, m/s.

Sound velocity is determined by Laplace relation:

$$Ws = \sqrt{\frac{XRT}{M}} \qquad \text{where}$$

X = adiabatic exponent

R = general constant of gases - 8312 J/Kmol

T = gas stack temperature °K

M = average molecular mass of gas.

Robert Mayer relation can be approximately used for adiabatic exponent calculation:

$$X = \frac{C_{pm}}{C_{pm} - R} \qquad \text{where}$$

C_{pm} = average molar specific heat of gas - J/Kmol grades

R = gas general constant with the value 8312 J/Kmol.

Permissible noise levels caused by industrial plants can be considered, as shown in table 3.5 below:

Table 3.5

Permissible noise levels

Zoned area	Noise level by night dB(A)
Industrial	70
Commercial	50
Residential	40-45
Hospitals	35

(b) The reduction of the thermal radiation effect of the flame is obtained by the correct size-up of flare stack height. As a starting point in establishing the unitary thermal flow radiated by flare, the flame is assumed to be a point source releasing heat into surroundings. The correlation between the unitary thermal flow (2) received by an area at a certain distance and the radiant flow of the source (flame) is given by Kepler law:

$$q = \frac{F \cdot Q}{4\pi r^2}$$ where

q = unitary thermal flow, $w/m^2.h$

Q = radiant flow of source, w/h

r = distance from the source to the receiving area

F = coefficient considering the share of the heat released by gas burning with flame and transmitied by radiation, usually taken as 0.35.

The unitary thermal flow allowed for the operation personnel has the following values:

Unitary thermal flow w/m^2 (sun radiation included)	Exposure time
1,900	infinite
2,360	1-2 h
2,800	0.5-1 h
3,500	5-10 minutes
4,400	15 sec.
6,300	no exposure

For determination of flare stack height one can use Kepler relation according to which values are taken for "q" and "F"; "Q" is calculated from the heat released by gas flow burning and subsequently "r" is determined as the distance between the flame and the concerned point at ground elevation.

$$r = \sqrt{X^2 + Y^2}$$ where

X = the distance, horixontally from the axis of flare stack to the closest unit where a steady activity is conducted

Y = flare stack height including the distance from flare stack top to the geometric center of flame.

(c) The reduction of the environmental pollution is achieved by using an adequate flare stack height. The higher the flare stack is, the lower the level of unitary thermal radiation at ground elevation and the lower the environmental noxious concentrations, while the investment and repairs and maintenance costs increase significantly.

3.3.2. Flare gases recovery

Waste gas recovery from refinery operations can be the most economically attractive energy saving option available; use of flare gas to provide fuel for process heaters and steam generation leaves more in fuel processing, thus increasing yields. Advantages are also obtained from reduced flaring pollution and extended tip life.

The design of a suitable gas recovery plant considered the following constraints:

- Flare relief is essentially a safety security system, thus its operation must not be affected by any gas recovery plant installation;
- In order to obtain maximum pressure on the plant suction side, the flare water seal design was altered such as not to affect the operation of the plant safety valves, particularly those set for low pressure relief.

Process description

There are two types of recovery systems:

- Recovery system with gasometer;
- Recovery system without gasometer.

Recovery system with gasometer (figure 3.9)

The normal flare gases flow through the flare header and reach the gasometer (2) via the flare gas separator (1).

The gas flows preferentially to the gasometer, where the back pressure is set lower than in the flare seal drum (250 mm WC/450 mm WC).

The liquid separated in separator (1) flows to separator (4), where waste water is separated from liquid hydrocarbons.

The gas from the gasometer is pressurized by compressor (3) to a pressure required by the fuel gas system. The gas flow to the fuel gas system shall take into consideration the water level in the gasometer. The maximum and minimum level is maintained by two level switches. At low or high level the respective control valves will close, respectively open.

If a failure in the plant leads to a large safety valve release, the gas flows through the flare header, the pressure rises, the pressure switch closes the access valve to the recovery system and the gas flows to the flarestack to be burned. Thus the gasometer is protected against overpressure.

At a released gas with a higher molecular weight, an overloading of the compressor results but only for a very short time.

If the released gas has a high temperature, the temperature switch also closes the access valve to the recovery unit. This protects the compressor and the gasometer.

If for a certain period of time the gas leakages are small the pressure in the flare line tends to drop. In order to avoid vacuum a low pressure switch disconnects the flare line from the recovery system.

Depending on the gas composition the recovered gas is sent directly to the fuel gas system or to a treating step like H_2S absorption.

<u>Recovery system without gasometer</u> (figure 3.1o)

By application of adequate control and instrumentation it is possible to design a flare gas recovery system without gasometer. The role of the gas accumulator is taken by the volume of the long and large flare gas header. The flare gas is sent to the compressor separator (1). Here, the liquid phase is separated, which flows into separator (4), where waste water is separated from liquid hydrocarbons. The gas phase from the separator is pressurized by compressor (2) cooled in cooler (5). The condensed liquid is separated in separator (3) and the gas at the top of this separator is sent to the fuel gas system.

To avoid air entering the system at low pressure in the gas header, the pressure switch in the header closes and the controller in the bypass line opens. Thus the forward gas flow is interrupted and is recycled to compressor suction.

When the pressure in the header rises again, the suction valve opens and the by-pass line control valve closes; tha gas flows again to the fuel gas network.

Fig.3.9. FLARE GAS RECOVERY SYSTEM WITH GASOMETER

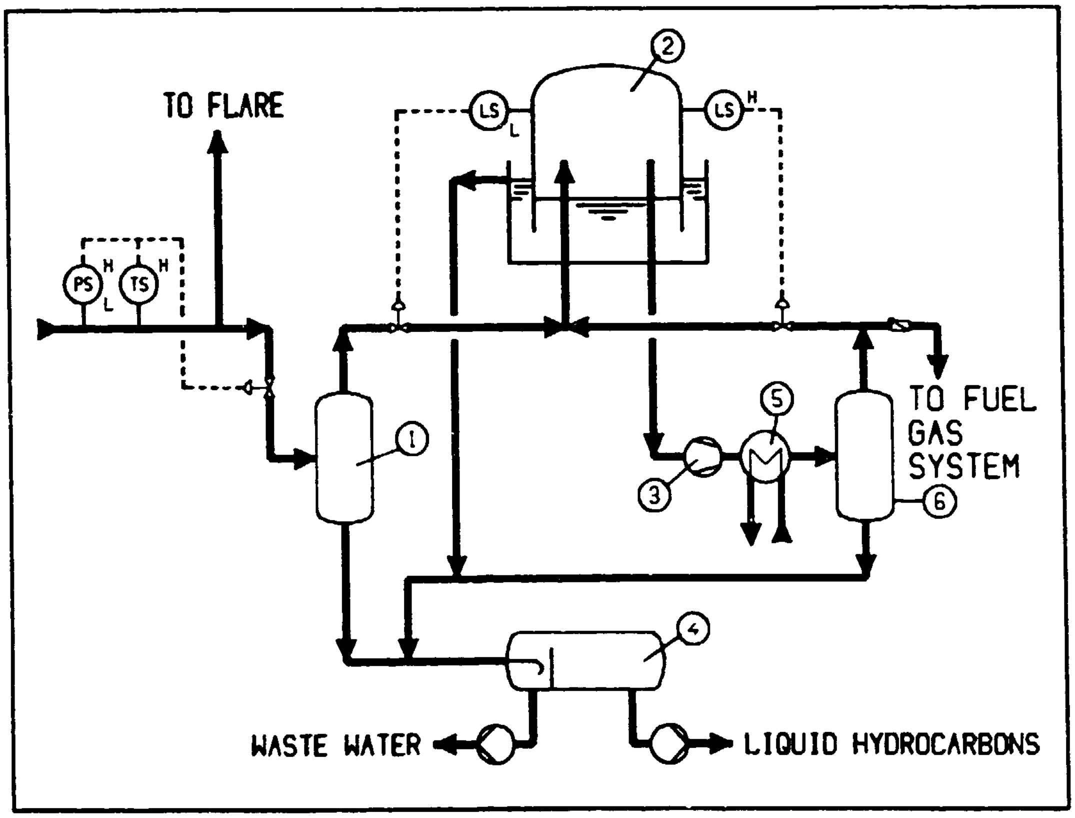
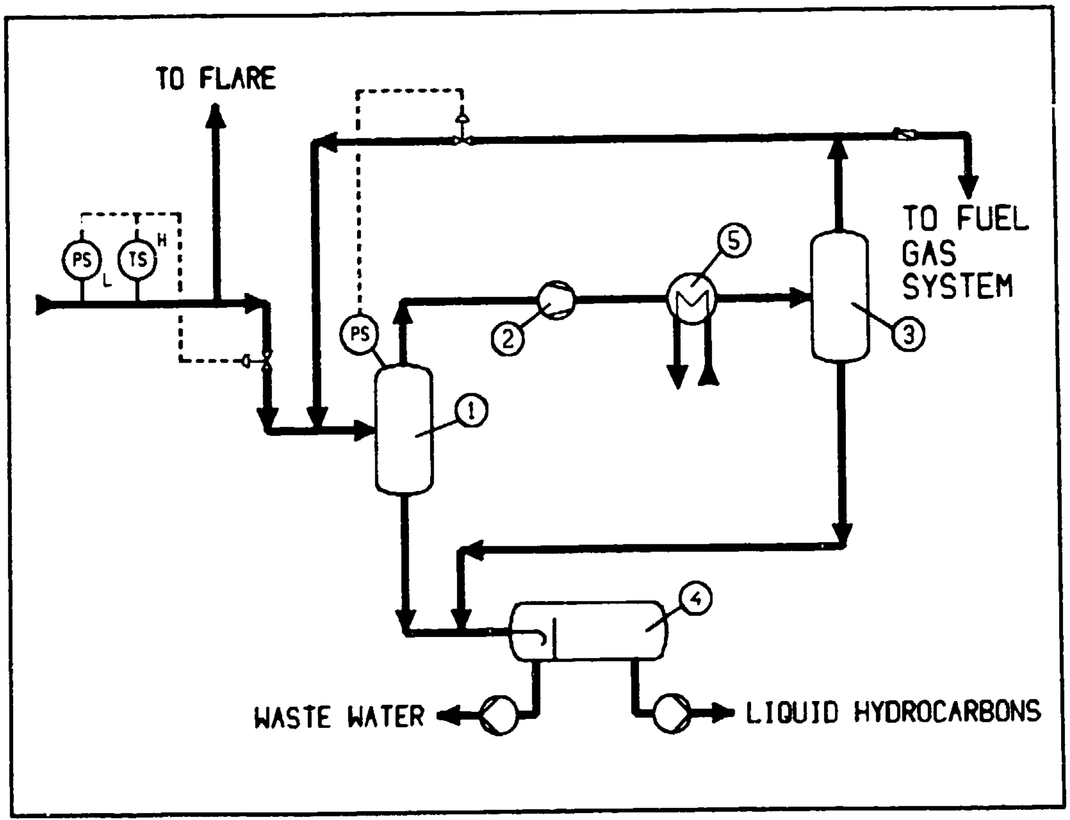


Fig. 3.10 **FLARE GAS RECOVERY SYSTEM WITHOUT GASOMETER**



If the incoming flare gas temperature exceeds a certain value, the temperature switch closes the suction valve to protect the compressor.

The compressor type has to be selected to allow variations in suction and discharge pressures and molecular weight. Good results were obtained with rotary and liquid ring compressors. For each case the adequate solution has to be studied and applied.

Comparison between the two alternatives

The gasometer has the advantage of the large volume, which levels out the fluctuations in flow and pressure. The amount of gas recovery is somewhat larger.

The advantages of the system without gasometer are the lower plan area requirement, lower investment cost, simpler design and less maintenance cost.

Economics

The payout time for a flare gas recovery unit depends on capacity and price of the fuel gas. It normally varies from 3 to 5 years, without taking into consideration the reduction in environmental pollution (hydrocarbons, SO_2, noise and light).

4. THE FUTURE SCOPE FOR CLEANER PETROCHEMICAL TECHNOLOGIES

Recent events have raised the issue of safety and emergency awareness and preparedness of people in all nations of the world. Industrial events caused serious damage to the environment and unacceptable loss of life and property, such as:

- Dioxin containing release in Sevesso, 1976;
- Propane explosion in Mexico City, in 1984;
- Release of methylisocyanate at Bhopal, in 1984;
- Fire and discharge of contaminated waters in Rhine, in 1986, from a warehouse in Bassel.

Is is now universally acknowledged that every disaster, no matter the cause, has an environmental impact. In 1986, following various industrial accidents that occurred in both highly industrialized and developing countries, resulting in adverse impacts on the environment, the UNEP suggested a series of measures to help governments, particularly of developing countries, to minimize the occurrence and harmful effects of chemical accidents and emergencies.

In this context, the UNEP Industry and Environment Office has developed a handbook on "Awareness and Preparedness for Emergencies at Local Level"(APELL), designed to assist decision-makers and technical personnel in improving community awareness of hazardous installations and in preparing response plans, should unexpected events at these installations endanger life, property and the environment.

APELL's overall goals are:

- Provide information to the concerned members of the community on the hazards involved in industrial operations in its neighbourhood and the measures taken to reduce these risks;
- Review- up-date or establish emergency response plans in the local area;
- Increase local industry involvement in community awareness and emergency response planning;
- Integrate industry emergency plans with local emergency response plans into one overall plan for the community to handle all types of emergencies;
- Involve members of the local community in the development, testing and implementation of the overall response plan.

Escalating environmental concerns in recent years have caused a proliferation of new environmental regulations, sometimes at the expense of sound energy policy. The environmental movement and consolidation of the petrochemical industry, has been and may well continue to be the dominant trends of the 1991-1995 period, affecting every sector of the petroleum, chemical and petrochemical industries (28).

It is imperative that the industry improve its performance with regard to product stewardship, plant safety, emissions and waste minimization. By the turn of the century, the chemical and petrochemical industry must produce less waste, reduce emissions drastically and operate even more safely than today and, just as importantly, the public must recogniz[illegible]g progress (28).

Indeed, 1991 begins a decade that [illegible] heralded as one of new environmental awareness. Apprehensions about man-induced global changes in the atmosphere and some recent tragic experiences with technological malfunctions such as human and environmental disaster at Bhopal, Chernobyl and Valdez have precipitated a strong current of public concern for the consequences of environmental deterioration. Other less tragic but still graphic events such as damage to the Black Forest or algae bloom in the Adriatic serve to reinforce the public sense of an environment in peril.

This concern has spawned organized groups that are effective in focusing media attention on environmental problems and in translating that attention into political action (28).

Great Britain's Parliament is expected to pass strict new environmental legislation applying measures of taxation to discourage industrial pollution.

The German Government is considering passage of an environmental liability law and an environmental penal law - both aimed at putting teeth into environmental regulation.

France has a new "plant vert" aimed at improving air and water quality and in Italy, the influence of the "Green List" on elections has resulted in the creation of a new Environmental Ministry and consideration of legislation to substantially improve air and water quality.

As Western Europe moves closer to 1992 and the unification of its markets, the European Community is attempting to standardize their environmental controls. In addition to focusing on the atmospheric ozone problem with an agreement to ban chloro-fluorocarbons by the end of the century, the European Community has regulations providing for the application of catalytic converts on medium and large size automobiles, and a total shift to lead-free gasoline.

Additionally, the European Community is developing regulation to cover hazardous waste disposal, volatile organic compounds and evaporative emissions. It is also examining the possible application of civil liability provisions to producers and disposer of chemical wastes.

While Pan-Asia cooperation and public advocacy have not been as strong a factor among the Pacific Rim nations, environmental and health concerns are having an impact on individual governmental actions in manu of those nations.

In Japan, advances have been made in energy efficiency and measures are being taken to sharply reduce particulate in diesel fuels. Stringent limitations have also been placed on sulphur, in oil fuels, causing Japan to pay a premium for law-sulphur, Asin crude and dramatically increase their imports of liquefied natural gas.

An active lead-fuel phasedown is under way in both Korea and Taiwan.

As for North America, clean air requirements are pressing a basic reformulation of petroleum-based fuels. Sulphur content in diesel is being reduced. Lower gasoline vapor pressures are being required, and the content of benzene and other aromatics in gasoline is being lowered. New US plant emission limitations reducing benzene release by 95% will require costly plant modifications.

The regulations aimed at controlling toxic pollutants will affect everything, from air and water emissions to sludge and waste disposal practices.

Environmentally driven fuel specifications will advance the production of reformulated fuels and alternative fuels such as methanol and compressed natural gas. Likewise, new requirements to lower hydrocarbon emissions from fossil fuel power generation plants will increase the demand in some markets for LNG. Large investments will be needed both to facilitate product changes in the industry and to meet new and existing environmental requirements.

Between now and the year 2000, costs of making technological changed driven by new industrial demands, together with costs of compliance for existing plants and facilities could exceed 120 billion US dollars, and this just for North America, Western Europe, Japan, Korea and Taiwan.

Then there will be capital demands for environmental compliance in other nations as well. Costs to upgrade and meet environmental quality control in Eastern Europe and the Soviet Union have been roughly estimated at 200 billion US dollars over the next two decades.

The prospects of nearly doubling worldwide capital requirements to satisfy environmental requirements may constitute its own "future shock" for the industry, its investors and consumers as well.

In Section 3 we examined the extent to which cleaner technologies had been adopted during the development of the petrochemical industry. In this section we assess the future scope for the development and adoption of cleaner technologies in petrochemical production and the constraints to this process.

We consider separately the future use of cleaner technologies with respect to:

- basic process technologies;
- recovery and recycle of unconverted feedstock and by-products;
- recovery and reuse/sale of by-products.

In the petrochemical products examined, only few could be said to have developed cleaner process options, although clearly the degree of reduction in emissions/wastes or energy/raw material requirements realized by these options varied considerably. So did the level of their adoption. It has also been pointed out that certain cleaner process options involved environmental trade-offs; for example reduction in difficult/toxic emissions may be achievable but sometimes at the expense of lower product yield.

Taking into consideration the petrochemical industry as a whole, considerable theoretical scope exists for further adoption of cleaner technologies, particularly in monomers synthesis and basic petrochemicals. The practical and economic reality may be different and, as it will be seen, is likely to vary considerably among petrochemicals.

In several of the larger petrochemical industry plants particularly those in more sensitive environmental situations, large and relatively sophisticated effluent treatment plants have been designed to receive emissions from several plant processes.

The existence of these treatment plants could well have some influence on whether or not cleaner technologies were selected in the future.

In the last 15 years the degree of recovery and recycle of by-products and unconverted feedstock, whether to the original process or to other processes in the same plant, has increased significantly in certain bulk chemical processes mostly petrochemical, polymer and organics production. In this sense the recycle of aqueous effluent can be considered a cleaner technology, although as certain contaminants build up in the recycle stream they have to be blend off and disposed of from time to time. Furthermore, in many large complex petrochemical plants there was an increase in the recycle of by-products.

Although the situation varies between the petrochemicals, it can be seen that for the case studies examined where future new capacity is being installed, overall there is a reasonable likehood that cleaner technologies will be adopted. However, as already stressed, local factors will play a strong influencing role in the particular process investment decision.

There is, however, undoubtedly considerable scope for furhter recovery/recycle of by-products and unconverted feedstocks.

The introduction of cleaner technologies in this form will take place:

- since they can be shown to be economic in terms of increased yields for given input of feedstock;
- because they offer lower cost alternatives to other waste disposal, emission treatment options;
- to comply with environmental controls when no other alternative exists.

However, even when the conditions listed in the preceding sub-section are potentially applicable, there may well be reluctance on the part of petrochemical companies to introduce such recovery/recycle systems for one or more of the following reasons:

- they may be seen as a high capital cost solution;
- uncertainty over whether potential increased yield will actually be achieved;
- general unfamiliarity with the processes;
- concern over contamination of desired end products with by-product derived impurities.

The theoretical scope for recovery and reuse/sale of by-products from the petrochemical industry is very large indeed.

The theoretical scope for recovery and reuse or sale (outside the plant) of organic by-products is also very considerable. Solvent recovery is the most widely practised non-in house recycle recovery method. The increase in energy costs has tipped the economic balance in favour of in house combustion of impure organic wastes versus purification/recovery of the organic by-product itself.

Constraints to recovery/resale are made of technical and economic factors and may be summarized as follows:

By-product purity. A major constraint to recovery and reuse/ sale of by-products has been in several instances the difficulty and associated costs of obtaining a product pure enough for the market. Such problems exist in certain plaster applications, and for ammonium sulphate when recovered from acrylonitrile/methyl methacrylate wastes to be used as a compound fertilizer ingredient.

Recovery costs. These may sometimes be very significant, as in acid concentration and certain recrystallization processes.

Costs of alternative raw material. The fact is that the cost of the alternative raw material is often not high enough for recovered by-product to be competitive. This is the situation with ammonium sulphate in most parts of the EEC and can be the case with sulphur (versus double contact SO_2 recovery). In the last few years, ammonium sulphate recovery economics have improved. The fluctuation in alternative raw material prices adds to the uncertainty of sufficient economic return being achieved in by-product recovery.

Location of plant in relation to market. Transport costs of the by-product to market outlets can be a critical element in influencing the economics of recovery/reuse of by-products.

Shortage of capital funds. Investment in plant capacity for by-product recovery often assumes low priority in competing for limited available investment funds.

In spite of the fact, recovery of many by-products for reuse is already a much studied subject, and the petrochemical industry is mostly well aware of the potential opportunities (and constraints) to this application of cleaner technologies, its significance in relation to reducing waste emissions is such as to warrant continual review.

Destruction of volatile organic compounds via catalytic incineration is used by a variety of industrial sources. Several catalyst formulations are sold for this purpose (platinum or palladium predominate), used in fixed bed or fluid bed systems.

These systems were distributed across the following industrial categories:

- solvent/coating application and drying:	60%
- organic chemical and petrochemical production:	15%
- miscellaneous processes	25% .

Results from study provide data showing effect of incinerator operating conditions and volatile organic compounds, waste gas characteristics on compound specific and overall mixture destruction efficiency (29).

5. ELEMENTS OF ECONOMIC ISSUES

Recycling and low waste technologies do not only decrease the environmental impacts of industrialization and hence development, but they usually also cut down the energy consumption of the process, hence additional economic and environmental advantages. Through recycling and low waste technologies we are approaching the cycle of energy and matter in nature, which takes place with minimum energy consumption and least environmental impacts.

A comprehensive cost/benefit analysis would give us a true account of the advantages of recycling and low waste technologies. But, unfortunately, these cannot be undertaken in every case because many of the environmental benefits of these technologies are long-term ones and it is usually difficult, if not impossible, to express all the environmental benefits in terms of money.

From an economic perspective one may summarize the state of the art in the analytical handling of risk management of environmental hazards. Economic theory is not able to provide general solutions given the present state of knowledge. Economists are groping for solutions of special cases and trying to overcome the difficulties involved. It is conceivable that is no general solution to the design problem in the face of uncertainty.

5.1. Recycling

Where recycling is the main solution, an entrepreneur will not undertake recycling unless his expected benefits are greater than predictable costs. Recycling costs include: energy, virgin materials, capital cost, operating costs, disposal of residues, storage and transportation.

Energy costs are an important variable and if for a given waste material requires large inputs of energy, this cost may become crucial in the decision whether or not to recycle. The most important factor here is whether the market price of a unit of untreated waste material is higher than the costs of energy required for its collection.

The cost of processing waste materials is particularly important among the operating costs of the recycling industry, which has some components such as:

- endogenous component derived from whatever production process is selected;
- exogenous component; additives, auxiliary materials (e.g. additives in lubricating oils have led to increases in recycling costs);
- other operating costs: labour, materials.

Available technologies affect the decision to recycle if if these technologies can improve the quality of the final product, could narrow the price gap between new and recycled materials.

Credit conditions available to recyclers are affected by the general political and economic situation and significantly influence the decision to start or expand recycling activities.

The costs of residues recovery depends in part upon the type and degree of contamination they have sustained. Furthermore, the type of resource will influence the decision as to reuse. Finally, effluent charges, fines, taxes or regulations about residues not recycled but discharged into the environment can directly increase the operating costs. If available technology can produce substitute for virgin products, then the price difference will be the primary criterion for recycling operation.

5.2. Anaerobic fermentation of sewage sludge

Anaerobic fermentation is not a new idea. The waste material, sewage sludge, is pumped into an airtight digester, where it is heated to 35°C and mixed with the material already present. The bacteria in the digester decompose the feed material producing methane, carbon dioxide and small amounts of other gases. The main factors affecting the economics of anaerobic digestion are the cost of the digester, the alternative cost of treating the sewage sludge and the value of biogas.

A sewage sludge digester of 4,000 m^3 will produce annually about 2,400,000 Nm^3 biogas, the net power of which is equivalent to 1120 kwh heat and about 675 kw of electricity.

In comparison with conventional fuels, biogas is considered a clean source, because it produces about 1/3 of the coal and oil cycles respectively, for the generation of the same amount of electricity. It also produces no particulates and about 1/3 the NOx of the coal, oil and natural gas cycle.

If the sewage sludge is not treated in a biogas plant, it should be treated in a biochemical plant; then the current cost of constructing such a plant is little higher than the biogas alternative.

5.3. Anaerobic fermentation of organic industrial waste

Petrochemistry, textile, leather and food production produce a great deal of waste containing organic substances. In many countries the legislation does not allow storing of this kind of waste without stabilization of sludge, which is normally done by neutralization, compusturing or burning. The above mentioned method of stabilization has the disadvantage of wasting the vast amount of energy of the sludge. In some countries it has been calculated that in this way an amount of energy corresponding even to 10% of the whole energy supply of the country is left unutilized.

The methane fermentor consists of one or more units, basins, stirrer, necessary armature and measuring instruments. In the process the volume of the organic substances diminishes up to 90% About 15% of the produced energy is needed by the fermentor itself. This results in small digester volume and simple, compact construction.

The process has low service costs and is adaptable on large scale. Apart from environmental advantages considerable cost savings are achieved in view of eliminating the stabilization or neutralization process used in case of conventional technology.

5.4. Fuel gas desulphurization

A considerable part of the air polluting sulphur dioxide emissions originates from coal and oil firing. There are several different processes available of which:

- regenerative methods sulphur dioxide utilized as sulphuric acid for making fertilizers;
- non-regenerative methods, producing calcium sulphate and calcium sulphite.

Most of plants operating in the world belong to the last method, which is typically chemical process, including several process phases and handling of solutions and sludges.

The most important raw material is limestone, needed for one tone of sulphur about 4-6 tons, consumptions of electricity o,2 kw/Mw and process water $60m^3$/Gwh. The investment costs of the low waste technology is about 320 US dollars/Mw heat of the output power.

The content of NOx in flue gases is fairly low thanks to the low combustion temperature of the fluidized bed boiler (850-900°C). Practically, there no thermal NOx develops at all. The NOx developing from air also remains small, in comparison with conventional boiler, A survey of present knowledge has shown that one of the promising method to reduce NOx-emission is the application of staged combustion at individual burners, the so-called "burner staging".

"Burner staging" involves mixing the fuel with only a part of the combustion air, so that initial reaction takes place under fuel-rich conditions and combustion is completed as the remainder of the air is mixed with the combustion products. By this process, fuel NO formation can be restricted in the primary oxygen-deficient combustion zone. About 30% of NOx could be reduced using the low-waste technology, but the necessary savings due to this production in NOx emission are difficult to estimate.

5.5. Petrochemical production

Any attempt to understand the likehood, or otherwise of available cleaner technologies being adopted in the future, requires an appreciation of the principal factors likely to influence the petrochemical industry.

The principal factors that enter into process investment decision-making are shown in figure 5.1, while the net effect of economic factors is almost certainly the principal influence on process technology selection, other factors also directly influence the decision.

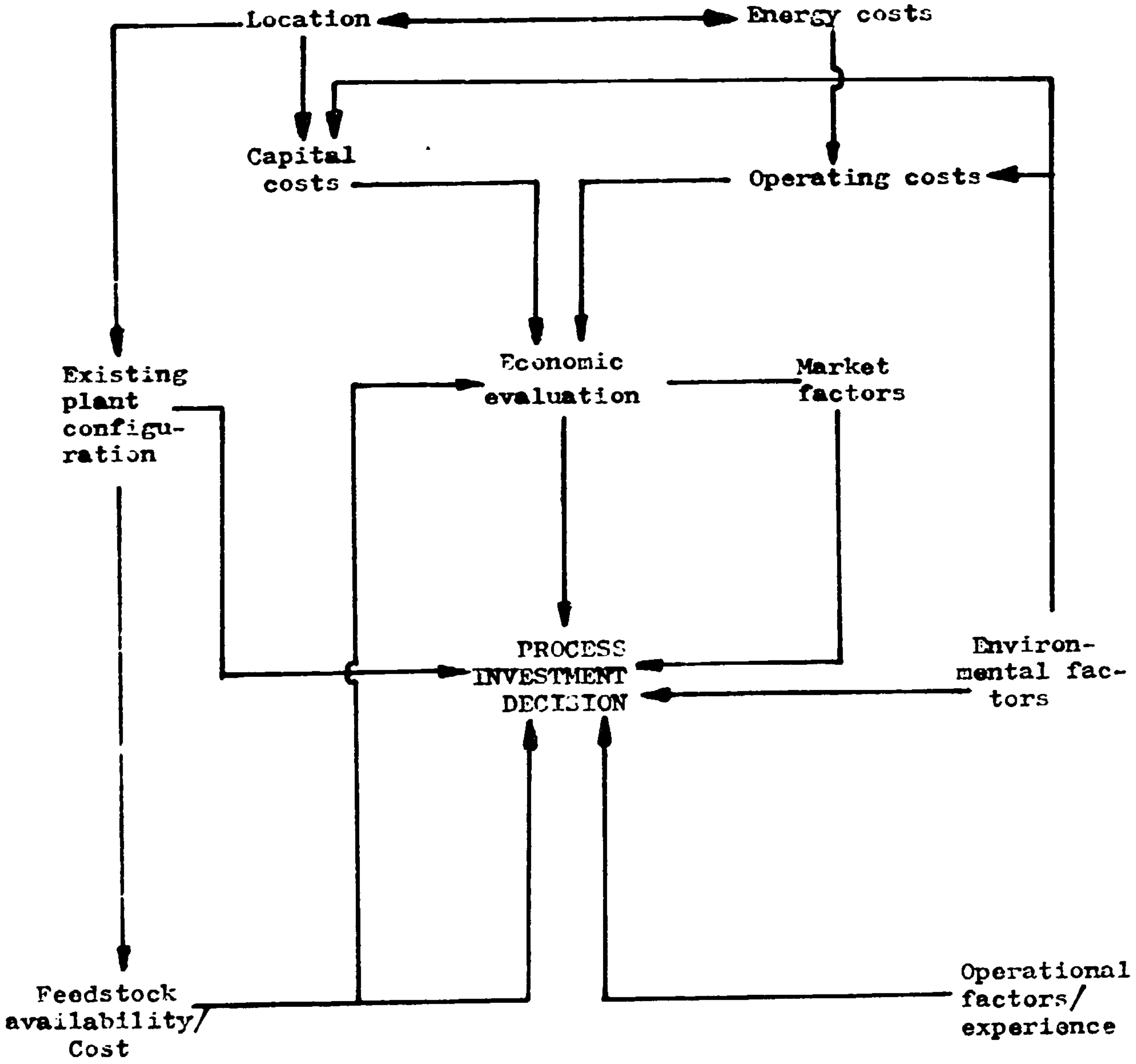


Figure 5.1 - Factors influencing petrochemical production

The particular situation, the petrochemical involved and the process options available will determine the relative weight of the influencing factors including environmental considerations. Environmental factors more often influence the decision indirectly because of their capital/operating cost implications, rather than directly. It can often be the case that this indirect influence is not very strong.

The following sub-sections discuss the manner in which the factors identified can bear upon the selection of the basic process technology.

Capital Costs

The relative importance of capital costs to overall manufacturing costs will depend, among other things, upon:

- plant size;
- sophistication/type of plant;
- new or existing site;
- environmental control regulations.

Plant size.

A crucial factor in influencing the development of process technologies has been the desire to achieve economies of scale, although it has been recognized that optimum size for plant capacity exist. Some process technologies, usually gaseous rather than liquid phase, lend themselves more easily to scale up (or expansion at a future date). These may be cleaner technologies, but not necessarily.

Another point is the importance of plant size with respect to the economies of scale, of emission/effluent treatment plant. This, in turn, will influence the apparent need to install cleaner technologies.

Type of plant

The type of plant, the number of stages, sophistication etc. will determine the overal cost of bulk chemical manufacture.

Location

The location of the plant will affect its capital cost in terms of local construction costs, and the level of grants/fiscal incentives available. But probably even more cost influence is whether construction takes plane on a new or existing site. The usually higher costs of building process plant on greenfield sites tends to favour construction of a new process plant on existing sites, where this is possible. This, in turn, introduces the important factor of the existing plant configuration, which will be discussed.

Environmental controls

Stricter environmental controls normally tend to increase the capital cost of process plant and in this way can indirectly influence the selection of process technology.

Operating Costs

Such costs can vary considerably between process options. The cost of environmental controls or waste disposal can sometimes be sufficient to influence the selection or process technology. Other elements of operating costs are discussed in the following subsections.

Although a capital intensive industry, the influence of labour costs on total petrochemical production costs should not be underestimated.

Catalyst Costs

The consumption of catalysts by the petrochemical industry is in itself an issue within the ambit of clean technologies, particularly where the material is a rare/precious metal, e.g. silver, platinum. The rarity of the catalyst raw material is, of course, reflected in its price.

Generally speaking, the benefit of increased yield/reduced operating costs conferred by catalysts considerably outweighs their costs, even when catalyst costs are high and life time is relatively short. In other words, normal petrochemical industry response to economic forces is unlikely to lead to adoption of process technologies using less rare catalyst raw materials. Nevertheless, where economically justified, operating practices will be geared to prolonging catalyst life, which will include protection from catalyst poisons.

Market Factors

Apart from having some, but by no means overriding, influence on the location of new bulk chemical process plant capacity, market factors can occasionally influence the choice of process technology in other respects. This may be a force acting either for or against the adoption of cleaner process technologies. For example:

The lower energy VCM suspension process cannot meet all market specifications required for the product.

The food industry required PVC producers to lower the VCM content of certain PVC packaging materials.

Indeed, the purity issue is undoubtedly a constraint to the market saleability of certain by-products.

Existing Plant Configuration

It has already been noted that petrochemical companies experience considerable economic advantages in expanding or building new petrochemical production capacity on existing rather than green fields sites. These advantages stem from:

- lower site preparation/off-site costs;
- lower overheads, cost of support infrastructure/services;
- often local availability of feedstocks.

The process plant already installed on the site usually exerts strong direct, as well as indirect influence on the process technology selected in the building of new petrochemical capacity. This may derive from one or more of the following reasons:

- type of feedstock available;
- local outlets for by products;
- existing spare capacity for by-product/waste/effluent treatment;
- size of new plant defined by other process capacities.

With regard to the last point, the design of existing plant may be such as to allow increased capacity to be gained through a de-bottlenecking operation rather than the building of a new train of process plants.

The net result of these factors on the selection of new process plant is a tendency to go on using the process technology already employed, unless there are other overriding economic or possibly environmental determinants. This tendency may be reinforced by operational factors whereby a company's successful working experience with one process technology will naturally incline towards persisting with the same technology. There may also be saving on process lincense fees.

The factors mentioned above do not only influence selection of process technologies for new capacity within a single plant. Because of the size of new plant capacities, large chemical companies plan their manufacturing operations on a national and usually an international level. Therefore, although feedstocks for one process may not be available in the same plant, it could be imported from another plant within the group. The same point can occasionally apply to the use of by-products as well.

An attempt to illustrate the expected situation in the year 2000, compared with the year 1986, regarding total amount of petrochemical wastes and its destination could be the following:

	1986 (%)	2000 (%)
Landfill	55	10
Incineration	10	25
Useful application	15	25
Reuse in the process	20	35
Quantitative prevention	-	5
	100	100

As it can be seen, in the year 2000 it could be:

- an increase in the reuse and useful application of waste from 35% to 60%;
- a decrease in the percentage of waste being landfilled from 55% to only 10%;
- a decrease of 5% in the total amount of waste.

From these figures the conclusion can be drawn that the key element in a strategy aimed at prevention and recycling of waste is the "hidden factor" of improving the process and waste quality, leading to a great increase in the percentage of waste that can be recycled.

An attempt to illustrate the expected situation for packaging materials could be the following:

	1986 (%)	2000 (%)
Landfill	50	-
Incineration	25	40
Reuse	25	60
	100	100

Possible measures and activities:

Harmful materials such as heavy metals and PVC must disappear within 5 years for certain applications.

The returned bottles ensure recycling for: PE, PET, PVC or PC

- Codes of practice on gelislation to be drawn up;
- Standardize/certify plastics to be recirculated;
- Forbid application of certain materials in plastics fillers: heavy metals.

The cost of construction of a new petrochemical processing plant usually will require that approximately 5 to 10 percent of the capital investment be in pollution control facilities. However, in the existing facilities it is frequently possible to make modification in the processes or install pollution control equipment that will recover the cost in a relatively short period of time.

6. INDUSTRIAL POLLUTION CONTROL IN DEVELOPING COUNTRIES

Governments of developing countries may have become aware of the vast amount of pollution and environmental control legislation which has been enacted in recent years.

However, if Governments of developing countries feel overwhelmed with the current growth of control legislation, and are finding it difficult to relate this to the limited amount of resources (both financial and technical) which they have available for pollution control, then, they may wish to concentrate their efforts on the major sources of pollution. These are most likely to be industrial installations involved with the processing of foodstuffs and the production of chemicals.

It is most important that Governments should encourage the co-operation of Industry in this matter because Industry is the main source of knowledge about its processes. This co-operation should start at the design stage of a project. One way to ensure this happens is to see that industrial control proposals are discussed when applications for industrial development licences are presented. This can be arranged by including a section on pollution control in the licence application. In this way when application has been made, projects managers/consultants can be invited to discuss their proposals for controlling the wastes likely to be produced.

These discussions should cover: gaseous emissions, liquid discharges, solid wastes disposal, control of factory atmospheres and plant safety, risk assessment.

Any form of pollution control must be capable of allowing discussion between Government technical staff and project engineers. Following these discussions the control procedures imposed by Governments should have taken into consideration the following:

a. Practical Aspects - Conditions of discharge must be related to the performance characteristics of the pollution control equipment available at the plant design stage.

b. Financial Aspects - Some regard must be paid to the cost of the proposed pollution control requirements. If Governments of Developing Countries are anxious to encourage new industries, this may be difficult to achieve if the cost of the pollution control equipment they require is as much as the rest of the plant.

c. Flexibility - The Control Authority should be able to study each application on it's own merits. It should be able to vary requirements according to the size and location of the project.

The information required from Developers can be obtained in the form of a questionnaire attached to an application for licence to build, such as:

General - Type of Product, quantity; Raw materials, quantity (degree of toxicity); Applicants to submit site layouts, flow sheets and Mass balance of processes involved.

Air Emmissions - Provide details of the flow and composition of exhaust gases, giving proposals for methods of treatment, including monitoring equipment.

Liquid Wastes - Provide details of flow and composition of liquid wastes (including an estimate of water consumption), giving proposals for methods of treatment and disposal.

Solid Wastes - Provide information on the amount of solid wastes and their composition. If there are likely to be toxic and hazardous materials, give proposals for rendering harmless.

Re-use/Recycling - Request information on methods to be used for conserving water and re-using waste materials. Obtain information on the possible uses of by-products.

Factory Atmospheres and Plant Safety - Give information on noise levels, temperature and ventilation, lighting and fire protection arrangements for the factory. Provide details of staffing, staff protection equipment, staff welfare (including number of toilets, wash basins, canteens, etc.) and medical supervision.

6.1. Control Procedure

On the basis of information submitted and discussions with the project engineers/consultants, etc. recommendations can be drawn up and attached to any Government approval document enabling the Developer to proceed with the purchase and erection of the installation. Approval is usually given subject to the Developer's complying with the pollution control recommendations. By this means the pollution control requirements are regarded as an integral part of the project and the pollution control equipment cost included in the initial capital cost of the project.

On completion of the erection of the plant, the Developer could then be required to apply for a licence to commence manufacture. Or, if the plant is located in an industrial estate or on Government-owned land the lease agreement could be extended to cover this additional control. The purpose of this is to provide the pollution control staff with the opportunity to check that the recommendations made in the original licence have been complied with. The pollution control requirements for the operation of the plant, including the expected composition of discharges can then be stated.

It is of the utmost importance that once pollution control equipment has been installed, it should be regarded as part of the production process. It should remain in operation whenever the plant is running and should be regularly maintained. It will be for the Government technical staff to ensure their monitoring procedures are adequate and that factory managers are made aware of any shortcomings in plant performance. In cases of persistent disregard by factory managers to pollution control matters, Government officers should be able to request closure of factories until errors have been rectified.

6.2. Pollution Control Processes and Equipment

The pollution control procedures suggested require the involvement of technical personnel for their implementation. They are particularly important in the initial stages of a project if sound working relationships with project engineers and consultants are to be established. Pollution control staff in developing countries may find it useful to have some information on the types of treatment processes and equipment which they are likely to encounter during the course of their work. Accordingly, the rest of the paper describes some of the processes available, together with some guidelines as to their performance characteristics.

6.2.1. Processes for Treating Gaseous Emissions

A. Dry Processes

1. Chimney Stacks - The height required for a particular chimney will be dependent on the nature, temperature and velocity of the exit gases. It will also be necessary to take into consideration the local weather conditions. The objective must be to prevent the emission being directed downwards to ground level, especially in populated areas. If temperature inversion layers are a regular feature of local meteorological conditions, then all practical steps should be taken to direct the emission above this layer.

2. Dust and Grit Separation - If it is necessary to remove dust and grit from gaseous emissions there are several types of equipment available. Gravity Settlement Chambers are designed to reduce the velocity of the gases so that heavy coarse particles can separate out by falling into a collecting hopper.

These chambers are capable of removing particles in excess of 150 microns with an efficiency of about 50%. The introduction of Baffle Chambers, in which particles collide with baffles, cause them to lose momentum. They then slide down the baffle into the hopper. The use of baffles permits the use of higher gas velocities (up to three times those for gravity settlement chambers) with a proportional reduction in the size of equipment. Impingement Separators consist of a number of baffles (trapezoidal in section) which can be fitted into an existing duct if necessary. They are capable of separating particulate matter down to 10-20 microns with an efficiency of 90%. They can be operated at velocities up to 30 metres per second with a pressure drop of about 37.5 mm water gauge.

3. Cyclones - The gaseous emissions are fed into the cylinder tangentially at the top. They then spiral downwards and are discharged via a vertical tube fitted in the lid of the cylinder. Cyclones can collect solids down to 10-20 microns in size with an efficiency of 85%. They can be operated at gas velocities of up to 15-30 metres per second (100 mm water gauge pressure drop) at high pressures and temperatures (up to 1000°C).

4. Bag Filters - They consist of a number of tubular fabric bags suspended in a suitable container. Gases are blown into the bags (velocity range 0.005-0.1m per second) when the particles are retained in the interstices of the fabric. As the layer of solids builds up, the pressure drop across the fabric increases. When the operation of the filter becomes impaired by the increase in pressure drop, it is taken off-stream automatically and the bags are cleaned by shaking the solids into a hopper situated in the base of the equipment. Bag filters can

operate up to 250°C (depending on the type of fabric used) and can remove solids down to 0.2 microns in size with an efficiency of 99%.

5. Electrostatic Precipitators - these are used when the temperature and corrosivity of the gaseous emission renders if unsuitable for treatment by the use of bag filters. The gases are passed between plate electrodes set 100 mm apart. In between the plates are wire electrodes carrying a high D.C. voltage (30-60 kV) and the dust particles acquire an electrical charge. They migrate to the collecting plates and are removed periodically by vibration. Electrostatic precipitators require a gas velocity in the range 0.5-3 metres per second, the electrical resistivity of the dust to be within 10^4-10^{10} Ohm per centimetre. They are capable of producing a removal efficiency of 99% and of collecting particles down to 2 microns in size.

B. Wet Processes

1. Gravity Spray Scrubbers - The waste gases are passed into a cylinder fitted with water sprays. The dust is captured by the falling water droplets and is collected in the hopper below. This method is capable of removing particles down to 10 microns with an efficiency of 70%. The exit velocity of the "cleaned" waste gas has to be kept below 6 metres per second to prevent the entrainment of water droplets.

2. Gravity Packed Tower Scrubbers - In this equipment the waste gases are passed up a cylinder containing suitable packing material , down which the liquid phase trickles. This process is more suitable for dilute dust suspensions (to avoid undue blockage of the interstices of the packing) it can re-

move particles down to 5 microns with an efficiency of 90%.

3. Venturi-type Scrubbers- These can exist in two forms; in one the waste gas passes through the Venturi and water is drawn in at the Venturi throat. Turbulent mixing occurs and the mixture then enters a cyclone unit for separation.In the other form water is pumped through the Venturi and the waste gas is drawn in at right angles to the flow at the throat. The mixture passes down into a separation chamber and the cleaned gases exit through a vent in the top. Both methods are capable of removing sub-micron sized particles (down to 0.5 micron) with a maximum removal efficiency of 90-99%.

4. Biological Scrubbers - These can be used in either of two forms. Biological Sprays are gravity spray type units in which the liquid spray contains a biological activated sludge. This system has been used for removing 80-90% of solvents present in waste air emissions from paint-spraying operations

Biological Filters are packed-bed scrubbers in which the packing can be peat or soil. They are capable of removing odours, sulphur dioxide and oxides of nitrogen and have been used for treating emissions from rendering plants and maggot farms.

6.2.2. Processes for Dealing with Liquid Discharges

Any liquid discharge from an industrial installation must be of such volume and composition that no damage is done to the sewer fabric nor should it cause any deterioration to the operation of the sewage treatment works. If the factory waste is intended to be discharged to a river, then it should not cause damage to the flora and the fauna.

If it is not possible to discharge liquid wastes directly to a public sewer then the following processes may be required to render the wastes suitable for discharge.

Physico/Chemical Processes

1. Flotation - In this process, particles less dense than water are collected in tanks from which they are removed by scraping the liquid surface. The removal of oils can be improved by allowing the waste to flow between inclined plates. The process can also be enhanced by releasing fine bubbles of compressed air at the base of the flotation tank.

2. Sedimentation - This involves the separation of suspended solids by reduction of waste flow velocity. The process is independent of the shape of the settlement vessel but these are usually rectangular or circular. They are fitted with equipment to remove the solids on a continuous basis, if the quantities involved warrant it. Chemical additives can be used to accelerate the settling rate, and to precipitate dissolved toxic metals. Suspended **solids** removal efficiency is usually about 60% (dependent on density and particle size) and this can be increased to 90-95% with the use of chemical flocculants.

Aerobic Biological Processes

These processes are carried out using aerobic micro-organisms, which assimilate carbon (present in the organic chemicals), nitrogen, phosphorus, sulphur and other trace elements present in the liquid wastes. In addition they require oxygen to complete the oxidation of the organic matter, with the production of new cells and the release of carbon dioxide, water, etc. There is a wide range of aeration/mixing devices available to provide the oxygen requirement and these can be collected into three groups.

1. Bubble Aerators - These include "fine bubble" (porous diffusers) "coarse bubble" (non-porous diffusers) and large bubble devices. "Fine bubble" diffusers have, for many years, been made from grains of silicon dioxide supported on a ceramic binder. More recent types have been manufactured from plastic-wrapped tubes and non-clog rubber. They have high aeration efficiencies (up to 2.2 kg /kWh) but are dependent on having a very clean air supply.

"Coarse bubble" aerators, are iin essence, perforated pipes with or without some form of non-return valve. The size of hole is not critical, as no oxygen transfer occurs at bubble formation. The degree of oxygen transfer is dependent on the length of time the bubbles remain in suspension.

A "Large bubble" device, which is also an efficient mixer, consists of a sunken chamber continuously filled with air. When the chamber is full, a large bubble is released up a vertical tube (drawing in tank liquors behind) to the tank or lake surface.

2. Mechanical Aerators - This type of aerator is basi-

cally a specially designed stirrer which rotates just below the surface of the liquid waste and is maintained in the optimum operating position by supports mounted on floats or by being attached to a rigid platform.

3. Fixed Bed Aerators - In the case of fixed bed aerators (historically known as trickling filters) the waste liquors and air pass over the micro-organisms which are retained on a support medium. In the past this supporting medium was inert inorganic material (for example basic slag, clinker, gravel,etc) but in recent years many forms of plastic supports have been produced. They have been found to be particularly effective in treating wastes from food processing factories,breweries, fermentation processes and chemical plants.

Anaerobic Biological Process

In the aerobic process the end products are carbon dioxide and bio mass. With the anaerobic process the main product of interest is methane (with smaller quantities of carbon dioxide and bio mass) and this can be used as an alternative fuel. The optimum temperature for this fermentation process is 33-38°C and the gas production that can be expected is in the range 0.26-0.5 m^3/kg C.O.D. applied, with a C.O.D. removal of 85-95%.

Processes for Dealing with Solid Waste Disposal

For the purpose of this paper the solid wastes likely to arise from industrial installations have been divided into the following three groups: Sludges produced during plant operations, non-hazardous wastes, hazardous wastes.

1. Sludges - There are several types of dewatering equipment available. Plate and Frame presses dewater the sludges through woven filter cloth, usually under a pressure of 6-7 bars. The resulting filter cake is likely to contain 50-60% moisture and will be in a suitable form for transportation. Rotary Vacuum Filters consist of a revolving drum fitted with a suitable filter cloth, and this is half submerged in a tank containing the sludge suspension. As the drum rotates, vacuum is applied and liquid is drawn through the filter cloth into the drum. Belt Presses are a more recent development and these provide a draining period (during which most of the liquid is removed) prior to pressing the sludge between rollers. Unlike the plate and frame presses, the belt presses operate continuously. They are capable of producing pressed cake with solids' concentration in the range 30-50%.

Centrifuges (both horizontal and vertical bowl types) are available for sludge dewatering applications, but they seem to be preferred for the dewatering of crystalline sludges. They have been used for the dewatering of biological sludges but floc breakdown can occur, due to shearing forces, when the feed makes contact with the centrifuge bowl.

2. Non-hazardous Wastes - Landfill Sites, whether in the control of the Local Community or Industry, require to be correctly designed before use. Initial surveys should be made to locate a suitable site. They should be sealed with an impervious layer (for example clay or suitable plastics) and a drainage system laid to collect any leachate. Any liquors draining

from tips will be highly polluting and will require treatment before discharge to rivers, etc.

3. Hazardous Wastes - These are likely to be only a small proportion of the total solid wastes requiring disposal. It has already been suggested that Industry should be responsible for dealing with all its hazardous wastes and that it should de-toxify them before releasing them outside its jurisdiction. In cases where it is not feasible to de-toxify hazardous wastes chemically, it may be necessary to resort to incineration. It may be possible to arrange to have wastes burnt in a nearby kiln (for example at a cement works). If not, a suitable incinerator will be required.

6.3. Plant Safety

1. Identification Systems - Considerable effort has been made in recent years to avoid confusion in the labelling of chemicals etc. There are now internationally recognised markings which should be used. Hazard Warning Signs should be fixed to all chemical containers so that the nature of the contents can be readily seen. Road tankers should be labelled in sufficient detail (for example, with HAZCHEM markings) to enable their contents to be safely handled by rescue workers in an emergency. Pipelines and Gas Cylinder Identification should be carried out using an internationally recognised colour code scheme and copies of the colour code in use should be displayed at suitable sites in the factory. Chemical Packaging should show visual warnings as well as written information to indicate any dangerous properties they may have, together with handling instructions.

2. Safety Equipment - Fire extinguishers will be selected for different duties (for example non-water types for use where electrical equipment is involved).

Breathing Apparatus will be required where potentially toxic atmospheres could occur.

Fire and Hazardous Gas Alarms both visual and audible, together with emergency lighting and exit indicators will also be required. It will be necessary to ensure that all safety equipment is regularly maintained and inspected and, in some countries, the local fire authority will carry out this work.

3. Training - All staff must receive training in the operation of all safety equipment and in plant process operations. This training is usually given by the equipment suppliers or plant commissioning engineers. It will be for the pollution control staff to ensure training is carried out to their satisfaction.

4. Storage - The storage facilities for raw materials and finished products should also be established at the design stage. There are labelling systems in use (for example one devised by the London Fire Brigade) and these should be adhered to, to prevent the adverse accidental reaction of non-compatible materials. Warehouses should have sprinkler systems installed (or inert gas systems) where inflammable substances are likely to be stored. Drainage from warehouses, or external storage areas (including tanker unloading and cleaning points) shouls be directed to emergency holding tanks or basins so that any dangerous chemicals can be rendered harmless before removal from site

6.4. Monitoring Procedures

The paper has endeavoured to show the need for pollution control to commence at the design and planning stages of industrial development. It has suggested that this work should be carried out by technical personnel, possible a small team with a combined experience of all aspects of industrial process design and operation.

Once an industrial plant has been commissioned, the main concern for the pollution control team is to see that the pollution control equipment and monitoring apparatus is properly calibrated and maintained. This aspect of the work must be taken very seriously, especially by plant managements,in view of the major factory accidents which have occured recently. The monitoring team will have to make regular, unannounced visits to establish the plant is being run correctly, and to offer advice.

With regard to monitoring factory atmospheres, this can be carried out using field testing kits in the first instance. There is portable equipment available for the measurement of temperature and humidity, noise, and the semiquantatative analysis of trace chemicals in air.

The monitoring team should also attend regular test runs of standby safety equipment (for example the testing of "cut-in" arrangements for standby Diesel electric generators for fire-fighting purposes). These commence operation automatically in the case of failure in the mains power supply. They should also witness the testing of safety gas scrubbing equipment such as the type installed to "neutralise" the accidental release of toxic gases (for example chlorine).

It is firmly believed that a small knowledgeable monitoring team, read to help and advise, rather than concentrating on the implementation of the fine detail of legislation, is likely to promote the respect of and obtain a fuller co-operation with Industry.

7. List of Manufactures

1. Kaldair Limited - Process Combustion Product and Services Profile, Pyrene House Staines Road West Sunbury-on-Thames Middlesex TW 167 A.L. Fax 093276 1375 - England
    a. Incineration: submerged combustion systems, rotary kilns, effluent treatment, scrubber systems for ermission control waste heat recovery, acid recovery
    b. vaporisation: heaters for direct or indirect vaporisation of low temperature fluids such as LNG, nitrogen, oxygen and LPG
    c. process heating: high-efficiency packaged heaters for all process heating applications
    d. service: Kaldair-Thurley offer a complete turn-key solution to Clients for process combustion requirements.

2. A.B.B. Lummus Crest GmbH - Germany
    a. Flare gases
    b. Safety valves
    c. Seal oil systems
    d. Recovery system

    Ludenstr. nn, D-W-6800 Manheim Fax (0621)3.88.26.58

3. Simmering-Graz-Pauker A.G. Brehmstrasse 16, A-1110 Wien Paukerwerk Siemensstrasse 89, A 1210 Wien, Tel (0222)252525 Fax 11 41 13 S6P

    Fluidized bed - combustion systems plant. Design based on practical experience. The fluidized bed system is basically suitable for the most varied fuels and has advantages: lower emissions than with steady-state process, higher burn-up rate due to the intense contact between fuel and oxygen and longer residuence time, economical application above 80 MW (thermal).

4. Petrodesign S.A. Bucharest, Căderea Bastiliei 56-58,
Romania - Fax 12 00 93
Flare gases, safety valves, seal oil systems, recovery systems, tanks, instruments. Turn-key services.

5. Krauss Maffei - Process equipment for environmental protection: centrifuges, filters, mixing equipment, centrifugal evaporators, reactors, liquid-solid separation lines, microprocessor controls.
Krauss-Maffei str. 2 D-W-8000 Munchen 50, Germany
Fax (089) 88993299

6. Alfa-Laval Industrie GmbH : centrifuges, plate heat exchangers, spiral heat exchangers, decanters, separators.
Wilhelm-Bergner-Str.1, D-W-2056 Glindeb-Hamburg.
Fax (040)72.70.15.15 Germany

7. Aerob Entestaubungsanlagen GmbH
Production and sale of dedusting installations, fibrons filters, with pneumatic and mechanic blowing-off for the removal of all dustlike products and the disposal of noxious matter in chemical production.
Voith str. 5, P.O.Box 12.24 D.W.7253 Renningen 2
Fax (07159)79.33 - Germany

8. Maschinenfabrik Karl Brieden GmbH - cooling water treatment units, filters systems for fluids, automatic backwash filters with "breathing filter elements".
Ettersheide 64, D.W.4630 Bochum 5 Fax (0234)41.71.106
Germany

9. B.S.-B Safety Systems Limited
Relief devices for the protection of personnel and plant.
Center House, 68 Sheen lane, London SW 148 LP, G.B.
Fax (071)8760573

10. Degussa A.G. Processes for the removal of SO_2, NO_x, H_2S and formaldehyde from waste gas and stack gas. Purification of drinking water, industrial and pool water with chlorine dioxide, to efficiently disinfect without the formation of chlorinated organic compounds. Detoxification of waste water containing: cyanide, phenol derivates, hydrogen sulfide, sulfite, hypochlorite, formaldehyde, etc.
Weistrauestr. 9, D.W. 6000 Frankfurt 11, Fax (069)2 18 32 18
Germany

11. D.T.S. Wasser - Abwasser Technik GmbH
Construction of installations for the purification of sewage with chemical and physical processes such as: neutralisation detoxification, precipitation of metal hydroxides, purification of emulsions, ion exchange-circulation installations, thermal and chemical disinfecting installations.
Eschborner Landstr. 134-138, D.W. Frankfurt 94,
Fax (069)78903178 - Germany

12. Edeleanu Gesellschaft MBH
Design and construction of plants forthe petroleum, gas and petrochemical industries, engineering, procurement, construction, start-up, personnel training, licensing of processes.
Stresenmannallee 36, DW-6000 Frankfurt 70, Fax (069)182020
Germany

13. Enviro-chemie Abwassertechnik GmbH
Complete problem solutions for all industrial waste waters.
Eichbergstr. 1-3, DW.6100, Darmstadt, Fax (06151)293238
Germany

14. Hydro Air Research S.R.L.

Membrane process technology for ultrapure water and waste water treatment, ultrafiltration

Via Cesare Pavese 5-7, 1-20090 Zerbo di Opera (Milano)
Fax (02) 55500571 - Italy

15. Krupp Koppers GmbH

Design, engineering, supply and erection of industrial plants in the field of petroleum, petrochemicals, chemicals and environmental protection

Altendorferstr. 120, DW-4300, Essen 1, Fax (0201)8-282566
Germany

16. Krupp Mak Maschinenbau GmbH

Plasma technical plant for the treatment of toxic residues such as fine and filter dusts from incineration plants; plants for drying of oil and water containing impurities

Falckensteiner str. 2, DW-2300, Kiel 17, Fax (0431)39952193
Bochum - Germany

17. Monsanto Europe S.A. , Enviro-chem and Permea Division

Gas scrubbing equipment, hollow-fiber membrane separators for hydrogen recovery in refining and petrochemical processing and for CO_2/CH_4 separation.

270-272 Avenue de Tervuren, B-1150 Bruxells Fax (02)7614040

18. Passavant-Werke A.G.

Processes, machines, apparatus and complete plants for the treatment and purification of industrial water and waste water, using chemical and biological methods

DW-6209 Aarbergen 7, Fax (06120)282931 Germany

19. Steuler-Industriewerke GmbH

Environmental engineering: processes and installations for maintaining clear air and water

Georgh-Steulerstr. 175 , DW-5410 Hohr-Grenzhausen
Fax (02624)13339

20. Sulzer-Chemtech.

Process engineering plants for chemical and environmental engineering industries, oil and gas processing, refineries
CH-8404 Winterthur, Fax (052) 2620101 - Germany

21. Thermo Environmental Instruments

Ambient, source and toxic analyzers, pH/ORP/conductivity process monitoring.
Martenerstrasse 539, 4600 Dortmund 70, Fax (0231) 614097
Germany

22. Westfalia Separator A.G.

Centrifugal, separators, decanters, extractors, mixers, rotary brush strainers for waste water purfication
Werner-Habigstr. 1, DW-4740, Oelde, Fax (02522)772288
Germany

23. Prematechnik

Flare systems, low-pollutant combustion devices, low nox burner, measuring equipment
Rathenauplatz 2-8, DW-6000 Frankfurt 1, Fax (069)288020
Germany

24. KSB Aktiengeselschaft

Polution control and industrial technology for air, waste gas, gaseous media
Johann-Kleinstr. 9, DW-6710, Frankenthal, Fax (06233)863311
Germany

8. List of Research and Development Institutions

1. A.R.L. Applied Research Laboratories S.A.
   Pollution control measurement
   En Vallaire ouest c. CH 1024 - Ecublens
2. Bayer A.G.
   Pollution control, environmental protection technology of:
   weste water, waste air, solid waste
   Bayerwerk, D-W 5090 Leverkusen, Fax (0214)3.06.64.11
   Germany
3. Laboratorium Prof. Dr. Berthold
   Measurement of radioactivity, pollution control for petrochemical plants, environmental behaviour of substances
   Calmbacherstr. 22, DW-7547, Wildbad 1, Fax (07081)177166
   Germany
4. Biosens GmbH
   Pollution control - measurement services for: water, waste water, liquid media and sludges
   Richthofenstr. 29, DW-3200, Hildeshum, Fax (05121)55714
   Germany
5. C. Borp and Co. A.G.
   Pollution control and industrial technology
   Bachmannweg 20, CH-8046 Zurich, Fax (01)3711880
6. Bran + Luebbe GmbH
   Pollution control and industrial technology
   Werkstr. 4, DW-2000 , Norderstedt, Fax (040)32202444
   Germany

7. Brown-Boveri York

   Pollution control, industrial technology. Simulation of environmental conditions in the field of petrochemical industry

   Gottlieb-Daimlerstr. 6, D-6800, Hanheim, Fax (0621)468245

   Germany

8. Cavitron vom Hagen

   Pollution control and industrial technology

   Am Leveloh 9, DW-4322 Sprockhovel 1, Fax (02324)77300

   Germany

9. Chematur A.B.

   Pollution control and industrial technology. Air purification and solvent recovery.

   Baggangsvagen 43, S-69127, Karlskoga, Fax (0586)59450-Sweden

10. Corning Process Systems

    Pollution control and industrial technology

    Tilling drive, stone, stoffs st. 15 OBC, Fax (0785)818785

    England

11. Czecholsovak Academy of Sciences. Institute of Chemical Process Fundamentals. Prague Institute of Chemical Technology

    Pollution control, industrial technology for water, waste water liquid media and sludges

    Technicka 5, CS 166, 28 Praha 6, Dejvice, Fax (0422)3114769

12. Analytical Bio-Chemistry Laboratories Inc.

    Pollution control and industrial technology

    7200 East ABC Lan P.O.Box 1097, Columbia, S.U.A.

13. Pennsylvania State University

    Environmental protection technology

    University Park W.P. 00151 OP , U.S.A.

14. American Society for Microbiology
    Microbiological technology for environmental protection
    Washington D.C. , S.U.A., 1325, Massachusetts Avenue,
    D C 20005, 4171
15. Petrodesign S.A.
    Engineering for petrochemical technology, environmental protection and clean technology
    56-58 Căderea Bastiliei str., Bucharest, Fax 120093- Romania
16. Degussa A.G.
    Industrial technology for : air, waste gas, gaseous media purification
    Weisfrauenstr. 9, DW-6000, Frankfurt 11, Fax (069)2183218
17. Ecole Centrale Paris
    Research on depollution of effluents, methanogenic fermentation bacterial desulphurization, aerobic treatment for C^{14} effluents, dynamic simulation of petrochemical processes.
    F-92295 Chatenay-Malabry CEDEX , Fax (01)46836437 - France
18. Ecole Nationale Superieure d'Ingenieurs de Génie Chimique
    Pollution control and industrial technology for water, waste water liquid media and sludges
    Chemin de la Loge F-31078 Toulouse, CEDEX, Fax (0)65583861
    France
19. Fluid System Corporation
    Industrial technology for water, waste . Pollution control and industrial technology for water, waste industrial water, and sludges
    10054 Old Grove Road, San Diego, CA 92131, FAx (0619)6952176
    U.S.A.

20\. Hoechst Actiengesellschaft

Industrial technology for pollution control by air, waste gas, gaseous media, polymers for filter and sound absorber elements

Bruningstr. 50, DW-6230, Frankfurt 80, Fax (069)3665766

Germany

21\. Institute Francais du Petrole

Controlling pollution by vehicles, refining processes, additives improving the octane number of gasoline, controlling pollution of industrial origin, desulfurisation of fuel, effluents and fumes, burner and furnaces

1-4 Avenue de Bois, Préan. F-92506 rue il Malmaison, CEDEX

Fax (01)47490411 France

22\. Linde A.G.

Treatment of vent air and off-gas, removal of noxious substances, SO_2, hydroarbers, solvents, and recovery of valuable materials

Dr. Carl von Lindestr. 6-14, DW-8023, Hollriegelskruth

(089)72731, Fax (089)72732946 - Germany

23\. Lurgi A.G.

Industrial technology for: water - sludge, waste and residue disposal, recycling and remedial site treatment, gas cleaning

Lurgi Allee 5, DW-6000, Frankfurt 11, FAx (069)58083888

Germany

24\. Monsanto Europe S.A. Enviro-Chem and Permea Division

Industrial technologies for waste gases, process gases, Monsanto most eliminators enable to meet most strongest air pollution standards

270-272 Avenue de Tervuren B-1150, Bruxelles

25. A/S Niro Atomizer
Pollution control and industrial technologies for waste, soil protection, waste water, air, waste gas and gaseous media
Sladsaxevey 305 , DK-2860 Soborg, Fax (031)691414-Danmark

26. Philips GmbH
Measurement of air pollution by means of chromatographic instruments. Determination of heavy metals and organic components by means of atom desorbtion and infrared spectrometers
Miramstr. 87, DW-3600 Kassel, Fax (0561) 50198 - Germany

27. Rhone-Poulenc
Environment and surface treatment
25, Quai Paul Doumer, F-92408, Courbevoie, CEDEX, Fax(01) 47680747, France

28. Sulzer Chemtech.
Process and environmental technology
CH 8404, Winterthur, Fax (052)2620101

29. Department of Chemical Engineering University of Nottingham
Environmental engineering, process development in the field of water quality, incineration of wastes, migration of methane in and around landfill sites
University Park, Nottingham, NG 7, 2 RD, Fax 0601-790239- U.K.

30. Universitatea Bucuresti, Institutul Politehnic Bucureşti, Facultatea de Chimie Industrială
Pollution control and industrial technology,
Fax 120093 - Romania

9. List of Technical Papers

9.1. Technical publications

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2. P. Payagopol	Towards Clean Chemical Technologies an Educational and Research Perspective for Developing Countries. Journal of Clean Technology and Environmental Sciences. Vol. 1. Number 1, 1991
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2. 107.204.094 W-Measuring stack emissions of micropolluants, woodfield M.J (Waren Spring Lab.4 K). Filtr. Sep. 1987 m (u) 272-4. A review, with 10 refs. on Sampling Systems for measuring stack emissions of org. pollutants from refuse incineration.

3. 107.204.105 a. - Sources of nitrogen oxide pollution in the indoor environment,KalL.P.D. (Brookhaven Natl. Lab. upton NY - USA). A review with refs. on indoor sources of NO_x. Major factor that influence the emissions are discussed and typical source levels are reported for use in exposure modeling.

4. 107.204.108 d - Compendium of methods for the determination of toxic organic compounds in ambient air. Supplement Riggin R.M. (Battelle Columbus Lab. OH SUA). A review of 5 methods covering 29 toxic air pollutants presented in the original compendium and included 4 new specific methods. With this addn., the compendium now contains 9 standardized sampling and anal. procedures covering 36 toxic air pollutants.

5. 107.204.109 e - Preliminary characterisation of the Southeastern Brasilian environment. Moreira Nordemann (Inst. Pesqui Espaciais, Sao Jose de Campos, Brasil). A review which covers information about environmental conditions of the Southeastern

region of Brasil. Emission and deposit of S and N compounds are discussed and direct related to pollution focus, coresponding to larger industrialized and urbanized areas.

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7. 107.204.119 h - What's wrong with the environment ? Benoit, Richard J. (Dep. Bot. Connecticut Call, New London, CT 06320 USA). A review with 27 refs. on the ecol. and human health impacts of acid rain, asbestos and P.C.Bs.

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and odores (eg. produced by manual frying equipment) on removed from air by an ap.p. comprising a scrubber with an inlet a shaped gate dividing the chamber into a channel-like upper part with variable cross-section and a lower scrubbing section contg. the scrubber unit with 1 nozzle and a cooling chamber consisting of a cooling set of battery.

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13. 107.204.460 n - Landfarming of oily wastes :design and operation. Amarol S.P. water Sci. Technol. 1987, 19 (8,use Soil Treat. Final Disposal Effluents Sludge) 75-86 Eng. The review with 10 refs. covers the technologye of land farming of oil wastes including design parameter such as: location, soil characterisation, dimensioning of the area of application, ground water protection, drainage, etc.

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11. Conclusions

1. Clean technologies can be regarded as both a goal or target and a policy so that its development is consequently a short and long term endeavour of great importance.

2. It would be necessary to distinguish between the concept of "waste" and the concept of "residuals". All production processes will generate a certain amount of "residual products". Depending upon the composition of the residual products part of not all of these residuals can be recovered and re-utilized. The remainder, which at the prevailing set of prices has no economic value, is defined as "waste".

3. In the past, environmental policy has been towards the installation of add-on control devices, treatment facilities rather than focusing on process changes to eliminate pollution sources.

4. Priority is now being given to the promotion of clean technologies:low and non waste technologies.

5. Emphasis is placed on tecnological modifications of processes which reduce the amount of residuals generated through greater physical efficiency of materials and energy use, as well as on those processes that convert the residual products into useful products.

6. The concept of clean technology also promote:

a. Increased durability of products, as the longer the consumer can use them, the less need there is for replacing them and thus less resources including energy are needed for manufacturing them.

b. Substitution of material of bio-accumulative, persistent, toxic nature by those which do not impair the environment once released as wastes or accidental spills.

7. The objectives of the compendium are to:

a. Share experience of practical application of the concept of clean petrochemical technologies in developing countries.

b. Reveal gaps in knowledge and thereby identify areas that require special attention in research and development.

c. Serve as a source of information decision makers in formulating policies for the purpose of stimulating the development of clean technologies.

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