BEST AVAILABLE TECHNIQUES GUIDANCE DOCUMENT ON PRODUCTION OF PETROCHEMICALS

FOREWORD

Best Available Techniques Economically Achievable (BAT) document had been prepared as a guidance notes for the nine (9) major industries in Malaysia and to support the implementation of the new Environmental Quality (Clean Air) Regulations 20xx. These documents were prepared based on the latest state-of-the-art technologies, internationally accepted limit values but had been adjusted and tailored to local requirements.

BAT is defined as the effective methods in preventing pollution and, where generally that is not practicable, to reduce emissions from industrial activities and their impact on the environment. This definition implies that BAT not only covers the technology used but also the way in which the installation is operated, to ensure a high level of environmental protection. Implementations of BAT in any specific industrial sectors are under economically and technically viable condition.

It is hope that the technical contents of these documents will prove beneficial to the industries in their endeavour to comply with the environmental regulations and standards through more cost-efficient means. In the identification of BAT, emphasis is placed on pollution prevention techniques rather than end-of-pipe treatment. These documents will be reviewed and updated from time to time.

These documents have been prepared in consultations with the University of Malaya Consultancy Unit (UPUM), Malaysia German Technical Cooperation (GTZ) and the relevant industries/stakeholders. The Department of Environment wishes to record appreciation to representatives of the relevant industrial sectors, government agencies and individuals for their invaluable input.

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ABS	-	Acrynitrile Butadiene Styrene
BAT	-	Best Available Techniques economically achievable
BT	-	Benzene Toluene
BTX	-	Benzene Toluene Xylene
BREF	-	Best Available Technique Reference Document
CAR	-	Clean Air Regulation
DOE	-	Department of Environment
DCS	-	Distributed Control System
EB	-	Ethyl Benzene
EDC	-	1,2-dichloroethane
EO	-	Ethylene Oxide
EPS	-	Control Expanded Polystyrene
g/Gj	-	gram/Giga Joule
GPPS	-	General Purpose Polystyrene
HDPE	-	High Density Polyethylene
HIPS	-	High Impact Polystyrene
IPPC	-	Integrated Pollution Prevention Control
KA	-	Ketone Alcohol
kg/h	-	kilogram per hour
kPa	-	kilopascal
LDAR	-	Leak Detection and Repair Program
LDPE	-	Low Density Polyethylene
LLDPE	-	Linear Low Density Polyethylene
LPG	-	Liquid Petroleum Gas
LVOC	-	Large Volume Organic Chemistry
mbarg	-	meter bar gauge
MEG	-	Mono Ethylene Glycol
MEK	-	Methyl Ethyl Ketone
mg/Nm^3	-	milligram per cubic metre at standard temperature (273K) and pressure (1atm)
NMVOCs	-	Non Methane Volatile Organic Compounds

PET	-	Polyethylene Terephtalate
PLC	-	Programmable Logical Computers
PP	-	Polypropylene
ppmv	-	parts per million of volume
PVC	-	Polyvinyl chloride
SCR	-	Selected Catalytic Reaction
SNCR	-	Selected Non-Catalytic Reaction
TA	-	Terephthalic Acid
TPM	-	Total Particulate Matter
VOCs	-	Volatile Organic Compounds
VCM	-	Vinyl Chloride Monomers

1.0 PREFACE

1.1 Status of This Document

This document forms a part of a series presenting the guidance notes for selected industries in Malaysia (list given at the end of this preface) to apply best available techniques economically achievable (BAT), associated monitoring and developments in them. This series is published by the Department of Environment (DOE) in accordance to the Environmental Quality (Clean Air) Regulations 2014(CAR 2014).

1.2 Definition of BAT

In order for the user of this document to understand the legal context of this document, the interpretation on the definition of BAT is taken from Regulation 2 – Interpretation of CAR 2014 and described as below:

"Best Available Techniques Economically Achievable" means the effective methods in preventing pollution and, where that is not practicable, generally to reduce emissions in the air from the industrial activities and their impact on the environment as a whole. In this regard:

"Techniques" includes both the technology used and the way in which the facility is designed, built, maintained, operated and decommissioned;

"Available Techniques" means those techniques that are accessible to the occupier and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and

"Best" means effective in achieving a high general level of protection of the environment as a whole;

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this document that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood to mean those levels representing the environmental performance that could be expected as a result of the application, of the techniques described, taking into account the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such.

In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

The actual cost of applying a technique will depend strongly on the specific situation such as taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific economic viability of techniques drawn from observations on existing installations.

The purpose of CAR 2014 is to achieve prevention and control of pollution arising from activities listed in its First Schedule. More specifically, it provides for a permit system for certain categories of industrial installations to conduct an integrated and comprehensive view of the pollution and consumption potential of their installation. The overall aim is to ensure a high level of protection of the environment as a whole based on appropriate preventative measures through the application of BAT.

1.3 Objective of This Document

The ‘emission minimization principle’ as cited in CAR 2014 requires that the goal of emission abatement is to achieve minimum emissions as a result of applying current BAT. Hence this guidance document is meant to provide the reference information for the approving authorities to take into account when determining approved conditions. This document should serve as valuable input to achieve better environmental performance.

1.4 Information Sources

The information is mainly based on the European IPPC BREF document where the assessment was achieved through an iterative process involving the following steps:

- identification of the key environmental issues for the sector
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in Implementation of these techniques;

- selection of the BAT and the associate emission and/or consumption levels for this sector

1.5 How to Use This Document

It is intended that the general BAT in this document could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate BAT based conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general BAT levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or perform better. This reference document does not set legally binding standards, but they are meant to give information for the guidance of industry, the relevant government bodies and the public on achievable emission and consumption levels when using specified techniques.

The structure of the guideline document is as follows:

An overview of each particular sector in the Malaysian context is firstly covered briefly followed by process description, process optimization, sources of pollution, emission control options, recommended practices and emission values and finally emission monitoring and reporting. More often than not, trade-off judgements between different types of environmental impacts and specific site condition are the influencing factors.

Another important point to note is that BAT change over time and this guidance document needs to be reviewed and updated as appropriate.

2.0 OVERVIEW OF CHEMICAL AND PETROCHEMICAL INDUSTRY IN MALAYSIA

The petrochemical industry can be defined as industrial processes utilizing petroleum or other hydrocarbon origin as raw materials. Although some of the chemical compounds that originate from petroleum may also be derived from other sources such as coal or natural gas, petroleum is a major source of many. The two main classes of petrochemical raw materials are olefins (including ethylene and propylene) and aromatics (including benzene and xylene isomers), both of which are produced in very large quantities.

A wide range of petrochemicals are produced in Malaysia, such as olefins, polyolefins, aromatics, ethylene oxides, glycols, oxo-alcohols, exthoxylates, acrylic acids, pthalic anhydride, acetic acid, styrene monomer, polystyrene ethylbenzene, vinyl chloride monomer and polyvinyl chloride.

Malaysia’s petrochemical sector has also contributed to the development of local downstream plastic processing activities. World scale producers of LDPE, LLDPE, HDPE, PP, EPS, GPPS, HIPS, PVC, ABS, SAN and PET resins have established plants in Malaysia, thus providing a steady supply of feedstock material for the plastic industry.

3.0 PROCESS DESCRIPTION

Natural gas and crude distillates such as naphtha from petroleum refining are used as feedstocks to manufacture a wide variety of petrochemicals that are in turn used in the manufacture of consumer goods. Due to the large number of petrochemical products and their associated production routes, petrochemical processes are extremely diverse and complex. However, most of these processes involve the same generic steps. Some examples of typical petrochemical processes are shown in **Figure 1** – **Figure 8**.

As shown in **Figure 1**, five main steps can be identified in any petrochemical plant:

i. Raw material supply and preparation: this activity consists of the receipt, storage, and charging of raw materials and other reagents into reactors.

ii. Synthesis: it is the core of every process where raw materials are transformed into crude products. This involves a chemical reaction (‘Unit Processes’). **Table 1** shows the main unit processes used in the manufacturing of 140 compounds. The characteristics of some of these processes are given in **Table 2.**

iii. Product separation and refinement: in this activity, the product is separated from other reaction components and purified using several ‘Unit Operations’ to meet market specifications. The characteristics of some of these unit operations are given in **Table 3**.

iv. Product handling and storage: storage, packaging and export of the product.

v. Emission abatement: the collection, re-use, treatment and disposal of unwanted liquids, gases and solids.

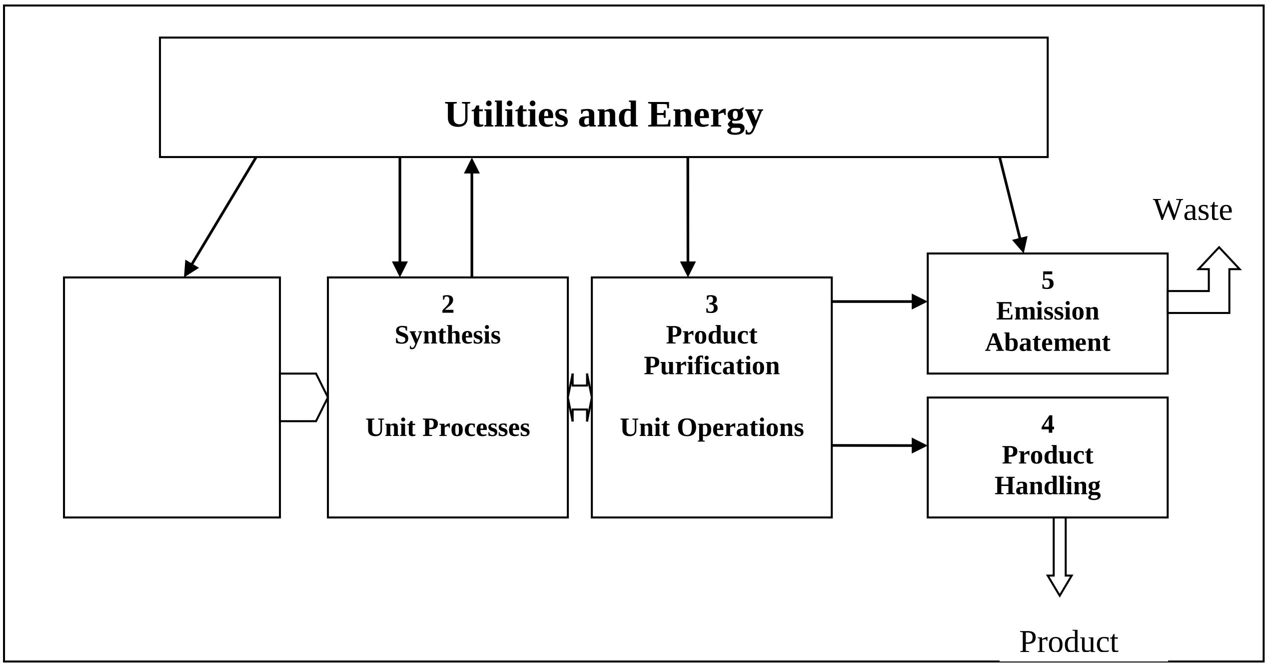

Figure 1: Schematic Production of Organic Chemicals

3.1 Production of Petrochemicals

The followings are the major reactions encountered in the production of petrochemicals:

Oxidation

Oxidation is the addition of one or more oxygen atoms to a compound. In this process oxidation agents such as atmospheric oxygen, nitric acid, hydrogen peroxide, organic peroxides, and pure oxygen are used. Important industrial oxidation processes are the silver catalysed gas phase reaction between ethylene and oxygen to form ethylene oxide, the production of acetic acid, formaldehyde, phenol, acrylic acid, acetone and adipic acid. Oxidation reactions are exothermic and heat can be re-used in the process to generate steam or to preheat other component streams.

Halogenation

Halogenation describes the introduction of halogen atoms into an organic molecule by addition or substitution reactions. In organic synthesis this may involve the addition of molecular halogens (e.g. Cl_2, Br_2, I_2 or F_2) or hydrohalogenation (with HCl, HBr or HF) to carbon-carbon double bonds. Chlorination is the most important industrial halogenation reaction. Production of 1,2-dichloroethane (EDC) and vinyl chloride (VCM) are examples of chlorination processes.

Hydrogenation

Hydrogenation is a catalytic reaction during which hydrogen is added to an organic molecule. It can involve direct addition of hydrogen to the double bond of an unsaturated molecule; amine formation by the replacement of oxygen in nitrogen containing compounds; and alcohol production by addition to aldehydes and ketones. Hydrogenation is an exothermic reaction and the equilibrium usually lies far towards the hydrogenated product under most operating temperatures. Nickel, copper, cobalt, chromium, zinc, iron and the platinum group are among the elements most frequently used as commercial hydrogenation catalysts. The general safety precautions that apply to highly flammable gases and vapours apply particularly to hydrogen.

Esterification

Esterification is the reaction between and organic acid and an alcohol to produce an ester. The main products from esterification reactions are dimethyl terephthalate, ethyl acrylate, methyl acrylate and ethyl acetate. They have considerable economic importance in many applications (e.g. fibres, films, adhesives and plastics). Some volatile esters are used as aromatic materials in perfumes, cosmetics and foods.

Alkylation

Alkylation is the introduction of an alkyl group into an organic compound by substitution or addition. Major alkylation products include ethylbenzene, cumene, linear alkylbenzene, tetramethyl lead and tetraethyl lead.

Sulphonation

Sulphonation is the process by which a sulphonic acid group (or corresponding salt or sulphonyl halide) is attached to a carbon atom. It is used to produce many detergents (by sulphonating mixed linear alkyl benzenes with sulphur trioxide or oleum (fuming sulphuric acid)) and isopropyl alcohol (by the sulphonation of propylene).

Dehydrogenation

Dehydrogenation is the process by which hydrogen is removed from an organic compound to form a new chemical (e.g. to convert saturated into unsaturated compounds). It is used to produce aldehydes and ketones by the dehydrogenation of alcohols. Important products include acetone, cyclohexanone, methyl ethyl ketone (MEK) and styrene. Dehydrogenation is most important in the ‘Cracking’ process, where saturated hydrocarbons are converted into olefins. The process is applied to appropriate hydrocarbon feedstocks (e.g. naphtha) in order to produce the very large volumes of ethylene, propylene, butenes and butadienes that are required as feeds for the chemical industry. The schematic diagram is shown in **Figure 2**.

Hydrolysis

Hydrolysis involves the reaction of an organic with water to form two or more new substances. Hydration is the process variant where water reacts with a compound without causing its decomposition. These routes are used in the manufacture of alcohols (e.g. ethanol), glycols (e.g. ethylene glycol, propylene glycol) and propylene oxide. The schematic diagram is shown in **Figure 3**.

Reforming

Reforming is the decomposition (cracking) of hydrocarbon gases or low octane petroleum fractions by heat and pressure. This is most efficient with a catalyst, but can be achieved without. Reforming is mainly used in refineries to increase the octane number of fuels. The main reactions are the dehydrogenation of cyclohexanes to aromatic hydrocarbons, the dehydrocyclisation of certain paraffins to aromatics, and the conversion of straight chains to branched chains (isomerisation). It is also used to make synthesis gas from methane.

Nitration

Nitration involves the replacement of a hydrogen atom (in an organic compound) with one or more nitro groups (NO_2). Nitration of aromatics is a commercially important process (e.g. explosives and propellants such as nitrobenzene and nitrotoluenes).

Dehydration

Chemical dehydration is a decomposition reaction in which a new compound is formed by the expulsion of water. The major product of this process, urea, is produced by the dehydration of ammonium carbamate.

3.2 Production of Organic Compounds

Tables 1 and **Table 2** summarise the applications and characteristics of major reactions used in the production of organic compounds.

Table 1: Unit Processes Used In the Manufacture of 140 Organic Compounds.

Unit process	Number of products produced using the unit process	Number of production activities using the unit process	Estimated contribution to total unit process air emissions prior to treatment (%)
Oxidation	63	43	48.3
Halogenation	67	43	14.5
Hydrogenation	26	13	10.8
Esterification	24	8	6.9
Alkylation	15	5	4.0
Sulphonation	11	6	3.4
Dehydrogenation	15	4	2.7
Hydrolysis	27	8	2.4
Reforming	1	1	2.2
Carbonylation	10	8	1.2
Oxyacetylation	1	2	1.0
Nitration	12	1	0.8
Dehydration	18	4	0.7
Ammonolysis	11	6	0.6
Condensation	51	4	0.5
Dealkylation	4	1	0

Note 1: The table was prepared in 1980 and no newer data was available from USEPA
Note 2: The table takes no account of other environmental issues (e.g. cross media effects, energy)

Table 2: Characteristics of Unit Processes Used In Organic Chemical Production.

Process	Feed Material		Conditions		Products
	Reagents	Substrates	Catalysis	Phase	
Oxidation	Oxygen (Air)	Parrafins, Olefins, BTX-Aromatics	Heterogeneous	Gas	Acids, Anhydries, Epoxides
			Homogeneous	Gas-Liquid	Alcohols, Aldehydes, Ketones, Acids
			None	Gas-Liquid	Hydroperoxides
Ammoxidation	Oxygen, NH_3	Olefins, Alkyl-aromatics	Heterogeneous	Gas	Nitriles
Chlorination	Chlorine	Olefins, Aromatics	Homogeneous	Gas-Liquid	Chloro-organics
		Olefins, Paraffins	None		
Hydrogenation	Hydrogen	CO, Aldehydes, Nitriles, Nitro-compound	Heterogeneous	Gas	Alcohols, Amines
Hydroformylation (Oxo-Synthesis)	H_2, CO	Olefins	Homogeneous	Gas-Liquid	Aldehydes, Alcohols
Dehydrogenation	-	Paraffins, Olefins, Alkyl-aromatics, Alcohols	Heterogeneous	Gas	Olefins, Diolefins, Aromatics, Aldehydes, Ketones
Alkylation	Olefins, Alcohols, Chloro-organics	Aromatics	Heterogeneous	Gas	Alkyl-aromatics
			Homogeneous	Gas-Liquid	Alkyl-aromatics

Reaction products rarely are obtained in a pure form from a reaction. Often there are byproducts and unreacted inputs. Therefore, the desired product must be isolated and purified in order to be used by customers or downstream manufacturers. Common separation methods include filtration, distillation, and extraction. Depending on the particular mixture and the desired purity, multiple separation methods can be used. The following are the major separation processes used in the production of organic compounds:

Absorption

Absorption is the uptakes of one substance into the inner structure of another; most typically a gas into a liquid solvent. The interaction of absorbed materials with the solvent can be physical or chemical in nature. In physical absorption, the gas molecules are polarised but remain otherwise unchanged. The concentration of dissolved gases in the solvent increase in proportion to the partial pressure of the gases. In chemical absorption, they are also chemically converted. Absorption equipment generally consists of a column with internals for heat and material exchange in which the feed gas is brought into counter-current contact with the regenerated absorbent. The internals direct the liquid and gas streams and increase the contact area between the two phases. Various designs are used, especially absorption plates, randomly poured packing and structured packing.

Distillation

Distillation is the most important industrial method of phase separation. Distillation involves the partial evaporation of a liquid phase followed by condensation of the vapour. This separates the starting mixture (the feed) into two fractions with different compositions; namely a condensed vapour (the condensate or distillate) that is enriched in the more volatile components and a remaining liquid phase that is depleted of volatiles.

Extraction

Extraction is the most important liquid-liquid separation process used in industrial chemistry. It is used mainly where other separation methods or direct distillation are ineffective or too expensive. In order to extract a substance, an extraction solvent must be added to form a second liquid phase solution. Generally the desired substance is then separated from the solvent by distillation and the solvent is recycled.

Solids separation

Solid-liquid and solid-gas separations have industrial importance for product finishing and for minimising emissions of particulate matter to the atmosphere. Product finishing applications include separating heterogeneous catalysts from a product stream or separating solid products, by-products or intermediates (e.g. ammonium sulphate in the acrylonitrile-process, BTX-aromatics at low temperatures). The principal solid-gas separation techniques are cyclones, fabric filters, ceramic filters, wet collection devices, electrostatic precipitators, dust separation equipment and high efficiency venturi scrubbers.

The main solid-liquid techniques are centrifuging, filtration, sedimentation & clarification, drying and crystallisation.

Adsorption

Adsorption is the physical accumulation of material (usually a gas or liquid) on the surface of a solid adsorbent. Industrial adsorption processes are used to remove certain components from a mobile phase (e.g. air or water) or to separate mixtures. The best adsorbents are characterised by a large number of different sized pores and so activated carbon, zeolites, silica gel and aluminium oxide are the most commercially important. Zeolites (molecular sieves) have a very narrow distribution of micro-pores and preferentially adsorb polar or polarisable materials (e.g. water or carbon dioxide). By contrast, activated carbon has a hydrophobic character and is especially suitable for the removal of organic substances.

Tables 3 present a summary of the applications and characteristics of the main separation processes used in industry.

Table 3: Applications of Some Selected Separation Techniques.

Technique	Separation Principle	Application
Fractional distillation	Different boiling points	Base materials, intermediates, final products
Extractive distillation	Different polarities	Unsaturates from saturates
Liquid-Liquid-extraction	Different polarities	Aromatics from non-aromatics
Molecular sieve technique	Different diameters of molecules	n-Alkenes from branched and cyclic hydrocarbons
	Different polarisability of molecules	n-Alkenes from n-alkanes; p-xylene from m-xylene
Crystallization	Different solubilities	Re-crystallization for purification
	Different melting points	p-Xylene from m-xylene

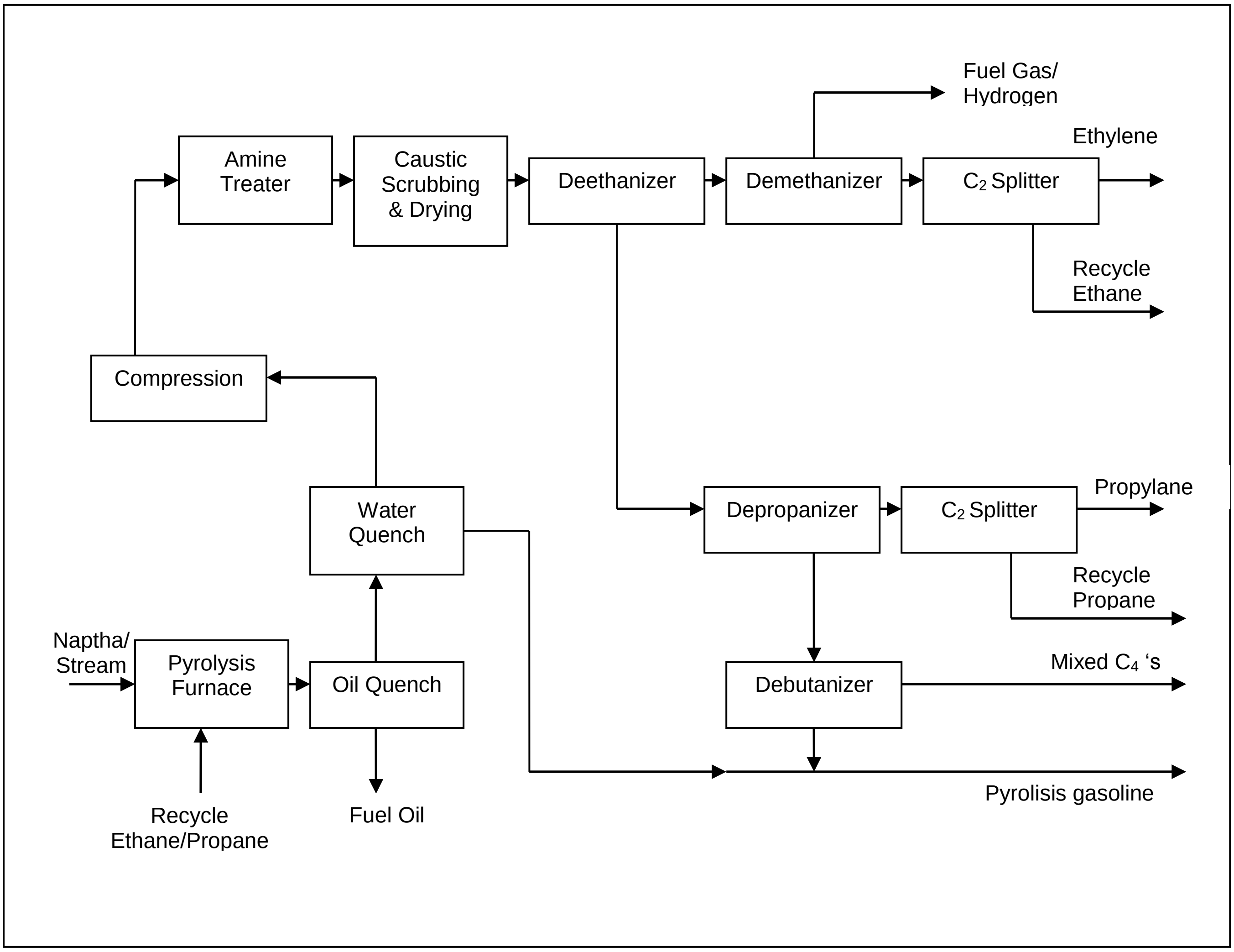

Figure 2: Ethylene Process: Steam Cracking of Naptha.

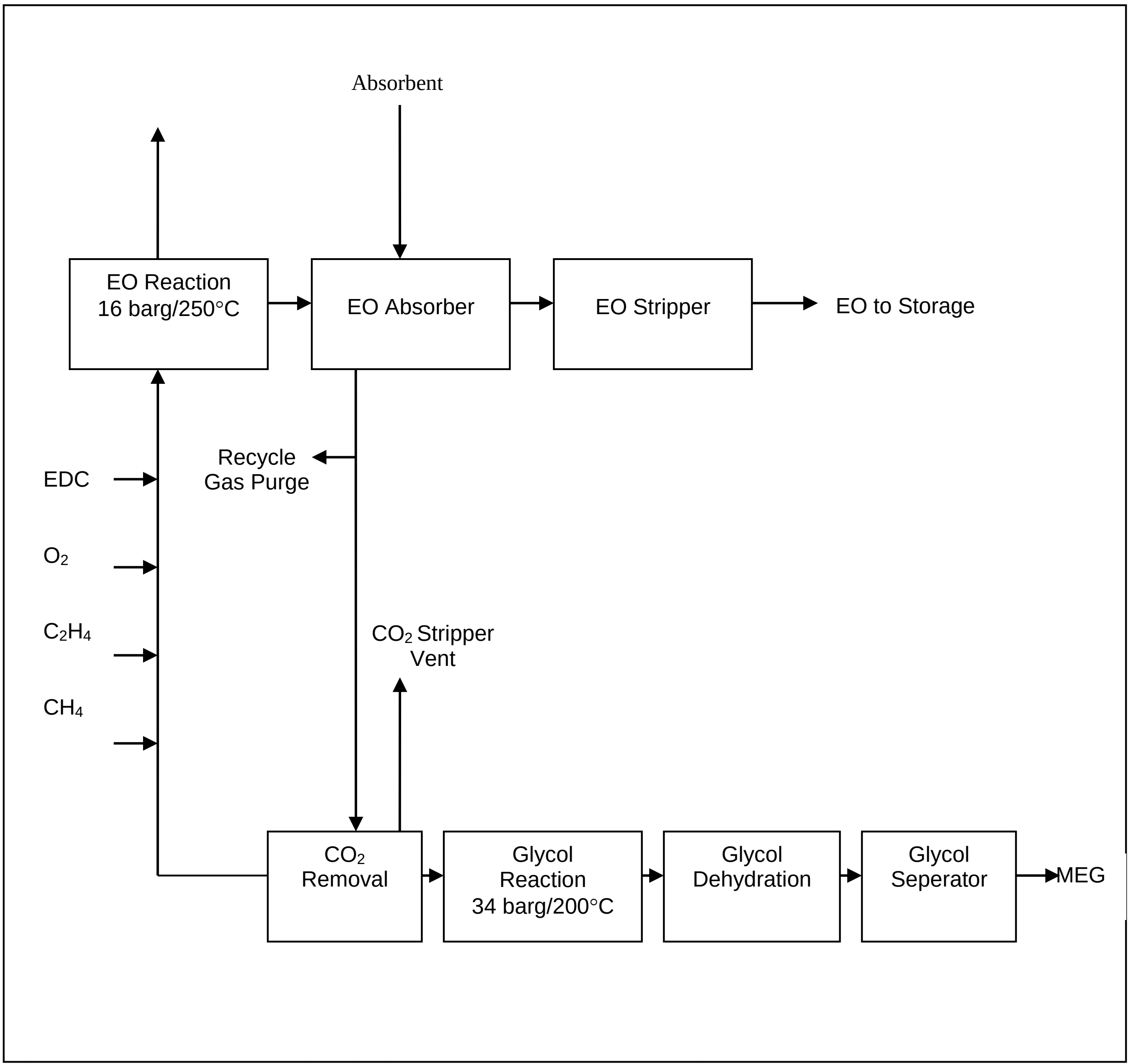

Figure 3: Ethylene Oxide/Ethylene Glycol Production.

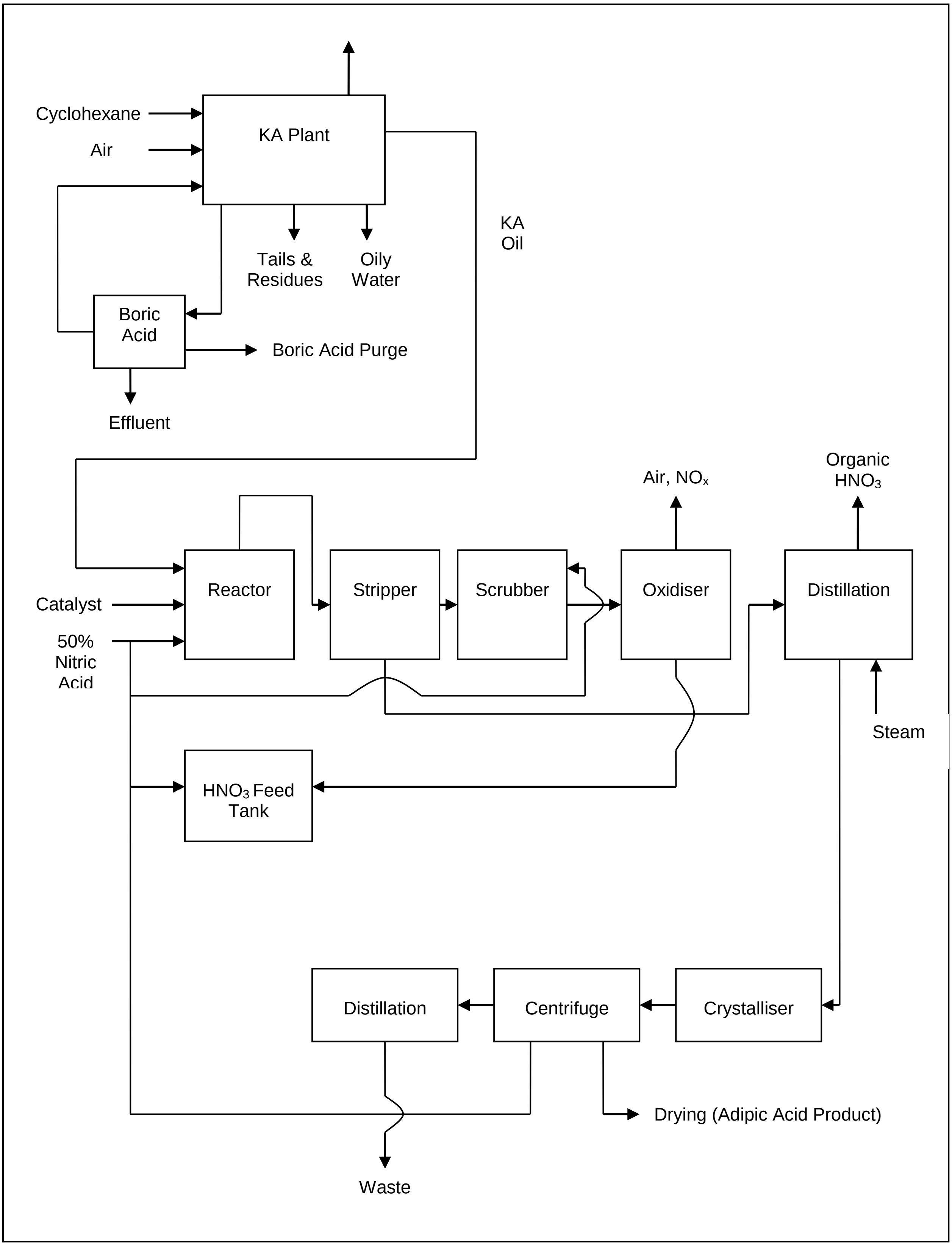

Figure 4: Adipic Acid Production.

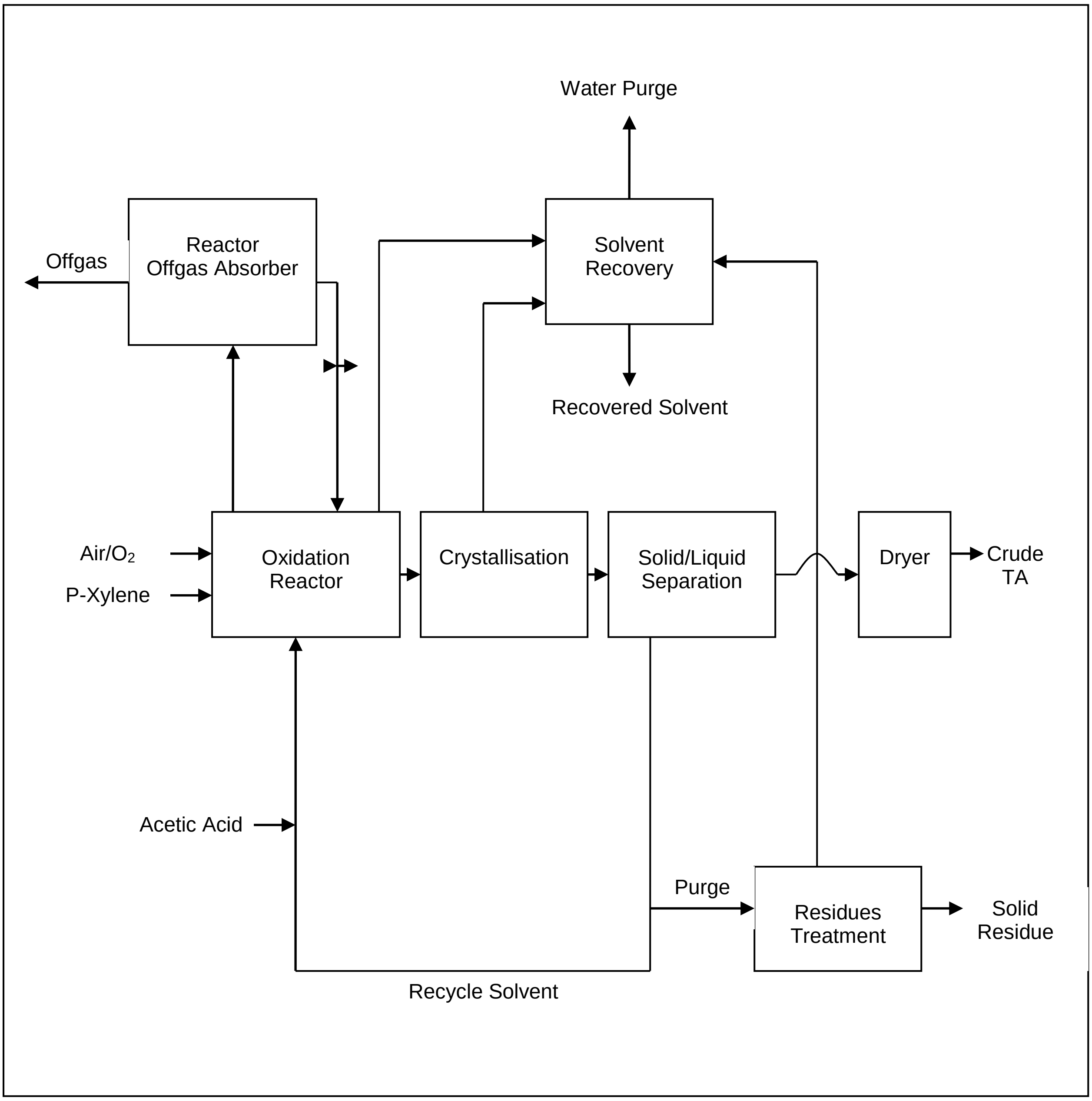

Figure 5: Terephthalic Acid Process: Oxidation.

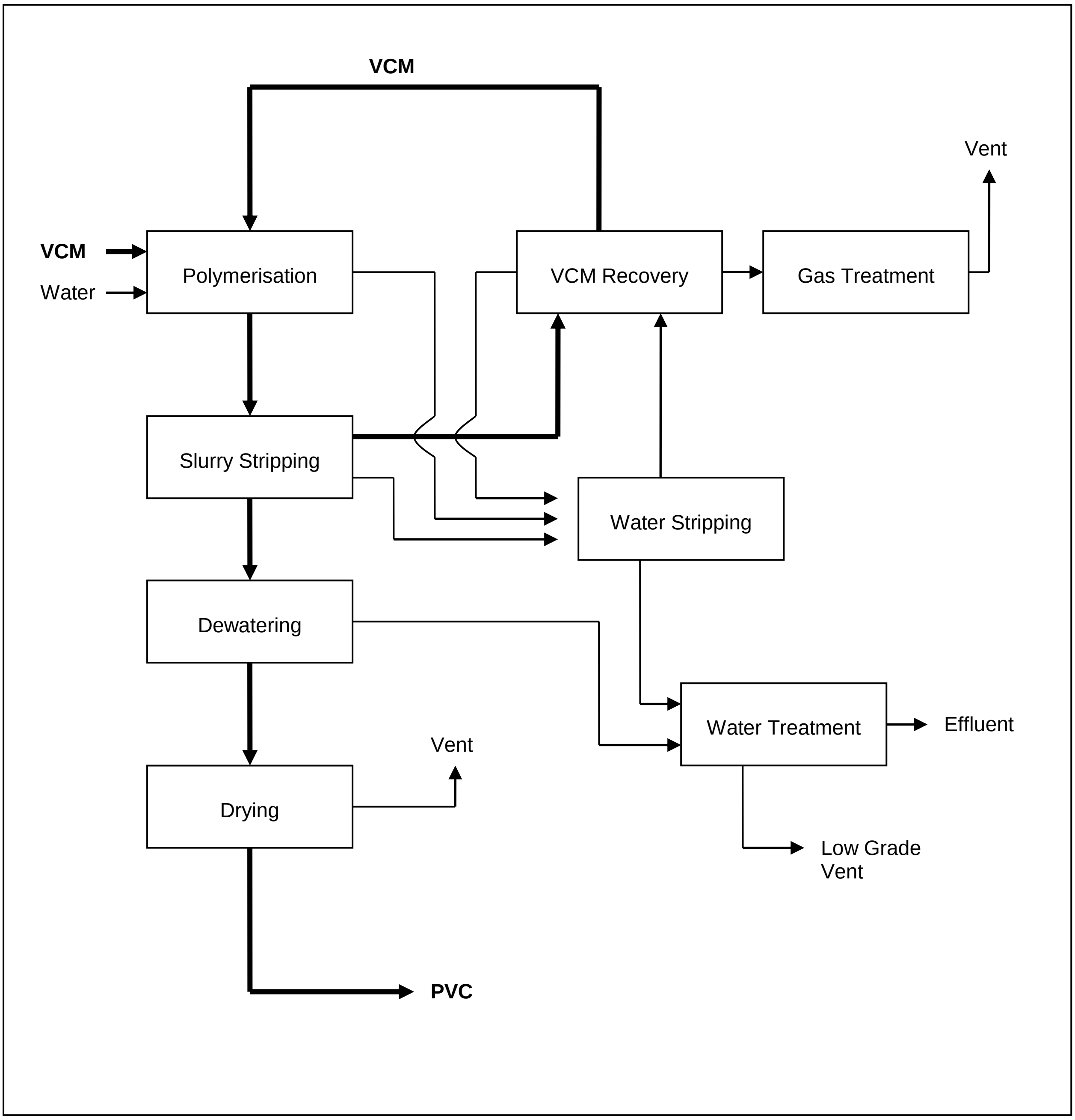

Figure 6: PVC Production: Suspension.

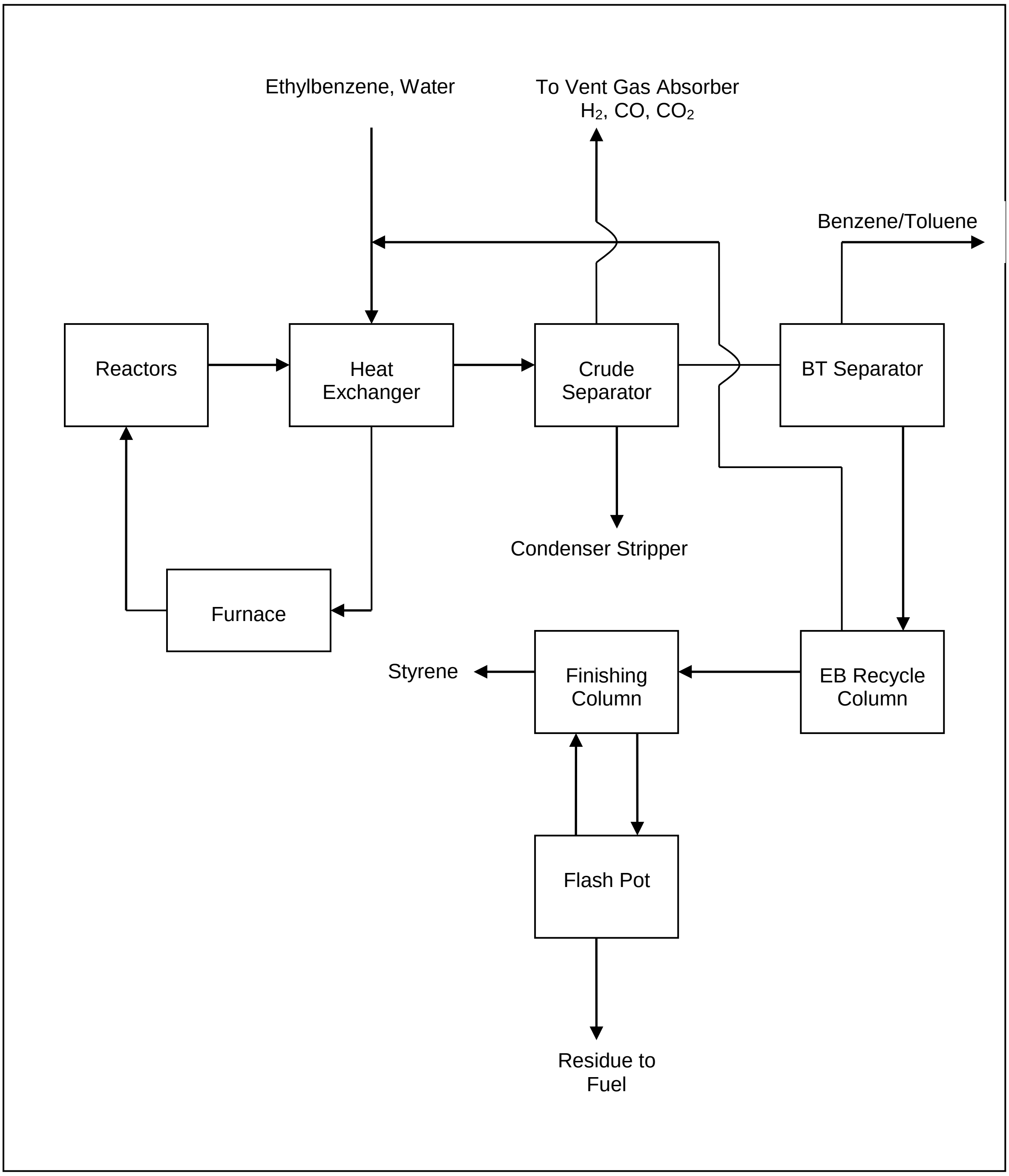

Figure 7: Manufacture of Styrene: Ethylbenzene Dehydrogenation.

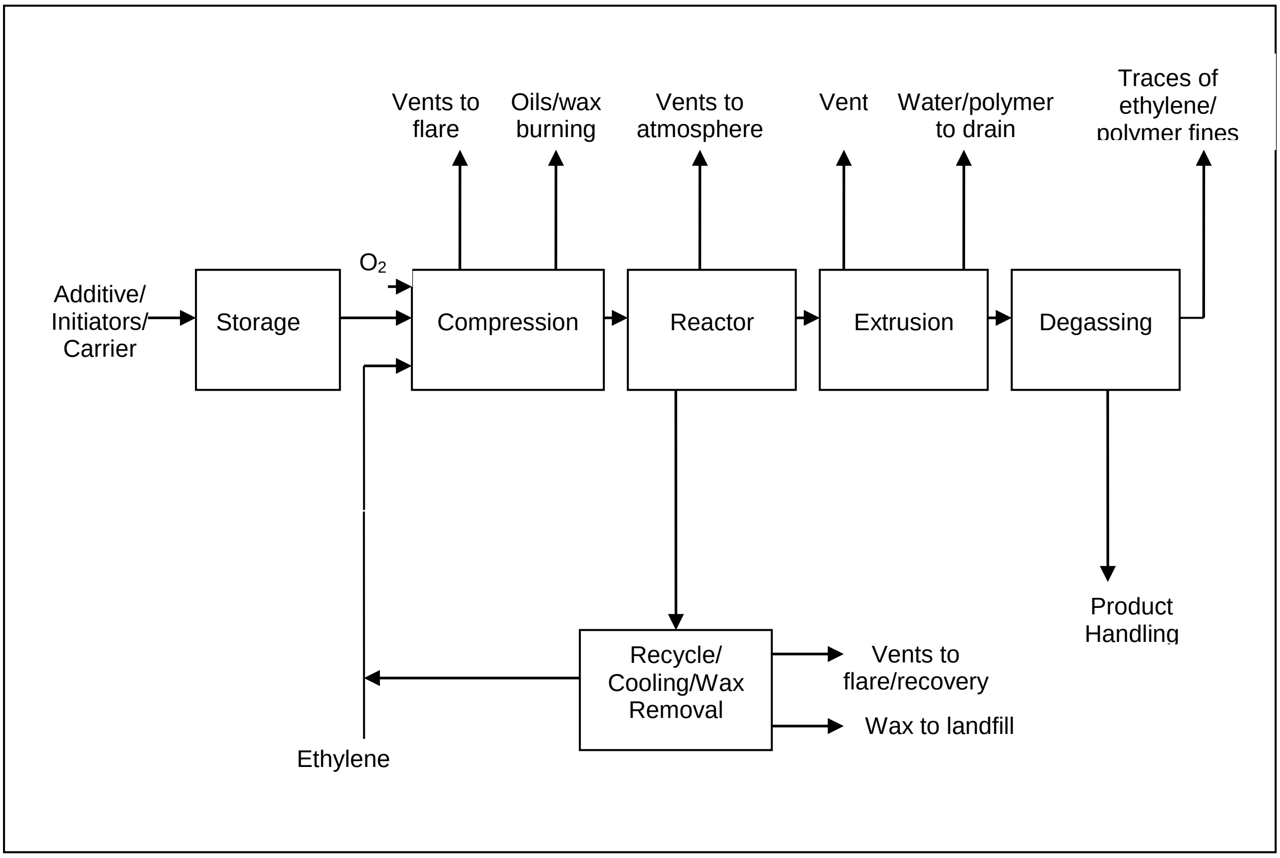

Figure 8: LDPE Production.

4.0 PROCESS OPTIMIZATION

To increase the yield, the first option is to use high quality raw material or further optimize the main process operating parameters.

The use of advanced computerized control systems such as DCS (Distributed Control Systems) or PLC (Programmable Logical Computers) in order to achieve stable operations and high yields is important to achieve good environmental performance.

5.0 SOURCES OF AIR POLLUTANT EMISSIONS

Table 4 gives the type of pollutants relevant to the petrochemical plants.

Table 4: Pollutants emitted and their sources

Pollutants	**Sources**
VOCs	Process vents Storage and transfer of liquids and gases Fugitive sources and intermittent vents Unit processes Distillation units
Particulate matter	Conditioning of solid raw materials Drying of solid products Catalyst regeneration Waste handling
Combustion gases: NO_x, CO, SO_x, HC, metals, soot	Furnaces Steam boilers Incinerators and flares
Acid gases (HCl, HF)	Halogenation reactions
Dioxins	Production processes that use chlorine Incinerators

Typical pollutant concentrations measured in some Malaysian petrochemical plants are given in **Table 5.** It is important to note that none of the petrochemical plants surveyed in the emission factor project in 2002, had provided estimation of fugitive emissions.

Table 5: Typical Pollutant Concentrations in Malaysian Petrochemical Plants

Plant	Process	Emission Concentrations (in mg/Nm^3, unless otherwise stated)						
		PM	CO_2	CO	SO_x	NO_x	VOC	Others
Petrochemical A	Oxidation reactor	9.9	149288	1328	5.2	-	-	Benzene :23.7
	Hot oil furnace	12.7	81683	1.6	-	-	-	Benzene : 0.7
	Hot oil furnace	11.4	96445	1.5	-	-	-	Benzene: 0.4
	Sludge incinerator	6.6	30983	2.6	0.8	-	-	Benzene: 1.7
	Crude TA transfer	13.2	153588	1113	28.1	-	-	Benzene: 4.0
	PTA reactor	5.9	102507	1439	23.0	-	-	Benzene: 0.8
	PTA drying	102	104408	910	10.8	-	-	Benzene: 2.5
	Off gas dryer	14.0	130847	701	14.3	-	-	Benzene: 82.4
Petrochemical B	Furnace	< 0.01	3.8 v/v%	-	< 0.01	< 0.01	-	-
Petrochemical C	Incinerator chimney	-	-	-	< 0.3	19.4	-	Moisture : 4.95 % Copper :< 0.01 Zinc : < 0.05 Cadmium : < 0.001 Lead : < 0.001 Arsenic : <0.001 Mercury : < 0.001 Antimony : < 0.001
	Boiler Chimney	10		< 100 ppm	< 0.30	20	-	Copper: < 0.01 Zinc: < 0.05 Cadmium: < 0.001 Lead: < 0.001 Arsenic: < 0.001 Mercury: < 0.001 Antimony: < 0.001
	ECS Stack	-	-	5 ppm	-	-	-	Formaldehyde: 0.1 ppm Benzene: 0.7 ppm
	Ambient Air	-	-	-	-	-	-	Ozone: 5.7 µg/Nm^3 PM_{10}: 9.28 µg/Nm^3 TPM: 60 µg/Nm^3

	Cleaning furnace	-	-	-	-	-	-	HCl: < 0.01 Cl_2: < 0.01 HS: < 0.01 ppm Arsenic: < 0.01 Mercury: < 0.01 Lead: < 0.01 Antimony: < 0.01 Cadmium: < 0.01 Copper: < 0.01 Zinc: < 0.01
	Finishing wet scrubber	-	-	-	-	-	-	Formaldehyde: 40 ppm
Petrochemical D	Cogeneration	-	-	34 ppm	69 ppm	560 ppm	-	-
	Cogeneration	-	-	34 ppm	69 ppm	560 ppm	-	-
	Cogeneration	-	-	34 ppm	69 ppm	560 ppm	-	-
Petrochemical E	Heater stack	-	-	-	3.9379	< 0.0001	-	-
	Dust collector	0.0054	-	-	-		-	-
	Dust collector	0.0039	-	-	-	-	-	-
Petrochemical F	Power generation	0.03	2.1 ppm	20 ppm	-	47 ppm	-	-
	Power generation	0.01	2 ppm	-	1 ppm	56 ppm	80 ppm	-
	Boiler system	-	10.5 ppm	-	6 ppm	113 ppm	130 ppm	-
Petrochemical G		-	-	-	< 0.001	< 0.001	-	-
Petrochemical H	Boiler	17.37	161750	15.66	< 2.59	< 1.84	-	NO: 2.91 O_2: 60100 H_2SO_4: 0.3
	Plasticizer	3.43	19340	15.66	12.80	9.20	-	O_2: 242960
	PA	10.68	68570	5.60	< 2.59	< 1.84	-	O_2: 180310 CH_3COOH: < 0.12

Source: *DOE Project on the Formulation of Emission Factors for Industrial Pollutants in Malaysia, 2002*

6.0 EMISSION CONTROL OPTIONS

Despite the wide range of processes, the key issues are often common. For example, the release of VOCs and the techniques for controlling them are central to all the processes.

6.1 Volatile Organic Compounds (VOCs)

As shown in **Table 6**, there are many sources of VOCs emissions in a petrochemical plant. Therefore, the control options for VOC will depend on the source.

6.1.1 Control options of VOC emissions from process vents

The techniques for VOCs emission control can be classified in two main classes:

i. Recovery and re-use techniques which include adsorption, condensation, and absorption.
ii. Destructive techniques namely thermal oxidation, catalytic oxidation and biological treatment.

The performance and costs of VOC control techniques depend on the VOC species, the VOC concentration, and the flow rate. **Table 6** summarises the strengths and weaknesses of VOC control techniques. **Figure 9** shows the applicability of the techniques in terms of VOC concentration and flow.

Table 6: Summary of the Strengths and Weaknesses of VOC Control Techniques

Issue	Recovery and re-use techniques			Destructive techniques		
	Adsorption	**Condensation**	**Absorption**	**Thermal oxidation**	**Catalytic oxidation**	**Biological**
Low flow/low concentration	A	B	A	B	D	A
High flow/low concentration	A	C	C	B	A	A
Low flow/high concentration	D	A	A	A	D	B - D
High flow/high concentration	D	A	B	A	D	E
Hydrocarbon gases	D	E	B - D	A	A	A - C
Halogenated or sulphonated organic gases	D	E	A	B	D	C - E
Aminated organic gases	D	E	C - D	C	C	B - C
Hydrocarbon condensables	A	A	B - C	A	A	A - C
Halogenated or sulphonated organic condensables	A	A	A - B	B	D	C - E
Aminated organic condensables	A	A	B	C	C	A - C
Continuous	A	A	A	A	A	A
Batch or variable	A	A	A	D	D	A
Removal efficiency	B	C	A	B	C	A - B
Pressure drop	C	B	B	A	C	A
VOC recovery	B	A	B	E	E	E
Key: **A**:Excellent, **B**:Good, **C**:Satisfactory, **D**:Poor, **E**:Unacceptable						

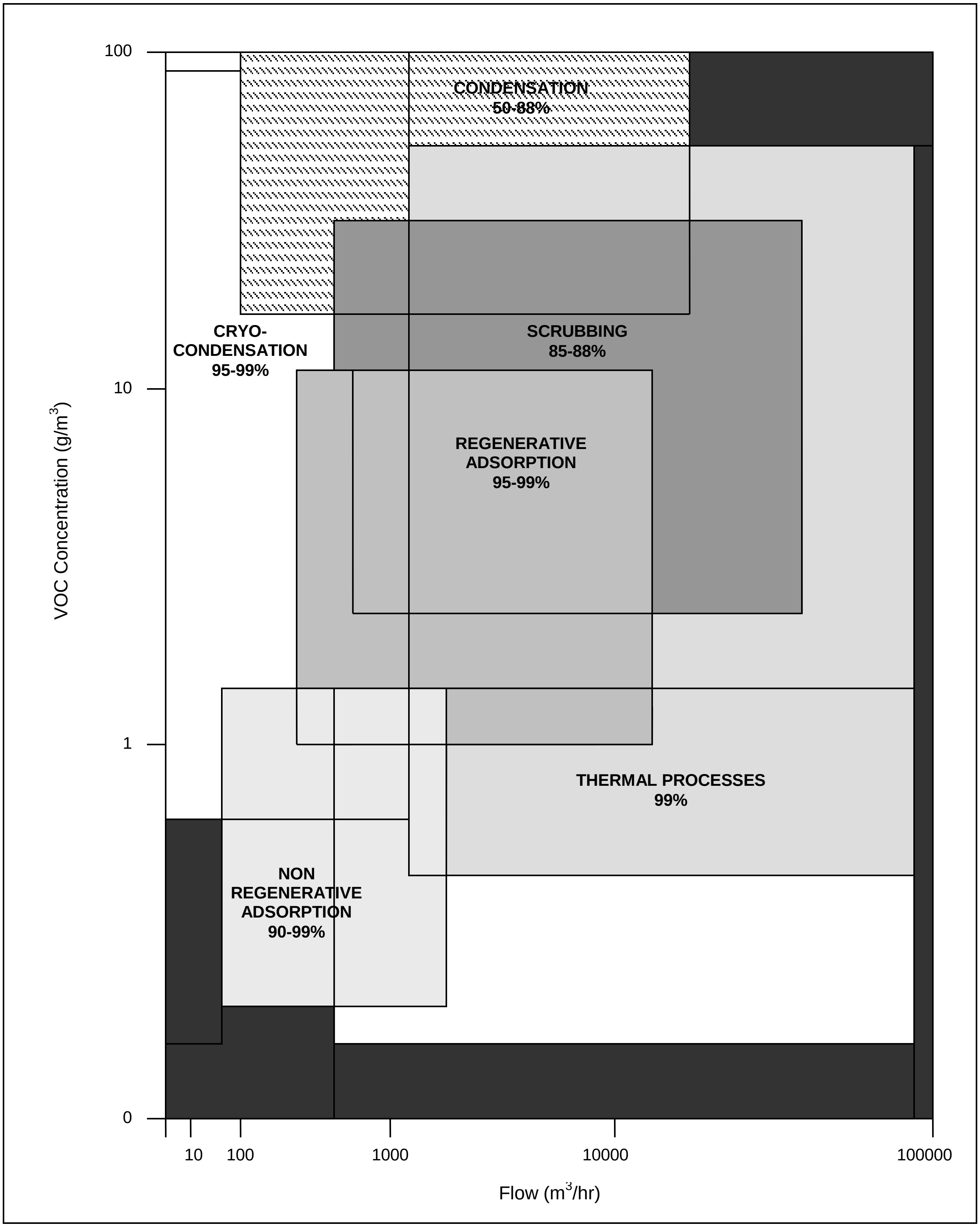

Figure 9: Flowrate and VOC Concentration Ranges Applicable to VOC Abatement Techniques.

6.1.2 Control Options of VOCs Emissions from Storage, Handling and Transfer

The techniques used to minimize VOCs emissions from storage tanks, handling and transfer of materials are given in **Table 7**.

Table 7: Control Options of VOCs Emissions from Storage, Handling and Transfer

Techniques	Reduction in losses
External floating roof	70-90 %
Secondary seals	up to 95 %
Fixed roof tanks with internal floating covers and rim seals (used for more volatile liquids)	70-85 %
Inter-connecting storage vessels and mobile containers with balance lines	75 %
Use of tank filling pipes that extend beneath the liquid surface	Minimal losses
Bottom loading to avoid splashing	
Vapour balance lines that transfer the displaced vapour from the container being filled to the one being emptied	
An enclosed system with extraction to suitable arrestment plant	
Recovery of displaced gases by condensation, absorption or adsorption.	
Fixed roof tank with inert gas blanket	
Storage under pressure	

More details on control options of VOCs emissions from storage, handling and transfer could be found in Storage & Handling of Petroleum Products BAT document.

6.1.3 Control Options of VOCs Fugitive Emissions:

Sources of fugitive emissions in petrochemical plants include stem packing on valves and control valves, flanges and connection, open ends, safety valves, pump and compressor seals, equipment manholes and sampling points. Furthermore, process operations (e.g. opening of vessels, filtering, stirring) and volatilization from liquid spills, effluent collection and treatment systems are also sources of fugitive emissions.

Generally reduction of fugitive emissions from equipment leaks can be achieved by:

- Minimizing the number of valves, control valves and flanges.
- Ensuring effective maintenance and leak detection.
- Using high quality equipment.

Table 8 gives the control techniques used to minimize VOC fugitive emissions from each source.

Table 8: Control Techniques Used to Minimize VOC Fugitive Emissions

Source	Control technique
Valves	Use high quality valves Use of quarter turn valves instead of rising stem valves Use of bellows valves (very costly)(recommended only in highly toxic or corrosive services)
Control valves	Use rotating control valves instead of raising stem control valves
Flanges	Minimise number of flanges (using welded connections)
Open ends (vents and drain outlets from pipes, equipment or sampling points)	Should be blinded, capped or plugged if not operated on a regular basis Should be fitted with two block valves Use ram-type sampling valves Use needle valve and a block valve for sampling Minimise the length of sampling lines
Safety valves	Installation of a rupture disk upstream of the safety valve Connection to a flare or abatement system (if safe)
Pumps	Use of high quality and double seal systems Use of seal-less pump when possible
Compressors	Use of high quality and double seal systems Collection of seal losses
Process operations	Operate the plant at below ambient pressure Obviate the need for vessel opening Enclose effluent collection systems and tanks Monitor cooling water

More details on control options of VOCs fugitive emissions could be found in Storage and Handling of Petroleum Products BAT document.

6.1.4 Control Options for VOCs from Intermittent Vents:

VOC releases can occur from intermittent activities such as pressure relief, blow-down and process start-up/shutdown. Reduction of these emissions can be achieved by:

- Minimizing inventories prior to shutdown.
- Minimizing purging to relief and blow-down during start-up and shutdown.
- Using enclosed blow-down drums.
- Directing vents to a flare or a boiler.
- Installing two tiers of pressure relief-one at a low trigger pressure and another at a higher trigger pressure.

6.2 Control options for combustion gases

Control options for combustion gases are given in **Table 9**.

Table 9: Control options for combustion gases.

Pollutant	Control option	Emission reduction
NO_x	Use of low NO_x burners	Up to 70 %
	Selective non catalytic reduction (SNCR)	60-80 %
	Selective catalytic reduction (SCR)	Up to 95 %
SO_2 (usually low)	Use low sulfur fuel	Significant reduction in emission
	Injection of alkali	
Particulates	Switch to natural gas	
	Bag filters, electrostatic precipitators	

7.0 RECOMMENDED PRACTICES AND EMISSION VALUES

The BAT for the control of VOCs and other pollutants are given in **Table 10** and **Table 11**, respectively. The achievable emission levels associated with the BAT are also given in these tables.

Table 10: BAT-Associated Values for the Recovery/Abatement of VOCs

Technique	BAT-associated values (1)	Remark
Selective membrane separation	90 – > 99.9 % recovery VOC < 20 mg/m^3	Indicative application range 1 – >10g VOC/m^3 Efficiency may be adversely affected by, for example, corrosive products, dusty gas or gas close to its dew point.
Condensation	Condensation: 50 – 98 % recovery + additional abatement. Cryo-condensation: (2) 95 – 99.95 % recovery	Indicative application range: flow 100 – > 100000 m^3/h, 50 – > 100 g VOC/m^3. For cryo-condensation: flow 10 – 1000 m^3/h, 200 – 1000 g VOC/m^3, 20 mbar – 6 bar
Adsorption (2)	95 – 99.99 % recovery	Indicative application range for regenerative adsorption: flow 100 – 100000 m^3/h, 0.01 – 10g VOC/m^3, 1 – 20 atm. Non regenerative adsorption: flow 10 – 1000 m^3/h, 0.01 – 1.2 g VOC/m^3.
Scrubber (2)	95 – 99.9 % reduction	Indicative application range: flow 10 – > 50000 m^3/h, 0.3 – > 5 g VOC/m^3.
Thermal incineration	95 – 99.9 % reduction VOC (2) < 1 – 20 mg/m^3	Indicative application range: flow 1000 – > 100000 m^3/h, 0.2 – > 10 g VOC/m^3. Range of 1 – 20 mg/Nm^3 is based on emission limits & measured values. The reduction efficiency of regenerative or recuperative thermal incinerators may be lower than 95 – 99 % but can achieve < 20 mg/Nm^3.
Catalytic oxidation	95 – 99.95 % reduction VOC (2) < 1 – 20 mg/m^3	Indicative application range: flow 10 – > 100000 m^3/h, 0.05 – 3 g VOC/m^3.
Flaring	Elevated flares > 99 % Ground Flares > 99.5 %	

1. Unless stated, concentrations relate to half hour / daily averages for reference conditions of dry exhaust gas at 0 °C, 101.3 kPa and an oxygen content of 3 vol% (11 vol% oxygen content in the case of catalytic / thermal oxidation.)
2. The technique has cross-media issues that require consideration

Table 11: BAT-associated Values for the Abatement of Other Air Pollutants

Pollutant	Technique	BAT-associated values (1)	Remark
Particulates	**Cyclone**	Up to 95 % reduction	Strongly dependent on the particle size. Normally only BAT in combination with another technique (e.g electrostatic precipitator, fabric filter)
	Electrostatic precipitator	5 –15 mg/Nm^3 99 – 99.9 % reduction	Based on use of the technique in different (non-LVOC) industrial sectors. Performance of is very dependent on particle properties.
	Fabric Filter	< 5 mg/Nm^3	
	Two stage dust Filter	~ 1 mg/Nm^3	
	Ceramic Filter	< 1 mg/Nm^3	
	Absolute Filter	< 0.1 mg/Nm^3	
	HEAF Filter	Droplets & aerosols up to 99 % reduction	
	Mist Filter	Dust & aerosols up to 99 % reduction	
Odour	**Adsorption Biofilter**	95 – 99 % reduction for odour and some VOC	Indicative application range: 10000 – 200000 ou/Nm^3
Sulphur dioxide & acid gases	**Wet limestone scrubbing**	90 – 97 % reduction SO_2 < 50 mg/ Nm^3	Indicative range of application for SO_2 < 1000 mg/m^3 in the raw gas.
	Scrubbers	HCl (2) < 10 mg/ Nm^3 HBr (2) < 5 mg/ Nm^3	Concentration based on Austrian permits limits.
	Semi Dry Sorbent Injection	SO_2 < 100 mg/ Nm^3 HCl < 10 - 20 mg/ Nm^3 HF < 1 - 5 mg/ Nm^3	Indicative range of application for SO_2 < 1000 mg/m^3 in the raw gas.
Nitrogen oxides	**SNC**	50 – 80 % NO_x reduction	
	SCR	85 to 95 % reduction NO_x < 50 mg/ m^3. Ammonia < 5 mg/ m^3	May be higher where the waste gas contains a high hydrogen concentration.
Dioxins	**Primary measures + adsorption 3-bed catalyst**	< 0.1 ng TEQ/Nm^3	Generation of dioxins in the processes should be avoided as far as possible.
Mercury	**Adsorption**	0.05 mg/Nm^3	0.01 mg/Nm^3 measured at Austrin waste incineration plant with activated carbon filter.
Ammonia & amines	**Scrubber**	< 1 - 10 mg/Nm^3	Acid scrubber.
Hydrogen sulphide	**Absorption (alkaline scrubber)**	1 - 5 mg/Nm^3	Absorption of H_2S is 99 %+. An alternative is absorption in an ethanolamine scrubber followed by sulphur recovery.
1.	Unless stated, concentrations relate to half hour / daily averages for reference conditions of dry exhaust gas at 0 °C, 101.3 kPa and an oxygen content of 3 vol%		
2.	Daily mean value at standard conditions. The half hourly values are HCl < 30 mg/m^3 and HBr < 10 mg/m^3.		

8.0 EMISSION MONITORING AND REPORTING

The emission monitoring should be carried out to determine the substances in the clean gas so that they can be reported.

For measurement methods, see the chapter on Monitoring in Pollution Prevention and Abatement Handbook, WORLD BANK GROUP, 1998.

8.1 Continuous Monitoring

Where appropriate, continuous monitoring techniques should be used. Wherever a combustion process (other than flaring) is used for the destruction of hydrogen sulphide or hydrocarbons, its effectiveness should be demonstrated indirectly by continuously monitoring the temperature and the oxygen content of the exhaust gas.

Visual and olfactory assessments of releases from incinerators, flares, furnaces and other sources liable to cause a nuisance emission should be made when appropriate, particularly during upset/start-up/shut-down conditions.

Additionally, all flare systems should be equipped with adequate monitoring and control systems necessary to operate smokeless and to be so observed at all times under nonemergency conditions. Such systems should include flow measurement, for which proven non-intrusive systems at the flare base are available, luminosity measurement with automatic steam control, remote visual observation using colour TV monitors in relevant plant control rooms with access to steam control, pilot flame detection, etc. The selection of one of the above features depends on the size and nature of flare installations (Source: IPC Guidance Notes, UK).

8.2 Stack Sampling

Direct measurement of the concentrations of the following emissions in samples of flue gases should be performed regularly (for example, on an annual basis). At least three data sets should be used (ref: Pollution Prevention and Abatement Handbook, WORLD BANK GROUP, 1998)

- PM (not relevant for natural gas fuel)
- PM_{10} (not relevant for natural gas fuel)
- $PM_{2.5}$ (not relevant for natural gas fuel)
- SO_2 (not relevant for natural gas fuel)
- NO_x
- CO
- Heavy metals (not relevant for natural gas fuel)
- HF
- HCl
- HC
- VOCs
- Dioxins and furans

The off-gas parameters that should be determined are:

- The volumetric off-gas flow
- The off-gas temperature
- The water vapour content of the gas
- The static pressure in the off-gas duct
- The atmospheric pressure
- Monitoring period

The stack dimensions should be also reported.

All emission concentrations should be reported under standard conditions, i.e. 273 K, 101.3 kPa.

8.3 Leak Detection and Repair Program (LDAR)

The site should be equipped with suitable portable hydrocarbon monitors so that all process vents and possible sources of fugitive losses are checked to assess hydrocarbon emissions from the site as a part of the leak detection and repair (LDAR) programme. The instrument(s) should also be used to check for leaks and other irregular venting at times of plant maintenance and shut-down. An assessment should be made of the total hydrocarbon emissions from the site on a regular basis. Records should be kept of the individual contributions to each total. The activities of the site LDAR programme should also be retained as records. Monitoring should be undertaken during commissioning, start-up, normal operation, and shut-down unless it is shown to be inappropriate to do so (Source: IPPC Guidance Notes, UK).

REFERENCE

1. European Integrated Pollution Prevention and Control Bureau (EIPPCB), (August 2006). Best Available Techniques (BAT) Reference Document for the Manufacture of Organic Fine Chemicals. Joint Research Centre, Institute of Prospective Technological Studies, EIPPCB

2. European Integrated Pollution Prevention and Control Bureau (EIPPCB), (February 2003). Best Available Techniques (BAT) Reference Document in the Large Volume Organic Chemical Industry. Joint Research Centre, Institute of Prospective Technological