

Commission of the European Communities

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CLEANER TECHNOLOGIES IN THE CHEMICAL INDUSTRY

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CLEANER TECHNOLOGIES IN THE CHEMICAL INDUSTRY

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1. INTRODUCTION

1.1 The Study

This final report presents the results of the first and second stages of ERL's study of 'Cleaner Technologies in the Chemical Industry', carried out for the Directorate for Environment and Consumer Protection. While ERL received considerable cooperation from the EEC chemical industry in the course of its investigations, in particular from the Clean Technology Sub-Committee of CEFIC, the conclusions and recommendations contained in the report are those reached independently by the consultants, and do not necessarily reflect the final view of DGXI of the European Chemical Industry.

Because of the differences in size, nature and the feedstocks of their production processes, together with other key factors including the economics of the industry, its organisation, etc., the two sectors of the industry deserve separate consideration.

1.2 Objectives of the Study

The principal purposes of the overall study are:

- o to examine the extent to which cleaner technologies have been introduced in the production of chemicals in response to normal business and market forces and also to pollution controls themselves;
- o to note the contribution cleaner technologies have made to reduced emissions, wastes, energy and raw material use in the industry;
- o to identify the principal factors which influence the selection of process technologies in chemical production and to point out potential conflicts with regard to the adoption of cleaner technologies;
- o to assess the scope for introducing cleaner technologies in future chemical production processes, and the constraints to this process;
- o to conclude what action on the part of the EEC Commission, Member State Governments and the industry itself might facilitate the adoption of cleaner technologies in this industry.

1.3 Approach and Scope of the Study

- 1.3.1 The methodology adopted to examine the status and factors influencing the use of cleaner technologies in the chemical industry has been a **case study** approach. However, because of the nature and organisation of the sectors, a rather more rigorous case study approach was possible with bulk chemicals than with fine chemicals. The approaches and scope of the study to the two sections are therefore discussed separately.

1.3.2 Bulk chemicals

Bulk chemicals for study have been selected according to certain pollution/waste and resource use criteria, considered most likely to illuminate the issues involved. These were described and the chemicals identified in an earlier working paper.

In total some 14 products/sectors were selected from the different parts of the bulk chemical industry:

Inorganics

Chlor-alkali industry
Aluminium production
Phosphoric acid
Sulphur industry
Titanium dioxide

Petrochemicals

Halogenated hydrocarbons,
Acrylonitrile
Olefin oxides

Organics

Certain nylon intermediates
Methyl methacrylate
Phthalic anhydride
Tolylene diisocyanate

Polymers

Nylon production
VCM/PVC

Within some of these sectors, e.g. nylon production, an examination of the production routes and the process technologies involving intermediate manufacture were considered.

In addition, a broader examination of bulk chemical production in general was undertaken, and the report draws upon other examples where appropriate.

The consultants carried out an extensive literature research supported by discussions held with chemical companies in the following Member States:

- o Belgium
- o France
- o Germany
- o Italy
- o Netherlands
- o United Kingdom.

A list of the companies consulted is given in Appendix 1.

1.3.3 Fine chemicals

The difficulty of adopting a similarly precise case study approach for fine chemicals lies in the fact that because of its very diverse structure, and the large number of small companies operating, it was not possible to identify and compare the process technologies/operations companies making precisely the same product.

Nevertheless, the same general principal has been adopted whereby, instead of examining selected individual chemicals for case studies, sub-sectors or product areas were identified within the

fine chemical industry. These comprised the following:

- i. pharmaceutical intermediates and finished products.
- ii. agrochemicals/pesticides,
- iii. dyestuffs,
- iv. food additives,
- v. fine inorganics (involving toxic metals),
- vi. fine inorganics (precious metals),

Within groups i and ii, being the largest sectors and with which the majority of interviews were held, we attempted where possible to focus discussions on processes involving the use or production of toxic or environmentally problematic chemical groups. These include products on the EEC black and grey list substances, such as:

persistent organohalogens,
organo phosphorus compounds,
halogenated phenols,
lead, chromium, antimony and arsenic compounds.

In addition to discussions held with companies involved with the production of these groups of compounds, ERL undertook more general discussions with representatives of the industry on the development of fine chemicals process technology. A list of the companies visited in this part of the study is also given in Appendix One.

1.4 Definition of Cleaner Technologies in the Chemical Industries

1.4.1 In view of what are often varying and sometimes rather loose references made to "cleaner" or "clean technologies", it is worth defining exactly what were included in this study of the issue in the chemical industry. In general terms, cleaner technologies embrace the notion that "prevention is better than cure" and that their adoption through change of manufacturing process reduces the level of polluting emissions/wastes and/or energy and/or raw material, catalyst, solvent requirements. In the chemical industry this change in manufacturing process could involve one or more of the following:

- i. adoption of manufacturing process, involving different feedstocks and /or significant change in reaction conditions, catalyst, etc.;
- ii. adoption of a different route to a final end product involving either fewer stages with less pollution/energy/wastes and/or less toxic intermediates/feedstocks;
- iii. the recovery and recycling of by-product or uncovered feedstock from waste streams into the process itself;
- iv. the recovery, usually involving purification, and use of a by-product as a feedstock in another chemical process or as a final marketable product in its own right.

There is a tendency for cleaner technologies to be considered mainly in terms of (i) above. However, the potential importance of the other forms that cleaner technologies can take in the chemical industry should be recognised.

We would note that 'clean' in respect of process technologies has been defined in terms of emissions rather than pollution. The latter will of course also be a function of the local receiving environment.

1.5

Organisation of the Report

Following Section 2, which summarises the **findings and conclusions** of the overall study, the report is separated into two main sections:

Section A covering Bulk Chemicals, contains:

Section 3: The use of cleaner technologies in EEC bulk chemical manufacture.

Section 4: Factors influencing the selection of bulk chemical process technology.

Section 5: The future scope for adoption of cleaner technologies in EEC bulk chemical production.

The findings in Section 3 concerning past and current development and use of cleaner technologies are supported by Appendix 2 containing case studies giving brief descriptions of basic process technologies available, and their principal characteristics.

Section B on Fine Chemicals contains:

Section 6: Nature and structure of the fine chemicals industry.

Section 7: Process technology of the fine chemicals industry.

Section 8: The environmental significance of the Fine Chemicals industry.

Section 9: Factors influencing the selection of fine chemical process technology.

Section 10: The use and development of cleaner technologies in EEC fine chemicals production.

A list of the principal reference material examined during the course of the study is shown at the end of the report.

1.6

Acknowledgements

ERL would like to express its thanks to the many individuals and companies in the chemical industry throughout the EEC Member States who provided their time and information to the consultants during the course of the study. However, it should be stressed that the conclusions expressed in the report are those of ERL and do not necessarily represent the views of what is a large and diverse industry.

2. CONCLUSIONS

2.1 Principal Findings of the Study on Bulk Chemicals

2.1.1 Past development and use of cleaner technologies

- i. The hypothesis that the adoption of cleaner technologies by the bulk chemical industry is coincident with the economic and operational interests of the industry is too simplistic and cannot always be supported by the facts.
- ii. However, the development of new basic bulk chemical processes has more often than not also involved significant reductions in associated emissions/wastes and/or reduced energy/raw material use. In some instances, the rationale for the new process development has been precisely to achieve such results.
- iii. Improvements in product yield and energy efficiency have been achieved as a matter of steady refinements and modifications to process technologies over many years, as well as by major change in process technology.
- iv. There can be conflicts or trade-offs in the emission and resource benefits to be realised in the introduction of new process technology. For example, less toxic by-products/wastes may be achieved at the expense of a fall in overall product yield. It is also important to recognise that apparent environmental gain in one production process achieved by a change in feedstock, may be offset by increased emission/wastes in producing that feedstock. Perhaps the most common cleaner technology trade-off occurs in the recovery and recycle of by-products/unconverted feedstock, which usually involves additional energy expenditure per unit of product for that process. This may be compensated by the reduction in energy required to produce less of the original feedstock.
- v. The adoption of available cleaner basic bulk chemical processes has occurred to a considerable extent in the development of many sectors of the bulk chemical industry. Particular progress has been made with recovery and recycle of certain toxic micro-pollutants (including black list substances). However, it should be noted that:
 - o there is considerable variation in the situation within the main sectors of the industry's inorganic, petrochemical, polymer and organics production;
 - o development and use of cleaner technologies is less widespread in inorganic bulk chemicals than in other sectors, probably a function of the inherent chemistry and more limited feedstock options, the somewhat slower economic growth and of the less integrated nature of the industry; in some inorganic processes, of course, very considerable cleaner technology development has taken place.

- vi. Selection of process technology is principally determined by direct considerations of capital and operating costs. However, local and intra-company factors are often of paramount importance in determining the selection of process technologies, particularly for organics. Major influences can include size/configuration of plant, availability of feedstock, familiarity with processes, waste/effluent disposal options and integration with existing operations.

2.1.2 Future Scope

- vii. In theory, there is considerable scope for the development and further use of cleaner technologies in many sectors of bulk chemical production. The potential varies from sector to sector, and also among countries and companies. There are good economic and operational reasons to believe that cleaner technologies will continue to be adopted in the future development of the industry, although again the degree of application will vary among sectors, countries and companies.
- viii. However, the changed economic circumstances and outlook for the bulk chemical industry from that prevailing up to 1975 are likely to slow or restrict this process, particularly with respect to the adoption of new basic process technologies. The following points may be made:
- o The requirement for additional capacity over the next 10-15 years will be small (and in some cases zero) in many bulk chemical sectors. New capacity built will therefore largely be replacement capacity or small additions achieved through debottlenecking on existing plants. In these circumstances, local factors and existing plant configurations will tend to have a strong and rather conservative influence on process type adopted.
 - o Research and development of new basic bulk chemical processes will generally be less than that of the past. One can also note that an increasing share of new cleaner basic process technologies is being developed outside the EEC, particularly Japan, where economic, raw material and emission/waste control circumstances are more conducive to such development.
 - o Research and development funds are being steered into the expanding and more profitable sectors of the industry. This includes fine chemical development.
- ix. Taking account of both the economic circumstances noted above, and the potential benefit to be derived from cleaner technologies, particular focus in further application should be given to:

- (a) recovery/recycle of by-products/wastes within plants and for reuse/sale outside plant;
- (b) cleaner technology applications (including (a)) to reduce the quantities of relatively insoluble inorganic wastes and weak acid effluents.

In making these remarks, it is recognised that in some plants, a great deal has already been achieved and further scope is limited. Also, there are very real economic and sometimes technical constraints to recovery and resale of by-products to a third party industry. Nevertheless there is undoubtedly also scope for further refinement and improvement of existing technologies, a particularly important aspect in a period of low investment new plant capacity.

2.2 Principal Findings relating to Fine Chemicals Industry

2.2.1 Structure and nature of the industry

- i. The industry is made up of very many (some 350-450 companies producing active ingredients) usually small companies. Most are highly product oriented, geared to supplying a particular market. Others specialise in producing certain kinds of intermediates or inorganic fine chemicals. Quantities produced mostly vary from less than one tonne to 1,000 tonnes/year produced in batch processes. Some pesticide products and certain other fine chemicals are produced in larger quantities (up to 20,000 tonnes/year), often in continuous or semi-continuous processes. Many of the market sectors for fine chemicals, particularly pharmaceuticals, certain pesticides, photographic chemicals, food additives/perfumes are still growing quite strongly. These faster growing and larger markets are mostly organic chemicals.
- ii. The principal environmental problems of fine chemicals plants tend to involve toxic micro-pollutants rather than heavy pollutant load. Most of the EEC Black and Grey List substances are included in the feedstocks, products and sometimes by-products of the fine chemicals industry. This is inevitable and integral to the nature of an industry specialising in the production of fine chemicals. As a result, the industry's plant and operations are specifically designed to cope with this fact. However, many fine chemical plants do not give rise to significant pollution effects, and impacts tend to be site specific.
- iii. The production of fine organics involves multi-stage (3-20), usually liquid phase, reactions, using a very wide selection of bulk or semi-bulk organic chemicals as feedstocks. Many of the processes are similar in type using common inorganic/organic reagents. Yields for individual stages are generally high, in the 80-95% range,

but can sometimes be much lower with large yields of by-products. Use of catalysts is growing but can give rise to metal pollution problems. Production of fine inorganics generally involves only 1-3 stages, often fairly simple solid/gaseous phase chemistry.

2.2.2 The use and future scope for cleaner technologies in fine chemical production

- iv The principal thrust of the industry is towards development of new products rather than new production processes. However, there is increasing emphasis on improving yields/reducing production costs of existing fine chemicals, and this process is generally, but not always, consistent with lower waste technologies. Also emission/waste questions are being given increasing emphasis in design of new processes, and sometimes force changes in existing ones. Conflicts can arise, such as the drive to higher purity products in some sectors and increasing use of catalysts can produce more contaminated effluent streams. In the latter case, catalytic processes have sometimes been prevented because of this problem.
- v. Given the number of reaction processes and the diversity of the fine organics industry, the theoretical scope for introduction of cleaner technologies is considerable. The process is likely to be gradual, bearing in mind the product orientation of the industry and the allocation of R&D resources, but should slowly increase, particularly as more resources are directed to production processes. This is partly a function of growing attention on fine chemicals from large multi-national companies. The scope for introduction of cleaner technologies in the fine inorganics industry, containing most of the Black/Grey List substances is much more limited.
- vi. However, by the nature of the industry, most production technologies in manufacturing fine chemicals are commercial secrets and unique to the companies that develop them.
- vii. Recovery of by-products is limited by the generally small quantities produced, and possibly contamination by other toxic compounds. Nevertheless, there is considerable scope in this respect and the fine chemicals industry in total recovers and reuses more by-products from waste streams than does the bulk chemical industry, mostly because product value is generally much higher. A very high level of waste recovery exists in production of precious metals/rare earth compounds.
- viii. The scope for reducing energy consumption is rather limited. For most processes energy is usually used in a number of relatively low temperature applications where the cost of waste heat recovery is high. Exceptions are some of the rare metal/inorganic solid/gaseous phase reactions, which take place at higher concentrations.

2.3 Conclusions and Recommendations for Action

Here we draw certain conclusions and make suggestions on areas for possible action on the part of the Commission, Member State Governments and the chemical industry. Most suggestions for positive action envisage collaboration between the parties mentioned above.

2.3.1 Bulk chemicals

- i. It does seem justified for the Commission or Member State Governments not to make **grants/fiscal incentives** available to chemical companies to encourage the adoption of cleaner technologies, except in respect of demonstration projects - see iv. Apart from the difficulty of devising an equitable scheme, the size of the fund required to have any impact would have to be very large.
- ii. Nor do we recommend that **funds be made available for supporting research and development of new basic process technologies** for bulk chemical manufacture. The principal reasons are:
 - a. again, there would be difficulties in drawing up criteria for selecting R&D projects for support which were equitable;
 - b. the amounts of money would again have to be large to have a significant impact;
 - c. without prior and independent financial commitment from industry there is less chance that the technologies would be developed to the point of commercialisation.
- iii. However, it is possible that some **R&D support could be justified** to encourage development of clean technologies aimed at:
 - recycle/reuse of by-products/unconverted feedstocks within plants;
 - purification processes of by-products to be used in outside plants or other industries;
 - use of by-products as alternative feedstocks.

Sometimes there will be no distinction between these recovery technologies and the basic production technologies. These technologies have probably received less attention in the past than the development of new production processes, and certain recovery processes may have wider application than to one particular by-product/waste stream. We would suggest further study is needed to examine the scope for these applications, particularly in organic chemicals production, and the case for financial support. Also see vii. below.

- iv. However it is suggested that the principal funding initiative of the Commission in respect of chemicals should be directed to support suitable demonstration projects, where the basic R&D has already been carried out. We believe support may be justified for **certain kinds of demonstration projects**, particularly in the recycle/reuse applications identified in iii. above, where the technology could be of wider application than being confined to specific chemicals.
- v. We support the **education** initiatives being adopted by the UN Economic Commission for Europe, by the French government and by industry itself in publishing compendiums of cleaner or low waste/low energy process technologies in the chemical industry. More emphasis by the Commission could be placed on recycle/reuse cleaner technology processes, rather than on basic process technology itself, which is more adequately covered by technical publications and probably better known to the industry itself.
- vi. The study has indicated that familiarity with process technology can considerably influence industry decisions to adopt cleaner technologies or not. Education may not be sufficient in its own right. Support and encouragement could therefore be usefully given to **appropriate chemical industry seminars/ symposiums**, where experience and problems with using certain cleaner technologies could be discussed among technical experts. Every effort should be made to invite participation of process engineers from countries outside the EEC, including Japan.

Priorities in v. and vi should be given to areas where current production processes:

- have wide application;
- give rise to major pollutant load or Black/Grey list micro-pollutant problems;
- have associated wastes in large quantity but potentially usable, or of high value.

2.3.2 Fine chemicals

- viii. The involvement of the Commission in promoting the use of cleaner technology applications in fine chemicals is by and large hard to justify for the following reasons:
- Support for a demonstration project on a particular reaction stage, even if subsequently commercialised, would have only limited application in the industry - see 2.2.2 vi. above.

- Because of the commercial confidence bound up in production process technology, attempts to share, distribute and discuss information in this respect are unlikely to be successful.

- ix. Nevertheless, there are probably a few production processes, relatively well known, which give rise to particular emission wastes problems. It is suggested that the Commission should explore possibilities in this respect further, with particular emphasis on the fast growing sectors of the industry.

- x. Again, the most cost/beneficial area for possible support in demonstration projects is likely to be in technologies that could be widely applied in recovering by-products, and slightly contaminated products from waste streams, where by-product value is high. Emphasis should be given to areas where high pollutant load or, more particularly, Black and Grey List substances are involved. It may be that waste disposal/solvent recovery contractors have a role to play in the development and commercialisation of such technologies.

2.3.3 Final remarks

From the conclusions above and the analysis in the text, any action on the part of the Commission with respect to promoting use of cleaner technologies in the chemical industry, should, we believe, emphasise the bulk rather than the fine chemicals sector. This conclusion is the opposite of what was foreseen at the start of the project.

We would, however, strongly suggest that examination of the scope for cleaner technologies in semi-bulk organics sector should be pursued, as we believe that cleaner technologies, of quite wide application, might play an important role in reducing wastes/emissions in this sector.

SECTION A: BULK CHEMICALS

3. THE USE OF CLEANER TECHNOLOGIES IN EEC BULK CHEMICAL MANUFACTURE

3.1 Introduction

This section of the report supported by Appendix 2 examines:

- i. the historical development of process technologies adopted by the bulk chemical industry, their environmental/resource characteristics and presents comments upon the chief rationale for their adoption;
- ii. growth in production of the bulk chemicals examined and, where possible, the share of total production taken by cleaner technologies.

In Section 5, the report discusses the extent to which the cleaner technologies available to the industry are likely to be adopted over the next 10-15 years.

However, before describing the development and use of process technologies for various bulk chemicals, brief comment is given upon the nature of bulk chemical production and the nature of emissions/wastes that may be associated with them.

3.2 The Nature of Bulk Chemical Production

3.2.1 The development of the bulk chemical industry and its production processes

Bulk chemical manufacture is almost by definition the initial or early stages of the production process in the chemical 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 1950's to the early to mid-1970's. The consequences of this growth were:

- i. Average plant capacities increased many times in size and became large unit consumers of raw materials and energy.
- ii. The economic incentive for minimising production costs resulted in considerable R&D effort being devoted to improving process technology, search for new feedstocks, etc. This was an innovative era for the development and introduction of new process technologies.
- iii. A high proportion of petrochemical, bulk organic and polymer production processes became continuous (often in the gas phase), utilising selective catalysts.

- iv. Final product yields have in most cases showed steady improvement although this has slowed over the 1960-1980 period as obviously a situation of diminishing returns on investment applies as yields exceed 85-90%.
- v. Changed feedstock availability/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.
- vi. Even before the 1974 and 1979 rise in energy production prices, energy costs have contributed a large share of total production costs; the bulk chemical industry has devoted considerable process research effort to improve energy efficiency.

3.2.2 Changes in economic situation

A radical change in the economic situation and outlook for the bulk chemical industry has occurred since the mid-1970s, induced principally, 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 has been:

- o excess production capacity in many sectors of the industry since 1975-78;
- o market growth rates much reduced and growth sometimes eliminated altogether;
- o low or negative profit margins;
- o less R&D funds being devoted to the development of new process technology for bulk chemicals production.

3.2.3 Emissions and wastes

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

- o While certain sectors of the industry do produce emissions of high toxicity, including 'black' and 'grey' list substances (some of these are examined), environmental problems mainly arise from the large effluent load for which adequate dispersal in certain environments may be difficult.

- o 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.
- o A particular environmental problem of certain bulk chemical manufacture is the production of large quantities of rather inert solid inorganic wastes/by-products.
- o Large quantities of aqueous weak acid effluent can also be associated with certain bulk chemical production processes.

3.3 Use of Cleaner Basic Process Technologies

3.3.1 In the following sub-sections we determine the extent to which cleaner process technologies, where they can be identified, have been adopted in the natural evolution and expansion of the bulk chemical 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. There can be trade-offs between processes. For example, one process may have less overall wastes/by-products associated with it, i.e. higher yield, but may produce a more toxic waste stream than the alternative. The report 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 ameliorate any consequent impacts. Clearly there is room for argument in assigning the label of cleaner technologies. Nevertheless, such potential controversy is inherent in the notion of cleaner technologies and no attempt to understand and examine the issues can completely avoid them. What of course must be emphasised, is the actual impact of emissions/wastes from a particular process will depend upon the receiving environment. In other words, the identification of a 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 analysis will point out such conflicts, by showing where the lower emissions/waste technology (cleaner) has a higher energy use than alternative processes.

3.4 Historical Development of Process Technologies

3.4.1 In this section we identify the extent to which cleaner basic process technologies have been adopted in the natural development and expansion of each bulk chemical in the case studies, taking account of remarks in the preceding section defining and qualifying the term 'cleaner'.

Appendix 2 describes in summary form for some 17 bulk chemicals the principal process technologies that have been used, their characteristics and the rationale for their adoption. In Tables 3.4(a), 3.4(b) and 3.4(c) below we identify where such basic process development and adoption has resulted in **significant** improvements in either reduced emissions/wastes or energy/feedstock use. They will not point out the gradual and continuous small improvements in yields and/or energy gained throughout the chemical industry through plant design, refinement of operating conditions/catalysts, heat recovery/insulation, process control, good housekeeping, etc. Increases in energy efficiency achieved in this manner range from 15-40%. The importance of such improvements should be recognized but such developments are not the principal focus of this study.

3.4.2 **Inorganics**

In Table 3.4(a) overleaf, we summarise the extent to which the introduction of cleaner technologies has taken place in the manufacturing development of these bulk inorganics, and what the principal environment/resource gains have been.

Further comment:

- i. Aluminium. Basic Hall Heroult process has not been replaced. Gradual refinement and improvements to process have reduced energy regularly. A lower energy chloride process exists which avoids hydrogen fluoride emissions, but higher capital and maintenance costs result because of the construction materials required.
- ii. Chlorine. The requirement for high purity caustic (NaOH), not obtainable from diaphragm cell (widely adopted in the USA) has to a considerable extent, constrained replacement of mercury cell chlor-alkali production. Continual improvements to mercury cell design, recycling of mercury (recovered in end-of-pipe treatment) has allowed mercury emissions to be reduced from 250-500g/tonne Cl₂ produced to <50g/tonne Cl₂ produced. New materials, improved design of anode have contributed to reduced energy use. Cleaner membrane cell technology has been developed, avoiding mercury and asbestos use, and offering at least comparable energy efficiency.

Here, cleaner technologies were developed at least in part in response to environmental regulations.

Table 3.4(a)
REDUCTION IN EMISSION/WASTES AND ENERGY/RAW MATERIAL USE ACHIEVED THROUGH PROCESS CHANGE IN BULK INORGANIC CHEMICAL PRODUCTION IN EEC 1950-80

| Bulk Chemical | Significant Process Change | Marked Improvement through Change in Basic Process Technology | | | Comment |
|------------------|----------------------------|---|-----------------------|-------|---|
| | | Emissions/Wastes | Energy | Yield | |
| ALUMINIUM | No | Some | Yes | - | Modifications to basic production process, e.g. electrode preparation (anode baking). Improved fluoride recovery/recycle. |
| CHLORINE | Some | Some | Some | - | Partial adoption of diaphragm over Mercury cell process. Improvements to Mercury cell. |
| SULPHURIC ACID | Yes | Yes | No. Higher energy use | - | Lead chamber to significantly cleaner single contact process. Since 1965-70 most new plants double contact process. |
| PHOSPHORIC ACID | No | No | Some but see comment | - | Wide adoption of wet process (low energy but waste producing) except for high purity product where electric furnace process adopted. Improved wet process able to make high purity product. |
| TITANIUM DIOXIDE | Some | - | - | - | Some installation of cleaner chloride process which avoids coperas and weak sulphuric acid by-products. However, feedstock constraint. Italian production uses imported steel slag feedstock which reduces FeSO ₄ waste. |

- iii. Sulphuric acid. The industry converted from the lead chamber to the cleaner contact process principally to realise economies of scale. Further conversion to the double contact process, which recovers additional SO₂ in gaseous emissions and so increases yield, cannot be justified on economic grounds alone, but is usually the most cost-effective means of meeting the stricter SO₂ regulations now usually required. However, it may be noted that one sulphuric acid manufacturer opted for ammonia scrubbing equipment rather than a double contact (cleaner technology) solution to reduce SO₂ emissions.

The double contact process is also a cleaner technology which offers the means to recover SO_x emissions from metal pyrites smelters and uses them as a sulphuric acid feedstock. To be economic, the SO_x concentration must be of a certain level.

- iv. Phosphoric acid. Industry has largely adopted the wet process for fertiliser grade phosphoric acid production, with its associated production of gypsum (5 tonnes CaSO₄ . 2H₂O to one tonne product P₂O₅). However, it is cheaper than the energy intensive electric furnace process which is still used for high purity phosphoric acid production. High purity product can now also be manufactured by an improved (solvent extraction) wet process, and may be used in future.

A cleaner wet process (hemi-hydrate/double stage recrystallisation), offering the means to higher purity gypsum by-product has been built in the EEC. Only one plant using the 'cleaner' nitrophosphate process, has so far been installed in EEC Member States.

- v. Titanium dioxide. Raw material constraint (decreasing availability of rutile ore) has limited the use of cleaner technology. Some economic penalty in using more expensive imported slag feedstock process to reduce wastes. Also, because of its situation, one German chemical plant recovers sulphuric acid from weak acid waste stream as this is cheaper than alternative disposal option. However, this concentrating process is energy intensive.

Japanese and certain East European TiO₂ plants are required to recover/reuse weak sulphuric acid and precipitate and recover ammonium sulphate from waste streams as well as recover ferrous sulphate/oxide from copperas sludge. The FeSO₄ in turn is used for pigment production on site or purified and sold as water treatment chemical. The use of copperas derivatives for water purification is being actively developed in France, Germany (FDR) and the UK. The recovery of ferrous iron is estimated to add 25% to titanium dioxide production capital and operating costs.

3.4.3 Petrochemicals

Table 3.4(b) overleaf shows the extent of historical adoption of cleaner basic process technology in the production of selected petrochemicals and polymers.

- i. Ethylene oxide. Process development resulted from the desire for scale economics to reduce costs. Use of O_2 vs. air avoids large volume of contaminated nitrogen emissions oxidation motivated by economies of scale/ capital costs reductions in large plant.
- ii. Chloromethanes/perchloroethylene. Process development has offered greater flexibility in petrochemical/chlorination plants by optimising use of by-products/raw materials.
- iii. Acrylonitrile. 1950/60's development of process was if anything a dirtier process. However, cost of feedstocks and problems with by-products stimulated improved ammoxidation process - complex catalyst.
- iv. VCM. Once acetylene based process replaced, newer processes also offered some advantages as in (ii) above.

3.4.4 Polymers/Intermediates

Table 3.4(c) overleaf shows significant changes in emissions/wastes and in energy/raw material use arising from past changes in basic process technology or in the intermediate route to certain polymers. In the case of nylon:

Nylon 66 - is manufactured from the hexamethylene diamine (HMD)/adipic acid route

Nylon 6 - from polymerised caprolactam.

i. PVC.

The improvement in yield in the 1970s from around 95% to 97% through additional VCM stripping stage, although initiated by environmental/health and pressures from food packaging industry, turned out also to be economically justified.

For further VCM recovery, up to 99.8% PVC yield in some plants facing very stringent controls, the costs of recovery are greater than the value of additional PVC yield. The additional recovery has an energy use penalty.

The VCM/PVC suspension process which avoids use of water (therefore avoids evaporation energy use) has been adopted to some extent, but cannot meet certain grade specs and has certain other operational disadvantages.

| Table 3.4(b) REDUCTION IN EMISSIONS, WASTES AND/OR ENERGY/RAW MATERIAL USE IN CERTAIN PETROCHEMICAL PRODUCTION ACHIEVED THROUGH BASIC PROCESS CHANGE IN EEC 1950-80 | | | | | |
|---|----------------------------------|---|---|----------------------|---|
| Petrochemical | Significant Process Change | Marked Improvement through Change in Basic Process Technology | | | Comment |
| | | Emissions/ Wastes | Energy/ Raw Material | Yield | |
| ETHYLENE OXIDE | Yes | Yes | Silver Catalyst | Reduced | Gaseous process replacing aqueous process. Lower waste gas O ₂ oxidation now favoured over air ox. process. |
| CHLORO- METHANES | Some | Some | - | - | Use of process largely determined by availability of feedstocks. Methanol hydrochlorination process to methylchloride enables waste HCl from other processes to be used. Old 'dirty' process to CHCl ₃ and CCl ₄ largely replaced. |
| PERCHLOR- ETHYLENE | Yes | Yes | | - | Clean process oxychlorination of lower chlorinated hydrocarbons allow such waste products from other process to be upgraded. |
| ACRYLONITRILE | Yes | Yes | Bismuth/ phospho- molybdenum. Now used uranium based catalyst. | Yes | Originally introduction of ammoxidation was 'dirtier' process (more difficult by-products, lower yield). Improved Sohio process reduces by-products. |
| VINYL CHLORIDE MONOMER (VCM) | Yes | Yes | Some | Slightly reduced. | First development from acetylene to ethylene feedstock. Oxychlorination allows use of waste HCl. |

Table 3.4(c)
REDUCTION IN EMISSIONS, WASTES AND/OR IN ENERGY/RAW MATERIAL USE IN CERTAIN POLYMER PRODUCTION
ACHIEVED THROUGH BASIC PROCESS CHANGE IN EEC 1950-80

| Polymer | Significant Process Change | Marked Improvement through Changes in Process Technology | | | Comment |
|---|----------------------------|--|----------------------------------|-------|---|
| | | Emissions/Wastes | Energy/Feedstock | Yield | |
| POLYVINYL CHLORIDE (PVC) | Some | Yes | No. Some increase in energy use. | Yes | Recovery of carcinogenic VCM (unreacted feedstock) in gaseous emissions achieved through add-on steps, e.g. stripping, adsorption. |
| NYLON 66 intermediates - Adipic acid | No | - | - | - | No basic changes in route - HMD/adipic acid route still predominates. Cyclohexane, rather than phenol, feedstock route developed as this cleaner but more inflammable petro-chemical became more widely available. Acrylonitrile route is somewhat cleaner (significantly reduces toxic wastes and has higher yield than butadiene route) but is less 'clean' feedstock; not adopted. |
| | Some | - | See comment. | - | |
| - HMD | Some | - | See comment. | Some | |
| NYLON 6 - caprolactam | No | - | - | - | Polymerisation of caprolactam remains. Ammonium sulphate by-product (formed from both phenol and cyclohexane feedstock) has been avoided in some countries by nitration or benzoic acid process. |
| | Yes | Solid wastes - Yes Other emissions - NO | - | - | |

The move to larger continuous process autoclaves also reduces gaseous releases inside plant (subsequently vented to the outside environment) inherent by avoiding opening of batch autoclaves.

ii. Nylon 66

In so far as avoidance of phenol feedstock for adipic acid manufacture is considered environmentally desirable (a marginal and arguable issue), the increased availability of cyclohexane has resulted in less use of the phenol route. However, local circumstances, including plant, configuration, feedstock availability, type of existing capacity) dictates which route is adopted.

In the case of HMD manufacture, there is an environmental trade-off. The lower toxic emission/waste acrylonitrile route is cleaner than the more widely and traditionally used butadiene feedstock route, but involves a toxic/carcinogenic feedstock, whose production has awkward by-products, including hydrogen cyanide. Again local considerations are paramount in determining process route.

iii. Nylon 6

The nitration and benzoic acid routes to caprolactam were developed specifically to avoid production of large quantities of ammonium sulphate by-product. The cleaner (less $(\text{NH}_4)_2\text{SO}_4$ and lower cost) photonitrosation route to cyclohexanone oxime final, the final intermediate before caprolactam, has been used in Japan but not yet adopted in Europe.

3.4.5 Bulk Organic Chemicals

Finally, in Table 3.4(d), we show significant changes in emissions/waste and/or energy use in the production of bulk organics, which have resulted from changes in basic process technology.

- i. Phthalic anhydride. A cleaner o-xylene oxidation process has been developed, using a lower air to o-xylene ratio, resulting in less aqueous effluent and energy use. This process has yet been installed in the EEC.
- ii. Methyl methacrylate. The acetone cyanhydrin process is still the only process used in the EEC. Little of the ammonium sulphate by-product (3 tonnes $(\text{NH}_4)_2\text{SO}_4$ to 1 tonne product) is currently recovered, and this aspect will be discussed later in Section 3.6.3. The iso-butylene process, using butadiene feedstock, has been used in the USA but only yields around 55-65% yield. The direct carboxylation of ethylene (Dow-Badische-Reppe process) has not had any commercial application.

Table 3.4 (d)
REDUCTION IN EMISSIONS, WASTES AND/OR IN ENERGY/RAW MATERIAL USE FROM BULK ORGANIC MANUFACTURE
ACHIEVED THROUGH BASIC PROCESS CHANGE IN EEC 1950-80

| Organic Chemical | Significant Process Change | Marked Improvement through Changes in Process Technology | | | Comment |
|-----------------------|----------------------------|--|----------------------|-------|---|
| | | Emissions/Wastes | Energy/Raw Materials | Yield | |
| PHTHALIC ANHYDRIDE | Yes | Some | Yes | Some | When demand expanded in 1950/60's, old 'dirty' liquid phase process was replaced by cleaner gaseous phase continuous process - air oxidation of naphthalene. This process was largely replaced by o-xylene oxidation due to feedstock availability. Some reduction in emissions, improvement in yield, 5% maleic anhydride by-product can be recovered. |
| METHYL METHACRYLATE | No | No | - | - | Other cleaner processes avoiding ammonium sulphate and other sulphate by-products/wastes, based on butadiene feedstock not adopted. Yield is lower in cleaner butadiene/isobutylene process. |
| TOLYLENE DIISOCYANATE | No | No | - | - | Process has continued to be based upon phosgene and tolylene diamine. |

- iii. Tolylene diisocyanate. No other commercial process, besides the 'dirty' phosgene/tolylene diamine route, has been developed as a full scale commercial process. The product is the principal feedstock for polyurethane elastomers, fibres and coatings.

3.5 Current Use of Cleaner Process Technologies

3.5.1 Share of Total 1980 Capacity/Rate of Demand Growth

In this section we identify where possible, the current share that cleaner basic process technologies occupy of total 1980 capacity. A process qualifies as "the cleaner technology" if it has been commercially available since 1965.

It is then of interest to show this share in relation to the growth in production experienced [1] for the bulk chemicals over the 1970-80 and 1960-70 periods. Such comparisons are made for the inorganic, petrochemical, polymer and organic case studies, in Figures 3.5(a) and 3.5(b) overleaf.

3.6 General Conclusions

From the previous examination of historical development and use of basic process technologies, the following general observations may be made:

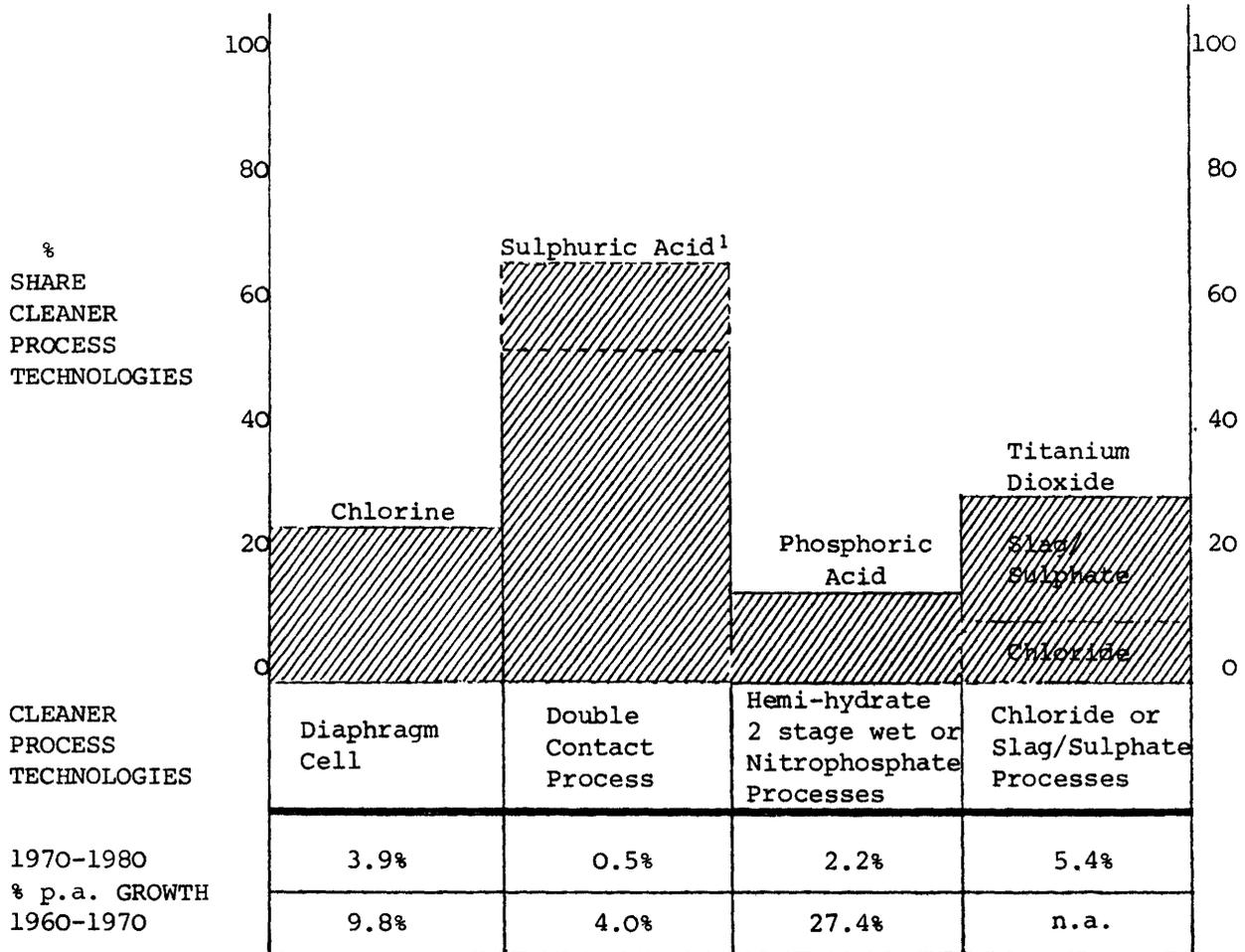
- i. In the 17 case studies selected, the development and use to date of essentially different [2] cleaner process technologies in the EEC may be summarised as:

| Table 3.6(e) | | | | |
|--|------|----------------|-------|--|
| LEVEL OF HISTORICAL ADOPTION OF CLEANER TECHNOLOGIES IN PRODUCTION OF SELECTED BULK CHEMICALS | | | | |
| High | Some | Little or None | Total | |
| 8 | 4 | 5 | 17 | |
| A more definitive assessment of the share of 1980 production capacity taken by cleaner basic process technologies is given in Section 3.5. | | | | |

[1] Not the same as production capacity, although the two are related over a long enough period. Growth in production capacity was generally faster in this period by some 2-3.5% per annum.

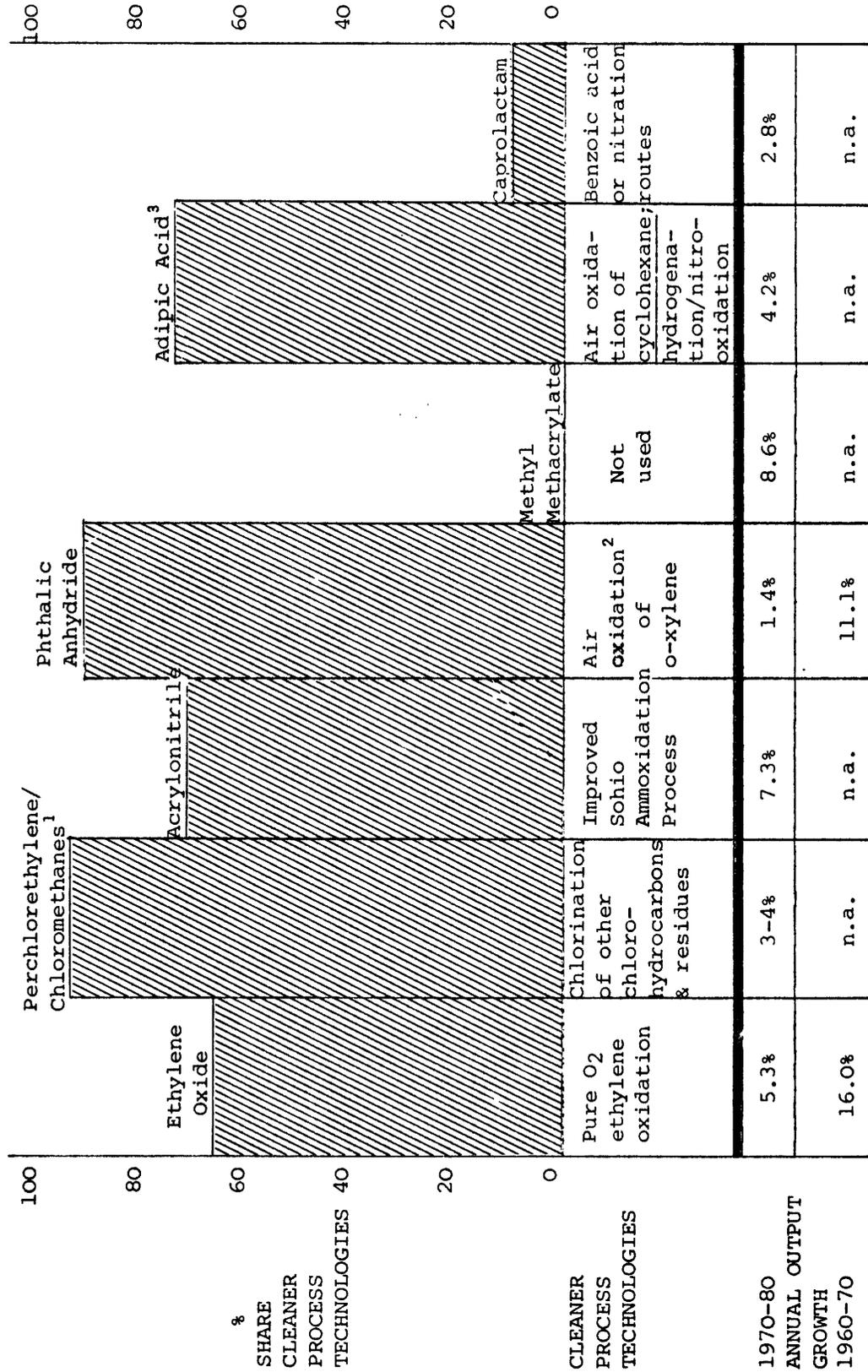
[2] We have already commented that there is a general trend over time to improve product yields and reduce energy requirements for any one given technology.

Figure 3.5(a): SHARE (%) CLEANER TECHNOLOGY OF SELECTED INORGANIC 1980 EEC PRODUCTION CAPACITY



¹dotted line implies very approximate estimate.

Figure 3.5(b): SHARE (%) CLEANER PROCESS TECHNOLOGIES OF SELECTED BULK ORGANIC 1980 EEC PRODUCTION CAPACITY



¹Excluding methyl chloride (manufactured from methanol or methane).

²Low air oxidation (cleaner) process only developed in 1970's.

³Process route not particularly clean but avoids alternative phenol feedstock.

- ii. There would appear to be a higher proportion of cleaner technologies adopted in petrochemical/organic production capacity than for inorganic. This probably reflects partially the faster growth of organics over the past 10-25 years, more alternative feedstock and process options and also the greater opportunity for recycling/re-use of by-products in these sectors of the industry. The latter is particularly well demonstrated in the manufacture of chlorinated lower aliphatic compounds.
- iii. Even so, it can be seen that there is considerable variation in the manufacture of petrochemicals and bulk organic intermediates with respect to the use of cleaner technologies. The more downstream the organic product involved, the more likely it is that local plant factors will limit the use of modern cleaner technologies - see Section 4.5.
- iv. Generally the development and adoption of new process technologies has been accompanied by increased yield (e.g. phthalic anhydride, PVC and sulphuric acid, but not always (e.g. HMD and ethylene oxide).
- v. The development of new basic process technologies has usually tended to improve the energy efficiency of production, in some cases significantly. However, where the cleaner technology involves recovery and recycle of a feedstock or by-product from a waste stream, this process will almost always require increased energy input, i.e. there is a conflict in such situations between reducing wastes and reducing energy use.
- vi. There has been greater use of catalytic processes (sometimes precious metals); catalyst efficiency has in many cases also been increased - longer life times. The replacement of liquid phase (often batch processing) by often higher yield continuous gaseous phase processes has occurred in several sectors of the petrochemicals industry. This has usually ameliorated the emission load.
- vii. The relationship between the adoption of cleaner technologies available and the rate of production growth would appear not to be close. Even so, the faster the rate at which new capacity has been added, the more likely it is for the majority of bulk chemicals that cleaner technologies will have been adopted and contribute to a larger share of current production capacity.
- viii. With inorganics, although the overall share occupied by cleaner technologies is not very high, the proportion that cleaner technologies takes of production capacity commissioned since 1970 is substantially higher.

- ix. Cleaner technologies are more readily taken up when they involve add-on or modification features to process plant, e.g. double contact sulphuric acid process, additional VCM recovery in PVC production, change from naphthalene to o-xylene feedstock in phthalic anhydride.

3.7 Other Cleaner Process Technology Application

3.7.1 **Cleaner alternative routes involving less toxic/fewer intermediates and/or waste streams**

Such examples can be found, e.g. use of cyclohexane rather than phenol in adipic acid, HMD or caprolactam production en route to nylon, but their incidence is mostly coincidental since other factors are likely to have a stronger influence in selection of process technology routes/feedstocks. However, if a process stage can be avoided, e.g. the photo-oxidation cyclohexane to cyclohexanone oxime en route to caprolactam (nylon 6 monomer), it is likely that there will be an economic incentive as well. For certain bulk chemical production processes have been specifically developed to avoid use of a certain toxic feedstock or production of a significant effluent/waste product, e.g. the toluene/benzoic acid feedstock en route to caprolactam, which avoids production of ammonium sulphate by-product.

There can, however, be conflicts or trade-offs between the cleanliness of a process and that of the feedstock. For example, acrylonitrile feedstock offers a cleaner route to the production of hexamethylenediamine (key intermediate for Nylon 66) than that from butadiene. Another case is the cleaner chloride process for titanium dioxide manufacture which can be undertaken with synthetic rutile, thus overcoming the natural scarcity of this raw material. However, acrylonitrile manufacture involves the by-product hydrogen cyanide; and in the second example, the production of synthetic rutile itself involves certain effluent and waste problems in the beneficiation process (there have been developments to reduce these effects). In other words, one should be aware that the adoption of an apparently much cleaner process technology may involve shifting environmental problems elsewhere [1].

[1] This phenomenon is particularly significant in fine chemical production and will be discussed more fully in the final report.

3.7.2 The Recovery/Recycle of a By-Product/Unconverted Feedstock from Waste Streams Into the Process Itself

Examples of this process in the case studies are:

| Production | Process | Feedstock/Chemical Recovered |
|------------------|-----------------------|------------------------------|
| Chlorine/NaOH | Mercury cell | Mercury |
| Sulphuric acid | Double contact | SO ₂ |
| Titanium dioxide | Chloride | Cl ₂ |
| PVC | Polymerisation | VCM (feedstock) |
| Aluminium | Cryolite electrolysis | HF |

It can be seen that this cleaner technology is of particular significance where the chemicals being recovered are considered as posing a particular potential impact as micropollutants upon human health or the environment, rather than a general problem because of the overall effluent load involved.

With the exception of chlorine recovery and recycle as HCl in the chloride TiO₂ production process, the other recovery/recycle processes identified above were introduced in response to environmental controls, i.e. they were not seen as being economically justified investments. However, as noted previously, a certain level of VCM recovery (PVC yield 95-97%) was in fact found to be economically justified in its own right. The double contact process recovery of SO₂ from gaseous emissions can show an economic return if the gaseous waste stream is concentrated enough and the value obtained for the sulphuric acid obtained is sufficiently high.

Also, wherever solvent extraction processes are employed, it has been normal practice to recover as much solvent as economically justified from waste streams.

3.7.3 The recovery and reuse/sale of by-products

In this instance we are concerned with the recovery of by-product and its reuse as a feedstock in other industrial or chemical processes, or for sale as a final product.

A principal example of such cleaner technology, currently practised widely in the petrochemical industry, is the recovery and reuse of:

- o hydrogen chloride
- o chlorinated aliphatic by-products
- o chlorinated organic residues.

These products/wastes are all produced as by-products in the manufacture of various chloromethanes and chlorinated C₂ compounds (see Appendix 2) and used as feedstocks in other chloro-aliphatic hydrocarbon manufacturing processes. The introduction of these cleaner technology processes was motivated by economic reasons - free chlorine, the alternative feedstock, has a high value as well as being a high energy content product.

The recovery of SO₂ from gaseous emissions of metal ore smelting processes is possible in new (non-reverberatory) pyrolytic furnaces through application of the double contact process. The by-product is sold as H₂SO₄ (70%), or reconverted to SO₂/S depending upon the proximity of the market.

The recovery and sale (or reuse in another plant) of liquid wastes is not widely practised. At one time acetonitrile was recovered as by-product in the manufacture of acrylonitrile and used as a specialised solvent. However, production has far outstripped demand with the result that production of this by-product is usually minimised. Most organic liquid wastes are recovered and burnt as fuel, thus saving energy, and avoiding the costs of purification. Maleic anhydride produced as 5% by-product in the manufacture of phthalic anhydride from o-xylene, is theoretically recoverable for reuse or sale, though the economics are marginal. Little other recovery of liquid organic solvents takes place other than solvent recovery which is widely practised.

The recovery and reuse/sale of other liquid wastes is relatively limited in the EEC. Weak sulphuric acid wastes are generated in large quantities from the bulk chemical industry. In the case studies examined, ferrous sulphate/weak acid sludges have been the subject of a good deal of study on the recovery/reuse. Only in the

Federal Republic of Germany is weak sulphuric acid recovered through a concentrating process estimated to cost 4-5 times the normal H₂SO₄ manufacturing process from roasting sulphur, but is cheaper than alternative disposal options. In Japan and several Eastern European countries sulphuric acid is regenerated from these wastes and ferrous sulphate recovered; the latter either for uses as a water treatment chemical or as in Japan and Czechoslovakia for manufacture of iron oxide pigments. Normally, these processes would undoubtedly be seen as increasing overall TiO₂ manufacturing costs. However, acid reutilisation is often economic in these countries as an input to an adjacent fertiliser/super phosphate plant where the costs of alternative sulphuric acid feedstock are seen to be higher (or involve foreign exchange expenditure).

Large quantities of solid waste by-products are produced in the following processes examined.

Gypsum/ammonium sulphate, these salts, gypsum being insoluble white solid, are produced in several inorganic but many organic chemical processes, particularly where control of acid effluent is undertaken through lime dosing. In the case studies examined:

- o a limited amount of gypsum (less than 10% that produced) is recovered from phospho-gypsum wastes in certain Member States; gypsum available in natural form is used chiefly in the construction (building block, plaster board) and cement industries;
- o in the past ammonium sulphate for sale as a compound fertiliser ingredient has been recovered from methyl methacrylate wastes, and it is currently recovered from some caprolactam and acrylonitrile process wastes, however overall only limited reuse of ammonium sulphate by-product takes place in the EEC.

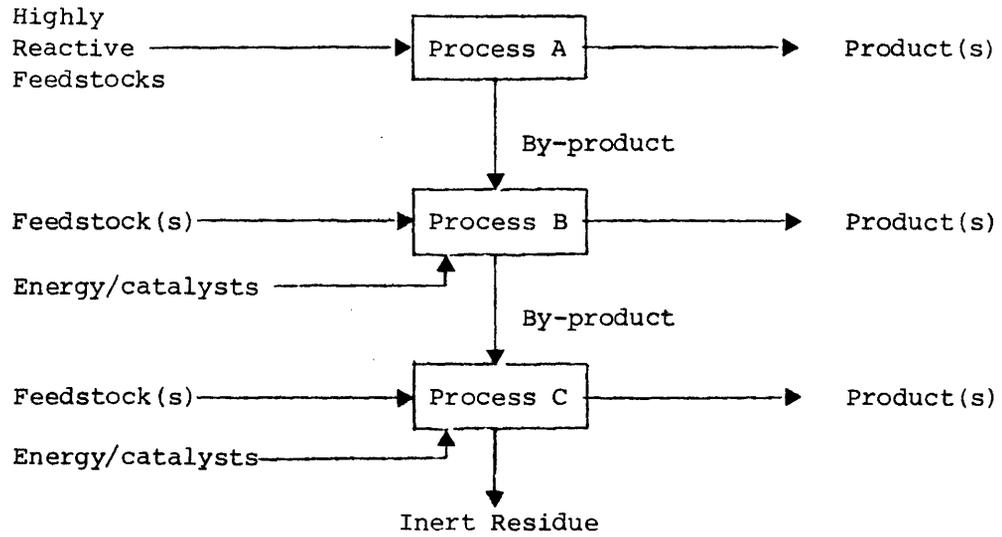
The potential for further recovery, and constraints limiting this process will be reviewed in Section 5.4.

| Product | Process | By-Product |
|---------------------|-----------------------------------|--|
| Phosphoric acid | Wet process | Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) |
| Titanium dioxide | Sulphate | FeSO_4 /Other sulphates, silicates |
| Methyl methacrylate | Acetone/ cyanhydrin | Ammonium sulphate |
| Caprolactam | Oxidation/ hydroxylamine route | Ammonium sulphate |

3.7.4 General comment on by-products

The total quantity of by-product production in EEC chemical manufacture is very large indeed (see Section 5.4.1). A proportion is recovered, recycled or reused in other processes, and as a result of stricter environmental controls, further introduction of such recycling technologies is taking place. However it should be recognised that a consequence of the Second Law of Thermodynamics is that the free energy/entropy loss involved in chemical reactions inevitably means that by-products are likely to have less chemical reactivity than the products from which they were derived. In other words, the majority of chemical by-products have fairly limited chemical applications and are relatively unreactive chemically - but not necessarily biochemically. The final result of recycling waste streams in various processes is a relatively inert solid residue (see Figure 3.6(a)).

Figure 3.6(a): SCHEMATIC REPRESENTATION OF DEGRADATION OF BY-PRODUCT REACTIVITY



4. **FACTORS INFLUENCING THE SELECTION OF BULK CHEMICAL PROCESS TECHNOLOGY**

4.1 **General Comment**

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

The principal factors that enter into process investment decision-making are shown in Figure 4.1(a) overleaf.

4.1.1 We have seen from Section 3 that the adoption of cleaner basic process technologies - assuming they exist - can vary appreciably from product to product.

4.1.2 The chart indicates that while the net effect of economic factors is almost certainly the principal influence on process technology selection, other factors also directly influence the decision [1]. The particular situation, the bulk chemical involved and the process options available will determine the relative weight of the influencing factors, including environmental considerations. As the chart shows, 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.

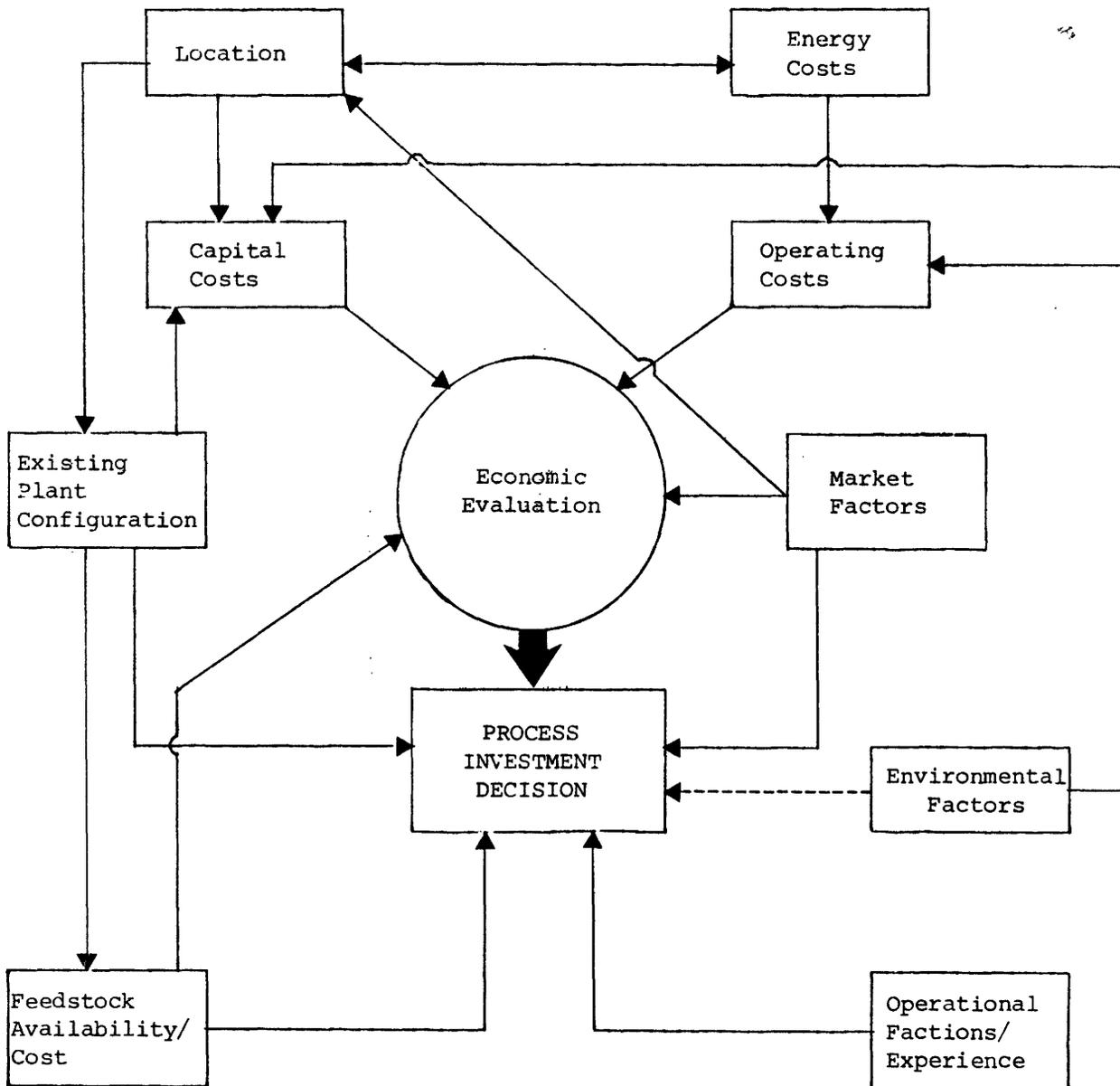
The following sub-sections discuss the manner in which the factors identified can bear upon the selection of the basic process technology.

4.2 **Capital Costs**

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

- o plant size
- o sophistication/type of plant
- o new or existing site
- o environmental controls.

[1] Several of them also indirectly affect plant capital and operating costs.

Figure 4.1(a): FACTORS INFLUENCING BULK CHEMICAL PROCESS DECISION MAKING

4.2.1 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 recognised that optimum sizes 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.

4.2.2 Type of plant

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

4.2.3 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 influential is whether construction takes place on a new or existing site. The usually higher costs of building process plant on greenfield sites tends to favour construction of 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 in Section 4.5.

4.2.4 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.

4.3 Operating Costs

4.3.1 Figure 4.1(a) indicated how **energy requirements** and the control and disposal of **emissions/wastes** influence 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 of process technology. Other elements of operating costs are discussed in the following sub-sections.

4.3.2 Labour

Although a capital intensive industry, the influence of labour costs on total bulk chemical production costs should not be underestimated. Indeed, during the course of discussions with the chemical industry, two companies mentioned that future selection of titanium dioxide process technology was likely to be heavily influenced by the fact that the chloride process - a continuous gaseous process - (happily, also the cleaner technology), had considerably lower labour costs than the batch liquid sulphate process. The sulphate process also could not benefit from economics of scale to the same extent.

4.3.3 Catalyst costs

The consumption of catalysts by the bulk chemical 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 times are relatively short. In other words, normal chemical 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.

4.4 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:

- o Chlor-alkali industry. The continued use of mercury cell technology has undoubtedly been influenced by the requirement to produce pure concentrated caustic.
- o PVC. The lower energy VCM suspension process cannot meet all market specifications required for the product.
- o PVC. 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, an issue which will be discussed further in Section 5.4.

4.5 Existing Plant Configuration

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

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

The process plant already installed on the site usually exerts strong direct as well as indirect (see Figure 4.1(a)) influence on the process technology selected in the building of new bulk chemical capacity. This may derive from one or more of the following reasons:

- i. type of feedstock available;
- ii. local outlets for by-products;
- iii. existing spare capacity for by-product/waste/effluent treatment;
- iv. 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, as shown in Figure 4.1(a) by **operational factors** whereby a company's successful working experience with one process technology will naturally incline it towards persisting with the same technology. There may also be saving on process license fees.

4.5.2 The factors i-iv noted in 4.5.1 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/will be imported from another plant within the group. The same point can occasionally apply to the use of by-products as well.

- 4.5.3** The influence of existing process plant configurations and capacities is very much more significant with respect to selection of petrochemical and bulk organic process technologies than for bulk inorganics.

5. THE FUTURE SCOPE FOR CLEANER TECHNOLOGIES IN THE EEC BULK CHEMICAL INDUSTRY

5.1 Introduction

In Section 3 we examined the extent to which cleaner technologies had been adopted during the development of the bulk chemical industry. In this final section on bulk chemicals we assess the future scope for the development and adoption of cleaner technologies in bulk chemical production and the constraints to this process. In this evaluation, we shall refer to the case studies and also to the more general situation applying in the EEC bulk chemical industry.

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

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

5.2 Basic Process Technologies

5.2.1 Theoretical Scope for Cleaner Process Technologies

In the **seventeen** bulk chemical products examined, all but 3 could be said to have developed cleaner process options, although clearly the degree of reduction in emissions/wastes or energy/raw material requirements realised 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.

Of the 14 or so case studies having cleaner technology options, there would appear to be scope for significantly increasing the share held by such process technologies in about 9 of the case studies. **Taking the EEC bulk chemical industry as a whole, considerable theoretical scope exists for further adoption of cleaner technologies, particularly in inorganics. The practical and economic reality may be different and, as will be seen, is likely to vary considerably among bulk chemicals.**

Before assessing the likelihood for future adoption of cleaner basic process technologies in the case studies, some more general issues are worth discussing.

5.2.2 The development of new processes

For certain bulk chemicals studied in Section 3.4, it was noted that cleaner process technologies had been become commercially available since 1970 but had not been so far taken up. As will be discussed in Section 5.2.5, other new cleaner process technologies have since been made commercially available or are being developed in certain other sectors.

However, taking the EEC bulk chemical industry as a whole, and there are obviously exceptions among companies, the amount of R&D funds being directed to new process technology development in bulk chemicals is significantly less than it used to be. The reasons are:

- i. the much lower profitability of the bulk chemical industry caused by the prevailing excess capacity and by the slowing and sometimes even fall in demand over the last 7 or 8 years;
- ii. the expected requirement for new process capacity over the next 10-15 years is very much less than that commissioned over the 1960-1975 period; this is a result partly of the much lower market growth currently anticipated for bulk chemicals and also of the current excess manufacturing capacity in many sectors.

Indeed, this situation has prevailed for some while, and it is noticeable that a much higher proportion of new process technologies is now being developed and introduced in countries outside the EEC, particularly Japan. The reasons can probably be found in the fact that they have experienced higher market growth than the EEC bulk chemical industry. But in some cases this has also been a response to stricter environmental controls. For the development of cleaner technologies in the chemical industry, there is some truth in the saying that "necessity is the mother of invention". It is also the case that their introduction cannot always be achieved without higher production costs.

5.2.3 Future expansion bulk chemical process capacity

The point has already been made that the introduction of new process capacity in the bulk chemical industry to meet a higher level of demand is likely to be slow, and for several sectors over the next five years, negligible. The reduced expansion prospects are also a result of the fact that new process capacity is now being built where the raw materials e.g. phosphates, are produced and/or where energy is cheap. This applies to aluminium and certain petrochemicals. Over the next 10-15 years therefore a considerable proportion of new process capacity built in the EEC Member States will be **replacement capacity** for old plant. Premature closure of existing plant is not very likely. Also a proportion of expanded capacity will be achieved through **de-bottlenecking** existing plant rather than the construction of large new increments of process

capacity. In both these situations, the influence of existing plant configurations discussed in Section 4.5, is likely to be considerable. In many sectors this will act as a constraint to the future adoption of new cleaner technologies.

5.2.4 Effluent treatment vs cleaner technologies

In several of the larger chemical industry plants in the EEC, 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.

5.2.5 Future adoption of cleaner technologies for certain bulk chemicals

Here we consider those case study bulk chemicals, for which both cleaner basic process technologies exist and where there is considerable theoretical scope in the EEC for increasing the contribution of such processes to overall future plant production capacity. Overlaying the assessments made in Table 5.2(a) (next page) are the comments made in the previous Sections 5.2.2 to 5.2.4 with regard to economic and other factors constraining the future adoption of cleaner basic process technologies in EEC bulk chemicals.

5.3 Recovery and Recycle of By-Products or Unconverted Feedstock

5.3.1 Scope

In the last 10 years or so 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 [1]. Furthermore, in some large complex organic plants of the EEC there has been an increase in the recycle of by-products.

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

There is, however, undoubtedly considerable scope for further recovery/recycle of by-products and unconverted feedstocks, particularly in the organic chemicals industry.

[1] 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 bled off and disposed of from time to time.

| Table 5.2(a) FUTURE LIKELIHOOD OF CLEANER PROCESS TECHNOLOGIES BEING ADOPTED IN THE EEC FOR CERTAIN BULK CHEMICAL PRODUCTION | | |
|--|---|--|
| Bulk Chemical | Cleaner Technology Process | Likelihood of being Adopted |
| 1. Inorganics | | |
| Aluminium | Chloride process. | <u>Small</u> . Not yet fully commercially proven. Cl ₂ expensive in EEC. Little or no future expansion of Al capacity in EEC. |
| Chlorine | Membrane process (lower energy use; avoids Mercury cells). | <u>Reasonable</u> . Already used in Japan. Economically competitive. However, as yet only one plant operating in Europe. |
| Sulphuric Acid | Double contact process. | <u>Good</u> . It is expected that nearly all new capacity will use this process. |
| Phosphoric Acid | a. Two stage crystallisation - hemi-hydrate wet process; b. Nitro phosphate process. | <u>Fairly small</u> . Little new P ₂ O ₅ capacity likely to be built in EEC. Some modification of existing wet process capacity to double stage crystallisation process. |
| Titanium Oxide | Chloride process. | <u>Quite good</u> . Environmental pressures combined with economic advantages of continuous gaseous process plus improvements in synthetic rutile beneficiation process. |
| 2. Petrochemicals/ Polymers and Organics | | |
| Ethylene Dioxide | Pure XO ₂ oxidation of ethylene. | <u>Quite good</u> . Economies of scale advantages, though local factors important. |
| EDC ¹ /Vinyl Chloride Monomer | Akzo lower energy route, avoiding electrolysis of brine (NaCl), with I ₂ , trimethyl ammonia and CuCl ₂ . | <u>Small</u> . Complex process and local plant configurations very important in organic chlorinations. Not yet commercially demonstrated. |
| Adipic Acid | Single stage high pressure route from butadiene with CO and water. | <u>Some</u> . However, opportunities for demonstration of project few. Local factors important. |
| Hexamethylene-diamine | via acrylonitrile. | <u>Some</u> but note previous remarks on HCN/acrylonitrile manufacture. |
| Caprolactam | Photo-oximation (with Cl ₂ with NO), single stage to cyclohexanone oxime. | <u>Reasonable</u> . Pressure from restrictions on (NH ₄) ₂ SO ₄ disposal; economics good; but local factors particularly important. |
| Methyl methacrylate | Isobutylene/butadiene process. | <u>Reasonable</u> but see later comments on ammonium sulphate recovery. |
| Acrylonitrile | Sohio improved ammoxidation process. | <u>Good</u> . Improved economics of this process established. |
| ¹ Ethylene Dichloride. | | |

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

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

5.3.2 Constraints

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

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

5.4 Recovery and Reuse/Sale of By-Products

5.4.1 Scope

The theoretical scope for recovery and reuse/sale of by-products from the bulk chemical industry is very large indeed. In quantitative terms these are principally made up of:

- i. certain inorganic salts;
- ii. aqueous weak acids.

The quantities involved are very large. Taking the case studies alone, the production of these by-products/acids are approximately as follows:

| <u>By-Product/Waste</u> | <u>Process</u> | <u>Approx. Quantity</u> <u>Million tonnes</u> |
|--|---------------------|--|
| Gypsum (CaSO ₄ 2H ₂ O) | Phosphoric acid | 12 |
| Ammonium sulphate | Methyl methacrylate | 0.5-1 |
| Ammonium sulphate | Acrylonitrile | 0.1 |
| Ammonium sulphate | Caprolactam | 1-1.5 |
| Mixed acids | HMD manufacture | 0.1-0.3 |
| FeSO ₄ slurry | Titanium dioxide | 1-1.5 |
| Sulphuric acid (15%) | Titanium dioxide | 9-11 |

Of these by-products:

- o Relatively little gypsum is currently recovered (10% of production) - gypsum plaster and combined phosphoric acid/cement plants utilising waste gypsum have in fact been closed down in Member States either for economic or technical reasons.
- o A proportion, approx. 25-35%, of ammonium sulphate is recovered and sold as compound fertiliser from methyl methacrylate and caprolactam by-product.
- o Little or no FeSO_4 or $\text{FeO/Fe}_2\text{O}_3$ is currently recovered from TiO_2 coproducts.
- o About 15-20% of acid wastes produced in TiO_2 production are recovered in a concentrating process.

This very approximate survey of the current position would indicate that the theoretical scope for additional recovery and reuse/sale of inorganic wastes is very substantial. This subject has received a great deal of attention in its own right, particularly phospho-gypsum and TiO_2 by-product recovery. The factors constraining to the recovery/re-use of by-products is discussed in 5.4.2.

The theoretical scope for recovery and re-use 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 vis-a-vis purification/recovery of the organic by-product itself. The potential for in-house recycle of organic wastes was discussed in Section 5.3.

5.4.2 Constraints to Recovery/Resale

These are made of technical and economic factors and may be summarised as follows:

- i. 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, for phospho-gypsum, and for ammonium sulphate when recovered from acrylonitrile/methyl methacrylate wastes to be used as a compound fertiliser ingredient.
- ii. Recovery costs. These may sometimes be very significant, as in acid concentration and certain recrystallisation processes.

- iii. Cost 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 calcium sulphate (anhydrite and gypsum) and to a considerable extent, ammonium sulphate in most parts of the EEC, and can be the case with sulphur (vis-a-vis double contact SO₂ 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.
- iv. 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.
- v. 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 that recovery of many by-products for reuse is already a much studied subject, and the chemical 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. In particular, the following aspects should be borne in mind:

- o the location of new plant in relation to market outlets for by-products;
- o improvement of purification processes for by-products;
- o the need to alter consumer insistence upon unnecessarily high purity standards, where such attitudes exist.

6. NATURE AND STRUCTURE OF FINE CHEMICALS INDUSTRY

6.1 Definition of Fine Chemicals

Before any description of the nature of the fine chemicals industry can take place it is necessary to define what is meant by fine or specialty chemicals. There is no rigid definition by the industry. For the purposes of this study it is not helpful to apply one, however it will be assumed that fine chemicals generally conform to the following:

- o chemicals produced in production units ranging approximately in size from 1-5,000 tonnes/year, the majority being below 1,000 tonnes/year;
- o chemicals produced in batch or sometimes semi-continuous processes.

There are of course certain categories of what may be thought of as fine chemicals which lie outside these guidelines. Some agrochemicals, for example the drins and thiocarbamate pesticides are produced in continuous processes up to 20,000 tonnes/year. Also, 1,000 tonnes/year fine chemicals are produced in continuous processes.

By contrast, bulk chemicals are produced in continuous processes from plant sizes of 10,000-200,000 tonnes/year.

6.2 Size of Industry

The fine chemicals industry is also characterised by the following features:

- i. a large number of relatively small companies;
- ii. low volume but generally high value output;
- iii. companies are either single product market oriented or, in some cases, specialists in certain types of process reactions.

It is difficult to be at all precise about the total production of the EEC fine chemicals industry. In most sectors of the industry, output is measured in terms of the value of the final products produced. But also, there are several stages and commercial transactions involving intermediate products which take place along the process to the marketed chemical. Very approximately it is estimated that EEC production of fine chemical end-products amounts to the order of 1 million tonnes/year, less than 1% of total chemical production in the EEC (about 140-160 million tonnes). However the consumption of initial feedstock to the fine chemicals industry is probably some 2-3 times the output.

The number of fine chemical plants operating in the EEC is estimated to number something of the order of 350-450 [1]. This excludes blenders or finished chemical formulators and very small units.

The diffuse nature and small size of the fine chemicals industry can be seen therefore to contrast markedly with the bulk chemicals industry.

6.3 Sectors of the Industry

While it is not always possible to be very specific, the fine chemicals industry can be broken down into the categories shown in Table 6.1 below. Where possible, we also show the relative size of the sector in terms of turnover, although the figures shown for the EEC should be considered as indicative only (some of them depend in part on ERL's estimates [2]). Figures are also shown for Italy since national statistics of that country are much the most comprehensive in the fine chemicals sector, and by showing them, some impression is given of the relative size of different sub-sectors. While obviously the relative importance of different sub-sectors varies from country to country, the situation in Italy does nevertheless give a broad indication of the relative situation and in particular shows the dominance of organic chemicals in the industry relative to inorganics.

[1] This estimate was based on an examination of the numbers of chemical or chemical producing companies in the Member States, consideration of the total size of the industry and of plant sizes within the fine chemical sectors.

[2] A more detailed study of individual sub-sectors would undoubtedly improve the statistics, but this was beyond the scope of the study.

| Table 6.1 | | |
|---|---|-------|
| PRINCIPAL CATEGORIES OF FINE CHEMICALS INDUSTRY | | |
| Category | Industry Production (1980) \$ x 10 ⁹ | |
| | EEC (v.approx.) | Italy |
| 1. Pharmaceuticals (1) | 13.2 | 4.4 |
| 2. Agrochemicals | 3.5-4.0 | 0.5 |
| 3. Industrial coatings/adhesives | na (3) | 0.4 |
| 4. Dyestuffs | 0.5 | 0.2 |
| 5. Paints & varnishes | 6.0(very approx) | 1.6 |
| 6. Food additives (1) | na | na |
| 7. Photographics | na | 0.5 |
| 8. Inorganics/metal oxides | na | 0.2 |
| 9. Detergents | na | 1.0 |
| 10. Cosmetics/perfumes | na | 1.3 |
| 11. Other fine chemicals (2) | na | 1.3 |

(1) Active ingredients plus final products.
(2) Includes fermentation products from cereal based starch and glucose.
(3) Indicates insufficient data available to provide any reliable estimates of category size.

Sources: UN (ECE) Annual Review of the Chemical Industry;
OECD, The Chemical Industry, 1979;
National Statistics of Netherlands, UK, France & Italy.

It can be seen that the **pharmaceutical** sector is by some way the largest in terms of value and also in terms of the number of companies and chemical processes involved. A sizeable proportion (perhaps around half) of companies in this sector are involved in the production of intermediates sold on to pharmaceutical companies. Indeed the existence of a large number of small to medium sized companies, employing 50-500 people producing fine organic intermediates is also a feature of other sub-sectors, most notably agrochemicals and food additives.

In volume terms **agrochemicals, dyestuffs, coatings and paints** are the largest sub-sectors. These categories all involve fewer process stages than pharmaceuticals as is discussed in Section 7.

6.4

Products

Apart from certain inorganics, metal oxides, salts and organo-metallic compounds of relatively simple structure and production chemistry, fine chemicals are mostly complex organic molecules. Indeed the principal driving force of the fine chemicals industry is the synthesis of highly selective compounds with a particular application in mind. That is to say, much of the industry is very market/product oriented, which, as will be discussed in later

sections, has significant implications for the allocation of R&D funds and the selection of process technologies. There is, however, a smaller but growing section of the industry, mainly producing organic intermediates, which is process oriented.

A consequence of the product orientation of the fine chemicals industry and the complexity of many fine organics, is that its products are generally high value. Most products sell in the range \$5-50/kilo (\$5,000-50,000 per tonne), with the majority being in the £20-40/kilo range. Some small quantity highly specialised products command considerably higher prices still. This price range compares to \$500-1,000/tonne for the majority of bulk chemicals. Again this feature has a bearing on the approach to production of fine chemicals and the allocation of R&D funds.

6.5 Growth of the Industry

Another feature of fine chemicals, which now mark them in contrast to bulk chemicals is the relatively high rate of growth experienced in many sub-sectors. In Table 6.2 below we show average annual production growth of EEC countries for pharmaceuticals. It is probable that for many countries these rates underestimate the overall growth of the industry since they were calculated using production values deflated by the national Wholesale Price Indices. In practice, it is known that the value of many pharmaceutical products fell in relation to industrial prices as a whole.

| Table 6.2 | | |
|--|-----------------------|---------|
| APPROXIMATE AVERAGE ANNUAL GROWTH OF PHARMACEUTICAL PRODUCTION | | |
| Country | Annual Average Growth | |
| | 1970-76 | 1975-80 |
| Belgium | 7.6% | 8.5% |
| Denmark | na | 8.5% |
| France | 2.1% | 6.5% |
| Germany | 4.6% | 4.0% |
| Italy | 4.0% | 8.5% |
| Netherlands | 3.5% | na |
| UK | 4.3% | 3.5% |

Source: UN(ECE) Annual Review of the Chemical Industry.

Even so, it may be seen that the production growth of the industry, particularly the 1975-80 period, considerably exceeded that of most other manufacturing industry, including bulk chemicals.

Strong growth in the latter half of the 1970's also continued for the agro-chemicals (particular herbicides) at around 3-5% per annum and for food additives, photographic and certain coatings and other fine organic chemicals. The requirement for organic and most inorganic chemicals generally grew less fast. And while for some

of these fine chemical sectors some slow down in market growth is now being experienced, in general they remain one of the fastest growing sectors in the economy, and certainly in relation to bulk chemicals.

The consequences of this is that fine chemicals companies, particularly those with a strong product orientation, have continued to attract R&D and investment funds, as well as increasing attention from the multi-national major chemical companies, who traditionally have been principally concerned with bulk and semi-bulk chemical production.

SECTION B: FINE CHEMICALS

7. PROCESS TECHNOLOGY OF FINE CHEMICALS INDUSTRY

7.1 General Production Process

7.1.1 In order to understand the scope for and significance of cleaner technologies in the context of fine chemicals, it is necessary to understand the principal types and manner of production process within the industry.

7.1.2 **Batch processes**

The point has already been made that a distinguishing feature of the fine chemicals industry is that the manufacture of both the final and intermediate products usually involves several stages of batch processes. A batch process in fine chemicals production normally involves the following steps:

- i. **introduction of reactants** into reaction vessel (usually 1,000-6,000 litres capacity), in aqueous phase and/or in organic solvent;
- ii. **reaction** under required conditions over set time duration - usually 2-48 hours;
- iii. **extraction and often, purification of products;**
- iv. **treatment/disposal of waste streams** and, if applicable, **recovery of solvents;**
- v. temporary **storage** of products before next batch process reaction.

Continuous or semi-continuous processes tend to be adopted only when production quantities of a particular chemical are sufficiently large, as with certain pesticides for example, to justify continuous utilisation of process plant. Even then, the process technology has to be developed and it can be the case that control of the reaction and/or extraction of the product intermediate cannot be achieved on a continuous basis. Nevertheless where continuous processes have been introduced, even on a small scale, improvements in yields, quality control and reduction in wastes have generally accompanied the development.

7.1.3 **Numbers of reaction stages**

The number of reaction stages involved in the production process of fine chemicals of course varies depending on the nature of the finished product involved. However, it is possible to give broad indications for certain product categories:

It is to some extent arbitrary, where organic reactions are concerned, to state exactly how many stages there are in a total process, since this depends on what are considered to be the starting points, i.e. the feedstocks for the fine chemical industry. It is the organisation of the industry that is the principal determining factor in this respect.

7.2 Feedstocks

7.2.1 Organics

For the organic fine chemicals industry the starting-point feedstocks are usually bulk organic chemicals and semi-bulk organics. By the latter is meant that the fine chemicals production process will quite often begin with chemicals, which although produced in relatively large quantities, usually in continuous processes, are themselves the result of several stages of synthesis. For example alkylated, halogenated, or nitrated benzenes and pyridine are often the starting point for several production processes in particular sub-sectors of the fine chemical industry. Likewise chemicals such as chloroacetic acid, chloral, chlorosulphuric acid etc., would not necessarily be considered bulk chemicals. Thus it is the case that the feedstocks themselves can be high value chemicals.

As already pointed out, fine chemicals themselves are feedstocks traded as intermediates in the industry. Some fine chemicals, although produced in relatively small quantities, are the starting points for a range of final products within certain sectors of the pharmaceutical, pesticide and dyestuffs industry.

Another important point in relation to feedstocks is that there is normally a wider choice of feedstocks and reaction routes available to the fine chemicals producer than for bulk chemical manufacturers. However, in practice, the choice may not always be as wide as the chemistry would suggest. Since the feedstock can have a critical impact on the wastes and emissions produced in a process, i.e. how "clean" is it, this feature is of obvious significance for consideration of cleaner technologies in this industry. Nor is it the case, as with bulk chemicals, that a company's up-stream plant configuration and production process can determine its feedstock for a given process [1].

7.2.2 Inorganics

For most inorganic fine chemicals, including organo-metallic compounds and salts of organic acids, the feedstock is often the metal itself, but can also be the oxide and sometimes, as with chromium derivative, for example the acid or its salts (dichromate, chromic acid). Inevitably, the feedstocks options for a given inorganic fine chemical product are more limited than with organic

[1] Sometimes, however, the availability of a by-product intermediate within a plant will mean that its low cost will suggest itself strongly as the most economic feedstock alternative.

fine chemical production, although it is often possible to obtain metal compounds in more and less toxic forms.

7.3 Chemical Processes - Organics

7.3.1 Principal characteristics

Because of the diversity of the industry, there are obvious dangers of generalisation in fine chemicals production. Notwithstanding this caveat, the principal characteristics of the chemical processes applying in most fine chemical production may be summarised as follows:

| Table 7.3 | |
|---|---|
| PRINCIPAL CHARACTERISTICS OF FINE ORGANICS PRODUCTION PROCESSES | |
| Characteristics | Comment |
| Mostly liquid phase | Aqueous and organic solvents |
| Low/medium temperature | Generally 40-150°C |
| Low pressure | Atmospheric - 100 psi |
| Some use of catalysts | |
| Yields | Usually 80-90% (see below) per stage |
| Biochemical processes in pharmaceuticals and starch industry | Fermentation technology particularly significant in anti-biotics and food additives |

7.3.2 Yields

In the summary Table 7.3, yields from single stage organic process are shown to be in the range 80-90%, and more often the figure is nearer to 90%. Indeed there are many fine chemical production processes where the product yield is 90% plus. This applies particularly in the final stages of a production where only minor chemical changes, such as hydrolysis, esterification, formation of salt etc., are being made to an active group of the intermediate.

However, yields on several fine chemical reaction stages can be as low as 50-60%. The phenomenon of low yields may particularly apply where a complex reaction is taking place involving major changes in the base structure of the molecule(s) of the intermediate(s); or when two or three isomers are formed in a chemical reaction and only one isomer is suitable. As will be discussed, there is usually a strong economic incentive to avoid reaction processes with such low yields.

Reaction yields have generally been improving over the last 20 years or so, although perhaps not as markedly as with bulk chemicals.

It will however be appreciated that the overall yield on original feedstocks of a finished fine chemical is significantly lower than 80-90%. For example in a 7-stage process averaging 85% product yield for each stage, the final product yield on original, say, phenol feedstock would be 32%. It also has to be recognised that reactions may often have to take place in the presence of excess reagents, e.g. nitric/sulphuric acid, or ammonia to maximise yield of product on the feedstock. This will also contribute to the volume of the waste streams.

7.3.3 Reaction process

Although the final products of the fine organics industry are remarkably diverse and complex, many of the process reactions in the manufacturing process are similar in type, involving the same reagents. The most common will now be mentioned:

i. Alkylations

The agents used are extremely varied but can involve chloro-paraffins in the presence of alkali, the use of the toxic/explosive dialkyl sulphates, methyl esters with sulphonic acids, methanol with sulphuric acid (for alkylating anilines), and occasionally Grignard's reagent. Grignard reactions are, if possible, avoided because of their rather low product and high by-product/waste yields associated with them.

ii. Halogenation

This process is used extensively as a chemical step in the manufacture of various intermediates. The chlorine atom is often then converted to another active group and the chloride ion appears in a waste stream as dissolved salt. Both chlorine (in the presence of FeCl_3 catalysts) and hydrochloric acid (in the presence of oxygen) are used as chlorinating agents. Brominations usually take place in the liquid phase using HBr . Where the bromide is subsequently replaced at a later stage, efforts are often made to recover HBr .

iii. Nitrations/Aminations

Nitration is often the first step to introducing N atoms into benzene or other aromatic rings, before conversion to amino compounds; this process is particularly prevalent in dyestuffs industry. It is usually achieved with the use of concentrated nitric/sulphuric acids in solution (usually in excess). Subsequent amination is achieved by a number of processes either using iron and an acid catalyst, zinc and an alkali, sodium sulphide or vapour phase catalytic hydrogenations.

iv. Sulphonation

Excess chlorosulphuric acid is most widely employed in this process.

v. Sulphuration

Thio-compounds are widely produced for both pharmaceutical and pesticide production. The highly toxic and reactive carbon disulphide is probably the principal agent involved, although elemental sulphur itself is also used.

vi. Phosphorations

Organo-phosphorus compounds are important intermediate (and final) products in the manufacture of certain pharmaceuticals. Elemental yellow phosphorus and P_2O_5 are the principal reagents, although di-alkyl-dithiophosphoric acid as a second stage intermediate has a wide number of uses in pesticide production processes.

vii. Oxidations

The conversion of alkyl groups to acids is sometimes necessary. Air (or O_2) oxidation is normally the oxidising agent in the presence of catalysts (e.g. vanadium pentoxide), although anodic oxidation and potassium permanganate have been used.

viii. Hydrogenation

Hydrogen in the presence of copper catalysts is probably the most usual method.

ix. Esterification

Esterification/alcoholysis can be realised in a number of ways, the most common being the addition of the alcohol in the presence of concentrated sulphuric acid.

x. Condensations and cyclisation

The binding together of several molecules by condensation or ring closure, without splitting out a smaller molecule, is a very important chemical conversion employed in the manufacture of a considerable number of pharmaceutical products. Such reactions involve bringing together molecules, often with an amino (N) group in one, usually in the presence of various catalysts or sometimes with concentrated sulphuric acid.

xi. Hydrolysis

This is usually achieved by alkaline fusion, using caustic soda, to replace $-SO_3H$ group by $-OH$ group. Some vapour phase reactions use steam in the presence of $AlCl_3$.

An example of a complete process, one to manufacture the herbicide trifluralin, is shown in Figure 7.3 overleaf. The figure shows how what is essentially a 3-step process in fact involves 4 waste streams because of the many extraction purification processes involved.

7.3.4 Chemicals used

From the above it can be seen that the fine organics industry generally uses as its reagents fairly common inorganic chemicals. They can be summarised as:

- Acids : Nitric, sulphuric, hydrochloric, acetic, HCN.
- Alkalis : Caustic soda, ammonia, lime and alkylamines.
- Salts : Sodium chloride, sulphate, sulphide, cyanide, nitrate, aluminium chloride, ferrous/ferric chloride.
- Other : Chlorine, bromine, hydrogen, phosphorus (P_2O_5), alcohol, formaldehyde, alkyl halides, alkyl sulphates, carbon disulphide.

The aqueous stream by-products formed from the use of these reagents will often be salts, excess acids/alkalis, compounds, which in low concentrations usually pose no particular environmental problems. The principal problem chemicals in these reactions will be catalysts (e.g. copper, zinc and aluminium chloride). Nevertheless toxic or difficult by-products can also be formed whose control or disposal can present difficulties.

7.4 Chemical Processes - Inorganics

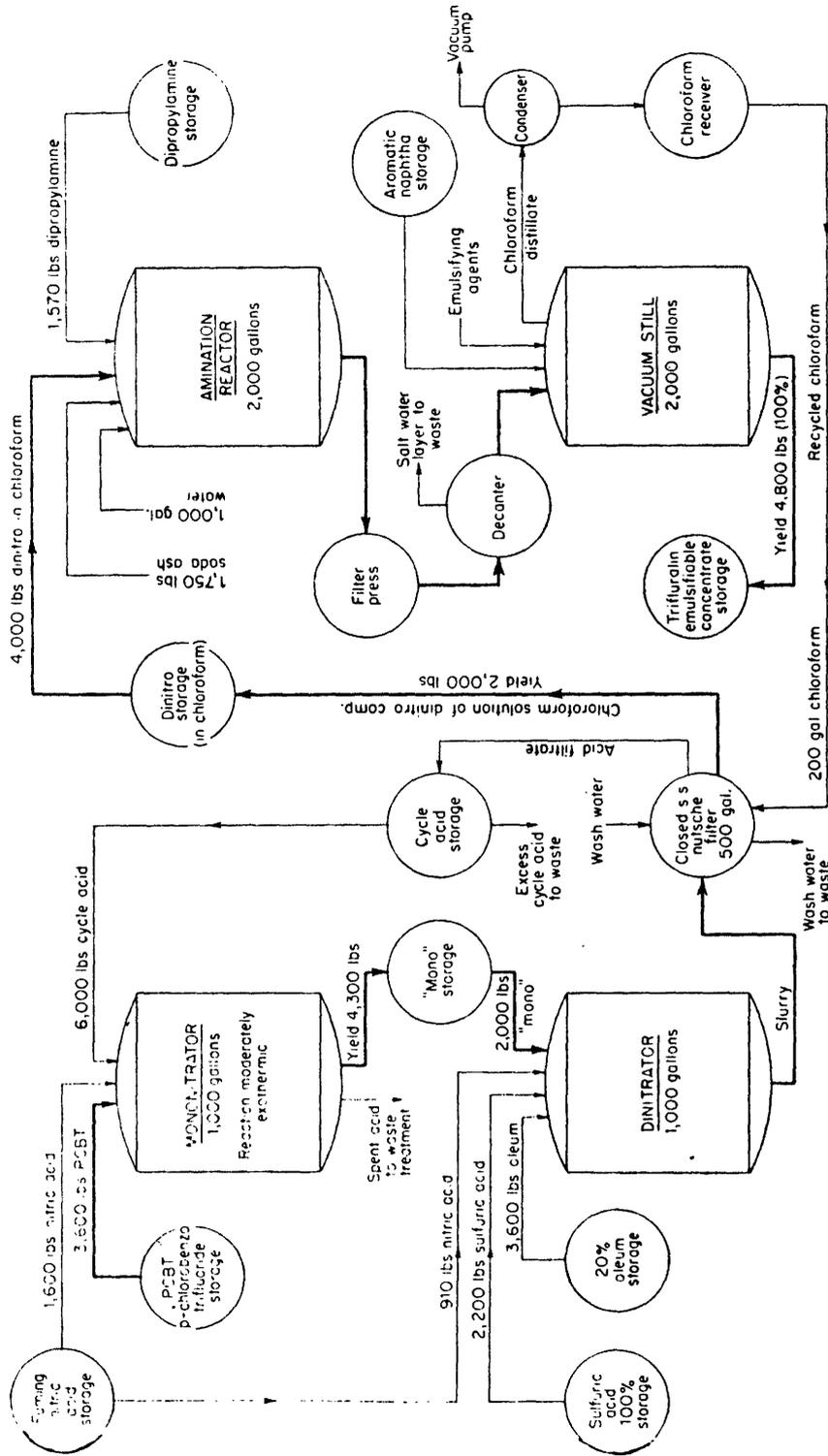
7.4.1 Products

Most fine inorganic chemicals are based on metals and tend to be in the following product groups:

- i. pigments/ corrosion inhibitors/coatings and fire retardants;
- ii. high purity precious metal/rare earth production for catalysts; coatings for electronics industry as metal-lising platings and semi-conductors; and small quantity fine chemicals;
- iii. special additives;
- iv. tanning chemicals and wood preservatives;
- v. pesticides.

It is the first three which represent the strongest growing sectors. A good many inorganic based pesticides have been replaced by organic products.

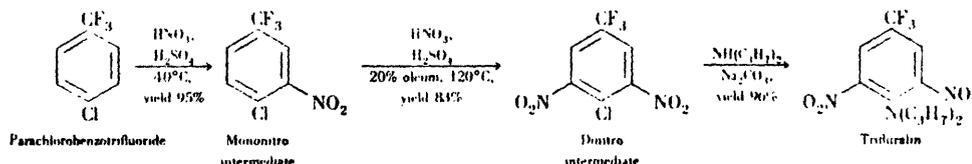
Figure 7.3: DESCRIPTION OF PRODUCTION STAGES OF TRIFLURALIN



Source: Eli Lilly and Co.

Figure 7.3 (Ctd.)

It is manufactured as follows:



Description

- o Charge the nitrator with cycle acid and fuming nitric acid and heat to 40°C.
- o Add the p-chlorobenzotrifluoride for mononitration, maintaining the temperature at 40° during the course of 4 h. Raise the temperature and hold it at 75°C over 4 h.
- o Cool and settle out the spent acid from the "mono" on top.
- o Draw off the spent acid from the "mono" on top.
- o Draw off the spent acid to waste treatment.
- o Charge the dinitrator with 100% sulfuric acid, 20% oleum, and fuming nitric acid. Raise the temperature to 120°C.
- o Run in the "mono" at 120°C over 6 h and hold at this temperature over the course of 4 h to effect dinitration. Cool to 20° and settle.
- o Filter off the solid "dinitro" on a closed Nutsch filter, running the spent acid to cycle acid storage.
- o Wash with water, running the wash water to waste. Dissolve in chloroform (from the recovery still).
- o Charge the amination reactor, water, soda ash, and the dinitro derivative (in chloroform solution). Adjust the temperature to 45°C.
- o Aminate with dipropylamine added at 45 to 50° over 4 h and heat 4 h more at 45°C.
- o Add the rest of the water and pass through a filter press and decanter to a vacuum still, the salt-water layer going to waste.
- o In the vacuum still distill the chloroform overhead (for recycle).
- o Add aromatic naptha and emulsifiers to the desired formulation.

In terms of quantity, it is probably the case that most fine inorganics are produced as the metal, metal oxides and sulphides. However, a large number of different salts and oxidised metal anions are also produced, e.g. chromates, molybdates, arsenates etc. P. de Reeder has pointed out [1] that for the 'black list' metals alone there are some 475 industrially produced compounds. Very many of these are produced in extremely small quantities (<10 tonnes).

7.4.2 Chemical processes

Metal and some metal oxide production usually takes place in the solid or solid/gaseous phases, by electrochemical processes. Solid/gaseous phase production of inorganic fine chemicals usually involve high temperatures.

The various metal salts and oxidised anions are usually produced in one or sometimes two stage processes, with the final product being precipitated from solution.

Generally speaking the chemistry involved in inorganic fine chemicals production technology is rather simple and yields can vary from 50 to 99%. However, certain sectors such as the precious metal catalyst, electronics coating and certain additives require very high purity (>99.5%) products, and the production technology in these situations can be quite sophisticated. Generally speaking most process technology development is directed to improving waste stream recovery rather than the basic processes themselves.

[1] 'Clean Technologies in the Chemical Industry', P.L. de Reeder. Paper presented at the European Symposium "Clean Technologies". The Hague, 4-7 November, 1980.

8. THE ENVIRONMENTAL SIGNIFICANCE OF THE FINE CHEMICALS INDUSTRY

8.1 Waste Streams

8.1.1 Liquid effluent

Because most of the reactions take place in the liquid phase, liquid wastes generally represent the most significant pollution load of the fine chemicals industry, although many production processes will also have sludges associated with them.

From examination in the previous section of the reactions and reagents employed, it can be seen that the larger part of aqueous effluent from the fine chemical industry is not very different from that of the bulk chemical industry. That is, it comprises, after primary settlement, weak acids and dissolved salts. The acids would usually be neutralised thus adding to the dissolved salts, or if limed, to solid inert anhydrite for subsequent disposal. While the concentrations of salts and BOD/solids may sometimes be quite high in relation to the volume of the effluent, and possibly relative to a local sewage treatment plant or confined local environment, in absolute terms the pollution load is small compared to the bulk chemical and to many other process industries.

However, because of the nature of certain reactants and the fact that the overall yield on organic feedstock(s) can be quite low (see Section 7.3.2), organic by-products, which may be difficult (e.g. by being coloured) or toxic can be formed. Also the aqueous effluent can contain concentrations of toxic metals such as copper and zinc if, for example, they are being used as catalysts, or an inorganic fine chemical operation is involved. Such by-products will often require separation before treatment/disposal (or recovery). Where organic solvents are in use, it is likely that some organics contamination of the aqueous effluent stream will take place. Also, it is inevitable that where extractions, separations etc., are involved, some of the products themselves will also contaminate the effluent.

8.1.2 Air pollutants

Air pollutants are generally not very significant in the fine chemicals industry except where solid/gaseous phase reactions involving metals or metal oxides are concerned. In these situations, normally a high level of dust emission control is installed. There is often have a strong economic incentive for such solid particulates recovery.

Some fine chemical reactions also have air pollutant nuisances associated with them, e.g. mercaptans (smell at very low concentrations), where sulphuration is involved, NO₂ (visible brown fumes at low concentrations) with certain metal treatment etc.

8.1.3 Solid wastes

The principal solid wastes occur in the form of sludges, partly from treatment of liquid effluent. These sludges can often be contaminated with micro-pollutants and disposal may well involve

incineration (which also leaves a residue for final disposal), either by the plant operator or by a toxic waste contractor. The actual volume of sludges can be quite small.

There are often particular difficulties with sludges/solid wastes formed in fermentation processes for pharmaceuticals/vitamins production, because of the nature of toxic contamination.

8.2 Overall Impact of the Fine Chemicals Industry

8.2.1 Location specific

Because of its relatively small size and dispersed nature (a large number of small plants), the environmental impact of the fine chemicals industry will tend to be location specific. That is to say, its impact is very largely determined by the sensitivity of its surrounding environment, including the capacity of the local sewage treatment plant. Many fine chemicals plants operate closely alongside other generally low-polluting factories on industrial estates. It is also the case that fine chemicals plants operate within or alongside large bulk chemical plants where their impact is therefore relatively minor. In this situation, wastes from fine chemical production can take advantage of the large capacity emission treatment facilities of bulk chemical plants.

8.2.2 Product specific

Nevertheless, it would be wrong to convey the impression that the fine chemicals industry gives rise to no significant environmental impacts. The nature of the feedstocks used and products and by-products manufactured are such that environmental concerns do arise for fine organic producers and can, as will be discussed in the next section, influence process technology and manufacturing operations. **It is a fact that most of the 'black and grey list' substances are either used or produced by the fine chemicals industry.** Also, with pharmaceuticals production, there can be biologically active by-products and impure product wastes involved.

However, it is important to keep these observations on the toxic nature of some fine chemical industry wastes/pollutants in perspective. The following points can be made:

- i. Where such high toxicity substances are involved in manufacturing operations, the quantities are often quite small.
- ii. Plants are specifically designed and operated for the protection of the internal and external environment, with careful separation of toxic micro-pollutants.
- iii. The industry will locate difficult plant so as to minimise impact.
- iv. Often the use of the fine chemicals industry's toxic products is likely to have more impact upon the environment than their manufacture. This obviously applies less to pharmaceuticals and to food additive production.

9. FACTORS INFLUENCING SELECTION OF PROCESS

9.1 General Discussion

9.1.1 A considerable number of factors go towards influencing the selection of process technologies in the fine chemicals industry. Although they are essentially the same as those given in Figure 4.1(a), page 34, they do differ somewhat in substance but particularly in emphasis from the bulk chemicals industry. Also, 'production or process route' is a somewhat better description than 'process technology' of the means of fine chemical manufacture, since multi-stage processes are involved, using fairly similar and well known chemical reactions. It is the selection of the feedstock(s) and the subsequent reaction route which are critical.

9.1.2 The influencing factors will be discussed under the following general headings:

- i. Market factors
- ii. Production economics
- iii. Environmental factors
- iv. Operational experience
- v. Existing plant configurations.

In terms of priority the first two factors tend to be much the most important in influencing the selection of fine chemical process technology, although, as will be discussed, environmental factors do receive significant attention in the development of a new production process.

9.2 Market Factors

9.2.1 Emphasis on product vs. process

As already mentioned a distinguishing feature of the fine chemicals industry, which applies to most but not all companies, is its strong market orientation. Thus, after having developed at laboratory scale a complex molecule found to exhibit particular properties for a very specific application, and having devoted considerable resources to its testing (in the case of pharmaceuticals and agrochemicals for side effects, human and ecotoxicity effects etc.) over a quite long period, the funds and time available for process technology development may be somewhat limited. The analogy with cooking is quite a good one. The finished product is what matters to the chef. He or she will not, within reason, spend an enormous amount of time and concern over analysing each step to the final product for its cost effectiveness. Nevertheless, overall costs are not without consideration.

To put this another way, the value of finished fine chemicals tends to be high in relation to the production costs. The critical management and resource considerations are therefore more likely to be allocated in such a way as to ensure that the fine chemical companies retain their competitive edge. For such fine chemicals producers, the average allocation of R&D resources, principally manpower, is roughly as follows:

| Table 9.2 | |
|--|-------------|
| ALLOCATION OF R&D RESOURCES OF FINE CHEMICALS INDUSTRY | |
| Product development | 70-80% |
| Production process | 20-30% |
| - of which pollution control | (0-15%) |
| | <u>100%</u> |
| Source: ERL based on industry discussions. | |

9.2.2 Purity considerations

In several sectors within pharmaceuticals, certain agrochemicals and other fine organics sectors and with inorganic fine chemicals involving precious metals and those produced for the electronics industry, purity of product can be particularly important. This can mean that a higher proportion of the final product can find its way into the waste stream (e.g. from a solvent extraction/separation process) than would otherwise be the case.

9.2.3 Product activity

The key aspect of a fine chemical product, particularly in the pharmaceuticals and agrochemicals sectors, is the degree of 'activity' of the active ingredients. There is therefore a strong incentive to produce more active fine chemicals. These are, if anything, likely to have a higher biological impact. So consequently the effluent stream is likely to have more environmentally damaging wastes. This environmentally unfortunate tendency will be offset by the fact that less product is needed if it is more active.

9.2.4 Process oriented fine chemicals producers

The remarks above regarding the high importance of market factors giving rise to strong product rather than process orientation of the fine chemicals industry, do not apply to the whole industry. There are exceptions which arise in the following situations:

- i. Some fine chemical companies specialise in producing well established intermediates for other fine chemical companies; such companies are strongly process oriented.
- ii. As products come out of patent, their production and marketing becomes more cost competitive, with increasing attention focused on production economics.
- iii. Certain producers of fine inorganic intermediates are concerned with manufacturing products whose chemistry is relatively simple. Marginal improvements in yield and process cost reductions are therefore of high priority.

The implications for process technology/production routes of concern with process costs are discussed in the following section.

9.3 Production Economics

9.3.1 Production costs

There are dangers in attempting to apportion production costs between the principal categories, and many exceptions can be found to generalisations in the fine chemicals industry. Nevertheless, based on information provided by representatives from different sectors of the fine chemicals industry, we present in Table 9.3 the break-down of the average contribution to product costs.

| Table 9.3 | |
|--|------------------------------|
| CONTRIBUTION TO PRODUCTION COSTS OF FINE CHEMICALS | |
| Category | Share of Total product Costs |
| Feedstock | 50-60% |
| Capital | 5-15% |
| Labour | 15-23% |
| Energy | 5-20% |
| Pollution control | 3-10% |

Feedstock costs can, in certain circumstances, be significantly less, most notably with fermentation processes where energy costs and capital costs are correspondingly higher.

The most important feature of this cost breakdown is the relatively much higher contribution of feedstock and labour costs of such batch processes compared to the bulk chemicals industry, and the lesser contribution of capital costs. Based on these contributions, it is probable that any drive to minimise production costs is likely to focus principally upon feedstock and labour costs. It is worth now explaining the process route implications of this.

9.3.2 Feedstock/process yield

There are two ways of effectively reducing feedstock costs:

- i. by using less feedstock for a given product output, i.e. by improving yield;
- ii. by using a cheaper feedstock.

The incentive to maximise yield, and therefore reduce wastes, is thus considerable in the fine chemicals industry. Coincidentally, of course, it will also lead to improved output per labour and capital employed.

Means of improving yield on initial feedstock can be:

- o **to reduce the number of stages involved in the process.** Such a change may or may not give rise to a more difficult by-product waste, but it is more likely that such a development would be environmentally benign, i.e. a "cleaner technology";
- o **substitution of a higher yield reaction stage for another.** Particular scope exists when the by-product yield is higher, perhaps because of isomer formation;
- o **conversion from batch to continuous or semi-continuous process.** Continuous processes nearly always offer improved yields and less wastes (often with higher product purity) as a result of better control; they also avoid contaminated reaction vessel wash-down water/solvent between batches;
- o **introduction of a catalyst.** Such catalysts as have been used are often metal ions, e.g. Fe, Cu and Zn; as a result there is an environmental trade-off between reduced waste production and metal ions in the effluent stream;
- o **recovery of product from waste stream.** Where product value is high, the incentive for recovery improves.

Changing to a cheaper feedstock is likely to have major implications for the subsequent reaction stages. These may or may not lead to wastes of potentially lesser environmental impact. On the whole, unless a very much cheaper feedstock with a new reaction process is developed, the consequent changes are unlikely to result in much higher yields of by-products or more difficult wastes as any such associated higher operating costs would offset the advantages of cheaper feedstock(s).

9.3.3 **Labour costs**

Reduction in unit labour costs can be most readily achieved through reduction in the number of process stages; or, if it is possible, through introduction of continuous or semi-continuous processes. Both of these process changes are, if anything, likely to lead to reduction in waste/by-products.

9.3.4 **Energy costs**

The cost and level of use of energy in fine chemicals production varies somewhat according to the process. In most liquid phase batch processes, energy is as much (or possibly more) applied in the separation, extraction, purification and drying processes as in applying heat to reaction vessels. In all these applications the process heat is normally of relatively low temperature and therefore heat recovery is likely to be uneconomic. The most likely means of conserving energy in such processes is again by reducing the number of process stages.

In solid/gaseous phase processes used in producing certain metals/metal oxides, energy use per unit output is likely to be higher with greater opportunities for reduction in energy costs through heat recovery or reduction through process change.

9.4 Environmental Factors

9.4.1 General comment

Before the 1970's, it is generally true to say that environmental factors had not greatly influenced the development of production processes in the fine chemicals industry. Since then such factors have increasingly entered into process considerations, particularly in the development of new products production. This is not to say that the cleanest available technology route has always been adopted. Market and economic factors will always predominate, although waste treatment and disposal do of course affect capital and operating costs of the process.

However, environmental considerations can directly (as opposed to indirectly through impact on costs) influence the production process through one or more of the following:

- i. choice of feedstock(s),
- ii. reagents and catalysts used in the process stages,
- iii. recovery/reuse of by-products.

9.4.2 Choice of feedstocks

This is probably the most important manner in which the emissions or "cleanliness" of a fine chemical production process can be determined. The initial feedstock(s) is often likely to influence significantly to subsequent 1-3 production stages at least. In considering the design of the production process for a new fine chemical, it is now unlikely that the industry would select a feedstock/process which gives rise to particularly difficult/toxic by-products unless there are no alternatives or these alternatives involve considerably higher costs.

The industry has also been known to seek and introduce alternative feedstocks to an existing process, where the introduction of stricter emission/waste disposal regulations has resulted in very much higher operating costs. This change tends to be effected in one of three ways:

- i. the operator has developed an alternative himself;
- ii. the operator has told his feedstock supplier(s) that he requires a 'cleaner' feedstock which produces the same intermediate at stage 'X';
- iii. the operator asks the feedstock supplier to take over the process himself because he may be in a better position to recover/treat/dispose of the toxic by-products/wastes involved.

It will be noted that the second two processes are shifting the environmental problem back to the bulk or semi-bulk chemical industry. This development in response to economic forces, is likely to be environmentally advantageous as it is probable that the larger plant will have more treatment facilities and/or R&D resources to solve any waste/emission problems.

9.4.3 Use of reagents

The industry will also give consideration to the environmental impact of use of reagents/catalysts in the selection of particular processes. Indeed during the course of its investigations, ERL learnt of two or three instances when a new lower cost production process, involving the use of metal catalysts, to particular fine chemicals were not adopted because of environmental controls (actual or anticipated) on the metal concentrations in the effluent. Indeed it is a point of general note that unlike the use of catalysts in bulk continuous (and usually gaseous phase) processes, in the production of fine chemicals catalytic processes offering lower cost/higher yield routes to a product, can often be "less clean" processes.

9.4.4 Recovery/reuse of by-products

This subject will be discussed at greater length in Section 10. In the context of influencing process routes to a desired end-product, we would just mention at this point that if a possible use is foreseen for a by-product produced in large quantities in a particular stage of the process, it is more likely that the process will be adopted.

9.5 Operational Experience

9.5.1 It is certainly the case that fine chemical manufacturers, whether large or small, tend to develop expertise in particular production stage reactions. As already remarked, some small independent fine chemical companies specialise in selling this expertise as contract intermediate producers. This aspect of the industry's development is generally likely to be consistent with the development of cleaner technologies in fine chemicals production.

9.6 Existing Plant Configurations

9.6.1 This factor is of lesser consequence in influencing the production route to a final chemical than in the bulk chemical industry. While it is true that a certain feedstock may be available at a cheaper price because it is produced "in-house", product considerations tend to come first in the development of new fine chemicals. This is likely to reduce the influence of the availability of a particular bulk chemical or semi-bulk chemical in influencing the process route adopted.

However, fine chemicals production plant is multi-purpose, that is to say it is usually designed with the aim of providing production facilities for several fine chemicals. This design may constrain the introduction of certain new process route options on fine chemicals, if substantial new plant investment were required.

The development of a fine chemicals plant, juxtaposed to a bulk chemicals plant, can have one significant influence in one other respect. As mentioned above, it can often reduce the treatment/disposal cost of difficult waste streams through access to large capacity central treatment systems, whose level of treatment would be quite uneconomic on a small scale.

9.7 Recent Developments in the Fine Chemicals Industry

9.7.1 In this final sub-section it is worth commenting upon more recent developments in the market place which could have a gradual impact on process technologies adopted in fine chemicals.

- i. **The rate is slowing at which new fine chemicals are introduced.** This is partly a function of the fact that new technical 'breakthroughs' in chemistry do not now occur so fast, but also because the costs of testing for new products has risen so that large markets must be guaranteed for new products. The impact of this is that increased attention will be paid to lowering production costs of existing fine chemicals and more R&D resources will tend to be devoted to this end.
- ii. **Large multi-national chemical companies, traditionally mostly bulk chemical producers, are becoming increasingly involved in the fine chemicals industry.** This is a result of the relatively much faster growth prospects and profit margins for many fine chemical sectors, and also because they are looking for a means of utilising spare plant and/or labour capacity. The first rationale is likely generally to be beneficial as it will bring additional R&D resources to process development in fine chemicals, together with expertise in continuous process technology. It is not to comment on whether the second development will enhance the use of cleaner technologies in fine chemicals production.
- iii. **In the longer term (10 years or more), increased application of biotechnology to fine chemical production processes is probable.** At the moment this is chiefly confined to pharmaceuticals and parts of the food industry. Although these sectors will continue to dominate in this respect, it is also likely that fermentation processes will be more widely applied in certain other organic sectors. Increased use of fermentation processes and biotechnology is generally considered as environmentally beneficial as it often

provides means of utilising waste materials as feedstock. However, fermentation reactions can also bring additional waste problems, often of a more toxic variety. These can present treatment and disposal difficulties.

In summary though, the structural and other developments taking place in the fine chemicals sector are generally likely to be consistent with the development and use of cleaner technologies.

10. THE USE AND DEVELOPMENT OF CLEANER TECHNOLOGIES IN EEC FINE CHEMICALS PRODUCTION

10.1 Introduction

In this final section of the report we comment upon the current use and scope for future development of cleaner technologies in fine chemicals production. We shall note the principal constraints to this process, also referring to those identified in Section 5, concerning constraints to use of cleaner technologies in bulk chemicals production, where these are also of relevance to fine chemicals.

Cleaner technologies in the context of fine chemicals will be considered with respect to:

- o basic production processes;
- o recovery and reuse of by-products and solvents.

10.2 Cleaner Technologies in Production Processes

10.2.1 Current use and future scope

In Sections 9.3 and 9.4 means by which changes in process technologies (or production routes, as they are better termed) can lead to reduction in emissions/wastes were discussed. The most significant of these included:

- i. reduction in number of process stages;
- ii. change from batch to continuous/semi-continuous process;
- iii. substitution of high yield reaction stage(s) in production route;
- iv. recovery of product from waste stream;
- v. change to 'cleaner' feedstock, or feedstock giving rise to less difficult/toxic by-products/wastes;
- vi. use of reagents/catalysts giving rise to less or 'cleaner' by-products/wastes.

The first three 'cleaner technology' routes, i, ii and iii will all tend to achieve the purpose of reducing wastes and energy consumed per unit of product, as well as certain other efficiency improvement, essentially by increasing yield on feedstock. Their adoption is generally likely to follow from the normal response of the industry to economic and market forces, although as will be noted below, there can sometimes be a certain conservatism to making major changes in the production process.

Recovery of product from waste stream (process iv); given that the quantities/concentrations are likely to be small, is really only likely to be technically and economically feasible when the product is of very high value, e.g. as with precious metal/rare earths, oxides and their compounds. This most particularly applies with solid/gaseous phase smelting/oxidising processes where elaborate metal dust/fume collecting systems are installed.

With regard to **process changes covered under v and vi above**, we commented in Section 9.4 that consideration of the environmental consequences of alternative feedstock(s) and/or reactions did enter into the decision making with regard to the design of process routes for new products, and could sometimes rule out the use of what would otherwise be acceptable lowest cost process routes to the final product. It is also the case that existing production lines have substituted 'cleaner' feedstocks when the wastes/emissions produced by the previous process have become unacceptable. The use of **catalysts** both contribute to cleaner technologies by achieving improved yields and reduced water use, and present additional effluent problems through metal ion contamination.

Most of the instances or means of achieving cleaner basic process routes apply to **fine organic chemicals**. Given the:

- i. reasonable expansion prospects of the industry;
- ii. fact that fine chemicals are mostly produced in multi-stage batch processes; and
- iii. increased resources likely to be made available for reducing production costs through process routes i to iii above;

it is reasonable to conclude that both the scope for use and the prospects for development of cleaner process technologies are quite considerable.

On the whole the situation with **inorganic fine chemicals** is much less promising, and it will be noted that many of these are 'black' and 'grey' list substances. This situation arises for the following reasons:

- o inorganic fine chemicals normally involve only 1-3 stage processes;
- o the scope for using alternative chemical processes tends to be much more limited;
- o by their very nature, the feedstocks, the products and the by-products have to be metallic compounds, often on the black and grey lists;
- o in many sectors of inorganic fine chemicals, the growth and investment prospects, and allocation of R&D resources tend to be less than for fine organics [1].

Even so, the economic incentive to maximise yield on feedstock can apply to inorganic fine chemicals in the same manner as it does for organics. It is just that the scope for achieving improvement through change of process is more limited.

[1] It is also true to say that the size of the fine inorganics industry is considerably smaller than that of fine organics.

10.2.2 Constraints

In certain important respects the constraints to development of cleaner process routes in fine chemicals are less than in bulk chemical production.

- **Growth prospects.** These are reasonable, certainly compared to bulk chemicals.
- **Finance.** There is a reasonable prospect that the funds available for process R&D will if anything improve in the future, even though profit margins become squeezed (as they already have) as competition increases.
- **Technical factors.** Technical know-how in fine chemicals will continue to grow and should benefit from the increased attention and expertise in continuous process technology of the major chemical companies. The number of small chemical firms specialising in particular process technologies has also been growing.

However two important **market constraints** to the spread of cleaner process technologies in fine chemicals must be noted.

The first, which has been referred to previously, is that the fine chemicals industry has been and will continue to be primarily product oriented both with respect to decision making on production process design and operation. For example the stress on purity of product is likely to increase and can conflict with yield improvement objectives, and to the allocation of R&D resources to development of cleaner technologies.

The second point relates to the very nature of competition within the industry. Unlike the situation in bulk chemicals, if a new cleaner (and lower cost) process route is developed by a company, it is not likely to advertise the means nor sell the process to others. The know-how bound up in the production route is an integral part of the commercial advantage of the new product. This tends to mean that when a new and cleaner technology is developed for a fine chemical, it is likely to remain the property of the company concerned and not become widely applied in the industry. This is perhaps somewhat less the case as the product becomes well established and increases in volume.

10.3 Recovery and Reuse of By-Products and Solvents

10.3.1 Current practice and future scope

As a generalisation it is true to say that the extent of recovery of by-products produced in the fine chemicals industry is not very high. This is largely a matter of economics, in that usually the unit cost of recovery, given the lowish yield and/or concentration

of the by-product(s) involved, are more than the value of the recovered product [1]. Solid wastes, such as gypsum and ammonium sulphate, theoretically recoverable, also arise from the treatment of acid wastes.

However, having said that, many instances of by-product recovery do occur in the fine chemicals industry, particularly where the yield is reasonably large or the unit value is high, as with precious metal/rare earth compounds. Indeed over half of the 17 companies interviewed regarding fine chemicals were able to give examples in their own company operations where recovery of by-product/wastes was taking place. Some of these are mentioned below:

- Halogenated aromatics
- Precious metals, oxides and their compounds
- Lead compounds (from bag filters)
- Sulphur
- Hydrogen sulphide
- Sodium sulphate
- Sodium acetate
- Sulphonamic acid
- Certain alkyl and benzo-phosphorus intermediates.

This could be considered at least as good a performance record as was found in the examination of bulk chemical production operations. Nevertheless it is true to say that considerable scope exists for further recovery of by-products, even recognising the aim of the industry to minimise production of by-products.

The situation with solvents is quite different. The very large majority of solvents used in fine chemicals production, and which become contaminated, are recovered. Recovery either takes place in-house, when the operation is relatively straightforward; or if a high level of contamination has taken place, the solvent is sold/given to a special contractor for recovery.

10.3.2 Constraints

Many of the same economic and technical constraints to by-product recovery noted in Section 5.4.2 for bulk chemicals apply also to fine chemicals. Attention is drawn to the following principal aspects which will tend to worsen the economic feasibility of by-product recovery:

- o **Economies of scale.** Because of the quantities in which they are produced, fine chemical by-product recovery tends to be more costly.
- o **Purity.** The need for high purity in recovered by-product (and recovered product for that matter) is usually greater than that with bulk chemicals, which again will raise the costs of technically acceptable by-product.

[1] Even though sometimes this value can be relatively high.

- o **Batch processing.** This tends to complicate the design and efficiency of recovery operations.
- o **Toxicity.** The recovery and reuse of some solid wastes is made more difficult by contamination with high toxicity materials. This applies to, for example, fermentation wastes.

On the other hand, when the by-product has a higher value, as is more often the case than with bulk chemicals, then this can offset the cost constraints. In one respect this is particularly important in that it reduces the relative importance of transport costs, thus making resale of by-products to a third party a much more likely possibility than with by-product recovery from bulk chemicals. Even so, it is more probable that by-product recovery will take place if an 'in-house' use can be found.

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Appendix One

COMPANIES INTERVIEWED

CHEMICAL COMPANIES INTERVIEWED**i. Bulk Chemicals**

Akzo
BASF
Bayer
BTP Tioxide Limited
Chem Systems International
Fisons
Hoechst/Uhde
ICI
Montedison
Produit Chimique Ugine Kuhlman
Rhone-Poulenc
Rio Tinto Zinc
Shell Chemicals International
Solvay

ii. Fine Chemicals

Akzo
Albright and Wilson
Bayer
Cheminova A/S
Farmoplant SpA
Farmitalia SpA
Fine Organics
Glaxochem
Grinsted Products A/S
ICI
Johnson Mathey Chemicals
Lead Industries Group
NL Chemicals
Oce-Andeno BV
Produit Chimique Ugine Kuhlman
Rhone-Poulenc
Shell Chemicals International
UCB

Appendix Two

**SUMMARY OF CASE STUDY
BULK CHEMICAL PROCESS TECHNOLOGIES AND
THEIR PRINCIPAL CHARACTERISTICS**

1. Aluminium
2. Chlorine
3. Sulphuric Acid/SO₂
4. Phosphoric Acid
5. Titanium Dioxide
6. Ethylene Oxide
7. Acrylonitrile
8. Chloromethanes
9. Perchlorethylene
10. Vinyl Chloride (VCM)
11. PVC
12. Nylon 66 - intermediates
13. Nylon 6 - intermediates
14. Phthalic Anhydride
15. Methyl methacrylate
16. Tolylene diisocyanate

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: ALUMINIUM Al 1.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|---|-------------------|---|---------------------------------|--|--|
| Electrolytic reduction of alumina in cryolite. Hall-Heroult Process | 1890's | Alumina Al_2O_3 , dissolved in fused cryolite ($3NaF \cdot AlF_3$) is electrolysed by means of carbon anodes. Two anode types a. prebaked b. self-baking or Sodaberg. | Emissions of Hydrogen fluoride. | High electricity use 9-12 kWh per lb. Al. | Offers means to avoid Al evaporation. |
| Improved Hall Heroult | 1960's/70's | More continuous process. Improved anode baking technologies. | More recycle of HF. | Electricity consumption lowered to 6 kWh per lb. in new processes. | Reduced energy costs. |
| Chloride process | 1970's in USA | Alumina chlorinated to $AlCl_3$ and electrolysis in mixed chloride bath. Very demanding on construction materials. | Avoids HF emissions. | Somewhat lower overall energy use. Requires 'cheap' Cl_2 to be economic. | Cleaner somewhat lower energy process. |

PRINCIPAL PROCESS TECHNOLOGIES IN ELECTROLYSIS MANUFACTURING: CHLORINE Cl₂ 2.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--------------------------------------|----------------------------------|--|--|--|--|
| 1. Mercury cell; graphite electrodes | 1890's Predominant in Europe. | Electrolysis of brine. Graphite block anodes. Mercury cathode. Pure 50% caustic soda and hydrogen gas derived by hydrolysis of the mercury/sodium amalgam. Chlorine evolved at the anode. Brine either once through or else reconcentrated and recirculated. | Mercury lost by spillage and in gaseous and liquid effluents, solid wastes, and in the products chlorine, hydrogen and caustic soda, originally amounted to about 500g/ton chlorine produced. Mercury losses can now be reduced to not more than 50g per ton chlorine. | Originally about 4000 kWhr electricity consumed per ton Cl ₂ . | High purity caustic soda; was the main product originally. Mercury mined in Spain & Italy. Pure solid salt commercially plentiful in Europe. |
| Improved mercury cell | Since 1960 | Dimensionally stable, titanium based anodes instead of graphite. Computerisation. | Lower mercury loss through better recycle and Hg recovery from waste stream. | Electrolysis consumes about 3300 kW hr/t.Cl ₂ | Lower electricity consumption. Lower impact. |
| 2. Diaphragm cell | 1890's Predominant in USA. | Asbestos diaphragm separates anode and cathode compartments to prevent caustic soda from coming into contact with Cl ₂ . 10% caustic soda concentrated by evaporation. The 50% concentrate is contaminated with 1% salt. | No mercury is involved. Plant staff and the environment must be protected from asbestos | Electrolysis consumes about 2700 kW hr/ton Cl ₂ in modern plants. 3 tons steam per ton Cl ₂ also required to concentrate NaOH. | Asbestos mined in Canada & USA. Steam, required to concentrate caustic soda, cheaper than in Europe. |
| 3. Membrane cell | Since 1970 | A resin membrane separates anode and cathode compartments. 30-40% caustic soda is produced. After concentration to 50% it contains 0.1-0.2% salt. | No mercury or asbestos is involved. Environmental problems (fluorine) may be met by membrane manufacturers. | 2800-3200 kW hr/t Cl ₂ and improving. Only 0.5 t steam required per ton Cl ₂ to concentrate caustic soda. | Preferred to diaphragm since less steam required & pure caustic soda obtained. Cleaner technology. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: SULPHURIC ACID H₂SO₄ (continued) 3.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|---------------------------|-------------------|---|--|---|---|
| 4. Double Contact process | 1960's | After absorption of SO ₃ in water, the gases are reheated and passed a second time over the V2O5 catalyst to form more SO ₃ . | Reduced SO ₂ discharge to atmosphere (less than 1/10th compared with Single Contact). | Up to 99.75% SO ₂ converted to SO ₃ and even 99.85% at 4 atmospheres pressure. Less energy efficient than single contact. | Usually only adopted when SO ₂ discharge is strictly controlled by law since extra investment and extra energy required. |

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|----------------------------------|-------------------|---|--|---|---|
| 1. Lead chamber process | 1750 | SO ₂ , air, steam & nitrogen oxides react in a lead chamber. Nitrogen oxides are recycled and H ₂ SO ₄ of max. 80% concentration obtained. | Nitrogen oxides caused severe air pollution during process upsets. | Can use dilute (down to 1%) SO ₂ from sulphide ore roasting. The SO ₂ is thus not wasted. High yield. | Some output from smaller plant therefore less lead used. Environmentally acceptable. Market for max. 80% H ₂ SO ₄ needed. |
| 2. Improved lead chamber process | 1978 | Continuous analysis for NO ₂ and accurate process control. Towers rather than chambers. | Discharges of NO ₂ almost eliminated. | | |
| 3. Contact process | 1920 | Combustion gases containing typically 6-15% SO ₂ and 8-12% oxygen are purified to remove catalyst poisons and passed over vanadium pentoxide at 400-600°C. SO ₃ is absorbed in weak sulphuric acid. | Unreacted SO ₂ discharged to the atmosphere. | 96-98% conversion of SO ₂ to SO ₃ . Heat economy achieved by heat exchange before SO ₃ absorption. | Concentrated H ₂ SO ₄ or oleum produced. Cheaper to operate than the Chamber process when 6-15% SO ₂ gases available. Plant capacity can be 700,000t/yr (Chamber process only about 40,000t/yr.) |

3.

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: SULPHUR DIOXIDE SO₂

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|---|--|---|--|--|---|
| 1. Roasting of sulphide ores of Zn, Pb, Ni, Cu etc. | 19th century | The sulphide ore is roasted to produce the oxide. SO ₂ is a byproduct. | | | Demand for non-ferrous metals. |
| 2. Roasting of Iron Sulphide | Mid 19th century | Roasting of iron pyrite at 800-850°C in layers or in fluidised beds. | Large amount of dust evolved. The iron oxide slag is a by-product. | 1.6 tons steam can be obtained by roasting 1 ton pyrite, (ie. 4.5 tons per ton sulphur). | The demand for H ₂ SO ₄ outstripped the availability of Sicilian sulphur. |
| 3. Burning of sulphur | 18th century and again in 1900 in the USA and 1950's in Europe | Clean molten sulphur is burnt in a stream of air. | A process with no solid residue. | About 3 tons steam can be produced per ton sulphur. | 1900 in the USA when Frasch sulphur available Louisiana and Texas. 1950's Europe, sulphur from oil & gas. |
| 4. Hydrogen sulphide | 1950's | Oxidise to sulphur and then to SO ₂ . | Removes an environmental nuisance. | | Availability of byproduct H ₂ S. |
| 5. From spent sulphuric acid | | Spent sulphuric acid, about 15-80%, cracked to produce SO ₂ . | Removes an environmental nuisance. | | Becomes economic if disposal of spent H ₂ SO ₄ is costly. |

4.

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: PHOSPHORIC ACID H₃PO₄

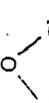
| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|------------------------------------|-------------------|---|---|---|---|
| 1. Wet process | 19th century | Decomposition of phosphate rock, usually with 94% sulphuric acid but occasionally with HCl or HNO ₃ instead. Filter off the solid byproduct. | Gypsum byproduct (about 5 tons per ton P ₂ O ₅) and fluorine compounds in tail gases are major environmental problems. | Fuel to dry phosphogypsum costs more than newly mined gypsum. | Slightly impure weak phosphoric acids (65% H ₃ PO ₄ or 52% P ₂ O ₅). Good enough for fertilisers |
| 2. Electric furnace process | 1900 | A mixture of phosphate rock, sand and coke is melted in an electric furnace to produce phosphorus. This is then burned to P ₂ O ₅ which is treated with water. | Byproduct slag and the fluorine compounds in tail gases are environmental problems. | 1.7 megawatts per 1000 tons per year phosphorus. Capital cost double cost of wet process. | Need to produce pure phosphoric acids. Ability to use lower grade ores. |
| 3. Improved wet process | 1970 | Solvent extraction of 65% H ₃ PO ₄ from the wet process gives some purified 100% acid and a crude acid byproduct containing the impurities from the original weak acid. | The phospho-gypsum and fluorine problems remain. | Electric furnace quality acid is obtained without the high capital cost or energy consumption of the furnace process. | Production of furnace quality at a lower cost |
| 4. Hemihydrate 2 stage wet process | late 1960's | Same as 1 but recrystallisation stage avoids steam evaporation. | Purer gypsum (less F) byproduct, therefore more marketable if recovered. | Lower energy use. | Cleaner process - see Environmental Aspects. |
| 5. Nitro-phosphate NPK-process | 1930 | Nitric acid digestion of phosphate rock; precipitation of Ca(NO ₃) ₂ with subsequent conversion to mixed N & P fertiliser products. | Avoids production of byproduct gypsum. Lower F ⁻ emissions. | Lower energy use. Requires CO ₂ feedstock from associated ammonia plant. | Cleaner process |

5.

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: TITANIUM DIOXIDE TiO₂

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|--|---|--|---|
| 1. Ilmenite sulphate process | 1920's | Digestion of Ilmenite with 95% sulphuric acid, removal of sludge and ferrous sulphate (Copperas), and purification and calcining of titanium hydrate. Ilmenite contains about 50% TiO ₂ . | For each ton TiO ₂ 4-5 tons of acidic ferrous sludge must be disposed of, plus several tons of weak sulphuric acid. | Per ton TiO ₂ , 4 tons H ₂ SO ₄ needed and about 2.5 tons ore. | |
| 2. Sulphate process on Canadian or South African slag from iron production | 1960's | As for Ilmenite, except that no Copperas waste is only 10-25% of Ilmerite process. Slag contains up to 85% TiO ₂ . | For each ton TiO ₂ , almost 400 Kg siliceous sludge to be disposed of plus several tons of weak sulphuric acid. | 2.8 tons H ₂ SO ₄ required per ton TiO ₂ and about 1.6 tons slag. | Reduction of the Copperas disposal problem. Cleaner process than 1. |
| 3. Chloride process on Rutile ore | 1940's | Chlorination of rutile in the presence of coke or carbon monoxide at 500-800°C gives TiCl ₄ vapour. After purification it is oxidised to TiO ₂ in a fluidised bed and chlorine recycled. | Only some 80 Kg acidic metal chlorides for disposal per ton TiO ₂ produced. Rutile contains about 95% TiO ₂ Requires disposal of FeCl ₃ e.g. in deep wells | Some 1.1 tons rutile and 200 Kg chlorine required per ton TiO ₂ . Rutile in short supply. | Waste disposal problems reduced in scale. Improved scale economies -continuous gaseous process Cleaner process than 1. & 2. |
| 4. Chloride process on 'beneficiated' Ilmenite (synthetic Rutile) | 1970's | As for natural rutile. The synthetic rutile contains over 90% TiO ₂ . | About 200-500Kg acidic metal chlorides for disposal per ton TiO ₂ . However the beneficiation plant may give environmental problems. | Some 2.5 tons of the original Ilmenite and energy for the beneficiation per ton TiO ₂ . | Shortage of rich ores of the rutile type Unlimited availability of ilmenites. |

6.

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: ETHYLENE OXIDE  CH₂ — Ch₂

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|------------------------------------|-------------------|---|---|---|---|
| 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 byproducts. | | Good yield (over 90%). |
| Air oxidation of ethylene | 1940 | Ethylene and air are passed over a <u>silver-based catalyst</u> at 200-300°C. | Less aqueous effluent. Large volumes of impure nitrogen evolved. | Silver catalyst. No chlorine used. Only about 75% yield on ethylene production. | Much more economic for large scale production. |
| Oxidation of ethylene using oxygen | 1960 | Ethylene and 95% or purer oxygen are passed over a <u>silver based catalyst</u> at about 250°C. | Minimal gaseous and liquid effluents. | Avoids chlorine use. New plant achieves 80% yield. Little difference vis air oxidation in primary energy terms. Air ox. process more delivered energy but less electricity consumption than O ₂ process. | Marginally better yields. Availability of cheap oxygen, e.g. if nitrogen also needed. Somewhat cleaner process. Improved economies of scale over air oxidation. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: ACRYLONITRILE CH₂ = CH

7.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|---|---|--|--|
| Ethylene Cyanohydrin route | 1940 in USA | Formed from ethylene oxide HCN, which was then dehydrated to acrylonitrile. | Significant aqueous organic impurities containing cyanides. Hydrogen cyanide (HCN) raw material. | | |
| Bayer acetylene/HCN route | 1940's Europe | Aqueous phase in presence of cuprous chloride. | Wide range of acetylenic byproducts. HCN feedstock. | CuCl ₂ catalyst. | Cheaper more convenient feedstocks. Purer byproduct 80% yield. |
| Ammoxidation 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. Complex ACN separation process involving sulphuric acid. | Significant quantities of byproducts, mainly - hydrogen cyanide - acetonitrile - ammonium sulphate. Not easily recoverable. | Yield originally ~30-50% on propylene catalyst - Bismuth energy or phospho-molybdate/bismuth. | More economic process to match strong demand. |
| Improved ammoxidation - Sohio process | 1970 | More selective catalyst. Sohio used fluidised bed. | Reduced byproduct yields especially acetonitrile and ammonium sulphate. | Improved overall Acrylonitrile yield to around 80% (Sohio). | Reduction of ammonium sulphate and acetonitrile byproducts. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: CHLOROMETHANES 1 Methyl Chloride CH₃Cl 8.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|---|-------------------|--|---|---|---|
| 1. From Methanol. Liquid phase | Late 19th century | Refluxing of methanol at 150°C with a dissolved zinc chloride catalyst and HCl. | Requires use of NaOH to remove HCl from product gases and oleum to remove water. Aqueous effluent stream. | 98% yield. | Process is a useful sink to absorb HCl byproduct from other chlorination reactions. |
| 2. From Methanol. Vapour phase | 1950's | Equimolar quantities of methanol and HCl passed as mixed vapour at 350°C over a catalyst, typically alumina, zinc chloride or active carbon. | Same as liquid phase. Only 0.5m ³ aqueous effluent per ton CH ₃ Cl. | 98% yield of CH ₃ Cl. H ₂ SO ₄ can be cleaned and reused/sold. | Lends itself to continuous operation. Improved control and new principal process. |
| 3. From Methane | Mid 1920's | Reaction of chlorine and methane at 400°C. | | HCl by product and higher chloro-methanes. | Saleable HCl can be produced. Product mix can be varied. |
| 4. Same as 2 but avoids use of NaOH/H ₂ SO ₄ | 1970's | Hi pressure (190 psi & 120°C) process. Byproduct hydro-carbon separated and recycled. | Produces weak acid effluent. | Avoids salt contaminated aqueous effluents. | Cleaner process. Not yet proven. |
| ¹ For description of process and High Volume Organic Chemicals. Mitre Corporation. | | - See Clean Technologies in Industrial Sectors of: 1981 pp.101-106. | | | Metal finishing, non-ferrous metals, |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: CHLOROMETHANES 2. Methylene Chloride CH_2Cl_2 8.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|--|---|--|---|
| 1. High temp. chlorination of methane | | Methane reacted with chlorine in excess at 500°C . | Only 0.5% of non-volatile residue. | $3\frac{1}{2}$ tons steam required to separate 1 ton of mixture. | Choice of conditions enables methylene chloride to predominate. |
| 2. High temp. chlorination of CH_3Cl | | Methyl chloride reacted with chlorine in excess at 500°C : | HCl and a large proportion of CCl_4 (>50%) by product. | | |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: CHLOROMETHANES 3. Chloroform CHCl_3

8.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|--|--|---|--|
| 1. Liquid phase chlorination of alcohols or ketones | 19th century | Acetone or ethyl alcohol warmed to 62°C in an aqueous suspension of bleaching powder. | Considerable aqueous effluent stream. | | |
| 2. Chlorination of methane | 1950's | Chlorine, methane and recycled carbon tetrachloride passed through a fluidised catalyst at 700°C . | Only 0.5% of non-volatile residue. Larger quantity of byproduct HCl than in 3. | $3\frac{1}{2}$ tons steam to separate 1 ton of mixture. | Availability of methanol as raw material. Minimal CCl_4 production. |
| 3. High temperature chlorination of CH_3Cl | | Methylchloride reacted with excess chlorine at 500°C . | HCl and a large proportion of CCl_4 by-product (>50%). | | |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: CHLOROMETHANES 4. Carbon Tetrachloride CCl₄ 8.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|---|--|---|--|
| 1. Chlorination of carbon disulphide | 1890's | 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's | Reaction of chlorine with methane at 650°C, or at 300° on a fluidised fuller's earth catalyst. | Only <0.5% of residue. | | Use of HCl as byproduct. |
| 3. Pyrolytic chlorination of higher hydrocarbons | 1950's | High temperature chlorination of ethane, propane or; | | The main byproducts are perchlorethylene and HCl. | Continuous operation. Integration with production of other chlorinated hydrocarbons. |
| 3a. or chlorinated residues | 1960's | non volatile organic residues from other chlorination plants. | Typically, pyrolytic chlorination of chlorinated organic residues produces an unusable residue less than 20% of the original weight. | | 3a. Cost of residue disposal Clean process - uses other waste streams of chlorinated aliphatics. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: PERCHLOROETHYLENE CCl₂=CCl₂

9.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|--|---|--|---|
| 1. Acetylene chlorination | 1900 | Chlorination and dehydrochlorination of acetylene to trichlorethylene and then chlorination. | | | Easy process when acetylene is available. |
| 2. Pyrolytic chlorination of aliphatic hydrocarbons | 1950's | Chlorination of individual or mixed aliphatic hydrocarbons at 550-700°C. | | | |
| 3. Pyrolytic chlorination of chlorinated hydrocarbons; or chlorinated residues | 1950's | Similar conditions. | Typically pyrolytic chlorination of chlorinated organic residues produces an unusable residue less than 20% of the original weight. | Carbon tetra-chloride is the major co-product and can be recycled to minimise its production rate. | High cost of acetylene. Abundance of other hydrocarbons and byproduct chlorohydrocarbons. |
| 3a. Chlorinated residues | | | | | 3a. Cost of residue disposal. Clean process - excellent means of using other chlorinated waste streams. |
| 4. Oxichlorination of ethylene dichloride, ethylene, or lower chlorinated aliphatic hydrocarbons | 1950's | ELC or 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. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: VINYL CHLORIDE MONOMER $\text{CH}_2=\text{CH}\cdot\text{Cl}$ 10.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|---------------------------|---|--|--|--|
| 1. Acetylene | World War II in Europe | 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. | Up to 99% yield on acetylene. Carbide for acetylene needs very large energy input. | Easy process when acetylene is available. Low demand for VCM and PVC. |
| 2. From ethylene via pyrolysis of EDC | World War II in USA | Addition of chlorine to ethylene at 50° and cracking of the resultant ethylene dichloride at 500°C over e.g. pumice and recycling of uncracked EDC. | Large quantities of co-product HCl neutralised for discharge as salt or preferably sold as hydrochloric acid. | Up to 95% overall yield of vinyl chloride. | High cost of acetylene. Falling cost and increasing availability of ethylene to meet growing demand for PVC. Suitable for large production capacities. |
| 3. Oxychlorination of ethylene with air | 1950 | Part of the EDC is produced by passing byproduct HCl and air with ethylene at 225°C over a copper catalyst. | Byproduct HCl from other manufacturers can be usefully employed. Large volumes of waste gases carry traces of EDC into the atmosphere. | Highly exothermic. High yields on ethylene consumed, e.g. 97%, and the 3% byproducts can be used in other processes. | Chlorine scarce and costly. Able to use the chlorine content of byproduct HCl |
| 4. Oxychlorination of ethylene with oxygen | 1970's | As 3, but using oxygen instead 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 |
| 5. Acetylene plus ethylene | 1950 in Italy and Germany | By balancing production rates a combination of processes 1 & 2 eliminates byproduct HCl. | As for 1 & 2 with advantage of elimination of HCl. | High yields but costs are high because of the small scale. | Suitable for exploiting HCl from process 2 in small scale units. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: POLYVINYL CHLORIDE, PVC

11.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|--|---|--|---|
| Suspension, emulsion and mass polymerisation | 1930-1960 | Vinyl chloride monomer polymerised in autoclaves, sometimes suspended in water, and using catalysts. Some recovery of unreacted VCM. | No problems recognised until the linking of acroosteolysis (1965) and liver angio-sarcoma (1974) with VCM. | About 95% yield VCM charged lost to the atmosphere from autoclaves and from finished polymer. | |
| Improved processes | 1970's | Large, automated autoclaves requiring cleaning only after several batches. Full recovery of unused VCM. VCM removed from polymer before storage or sale. | Almost no discharge of VCM from the plant and almost no VCM left in the polymer product. Overall loss say 0.3%. | Improved yields, no waste of VCM. Cost of catching last traces of VCM is higher than the credit for the traces recycled. | 95-97% yield improvement economically justified. Market pressures forcing further VCM removal - 98.6%→99.8% yield. 99.8% yield only required under certain regulations. |
| Rhone-Poulanc VCM suspension process | | Process used VCM instead of water as suspension medium. | | Reduced energy costs in drying. | Lower op. costs but cannot meet all PVC grades. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: NYLON 66 -NH(CH₂)₆NH.CO(CH₂)₄CONH(CH₂)₆NH- (Polyhexamethylenediamine adipate) 12.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|-------------------------------------|-------------------|---|---|--|--|
| 1. From phenol via adipic acid | 1930's USA | Phenol is hydrogenated to cyclohexanol and by nitric acid oxidation to adipic acid. Half this acid is ammoniated to adipamide and reduced to hexamethylene diamine. Mixing produces Nylon salt and the polymer is produced by heating the salt in autoclaves. | Nitrous fumes evolved during nitric acid oxidation. | About 90% yield on phenol. | |
| 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. | About 90% yield on cyclohexane. | 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. | A yield of about 75% HMD on the butadiene is obtained. | Plentiful supply of butadiene available. |
| 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. | A yield of about 85% HMD on the acrylonitrile is obtained. | Availability of acrylonitrile Relatively clean process. |

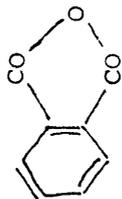
(Polymerised Caprolactam)

13.

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: NYLON 6 -NH(CH₂)₅CO.NH(CH₂)₅CO-

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|-------------------------|-------------------|--|---|---|--|
| 1. Phenol process | 1940's Germany | Caprolactam is traditionally made via Beckmann 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 byproduct ammonium sulphate. | 90% yield from the cyclohexanone. | |
| 2. Cyclohexane process | 1950's USA | The same as above except that the cyclohexanone is obtained by oxidation of cyclohexane. | Large amount of byproduct ammonium sulphate. | 90% yield from the cyclohexanone. | Feedstock availability. |
| 3. Nitration process | 1960's | Cyclohexane nitrated to nitro-cyclohexane and this reduced to cyclohexanone oxime. | Much reduced ammonium sulphate byproduct involved. | | |
| 4. Photo | 1960's Japan | Action of chlorine, nitric oxide and light produces cyclohexanone oxime directly. | Much reduced ammonium sulphate byproduct involved. | Lower energy requirement. | Low cost route, 'cleaner route', assuming (NH ₄) ₂ SO 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 byproduct. Oleum required to absorb nitrogen oxides. Alkyl phenol solvent extraction in process. | Requires H ₂ and palladium catalyst. | Avoids ammonium sulphate. |

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: PHTHALIC ANHYDRIDE



14.

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|---|-------------------|---|--|---|---|
| 1. Oxidation of naphthalene by oleum | 1896 | Mercuric sulphate catalyst. Sulphur dioxide by product. Liquid phase. | Large amounts of sulphur dioxide evolved. | Sulphur dioxide could be recycled to sulphuric acid production. | Mercury gave better yields and a faster reaction than earlier processes. |
| 2. Vapour phase oxidation of naphthalene | 1920's | Air oxidation over vanadium pentoxide catalyst. Highly exothermic. | Large amounts of heat to dissipate or utilise. Waste gases contain volatile by-products. | 60-85% yield on naphthalene. | Increasing demand. Better economics. |
| 3. Oxidation of o-xylene | 1950's | Liquid or gas phase, air oxidation of o-xylene over vanadium pentoxide based catalysts. | Waste gases should be washed. About 5% maleic anhydride by-product; can be recovered. | 70-88% yield on o-xylene. | Increasing demand. Shortage of naphthalene feedstocks. Abundance of o-xylene. |
| 4. Low air ¹ 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. | Electricity consumption cut by 85%. | Cleaner (low energy) process; not yet proven in Europe. |
| ¹ For description of process and High Volume Organic Chemicals. Mitre Corporation. | | - See Clean Technologies in | Industrial Sectors of: 1981, pp.95-100. | Metal finishing, non-ferrous metals, | |

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|----------------------------|-------------------|--|---|--|--|
| 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 byproducts. (3 tonnes of waste acid per tonne product) Acid residues. | Some companies use the $(\text{NH}_4)_2\text{SO}_4$ as a fertiliser and pyrolyse the weak H_2SO_4 to produce SO_2 . | Reasonable yield ~85% |
| 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 byproducts. | 55-65% yield of methacrylic acid on isobutylene. Esterification yield better than 95%. | Availability of butadiene raw material and specific long life catalysts. Avoids hazardous and scarce HCN. Now little used. |
| 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. Not commercially proven. |

16.

PRINCIPAL PROCESS TECHNOLOGIES IN MANUFACTURING: TOLYLENE DIISOCYANATE (TDI)

| PROCESS | PERIOD INTRODUCED | PRINCIPAL CHARACTERISTICS | ENVIRONMENTAL ASPECTS | ENERGY/RAW MATERIAL USAGE | RATIONALE FOR ADOPTION |
|--|-------------------|--|--------------------------------|---------------------------|---|
| Phosgene/ tolyl diamine process | 1950's | Three stage batch process involving mixing of reactants in presence of inert organic solvent, extraction and slurry, further reaction with phosgene and final conversion purification. | Toxic reactants HCl emissions. | | Growth in poly-urethane products. Two/three stage process better yield than older single stage process. |

