IEA GREENHOUSE GAS R&D PROGRAMME

The reduction of greenhouse gas emission from the oil refining and petrochemical industry

Report Number PH3/8
June 1999

Title: **The reduction of greenhouse gas emissions from the oil refining and petrochemical industry**
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Other remarks:

Background to the Study

The IEA Greenhouse Gas R&D programme (IEA GHG) is systematically evaluating the cost and potential for reducing emissions of greenhouse gases arising from anthropogenic activities, especially the use of fossil fuels.

Greenhouse gases are produced from a variety of industrial activities. The main sources, not related to power generation, are those energy intensive industries, which chemically or physically transform materials from one state to another. During these processes, many greenhouse gases (carbon dioxide, methane, nitrous oxide) are released. One notable example is oil refining and petrochemicals where considerable amounts of greenhouse gases are produced. Relatively little attention has been focused on the abatement/mitigation of greenhouse gas emissions from the industrial sector. This study is the second in a series looking at greenhouse gas abatement/mitigation options for energy intensive industries.

Carbon dioxide, methane and other hydrocarbons are emitted during the refining of oil, production of petrochemicals and the storage of feedstocks and products. The purpose of this study is to consider the abatement/mitigation options in the oil refining and petrochemicals industry.

The study was carried out by AEA Technology of the United Kingdom.

Industry overview

Oil refining involves breaking down and separating the complex mixture of hydrocarbons in crude oils into standard fuel and non-fuel products. These products include; gasoline, diesel oil, heavy fuel oil, liquefied petroleum gas (LPG), bitumen and lubricants. Crude oil and natural gas are also raw materials for petrochemicals such as polymers, certain alcohols and other chemical products.

Refineries, worldwide, process 10 million tonnes of crude oil per day. Large refineries produce the full range of products while smaller refineries may make only gasoline, diesel and heating fuels. Refining processes can be grouped into three classes:

- separation (usually distillation)
- conversion (usually thermal, catalytic or hydrocracking)
- upgrading (e.g. HDS[1], demetallisation, hydrocracking, catalytic cracking, coking)

A refinery is a highly complex and integrated installation requiring many auxiliary facilities, including large storage facilities for feedstocks and products, extensive port and dock facilities, and on-site services such as electricity, heat and cooling. Heat is used in the many distillation, conversion, reforming and finishing (product purification) processes in the refinery, with considerable attention paid to heat integration. Motive power to turn pumps and other equipment is normally provided by

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[1] Hydro-desulphurisation

electricity, often generated on site. Refineries are typically fuelled by crude oil or by waste products from the conversion processes, but sometimes use coal or natural gas as well, depending on local supplies.

Refining is closely related to the marketing of refined products. Both parts of the industry are closely regulated by legislation. It is essentially a commodity industry with stiff competition. The rate of return on capital is, in general, relatively low, at least in Europe. Despite this general situation, the refining industry in OECD countries has been able to adjust to stricter product quality requirements, making the necessary investments as regulations change.

When addressing emissions from the refining industry it should be made clear that this is only one of the elements in the total chain from production of oil to delivery of the final service to the user, i.e. transport, work or heat. Life cycle analysis, both at the level of the overall chain and at the more detailed level of individual products, can be a revealing way of understanding the impact of different options but is outside the scope of this report.

This report covers the following areas

- Greenhouse gas emissions from oil refining and petrochemical processes globally.
- The principal types and sizes of refining operations within (i) Europe (ii) North America (iii) South America (iv) Japan (v) Asia, identifying areas of likely expansion, outlining the main processing steps, the chemistry involved and the types of fuels used.
- Current environmental legislation, pressure for 'green' products and how these will affect future refinery practice and the products produced.
- All emissions from a typical plant as well as current recovery processes for minimising waste.
- Future technological developments and any barriers to development of these technologies together with potential costs and timescales of implementation.
- Future emissions to the year 2020 with consideration of future developments.

Results and Discussion

Many changes have occurred in the refining business, dictated largely by the demands of the market place with decreasing demand for heavy fuel oils and increasing demand for lighter transportation fuels, together with increasing environmental constraints. At the same time, there has generally been an increase in pressure to produce 'greener' products, such as unleaded petrol, low benzene and low sulphur fuels, and low aromatic solvents. Restrictions on sulphur content, in particular, have greenhouse gas implications for refineries. Future trends will continue towards larger and more complex refineries with the capacity for deep conversion processing of heavier crudes to lighter products. To compete with this trend, current refineries will have to expand to incorporate more processing units and increased desulphurisation capacity.

Refineries and petrochemical plants are a potential source of atmospheric emissions of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), Volatile Organic Compounds (VOCs[2]), sulphur, reduced sulphur compounds and oxides of sulphur, ammonia, oxides of nitrogen, toxic organic micropollutants (dioxins, PAHs[3]), heavy metals, particulates and odour. Global estimates of greenhouse gases from oil refining and petrochemicals production are shown in Table 1.

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[2] Volatile Organic Compounds

[3] Polyaromatic Hydrocarbons

	CO_2	CH_4	N_2O
Refineries	686.9 Mt/yr in 1994	5-45 Kt/yr in 1994	1-6 Kt/yr
Petrochemicals	520 Mt/yr in 1996	Not estimated	150-600 Kt/yr (adipic acid manufacture)

Table 1. Global emissions from oil refining and petrochemicals

The largest emission sources are associated with energy use, as shown by the breakdown of sources given in Table 2:

Source	**Percent of refinery CO_2 emissions**
Oil and gas fuel firing of furnaces and boilers	65%
Regeneration of cat cracker catalyst	16%
Flares	< 3%
Methane steam reforming to make hydrogen	2%
Incineration and effluent processes	1%
Power (55% imported)	13%

Table 2 Sources of refinery CO_2 emissions

Typical CO_2 concentrations in refinery vent gases are:

- From combustion plant, furnaces, boilers, flares and FCC[4] regenerators: about 13% CO_2.
- From gas turbine power generators or machinery-drives: about 3% CO_2.
- From steam reforming process for H_2 generation: up to 100% CO_2.

Options for reducing greenhouse gas emissions from refineries include:

- refinery process optimisation;
- refinery use of non-carbon-based energy sources;
- reducing the carbon content of fuels;
- optimising the efficiency of heat and power production and use;
- reducing the amount of wastes flared;
- CO_2 capture and disposal.

Refinery operators aim to obtain the maximum yield of valuable products for the minimum cost. These aims are consistent with minimising greenhouse gas emissions from refineries - any carbon in crude, which is not incorporated into fuels, petrochemical feedstocks or other products will mostly, sooner or later, be emitted into the atmosphere as CO_2, CO or VOCs. Carbon monoxide and VOCs in their turn will be converted by atmospheric processes into CO_2.

An important aspect of refinery design and operation is to ensure that every process operates with maximum efficiency and minimum energy input. Low-value product or waste such as process off-gases provides much of the energy requirement.

Natural gas, LNG, LPG, coal-bed methane or indeed refinery gas have lower carbon-to-hydrogen ratios than fuel oils, and will give lower greenhouse gas emissions for a given unit of energy. Gas-fired power generation is highly efficient, and future developments are expected to focus on incremental improvements to combined-cycle gas turbine technology which could allow efficiencies of up to 60% to be reached over the next decade.

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[4] Fluid bed catalytic cracker

Refineries may generate their own power or purchase it from outside. Some alternative energy sources may be more suitable for internal use, some will only be usable as an external source; possible examples range through nuclear, solar, wind, geothermal, hydro. Following a series of incidents around the world, in much of Europe and North America, nuclear power has lost its mid-century image as the clean technology of the future. Elsewhere nuclear power retains importance, particularly in countries without substantial oil reserves. In Japan, for example, where nuclear power meets about 14% of the national energy needs, the nuclear share of electricity generation is likely to stay at about 35% up to 2010. Hydroelectric power already represents several percent of the national energy supply in some parts of the world, and demand is growing rapidly for solar photovoltaic systems and other renewable energy sources. Nevertheless, fossil carbon (coal, oil, and gas) will remain the principal national energy sources during the period considered in this report.

Cogeneration is finding increasing application in the refinery sector. An example[5], from the early 1990s, at Shell's refinery in Fredericia, Denmark uses 150 t/day of refinery off-gas to drive a gas turbine-generator with 27 MW output capacity. The flue gases leave the turbine at a temperature of 485°C and are used to heat crude oil from 165 °C to 365 °C - recovering over 35 MW. The flue gases are then cooled further by heating water for a district heating system, recovering a further 9 MW. This system makes good use of the potential work available from the fuel as well as achieving good overall energy efficiency (up to 76%).

Barriers to implementing energy efficiency measures are:

- lack of awareness;
- investment hurdles;
- split responsibility for emissions.

CO_2 capture using an absorption-based technique appears to be a viable option for refinery exhaust streams from on-site power generation, from process furnaces and boilers, and from catalyst regeneration. High concentrations of CO_2 are found in the off-gases from the steam reforming process and from some petrochemical streams, such as ethylene oxide manufacture; for these relatively small, high concentration emission sources, cryogenic separation is a promising option.

Economics

A number of scenarios up to the year 2020 have been examined. A baseline scenario was developed which has projected current industry emissions until 2020 using compound growth rates and The World Energy Council projections for oil use as primary energy. This scenario shows a rise in emissions from 1083 Mt CO_2/y in 1990 to 1578 Mt CO_2/y in 2020, from refineries and petrochemicals together. To examine the impact of energy efficiency improvements and CO_2 capture/storage on oil and petrochemical industry emissions two scenarios are examined as variants on the baseline. These scenarios are summarised as follows:

(1) "Energy efficiency" - focusing on reductions which can be achieved through reducing energy use, with consequent cost savings. This scenario assumes that the products meet existing desulphurisation requirements and environmental standards (e.g. sulphur and particulate emissions).

(2) "Maximum CO_2 reduction" - in which CO_2 capture/storage is added on top of the "Energy efficiency" scenario.

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[5] Bodewes, H. and Lutgen, M.C., " A Cogeneration Unit at the Shell Refinery in Frederica", Energy Economy, NR8, 1992.

These two scenarios represent extreme cases and it is accepted that there are potentially a number of intermediate measures that could be considered within the boundaries of the two scenarios studied. The aim of these two scenarios was to examine the limits of CO_2 reductions that could be achieved by established technological modifications and assess what the implications for costs might be.

One further scenario was examined, which considers the impact on baseline emissions of potential future trends in low sulphur/low VOC transport fuels i.e. the fuels of the future. This scenario, called the "Low sulphur future" - is one in which energy use, and hence greenhouse gas emissions, rise due to increased upgrading and desulphurisation required to meet what are considered to be the future legislative requirements for emissions from transport fuels. This scenario shows the effect of tighter regulation of products on greenhouse gas emissions, which could make the challenge of emission reduction much more severe.

The "Energy efficiency" scenario assumes that the refineries introduce a package of energy efficiency measures that have the potential to reduce emissions from process operations by 20%. This scenario enables refineries to hold emissions steady up to about 2010, before emissions rise in line with growth in throughput. On the other hand, in the same scenario for petrochemicals, the reduction in emissions is swamped by growth in throughput. Overall emissions of CO_2 would be reduced by about 15% below baseline by 2020. This scenario gives average cost-savings of US$ 20/t CO_2 avoided.

The "Maximum CO_2 reduction" scenario assumes that additional end of pipe CO_2 capture and disposal techniques are applied to the process operations coupled with an increase in flare gas recovery from 25 to 50%. The CO_2 capture/storage measures are additional to those energy efficiency measures considered in the "Energy efficiency" scenario. In this scenario, there is a substantial decrease in refinery emissions by 2010, but this is still offset by a substantial increase in petrochemical emissions. By 2020, both sectors are decreasing their emissions, with CO_2 emissions 75% below the baseline, at a cost of about US$ 45/t CO_2 avoided.

Emissions in the various scenarios to the year 2020 are summarised in Tables 3, 4 and 5.

Source	**CO_2 emissions, Mt CO_2/yr**			
	1990	**2000**	**2010**	**2020**
Refineries	685	694	682	722
Petrochemicals	399	548	702	856
Refineries plus petrochemicals	1083	1242	1384	1578

Table 3 Scenario 1, energy efficiency.

Source	**CO_2 emissions, Mt CO_2/yr**			
	1990	**2000**	**2010**	**2020**
Refineries	685	584	543	252
Petrochemicals	399	526	518	228
Refineries plus petrochemicals	1083	1110	1061	480

Table 4 Scenario 2, maximum carbon dioxide reduction.

The results for the "Low Sulphur Future" are shown in Table 5. In this scenario, there is a significant increase in emissions - overall CO_2 emissions are 7% above baseline scenario, all of this due to increased emissions from refineries.

Source	CO_2 emissions, Mt CO_2/yr			
	1990	**2000**	**2010**	**2020**
Refineries	685	784	892	980
Petrochemicals	399	625	878	1070
Refineries plus petrochemicals	1083	1409	1769	2050

Table 5 Scenario 3, low sulphur future.

In conclusion, the modelling indicates that substantial emission reductions can only be achieved through significant expenditure - for every US$ spent on end-of-pipe capture, CO_2 emissions can be reduced by 0.024 t CO_2. In order to bring emissions back to 1990 levels by 2020 would require all the US$ 6.7 billion savings from energy efficiency measures to be spent on end-of-pipe controls, plus an additional US$ 14 billion.

Expert Group Comments

The draft version of this report was sent to eight experts identified by members of the Programme. The general opinion was favourable and many of the comments were editorial, although there were a number of specific requests. The requests recommended by the expert group have been incorporated into the report.

Major Conclusions

The energy efficiency scenario can be achieved and costs reduced by use of appropriate measures, although by 2020 overall emissions still increase due to increased throughput.

Substantial emission reductions can be achieved only through substantial expenditure, such as for CO_2 capture and storage; a major barrier to implementation of these measures is cost.

Responding to increased environmental pressures, such as further reduction in the sulphur content of fuels, will increase CO_2 emissions significantly.

There may be opportunities for CDM[6]-type activities in which companies in developed regions make available investment capital, expertise and training to companies in less developed regions, thereby accelerating implementation of energy efficiency measures at the global scale. The emergence of a trading system for CO_2 emissions credits may encourage this.

Recommendations

Opportunities identified in this study and in related studies (e.g. precombustion decarbonisation) should be followed up with more in-depth examination of the particular options, focussing on a number of example plants and including consideration of life-cycle emissions.

Refineries may have opportunities to vary their range of products, even to the extent of generating electricity for sale. This may give rise to low-cost opportunities for mitigation, which should be examined once the results of the current multi-products study have been reported. This would include considering the impact on demand for other fossil fuels for power generation, both in developed and developing countries, and the impact of residue conversion and the use of CO_2 sequestration. In fact, there may a number of opportunities for the refining sector to work with developing countries to

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[6] Clean Development Mechanism

reduce greenhouse gas emissions and energy costs. The impact of tradable credits on investment decisions should also be considered.

The technology needs in relation to scenarios of radical change, such as scenario 3, should be considered in more detail, once the examination of future transport fuels has been completed. Such investigation of long-term options should include consideration of the scope for radical change in refining technologies.

Greenhouse gases from major industrial sources II: Oil refining & petrochemicals

A report produced for the IEA Greenhouse Gas R&D Programme

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April 1999

Title	Greenhouse gases from major industrial sources II: Oil refining & petrochemicals
Customer	The IEA Greenhouse Gas R&D Programme
Customer reference	IEA/CON/98/32
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File reference	AEAT/20642001
Report number	AEAT-4975/20642001
Report status	Issue 2

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Executive Summary

This report was prepared for the IEA Greenhouse Gas R&D Programme by AEA Technology Environment under contract reference IEA/CON/98/32 "*Greenhouse gases from major industrial sources - II: Oil refining and petrochemicals*".

The contract specification is reproduced in full in **Appendix 1**. In summary, the main tasks of the project were to:

- Describe and quantify greenhouse gas emissions from oil refinery and petrochemical processes globally.
- Describe the principal types/ sizes of refining operations within (i) Europe (ii) North America (iii) South America (iv) Japan (v) Asia, identifying areas of likely expansion. Outline the main processing steps, the chemistry involved and the types of fuels used.
- Discuss current environmental legislation in the above regions; pressures for 'green' products and how these will affect future refinery practise and expected products.
- Estimate all emissions from a typical plant and describe current recovery processes for minimising waste.
- Outline future technological developments, *e.g.* separation membranes, carbon dioxide capture and storage, possible recycling options. Identify any barriers to development of these technologies, together with potential costs and timescales of implementation.
- Estimate future emissions to the year 2020 with consideration to future developments.
- Estimate the optimum for greenhouse gas reduction in a total perspective.

Historically, many changes have occurred in the refining business, dictated largely by the demands of the market place with decreasing demand for heavy fuel oils and increasing demand for lighter transportation fuels, together with increasing environmental constraints. At the same time there has generally been an increase in pressure on the industrial sector to produce 'green products', such as unleaded petrol, low benzene and sulphur fuels, and low aromatic solvents. Restrictions on fuel sulphur content, in particular, have greenhouse gas implications for refineries. Future trends will continue towards larger and more complex refineries with the capacity for deep conversion processing of heavier crudes to lighter products. To compete with this, current refineries will have to expand to incorporate more processing units and increased desulphurisation capacity.

The overall picture is one of rapidly converging technologies based around the domination of a relatively small number of multi-national oil producers, an increasing role for large national oil companies, and the wide-spread licensing of technologies. Where significant differences do exist, they are generally based around the demand profile for products of the particular region.

Refineries and petrochemical plants are a potential source of atmospheric emissions of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), Volatile Organic Compounds (VOCs), sulphur, reduced sulphur compounds and oxides of sulphur, ammonia, oxides of nitrogen, toxic organic micropollutants (dioxins, PAHs), heavy metals, particulates and odour.

We have estimated global emissions of greenhouse gases as follows:

	CO_2	CH_4	N_2O
Refineries	686.9 Mt/yr in 1994	5-45 kt/yr in 1994	1-6 kt/yr
Petrochemicals	520 Mt/yr in 1996	Not estimated	150-600 kt/yr (adipic acid manufacture)

The largest emission sources are associated with energy use:

Source	Percent of refinery CO_2 emissions
Oil and gas fuel firing of furnaces and boilers	65%
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Power (55% imported)	13%

In refineries typical CO_2 concentrations are:

- From combustion plant, furnaces, boilers, flares and FCC regenerators: about 13% CO_2.
- From gas turbine power generators or machine drivers: about 3% CO_2.
- From steam reforming process for H_2 generation: 100% CO_2.

Options for reducing greenhouse gas emissions from refineries include:

- alternative societies which are not based on crude oil;
- refinery process optimisation;
- refinery use of non-carbon-based energy sources;
- reducing the carbon content of fuels;
- optimising the efficiency of heat and power production and use;
- reducing the amount of wastes flared;
- CO_2 capture and disposal.

Co-generation appears to offer significant potential to reduce net emissions in the combined power grid/refinery system.

CO_2 absorption appears to be a viable option for refinery exhaust streams from on-site power generation, from process furnaces and boilers, and from catalyst regeneration. High concentrations of CO_2 are found in the steam reforming process and in some petrochemical offgas streams such as ethylene oxide manufacture ; for these relatively small emission sources cryogenic techniques may be a promising option.

We have modelled three future scenarios of CO_2 emissions up to the year 2020, together with baseline emissions, and we have examined costs for two of the scenarios. The three scenarios may be summarised as:

(1) “Energy efficiency” - focusing on reductions which can be achieved through reducing energy use, with cost savings.

(2) “Maximum CO_2 reduction” - in which CO_2 capture/disposal is added on top of the first scenario.

(3) “Low sulphur future” - a scenario in which energy use and hence greenhouse gas emissions increase due to requirements for increased upgrading and desulphurisation.

The “Energy efficiency” Scenario enables refineries to hold emissions steady up to about 2010, before emissions rise in line with growth in throughput; whereas for petrochemicals any reduction is swamped by growth in throughput. This scenario gives savings of US$ 20/t CO_2.

In the “Maximum CO_2 reduction” Scenario we see a substantial decrease in refinery emissions by 2010 offset by a substantial increase in petrochemical emissions; but by 2020 both sectors are decreasing; the maximum reduction modelled in the summed sectors by 2020 is 56 % reduction at a cost of about US$ 45/t CO_2.

The “Low sulphur future” Scenario is defined as having an increase in emissions. Relative to the 2020 baseline, this increase is + 16% for refineries; zero for petrochemicals (by definition); and + 7% for the combined sectors.

In conclusion our modelling indicates that significant emission reductions can only be achieved through significant expenditure - for every US$ spent on end-of-pipe capture, CO_2 emissions can be reduced by 0.024 t CO_2. In order to bring emissions back to 1990 levels by 2020 would require all the US$ 6.7 billion savings from energy efficiency measures to be spent on end-of-pipe controls, plus an additional US$ 14 billion.

The barriers to implementing energy efficiency measures may be summarised as:

- issues relating to awareness;
- investment hurdles;
- the perceived need;
- ownership of emissions.

The principal barrier to implementation of CO_2 capture is cost.

We have postulated an opportunity for Joint Implementation activities in which companies in developed regions make available investment capital, expertise and training to companies in less developed regions, thereby accelerating implementation of energy efficiency measures at the global scale.

Contents

Appendices

1 Introduction

This report was prepared for the IEA Greenhouse Gas R&D Programme by AEA Technology Environment under contract reference IEA/CON/98/32 "*Greenhouse gases from major industrial sources - II: Oil refining and petrochemicals*".

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- Discuss current environmental legislation in the above regions; pressures for 'green' products and how these will affect future refinery practise and expected products.
- Estimate all emissions from a typical plant and describe current recovery processes for minimising waste.
- Outline future technological developments, *e.g.* separation membranes, carbon dioxide capture and storage, possible recycling options. Identify any barriers to development of these technologies, together with potential costs and timescales of implementation.
- Estimate future emissions to the year 2020 with consideration to future developments.
- Estimate the optimum for greenhouse gas reduction in a total perspective.

The report is structured as follows:

> **Chapter 2** describes refining processes in general, and provides example information from the five target regions plus Africa which was added at the request of the IEA Greenhouse Gas R&D Programme.
>
> **Chapter 3** describes the petrochemicals industry together with several important production processes, illustrated with data from the five regions.
>
> **Chapter 4** seeks to quantify all emissions from refineries, with focus on the main air pollutants, and presents estimates of air pollutant emissions from petrochemicals.
>
> **Chapter 5** presents various options for reducing greenhouse gas emissions from refineries and petrochemicals, and summarises techniques for other pollutants.
>
> **Chapter 6** briefly reviews market and product trends which may influence greenhouse gas emissions in the future.
>
> **Chapter 7** presents an overview of relevant environmental regulations from around the world.

Chapter 8 develops a number of scenarios of future CO_2 emissions for the years 1990 to 2020, and estimates the associated global costs.

The key conclusions from the report are summarised in **Chapter 9**.

In addition there are a number of supporting Appendices which provide additional detail or present case study material.

During the progress of the project, a number of individuals and organisations kindly provided advice and information. **Appendix 2** lists organisations contacted during the study.

2 Refinery processes

2.1 GENERAL INTRODUCTION TO REFINERY PROCESSES

2.1.1 Definitions of Crude Oil, Refining and Petrochemicals

The raw material in the petroleum industry is **crude oil**, which comprises mainly of a variable and complex mixture of hydrocarbons and substituted hydrocarbons containing different numbers of atoms of hydrogen and carbon.

The purpose of a **refinery** is to:

(i) separate the crude oil into different 'fractions' or saleable components;
(ii) shift the original component ratio and properties to meet the customer's demand; and
(iii) remove impurities detrimental to product quality.

The products of refining are 'fractions' of crude oil which themselves contain a large number of individual hydrocarbons; for example, LPG (liquid petroleum gases), petrol (gasoline) and lubricants. Further processing of these fractions yields **petrochemicals**, which contain a smaller number (one or two) of specific hydrocarbons of high purity; for example, ethylene and toluene. More complicated petroleum chemicals may then be made from these feedstocks at another plant, often located near to or adjoining the refinery.

2.1.2 Composition of crude oils

As noted above, the composition of crude oil is highly variable and each oil field yields a crude of unique composition (BP, 1970). Generally, the elemental composition includes carbon (85-90 %), hydrogen (10-14 %), sulphur (usually 0.2-3 %), nitrogen (usually below 0.1 %) and oxygen (up to 1.5 %), together with trace amounts (ppm or ppb) of elements such as nickel, vanadium and lead. Variation in composition leads to different boiling point curves (yield of distillate *vs.* temperature) by which oils may be assessed by a refiner.

Different oils are also compared in terms of gravity (density), ranging from very heavy crudes (*e.g.* some Venezuelan oils), containing a high proportion of materials such as asphaltenes and naphthenes, to very light crudes (*e.g.* oil from the Middle Eastern Qatar oil field). Oils from large fields, as used in most UK refineries, are of intermediate gravity.

Another property by which oils are assessed is their sulphur content. Sulphur is present in virtually all crude oils in varying amounts, ranging from 0.1-7 wt % sulphur. The majority of this sulphur is usually found in the higher boiling point component of an oil, and so within any geographical region heavy crudes generally have a higher sulphur content than lighter crudes. In terms of regional variations, high sulphur crudes are mainly found in the Middle East, Syria, Turkey and some regions of the USA (*e.g.* Texas) and Canada, whilst the light crudes of the USA and Canada and oils from North Africa and Nigeria typically have a low sulphur content. The significance of the sulphur content of a crude is that, depending upon the form in which it is present, it may lead to corrosion of equipment and poisoning of catalysts during the refining process or may result in products with undesirably high sulphur contents. The H_2S content also renders the vapours toxic, requiring more complex safety and emergency procedures, and volatile high sulphur content products have an unpleasant odour. So additional processing may be necessary, as described below. This has become an increasingly important consideration with increased pressure in recent years for 'green', low sulphur products.

Normally the feed used in an oil refinery is a mixture of different crudes, dependent upon the market situation.

2.1.3 Descriptions of refinery processes

Due to its numerous and varied components and the range of products derived from it, the processing of crude oil is extremely complex. The various refinery stages are summarised in **Box 1** and described in more detail below (Kirk Othmer, 1992, 1996; Institute of Petroleum, 1990).

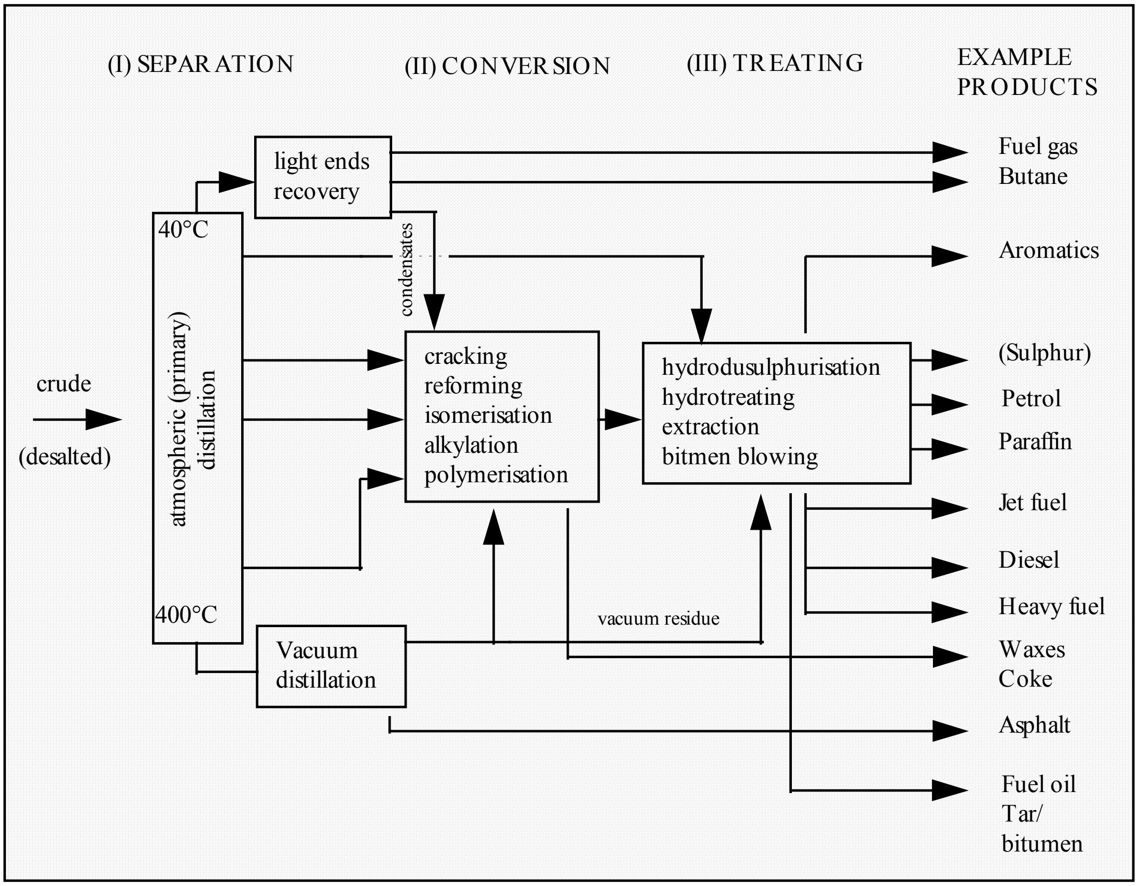
Box 1: Refinery processes

(I) SEPARATION	crude oil desalting/dewatering atmospheric distillation vacuum distillation light ends recovery
(II) CONVERSION	thermal cracking - coking, visbreaking catalytic cracking hydrocracking steam cracking catalytic reforming isomerisation alkylation and polymerisation
(III) TREATING PROCESSES	hydrodesulphurisation hydrotreating extraction bitumen blowing lube oil manufacture (large or specialist refineries only)
(IV) CRUDE & PRODUCT HANDLING	unloading storage blending loading
(V) AUXILIARY FACILITIES	boiler/process heaters hydrogen production sulphur recovery and production cooling towers compressor engines power generation blowdown system wastewater treatment

flares

Some unit processes are common to all refineries, *e.g.* primary distillation, but in general a refinery will be made up of a selection of unit processes, such that each refinery has a different make-up to suit its specific purpose, dependent upon the composition of the crude oil and what products are required from it. A schematic diagram representing an example refinery is shown in **Figure 2.1.**

Figure 2.1: Flow diagram illustrating the overall processes typically occurring in a refinery



The crude oil received at a refinery may have undergone various degrees of processing already at production facilities both onshore and offshore. Principally, the crude will have been dewatered in process separators, and separation from the gases will have been performed in the same units. However, it may also have been stabilised (dissolved gases driven off) and may already have been desalted and sweetened (stabilisation of sulphur compounds), prior to arrival at the refinery. Some gas fields are also associated with significant quantities of CO_2 which may also have been separated and some gas condensate may have been added back into the crude once associated gas has been separated. The extent of this processing depends largely on the requirements of local markets and transport systems and the nature of the produced oil. As discussed elsewhere, the basic composition of crude oil also varies form field to field, from the light Arabian crudes to the heavy Venezuelan crudes. The majority of refineries are designed around the crude feedstock they normally process and this affects the type and extent of the units which are present. However a number of (generally smaller) refineries do take a wide variety of feedstock from the spot market and many refineries may take a “spot cargo” of different specification from time to time; these changes in feedstock can significantly alter the efficiency and throughput of units on a given refinery.

Key processes, which are common to the majority of refineries, are:

(I) Separation

Crude oil desalting/ dewatering

Crude oil often contains salt and ash, either incorporated during its formation or from associated water in formation or subsequently from contamination by sea water during transportation. The first step in refining is to remove these impurities in order to prevent problems during later steps in the process, such as unwanted deposition in heater tubes or reaction at higher temperature.

The crude oil is desalted by washing with fresh water at about 120 °C under pressure. This forms an emulsion which picks up and retains other contaminants. The wash water is then separated by electrostatic precipitation with some chemical additives.

Distillation

The desalted crude oil is then preheated prior to separation according to boiling point (distillation) by refluxing in large fractionating towers to a maximum temperature of *ca.* 400°C. This produces a number of fractions containing hydrocarbons which boil within a series of temperature ranges. Primary distillation at atmospheric pressure separates the crude into four or five main fractions. Further separation of the bottom fraction (high boiling point material) may be achieved, if required, by vacuum distillation; by reducing the gas/ liquid equilibrium temperature this allows further separation without cracking (thermal degradation) occurring. Each fraction may then be processed further separately.

Light ends recovery

The highest fraction from the initial atmospheric distillation includes low boiling point gases. These are fed to the light ends processing unit, together with uncondensed gases from other sources. Condensable gases are frozen out by compression and then subject to further processing, while the lightest non-condensable gases are scrubbed and then burnt as refinery fuel.

(II) Conversion

Conversion processes involve the physical or chemical conversion of middle and lower fractions into materials which are in greater demand.

Cracking processes

Cracking involves breaking up large molecules into smaller ones. In thermal cracking this is achieved using heat alone. This method was used extensively in the past to yield material in the more commercially desirable gasoline range (30-200 °C) from larger, higher boiling materials. Petrol produced by this method is, however, of insufficient quality for use in modern engines and so catalytic cracking methods are now employed for this purpose (see below).

More recently, thermal cracking has been used as a convenient method for converting waxy or viscous distillates to less viscous oils which are more easily handled. This process is called viscosity breaking or visbreaking.

A further thermal cracking process is delayed coking, in which unwanted crude oil residue is heated to about 500 °C in a large drum; this converts the residue to lower boiling components, such as gas, naphtha and fuel oil, which are distilled off for further processing, and coke, which remains in the drum. The coke is then collected and either sold for use in other industries or used as fuel in the refinery. The coke produced may be up to 50% richer in sulphur than the original crude; combustion of high-sulphur coke therefore requires SO_x control.

The selectivity and efficiency of the cracking process has been improved by the development of catalytic cracking, thermal decomposition in the presence of a catalyst, which is the method now used to convert heavy distillates to gasoline products. In the course of this process, however, the catalyst (usually a crystalline aluminosilicate or molecular sieve) becomes coated with carbon and so is rapidly deactivated; the catalyst therefore undergoes constant regeneration. Originally catalytic cracking was introduced as a cyclic fixed-bed process, but now fluid catalytic cracking (FCC) predominates. In the latter process, small particles of catalyst (typically ~ 100 μm diameter) are suspended in gas, enabling it to be handled as a liquid. This process has a number of advantages over the fixed-bed process. Firstly, fluidisation facilitates the regeneration process, as the suspended catalyst is easily circulated between reaction and regeneration vessels; also, it enables better heat transfer; further, it allows processing of both liquid and feeds whereas the fixed-bed process was suitable for gas feed only.

Hydrocracking, which involves catalytic cracking in the presence of high pressure hydrogen, to produce low-boiling point saturated compounds, and steam cracking, which is used to produce light olefins such as ethylene from naphtha, are further methods which are very flexible and can produce high yields of desirable products (mainly petrochemical feedstocks).

Catalytic reforming

Reforming processes involve the re-arrangement of molecules to more useful forms in the presence of a catalyst. This may involve a change in the types of bond (saturated/ unsaturated) present, with associated loss or gain of hydrogen as controlled by the conditions. The process is used to produce higher octane level stocks, generally aromatics, from paraffins and naphtha (distillates in the temperature range 70-200 °C), using a platinum based catalyst at temperatures of 500 °C. The hydrogen produced is sufficient to supply the hydrotreating and hydrodesulphurisation units.

Isomerisation

Isomerisation has the same aim as catalytic reforming, and is used for straight chain C_5 and C_6 molecules in the lower boiling range of 20-70 °C. The main difference between the two techniques is that isomerisation involves re-arrangement only (no change in bond types or addition/ loss of hydrogen), such that the empirical formula of the compound remains the same; only its structure is changed to generate higher octane components.

Alkylation and polymerisation

The principles of these two processes are the same, namely the conversion of gaseous C_3 - C_5 olefins (unsaturated by-products from cracking procedures) to longer chain gasoline (saturated) molecules. In alkylation this is achieved by combining the molecules with isobutane, while in polymerisation the molecules join to each other to form longer chain saturated molecules. These processes occur under controlled conditions of temperature and pressure in the presence of a strong acid catalyst. They are the only major processes in refining which result in products with a higher boiling point than the feed.

(III) Treating Processes

Hydrodesulphurisation

In light distillates sulphur is present in low boiling point materials such as hydrogen sulphide (H_2S), mercaptans (compounds of general formula $HS\text{-}C_nH_{2n+1}$), sulphides, disulphides and thiophenes. As well as being highly odorous, these compounds are very corrosive to metals and can poison many catalysts, which is a problem for both the refiner and the end user. They may be removed by a variety of processes, most commonly by hydrodesulphurisation, which involves high pressure destructive hydrogenation, resulting in breakage of the C-S bonds and production of hydrogen sulphide gas. The latter is then subsequently removed as described below.

As previously noted, the majority of the sulphur usually exists in the heavier fractions of crude oil (higher boiling point). At such temperatures the sulphur exists in complex ring structures which are very stable and non-reactive and their removal subsequently requires high pressure destructive hydrogenation in the presence of a catalyst. This is an expensive process, and is only employed as required and when economically viable. For example, if a heavy fraction is to undergo catalytic reforming to a product which is in sufficiently high demand it may be cost effective to desulphurise the fraction to prevent catalyst poisoning. However, for a product which is in lower demand it may be more cost effective to blend the fraction with the equivalent fraction from a low sulphur crude. For certain end uses, generally where the product is not burnt (*e.g.* lubricating oils), the removal of stable sulphur compounds may not be required. The extent of hydrodesulphurisation is therefore dependent upon both end use and economics.

Hydrogen sulphide may be removed by a variety of processes. For example it can be removed by washing in alkali to form less nocuous disulphides. Alternatively, it can be burned to form SO_2 in an oxygen supply which is limited such that one third of the H_2S burns; this yields a mixture of two-thirds H_2S and one-third SO_2 which subsequently react to form sulphur and water :

$$\begin{array}{llllllllll} & 3H_2S & + & 1.5\ O_2 & = & 2H_2S & + & SO_2 & + & H_2O \\ & 2H_2S & + & SO_2 & = & 3S & + & 2H_2O & & \\ \hline \text{Overall :} & 3H_2S & + & 1.5\ O_2 & = & 3S & + & 3H_2O & & \end{array}$$

The sulphur is then collected and can be sold.

In many cases, particularly historically, H_2S rich gas streams were simply flared, converting the H_2S to SO_2 in an acid gas flare to give a characteristic yellow smoke and of course the potential for acid rain. Whilst this has become less common, there are still areas where it is done, although it is tending to be phased out by regulations and good practice.

Hydrotreating

Hydrotreating is similar to hydrocracking but is carried out under far less severe conditions, with the aim of removing impurities and converting olefins to saturated compounds. It converts sulphur- and/ or nitrogen-containing hydrocarbons into low sulphur/ nitrogen liquids and hydrogen sulphide and ammonia gases which can be removed. The hydrogen supply for this process comes from the catalytic reforming unit.

Extraction

There is a large range of extraction processes, which are employed to remove impurities which cannot be removed by distillation methods. The processes generally involve the use of a suitable organic solvent, which can be recycled, after separation from the product, to be used again. The product is then treated to remove any excess solvent.

Bitumen blowing

Bitumen is the lowest fraction of vacuum distillation and is also known as vacuum residue. Viscous vacuum residue is converted to a more usable form by blowing, in which air is blown though molten bitumen, oxidising it such that partial polymerisation occurs. This modified bitumen then has the ideal properties for use in road-making and in roofing.

(IV) CRUDE AND PRODUCT HANDLING

Unloading and storage of crude

Crude oil and its refined products may be transported by pipeline, sea, inland waterways, rail or road, as determined by location (of source and customer) and economics. Most refineries are sited on the coast and generally crude oil is transported by oil tankers to an oil terminal located at a port, where it is then unloaded. Inland terminals are generally fed by pipeline or barge or river traffic. Prior to docking, the crude oil is preheated on the vessel to a suitable temperature (20 °C) to enable it to be pumped into holding tanks at the terminal where it is stored. Typically there is enough storage capacity to hold 30 days supply of crude (and 30 days of products).

Blending

Products such as gasoline and diesel are blended to achieve an optimum formulation to meet market demand or regulatory specifications. ‘Premium’ diesel fuel, for example, may have anti-oxidants, anti-rust agents, cetane improvers, corrosion inhibitors and de-emulsifiers added to improve performance.

Loading

The refined products are then loaded for appropriate transportation to the customer.

These processes and associated environmental aspects are considered in more detail in section 6.

(V) AUXILIARY FACILITIES

The term auxiliary facilities incorporates all the supporting processes and utilities which are integral to the running of the above refinery operations. For example, nearly all processes involve heating/ cooling and all products have to be pumped. This requires facilities such as power generators, boiler and process heaters, and cooling towers, together with utilities such as steam, air, water and electricity. UK EA (1997) gives a range of large combustion plant capacities in the UK of 160-1680 MWth.

Other auxiliary facilities include wastewater treatment and hydrogen production plants. The latter is required since there is a greater demand for hydrogen for hydrotreating processes than is produced as a by-product in other procedures (mainly catalytic reforming). Extra hydrogen is commonly obtained by catalytic steam reforming of low sulphur methane, refinery gas or naphtha; this produces CO_2 and H_2. Hydrogen can also be produced from low quality residual stocks or petroleum coke by non catalytic partial oxidation with oxygen and steam.

Flares are commonly used during refining for the safe disposal of waste gases during process upsets (e.g. start-up, shut-down, system blow-down) and emergencies to combust the organic content of waste emission streams without recovering/using the associated energy.

2.1.4 Categorisation of refineries

As defined by the American Petroleum Industry (API), based upon processing complexity and product state, refineries may be split into five categories, namely:

1) Topping refineries (T), also know as ‘hydroskimming’ type in the EEC
include atmospheric distillation units, vacuum distillation units, naphtha hydrotreating units, catalytic reforming units, middle distillate hydrotreating units and asphalt processing units.

2) Topping and cracking refineries (T & C)
as above plus fluid catalytic cracking units (FCCU), hydrocracking units (HCCU), thermal cracking units (TCCU), delayed cracking units, gas oil hydrotreating units, alkylation units, aromatic extraction units

3) Topping, cracking and lubes refineries (T, C & L)
as above (1) and (2) plus modules for processing lubricating oils.

4) Topping, cracking and petrochemical refineries (T, C & P)
as above (1) and (2) plus some primary and secondary petrochemicals such as olefins, butane, toluene, xylene, cyclohexane, cumene, styrene, ketones, alcohols *etc.*

5) Integrated refineries (I)

full range of processes for production of fuels, petrochemicals and lubricants.

This categorisation has been discussed with a number of refinery operators who consider it quite representative. Simple refineries (some T, mostly T&C) are common in Europe, while in the US refineries are generally large and of greater complexity. These differences are discussed in more detail in following sections.

2.2 OVERVIEW OF WORLD-WIDE REFINERY TECHNOLOGY

Refinery technology tends to be quite consistent throughout the world for two reasons:

- The basic processes which have been used for many years are essentially those of distillation; whilst details may differ, the major drive in all areas has been improved efficiency.

- Most of the additional conversion processes are licensed by a small number of organisations to oil companies operating throughout the world.

Historically, many changes have occurred in the refining business, dictated largely by the demands of the market place with decreasing demand for heavy fuel oils and increasing demand for lighter transportation fuels, together with increasing environmental constraints. Demand for lighter fuels (particularly petrol) has led to the increasing use of conversion processes throughout the world, particularly in the American and European markets, but also in the Far East, since the demand for these products now outstrips the proportion present in most crude oils. Light Arabian crudes may contain a more appropriate proportion of light materials to satisfy average demand, but lowering demand for the heavier fractions in most markets has still led to an increase in the use of cracking world-wide to convert these less desirable fractions.

One of the principal requirements for petrol is to satisfy the appropriate octane number. The addition of lead compounds (TML/TEL) helped to increase the octane number substantially. The move towards lead free fuel has meant that alternative methods of increasing octane number have had to be found. Generally this has led to an increase in the numbers of reforming units (aromatic molecules generally have higher octane numbers than aliphatic ones) and alkylation units (which use the less useful butane fraction to produce iso-octane and similar products with high octane numbers).

The majority of oil is shipped from the production area to the market in the form of crude oil and refined close to the final point of sale. Finished products tend to be transported over much shorter distances and intermediate naphthas may frequently be exchanged between nearby refineries to optimise processing capabilities between them.

An increasing trend is the increased production of natural gas and LNG as cleaner burning fuels over the past years. The extent to which this production has increased is evidenced by the building of entire facilities, particularly in the Middle East, around refining condensate from the gas stream into saleable products in addition to selling the gas or LNG. The increasing sales volume of gas and LNG has turned what was once considered as a waste product of oil production, and flared, in areas such as the Middle East into a valuable and sought after reserve, even in remote areas. The availability of clean LNG in bulk to economies such as Japan and South Korea, which have no significant gas reserves, has changed the fuel of choice for heating and power generation over the past decade or so, and there is strong evidence of increasing trends in this direction.

An interesting difference between refineries is the choice of fuel to operate the refinery furnaces and boilers. This is a complex issue, but ideally involves burning the lowest value products which can efficiently be used in the combustion processes. For simplicity, there will always be a refinery fuel gas system, and the majority of process furnaces are designed to run on surplus fuel gas. This is principally because gas is not a significant refinery export, having mainly been removed from the feedstock, and is very easy to use in furnaces. Fuel oil is also commonly used as one of the lower value products, and may also contain significant contaminants, and furnaces are frequently designed with the flexibility to accept both gas and fuel oil feeds. Some refineries which have only a small market in LPG for heating or automotive uses may choose preferentially to use LPG as part of the fuel gas system. The market is, to a large extent, dependent on the tax regimes for fuel in specific countries. Even within Europe, there is a large disparity in the usage of automotive LPG - the higher consumption being principally in the south. There is also an increasing use of LPGs as fuels in the Far East, as they can be readily imported economically.

In North America and Europe, the predominant demand is for motor gasolines, with relatively low demand for fuel oils, particularly in America. This leads automatically to the necessity for a significant cracking capacity in the refineries, particularly the use of FCC units. Similarly, the stricter regulations on the use of lead compounds and sulphurous emissions has lead to an increase in reforming and hydrotreating units.

In Asia Pacific, the demand for fuel oils is significantly higher, for marine transportation and power generation, meaning that less cracking capacity is required, although large refineries may still have both FCC and hydrocrackers. Similarly older, simpler types of refineries are often employed in regions where less stringent regulations currently apply, and older technology is often used, generally with reduced conversion capacity, in some of the poorer countries. This is clearly not the case in the highly industrialised countries of the Pacific rim.

In the Middle East, there is a lower demand for motor fuels, and higher demand for fuel oil and middle distillates for power generation and shipping. Whilst the Middle East exports the majority of its crude oil, the local demand is relatively low and the oil both plentiful and cheap. There is therefore relatively little incentive to provide extensive conversion facilities, when relatively simple topping operations can produce sufficient gasoline for local demand. However, conversion facilities are increasingly being built to upgrade low value products to increase the overall saleable value for export.

The African demand profile is relatively similar to the Middle East and again relatively simple topping facilities can generally be employed. However, South Africa has been something of an exception due to past sanctions on oil imports. This has led to motor gasoline being produced, at least in part, by steam reformation of water gas produced from the plentiful reserves of coal. Due to the complexity of this process in comparison to crude oil refining, and the easier availability of crude oil, the tendency is to move from these processes to more conventional refining.

In the Former Soviet Union, most of the basic refinery units employed are very similar. However, historically, units were built more as autonomous units, with more extensive use of intermediate storage. A greater demand for heating oils fitted in with the generally heavier crudes available, but increasing use is being made of cracking facilities to supply increasing demand for motor fuels, and increasing Western involvement is leading to a move to more fuel efficient refinery designs.

The overall picture is one of rapidly converging technologies based around the domination of a relatively small number of multi-national oil producers, an increasing role for large national oil companies, and the wide-spread licensing of technologies. Where significant differences do exist, they are generally based around the demand profile for products of the particular region.

2.3 NORTH AMERICA

2.3.1 United States

The US total crude oil distillation capacity as reported at 1st January 1997 is 15,451,785 barrels per calendar day (bpcd), with over 5.2 million barrels processed in 1996. This total incorporates 81 different refining corporations, running 164 refineries in total, mostly T & C. The corporations range in size from the Petrolite Corporation, which runs one refinery of capacity 600 bpcd, up to the Chevron Corporation which runs seven refineries within six different states, each of capacity up to 300,000 bpcd, totalling 1,047,000.

Chang (1998a) gives process capacities as at 1st January 1999:

	Capacity, bpcd
Crude	16,422,670
Vacuum distillation	7,423,805
Coking	2,039,450
Thermal operations	56,300
Catalytic cracking	5,419,931
Catalytic reforming	3,579,268
Catalytic hydrocracking	1,485,620
Catalytic hydrorefining	1,681,590
Catalytic hydrotreating	8,945,160

2.3.2 Canada

Canada has 22 refineries (1st January 1999). Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	1,872,700
Vacuum distillation	621,950
Coking	39,550

Thermal operations	136,750
Catalytic cracking	398,100
Catalytic reforming	350,500
Catalytic hydrocracking	253,150
Catalytic hydrorefining	36,600
Catalytic hydrotreating	780,450

Imperial is Canada's largest refiner of petroleum products and a major producer of petrochemicals. The company operates four refineries nationally; two T & C, one T, C & L and one integrated with a full chemical manufacturing plant. Total refinery capacity is in the region of 492,500 barrels of crude oil per day.

Petro-Canada is one of the largest oil and gas companies, operating in both the upstream (exploration and production) and downstream (refining and marketing). It is the second largest petroleum refining and marketing company in Canada, owning and operating three major T & C refineries together with a separate lubricants facility. In response to the government's VCR programme, voluntary actions by Petro-Canada have reportedly reduced their greenhouse gas emissions by 6% from 1990 - 1996, despite growth in production of 10.9%. Initiatives to reduce emissions in refineries have included the introduction of leak detection and repair programmes, improvements in processing and recovery of flare gases.

2.3.3 Mexico

Mexico has 6 refineries (1st January 1999). Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	1,525,000
Vacuum distillation	761,700
Coking	41,000
Thermal operations	100,000
Catalytic cracking	332,000
Catalytic reforming	243,000
Catalytic hydrocracking	18,500
Catalytic hydrorefining	-
Catalytic hydrotreating	748,000

Mexico's state oil company Pemex maintains monopoly control over refining of crude oil. The refineries are: Salina Cruz (330,000 bbl/d), Tula Hidalgo (320,000 bbl/d), Salamanca (236,000 bbl/d), Cadereyta (235,000 bbl/d), Minatitlan (204,000 bbl/d) and Ciudad Madero (195,000 bbl/d) (EIA, 1998e).

2.4 SOUTH AMERICA

Refining capacity in South America is given by Chang (1998a) for 1st January 1999:

Country	Number of refineries	Crude capacity, bpcd
Argentina	11	652,675
Bolivia	3	47,888
Brazil	13	1,772,273
Chile	3	204,640
Colombia	5	248,850
Ecuador	3	176,000
Paraguay	1	7,500
Peru	5	182,250
Uruguay	1	37,000
Venezuela	6	1,187,200

2.4.1 Brazil

Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	1,772,273
Vacuum distillation	551,310
Coking	78,683
Thermal operations	9,000
Catalytic cracking	395,541
Catalytic reforming	24,060
Catalytic hydrocracking	-
Catalytic hydrorefining	85,411
Catalytic hydrotreating	62,085

Major refineries and their capacities as of 1997 are: Paulinia in São Paulo (272,930 b/d); Duque de Caxias in Rio de Janeiro (225,730 b/d); São Jose dos Campos in São Paulo (204,700 b/d); Araucaria in Parana (159,210 b/d); Betim in Minas Gerais (136,470 b/d); and Mataripe in Bahia (117,960 b/d) (US DoE, 1998a).

Oil consumption in Brazil has risen by about 20% since the mid-1980's. Despite significant domestic production, Brazil imports more than 40% of its petroleum consumption (mainly from Argentina, Venezuela and Saudi Arabia). Outputs of refined petroleum products are given below (US DoE, 1998a):

	Output, 1000 b/d
Distillate fuel oil	433
Automobile gasoline	298
Residual fuel oil	248
Other[*]	212
Liquified petroleum gas	121
Jet fuels	49
Kerosene	3
Total	**1,363**
[*] Includes asphalt, coke, aviation gasoline, naphthas, paraffin wax, petrochemical feedstocks.	

2.4.2 Venezuela

Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	1,187,200
Vacuum distillation	548,370
Coking	52,100
Thermal operations	82,000
Catalytic cracking	234,900
Catalytic reforming	47,200
Catalytic hydrocracking	-
Catalytic hydrorefining	-
Catalytic hydrotreating	284,600

Petroleos de Venezuela is the world's fourth largest oil refiner and owns the country's 6 refineries. Amuay and Cardon refineries merged to form the Paraguana Refining Centre (940,000 b/d), one of the largest refineries in the world. The other refineries are: Puerto La Cruz (200,000 b/d); El Palito (130,000 b/d); Bajo Grande (51,000 b/d); and San Roque (5,000 b/d) (US DoE, 1998b).

Outputs of refined petroleum products are given below (US DoE, 1998a):

	Output, 1000 b/d
Automobile gasoline	376
Residual fuel oil	307
Distillate fuel oil	258
Kerosene	76
Liquified petroleum gas	9
Other[*]	64
Total	**1,090**
[*] Includes asphalt, coke, aviation gasoline, naphthas, paraffin wax, petrochemical feedstocks.	

2.5 EUROPE

2.5.1 Western Europe

Process capacities are given by Beckman (1995):

Process	Total Western European capacity, b/d
Atmospheric distillation	13,212,833
Vacuum distillation	4,960,004
Thermal	1,838,686
Catalytic cracking	2,041,010
Catalytic reforming	2,109,394
Catalytic hydrocracking	619,181
Catalytic hydrorefining	1,864,361
Catalytic hydrotreating	5,044,590
Alkylation/ polymerisation/ dimerisation	265,297
Aromatics/ isomerisation	563,132
Lubes	123,800
Oxygenates	40,919
Hydrogen	1,381.5
Asphalt	327,376
Coke	9,991

Individual refineries and their capacities in 1995 are listed in **Appendix 3**.

Elf's Mider refinery at Leuna (Germany), on-stream in 1997, was the first refinery to be built in Europe for 15 years (Elf, 1998).

2.5.2 Central and Eastern Europe

Refining capacity in Central and Eastern Europe is given by Chang (1998a) for 1st January 1999:

Country	Number of refineries	Crude capacity, bpcd
Albania	2	26,300
Bulgaria	1	133,500
Croatia	3	235,900
Czech Republic	4	198,000
Hungary	3	232,000
Lithuania	1	263,420
Poland	7	382,000
Romania	10	521,715
Serbia	2	167,264
Slovakia	1	115,000

Slovenia	1	12,000

2.5.2.1 Bulgaria

Neftochim is a state refining company operating the refinery at Bourgas. Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	133,500
Vacuum distillation	58,700
Coking	-
Thermal operations	24,700
Catalytic cracking	24,800
Catalytic reforming	6,400
Catalytic hydrocracking	-
Catalytic hydrorefining	-
Catalytic hydrotreating	78,400

2.5.2.2 Slovak Republic

Slovnaft a.s. operates the country's refinery in Bratislava. Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	115,000
Vacuum distillation	53,030
Coking	-
Thermal operations	-
Catalytic cracking	-
Catalytic reforming	22,270
Catalytic hydrocracking	16,970
Catalytic hydrorefining	-
Catalytic hydrotreating	73,830

Most of the oil is imported from the Russian Federation (US DoE, 1998c).

2.6 JAPAN

The Japanese petroleum industry has undergone a number of changes in recent years. Until 1987 the industry was strictly controlled by the Petroleum Industry Law of 1962. Under this law, the construction of refining facilities required permission from the government, with priority being given to the establishment of refineries to supply feedstocks to internal petrochemical or power companies. Oil refining and the marketing activities of the Japanese petroleum industry were decontrolled in a series of steps between 1987 and 1992, in accordance with the policy "oil supply in ordinary times is left to the autonomous activity of the oil industry, while the government supplements it in case of emergency".

Following this, there has been an attempt to bring the Japanese petroleum industry more closely into line with the international oil market, for example to bring about reduction in the price of gasoline in Japan (which was higher than in most other countries) and to make the industry more competitive internationally. To facilitate this, there has been further deregulation concerning the import of refined products (April 1996), together with a variety of measures designed to improve the efficiency of product distribution inside Japan and to promote competition within the home industry. This is to be followed by further deregulation of the petroleum industry including export liberalisation of refined products.

Japan holds almost no oil of its own (60 million barrels of proven oil reserves), but is the second largest world oil consumer. Japan consumed (and imported) 5.9 million barrels per day of oil in 1996.

EIA (1998d) reports that Japan has 44 refineries, "considered by analysts to be excessive and inefficient". Process capacities reported by Chang (1998a) are:

	Capacity, bpcd
Crude	5,059,4760
Vacuum distillation	1,655,267
Coking	86,100
Thermal operations	-
Catalytic cracking	791,200
Catalytic reforming	733,808
Catalytic hydrocracking	160,100
Catalytic hydrorefining	2,296,830
Catalytic hydrotreating	2,048,281

Major refineries include: Negishi (367,000 bbl/d), Ichihara-Chiba (237,500 bbl/d), Mizushima (230,000 bbl/d), Cosmo-Chiba (228,000 bbl/d), Showa Yokkaichi (220,300 bbl/d), and Tonen Kawasaki (217,350 bbl/d) (EIA, 1998d).

The top three refiners in Japan are (in order):

1. Nippon Oil Company
2. Idemitsu Kosan Company
3. Cosmo Oil Company

Idemitsu Kosan operates six refineries that produce about 900,000 barrels per day (gasoline and fuels; kerosene; lubricants; and LPG). These are located in Hokkaido, Chiba, Aichi, Hyogo, Tokuyama, and Okinawa (Okinawa Refining Company). Cosmo Oil Company has four refineries, mainly importing Middle Eastern crude.

In August 1997, an official of Japan's Ministry of International Trade and Industry (MITI) said that Japan and China are considering a joint coal liquefaction project as a possible substitute for oil. A $5.9 million feasibility study on the project, which would utilise coal from China's Yilan mine and Japanese liquefaction technology, is expected to be completed in 1999 (EIA, 1998d).

2.7 OTHER ASIA

China: The total refining capacity at the start of 1998 was 3.0 million bbl/day; China's current strategy is to debottleneck and upgrade existing refining capacity rather than build new refineries (EIA 1998a). The goal is to reach 3.6 million bbl/d capacity by 2000, and 5 million bbl/d by 2010. Major refineries (1/1/98 capacity) include: Fushun (174,000 bbl/d), Maoming (170,000 bbl/d), Qilu (160,000 bbl/d), Gaoqiao (Shanghai) (146,000 bbl/d), Dalian (142,000 bbl/d), Yanshan (140,000 bbl/d), and Jinling (134,000 bbl/d). An example of a small specialised refinery is the Jingxi Yunhua Petroleum Refinery, with an annual capacity of 60,000 t of lubrication oil and "industrial oil". The Shanghai Oil Refinery is described in **Appendix 6**.

India had a crude oil refining capacity of 1.1 million bbl/d at 1 January 1998. India currently has 12 operating refineries, with 2 under construction and 5 more planned by 2002. These projects will double India's refining capacity, to 2.2 million bbl/d. Major oil refineries (1/1/98 capacity) include: Koyali-Gujarat (185,100 bbl/d), Mathura-Uttar Pradesh (156,000 bbl/d), Mahul-Bombay (Bharat Petroleum) (134,860 bbl/d), Madras (130,660 bbl/d), and Mahul-Bombay (Hindustan Petroleum) (110,452 bbl/d) (EIA 1998b).

Indonesia has a crude refining capacity (1/1/98) of 930,000 bbl/d. Indonesia has eight refineries with a combined capacity of 930,000 bbl/d: Cilacap, Central Java (285,000 bbl/d); Pertamina-Balikpapan, Kalimantan (240,920 bbl/d); Musi, South Sumatra (109,155 bbl/d); EXOR-1, Balongan, Java (125,000 bbl/d); Dumai, Central Sumatra (114,000 bbl/d); Sungai Pakning, Central Sumatra (47,500 bbl/d); Pangakalan Brandan, North Sumatra (4,750 bbl/d); Cepu, Central Java (3,420 bbl/d). In September 1997, the Mines and Energy Ministry reported that Indonesia has been studying ways to increase production capacity at its oil refineries in order to avoid building expensive new refineries the country cannot afford in light of the current economic crisis. Pertamina estimates that the country's domestic demand for refined products will continue to grow at an annual rate of 6-7% and that Indonesia will need an additional 350,000 bbl/d of capacity by the year 2000. The Ministry indicated that Indonesia is considering debottlenecking existing plants to increase production and efficiency and adding catalytic reformers to produce higher quality and lower lead petrol, and naphtha reformers to convert surplus heavy residue into lighter products (EIA, 1998c).

2.8 AFRICA

The refineries in Africa are shown in the table (MBendi, 1997):

Country	Name, location
Algeria	Raffinerie d'Alger, El Djazair/Maison Carre Raffinerie d'Arzew, Arzew Raf de H Messaoud, Hassi Raf de Skikda, Skikda
Angola	Fina Refinery, Luanda
Cameroon	Sonara, Limbe

Democratic Republic of Congo	Sozir Refinery, Muanda
Republic of Congo	Coraf Refinery, Pointe Noire
Country	**Name, location**
Cote d'Ivoire	Raffinerie SIR, Vridi, Abidjan
Egypt	El Mex Refinery, Alexandria Amerya Refinery, Alexandria El Suez Refinery, Suez El Nasr Refinery, Suez Cairo Oil Refinery, Mostorod Cairo Oil Refinery, Tanta El Nasr Refinery, Wadi Feiran Assyout Oil Refinery, Assyout
Eritrea	Assab Refinery, Assab
Gabon	SGR Refinery, Port Gentil
Ghana	Tema Refinery, Tema
Kenya	Kenya Petroleum Refinery, Mombasa
Libya	Sirte Oil Company, Brega Ras Lanuf, Ras Lanuf Azzawiya, Zaria
Madagascar	Solima Refinery, Tamatave
Mauritania	Somir Refinery, Nouadhibou
Morocco	Samir Refinery, Mohammedia Sidi Kacem Refinery, Sidi Kacem
Nigeria	Kaduna Refinery, Kaduna Port Harcourt I & II, Port Harcourt Warri Refinery, Warri
Sénégal	SAR Refinery, Dakar
South Africa	Caltex Refinery, Cape Town Engen Refinery, Durban Natref Refinery, Sasolburg Sapref, Durban Sasol I, Sasolburg Sasol II & III, Secunda Mossgas, Mossel Bay
Somalia	Mogadishu Refinery, Mogadishu
Sudan	Port Sudan Refinery, Port Sudan
Tanzania	Tiper Refinery, Dar-es-Salaam
Tunisia	STIR Refinery, Bizerte
Zambia	Indeni Refinery, Ndola

The following descriptions for specific countries are summarised from MBendi (1997).

South Africa: Because of South Africa's abundant supplies of cheap coal, liquid fuels only provide 21% of the country's energy requirements. South Africa is also very unusual in having synfuel plants which were established to produce oil from coal during the period of political isolation. The synfuel technology is based on a two-step process: coal is gasified at high temperature to produce a “syngas” which is reacted with a catalyst to produce a range of olefins and other hydrocarbon products (Fischer Tropsch synthesis).

The Sasol I synfuels plant at Sasolburg was built in 1956. Sasol II and III were built in the 1970’s over the coalfields at Secunda. Sasol II and III produce more than 5.7 million tons of product per year, equivalent to a refinery with a crude capacity of 170 tbpd. In May 1996 Sasol announced a US$ 200 million project to replace sixteen 17-year-old synfuel reactors with six new generation advanced synfuel reactors using fluidised bed technology.

The Sasol I synfuels plant was converted in the early 1980’s into a chemicals producer, and liquid fuels have not been produced since. Sasol I can process 6.5 million tons of coal per year to pipeline gas, ammonia, waxes, solvents and other chemical products.

In 1987 the South African Government approved the Mossgas project in Mossel Bay to produce synthetic products (diesel and petrol fuels, LPG, kerosene and alcohol) from natural gas and condensates from offshore fields using similar technology.

The Natref refinery in Sasolburg is one of the crude refineries in South Africa. First on line in 1971 it has had several revamps and upgrades. It has a distillation capacity of 4.28 Mt/yr. The main process units and their capacities are shown in the table:

Units	Capacity, bpd
Integrated atmospheric and vacuum distillation units	86,000
Two catalytic desulphurisers	26,500
Catalytic reformer	14,500
Fluid catalytic cracker	18,100
HF alkylation unit	3,900
Butane isomerisation unit	3,600
Distillate hydrocracker	10,500
Residual crude desulphuriser	13,000
Two amine units and a sulphur recovery unit	130 t/day
Steam reforming H_2 unit	30,000 m^3/hr
Six Merox treating units	-
Bitumen blowing unit	-

The Natref refinery product spread includes:

- propane;
- gasoline (three grades);
- diesel;
- jet fuel;
- illuminating kerosene;
- power paraffin;
- bitumen;
- fuel oil (eight grades);
- liquid sulphur.

Nigeria: There are two refineries at Alesa-Eleme near Port Harcourt. Port Harcourt I is a topping and reforming refinery. It was rebuilt following a fire in 1989, and has a distillation capacity of 3 Mt/yr. Port Harcourt II is a complex refinery with a distillation capacity of 7.5 Mt/yr. Both are reported to be in a dilapidated state of repair. The main production units are summarised in the table:

Refinery	Unit	Capacity, bpd
Port Harcourt I	Crude Unit	60,000
	Catalytic reformer	6,000
Port Harcourt II	Crude unit	110,000
	Vacuum unit	54,000
	FCCU	40,000
	Catalytic reformer	33,000
	Distillate hydrotreater	33,000
	Alkylation unit	7,020
	Isomerisation unit	3,600
Kaduna	Crude unit	110,000
	Vacuum unit	36,300
	FFCC	18,000
	Pretreater	14,500
	Catalytic reformer	15,300
	Catalytic hydro desulphuriser	15,700
	Distillate hydrotreater	21,600
	Isomerisation unit	300

The Kaduna refinery is a complex refinery with a distillation capacity of 5.5 Mt/yr and came on stream in 1980. The refinery also has capacity to manufacture petrochemical products such as linear alkyl benzene (30,000 t/yr), benzene (15,000 t/yr) and kero solvent (30,000 t/yr). The refinery has been plagued by technical malfunctions and breakdowns - overall costs for repairs and restoration are estimated at US$ 55 million.

The Kaduna refinery has the units shown in the table above.

The Warri refinery has downstream petrochemical plants which produce 13,000 t/yr of polypropylene and 18,000 t/yr of carbon black.

3 Petrochemical processes

3.1 INTRODUCTION TO PETROCHEMICAL PROCESSES

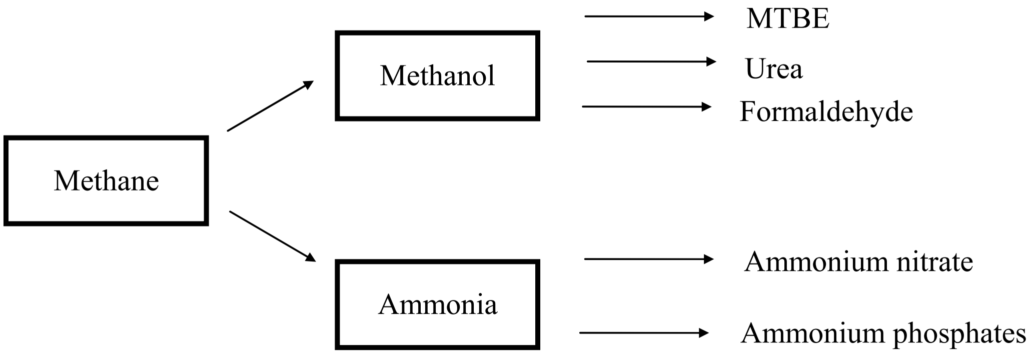
3.1.1 Outline description

The petrochemicals industry is based upon the production of chemicals from raw materials mainly of natural gas or petroleum origin. The processes involved in the petrochemical industry are similar to those described for the oil refining industry; similar emission sources must therefore be considered.

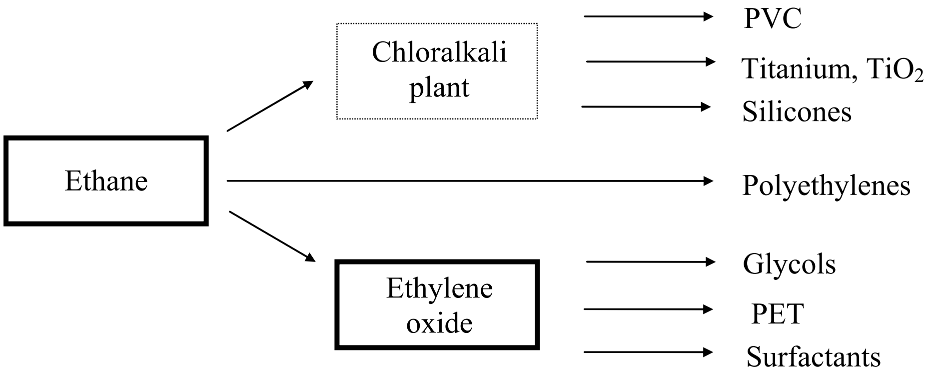
Petrochemicals may be broadly broken down into three groups:

- gas-based petrochemicals derived from methane and ethane;
- naphtha or oil-based petrochemicals derived from propane or butanes;
- aromatics, derived from LPG or naphtha

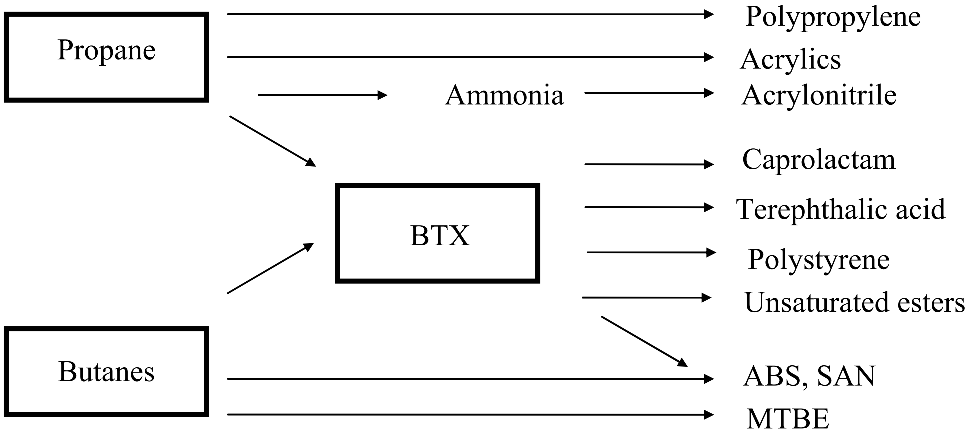
Methane is the largest component of natural gas and is used to make a variety of chemicals:



Ethane is used in chloralkali plant, in the production of polyethylenes and derivatives of ethylene oxide:



Propane and butanes are components of LPG but are commonly produced in refineries by naphtha cracking.



3.1.2 Global petrochemical capacity and production data

The world-wide capacity for ethylene in 1998 was 89.6 Mt/yr (Chang, 1998b):

Region	1998 capacity, t/yr
Asia/Pacific	21,888,700
Eastern Europe/Former Soviet Union	7,478,000
Middle East/Africa	6,521,860
North America	30,177,731
South America	3,457,800
Western Europe	20,081,295

The following table gives world ethylene capacity and demand for the years 1990 to 1998 (Chang, 1998b) and Western European ethylene capacity and production (1991 to 1996 data from Financial Times, 1997; 1998 data from Chang, 1998b).

Year	World capacity, t/yr	World demand, t/yr	World demand as % of capacity	W. Europe capacity, t/yr	W. Europe production, t/yr	W. Europe production as % of capacity
1990	63,000,000	56,000,000	88.9			
1991	66,500,000	58,000,000	87.2	17,280,000	14,470,000	83.7
1992	69,500,000	60,000,000	86.3	18,044,000	15,535,000	86.1
1993	72,000,000	62,000,000	86.1	18,760,000	15,650,000	83.4
1994	74,000,000	67,000,000	90.5	19,111,000	17,517,000	91.7
1995	77,000,000	70,000,000	90.9	19,416,000	17,708,000	91.2
1996	81,500,000	73,000,000	89.6	19,370,000	17,752,000	91.6
1997	84,975,017	77,000,000	90.6			
1998	89,605,386	81,500,000	91.0	20,081,295		

The world-wide capacity for polypropylene was about 1 Mt/yr in 1990; the largest producer was Himont (USA) followed by the Shell group (Chemical Intelligence Services, 1991).

3.1.3 Trends in production

The petrochemicals business tends to be cyclic in nature. In part this reflects the general state of the world economy and demand for products. Another cyclicity follows investment: expanded capacity can increase supplies to outstrip demand and so suppress margins.

In 1993 the Royal Dutch Shell Group of companies and Exxon Corporation together accounted for about 20% of world production of primary petrochemicals; the United States, Western Europe and Japan represented almost 65% (SRI International, 1995). The same reference suggests demand projections for the period 1995 to 2005:

Region		Average annual growth in demand for petrochemicals
United States, Western Europe and Japan		2% per year
Rest of the World		6% per year
of which:	Middle East	11% per year
	South America	7% per year
	Asia excluding Japan	6% per year

Although the recent Asian financial crisis is having a global impact on petrochemicals, analysts are still predicting substantial growth - estimated at 5.2% per year compound between 1995 and 2005 for ethylene (Chang, 1998b).

3.2 DESCRIPTIONS OF INDIVIDUAL PETROCHEMICAL PROCESSES

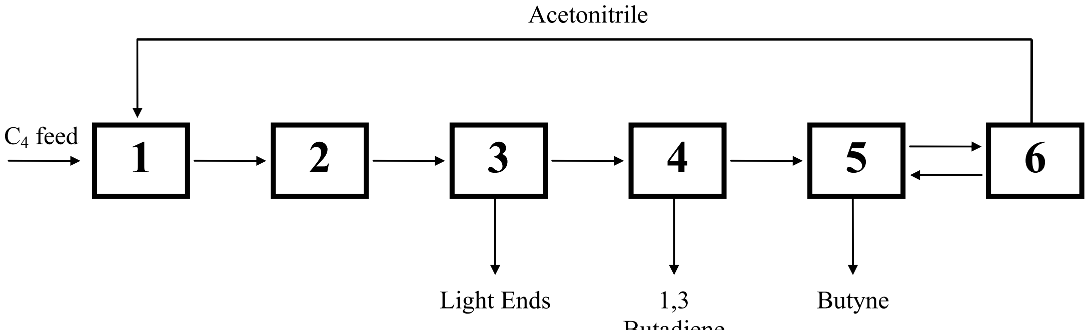
The following process descriptions are summarised from Fowler *et al*. (1993) except where otherwise indicated.

3.2.1 Adipic acid

Adipic acid, HOOC$(CH_2)_4$COOH, is used primarily in the manufacture of nylon. It is manufactured from cyclohexane in two steps. The first step is the oxidation of cyclohexane to cyclohexanone and cyclohexanol. This mixture is then converted to adipic acid by oxidation with nitric acid in the presence of copper and vanadium catalysts. The gaseous effluent from oxidation contains NO_x, CO_2, CO, N_2O and dibasic acids (US EPA, 1994a).

3.2.2 Butadiene

Butadiene can be derived by catalytic dehydrogenation of butenes, and by extractive distillation from C_4 streams arising from a variety of cracking operations. A typical process diagram for extraction with acetonitrile is shown in the Figure:



Key

1 - Extractive distillation column
2 - Solvent stripper column
3 - Light ends column
4 - Heavy ends column
5 - Water wash column
6 - Solvent recovery column

3.2.3 C_1 chlorinated products

Several products can be formed by successive chlorination of methane:

$$CH_4 + Cl_2 + O_2 \rightarrow CH_3Cl,\ CH_2Cl_2,\ CHCl_3,\ CCl_4,\ H_2O$$

Typical process units would include:

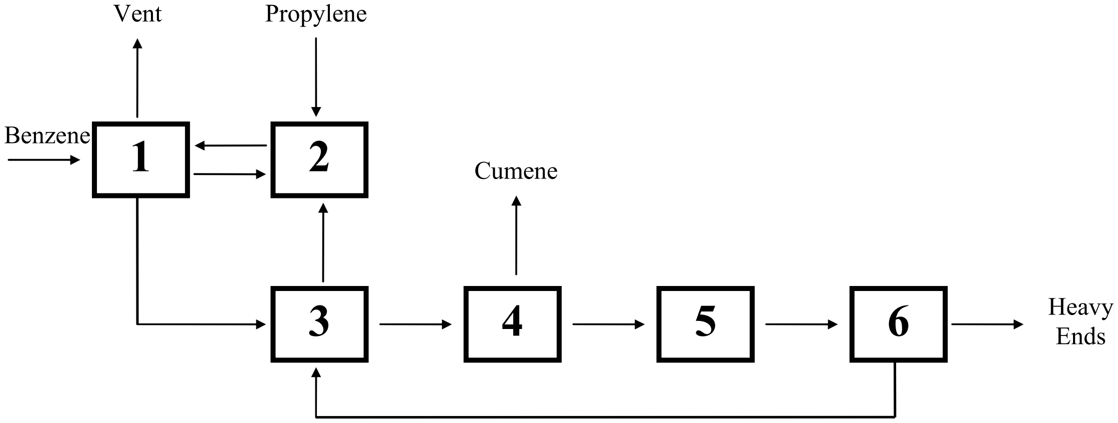
- chlorination reactors;
- product absorbers;
- product strippers;
- hydrochloric acid scrubbers;
- neutraliser wash columns;
- drying columns.

3.2.4 Cumene

Cumene can be obtained by distillation of petroleum fractions; or by alkylation of benzene with propylene:

$$2C_6H_6 + 3C_3H_6 \rightarrow C_9H_{12} + C_{12}H_{18}$$

The alkylation process is summarised in the figure:



Key

1 - Two stage flash column and depropaniser
2 - Fixed bed catalytic reactor
3 - Benzene recovery column
4 - Cumene recovery column
5 - Transalkylation unit
6 - Heavy ends column

The vent gas is mainly propane, which feeds to process heaters. Process heat required is 1 GJ per tonne of product.

3.2.5 Ethanol

Ethanol can be produced by hydrolysis of ethylene:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

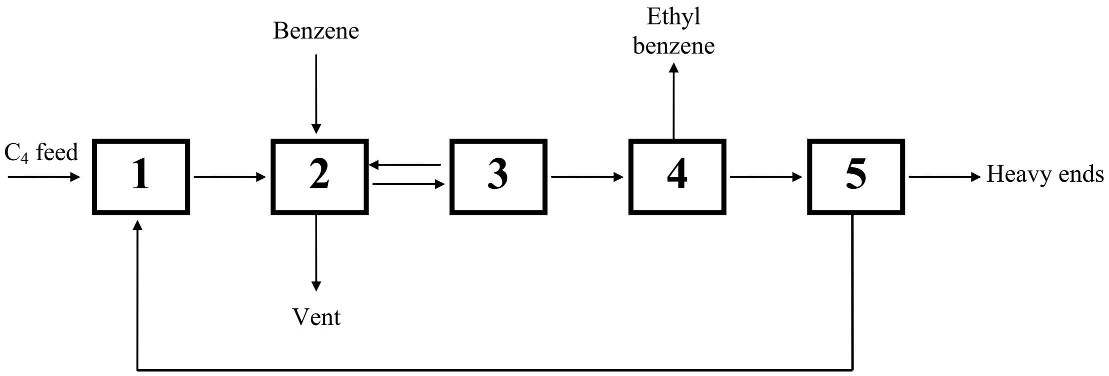
Process units typically include a catalytic reactor, and various product separation and recovery columns. Vent gas is mainly ethane and propane and is fed to process heaters. Process heat required is 2.5 GJ per tonne product.

3.2.6 Ethyl benzene

Ethyl benzene is mainly produced by catalytic alkylation of benzene with ethylene:

$$2C_6H_6 + 3C_2H_4 \rightarrow C_8H_{10} + C_{10}H_{14}$$

The process is summarised in the figure:



Key

1 - Extractive distillation column
2 - Solvent stripper column
3 - Light ends column
4 - Heavy ends column
5 - Water wash column
6 - Solvent recovery column

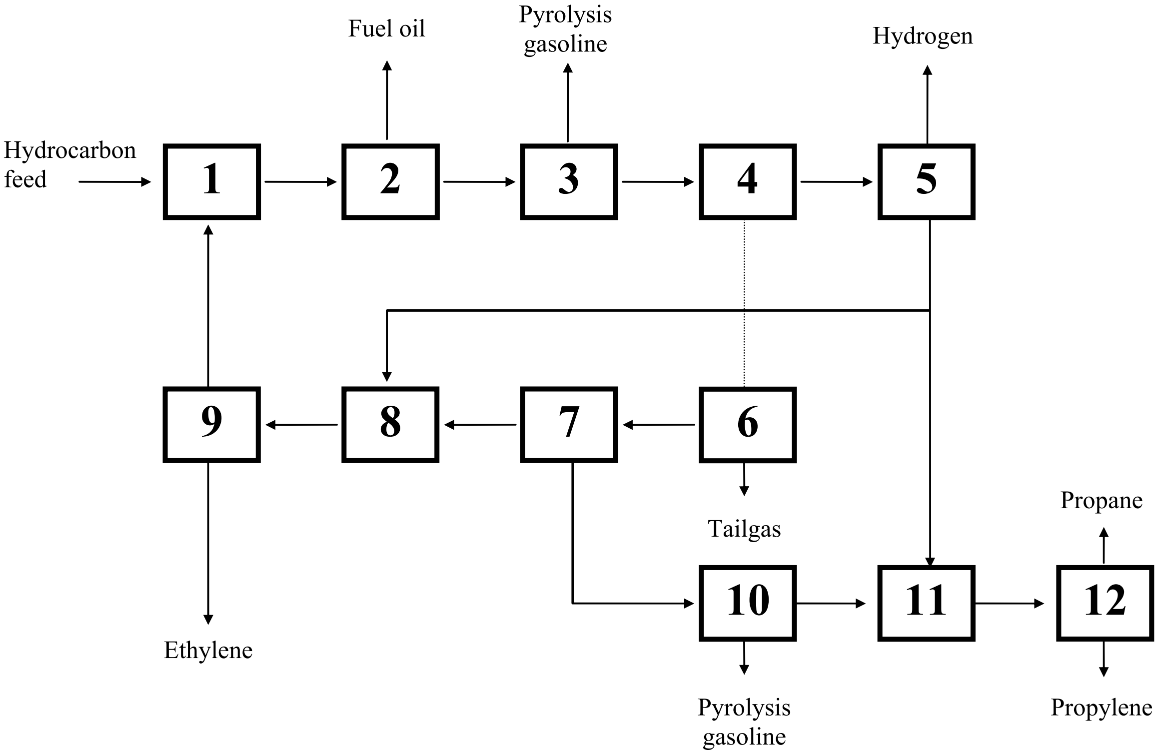
Vent gas is mainly hydrocarbons and is fed to process heaters.

3.2.7 Ethylene and propylene

Ethylene is produced from high temperature pyrolysis of ethane or propane and from thermal cracking of liquid hydrocarbons, such as naphtha or gas oil. It can also be recovered from refinery off-gas streams. Propylene is produced mainly as a co-product of ethylene by steam cracking of naphtha, gas oil or LPG; it is also obtained by extraction from refinery gas produced by catalytic cracking of oil fractions.

Vent gases are mainly hydrocarbons and are routed to process heaters for destruction.

The figure shows a typical process for co-production of ethylene and propylene:



Key

1 - Pyrolysis reactor
2 - Gas/liquid separator
3 - Compression, heat exchange, gas/liquid separation
4 - Compression, heat exchange, gas/liquid separation
5 - Compression, heat exchange, gas/liquid separation
6 - Demethaniser column
7 - Product splitter
8 - Hydrogenation reactor
9 - Ethylene column
10 - Heavy ends column
11 - Hydrogenation reactor
12 - Propane/propylene splitter

3.2.8 Ethylene dichloride

Ethylene dichloride is produced by chlorination or oxychlorination of ethylene (Chemical Intelligence Services, 1991).

3.2.9 Ethylene glycol

Ethylene glycol is produced by hydration of ethylene oxide:

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2$$

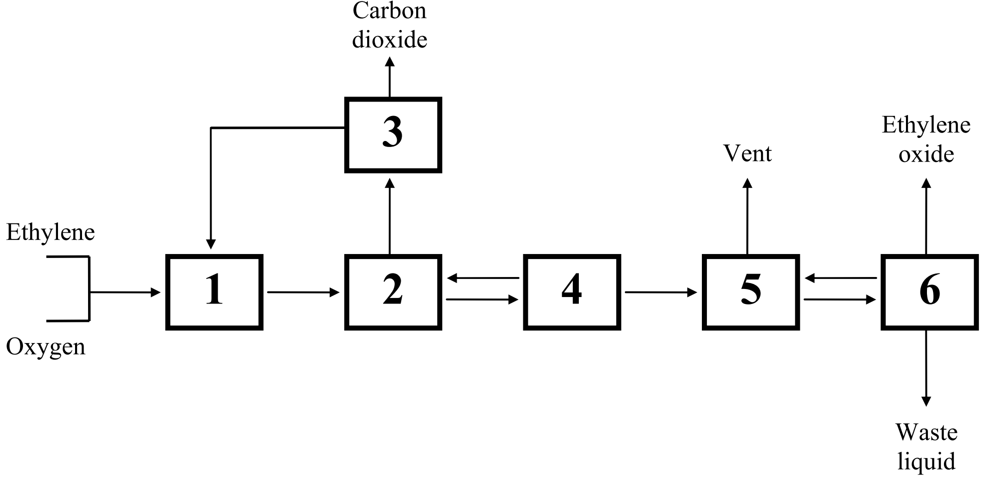
The feeds are reacted in a non-catalytic reactor, and passed through a series of evaporators and a light ends column to the main product column and a by-product column which give di- and tri-ethylene glycols.

3.2.10 Ethylene oxide

Ethylene oxide is produced by catalytic oxidation of ethylene with oxygen or air:

$$4C_2H_4 + 7O_2 \rightarrow 2C_2H_4O + 4CO_2 + 4H_2O$$

Vent gas is mainly carbon dioxide, estimated as 0.73 t CO_2 per tonne of ethylene oxide produced.



Key

1 - Gas phase catalytic reactor
2 - Water scrubber and gas/liquid separator
3 - Carbon dioxide separation plant
4 - Water recovery column
5 - Product recovery column
6 - Product purification column

3.2.11 Higher olefins

Chemical Intelligence Services (1991) describes several processes for the production of higher olefins. Linear higher olefins can be produced:

- by thermal cracking of waxy distillates from crude oil;
- from *n*-paraffins, either by chlorination followed by dehydrochlorination, or by direct dehydrogenation;
- or by oligomerisation of ethylene.

Branched chain olefins are prepared by selective oligomerisation of propylene and butylene fractions.

Fowler *et al*. (1993) report that vent gases are mainly hydrocarbons which are usually routed to process heaters.

3.2.12 Higher alcohols

Higher alcohols (oxo alcohols) may be produced by catalytic reaction of propylene with synthesis gas (carbon monoxide and hydrogen) to form intermediate aldehydes which are then hydrogenated. Vent gases contain unspent carbon monoxide and hydrogen which can be routed to process heaters.

3.2.13 Isopropanol

Isopropanol may be produced either by catalytic hydration of propylene with water:

$$3C_3H_6 + 2H_2O \rightarrow C_3H_7OH + C_6H_{14}O$$

or by absorption of propylene in sulphuric acid and subsequent hydrolysis:

$$C_3H_6 + H_2SO_4 \rightarrow C_3H_7HSO_4$$

$$C_3H_7HSO_4 + H_2O \rightarrow C_3H_7OH + H_2SO_4$$

In both cases the vent gas is mainly propane and so can be routed to process heaters.

3.2.14 Perchloroethylene

Perchloroethylene (tetrachloroethylene) is produced by chlorination of propylene via propylene dichloride, or by catalytic oxychlorination of ethylene dichloride (with co-production of trichloroethylene). In the latter case the vent gas is mainly carbon dioxide, with an estimated emission factor of 0.059 t CO_2 per tonne of product.

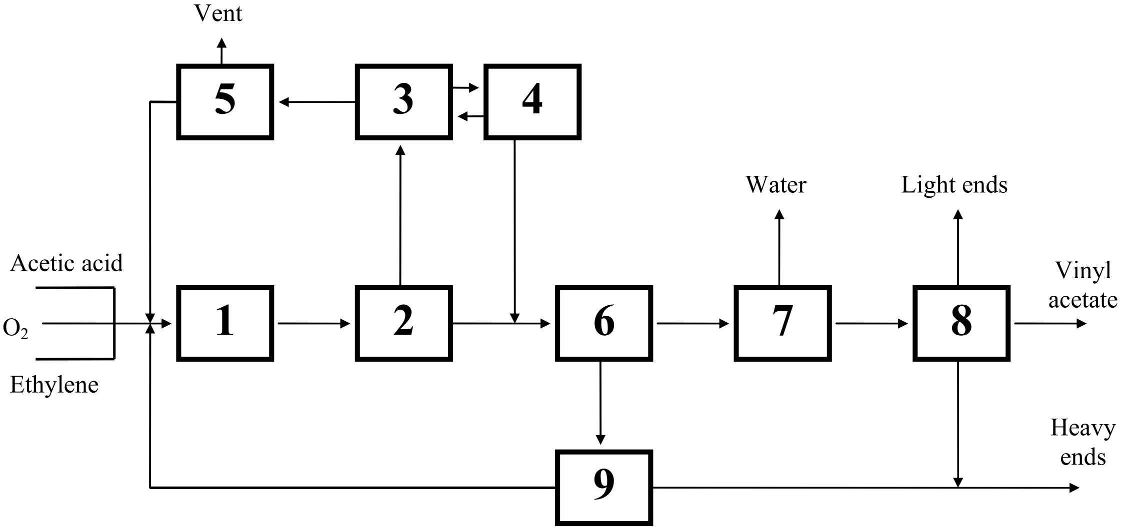
3.2.15 Trichloroethylene

Trichloroethylene is produced either by catalytic oxychlorination of ethylene dichloride (with co-production of perchloroethylene) or by decomposition of tetrachloroethane with lime or alkali in the presence of water.

3.2.16 Vinyl acetate

Vinyl acetate is mainly produced by the vapour phase reaction of ethylene, acetic acid and oxygen on a fixed bed palladium-based catalyst:

$$C_2H_4 + CH_3CO_2H + \tfrac{1}{2}O_2 \rightarrow CH_3CO_2C_2H_3 + H_2O$$



Key

1 - Fixed bed catalytic reactor
2 - Gas/liquid separator
3 - Glycol scrubber
4 - Gas desorber
5 - CO_2 absorber/scrubber
6 - Crude product splitter
7 - Liquid/liquid separator
8 - Product column
9 - Acetic acid recovery column

3.3 NORTH AMERICA

United States: The ethylene capacity in 1998 was 25,482,563 t/yr or 28% of global capacity (Chang, 1998b).

Canada: Canada's ethylene capacity in 1998 was 3.3 Mt/yr (Chang, 1998b). Petro-Canada (based in Calgary, Alberta) has cut its greenhouse gas emissions by 6% during 1990 to 1996 while increasing production by 11% over the same period (Calstart, 1997).

Mexico: The petrochemicals industry in Mexico has recently been reviewed by the Mexican Bank for Foreign Trade (1998). With 3% of the world's installed capacity, Mexico is the fifteenth largest producer world-wide. Installed ethylene capacity in 1998 is 1.391 Mt/yr (Chang, 1998b). Accumulated investment in the industry stands at US$ 16.3 billion, of which the state-owned Petroleos Mexicanos (PEMEX) represents US$ 8.54 billion. There are 28 other companies manufacturing petrochemicals.

PEMEX is the sole producer of basic petrochemicals: 59 plants manufacture 16 products with an output of 11 Mt/yr. Three products (ethane, ammonia and ethylene) account for 73% of capacity.

Mexico has 4.3 Mt/yr of installed capacity for intermediate petrochemicals. PEMEX has 34 plants with a capacity of 2 Mt/yr. The 28 other companies collectively have 32 plants and include Celanese, Petrocel, Tereftalatos, Maxicanos, Polioles, Glicoles Mexicanos, IDESA and Univex.

Other installed capacities are: fertilisers 1.7 Mt/yr; fibres 494,000 t/yr (8 producers in 13 plants); synthetic resins 1.6 Mt/yr (more than 80 producers); elastomers 351,000 t/yr (three producers).

3.4 SOUTH AMERICA

Ethylene capacities in 1998 are given by Chang (1998b):

Country	Ethylene capacity, t/yr
Argentina	308,000
Brazil	2,389,800
Chile	60,000
Colombia	100,000
Venezuela	600,000
Total	**3,457,800**

Brazil: There are three petrochemical complexes, located in the states of Bahia (Northeast), Rio Grande do Sul (South) and São Paulo (Southeast) with an overall total ethylene production capacity of 1.4 Mt/yr (early-mid 1990's); Chang (1998b) reports that ethylene capacity had risen to 2.39 Mt/yr in 1998.

3.5 EUROPE

Ethylene capacities in 1998 are given by Chang (1998b):

Country	Ethylene capacity, t/yr
Austria	345,000
Belgium	1,730,000
Bulgaria	400,000
Croatia	110,000
Czech Republic	441,000
Finland	290,000
France	3,435,000
Former Soviet Union	4,868,000
Germany	4,645,000
Greece	15,000
Hungary	290,000
Italy	2,100,000
Netherlands	2,307,710
Norway	410,000
Poland	395,000
Portugal	330,000
Romania	744,000
Slovakia	230,000
Spain	1,242,585
Sweden	400,000
Switzerland	31,000
United Kingdom	2,400,000
Total	**27,158,585**

The following table shows UK production data for the late 1980’s taken from Chemical Intelligence Services (1991). It should be noted that this publication does not give production data where they can be identified to a particular site or company, consequently data are not available for a number of petrochemicals known to be manufactured in the UK.

Substance	Production, t/yr
Ethylene	1490803
Benzene	837018
Propylene	640293
Polyethylene	514079
Polypropylene	353022
Styrene-butadiene rubber	216186
Butadiene	195128
Polyvinyl chloride	168024
Vinyl acetate homo/copolymers	154587
Carbon black	150000

Acetone	128462
Substance	**Production, t/yr**
Acrylic resins	122169
Toluene	108000
Polyester resins	81129
Formaldehyde	79756
Phthalic anhydride	72982
Polystyrene	63836
Isopropanol	61426
Phenol	52946
Urea	46000
ABS & SAN resins	43197
Epoxy resins	40145
Glycerol	37605
Fatty acids	25937
Silicones	24784
Polyamides (nylon)	21813
Naphthalene	14354
Polyurethanes	13852

3.6 JAPAN

Idemitsu Kosan Company owns seven petrochemical plants - two in Japan (next to its refineries in Chiba and Tokuyama) manufacturing olefins, aromatics, and styrene products. Installed ethylene capacity in 1998 was 7,473,000 t/yr (Chang, 1998b).

3.7 OTHER ASIA

The petrochemicals industry has been one of the fastest growing sectors in Asia over the last two decades. Increasing demand was initially met by exports from the more developed countries, but huge investment in local capacity soon followed - and in India (Indian Express Newspapers, 1997) and elsewhere the local sector has been strengthened and protected by high import duties. The recent monetary crisis has however meant that a number of projects have been rescheduled or put on hold.

Ethylene capacities in 1998 are given by Chang (1998b):

Country	Ethylene capacity, t/yr
China	3,698,000
China, Taiwan	1,015,000
India	1,695,000
Indonesia	550,000
Iran	694,000
Israel	200,000

Kuwait	650,000
Country	**Ethylene capacity, t/yr**
Malaysia	630,000
North Korea	60,000
Qatar	525,000
Saudi Arabia	3,350,000
Singapore	965,000
South Korea	4,525,000
Turkey (undefined)	400,000
Total	**18,957,000**

China: The petrochemical industry has recently been reviewed by Dechema (1998). The sector is growing at rates of 10-15% per year. The Ninth Five-Year Plan has established an ambitious construction programme which is well illustrated by the case of ethylene. In May 1998 China had an ethylene capacity of 3.08 Mt/yr (3.698 Mt/yr at an undefined date in 1998 reported by Chang, 1998b), which was estimated to rise to more than 5 Mt/yr by 2000 and to between 8 and 10 Mt/yr by 2010. Three 1 Mt/yr capacity plants are due for completion by 2002 (Yangzi Petrochemical Corp., Yanshan Petrochemical Corp., Shanghai Petrochemical Co.). Beyond 2000, China is planning to construct nearly a dozen ethylene plants in the range of 450,000 to 600,000 t/yr:

Location	Capacity, t/yr
Liaoning	450,000
Qingdao	450,000
Tianjin	600,000
Gansu	500,000
Xinjiang: new plant expansion of existing plant	450,000 60,000
Yangzi Petrochemical Corp.	600,000
Jinshan	600,000
Shanghai Petrochemical Corp.	700,000
Nongbo, Zhejiang	900,000
Xiaocuo Industrial Zone, Fujian	500,000
Huizhou, Guangdong	450,000
Guangzhou Ethylene Co.	300,000

Many Chinese petrochemical sectors still use obsolete technologies that are both inefficient and environmentally unfriendly (Dechema, 1998). For example, more than 60% of China's PVC capacity is produced with acetylene generated from calcium carbide as raw material. The Ninth Plan's goal to modernise these industries means that the plants will have to employ newer processes. Because of the enormous investments required, China has invited US, European and Japanese companies to join as joint venture partners in many of the projects. But dozens of small- and medium-scale projects are also planned.

India: Ethylene capacity in 1998 was 1.695 Mt/yr (Chang, 1998b). Indian Express Newspapers (1997) have indicated a likely growth in demand for petrochemical products from 5.1 Mt in 1995 to 8.7 Mt in 2000. But with higher raw material and energy costs their description of the Indian petrochemicals sector pointed to specialisation of local capacity:

> "...small plant sizes, higher capital cost, poor infrastructural facilities and obsolete technology make the Indian petrochemical industry highly uncompetitive... Most of the small- and medium-scale manufacturers are either operating at very low capacity utilisation or have closed down. As for the larger players, their performance has taken a beating, which has also been aggravated by a prolonged downward petrochemical cycle. There is... a likely government decision to allow multinationals to set up trading subsidiaries in the country... A process of consolidation of capacities can be seen in future, with companies sticking to their competence rather than manufacturing a range of products. The number of units is likely to come down too."

Indonesia: The Indonesian petrochemicals industry has been reviewed recently by Data Consult (1998). Between 1992 and 1996 the industry's market size grew at an average annual rate of 13.8%. The following table summarises the current plant reported by Data Consult as of March 1998:

Product	Plant	Capacity (Production) t/yr	Age
BTX	Pertamina, Cilicap Paraxylene Plant, Central Java	120,000 (benzene) 270,000 (*p*-xylene)	1990
Alkyl benzene	PT Unggul Indah Corporation	(138,600 in 1996)	-
Purified terephthalic acid	Pertamina; PT Polysindo Eka Perkasa; PT Amoco Mitsui PTA Indonesia; PT Polyprima Karyareksa; PT Bakrie Kasei Corp.	1,810,000	1,335,000 t/yr increase in capacity in 1995-1997
Phthalic anhydride	PT Petrowidada	70,000	1989 (30,000 t/y) 1996 (40,000 t/yr)
Dioctyl phthalate	PT Petronika; PT Eternal Buana Chemical Industries; PT Eterindo Nusa Graha	90,000	-
Ethylene	PT Chandra Asri Petrochemical Centre	510,000[1]	1995

Propylene	Pertamina (Plaju; Exor I); PT Chandra Asri Petrochemical Centre	470,000	-
Product	**Plant**	**Capacity (Production) t/yr**	**Age**
Vinyl chloride monomer	PT Asahimas Subentra Chemical	400,000	1989 onwards
Ethylene glycol	PT Prima Ethycolindo	-	1993
Polyol	PT Arco Chemical Indonesia	32,000	1989
2-Ethyl hexanol	PT Petro Oxo Nusantara	-	1997
Ethyl benzene	PT Styrindo Mono Indonesia	110,000	1996
Styrene monomer	PT Styrindo Mono Indonesia	100,000	1993
Ethyl acetate	PT Indoacidatama Chemical Industry; PT Molindo Raya Industrial Co.	30,000	-
Acrylic acid & acrylic ester	PT Nisshoku Tripolyta Acrylindo	-	1998
Methanol	PT Medco Methanol Bunyu; PT Kaltim Methanol Industry	990,000	-
Ammonia and urea	Six state-owned companies	4,360,000 (ammonia) 6,490,000 (urea)	-
Vinyl acetate monomer	PT Sri Melamine Rejeki; PT DSM Kaltim Melamine	70,000	1993 and 1996
Adhesive resin	35 producers, mostly owned by plywood companies	(1,240,000 in 1996)	-
Alkyl benzene sulphonate	-	172,000	-
Polystyrene resin	Four producers	106,300	-
Polyester	-	(843,150 in 1996)	-
Polyamide	Five producers	39,000	-
Polyethylene resin	PT Chandra Asri Petrochemical Centre; PT PENI	550,000	1995
PVC resin	Three producers	403,000	-
Acetic acid	-	34,000	-
Polypropylene resin	PT Tri Polyta	585,000	-

	Indonesia and others		
Polyurethane resin	-	(5,040 in 1996)	-
Styrene butadiene rubber	PT Sentra Sintetika Jaya	-	1998
Hydrogen peroxide	Three producers	66,000	1991; 1992; 1996
Product	**Plant**	**Capacity (Production) t/yr**	**Age**
Formic acid	-	(11,097 in 1996)	-
Carbon black	PT Continental Carbon Indonesia; PT Cabot Indonesia	260,000	-
Nitric acid & ammonium nitrate	-	55,000 (nitric acid) 26,400 (NH_4NO_3)	1991 onwards
Alkyd resin	-	(67,670 in 1996)	-
PET resin	Five producers	250,750	1995 onwards
Styrene butadiene latex	PT Rhone Poulenc Indolatex; PT BASF Indonesia; PT Dow Polymers Indonesia	56,000	-

[1] Ethylene capacity was reported as 550,000 t/yr in 1998 by Chang (1998b).

Indonesia imports all its consumption of toluene, phenol, acetone, caprolactam, adipic acid, toluene diisocyanate, butylene, acrylonitrile, propylene oxide, propylene glycol, acrylic polymer, pentaerythritol, polyvinyl acetate resin, polyvinyl alcohol, and polycarbonate.

4 Emissions and wastes

4.1 REFINERIES

Refineries are a potential source of atmospheric emissions of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), Volatile Organic Compounds (VOCs) including hazardous substances such as benzene and 1,3-butadiene, sulphur, reduced sulphur compounds and oxides of sulphur, ammonia, oxides of nitrogen, toxic organic micropollutants (dioxins, PAHs), heavy metals, particulates and odour.

The following sections present global and regional emission estimates. **Appendix 4** contains a description of emissions from two refineries in Finland.

4.1.1 Carbon dioxide

The main sources of CO_2 emission in a refinery are:

- power plants (producing steam and/or electricity);
- process furnaces and boilers;
- flares;
- process vent emissions.

BP Oil (1999) has provided a breakdown of CO_2 sources averaged across their operations world-wide:

Source	Percent of refinery CO2 emissions
Oil and gas fuel firing of furnaces and boilers	65%
Regeneration of cat cracker catalyst	16%
Flares	< 3%
Methane steam reforming to make hydrogen	2%
Incineration and effluent processes	1%
Power (55% imported)	13%

BP Oil also provided typical CO_2 concentrations:

- From combustion plant, furnaces, boilers, flares and FCC regenerators: about 13% CO_2.
- From gas turbine power generators or machine drivers: about 3% CO_2.
- From steam reforming process for H_2 generation: 100% CO_2.

4.1.1.1 Refinery power generation and process heaters

The IPCC Reference Approach (IPCC/OECD/IEA, 1997) for estimating CO_2 emissions from fuel combustion involves the following six steps:

1. Estimate consumption of fuels by fuel/product type.
2. Convert the fuel data to a common energy unit (TJ), if necessary
3. Select carbon emission factors for each fuel/product type and estimate the total carbon content of the fuels
4. Estimate the amount of carbon stored in products for long periods of time
5. Account for carbon not oxidised during combustion
6. Convert emissions of carbon to full molecular weight of CO_2.

For fuels used in refineries, we can assume that step 4 above may be omitted.

OECD/IEA (1996) identifies refinery fuel use of:

- gas/diesel oil;
- residual fuel oil;
- total fuel use (all products);

and defined as oil consumed in refineries for the operation of equipment, heating and light (i.e. including both power plants and process heaters). These data are summarised for 1994 in the following table, by region:

Region	Refinery fuel use of gas/diesel oil, t	Refinery use of residual fuel oil, t	Total refinery fuel use, t
North America	1,295,000	5,383,000	64,274,000
Pacific	49,000	2,442,000	11,879,000
OECD Europe	164,000	11,839,000	37,069,000
Total OECD	**1,508,000**	**19,664,000**	**113,222,000**

OECD/IEA (1996) also gives equivalent data for most of the countries of the OECD region.

It is not possible to use these data directly in the IPCC Reference Approach to calculate a global CO_2 emission as some important refinery fuels are not included, and no data are given for non-OECD countries. However it is possible to derive global CO_2 emission estimates if we assume that the more complete UK fuel use data are typical. The derivation is described below, and the assumption is tested where possible.

Salway (1995) lists UK refinery fuel use for 8 fuels in 1993 in petajoules (PJ), which may be converted to tonnages using net calorific values for fuels given in the IPCC Reference Approach (Table I-3 in IPCC/OECD/IEA, 1997):

Fuel	Published 1993 refinery fuel use, PJ	Net calorific value, $TJ/10^3$ tonnes	Calculated 1993 refinery fuel use, tonnes
Gas/diesel oil	0.2	43.33	4,616
Residual fuel oil	95.6	40.19	2,378,701
LPG	0.8	47.31	16,910
Naphtha	1.1	45.01	24,439
Petroleum coke	43.0	31.00	1,387,097
Refinery gas	147.8	48.15	3,069,574
Natural gas	6.9	46.89	147,153
Other	2.3	40.19	57,228
Total	**297.7**	**-**	**7,085,718**

OECD/IEA (1996) give 1993 data for the UK, which compare reasonably well with their equivalents derived from Salway (1995):

Fuel	Refinery fuel use in 1993, tonnes		Ratio of derived data to OECD/IEA data
	OECD/IEA (1996)	Derived from Salway (1995)	
Gas/diesel oil	5,000	4,616	0.92
Residual fuel oil	2,356,000	2,378,701	1.01
Total - all fuels	6,383,000	7,085,718	1.11

If we assume that the UK refinery fuel use data are typical of the rest of the world, it should be possible to reproduce the OECD/IEA (1996) regional data by scaling up with an appropriate scaling factor. The following table makes this comparison for total refinery fuel use using refinery output data for 1994 (Table 15 on page II.12 of OECD/IEA, 1996):

Region	Refinery output in 1994, tonnes	OECD/IEA refinery fuel use, tonnes	Predicted refinery fuel use, tonnes	Ratio of predicted to OECD/IEA
United Kingdom	93,037,000	6,256,000	-	-
North America	911,445,000	64,274,000	61,287,444	0.95
Pacific	248,942,000	11,879,000	16,739,374	1.41
OECD Europe	673,383,000	37,069,000	45,279,663	1.22
Total OECD	1833,770,000	113,222,000	123,306,482	1.09

The comparison indicates a reasonable degree of prediction using this approach. There are insufficient data to make a statistical analysis of the uncertainty, so we guesstimate an uncertainty range of ± 50% which we will also apply to the estimates of CO_2 emissions derived below.

The IPCC Reference Approach suggests emission factors for refinery fuels (Table I-1 in IPCC/OECD/IEA, 1997):

Fuel	Carbon emission factor, t C/TJ
Gas/diesel oil	20.2
Residual fuel oil	21.1
LPG	17.2
Naphtha	20.0
Petroleum coke	27.5
Refinery gas	20.0
Natural gas	15.3
Other	20.0

The tables above provide the means to reach step 3 of the IPCC Reference Approach. There are various ways in which the data could be combined. For example, we could assume that refinery energy requirements world-wide are met by the same mix of fuels as in the UK. This is an unlikely assumption and is not borne out by the country-specific data in OECD/IEA (1996). Instead we have assumed that the total energy requirement per unit output is broadly the same.

First, using the detailed 1993 UK fuel use tonnages derived above together with the carbon emission factors, we can calculate UK carbon emissions from refinery fuel use by fuel type:

Fuel	1993 UK fuel use, t	Carbon emission factor, t C/TJ	Derived carbon emissions, t C
Gas/diesel oil	4,616	20.2	4,040
Residual fuel oil	2,378,701	21.1	2,017,160
LPG	16,910	17.2	13,760
Naphtha	24,439	20.0	22,000
Petroleum coke	1,387,097	27.5	1,182,500
Refinery gas	3,069,574	20.0	2,956,000
Natural gas	147,153	15.3	46,000
Other	57,228	20.0	105,570
Total	**7,085,718**	**-**	**6,347,030**

Next, we can divide the total emissions of 6,347,030 t C by the total fuel use of 7,085,718 t to derive an overall emission factor of 0.896 tonnes carbon emitted per tonne of fuel used.

This factor compares favourably with emission factors of 0.800 to 0.940 t C/t fuel for various fuels provided by the United Kingdom Petroleum Industries Association in 1989 (referenced in Salway, 1995).

If we now consider step 5 of the IPCC Reference Approach, we need to take account of the fraction of carbon oxidised. For this we have taken a fraction of 0.99 (Table I-6 in IPCC/OECD/IEA, 1997). This modifies the factor of 0.896 t C/t fuel to 0.887 t C/t fuel.

For step 6, the emissions in t C are multiplied by (44/12) to give emissions in t CO_2.

Now we can complete the emission estimation. The table below gives regional refinery outputs for 1994 taken from OECD/IEA (1996); refinery fuel use calculated pro rata from the 1994 UK fuel use data as described above; and emissions in t C and t CO_2 calculated using the emission factor of 0.887 t C/t fuel.

Region	Published 1994 refinery output, t	Calculated 1994 refinery fuel use, t	CO_2 emissions	
			t C	t CO_2
North America	911,445,000	61,300,000	54,300,000	199,300,000
Central/South America	198,154,000	13,300,000	11,800,000	43,300,000
Europe excluding FSU	735,675,000	49,500,000	43,900,000	160,800,000
Former Soviet Union	256,054,000	17,200,000	15,300,000	56,000,000
Africa	112,794,000	7,600,000	6,700,000	24,700,000
Pacific	248,942,000	16,700,000	14,800,000	54,400,000
Middle East	246,833,000	16,600,000	14,700,000	54,000,000
Asia excluding China	303,259,000	20,400,000	18,100,000	66,300,000
China	128,471,000	8,600,000	7,700,000	28,100,000
World total	**3,141,627,000**	**211,200,000**	**187,300,000**	**686,900,000**

Thus we estimate that global emissions of CO_2 from refinery fuel use (power generation plus process heaters) were 686.9 Mt CO_2 in 1994. As noted above we assign an uncertainty of ± 50% to this estimate. The key assumption in the calculation, and the origin of much of the uncertainty, is that regional and global fuel requirements can be predicted from the UK data.

Using a global refinery energy use of 9,853 PJ in 1994 (see under methane below) we can calculate an emission factor of 0.0697 t CO_2/GJ.

EEA (1996) has published emission factors for CO_2 emissions from process heaters. The emission factors range between 10 and 101 kg/GJ, depending on fuel type. We were unable to locate global fuel use data for process heaters during this study, and so are unable to separate out this source from total fuel use.

4.1.1.2 Refinery flares and process vents

The IPCC guidelines do not suggest how to estimate CO_2 emissions from refinery flares. EEA (1996) contains a chapter dealing with flaring in oil refineries, but also does not give a methodology for CO_2 emissions. The latter publication does however report that the contribution of miscellaneous vent and flare emission sources represented approximately 9% of the total petroleum refinery CO_2 emission in Canada during 1988. If we assume that this contribution is typical of the global picture and has not changed over recent years, we can calculate vent plus flaring emissions from the fuel combustion emissions derived in the previous section. The calculation gives a global estimate of CO2 emissions from refinery vents and flaring of 67.9 Mt CO_2 in 1994.

4.1.1.3 All sources

The authors have confidential data for several refineries in 1997 which, if scaled up to global level using the capacities given in Appendix 3, give a global emission estimate for CO_2 from all refinery sources of 796 Mt in 1997.

4.1.2 Methane

Methane is an important greenhouse gas. IPCC (1995) gives global emissions from the petroleum industry as 5 to 30 Mt/yr, with a central estimate of 15 Mt/yr.

Sources of methane emission in refineries include:

- power generation;
- process heaters;
- flares;
- process vents;
- fugitive losses.

4.1.2.1 Power generation and process heaters

Methane is a product of incomplete combustion.

The revised 1996 IPCC guidelines (IPCC/OECD/IEA, 1997) suggest simple (Tier 1) and detailed (Tiers 2, 3) approaches to estimating methane emissions from the energy industries. The detailed approaches require knowledge of the mix of burner/boiler technologies which we were unable to identify for this study. Instead we present here a Tier 1 estimate. In the Tier 1 method the IPCC guidelines give two emission factors for methane emissions from energy use in energy industries (Table 1-7 in IPCC/OECD/IEA, 1997):

- 3 kg/TJ for oil combustion;
- 1 kg/TJ for natural gas combustion.

As we have seen above, refineries world-wide combust considerable quantities of oil products, while in the UK and probably elsewhere a substantial proportion of the refinery energy requirement is met by refinery gas. We have therefore taken the two emission factors from the IPCC guidelines to represent a range.

To calculate the emissions we also need the fuel use expressed in TJ. The UK fuel use data presented above gives an overall refinery energy requirement of 46.64 GJ per tonne of output (as a weighted average across all fuel types). The OECD/IEA (1996) refinery outputs can thus be converted to TJ and multiplied by the above emission factor range to derive methane emissions from refinery fuel use by region:

Region	Published 1994 refinery output, t	Calculated 1994 refinery fuel use, PJ	CH_4 emissions, t CH_4	
			Low estimate	High estimate
North America	911,445,000	2,858	2,858	8,575
Central/South America	198,154,000	621	621	1,864
Europe excluding FSU	735,675,000	2,307	2,307	6,922
Former Soviet Union	256,054,000	803	803	2,409
Africa	112,794,000	354	354	1,061
Pacific	248,942,000	781	781	2,342
Middle East	246,833,000	774	774	2,322
Asia excluding China	303,259,000	951	951	2,853
China	128,471,000	403	403	1,209
World total	**3,141,627,000**	**9,853**	**9,853**	**29,558**

Thus we have calculated that global emissions of CH_4 from refinery fuel use (power generation plus process heaters) were between about 10 and 30 kt CH_4 in 1994. As with the equivalent CO_2 estimate we assign an uncertainty of ± 50% to each estimate, giving an overall range of 5 to 45 kt CH_4 in 1994.

EEA (1996) has published emission factors for CH_4 emissions from process heaters. The emission factors range between 0.1 and 6 g/GJ, depending on fuel type. We were unable to locate global fuel use data for process heaters during this study, and so are unable to separate out this source from total fuel use.

4.1.2.2 Flares

Radian Corporation (1992) has published emission factors for methane from refineries:

Source	Emission factor
Flaring	4.00×10^{-7} short tons per barrel of refinery capacity

4.1.2.3 Process vents and fugitive losses

Methane is present in crude oil and may be lost from storage tanks. During refining processes too, wherever methane is present it can leaked from components. It is also vented from some processes.

The revised 1996 IPCC guidelines (section 1.8.6 in IPCC/OECD/IEA, 1997) give two emission factors:

- 90 to 1,400 kg CH_4/PJ of oil refined, from refinery vents and fugitive losses (excluding storage tanks);
- 20 to 260 kg CH_4/PJ of oil refined, from refinery storage tanks.

If we approximate that the world refinery output for 1994 of 3,141,627,000 t is equivalent to the amount of oil refined, we can calculate this as PJ using Table 1-2 in IPCC/OECD/IEA (1997). The table gives country-specific net calorific values, mostly lying in the range 42 to 43 TJ/kt. We have used this range to calculate a 1994 global refinery throughput of 131,948 to 135,090 PJ. Applying the above emission factors gives global methane emissions for each of the two sources:

- refinery vents and fugitive losses (excluding storage tanks): 11,875 to 189,126 t CH_4 in 1994;
- refinery storage tanks: 2,639 to 35,123 t CH_4 in 1994.

Radian Corporation (1992) has published emission factors for methane from refineries:

Source	Emission factor
Fugitive emissions	1.635×10^{-5} short tons per barrel of refinery capacity
Tank farms	4.37×10^{-7} short tons per barrel of refinery throughput

These may be converted into units of metric tonnes using the conversions:

- 1 metric tonne = 1.1023 short tons;
- 1 tonne ≡ 7.400 barrels in the USA (Table 7.4 on page I.31 of OECD/IEA, 1996).

Source	Emission factor
Fugitive emissions	2.004×10^{-6} tonnes per tonne of refinery capacity
Tank farms	5.36×10^{-8} tonnes per tonne of refinery throughput

OECD/IEA (1996) gives the world distillation capacity at year end 1994 as 73.15 million barrels per calendar day. Using the USA conversion factor above this gives an equivalent annual tonnage capacity of 3,608,000,000 tonnes. Applying the above emission factor gives a global fugitive emission estimate of 7,230 t CH_4, which is broadly comparable with the (fugitive + vent) range given above.

Multiplying the tank farm emission factor by our assumed throughput of 3,141,627,000 t gives a global emission of 168 t CH_4 from tank farms, which is considerably less than the above estimate derived from IPCC emission factors.

Apparently using the same Radian emission factors the EIA (1994) has calculated methane emissions for US refineries during 1987 to 1992:

Emissions of methane from US refineries (kt methane per year)

Source	1987	1988	1989	1990	1991	1992
Fugitives	70	72	73	73	72	73
Tank farms	2	2	2	2	2	2
Flaring	2	2	2	2	2	2
Total	**73**	**75**	**76**	**76**	**76**	**77**

4.1.3 Carbon monoxide

Carbon monoxide (CO) does not contribute to global warming directly, but rather through its role in atmospheric chemistry: it is oxidised to carbon dioxide and is also a precursor of tropospheric ozone; and it can react with the hydroxyl radical ($^{\cdot}OH$) which is an important scavenger of the greenhouse gas methane.

Carbon monoxide is an intermediate product of combustion processes, and is also produced by some refinery processes. Refinery sources include:

- power generation;
- process heaters;
- flares;
- vacuum distillation;
- catalytic cracking (mainly catalyst regeneration);
- thermal cracking;
- blowdown systems.

In the Tier 1 method the IPCC guidelines give two emission factors for carbon monoxide emissions from energy use in energy industries (Table 1-10 in IPCC/OECD/IEA, 1997):

- 15 kg/TJ for oil combustion;
- 20 kg/TJ for natural gas combustion.

Using a similar approach to that described above for methane, we have calculated carbon monoxide emissions from refinery fuel use by region:

Region	**Published 1994 refinery output, t**	**Calculated 1994 refinery fuel use, PJ**	**CO emissions, t CO**	
			Low estimate	**High estimate**
North America	911,445,000	2,858	42,877	57,169
Central/South America	198,154,000	621	9,322	12,429
Europe excluding FSU	735,675,000	2,307	34,608	46,144
Former Soviet Union	256,054,000	803	12,045	16,061
Africa	112,794,000	354	5,306	7,075
Pacific	248,942,000	781	11,711	15,614
Middle East	246,833,000	774	11,612	15,482
Asia excluding China	303,259,000	951	14,266	19,021
China	128,471,000	403	6,044	8,058
World total	**3,141,627,000**	**9,853**	**147,790**	**197,054**

Thus we have calculated that global emissions of CO from refinery fuel use (power generation plus process heaters) were between about 148 and 197 kt CO in 1994. As with the equivalent CO_2 estimate we assign an uncertainty of ± 50% to each estimate, giving an overall range of 74 to 99 kt CO in 1994.

IPCC/OECD/IEA (1997) suggests a simple method for estimating CO emissions from catalytic cracking using an emission factor of 0.08 kg/m^3 of refinery feedstock. If we assume that the above refinery output data approximate to refinery input, and taking a typical density of 1.117 m3/t (USA value in Table 7.4 on page I.31 of OECD/IEA, 1996), we can estimate these emissions on a regional basis:

Region	Published 1994 refinery output, t	CO emissions, t CO
North America	911,445,000	61,950
Central/South America	198,154,000	13,468
Europe excluding FSU	735,675,000	50,003
Former Soviet Union	256,054,000	17,404
Africa	112,794,000	7,667
Pacific	248,942,000	16,920
Middle East	246,833,000	16,777
Asia excluding China	303,259,000	20,612
China	128,471,000	8,732
World total	**3,141,627,000**	**213,535**

Thus we have calculated that global emissions of CO from catalytic cracking were about 214 kt CO in 1994.

The authors have confidential data for several refineries in 1997 which, if scaled up to global level using the capacities given in Appendix 3, give a global emission estimate for CO from all refinery sources of 169 kt in 1997.

4.1.4 Sulphur compounds

In this section we consider the following sulphur compounds:

Sulphur dioxide (SO_2)

Sulphur trioxide (SO_3)

We do not consider sulphurous or sulphuric acids or other sulphur compounds.

Sulphur dioxide and sulphur trioxide can both be formed during combustion of fuels containing sulphur. The former compound predominates but the proportions vary; they are usually considered together as “SO_x” but often reported as SO_2. Crude oil contains around 1.3% sulphur on average (IPCC/OECD/IEA, 1997).

Sulphur dioxide is not a greenhouse gas, but it is thought that it might influence climate by forming sulphate aerosols in the atmosphere.

Refinery sources of emissions of sulphur compounds include:

- power generation;
- process heaters;
- flares;
- vacuum towers;
- catalytic crackers;
- fluid coking;
- sulphur recovery plant;
- incinerators;
- caustic regeneration.

The IPCC Tier 1 approach for estimating SO_x emissions (there is no Tier 2) recommends deriving an emission factor in kg/TJ from the fuel sulphur content, then multiplying this by an activity statistic in TJ to give the emissions:

$$\mathbf{EF_{SO_2} = 2 \text{ x } (s/100) \text{ x } 1/Q \text{ X } 10^6 \text{ x } ((100-r)/100) \text{ x } ((100-n)/100)}$$

where:

EF = Emission factor [kg/TJ];
2 = SO_2/S [kg/kg];
s = Sulphur content in fuel [%];
r = Retention of sulphur in ash [%];
Q = Net calorific value [TJ/kt];
10^6 = (Unit) conversion factor;
n = Efficiency of abatement technology and/or reduction efficiency [%];

and:

$$\mathbf{Emissions = \Sigma \left(EF_{ab} \text{ x } Activity_{ab} \right)}$$

where:

EF = Emission factor [kg/TJ];
Activity = Energy input [TJ];
a = Fuel type; and
b = Sector activity.

For liquid fuels the sulphur retention in ash is minimal and can be disregarded (IPCC/OECD/IEA, 1997).

Table 1-12 in IPCC/OECD/IEA (1997) lists default values of sulphur content in various fuels, including:

Fuel	Default sulphur content, %
Heavy fuel oil	1.0 to 4.0
Light fuel oil/diesel	0.3 to 1.0
Natural gas	negligible

EEA (1996) has also published fuel sulphur contents:

Fuel	Sulphur content, %
Residual oil	0.3 to 3.5
Gas oil	0.08 to 1.0 (0.3 recommended)
Diesel oil	0.3
LPG	-
Refinery gas	< 8 g/m^3
Naphtha	listed but no data
Petroleum coke	listed but no data

Salway (1998) has provided sulphur contents as follows:

Fuel	Sulphur content, %
Refinery gas	0 to 0.05
Naphtha	0.05 to 0.15
Petroleum coke	0 to 5

We have estimated emissions using the sulphur contents shown below:

Fuel	Sulphur content, %	
	Lower	Upper
Gas/diesel oil	0.3	1.0
Residual fuel oil	0.3	4.0
LPG	0	0
Naphtha	0.05	0.15
Petroleum coke	0	5
Refinery gas	0	0.05
Natural gas	0	0
Other	0	1.0

In the first step we calculated emissions for the UK, assuming no sulphur retention in ash (r = 0) and no abatement (n = 0):

Fuel	**Activity, TJ**	**Net calorific value (Q), TJ/kt**	**Sulphur content (s), %**		**Emission factor (EF), kg/TJ**		**Emissions, t SO2**	
			Lower	Upper	Lower	Upper	Lower	Upper
Gas/diesel oil	200	43.33	0.3	1	138.5	461.6	28	92
Fuel oil (residual)	95,600	40.19	0.3	4	149.3	1990.5	14,272	190,296
LPG	800	47.31	0	0	0.0	0.0	0	0
Naphtha	1,100	45.01	0.05	0.15	22.2	66.7	24	73
Petroleum coke	43,000	31	0	5	0.0	3225.8	0	138,710
Refinery gas	147,800	48.15	0	0.05	0.0	20.8	0	3,070
Natural gas	6,900	46.89	0	0	0.0	0.0	0	0
Other	2,300	40.19	0	1	0.0	497.6	0	1,145
Total	**297,700**						**14,324**	**333,386**

From these data we can calculate lower and upper overall emission factors of 48.12 and 1120 kg SO_2/TJ fuel. These can be applied to the regional fuel use statistics derived in the methane section above to give regional and global emission estimates:

Region	**Published 1994 refinery output, t**	**Calculated 1994 refinery fuel use, PJ**	**SO_x emissions, t SO_2**	
			Low estimate	**High estimate**
North America	911,445,000	2,858	137,539	3,201,091
Central/South America	198,154,000	621	29,902	695,938
Europe excluding FSU	735,675,000	2,307	111,015	2,583,768
Former Soviet Union	256,054,000	803	38,639	899,289
Africa	112,794,000	354	17,021	396,144
Pacific	248,942,000	781	37,566	874,310
Middle East	246,833,000	774	37,248	866,903
Asia excluding China	303,259,000	951	45,762	1,065,077
China	128,471,000	403	19,387	451,204
World total	**3,141,627,000**	**9,853**	**474,078**	**11,033,724**

Thus we have calculated that global emissions of SO_x from refinery fuel use (power generation plus process heaters) were between about 474 and 11,034 kt SO_2 in 1994.

IPCC/OECD/IEA (1997) suggests a simple method for estimating non-combustion emissions of SO_2 for refineries using an emission factor of 0.8 kg/m^3 of refinery feedstock. If we assume that the above refinery output data approximate to refinery input, and taking a typical density of 1.117 m3/t (USA value in Table 7.4 on page I.31 of OECD/IEA, 1996), we can estimate these emissions on a regional basis:

Region	Published 1994 refinery output, t	SO_2 emissions, t SO_2
North America	911,445,000	619,504
Central/South America	198,154,000	134,684
Europe excluding FSU	735,675,000	500,034
Former Soviet Union	256,054,000	174,038
Africa	112,794,000	76,665
Pacific	248,942,000	169,204
Middle East	246,833,000	167,771
Asia excluding China	303,259,000	206,123
China	128,471,000	87,321
World total	**3,141,627,000**	**2,135,345**

Thus we have calculated that global emissions of SO_2 from non-combustion sources in refineries were about 2,135 kt SO_2 in 1994.

In 1994 the US EPA published emission factors for modified Claus sulphur recovery plants, reproduced here from EEA (1996):

Number of catalytic stages	Average percent sulphur recovery	SO_2 (kg/Mg sulphur produced)
Two, uncontrolled	93.5	139
Three, uncontrolled	95.5	94
Four, uncontrolled	96.5	73
Two, controlled	98.6	29
Three, controlled	96.8	65

4.1.5 Nitrogen compounds

In this section we consider four compounds of nitrogen:

Nitrous oxide (N_2O) - also known as dinitrogen monoxide

Nitric oxide (NO) - also known as mononitrogen monoxide, and sometimes (confusingly) nitrogen oxide.

Nitrogen dioxide (NO_2)

Ammonia (NH_3)

In this report we do not consider the unstable oxides N_2O_3, N_2O_4, N_2O_5; other inorganic compounds such as nitric acid; or organic nitrogen compounds (which are treated as VOCs - see below).

Nitrous oxide is a greenhouse gas. Nitric acid and nitrogen dioxide are not themselves greenhouse gases but are involved in the atmospheric chemistry of the greenhouse gas ozone. In common with the IPCC and other inventory workers we will treat nitrous oxide separately, but combine (nitric oxide + nitrogen dioxide) as "NO_x" (not to be confused with "NO_y" which is the sum of all oxidised nitrogen species and therefore also includes NO, NO_2, nitric acid, peroxy acetyl nitrate (PAN) and various other organic and inorganic forms of nitrogen).

Ammonia is not a greenhouse gas but is involved in the atmospheric chemistry of sulphur and nitrogen oxides.

4.1.5.1 N_2O

Nitrous oxide is produced from combustion processes by oxidation of oxygen in air or in the fuel. Refinery sources include:

- power generation;
- process heaters;
- flares.

In the Tier 1 method the IPCC guidelines give two emission factors for nitrous oxide emissions from energy use in energy industries (Table 1-8 in IPCC/OECD/IEA, 1997):

- 0.6 kg/TJ for oil combustion;
- 0.1 kg/TJ for natural gas combustion.

Using a similar approach to that described above for methane, we have calculated nitrous oxide emissions from refinery fuel use by region:

Region	**Published 1994 refinery output, t**	**Calculated 1994 refinery fuel use, PJ**	**N_2O emissions, t N_2O**	
			Low estimate	**High estimate**
North America	911,445,000	2,858	286	1,715
Central/South America	198,154,000	621	62	373
Europe excluding FSU	735,675,000	2,307	231	1,384
Former Soviet Union	256,054,000	803	80	482
Africa	112,794,000	354	35	212
Pacific	248,942,000	781	78	468
Middle East	246,833,000	774	77	464
Asia excluding China	303,259,000	951	95	571
China	128,471,000	403	40	242
World total	**3,141,627,000**	**9,853**	**985**	**5,912**

Thus we have calculated that global emissions of N_2O from refinery fuel use (power generation plus process heaters) were between about 1 and 6 kt N_2O in 1994. As with the equivalent CO_2 estimate we assign an uncertainty of ± 50% to each estimate, giving an overall range of 0.5 to 9 kt N_2O in 1994.

4.1.5.2 NO_x

Sources of emission of oxides of nitrogen (NO_x) include process heaters, boilers, compressor engines, catalyst regenerators and flares.

In the Tier 1 method the IPCC guidelines give two emission factors for NO_x emissions from energy use in energy industries (Table 1-9 in IPCC/OECD/IEA, 1997):

- 200 kg NO_2/TJ for oil combustion;
- 150 kg NO_2/TJ for natural gas combustion.

Using a similar approach to that described above for methane, we have calculated NO_x emissions from refinery fuel use by region:

Region	Published 1994 refinery output, t	Calculated 1994 refinery fuel use, PJ	NO_x emissions, t NO_2	
			Low estimate	**High estimate**
North America	911,445,000	2,858	428,767	571,689
Central/South America	198,154,000	621	93,217	124,289
Europe excluding FSU	735,675,000	2,307	346,080	461,440
Former Soviet Union	256,054,000	803	120,454	160,606
Africa	112,794,000	354	53,061	70,748
Pacific	248,942,000	781	117,109	156,145
Middle East	246,833,000	774	116,117	154,822
Asia excluding China	303,259,000	951	142,661	190,214
China	128,471,000	403	60,436	80,581
World total	**3,141,627,000**	**9,853**	**1,477,901**	**1,970,535**

Thus we have calculated that global emissions of NO_x from refinery fuel use (power generation plus process heaters) were between about 1,478 and 1,971 kt NO_2 in 1994. As with the equivalent CO_2 estimate we assign an uncertainty of ± 50% to each estimate, giving an overall range of 739 to 2,956 kt NO_2 in 1994.

IPCC/OECD/IEA (1997) suggests a simple method for estimating emissions of NO_x from refinery catalytic cracking using an emission factor of 0.05 kg/m^3 of refinery feedstock. If we assume that the above refinery output data approximate to refinery input, and taking a typical density of 1.117 m3/t (USA value in Table 7.4 on page I.31 of OECD/IEA, 1996), we can estimate these emissions on a regional basis:

Region	Published 1994 refinery output, t	NO_x emissions, t NO_2
North America	911,445,000	38,719
Central/South America	198,154,000	8,418
Europe excluding FSU	735,675,000	31,252
Former Soviet Union	256,054,000	10,877
Africa	112,794,000	4,792
Pacific	248,942,000	10,575
Middle East	246,833,000	10,486
Asia excluding China	303,259,000	12,883
China	128,471,000	5,458
World total	**3,141,627,000**	**133,459**

Thus we have calculated that global emissions of NO_x from catalytic cracking were about 133 kt NO_2 in 1994.

4.1.5.3 Ammonia

Emissions from Canadian refineries in 1996:

Refinery	NH_3 emissions, t NH_3	Comments
Husky Oil, Lloydminster, Alberta	0	
Husky Oil, Prince George	0	
Imperial Oil, Dartmouth	1.77	Fugitive releases
Imperial Oil, Nanticoke, Ontario	0.18	Fugitive releases
Imperial Oil, Sarnia, Ontario	2.14	Fugitive releases
Imperial Oil, Strathcona Refinery, Edmonton, Alberta	0	
Irving Oil, Saint John	0.1	Storage/handling releases
North Atlantic Refining, Come by Chance, New Foundland	0	
Parkland Refining, Bowden, Alberta	0	
Petro-Canada, Edmonton, Alberta	0	
Petro-Canada, Oakville, Ontario	1.84	Fugitive releases
Petro-Canada, Montreal, Quebec	3.75	Fugitive releases
Shell Canada Products, Shellburn Refinery, Burnaby	0	
Shell Canada Products, Shell Scotford Refinery, Fort Saskatchewan, Alberta	0	
Sunoco, Sarnia, Ontario	0.02	Fugitive releases
Ultramar, St-Romuald, Quebec	218.52	Stack/point releases

4.1.6 Hydrocarbons and other volatile organic compounds

Volatile organic compounds (VOCs) are a broad and often ill-defined class of pollutants. In this section we have not attempted to analyse these definitions; readers are referred to the references we quote for definitions (if given). As far as is possible we have sought out data for non-methane volatile organic compounds (NMVOC), which we label hereinafter as "VOC".

Some VOCs may have a weak greenhouse potential, but their main greenhouse impact is their role in photochemical formation of the greenhouse gas ozone.

The major direct process emission sources of VOCs are vacuum distillation, catalytic cracking, coking, chemical sweetening and asphalt blowing (EEA, 1996 and references therein).

In the Tier 1 method the IPCC guidelines give an emission factors for VOC emissions from energy use in energy industries (Table 1-11 in IPCC/OECD/IEA, 1997) of 5 kg VOC/TJ for both oil combustion and natural gas combustion.

Using a similar approach to that described above for methane, we have calculated VOC emissions from refinery fuel use by region:

Region	Published 1994 refinery output, t	Calculated 1994 refinery fuel use, PJ	VOC emissions, t VOC
North America	911,445,000	2,858	14,292
Central/South America	198,154,000	621	3,107
Europe excluding FSU	735,675,000	2,307	11,536
Former Soviet Union	256,054,000	803	4,015
Africa	112,794,000	354	1,769
Pacific	248,942,000	781	3,904
Middle East	246,833,000	774	3,871
Asia excluding China	303,259,000	951	4,755
China	128,471,000	403	2,015
World total	**3,141,627,000**	**9,853**	**49,263**

Thus we have calculated that global emissions of VOC from refinery fuel use (power generation plus process heaters) were about 49 kt VOC in 1994.

IPCC/OECD/IEA (1997) suggests a simple method for estimating fugitive and process emissions for VOCs in refineries using an emission factor of 0.53 kg/m^3 of refinery feedstock. If we assume that the above refinery output data approximate to refinery input, and taking a typical density of 1.117 m3/t (USA value in Table 7.4 on page I.31 of OECD/IEA, 1996), we can estimate these emissions on a regional basis:

Region	**Published 1994 refinery output, t**	**VOC emissions, t VOC**
North America	911,445,000	410,421
Central/South America	198,154,000	89,228
Europe excluding FSU	735,675,000	331,273
Former Soviet Union	256,054,000	115,300
Africa	112,794,000	50,791
Pacific	248,942,000	112,098
Middle East	246,833,000	111,148
Asia excluding China	303,259,000	136,557
China	128,471,000	57,850
World total	**3,141,627,000**	**1,414,666**

Thus we have calculated that global emissions of VOC from fugitive and process sources in refineries were about 1,415 kt VOC in 1994.

The National Physical Laboratory (NPL) has measured emissions of VOCs from a number of refineries in Europe using lidar techniques. Averaged results are shown in the table (Woods *et al*., 1995):

	Range	**Average value**
Refinery throughput	4.5 to 11.9 Mt/yr	6.8 Mt/yr
Measured emissions to atmosphere	840 to 2,810 kg/hr	1,320 kg/hr
Emissions as a percentage of throughput	0.12 to 0.30 %	0.19 %

These were broken down by refinery area as follows:

Refinery area	**Emissions for the average 6.8 Mt/yr refinery, kg/hr**
Storage of crude oil	340
Process plant	357
Storage of product/intermediate	574
Waste water treatment	51
Total	**1322**

If we multiply global refinery output by NPL's emission factors of 0.12 to 0.3% we obtain a range of estimates of global VOC emissions for refineries between 3,770 and 9,425 kt VOC in 1994. This range is somewhat higher than the estimate derived from the IPCC methodology but is of the same order of magnitude.

Another estimate can be made by scaling up a UK estimate of 103 kt in 1994 (UKPIA, 1998). Scaling by refinery outputs for 1994 gives a global VOC emission estimate of 3,478 kt VOC, which is close to the lower end of the range derived from NPL emission factors.

4.1.7 Toxic organic micropollutants

While there are probably small emissions of a variety of toxic organic micropollutants from refineries there appear to have been no major studies in this area (Coleman, 1999). **Appendix 5** gives some example data for PAH emissions from Californian refineries.

4.1.8 Heavy metals

Various metals can be emitted by refineries into the atmosphere. These derive mainly from trace quantities present in crude, and from catalysts. Example data for several Californian refineries are presented in **Appendix 5**.

4.1.9 Particulates

Catalytic cracking is an important process source of particulate emissions; other process sources include vacuum distillation, thermal cracking and blowdown systems (EEA, 1996).

EEA (1996) suggests a simple method for estimating emissions of particulates from refinery catalytic cracking using an emission factor of 0.006 kg/m^3 of refinery feedstock. If we assume that the refinery output data given in previous sections approximate to refinery input, and taking a typical density of 1.117 m3/t (USA value in Table 7.4 on page I.31 of OECD/IEA, 1996), we can estimate global particulate emissions from this source of 16 kt in 1994.

The authors have confidential data for several refineries in 1997 which, if scaled up to global level using the capacities given in Appendix 3, give a global emission estimate for particulates from all refinery sources of 157 kt in 1997.

4.2 PETROCHEMICALS

4.2.1 Carbon dioxide

Lord Marshall (1998) gives UK energy consumption in the manufacture of basic chemicals and plastics of 4,934,000 toe in 1996; and CO_2 emissions from these sectors as 3,947,000 t C in 1996; based on Department of Trade and Industry estimates.

We have scaled the UK data to give an estimate of global CO_2 emissions from petrochemicals, assuming that:

- “basic chemicals and plastics” equates with “petrochemicals”;
- total petrochemicals production may be scaled according to ethylene production.

Ethylene production statistics for the world and for Western Europe were presented in **Chapter 3** above. In 1996 the UK ethylene capacity was 2,270,000 t/yr; we have estimated UK production of 2,080,384 t from the western European proportion of production-to-capacity in that year (91.6% - see Chapter 3). Multiplying by the proportion of world-to-UK ethylene production, and converting from t C to t CO_2 gives an estimate of global CO_2 emissions from “petrochemicals” of 520 Mt CO_2 in 1996.

As 1 toe is 41.87 GJ (UK DTI, 1998), we can calculate by a similar method a global energy use for petrochemicals production of 7,420 PJ; and an emission factor of 0.07 t CO_2/GJ. This may be compared with the refinery emission factor (fuel use) of 0.0697 t CO_2/GJ - derived in **Section 4.1.1** above.

For further comparison, Appendix 7 contains emissions and energy use data for individual companies from which emission factors may be derived: Elf emit 0.0366 t CO_2/GJ in chemicals production; Shell Chemicals emit 0.0546 t CO_2/GJ in petrochemicals production; the Shell group emits 0.0754 t CO_2/GJ in refining. The range of energy use per unit production for Shell Chemicals and BP Chemicals is 2.9 to 16.7 GJ/t product; and Shell Chemicals have an emission factor of 0.667 t CO_2/t product.

4.2.2 Methane

The EIA (1994) have estimated US methane emissions from the manufacture of some petrochemicals:

Emissions of methane from US chemical manufacturing (kt methane per year)

Source	1987	1988	1989	1990	1991	1992
Ethylene	16	17	16	17	18	18
Ethylene dichloride	2	2	2	3	2	3
Styrene	15	16	15	15	15	16
Methanol	7	7	7	8	8	8
Carbon black	14	14	15	14	13	15

We can use the ethylene data to estimate global methane emissions by assuming:

- US ethylene capacity in 1992 was the same proportion of global capacity as it was in 1998 (28.4% - derived from Chang, 1998b);
- the US proportion of production-to-capacity in 1992 was the same as the global ratio (86.3%).

From these assumptions we can calculate:

- US production of 17,070,000 t ethylene in 1992;
- global methane emissions from ethylene production of 63,400 t CH_4 in 1992;
- an emission factor of about 0.001 t CH_4/t ethylene produced.

Likewise we have a European estimate of 4,000 CH_4 emitted from ethylene production in 1990 (EEA, 1996), from which we can derive a global estimate of 15,400 t CH_4 in 1990.

We do not have suitable production statistics from which to estimate methane emissions from other petrochemical processes.

4.2.3 Carbon monoxide

The US EPA (1994b) have published an estimate of US CO emissions from organic chemical manufacturing of 259,000 t/yr in 1990, from which we have derived a global estimate of 911,000 t CO/yr in 1990.

4.2.4 Nitrogen compounds

Nitrous oxide is emitted during the manufacture of adipic acid. An emission factor of 0.3 tonne N_2O per tonne of adipic acid formed has been published by Thiemans & Trogler (1991). Global emissions from this source are estimated at 0.4 to 0.6 Mt/yr (IPCC, 1992). Emissions in Canada have been estimated as 35,000 t/yr during 1990 to 1995 (Environment Canada, 1997). Emissions in the USA have been estimated by EIA (1994) as 50,000 to 57,000 t/yr during 1987 to 1993. The USA accounts for approximately one third of the total annual global production of adipic acid (US EPA, 1994b and references therein), giving global emissions of N_2O from this source of about 150,000 to 171,000 t/yr during the same period.

The US EPA (1994b) have published an estimate of US NO_x emissions from organic chemical manufacturing of 38,000 t/yr in 1990, from which we have derived a global estimate of 134,000 t NO_x/yr in 1990.

4.2.5 Hydrocarbons and other volatile organic compounds

In 1994 the National Physical Laboratory, Warren Spring Laboratory and Shell Research Ltd conducted a series of measurements of volatile organic compound emissions at the Shell Carrington Manufacturing Complex, UK (Woods *et al*., 1995). A suite of studies were made on the low-density polyethylene production plant which comprised two units with a combined capacity of 170,000 t/yr. Several techniques were employed:

- Lidar measurements
- Component counts and average US EPA/SOCMI emission factors
- Leak/no leak and other screening tests of components
- Low-level downwind sampling and dispersion modelling
- Mass balance calculations

Using the lidar technique emissions were measured from the whole plant in the range 55 to 63 kg/hr, corresponding to equivalent annual emissions of 440 to 500 t/yr or about 0.26% of throughput. Emissions near ground-level were found to be low (about 38 t/yr), probably associated with valve and flange fugitive losses; the majority of the emissions derived from high-level sources, most probably the vent stacks.

Fugitive losses from components were assessed using several methods. Component counts were made for one of the two units, and emissions estimated using average emission factors published by the Chemical Manufacturers Association (1989) and the US Environmental Protection Agency (1993):

Component type	Average emission factor, kg/hr per component	Number of components	Calculated emissions, kg/hr
Valve, gas/vapour	0.0056	115	0.64
Valve, light liquid	0.0071	76	0.54
Flange	0.00083	1566	1.30
Relief valve	0.104	14	1.46
Total emissions			**3.94**

Screening tests were carried out for the same unit using a flame ionisation detector (FID) and interpreted with published emission factors and correlation coefficients. Three different methodologies were employed, the "screening ranges" approach; the "stratified emission factor" approach; and the "EPA correlation" approach. The following table compares estimated emissions using these three approaches and the above average emission factor approach:

	Estimated emissions, t/yr
Average emission factor approach	23
Screening ranges approach	14
Stratified emission factor approach	12
EPA correlation approach	14

Upper and lower limits (95% confidence level) on these emission estimates were 2.5 to 50 t/yr, with a most probable emission rate of 13 t/yr.

Downwind sampling measurements and mass balance calculations indicated emission rates of 250 to 4,300 t/yr.

Lidar measurements were also made of pentane emissions from a polystyrene plant (capacity not reported). The emissions were found to be about 4.8% of the pentane throughput of the process. The majority of these emissions were from vent stacks at high elevations on the process unit.

The US EPA (1994b) have published an estimate of US non-methane VOC emissions from organic chemical manufacturing of 621,000 t/yr in 1990, from which we have derived a global estimate of 2,184,000 t VOC/yr in 1990.

4.3 RELEASES TO WATER

Water is used as a coolant in many refining and petrochemical processes and picks up many impurities, from both the crude itself (such as heavy metals, sulphide and phenols) as well as by-products from processing such as cyanide, dioxins and furans. The type and concentration of pollutants in a refinery's effluent are dependent upon both the composition of the crude and the processes and chemicals used in conversion.

Water pollutants include oil, H_2S or other sulphur compounds, ammonia, phenols, chromium compounds, and chlorine (used in water treatment to control corrosion and biological fouling). Water contaminants are usually monitored in terms of their biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, total organic carbon (TOC) and total dissolved solids (TDS).

The wastewater from a refinery is treated prior to discharge. This involves a number of steps including oil/ water separation, primary treatment to remove solids and biological treatment. Process wastewater which has to be treated often contains H_2S, ammonia and oil and is termed sour water. The inorganic material is removed by steam treatment, followed by incineration; the oil is removed in separators. The latter are generally large tanks where oil droplets can rise to the surface, usually with the aid of air flotation, and so be separated from the water. Evaporation can occur from this large surface area, resulting in air emissions. To minimise such evaporative losses and odours the separators are covered.

Following separation, the wastewater is treated further by biological oxidation and passed through filters; sometimes nutrients are added and if required the water may be further cleaned using activated carbon.

Shell has reported the quantities of oil in effluent water from its global refining operations: 12.7 grams per tonne of throughput in 1996, and 8.9 grams per tonne of throughput in 1997 (Shell, 1998).

4.4 SOLID WASTES

Solid waste comprises mainly of spent catalysts, together with ash if coal is burned as a fuel in the refinery. Solid wastes are treated by standard techniques, both on site and off, such as land farming, land filling and ponding. Emissions are minimal.

Shell has published data for waste which indicates waste generation of 1.1 grams of waste per tonne of throughput in 1996, falling to 0.42 grams of waste per tonne of throughput in 1997.

Amerada Hess (1998) have published 1997 waste generation at the St. Croix and Port Reading refineries: 4,696 t/yr of hazardous waste, and 4,130 t/yr of non-hazardous waste. Taking the combined throughput of 411,000 bbl/day indicates total waste generation of 435 grams of waste per tonne of throughput.

The large difference in these reported waste arisings may be related to how waste is defined, and especially whether water content is included or excluded.

4.5 EMISSIONS FROM LOADING/UNLOADING AND STORAGE

Refineries are usually supplied with crude by pipeline or ship. The majority of products are typically likewise moved in bulk; although some refineries have associated road distribution terminals to supply the local region. Some products may be exported via rail tankers; and barge transportation is not uncommon for intermediate coastal or river-borne loads.

This section considers loading/unloading operations and storage at the refinery; emissions during transportation, or elsewhere in the distribution chain, are not considered.

4.5.1 Unloading

Lidar measurements of fugitive losses from pentane storage tanks were made at Shell Carrington in 1994 (Woods *et al*., 1995). Measurements made during periods when pentane was being loaded from road tankers into the storage tanks indicated a loss of 0.04% by mass of pentane transferred.

4.5.2 Storage

The material presented in this section relates to refineries - it is difficult to make generalisations for the storage of petrochemicals.

Crude oil storage

All refineries require crude oil storage to ensure continuity of feed to processing. The sizes and numbers of tanks are determined by the number of grades to be handled, the extent to which these grades may need to be kept separate for processing, the size and frequency of batches of oil to be delivered, and to some extent the geographical constraints of the site.

Crude oil tanks in refineries vary greatly in size, typically between about 30,000 and 130,000 m^3 capacity. It is usual to store crude oil and products with vapour pressures above 1.5 psi in external floating roof tanks, although fixed roof tanks may be used for some heavy crudes. External floating roof tanks produce far smaller vapour emissions than fixed roof tanks, but their performance is affected by the choice of rim seal system. All primary rim seal systems can be enhanced by the use of secondary seals. The state of maintenance of the tank is very important to seal efficiency.

Storage of intermediate products

In older refineries it was normal for partially processed oils to be held in intermediate tankage before it was fed to the next stage of processing. For example kerosene would be run to intermediate tanks from the distillation units, and later brought back to treatment in a sweetening process to remove odorous sulphur compounds. Recent refineries have a high degree of process integration: oil streams pass directly from one process unit to another whenever possible to improve overall thermal efficiency and to reduce handling and storage costs.

Finished products

The storage configuration depends on the number and grades of each product type and on the size and frequency of batches to be despatched. In addition, it is often operationally convenient to have a limited number of small tanks to handle the much smaller batches for road and rail loading.

Products with very high vapour pressures (above, say, 12 psi) and including propane, butane and pentanes, are stored in pressure vessels with relief valves venting to flare.

Products with vapour pressures in the range 1.5-1 psi include motor gasolines and most of the intermediate products used in blending them, plus wide-cut jet fuel and light distillate feedstocks for petrochemical manufacture. These materials are generally stored in external floating roof tanks of the same general pattern and construction as those used for crude oil, but in the smaller size range of 3,000 to 30,000 m^3.

Low volatility products are usually stored in fixed roof tanks - including kerosene, gas oil and diesel fuels, feedstocks for downstream processes, lubricants, heavy residual fuel oil and bitumen.

Internal floating roof tanks are finding increasing usage in Europe and North America for volatile products due to environmental regulations. Elsewhere their use is often limited to products where it is important to exclude water - such as alcohols or ethers.

Emissions from storage

Losses of vapour can arise as follows:

- as displacement losses during filling operations when vapours in an empty or part-filled tank are displaced by the incoming liquid;
- as “breathing” losses due to expansion of the vapours when the tank is warmed during the day.

Losses from storage tanks are usually calculated using methodologies developed by the American Petroleum Institute (API), which take into account a large number of factors dealing with tank design, properties of the stored material, and local meteorology. For example, UKPIA (1998) has estimated UK emissions using a methodology adapted from API by CONCAWE: the estimate for 1997 is 10,000 t VOC/yr.

In 1992 the National Physical Laboratory conducted a series of measurements of hydrocarbon losses from storage tanks at the Shell Stanlow refinery, UK using a lidar technique (Woods *et al*., 1993). The measured emissions were then compared with estimates made using API methodologies. It was found that measured emissions were generally higher than calculated emissions. The lidar-to-API ratio ranged between 0.8 and 5.8, with a weighted mean value of 2.7 (32 measurements).

4.5.3 Loading operations

Refinery products are distributed by road, rail, water or pipeline; or a combination of these routes. Emissions from transfers into pipelines are likely to be small. For the other loading operations, emissions depend on the nature of the loading system which can be of three types:

- top (splash) loading - in which the loading arm is positioned with the outlet above the tank bottom so that the product splashes onto the liquid surface, leading to a high vapour evolution than the other two systems;

- bottom loading - in which petroleum products are loaded into the cargo tank from the bottom, minimising disturbance of the liquid and hence volatilisation;
- submerged top loading - in which the product is loaded by means of a pipe to provide entry below the liquid surface, again minimising splash and vapour formation.

EEA (1996) gives emission factors for various types of gasoline loading operations at refineries:

Operation	**Emission factor g VOC / t gasoline throughput**
Pipeline	0
Ship/ocean barge	300-430
Shallow draft barge	560-640
Rail cars	
Top-submerged	500-800
Top-partial splashing	1060-2000
Road trucks:	
Splash loading	2050
Top - partial splashing	870
Top - submerged	450-670
Bottom	410-670

4.6 WASTE HEAT

Heat may be lost from any process above ambient temperature. The biggest loss is likely to be in flue gases from combustion processes (power generation; process heaters).

EEBPP (1997) has published heat balances for three fired heaters at the Conoco Humber refinery (UK):

	Heat absorbed by process	**Heat absorbed by waste heat boiler**	**Flue gas heat loss**	**Casing heat loss**
Heater 1	61%	26%	12%	1.5%
Heater 2	80%	-	18%	1.5%
Heater 3	72%	-	26%	1.5%
Heater 3 after addition of waste heat boiler	72%	12%	14%	1.5%

4.7 SUMMARY OF GLOBAL ESTIMATES OF EMISSIONS FROM REFINERY AND PETROCHEMICAL PROCESSES

The various global estimates of emissions of gases from refineries into the atmosphere presented in section 4.1 are summarised in the table below. The table also contains global estimates derived from Californian data (see **Appendix 5**).

Source	**Global emissions, kt pollutant/yr in 1994**						
	CO_2	**CH_4**	**CO**	**SO_x[a]**	**N_2O**	**NO_x[b]**	**VOC**
Refineries							
Refinery fuel use	686,900	5-45	148-197; 418[d]	474-11,034; 46[d]	1-6	1,478-1,971; 1,085[d]	49; 573[d]
Process vents plus flares	67,900						
Process vents plus fugitive losses		12-189					1,415
Fugitive losses		7.2					
Storage tanks		0.2-35					
Catalytic cracking			214			133	
Non-combustion sources			93[d]	2,135; 930[d]		294[d]	744[d]
All sources	796,000[c]		169[c]; 511[d]	976[d]		1,379[d]	3,478-9,425; 1,317[d]
Petrochemicals							
Undifferentiated sources	520,000[e]		911[g]			134[g]	2,184[g]
Ethylene production		63.4[f]; 15.4[g]					
Adipic acid production					150-600[h]		

[a] As kt SO_2/yr.
[b] As kt NO_2/yr.
[c] 1997 data.
[d] Estimate derived from Californian data and representing the mid-1990's; see Appendix 5.
[e] 1996 estimate.
[f] 1992 estimate.
[g] 1990 estimate.
[h] Estimates from early 1990's.

In Section 4.1.9 we presented an estimate of global emissions of particulates from all refinery sources of 157 kt in 1997. The Californian data presented in **Appendix 5** scales up to a global estimate of 124 kt (mid-1990's), of which 93 kt is PM_{10}.

5 Emission reduction techniques and costs

This Chapter focuses primarily on technologies for reducing greenhouse gas emissions from *refineries*. The basic techniques for reducing greenhouse gas emissions from the *petrochemicals* sector are similar. Emphasis is given to techniques for reduction of CO_2 emissions as these are the largest greenhouse gas emissions from these sectors.

Options for reducing greenhouse gas emissions from refineries include:

- alternative societies which are not based on crude oil;
- refinery process optimisation;
- refinery use of non-carbon-based energy sources;
- reducing the carbon content of fuels;
- optimising the efficiency of heat and power production and use;
- reducing the amount of wastes flared.

5.1 ALTERNATIVE SOCIETIES NOT BASED ON CRUDE OIL

Crude oil refining is driven by demand for gasoline and other fuels, petrochemical feedstocks, and a variety of other products which have seen expansive consumption throughout much of the world during the 20th Century.

There are two broad directions in which this pattern could potentially change:

- demand for alternative energy sources and alternative products could reduce the reliance on oil-based economies or shift the distribution of oil-derived products;
- alternative sources of carbon could be used to produce a broadly similar product mix

Examples of alternative energy sources include nuclear, solar, wind, geothermal, hydro. Following a series of incidents around the world, nuclear power has lost its mid-century image as the clean technology of the future, and nuclear programmes have been cut considerably in Europe and North America. Elsewhere nuclear power retains importance, particularly in countries without substantial oil reserves. In Japan, for example, where nuclear power meets about 14% of the national energy needs, the nuclear share of electricity generation is likely to stay at about 35% up to 2010 (EIA 1998d). Hydroelectric power already represents several percent of the energy supply in some parts of the world, and demand is growing rapidly for solar photovoltaic systems and other renewable energy sources. Nevertheless fossil carbon (coal, oil, gas) will remain the principal energy sources during the period considered in this report.

In the developed world, gasoline to fuel automobiles has been the largest market for refinery products. In the last two decades considerable R&D has been invested in alternative fuels for automobiles, particularly methanol, ethanol, hydrogen and electricity. A particularly promising direction appears to be automobiles which use gasoline or alcohol fuels reformed to hydrogen which then powers fuel cells to produce electricity to drive the vehicle.

Research by the Tennessee Valley Authority into the production of fuel ethanol from cellulosic feedstocks dates back to the 1950's; "refinery" systems and yields for four alternative feedstocks are described in Broder & Barrier (1990). Petro-Canada has announced a joint venture with Iogen Corporation to develop and commercialise technology to produce ethanol fuel from biomass in the form of cellulose from grasses or agricultural by-products (Petro-Canada, 1998). Petro-Canada quote a US Department of Energy finding that greenhouse gas emissions associated with fuel produced through this process are more than 90% lower, on a full life-cycle basis, than emissions associated with the production and combustion of gasoline.

Other alternative sources of carbon which might be used to manufacture useful products include coal, natural gas, coal-bed methane, deep sea gas hydrates, wastes and sewage. In **Chapter 2** we outlined the synfuel technology used in South Africa to produce a range of products from coal. The USA is also pursuing this possibility, as described by the US DoE (1997). In the US programme, it is envisaged that Integrated Gasification Combined Cycle (IGCC) technology could be used both as a power source and as a route to manufacturing a range of fuels and chemicals. One of the most efficient and environmentally friendly technologies for producing low-cost electricity, IGCC can process many feedstocks including coal, petroleum coke, biomass, and municipal wastes. The coal or other carbonaceous feedstock is first gasified with air or oxygen, and optionally steam, to produce a fuel gas consisting mainly of hydrogen and carbon monoxide (although gasification to pure hydrogen, with CO_2 collected as a sidestream for use or disposal is an option). The gas is cleaned of particulates, sulphur, and other contaminants to permit further processing and combusted in a high-efficiency gas turbine/generator. The heat from the turbine exhaust gas is extracted to produce steam to drive a steam turbine/generator. In "co-production" mode, feedstocks can be processed before gasification to extract valuable components, or the synthesis gas can be converted to products. Clean synthesis gas can be catalytically converted into environmentally superior transportation fuels, high-value chemicals, or hydrogen. Transportation fuels produced from synthesis gas contain no sulphur and aromatics and reduce hydrocarbon, CO, and particulates emissions by 25–40% compared with low-sulphur, low-aromatic petroleum diesel. In the co-production mode, carbon emissions are expected to be a third lower than from separate facilities producing the same amount of power and fuel. In the long term the US DoE envisages using synergies between energy generation, fuels production, and chemical production by integrating these into a single entity, an "energyplex". This would optimise the entire cycle of carbon utilisation by incorporating co-processing concepts, the integral capture of CO_2, and leading to incorporation of carbon into useful products or sequestration (US DoE, 1997).

IGCC demonstration projects using coal, petroleum coke, or other petroleum refinery wastes are operating or under construction in the USA and world-wide. Many are designed for co-production to allow improved thermal efficiencies. For example liquid-phase methanol synthesis is being demonstrated at an Eastman Chemical coal gasification facility. The project is demonstrating a new cost-effective route for producing liquid fuels and chemicals in a mode that could be readily integrated with an IGCC plant to co-produce power and fuels/chemicals (US DoE, 1997).

Liquefied natural gas (LNG) offers another feedstock for producing fuels and products. In the USA industry is using slurry reactor and catalyst technology to convert natural gas to methanol, chemicals, and liquid fuels (US DoE, 1997). Shell has built a plant to convert natural gas to fuels in Malaysia.

There have been a number of studies of the economics of electricity generation from biomass and biomass gasification (for example Morris, 1994; Craig & Mann, 1996; Graham et al., 1996) but we have not identified studies on the costs of chemicals production. Santos-Leon *et al.* (1997) have examined the costs and climate change benefits of cellulose-derived ethanol and concluded that 200-250 Mt C could be avoided from gasoline combustion in the USA at an average cost of US$ 30-100/t C (US$ 8-27/t CO_2).

5.2 CRUDE OIL REFINERY PROCESS IMPROVEMENTS

Refinery operators aim to obtain the maximum yield of valuable products for the minimum cost. These aims are consistent with minimising greenhouse gas emissions from refineries - any carbon in crude which is not incorporated into fuels, petrochemical feedstocks or other products will mostly, sooner or later, be emitted into the atmosphere as CO_2, CO or VOC (and CO and VOC in their turn will be converted by atmospheric processes into CO_2).

An important aspect of refinery design and operation is to ensure that every process operates with maximum efficiency and minimum energy input. Much of the energy requirement is provided by low-value product or waste such as process off-gases.

5.2.1 Individual processes

Numerous opportunities exist to improve the efficiency/economics of individual processes in crude oil refineries. For example improved catalysts could reduce the energy requirements for cracking processes, while membranes could improve separation processes. Membrane technologies for the separation of hydrogen in several different refinery streams are being investigated (US DoE, 1997).

The US DoE (1997) estimate that a combination of improved off-gas separation, more selective catalysts, and effective methane capture could reduce US greenhouse gas emissions from refineries by 10-20% in a decade.

5.2.1.1 Improved catalysts

Trends in catalysis research have been reviewed by Absi-Halabi *et al.* (1997). Benefits of specified improved catalysts which they list include:

- increased conversion/yields;
- reduced coking;
- octane enhancement;
- reduced temperatures/pressures;
- improved catalyst stability;
- increased throughput;

- increased selectivity.

They also describe a number of long-term trends including:

- new catalysts for converting methane and natural gas to liquid transportation fuels;
- new routes and catalysts to improve conversion economics of alternative fuel sources;
- new catalysts and catalytic routes for hydrogen production and recovery;
- R&D in new zeolitic materials specific to environmental fuel issues;
- new catalysts for energy-efficient and economic routes for converting syngas into fuels;
- new catalytic materials such as carbides, nitrides and solid super-acids.

5.2.1.2 Bioprocessing/biocatalysis

Crude oils can be biochemically converted to lighter oils through removal of heteroatoms, with simultaneous reduction in sulphur, trace metals, and nitrogen compounds (US DoE, 199?a). Research carried out at the Brookhaven National Laboratory has demonstrated the technical feasibility at laboratory-scale of bioprocessing under a variety of processing conditions; they have now teamed with Energy Consultants International to investigate the economic feasibility. Similar research has been conducted by Energy BioSystems Corporation in the USA and by the Petroleum Energy Centre in Japan (Monticello, 1998).

Research is also under way to develop cheaper methods for removing nickel and vanadium from heavy crude oil before it enters the refinery.

In another example, the US DoE is funding work by Engineering Resources Inc. who have developed a biological process for utilising waste gases from carbon black production (US DoE, 1996a). The waste gases contain CO_2, CO and H_2 which are converted into acetic acid by anaerobic bacteria. As well as reducing the quantities of waste gases, it is anticipated that the process would use substantially less energy than existing acetic acid manufacturing processes: about 14,000 Btu per pound compared to 57,000 Btu per pound. It is estimated that if all the 30 carbon black plants in the USA were to convert to this process, replacing all current US acetic acid production, 100 to 150 trillion Btu would be saved annually.

5.2.1.3 Membrane technologies

Membrane technologies provide a means of separating gases by selective permeation - molecules can separated on the basis of size, shape, or chemical properties according to the nature of the membrane.

Refiners have long used organic membranes as a way to recover hydrogen for use as a fuel (US DoE, 199?a); a design for membrane reactor for methanol reforming is given in Buxbaum (1997). Other potential applications can be envisaged wherever separation processes occur in refineries and petrochemical plants. For example, the US Department of Energy is investigating a hybrid membrane/distillation process to recover products from waste gas streams (US DoE, 1996b). The project has focused on recovery of olefins from catalytic cracking. Conventional technology uses a distillation system to separate propylene from a propylene/propane gas stream. The distillation process is very energy-intensive, with energy efficiencies seldom exceeding 10%. The hybrid membrane/distillation system is estimated to save 500 billion Btu per year for a 10,000 bbl/day facility.

Use of membranes in CO_2 capture is discussed below.

5.2.1.4 Recycling refinery sludges

Refinery sludge is typically an emulsion of oil, solids and water. Traditional disposal options include lagooning, deep land injection, or incineration. Waste sludges can also be recycled into the refinery coker. Coking treats heavy residues to recover and thermally crack high boiling point residues into lighter fuel fractions and to produce fuel-grade coke. Addition of sludge into the coker enables recovery of the sludge solids but has various problems such as introducing water which increases the energy requirements. Scaltech (1995) have described a system which first centrifuges the sludge before injecting it into the coker in place of water during the quenching stage. Oil is recovered from the centrifuge for reprocessing; and many of the problems associated with sludge injection are avoided. The Scaltech system has been used by Chevron’s Port Arthur refinery where nearly twelve times as much sludge solids were recycled compared with raw sludge injection; and at CITGO Petroleum Corporation’s Lake Charles refinery.

5.2.1.5 Other process developments

Other novel process developments being investigated by programmes funded by the US Department of Energy include:

- inorganic membrane reactor technology to provide improved energy utilisation in high-temperature petrochemical applications;
- high-temperature catalytic membrane reactors;
- production of ethanol from refinery waste gases.

One project seeks to aid small refiners in California to upgrade heavy crude oils and residues to higher grade material using aqueous pyrolysis, vacuum distillation followed by pyrolysis, or fluidised bed conversion.

5.2.2 Whole refinery optimisation

For the last 30 years it has been normal practice in western countries for crude oil refineries to be scheduled using a computerised optimisation technique known as “linear programming”. This methodology matches available resources (e.g. types and quantities of crude oil, types of process units and their capacities) with required products (e.g. quantities and specifications of products), and indicates the optimum processing sequence. A computer model is set up for the refinery, into which is built the characteristics and constraints of each process unit. These include mathematical relationships for process yields, utility and energy consumptions and costs, and limits on throughputs or other parameters. The nature and quantities of environmental emissions can form an integral part of the model (description taken from Mott MacDonald, 1996).

5.3 REFINERY USE OF NON-CARBON-BASED ENERGY SOURCES

We mentioned above the possibilities for society as a whole replacing petroleum-derived fuels by other energy sources such as nuclear, solar, wind, geothermal, or hydro. These energy sources could, of course, also be exploited by crude oil refineries - usually for imported power, although refineries in suitable locations could in principle exploit locally available renewables. The authors are not aware of any examples, although we noted that Texaco is a participant in an electric power generating plant in Indonesia which is fuelled by geothermal energy (Texaco, 1998).

This is unlikely to be a significant option during the timescale addressed by this study.

5.4 REDUCING THE CARBON CONTENT OF FUELS

Natural gas, LNG, LPG, coal-bed methane or indeed refinery gas have lower carbon-to-hydrogen ratios than fuel oils, and will give lower greenhouse gas emissions for a given amount of energy. Gas-fired power generation is highly efficient, and future developments are expected to focus on incremental improvements to combined-cycle gas turbine technology which could allow efficiencies of up to 60% to be reached over the next decade (Smith *et al.*, 1998).

The exploitation of gas fields is still at early stages in many parts of the world, but demand for natural gas is expected to develop rapidly and major distribution networks are being implemented. For example, China is in discussion with Russia over long-distance pipeline gas imports from Russia, including plans for a pipeline that would extend to Japan via the Korean peninsula (EIA, 1998a). In India, natural gas meets 7% of energy demand; consumption is expected to double by 2000 and treble by 2005. At the moment this is mostly met through import of LNG, and future plans include gas pipelines from Oman, Iran and Turkmenistan. In the longer term, India is developing plans to exploit domestic gas fields, coal-bed methane and deep sea gas hydrates (EIA, 1998b).

Opportunities to exploit low-carbon fuels will be very plant-specific, determined by the availability and price of off-site gas versus other energy sources; and the product mix and process configuration of the refinery (affecting availability of refinery gas). It is likely that opportunities for fuel-switching will be rare; in most refineries low-value heavy ends and refinery gas will be economically preferable.

5.5 OPTIMISING THE EFFICIENCY OF HEAT AND POWER PRODUCTION AND USE

The major energy use in refineries is for process furnaces and boilers, with a significant proportion as power. The power may be imported, and this is usually the case in the USA, although in Europe a lot of sites have on-site power generation.

5.5.1 Cogeneration

Cogeneration is the generation of heat and power in the same plant, usually using a gas turbine with heat recovery. This reduces CO_2 production relative to other systems:

- gas turbines are more efficient than oil-fired boilers;
- the recovered heat may be used on site or sold, avoiding combustion emissions from a separate heat generator;
- there are potential benefits from power sales to the electricity grid to reduce net CO_2 emissions.

Cogeneration is finding increasing application in the refinery sector. An example from the early 1990's was installed at Shell's refinery in Fredericia, Denmark (Bodewes & Lugten, 1992). In their system, 150 t/day of refinery gas drives a generator with 27 MW output capacity. The flue gases leave the turbine at a temperature of 485^{o}C and are used to heat crude oil from 165 ^{o}C to 365 ^{o}C - recovering over 35 MW. The flue gases are cooled to 230 ^{o}C by the crude; they are then used to heat water for a district heating system, recovering a further 9 MW. The overall energy efficiency is up to 76%; the investment was DKK 165 million. Reading data from a graph given in the reference indicates a net global CO_2 reduction from 340 kt to 150 kt, or 56% reduction, taking into account the avoidance of electricity generation at a coal-fired power station; and avoidance of gas oil combustion for the district heating system.

Shell's Pernis refinery (the Netherlands) has a 127 MWe cogeneration unit fired by syngas (de Zilwa & van Kooten, 1995). The syngas (a mixture of CO and H_2) is produced in a Shell gasification hydrogen process plant (SGHP), in which heavy residues are reacted with oxygen. Much of the hydrogen is used in a hydrocracker, while some is retained with the CO for fuel. In addition to electricity, the cogeneration plant produces about 400 t/hr of 70 bar steam for the refinery steam systems. The surplus of syngas from the SGHP (about 300-1700 t/day) is not always sufficient for the desired load of the gas turbine, in which case LPG and/or natural gas is mixed in as supplementary fuel.

Appendix 9 presents data on the performance of a cogeneration system at Conoco's Humber refinery (UK) where the costs were found to be:

- US$ -6.5/t CO_2 (i.e. savings) relative to on-site generation using oil-fired steam turbines (21% energy saving);
- US$ -48/t CO_2 (i.e. savings) relative to electricity purchased from a coal-fired power station.

Other examples include:

- Amoco Canada has invested US$75m in cogeneration facilities (Amoco, 1998).
- ARCO (1996) has installed a turbine-powered cogeneration plant at its Los Angeles refinery. This generates 385 MW of power ("enough to meet the needs of 200,000 homes") and 1.2 million pounds per hour of steam to refine 200,000 barrels of crude per day. Energy savings equal 4,000 barrels of crude a day.

- Bharat Petroleum is installing a gas turbine cogeneration plant at its Mahul (India) refinery (Bharat Petroleum, 199?).
- Elf is planning to install cogeneration (Elf, 1998).
- Phillips Petroleum has installed three cogeneration plants (Phillips Petroleum, 1998), and will buy steam from a $100 million 216 MW facility under construction (1998) for Southwestern Public Service at the Phillips Petroleum's Borger (Texas) refinery complex (Lubbock Avalanche-Journal, 1997);
- Texaco operates 10 natural gas-fired cogeneration facilities in the US producing "enough electricity to power over one million homes" (Texaco, 1998).
- Wood River Refining Company in Roxana, Illinois, will buy steam from a new cogeneration plant announced in 1998 (HIPG, 1998).

Many refineries buy in power as an alternative or supplement to on-site generation. Co-generation offers an opportunity to reduce net greenhouse gas emissions from the combined power grid/refinery system through more efficient combustion compared with many existing power generation technologies, and through use of recovered heat.

5.5.2 Advanced turbine systems

A US$700 million programme (1992 to 2000) jointly funded by the US Department of Energy and industry has been working on advanced gas turbine systems for both utility and industrial applications, including cogeneration. The programme aims for 60% efficiency for > 20 MW facilities against 54% quoted as current technology.

5.5.3 Fuel cells

Fuel cells are electrochemical devices in which a fuel is supplied to an anode, and an oxidant to a cathode. The fuel is electrochemically oxidised, producing electrons which flow between the cathode and the anode to create an electric current. Individual cells are small (less than 1 kW), and are therefore assembled into "stacks" to provide larger outputs (ETSU, 1997). Fuel cells may be fuelled by hydrogen, methane, or other organic fuels. Fuel cells produce heat as well as electrical power, and are suited to use in cogeneration systems. It is estimated that there is typically a full fuel cycle CO_2 saving of around 25% relative to a gas turbine (Smith *et al.*, 1998); while generated electricity prices are about double (Marsh, 1999).

It is unlikely that fuel cells will be available for bulk capacity applications before about 2015 (Marsh, 1999).

5.5.4 Distillation

BP Oil and MW Kellogg Ltd have piloted dividing wall distillation technology at the Coryton refinery (UK). The technology is applicable as a method of separating three components (or groups of components). Usually this would be done using two columns, with heating and cooling provided for each column. The dividing wall technology combines the separation process into a single vessel, with energy savings of about 30% and capital savings of 25% (MW Kellogg, 1998).

5.5.5 Compact heat exchangers

Compact heat exchangers are generally made from thin metallic plates rather than tubes. The plates form convoluted and narrow flow passages which give a large heat transfer surface area per unit volume. Multi-stream versions can incorporate 12 or more streams. Compact heat exchangers can give energy savings as well as reduced capital and installation costs. In a case study at a UK refinery, potential capital savings amounted to between 69% and 84% (EEO, 1993).

5.5.6 Refrigeration technology

Planetec Utility Services and Energy Concepts Co. have developed a refrigeration system which has been trialled at Ultramar Diamond Shamrock's Commerce City refinery (near Denver, Colorado, USA). Their process transforms waste heat into cold energy which can be used to recover volatile products such as butane. The investment was US$2.3 million. Based on the first five months of operation it is projected that the system will save US$175,000 to US$200,000 a year in electricity costs compared with traditional electricity-powered refrigeration systems; extra revenue will be an estimated US$1 million per year; and carbon emissions will be reduced by about 66,000 pounds per year (Aven, 1998).

5.5.7 Waste heat boilers

Waste heat boilers recover heat from combustion exhaust gases for steam generation. Data presented in Chapter 4 show how addition of a waste heat boiler to an existing process heater at Conoco's Humber refinery reduced heat loss in flue gases from 26% of energy input to 12% of energy input (EEBPP, 1997).

5.5.8 Miscellaneous energy efficiency improvements

There are numerous ways to reduce energy use (and hence combustion-related greenhouse gas emissions) from refineries. Important opportunities include:

- optimising combustion efficiency of boilers and furnaces;
- optimising heat exchanger efficiency;
- recovering waste heat to pre-heat combustion gases or to export to district heating systems.

Appendix 6 describes some energy efficiency opportunities at a large Chinese refinery, where the long-term potential for savings has been estimated as 15-20%. Good combustion control was likely to save about 2% of energy use for a saving of US$ 28/t CO_2. The source reference gave no indication of the capital required; we estimate that the net saving would be of the order of US$ 14/t CO_2.

Appendix 7 describes various emissions data, energy efficiency improvements and greenhouse gas emission reductions and targets reported by several companies. The following table summarises targets and achievements for five companies.

Company	Reduction	Dates	Means
Amoco	10% reduction in greenhouse gas emissions per unit production	Achieved during 1993 to 1997	Means unspecified
Elf	15% reduction in greenhouse gas emissions	Target for 1990 to 2000	Means unspecified
Mobil	10% reduction in energy consumption	Achieved during 1990 to 1996	Various energy efficiency measures

Company	Reduction	Dates	Means
Petro-Canada	1% improvement in energy efficiency per year	Achieved 3.9% in 1996 and 0.4% in 1997; 1.1% target for 1998	Various energy efficiency measures
Shell Canada	Stabilisation	1990 levels of greenhouse gas emissions by 2000	Various energy efficiency measures

Petro-Canada's plans, in particular, stress the importance of training staff in good energy management practice.

Data published by Shell Canada and reproduced in Appendix 7 enable calculation of cost effectiveness of the measures. We have assumed 5% (10%) discount rates, 15 year plant lifetime, and an exchange rate of CS$ 1 = US$ 0.7227; and we have used the Discounted Cash Flow method given in EEA (1999) to calculate the following data:

- US$ 35.8 (27.0)/t CO2 saved at Montreal East Refinery through improved heating arrangements on the FCC;
- US$ 25.5 (23.2)/t CO2 saved at Montreal East Refinery through improved management of six steam turbines;
- US$ 27.5 (24.3)/t CO2 saved at the Sarnia refinery through increased heat recovery from the hydrocracker by installing a new heat exchanger.

According to a 1996 study conducted by RIVM, the average energy efficiency improvement potential for refineries in the European Union (EU-12) is 15% (Phylipsen & Blok, 1996).

In 1990 a UK Department of Trade and Industry study (ETSU, 1990) estimated the energy saving potential of the organic chemicals sector, which included petrochemicals as well as speciality chemicals. The key findings are reproduced in **Appendix 8**. The overall energy saving potential was estimated as 23 % in 2000, and 47 % in 2020, relative to 1988 energy use.

In a current study on the cost implications of the IPPC Directive, AEA Technology Environment and the Fraunhofer Institute have examined a number of energy saving measures for petrochemical processes (Howarth, 1999). Some early findings are summarised in the table:

Process	Process energy requirement, GJ/t throughput	Efficiency measure	Energy saving, GJ/t throughput	Investment, ECU/t throughput	Net operating cost, ECU/t throughput
Styrene	7.10	Improved catalysts	0.9 to 2.1	0	-1.3 to -4.3
		Packed columns	0.9	23	-1.3
Olefins - steam cracking	19.6	Improved insulation	0.4 to 0.5	4.5	-1.0 to -1.3
		Integrated gas turbine	1.6 to 2.0	20	-4 to -5
		Good housekeeping	1.2 to 1.5	14	-3 to -3.8
		Feedstock control	0.8 to 1.0	9.3	-2 to -2.5
		Improved reactor design	2.0 to 2.6	0	-5 to -6.6
		Divided wall column	7.8 to 10.2	0	-20 to -26
Methanol - steam reforming	9.7 to 14.5	Heat recovery	0.7 to 1.0	5.2	-1.8 to -2.5
		Hydrogen recovery	0.6	3.1	-1.5
		Good housekeeping	0.3 to 0.4	4.7	-0.8 to -1.0
		New amv-process	2.3	221	0.4
		Adiabatic prereformer	1.2	8.1	-2.5
All processes - process heat	1.5 to 11.2	Heat recovery	0.1 to 3.9	1.9 to 51	-0.3 to -8.9

We have used these data to estimate CO_2 reduction potentials and costs in US$/t CO_2 by:

- assuming an emission factor of 0.07 t CO_2/GJ (see **Chapter 4**);
- using the Discounted Cash Flow approach given in EEA (1999) with real discount rates of 5% and 10% per year and an assumed plant lifetime of 15 years;
- assuming that the fuel requirement for the processes is met by heavy fuel oil at a price of 2.5 ECU/GJ (Howarth, 1999);
- a currency exchange rate of 1 ECU = US$ 1.1710.

Process	Efficiency measure	CO_2 emission reduction, %		Cost, US$/t CO_2 at 5% (10%) discount rate	
		Minimum	Maximum	Minimum	Maximum
Styrene	Improved catalysts	12.7	29.6	-34 (-34)	-24 (-24)
	Packed columns	12.7	12.7	+17 (+32)	+17 (+32)
Olefins - steam cracking	Improved insulation	2.0	2.6	-29 (-24)	-24 (-17)
	Integrated gas turbine	8.2	10.2	-26 (-20)	-22 (-14)
	Good housekeeping	6.1	7.7	-28 (-22)	-24 (-16)
	Feedstock control	4.1	5.1	-27 (-21)	-23 (-16)
	Improved reactor design	10.2	13.3	-42 (-42)	-42 (-42)
	Divided wall column	39.8	52.0	-43 (-43)	-43 (-43)
Methanol - steam reforming	Heat recovery	4.8	10.3	-46 (-40)	-22 (-20)
	Hydrogen recovery	4.1	6.2	-50 (-46)	-22 (-20)
	Good housekeeping	2.1	4.1	-29 (-15)	-15 (-11)
	New amv-process	15.9	23.7	+105 (+143)	+236 (+320)
	Adiabatic prereformer	8.3	12.4	-35 (-30)	-16 (-13)
All processes - process heat	Heat recovery	6.7	34.8	-20 (-9)	-17 (-8)

Most of the techniques show cost savings, in the range US$ 17/t CO_2 to US$ 50/t CO_2 (5% discount rate) or US$ 8/t CO_2 to US$ 46/t CO_2 (10% discount rate). Two of the options show positive net costs.

5.6 REDUCING THE AMOUNT OF WASTES FLARED

Reducing the amount of waste gases sent to flare will reduce greenhouse gas emissions from this source, and recover product.

Normally the amount of gas flared is small; condensable liquid fractions are recovered, and the separated gases are sent to flare. Large releases to flare can occur during process upsets. An option for this situation is to collect the gases in a holding tank, for subsequent compression and recycle into the gas separation units.

The Petroleum Technology Alliance Canada is investigating the use of mini-turbines for on-site electrical generation from flare gas.

We did not identify any reports or case studies of the potential for flare gas recovery, although we note a stringent requirement in Rule 359 of the Santa Barbara County Air Pollution Control District (SBCAPCD, 1994). This required refineries and other flare operators to establish a Flare Minimisation Plan which would achieve a 50% reduction in average monthly flare gas volume within 5 years.

5.7 TECHNOLOGIES SPECIFIC TO CARBON DIOXIDE

In recent years there has been considerable research into methods for capturing CO_2 from waste streams, either for use or for disposal.

5.7.1 CO_2 capture technologies

Options for CO_2 capture include:

- adsorption;
- absorption;
- cryogenics;
- membrane systems.

5.7.1.1 Adsorption

CO_2 can be adsorbed using molecular sieves - materials which are 'porous' at the molecular level and which loosely bind the adsorbed gas by weak physico-chemical means. Riemer (1996) reports that this technique is most effective when the concentration of CO_2 in the waste stream is between 400 and 15,000 ppm. The adsorbed CO_2 may be released from the adsorbant by reducing the pressure or increasing the temperature.

The disadvantages of this technique are that it is not particularly selective, so other gases are captured as well; and the capacity is limited.

The CO_2 concentrations of refinery waste streams all lie above the optimum range for adsorption, and so this technology is not likely to have significant potential in this sector.

5.7.1.2 Absorption

There are two options for absorption: chemical absorption or physical absorption. In chemical absorption the CO_2 reacts with the solvent to form a weakly bonded intermediate compound which can later be broken down by applying heat, regenerating the solvent and producing a CO_2 stream. With a physical solvent, the CO_2 is dispersed into the solvent without forming chemical bonds and can later be released by the application of heat or by lowering the pressure of the atmosphere over the solvent.

For low partial pressures of CO_2 in flue gases, a chemical solvent such as monoethanolamine can be used. Where the CO_2 partial pressure is high, a physical solvent is preferred, such as Selexol (dimethylether of polyethylene glycol), Purisol, Rectisol (cold methanol) or Sepasolv.

Disadvantages of monoethanolamine include high volatility, chemical instability in the presence of oxygen, and corrosivity (Erga *et al*., 1995).

Chakma (1995) has reported that the cost of aqueous ethanolamine absorption of CO_2 is US$40-70/t CO_2 in power generation. The IEA Greenhouse Gas R&D Programme (199?) has reported costs in the range US$ 16-87/t CO_2 for a range of power generation technologies, for a capture efficiency of 82 to 99%. In refineries, CO2 absorption appears to be a viable option for exhaust streams from on-site power generation, from process furnaces and boilers, and from catalyst regeneration. For these sources the CO_2 concentrations will be similar to power generation; the required capacity will be lower but uncontrolled CO2 emissions will be correspondingly lower, so costs per tonne are likely to be similar. For modelling purposes (see below) we assume a range of costs of US$ 20-90/t CO_2 and capture efficiency of 80 to 99%.

5.7.1.3 Cryogenic techniques

Cryogenic processes are only viable where there is a high concentration of CO_2 in the waste stream.

High concentrations of CO_2 are found in the steam reforming process (100% CO_2) and in some petrochemical offgas streams such as ethylene oxide manufacture (see **Section 3.2.9**). For these relatively small emission sources cryogenic techniques may be a promising option. We surmise that the technique will have a net cost, probably of some tens of US$ per tonne of CO_2 captured.

5.7.1.4 Membrane systems

Membrane separation operates through selective permeation - the membrane acts as a barrier to some gases while allowing other gases to pass through. The process can be enhanced by using an absorption liquid on the capture side of the membrane.

Membrane systems suitable for isolating CO_2 from exhaust gases are still the subject of basic research. Various systems have been tested by a number of researchers such as Chakma (1995), Feron and Jansen (1995), Falk-Pedersen *et al*. (1995)

The application of the above techniques to CO_2 emissions from power generation have been reviewed by Riemer (1998). The IEA Greenhouse Gas R&D Programme (199?) has reported the cost of a membrane system for one power generation case of US$ 45/t CO_2.
Studies in the power generation sector suggest that membranes offer greatest potential in combination with other capture techniques, notably absorption.

5.7.2 CO_2 use/disposal options

Having captured CO_2, options for its use or disposal include:

- utilisation in industry: manufacture of useful products;
- enhanced photosynthesis;
- enhanced oil recovery;
- underground geological storage;
- deep ocean storage.

5.7.2.1 Utilisation in industry: manufacture of useful products

In the mid-1990's the US Department of Energy funded a research programme at Sandia National Laboratories to develop catalysts that electrochemically reduce carbon dioxide to chemicals that are commercially useful, such as methanol and formaldehyde (Shelnutt, 1999). The work involved designing porphyrin based catalysts, mainly cobalt porphyrins, with improved activity in electrochemical CO_2 reduction to CO. The conversion of CO_2 is almost 100% to CO. The first idea was to improve the electrochemical potentials at which the conversion occurs by computer designing new porphyrin catalysts. There was some success by using porphyrins with electron-withdrawing substituents.

Toward the end of the programme, Sandia attempted to develop catalysts with hydrogen-bonding substituents near the active metal centre. This was expected to increase activity by hydrogen-bonding to the CO_2. This approach could also be used to hold the CO product at the active site for further conversion to more useful products, such as formaldehyde.

5.7.2.2 Enhanced photosynthesis

The concept is that by increasing CO_2 concentration, crops will be able to sequester more carbon and so increase crop yields. Feron & Jansen (1995) report that increasing the carbon dioxide concentration in the greenhouse from 350 ppm to 500 ppm results in a production increase of 25% for certain bulk crops.

US DoE (199?b) suggest that microalgal systems represent the best biological technology for direct capture and use of CO_2 emitted by industrial sources, because of their fast growing time. After harvesting the biomass could be used to produce fuels or other products (see **Section 5.1** above). The US DoE article indicates a cost of up to US$ 100/t CO_2 for the case of power plants.

5.7.2.3 Enhanced oil recovery

In oil production, injection of materials into the "void" left by recovered oil can increase the amount of oil recovered. This technique has been used with a variety of materials, including water and liquid wastes. Carbon dioxide has been extensively used in regions where supplies of CO_2 are readily available. For example, CO_2 rich reservoirs occurs in the Permian Basin in Texas/New Mexico; the CO_2 is piped to other parts of the basin for enhanced oil recovery.

US DoE (199?b) indicates that US industries consume about 40 Mt CO_2/yr, of which about 80% is used for enhanced oil recovery, using CO_2 from CO_2 gas wells which is much cheaper than power plant capture options.

In principle enhanced oil recovery using refinery CO_2 could be a viable option in locations where a refinery is located near a production area where no natural CO_2 reserves are available.

5.7.2.4 Underground geological storage

Bergman & Winter (1995) report that estimates of the global capacity for storage of carbon dioxide in aquifers is 100 to 10,000 Gt of CO_2; for the USA the capacity is 5 to 500 Gt of CO_2. Tanaka *et al*. (1995) calculated a capacity in Japan of 3 Gt (in oil and gas reservoirs and neighbouring aquifers, and in aquifers in anticlinal structures) and 80 Gt (in aquifers in monoclinal structures on land and offshore). Costs are associated with: construction of CO_2 recovery plants, pipelines for transportation, surface facilities for CO_2 injection, and drilling wells (Tanaka *et al*., 1995). The costs for storage in onshore aquifers have been estimated by Hendriks & Blok (1995) to be 2 to 8 US$/t CO_2 not including recovery plant; the corresponding costs for onshore natural gas fields were 0.5 to 3 US$/t CO_2.

5.7.2.5 Deep ocean storage

This option has been reviewed recently by Ormerod (1998). The basic concept is to inject CO_2 into deep ocean waters. Unlike surface waters, these are not saturated with CO_2, and have theoretical capacity to store the gas for up to 1,000 years. After this time, much of the CO_2 would be released back into the atmosphere after upwelling (which mainly occurs in the tropical latitudes in today's climatic situation). The most practical way to achieve injection into the deep ocean would be to pump the CO_2 via pipeline, either as a dense phase gas or as a liquid, although other options have been mooted. Ormerod (1998) suggests disposal costs of between US$ 10-40/tC (about US$ 3-11/t CO_2).

Adams *et al.* (1995) have estimated a capital cost of $300 million for an offshore disposal system at a depth of 1000m, at a distance of 100 km, serving a 1000 MW power plant.

Riemer (1996) has summarised estimates of storage costs for several of these techniques:

CO_2 storage option	**Cost, $/tC**
Ocean disposal	4.1
Saline aquifers	4.7
Depleted gas reservoirs	8.2
Depleted oil reservoirs	8.2
Improved forestry and reforestation	5-20

5.8 TECHNOLOGIES SPECIFIC TO METHANE

The data presented in Chapter 4 indicated that the major sources of methane emissions in refineries are heat/power combustion sources and fugitive losses from processes; storage tanks and flares are relatively small sources.

Control of emissions from heat/power sources are described above.

It should be noted that care must be taken in interpreting cost data for methane control measures since the same measures reduce non-methane VOCs. It would be wrong to apportion the full costs of the measures to methane since emission reductions and cost savings in VOCs are also made.

5.8.1 Fugitive loss control

Fugitive sources include valves, pumps, compressors and flanges.

One of the most effective control measures for fugitive losses is regular inspection and maintenance, which can reduce emissions typically by about 40% to 80% (Wenborn *et al.*, 1995). Chem Systems and ERM Economics (1996) have published a cost range for leak detection and repair programmes of £50/t VOC to £90/t VOC but did not report savings associated with product loss prevention. UN ECE (1990) reported that a programme to reduce fugitive emissions by 50% would give savings, whereas a reduction of 80% by quarterly inspection and maintenance would have a net cost of 193 ECU/t VOC. de Jager *et al.* (1996) have reported implementation costs of US\$ 76/t CH_4 for a 70% effective programme yielding savings of US\$ 342/t CH_4, i.e. a net saving of US\$ 266/t CH_4.

Losses from leaking pumps, valves, flanges, compressors and other components can sometimes be reduced by using low- or zero-loss components such as seal-less pumps; double-sealed flanges; or replacement of flanges by continuously welded piping. Costs have been estimated by Wenborn *et al.* (1995) as ranging from cost-neutral to an expenditure of 125 ECU/t VOC. de Jager *et al.* (1996) report cost savings of US\$ 34/t CH_4 by improving compressor valve sealing.

5.8.2 Storage losses

Emissions from storage tanks may be minimised through vapour recovery systems (in which methane and other vapours in the headspace of a filling tank are returned to the unloading vessel, tanker etc; or into production processes or the flare system); fixed roof tanks with internal floating covers; floating roof tanks; secondary seals on floating roof tanks.

Good control of storage losses are likely to produce savings if designed into new plant. Retrofitting of floating roof tanks with secondary seals returns investment in a short time (UN ECE, 1990).

5.8.3 Flares

The most effective control technique for flares is to reduce the amount of gas flared - see **Section 5.6** above.

Combustion efficiency in the flare can be improved from 95-98% up to over 99% by injecting steam into the combustion zone to provide turbulence and air. Steam injection also reduces emissions of nitrogen oxides by lowering the flame temperature.

5.9 TECHNOLOGIES SPECIFIC TO NITROUS OXIDE

Emissions of N_2O from combustion processes are very small (see Chapter 4), and generally the most effective emission reduction options are the various energy efficiency measures described above.

Bates (1998) has described some N_2O emission reduction options for adipic acid manufacture:

- In catalytic destruction, a catalyst bed (of metal oxides) is used to decompose the N_2O into N_2 and O_2. The reaction is strongly exothermic, giving the possibility of heat recovery for steam production.
- Another catalytic destruction technique involves the use of catalysts to decompose the N_2O to NO, which can then be oxidised and converted to nitric acid. This process has been tested but abandoned as the estimated capital cost of the process was very high.
- An alternative process is combustion of the off-gases in the presence of methane. The N2O acts as an oxygen source and is reduced to N_2, leaving non-negligible quantities of NO and some residual N_2O.
- Alternative production processes could be envisaged: in the past, some manufacturers used air oxidation rather than nitric acid oxidation to produce adipic acid, but this process was abandoned because of poor product quality; research has been carried out on a butadiene carbonylation process, but it was too costly.

The effectiveness of the end-of-pipe technologies ranges from 90% to 99%. Bates (1998) quotes a reference which stated that the cost of abatement is below 160 ECU/t N_2O without giving any details of the cost assumptions (which we have converted to US$ 179/t N_2O using an average 1998 exchange rate of 1 ECU = US$ 1.12109).

5.10 SUMMARY OF CONTROL TECHNIQUES FOR NON-GREENHOUSE GAS EMISSIONS

5.10.1 Carbon monoxide

Sources of CO emission include vacuum distillation, catalytic cracking (mainly catalyst regeneration - usually the major source), thermal cracking, blowdown systems, and exhaust from boilers and compressor engines. Waste heat CO boilers may be used to reduce CO emissions from fluidized-bed catalytic cracking, while emissions from moving-bed catalytic cracking are incinerated to negligible levels by passing the flue gases through a process heater fire-box or smoke plume burner.

5.10.2 Sulphur compounds

Sources of emissions of sulphur compounds include vacuum towers, catalytic crackers, fluid coking, sulphur recovery plant, incinerators, caustic regeneration, flares, vents and boilers. Oxides of sulphur from catalyst regeneration may be removed by passing the flue gases through a water or caustic scrubber. Tail gas from a Claus sulphur-recovery unit (which recovers up to 97% of the sulphur deriving from sour gas streams) contains a variety of pollutants from direct process oxidation reactions including sulphur compounds including SO_2 and unreacted H_2S, and other furnace side reaction products such as reduced sulphur compounds and mercaptans (e.g. COS, CS_2). Emission reduction from the Claus process is normally achieved by one of three techniques. Extending the Claus reaction into a lower temperature liquid phase results in overall higher sulphur recoveries (over 99%) with a corresponding reduction in sulphur compound emissions in the tail gas. Tail gas scrubbing (with oxidation or reduction) enables recovery and recycling of sulphur compounds back into the Claus process. Claus plant emissions may also be directly incinerated to convert the more hazardous reduced sulphur compounds to SO_2 under proper combustion conditions for release to a stack.

5.10.3 Nitrogen compounds

Sources of emission of oxides of nitrogen (NO_x) include process heaters, boilers, compressor engines, catalyst regenerators and flares. During the combustion of fuel, NO_x are formed in the boiler from the oxidation of nitrogen contained in the air and in the fuel. Factors that affect NO_x formation include the combustion chamber design and temperature, the amount of excess air present, and the amount of nitrogen in the fuel itself. The most effective measure for controlling NO_x emissions is to minimise their formation through modified combustion techniques. This includes controlling operational parameters and changing furnace design for new facilities.

Ammonia may be emitted from catalyst regenerators and sour water strippers. CO boilers (see above) convert the ammonia in catalyst regenerator gas to oxides of nitrogen.

5.10.4 Hydrocarbons

Sources of VOC emission include process plant, fugitive losses from components, tanks and transfer operations, and products of incomplete combustion in flares, boilers and compressor engines. Losses from vacuum distillation, catalytic and thermal cracking, sweetening and other process units may be vented into blowdown systems or fuel gas systems, or incinerated in flares, furnaces, or waste heat boilers (generally >99% efficiency). Control of fugitive sources is described above under methane. Flares routinely burn relatively small volumes of off-gases but potentially may take large volumes during an emergency shut-down. Under good operating conditions over 98% VOC destruction efficiency is possible in a flare, with most of the residual VOC in the form of methane. Flare performance can be optimised (to over 99% destruction efficiency) through the use of steam injection to provide turbulence for efficient mixing and to entrain air for improved combustion; and through good maintenance (£80/t to £400/t). Vapour displacement losses during tankage movements may be largely eliminated (99% efficiency) using vapour return systems (£225/t to £1125/t). Floating covers which rise or fall with the level of liquid in the tank can reduce emissions by up to 95% by minimising the headspace volume. Secondary seals may be fitted to minimise evaporative emissions from the space between the tank shell and the floating roof rim. Breathing losses due to changes in ambient temperature can be reduced by painting tanks with a light coloured reflective material. Controls for storage tanks are estimated to be 90% effective at a cost of £100/t to £900/t. The vent on a ship or rail tanker that is being loaded or off-loaded into a stock tank can often be connected to the stock tank vent system in order to transfer the gases displaced from the vessel being filled into the vessel being emptied. This system of total containment is sometimes known as “back-balancing”.

5.10.5 Toxic organic micropollutants

Refineries are unlikely to be a significant source of dioxins, although they might be present in trace amounts in combustion exhausts. Polyaromatic hydrocarbons (PAH's) are likely to be emitted from boilers, flares and other combustion sources. The most effective abatement measures will focus on optimising combustion conditions (higher temperature, improved turbulence, improved combustion control).

5.10.6 Heavy metals

Trace quantities of heavy metals may be released from combustion sources, probably mainly in the form of particulates (see below).

5.10.7 Particulates

Sources of particulate emission include vacuum distillation, catalyst regenerators, thermal cracking, blowdown systems, boilers (particularly burning heavy fuel oil), process heaters, and incinerators. In fluidized-bed catalytic cracking, particulate emissions are controlled by cyclones and/or electrostatic precipitators. In moving-bed catalytic cracking, particulates may be controlled by high-efficiency cyclones. Particulate emissions from boilers and other combustion sources can be reduced by optimising the boiler design and operating conditions coupled with electrostatic precipitators.

5.10.8 Fugitive sources

Control techniques for fugitive sources are given in EEA (1996):

Component	Fugitive control techniques
Pipeline valves	monitoring and maintenance programs
Open-ended valves	Installation of cap or plug on open end of valve /line
Flanges	Monitoring and maintenance
Pump seals	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Compressor seals	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Process drains	Traps and covers
Pressure/relief valves	Rupture disks upstream of relief and/or venting to a flare

5.11 SYNTHESIS OF GREENHOUSE GAS REDUCTION OPTIONS

As we saw in **Chapter 4**, CO_2 represents by far the largest emissions of greenhouse gases in refineries; the largest emission sources are associated with energy use:

Source	**Percent of refinery CO_2 emissions**
Oil and gas fuel firing of furnaces and boilers	65%
Regeneration of cat cracker catalyst	16%
Flares	< 3%
Methane steam reforming to make hydrogen	2%
Incineration and effluent processes	1%
Power (55% imported)	13%

and typical CO_2 concentrations are:

- From combustion plant, furnaces, boilers, flares and FCC regenerators: about 13% CO_2.
- From gas turbine power generators or machine drivers: about 3% CO_2.
- From steam reforming process for H_2 generation: 100% CO_2.

The table on the following pages summarises CO_2 emission reduction options for refineries. Those techniques which reduce energy consumption will also reduce associated CH_4 and N_2O emissions.

Source	Percent of sector CO_2 emissions associated with source	CO_2 reduction technique	CO_2 reduction efficiency for this source	Maximum CO_2 reduction potential for whole sector	Cost, US$/t CO_2
Entire refinery sector	100 %	Carbon-free energy sources: nuclear, solar, wind, geothermal, hydro	100 %		Not known
		Alternative carbon sources[*]: (coal), natural gas, coal-bed methane, deep sea gas hydrates, biomass, wastes and sewage	Up to 33% reduction projected for 'co-production' facilities. Up to 90% reduction for ethanol fuel produced from biomass (full life-cycle basis)		30-100 for ethanol fuel from biomass
		Refinery process optimisation: linear programming	Not known		Savings
Specific refinery processes	Refinery-specific	Improved catalysts Improved separation using membranes Bioprocessing Recycling refinery sludges	Process-specific; published data not identified	10-20% reduction in US refinery emissions achievable within a decade	Savings; published data not identified

[*] Alternative carbon sources only lead to emission reductions where they enable more efficient carbon utilisation or energy efficiency.

Source	Percent of sector CO_2 emissions associated with source	CO_2 reduction technique	CO_2 reduction efficiency for this source	Maximum CO_2 reduction potential for whole sector	Cost, US$/t CO_2
Power generation	13 %	Cogeneration	21 % relative to on-site oil-fired generation	1.2 % taking into account that 55% of power is imported	- 6.5 relative to onsite generation; - 48 relative to purchased power
		Fuel cells	25%	1.5 % taking into account that 55% of power is imported	Not known
Process furnaces and boilers	65 %	Dividing wall distillation technology	30 % reduction on energy used in distillation processes	Not known	Capital savings of 25%
		Compact heat exchangers	Not known	Not known	Capital savings of 69-84%
		Waste heat boilers	14 %	11 %	Not known
		Miscellaneous energy efficiency measures	10-20 %	8-16 %	-20 to -50
Power generation, process furnaces and boilers, FCC catalyst regeneration, incineration processes	95 %	CO_2 capture and disposal	80-99 %	76-94 %	20-90 (capture by absorption); 2-11 (ocean/geological storage)
Methane steam reforming	2 %	Cryogenic CO_2 capture	High	2 %	10’s
Flares	< 3 %	Reduced flaring	50 %	1.5 %	Savings
Entire refinery plus petrochemicals sector	100 %	“Energyplex” concept	100 %	100 %	Not known

6 Other trends influencing greenhouse gas emissions

6.1 PRODUCT MIX AND SPECIFICATION

In recent years there has generally been an increase in pressure on the industrial sector to produce ‘green products’, such as unleaded petrol, low benzene and sulphur fuels, and low aromatic solvents.

Restrictions on fuel sulphur content, in particular, have greenhouse gas implications for refineries. Product specifications are tightening - in the EU, for example, diesel sulphur content has been limited to 0.05% w/w since 1996; provisional specifications for 2000 indicate gasoline sulphur content of 100 ppm; and some countries have limited the sulphur content of fuel oil to 1%. These pressures are not restricted to the heavily industrialised nations - in India, for example, a directive issued by the Supreme Court will require all diesel to meet a 0.25% maximum sulphur content requirement by April 1, 1999 (currently most diesel for vehicle use has a sulphur content of 1%) and refineries are required to install diesel hydrodesulphurization units.

At the same time, reserves of low sulphur crude are diminishing and over the next twenty years crudes will on average become heavier and with a higher sulphur content. This means that the crudes will require more processing, both to maintain the yield of lighter ends and to remove increased amounts of sulphur. This in turn will increase the amount of energy required.

Hydrodesulphurisation is a high-pressure (150-250 psi) and high-temperature (200-425^{o}C) process that uses hydrogen gas to reduce the sulphur in petroleum fractions to H_2S, which is then separated from the fuel and oxidised to elemental sulphur in the sulphur recovery plant. The energy requirement for hydrodesulphurisation in 1992 was reported by Comprimo (1992) as 105-135 tonnes of standard refinery fuel (SRF) per day for a European 30,000 t/day refinery, where SRF has an energy content of 40,200 MJ/t SRF. From this we can calculate an energy requirement of about 4,200 to 5,400 GJ per tonne crude processed at a time when European diesel was restricted to 0.3% sulphur content. Modelling changes in the sulphur content of various fuels; and restrictions on gasoline lead, benzene and aromatics content; Concawe (1995) concluded that by 2010 refinery specific energy consumption would rise by 50% (for a scenario in which fuel oil demand remained a constant proportion of refinery intake) or 75% (for a scenario in which fuel oil demand falls by one third, from 18% to 12% of refinery intake) relative to a 1990 baseline. ERM (1994) indicated increased CO_2 emissions of 5 to 14 t CO_2 per tonne of additional sulphur removed.

In California, where diesel sulphur content was capped at 0.05% in 1993 compared with pre-1993 levels of about 1%, diesel cost about 1 to four cents more than in other US states (CARB, 1997).

6.2 MARKET FACTORS

Changes in operation of current refineries and the construction of future refineries are governed by a number of factors. For example, future trends in crude availability and market demand, together with environmental issues and the previously described pressure for green products, will all have a significant effect and must be considered.

There is obviously a finite amount of crude oil reserve available. As a result of a shift in market demand towards lighter products and a general awareness that limited supplies should be used as efficiently as possible, there has gradually been a move towards maximising the conversion to marketable products which currently can only come from crude (such as car and aviation fuel), rather than products for use in sectors (such as power generation) where other fuels (fossil or renewable) could be used.

Further, as previously described, there is great variation in the composition of crudes and light, low sulphur crudes are in greater demand than crudes which require more, deeper processing. It is anticipated that demand for light crudes will continue to grow disproportionately with supply. This will result in a more marked price differentiation between crudes of different gravity, so that the extra cost of processing heavy crudes is offset by a cheaper feed.

In combination, the above two factors strongly indicate that future trends will continue towards larger and more complex refineries with the capacity for deep conversion processing of heavier crudes to lighter products. To compete with this, current refineries will have to expand to incorporate more processing units and increased desulphurisation capacity. The latter will require more hydrogen, but the extra can be produced by steam reforming of residual matter in gasification units.

Demand for petroleum products is likely to grow over the next twenty years, although there are likely to be strong regional differences in the growth. The following table shows projections of oil use for primary energy supply in 1990 and 2020, taken from the IIASA/WEC (1998) “middle course” scenario B.

Region	**Oil use for primary energy supply, Mtoe**		**% change**
	1990	**2020**	
World	3060	3780	+ 24
North America	834	781	- 6
Latin America plus Caribbean	244	503	+ 106
Middle East plus Africa	245	505	+ 106
Europe	683	494	- 28
Former Soviet Union	409	311	- 24
Asia	202	539	+ 167
Pacific	448	652	+ 46

Forecasts of petrochemicals production were presented in **Chapter 3**.

The greenhouse gas implications of these trends are modelled in **Chapter 9**.

7 Regulatory regimes

This Section focuses on environmental regulations and agreements directly implicating greenhouse gases. These can be thought of as falling into two groups:

- regulations/agreements which are driven by the greenhouse effects of greenhouse gases;
- regulations/agreements which are driven by other environmental impacts of greenhouse gases.

Many countries around the world, and various international bodies, have introduced other environmental regulations and agreements which do not directly concern greenhouse gas emissions; and non-environmental regulations which affect emissions and wastes. These regulations are not dealt with in this report, except in broad terms in the section concerning future trends.

7.1 THE UN FRAMEWORK CONVENTION ON CLIMATE CHANGE (UNFCCC) AND THE KYOTO PROTOCOL

The emission of greenhouse gases and the subsequent warming effect is one of the major global environmental issues. The global warming issue was discussed at the United Nations' Conference on Environment and Development (UNCED), held in June 1992 in Rio de Janeiro, Brazil. This resulted in “Agenda 21”, consisting of a series of international programs designed to avoid future environmental problems. A key aspect of these programs is the need for sustainable development, which means achieving economic development compatible with environmental protection.

In 1992 the United Nations Framework Convention on Climate Change (UNFCCC) was also established, to address and promote awareness of problems linked to climate control. One of the primary objectives of the UNFCCC is to reduce emissions of greenhouse gases on a global basis. With this aim, countries (known as Parties) participating in the Convention adopted the Kyoto Protocol in 1997 (United Nations, 1997).

The Kyoto Protocol was adopted by 166 nations. It quantifies greenhouse gas emission limitation/ reduction targets for 38 developed countries (those most responsible for current levels of greenhouse gas pollution), and creates significant incentives for developing countries to control their emissions as their economies grow. The developed countries are referred to as ‘Annex B Parties’, where a Party is either a single nation, such as the US, or a group of nations, such as the European Union.

The Protocol is still a work in progress and is subject to further negotiations later this year. It has yet to be agreed by all member states, and will only enter into force after it has been ratified by at least 55 Parties with combined emissions equal to at least 55% of the total 1990 emissions by Annex B Parties.

As the Protocol currently stands, Annex B Parties are together committed to reducing emissions from developed countries in the years 2008 - 2012 to an average of 5.2 % below levels from a chosen base year. The Protocol restricts (by varying amounts) emissions of the six main greenhouse gases, namely; carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6). Most of the Annex B Parties have targets for CO_2, CH_4 and N_2O based on their 1990 levels and may select either a 1990 or 1995 base year for HFCs, PFCs and SF_6. Parties that are developing market economies, such as the Ukraine, may select a different base year for all six gases. To illustrate that they are complying with the Protocol, Parties are required to inventory and report emissions.

Individually, the Parties have accepted varying targets based on the principle of ‘differentiation’. This system allows for the fact that some countries are more capable of reducing their emissions than others, due to a number of factors, such as their current levels of pollution, how they produce and use energy, their access to clean technologies *etc*. For example, EC countries are committed to reducing their emissions to be 8% lower than they were in 1990, while Japan has a target of 6% reduction. It has been estimated that in real terms in the US, at the current economic growth rate, this actually represents a 30% reduction in the emissions which would be occurring by 2008.

The emission targets for all Annex B Parties are listed in the following table:

Party	Emission commitment/ % of (base year) levels
Australia	108 (1990)
Austria	92 (1990)
Belgium	92 (1989)
Bulgaria	92 (1990)
Canada	94 (1990)
Croatia*	95
Czech Republic*	92
Denmark	92 (1990)
Estonia*	92
European Community	92 (1990)
Finland	92 (1990)
France	92 (1990)
Germany	92 (1990)
Greece	92 (1990)
Hungary	94 (1990)
Iceland1	110 (1990)
Ireland	92 (1990)
Italy	92 (1990)
Japan	94 (1990)
Latvia*	92
Liechtenstein	92 (1990)
Lithuiania*	92
Luxembourg	92 (1990)
Monaco	92 (1990)
Netherlands	92 (1990)
New Zealand	100 (1990)

Norway	101 (1990)
Party	**Emission commitment/ % of (base year) levels**
Poland	94 (1988)
Portugal	92 (1990)
Romania	92 (1989)
Russian Federation*	100
Slovakia*	92
Slovenia*	92
Spain	92 (1990)
Sweden	92 (1990)
Switzerland	92 (1990)
Ukraine*	100
United Kingdom	92 (1990)
USA	93 (1990)

* Countries that are undergoing the process of transition to a market economy and have not yet selected a base year for emissions reductions.

It is intended that developing countries, such as India and China, should be encouraged to participate by the market-based policies in the Protocol. Policies included in the Protocol are also designed to generally help to lower the cost of reducing emissions and to spur the creation of clean technology in all countries. The implementation and operation of such policies has yet to be decided, but they include emissions trading, project-based credit trading (joint implementation, JI) and the clean development mechanism (CDM). These are described in further detail below. Activities which produce ‘sinks’, which absorb and store carbon, such as planting trees, can also be offset against emissions targets.

Emissions trading enables an Annex B Party which is exceeding its emissions target to buy emissions permits from a Party which has emissions below its target. Thus an Annex B Party would be able to choose between reducing emissions through domestic measures *vs*. purchasing those reductions on the emissions permit market. This enables greater flexibility in terms of cost control, while the required net effect of reduction in global emissions is still met. This policy may also be extended to allowing trading between specific companies within an Annex B Party.

Through project-based credit trading, also referred to as joint implementation (JI), an Annex B Party will receive credit towards meeting its emissions target by supporting specific projects that reduce or sequester emissions in another Annex B Party. This may also be extended to specific companies within an Annex B Party; for example, an EC-based company would have the option to reduce emissions at its home facility, or to trade those reductions for financing an emissions reduction project in another Annex B Party.

The clean development mechanism (CDM) essentially involves joint implementation between Annex B Parties and developing countries, enabling both emissions permit trading and project investment. The aim of CDM is to lower the cost of compliance for Annex B Parties, while promoting clean technology and participation in the developing world. There is also significant incentive for early action since Annex B Parties may count reductions acquired through the CDM starting in 2000 against their first budget period of 2008 - 2012.

7.2 UN ECE PROTOCOLS

The United Nations Economic Commission for Europe (UN ECE) covering UN ECE Europe (which is most of geographical Europe) and North America has established a number of Protocols under the Long Range Transboundary Air Pollution Convention aiming to reduce pollution which crosses international frontiers. These Protocols are not legally binding on signatories but are seen as very influential in the UN ECE region.

7.2.1 SO_2 Protocol

The 1985 Helsinki Protocol on the reduction of sulphur emissions or their transboundary fluxes entered into force in 1987. The Protocol called on signatories to reduce their national annual sulphur emissions by at least 30% by 1993 from a 1980 baseline.

7.2.2 NO_x Protocol

The 1988 Sofia Protocol concerning the control of emissions of nitrogen oxides or their transboundary fluxes entered into force in 1991. The Protocol called on signatories to reduce their national total emissions of nitrogen oxides to 1987 levels by the end of 1994. Signatories were also to apply national emission standards to major new or substantially modified stationary sources.

7.2.3 VOC Protocol

The 1991 Geneva Protocol concerning the control of emissions of volatile organic compounds or their transboundary fluxes calls for a 30% reduction in emissions of total non-methane VOCs by 1999, relative to a baseline year which each signatory may select between 1985 and 1990. A number of exclusions were successfully introduced by signatories - for example, North Sea oil exploration and production was excluded. An annex gives guidance on the application of POCP and similar approaches for minimising the environmental impact of residual emissions, so giving international credibility to a differential approach.

7.2.4 POPs Protocol

On 24 June 1998 in Aarhus the Executive Body of the UNECE adopted the Protocol on Persistent Organic Pollutants. It focuses on a list of 16 substances that have been singled out according to agreed risk criteria. The substances comprise eleven pesticides, two industrial chemicals and three by-products/contaminants. The objective is to eliminate any discharges, emissions and losses of POPs to the atmosphere. The Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (DDT, heptachlor, hexaclorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that will be banned. It also requires signatories to reduce their emissions of PCDD/Fs, PAHs and HCB below their emissions in 1990 (or an alternative year between

1985 and 1995 selected by the party). For the incineration of municipal, hazardous and medical waste, it lays down specific limit values which shall not be exceeded.

7.2.5 Multi-Pollutant, Multi-Effects Protocol

A new multi-pollutant Protocol is currently under development. This will address photochemical pollution and acid rain through provisions for VOCs, NO_x, sulphur oxides and ammonia.

7.3 DIRECTIVES AND OTHER MEASURES OF THE EUROPEAN UNION

7.3.1 The Integrated Pollution Prevention and Control Directive

In the IPPC Directive[1] installations, rather than processes, are the regulated entities. Refinery facilities will be covered by IPPC. The IPPC Directive does not require that each installation be regulated by a single regulatory authority, but it does require that each site has a single permit. This is described as "co-ordinated" permitting.

Although the IPPC directive uses the term Best Available Techniques (BAT) rather than Best Available techniques not Entailing Excessive Costs (BATNEEC) it is clear that costs, advantages and economic feasibility are to be taken into account.

The European Commission will publish a series of BAT reference documents and organise an information exchange between member states and industry. The European Commission must publish the results of this information exchange every three years. However, the final decision on what is or is not BAT for a particular site will be taken on a site specific basis. The competent authority will simply have to "take into account" the techniques published in the BAT reference documents. The Directive does not say that the regulators should specify BAT. It says that he shall write conditions *based on* BAT, taking into account local conditions.

The BAT reference documents are being developed by the European IPPC Bureau, based in Seville. The production of the BAT reference documents as a whole is a 5 year project starting in 1997; the document for refineries is due for development in 1999.

As well as emissions and releases, IPPC will also cover contaminated land, energy efficiency, noise, raw material consumption, accident prevention, environmental impact assessment and waste issues.

The IPPC directive could allow the Commission to promulgate daughter directives setting community wide uniform emission limits. However, this approach is probably unlikely as one of the principles of IPPC is a site specific approach.

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[1] Council Directive 96/61/EC concerning integrated pollution prevention and control- OJ No L 257/26, 10.10.96.

7.3.2 The “Stage 1” Directive

This Directive[2] aims to reduce VOC emissions arising during the loading/unloading, transportation/distribution and storage of gasoline during all stages from the refinery to the filling station storage tank.

The types of measures envisaged involve modified tanks to prevent losses and vapour return systems to contain and recover losses.

7.3.3 The draft Directive on petrol and diesel fuel quality

This draft Directive[3] specifies a maximum permitted benzene content of 1.0% v/v for petrol, to be achieved by 1 January 2000 (or 1 January 2005 in the event that a permitted derogation is allowed for a given Member State). In exceptional circumstances, where a sudden change in the supply of crude oils renders compliance difficult, the Commission may authorise higher limits for a period not exceeding six months. Presently typical benzene contents of petrol vary between 0.3% v/v and 4.7% by volume for both leaded and unleaded fuels.

7.3.4 Air quality directives

Air quality standards and guidelines have been set for nitrogen dioxide by EC Council Directive 85/203/EEC and are summarised in the table below:

Description	Criteria based on	Value, μg/m^3
	Calendar year of data:	
Limit value	98%ile of hourly means	200
Guide value	98%ile of hourly means	135
Guide value	50%ile of hourly means	50

The Directive sets a *limit value* for nitrogen dioxide of 200 μg/m^3 for the 98th percentile of hourly mean concentrations - i.e. the average concentration during 98% of the hours during a year should be less than 200 μg/m^3 - which conversely implies that the limit value may be exceeded for 2% of the hours. The Directive also sets two *guide values*.

Air quality standards and guidelines which have been set for sulphur dioxide are summarised in the following table:

Description	Criteria based on	Value μg/m^3
Limit value	Pollution year; median of daily values	80 if smoke(1) >34 120 if smoke <= 34
Limit value	Winter; median of daily values October-March	130 if smoke > 51 180 if smoke <=51

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[2] European Parliament and Council Directive 94/63/EC on the control of VOCs resulting from the storage of petrol and its distribution from terminals to service stations. Published in the Official Journal of the European Communities, No C365 of 31.12.94.

[3] Common position (EC) No .../97 adopted by the Council on .... with a view to adopting Directive 97/.../EC of the European Parliament and of the Council relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC.

Limit value[2]	Pollution year; 98%ile of daily values	250 if smoke>128 350 if smoke <= 128
Guide value	Pollution year; mean of daily values	40-60
Guide value	24 hours; daily mean values	100-150

Until recently, air quality standards and guidelines for sulphur dioxide were expressed in conjunction with values for black smoke or other measures of particulate concentrations. This forms the basis of the current EC Directive (80/779/EEC), which sets a range of criteria.

The Framework Directive on Air Quality (Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management) sets out the objectives and requirements of legislation on air quality across the European Union. The objectives of the Directive are to:

- define and establish objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole;
- assess the ambient air quality in Member States on the basis of common methods and criteria;
- obtain adequate information on ambient air quality and ensure that it is made available to the public as necessary;
- maintain ambient air quality where it is good and improve it in other cases.

The Directive defines the rationale for:

- selecting pollutants for consideration in subsequent daughter directives;
- setting limit values, target values and alert thresholds;
- defining the time frame for derivation of values;
- quantifying the number of sampling points needed, and criteria related to the siting of monitors;
- selecting methods for measuring and estimating pollutant levels.

The Directive notes a number of factors which may be taken into account when setting limit values and alert thresholds, though the list is indicative, rather than exhaustive. These factors include:

- degree of exposure of sectors of the population, and in particular sensitive sub-groups;
- climatic conditions;
- economic and technical feasibility of attaining targets;
- long-range transmission of pollutants, including secondary pollutants such as ozone.

Under this Directive so far, technical work on SO_2, NO_x, fine particles, lead, benzene and CO has already been completed.

7.4 SOME NATIONAL REGULATIONS

The following sections aim to illustrate some of the approaches adopted by individual countries; it is not intended to be a comprehensive survey all relevant national regulations.

7.4.1 Germany

The basis of all German regulations for air quality control is the “Act for Protection from Harmful Environmental Effects of Air Pollution, Noise, Vibrations and Similar Occurrences” or Bundes-Immissionsschutzgesetz (BImSchG) of 1974 amended in 1985.

This act states that sites which are capable of causing environmental damage may require a permit to operate. It also requires permitted sites to operate in such a way as to avoid environmentally damaging effects and to make provision to limit environmental releases through implementation of “Stand der Technik” (state of the art). Stand der Technik is the current state of developing techniques, facilities or industrial practice that have been proven effective for reducing emissions.

The Act is implemented by 22 Federal Ordinances or Bundes-Immissionsschutzverordnung (BImSchV). The purpose of these Ordinances is to enable the licensing authorities to ensure uniform implementation of statutory regulations across all the Länder of the Federal Republic of Germany.

The most important of these is the fourth Federal Ordinance (4. BImSchV) on Facilities Subject to Licensing. This lists and describes the categories of installation that require permits under the BImSchG.

The next tier of regulation is the Technical Instruction on Air Quality Control or “Technische Anleitung zur Reinhaltung der Luft -TA Luft, vom 27 Februar 1986”. This sets out emission limits and suggests abatement techniques. It is at this lowest tier of legislation that detailed requirements affecting the operation of specific processes are specified.

The TA Luft instructions determine the requirements to be met by installations that require a licence. The TA Luft of 1986 has been updated by the 1992 “Dynamisierungsklausel TA Luft”. This presents refined emission limits and a more up to date description of the “state of the art”.

Work has started to prepare BAT notes for refineries in terms of emission reduction and energy use. A preliminary report is expected in summer 1999, and the work is due for completion at the end of 1999 (UBA, 1999).

7.4.2 Italy

The Italian Constitution of 1948 does not contain any specific provision providing for the protection of the environment. Italian environmental legislation is contained mainly in statutes passed by Parliament. Most of the legislation originates from EC Directives. Jurisdiction over environmental matters is divided between state, regions, provinces and municipalities.

The national government has authority to set law and regulations relating to the environment. The regional authorities must then comply with these. For new plant, the regions are not pre-empted by national requirements and are able to set guidelines (although not regulations) for use within their own territory. The provinces and municipalities are mainly in charge of monitoring compliance with environmental regulations and may intervene if necessary to ensure compliance.

Air pollution is governed by Presidential Decree No. 203 of 24 May 1988 (DPR 203) and by Ministerial Decree No. 51 of 12 July 1990 which gives guidelines for the control of polluting emissions from existing industrial plants and the fixing of maximum emission values.

For a new installation authorisation is needed to operate and the authorising authority sets emission control criteria within this. Our best information is that the authorising authority will set emission limits rather stricter than those specified for existing plants in ministerial decree number 51.

The authority in charge of monitoring compliance requirements as prescribed in the plant authorisation (usually the province) is authorised to inspect the plants. If violations of the authorisation occur, the region can send warnings, suspend the operation of the plant or even revoke the authorisation. Violations of emission limits and failure to obtain the prescribed authorisations carry criminal sanctions.

Ministerial Decree No. 51 applies to existing plants only, and seems to be modelled on the German TA Luft. Annex 5 to the Ministerial Decree No. 51 gives very limited guidance on the selection of abatement technologies. The frequency of emission sampling and measurement is laid down in the plant authorisation by the relevant competent authority but Ministerial Decree No. 51 states that the frequency will normally be annual.

7.4.3 Sweden

Swedish law is based on a statute law system. The parliament (*Riksdag*) enacts legislation but can delegate to the government the task of making more detailed prescriptions in ordinances. Statutory texts are usually quoted by year and number in the official series *Svensk forfattningssamling* (SFS).

Environmental legislation was introduced around the late 1960s. There are about 200 acts and ordinances containing environmental regulations. Public administration is carried out by the State, the 24 counties and 227 municipal authorities. These latter two parties are responsible for implementing and enforcing statutes. The National Environment Protection Agency is the central supervisory agency. County administrations and municipal environment committees supervise individual environmentally hazardous activities.

The central framework law is the Environment Protection Act (SFS 1969:387), and the related implementing ordinance is the Environmental Protection Ordinance (SFS 1989:364). The Environmental Protection Act covers pollution of land, water, air and almost all other forms of pollution (including aesthetics) but not radiation. The Act only applies to stationary sources of pollution (control of mobile sources is the subject of other statutes, including the Automobile Exhaust Act (SFS 1986:1386)).

The Environment Protection Act brings together a body of provisions governing various kinds of hazard originating from permanent facilities. The basic principle is that such hazards should be prevented as far as practically possible. The obligation to take preventive measures should be decided on the basis of what is technically feasible. The authorities enforcing the act may order action to be taken, in some cases with fines for non-compliance, or they may prohibit activities if the conditions governing them are not observed.

There are no general standards for air emissions in Sweden, with processes being considered on a case by case basis.

A large number of activities are subject to approval before being started or altered. The Environment Protection Ordinance lists three categories of activities. The enterprises which are the most polluting or likely to cause a nuisance, numbering about 3,000, are subjected to inspection procedures prior to receiving a permit. As a basis for the examination of the individual permit applications, use is sometimes made of guidelines from the national Environmental Protection Agency, which is Sweden's central environment control authority. These guidelines are not legally binding on the decision makers. Permits under the Environment Protection Act are issued by the National Licensing Board for Environment Protection (*Koncessionsnämnden för miljöskydd*) in Stockholm or by the county administrative boards.

The Chemical Products Act (1985) applies to all handling, import and export of chemical products. The emphasis is on the marketing of chemical products, but the Act also covers all stages of a chemical's life-cycle. The Act introduced the principle that if a specific product could be replaced by another product or another technology, resulting in reduced environmental impacts, then the first product should not be used.

7.4.4 Brazil

Brazil is a federal republic comprising 26 States and a Federal District (Brasilia). In 1973 the federal government brought environmental administrative and regulatory issues into a formal ministry called the Special Secretariat of the Environment (SEMA). Under Decree 73030 SEMA co-ordinated all federal pollution control activities, developed pollution standards and provided education and assistance to the state agencies (SEPA's). Law 1413 allowed state and municipal governments to regulate industrial operations. Decree 76.389 provided the federal government with the authority to shut down an industrial facility because of pollution problems. National air standards for particulates, sulphur dioxide, carbon monoxide and photochemical oxidants were defined in 1976 under Regulation 13.

In 1981 Law 6938 created the National Environmental System (SISNAMA), an environmental council administered by SEMA and mandated to implement a National Environmental Policy (PNMA). The PNMA's main goals were to identify priority areas for government action, develop pollution standards and promote sustainable development.

In 1988 a new federal Constitution reorganized the country's environmental strategy. Article 23 confirms that the federal Congress is responsible for environmental laws, but states can pass supplementary laws on industrial pollution control and several other areas of environmental protection. Article 225 requires environmental impact assessments for any projects potentially affecting the environment. A Secretary for the Environment (SENAM) was created to serve as a central agency; SEMA was replaced by the Institute of the Environment and Natural Renewable Resources (IBAMA) which was placed under the SENAM's authority. IBAMA's responsibilities are monitoring and enforcement and to provide technical assistance to the state agencies. CONAMA was created to serve SENAM as an advisory council, to help set standards and to institute licensing requirements for polluting activities.

While IBAMA's regulations and standards are as strict as those in the developed world, enforcement has been variable according to the differing needs and priorities of individual states. Two of the leading states are São Paulo, where the state SEPA is CETESB, and Rio de Janeiro where FEEMA is the SEPA. The 70,000 industrial sites between São Paulo and Rio de Janeiro make this corridor the most concentrated in all of Latin America and Brazil one of the most industrialised countries in the developing world. The most dominant industrial sectors in the region are petrochemicals, steel and mining. The federal government has based much of its legislation on laws set by the state agencies in São Paulo and Rio de Janeiro, who in turn took their regulations an standards from existing models in the United States.

The city of São Paulo established its first air and water regulations in 1964. CETESB was set up in 1973, and in 1975 the state Law 997 provided CETESB with the authority and mandate to register and license all enterprises. State Law 1.817 (1978) required any industry seeking a new location or expansion to obtain a license which set limits on what type and level of pollution was allowable. General air and water standards were set by the state legislature. CETESB defined eleven air quality control areas and used zoning and licensing requirements to relocate industries away from highly populated areas. Before a plant wishing to do business in São Paulo can begin operations, they must provide CETESB with details of pollution control equipment to be installed, treatment procedures and expected emission levels.

In the state of Rio de Janeiro, since November 1991, facilities in a number of industrial sectors have been required by law to undergo an annual environmental audit, the results of which are publicly available. This includes both oil refineries and petrochemical facilities. This has also been introduced in other states, Minas Gerais and Espirito Santo (1992), and some municipalities.

7.4.5 Japan

EIA (1998d) describes a number of measures taken in Japan as follows:

> "In 1989, the Japanese government established the Council of Ministers for Global Environment Conservation, a select group of public officials, to work on global environmental issues. In October 1990, the Council developed The Action Programme to Arrest Global Warming, Japan's national climate change programme for the period 1991 to 2010. The programme consists of a wide range of actions to be taken by both the government and the private sector to achieve CO_2 emissions targets as well as to reduce emissions of methane and other greenhouse gases, enhance carbon dioxide sinks (such as oceans and trees), and foster international co-operation on environmental issues.

> In November 1993 the Japanese Parliament (Diet) enacted the country's "Basic Environment Law", which provides a legal framework for coping with global warming and other environmental problems. The Basic Environment Plan, the operational part of this initiative, specifies measures that the national government must take, including surveys and research related to economic measures, as well as provisions for international co-operation on global environmental protection. The Action Program To Arrest Global Warming was incorporated into this broader plan. The Japanese Environment Agency is charged with implementing The Basic Environment Plan. In an effort to reduce carbon dioxide emissions in industry, the sector which accounts for about 60% of Japan's total carbon emissions, the government has promoted energy-saving technology under "The Energy Conservation Law". The law has improved standards on fuel combustion and provided for assistance in energy-saving capital equipment through special taxation measures and low-interest financing."

Environmental measures reported by the Petroleum Association of Japan (PAJ) include:

- As well as striving to produce clean and high quality petroleum products, the industry is also trying to harmonise with the environment in producing and transporting products.
- The industry is investing in research into technologies to improve the efficiency of petroleum refining processes.
- The industry is investing in research to make effective use of wastes from oil refineries. The Petroleum Energy Centre (PEC) is developing technologies to enable the use of some of the wastes generated by the refining process, including technologies for converting sludge and other wastes to new types of fuels, recovering metals from used catalysts, and creating improved asphalt pavement from spent FCC catalysts. They are also developing technologies that enable hydrogen sulphide from desulphurisation plants and recovered sulphur to be used effectively.
- The PEC is also conducting research into technologies that can improve the storage stability of petroleum products, including analysis of the mechanism by which petroleum products deteriorate and development of technologies to prevent sludge production.
- The industry has installed high performance flue gas desulphurisation facilities, denitrification equipment and waste water treatment facilities in oil refineries, and operates them using the best technology available. Accumulated investment in these facilities will amount to 1,250 billion yen between FY1969 to FY1995.
- The industry also seeks harmony with its surroundings through the planting of trees and the provision of "Green Belt" areas.
- The petroleum industry has also installed environmental control systems to carry out appropriate environmental measures in refineries and depots.
- Since September 1996, ISO environmental management systems have been put into effect and enacted as Japan Industry Standard (JIS).
- Each oil company makes every effort to improve further control systems for environmental conservation, including the adoption of the international environmental management systems.

Air pollution preventive measures reported:

Sulphur Oxides (SOx) reduction measures -

- To reduce SOx emitted from furnaces and boilers at refineries, the petroleum industry has installed high performance facilities to desulphurise flue gas generated in various processes, as well as removing sulphur oxide contained in the stack gas. The average sulphur content in home fuel has been substantially reduced to approximately 0.5% in recent years from 1.5% in 1970. Seventeen flue gas desulphurisation facilities have been installed at Japanese refineries at present, at a cost of approximately 3.2 billion yen.

Nitrogen Oxides (NOx) reduction measures -

- To reduce NOx emitted from furnaces and boilers at refineries, the industry has improved the combustion method through low NOx burners, as well as removing NOx in flue gas by denitrification facilities. At present, 45 flue gas denitrifiers have been installed at refineries in Japan.

Hydrocarbon(HC) emission preventive measures -

- Hydrocarbon is a principal component of petroleum. When evaporated and released into the air, hydrocarbon becomes one of the causes of photochemical oxidants. Therefore, the industry uses floating roof tanks or inner floating roof tanks to contain hydrocarbon vapour at refineries. In addition, hydrocarbon generated when shipping by tank trucks is collected using hydrocarbon recovery equipment.

Poisonous air pollution substance preventive measures -

- Countermeasures for environmental pollution problems by chemical substances have been focused mainly on health conditions by pollution from a few individual substances. The Air Pollution Control Law was amended in May 1996. Under this law, substances which already have a high environmental density level, like benzene, will be controlled by legislation. Other substances will be subject to further measures by 2000, through a framework relying on the self-controlling business. The petroleum industry published its "Control Program on Poisonous Air Pollution Substances", compiled by PAJ on 16th October 1996, and decided to proceed with various measures including a measure to reduce benzene density in gasoline to 1 vol% by the end of 1999.

Water pollution preventive measures reported:

- Water use and waste water at refineries is reduced through the recycling of industrial water. The industry also recovers oil from waste water by using oil separators. Furthermore, processed waste water is treated by sophisticated waste water equipment, including chemical treatment using coagulants, activated sludge, and activated charcoal. The water is then drained as clean water through guard basins and reservoirs positioned in front of the final drain outlet.

Based on the international movement established at the UN conference of 1992, the "Basic Environmental Law" was enacted in November 1993, and the "Basic Environmental Plan" was authorised by the Cabinet in December 1994.

The PAJ have also initiated the following steps to deal with environmental problems:

- Improvement in organisational and regulatory frameworks.

- Consideration for the environment in business activities and technological development.
- Consideration for the environment in international co-operation, emergency response, public relations, government policy and overseas activities.
- Based on the government's “Program to Arrest Global Warming”, formulated in October 1990, Japan has promoted specific measures to restrict CO_2 emissions. There is a movement to impose a tax on fossil fuels in order to restrict demand and to secure financial resources; however, there are many problems related to the introduction of new indirect tax, such as environmental tax (CO_2 tax). There is strong opposition to the latter from the oil industry, as petroleum products in Japan are already heavily taxed, reducing oil’s competitiveness relative to other energy sources. In order to restrict CO_2 emissions, the petroleum industry is actively developing and introducing new technology, including energy saving at oil refineries and co-generation systems.
- The PAJ also decided to study a self-active action program of global environmental conservation in all fields of the industry with co-operation of related committees concerned, centring around its Environmental Safety Committee. As a result, Self-Active Action Program Committee, composed of principals and vice chairmen of twelve special committees, was set up and the Committee drew up an action program. As its result, PAJ published in February 1997 the Self-Active Action Program for Global Environmental Conservation by the petroleum industry.

7.5 FUTURE TRENDS IN REGULATIONS

Around the world much of the focus of pollution control has been aimed at reducing local nuisance (such as visible plume, odour) or hazard (e.g. air toxics); or regional acidification (SO_x, NO_x). Such regulations are likely to spread geographically, and to see ever-tightening release standards.

Historically, regulations have tended to focus on one medium at a time, and often one pollutant. This has sometimes created situations in which a release limit for a given substance could be achieved by means which would increase the release of another pollutant. In the future more and more countries are likely to follow an integrated approach whereby the best overall environmental solution is sought.

In the USA, a variety of standards have been developed for individual source types. National emission standards for hazardous air pollutants (NESHAP) have been set for refineries which requires major refineries to meet emission standards reflecting the implementation of the maximum achievable control technology (MACT). The UK process guidance notes similarly set standards according to source. Other countries around the world continue to establish similar standards. Refineries and petrochemical processes, being significant point sources, usually attract attention.

These regulations have not, hitherto, specifically dealt with CO_2 or other greenhouse gas emissions. Action to date has generally focused on voluntary programmes such as Canada’s Climate Change Voluntary Challenge and Registry (VCR), launched by the Federal Government in 1995 to encourage and co-ordinate voluntary action. There has been much debate over the implementation of carbon taxes, but only a few countries have introduced them to date. The EU’s IPPC Directive (see above) includes requirements for energy efficiency which are intended to reduce greenhouse gas emissions. It remains to be seen to what extent countries set specific CO_2 emission limits in the future.

8 Modelled scenarios

We have modelled three future scenarios of CO_2 emissions up to the year 2020, together with baseline emissions, and we have examined costs for two of the scenarios. The three scenarios may be summarised as:

(1) "Energy efficiency" - focusing on reductions which can be achieved through reducing energy use, with cost savings.

(2) "Maximum CO_2 reduction" - in which CO_2 capture/disposal is added on top of the first scenario.

(3) "Low sulphur future" - a scenario in which energy use and hence greenhouse gas emissions increase due to requirements for increased upgrading and desulphurisation.

The baseline projection and scenarios are described in more detail in **Section 8.1** below. **Sections 8.2 and 8.3** present emission projections and cost projections respectively. All figures referred to are to be found at the end of Chapter 8.

8.1 DESCRIPTIONS OF SCENARIOS

8.1.1 Baseline projections

A refinery baseline projection of CO_2 emissions from 1990 to 2020 is shown in **Figure 8.1**. This is based on:

- the 1994 CO_2 emission estimate given in **Chapter 4**:

Region	Emissions, Mt CO_2/yr
North America	199.3
Central/South America	43.3
Europe	160.8
Former Soviet Union	56.0
Africa + Middle East	78.7
Pacific	54.4
Asia	94.4
World total	**686.9**

- emissions for 1990-1997 were scaled from the 1994 estimates using historical trend data from BP (1998) for refinery throughputs;
- emissions for 1998 to 2000 were projected linearly from 1997, so that the overall 1990-2020 changes by region match the World Energy Council Scenario B for oil used as primary energy (IIASA/WEC, 1998):

Region	**Oil use as primary energy, Mtoe/yr**		**% change, 1990 to 2020**
	1990	2020	
World	3065	3785	23
N. Am.	834	781	-6
SAm/Carib	244	503	106
Mid-East+NAfrica	245	505	106
Euro	683	494	-28
FSU	409	311	-24
Asia	365	985	170
Pacific	285	206	-28

The baseline indicates CO_2 emissions rising from 685 Mt CO_2/yr in 1990 to 843 Mt CO_2/yr in 2020.

A petrochemicals baseline projection of CO_2 emissions from 1990 to 2020 is shown in **Figure 8.2**. This is based on:

- the 1996 CO_2 emission estimate given in **Chapter 4** (world total of 520 Mt CO_2/yr);
- scaled by region during 1990-1998 using a 1998 regional distribution of ethylene capacity (Chang, 1998b);
- regional and world emission estimates for 1990-1998 scaled using historical trends in ethylene capacity (Chang, 1998b);
- projections for 1999-2005 using projected compound growth rates given by Chang (1998b), and more modest compound growth rates for 2005-2020:

Region	**Compound growth rate, %/yr**		
	1999-2005	**2005-2010**	**2010-2020**
North America	2.62	2	2
Central/South America	7	4	2
Europe	2.47	2	2
Former Soviet Union	6	3	2
Africa plus Middle East	10.2	5	2
Pacific	2.25	2	2
Asia	6	3	2

The baseline indicates CO_2 emissions rising from about 400 Mt CO_2/yr in 1990 to over 1,000 Mt CO_2/yr in 2020.

8.1.2 Scenario (1): "Energy efficiency"

In this scenario we have assumed that:

- refineries introduce a package of energy efficiency measures (not defined in detail but see **Chapter 5** for example measures) which reduced emissions from process furnaces and boilers by 20%;
- of the 45% of refinery power generation which is on-site, 50% moves to cogeneration which reduces those emissions by 21%;
- refineries introduce measures to reduced flaring by 25%;
- the petrochemicals sector would introduce energy efficiency measures which would reduce emissions by 20%.

We further assumed that these measures would be introduced (linearly) over a 10-year period. We varied the ten-year period according to region:

Region	Implementation period
North America	1991-2000
Central/South America	2001-2010
Europe	1991-2000
Former Soviet Union	2001-2010
Africa plus Middle East	2001-2010
Pacific	1996-2005
Asia	2001-2010

8.1.3 Scenario (2): "Maximum CO_2 reduction"

In this scenario we have assumed that:

- additional measures are introduced on top of the Scenario (1) measures;
- the additional measures consist of end-of-pipe CO_2 capture/disposal techniques (not defined, but see **Chapter 5** for techniques) applied to process heaters, catalyst regeneration, reforming, and power; plus an increase in flare gas recovery from 25% to 50%;
- the end-of-pipe measures have an overall average CO_2 removal efficiency of 90%.

Again we assumed that the measures would be introduced (linearly) over a 10-year period. We varied the ten-year period according to region:

Region	Implementation period
North America	2006-2015
Central/South America	2011-2020
Europe	2006-2015
Former Soviet Union	2016-2025[a]
Africa plus Middle East	2016-2025[a]
Pacific	2006-2015
Asia	2016-2025[a]
[a] i.e. the measures are only half-implemented by the end of the period modelled.	

8.1.4 Scenario (3): "Low sulphur future"

In this scenario we assumed that:

- there are no CO_2 controls introduced;
- energy use in refineries increases to meet (undefined in detail) legislative limits on the sulphur content of fuels;
- energy use in refineries also increases through increasing requirements to upgrade heavier crude feedstocks;
- energy use and CO_2 emissions rise by 25% as a result.

Again we assumed that the measures would be introduced (linearly) over a 10-year period. We varied the ten-year period according to region:

Region	Implementation period
North America	1996-2005
Central/South America	2006-2015
Europe	1996-2005
Former Soviet Union	2006-2015
Africa plus Middle East	2006-2015
Pacific	1996-2005
Asia	2006-2015

8.2 MODELLED FUTURE EMISSIONS

The emissions under Scenarios (1-3) are shown for refineries in **Figure 8.3**; and for petrochemicals (Scenarios 1 & 2 only) in **Figure 8.4**. The projections for the two sectors are combined in **Figure 8.5**.

8.2.1 Scenario (1): "Energy efficiency"

The achieved emissions are summarised in the following table for decade years:

Source	CO_2 emissions, Mt CO_2/yr			
	1990	2000	2010	2020
Refineries	685	694	682	722
Petrochemicals	399	548	702	856
Refineries plus petrochemicals	1,083	1,242	1,384	1,578

The corresponding changes in emissions relative to 1990 are given below:

Source	Change in CO_2 emissions relative to 1990, percent			
	1990	2000	2010	2020
Refineries	-	+ 1	- 0.4	+5
Petrochemicals	-	+ 37	+ 76	+ 115
Refineries plus petrochemicals	-	+ 15	+ 28	+ 46

Thus Scenario (1) enables refineries to hold emissions steady up to about 2010, before emissions rise in line with growth in throughput; whereas for petrochemicals the high growth predicted by Chang (1998b) up to 2005 and extended by us to 2020 means that any reduction is swamped by growth in throughput.

8.2.2 Scenario (2): "Maximum CO_2 reduction"

The achieved emissions are summarised in the following table for decade years:

Source	**CO_2 emissions, Mt CO_2/yr**			
	1990	**2000**	**2010**	**2020**
Refineries	685	694	543	252
Petrochemicals	399	548	518	228
Refineries plus petrochemicals	1,083	1,242	1,061	480

The corresponding changes in emissions relative to 1990 are given below:

Source	**Change in CO_2 emissions relative to 1990, percent**			
	1990	**2000**	**2010**	**2020**
Refineries	-	+ 1	- 21	- 63
Petrochemicals	-	+ 37	+ 30	- 43
Refineries plus petrochemicals	-	+ 15	- 2	- 56

Thus in Scenario (2) we see a substantial decrease in refinery emissions by 2010 offset by a substantial increase in petrochemical emissions; but by 2020 both sectors are decreasing; the maximum reduction modelled in the summed sectors by 2020 is 56 % reduction.

8.2.3 Scenario (3): "Low sulphur future"

The achieved emissions are summarised in the following table for decade years:

Source	**CO_2 emissions, Mt CO_2/yr**			
	1990	**2000**	**2010**	**2020**
Refineries	685	784	892	980
Petrochemicals[a]	399	625	878	1070
Refineries plus petrochemicals	1,083	1,409	1,769	2,050
[a] Baseline projection				

The corresponding changes in emissions relative to 1990 are given below:

Source	**Change in CO_2 emissions relative to 1990, percent**			
	1990	**2000**	**2010**	**2020**
Refineries	-	+ 14	+ 30	+ 43

Petrochemicals[a]	-	+ 57	+ 120	+ 168
Refineries plus petrochemicals	-	+ 30	+ 63	+ 89
[a] Baseline projection				

Scenario (3) is defined as having an increase in emissions. Relative to the 2020 baseline, this increase is + 16% for refineries; zero for petrochemicals (by definition); and + 7% for the combined sectors.

8.3 MODELLED COSTS

We have modelled the costs of Scenarios (1) and (2) assuming:

- average savings of US$ 20/t CO_2 in the "Energy Efficiency" scenario;
- average costs of US$ 61.50/t CO_2 for CO_2 capture/disposal (average of US$ 20-90/t CO_2 for capture; plus average of US$ 2-11/t CO_2 for disposal).

In the "Maximum CO_2 reduction" scenario, as we lack unit cost data and for ease of modelling, we have used the same add-on cost for reduced flaring as for end-of-pipe capture. This, it may be recalled, is assuming application of the Californian ruling for 50% reduction in flaring, which we effectively assume goes well beyond the point of break-even.

The cost profiles are summarised in **Figures 8.6** (refineries); **8.7** (petrochemicals) and **8.8** (combination of both sectors). The key results for the year 2020 are summarised in the following table:

	Emission relative to baseline, Mt CO_2/yr		**Cost, US$ million/yr**		**Cost effectiveness, US$/t CO_2**	
	Scenario (1)	**Scenario (2)**	**Scenario (1)**	**Scenario (2)**	**Scenario (1)**	**Scenario (2)**
Refineries	- 121	- 591	- 2, 422	+ 26, 485	- 20[a]	+ 45
Petrochemicals	- 214	- 842	- 4,279	+ 34,349	- 20[a]	+ 41
Refineries plus petrochemicals	- 335	- 1,433	- 6,701	+ 60,834	- 20[a]	+ 42
[a] By definition						

As we saw in the previous section, although Scenario (1) can be achieved for cost savings, emissions still increase due to increased throughput. Significant emission reductions can only be achieved through significant expenditure.

The figure of US$ 42/t CO_2 may be inverted: for every US$ spent on end-of-pipe capture, CO_2 emissions can be reduced by 0.024 t CO_2. Looking at the combined refinery plus petrochemicals sector, if the US$ 6.7 billion saved in Scenario (1) were all spent on end-of-pipe control, emissions would be reduced by 160 Mt CO_2/yr. This would still mean emissions rising by 335 Mt CO_2/yr. In order to bring the emissions back to 1990 levels by 2020 would require all the US$ 6.7 billion savings to be spent, plus an additional US$ 14.0 billion.

8.4 DISCUSSION OF BARRIERS AND OTHER FACTORS AFFECTING TIMESCALES

8.4.1 Energy efficiency measures

The barriers to implementing energy efficiency measures may be summarised as:

- issues relating to awareness;
- investment hurdles;
- the perceived need;
- ownership of emissions.

Awareness: the case of the Shanghai refinery (**Appendix 6**) suggests that there may be a widespread lack of awareness of opportunities to improve energy efficiency; it is predictable that there is also poor awareness of the greenhouse emission savings which may result from energy efficiency improvements. Even in companies which are well focused in this area, the importance of staff training is recognised (see for example the efforts made by Petro-Canada (**Appendix 7**). There is clearly a potential role for some form of technology transfer programme whereby the more experienced countries/companies might pass on experience/know-how to less experienced countries/companies. The barrier here is that advanced companies have a commercial advantage (in terms of a lower cost base) over the less well-advanced companies, so there needs to be some benefit for the former in participating in technology transfer. The benefit could possibly come from some form of Joint Implementation activity (see below).

Investment: although energy efficiency measures can lead to substantial savings, the measures described in **Chapter 5** require significant investment. The availability of capital may therefore be a barrier, particularly when the industry is under pressure from a number of different directions. In the USA, the government has recognised the economic importance of the refining and petrochemicals sectors, and is investing substantial R&D funds into developing more efficient processing methods in order to protect the long-term competitiveness of US industry. Major multinational companies are likewise investing in developing technologies. But smaller companies may need assistance from national governments in the form of grants, loans, tax incentives and so on.

Perceived need: greenhouse gas control is still a recent issue compared with the life of refinery and petrochemical plant. In earlier decades, energy efficiency and cost control had lower priority than it has in today's economic situation. Prioritisation remains an issue even for the most environmentally conscious company - in the USA, for example, much attention has been focused by the regulators on air toxics rather than greenhouse gases; and in Europe the impending IPPC directive will place emphasis on water and ground pollution as much as on air pollution. In some countries state monopolies have historically protected the industry to some extent from the commercial pressures faced by companies trading in the world economy, again reducing the perceived importance of cost cutting.

Ownership of emissions: in the scenarios modelled in this report, ownership of emissions is an issue for power generation. If a company currently imports all its power, it may feel reluctant to switch to on-site cogeneration even if this leads to cost savings and a net reduction in greenhouse emissions - because the company would effectively be increasing its on-site emission inventory. This barrier could be minimised if regulators around the world are seen to take into account the *global* benefits of emission reduction measures rather than merely the situation on a given site.

8.4.2 End-of-pipe measures

The principal barrier to implementation of CO_2 capture is cost, and it is unlikely that the industry will implement such measures beyond token efforts for public relations purposes. This barrier could be reduced through suitable economic incentives such as tax benefits - but here the barrier may be the perceptions of governments. Again the question is one of prioritisation - of greenhouse emissions versus other pollution issues relating to this industry; and of the industry's importance relative to other sources of greenhouse gas emission.

Another barrier is site-specific, and relates to the local availability of viable options for CO_2 use or disposal.

8.4.3 An opportunity for Joint Implementation

In our modelled scenarios we have assumed that implementation of energy efficiency measures will proceed more rapidly in the developed regions. This indicates a possibility for Joint Implementation activities in which companies in developed regions make available investment capital, expertise and training to companies in less developed regions, thereby accelerating implementation of energy efficiency measures at the global scale. This is effectively already happening where the large multinationals are investing in their own sites in developing regions, but the practice could be widened if sites in developed regions gained greenhouse emission credits which could be offset against their own emissions - thus potentially saving some of the investment envisaged in the longer term for CO_2 capture.

Figure 8.1: Baseline projection of CO_2 emissions from refineries, 1990-2020

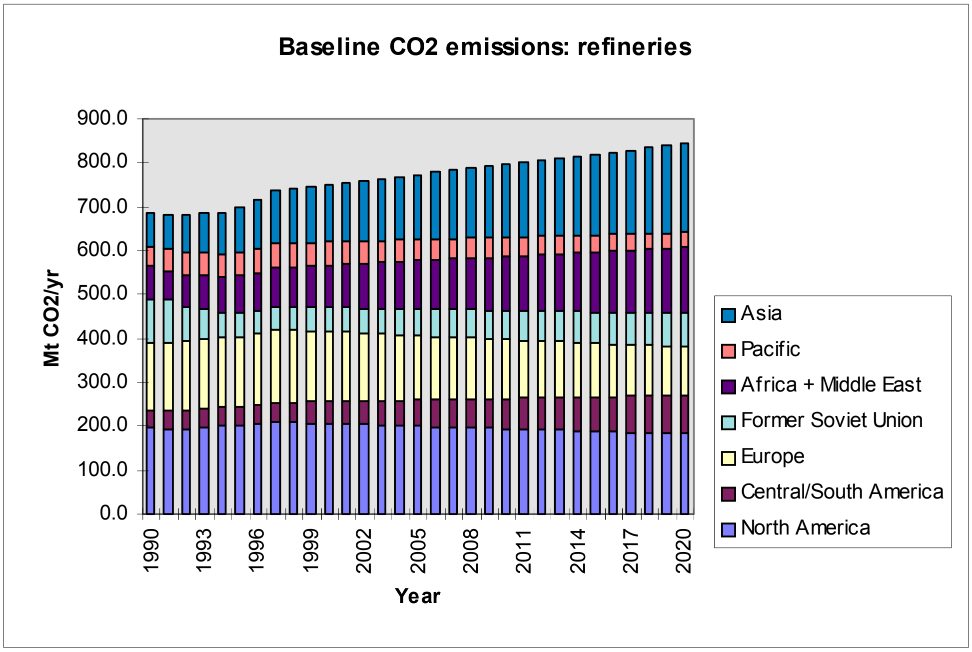


Figure 8.2: Baseline projection of CO_2 emissions from petrochemicals, 1990-2020

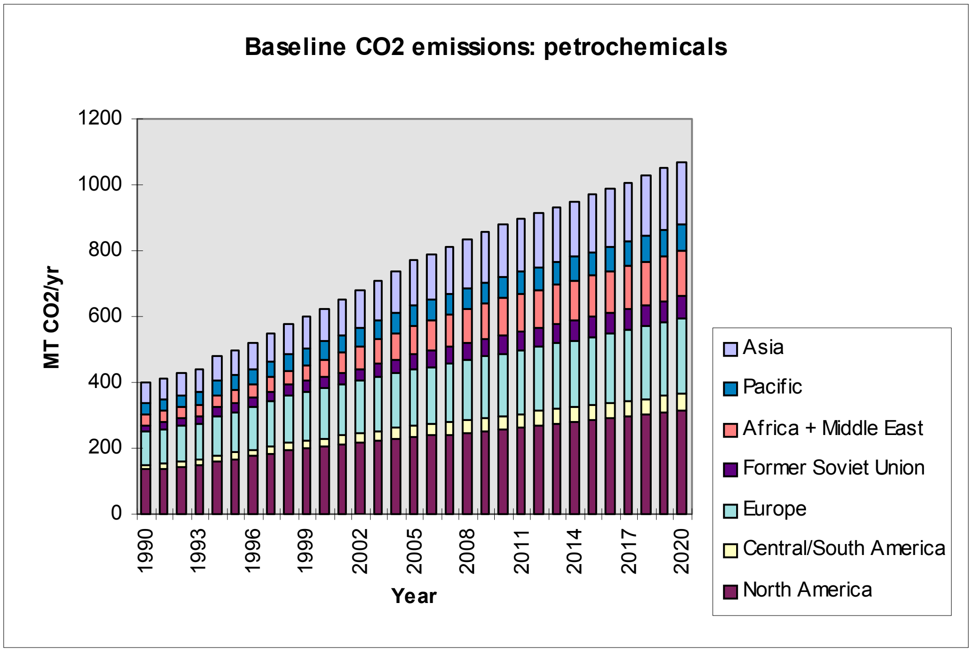


Figure 8.3: Scenario projections of CO_2 emissions from refineries, 1990-2020

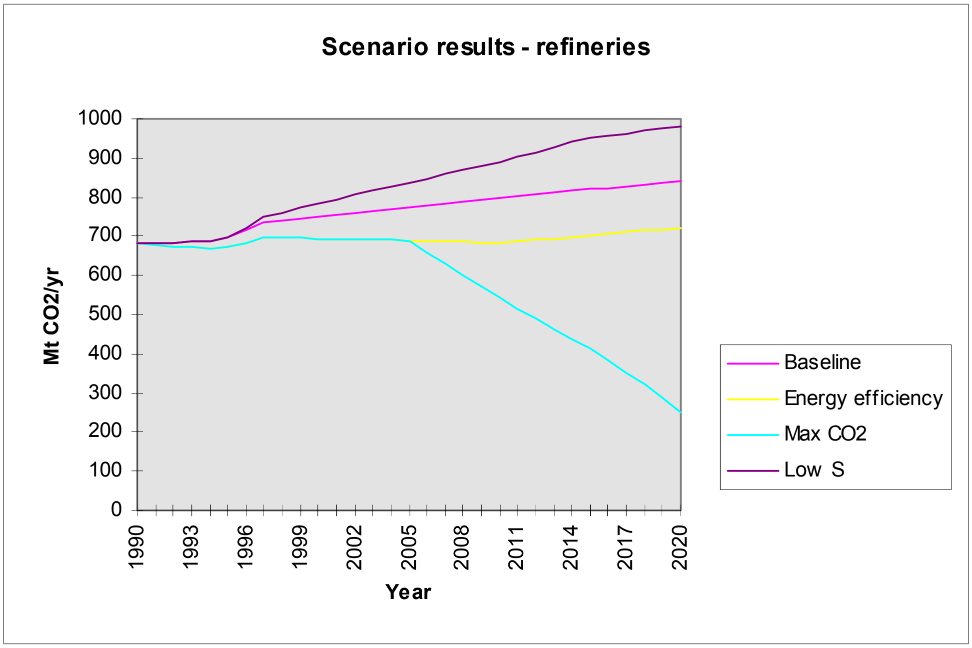


Figure 8.4: Scenario projections of CO_2 emissions from petrochemicals, 1990-2020

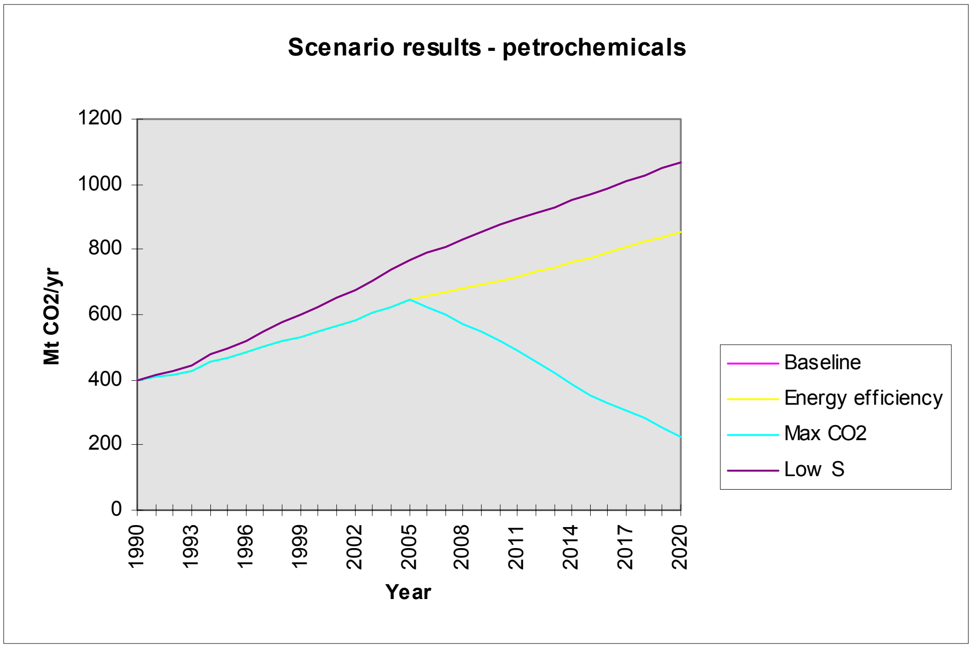


Figure 8.5: Combined scenario projections of CO_2 emissions from refineries plus petrochemicals, 1990-2020

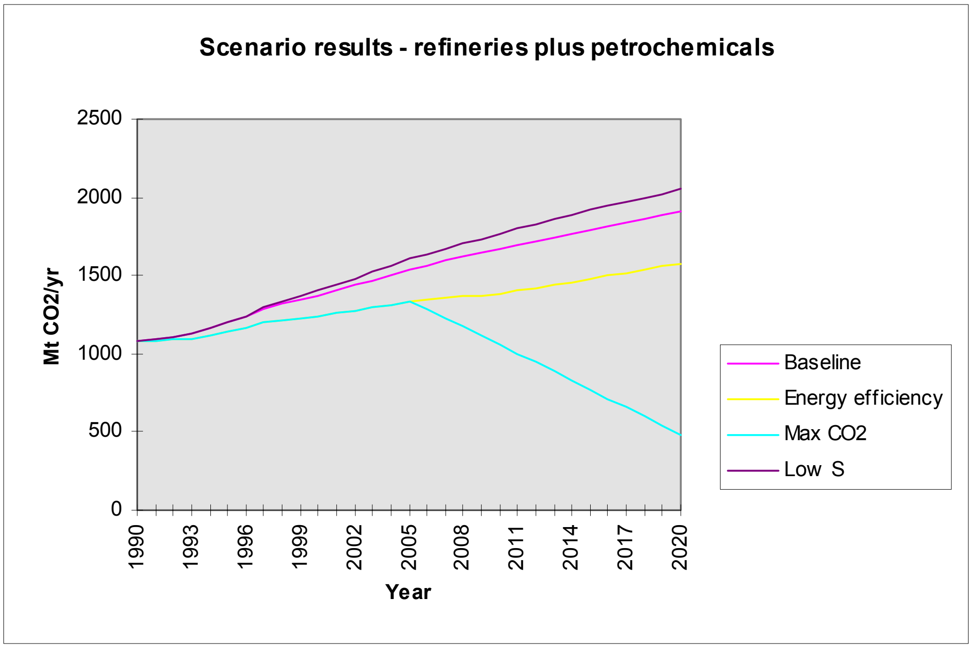


Figure 8.6: Cost profile for CO_2 reductions from refineries, 1990-2020

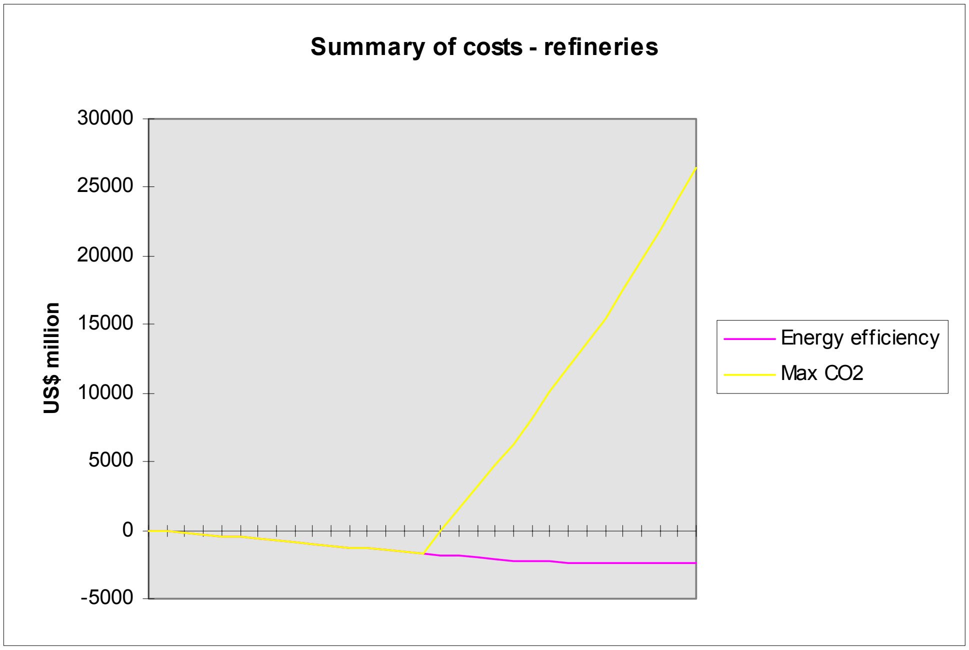


Figure 8.7: Cost profile for CO_2 reductions from petrochemicals, 1990-2020

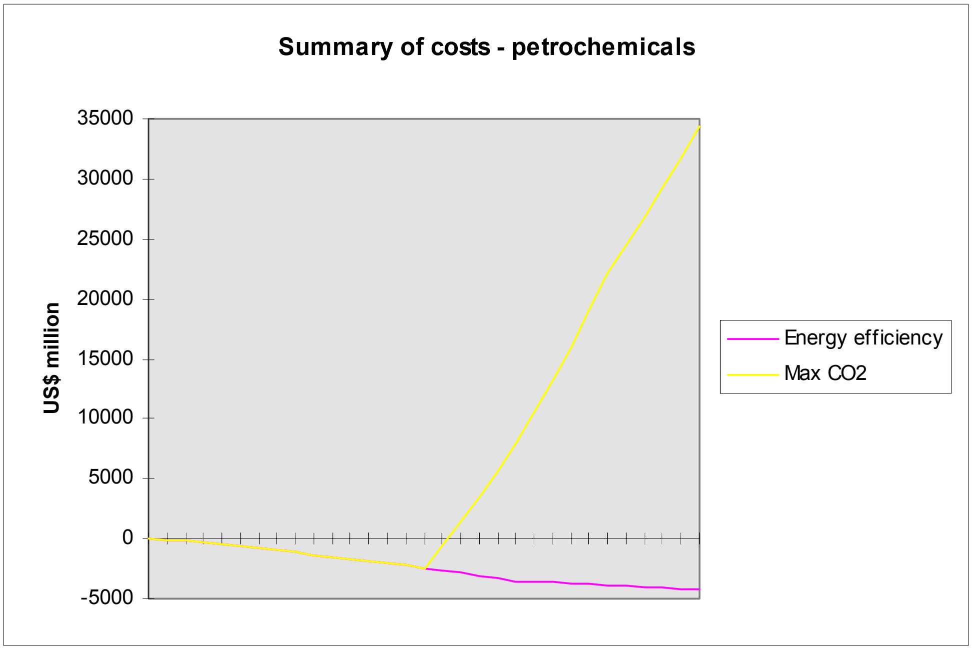
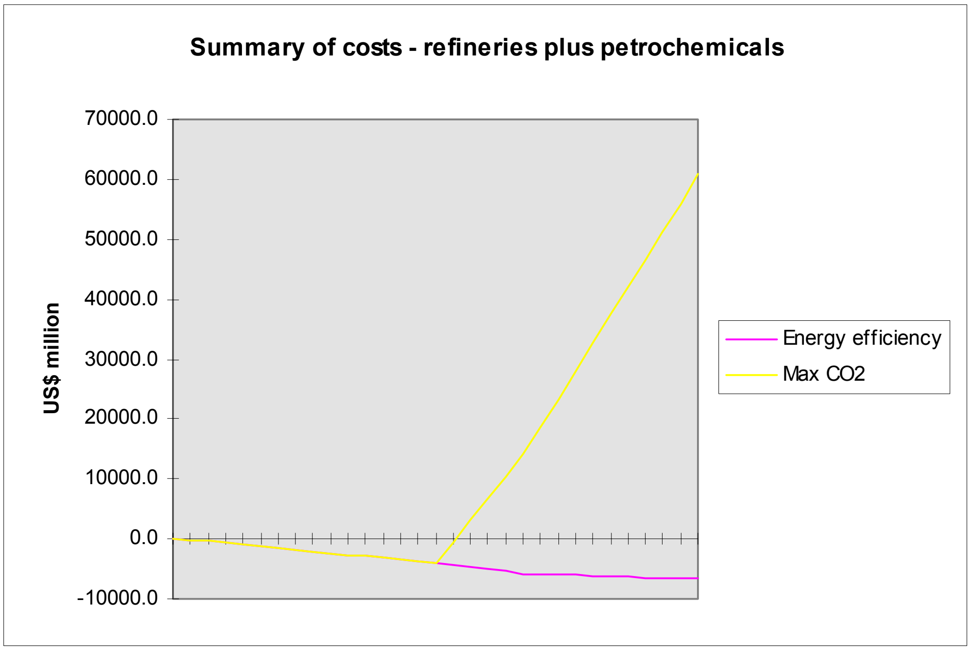


Figure 8.8: Cost profile for CO_2 reductions from refineries plus petrochemicals, 1990-2020



9 Conclusions

This report presents an overview of the refinery and petrochemical sectors; their greenhouse gas emissions; trends in process development; product formulation and regulation; options for reducing greenhouse gas emissions and associated costs.

Historically, many changes have occurred in the refining business, dictated largely by the demands of the market place with decreasing demand for heavy fuel oils and increasing demand for lighter transportation fuels, together with increasing environmental constraints. At the same time there has generally been an increase in pressure on the industrial sector to produce ‘green products’, such as unleaded petrol, low benzene and sulphur fuels, and low aromatic solvents. Restrictions on fuel sulphur content, in particular, have greenhouse gas implications for refineries. Future trends will continue towards larger and more complex refineries with the capacity for deep conversion processing of heavier crudes to lighter products. To compete with this, current refineries will have to expand to incorporate more processing units and increased desulphurisation capacity.

The overall picture is one of rapidly converging technologies based around the domination of a relatively small number of multi-national oil producers, an increasing role for large national oil companies, and the wide-spread licensing of technologies. Where significant differences do exist, they are generally based around the demand profile for products of the particular region.

Refineries and petrochemical plants are a potential source of atmospheric emissions of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), Volatile Organic Compounds (VOCs), sulphur, reduced sulphur compounds and oxides of sulphur, ammonia, oxides of nitrogen, toxic organic micropollutants (dioxins, PAHs), heavy metals, particulates and odour.

We have estimated global emissions of greenhouse gases as follows:

	CO_2	CH_4	N_2O
Refineries	686.9 Mt/yr in 1994	5-45 kt/yr in 1994	1-6 kt/yr
Petrochemicals	520 Mt/yr in 1996	Not estimated	150-600 kt/yr (adipic acid manufacture)

The largest emission sources are associated with energy use:

Source	Percent of refinery CO_2 emissions
Oil and gas fuel firing of furnaces and boilers	65%
Regeneration of cat cracker catalyst	16%
Flares	< 3%
Methane steam reforming to make hydrogen	2%
Incineration and effluent processes	1%
Power (55% imported)	13%

In refineries typical CO_2 concentrations are:

- From combustion plant, furnaces, boilers, flares and FCC regenerators: about 13% CO_2.
- From gas turbine power generators or machine drivers: about 3% CO_2.
- From steam reforming process for H_2 generation: 100% CO_2.

Options for reducing greenhouse gas emissions from refineries include:

- alternative societies which are not based on crude oil;
- refinery process optimisation;
- refinery use of non-carbon-based energy sources;
- reducing the carbon content of fuels;
- optimising the efficiency of heat and power production and use;
- reducing the amount of wastes flared;
- CO_2 capture and disposal.

CO_2 absorption appears to be a viable option for refinery exhaust streams from on-site power generation, from process furnaces and boilers, and from catalyst regeneration. High concentrations of CO_2 are found in the steam reforming process and in some petrochemical offgas streams such as ethylene oxide manufacture ; for these relatively small emission sources cryogenic techniques may be a promising option.

We have modelled three future scenarios of CO_2 emissions up to the year 2020, together with baseline emissions, and we have examined costs for two of the scenarios. The three scenarios may be summarised as:

(1) “Energy efficiency” - focusing on reductions which can be achieved through reducing energy use, with cost savings.

(2) “Maximum CO_2 reduction” - in which CO_2 capture/disposal is added on top of the first scenario.

(3) “Low sulphur future” - a scenario in which energy use and hence greenhouse gas emissions increase due to requirements for increased upgrading and desulphurisation.

The “Energy efficiency” Scenario enables refineries to hold emissions steady up to about 2010, before emissions rise in line with growth in throughput; whereas for petrochemicals any reduction is swamped by growth in throughput. This scenario gives savings of US$ 20/t CO_2.

In the “Maximum CO_2 reduction” Scenario we see a substantial decrease in refinery emissions by 2010 offset by a substantial increase in petrochemical emissions; but by 2020 both sectors are decreasing; the maximum reduction modelled in the summed sectors by 2020 is 56 % reduction at a cost of about US$ 45/t CO_2.

The “Low sulphur future” Scenario is defined as having an increase in emissions. Relative to the 2020 baseline, this increase is + 16% for refineries; zero for petrochemicals (by definition); and + 7% for the combined sectors.

In conclusion our modelling indicates that significant emission reductions can only be achieved through significant expenditure - for every US$ spent on end-of-pipe capture, CO_2 emissions can be reduced by 0.024 t CO_2. In order to bring emissions back to 1990 levels by 2020 would require all the US$ 6.7 billion savings from energy efficiency measures to be spent on end-of-pipe controls, plus an additional US$ 14 billion.

The barriers to implementing energy efficiency measures may be summarised as:

- issues relating to awareness;
- investment hurdles;
- the perceived need;
- ownership of emissions.

The principal barrier to implementation of CO_2 capture is cost.

We have postulated an opportunity for Joint Implementation activities in which companies in developed regions make available investment capital, expertise and training to companies in less developed regions, thereby accelerating implementation of energy efficiency measures at the global scale.

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Appendices

CONTENTS

Appendix 1
Contract specification

Appendix 2
Organisations contacted

The following organisations were contacted during this study, and the authors would like to express their gratitude for all the assistance received:

Amerada Hess Corporation, New York, USA.
Amoco Corporation, Chicago, USA.
Australian Institute of Petroleum, Melbourne, Australia.
British Library, London, UK.
British Petroleum, London, UK.
BP Chemicals, Saltend, UK.
BP International Ltd, Sunbury on Thames, UK.
BP Oil, Sunbury on Thames, UK.
Cefic, Brussels, Belgium.
Chemical Industries Association, London, UK.
Chevron Corporation, San Francisco, USA.
China National Petroleum Corporation, Beijing, China.
Concawe, Brussels, Belgium.
Conoco Inc., Houston, USA.
Conoco, Humberside, UK.
David Reay & Associates, Whitley Bay, UK.
Deutsche Shell, Köln-Godorf, Germany.
Elf Aquitaine, Courbevoie, France.
Empresa Colombiana de Petroleos, Bogota, Colombia.
Environment Agency, London, UK.
Environment Agency, Worthing, UK.
Environment Canada, Quebec, Canada.
Environmental Protection Agency (EPA), Philadelphia, USA.
Environmental Protection Agency (EPA), Washington DC, USA.
Esso Nederland BV, Rotterdam, The Netherlands.
European IPPC Bureau, Seville, Spain.
Exxon Corporation, Irving, USA.
Foster Wheeler Energy Ltd, Reading, UK.
Hyprotech, Barcelona, Spain.
ICI, London, UK.
Infomil, The Hague, The Netherlands.
Institute of Petroleum, London, UK.
International Institute for Applied Systems Analysis, Laxenburg, Austria.

Iplom SpA, Busalla, Italy.
Kvaerner Oil & Gas International, London, UK.
Lukoil, Moscow, Russia.
Marathon Group, Houston, USA.
MIDER GmbH (Leuna 2000), Spergau, Germany.
Ministry of Housing, Spatial Planning and the Environment, The Hague, The Netherlands.
Mobil Corporation, Fairfax, USA.
M.W. Kellogg Ltd, Sudbury, UK.
National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands.
Norsk Hydro ASA, Oslo, Norway.
OLF (Norwegian Oil Industry Association), Stavangar, Norway.
OMV, Vienna, Austria.
Pemex, Mexico City, Mexico.
Pertamina, Jakarta, Indonesia.
Petrobras International, Rio de Janeiro, Brasil.
Petro-Canada, Calgary, Alberta, Canada.
PetroEquador, Quito, Equador.
Petrofina, Brussels, Belgium.
Petronas, Kuala Lumpar, Malaysia.
Preem, Sweden.
RAO Gazprom, Moscow, Russia.
Rosneft, Moscow, Russia.
Royal Dutch/ Shell Group, The Hague, The Netherlands.
Sandia National Laboratories, Albuquerque, USA.
Scandinaviska Raffinaderi AB (Scanraff), Brofjorden-Lysekil, Sweden.
Shell UK Ltd, London, UK.
Shell Canada, Calgary, Canada.
Statistics Canada, Ottawa,Canada.
Sibneft, Tyumenskaya Oblast, Russia.
Sidanko, Moscow, Russia.
Slavnet, Moscow, Russia.
Statoil, Stavanger, Norway.
Surgutneftegaz, Surgur Tyumenskaya Oblast, Russia.
Texaco Inc., White Plains, USA.
Total, Paris, France.
Turner Industries, Baton Rouge, USA.
Tyumen Oil, Tyumenskaya Oblast, Russia.
UK Petroleum Industries Association, London, UK.
Umweltbundesamt, Berlin, Germany.
Unocal Corporation, El Segundo, USA.
World Energy Council, London, UK.
Yacimientos Petroliferos Fiscales, Argentina.
Yukos, Moscow, Russia.

Appendix 3
Western European refineries

The information in the Appendix is taken from Beckman (1995).

Site ID	Site Name	Owning Company	Town	Country	Crude/ bpcd
1	Conoco Ltd, South Killingholme	Conoco Ltd	South Killingholme	England	130000
2	Eastham Refinery Ltd, Eastham	Eastham Refinery Ltd.	Ellesmere Port	England	22000
4	Esso Petroleum Co. Ltd., Fawley	Esso Petroleum Co. Ltd.	Fawley	England	303000
5	Lindsey Oil Refinery Ltd., Killingholme	Lindsey Oil Refinery Ltd.	Killingholme	England	182000
6	Mobil Oil Company Limited, Coryton	Mobil Oil Company Limited	Coryton	England	178000
7	Philips Imperial Petroleum Ltd, Port Clarence	Phillips Imperial Petroleum Ltd	Port Clarence	England	100000
8	Shell UK Ltd, Shell Haven	Shell UK Ltd	Shell Haven	England	92000
9	Shell UK Ltd, Stanlow	Shell UK Ltd	Stanlow	England	262000
10	BP Refinery Grangemouth Ltd.	BP Refinery Grangemouth Ltd	Grangemouth	Scotland	190000
11	Nynas UK AB, Dundee	Nynas UK AB	Dundee	Scotland	10240
12	BP Refinery Llandarcy Ltd	BP Refinery Llandarcy Ltd	Llandarcy	Wales	0
13	Elf Oil UK, Milford Haven	Elf Oil UK	Milford Haven	Wales	108000
14	Gulf Oil GB, Milford Haven (+35% Pembroke)	Gulf Oil GB	Milford Haven	Wales	112000
15	Texaco Ltd, Pembroke (+65% Pembroke)	Texaco Ltd	Pembroke	Wales	180000
16	Belgian Refining Corp. NV - Antwerp	Belgian Refining Corp NV	Antwerp	Belgium	85000
17	Esso Belgium, Antwerp	Esso Belgium	Antwerp	Belgium	246000
18	Fina Raffinaderij Antwerp	Fina Raffinaderij Antwerp	Antwerp	Belgium	268000
19	Nynas Petroleum NV, Antwerp	Nynas Petroleum NV	Antwerp	Belgium	15000
20	AS Dansk Shell, Frederica	AS Dansk Shell	Frederica	Denmark	66700
21	Kuwait Petroleum Refining (Danmark) AS,Skaelskoer	Kuwait Petroleum Refining (Danmark), AS	Skaelskoer	Denmark	56500
22	Statoil AS, Kalundborg	Statoil AS	Kalundborg	Denmark	65000
23	Cie. Rhenane de Raffinage, Reichstett-Vendenheim	Cie. Rhenane de Raffinage	Reichstett-Vendenheim	France	82000
24	Elf France, Donge	Elf France	Donge	France	214300
25	Elf France, Feyzin	Elf France	Feyzin	France	128130
26	Elf France, Grandpuits	Elf France	Grandpuits	France	98000
27	Esso SAF, Fos sur Mer	Esso SAF	Fos sur Mer	France	106000
28	Esso SAF - Port Jerome	Esso SAF	Port Jerome	France	151000
29	Mobil Oil Francaise, Notre Dame de Gravenchon	Mobil Oil Francaise	Notre Dame de	France	66000
30	Societe de Petroles Shell, Berre l'Etang	Societe de Petroles Shell	Berre l'Etang	France	127000
31	Societe des Petroles Shell, Petit Couronne	Societe des Petroles Shell	Petit Couronne	France	141000
32	Ste. Francaise des Petroles BP, Dunkirk	Ste. Francaise des Petroles BP	Dunkirk	France	0
33	Ste. Francaise des Petroles BP, Lavera	Ste. Francaise des Petroles BP	Lavera	France	190000
34	Total France, Gonfreville L'Orcher	Total France	Gonfreville L'Orcher	France	211000
35	Total France, La Mede	Total France	La Mede	France	127000
36	Total France, Mardyck	Total France	Mardyck	France	127000
37	Addinol Mineralol GmbH Lutzkendorf, Krumpa, Kreis Mersberg	Addinol Mineralol GmbH Lutzkendorf	Kreis Merseburg	Germany	11800
38	Beta Raffineriegesellschaft Wilhelmshaven mbH	Beta Raffineriegesellschaft	Wilhelmshaven	Germany	180000
39	BP Oil Deutschland GmbH, Hamburg	BP Oil Deutschland GmbH	Hamburg	Germany	0
40	DEA Mineraloel AG, Heide	DEA Mineraloel AG	Heide	Germany	80000
41	DEA Mineraloel AG, Wesseling	DEA Mineraloel AG	Wesseling	Germany	120000
42	Deutsche Shell AG, Godorf	Deutsche Shell AG	Godorf	Germany	170000

Site ID	Site Name	Owning Company	Town	Country	Crude/ bpcd
43	Deutsche Shell AG, Harburg-Grasbrook	Deutsche Shell AG	Harburg-Grasbrook	Germany	98000
44	Erdoel Raffinerie Neustadt GmbH, Neustadt-Donau	Erdoel Raffinerie Neustadt GmbH	Neustadt-Donau	Germany	144000
45	Esso AG, Ingolstadt	Esso AG	Ingolstadt	Germany	105000
46	Esso AG, Karlsruhe	Esso AG	Karlsruhe	Germany	151800
47	Holborn Europa Raffinerie GmbH, Harburg	Holborn Europa Raffinerie GmbH	Harburg	Germany	78000
48	Hydrierwerk Zeitz GmbH, Zeitz	Hydrierwerk Zeitz GmbH	Zeits	Germany	73700
49	Leuna Raffineriegesellschaft mbH, Leuna	Leuna Raffineriegesellschaft mbH	Leuna	Germany	100000
50	Mobil Oil AG, Woerth	Mobil Oil AG	Woerth	Germany	105000
51	Oberrheinische Mineralolwerke GmbH, Karlsruhe	Oberrheinische Mineralolwerke GmbH	Karlsruhe	Germany	174000
52	OMV Aktiengesellschaft, Burghausen	OMV Aktiengesellschaft	Burghausen	Germany	72000
53	PCK Schwedt AG, Schwedt	PCK Schwedt AG	Schwedt	Germany	230000
54	Raffineriegesellschaft, Vohburg/ Ingolstadt	Raffineriegesellschaft	Vohburg/ Ingolstadt	Germany	114000
55	Schmierstoff Raffinerie, Salzbergen	Schmierstoff Raffinerie	Salzbergen	Germany	3100
56	Veba Oel/ Ruhr Oel GmbH, Gelsenkirchen	Veba Oel/ Ruhr Oel GmbH	Gelsenkirchen	Germany	227000
57	Wintershall AG, Lingen	Wintershall AG	Lingen	Germany	79460
58	Eko-Hellenic Refineries & Chemicals of Macedonia Industrial & Commercial	Eko-Hellenic Refineries	Thessaloniki	Greece	66500
59	Hellenic Aspropyrgos Refinery SA, Aspropyrgos	Hellenic Aspropyrgos Refinery SA	Aspropyrgos	Greece	126000
60	Motor Oil (Hellas) Corinth Refineries SA	Motor Oil (Hellas) Corinth Refineries SA	Aghii Theodori	Greece	100000
61	Petrola Hellas SA - Elefsis	Petrola Hellas SA	Elefsis	Greece	108000
62	Irish National Petroleum Corp., Whitegate	Irish National Petroleum Corp	Whitegate	Ireland	52500
63	Agip Plas SpA, Livorno	Agip Plas SpA	Livorno	Italy	84000
64	Agip Raffinazione SpA, P. Marghera, Venice	Agip Raffinazione SpA	Venice	Italy	80000
65	Agip Raffinazione SpA, Sannazzaro, Pavia	Agip Raffinazione SpA	Pavia	Italy	200000
66	Agip Raffinazione SpA, Taranto	Agip Raffinazione SpA	Taranto	Italy	84000
67	API Raffineria di Ancona SpA, Falconara, Marittima	API Raffineria di Ancona SpA	Marittima	Italy	78000
68	Arcola Petrolifera SpA, La Spezia	Arcola Petrolifera SpA	La Spezia	Italy	33000
69	Esso Italiana SpA, Augusta, Siracusa	Esso Italiana SpA	Siracusa	Italy	182500
70	Iplom SpA, Busalla	Iplom SpA	Busalla	Italy	46500
71	Isab, Priola Gargallo	Isab	Priola Gargallo	Italy	232000
72	Italiana Energia E Servizi SpA, Frassino, Mantova	Italiana Energia E Servizi SpA	Mantova	Italy	50318
73	Praoil, Gela, Ragusa	Praoil	Ragusa	Italy	105000
74	Praoil, Priolo, Siracusa	Praoil	Siracusa	Italy	220000
75	Raffineria di Roma SpA, Rome	Raffineria di Roma SpA	Rome	Italy	81500
76	Raffineria Mediterranea SpA, Milazzo, Messina	Raffineria Mediterranea SpA	Messina	Italy	160000
77	Saras SpA, Sarroch	Saras SpA	Sarroch	Italy	285000
78	Sarpom, S. Martino Di Trecate	Sarpom	S. Martino Di Trecate	Italy	248000
79	Tamoil Italia SpA, Cremona	Tamoil Italia SpA	Cremona	Italy	90000
80	Esso Nederland BV, Rotterdam	Esso Nederland BV	Rotterdam	Netherlands	180000
81	Kuwait Petroleum Europoort BV, Rotterdam	Kuwait Petroleum Europoort BV	Rotterdam	Netherlands	75500
82	Netherlands Refining Co., Europoort & Pernis	Netherlands Refining Co.	Europoort & Pernis	Netherlands	399000
83	Shell Nederland Raffinaderij BV, Pernis	Shell Nederland Raffinaderij BV	Pernis	Netherlands	374000

Site ID	Site Name	Owning Company	Town	Country	Crude/ bpcd
84	Smid & Hollander Raffinaderij BV, Amsterdam	Smid & Hollander Raffinaderij BV	Amsterdam	Netherlands	10000
85	Total Raffinaderij Nederland NV, Vlissingen	Total Raffinaderij Nederland NV	Vlissingen	Netherlands	148000
86	Asfaltos Espanoles SA, Tarragona	Asfaltos Espanoles SA	Tarragona	Spain	21000
87	Cia. Espanola de Petroleos, San Roque, Cadiz	Cia. Espanola de Petroleos	Cadiz	Spain	180000
88	Cia. Espanola de Petroleos, Tenerife	Cia. Espanola de Petroleos	Tenerife	Spain	90000
89	Ertoil SA, La Rabida, Huelva	Ertoil SA	Huelva	Spain	80000
90	Petromed, Castellon de la Plana	Petromed	Castellon de la Plana	Spain	102000
91	Petronor SA, Somorrostro, Vizcaya	Petronor SA	Vizcaya	Spain	240000
92	Repsol Petroleo SA, Cartagena, Murcia	Repsol Petroleo SA	Murcia	Spain	120000
93	Repsol Petroleo SA, La Coruna	Repsol Petroleo SA	La Coruna	Spain	135000
94	Repsol Petroleo SA, Ciudad Real	Repsol Petroleo SA	Ciudad Real	Spain	135000
95	Repsol Petroleo SA, Tarragona	Repsol Petroleo SA	Tarragona	Spain	180000
96	Petrogal-Leca da Palmeira, Porto	Petrogal-Leca da Palmeira	Porto	Portugal	91390
97	Petrogal-Leca da Palmeira, Sines	Petrogal-Leca da Palmeira	Sines	Portugal	212895
98	OMV-Schwechat	OMV	Schwechat	Austria	210000
99	Neste Oy, Naantali	Neste Oy	Naantali	Finland	40000
100	Neste Oy, Porvoo	Neste Oy	Porvoo	Finland	160000
101	Esso Norge AS, Slagen-Toensberg	Esso Norge AS	Slagen-Toensberg	Norway	89540
102	Norske Shell AS, Sola	Norske Shell AS	Sola	Norway	53000
103	Statoil Division Mongstad	Statoil Division Mongstad	Mongstad	Norway	142200
104	AB Nynas Petroleum, Gothenburg	AB Nynas Petroleum	Gothenburg	Sweden	12500
105	AB Nynas Petroleum, Nynashamn	AB Nynas Petroleum	Nynashamn	Sweden	28000
106	OK Raffinaderi, Gothenburg	OK Raffinaderi	Gothenburg	Sweden	106000
107	Shell Raffinaderi AB, Gothenburg	Shell Raffinaderi AB	Gothenburg	Sweden	81000
108	Skandinaviska Raffinaderi AB, Brofjorden-Lysekil	Skandinaviska Raffinaderi AB	Brofjorden-Lysekil	Sweden	200000
109	Raffinerie de Cressier SA, Cressier	Raffinerie de Cressier SA	Cressier	Switzerland	60000
110	Raffinerie du Sud-Ouest SA, Collombey	Raffinerie du Sud-Ouest SA	Collombey	Switzerland	72000
111	Anadolu Tasfiyehanesi AS, Mersin	Anadolu Tasfiyehanesi AS	Mersin	Turkey	100000
112	Turkish Petroleum Refineries Corp., Aliaga, Izmir	Turkish Petroleum Refineries Corp.	Izmir	Turkey	226440
113	Turkish Petroleum Refineries Corp., Batman, Siirt	Turkish Petroleum Refineries Corp.	Siirt	Turkey	22015
114	Turkish Petroleum Refineries Corp., Izmit	Turkish Petroleum Refineries Corp.	Izmit	Turkey	251600
115	Turkish Petroleum Refineries Corp., Kirikkale	Turkish Petroleum Refineries Corp.	Kirikkale	Turkey	113220

Appendix 4
Case study: Emissions from Finnish refineries

Neste Oy AB operates the Naantali and Porvoo refineries in Finland. Emissions to atmosphere from these two refineries are described in this Appendix.

NAANTALI REFINERY

Production in 1997:

Products	Production, tonnes
Gases	35,000
Gasolines	720,000
Diesel fuels and light fuel oils	1,191,000
Heavy fuel oil	221,000
Bitumens	268,000
Sulphur	9,500
Solvents	71,000

Emissions, t/yr:

	1994	1995	1996	1997	Permit level
Air					
CO_2	353,000	357,000	332,000	391,000	-
VOC	2,040	1,850	1,640	1,700	-
NO_x	690	570	350	400	350
SO_2	2,200	2,800	1,000	1,300	2,000
Water					
Oil	4.6	4.1	2.8	2.9	8
Waste					
Disposal	6,350	5,840	5,900	2,485	-
Hazardous	370	170	360	54	-

PORVOO REFINERY

Production in 1997:

Products	Production, tonnes
Gases	255,000
Gasolines	3,354,000
Diesel fuels and light fuel oils	4,010,000
Heavy fuel oil	888,000
Bitumens	21,000
Sulphur	36,000

Emissions, t/yr:

	1994	1995	1996	1997	Permit level
Air					
CO_2		2,229,000	2,415,000	2,035,000	-
VOC	3,400	2,800	1,700	1,900	-
NO_x	4,300	3,800	4,100	3,900	-
SO_2	4,700	4,700	5,300	4,700	6% of S in feedstock
Water					
Oil	6.7	2.9	1.6	2	21.6
COD	900	700	400	500	-
Waste					
Disposal	3,000	2,700	3,300	3,500	-
Hazardous	200	300	950	340	-

Appendix 5
Case study: Emissions from Californian refineries

PRODUCTION DATA

We have derived an estimate of Californian refinery production from a statement that the two refineries operated by Huntway Refining process up to 15,000 bbl/day which represents 1% of California's production (Hoover's, 1998).

Using a conversion of 1 t = 7.4 bbl (Table 7.4 on page I.31 of OECD/IEA, 1996), the Hunway Refining production can be converted to 2027.027 t/day. Multiplying this by 365 (days/year) and by 100 (%) gives a total Californian production of about 74 Mt/yr.

Below we have scaled up Californian emissions data to global emission estimates using 1994 a global production of 3141.627 Mt (OECD/IEA, 1996).

GLOBAL ESTIMATES DERIVED FROM CALIFORNIAN EMISSIONS DATA

The Californian Air Resources Board has published state-wide emission estimates for 1995 (CARB, 199?):

Source	**Californian refinery emissions, t pollutant per day**					
	VOC	CO	NO_x	SO_x	Particulate	PM_{10}
Combustion	37	27	70	3	3	3
Other	48	6	19	60	5	3
Total	85	33	89	63	8	6

We have converted these data into annual emissions by multiplying by 365:

Source	Californian refinery emissions, t pollutant per year					
	VOC	CO	NO_x	SO_x	Particulate	PM_{10}
Combustion	13505	9855	25550	1095	1095	1095
Other	17520	2190	6935	21900	1825	1095
Total	31025	12045	32485	22995	2920	2190

We can derive global emission estimates by scaling up according to the relative proportions of Californian to global production statistics. It should be borne in mind that the production data refer to different years in the mid-1990's, which introduces some error. Note that the units are now kt/yr:

Source	Global refinery emissions, kt pollutant per year					
	VOC	CO	NO_x	SO_x	Particulate	PM_{10}
Combustion	573	418	1085	46	46	46
Other	744	93	294	930	77	46
Total	1317	511	1379	976	124	93

DATA FOR INDIVIDUAL CALIFORNIAN REFINERIES

The Californian Air Resources Board has published 1996 emission estimates for a number of refineries (CARB, 199?). The following tables summarise the data for selected pollutants.

Annual emissions of VOC, CO, NO_x, SO_x, PM and PM_{10}:

Refinery	Emissions, t pollutant per year					
	VOC	CO	NO_x	SO_x	PM	PM_{10}
Exxon Corporation, Benicia	1,184	454	2,607	6,042	253	180
Fletcher Oil & Refining Co, Carson	136	2.5	6.8	0.4	1	0.95
Golden West Refining Co, Santa Fe Springs	31	7.3	2.9	n.d.	0.4	0.38
Huntway Refining Co, Benicia	60	8.7	28	n.d.	0.8	0.782
Pacific Refining Co, Hercules	439	66	386	290	13	12
Santa Maria Refining Co, Santa Maria	42	6.4	27	26	2.7	2.7
Shell Martinez Refining Co,	2,024	531	4,448	2,518	533	446

Martinez						

Refinery	**Emissions, t pollutant per year**					
	VOC	CO	NO_x	SO_x	PM	PM_{10}
Texaco, Wilmington	1,126	180	1,008	726	259	181
Tosco Corp, Martinez	2,845	329	2,570	4,460	193	125
Tosco Corp, Rodeo	892	235	1,663	728	55	53
Unocal, Arroyo Grande	201	33	96	225	12	11

Annual emissions of PAH's:

Refinery	**Emissions, lb pollutant per year**						
	PAH	B[a]A[a]	B[a]P[b]	B[b]F[c]	B[k]F[d]	D[a,h]A[e]	In[...]P[f]
Exxon Corporation, Benicia	10.668	n.d.	-	-	-	-	-
Fletcher Oil & Refining Co, Carson	120.56	8.45	-	-	-	-	-
Golden West Refining Co, Santa Fe Springs	-	3.537	9.224	3.534	3.537	3.537	3.537
Huntway Refining Co, Benicia	-	-	-	-	-	-	-
Pacific Refining Co, Hercules	2.285	-	-	-	-	-	-
Santa Maria Refining Co, Santa Maria	0.282	-	-	-	-	-	-
Shell Martinez Refining Co, Martinez	127.431	-	-	-	-	-	-
Texaco, Wilmington	0.072	-	-	-	-	-	-
Tosco Corp, Martinez	100.72	-	-	-	-	-	-
Tosco Corp, Rodeo	45.27	-	-	-	-	-	-
Unocal, Arroyo Grande	103.215	-	-	-	-	-	-

[a] Benzo[a]anthracene.
[b] Benzo[a]pyrene.
[c] Benzo[b]fluoranthene.
[d] Benzo[k]fluoranthene.
[e] Dibenzo[a,h]anthracene.
[f] Indeno[1,2,3-cd]pyrene.

Annual emissions of metals:

Refinery	**Emissions, lb pollutant per year**												
	Al	**As**	**Be**	**Cd**	**Cu**	**Cr(VI)**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Va**	**Zn**
Exxon Corporation, Benicia	-	0.179	-	17.6	293	0.35	24.7	221	333	-	-	-	595
Fletcher Oil & Refining Co, Carson	-	-	-	-	-	0.204	16.4	-	6.74	-	-	-	122
Golden West Refining Co, Santa Fe Springs	-	1.34	0.36	0.886	7.82	0.168	0.404	49.5	42.6	16.4	1.02	-	508
Huntway Refining Co, Benicia	-	-	-	-	-	-	-	-	-	-	-	-	-
Pacific Refining Co, Hercules	-	0	0	0.003	1.09	0	0.164	7.80	0.31	0.065	-	-	1.64
Santa Maria Refining Co, Santa Maria	-	-	-	-	-	-	-	-	-	-	-	-	-
Shell Martinez Refining Co, Martinez	-	2.06	-	0.587	23.2	2.00	9.27	60.3	5.40	-	-	-	131
Texaco, Wilmington	-	6.32	0.002	6.16	0.005	1.47	0.002	293	164	15.2	578	-	509
Tosco Corp, Martinez	-	0.873	0.047	0.392	-	0.508	2.05	35.8	19.1	0.309	-	-	34.4
Tosco Corp, Rodeo	-	1.72	-	8.64	-	1.72	86.4	14.7	0.864	-	-	-	-
Unocal, Arroyo Grande	347		0.3	1.7	63	0.208	13.2	2,231	1,405	4		600	178

Appendix 6
Case study: Energy saving opportunities at the Shanghai Oil Refinery

BACKGROUND

The Shanghai Oil Refinery is owned by the SINOPEC Shanghai Gaoqiao Petrochemical Corporation, and is located in the Pudong area on the eastern bank of the Huangpu River to the north-east of Shanghai city. It was established over 50 years ago, and is one of the largest refineries in China with a mid-1998 capacity of 8 Mt/yr, 33 units, 16 docks and 1.26 million m^3 of storage tanks. Products include fuel oils, LPG, asphalt, lubricating oils, solvents, waxes and chemical feedstocks.

Units at the refinery include three distillation units, three fluid catalytic crackers, two propane deasphalting units, and three dewaxing units. Feedstock for the refinery is predominantly low sulphur domestic crude oil from Daqing (0.14% w/w S).

In 1996 two site audits were carried out for SPURS (the Support Programme for the Urban Rehabilitation of Shanghai) by Mott MacDonald in association with Acer Environmental, AEA Technology, Environmental Resources Management and Hyder Consulting (Mott MacDonald, 1996 & 1997). In the recent period prior to the audits, throughput was about 5 Mt/yr.

The general degree of maintenance observed during the audits was good, and the plant has gained many certificates for high product quality, good environmental performance and safety consciousness.

The site does not generate any electricity but purchases all requirements. The refinery purchases steam from a local power plant, and also raises its own steam in a boilerhouse with seven boilers capable of firing oil or gas. The process units are served by fuel oil and fuel gas networks. There are about 30 furnaces around the refinery.

The total amount of fuel burned in 1995 was about 130,000 tonnes of standard oil equivalent, of which 54% was fuel oil and 46% was fuel gas.

Combustion conditions are monitored at most furnaces about every three days. Stack gases are analysed for oxygen, CO and CO_2. The excess air rate and combustion efficiency are then calculated for each furnace. **Table A6.1** gives the ranges of values found in January 1996 for two furnaces at the Furfural Extraction Unit.

Table A6.1: Combustion conditions for two furnaces at the Shanghai Refinery Furfural Extraction Unit

	Furnace 1	**Furnace 2**
Stack temperature, ^oC	168-193	216-230
CO_2, vol %	3.6-12	4-9.8
O_2, vol %	1.8-11.8	7.6-11.4
CO	0	0
Excess air, %	8-112	51-108
Efficiency, %	83-90	80-84.5

The most important observation is the high excess air rates. The average value over 14 tests was 70% excess air. The auditors were informed that the combustion problems were generally similar in many of the other furnaces on site. It appeared that the basic problem was “instability” of the fuel gas system. The pressure of fuel gas fluctuated to such an extent that it was difficult to manage the air flow rate consistently - at low air rates, there was a risk that flames would be forced out of gaps between plates at the base of the furnace. A high air rate was therefore maintained to ensure that there was a good upward air flow from the bottom of each furnace under all conditions. Solutions identified included measures to reduce fluctuations in the fuel gas system, and continuous monitoring of combustion conditions, and frequent monitoring of the pressure and composition of fuel gas.

The potential savings across the refinery for proper combustion control were estimated by the auditors to be an increase in efficiency of about two percentage points, or over 3,000 tonnes oil equivalent (about 140 TJ), worth over 2.4 million yuan per year. [The present authors have used an exchange rate of US$1 = 8.3

yuan to convert this saving to over US$289,000 per year. Using a default carbon emission factor of 20.0 t C/TJ (see section 4.1) we can calculate the avoided CO_2 emissions as about 10,300 t CO_2 per year. The potential savings are thus equivalent to about US$28/t CO_2].

Examination of the dewax unit suggested that energy savings of 20-30% could be achieved by a reorganisation of the heat exchanger network. Other potential savings were identified in the distillation units.

Control of the site boilers was found to be relatively good; about 78% efficiency of steam raising was achieved at 30-40% excess air.

When the auditors looked at the monthly energy use of the whole refinery, and compared this with oil input, they found a variation of about 25% from the from the best month to the worst for the same production level. The variation in electricity consumption was 35-40%. The auditors estimated a realistic long-term energy saving potential across the refinery of 15-20%. The savings are again presumably US$28/t CO_2. We have no indication of the investment required.

There were two flare stacks at the refinery, which burnt an estimated 15,000 t in 1995. The flares were frequently seen to be burning large quantities of material, often with a pulsing flame which suggested that the flare lines were not draining properly (and therefore condensing liquids were not being completed recovered for reprocessing); or that a compressor system was connected to the flare. At the time of the audits a flare gas recovery system was under design. We understand that the flare system has been replaced since the audit, and the new flare now routinely burns only a pilot flame.

Appendix 7
Case studies: Emissions and reductions from company publications

This Appendix contains example emissions data and greenhouse gas reduction plans and achievements reported by companies in recent environmental reports.

Amoco Canada has set greenhouse gas reduction targets from 1993 levels to be attained by 2000, and by 1997 had achieved a 10% reduction in greenhouse gas releases per unit production (Amoco, 1998).

BP Chemicals has published data for a number of its sites (BP Chemicals, 1997). **Table A7.1** at the end of this Appendix gives 1996 data.

Elf has set a target of 15% reduction in greenhouse gas emissions by 2010 from a 1990 baseline (Elf, 1998). In 1990, greenhouse gas emissions were 43 Mt CO_2 equivalent, of which 34 Mt were CO_2. 1997 CO_2 emissions were about 7.5 Mt from refining, and about 7.5 Mt from chemicals; other emissions from refining in 1997 included SO_2, about 50,000 t/yr; and NO_x, about 11,000 t/yr. Energy consumption was equivalent to 24% of 8.3 Mt oil equivalent in refining, and 59% in chemicals.

Mobil: carbon emissions have been reduced by > 1 Mt over 3 recent years (Mobil, 199?). SO_x emissions from their 5 US refineries have been reduced from 162 t per million barrels (Mbbl) in 1991, to 109 t/Mbbl in 1996. NO_x emissions are down from 76 t/Mbbl in 1990 to 46 t/Mbbl in 1996 (largely due to installation of low-temperature burners at Beaumont refinery, Texas, and new power plant at Paulsboro refinery, New Jersey). VOC emissions are down from 60 t/Mbbl in 1990 to 30 t/Mbbl in 1996 (mainly due to enhanced leak detection and control programmes). Energy consumption has been reduced by 10% since 1990. Some recent energy saving measures include (Mobil, 199?):

- 1,580,000 kWhr saved at the Joliet refinery (Illinois) by introducing automatic condensate drains for compressed air systems;

- 5,260,000 kWhr saved at the Chalmette refinery (Louisiana) by installing controls on water pumps;
- 1,250,000 kWhr saved at Edison Chemical Products (New Jersey) through improved operation of closed-loop coolers.

Petro-Canada has committed to achieving a minimum annual one percent improvement in energy efficiency (Petro-Canada, 1998). In 1996 the company reduced energy use per unit production in its refineries by 3.9% and greenhouse gas emissions by 6.3% (Canada NewsWire, 1997). Further emission reductions were achieved in 1997 (Petro-Canada, 1998), including: 5,300 t CO_2 equivalent (CO_2E) per yr through process heater and steam system optimisation at the Oakville refinery; 1,200 t CO_2E/yr through heat exchanger cleaning (Oakville); 2,900 t CO_2E/yr through condensate system upgrade (Oakville); and 4,400 t CO_2E/yr by installing a new heat exchanger at the Montreal refinery. Together these reductions represented 0.4% of company-wide refinery emissions of CO_2 in 1997. Greenhouse gas emissions from Petro-Canada's refineries in 1997 were: 3,634,000 t CO_2; 80 t N_2O; 1,700 t CH_4; 821,000 t CO_2E in imported electricity. Plans for 1998 are shown in Table A7.2 below.

Table A7.2: Greenhouse gas emission reductions planned for Petro-Canada's refineries in 1998

Location	Planned measure	Reduction, t CO_2E/yr	Reduction as % of 1997 total refinery CO_2E
All refineries	Energy efficiency training: boilers and heater operation	2,000	0.044 %
All refineries	Plant energy use optimisation	14,000	0.31 %
Montreal refinery	Improved heat exchanger heat recovery	4,200	0.093 %
Montreal refinery	Crude unit process improvements	9,500	0.21 %
Oakville refinery	Propane/propylene splitter condensate recovery	700	0.016 %
Oakville refinery	Nitrogen steam vaporiser optimisation	900	0.020 %
Oakville refinery	Process heater and steam system optimisation	5,800	0.13 %
Oakville refinery	Heat exchanger cleaning and operating efficiencies	14,000	0.31 %
Totals		**51,100**	**1.13 %**

Shell has reported emissions in 1997 from world-wide refining operations (Shell, 1998). In 1997 CO_2 emissions were 28.587 Mt (19.04t/100t throughput); SO_x emissions were 196,469 t (0.13 t/100t throughput); NO_x emissions were 42,438 t (0.029t/100t throughput); and VOC emissions were 246,440 t. Refinery throughput in 1997 was 150,112,000 t. Energy consumption was 379 million GJ.

Shell Canada has set a target of achieving 1990 levels of greenhouse gas emissions by 2000 for a 1994 level of business activity (Shell Canada, 1998a). Reported energy savings in refineries is 12% between 1990 and 1997, through upgraded furnaces; reconfigured heat exchangers; and process improvements (Shell Canada, 1998a). In 1997 a "revamped crude unit" at the Sarnia refinery (capacity 11,400 m^3/day; Shell Canada, 1998b) reduced energy demand by almost 50%, saving 45,000 t CO_2 per year, for an investment of nearly C$20 million.

Shell Canada modified the Fluid Catalytic Cracking unit in its Montreal East Refinery at a cost of C$4.2 million. Anticipated CO_2 emission savings are 12,000 t/yr; about C$1,000,000 per year will be saved in fuel and electricity. Modifications included a new steam generator, an additional reboiler and a new feed preheater (Shell Canada, 1997). The 1997 year end capacity at Montreal East was 20,600 m^3/day (Shell Canada, 1998b).

Also at the Montreal East Refinery, controls were added to six steam turbines to allow for variable speed control. These modifications significantly reduce steam consumption and resultant generation of excess low pressure steam. The project cost about C$100,000 and will save about C$270,000 per year in fired fuel, reducing CO_2 emissions by 8,000 t/yr (Shell Canada, 1997).

At Shell Canada's Sarnia refinery a new heat exchanger was added to the hydrocracking unit to recover heat from the reactor effluent stream. The recovered heat is used to reduce fuel use in a downstream reboiler furnace. The project cost about C$750,000 and will save about C$300,000 per year in fired fuel, reducing CO_2 emissions by 6,000 t/yr (Shell Canada, 1997). The 1997 year end capacity at Sarnia was 11,400 m^3/day (Shell Canada, 1998b).

At Shell Canada's Scotford Refinery an on-line energy monitoring system has been installed. This system provides operators and staff with current energy consumption on each process unit and compares it with a target number. A series of computer screens allow the user to trace the cause of any significant change in consumption or deviation from target. The project cost about C$100,000 and is expected to save at least C$100,000 per year in energy use (Shell Canada, 1997). The 1997 year end capacity at Scotford was 14,200 m^3/day (Shell Canada, 1998b).

Shell Chemicals produced 19.5 Mt of product in 1997, worth US$14.2b (Shell Chemicals, 1998). Emissions were 13 Mt CO_2; 21 kt SO_2; 17 kt NO_x; 17 kt VOC. Energy use was 238 million GJ (10.0 GJ per tonne of production).

Table A7.1: Production, energy use, and emissions data for BP Chemicals sites in 1996.

Site	Production t/yr	Main products	Energy use, GJ/t	Emissions, t/yr				
				HCs	SO_x	CO	NO_x	Partics
Baglan Bay, UK	614,000	ethanol, isopropanol, vinyl actetate monomer, styrene	16.7	1,199	8,620	21	2,095	210
Grangemouth, UK	1,565,000	ethylene, propylene, butadiene, ethanol, polybutenes, benzene	3.1	6,033	15	451	856	0
Green Lake, Texas	412,000	acrylonitrile, acetone cyanohydrin, acetonitrile	2.2	64	3	59	713	12
Hull, UK	1,441,000	acetic acid, acetic anhydride, acetone, acetate esters, phthalic anhydride, phthalate esters, formic acid, propionic acid, oil additives	10.4	15,069	1,659	20,723	2,296	4
Lavéra, France	529,000	polyethylene, ethylene glycol, ethylene oxide, polyisobutenes, glycol ethers and esters, acetates	6.6	878	1,707	0	90	70
Lima, Ohio	215,000	acrylonitrile, acetonitrile, barex resin	2.9	426	16	866	804	107
Wingles, France	184,000	polystyrene, expandable polystyrene	3.0	713	2	0	36	0

Appendix 8

Case study: Energy saving potentials in the UK organic chemicals sector

This Appendix contains information about the energy saving potential in the UK organic chemicals sector, taken from a Department of Trade and Industry study (ETSU, 1990).

Table A8.1: Energy saving potential for the UK organic chemicals sector

Potential energy savings, %	**2000**				**2020**			
	Electricity	**Gas**	**Fuel oil**	**Solid fuel**	**Electricity**	**Gas**	**Fuel oil**	**Solid fuel**
Good housekeeping/ energy management	2	4	4	4	3	5	5	5
Retrofit	8	8	8	8	15	15	15	15
Process changes	3	7	7	7	10	20	20	20
Boilers	-	2	4	-	-	4	7	-
Space heating	-	2	2	-	-	3	3	-
Motors and drives	5	-	-	-	16	-	-	-
Total potential energy saving, %	**18**	**23**	**25**	**19**	**44**	**47**	**50**	**40**
Energy use in 1988, Therms x 10^6	195	405	340	3	195	405	340	3
Energy saving potential, Therms x 10^6	35	93	85	1	86	190	170	1

The overall weighted energy saving potential (all fuels) can be calculated as 23 % in 2000, and 47 % in 2020, relative to 1988 energy use.

Appendix 9
Case study: Cogeneration at the Conoco Humber refinery

A cogeneration system was installed at Conoco's Humber refinery (UK) in 1982. Because the project received support from the Energy Efficiency Office as a demonstration scheme, long-term monitoring of its reliability and cost-effectiveness was carried by and reported (EEO, 1994; EEBPP, 1997). This Appendix summarises the findings.

In 1979 the site electrical load was 14 MWe. A 10 MWe gas turbine was installed which was fuelled primarily by a hydrogen-rich gas; with gas oil used as a standby fuel. The exhaust gases leave the gas turbine at 540°C (27 MW thermal, 15% O_2) and are used as pre-heated combustion air for a group of three fired process heaters. Initial problems with sticking dampers used to control exhaust gas pressure were overcome in the first months of operation; by 1993 the gas turbine and generator had operated reliably for more than 75,000 hours.

An energy audit in 1993 showed that the cogeneration system used about 21% less energy than the previous generating system (oil-fired boilers; 37 GJ/h saving) and operation of the fired heaters using ambient air (63 GJ/h saving). Overall thermal efficiency for the system was 74.1% (gross calorific value) and 82.2% (net).

During 1983 to 1993 the site electrical load increased from 14 MWe to 35 MWe. Instead of replacing existing steam turbine generating capacity, the gas turbine output was used to reduce the quantity of electricity purchased (by about 9 MWe). Energy savings against on-site steam turbines were assessed as 818 TJ/yr, or against purchased electricity from a coal-fired power station as 328 TJ/yr. The auditors estimated that the project reduced CO_2 emissions by at least 37,000 t CO_2/yr against emissions from a coal-fired power station; and also reduced SO_2 emissions by 600 t SO_2/yr; savings relative to on-site steam turbine generation were estimated as 56,000 t CO_2/yr and 1,070 t SO_2/yr.

The system cost £3.6 million to install and achieved initial energy cost savings of £2 million per year (1983 capital and energy prices).

Table A9.1 gives an economic analysis for 1983 and 1993 prices.

Table A9.1: Economic analysis of cogeneration system at Conoco Humber refinery

	1983 £s	**1993 £s**
Energy prices	114.40	56.00
Heavy fuel oil (£/tonne)	30.00	41.20
Purchased electricity (£/MWh)		
Cost savings against on-site boilers and condensing steam turbines (£'000/yr)		
Fuel cost saving	2,035	997
Cooling water cost saving	120	200
Maintenance costs	(110)	(220)
Net cost saving	**2,045**	**977**
Cost saving against purchased electricity (£'000/yr)		
Electricity cost saving	2,002	2,750
Less cost of additional fuel	(1,218)	(597)
Net energy cost saving	784	2,153
Maintenance costs	(110)	(220)
Net cost saving	**674**	**1,933**
Installed cost of system (£'000)	**3,600**	**7,600**
Simple payback period (years) against on-site boilers and condensing steam turbines	**1.76**	**7.78**
Simple payback period (years) against purchased electricity	**5.34**	**3.93**

We have used these data to calculate cost-effectiveness as US$/t CO_2 as follows:

- we have used the 1993 data from Table A9.1 and allocated all the costs and savings to CO_2;
- we have calculated annual costs using real annual discount rates of 5% and 10% (i.e. no adjustment for inflation);
- we have used the Discounted Cash Flow Approach described by EEA (1999);
- we have assumed an equipment lifetime of 15 years;
- we have used a 1993 exchange rate of £1 = US$ 1.4795.

The data are summarised in **Tables A9.2** (at 5% discount rate) and **A9.3** (at 10% discount rate).

Table A9.2: Cost-effectiveness of cogeneration at Conoco Humber refinery (using a 5% discount rate)

	Savings relative to on-site generation	**Savings relative to purchased electricity**
Discounted net savings	US$ 362,000 per year	US$ 1,777,000 per year
CO_2 emissions avoided	56,000 t CO_2/yr	37,000 t CO_2/yr
Cost-effectiveness	**US$ 6.46/t CO_2**	**US$ 48.0/t CO_2**

Table A9.3: Cost-effectiveness of cogeneration at Conoco Humber refinery (using a 10% discount rate)

	Savings relative to on-site generation	**Savings relative to purchased electricity**
Discounted net savings	US$ 33,000 per year	US$ 1,382,000 per year
CO_2 emissions avoided	56,000 t CO_2/yr	37,000 t CO_2/yr
Cost-effectiveness	**US$ 0.59/t CO_2**	**US$ 24.7/t CO_2**

Appendix 10
Glossary

ABS	acrylonitrile-butadiene-styrene copolymer
API	American Petroleum Institute
BAT	best available technology
BATNEEC	best available technology not entailing excessive cost
b/d, bbl/d	barrels per day
bpcd	barrels per calendar day
BOD	biological oxygen demand
Btu	British thermal unit
BTX	benzene, toluene, xylene
CARB	California Air Resources Board
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
COD	chemical oxygen demand
DKK	Danish krone
EEA	European Environment Agency
ECU	European currency unit
EEBPP	Energy Efficiency Best Practice Programme
EEO	Energy Efficiency Office
EIA	Energy Information Administration
ETSU	Energy Technology Support Unit
FCC(U)	fluid catalytic cracker/cracking (unit)
GJ	gigajoule, = 10^9 joules
HCCU	hydrocracking unit
hr	hour
IEA	International Energy Agency
IGCC	integrated gasification combined cycle
IIASA	International Institute for Applied Systems Analysis
IPCC	Intergovernmental Panel on Climate Change
IPPC	integrated pollution prevention and control
kg	kilogramme, = 10^3 grams
kt	kilotonne, = 10^3 metric tonnes
£	pounds sterling
LNG	liquified natural gas
LPG	liquified petroleum gas

Mt	megatonne, = 10^6 metric tonnes
MTBE	methyl *t*-butyl ether
MW	megawatt, = 10^6 watts
NO	nitric oxide
NO_2	nitrogen dioxide
N_2O	nitrous oxide
NO_x	oxides of nitrogen (nitric oxide + nitrogen dioxide)
NPL	National Physical Laboratory
OECD	Organisation for Economic Co-operation and Development
PAH	polycyclic aromatic hydrocarbon(s)
PCB	polychlorinated biphenyl
PET	polyethylene
PJ	petajoule, = 10^{15} joules
PM_{10}	particulate matter with diameter of 10 micrometer or less
POCP	photochemical ozone creation potential
psi	pounds per square inch
PVC	polyvinyl chloride
SAN	styrene-acrylonitrile polymer
SO_2	sulphur dioxide
SO_3	sulphur trioxide
SO_x	oxides of sulphur (sulphur dioxide + sulphur trioxide)
SRF	standard refinery fuel
t	metric tonne
TCCU	thermal cracking unit
TDS	total dissolved solids
TEL	tetraethyl lead
TJ	terajoule, = 10^{12} joules
TML	tetramethyl lead
TOC	total organic carbon
toe	tonnes oil equivalent, = 10^7 kcal (kilocalories), = 41.87 GJ (gigajoules), = 11,630 kWh (kilowatt hours)
UBA	Umweltbundesamt
UK	United Kingdom
UK DTI	United Kingdom Department of Trade and Industry
UK EA	United Kingdom Environment Agency
UKPIA	United Kingdom Petroleum Industry Association
UN ECE	United Nations Economic Commission for Europe
US, USA	United States of America
US DoE	United States Department of Energy
US EPA	United States Environmental Protection Agency
US$	United States dollar
VOC	volatile organic compound(s)
WEC	World Energy Council
yr	year