The Chemical Industry introduction to chemical engineering students

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Introductory statement

With more than 95% of all manufactured products relying on chemistry, the chemical industry provides solutions for sectors such as alternative energy, transportation, communications, building and information technology. It provides active ingredients for pharmaceuticals, and countless goods used every day by consumers, such as paints and household cleaning products.



Main source



Welcome to The Essential Chemical Industry - online

This is a reference library of the world's principal industrial chemicals, their uses and their manufacture using current industrial processes and innovations. This new web-based edition was first developed in 2013 from the book of the same title, which went through five editions. It is intended for:

- school, college and university students and their teachers
- industrial chemists and employees of chemical companies needing a quick reference or overview

About the The Essential Chemical Industry - online

Like the book was, *The Essential Chemical Industry (ECI) - online* is now one of the most highly respected and up-to-date resources about the chemical industry. This innovative website has easy cross-referencing and drill-down capability and achieves a new level of access for the student, researcher and industrial chemist alike. It has an exciting interactive research capability.

It is produced by Centre for Industry Education Collaboration (CIEC) formerly the Chemical Industry Education Centre, an independent non-profit organization in the Department of Chemistry, University of York, UK.

Written by members of the Centre's staff, and with the advice of over 200 experts in the field, the site is systematically reviewed and updated to ensure that it remains relevant and authoritative.

How to use this site

You can simply dive in and enjoy a journey of exploration - OR you can research information with more precision. Follow the **link** for some useful tips on finding your way around the site.

Outline

- 1. Introduction
- 2. What does the chemical industry produce?
- 3. How does the chemical industry contribute to an economy?
- 4. What is the value of the industry geographically?
- 5. How large are the world's chemical companies?
- 6. Where are chemical sites located and why?
- 7. Capital investment
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- 11. The chemical industry: how safe and how environmentally regulated?
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Technical Note #1: Basic Chemicals

Technical Note #2: Methanol

Technical Note #3: Ethylene

Technical Note #4: Acetic Acid

Technical Note #5: Ethene 1,2 Diol

1. Introduction

The chemical industry creates a wide variety of products which affect virtually every aspect of our lives.



Figure 1 The chemical industry is one of the largest manufacturing industries in all developed and emerging countries. This is a view of the largest site in the world devoted to the industry, at Ludwigshaven in Germany.

1. Introduction Cont.'d

While many of the products from the industry, such as detergents, soaps and perfumes, are purchased directly by the <u>consumer</u> others are used as <u>intermediates</u> to make other products. In Europe, 70% of chemicals manufactured are used to make products by other industries including other branches of the chemical industry itself. The industry uses a wide range of raw materials, from <u>air and minerals to oil.</u>

Figure 2. There have been breath-taking changes in the chemical industry over the last 10 years or so, not only in Europe and in the US but particularly in China, India, the rest of Asia and Brazil. This is a view of the chemical industry plant at Daya Bay in the south-east of China.



 With increasing <u>competition</u> worldwide, <u>innovation</u> remains crucial in finding new ways for the industry to satisfy its increasingly sophisticated, demanding and <u>environmentally-conscious</u> <u>consumers.</u>

- The products of the chemical industry can be divided into three categories:
 - Basic chemicals
 Technical Note #1
 - Specialty chemicals
 - Consumer chemicals
- Outputs range widely, with basic chemicals produced in huge quantities (millions of tons) and some specialty chemicals produced in modest kilogram quantities but with very high value. The choice of reactor is often governed by the amount of chemical that is to be produced.
- The value of sales per category for both Europe and the US are broadly similar, as shown in Table 1.

	Europe		US	
Basic chemicals	60		61	
Polymers		27		18
Petrochemicals		20		28
Basic Inorganics		13		15
Specialty chemicals	28		24	
Consumer chemicals	12		15	

Table 1. Products from the chemicalindustry in 2014 by category (%).Facts and Figures, CEFIC; 2016 Guideto the Business of Chemistry,American Chemistry Council, 2015.

Basic chemicals

- Basic chemicals are divided into
 - chemicals derived from oil, known as petrochemicals
 - > polymers
 - basic inorganics
- The term 'petrochemical' can be misleading as the same chemicals are increasingly being derived from sources other than oil, such as coal and biomass. An example is <u>methanol</u>, <u>Technical Note #2</u> commonly produced from oil and natural gas in the US and Europe but from coal in China. Another is <u>ethene</u>, <u>Technical Note #3</u> derived from oil and gas in the US and Europe but increasingly from biomass in Brazil.
- Basic chemicals, produced in large quantities, are mainly sold within the chemical industry and to other industries. For example, ethanoic acid Technical Note #4 is sold on to make esters, much of which in turn is sold to make paints and at that point sold to the consumer. These are then sold on to manufacturers of plastic components before being bought by the actual consumer. Figure 3 shows a plant producing chemicals which it then immediately uses to manufacture other chemicals.



Many companies use some of their chemical products as intermediates in their own manufacturing processes. There are often clusters of processes which use the output of one as the input to another. This site, at Billingham in the north-east of England, is a good example of such an integrated chemical plant. All the plants are also interconnected by steam pipes to make the most efficient use of energy released during manufacturing processes.

1. <u>Ammonia</u> is made from natural gas which is imported by pipeline from the North Sea.

2. Some ammonia is used to make <u>nitric acid</u>.

3. Ammonia and nitric acid are used to make the fertilizer, ammonium nitrate.

4. Ammonia is also converted into hydrogen cyanide.

5. Hydrogen cyanide is used in the process to make <u>methyl 2-</u> <u>methylpropenoate</u>, a key monomer for the manufacture of various acrylic polymers.

6. The stream of 'waste' sulfuric acid and ammonium sulfate from the process to make methyl 2-methylpropenoate is converted to pure sulfuric acid, which can then be reused in the process.
7. The tank farm stores imported reactants and products prior to

7. The tank farm stores imported reactants and products prior to export.

Basic chemicals Cont.'d

Petrochemicals and polymers

- The production of chemicals from petroleum (and increasingly from coal and biomass) has seen many technological changes and the development of very large production sites throughout the world. <u>The hydrocarbons in crude oil and gas</u>, which are mainly straight <u>chain alkanes</u>, are first separated using their differences in boiling point (unit operation: <u>Distillation</u>). They are then converted to hydrocarbons that are more useful to the chemical industry, such as branched chain alkanes, alkenes and aromatic hydrocarbons.
- In turn, these <u>hydrocarbons are converted into a very wide range of basic chemicals</u> which are immediately useful (e.g ethanol, ethane-1,2-diol) or are subjected to further reactions to produce a useful end product (for example, phenol to make resins and ammonia to make fertilizers). The main use for petrochemicals is in the manufacture of a wide range of polymers.

Basic chemicals Cont.'d

Basic inorganics

- These are relatively <u>low cost chemicals</u> used throughout manufacturing and agriculture. They are produced in very large amounts, some in millions of tones a year, and include <u>chlorine, sodium hydroxide, sulfuric and nitric acids and chemicals for fertilizers</u>.
- As with petrochemicals, many emerging countries are now able to produce them more cheaply than companies based in the US and Europe. This has led to tough competition and producers of these chemicals worldwide work continuously to reduce costs while meeting ever more stringent environmental and safety standards.

Specialty chemicals

- This category covers a wide variety of chemicals for <u>crop protection, paints and inks</u>, <u>colorants (dyes and pigments)</u>. It also includes chemicals used by industries as diverse as <u>textiles, paper and engineering</u>.
- There has been a tendency in the US and Europe to focus on this sector rather than the basic chemicals discussed above because it is thought that, with active research and development (R & D), <u>specialty chemicals deliver better and more stable profitability</u>. New products are being created to meet both customer needs and new environmental regulations. <u>An everyday example is household paints which have evolved from being organic solvent-based to being water-based. Another is the latest ink developed for inkjet printers.</u>

Consumer chemicals

- Consumer chemicals are sold directly to the public. They include, for example, <u>detergents, soaps and other toiletries</u>.
- The search for more effective and environmentally safe detergents has increased over the last 20 years, particularly in finding surfactants that are capable of cleaning anything from sensitive skin to large industrial plants. Parallel to this, much work has been done in producing a wider range of synthetic chemicals for cosmetics and fragrances.

Technical Note #1: Basic Chemicals

Basic chemicals Cont.'d

Basic chemicals, produced in large quantities, are mainly sold within the chemical industry and to other industries before becoming products for the general consumer. In the essential chemical industry website, each chemical is described in one unit following the same way, in three main sections which guides you instantly to relevant information:

- Uses
- Annual production quantities
- Manufacture

There are units on major organic and inorganic compounds.

The organic compounds are either building blocks such as ethene, propene, butadiene and benzene and how they are used to make plastics and pharmaceuticals, or compounds made from these building blocks, such as ethane-1,2-diol, ethanoic acid and methanal, useful in their own right or are used to make other useful compounds.

The inorganic chemicals included in the web site are compounds such as calcium carbonate, chlorine, hydrogen chloride, nitric acid, sodium hydroxide, sodium carbonate and sulphuric acid, which are used to make other compounds, including plastics, fertilizers, soaps and surfactants, and building materials.

Basic chemicals Cont.'d

Inorganic basic chemicals

•<u>Ammonia</u>

•Bromine

•Calcium carbonate

•Chlorine

•Fluorine

•<u>Hydrogen</u>

•Hydrogen chloride

•Hydrogen fluoride

•<u>Hydrogen peroxide</u>

•lodine

•<u>Nitric acid</u>

•Oxygen, nitrogen and the rare gases

Phosphoric acid

•Phosphorus

Sodium carbonate

Sodium hydroxide

•<u>Sulfur</u>

•Sulfuric acid

•<u>Titanium dioxide</u>

Organic basic chemicals

•Benzene and methylbenzenes

•Buta-1,3-diene

•<u>Epoxyethane</u> (Ethylene oxide)

•<u>Ethane-1,2-diol</u> (Ethylene glycol)

•Ethanoic acid (Acetic acid)

•<u>Ethanol</u>

•<u>Ethene</u> (Ethylene)

•<u>Methanal</u> (Formaldehyde)

•<u>Methanol</u>

•Methyl tertiary-butyl ether

Phenol

•<u>Propanone</u> (Acetone)

•<u>Propene</u> (Propylene)

•<u>Urea</u>

Technical Note #2: Methanol

Methanol

Methanol is produced from <u>synthesis gas (carbon monoxide and hydrogen)</u>, itself derived from oil, coal or, increasingly, biomass. It may become central to the development of biorefineries as an intermediate in the conversion of biomass to useful products.



Uses of methanol

Technical Note #2



Uses of methanol Cont.'d

(a) Polymers

The largest use for methanol is as a feedstock for the plastics industry.

(i) Plastics derived from methanol (formaldehyde)

Methanol is used to make methanal (formaldehyde) and hence a variety of plastics, based on reactions with phenol, carbamide (urea) and melamine.

(ii) Polyesters

The production of polymers such as the polyester Terylene use methanol as the original feedstock. (iv) Poly(ethene) and poly(propene)

A most remarkable increase is in the use of methanol to produce alkenes by the MTO and MTP processes, from 6 million tons in 2015 to an expected 20 million tons in 2020, which will mean that a large proportion of plastics such as poly(ethene) and poly(propene) will, in the near future, be derived from synthesis gas.

(b) As a fuel

<u>Methanol is destined to be a major fuel for cars</u>, either as a liquid fuel, mixed with petrol, or in fuel cells where it has been used to prepare, in situ in the car, hydrogen for the fuel cell. Whereas a few years ago, only a small amount of methanol was used directly as a fuel in cars, this use is now increasing rapidly. In China petrol is mixed with methanol (15%) without the need for engines to be redesigned. With some redesigning, more methanol (up to 85%) can be used. The advantage for China is that the methanol can be produced from both coal and biomass via synthesis gas. This emphasis of using methanol as a fuel is reflected in the global production figures for methanol. Thus worldwide, use of methanol as a fuel now accounts for 10% (about 7 million tons a year) but is expected to increase in the coming years.

China's use of methanol as a fuel increased 25% annually from 2000 to 2015.

Uses of methanol Cont.'d

Technical Note #2



M-85 is a mixture of methanol (85%) and petrol used in many cars in China.



Pure methanol is used in diesel engines in some buses in China.

Uses of methanol Cont.'d

Technical Note #2



Stena Line is converting its fleet of ships to run on methanol in order to reduce the pollution that occurs when burning fuel oil which is of particular concern in the Baltic. The Stella Germanica, here in Gothenburg, Sweden, getting ready to sail to Kiel in Germany, underwent extensive sea trials using methanol before the decision was made to convert over 20 other ships.

(c) To make fuels

The Methanol to Gasoline (MTG) process

Synthesis gas can be converted into liquid fuels. One way is by using the Mobil MTG (methanol to gasoline) process.

Methanol is converted into alkanes and aromatic hydrocarbons suitable for petrol (hydrocarbons with 5 to 8 carbon atoms), by passing the vapor over alumina at ca 600 K. An equilibrium mixture of methanol, dimethyl ether (DME) and steam is produced, containing about 25% methanol:

$2CH_3OH(g) \implies H_3C-O-CH_3(g) + H_2O(g)$

dimethyl ether

This mixture of gases is then passed over a bed of a zeolite in its acid form, HZSM-5, heated to ca 650 K, to produce the mixture of hydrocarbons (with 5-10 carbon atoms) for use as petrol.

Annual production of methanol

World	70 million tons
Asia	44 million tons
Middle East	9 million tons
US	2 million tons

In 2000, China accounted for about 12% of the world's consumption of methanol while North America and Europe consumed 33% and 22% respectively. By 2015, China consumed 54% while North America and Europe consumed 11% and 10%.

Manufacture of methanol

a) Production of synthesis gas

(i) Traditional methods

Methanol is manufactured from synthesis gas which is a mixture of carbon monoxide and hydrogen.

Technical Note #2

The feedstock, over the last 40 or more years, has been oil or natural gas. Coal, particularly in China, coal, rather than natural gas or oil, is being used as the feedstock.

(ii) 'Green' methanol

There have been major developments to produce methanol which is largely 'green'.

Any solid biomass including for example agricultural, city and industrial waste can be used to make synthesis gas using techniques similar to its production from coal.

a) Production of synthesis gas Cont.'d

(ii) 'Green' methanol

More recent developments include a plant in the Netherlands, which is using liquid propane-1,2,3-triol (glycerol), a by-product from the production of biodiesel, from animal fats and vegetable oils, to produce the gas.

Another 'green' route is to use waste carbon dioxide. Although the first such plant is linked to geothermal energy, it could be used to convert carbon dioxide waste from, for example, lime kilns and steel manufacture, to methanol.

Annual production of methanol Cont.'d

(b) Synthesis of methanol

Synthesis gas is catalytically converted to methanol at elevated temperatures and pressures in a fixed bed reactor. The catalyst is an alumina pellet coated with copper and zinc oxides.

The main methanol synthesis reaction may be written:

$$CO + 2H_2 \implies CH_3OH \quad \Delta H^{\oplus} = -91 \text{ kJ mol}^{-1}$$

One plant, for example, operates at 525- 575 K and 100 atmospheres. It eventually achieves a 97% conversion of the reactants.

Annual production of methanol Cont.'d

ENTRI

The converter in which methanol is being produced from synthesis gas

Technical Note #2

Technical note #3: Ethene (Ethylene)

Ethene (Ethylene)

<u>Ethene (ethylene) is the most important organic chemical</u>, by tonnage, that is manufactured. It is the building block for a vast range of chemicals from plastics to antifreeze solutions and solvents.



Ethene (Ethylene) Cont.'d

Technical Note #3



On the site at Grangemouth in Scotland, ethene is produced by steam cracking of naphtha.

Uses of ethene (ethylene)

The principal uses of ethene are to produce:

a) polymers

- poly(ethene)
- chloroethene (vinyl chloride) and hence poly(chloroethene), i.e. poly(vinylchloride), PVC
- ethylbenzene and hence phenylethene and poly(phenylethene), i.e. polystyrene

b) other chemicals

- epoxyethane and hence the diols, such as ethane-1,2-diol
- ethanol

The manufacture of polymers is the main use of ethene. Poly(ethene) accounts for about 60% of the world demand for ethene (HDPE 28%, LLDPE 18%, LDPE 14%), while dichloro-1,2-ethane, the precursor for chloroethene and thence PVC, accounts for a further 11%. Ethylbenzene, the route to poly(phenylethene), uses another 5%¹.

About 16% of ethene is used worldwide to make epoxyethane (ethylene oxide).

Annual production of ethene (ethylene)

Much of the ethene produced in the Middle East comes from Saudi Arabia, 17 million tons a year, with one refinery producing over 2 million tons a year, the 4th largest ethene production plant in the world.

World	134 million tons
Asia Pacific	50 million tons
U.S.	25 million tons
Europe	20 million tons
Middle East	20 million tons

Manufacture of ethene (ethylene)

Technical Note #3

Ethene is produced from the cracking of fractions obtained from distillation of natural gas and oil.

The processes are:

- a) the steam cracking of ethane and propane (from natural gas and from crude oil)
- b) the steam cracking of naphtha from crude oil
- c) the catalytic cracking of gas oil from crude oil. The choice of feedstock depends on availability, price (which can vary considerably), and what other products from cracking are needed.

The vast majority of ethene is produced by steam cracking. Some crackers are capable of producing 3 600 tons of ethene a day.



Distribution of ethene by pipeline across Europe.

Manufacture of ethene (ethylene) Cont.'d

Technical Note #3

New plants based on bioethanol produced from sugar cane are in operation and are also being constructed in Brazil. High yields of bio-based ethene are obtained by dehydrating ethanol vapor using a catalyst containing a mixture of magnesium oxide, alumina and silica at 600-750 K:

$$C_2H_5OH(g) \xrightarrow{\text{catalyst}} C_2H_4(g) + H_2O(g) \Delta H^{\oplus} = + 45 \text{ kJ mol}^{-1}$$

The ethene is used principally to produce bio-based poly(ethene).
Technical Note #4:Ethanoic acid (Acetic acid) Up to the last few years, ethanoic acid was manufactured by the non-catalytic oxidation of

naphtha which gave large quantities of side-products. It is now mostly manufactured from methanol with yields of over 99%.

CH₃COOH H₃C-C

Uses ethanoic acid (acetic acid)

Much of the ethanoic acid produced is converted into vinyl acetate which is the monomer for poly(ethenyl ethanoate) and acetic anhydride which is used principally to make cellulose ethanoate.

The acid itself is the solvent for the liquid phase oxidation of 1,4-dimethylbenzene (p-xylene), leading to the production of polyesters.



The uses of ethanoic acid.

Technical Note #4

Uses ethanoic acid (acetic acid) Cont.'d

Technical Note #4



he road surface on the Pont de Normandie, in Northern France, has been made from co-polymers, including one using ethene and ethenyl ethanoate. The ester is produced from ethanoic acid.

Annual production of ethanoic acid (acetic acid)

The newly manufactured acid is sometimes known as virgin ethanoic acid (virgin acetic acid). About another 2 million tons is recovered annually, particularly from the process leading to polyesters.

World	12.1 million tons
China	4.4 million tons
Rest of Asia	3.1 million tons
U.S.	2.8 million tons
Europe	1.8 million tons

Manufacture of ethanoic acid (acetic acid)

The main route is from methanol:

Methanol and carbon monoxide, both formed via synthesis gas are reacted together in the liquid phase, with some water to keep the catalyst in solution, at moderate temperatures of about 450 K and a pressure of 30 atm:

 $CH_3OH(I) + CO(g) \longrightarrow CH_3COOH(I) \Delta H^{\oplus} = -137 \text{ kJ mol}^{-1}$

A rhodium/iodine based catalyst system was first used. The catalyst has recently been improved, based on iridium in place of rhodium, the Cativa process. Yields of more than 99% ethanoic acid are obtained.

Manufacture of ethanoic acid (acetic acid) Cont.'d



The manufacture of ethanoic acid using the Cativa process. 1 The reactor. 2 Distillation column to remove methanol, water and carbon monoxide. Propionic acid is removed on further

Propionic acid is removed on further distillation.

3. How does the chemical industry contribute to an economy?

- <u>The chemical industry is a very important contributor to the wealth of a country</u>. For example it contributes over 1% to the Gross National Product (GNP) of European countries, which is over 6% of the total GNP produced by all manufacturing industries.
- Generally personnel in the industry are among the most well rewarded of all manufacturing industries because the industry has the largest proportion of highly qualified people and generally it is the most productive.

4. What is the value of the industry geographically?

- In 2011, worldwide, it was estimated that world sales of chemicals amounted to over \$3500 billion (Table 2). This means every man, woman and child in the world, on average, uses \$500 worth of chemicals a year.
- The main users of the chemicals are in the developed countries with each person using approximately \$1200 worth of chemicals annually.

Table 2. The geographic breakdown (%) of the
worldwide chemical sales in 2001, 2011 and 2014.

Year	2001	2011	2014
Total sales in (billion \$)	1829	3567	3555
China	8,1	26,8	30,4
Europe (EU)	29,8	19,6	17,0
Rest of Asia	14,0	18,8	16,3
North America	27,6	17,1	12,8
Japan	10.7	6,4	4,7
South America	4,5	5,5	4,4
Rest of World	5,3	5,8	1,4

4. What is the value of the industry geographically? Cont.'d

Production in China and other Asian economies is rising rapidly (Table 2). China has • increased its percentage share from 8.1 to 30.4 in ten years. In contrast the proportion has shrunk in Europe from 29.8 to 17.0% and that in North America from 27.6 to 16.3%. It is not as dire for Europe and North America as these numbers suggest as the total sales have increased from \$545 to \$1087 billion. Overall they are taking smaller slices of a much larger cake, but the mass of the slice is still growing. Thus chemical manufacture has increased by 80% in 20 years but its world share has nearly halved. Nevertheless, the manufacturing core of the industry is now decisively in Asia.

Table 3 shows the sales of the countries which have large sales.

4. What is the value of the industry geographically? Cont.'d

Sales(billio	n \$)
China	1222
US	515
Germany	162
Japan	156
South Korea	133
Brazil	87
France	87
India	80
Taiwan	77
Italy	57
Netherlands	55
United Kingdom	44
Spain	43

Table 3. Chemical sales by country in 2014 (billion \$).

4. What is the value of the industry geographically? Cont.'d

These figures can be put into a different perspective when the size of the country's population is considered (Table 4)

Country	Sales (billion \$)	Population (million)	Sales/per head of population (\$)
China	1222	1382	884
US	515	324	1590
Germany	162	126	1286
Japan	156	81	1926
South Korea	133	51	2608
Brazil	87	210	414
France	87	65	1338
India	80	1327	603
Taiwan	77	23	3348
Italy	57	60	950
Netherlands	55	17	3235
United Kingdom	44	65	677
Spain	43	46	935

Table 4. Chemical sales per head of population by country in 2014 (\$).

5. How large are the world's chemical companies?

It can be seen (Table 5) that the head offices of big companies are spread around the world and reflect not only the high growth of chemical markets in the Middle East and in Asia but also the desire of oil producers to participate in making chemicals.

Company	HQ location	Sales (billion \$)
BASF	Germany	63,7
Dow Chemical	USA	48,8
Sinopec	China	43,8
SABIC	Saudi Arabia	3,34
Formosa Plastics	Taiwan	29,2
Ineos	Switzerland	28,4
ExxonMobil	USA	28,1
LyonnellBasell	Netherlands	26,7
Mitsubishi Chemical	Japan	24,3
DuPont	USA	20,7
LG Chem	South Korea	18,2

Table 5. Chemical companies: Sales in 2015 and the location of their head office.

5. How large are the world's chemical companies? Cont.'d

- The chemical industry is highly multi-national. BASF is shown in Table 5 as a German company, but it has manufacturing plants in the US, UK, China and in many other countries worldwide, as well as in Germany.
- SABIC, whose Head Office is in Saudi Arabia, has manufacturing plants across Europe, the Americas, Asia as well as the Middle East. This company exemplifies the changes occurred in the chemical industry. From manufacturing its first chemicals in 1981, it is now the world's largest producer of basic chemicals such as poly(phenylethene) (polystyrene), and <u>ethane-1,2-diol</u> (ethylene glycol).

Company	HQ location	Sales (billion \$)
Air Liquide	France	17.3
Linde	Germany	16.8
AkzoNobel	Netherlands	16,5
Toray Industries	Japan	15.5
Evonik	Germany	15.0
PPG Industries	US	14.2
Braksem	Brazil	14.2
Yara	Norway	13.9
Covestro	Germany	13.4

Table 5 Cont'd. Chemical companies: Sales in2015 and the location of their head office.

The siting of many of the world's major chemical companies may seem random or puzzling. In fact there are very good reasons for the choice of sites, reasons which also reflect the industrial and consumer landscape of the day.

(a) In the beginning - the nineteenth century

- At first sight it seems strange that what are currently the fourth and seventh largest chemical companies in the world, Dow and DuPont, are situated in two small US cities, Midland, Michigan and Wilmington, Delaware. However, the reason that Henry Dow founded his company at Midland in 1897 was because the salt deposits in the area contain particularly high concentrations of bromide ions, and Dow had patented two methods for obtaining elemental bromine from these deposits.
- At this time, two great German companies were established Bayer in 1863 and BASF in 1865. Bayer's incentive was principally the river Rhine, a tributary of which ran through the city of Barmen (now part of the city of Wuppertal). There Friedrich Bayer set up a factory to manufacture synthetic dyestuffs from coal-tar for the textile industry. The city was near extensive coal fields, and the Rhine's tributary offered both a source of power and a means of transport.

(b) Up to the present - the twentieth and twenty-first centuries Cont.'d

- One thing that changed during the twentieth century was the importance of oil and natural gas feedstocks in supporting the growing petrochemical/polymer industry which developed principally after 1945. This explains why some installations are sited adjacent to oil fields. For example, there is a cluster of companies adjacent to the oil fields in Texas, and the discoveries and development of gas shale (still a controversial process in many countries) in places like Texas, Colorado and Pennsylvania are leading to new investment in chemical plants nearby.
- Access to the sea for transport remains a huge influence. Refineries and chemical companies have been built on the coast of many countries, whether they have their own indigenous oil and gas or whether they import it.

(b) Up to the present - the twentieth and twenty-first centuries Cont.'d

Figures 4 and 5 Refineries are located near the sea, allowing for the ready import and export of raw materials and products.



Figure 4 Storage tanks and docks at the Kwinana refinery near Perth, Western Australia.



Figure 5 An aerial view of Bukum Refinery, just off the shore of Singapore.

(b) Up to the present - the twentieth and twenty-first centuries Cont.'d

There are many examples along the US coastline of the Gulf of Mexico and in the UK. Similarly, there are refineries on the coast of mainland Europe, for example near Antwerp (Belgium) and Rotterdam (Netherlands). There are even pipelines that connect refineries, enabling easy transport of the ethene and, in the Netherlands and Belgium, the propene produced by them.



Figure 6 Distribution of ethene by pipeline across Europe.

(b) Up to the present - the twentieth and twenty-first centuries Cont.'d

 Other examples of very large refineries with chemical plants either integrated into them or nearby can be seen in Saudi Arabia (Al-Jubail, which has a large chemical complex built near a deep sea water harbor of Ras Tenura on the east coast near Bahrain), India (Jamnagar in the state of Gujarat on the north west coast) and South Korea (Ulsan on the south-east coast on the Sea of Japan). All three are among the world's largest refineries, Jamnagar actually being the largest.

(b) Up to the present - the twentieth and twenty-first centuries Cont.'d

- Another major factor determining location has always been a profitable market for the end products. Since the chemical industry is its own biggest customer, it makes good sense to group together companies that use chemical products as intermediates in their own manufacturing process. This has led to clusters of plants which successively use the output of one process as the input to another. For example, the manufacture of fertilizers, such as ammonium nitrate and urea, can be found adjacent to ammonia plants which are themselves close to plants with a ready source of raw materials, either methane or naphtha, used to make ammonia.
- More recently, close proximity to other high technology industries, as well as easy airport access, have been influential factors particularly for plants producing specialty chemicals.

7. Capital Investment

- Capital investment—the investment in new developments is made up of two main components:
 - \circ structures (e.g., buildings), and
 - \circ equipment.
- Investment in structures is mostly for industrial buildings and related structures (loading docks, terminals, etc.).
- The investment in equipment includes process equipment such as pressure vessels, storage tanks, heat exchangers, pumps, compressors and electrical equipment. These are discussed in the unit Chemical reactors.
- High priority is given to instrumentation, computers, and related automation or information processing technologies.
- New investment needs include expanding production capacity for both new and existing products, replacing worn-out or obsolete plant and equipment, and improving operating efficiencies (saving energy, increasing protection for the environment.

8. Research and Development (R&D)

Although expensive and time-consuming, research and development is crucial to the industry's evolution. To keep competitive the industry must:

- find new products which enhance the quality of life
- adapt rapidly to changes in consumer demand around the world, produce and sell chemicals in quantities that achieve economies of scale
- select locations for bulk chemical companies so that they can access the cheapest raw materials and energy
- improve existing processes for making chemicals in order to use less capital expenditure and save raw materials
- find methods of manufacturing that use and dispose of chemicals which do not harm the environment
- locate specialty chemical companies near good centers of R&D within both the commercial and university sectors.

8. Research and development (R&D) Cont.'d

The R & D cycle - deciding to carry out research on a particular topic, to spend money on development and then to manufacture - involves not only chemists and chemical engineers but other experts; financial (for borrowing the large sums of money needed), marketing (for ensuring that their new or improved product can be sold), legal (to ensure that the patents are secure) and many others.

9. Discoveries

- Sometimes discoveries have been made by accident, for example, the discoveries of both low density and high density poly(ethene). However, neither would have been discovered had chemists not already been doing fundamental research on the reactions of ethene. Other discoveries are the direct results of the clever ideas of chemists with specific aims in mind, for example the discoveries of polyamides, polyesters and, much later, linear low density poly(ethene).
- Research into new catalysts is still very fruitful. In recent years, a new catalyst for the manufacture of methanol has meant that the plant can operate at lower temperatures and lower pressures than before, thus saving much energy to the benefit of the environment. A new class of catalysts, the metallocenes have been developed for the manufacture of poly(ethene) and poly(propene) which give superior properties to these plastics for specialized uses.
- Other research areas that are now being commercialized include nanotechnology, biotechnology and the development of biofuels to supplement oil supplies. Significant benefits to the environment have come from research to develop processes which lead to improved octane rating of petrol, water-based paints, replacements for chlorofluorocarbons (CFCs) and the development of Green Chemistry as an active research area.

- Research carried out in the laboratories of industry and universities is only the first step. These discoveries have to be converted into realistic industrial processes. <u>This is the job</u> <u>of the chemical engineer</u> who is responsible for translating the laboratory chemistry to a larger scale. Scaling up production from grams under laboratory conditions to thousands of tones in a full scale industrial plant is very painstaking work for chemists and chemical engineers.
- The intermediate stages between laboratory and full scale production involve <u>pilot plants</u> with equipment that is able to mimic the large scale process and enable the most favorable conditions to be found for a high yield of product obtained at a suitable rate (Figure 7).

From research to production Cont.'d



Figure 7 An example showing some pilot <u>batch reactors</u> which are separate and operate in parallel. A computer controls each one and users can perform series of experiments, changing temperature, pressure and catalyst composition.

From research to production Cont.'d

- Figure 8 shows an intermediate stage in which a a pilot plant, has been made, to find the most suitable conditions for the new OMEGA process to produce <u>ethane-1,2-diol</u> <u>Technical Note #5</u>
 This is a very important step as often the conditions that are suitable for the process in the laboratory are not necessarily suitable when the process is transferred to larger scale equipment.
- Thus many experiments under carefully controlled conditions are carried out to obtain the maximum yield. The chemists and chemical engineers doing this work must also bear in mind the maximum yield may involve additional costs which make the process uneconomic.

From research to production Cont.'d



Figure 8 The pilot plant for the new OMEGA process to make ethane-1,2-diol.

From research to production Cont.'d

If the <u>pilot-scale</u> work is successful, the next stage is to <u>scale-up to the commercial scale</u> which, as in the case of ethane-1,2-diol, is many hundreds of thousands of tones a year (Figure 9). The profitability of the product lies in the design of the <u>industrial scale</u> <u>reactor</u> necessary for the safe manufacture of the desired products. The capital cost of such a plant is likely to be millions of dollars.

Figure 9 The actual plant for the new OMEGA process to make ethane-1,2-diol, built after successful trials on the pilot plant. This plant produces 750 000 tons of the diol each year.



From research to production Cont.'d

- <u>Designing a plant is a team project and chemical engineers, plant designers and chemists</u> select suitable materials for the construction of the plant. Although the common image is of chemical plants made from gleaming <u>steel</u>, many other materials are used in their construction including a wide variety of <u>metals</u>, plastics, glass and rubber. As construction materials are themselves chemicals, choosing materials which do not react with the chemicals involved in the process is essential to avoid hazardous interactions, the breakdown of the plant, or the contamination of the product.
- Construction materials must be
 - $\circ~$ inert to reactants, intermediates and products
 - o capable of withstanding very high pressures and temperatures when necessary
 - \circ durable.

Technical Note #5: Ethane-1,2-diol (Ethylene glycol)

Ethane-1,2-diol, (ethylene glycol, monoethylene glycol, MEG) which is manufactured from ethene via epoxyethane, is used to make polyester fibers, resins and films although it is probably better known for its use as a coolant in cars. <u>It is miscible with water and it lowers</u> the freezing point of water so it is used as an antifreeze.

$HO-CH_2-CH_2-OH$

Uses of ethane-1,2-diol (ethylene glycol) Technical Note #5

By far the most important uses of the diol is in the manufacture of polyesters, particularly (polyehylene terephthalate), PET used widely for clothes and for packaging. Indeed 45% of the polyester is used for bottles. Uses of ethane-1,2-diol.

others 6% antifreeze 8% PET (polyester) 86%

Uses of ethane-1,2-diol (ethylene glycol)

Another important use is as a coolant in engines. In modern engines, higher running temperatures mean better fuel efficiency and reduced emissions. Water is by far the best coolant, having a low viscosity, high specific heat capacity and high thermal conductivity, but is limited in its use because of its relatively high freezing point, low boiling point and it corrodes metals. Ethane-1,2-diol (antifreeze) mixed with water up to 60% volume gives a solution with a freezing point down to 223 K. The boiling point of the mixture also increases. The corrosion problem is addressed with corrosion inhibitors.

Annual production of ethane-1,2-diol (ethylene glycol)

World	18 million tons
Europe	5 million tons
North America	3 million tons
US	1.1 million tons
Manufacture of ethane-1,2-diol (ethylene glycol)

Epoxyethane, produced from ethene, reacts with water to form ethane-1,2-diol:

2

$$H_2C \longrightarrow HO-CH_2CH_2-OH \Delta H^{\odot} = -79.4 \text{ kJ mol}^{\circ}$$

The hydration takes place under a variety of conditions, neutral, acid-catalyzed and basecatalyzed. Usually the reaction in industry is carried out in neutral conditions or is catalyzed by acid (0.5% sulfuric acid) at 320-340 K, under pressure.

Manufacture of ethane-1,2-diol (ethylene glycol) Cont.'d



A new integrated refinery and petrochemicals facility is under construction in Singapore, known as the Shell Eastern Petrochemicals Complex. It will include a very large steam cracker to produce ethene together with additions to the existing refinery on Bukom Island. A new plant to produce ethane-1,2-diol using the Shell OMEGA process, is being built on nearby Jurong Island. Bukom and Jurong llands are close together, about 5 kilometres south of the tip of Singapore.

11. The chemical industry: how safe and how environmentally regulated?

<u>Safety must be at the top of the chemical industry's agenda</u> and for good reason. Many of its products are <u>potentially hazardous</u> at some stage during their manufacture and transport. <u>These chemicals may be solids, liquids or gases, flammable, explosive, corrosive and/or toxic</u>. Manufacturing processes frequently involve high temperatures, high pressures, and reactions which can be dangerous unless carefully controlled. Because of this the industry operates within the safety limits demanded by national and international legislation.



Figure 10 Hydrofluoric acid is a very corrosive liquid. Here it is being loaded automatically into a road tanker.

11. The chemical industry: how safe and how environmentally regulated? Cont.'d

Risks and injuries

In spite of dealing with hazardous operations, the chemical industry actually has a lower number of accidents than industry as a whole. Between 1995 and 2005, across the whole of European manufacture of all types, there were over 4 injuries for every 1000 employees, twice that sustained in the chemical industry. US data, recorded as days lost due to accidents, show an even starker difference; the number of days lost in major companies in the chemical industry is 4 times less than in manufacturing generally.

Figure 11 Personnel are given extensive training in the use of safety clothing and equipment. In this photograph, maintenance is being carried out on a reactor used to produce hydrofluoroalkanes.



11. The chemical industry: how safe and how environmentally regulated? Cont.'d

Environmental regulations

There are serious concerns about the potential impact of certain manufactured chemicals on living organisms, including ourselves, and on the natural environment. These concerns include air, land and sea pollution, global warming and climate change, ozone depletion of the upper atmosphere and acid rain. 11. The chemical industry: how safe and how environmentally regulated? Cont.'d

Environmental regulations

The chemical industry has a world-wide initiative entitled Responsible Care. It began in Canada in 1984 and is practiced now in over 60 countries. It commits national chemical industry associations and companies to:

- Continuously improve the environmental, health, safety and security knowledge and performance of our technologies, processes and products over their life cycles so as to avoid harm to people and the environment.
- Use resources efficiently and minimize waste.
- Report openly on performance, achievements and shortcomings.
- Listen, engage and work with people to understand and address their concerns and expectations.
- Cooperate with governments and organizations in the development and implementation of effective regulations and standards, and to meet or go beyond them.
- Provide help and advice to foster the responsible management of chemicals by all those who manage and use them along the product chain.

11. The chemical industry: how safe and how environmentally regulated? Cont.'d

Environmental regulations Cont.'d

- In the US, chemical companies spend over \$12 billion a year on environmental, health and safety programs. This, for example, has led to the reduction of hazardous releases to the air, land and water by 80 percent over the last 25 years.
- Another environmental measure concerns the use of energy. In the 20 years from 1994, the chemical industry in the US saved about 20% energy per unit of production and in the same period energy saved per unit of production in the EU fell by 55%. Greenhouse gas emission per unit of production (the greenhouse gas intensity) decreased by 58% and 75% in the US and EU, respectively between 1990 and 2014.

11. The chemical industry: how safe and how environmentally regulated? Cont.'d

Environmental regulations Cont.'d

Only a small proportion of chemical wastes are toxic or hazardous. Most of these, together with materials which resist natural breakdown, are incinerated at high temperature. Whenever possible, the waste itself provides the fuel for this process. The gases produced are thoroughly cleaned and 'scrubbed' before release into the atmosphere, leaving only ash for disposal. Examples of how by-products are dealt with are seen throughout the units on this web site.

12. What are the challenges for the chemical industry today?

- The chemical industry is undergoing huge changes worldwide. As we have seen above, one concerns the emergence of Middle Eastern countries and China, India and Brazil as manufacturers of chemicals on a huge scale, for their own consumption and also for export worldwide.
- Companies in these countries are also investing in plant in the US and Europe whilst US and European companies are investing in plant in these large emerging countries, making the industry as a whole totally international in the way it conducts business. The challenge for companies in the US and Europe is to cut their costs while ensuring that they conform to the best practice in protecting the environment.
- As <u>oil and natural gas become ever scarcer and more expensive</u>, chemists are searching for new feedstocks to supplement or even replace oil and natural gas. And they are rediscovering the virtues of coal (still in huge supply, even though it is a fossil fuel that cannot be replaced) and biomass.

12. What are the challenges for the chemical industry today? Cont.'d

- Thus we are coming full circle. In the late 19th and the first part of the 20th centuries, the organic chemical industry was based largely on coal and biomass. Coal was heated strongly in the absence of air to form coal gas (a mixture of hydrogen, methane and carbon monoxide). A liquid (coal tar) was formed as a by-product which contained many useful organic chemicals, including benzene, and the solid residue was coke, an impure form of carbon. Coke was the source of what we now call synthesis gas. Steam was passed over it at high temperatures to yield carbon monoxide and hydrogen. Another source of organic chemicals was biomass. For example, the source of many C2 chemicals was ethanol, produced by fermentation of biomass. C3 and C4 chemicals such as propanone and butanol were also produced on a large scale by fermentation of biomass.
- Since then, from the 1940s onwards, the industry has found better and better ways of using the products from the refining of oil to produce not only all the chemicals mentioned above but many more. An example is the growth of the petrochemical industry, with the array of new polymers, detergents, and myriad of sophisticated chemicals produced at low cost.

12. What are the challenges for the chemical industry today? Cont.'d

- <u>Therefore the greatest challenge lies in finding ways to reduce our dependence on non-renewable resources</u>. Thus, as oil and natural gas supplies dwindle, we must find ways to use the older technologies based on biomass to produce chemicals in as an environmentally acceptable way as possible, in terms of energy expended and effluents produced. For example, some ethene and a range of polymers, as well as very large quantities of ethanol, are now being produced from biomass.
- Another challenge is to reduce our dependence on non-renewable resources to produce energy. The easiest way to do this is to find ways to run our chemical plants at lower temperatures with the aid of catalysts or by using alternative routes. The consumption of energy per unit of production has fallen by about 55% in the EU since 1994 and about 22% in the US since 1990. In consequence, the emission of carbon dioxide has fallen by approximately the same over the same time scales.

12. What are the challenges for the chemical industry today? Cont.'d

- The new technologies based on <u>nanomaterials</u> will also be to the forefront in future advances in the chemical industry and it will be important to ensure that the production of these revolutionary materials is safe and of economic benefit.
- The chemical industry has many challenges in the 21st century. It is only through meeting these challenges, that the industry can help society to maintain and improve its standard of living and do so in a sustainable way.