CL6 - THE MANUFACTURE OF EHTANOIC ACID

ETHANOIC ACID IN OUR WORLD

▲ **Figure 1** *A vinegaroon spider*

Ethanoic acid is the largest component, other than water, by volume in vinegar (under water). Vinegar is typically made up of 4-5% ethanoic acid by volume.

The Vinegaroon spiders are carnivorous that feed on organisms living on crops. They are a good example of natural pesticides for organic farming. When threatened, they spray a mist of about 85% ethanoic acid from an opening beneath their tail. This affects the eyes and skin of a predator, giving the Vinegaroon spider a chance to flee when in danger.

Vinegaroon spiders are helpful to agricultural industry given that vast amounts of money requires to be spent on protecting crops from other organisms that compete for them. Such natural pesticides reduce crop loss.

It was reported in 2008 that the total potential loss of crops due to pests varied from ~50% in wheat to >80% in cotton production.

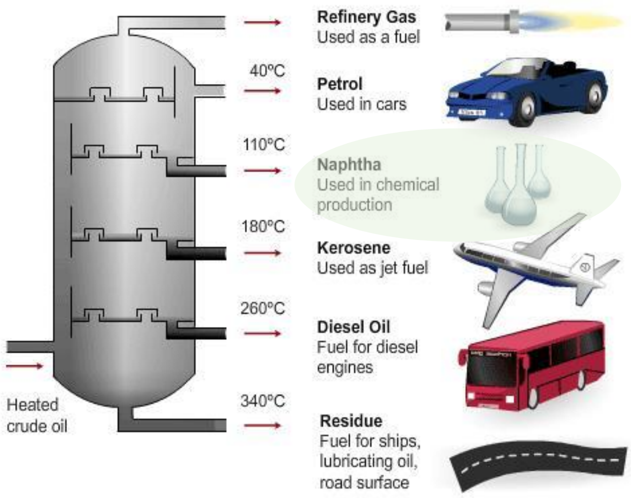
ETHANOIC ACID PRODUCTION INTRODUCTION

Ethanoic acid is mainly manufactured in industry using methanol and carbon dioxide, reacting under liquid phases with some water to keep the catalyst in solution.

$$CH_3OH_{(l)} + CO_{(g)} \rightarrow CH_3COOH_{(l)} \qquad \Delta H = -137\,\text{kJ}\,\text{mol}^{-1}$$

It works with yields and efficiency > 99%.

Until recently, much of ethanoic acid was manufactured by the non-catalytic oxidation of naptha (a fraction of crude oil distillation), giving large quantities of co-products.



Ethanoic acid, manufactured in bulk to keep production costs low, is used for a wide variety of purposes.

Some of which include making the monomer ethenyl ethanoate (for the polymer poly (ethenyl ethanoate), a polyester and another example is making ethanoic anhydride.

These are both good chemicals for emulsion paints.

An industry must consider the economy of the operating system (getting a balance between rate and yield).

THE OPERATION OF A CHEMICAL MANUFACTURING PROCESS

Principles of equilibrium and rates are required

Synthesis gas is a mixture of carbon monoxide and hydrogen. It is used to produce methanol.
The carbon is from coke (heating coal at high temperatures)

1. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad \Delta H = +131\,kJ\,mol^{-1}$ **800 – 1200^{0}C, atp**
2. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90\,kJ\,mol^{-1}$ **250^{0}C , 100 atm**
3. $CH_3OH(l) + CO(g) \rightarrow CH_3COOH(l) \quad \Delta H = -137\,kJ\,mol^{-1}$

Reaction	Temperature to increase yield	Pressure to increase yield
1.	High temperature (800 – 1200^0 C) favors the forward reaction that is endothermic. Reaction rate is also is increases exponentially since the frequency of pairs of reactant particles colliding with the combined required (activation) energy increases. The frequency of collisions also increases generally.	Carried out at atp since pressure will not increase the rate of formation of carbon monoxide and hydrogen since there a compromise made with a lower yield. 1 mole of gas on the reactant side but 2 moles on the product size so increasing pressure would decrease yield. Decreasing pressure becomes expensive.
2.	There are 3 moles of gas on the reactant side but 1 mole on the product side so increasing pressure favours the forward reaction that will reverse the affect to restore equilibrium. Therefore a high pressure of ~ 100 atm (10 X 10^6 Pa)	A high lower temperature would favor the forward reaction that is exothermic. HOWEVER, using lower temperatures will decrease the rate of reaction exponentially so a compromise is made to create a balance between rate and yield. This reaction is carried out at 250^{0}C

THE COSTS OF CHEMICAL PROCESSES

Feedstocks are the reactants that go into a chemical process

Raw materials are those which are required to obtain feedstocks. They must be prepared or treated to ensure they are sufficiently pure and present in the correct proportions to use as feedstock.

e.g. the largest part of an ammonia plant is concerned with making the nitrogen and hydrogen mixture for direct conversion of ammonia. The **raw materials for ammonia are therefore air, water and natural methane gas.**

Feedstocks needs to be prepared in a form which is easy to handle. **Gases and liquids can easily** be transferred via pies or pipelines across the world. Even so, the cost of pumping is high and pumps and pipe length is kept to a minimum.

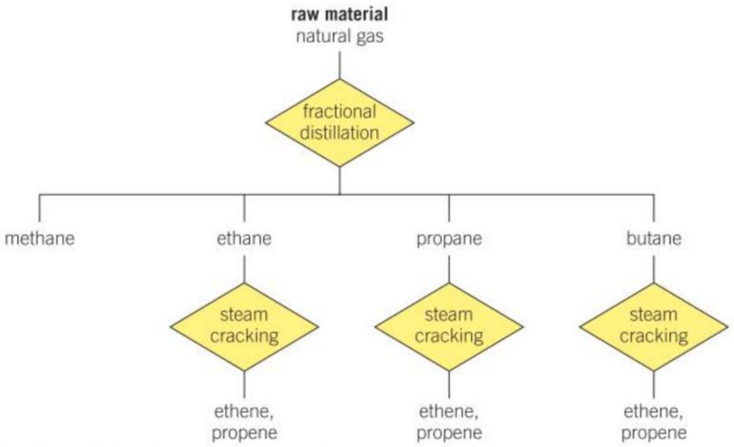
Solids are expensive to handle and so are sometimes **melted into a liquid** for transportation to **reduce costs**. Another method is to **mix solids with a liquid to form a slurry** that can be transported along a pipeline.
Sulfur is transported as a molten liquid to a plant that makes sulfuric acid.

▼ **Table 1** *Feedstocks and raw materials for some inorganic chemicals*

Product	Feedstock	Raw materials
ammonia	methane, air, water	natural gas, air, water
nitric acid	ammonia, air, water	natural gas/oil, air
sulfuric acid	sulfur, air, water	natural gas/oil (desulfurisation yields the sulfur), air, water
ethanoic acid	methanol, carbon monoxide, water	coal/natural gas, air, water

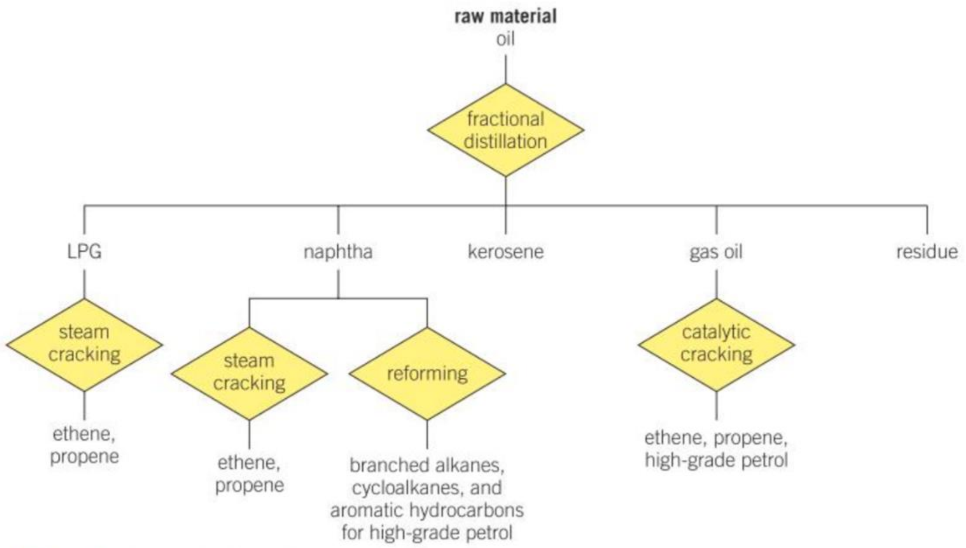
A vast majority of manufactured organic chemicals are derived from oil and natural gas.

Natural gas = mainly methane with some ethane, propane and butane present too. These are steam cracked to produce ethene and propene.



▲ **Figure 4** *Feedstocks from natural gas*

The fractions / distillates from crude oil are converted into a wide range of chemicals. The building blocks are often alkenes. However, branched-chain alkanes, cycloalkanes , and aromatic hydrocarbons are also produced for the use in unleaded petrol.



▲ **Figure 5** *Feedstocks from oil*

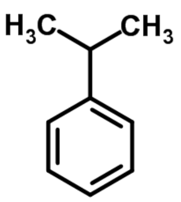
CO-PRODUCTS AND BY-PRODUCTS

- **The reaction may only form one product.**

  $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3(g)}$

- **The reaction may form two products.**

  When phenol is manufactured from 1-methylethylbenzene (cumene), he co-product propanone is also produced:



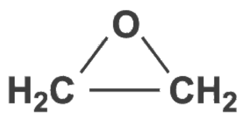
$$\underset{\text{cumene}}{C_6H_5CH(CH_3)_2} + O_2 \rightarrow \underset{\text{phenol}}{C_6H_5OH} + \underset{\text{propanone}}{(CH_3)_2CO}$$

The ratio of product to co-product is always fixed as a constant for the reaction. In this example, if 10 tonnes of phenol are produced then 6 tonnes of propanone are also produced. The molar ratio is 1:1 so this gives $\frac{10,000}{94} \approx \frac{6,000}{58}$

Proceeds from the sale of propanone (the co-product) make significant contribution to profits. The route would become uncompetitive if demand for propanone were to fall.

- **A reaction other than the one that was intended may occur (a side reaction).**

e.g. **epoxyethane, $(CH_2)_2O$**, can be made in a one step process of mixing ethene with oxygen and passing it over a **silver catalyst at 300^{0}C and a pressure of ~ 3atm.**



$$2C_2H_{4\,(g)} + O_{2\,(g)} \rightarrow (CH_2)_2O$$

However, under these conditions there is also a possibility of ethene being completely oxidized (combusted):

$$C_2H_{4\,(g)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 2H_2O_{\,(l)}$$ (unwanted side reaction)

The carbon dioxide and water form this reaction are what is known as **by-products**. Reducing the amount of side reactions occurring will help to reduce by-products.

- **Some feedstock may remain unreacted**.

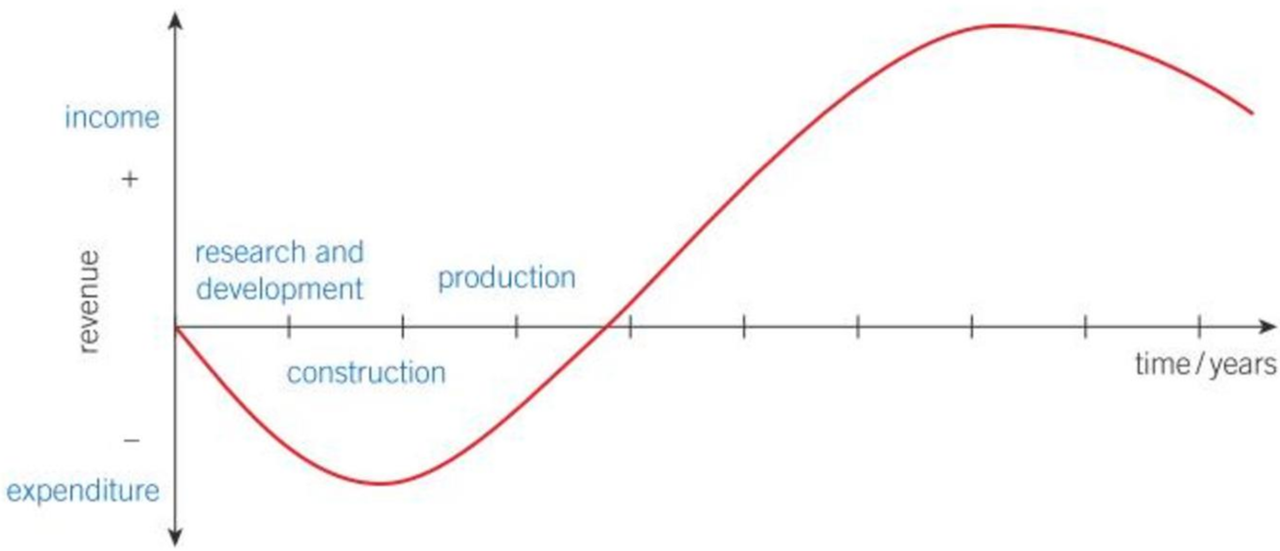
Especially if stoichiometric proportions are not accounted for.

COST

There are many costly aspects to chemical production before the end-product is even sold…

- Research and development
- Plant design
- Construction
- Initial production of chemicals

Sales of the product must generate enough return to offset these initial costs and generate a profit for the company.



The profit must eventually surplus the money invested in the development or the industrial process. Eventually, demand for the product or increasing maintenance costs, as the plant gets older, may reduce profits.

End revenue = Costs of production – (selling price X number sold)

Production costs may be fixed or variable.

Fixed (or **indirect) costs** are those incurred by the company, regardless on the quantity of product produced or sold. As soon as the production plant has been built it starts to lose value regardless of how much product is made. *Examples include: Labour costs, land purchase or rental, sales expenses and many more.*

The fixed cost element in the production cost is calculated by spreading the total annual charges over the number of units of the product produced per year.

If only 1 tonne of product is produced annually then the fixed cost element of production is significantly high than if 100 tonnes are produced with the same fixed costs.

Variable (or **direct) costs** are those incurred by the unit of production. They are dependent on the quantity of product produced. If no production occurs then these variable costs will not occur, but fixed costs will continue.

Examples include: raw materials, effluent treatment and disposal, and the cost of distribution / packaging of the product.

EFFICIENCY

The efficiency of a chemical process will also affect total costs an depends on various physical factors such as temperature, pressure, and rate of mixing.

It is necessary to find conditions that give the most economical conversion. A fine balance must be found between equilibrium and reaction rate. **The balance means that industry can maximize the output of product per unit time in order to maximize profits.**

Using extreme conditions to increase yields may exceed the cost of the end product or in some cases reduce the rate at which the reaction occurs, making it uneconomical. High temperatures and high pressures require a very specialized chemical plant that is costly to maintain, and add to the difficulty of controlling chemical reactions.

<u>Cost control often utilizes ideas of Green chemistry which aims to:</u>

Recycle unused reactants and solvents
Reduce the use of feedstocks to a minimum
Reduce energy consumption to a minimum
➔ This usually results in less waste.

▼ Table 1 *The 12 principles of green chemistry*

Principles	Explanation
Better atom economy	Means more of the feedstock is incorporated into the product and less waste products are produced.
Prevention of waste products	This is better than treating and disposing of waste.
Less hazardous chemical synthesis	Using less hazardous chemicals in the chemical reaction.
Design safer chemical products	Less toxic and hazardous chemical products.
Use safer solvents	Minimise the use of organic solvents.
Lower energy usage	Lower temperature and pressure processes.
Use renewable feedstocks	Instead of depleting natural resources.
Reduce reagents used and the number of steps	As these can generate waste.
Use catalysts and more selective catalysts	These generally reduce energy usage and waste products.
Design chemical products for degradation	When released into the environment should break down into innocuous products.
Employ real time process monitoring	Better monitoring of chemical processes reduces waste products.
Use safer chemical processes	Choose processes that minimise the potential for releasing gases, fires and explosions.

The costs of process is significantly reduced if an effective catalysts is found.

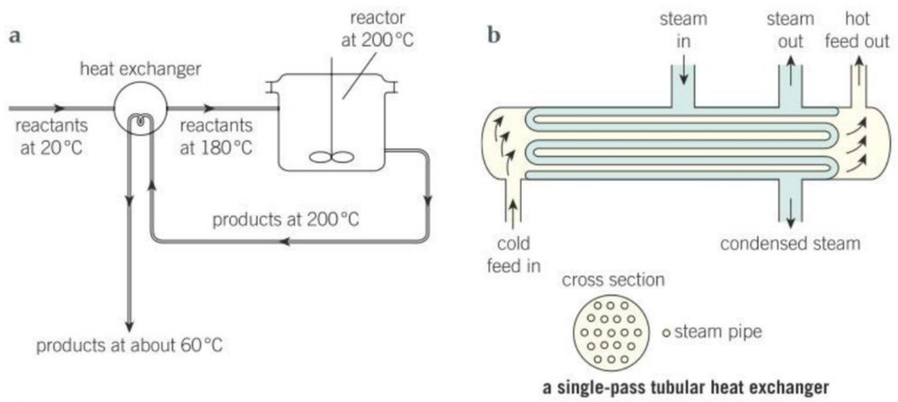
Huge savings are made by recycling unreacted feedstock.

Saving energy that would otherwise be lost to the environment also helps.

Sometimes, the ability to sell on a co-product can be the difference between making a profit or not (a co-product or a bi-product).

SAVING ENERGY

Efficient use of energy is an aim in most chemical processes, particularly in response to rising energy prices and environmental awareness. Many chemical reactions are exothermic. This thermal energy can be conserved by lagging pipes and by using heat exchangers. Thermal energy from exothermic parts if transferred to endothermic parts. This is done to raise reactant temperatures where it is safe to do so. When flammable substances are involved, it is much safer to use steam to transfer heat energy within a chemical plant. The steam is generated in a separate chemical plant away from the process, a much safer alternative to gas, electricity or oil.



▲ Figure 7 *Conserving thermal energy with heat exchangers*

AN integrated plant makes use of steam/hot liquids/gas streams to transfer heat form one process to a completely different part of the plant. This reduces the costs of electricity, gas or oil.

By comparison, a smaller plant would have to raise steam in a special boiler using purchased gas or oil or electricity. The price of energy would be considerably higher in relative terms than that in an integrated plant.

HEALTH AND SAFTEY

A balance must be made between the risk and the likelihood of that risk occurring against the benefits the chemical industry can bring to the quality of life.

Safety aspects in chemical industry are affected by national and European Union legislation. While legislation and planning are essential, the key factor ensuring safety is for everyone within the chemical plant to recognise that it is in their best interest to work safety.

Main pieces of legislation affecting industry are:

The Heath and Safety at Work Act, 1974	UK legislation places responsibility for **health and safety with the employer**. Personal safety is rated very highly and it is not uncommon to see **eye-baths, showers, toxic gas refuges, breathing apparatus, emergency control rooms** and (on larger sites) the company's own **fire brigade, ambulance service,** and a well-equipped **medical centre** with its own qualified **doctors and nurses**.
The Control of Substances Hazardous to Health (COSHH) Regulations, 2002	These control the **amount of exposure employees** have to hazardous chemicals. Where possible, the production of hazardous chemicals is minimized early on in production by **utilizing reaction conditions that reduce the amount of toxic by-products being produced** *(e.g. using lower temperatures may work for some reactions).* Steps taken might also include the use of **extractors** and the implementation of **safe handling and storage** of hazardous chemicals. These may be raw materials, by-products, products or reactants.

Hazard	Risk	Precaution(s)
Flammable gases	Explosions / fires	• Stored in **flameproof,** pessurised **cylinders.** • Incinerate under **controlled conditions.** • **Extractor fans.**
Acidic gases	Corrosive, irritant, acid rain is made for the environment	• **Neutralise** by passing through a **scrubber** contianing an alkaline material. • Regular **checking** of the plant **for leaks.**
Toxic emissions	Various, depending on the material	• Check **protocol** for the process to **minimise emissions** • **Monitor** levels of **emissions** • Ensure that all personnel are familiar with the **evacuation procedure.**

The Control of Major Accident Hazards (COMAH) Regulations, 1999	Some reagents used by chemical companies could become a hazard to **people living near the plant** in the event of an accident. This applies particular to **poisonous gases or volatile liquids**. If a plant requires the use of a reagent such as chlorine then the company works with the **local authority and emergency services. Emergency procedures and sirens** are r**ehearsed** so that everyone **understands the warning signs** and procedures to go **indoors and close all windows** until he all clear is given.
Registration, Evaluation, Authorisation, and Restriction of Chemicals, 2007  ▲ **Figure 9** *Bioaccumulation is a big environmental issue. The pesticide DDT was widely used before it was discovered to cause thinning in eggshells of birds of prey, such as the Bald Eagle, through bioaccumulation (build up in food chains). Since DDT was banned in the USA, the Bald Eagle's population has recovered significantly*	**EU regulation** addresses the **production and use** of chemicals, and **any potential effects** on **human health** and the **environment.** The **REACH regulation** puts responsibility on the company and requires that **any manufactured or imported chemical substances** must be **registered** with the **European Chemicals Agency (ECHA).** The ECHA must be i**nformed if the use of chemicals classified as `substance of very high concern` (SVHC)** are used in **significant quantities**. Substances are SVHC if they are: **carcinogenic (caner causing), mutagens (cause genetic mutations), interfere in normal reproduction** or **bioaccumulate (build up in food chains).**

RISKS VERSUS BENEFITS (DON'T JUST KEEP THE RISKS INTO PERSEPECTIVE)

The chemical industry in the UK generated $60 billion US dollars' worth of chemical sales, provided the world with biofuels, colourants, foodstuffs, paints, fertilisers, and so on.
The chemical industry improves the day to day quality of life for millions of humans and animals.

Sun cream (nanotechnology), hydropolymers (for contact lenses), water treatment chemicals (helping provide sanitary living conditions, food additives (extending shelf lives and improving tastes and appearances), the ever expanding range of pharmaceutical products….