Prepared by

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Industrial Chemistry

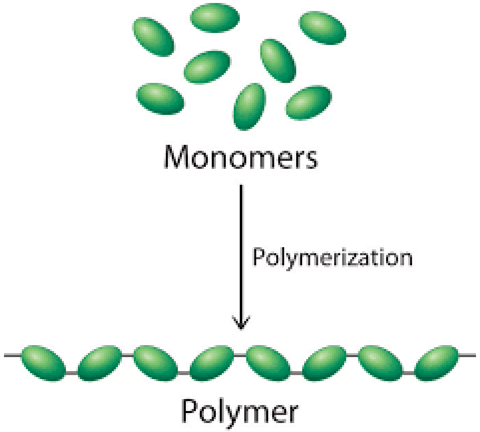
Is the branch of chemistry which applies physical and chemical processes towards the transformation of raw materials into products that are of benefit to humanity.

This is a view of the largest site in the world devoted to the industry, at Ludwigshaven in Germany.

Importance of Chemical Industry

- Chemicals play a major role in our food. The **preservatives**, **taste enhancers and flavours** helps the food to be palatable and increase the shelf life.

- More than **80%** of the chemical industry concentrates on producing **polymers, and plastics**. They are not only used in packing, but also in numerous other things, like wiring, furniture, clothing, home décor, prosthesis and electronics. PVC piping, water tanks, huge storage containers are made out of plastics.



Importance of Chemical Industry

- Fertilizers, and pesticides aids in the agriculture and development. The fertilizers and pesticides, not only increase the yield of the crop, but prevent from pest attacks.

Importance of Chemical Industry

- Pharma industries and life-saving drugs

Importance of Chemical Industry

- Toiletries like soaps, detergents, scents, perfumes, cosmetics are personnel care products that we use every day.

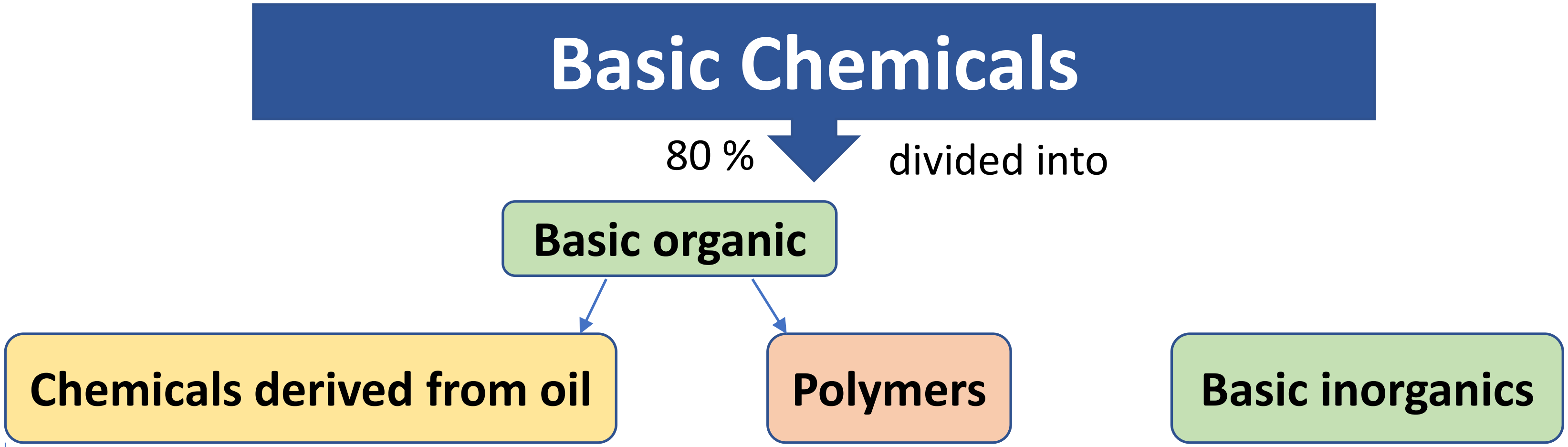
Classification of chemical industry products

The products of the chemical industry can be divided into two categories:

- Organic chemical industries
- Inorganic chemical industries

Also, it can be divided into

- Basic Chemicals
- Speciality Chemicals
- Consumer Chemicals



Basic Chemicals

80 %

divided into

Basic organic

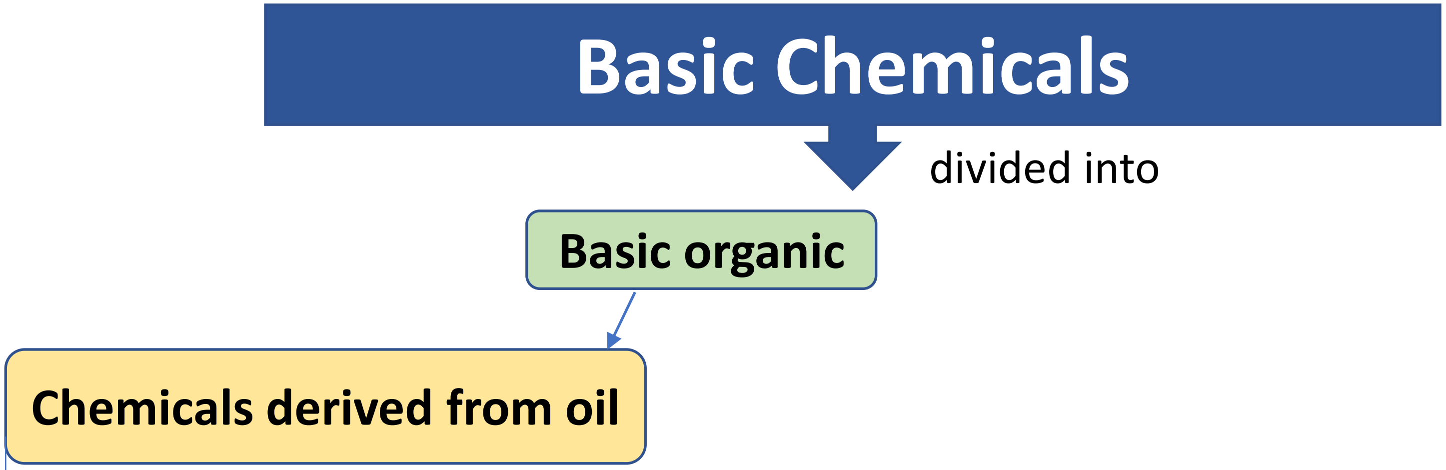
Chemicals derived from oil

Polymers

Basic inorganics

petrochemicals

The term can be misleading as the same chemicals are increasingly being derived from sources other than oil, such as **coal** and **biomass**. An example is methanol, commonly produced from **oil and natural gas** in the US and Europe but from **coal** in China. Another is ethene, derived from **oil and gas** in the US and Europe but increasingly from **biomass** in Brazil.



Basic Chemicals

divided into

Basic organic

Chemicals derived from oil

petrochemicals

Hydrocarbons are the main products in crude oil and gas, which separated using their differences in boiling point (diffraction distillation), They are then converted to hydrocarbons that are more useful to the chemical industry, such as branched chain alkanes, alkenes and aromatic hydrocarbons. these hydrocarbons are converted into a very wide range of basic chemicals which are immediately useful (petrol, ethanol, ethane glycol, acetic acid, esters, benzene and methylbenzenes …………etc).

Basic Chemicals

divided into

Basic organic

Chemicals derived from oil

petrochemicals

Hydrocarbons are the main products in crude **oil and gas**, separated by (diffraction distillation). These hydrocarbons are **converted into a very wide range of basic chemicals which are immediately useful** (petrol, ethanol, ethylene glycol, acetic acid, esters, benzene and methylbenzenes ....etc).

Basic Chemicals

divided into

Chemicals derived from oil

Polymers

Basic inorganics

The main use for petrochemicals is in the manufacture of a wide range of polymers.

Ex:

Ethylene → Poly ethylene

Propylene → poly propylene

Esters → Poly ester

Basic Chemicals

divided into

Chemicals derived from oil

Polymers

Basic inorganics

These are relatively low cost chemicals

used throughout manufacturing and agriculture

produced in very large amounts

some in millions of tonnes a year

Basic Chemicals

divided into

Chemicals derived from oil

Polymers

Basic inorganics

The top basic inorganic chemicals

sulphuric acid, nitrogen, oxygen, ammonia, lime, sodium hydroxide, phosphoric acid, nitric acid and chlorine dominate.

The reason sulphuric acid is always number one is because it is used in the manufacture of **fertilizers, polymers, drugs, paints, detergents and paper**. It is also used in petroleum refining, metallurgy and in many other processes. The top ranking of oxygen is to do with its use in the steel industry.

Basic Chemicals

It produced in large quantities, are mainly sold within the chemical industry and to other industries before becoming products for the general consumer. For example, **ethanoic acid** is sold on to make **esters**, much of which in turn is sold to make **paints** and at that point sold to the consumer. Huge quantities of **ethene** are transported as a gas by pipeline around Europe and sold to companies making **poly(ethene)** and other polymers. These are then sold on to manufacturers of **plastic** components before being bought by the actual consumer.

Chemical industry produce

Basic Chemicals

Speciality Chemicals

Consumer Chemicals

High-value adding produced in small quantities for specific end uses

- Medicinal chemicals
- Colorants (dyes and pigments)
- Paints and inks
- Flavour and fragrances
- Surfactants
- Adhesives
- Crop protection

Chemical industry produce

Basic Chemicals

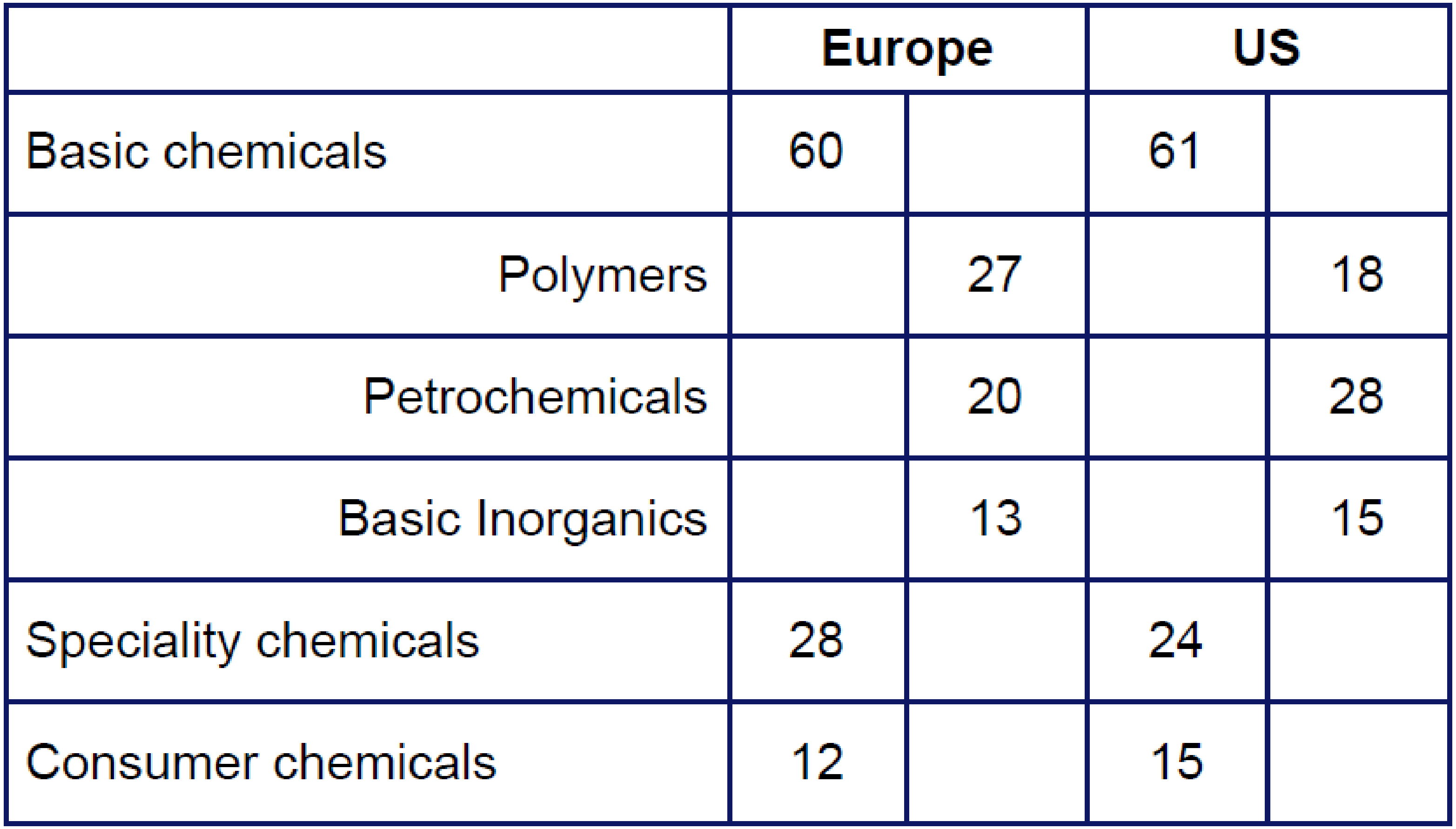
Speciality Chemicals

Consumer Chemicals

It sold directly to the public

detergents, soaps and other toiletries

Table 1: Products from the chemical industry in 2014 by category (%).

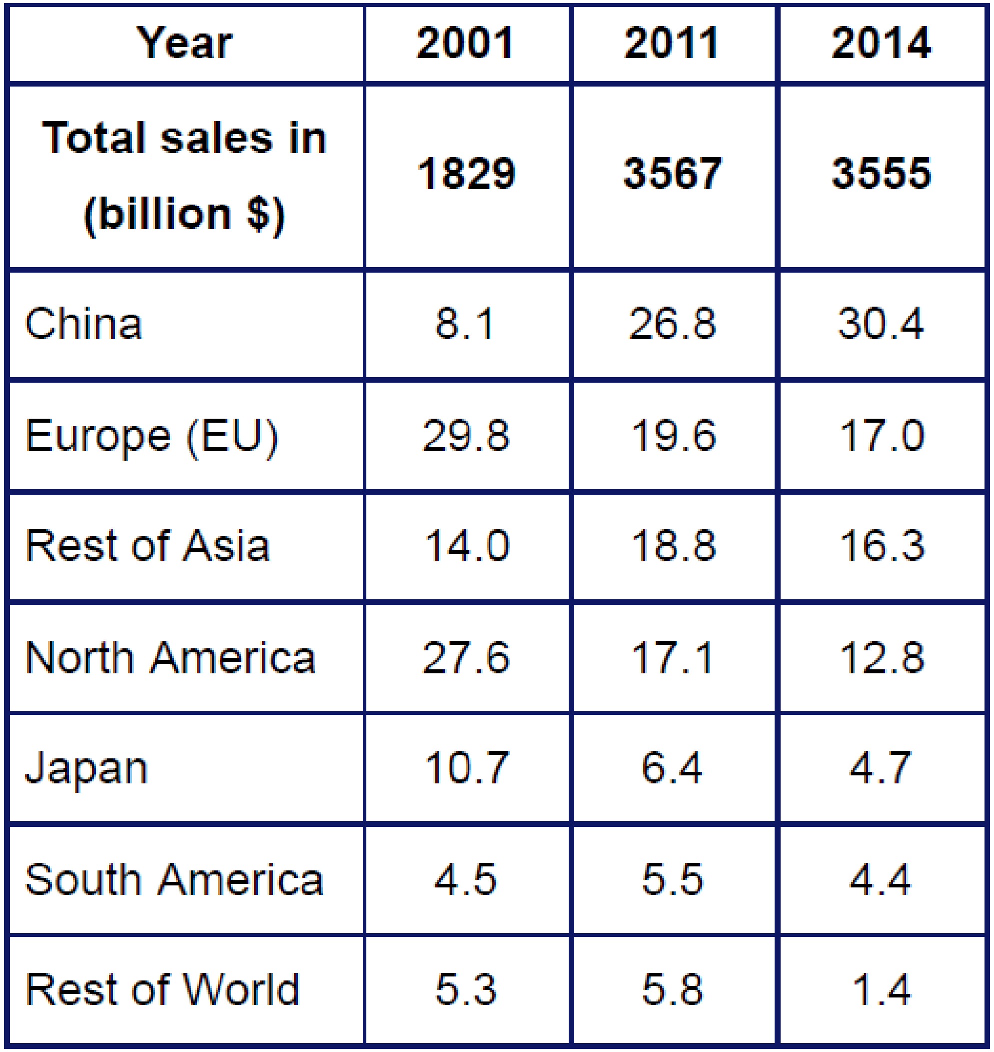


	Europe		US	
Basic chemicals	60		61	
Polymers		27		18
Petrochemicals		20		28
Basic Inorganics		13		15
Speciality chemicals	28		24	
Consumer chemicals	12		15	

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. Of course 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

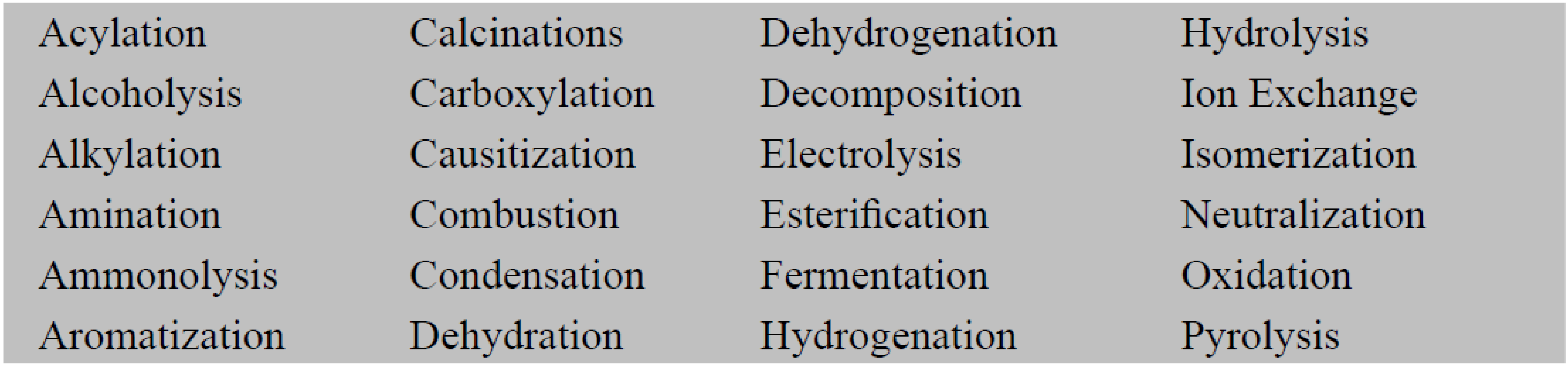
Chemical Processes in chemical industry

Every industrial process is designed to produce a desired product from a variety of starting raw materials using energy through a succession of treatment steps integrated in a rational fashion. The treatments steps are either physical or chemical in nature.

Units that make up a chemical process

A chemical process consists of a combination of chemical reactions (**Unit processes**) such as synthesis, calcination, ion exchange, electrolysis, oxidation, hydration and operations based on physical phenomena (**Unit operation**) such as evaporation, crystallization, distillation and extraction

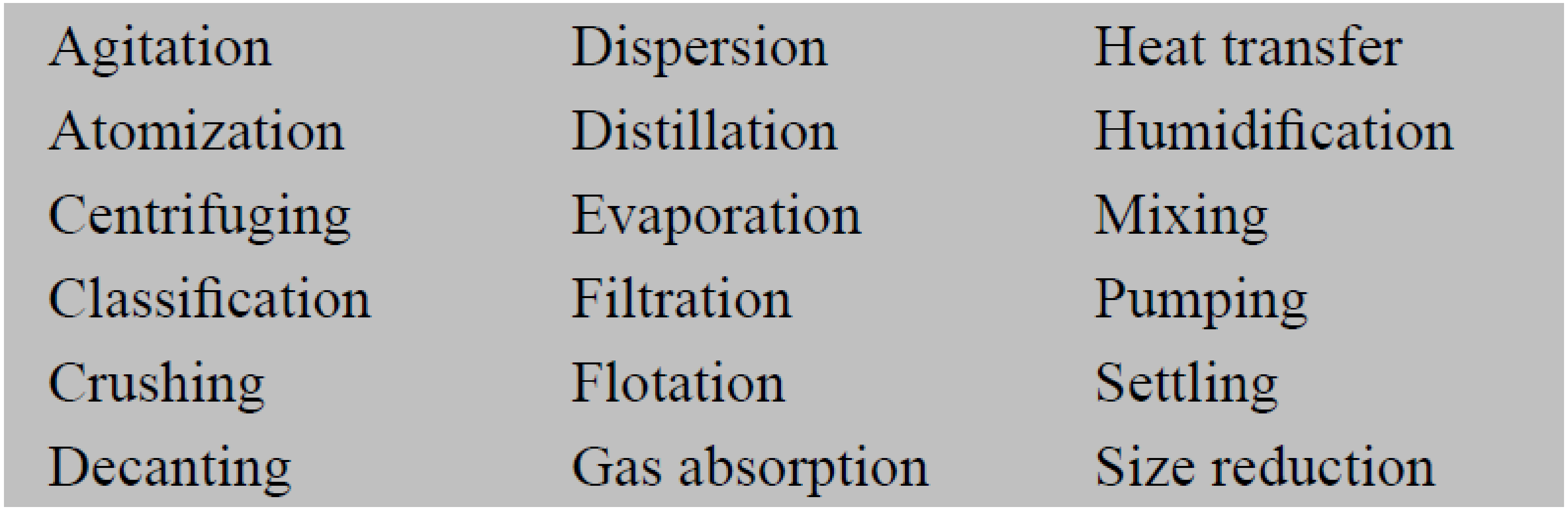
Examples of unit processes chemical transformations or conversions



Acylation
Alcoholysis
Alkylation
Amination
Ammonolysis
Aromatization
Calcinations
Carboxylation
Causitization
Combustion
Condensation
Dehydration
Dehydrogenation
Decomposition
Electrolysis
Esterification
Fermentation
Hydrogenation
Hydrolysis
Ion Exchange
Isomerization
Neutralization
Oxidation
Pyrolysis

Examples of unit operations

These are the physical treatment steps



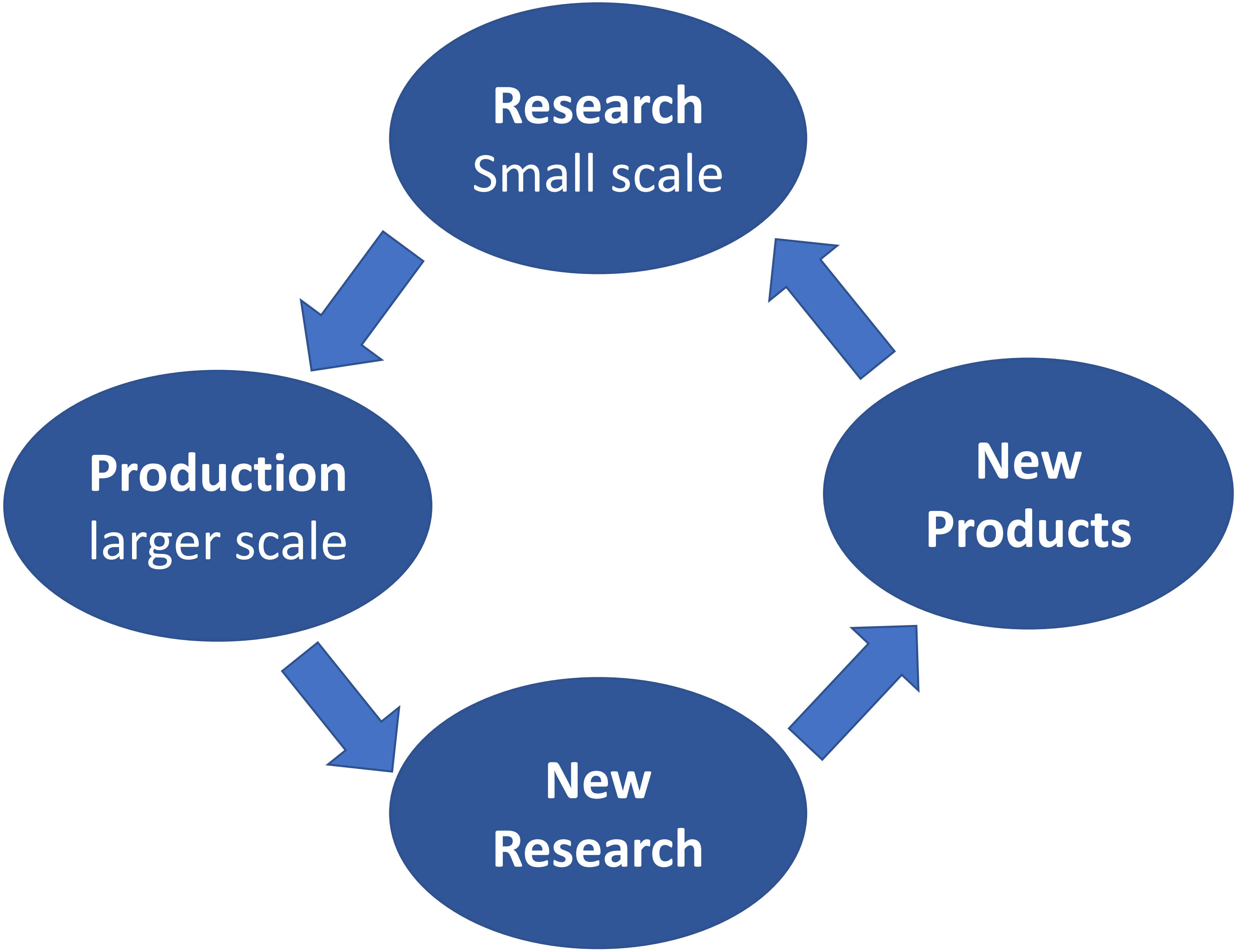
- Agitation
- Atomization
- Centrifuging
- Classification
- Crushing
- Decanting
- Dispersion
- Distillation
- Evaporation
- Filtration
- Flotation
- Gas absorption
- Heat transfer
- Humidification
- Mixing
- Pumping
- Settling
- Size reduction

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
- 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 speciality chemical companies near good centres of R&D within both the commercial and university sectors.

Research and development (R&D)



Research
Small scale

Production
larger scale

New Research

New Products

Safety

- Safety must be at the top of the chemical industry’s agenda. These chemicals may be solids, liquids or gases, flammable, explosive, corrosive and/or toxic.
- 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.

In our course we will focus on some important industries like

1- Sugar

2- Soap and detergents

3- Perfumes

4- Polymers (rubber) Silicone

5- Ethanol (Biofuels) 6- Paper………

……………………………………etc.

Sugar

by

Dr. Mohamed Y. Mahgoub

Sugar | How it's made?

Sugar is a broad term applied to a large number of **carbohydrates** present in many plants and characterized by a more or less sweet taste.

Raw materials

Juices of **sugarcane and beet** are rich in pure **sucrose**, although beet sugar is generally much less sweet than cane sugar. *These two sugar crops are the main sources of commercial sucrose.*

Global production of sugarcane and Beet in 2016

Brazil producing 41%

Sugarcane production – 2016	
Country	**Production (millions of tonnes)**
Brazil	768.7
India	348.4
China	122.7
Thailand	87.5
World	**1890.7**
Source: FAOSTAT, United Nations[42]	

Russia producing 18%

Top Ten Sugar Beet Producers—2016 (FAO)[3]

Rank	Country	Production (million tonnes)
1	Russia	51.36
2	France	33.79
3	United States	33.49
4	Germany	25.50
5	Turkey	19.46
6	Ukraine	14.01
7	Poland	13.52
8	Egypt	13.32
9	China	8.09
10	United Kingdom	5.69
Total	World	**277.23**

Other sugar crops include corn sugar

The Manufacturing Process

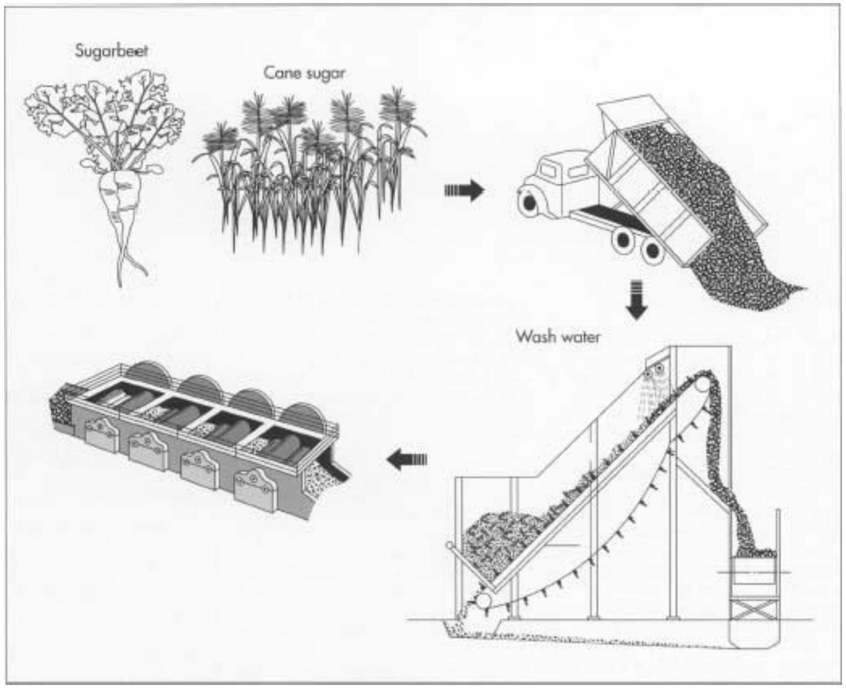
Planting and harvesting

Sugarcane requires an average temperature of **25 ^oC**

- It is grown in tropical (7 months) or subtropical areas (12-22 months)
- Sugar cane is harvested by **chopping down the stems** but leaving the roots so that it re-grows in time for the next crop.

The Manufacturing Process

Preparation



- Cutting in small pieces
- soil and rocks are removed
- It cleaned by flooding the carrier with warm water
- After that, The cane is clean and ready to be milled.

The Manufacturing Process

Processing _ juice Extraction

The first stage of processing is the extraction of the cane juice.

The pressing process involves crushing the stalks between the heavy and grooved metal rollers to separate the fiber *(**bagasse**)* from the juice that contains the sugar.

The extracted juice contains about **95** % or more of the **sucrose**

The Manufacturing Process

Purification of juice _Clarification and evaporation

- The extracted juice from the mills, green colour, is acid and turbid

- The clarification process is designed **to remove both soluble and insoluble impurities** (such as sand, soil, and ground rock) that have not been removed by preliminary screening.

The Manufacturing Process

Purification of juice _*Clarification*

Chemical treatment

- The process employs **lime** and heat as the clarifying agents. Milk of lime (*about 500 gm per ton of cane*) **neutralizes** the natural acidity of the juice, forming insoluble lime salts (**Sulphate, Phosphate, Citrate, and Oxalate**).

The Manufacturing Process

Purification of juice _*Clarification*

Chemical treatment

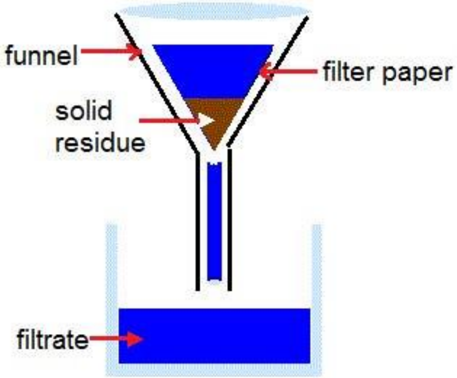
- Heating the lime juice to boiling **coagulates** the albumin and some of the fats, waxes, and gums, and the precipitate formed entraps suspended solids as well as the microparticles.

The Manufacturing Process

Purification of juice _Clarification

Chemical treatment

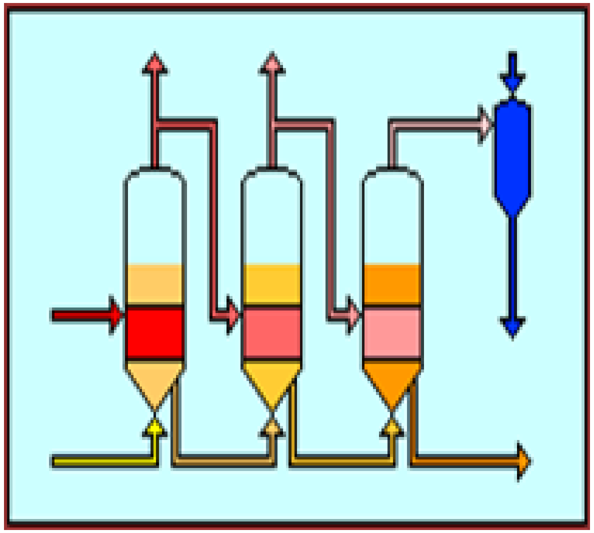
- The muds separate from the clear juice through **sedimentation**. The non-sugar impurities are removed by continuous **filtration.**



The Manufacturing Process

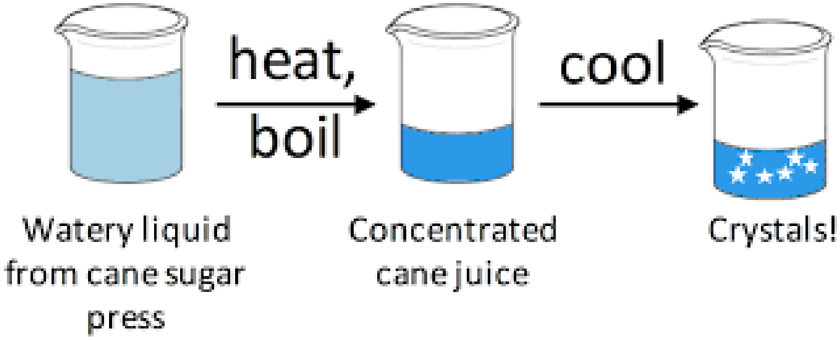
Evaporation

- To concentrate this clarified juice, about **two-thirds** of the water is removed through vacuum evaporation
- The syrup leaves the last body continuously with about **65 % solids** and **35 % water**



The Manufacturing Process

Crystallization



- Crystallization takes place in a single-stage vacuum pan. The syrup is evaporated until saturated with sugar.

- As soon as the saturation point has been exceeded, **small grains of sugar are added to the pan**, or "strike." These small grains, called *seed*, serve as nuclei for the formation of sugar crystals (Massecuite).

The Manufacturing Process

Centrifuging

- Separate sugar from molasses
- Centrifuge operates at 1000-1800 rpm
- Sugar crystals are washed with 80 °C water

The Manufacturing Process

Drying and packaging

- Once the sugar is centrifuged, it is "cut down" and sent to a granulator for **drying**

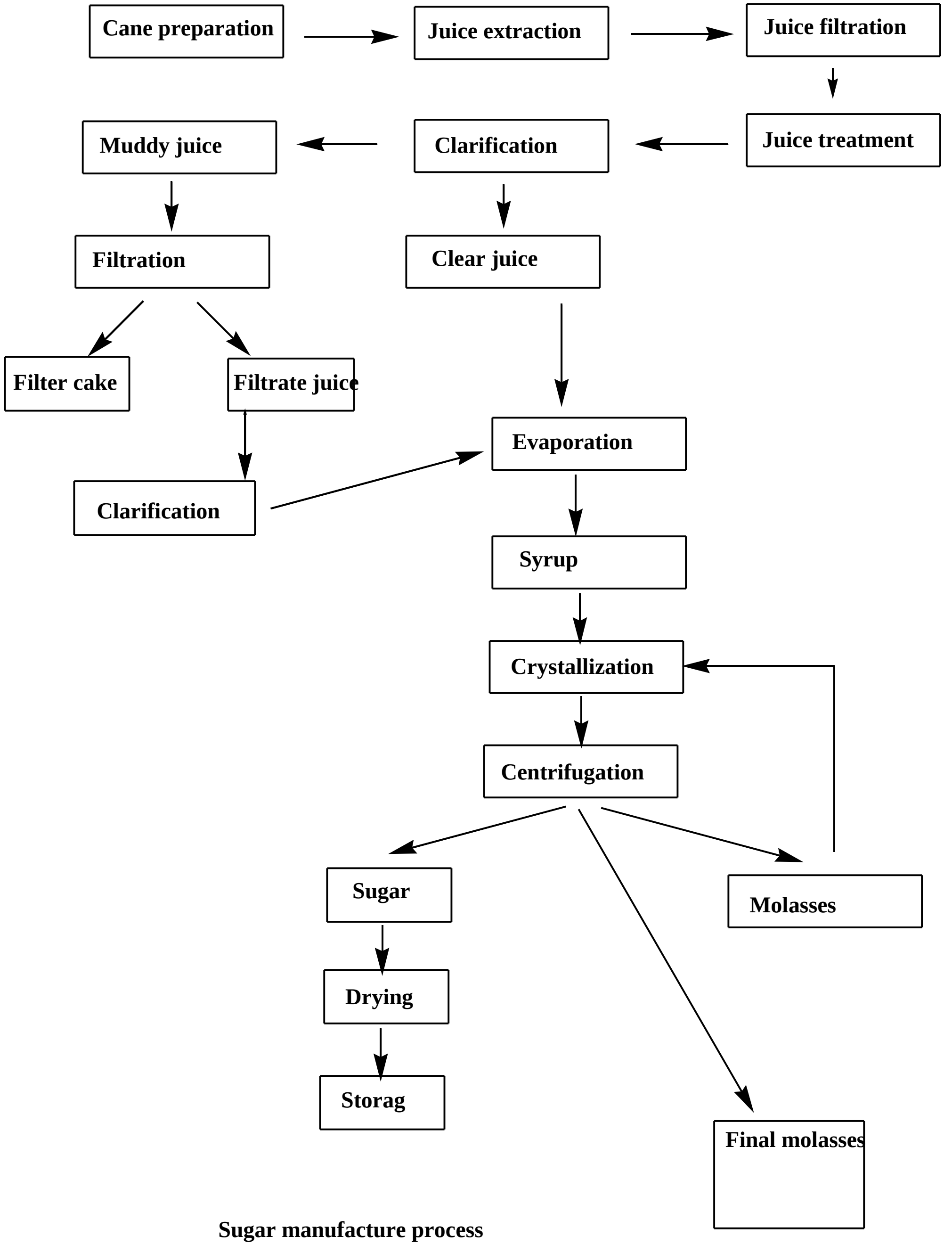
- After drying, sugar crystals are sorted by size and then **sent to be packed**

The Manufacturing Process

Drying and packaging

Sugar Manufacturing Process:

1. Growing & Harvesting the Cane.
2. Cane preparation for Milling.
3. Milling.
4. Clarification.
5. Evaporation.
6. Crystallization.
7. Centrifugation.
8. Drying.
9. Refining.



Sugar manufacture process

Soaps

by

Dr. Mohamed Y. Mahgoub

What is Soap?

Soap is a **salt of a fatty acid** used as a **surfactant** for washing, bathing, and cleaning.

Surfactant: a compound that lowers the surface tension between two liquids. (*Surface active agent*)

Made from naturally

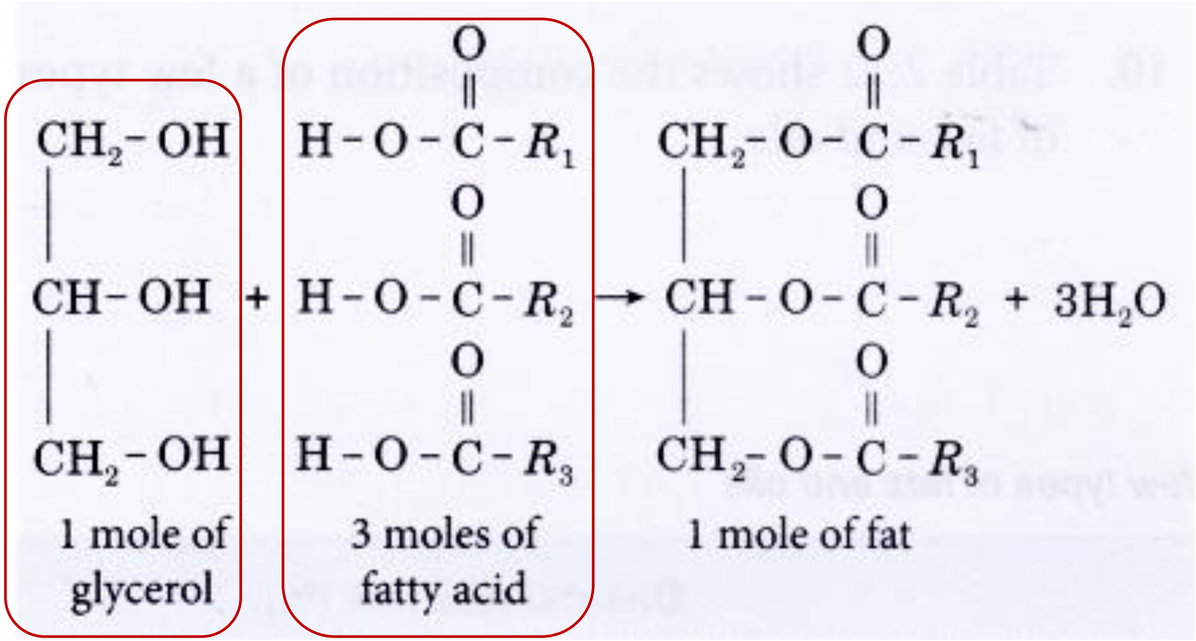
animal fats and vegetable oils

Triglycerides

Are esters of the glycerol with fatty acids (R-COOH),

R contain 7-21 carbon atoms

Esterification

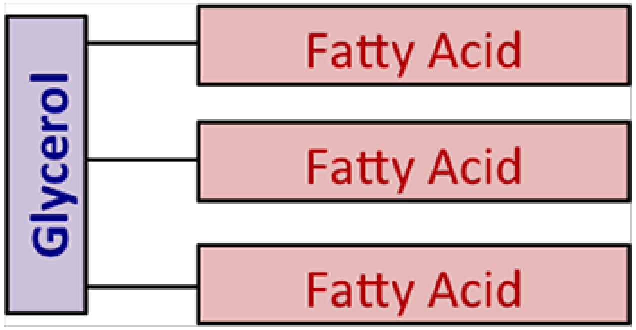


$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \begin{array}{l} H-O-\overset{O}{\overset{\|}{C}}-R_1 \\ H-O-\overset{O}{\overset{\|}{C}}-R_2 \\ H-O-\overset{O}{\overset{\|}{C}}-R_3 \end{array} \rightarrow \begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R_1 \\ CH-O-\overset{O}{\overset{\|}{C}}-R_2 \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R_3 \end{array} + 3H_2O$$

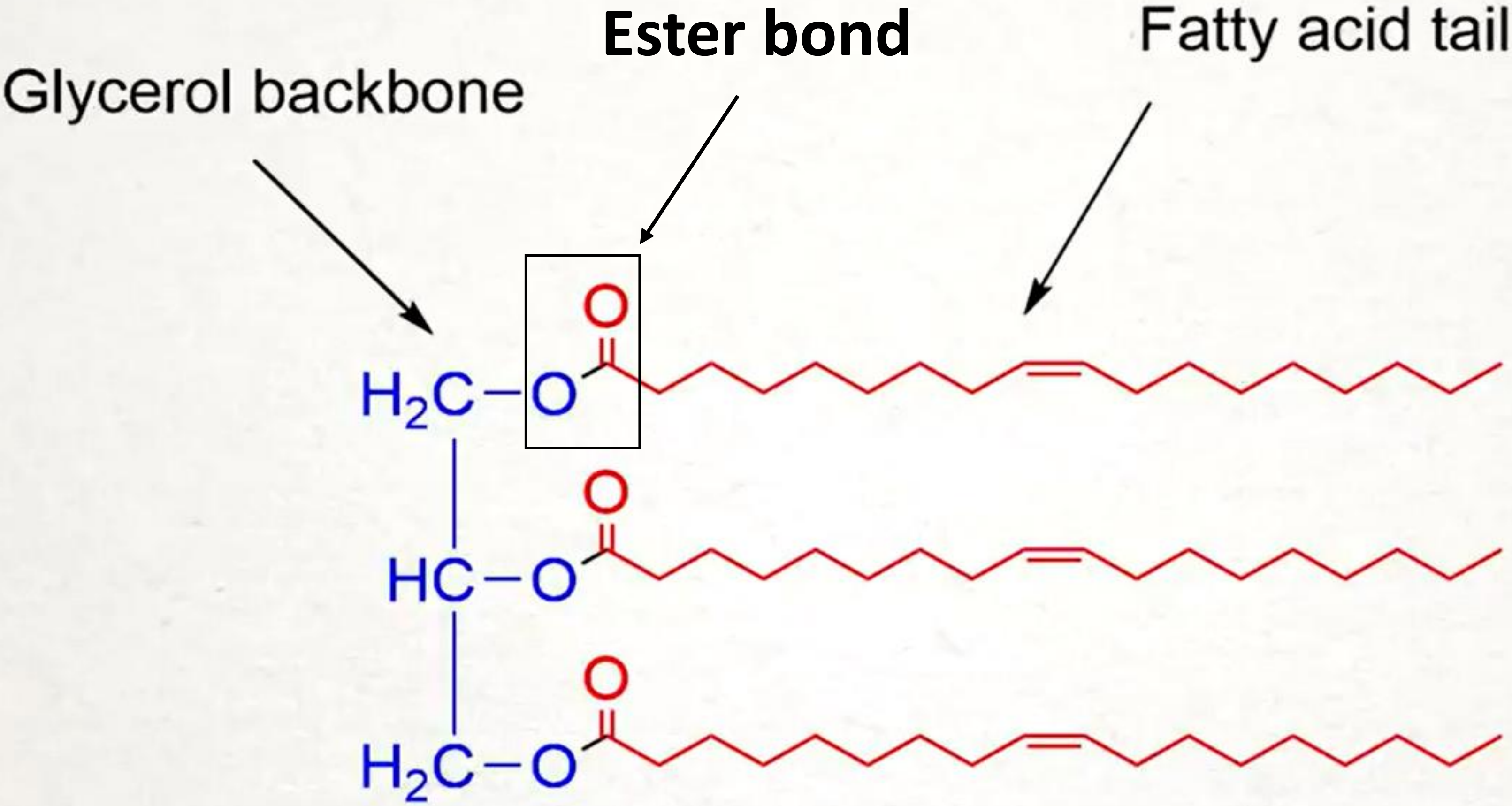
1 mole of glycerol

3 moles of fatty acid

1 mole of fat

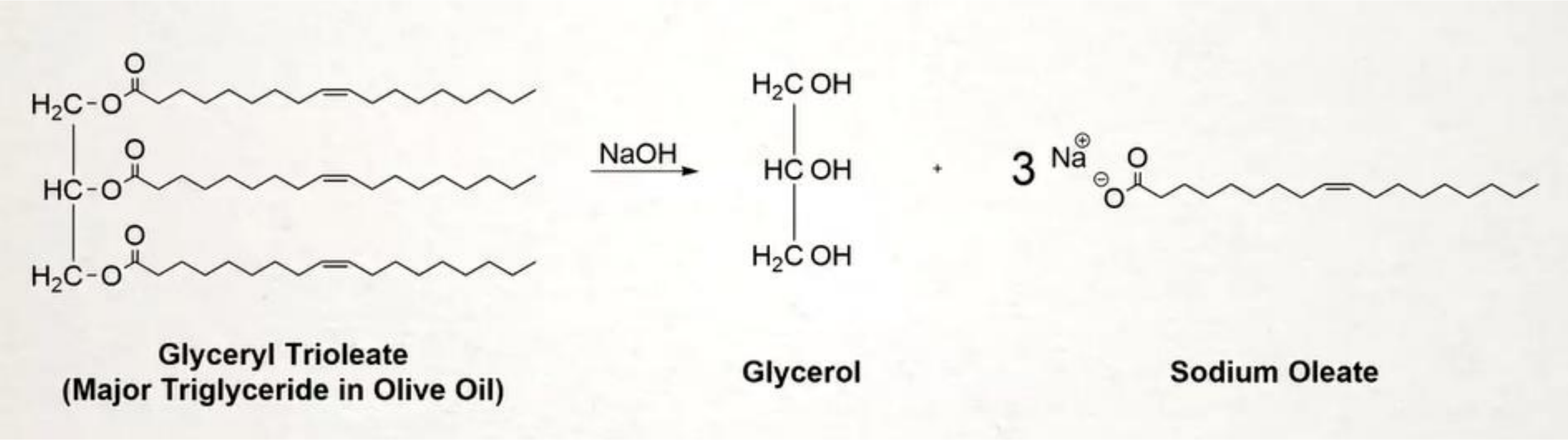


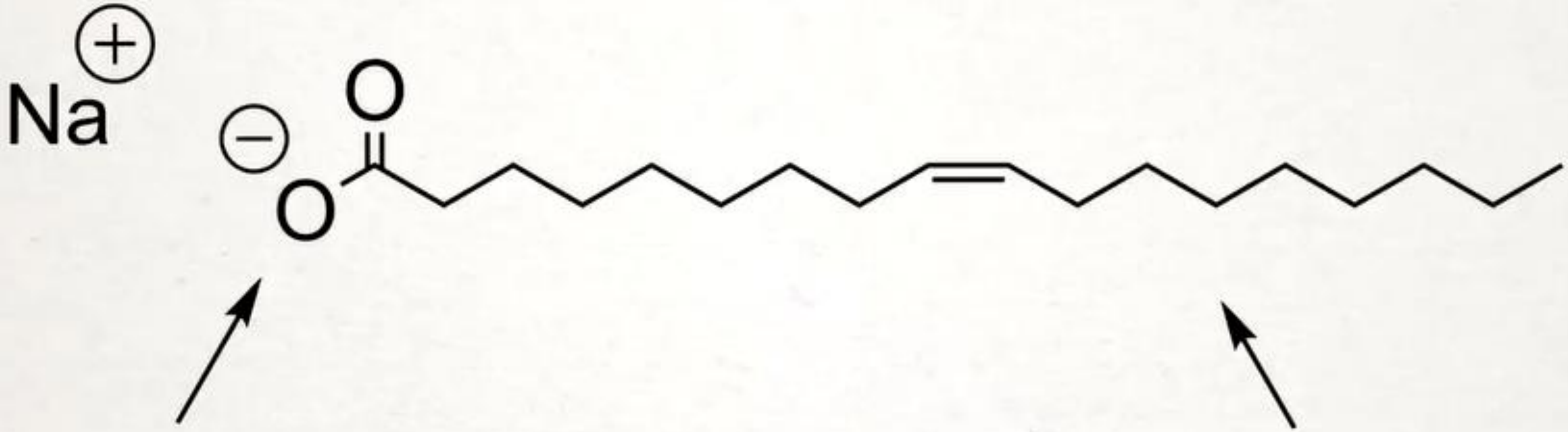
Fat or Oil



Glyceryl Trioleate
(Major Triglyceride in Olive Oil)

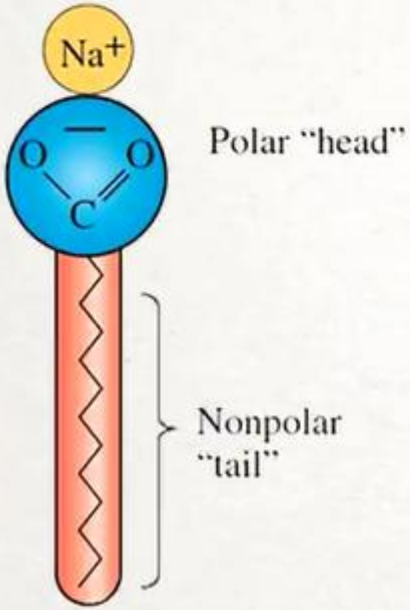
Saponification reaction



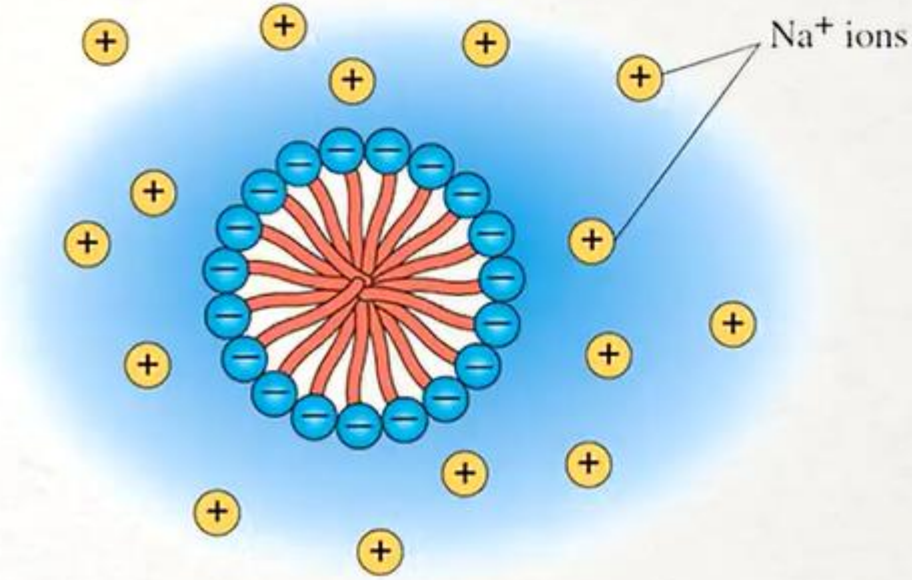


Polar
(hydrophilic)

Non-polar
(hydrophobic)



(a) A soap



(b) Cross section of a soap micelle in water

Images from: Organic Chemistry By William Brown

Soap micelle with “dissolved” grease

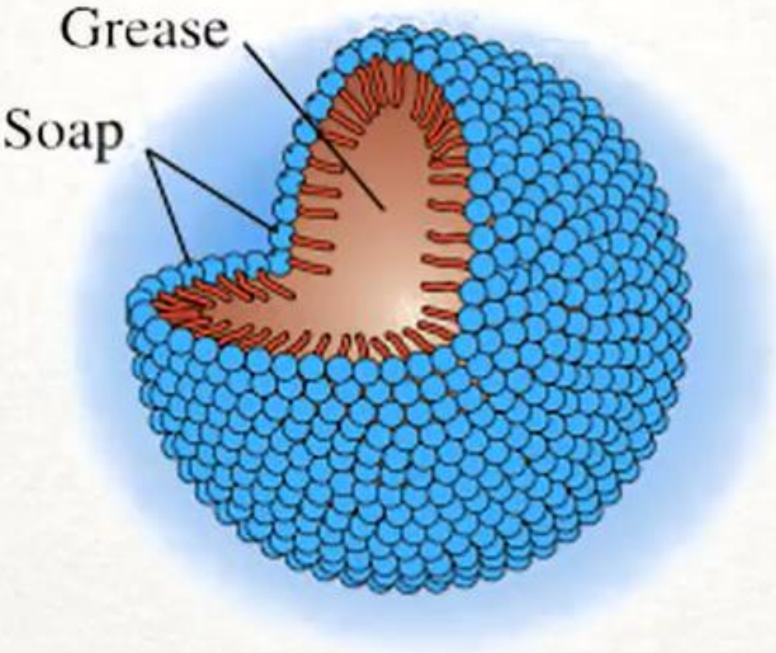
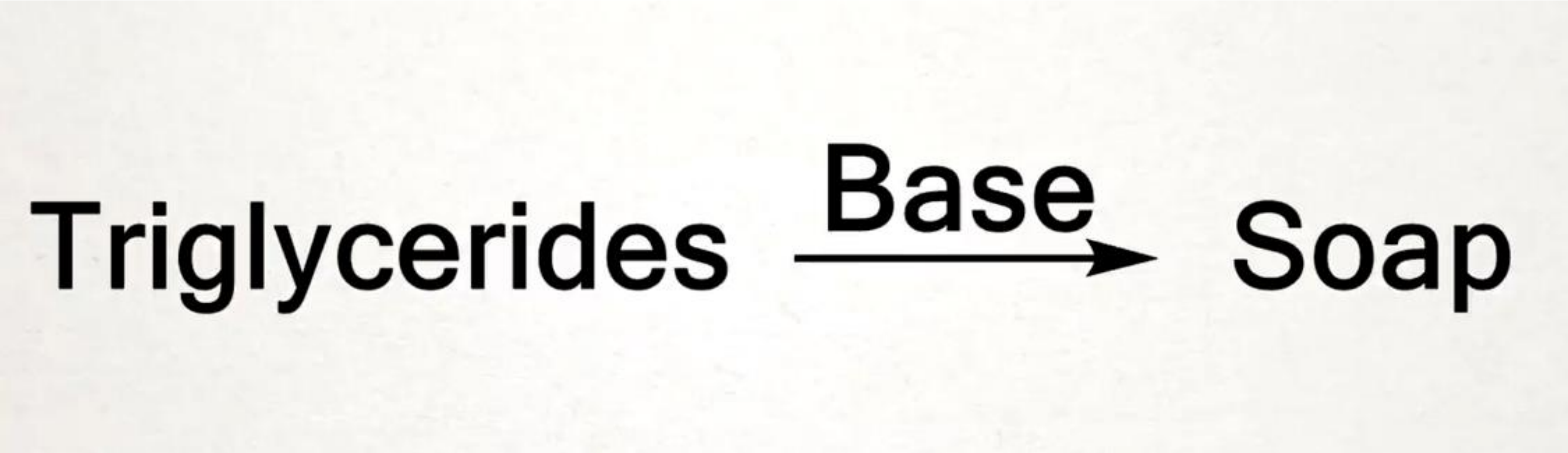


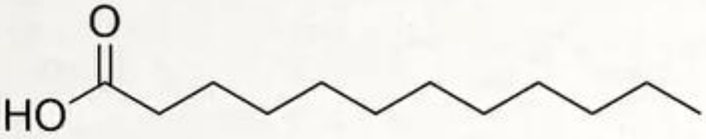
Image from: Organic Chemistry By William Brown



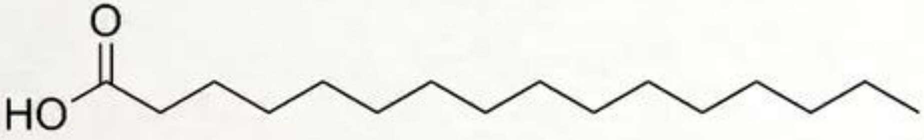
$$\text{Triglycerides} \xrightarrow{\text{Base}} \text{Soap}$$

Depending on the base that is used and the source of triglycerides, the final soap can have very different Properties.

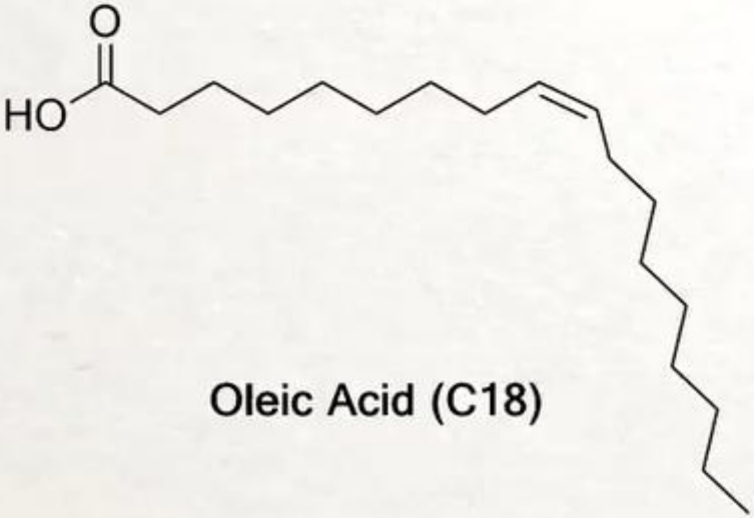
Fatty acid



Lauric Acid (C12)



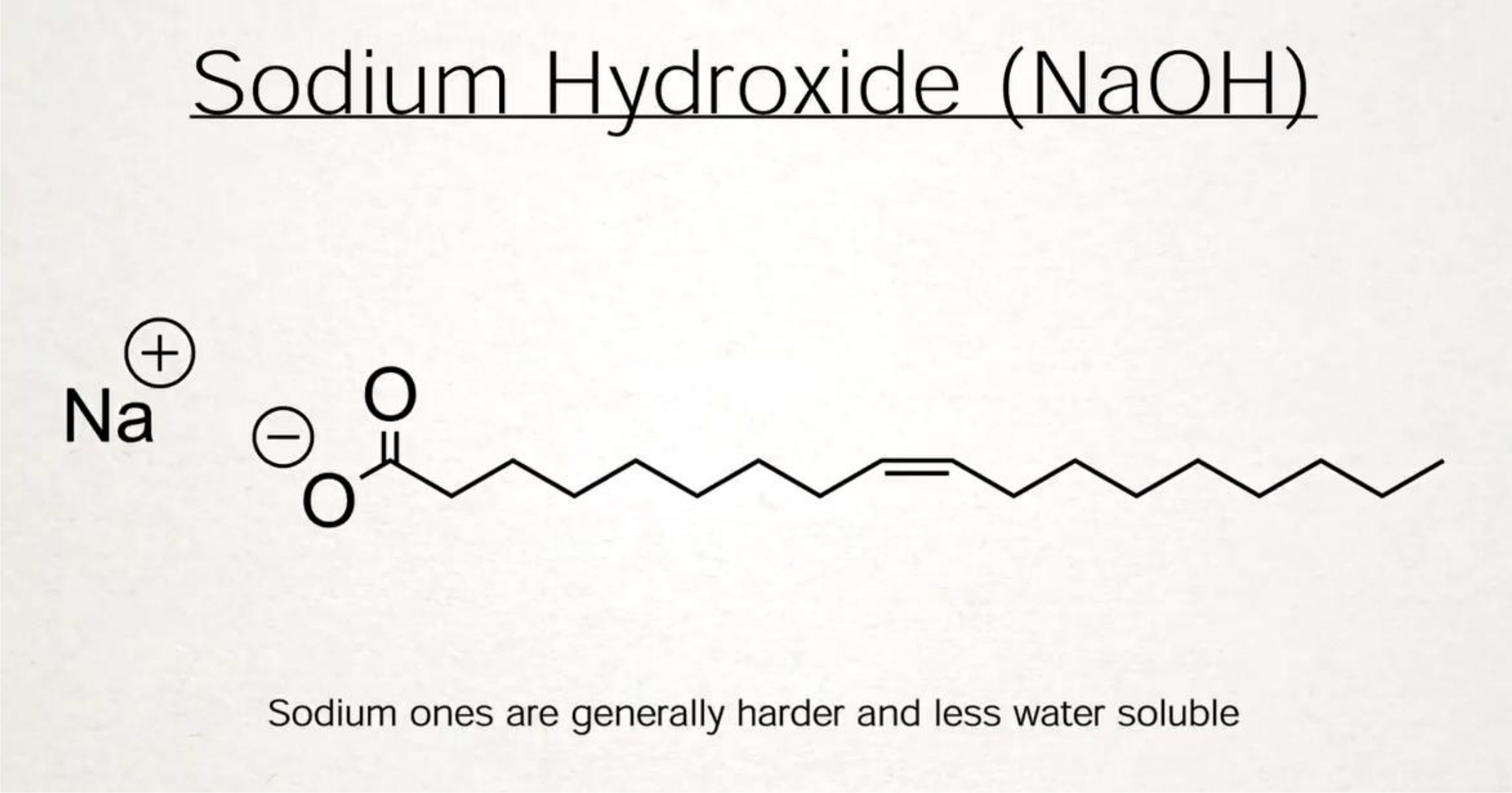
Palmitic Acid (C16)



Oleic Acid (C18)

The most important characteristic is the chain length

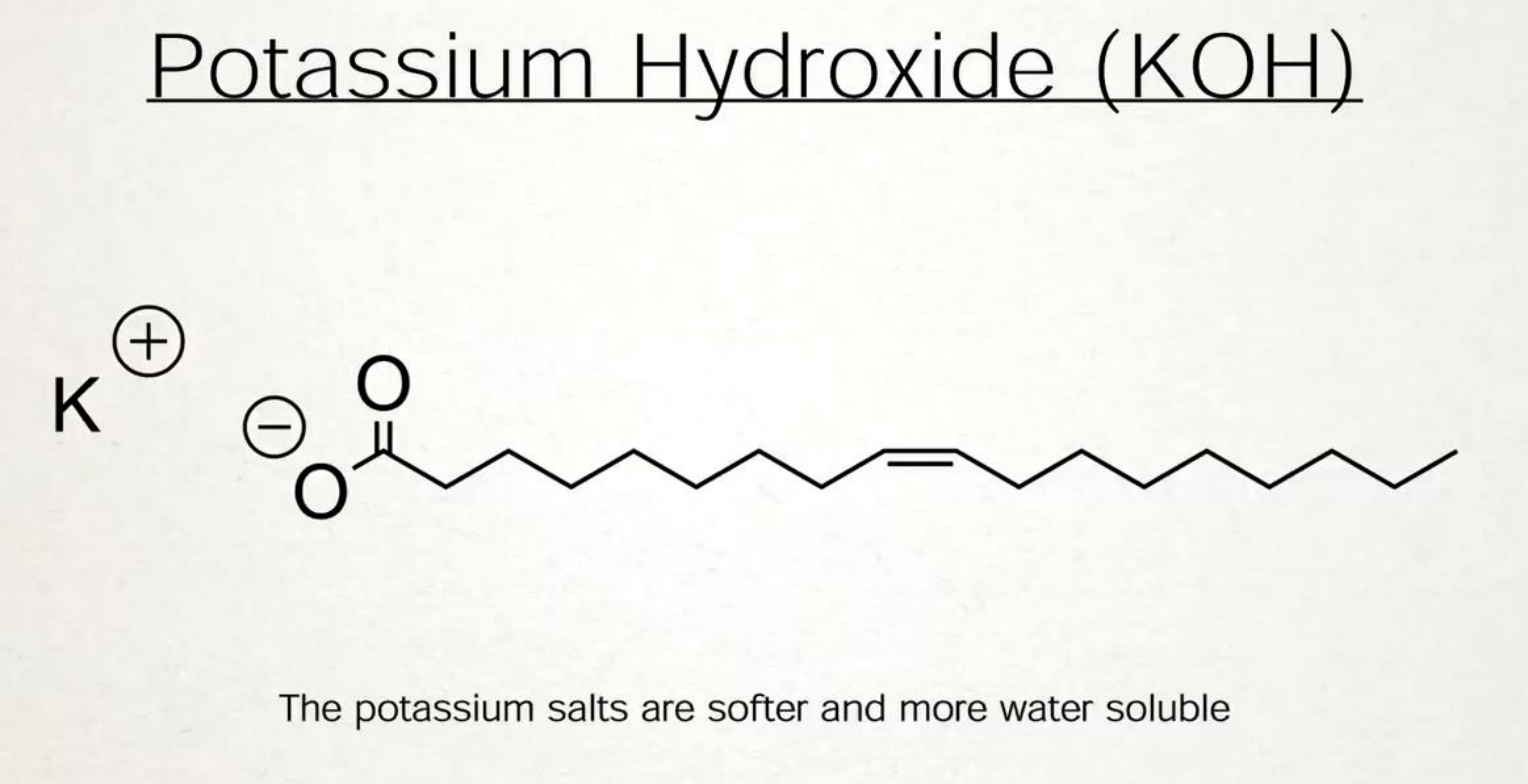
Soap with long chain fatty acid is more harder and less soluble in water



Sodium Hydroxide (NaOH)

Sodium ones are generally harder and less water soluble

It’s suitable for making solid soap

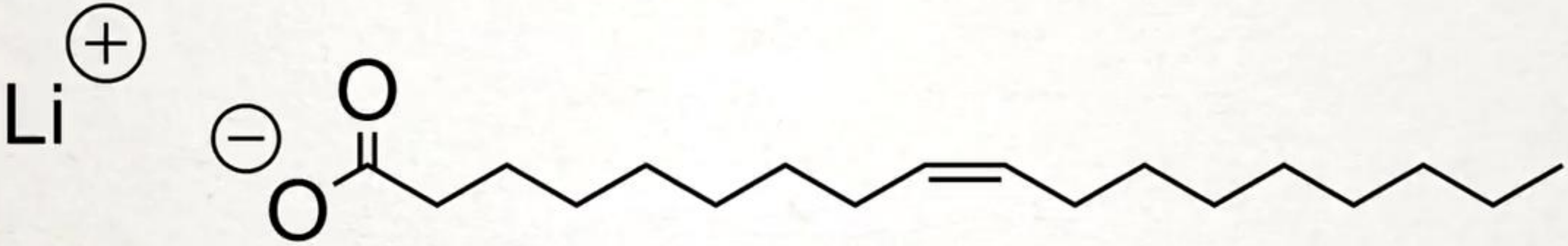


Potassium Hydroxide (KOH)

The potassium salts are softer and more water soluble

It’s suitable for making liquid soap

Lithium Hydroxide (LiOH)



Mixed with oils to make lubricants and greases

Manufacture

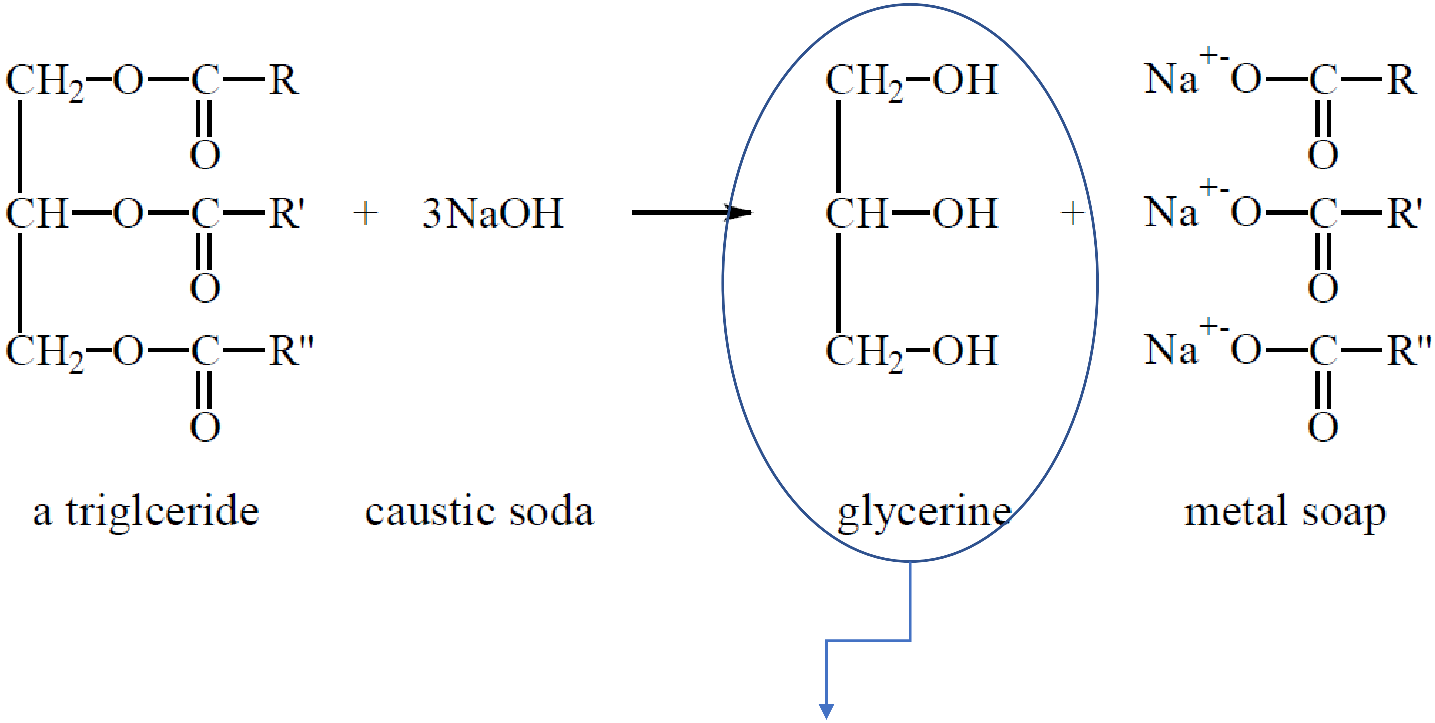
(A) Hot process

(B) Cold process

Manufacture (A) Hot process

Step 1 - Saponification

The **fats and oils** are heated with an **alkali**, usually sodium hydroxide. This process called **saponification**

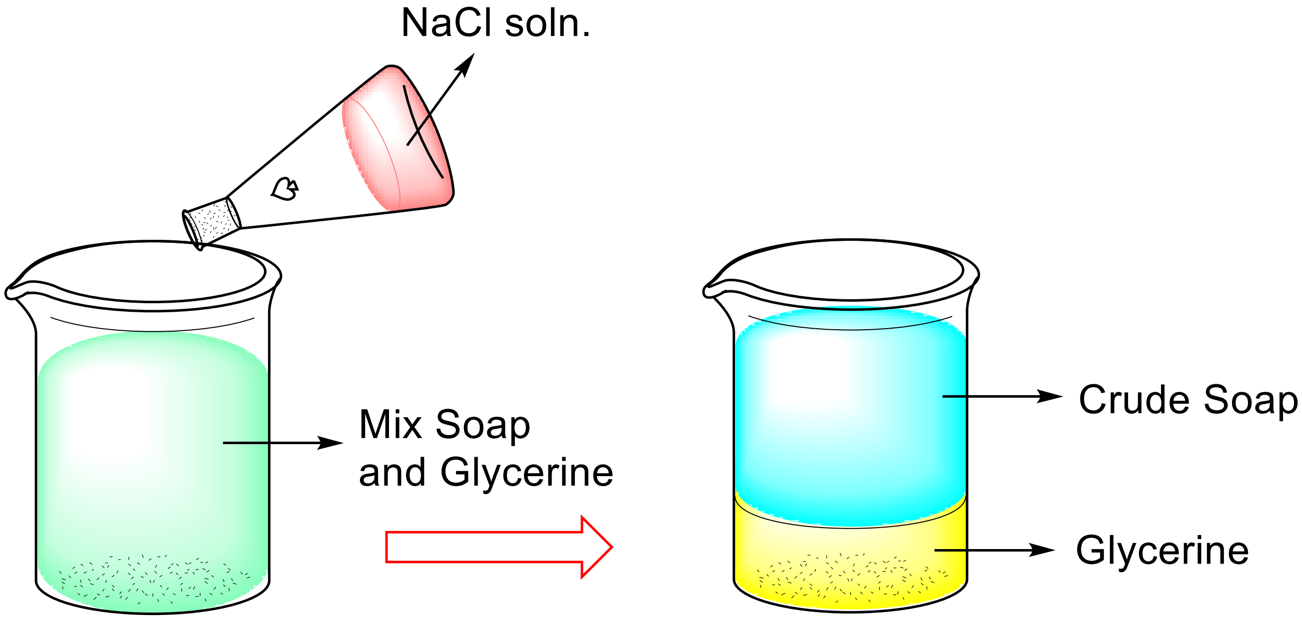


Most of it is recovered

Manufacture (A) Hot process

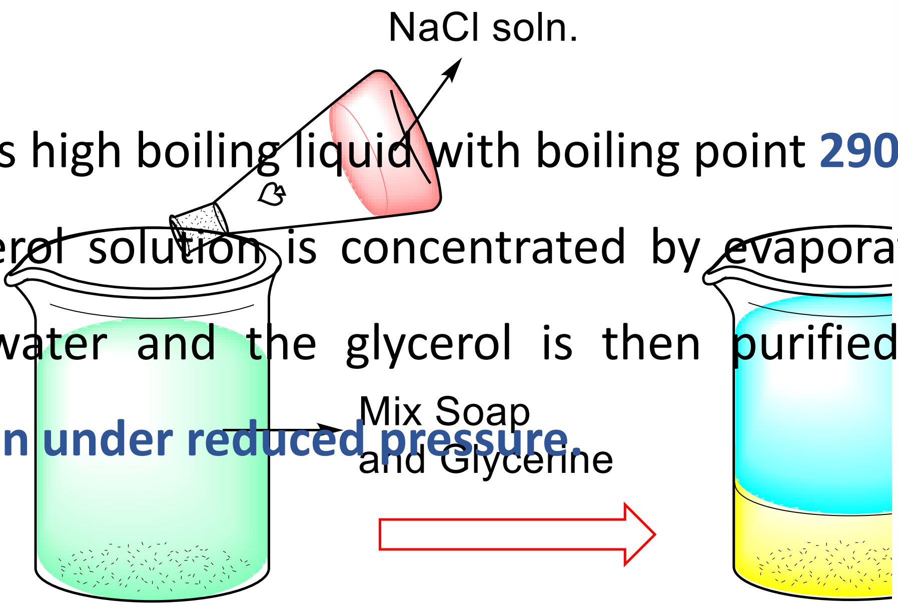
Step 2 - Glycerine removal

Some is left in the soap to help make it soft and smooth. Soap is not very soluble in salt water, whereas glycerine is, so salt (NaCl soln.) is added to the wet soap causing it to separate out into soap and glycerine in salt water.



Manufacture (A) Hot process

Step 2 - Glycerine removal



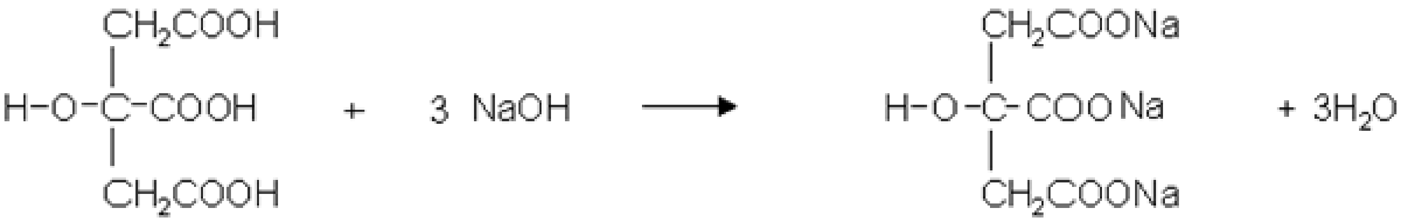
Glycerol is high boiling liquid with boiling point **290°C**

The glycerol solution is concentrated by evaporating off the water and the glycerol is then purified by **distillation under reduced pressure.**

EL LABORATORIO DE QUÍMICA ORGÁNICA

Step 3 - Soap purification

Any remaining sodium hydroxide is neutralised with a weak acid such as **citric acid** and two thirds of the remaining water removed.



$$\begin{array}{c} CH_2COOH \\ | \\ H\text{-}O\text{-}C\text{-}COOH \\ | \\ CH_2COOH \end{array} + 3\ NaOH \longrightarrow \begin{array}{c} CH_2COONa \\ | \\ H\text{-}O\text{-}C\text{-}COONa \\ | \\ CH_2COONa \end{array} + 3H_2O$$

Citric acid

Sodium citrate

Step 4 - Finishing

Additives such as **preservatives**, **colour** and **perfume** are added and mixed in with the soap and it is shaped into bars for sale.

Cold process VS. Hot Process

Cold process

Advantages

- Much easier to control the reaction
- More designs and additive options
- Fewer supplies needed

Disadvantages

- Takes a long time, 4-6 weeks

Hot process

Advantages

- Much faster, only takes a few hours

  (Plus a day or so far a final cure)
- Has a rustic appearance that some people think is cool

Disadvantages

- Much harder to make specialized designs
- Can’t use many ingredients because some can not tolerate the heat

Attached file

More details for soap manufacturing

Soap

Background

Soap is a combination of animal fat or plant oil and caustic soda. When dissolved in water, it breaks dirt away from surfaces. Through the ages soap has been used to cleanse, to cure skin sores, to dye hair, and as a salve or skin ointment. But today we generally use soap as a cleanser or **perfume.**

The exact origins of soap are unknown, though Roman sources claim it dates back to at least 600 B.C. , when Phoenicians prepared it from goat's tallow and wood ash. Soap was also made by the Celts, ancient inhabitants of Britain. Soap was used widely throughout the Roman empire, primarily as a medicine. Mention of soap as a cleanser does not appear until the second century A.D. By the eighth century, soap was common in France, Italy, and Spain, but it was rarely used in the rest of Europe until as late as the 17th century.

Manufacture of soap began in England around the end of the 12th century. Soap-makers had to pay a heavy tax on all the soap they produced. The tax collector locked the lids on soap boiling pans every night to prevent illegal soap manufacture after hours. Because of the high tax, soap was a luxury item, and it did not come into common use in England until after the tax was repealed in 1853. In the 19th century, soap was affordable and popular throughout Europe.

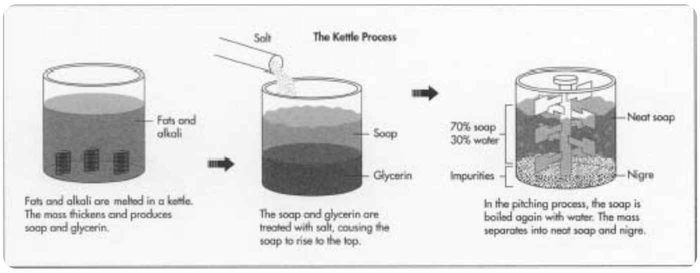
Early soap manufacturers simply boiled a solution of wood ash and animal fat. A foam substance formed at the top of the pot. When cooled, it hardened into soap. Around 1790, French soapmaker Nicolas Leblanc (/knowledge/Nicolas_Leblanc.html) developed a method of extracting caustic soda (sodium hydroxide) from common table **salt (../Volume-2/Salt.html)** (sodium chloride), replacing the wood ash element of soap. The French chemist Eugene-Michel Chevreul put the soap-forming process (called in English saponification) into concrete chemical terms in 1823. In saponification, the animal fat, which is chemically neutral, splits into fatty acids, which react with alkali carbonates (/knowledge/Carbonates.html) to form soap, leaving glycerin (/knowledge/Glycerol.html) as a byproduct. Soap was made with industrial processes by the end of the 19th century, though people in rural areas, such as the pioneers in the western United States, continued to make soap at home.

Raw Materials

Soap requires two major raw materials: fat and alkali. The alkali most commonly used today is sodium hydroxide. Potassium hydroxide (/knowledge/Potassium_hydroxide.html) can also be used. Potassium-based soap creates a more water-soluble (/knowledge/Solubility.html) product than sodium-based soap, and so it is called "soft soap." Soft soap, alone or in combination with sodium-based soap, is commonly used in shaving (/knowledge/Shaving.html) products.

Animal fat in the past was obtained directly from a slaughterhouse. Modern soapmakers use fat that has been processed into fatty acids. This eliminates many impurities, and it produces as a byproduct water instead of glycerin. Many vegetable fats, including olive oil, palm kernel oil, and coconut oil, are also used in soap making.

Additives are used to enhance the color, texture, and scent of soap. Fragrances and perfumes are added to the soap mixture to



The above illustrations show the kettle process of making soap.

cover the odor of dirt and to leave behind a fresh-smelling scent. Abrasives to enhance the texture of soap include talc, silica, and marble pumice (volcanic ash). Soap made without dye is a dull grey or brown color, but modern manufacturers color soap to make it more enticing to the consumer.

The Manufacturing Process

The kettle method of making soap is still used today by small soap manufacturing companies. This process takes from four to eleven days to complete, and the quality of each batch is inconsistent due to the variety of oils used. Around 1940, engineers and scientists developed a more efficient manufacturing process, called the continuous process. This procedure is employed by large soap manufacturing companies all around the world today. Exactly as the name states, in the continuous process soap is produced continuously, rather than one batch at a time. Technicians have more control of the production in the continuous process, and the steps are much quicker than in the kettle method—it takes only about six hours to complete a batch of soap.

The Kettle Process

Boiling

- 1 Fats and alkali are melted in a kettle, which is a steel tank that can stand three stories high and hold several thousand pounds of material. Steam coils within the kettle heat the batch and bring it to a boil. After boiling, the mass thickens as the fat reacts with the alkali, producing soap and glycerin.

Salting

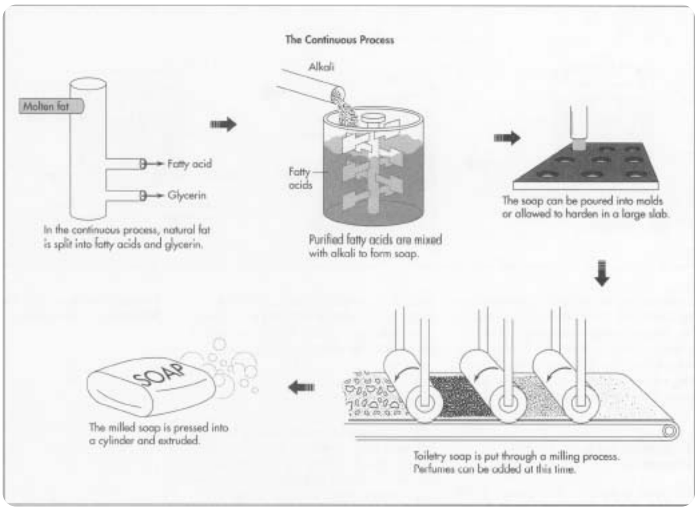
- 2 The soap and glycerin must now be separated. The mixture is treated with salt, causing the soap to rise to the top and the glycerin to settle to the bottom. The glycerin is extracted from the bottom of the kettle.

Strong change

- 3 To remove the small amounts of fat that have not saponified, a strong caustic solution is added to the kettle. This step in the process is called "strong change." The mass is brought to a boil again, and the last of the fat turns to soap. The batch may be given another salt treatment at this time, or the manufacturer may proceed to the next step.

Pitching

- 4 The next step is called "pitching." The soap in the kettle is boiled again with added water. The mass eventually separates into two layers. The top layer is called "neat soap," which is about 70% soap and 30% water. The lower layer, called "nigre," contains most of the impurities in the soap such as dirt and salt, as well as most of the water. The neat soap is taken off the top. The soap is then cooled. The finishing process is the same as for soap made by the continuous process.



Developed around 1940 and used by today's major soap-making companies, the above illustrations show the continuous process of making soap.

The Continuous Process

Splitting

- 1 The first step of the continuous process splits natural fat into fatty acids and glycerin. The equipment used is a vertical stainless steel column with the diameter of a barrel called a hydrolizer. It may be as tall as 80 feet (24 m). Pumps and meters attached to the column allow precise measurements and control of the process. Molten fat is pumped into one end of the column, while at the other end water at high temperature (266°F [130°C]) and pressure is introduced. This splits the fat into its two components. The fatty acid and glycerin are pumped out continuously as more fat and water enter. The fatty acids are then distilled (/knowledge/Distillation.html) for purification.

Mixing

- 2 The purified fatty acids are next mixed with a precise amount of alkali to form soap. Other ingredients such as abrasives and fragrance are also mixed in. The hot liquid soap may be then whipped to incorporate air.

Cooling and finishing

- 3 The soap may be poured into molds and allowed to harden into a large slab. It may also be cooled in a special freezer. The slab is cut into smaller pieces of bar size, which are then stamped and wrapped. The entire continuous process, from splitting to finishing, can be accomplished in several hours.

Milling

- 4 Most toiletry soap undergoes additional processing called milling. The milled bar lathers up better and has a finer consistency than non-milled soap. The cooled soap is fed through several sets of heavy rollers (mills), which crush and knead it. Perfumes can best be incorporated at this time because their volatile oils (/knowledge/Essential_oil.html) do not evaporate in the cold mixture. After the soap emerges from the mills, it is pressed into a smooth cylinder and extruded (/knowledge/Extrusion.html). The extruded soap is cut into bar size, stamped and wrapped.

Byproducts

Glycerin is a very useful byproduct of soap manufacture. It is used to make hand lotion, drugs, and nitroglycerin, the main component of explosives such as **dynamite.**

Where To Learn More

Books

Cavitch, Susan M. *The Natural Soap Book: Making Herbal and Vegetable-Based Soaps.* Storey Communications, 1995.

Maine, Sandy. *The Soap Book: Simple Herbal Recipes.* Interweave Press, 1995.

Spitz, Luis, ed. *Soap Technologies in the 1990s.* American Oil Chemists Society, 1990.

Other

About Soap. Procter & Gamble, 1990. (513) 983-1100.

— *Sheila Dow*

Also read article about Soap (/knowledge/Soap.html) from Wikipedia

User Contributions:

1 (/Volume- **Lacey** Mar 20, 2008 @ 2:14 pm

Abdullah,
I do not know much about making soap, which method you will be using or how much you will make, but I was able to find basic measurements that might help you.

12 oz or 340 grams 100% lye
605 grams ice cold or part frozen distilled water
2.48 kg lard or all vegetable shortening

Good luck, Lacey J.

2 (/Volume- **RANJAN** Dec 29, 2009 @ 12:00 am

Nice article.Kindly let me know how much quantities of raw material to take to make soap at home.

3 (/Volume- **Aadhish (mailto:metaldead_adi [at] hotmail [dot] com)** May 30, 2010 @ 10:22 pm

good one but i think chemical reactions should be given to make it more like chemistry.

4 (/Volume- **karamat (mailto:karamat_ullaha [at] yahoo [dot] com)** Jun 22, 2011 @ 1:01 am

Nice information i want to know that soapstone (/knowledge/Soapstone.html) powder is also used in soap manufacturing process

5 (/Volume- **uteno james (mailto:uteno_jame [at] yahoo [dot] com)** Aug 19, 2011 @ 5:05 am

my soap get shrinking after some day of production using cold process please help me Can i use beeswax as incredient in my in my formulation?

6 **ZABED.DIU** Mar 25, 2012 @ 9:21 pm

nice artile. BUT some info missing.indly let me know how much quantities of raw material to take to make soap at home.

7 (/Volume- **haji m amin** Aug 14, 2014 @ 10:10 am

I like to know how to laundry bar soap these days commercial way for the market

8 (/Volume- **Farzad** Aug 20, 2014 @ 2:02 am

I saw that in a factory line soap they use soap noodles (chips), a kind of color ,a kind of fragrance and some chemical ingredients. What are those ingredients and how to know amount (measure)?Thx

9 (/Volume- **Lidya** Apr 19, 2015 @ 2:02 am

1 The first step of the continuous process splits natural fat into fatty acids and glycerin. The equipment used is a vertical stainless steel column with the diameter of a barrel called a hydrolizer. It may be as tall as 80 feet (24 m). Pumps and meters attached to the column allow precise measurements and control of the process. Molten fat is pumped into one end of the column, while at the other end water at high temperature (266°F [130°C]) and pressure is introduced. This splits the fat into its two components. The fatty acid and glycerin are pumped out continuously as more fat and water enter. The fatty acids are then distilled for purification.

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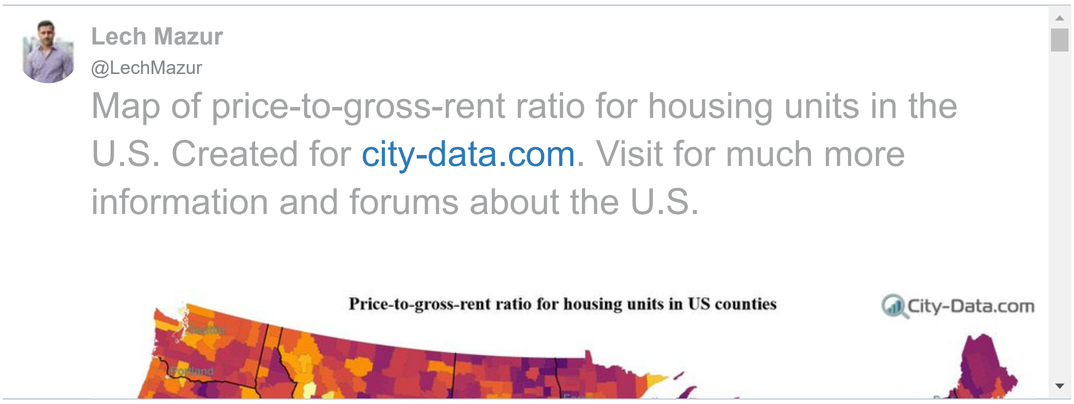


Lech Mazur
@LechMazur

Map of price-to-gross-rent ratio for housing units in the U.S. Created for city-data.com. Visit for much more information and forums about the U.S.

Embed

View on Twitter

Soap forum (/forum/)

< Smoke Detector (Smoke-Detector.html)

Soft Drink > (Soft-Drink.html)

Detergents

by

Dr. Mohamed Y. Mahgoub

Practical challenges

Human body

Clothes

Dishes

Glass

Toilette

Furniture

Cars

Water challenge

Soft water

Hard water

To successfully meet this challenges, it is essential to thoroughly **understand** not only all the properties of the raw materials present in the final products but also all the **potential interactions** between the raw materials before, during and even after making and use.

The detergents composition is a formulated mixture of raw materials that can be classified into different types based on their properties and function in the finished product

Surfactants

Builders

Bleaching agents

Enzymes

Minors

Surfactants

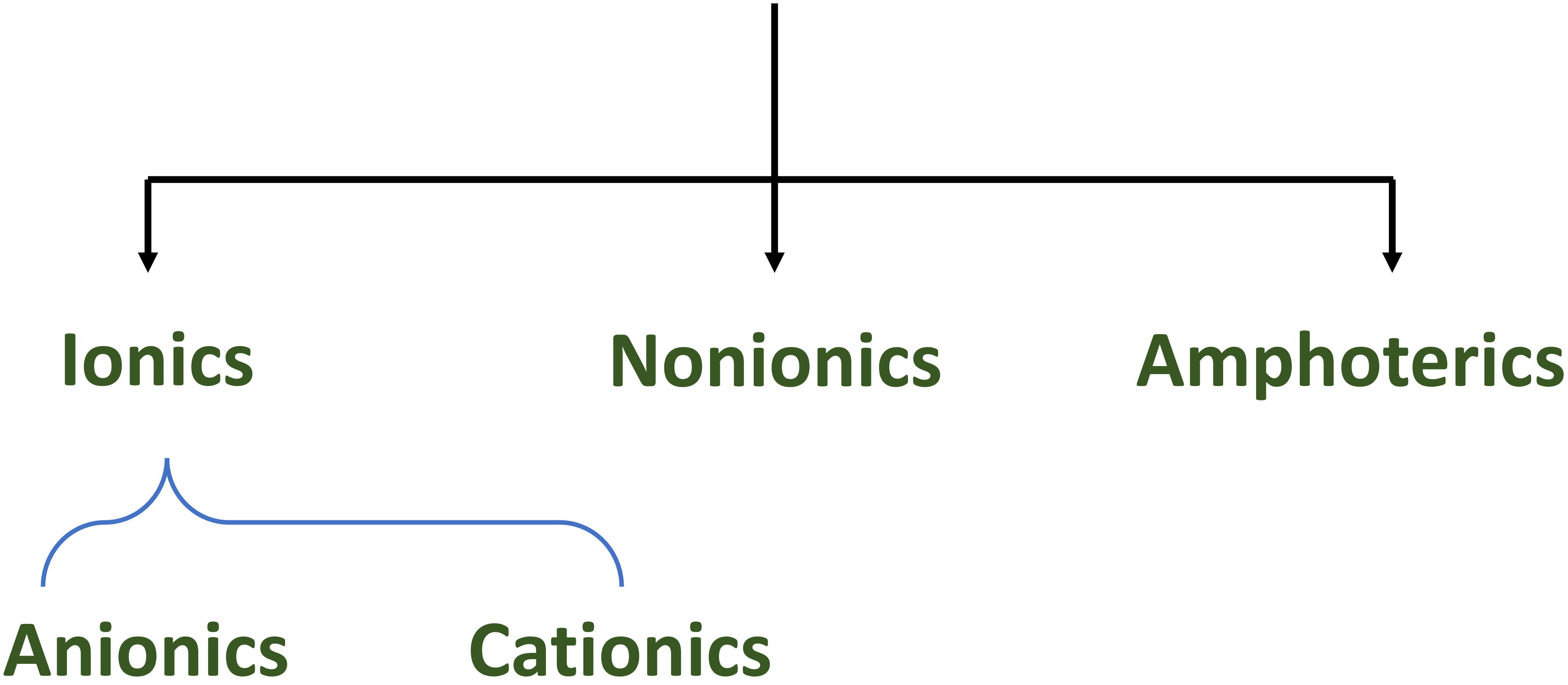
Surface active agent

They are added to remove dirt from skin, clothes and household articles particularly in kitchens and bathrooms.

The type of detergent dependent on type of surfactants

Classification of surfactants

Depending on the nature of the hydrophilic group



- Ionics
  - Anionics
  - Cationics
- Nonionics
- Amphoterics

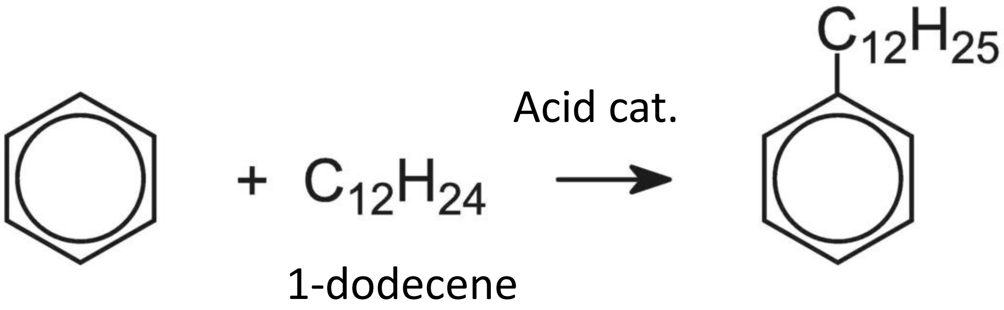
Anionic surfactants

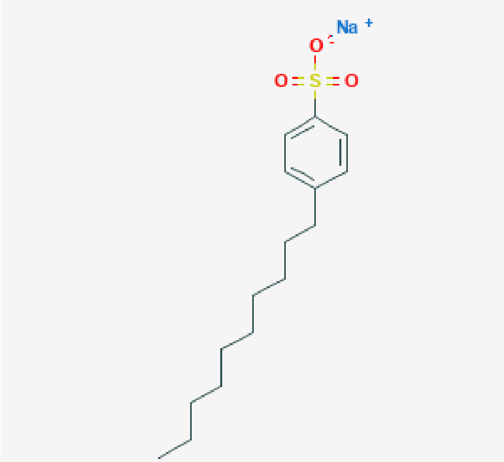
The hydrophilic group is **negatively charged**

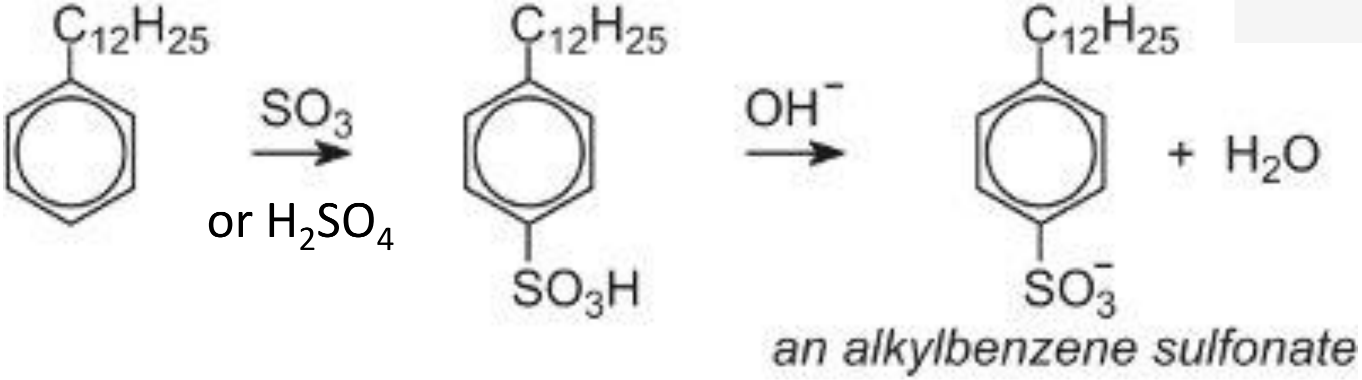
They are the most widely used type of surfactants for **laundering and dishwashing liquids**

Anionic surfactants

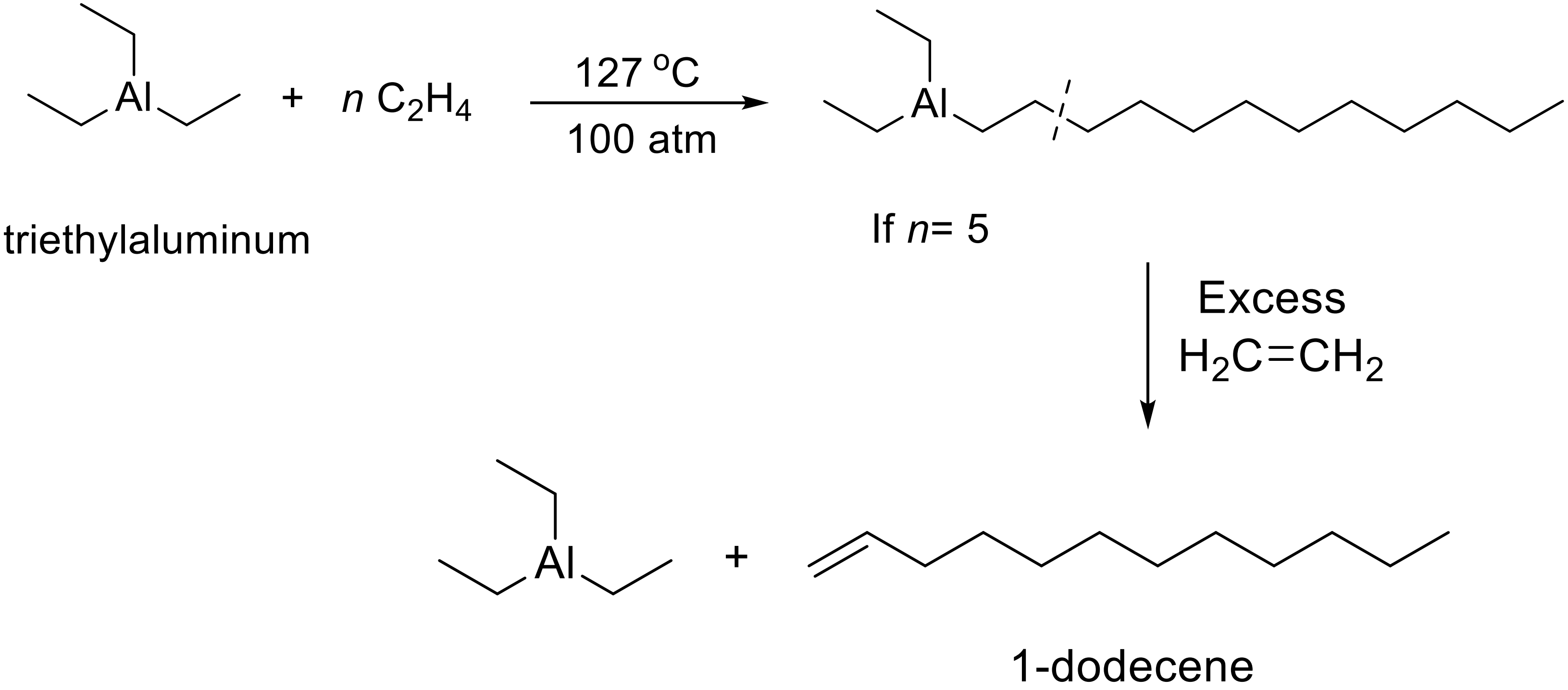
a) alkylbenzene sulfonates





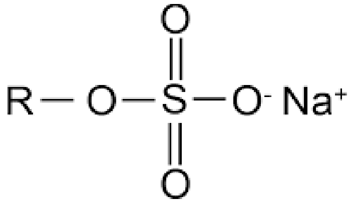


Straight chain alkenes for the previous process can be produced from ethene using a Ziegler catalyst (**Triethyl Aluminium**)



Anionic surfactants

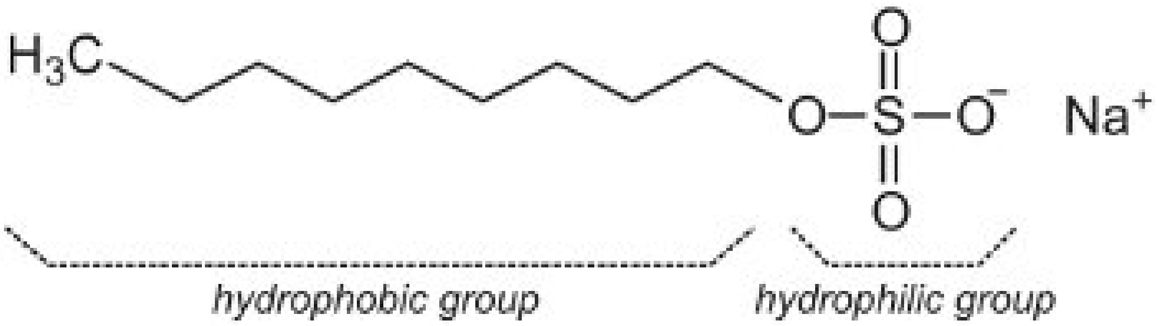
b) Alkyl sulfates



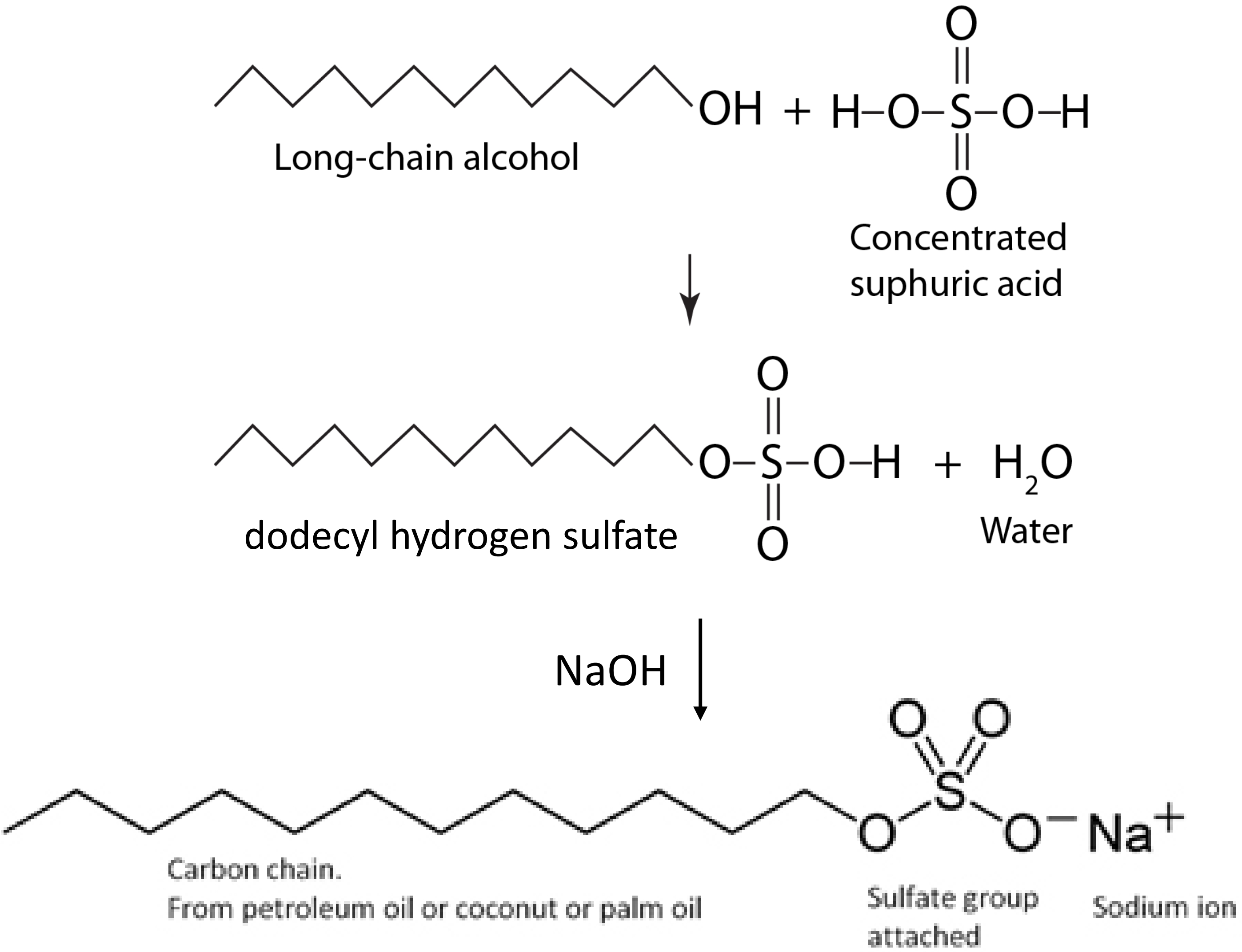
$$R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{-}\ Na^{+}$$

Sodium Alkyl Sulphate
(Detergent)

EX



an alkyl sulfate



Sodium Lauryl Sulfate (SLS)

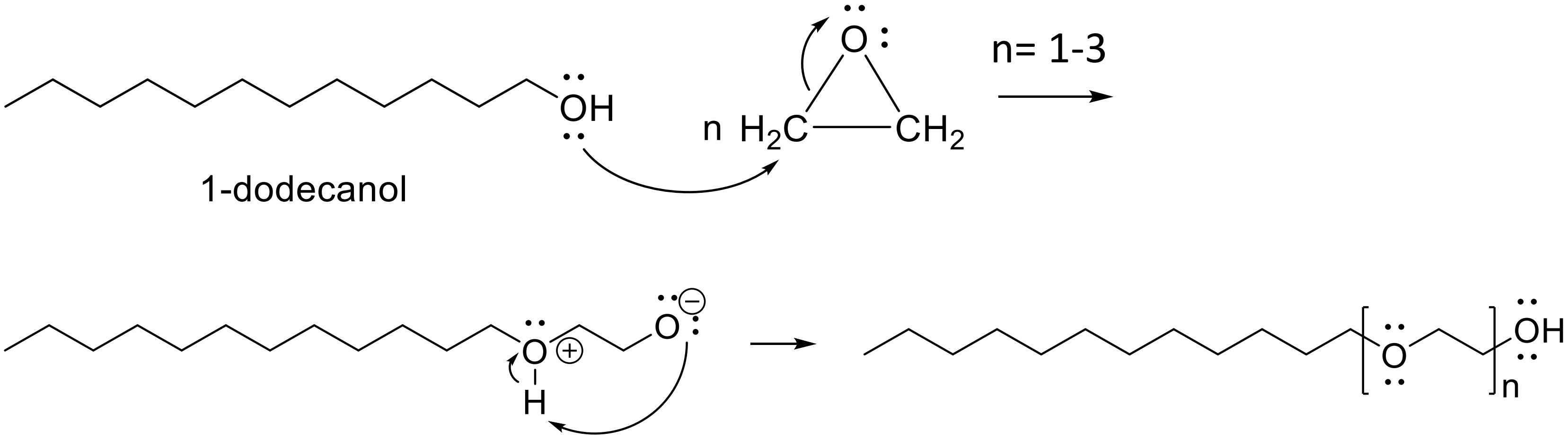
Sodium Dodecyl Sulfate (SDS)

Anionic surfactants

c) Alkyl ether sulfates

More widely used than simple alkyl sulfates

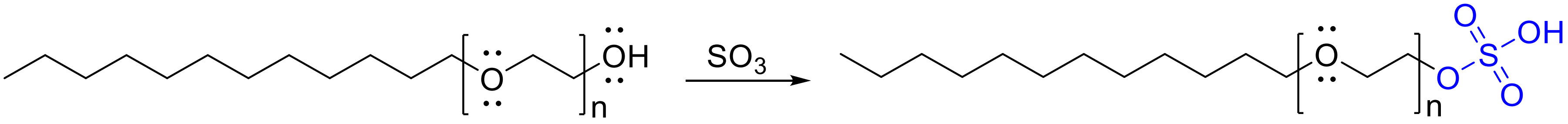
Primary alkyl alcohol is first ethoxylated with 1 to 3 molar equivalents of **epoxyethane**

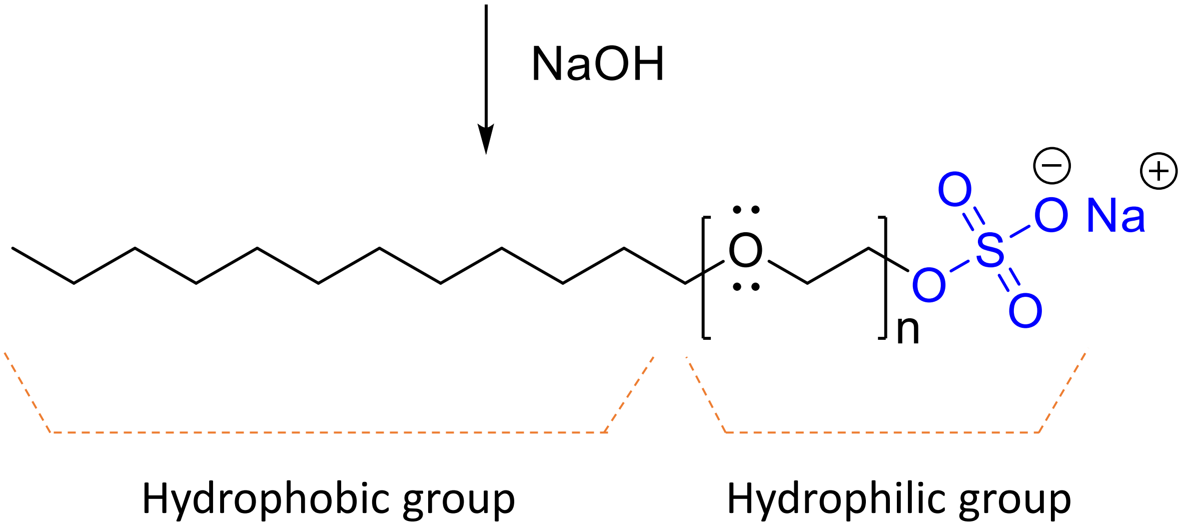


Anionic surfactants

c) Alkyl ether sulfates

The product is then sulfated using sulfur trioxide and neutralized with alkali to form the alkyl ether sulfate:





Texapon

Sodium Lauryl Ether Sulfate (**SLES**)

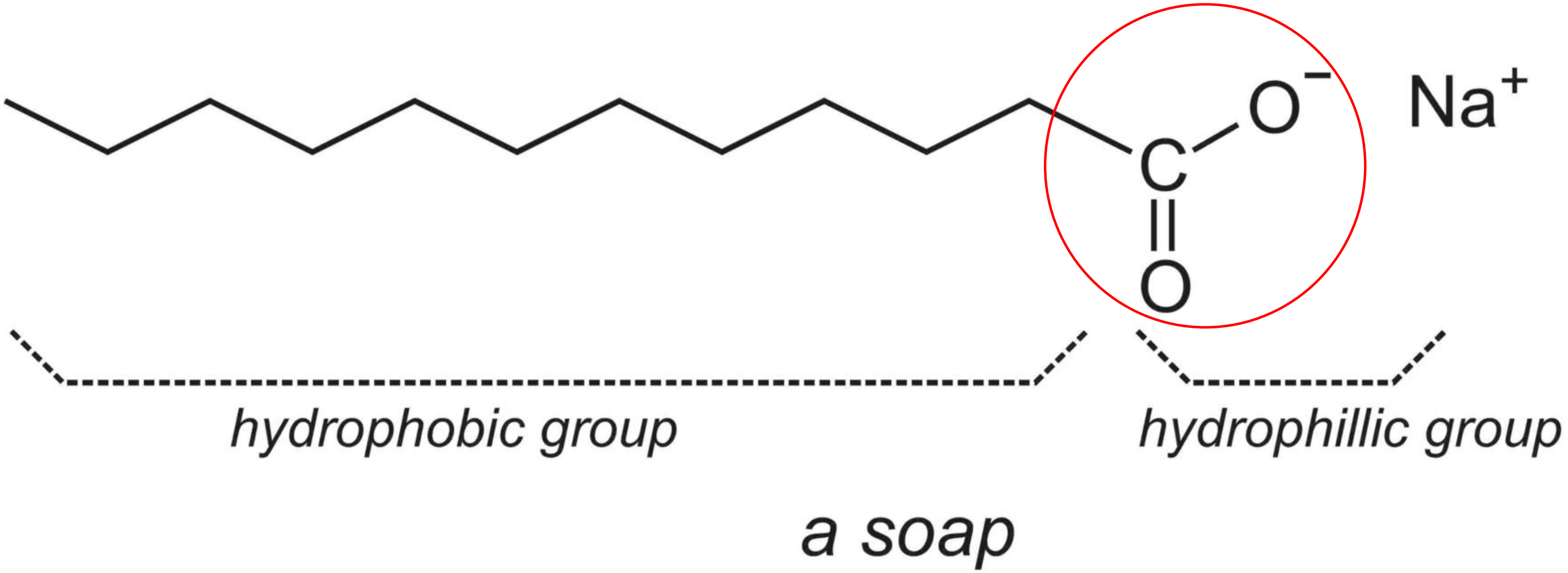
SLES applications

dishwashing liquids, shower gels, shampoo, glass cleaners, floor cleaners…….etc

because they are milder to the skin than alkyl sulfates. They also generate less foam which is an advantage in the formulation of **laundry machine products.**

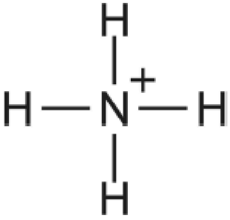
Anionic surfactants

d) Soaps

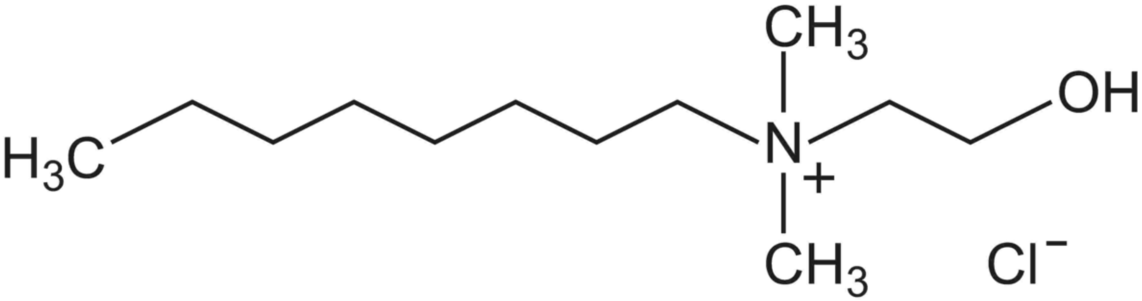


Cationic surfactants

The hydrophilic head is **positively charged**, have quaternary ammonium (quats) as the polar end.



(a) Mono alkyl quaternary systems



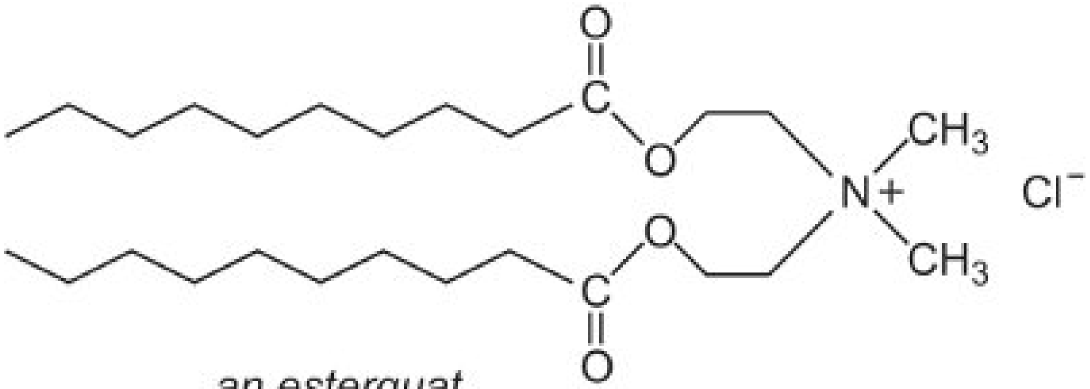
an alkyl quaternary system

They are used as fabric softeners

Cationic surfactants

(b) Esterquats

There is an ester linkage between the alkyl chains and the quaternary head-group as these are more biodegradable and less toxic



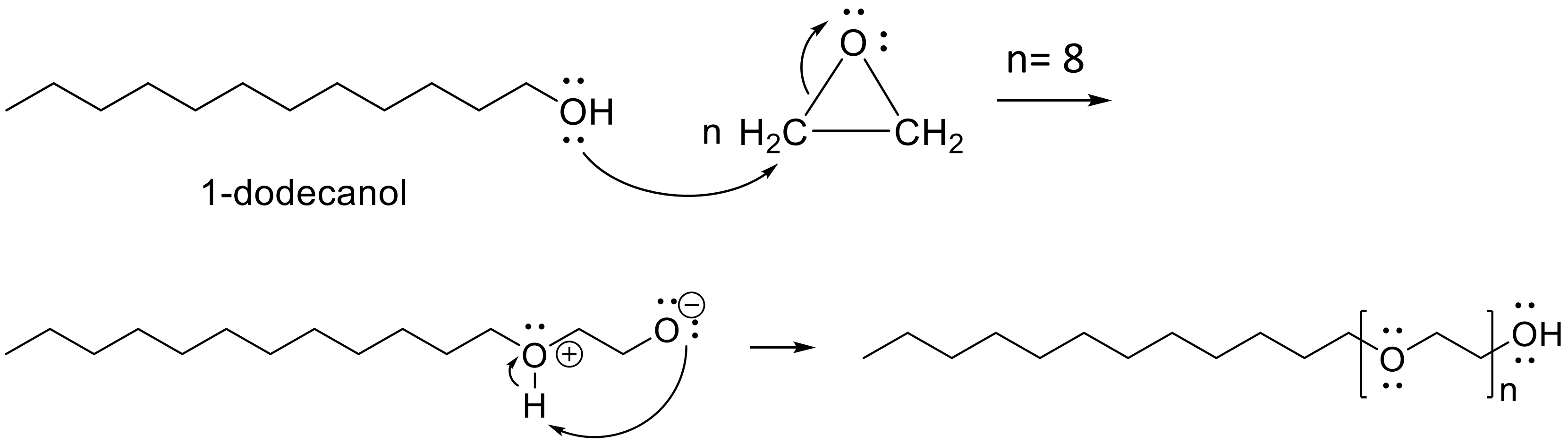
an esterquat

Esterquats give detergents their fabric softening qualities.

Nonionic surfactants

These surfactants do not bear an electrical charge and are often used together with anionic surfactants

The major group of nonionics are the **ethoxylates**



a nonionic surfactant

An advantage is that they do not interact with calcium and magnesium ions in hard water.

As the temperature of the surfactant solution is increased the hydrogen bonds gradually break causing the surfactant to come out of solution. This is commonly referred to as the cloud point and is characteristic for each nonionic surfactant. Nonionics are more surface active and better emulsifiers than anionics at similar concentrations. They are less soluble than anionics in hot water and produce less foam. They are also more efficient in removing oily and organic dirt than anionics.

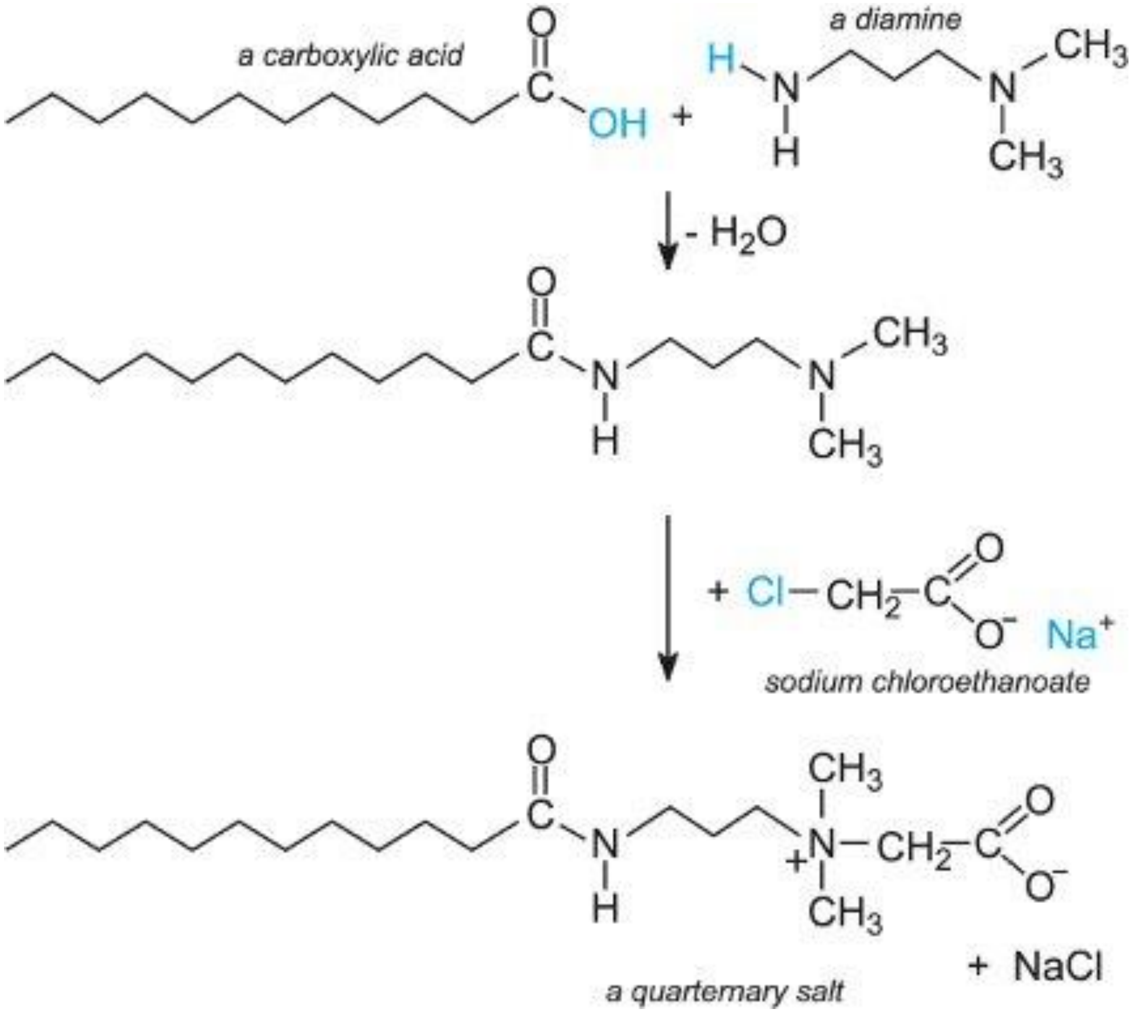
Amphoteric (Zwitterionic) surfactants

The head-group carries both a **negative** and **positive** charge

The **positive** charge is almost quaternary ammonium ion

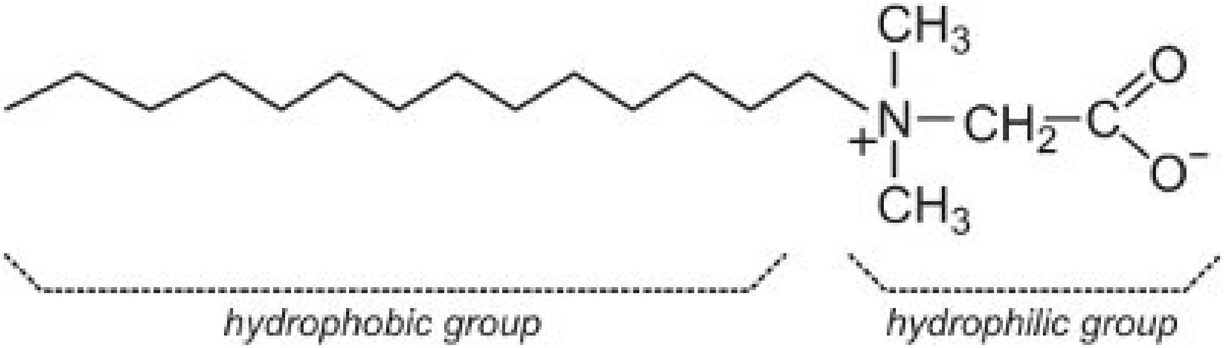
The **negatively** charged group can be carboxylate, $-CO_2^-$, sulfate, $-OSO_3^-$ or sulfonate, $-SO_3^-$.

Amphoteric (Zwitterionic) surfactants

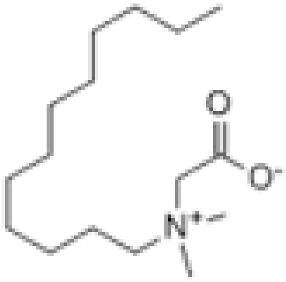


Amphoteric (Zwitterionic) surfactants

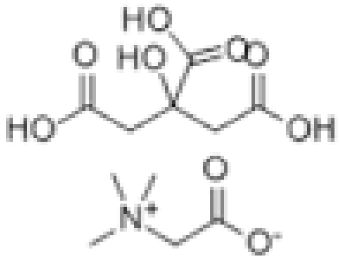
Betaines are neutral compounds with a cationic and an anionic group which are not adjacent to one another.



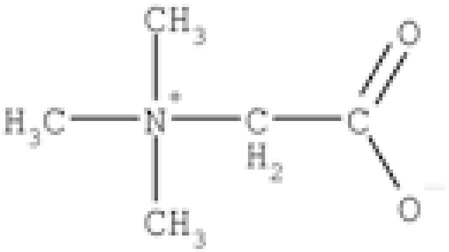
an alkyl betaine



Lauryl betaine



betaine citrate



betaine group

The quantity of foam produced order :

Anionics > Soaps > Nonionics > Cationics

Attached file

More details for Detergents manufacturing

Surfactants

Surfactants are one of many different compounds that make up a detergent. They are added to remove dirt from skin, clothes and household articles particularly in kitchens and bathrooms. They are also used extensively in industry. The term surfactant comes from the words surface active agent.

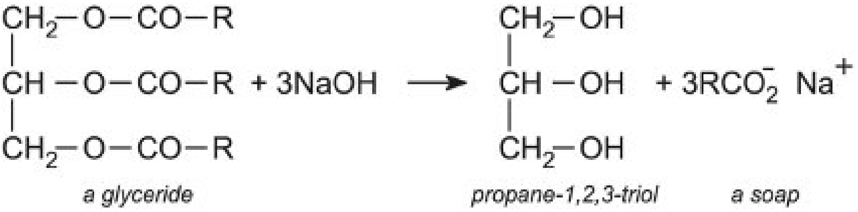
Figure 1 Surfactants aid the effective washing of dirty rugby kit using low temperature wash cycles, resulting in environmental benefits.

By kind permission of Stephen Garnett/Wharfedale RUFC.

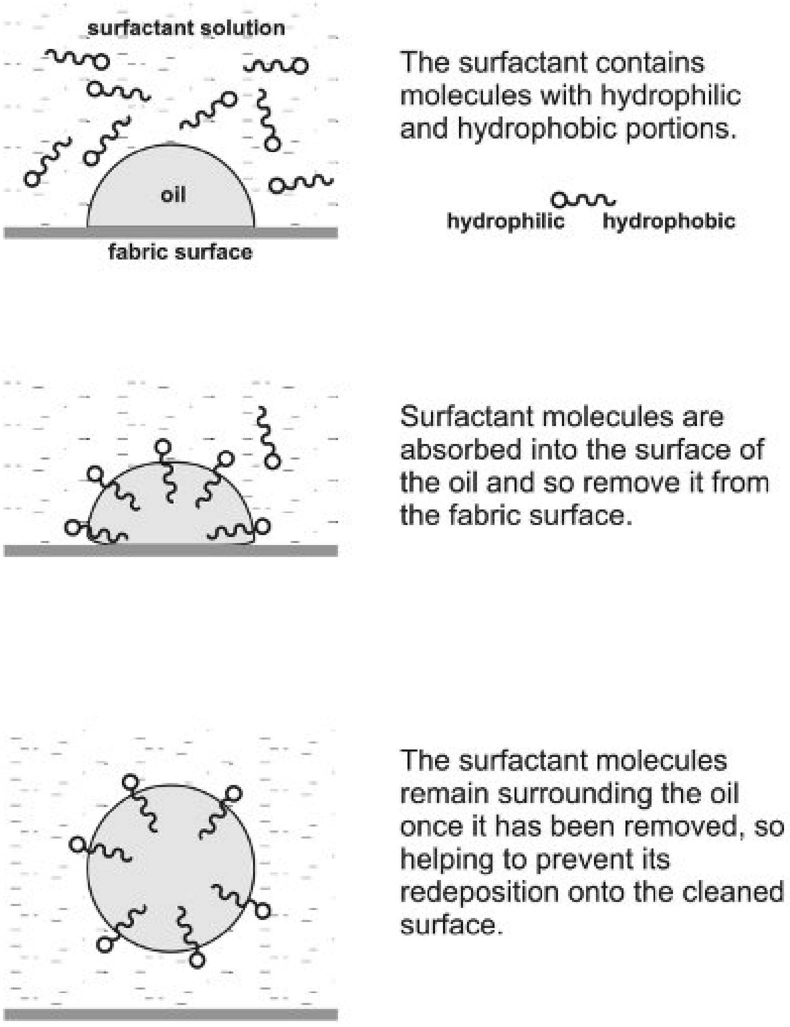
Scroll to Top

Surfactants function by breaking down the interface between water and oils and/or dirt. They also hold these oils and dirt in suspension, and so allow their removal. They are able to act in this way because they contain both a hydrophilic (water loving) group, such as an acid anion, ($-CO_2^-$ or SO_3^-) and a hydrophobic (water hating) group, such as an alkyl chain. Molecules of water tend to congregate near the former and molecules of the water-insoluble material congregate near the latter (Figure 2).

Soaps were the earliest surfactants and are obtained from fats which are known as glycerides because they are esters formed by the trihydric alcohol, propane-1,2,3-triol (glycerol), with long chain carboxylic acids (fatty acids) (/materials-and-applications/edible-fats-and-oils.html). The glycerides are hydrolyzed by heating with sodium hydroxide solution to form soaps, the sodium salts of the acids, and propane-1,2,3-triol. The process is known as saponification.



$$\begin{array}{l} CH_2-O-CO-R \\ | \\ CH-O-CO-R \\ | \\ CH_2-O-CO-R \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3RCO_2^- \, Na^+$$



The surfactant contains molecules with hydrophilic and hydrophobic portions.

Surfactant molecules are absorbed into the surface of the oil and so remove it from the fabric surface.

The surfactant molecules remain surrounding the oil once it has been removed, so helping to prevent its redeposition onto the cleaned surface.

Figure 2 Action of a surfactant.

Scroll to Top

Manufacture

The glycerides used to make surfactants contain saturated and unsaturated carboxylic acids which have an even number of carbon atoms, generally within the range 12-20, for example, octadecanoic acid (stearic acid), $CH_3(CH_2)_{16}CO_2H$.

Synthetic surfactants have one very important advantage over soaps. Because soaps form insoluble calcium and magnesium salts with the calcium and magnesium ions in hard water and in the clays which are present in dirt, much of the soap is wasted forming an insoluble scum. However, this is avoided when using a synthetic surfactant. For example, in the anionic surfactants, the carboxylate group in soap is replaced by a sulfonate or sulfate group as the hydrophilic component. The corresponding calcium and magnesium salts are more soluble in water than the calcium and magnesium salts of carboxylic acids.

Surfactants are classified based upon the nature of the hydrophilic "head-groups" as:

- anionics cationics
- nonionics
- amphoterics

Anionic surfactants

In these surfactants the hydrophilic group is negatively charged. They are the most widely used type of surfactants for laundering, dishwashing liquids and shampoos. They are particularly good at keeping the dirt, once dislodged, away from fabrics.

Four anionic surfactants are used:

a) alkylbenzene sulfonates
b) alkyl sulfates

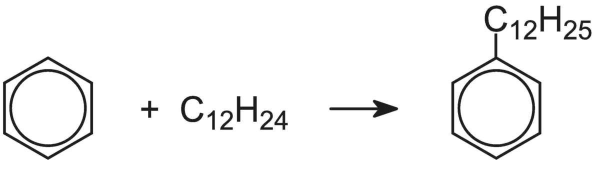
c) alkyl ether sulfates

d) soaps

(a) Alkylbenzene sulfonates

The most common of the synthetic anionic surfactants are based on the straight chain alkylbenzene sulfonates. Benzene, in slight excess, is mixed with an alkene or chloroalkane in the presence of an acid catalyst, usually a solid zeolite (/processes/catalysis-in-industry.html#zeolite) (ion exchange), aluminium chloride ($AlCl_3$) or hydrofluoric acid (HF), to produce an alkylbenzene (sometimes called detergent alkylate).

For example:

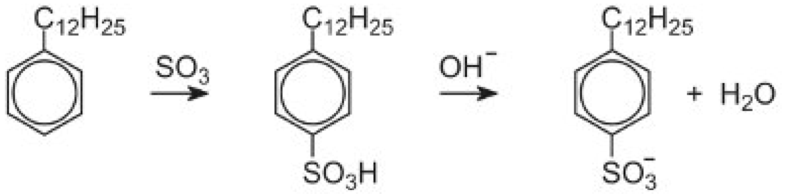


The alkylbenzene varies in average molecular mass, depending upon the starting materials and catalyst used and is often a mixture in which the length of the alkyl side chain varies between 10 and 14 carbon atoms. Historically these included branches in the side chains with

Scroll to Top

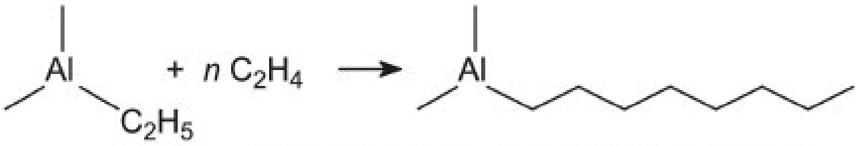
the result that they biodegrade very slowly and lead to foaming in rivers and sewage plants. By law, in most countries today, the surfactant must have side chains which are not branched so they degrade more rapidly.

The alkylate is sulfonated using an air/sulfur trioxide mixture, and the resulting sulfonic acid is then neutralised with an aqueous solution of sodium hydroxide (often in situ), for example:



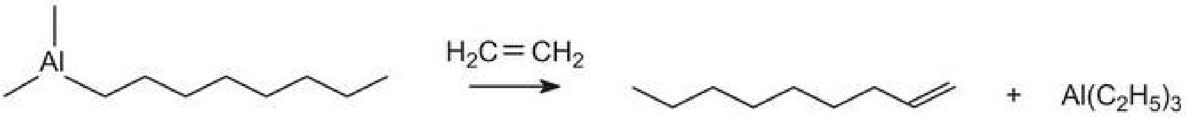
an alkylbenzene sulfonate

Straight chain alkenes for the above process can be produced from ethene using a Ziegler catalyst (/processes/catalysis-in-industry.html#ziegler_natta) (triethyl aluminium). Triethyl aluminium reacts with ethene at *ca* 400 K and 100 atm to form aluminium alkyls, for example:



This reaction will take place at all three ethyl groups.
For clarity, only one is shown.

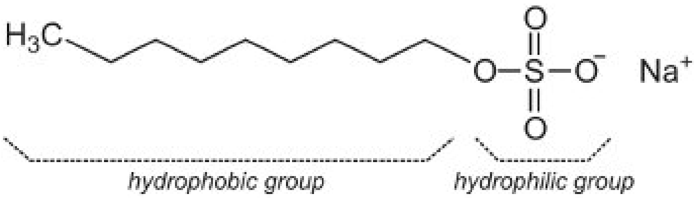
When heated in excess ethene, straight chain alkenes, with the double bond at the end of the chain (an a-alkene), are produced:



The mixture is then separated into fractions by distillation, the fraction of alkenes containing 10 to 14 carbon atoms being used to make the surfactants.

These are used together with other surfactants in powder and liquid laundry detergents such as Ariel, Daz, Persil and Surf.

(b) Alkyl sulfates



an alkyl sulfate

Many detergent products, particularly liquids, contain other synthetic anionic surfactants such as alkyl sulfates, esters of linear alcohols (C_{10}-C_{18}) and sulfuric acid. The alkyl sulfates are also used in personal care products such as toothpaste and are manufactured by treating the alcohol with sulfur trioxide. The product is then neutralised with aqueous sodium hydroxide solution to form a sodium alkyl sulfate:

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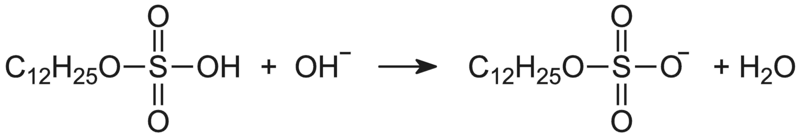
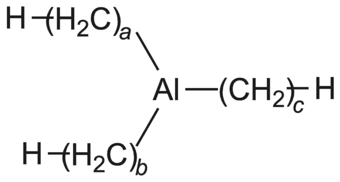


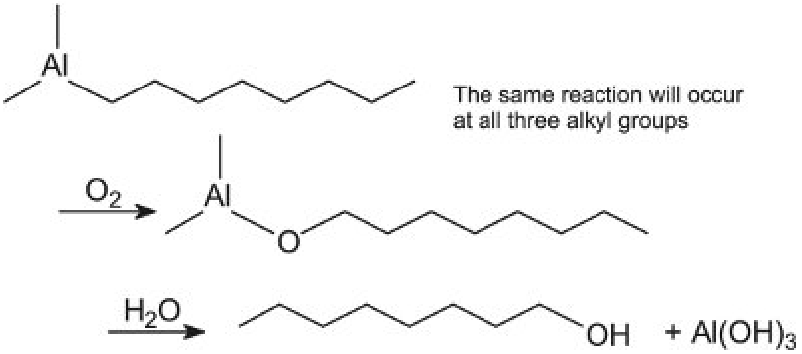
$$C_{12}H_{25}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH + OH^{-} \longrightarrow C_{12}H_{25}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{-} + H_2O$$

The alcohols are either produced from carboxylic acids obtained from oils, obtained naturally, for example from palm kernel oil or coconut oil, or alternatively from long-chain alkenes, manufactured from ethene.

There are two processes for making the alcohols from ethene. As described above, aluminium triethyl reacts with ethene to produce compounds such as:



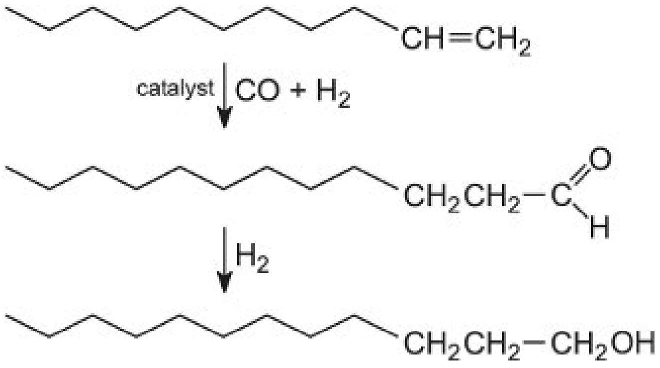
where a,b,c are even numbers from 2 to 12. Instead of heating with excess ethene to produce a-alkenes, the aluminium alkyl is treated with oxygen and then water to produce long chain alcohols:



The same reaction will occur at all three alkyl groups

Alternatively, a different process for making the alcohols from ethene is used, known as SHOP (Shell Higher Olefins Process). In the first stage, ethene is passed, under pressure of ca 100 atm, into a solvent (usually a diol, such as butane-1,4-diol) containing a nickel salt at 400 K. It yields a mixture of a-alkenes which are separated by fractional distillation. About 30% are in the range C_{10}-C_{14}.

These are reacted with carbon monoxide and hydrogen (hydroformylation) to yield straight-chain aldehydes, which on reduction form alcohols. For example:



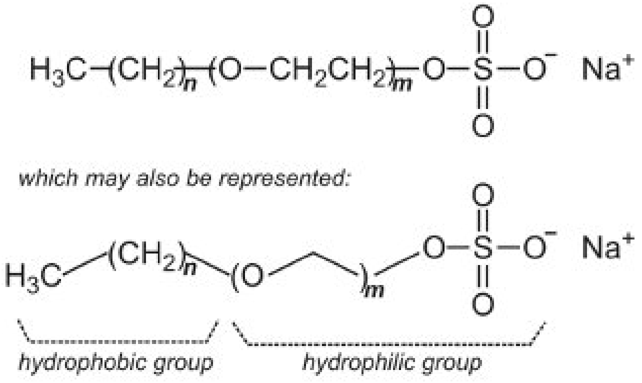
It is possible to convert the other a-alkene fractions (C_4-C_{10} and C_{14}-C_{40}) into the more desirable C_{10}-C_{14} fraction.

Scroll to Top

(c) Alkyl ether sulfates

More widely used than simple alkyl sulfates are various types of sodium alkyl ether sulfates (SLES).

In the manfacture of SLES the primary alkyl alcohol (from a synthetic or natural source and typically a blend based around dodecanol) is first ethoxylated with 1 to 3 molar equivalents of epoxyethane (/chemicals/epoxyethane.html#glycol_ether) (as described below for the manufacture of nonionic surfactants). The product is then sulfated using sulfur trioxide and neutralized with alkali to form the alkyl ether sulfate:

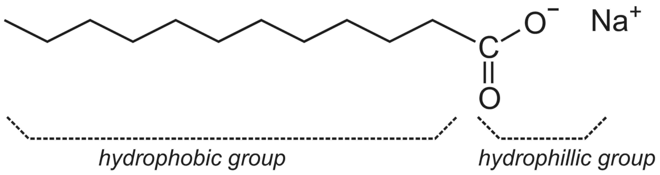


an alkyl ether sulfate

These materials are preferred by product formulators for many applications (dishwashing liquids, shower gels, shampoo, etc) because they are milder to the skin than alkyl sulfates. They also generate less foam which is an advantage in the formulation of laundry machine products.

(d) Soaps

Soaps are anionic detergents:



a soap

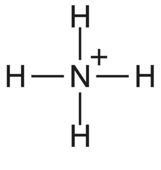
Cationic surfactants

With these surfactants, the hydrophilic head is positively charged.

Although they are produced in much smaller quantities than the anionics, there are several types, each used for a specific purpose.

(a) Mono alkyl quaternary systems

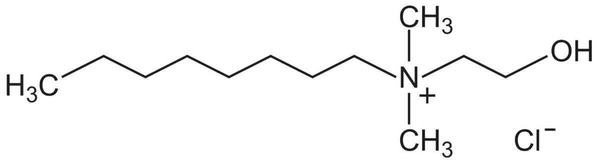
The simplest quaternary system is the ammonium ion:



NH_4^+

An alkyl quaternary nitrogen system has alkyl groups attached to the nitrogen atom. An example is:

Scroll to Top



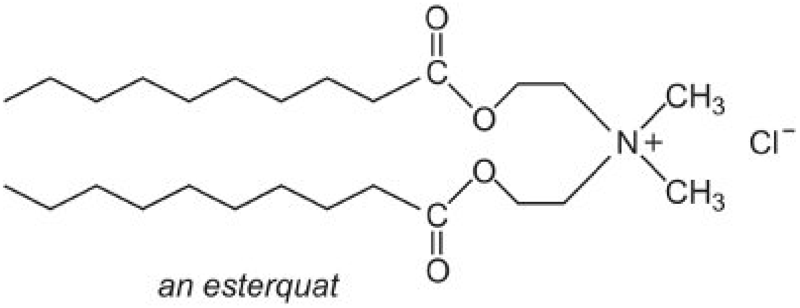
an alkyl quaternary system

They are used as fabric softeners with anionic surfactants, helping them to break down the interface between the dirt/stain and the water.

(b) Esterquats

The directly quaternised fatty acid surfactants described above have been replaced for laundry applications by more complicated structures in which there is an ester linkage between the alkyl chains and the quaternary head-group as these are more biodegradable and less toxic. They are known as esterquats.

An example is:



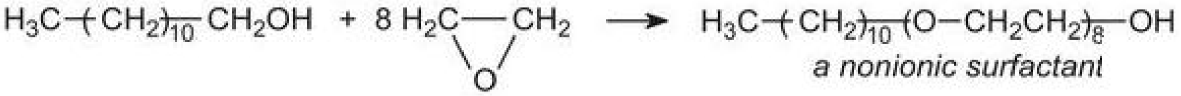
an esterquat

Esterquats give detergents their fabric softening qualities.

Nonionic surfactants

These surfactants do not bear an electrical charge and are often used together with anionic surfactants. An advantage is that they do not interact with calcium and magnesium ions in hard water.

They account for nearly 50% of surfactant production (excluding soap). The major group of nonionics are the ethoxylates made by condensing long chain alcohols with epoxyethane (ethylene oxide) (/chemicals/epoxyethane.html#glycol_ether) to form ethers, for example:

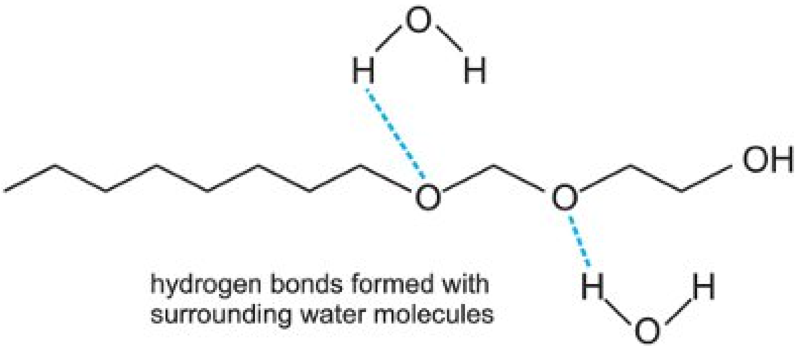


a nonionic surfactant

The long-chain alcohol can come from either a synthetic or natural source.

Although they do not contain an ionic group as their hydrophilic component, hydrophilic properties are conferred on them by the presence of a number of oxygen atoms in one part of the molecule which are capable of forming hydrogen bonds with molecules of water.

Scroll to Top

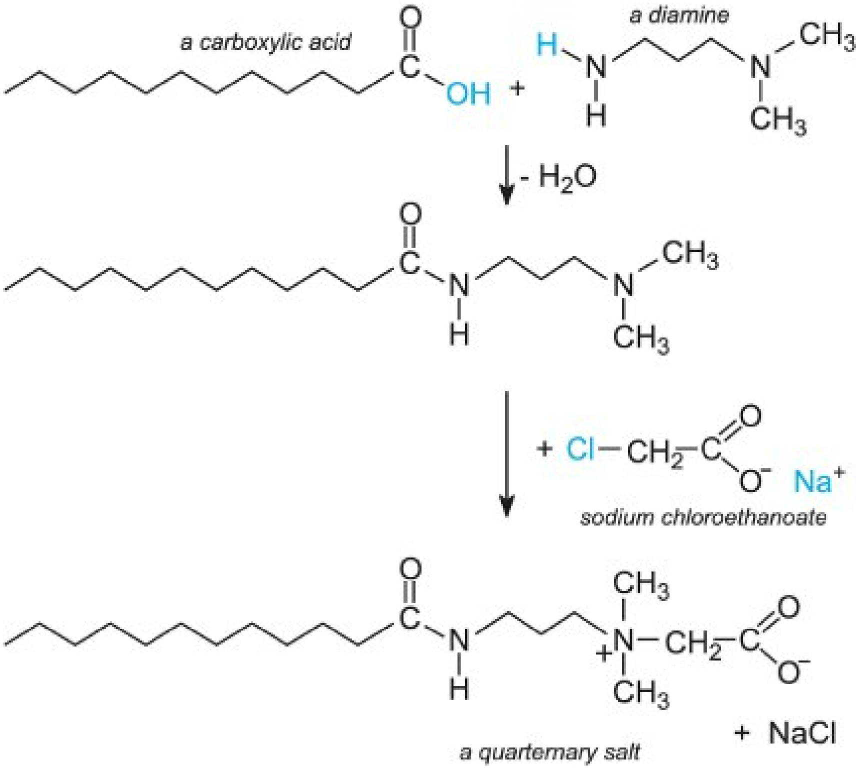


As the temperature of the surfactant solution is increased the hydrogen bonds gradually break causing the surfactant to come out of solution. This is commonly referred to as the cloud point and is characteristic for each nonionic surfactant. Nonionics are more surface active and better emulsifiers than anionics at similar concentrations. They are less soluble than anionics in hot water and produce less foam. They are also more efficient in removing oily and organic dirt than anionics. Depending on the type of fibre, they can be active in cold solution and so are useful in countries which lack hot water supplies and in developed countries where there is a desire to lower the wash temperatures either to save energy or because of the type of fabric being washed. Nonionics are used in fabric washing detergents (both powders and liquids), in hard surface cleaners and in many industrial processes such as emulsion polymerization and agrochemical formulations.

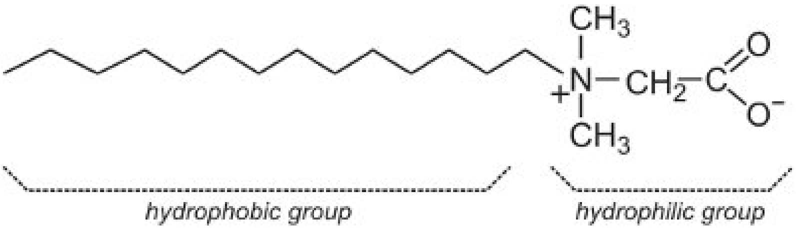
Amphoteric surfactants

Amphoteric (or zwitterionic) surfactants are so called because the head-group carries both a negative and positive charge. A range of methods is used to produce such materials, almost all of which contain a quaternary ammonium ion (a cation). The negatively charged group can be carboxylate, $-CO_2^-$, sulfate, $-OSO_3^-$ or sulfonate, $-SO_3^-$. One such well-used class is the alkyl betaines which have a carboxyl group. A long-chain carboxylic acid reacts with a diamine to form a tertiary amine. On further reaction with sodium chloroethanoate, a quaternary salt is formed:

Scroll to Top



Betaines are neutral compounds with a cationic and an anionic group which are not adjacent to one another.



an alkyl betaine

Amphoteric surfactants are very mild and are used in shampoos and other cosmetics. They are said to be pH balanced.

Applications

Laundry detergents

A detergent is made up of many ingredients, some of which are surfactants. An example of the mixture of compounds in a detergent is shown in Table 1.

In this formulation there are seven surfactants, two anionic, three non-ionic and two soaps. However, there are other ingredients, each with specific functions:

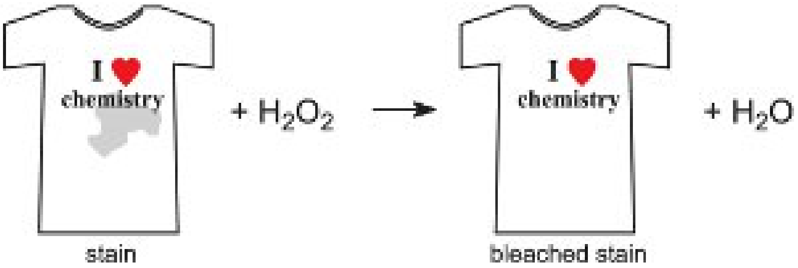
Bulking agents, such as sodium sulfate and water.

Some detergents need anti-caking agents, for example aluminium silicate, which keep the powder dry and free-flowing.

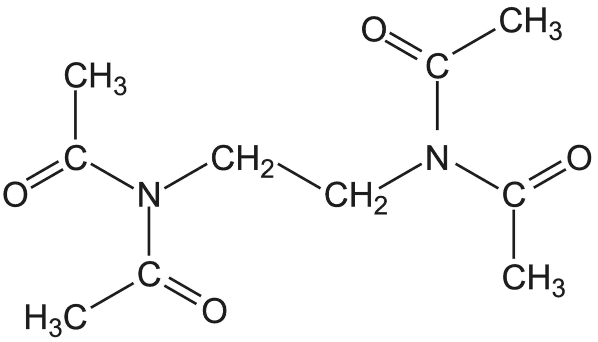
Builders, usually sodium aluminosilicates, a type of zeolite (/processes/catalysis-in-industry.html#zeolite), remove calcium and magnesium ions and prevent the loss of surfactant through scum formation.

Scroll to Top

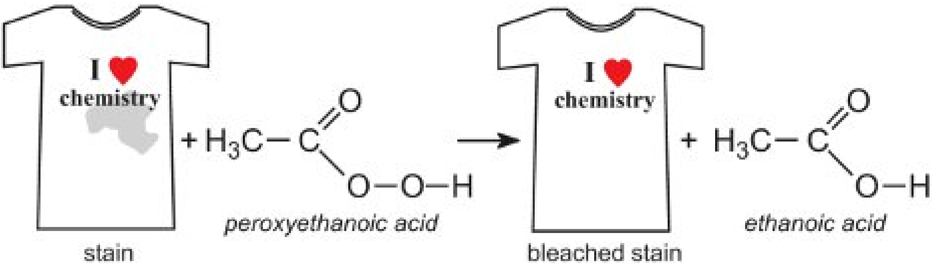
Stains can be bleached with oxidizing agents such as sodium perborate ($NaBO_3.4H_2O$) and sodium percarbonate ($2Na_2CO_3.3H_2O_2$) which react with hot water to form hydrogen peroxide (/chemicals/hydrogen-peroxide.html) which in turn reacts with the stain:



However *bleach activators* are needed for low temperature washes. Sodium perborate and sodium percarbonate do not liberate hydrogen peroxide in cool water. A compound is added to react with them to liberate a peroxycarboxylic acid, RCO_3H, which oxidizes stains readily. The most commonly used activator is:



It is known by its trivial name, TAED, and reacts with the oxidizing agent to form peroxyethanoic acid:



Other ingredients which can be added to a detergent include:

Buffering agents - to keep the pH at the appropriate value

Structurants - to give shape to the fabric being washed

Sequestrants - to react with free metal ions which might otherwise cause problems with appearance or scum formation

Ingredient	Function
Sodium silicoaluminate	Builder
Sodium carbonate	Buffering agent
Sodium sulfate	Bulking agent
Sodium carbonate peroxide (sodium percarbonate)	Oxidizing agent
Sodium dodecylbenzenesulfonate	Surfactant

Scroll to Top

Optical brighteners - to make the fabrics look brighter and whiter

Antifoaming agents

Enzymes - to remove specific stains: proteases (to remove proteins), amylases (to remove starches), lipases (to remove fats)

Fragrance

Anti-redeposition agents - to prevent dirt being redeposited on fabrics

Skin conditioning agent - to help to keep the skin in good condition

Softness extender - to help keep the clothes 'soft'

Emulsifier - to help keep immiscible liquids as an emulsion

Colorant

Domestic automatic machine laundry liquids are formulated using blends of anionic, nonionic and soap surfactants and various other functional substances. Bleach systems are not compatible with the higher water temperature and cannot be used above ca 315 K.

For hand washing (used for delicate fabrics such as wool or silk), foam-stabilisers are included, to maintain foam. The customer equates the quantity of foam produced with the detergent cleansing action. For the quantity of foam produced the order is:

anionics > soap > nonionics > cationics

Water	Bulking agent
C12-15 pareth-5	Surfactant
Tetraacetyl ethylene diamine (TAED)	Bleach activator
Ceteareth-25	Surfactant
Citric acid	Builder
Sodium silicate	Builder
Sodium acrylic acid/MA co-polymer	Structurant
C12-15 pareth-7	Surfactant
Sodium stearate	Surfactant
Stearic acid	Surfactant
Tetrasodium etidronate	Sequestrant
Ethylenediaminetetra methylene phosphoric acid Ca/Na salt	Sequestrant
Maize starch	Bulking agent
Cellulose gum	Anti-redeposition agent
Parfum	Fragrance
Dimorpholinopyridazinone	Optical brightener
Sodium bentonite	Softness extender
Simethicone	Antifoaming agent
Sodium chloride	Bulking agent
Sodium polyacrylate	Structurant
Glyceryl stearate	Emulsifier
Sodium polyarylsulfonate	Surfactant

Table 1 Ingredients of a detergent for washing clothes.

Machine dishwashing powders and tablets

The products used in dishwashers are usually powders and contain builders (90-95%), a nonionic surfactant (1-5%), bleach agents with an activator and enzymes. They are formulated with sodium carbonate and sodium silicate to create a very alkaline environment that helps to denature (break down) the fats and proteins left on the used dishes and utensils.

Scroll to Top

Washing up liquids

These formulations contain between 13-40% of surfactants which are predominantly alkyl ether sulfates but also include nonionics and amphoterics (betaines).

Shampoos and shower gels

These tend to be based on alkyl ether sulfates and usually contain small amounts of other surfactants (most typically amphoterics) which help protect the skin from irritation and also condition the hair.

Hair conditioners and fabric softeners

These products are formulated using cationic surfactants (sometimes combined with small amounts of non-ionic surfactants). These are not cleansing products and the cationic surfactant is deposited onto the slightly negatively charged hair or cotton fibre surface, thus giving a lubrication benefit.

Environmental considerations

In Western Europe all surfactant components of domestic detergents must be biodegradable. This requirement resulted from the fact that the original alkylbenzene sulfonate anionics were based on branched alkenes and these proved resistant to degradation by bacteria at sewage treatment works causing many rivers to suffer from foam. There was also a fear that surfactants could be "recycled" into drinking water. Similar concerns were expressed about nonylphenol ethoxylates and so in the 1980s the industry moved to linear alkylbenzene sulfonates and alcohol ethoxylates as the major ingredients of their formulations. Effective sewage treatment ensures that detergent components which are part of household effluent water are not discharged untreated into rivers and water courses.

The development of compact powders and liquids and refillable packages is designed to reduce packaging waste.

Redesign of washing machines and laundry detergent products (including the addition of bleach activators and enzymes to ensure good stain removal at low temperatures) has resulted in energy savings by reducing water heating and using shorter wash cycles.

Date last amended: 18th March 2013

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Scroll to Top

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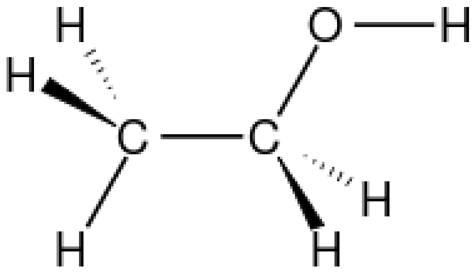


Ethanol

by

Dr. Mohamed Y. Mahgoub

Uses of ethanol

- Alcoholic drinks (e.g. beer, whiskey, and vodka).

- Biofuels for cars.

- Manufacture of ethene as a route to polyethene.

- The other main uses of ethanol as a chemical solvent and intermediate are for: **glycol ethers**, **ethanolamines**/**ethylamines** and **ethyl propenoate**.

Uses of ethanol

Detergents

Cosmetics

Perfumes

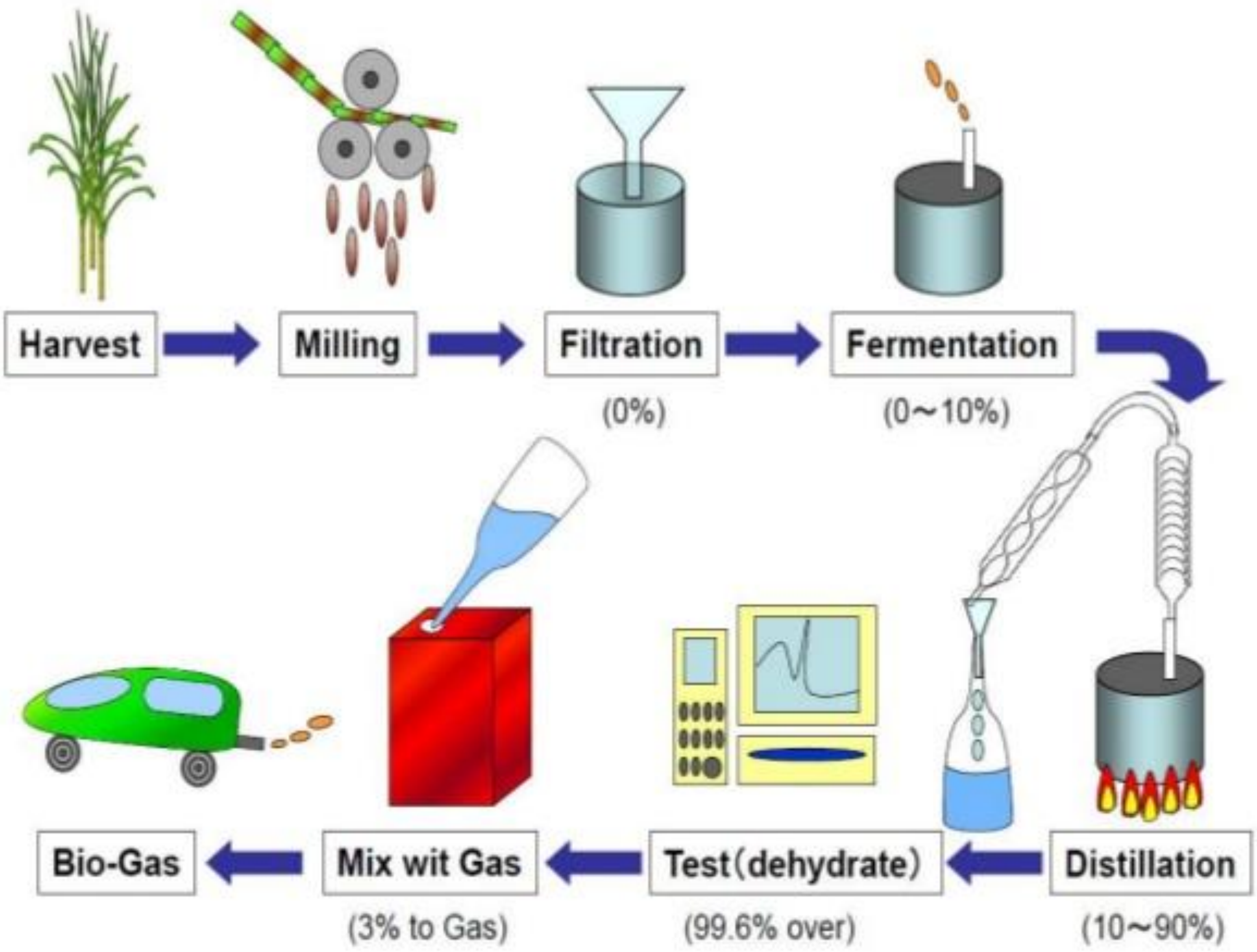
Paints

Manufacture of ethanol

Worldwide Ethanol is produced by

- **Fermentation of crops** (**93%**)
- **Synthetic ethanol** (**7%**) by direct hydration of ethene.

Fermentation of crops



Fermentation of crops

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\alpha\text{-amylase}} nC_{12}H_{22}O_{11}$$

Starch **Maltose**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\alpha\text{-amyloglucosidase}} 2C_6H_{12}O_6$$

glucose

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + 2CO_2$$

Ethanol

Manufacture of ethanol

By direct **catalytic hydration of ethene** in the presence of steam, using phosphoric acid adsorbed on the surface of a solid (silica) as a catalyst in a fixed bed reactor

$$C_2H_4(g) + H_2O(g) \xrightleftharpoons{\text{catalyst}} C_2H_5OH(g)$$

The reaction is reversible and exothermic

Annual production of ethanol

World 850 000 tonnes

Europe 470 000 tonnes

Compost

by

Dr. Mohamed Y. Mahgoub

Compost is organic matter that has been decomposed in a process called composting.

- This process **recycles various organic materials** otherwise regarded as waste products and produces a soil conditioner (the compost).

COMPOSTABLES

Food Scraps • Soiled Paper • Plants • Yard Waste

Breads, grains, pasta, cereal

Fruits and vegetables

Meat, poultry, seafood, eggs, dairy (including bones)

Leftovers, kitchen scraps (including coffee grounds/filters)

Once kitchen pail is full, empty into the large, green composting bin

NO PET LITTER OR WASTE
NO DIRT OR ROCKS
NO HAZARDOUS WASTE
NO PLASTIC BAGS
NO CONSTRUCTION MATERIALS

Attached file

More details for Ethanol manufacturing

The Essential Chemical Industry - online

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Ethanol

C_2H_5OH

Most of the world's ethanol is produced by fermentation of crops (93%) with synthetic ethanol (7%) being produced by direct hydration of ethene.

Uses of ethanol

The fermentation of plant material (for example, barley and rice) is the route by which alcoholic drinks (e.g. beer, whiskey, gin and vodka) are produced. It is also how bioethanol (/materials-and-applications/biofuels.html#bioethanol) for biofuels is produced.

Of the uses of bioethanol, easily the most important is as a fuel for cars. However an increasing one is in the manufacture of ethene (/chemicals/ethene.html) as a route to poly(ethene) (/polymers/polyethene.html). The other main uses of ethanol as a chemical intermediate are for:

- glycol ethers (/chemicals/epoxyethane.html#glycol_ether)
- ethanolamines/ethylamines (/chemicals/epoxyethane.html#e_amine)
- ethyl propenoate (/polymers/polypropenoic-acid.html#ethyl_propenoate)

It is also used as a solvent in the manufacture of cosmetics, pharmaceuticals, detergents, inks and coatings.

Scroll to Top

Figure 1 Ethanol is one of the starting materials for production of ethyl propenoate, a co-monomer for polymers used in emulsion paints.

By kind permission of AkzoNobel.

Annual production of ethanol

World	850 000 tonnes
Europe	470 000 tonnes

These figures relate to synthetic alcohol (i.e. does not include alcohol produced biosynthetically, bioethanol (/materials-and-applications/biofuels.html#bioethanol)).

The amount of bioethanol produced is enormous in comparison[1]. In 2015, 25.7 billion gallons (*ca* 80 million tonnes) were produced. Of these, 14.6 billion gallons (*ca* 44 million tonnes) were produced in the United States, mainly from corn, 7.1 billion gallons (*ca* 21 million tonnes) in Brazil, mainly from sugar. Europe produced significantly less, 1,4 billion gallons (*ca* 1 million tonnes).

1. Renewable Fuels Association, 2016

Manufacture of ethanol

Ethanol is manufactured by the direct catalytic hydration of ethene in the presence of steam, using phosphoric acid adsorbed on the surface of a solid (silica)
as a catalyst in a fixed bed reactor (/processes/chemical-reactors.html#fixed_bed). The reaction is reversible and exothermic:

$$C_2H_4(g) + H_2O(g) \overset{\text{catalyst}}{\rightleftharpoons} C_2H_5OH(g)$$

Scroll to Top

From the equilibrium equation, it can be seen that conversion of the feedstock to ethanol is favoured by low temperature, high pressure and high steam concentration.

To achieve acceptable reaction rates, a temperature of *ca* 500 K is used in the presence of the catalyst. Increasing the pressure pushes the reaction to the product side but also causes polymerization of the ethene. Higher pressures also mean increased capital and operating costs. In practice, the process is generally operated under a pressure of 60-70 atm.

Figure 2 The purification of ethanol by distillation.
The volatile impurities (for example, ethoxyethane) are removed in columns 1 and 2.
The azeotropic mixture (95% ethanol) is produced in column 3.
Other high boiling impurities (for, example, butanol) are removed by fractional distillation.
By kind permission of Sasol.

Higher ethene conversion can be obtained using an excess of water (steam). But at high pressures the catalyst takes up water, its activity drops and it becomes diluted, draining away from the catalyst support. A mole ratio of water : ethene around 0.6 : 1 is commonly used.

Great care is exercised to minimise the emissions of ethanol from the plant, together with the small amounts of by-products that are produced, principally ethanal (acetaldehyde) and diethyl ether.

Considerable work is being done to improve the catalyst so that the temperature of the furnace can be reduced. This means that less fuel will be used to heat the furnace, and the position of equilibrium will be 'shifted' to favour the product.

With the above conditions, around 5% conversion per pass is obtained. To obtain the 95% yield achieved, unreacted ethene is separated from the liquid products and recycled.

Scroll to Top

The product contains a high proportion of water and is distilled to produce a 95% (w/w) solution of ethanol.

Production of pure ethanol

(i) Distillation

Further distillation of the 95% solution of ethanol in water does not improve the purity as an azeotrope (constant boiling mixture) is produced. This can be overcome by adding a third compound (e.g. benzene) which 'breaks up' the azeotrope but this involves more distillations and consequently more energy.

(ii) Pressure swing adsorption

A zeolite molecular sieve (/processes/catalysis-in-industry.html#zeolite) is being increasingly employed to remove the water to produce pure ethanol by a process known as pressure swimg adsorption.

The mixture of ethanol and water is passed through a column containing pellets of a molecular sieve of 3 A (i.e. the pores have diameters of 3 angstroms, 3×10^{-10} m or 0.3 nm).

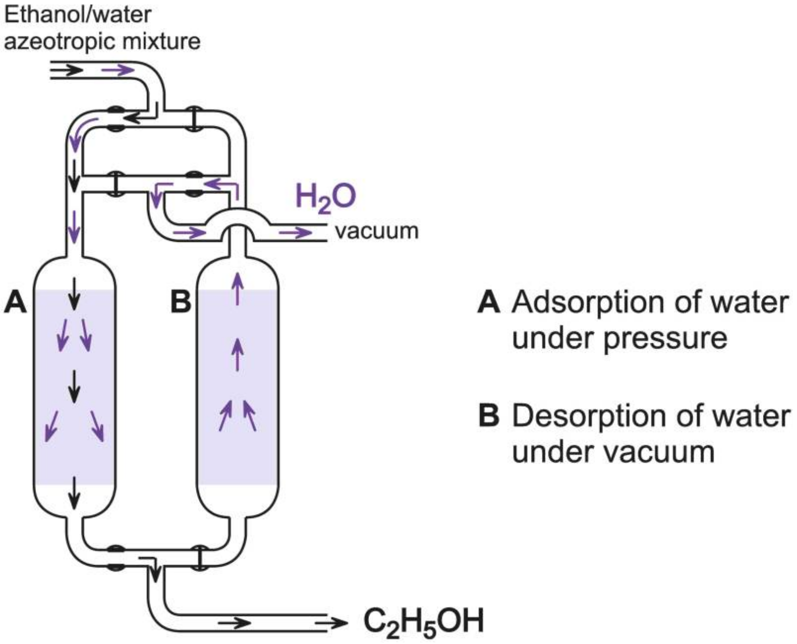

Figure 3 Purification of ethanol by pressure swing adsorption using a zeolite.

Although both ethanol and water are polar, only water molecules (diameter 0.28 nm) are able to pass through the pores as the diameter of ethanol molecules is too large (0.44 nm). Thus the water molecules enter through the pores and are trapped in the cages of the zeolite. The ethanol passes through the column and is collected.

In one method, which is usually used, the ethanol-water mixture is passed through the column in the gas phase at about 420 K, under pressure (4 atm) (Figures 3 and 4). The water vapour passes through the pores and is adsorbed, as a liquid, in the cages.

Scroll to Top

Figure 4 The purification of ethanol using a molecular sieve. The tanks are being filled at their base with a zeolite. The ethanol has been produced from biomass (wheat).

By kind permission of Ensus.

The term 'swing' is used because two columns are used in parallel. In Figure 3 the left hand column is being used to dry ethanol while the other, right hand one, is being used to regenerate the zeolite.

In the second method, the liquid solution of ethanol and water is passed through a column of the zeolite and the pure ethanol is collected. After several hours, the bed is drained and heated to over 500 K using a stream of heated nitrogen. The water is expelled. This technique is called *thermal (or temperature) swing adsorption.*

Date last amended: 27th October 2016

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Scroll to Top

Perfumes

by

Dr. Mohamed Y. Mahgoub

Perfume

Is a mixture of **fragrant essential oils** and **aroma compounds**, **fixatives**, and **solvents** used to give the human body, objects, and living spaces a pleasant smell.

What is the difference between essential oils and fragrance oils? Real vs fake?

Essential oils (EO’s) are volatile plant extracts made from steam distilling or cold-pressing flowers, bark, stems, leaves, peel, roots, seeds, or other parts of a plant.

Fragrance oils (FO's) are synthetically made chemical scent compounds. Fragrance oils are problematic because these synthetic compounds, they are drying and irritating to the skin.

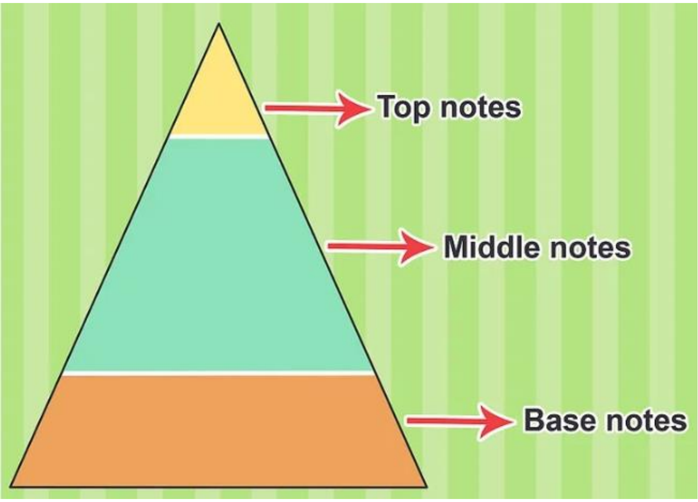
Description of a perfume

It is impossible to describe a perfume according to its components because the formulas are kept secret.

But, it is possible to group perfumes into **olfactive families** and describe them through the **notes** that appear as they slowly evaporate

Perfume’s notes

Understanding the Science of Perfume



Top notes are what you smell first. They are also what disappears first, usually within 10 to 15 minutes.

Middle notes appear as the top notes die off. These are the fragrance's core, determining which family the perfume belongs to — for example, oriental, woody, fresh, or floral.

Base notes accentuate and fix the fragrance's middle notes, also known as its theme. They comprise the fragrance's foundation, making the scent last up to 4 or 5 hours on your skin.

Understanding the Science of Perfume

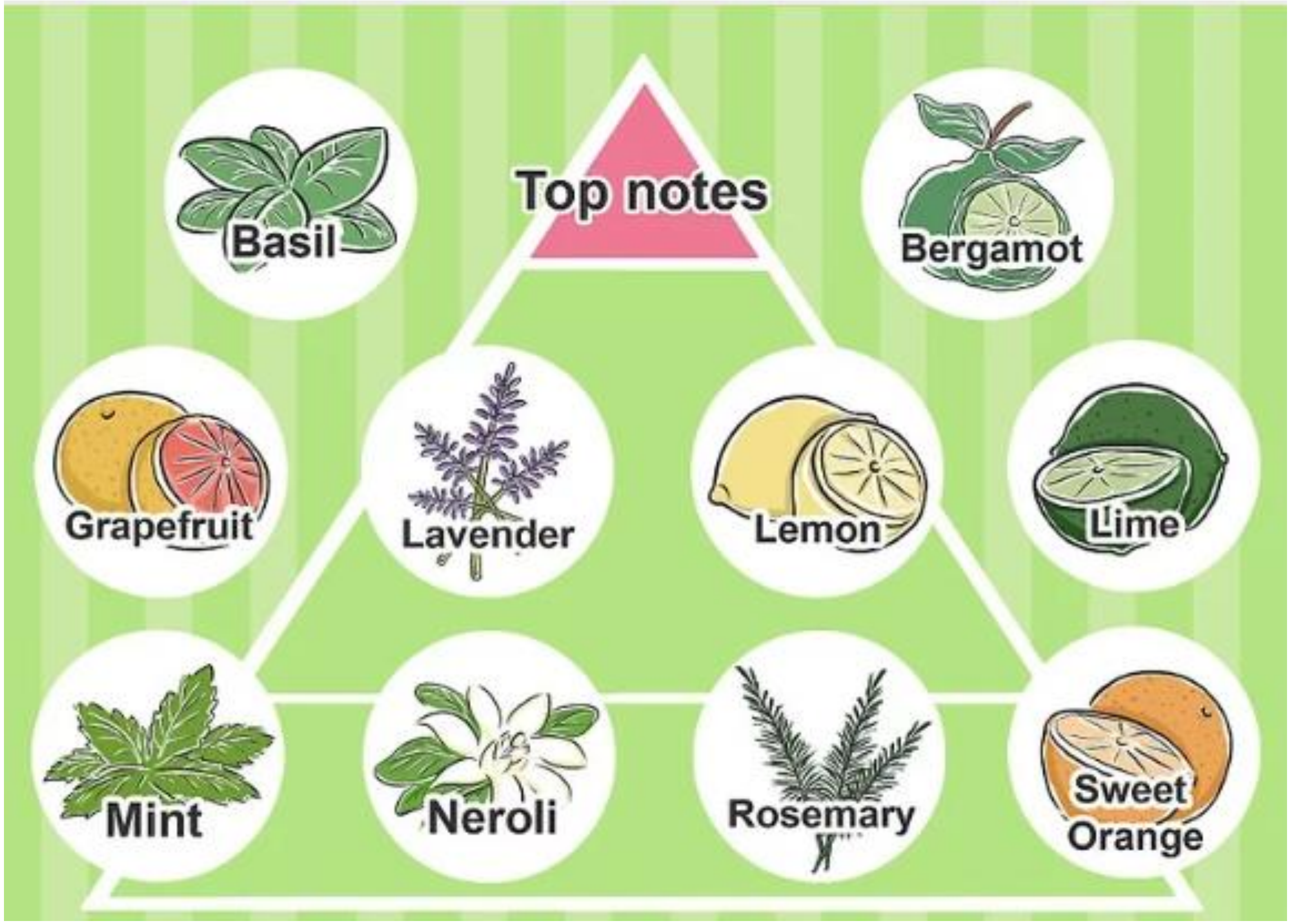
Perfumes are a blend of different levels of scent, also called “notes”. When you spray a fragrance on your skin, it moves through these notes in the following order:

[1] **Top notes** are what you smell first. They are also what disappears first, usually within 10 to 15 minutes.

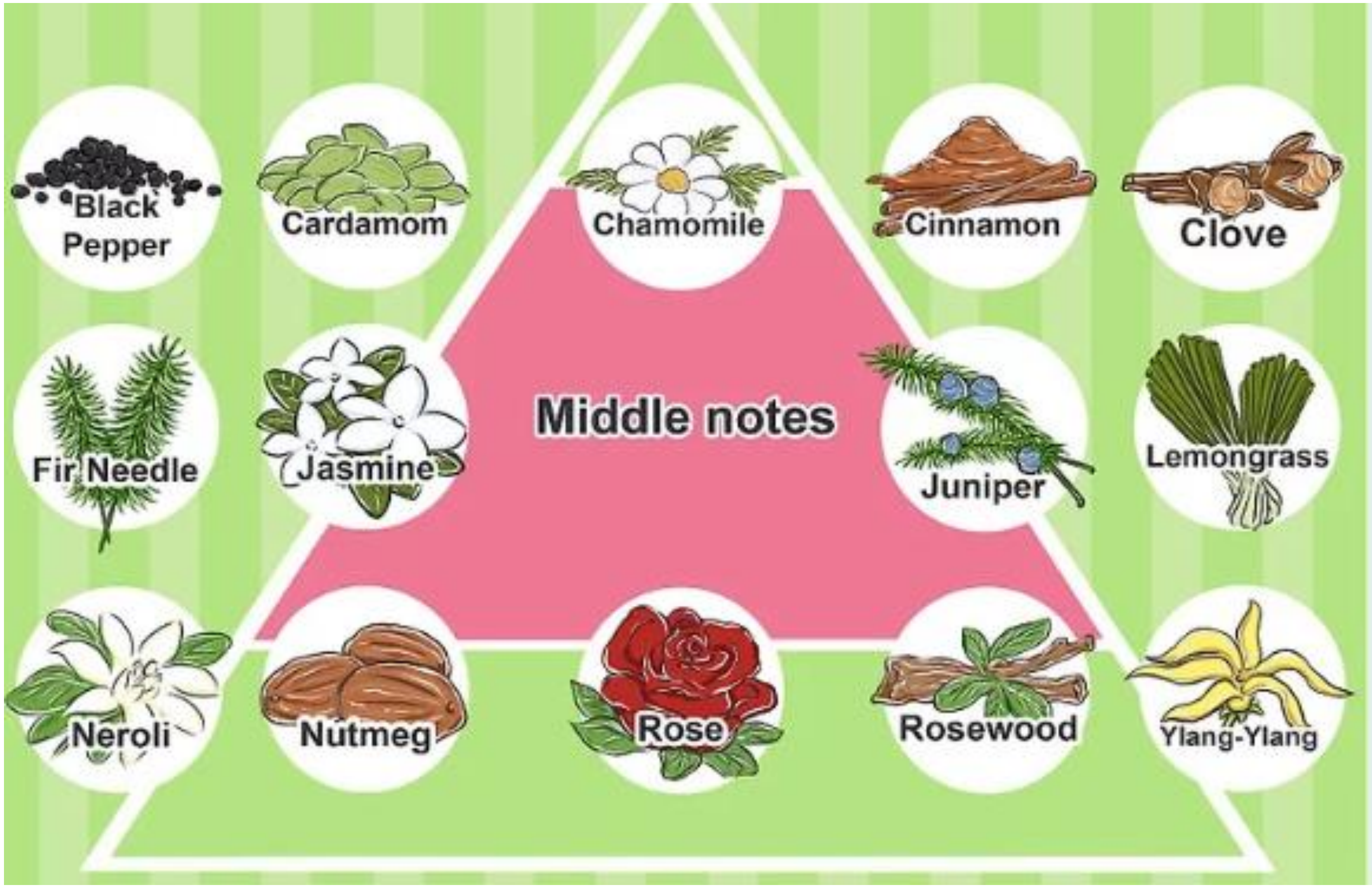
[2] **Middle notes** appear as the top notes die off. These are the fragrance’s core, determining which family the perfume belongs to — for example, oriental, woody, fresh, or floral.

[3] **Base notes** accentuate and fix the fragrance’s middle notes, also known as its theme. They comprise the fragrance’s foundation, making the scent last up to 4 or 5 hours on your skin.

Popular top notes include basil, bergamot, grapefruit, lavender, lemon, lime, mint, neroli, rosemary, and sweet orange.



The popular middle notes include black pepper, cardamom, chamomile, cinnamon, clove, fir needle, jasmine, juniper, lemongrass, neroli, nutmeg, rose, rosewood ….. Etc.



The popular base notes include cedarwood, cypress, ginger, patchouli, pine, sandalwood, vanilla, and vetiver

The ratios of notes

When mixing a fragrance, first add your base notes, then your middle notes, then finally, your top notes. The ideal ratio for blending notes is **30%** top notes, **50%** middle notes, and **20%** base notes.

Description of a perfume

It is impossible to describe a perfume according to its components because the formulas are kept secret.

But, it is possible to group perfumes into **olfactive families** and describe them through the **notes** that appear as they slowly evaporate

Olfactive Families

Perfumes olfactive families can be classified into

Traditional Modern

Single Floral: Fragrances that are dominated by a scent from **one** particular flower; in French called a **soliflore**. (e.g. Serge lutes' Sa Majesty La Rose, which is dominated by rose.)

Floral Bouquet: Is a combination of fragrance of several flowers in a perfume compound.

Perfumes olfactive families can be classified into

Traditional

Amber or Oriental: **A large fragrance class** featuring the sweet slightly animatic scents of ambergris, often combined with vanilla, flowers and woods.

Woody: Fragrances that are dominated by **woody scents**, typically of agarwood, sandalwood, cedarwood. A modern example would be Balenciaga **Rumba**.

Perfumes olfactive families can be classified into

Modern

Due to great advances in the technology of perfume creation (i.e., compound design and synthesis), new categories have emerged to describe modern scents:

Bright Floral: combining the traditional Single Floral & Floral Bouquet categories. Ex: **Estée Lauder's Beautiful**.

Green: a lighter and more modern Ex: **Calvin Klein's Eternity**.

Perfumes olfactive families can be classified into

Modern

Aquatic, Oceanic, or Azonic: the newest category in perfume history, first appearing in 1988. **Ex:** **Davidoff Cool Water, Christian Dior's Dune**. Generally, contains a synthetic scent discovered in, or other more recent synthetics.

Perfumes olfactive families can be classified into

Modern

Citrus: An old fragrance family that until recently consisted mainly of **"freshening" eau de colognes**, due to the low tenacity of citrus scents. **Ex:** Faberge Brut.

Fruity: featuring the aromas of fruits other than citrus, such as peach, cassis (black currant), mango, passion fruit, and others.

Product details and Its uses

❖ **Traditional**

The traditional classification which emerged around 1900 comprised the following categories:

Single Floral: Fragrances that are dominated by a scent from one particular flower; in French called a soliflore. (e.g. Serge lutes' Sa Majesty La Rose, which is dominated by rose.)

Floral Bouquet: Is a combination of fragrance of several flowers in a perfume compound.

Amber or "Oriental": A large fragrance class featuring the sweet slightly animatic scents of ambergris or labdanum, often combined with vanilla, tonka bean, flowers and woods.

Can be enhanced by camphor us oils and incense resins, which bring to mind era imagery of the Middle East and Far East.

Woody: Fragrances that are dominated by woody scents, typically of agarwood, sandalwood, cedar wood, and vetiver. Patchouli, with its camphorates smell, is commonly found in these perfumes. A traditional example here would be Mercuria’s Madera’s De Oriented or Chanel Bios des Lies. A modern example would be Balenciaga Rumba.

❖ **Modern :** Since, due to great advances in the technology of perfume creation (i.e., compound design and synthesis) as well as the natural development of styles and tastes, new categories have emerged to describe modern scents:

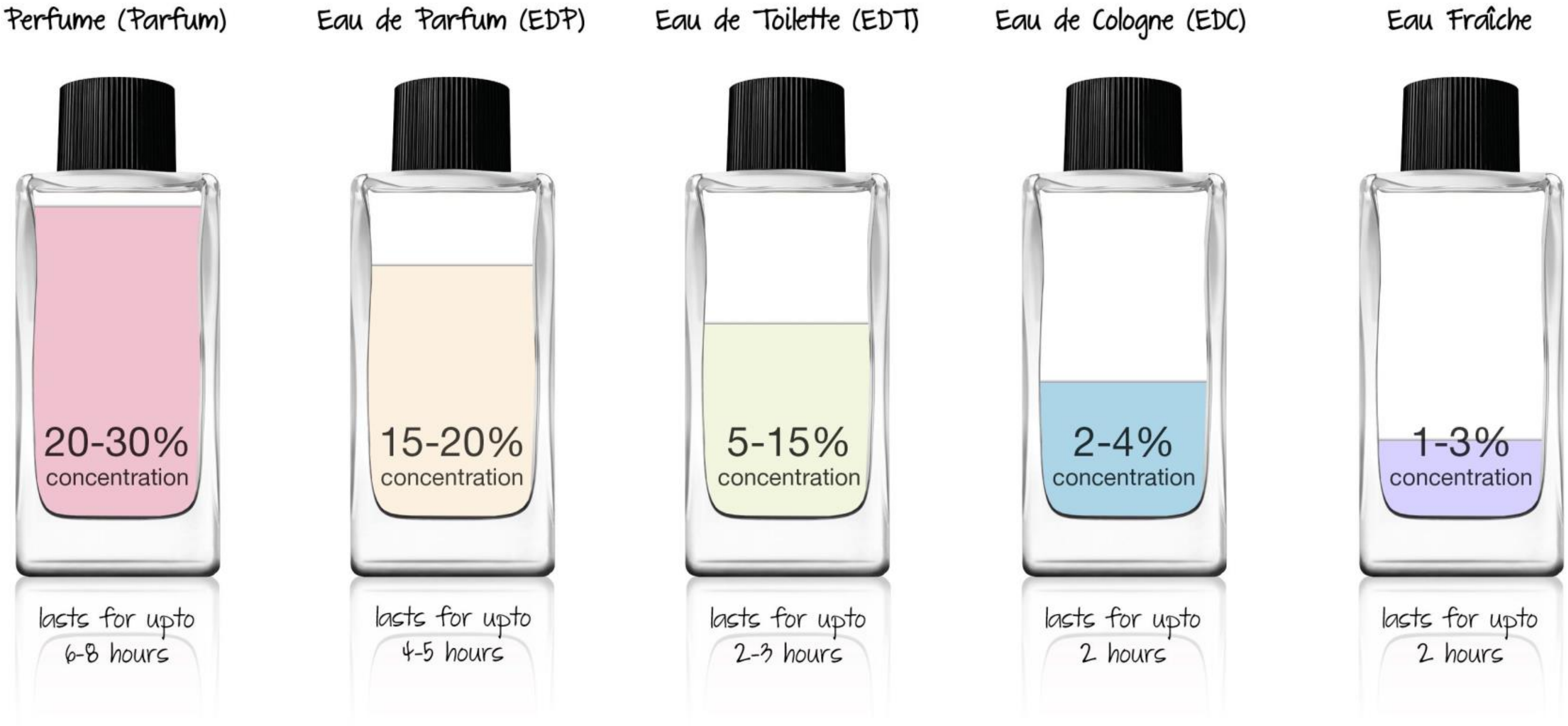
Bright Floral: combining the traditional Single Floral & Floral Bouquet categories. A good example would be Estée Lauder's Beautiful.

Green: a lighter and more modern interpretation of the Chypre type, with pronounced cut grass, crushed green leaf and cucumber-like scents. Ex: Calvin Klein's Eternity.

Aquatic, Oceanic, or Azonic: the newest category in perfume history, first appearing in 1988 Davidoff Cool Water , Christian Dior's Dune , and many others. A clean smell reminiscent of the ocean, leading to many of the modern androgynous perfumes. Generally, contains clone, a synthetic scent discovered in , or other more recent synthetics. Also used to accent floral, oriental, and woody fragrances.

Citrus: An old fragrance family that until recently consisted mainly of "freshening" eau de colognes, due to the low tenacity of citrus scents. Development of newer fragrance compounds has allowed for the creation of primarily citrus fragrances. A good example here would be Faberge Brut. **Fruity**: featuring the aromas of fruits other than citrus, such as peach, cassis (black currant), mango, passion fruit, and others.

Different classes of basic perfumes



CLASSIFICATION OF PERFUMES

- Perfumes are classified into five major groups on the basis of concentration of fragrance and duration of lasting:

Class	% of aromatic compound	Duration (hours)
Parfume(perfume)	20-30	6-8
Eau de parfume	15-20	4-5
Eau de toilette	5-15	2-3
Eau de cologne	2-4	2
Eau fraiche	1-3	2

Underneath the name of the perfume on a bottle will normally be the fragrance concentration. A fragrance concentration refers to the strength that a fragrance has. Perfumes with a higher fragrance concentration contain more perfume oils and less alcohol. Fragrance concentrations are broken into categories including parfum, eau de parum, eau de toilette, eau de cologne, and eau fraiche.

Parfum

Parfum, also known as extrait de parfum or pure perfume, has the highest fragrance concentration. Parfum will contain anywhere from 15% to 40% fragrance however concentration is generally between 20% to 30% for most parfums. Of all scents, parfums last the longest; usually six to eight hours. Parfum generally also commands the highest price of all the fragrance types due to the high concentration of fragrance. People with sensitive skin may do better with parfums as they have far less alcohol than other fragrance types and therefore are not as likely to dry out the skin.

Eau de Parfum

After parfum, eau de parfum (EDP) has the next highest concentration of fragrance. Eau de parfum generally has a fragrance concentration of between 15% and 20%. On average, eau de parfum will last for four to five hours. It is also generally less expensive that parfum and while it does have a higher concentration of alcohol than parfum, it is better for sensitive skin than other fragrance types. Eau de parfum is one of the most common fragrance types and is suitable for everyday wear.

Eau de Toilette

Eau de toilette (EDT) has a fragrance concentration of between 5% and 15%. It is cheaper than eau de parfum and is one of the most popular types of fragrance available. EDT fragrance will normally last for two to three hours. Eau de toilette is considered by some to be for daywear while eau de parfum is considered nightwear. The term eau de toilette came from the French term "faire sa toilette" which means getting ready.

Eau de Cologne

Eau de cologne, or EDC, has a much lower concentration of fragrance than the above types of perfume. EDC generally has a 2% to 4% percent concentration of fragrance and a high concentration of alcohol. It is cheaper than other types of fragrance however the scent generally only lasts for up to two hours. EDC generally comes in bigger bottles and more of the fragrance needs to be used. Originally eau de cologne referred to a traditional recipe that used herb and citrus notes with little anchoring with base notes.

Eau Fraiche (products sold as "splashes“ or mists)

Eau fraiche is similar to eau de cologne in that the scent will generally last for up to two hours. Eau fraiche has an even lower concentration of fragrance than eau de cologne, normally only 1% to 3%. While eau fraiche has a low fragrance concentration, it does not contain a high amount of alcohol. Along with the fragrance, the remainder of eau fraiche is mostly water.

Along with the types of perfume listed above, there are mists, aftershaves, and other types of fragrances available. Higher end fragrances can cost a significant amount of money so doing research beforehand will ensure that you get the type of fragrance you are looking for. Along with fragrance types there are also fragrance notes which determine the final scent. With all of the types and scents available, shopping for perfume is not always easy but it is possible.

Extraction Methods

Solvent Extraction

Cold expression

Steam Distillation

Extraction Methods

Solvent Extraction

This method is performed by putting plants into big, rotating drums. The plants are then covered with petroleum ether or benzene. The plant parts eventually dissolve in whatever solvent is used, leaving a waxy substance that contains the oils. This substance is then placed in ethyl alcohol. The oil dissolves in the alcohol, which is then burned off, leaving a highly concentrated perfume oil.

Cold expression

As one of the oldest forms of extraction, the expression method is quite simple. This process, often used for extracting citrus oils, involves pressing the plant, either mechanically or manually, until all of the oils are extracted.

Steam Distillation

Steam Distillation

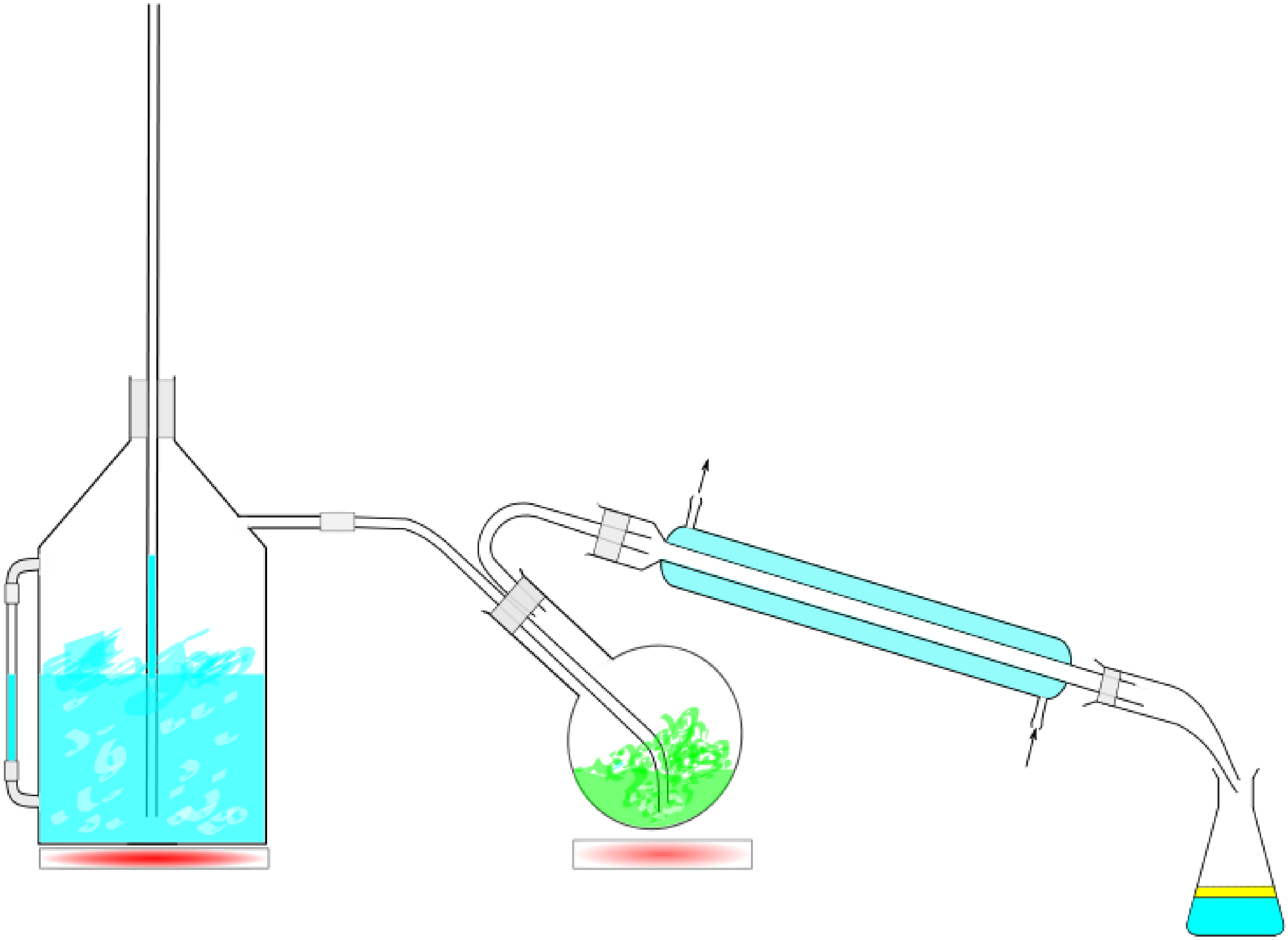
Steam Distillation

This method is used for extraction of **essential oils** from their original plant sources

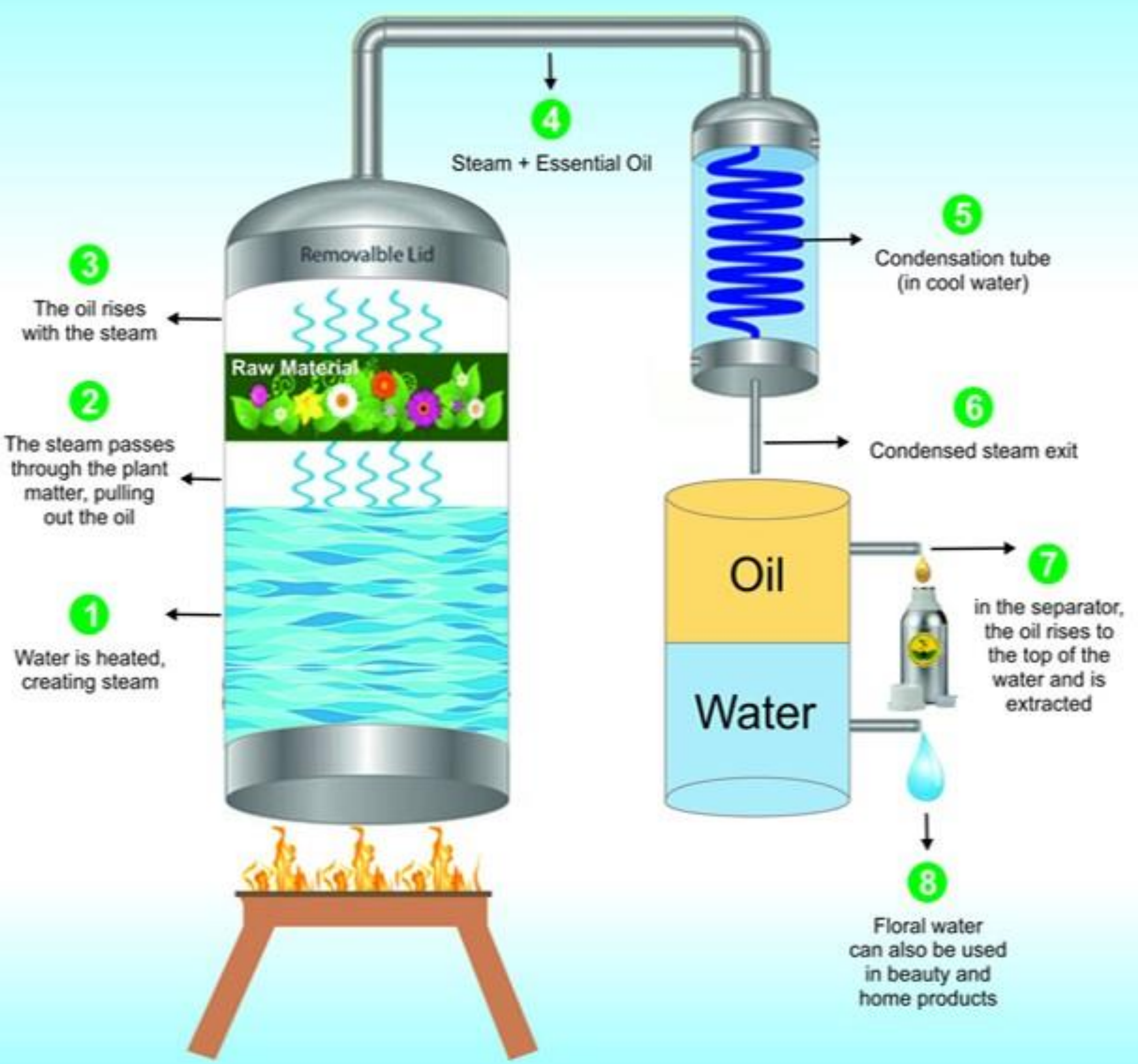
Ex:

Limonene from orang or lemon – Lavender oil – rose oil ……etc.

Steam distillation apparatus



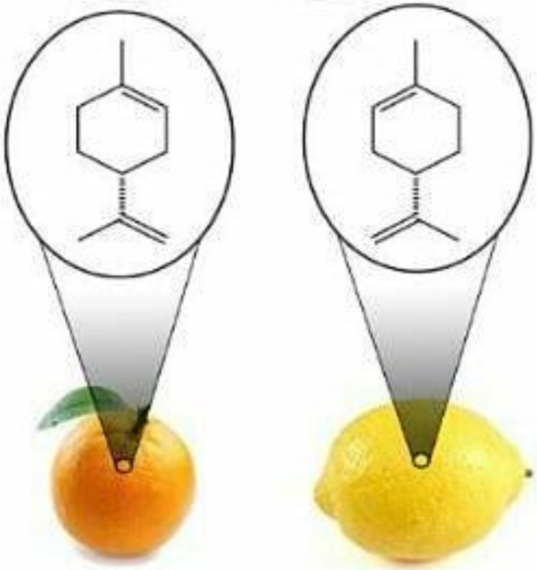
Steam Distillation Process



1. Water is heated, creating steam
2. The steam passes through the plant matter, pulling out the oil
3. The oil rises with the steam
4. Steam + Essential Oil
5. Condensation tube (in cool water)
6. Condensed steam exit
7. in the separator, the oil rises to the top of the water and is extracted
8. Floral water can also be used in beauty and home products

ليمونين
limonene

الليمونين مركب تربيني يتواجد طبيعياً في الفواكة الحمضية كالليمون والبرتقال هذا المركب له متماكبان ضونيان هما إس-ليمونين هو المذاق المميز لليمون ، و أر-ليمونين وهو المذاق الخاص بالبرتقال. يمكن أستخلاص الليمونين من قشور الليمون أو البرتقال بأستخدام التقطير البخاري يستعمل الليمونين كمنكة في الأطعمة و في منتجات التجميل وفي صناعة معطرات الجو وغيرها.....



البرتقال (R)-limonene

الليمون (S)-limonene

Do you want to make your own signature scent? Or maybe you’re looking for a unique homemade gift idea.

Perfume formula__ Dr. M. Y. Mahgoub

Ingredients for 50 ml

1- Essential oil 10-15 ml

2- Fixatives Ex: Glycerol or benzyl benzoate 1 ml

3- Ethyl alc. (without odour > 99%) up to 50 ml

4- Distilled water 4 ml

Industrial
Chemistry

Papers

by

Dr. Mohamed Y. Mahgoub

Paper is made in two steps:

1- Cellulose fibers are extracted from a variety of sources and converted to pulp.

2- Pulp is combined with water and placed on a paper making machine where it is flattened, dried, and cut into sheets and rolls.

Cellulose Sources

- The raw materials containing cellulose fibers, generally **Wood**, **Recycled paper**, **Agricultural residues,** and **Cotton & Other Natural Fibers**.

- In developing countries, about 60% of cellulose fibers originate from **nonwood raw materials** such as **bagasse**, **cereal straw**, **bamboo** ... etc.

Cotton & Other Natural Fibers

Natural fibers such as cotton are used in some cases because its fibers are very strong. This makes it an excellent choice for **documents that may need to be archived**. This strength, combined with its unique feel is why cotton paper is popular for letterhead and other corporate stationary products.

Recycled Fibers

Many papers include different types of recycled content, these include:

Pre Consumer Waste (paper waste from the paper manufacturing and printing processes)

Post Consumer Waste (paper waste that has already touched a consumer, like a recycled newspaper)

Pulp Making Process

There are three main components in the most of Cellulose sources:

Bark – Fiber – Lignin

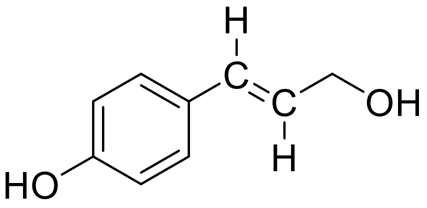
- The **bark** protects the fibers, which are held together by lignin.

lignin

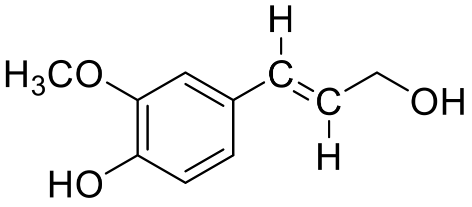
- The main component that needs to be removed to make paper.

lignin

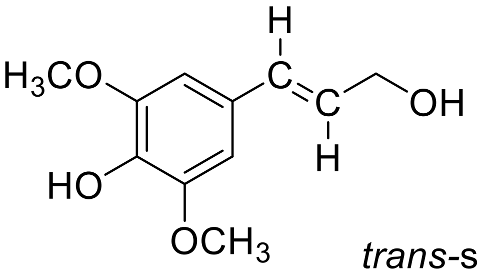
This name refers to a group of chemicals that are essentially three dimensional polymers of *trans*-coniferol, *trans*-sinapol and *trans*-*p*-coumarol (see below), along with hemicelluloses and aromatic carboxylic acids.



trans-*p*-coumarol



trans-coniferol



trans-sinapol

Pulp Making Process

Step 1- Pulp Preparation

Cellulosic pulp is manufactured from the raw materials, using

Mechanical and **Chemical means**.

Mechanical pulping

mechanical energy applied

The main processes are

- Stone Groundwood Pulping (SGW),
- Pressure Groundwood Pulping (PGW),
- Thermo-Mechanical Pulping (TMP),
- or Chemi-Thermo-Mechanical Pulping (CTMP).

Stone Groundwood Pulping (SGW)

- Usually this involves taking a log and pressing it against a rotating surface to **grind off small pieces**.
- The groundwood pulp is then often **cooked to soften it**.
- This pulp is used in newsprint and other low cost book grades.
- Groundwood pulp is economical since **all the wood is used**; however, it contains impurities that can cause discoloration and weakening of the paper.

Thermomechanical pulps (TMP)

Which are used for making products such as newsprint, are manufactured from raw materials by the application of **heat, in addition to mechanical operations.**

Chemimechanical and chemi-thermo-mechanical processes

Involve mechanical and the use of chemicals. The pulps show good strength properties, even when using hardwood as a fiber source

TMP pulps are generally stronger than groundwood pulps

Chemical pulping

- Is used on most papers produced commercially in the world today

- This has involved a **full chemical treatment** in which the objective is to remove non-cellulose wood components leaving intact the cellulose fibers.

Chemical pulping

- Chemical pulps are made by cooking (digesting) the raw materials, using the **kraft (sulfate)** and **sulfite** processes to remove lignin.
- **The kraft** (sulfate) process is the most dominating chemical pulping process worldwide.

Chemical pulping

- In the kraft pulp process the active cooking chemicals (white liquor) are sodium hydroxide (**$NaOH$**) and sodium sulfide (**Na_2S**).
- Kraft process is applicable to all types of wood species.

Chemical pulping

- **Sulfite process** uses different chemicals to attack and remove lignin

- The main sulphite pulping processes are Acid (bi)sulphite, and Alkaline sulphite.

- **Kraft pulp** possesses superior pulp strength properties in comparison to **sulphite pulp**.

Step 2- Pulp washing

The pulp is washed with water to wash out the cooking chemicals and lignin from the fibre so that they will not interfere with later process steps.

Step 3 – Bleaching OR/AND Colouring

- ✓ The objective of bleaching is to remove the small fraction of the lignin remaining after cooking.

- Oxygen, hydrogen peroxide, ozone, peracetic acid, sodium hypochlorite, chlorine dioxide, chlorine, and other chemicals are used to transform lignin into an alkali soluble form.

- An alkali, such as sodium hydroxide, is necessary in the bleaching process to extract the alkali-soluble form of lignin.

Step 4 – Beating / Mixing

- ✓ At this point, various filler materials can be added such as chalks ($CaCO_3$), clays, starch, or chemicals such as titanium oxide.

- ❖ These additives will influence the opacity and other qualities of the final product

Paper making

The pulp fibres are mechanically and chemically treated, formed into a dilute suspension, spread over a mesh surface, the water removed by suction, and the resulting pad of cellulose fibres pressed and dried to form paper.

The pulp is rolled smooth and dried.

Attached file

More details for Paper manufacturing

THE PULP AND PAPER INDUSTRY

In New Zealand, paper is made from wood using the "Kraft" process. This is a part mechanical, part chemical process that produces a strong pulp. It has several disadvantages, in terms of complexity and set up costs as well as having a low pulp yield and producing unpleasant-smelling sulfur compounds, but it is still internationally the most widely used pulp and paper process. The manufacturing process is outlined below.

Step 1 - Wood preparation
The bark is removed from in-coming logs, and these are then chipped. Sometimes, the wood arrives at the plant already chipped, meaning that this step is unnecessary.

Step 2 - Cooking
The wood chips are heated in a solution of NaOH and Na_2S in a pressure cooker, during which time a lot of the lignin (the reinforcing susbstance that make tree cells wood hard and 'woody' rather than soft like those of other plants) is removed from the wood. The pressure is then released suddenly, causing the chips to fly apart into fibres.

Step 3 - Pulp washing
The pulp is washed with water to wash out the cooking chemicals and lignin from the fibre so that they will not interfere with later process steps.

Step 4 - Pulp screening
A sieve is used to remove knots and clumped-together uncooked fibres from the pulp.

Step 5 - Bleaching
This is done in two stages. Firstly the pulp is treated with NaOH in the presence of O_2. The NaOH removes hydrogen ions from the lignin and then the O_2 breaks down the polymer. Then, the pulp is treated with ClO_2 then a mixture of NaOH, O_2 and peroxide and finally with ClO_2 again to remove the remaining lignin.

Step 6 - Paper making
The fibres are mechanincally treated to make them bond better to each other (strengthening the paper), chemicals added to provide special properties such as colour or water resistance, and then the water is squeezed out and the pulp is rolled smooth and dried.

Various ancilliary processes result in the recovery of CaO, NaOH and Na_2S, the major chemicals used in the process. Various utilities ensure that such conditions as sufficient reaction times and adequate mixing are met.

On site processing removes the lignin from the liquid wastes, and solid wastes are generally taken to a landfill. Efforts continue to be made to reduce water consumption by recycling, as smaller volumes are easier to process. The most obvious environmental problem continues to be the sulfurous emissions that give Kraft pulping plants their characteristic smell. These are decreased by gas incineration, but are not able to be wholly eliminated.

INTRODUCTION

Paper is a major product of the forestry industry, and is used widely in our society. Paper products are used not only in their obvious applications in the publishing industry and for writing on, but also in a variety of specialty papers, cardboards, brown papers etc. In addition, various chemicals are produced as a byproduct of the pulp and paper industry (see articles).

Paper is made by pulping wood, bleaching this pulp and then spreading it out into sheets to make it into paper. At various stages of the process, chemicals are used to give the paper particular properties, such as the bleaching chemicals that make paper white (and which also enable it to subsequently be coloured). The pulping process that is used in New Zealand is known as "kraft pulping" which relies on a combination of heat, chemicals and mechanical pulping to convert the wood into a smooth, soft pulp suitable for use in paper making.

Kraft pulping is the main pulping process (together with mechanical pulping) used today, and is the only one discussed below. The kraft process has several advantages:

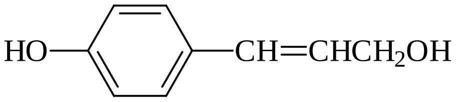
- It can be used with virtually all wood species
- It can easily handle the extractives in most coniferous wood
- The pulp has very good strength (the word 'kraft' means 'strong' in Swedish)
- The recovery process for the chemicals is well established

However, there are also disadvantages:

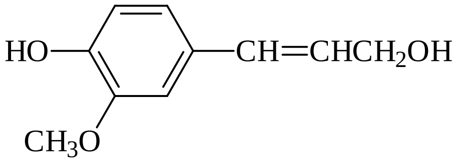
- The pulp yield is quite low at about 45 - 50%
- The equipment used for the chemical recovery is extensive and costly to install
- Sulphurous compounds, which are odorous in the parts per billion range, are formed in the process
- Fairly complicated processes are required for bleaching the pulp

Lignin

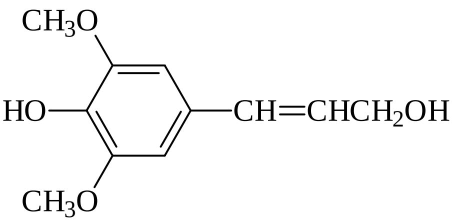
The main component of wood that needs to be removed to turn it into paper is a compound known as lignin. This name refers to a group of chemicals that are essentially three dimensional polymers of *trans*-coniferol, *trans*-sinapol and *trans*-*p*-coumarol (see below), along with hemicelluloses and aromatic carboxylic acids. Lignin is the reinforcing compound that is deposited on tree cell walls to make the wood strong enough to carry the weight of the tree crown. However, it is also the compound that makes wood pulp brown, so it is removed from all wood pulp except that used to make brown paper and some cardboards.



trans-*p*-coumarol



trans-coniferol



trans-sinapol

THE MANUFACTURING PROCESS

The process whereby timber is converted into paper involves six steps. The first four convert the logs into a mass of cellulose fibres with some residual lignin using a mixture of physical and chemical processes. This pulp is then bleached to remove the remaining lignin and finally spread out into smooth, pressed sheets (often with chemicals added to provide particular properties such as colour or water resistance). For some papers (e.g. cardboards and 'brown paper') the bleaching step is unnecessary, but all white and coloured papers require bleaching.

Step 1 - Wood preparation

Wood is delivered to the kraft mill in one of two ways: whole logs and sawmill chips (residuals from sawmills). The logs have their bark removed, either by passing through a drum debarker or by being treated in a hydraulic debarker. The drum debarker, which consists of a slightly inclined, rotating drum is best suited to small diameter logs. The hydraulic debarker, which uses high pressure water jets, can handle large diameter logs. The removed bark is a good fuel, and is normally burnt in a boiler for generating steam.

After debarking, the logs are chipped by multi knife chippers into suitable sized pieces, and are then screened to remove overlarge chips. The *thickness* of the chips is the most important parameter, as this determines the speed and the thoroughness of the impregnation of the cooking chemicals into the wood chip. Neither debarking nor chipping are usually necessary for sawmill chips.

Step 2 - Cooking

The "cooking process" is where the main part of the delignification takes place. Here the chips are mixed with "white liquor" (a solution of sodium hydroxide and sodium sulphide), heated to increase the reaction rate and then disintegrated into fibres by 'blowing' - subjecting them to a sudden decrease in pressure. Typically some 150 kg of NaOH and 50 kg of Na_2S are required per tonne of dry wood. This process is, like any chemical reaction, affected by time, temperature and concentration of chemical reactants. Time and temperature can be traded off against each other to a certain extent, but to achieve reasonable cooking times it is necessary to have temperatures of about 150 - 165^{o}C, so pressure cookers are used. However, if the temperature is too high then the chips are delignified unevenly, so a balance must be achieved.

The kinetics of the kraft pulping is quite well understood, but the reaction is heterogenous and therefore difficult to examine. To determine when to interrupt the cooking, a model relating time, temperature and cooking chemical charge is used. The degree of delignification is the most important parameter for determining pulp quality, and is normally expressed in what is called a "Kappa number". This number is directly related to the amount of lignin still remaining in the cooked pulp.

There are two different cooking systems; batch and continuous. In batch cooking, chips and white liquor are charged to a pressure vessel and are then heated with steam to a set temperature for a set time. When the correct delignification has been achieved, the cook is "blown" (the pressure is suddenly released so that the cooked chips disintegrate into fibres). In the continuous process, chips and white liquor are fed continuously to the top of a tall pressure vessel. The chips move down the 'digester' by gravity (as a plug) to be finally blown from the bottom of the vessel. The cooking time cannot be varied in this case (it is set by the production rate) and only the temperature and the chemical charge can be controlled.

Many developments have taken place during the last decade to improve the 'science' of kraft pulping. The challenge has been to remove as much of the lignin as possible with out degrading the cellulose and without losing too much yield. It is now well known that the concentrations of NaOH, Na_2S and dissolved lignin during the various phases of the delignification are of crucial importance for the pulp strength. Generally speaking, it is desirable to have a high sulphide concentration in the beginning of the cook, a low lignin concentration in the liquid phase towards the end of the cook, and an even alkali concentration during most parts of the cook. How to achieve this in practice under conditions of high temperature and high pressures has been a challenge, and much development is still going on.

Step 3 - Pulp washing

Because of the high amounts of chemicals used in the cooking wood in kraft pulping, the recovery of the chemicals is of crucial importance. The process where the chemicals are separated from the cooked pulp is called pulp washing. A good removal of chemicals (inorganic and organic) is necessary for several reasons:

- The dissolved chemicals interfere with the downstream processesing of the pulp
- The chemicals are expensive to replace
- The chemicals (especially the dissolved lignin) are detrimental to the environment

There are many types of machinery used for pulp washing. Most of them rely on displacing the dissolved solids (inorganic and organic) in a pulp mat by hot water, but some use pressing to squeeze out the chemicals with the liquid. An old, but still common method is to use a drum, covered by a wire mesh, which rotates in a diluted suspension of the fibres. The fibres form a mat on the drum, and showers of hot water are then sprayed onto the fibre mat.

Step 4 - Pulp screening

Apart from fibres, the cooked pulp also contains partially uncooked fibre bundles and knots. Modern cooking processes (together with good chip screening to achieve consistent chip thickness) have good control over the delignification and produce less "rejects". Knots and shives are removed by passing the pulp over pulp screens equipped with fine holes or slots.

Step 5 - Bleaching

Pulp produced by the kraft process is brown. This presents no problem for certain uses, e.g. for sack paper, most corrugated boxes, some bag paper etc. However, a major proportion of the kraft pulp that is made is used for white or coloured papers such as writing and printing papers, and then the pulp needs to be bleached.

Bleaching involves removing virtually all of the lignin that still remains after cooking, as the lignin contains the chromophoric groups which make the pulp dark. Strictly speaking, bleaching and cooking are both delignification processes, and modern developments have tended to blur the difference between the two processes. However, traditionally the name 'bleaching' is reserved for delignification that is taking place downstream of the cooking process. In practice, there are two separate "bleaching" process steps: oxygen delignification and final bleaching.

To measure the lignin content in pulp, a number called the "Kappa number" is used. The Kappa number is directly proportional to the lignin content of the pulp. Pulp from the digester has a Kappa number of 20-35 for softwood and 15-20 for hardwood (hardwood contains less lignin and can therefore be cooked to a lower Kappa number). Oxygen delignification removes about half of the lignin remaining after the cooking process, so that the Kappa number of the oxygen delignified pulp is typically 12-18 for softwood. The final bleaching removes all remaining lignin and decreases the Kappa number to zero.

Oxygen delignification

In oxygen delignification, washed pulp is treated with a highly alkaline solution of sodium hydroxide. The high pH ionizes phenolic groups in the lignin, which are then attacked by molecular oxygen. The aromatic part of the lignin is partly destroyed and it is then depolymerised to lower molecular weight compounds. These are more soluble in water and can be removed from the fibres. It is important that the pulp has been at least partly washed beforehand because the black liquor solids in unwashed pulp consume oxygen. After the oxygen delignification stage, the pulp has to be washed very well, as otherwise the organics carry over to the final bleaching process, consuming chemicals there and also decreasing the environmental benefits.

The highly alkaline conditions of oxygen delignification also make carbohydrate fractions in the fibres react with oxygen to a certain extent. As these reactions break down the polymer chains of cellulose, and thus decrease the pulp strength, these reactions must be kept to a minimum. It has been found that it is the radical species of oxygen which are particularly harmful to the carbohydrates. The formation of radicals is promoted by the presence of certain metal ions. However, it has been found that magnesium salts inhibit metal ion activity, and magnesium sulphate is therefore normally added as a protector in oxygen delignification.

Oxygen is only sparingly soluble in water, and the controlling factor on the reaction rate is therefore normally the concentration of dissolved oxygen around the fibre. Originally a high pulp consistency (30-40%) was used to overcome this restriction. However, modern high intensity mixers can distribute the oxygen in very small bubbles on the fibres, and these mixers have made it possible to operate at "medium consistency" (10-12%). Medium consistency has several advantages: the equipment is simpler and the risk of fire (because of the use of oxygen) is virtually eliminated.

Oxygen delignification can significantly decrease the water pollution from the final (normally chlorine or chlorine dioxide based) bleaching. In addition, it is an effluent free process. All dissolved lignin and other organics (as well as the inorganic chemicals) are recovered in the black liquor and returned to the chemical recovery system, rather than being discharged as effluent as they are in chlorine-based bleaching. Finally, oxygen is a fairly cheap bleaching chemical, although the capital costs are high for an efficient system. On the negative side, the process has the potential to degrade the pulp strength if it is not controlled properly.

Final bleaching

The final bleaching is always carried out in several stages to improve the efficiency of the chemicals used, and to decrease the strength loss of the pulp. There are quite a number of bleaching chemicals used commercially, and many more have been tried in the laboratory. The chemicals used are:

- Chlorine
- Chlorine dioxide
- Sodium hypochlorite
- Oxygen
- Peroxide
- Ozone

Of these chemicals, the first three contain chlorine atoms, whilst the last three use non-chlorine oxidizing compounds. Elemental chlorine (Cl_2) was for many years the work horse of the bleaching process. It is efficient in bleaching the pulp and (if properly used) does not degrade the pulp strength. However, it produces a large amount of chlorinated organic compounds in the effluent, and strenuous efforts have therefore been made to decrease its usage. For the same reason, the use of sodium hypochlorite (which also tended to affect the pulp strength) is now virtually eliminated.

Modern bleach plants therefore use no *elemental* chlorine. They are what is called ECF plants: elemental chlorine free bleach plants. Chlorine dioxide, which is used instead (in addition to non-chlorine compounds), is environmentally much more benign than Cl_2. However, while chlorine dioxide is good at preserving pulp strength, it is not as effective as elemental chlorine in delignification/bleaching. ECF plants therefore have to have a rather low incoming Kappa number, and this is normally achieved by using oxygen delignification ahead of the final bleaching.

Most ECF plants use a three step bleaching process of chlorine dioxide followed by a mixture of NaOH, O_2 and peroxide (the 'extraction' stage) and then finally chlorine dioxide again. At Kinleith, because of the efficiency of the oxygen delignification, the peroxide is no longer necessary and a sequence of chlorine dioxide then NaOH and O_2 followed by more chlorine dioxide is used. The chlorine dioxide stages normally run at a pH of 3-4.5, and the'extraction' stages at a pH of 10-11. The temperature is kept at 70-80 ^oC to achieve sufficiently fast rate of reaction.

The amount of chlorinated toxic compounds in the effluent from a correctly operated ECF plant is small (especially after secondary treatment) and the effects on the environment appear rather insignificant. However, especially in Europe, there is a perception that using "chlorine" in any form when bleaching is undesirable, and bleaching without using any form of chlorine compounds, so-called total chlorine free bleaching (TCF bleaching) has been developed. In TCF bleaching only oxygen, peroxide and ozone (in addition to caustic and certain chelating agents) are used. TCF bleached pulp can nowadays reach virtually the same brightness as ECF bleached pulp, but the strength is somewhat lower. Such plants require inevitably oxygen delignification and also, usually, cooking to a lower Kappa number. Chemical costs are also normally higher. TCF pulp is not made in New Zealand.

Step 6 - Paper making

Paper making is the process whereby pulp fibres are mechanically and chemically treated, formed into a dilute suspension, spread over a mesh surface, the water removed by suction, and the resulting pad of cellulose fibres pressed and dried to form paper.

The mechanical treatment of the fibre normally takes place by passing it between moving steel bars which are attached to revolving metal discs - the so-called refiners. This treatment has two effects: it shortens the fibre (fibre cutting) and it fibrillates the fibre. The latter action increases the surface area, and as the fibres bond together in the paper sheet by hydrogen bonding, the increased surface area greatly increases the bonding and strength of the paper. Paper strength is dependent on the individual fibre strength and the strength of the bonds between the fibres. It is usually the latter, which is the limiting factor. Refining increases the interfibre bonding at the expense of the individual fibre strength, but the net result will be an increase in paper strength. Pressing and calendering (feeding through rollers) increase density and promote smoothness.

Various chemicals are added, e.g. to give water resistance, to give increased strength (see Industrial Resins article), to produce coloured paper, or to serve as inorganic filters.

Henry and Sealy Fourdrinier have given their name to the Fourdrinier paper machine, the first of which was first used in 1804. The stock is diluted to 0.5-1.0% consistency, and then flows as a flat stream onto an endless travelling wire screen. Water (containing a considerable amount of filter and fine material) is extracted through the wire screen, and this is then circulated back to dilute the oncoming stock. The wire and the web pass over suction boxes, and the web is finally removed from the wire at about 20% solids. After being pressed to some 35-40% solids, the web passes round a large number of steam heated cylinders to be dried until it finally contains some 95% solids and 5% water.

Modern developments have tended towards so-called twin-wire machines, which overcomes the difference in two-sidedness caused by water draining through the bottom side of the web only. The twin wires are nowadays usually synthetic fibre fabrics, between which the stock is introduced.

ANCILLIARY PROCESSES

A variety of ancilliary processes are used to recover the chemicals used at various stages of the process. The dilute liquor from the pulp washing (containing the dissoved inorganic and organic solids) is called "black liquor". The dissolved organics have to be removed for environmental reasons,and their burning also generates most of the heat energy required by the kraft mill. The dissolved sodium hydroxide and sodium sulphide are regenerated so that they can be reused in the white liquor, and thus the escape of an environmental pollutant is prevented.

The four steps involved in chemical recovery are outlined below.

Step 1 - Evaporation
The black liquor from the pulp washing contains 15-17% solids, and this needs to be concentrated to about 60-70% solids before it can be burnt in the recovery furnace. "Spill liquors" may also be recovered from various places in the mill, and these dilute liquors supply further amounts of water, which needs to be evaporated.

Evaporation is carried out using multiple effects, normally 5 to 7 effects in series. In systems of this type, the vapour obtained in one evaporatorer effect becomes the heating steam for the next effect. Process steam enters the system at effect no. 1, while the vapour from the last effect is condensed, producing a vacuum in the latter effects.

Black liquor evaporation consumes a substantial part of the heat energy required in the kraft process. However, it is much more efficient to carry out this evaporation in multiple effect evaporators than in the subsequent recovery boiler. Because of this, there has been a constant effort to try to reach higher liquor solids from the evaporators. The limit is set by the increase in viscocity and boiling point that takes place when the solids increase.

Step 2 - Combustion of the black liquor in the recovery boiler
The recovery boiler burns the organic material in the concentrated black liquor, at the same time reducing the oxidised sulphur compounds to sulphide. The burning of the organics generates high pressure steam in the boiler, which is normally passed through a turbine, generating electricity. The low pressure steam, which is exhausted from the turbine, is then used for process heat in the pulpmill and papermill.

A modern recovery boiler is a complex and expensive chemical reactor, and the chemical reactions taking place inside it are many and complicated. The inorganic material is recovered as molten salts (a 'smelt'), which is then dissolved in dilute alkali. The resulting liquor is called 'green liquor' and consists mainly of sodium carbonate and sodium sulphide.

To compensate for chemicals that are being lost in the pulp mill cycle, sodium and sulphur chemicals are added to the black liquor before combustion. Traditionally, sodium sulphate has been the normal 'make-up' chemical, supplying both sodium and sulphur. However, modern mills only lose small amounts of sulphur, and it has become necessary to partially use 'sulphur free' make-up chemicals in form of caustic (NaOH) or soda ash (Na_2CO_3).

The following reactions very simply explain the combustion of the combustible organic compounds:

$$C + O_2 \rightarrow CO_2 + \text{heat}$$

$$2C + O_2 \rightarrow 2CO + \text{heat}$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 + \text{heat}$$

$$2H_2 + O_2 \rightarrow 2H_2O + \text{heat}$$

In conjunction with the above combustion the following chemical reactions are also occurring:

$$H_2S + 1\frac{1}{2}O_2 \rightarrow SO_2 + H_2O$$

$$Na_2O + SO_2 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$$

$$NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

The chemical transformation that takes place in the recovery boiler is not just due to combustion, but also involves the reduction of sodium sulfate to sodium sulfide. The main reaction is:

$$Na_2SO_4 + 2C + \text{heat} \rightarrow Na_2S + 2CO_2$$

This reaction consumes heat, i.e. it is endothermic.

Since sodium sulfate does not help in the cooking process, it is important to obtain maximum reduction of sulfate into sulfide within the recovery boiler. A measure of the quality of this reduction (in the smelt or green liquor) is called reduction efficiency. It is expressed as follows:

$$Reduction\ efficiency(\%) = \frac{Na_2S\ x\ 100}{Na_2S + Na_2SO_4}$$

Poor or low reduction efficiency results in extra energy consumption in the digester and recausticizing areas. Modern recovery boilers firing high dry solids content black liquor typically have very high reduction efficiencies, up to 99% - 100% when measured from the smelt. Reduction efficiency measured from the green liquor is typically somewhat lower, since some Na_2S gets oxidized by the oxygen in air.

The 'green liquor' (a solution of the Na_2CO_3 and Na_2S - the non-volatile combustion components) is then causticised as the first step to Na_2CO_3 removal.

Step 3 - Causticising

As well as dissolved sodium based chemicals (Na_2CO_3, Na_2S and smaller amounts of NaOH, Na_2SO_4 and NaCl), the green liquor also contains small amounts of suspended solids, called “dregs”. This material mostly consists of unburned carbon and insoluble metal hydroxides. To avoid problems in the causticising and lime burning processes, these dregs must be removed as much as possible. This can be done either using a gravity clarifier (as described below) or using the more recently developed green liquor filter.

In essence, clarifiers are large circular tanks so sized that the liquid rise rate is slower than the terminal velocity of the settling particles. A typical rise rate is 0.5 m/h. The dregs particles collect in the bottom of the clarifier and are then raked by a very slowly rotating scraper to a central removal point. The thickened dregs are washed to remove dissolved chemicals and are then discharged, normally to the sewer or to landfill. The dilute alkali solution resulting from the wash is recycled.

Clarified green liquor and burned lime (calcium oxide) are fed continuously in metered amounts into a reaction vessel, called a slaker. The calcium oxide reacts with the water in an exothermic reaction to form calcium hydroxide or milk-of-lime:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat}$$

The slaker also contains a “classifier” section which removes unreacted particles (grit). These are taken to landfill.

After slaking, the slurry is carried through a series of agitated tanks, which provide the retention time for the causticising reaction as shown below:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH$$

As with all chemical reactions, an equilibrium exists between the reactants and the products. The causticising reaction is also relatively slow (while the slaking reaction is fast), so in order to achieve close to equilibrium in a reasonable time, a high temperature (about 100°C) is maintained.

The overall reaction for the slaking and causticizing reactions are:

$$CaO + Na_2CO_3 + H_2O \rightarrow CaCO_3 + 2NaOH + \text{heat}$$

Step 4 - Conversion of $CaCO_3$ to CaO

The slurry from the causticisers is pumped to a clarifier which, as for the green liquor clarifier mentioned previously, is a gravity settling device. Generally the white liquor clarifier also serves as a white liquor storage tank.

The thickened “lime mud” underflow from the clarifier contains about 40 % suspended solids. This slurry is washed by diluting it with water or dilute alkali and then allowing the suspended solids to settle in another clarifier (similar to the white liquor clarifier) called “mud washer”. The resulting dilute alkali solution (“weak wash”) is used for dissolving the smelt coming from the recovery boiler to make new green liquor. The thickened washed mud is stored before a final washing and dewatering stage on a rotary drum washer.

Just as for green liquor clarification, filters are nowadays becoming more common both in white liquor clarification and in mud washing.

The Ca_2CO_3 sludge (“mud”) coming from storage is washed and dewatered on a filter, which increases the solids content to 70 - 80 %. Washing out the sodium compounds as much as possible is important for several reasons:

- The sodium sulphide can contribute to the emission of H_2S from kiln stack
- Sodium salts melt and function as a glue for the lime particles, producing rings and balls inside the kiln

After washing and dewatering, the mud is then dried and reburnt (calcined). Usually both operations are carried out in a slowly rotating lime kiln. In such a kiln, wet mud is fed into one end of the inclined kiln, and is slowly transported towards the other end. A burner, fed with natural gas or fuel oil, supplies hot gases which travel countercurrently to the mud. The mud dries and is then calcined at a temperature of about 1,000 - 1,200 deg. C in a heat absorbing reaction as follows:

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

To increase the heat transfer in the cooler end of the kiln, an extended area is provided by using steel chains attached to the kiln shell and hanging in the hot gases. The hotter part of the kiln is lined with refractory bricks.

Modern kilns are equipped with tube coolers to cool the outgoing lime and to recover the heat. This is done by heating the incoming combustion air.

The gases leaving the kiln are laden with lime dust, which must be removed. This is done either in venturi-type scrubber or, in more modern plants, by electrostatic precipitators.

UTILITIES

Reaction towers

For each stage in the bleaching sequence a “tower” is used to achieve sufficient retention time. Typical retention times required are 1 - 4 hours, depending on type of reaction. The towers have to be able to withstand the required temperature and chemical environment. Chlorine dioxide especially is a very aggressive chemical and such towers usually have a ceramic tile lining on a steel base, or they can be made from more exotic materials such as titanium.

Chemical mixers

Good mixing of the bleaching chemicals into the pulp is absolutely critical for efficient bleaching, and over the last decade there has been a major breakthrough in this area. In the early 1980’s the art of mixing was revolutionized with the arrival of the Medium Consistency (MC) mixer. These mixers are based on the principle of fluidisation of the pulp with a consistency of about 10 %. The fluidisation of the pulp is achieved by subjecting the pulp to heavy shear forces to destroy its network strength while it “flows” through narrow slots. The normally rather thick, almost solid pulp slurry behaves like water under these conditions, and it is comparatively easy to disperse liquids and also gases efficiently into the pulp.

Washers

The solubilized lignin is removed by washing the pulp, normally after each stage in the bleaching sequence. Such washing is particularly important when there is a change in pH.

The same washing equipment as in the washing of cooked pulp can be used, e.g. drum filters, presses or so called “diffuser washers”. However, it is important that the corrosive nature of the chemicals is taken account when choosing the material for these washers. Highly alloyed stainless steel or titanium are common, but reinforced plastic can also be used for certain components.

Pumps

Pumps are used for transporting pulp, chemicals, water and wash liquors. For liquids and pulp up to a consistency of 4-5 % (low consistency), centrifugal pumps can be used.
For pulp with a consistency of 10-12 % (medium consistency), positive displacement pumps were used in the past. However, since the discovery of fluidisation mentioned above, these

pumps have mostly been replaced with specialized so called MC-pumps, which fluidize the pulp and then use conventional centrifugal forces for imparting the pressure increase that is required.

ENVIRONMENTAL CONSIDERATIONS

Liquid effluent

Traditionally, the pulp and paper industry have been large users of water. Nowadays, strenuous efforts are being made to decrease the water usage, as any treatment of the effluent is made easier if the volume is decreased. Also, by intensive recirculation and reuse of liquid waste streams within the mill, the amounts of contaminants can be reduced in the effluent.

The major categories of water pollution of concern to the pulp and paper industry are: suspended solids (mainly fibre), biological oxygen demand, toxicity and colour. Each of these effects can be minimized by internal or external means, external meaning treatment of the final effluent outside the mill.

The suspended solids can be decreased internally by recirculating fibre containing process streams within the mill. Externally, suspended matter can be removed from the effluent in a conventional clarifier by settling. Removal efficiencies in the order of 80-90% of the suspended solids are generally achieved. The recovered sludge can be taken to landfill or further dewatered and burnt.

Oxygen demand (usually measured as BOD - biological oxygen demand - or COD - chemical oxygen demand) in the effluent can be decreased by in-mill measures, like good washing, recovery of black liquor spills, treatment of methanol containing condensates, and especially by the oxygen delignification process, described in the section on bleaching. However, biological treatment of the effluent is usually required to decrease the BOD sufficiently. This can be done in large stabilisation basins with oxygen supplied by surface diffusion, or in aerated basins in which the oxygen transfer rates are increased by the use of mechanical aerators. Nutrients are often added to enhance bacterial activity and thus promote the biological breakdown of wastes. When space is limited, more intensive processing of effluent is possible by using the activated sludge process.

Effluents from pulp and paper mills are only weakly toxic by conventional measurements, especially if they have been through biological treatment. However, the effluent from the bleaching process contains of variety of substances, some of which are known or suspected of being toxic, genotoxic or mutagenic. Chlorinated organics that are produced in the chlorine bleaching processes are of particular concern. There has therefore been a trend to change from chlorine to the much more benign chlorine dioxide as a bleaching agent as described above. If oxygen delignification is used, it will substantially decrease the amount of chlorinated compounds in the effluent.

Colour can be a problem, especially when the effluent is discharged into receiving waters with a high transparency. Most of the colour derives from the bleaching process, and oxygen delignification will help substantially against this pollutant as well. External removal of colour can be carried out, but it is difficult and expensive.

The wastewater that finally leaves the plant is discharged into the Waikato River. It routinely monitored and the results reported to the Reguality Authority, Environmental Waikato.

Atmospheric emissions
Chemicals are emitted to the atmosphere as gaseous and particulate emissions (dust).

Gaseous emissions consist of sulphur dioxide, nitrogen oxides, chlorine dioxide and reduced sulphur gases. The first two are not generally a problem, and chlorine dioxide emissions can be virtually eliminated by scrubbing with suitable liquids. However, reduced sulphur gases are a major problem because of their intensive odour. The typical kraft mill odour is due to small discharges of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide. Recovery boilers used to be the major source of emissions of reduced sulphur, but improved technology has mainly eliminated this problem. Collection of sulphurous gas streams from various vents in the pulp mill, and incinerating these gases in the lime kiln or in a dedicated incinerator has also decrease the odour problem, but not wholly eliminated it.

Dust (particulate) emissions are in the form of 'saltcake' (sodium sulphate) from the recovery boiler, lime dust from the lime kiln and fly ash from the bark boiler. All these emissions can be decreased to low levels by using efficient scrubbers, and especially by using electric precipitators, which is now the method of choice for removing particulates from all these sources.

As for water all discharges into the air are routinely monitored and reported.

PULP AND PAPER MILLS IN NEW ZEALAND

Below brief facts about all the pulp and paper mills in New Zealand are given.

Carter Holt Harvey

Kinleith
2 Paper Machines - 235 000 tonnes per annum
1 Pulp Dryer - 420 000 tonnes per annum
2 Kraft Pulp Mills

Penrose
1 Paper Machines - 67 000 tonnes per annum
(uses paper given for recycling, not wood chips or logs)

Whakatane
1 Paperboard machine - 80 000 tonnes per annum
Pulp mill

Kawerau
3 Paper Machines - 55 000 tonnes per annum
Pulp Mill

Mataura
2 Paper Machines - 25 000 tonnes per annum

Tasman Pulp and Paper Company Limited
Kawerau
3 Paper Machines - 400 000 tonnes per annum
2 Mechanical Pulp Mills - 315 000 tonnes per annum
2 Kraft Pulp Mills - 290 000 tonnes per annum

Pan Pacific Forests Industries (NZ) Ltd.
Karioi
1 Pulp Mill - 125 000 tonnes per annum

Originally three articles written by Sven Johnsson (Carter Holt Harvey) as revisions of articles in the first edition. Combined and edited by Heather Wansbrough with assistance from Mikael Lindstrom and with reference to http://swsmail.atlanta.com/~japi/kraft.htm (information on the Kraft Recovery Process provided by the Tampella Power Corporation).

Editorial addition: The introduction to the forestry section of the first edition included a comprehensive flow diagram of the whole Kinleith site. We reproduce this as **Figure 1** on the next page. Although probably no longer accurate, it does illustrate what is involved in the engineering design of a large complex, and could still be relevant to this current article.

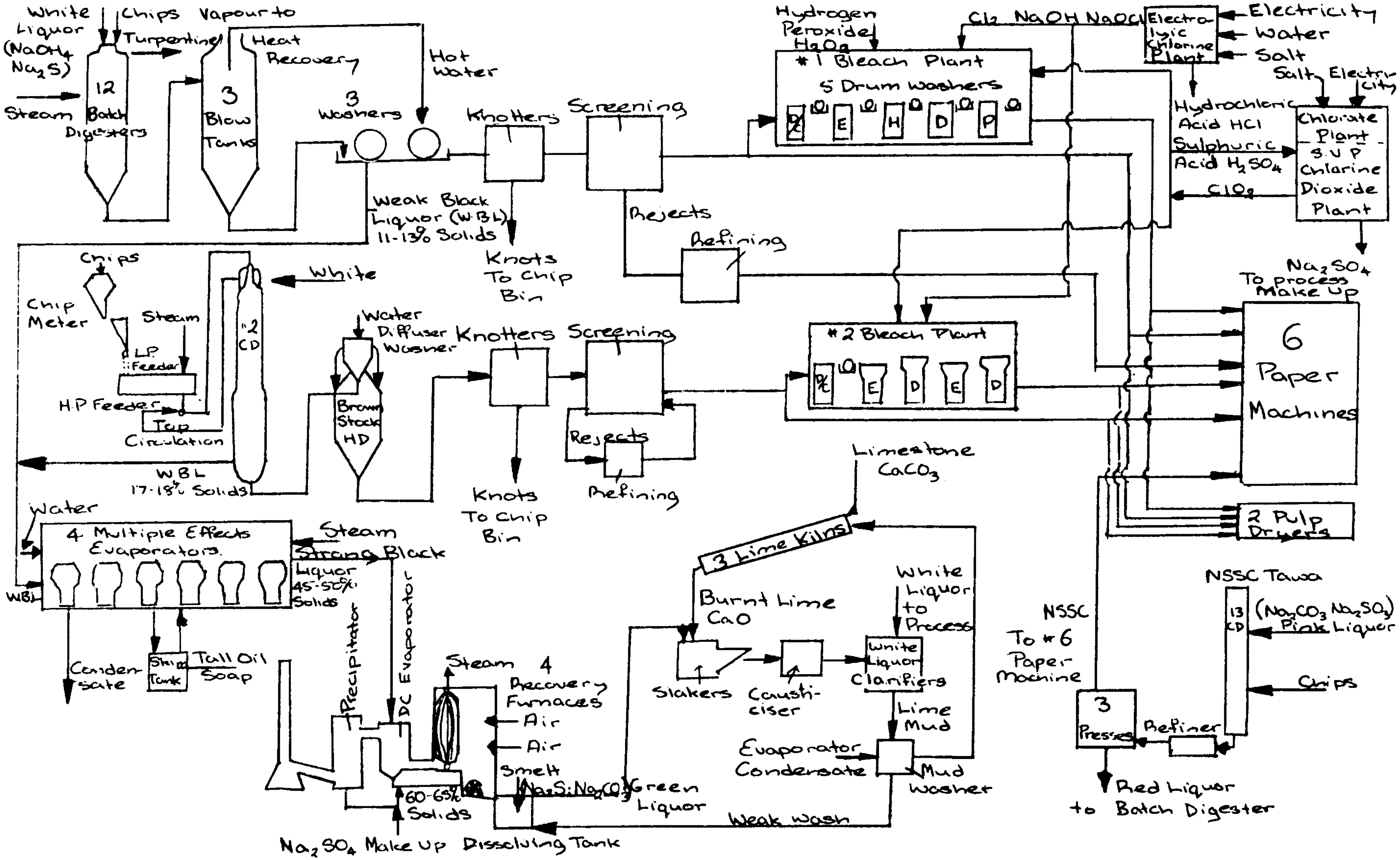


Figure 1 - Flow sheet of Kinleith site in 1976

Industrial Chemistry

Plastics

by

Dr. Mohamed Y. Mahgoub

Two main processes are used to produce plastics

- **polymerisation**
- **polycondensation**

They both require specific catalysts

In a polymerisation reactor, monomers such as ethylene and propylene are linked together to form long polymer chains. Each polymer has its own properties, structure and size depending on the various types of basic monomers used.

There are many different **types of plastics**, and they can be grouped into two main polymer families:

- **Thermoplastics** (which soften on heating and then harden again on cooling).
- **Thermosets** (which never soften once they have been moulded).

Examples of Thermoplastics

Polyethylene (PE)

Polypropylene (PP)

Polystyrene (PS)

Polyethylene terephthalate (PET)

Polyvinyl chloride (PVC)

Polymethyl methacrylate (PMMA)

Expanded Polystyrene (EPS)

Acrylonitrile butadiene styrene (ABS)

Polycarbonate (PC)

Examples of Thermosets

Epoxide (EP)

Phenol-formaldehyde (PF)

Polyurethane (PUR)

Polytetrafluoroethylene (PTFE)

Unsaturated polyester resins (UP)

Polyolefins

Are a family of polyethylene and polypropylene thermoplastics

There are four types of polyolefins:

- **LDPE** (low-density polyethylene): LDPE is defined by a density range of 0.910–0.940 g/cm^3.

Ex: Carrier bags, milk carton coatings, electrical cable coating, heavy duty industrial bags.

- **LLDPE** (linear low-density polyethylene): is a substantially linear polyethylene, with significant numbers of short branches.

Ex: Stretch film, industrial packaging film, thin-walled containers.

Polyolefins

- **HDPE** (high-density polyethylene): HDPE is known for its large strength-to-density ratio. The density of HDPE can range from 0.93 to 0.97 g/cm3 or 970 kg/m^3.

Ex: Boxes, bottles (for food products, detergents, cosmetics), food containers, toys, petrol tanks,

- **PP** (polypropylene): The density of PP is between 0.895 and 0.92 g/cm^3. Therefore, PP is the commodity plastic with the lowest density.

Ex: Food packaging, microwave-proof containers, medical packaging, kitchen tools.

Applications

- LDPE: cling film, carrier bags, agricultural film, milk carton coatings, electrical cable coating, heavy duty industrial bags.
- LLDPE: stretch film, industrial packaging film, thin-walled containers, and heavy-duty, medium and small bags.
- HDPE: boxes, bottles (for food products, detergents, cosmetics), food containers, toys, petrol tanks, industrial wrapping and film, pipes and houseware.
- PP: food packaging, including yoghurt, margarine pots, sweet and snack wrappers, microwave-proof containers, carpet fibres, garden furniture, medical packaging and appliances, luggage, kitchen appliances, and pipes.

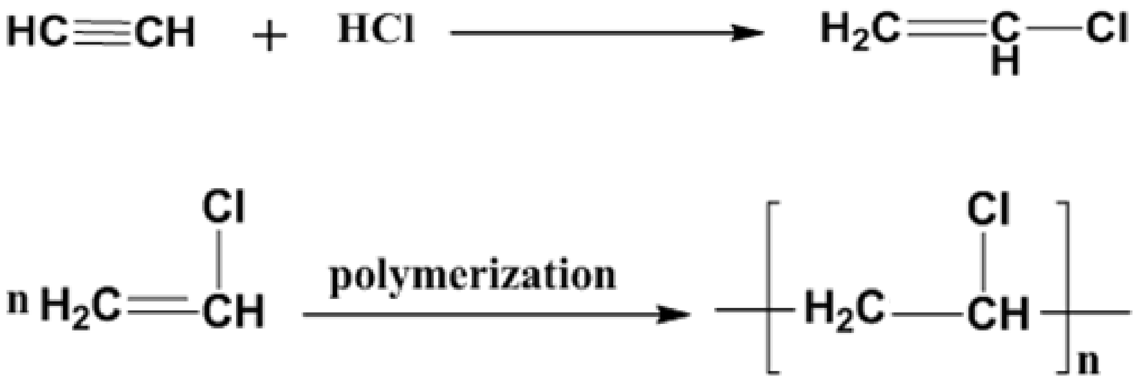
Poly ethylene (PE)

$$n\ CH_2{=}CH_2 \xrightarrow{\text{polmerization}} \left[CH_2{-}CH_2 \right]_n$$

polyethylene

Polyvinyl chloride (PVC)

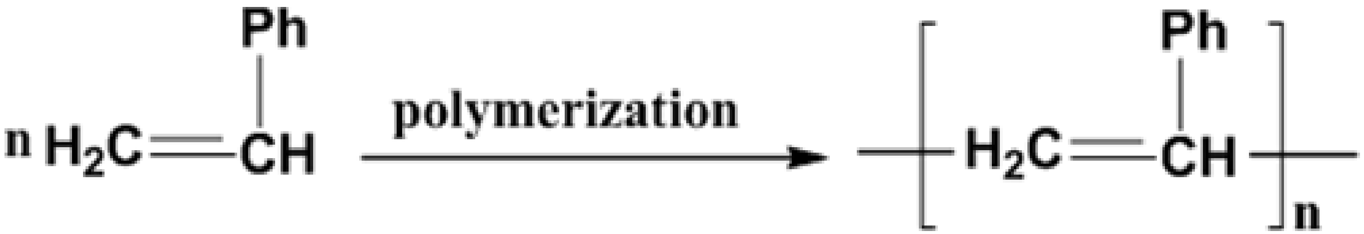
Polyvinylchloride can be prepared from acetylene:



$$HC{\equiv}CH + HCl \longrightarrow H_2C{=}\underset{H}{C}{-}Cl$$

$$n\ H_2C{=}\overset{Cl}{CH} \xrightarrow{\text{polymerization}} \left[H_2C{-}\overset{Cl}{CH} \right]_n$$

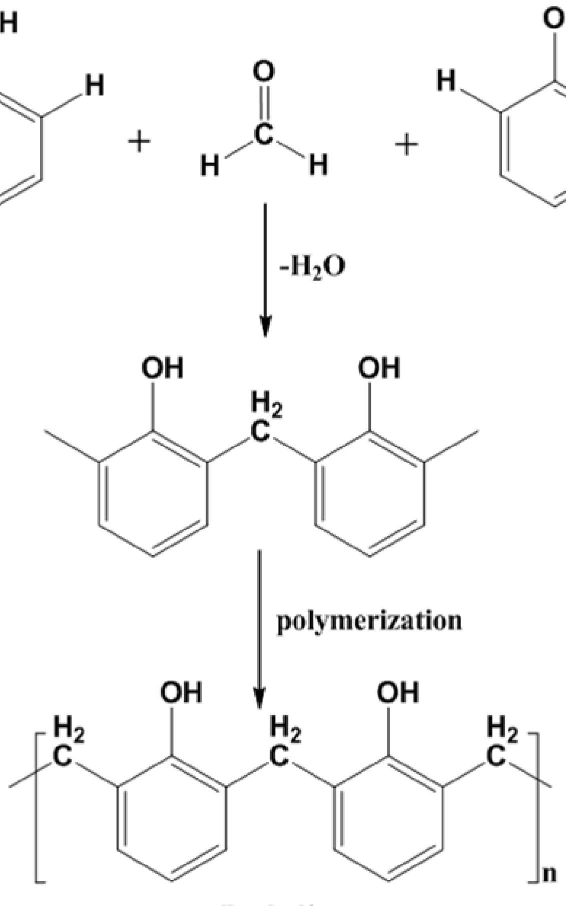
Polystyrene (PS)



$$n\ H_2C{=}\overset{\overset{\displaystyle Ph}{|}}{C}H \xrightarrow{\text{polymerization}} \left[H_2C{=}\overset{\overset{\displaystyle Ph}{|}}{C}H \right]_n$$

Thermosetting Plastics

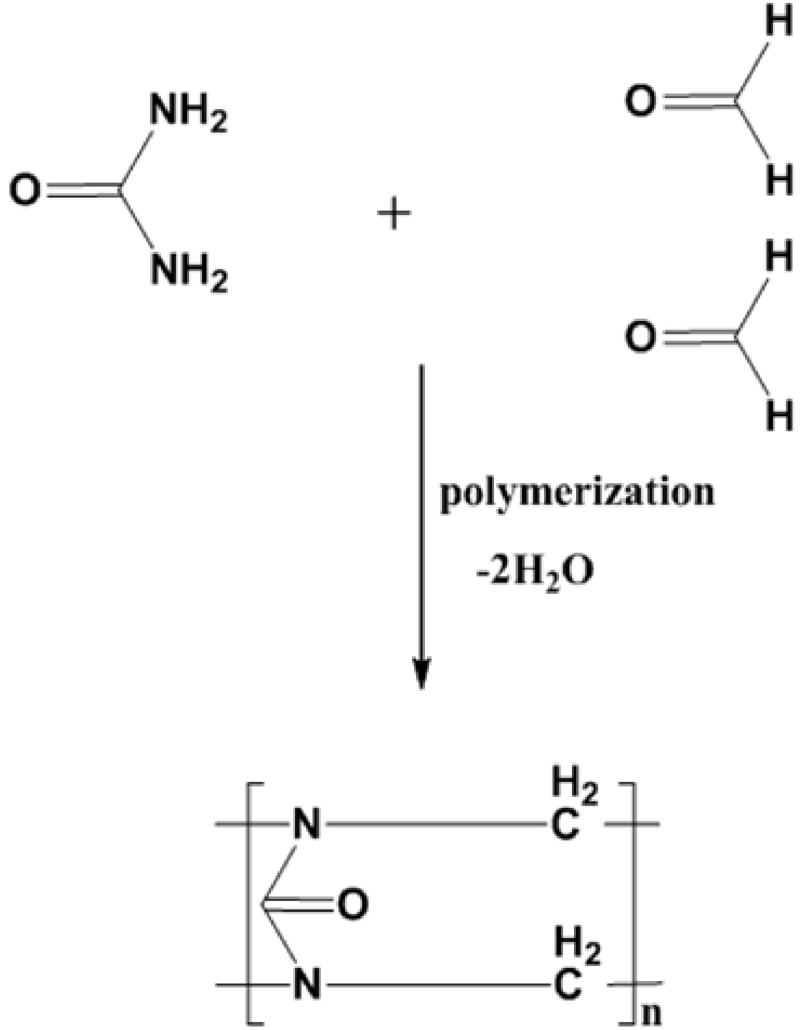
1- Phenol-aldehyde plastics (Backalite)



Backalite

2- Urea or Amino Plastics:

Prepared form condensation of urea with formaldehyde:



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Polymers: an overview

When many molecules of a simple compound join together, the product is termed a polymer and the process polymerization. The simple compounds whose molecules join together to form the polymers are called monomers. The polymer is a chain of atoms, providing a backbone, to which atoms or groups of atoms are joined.

This unit provides an overview of the main types of polymers characterised by how they are made, how their structures govern their general properties and how these properties can be refined by their formulation using a range of additives. Finally the unit summarises the range of processing techniques that can be used to convert polymers into a vast range of different products.

Each of the other units in the Polymers section describes the manufacture, properties and uses of an individual polymer or group of polymers in more detail.

Polymers are large molecules, a type of macromolecule. Their chemical properties are similar to those of simple molecules. For example, if the polymer contains a carbon-carbon double bond, as in poly(but-1,3-diene), it will undergo additions reactions with, say hydrogen or bromine.

$$\cdots-CH_2-CH{=}CH-CH_2-CH_2-CH{=}CH-CH_2-\cdots$$

poly(buta-1,3-diene)

If it contains an aromatic ring, as in poly(phenylethene) (often known as polystyrene), it will undergo substitution reactions, say with nitric acid.

poly(phenylethene)

The major differences between smaller molecules and polymers lie not with their chemical properties but with their physical ones. Their larger sizes lead to much stronger intermolecular forces leading in turn to much higher melting points, and the characteristic properties of hardness and flexibility. These intermolecular forces are even stronger when the polymer chains pack together in a regular way as in HPDE (high density poly(ethene)) and have regions of crystallinity.

When heated, it melts and the crystallinity is lost. As it does not have a sharp melting point, the temperature at which this occurs is termed the *melt transition temperature*, T_m. Above this temperature, the polymer is amorphous.

Some polymers are hard and amorphous, having no regions of crystallinity, for example, poly(methyl 2-methylpropenoate). The temperature at which they become soft and pliable is termed the *glass transition temperature*, T_g.

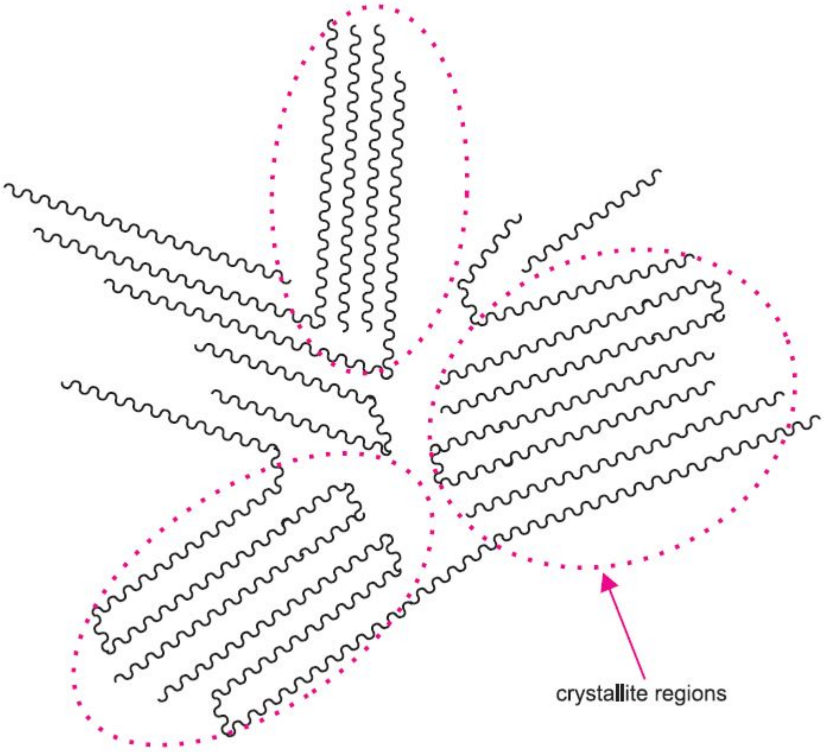


Figure 1 These crystallites have order in which the zigzag polymer chains are held together in a regular pattern by intermolecular forces.

There are many examples of polymers that occur naturally, for example, starch, cellulose and proteins. Over the last 70 years, synthetic polymers have been invented, often mimicking nature and they are now manufactured in millions of tonnes a year and are one of the most essential materials we use. Many are used as fibres. Others are moulded into required shapes and when they are used in this way, they are often termed plastics.

Characterising polymers

There are several ways in which polymers can be characterised:

a) how they are made, by addition or by condensation

b) whether they are homopolymers or heteropolymers (co-polymers)

c) whether they are themoplastics, thermosets, elastomers or fibres

d) by their steric structure

(a) Addition and condensation polymers

In **addition polymerization**, the polymer has the same empirical formula as the monomer but a higher molecular mass (Table 1). An example is the polymerization of chloroethene (vinyl chloride) to form poly(chloroethene), PVC:

$$n\,CH_2{=}CHCl \longrightarrow \left[CH_2-CHCl \right]_n$$

chloroethene poly(chloroethene)

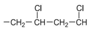
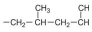
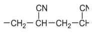
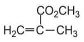
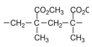
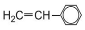
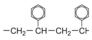
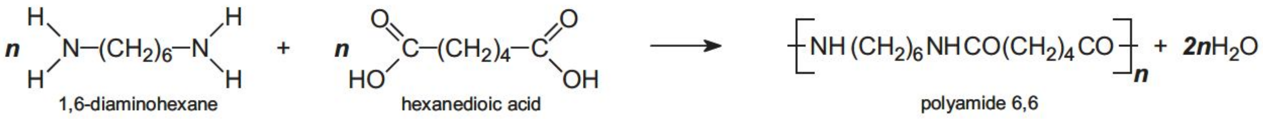
Monomer	Formula	Polymer	Trivial name	Structu
Ethene	$H_2C{=}CH_2$	LDPE Low density poly(ethene) (/polymers/polyethene.html#poly(ethene))	low density polythene	$-CH_2-CH_2-CH_2-CH$
Chloroethene	$H_2C{=}CHCl$	Poly(chloroethene) (/polymers/polychloroethene.html)	polyvinyl chlorine, PVC	 $-CH_2-\overset{Cl}{CH}-CH_2-\overset{Cl}{CH}$
Propene	$H_2C{=}CH-CH_3$	Poly(propene) (/polymers/polypropene.html)	polypropylene	 $-CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH}{CH}$
Propenonitrile	$H_2C{=}CH-CN$	Poly(propenonitrile) (/polymers/polypropenonitrile.html)	polyacrylonitrile	 $-CH_2-\overset{CN}{CH}-CH_2-\overset{C}{CH}$
Methyl 2-methylpropenoate	 $H_2C{=}\overset{CO_2CH_3}{C}-CH_3$	Poly(methyl 2-methylpropenoate) (/polymers/polymethyl.html)	polymethyl methacrylate	 $-CH_2-\underset{CH_3}{\overset{CO_2CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CO_2C}{C}}-$
Phenylethene		Poly(phenylethene) (/polymers/polyphenylethene.html)	polystyrene	
Tetrafluoroethene	$F_2C{=}CF_2$	Poly(tetrafluoroethene) (/polymers/polytetrafluoroethene.html)(PTFE)	polytetrafluoroethylene PTFE	$-CF_2-CF_2-CF_2-CF$

Table 1 Some addition polymers.

In **condensation polymerization**, polymerization of one or more monomers is accompanied by the elimination of small molecules (such as water or ammonia) (Table 2). For example, in producing polyamide 6,6, two monomers are used.



Another type of condensation polymer is said to be formed if the polymer chain contains (rather than appended to the chain) a functional group such as an ester, amide or urethane (Table 2).

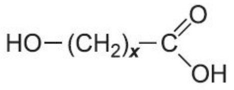
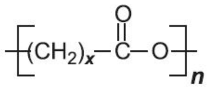
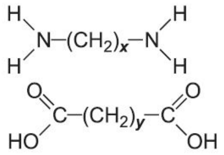
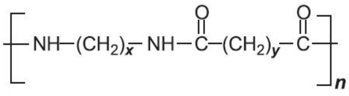
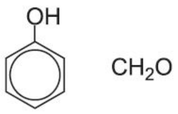
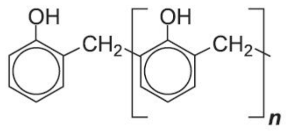
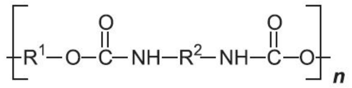
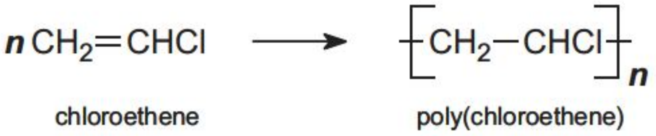
Polymer	Monomer	Formula
Polyesters (/polymers/polyesters.html)		
Polyamides (/polymers/polyamides.html)		
Phenol-methanal plastics (/polymers/methanal-plastics.html)		
Polyurethanes (/polymers/polyurethane.html)	$HO-R^1-OH$ $O=C=N-R^2-N=C=O$	

Table 2 Some condensation polymers.

(b) Homopolymers and heteropolymers (co-polymers)

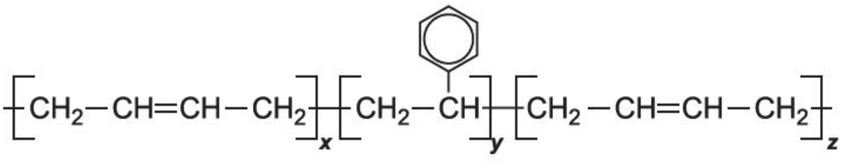
Another way of characterising polymers is to divide them into *homopolymers* and *heteropolymers*. Many of the well known polymers such as poly(chloroethene) are produced from a single monomer and so are referred to as homopolymers (Table 1):



A heteropolymer, or as they are more commonly known, a *co-polymer*, is produced from two or more monomers.

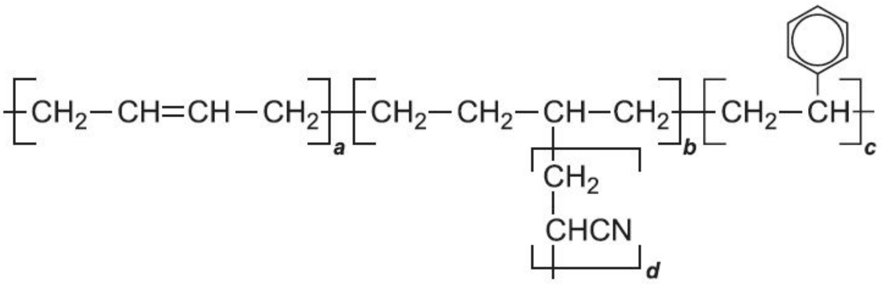
There are several types of co-polymer. One type is produced when two or more monomers are mixed and polymerized together. Depending on the reactivities of the monomers, they may form polymers with different arrangements of the monomer units (Figure 2).

SBS is an example of a *block co-polymer*. SBS is so named with S referring to Styrene (phenylethene) and B for Buta-1,3-diene. First, phenylethene is polymerized. Buta-1,3-diene is then added and adds on to both the reactive ends of the poly(phenylethene) molecules to form SBS:



Another type of co-polymer is known as a *graft co-polymer*. An example is ABS. A is Acrylonitrile, the trivial name for propenonitrile.

The backbone of the polymer is formed from phenylethene (styrene) and buta-1,3-diene. Propenonitrile (acrylonitrile) is added to the system and forms a grafted side chain onto the backbone. The nitrile adds to the double bond on the butadiene unit:



Co-polymers are very useful as they have the properties of the constituent polymers and thus can be produced for specific purposes. For example, poly(phenylethene) (polystyrene) is brittle but when it is co-polymerized with buta-1,3-diene, the latter gives the polymer resilience and strength. Known as High Impact Polystyrene (HIPS) (/polymers/polyphenylethene.html#ABS), it can now receive impacts without damage.

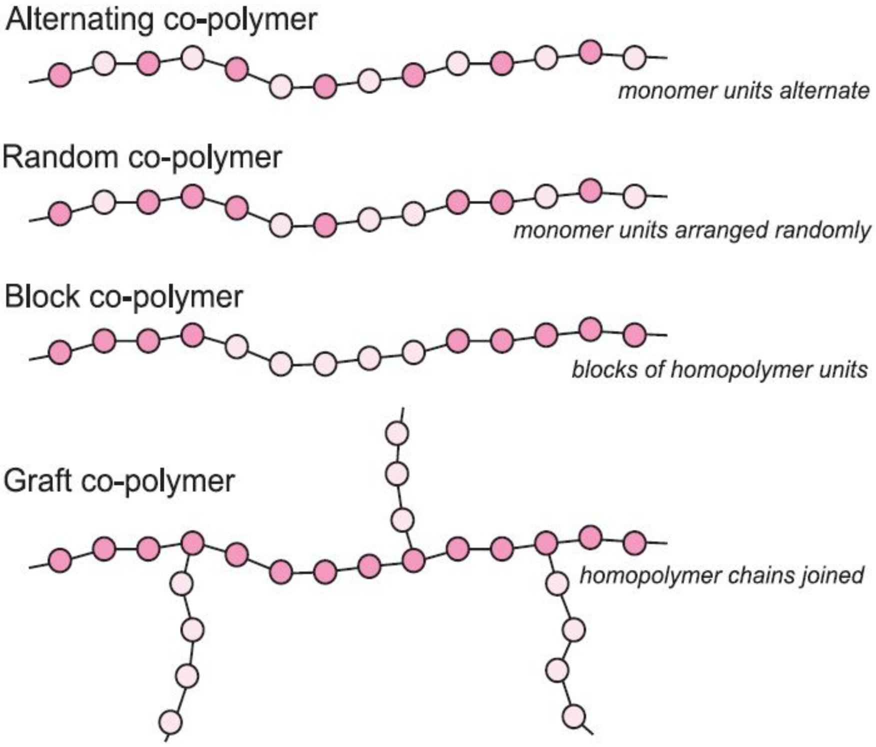


Figure 2 Structures of different types of co-polymer.

Figure 3 Different types of co-polymer have different properties. On the right, the medical vials are made of a random co-polymer (/polymers/polypropene.html#co-polymer) of ethene and propene which give a flexible and clear material. Below, the covering of the cable is a block co-polymer of the two alkenes, giving a very tough material with rubber-like properties.

By kind permission of Total.

(c) Thermoplastics, thermosets, elastomers and fibres

Polymers can also be characterised into four classes:

- thermoplastics
- thermosets (thermosetting resins)
- elastomers
- fibres

Thermomplastics consist of individual molecules with no covalent bonding between them but held together by intermolecular bonding. The polymers become soft on warming and can be moulded. They can be repeatedly warmed, softened and remoulded. A list of examples is given in Table 1.

Thermosets, on the other hand, have many covalent bonds between the chains, leading to a three-dimensional structure, which can be regarded as a single molecule. They can be moulded by heat and pressure, but once moulded they cannot be remoulded. The most important examples include the plastics made from methanal (formaldehyde). **Elastomers** are amorphous solids which, as the name suggests, are elastic (Table 3). They have coiled chains which can be stretched out but spring back to their original shape when the stretching force is released.

Fibres are thin threads which are produced by extruding a molten polymer through a die in which there are small holes.
Fibres produced in this way include the polyamides (such as nylon), the polyesters (such as terylene) and poly(propene) (Table 4).

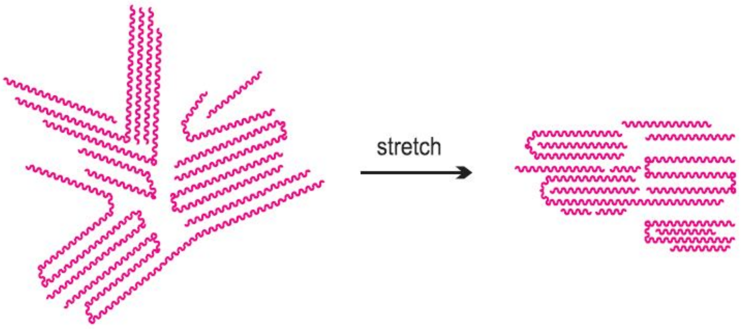


Figure 4 After stretching to make a fibre, the crystallite regions are aligned along the axis of the fibre, and this adds strength to it.

Having been extruded and stretched, the polymer molecules become aligned in the direction of the fibre. Any tendency to return to a random orientation is prevented by the strong intermolecular forces between the molecules (Figure 4).

Fibres are twisted into threads and can then be woven into cloth or imbedded in a plastic to give it much greater strength (Table 4).

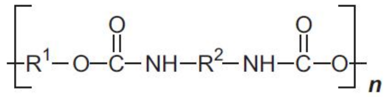
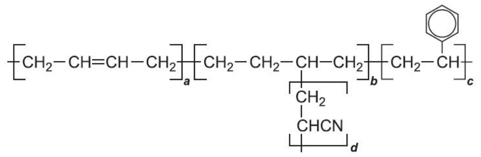
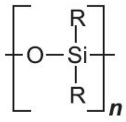
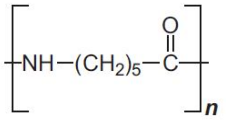
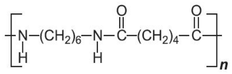
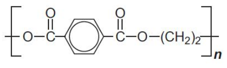
Polymer	Formula
Poly(buta-1,3-diene) (/chemicals/buta-13-diene.html)	$\left[CH_2-CH=CH-CH_2 \right]_n$
Polyurethanes (/polymers/polyurethane.html)	 $\left[R^1-O-\overset{O}{\overset{\|}{C}}-NH-R^2-NH-\overset{O}{\overset{\|}{C}}-O \right]_n$
ABS (/polymers/polyphenylethene.html#ABS)(Acrylonitrile butadiene styrene)	
Silicones (/polymers/silicones.html)	 $\left[O-\underset{R}{\overset{R}{Si}} \right]_n$

Table 3 Some elastomers.

Polymer	Formula
Polyamide 6 (/polymers/polyamides.html)	 $\left[NH-(CH_2)_5-\overset{O}{\overset{\|}{C}} \right]_n$
Polyamide 6,6 (/polymers/polyamides.html)	 $\left[\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$
The polyester (terylene) (/polymers/polyesters.html) formed from the dimethyl ester of 1,4-benzenedicarboxylic acid and ethane-1,2-diol	

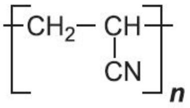
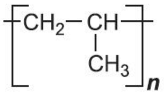
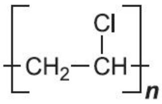
Poly(propenonitrile) (/polymers/polypropenonitrile.html)	 $\left[CH_2-\underset{CN}{CH}\right]_n$
Poly(ethene) (/polymers/polyethene.html)	$\left[CH_2-CH_2\right]_n$
Poly(propene) (/polymers/polypropene.html)	 $\left[CH_2-\underset{CH_3}{CH}\right]_n$
Poly(chloroethene) (/polymers/polychloroethene.html)	 $\left[CH_2-\overset{Cl}{CH}\right]_n$
Poly(tetrafluoroethene) (/polymers/polytetrafluoroethene.html)	$\left[CF_2-CF_2\right]_n$

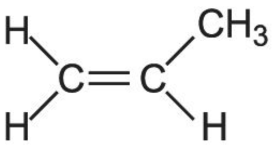
Table 4 Some polymers used to make fibres.

(d) Steric structure

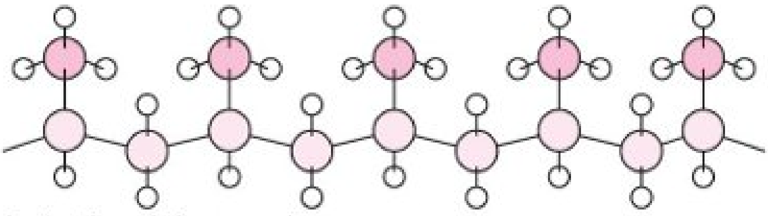
Another way of classifying polymers is by examining their steric structure. Polymers with side chains can be divided into two classes, one (stereoregular) which has a recurring pattern in terms of stereochemistry and one (atactic) with no regular structure.

A simple example of a polymer with a side chain is poly(propene).

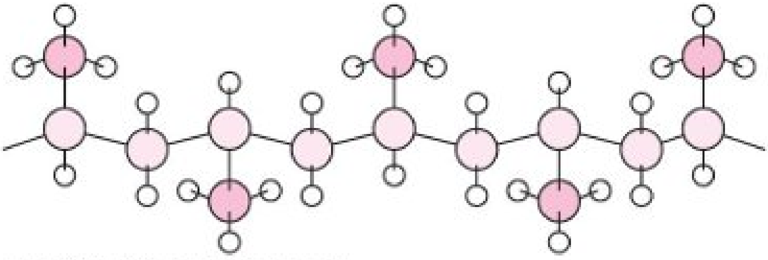
The propene molecule is asymmetrical,



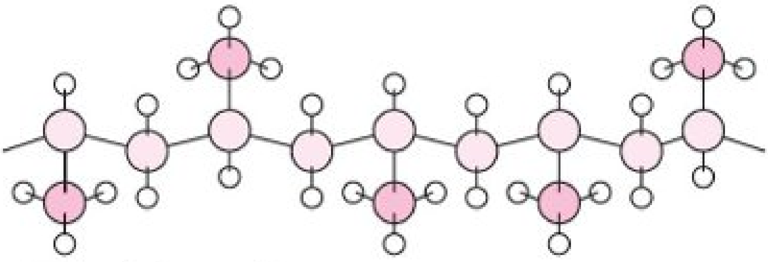
and, when polymerized, can form three basic chain structures dependent on the position of the methyl groups: two are stereoregular (isotactic and syndiotactic) and the third does not have a regular structure and is termed atactic as shown diagrammatically below:



isotactic poly(propene)



syndiotactic poly(propene)



atactic poly(propene)

Figure 5 Molecular structures of poly(propene).

The 'one handed' structure of isotactic poly(propene) causes the molecules to form helices. This regular form permits the molecules to crystallize to a hard, relatively rigid material, which, in its pure form, melts at 440 K.

The syndiotactic polymer, because of its regular structure, is also crystalline.

Atactic chains are completely random in structure and consequently they do not crystallize. High molecular mass atactic poly(propene) is a rubber-like material.

Commercial poly(propene) is a predominantly isotactic polymer containing 1-5% by mass of atactic material.

Stereoregular polymers are produced when using many Ziegler-Natta (see below) or metallocene (/polymers/polypropene.html#metallocene) catalysts.

Manufacture of polymers

As discussed above, polymers can be characterised by the method of polymerization, addition and condensation (/polymers/polymers-an-overview.html#addition).

Many addition polymers are produced by using an organometallic compound, known as a Ziegler-Natta catalyst. They were first developed by Karl Ziegler and Giulio Natta which led to the two chemists being awared the Nobel Prize in 1963 for this brilliant work.

Other addition polymers are produced by generating free radicals (/polymers/polymers-an-overview.html#radical) using a compound, known as an initiator, to catalyse the reaction.

Many condensation polymeriztion reactions, in which one or two monomers are the starting materials, also need catalysts. The catalysts are described in the unit devoted to each condensation polymer.

Catalysts for polymerization reactions

Ziegler-Natta catalysts

Ziegler-Natta catalysts are organometallic compounds, prepared from titanium compounds with an aluminium trialkyl which acts as a promoter:

The alkyl groups used include ethyl, hexyl and octyl.

The role of the titanium catalyst can be represented as shown in Figure 6.

The alkene monomer attaches itself to an empty coordination site on the titanium atom and this alkene molecule then inserts itself into the carbon-titanium bond to extend the alkyl chain. This process then continues, thereby forming a linear polymer, poly(ethene) (/polymers/polyethene.html).

The polymer is precipitated when the catalyst is destroyed on addition of water. Because it is linear, the polymer molecules are able to pack together closely, giving the polymer a higher melting point and density than poly(ethene) produced by radical initiation.

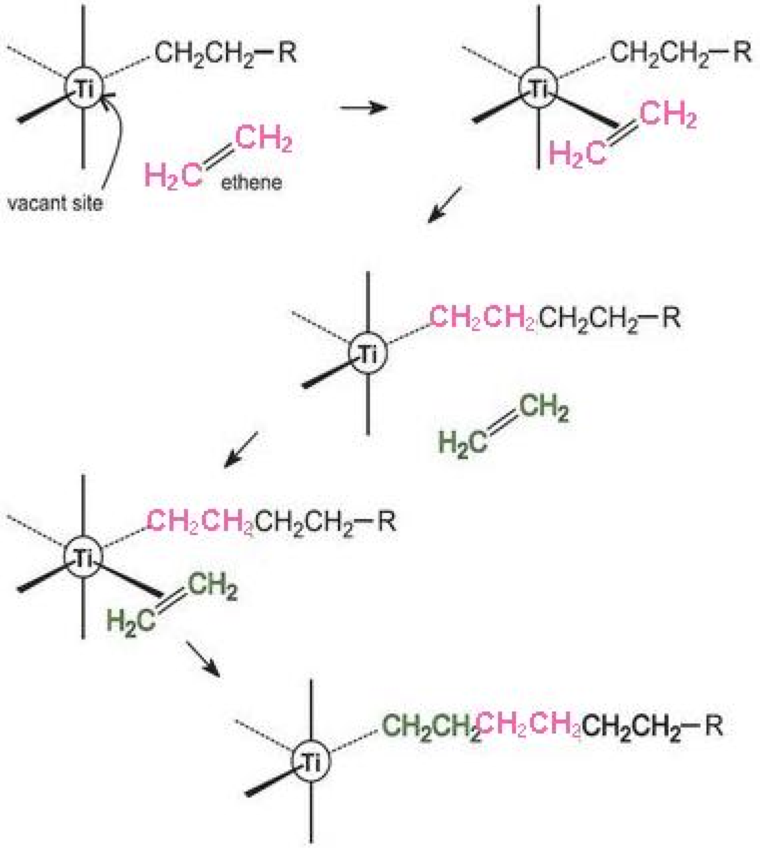


Figure 6 Illustrating the role of a Ziegler-Natta catalyst.

Not only do Ziegler-Natta catalysts allow for linear polymers to be produced but they can also give stereochemical control. Propene, for example can polymerize in three ways, as shown above in Figure 5, to produce either atactic, isotactic or syndiotactic poly(propene).

However, this catalyst only allows the propene to be inserted in one way and isotactic polypropene is produced.

Even greater control of the polymerization is obtained using a new class of catalysts, the metallocenes (/polymers/polypropene.html#metallocene).

Radical polymerization

Many polymers, including all of the addition polymers in Table 1, are produced using radical initiators, which act as catalysts. For example the polymerization of chloroethene is started by warming it with a minute trace of a peroxide (R-O-O-R):

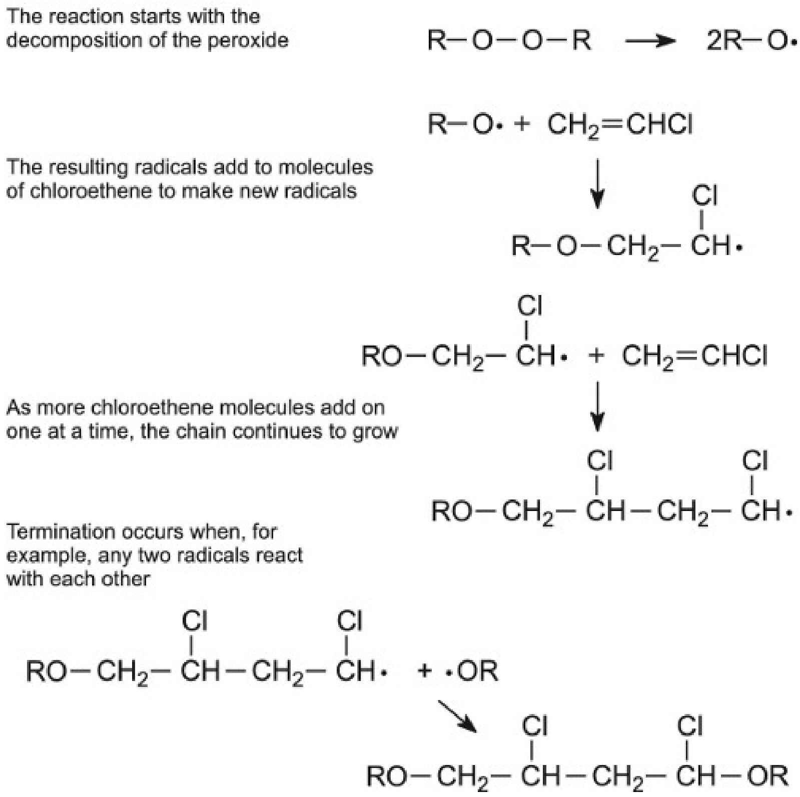
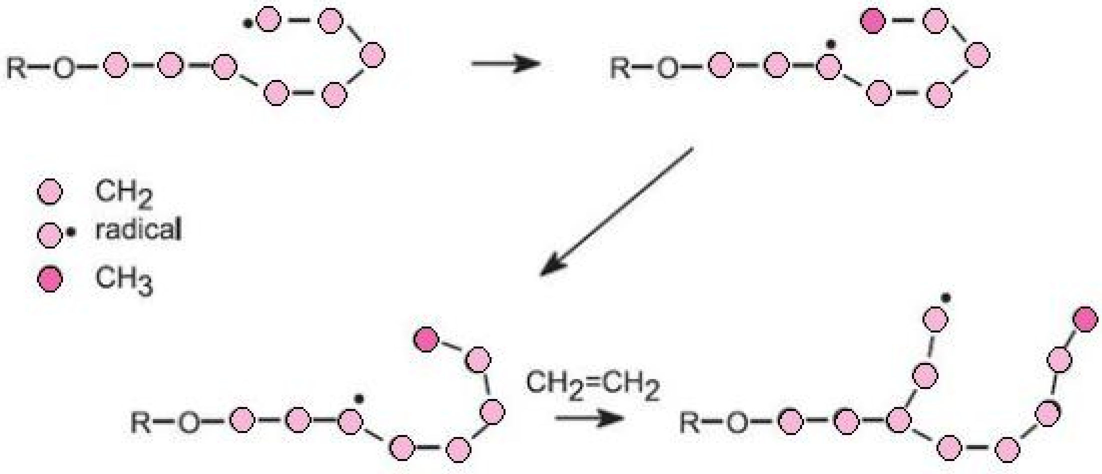


Figure 7 A mechanism for the free radical polymerization of chloroethene to poly(chloroethene).

In the case of ethene, by using the free radical process, the resulting polymer has a lower density and a lower softening point than the poly(ethene) produced using a Ziegler-Natta catalyst or a metallic oxide. The low density poly(ethene), LDPE, has side chains because the radicals react not only with molecules of ethene, by addition, but also with polymer molecules, by a process known as hydrogen abstraction. The polymer radical can also abstract a hydrogen atom from its own chain:



Both of these reactions lead to side chains so that the molecules of the polymer cannot pack together in a regular way. The polymer thus has a lower melting point and lower density.

Plastics formulation

The properties of many plastics can be modified by varying their formulation. For example, one of the most versatile plastics is poly(chloroethene) (PVC).

It can be made in either a flexible or a rigid form (and every combination between these extremes) by using various additives (Table 5).

Figure 8 Specific properties can be produced by mixing polymers. For example this shirt is made from a mixture of poly(propenoate) (acrylic) (/polymers/polypropenoic-acid.html), aramid (/materials-and-applications/composites.html#aramid) and polyamide (/polymers/polyamides.html) fibres which gives protection against heat and yet remains comfortable to wear.

By kind permission of DuPont.

Additive	Examples	Function
Plasticiser	e.g. esters of benzene-1,2-dicarboxylic acid	Acts as a lubricant for polymer chains. Large amounts give a flexible product, low quantities produce a rigid one.

Stabiliser	e.g. lead carbonate (<1%), lead phosphate or, for non-toxic requirements, mixtures of metal octadecanoates and epoxidized oil	Prevents decomposition of polymer. Without a stabiliser, poly(chloroethene), for example, decomposes on heating to give a brittle product and hydrogen chloride. Some plastics become coloured (yellowing) when exposed to long periods of sunlight.
Extender	Chlorinated hydrocarbons	Extends the effect of the plasticiser, but generally cannot plasticise alone. They are cheaper than plasticisers, so help reduce costs.
Fillers	Chalk, glass fibre	Tailor the plastic for special requirements, or make it cheaper.
Miscellaneous	Flame retardants, UV stabilisers, antistatics, processing aids, pigments	Impart specially required properties to the plastic for the manufacturing process or for end-use.

Table 5 Additives used to enhance the properties of plastics.

Processing plastics

Processing converts plastics into useful articles. Processing methods are given in Table 6.

Process	**Application**
Compression moulding	Usually for thermosets - powder moulded under heat and pressure.
Injection moulding	Usually for thermoplastics - molten plastics injected into a mould under pressure. The mould surface detail can be accurately reproduced. Very widely used.
Rotational moulding	Usually for thermoplastics. The powder is heated in a closed mould which is rotated, fairly slowly, simultaneously about two axes. Surface detail is poor but this method can be used to make large hollow articles.
Reaction injection moulding	Usually for thermosets, polymerization takes place in the mould thereby producing the finished article directly from a resin.
Extrusion	Usually for thermoplastics - the molten plastics are fed by a screw through a die, which for sheet or film, for instance, is a slit. Various extensions to the process are possible - e.g. a tube may be inflated by air whilst still hot to produce a tubular film (for bags, etc.), or short lengths of hot extruded tube can be inflated in moulds to form bottles.
Calendering	Usually for thermoplastics - molten plastics squeezed between hot rollers to form foil and sheet.

Thermoforming	Heat-softened thermoplastic sheet is drawn into or over a mould. If a vacuum is used to 'suck' the sheet into a mould, the process is known as vacuum forming. This process is used for a variety of articles, ranging from chocolate box liners to acrylic baths.

Table 6 Methods of processing plastics.

Polymers: their manufacture and uses

While this unit is concerned with the general principles underlying the structure, formulation and processing of polymers produced today, the manufacture and properties of the polymers vary considerably. The following are discussed in other units:

Methanal plastics (/polymers/methanal-plastics.html)

Polyamides (/polymers/polyamides.html)

Polycarbonates (/polymers/polycarbonates.html)

Poly(chloroethene) (/polymers/polychloroethene.html)

Polyesters (/polymers/polyesters.html)

Poly(ethene) (/polymers/polyethene.html)

Poly(methyl 2-methylpropenoate) (/polymers/polymethyl.html)

Poly(phenylethene) (/polymers/polyphenylethene.html)

Poly(propene) (/polymers/polypropene.html)

Poly(propenoic acid) (/polymers/polypropenoic-acid.html)

Poly(propenonitrile) (/polymers/polypropenonitrile.html)

Poly(tetrafluoroethene) (/polymers/polytetrafluoroethene.html)

Polyurethanes (/polymers/polyurethane.html)

Silicones (/polymers/silicones.html)

Important developments in recent years include degradable plastics (/polymers/degradable-plastics.html) and methods of recycling polymers (/processes/recycling-in-the-chemical-industry.html#recycling_polymers) which include reusing the polymer and degradation followed by repolymerization.

Date last amended: 18th March 2013

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Please send these comments to:
eci@essentialchemicalindustry.org (mailto:eci@essentialchemicalindustry.org)

References:
Industrial books and websites attached in the file.