THE MANUFACTURE OF HYDROGEN PEROXIDE

Hydrogen peroxide (H_2O_2) is a weakly acidic, colourless liquid, miscible with water in all proportions. It is the simplest peroxide (molecules containing two oxygen atoms covalently bonded to one another) and is commercially available in aqueous solution over a wide concentration range.

The main uses of hydrogen peroxide are in the preparation of other peroxides and as an oxidising agent.

The manufacturing process involves the catalysis of the reaction of H_2 (obtained from processing Maui Gas) with atmospheric O_2 to give H_2O_2. Anthraquinone (Q) is used as a H_2 carrier.

Step1 - Hydrogenation
Palladium catalyses the reaction between H_2 and anthraquinone to create anthrahydroquinone (H_2Q):

$$Q + H_2 \rightarrow H_2Q$$

Step 2 - Filtration
The palladium catalyst is filtered out of the solution.

Step 3 - Oxidation
The solution is oxidised by blowing air through the solution, forming the H_2O_2:

$$H_2Q + O_2 \rightarrow Q + H_2O_2$$

Step 4 - H_2O_2 Extraction
The hydrogen peroxide is removed in a liquid-liquid extraction column and concentrated by vacuum distillation.

INTRODUCTION

Hydrogen peroxide, a weakly acidic colourless liquid, was discovered by Thenard in 1818 and has been uses industrially since the mid-19th century. Its scale of manufacture and use have increased markedly since about 1925 when electrolytic processes were introduced to the United States and industrial bleach applications were developed. Now prepared primarily by anthraquinone autoxidation (where a molecule is oxidised by oxygen), hydrogen peroxide is used widely to prepare other peroxygen compounds and as a nonpolluting oxidising agent. Some of its physical properties are shown in **Table 1**.

Uses of hydrogen peroxide
The major uses of peroxide in New Zealand utilise its strongly oxidising nature to oxidise various chemical groups. These oxidisable groups primarily include lignins, cyanides, sulphides and phenols (benzyl alcohols). Hydrogen peroxide can react to form $HO^{\cdot}$ or HOO^- or other species depending of the conditions chosen. Pulp bleaching generally uses alkaline pH to generate HOO^-:

$$H_2O_2 + HO^- \rightarrow HOO^- + H_2O$$

Table 1 – P hysical properties of H_2O_2

Property	Value
melting point / ^oC	-0.41
boiling point / ^oC	150.2
density at 25^oC / g mL^{-1}	1.4425
viscosity at 20^oC / mPa s	1.245
surface tension at 20^oC / mN m^{-1}	80.4
specific conductance at 25^oC / Ω.cm	4×10^{-7}
enthalpy of fusion / J g^{-1}	367.52
specific heat at 25^oC / J g^{-1}	2.628
heat of vapourisation at 25^oC / J g^{-1}	1517
pK_a at 20^oC	11.75
heat of dissociation / kJ mol^{-1}	34.3

Phenol destruction normally uses peroxide to generate free radicals. This can be achieved by either UV light or metallic catalysis (Fenton's Chemistry).

Some industrial uses of hydrogen peroxide are shown in **Table 2**.

Table 2 - Uses of Hydrogen Peroxide

Industry	Application
Pulp and paper (see article)	Bleaching wood pulp
Mining (see article)	Detoxification of cyanide tailings
Textile bleaching	Bleaching of cotton fabrics
Wool scouring (see article)	Bleaching of wool
Waste water treatment (see article)	Measuring dissolved oxygen. Destroying soluble cyanides, sulfides and phenols
Packaging	Aseptic packaging of milk and fruit juice

Chemical Reactions of hydrogen peroxide

Some of the more significant reactions of hydrogen peroxide are listed below.

- Decomposition $2H_2O_2 \rightarrow 2H_2O + O_2$
- Molecular addition $H_2O_2 + Y \rightarrow Y.H_2O_2$
- Substitution $H_2O_2 + RX \rightarrow ROOH + HX$

$$H_2O_2 + 2RX \rightarrow ROOR + 2HX$$

- Oxidation $H_2O_2 + W \rightarrow WO + H_2O$
- Reduction $H_2O_2 + Z \rightarrow ZH_2 + O_2$

Where R, W, X, Y, Z represent various functional groups or molecules.

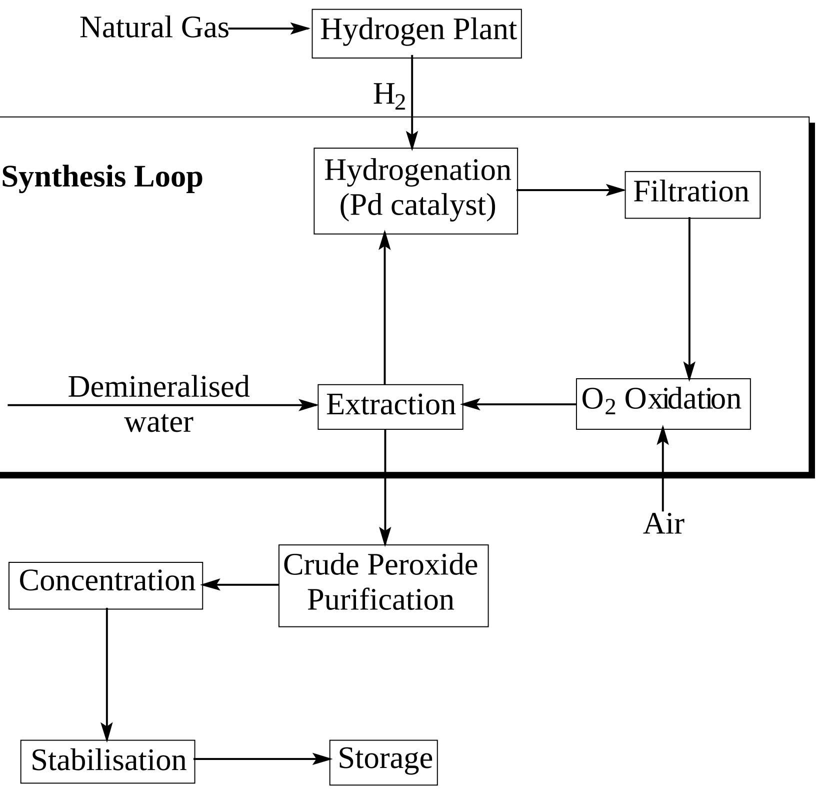


Figure 1 – The Anthraquinone Process for H_2O_2 Manufacture

THE MANUFACTURING PROCESS

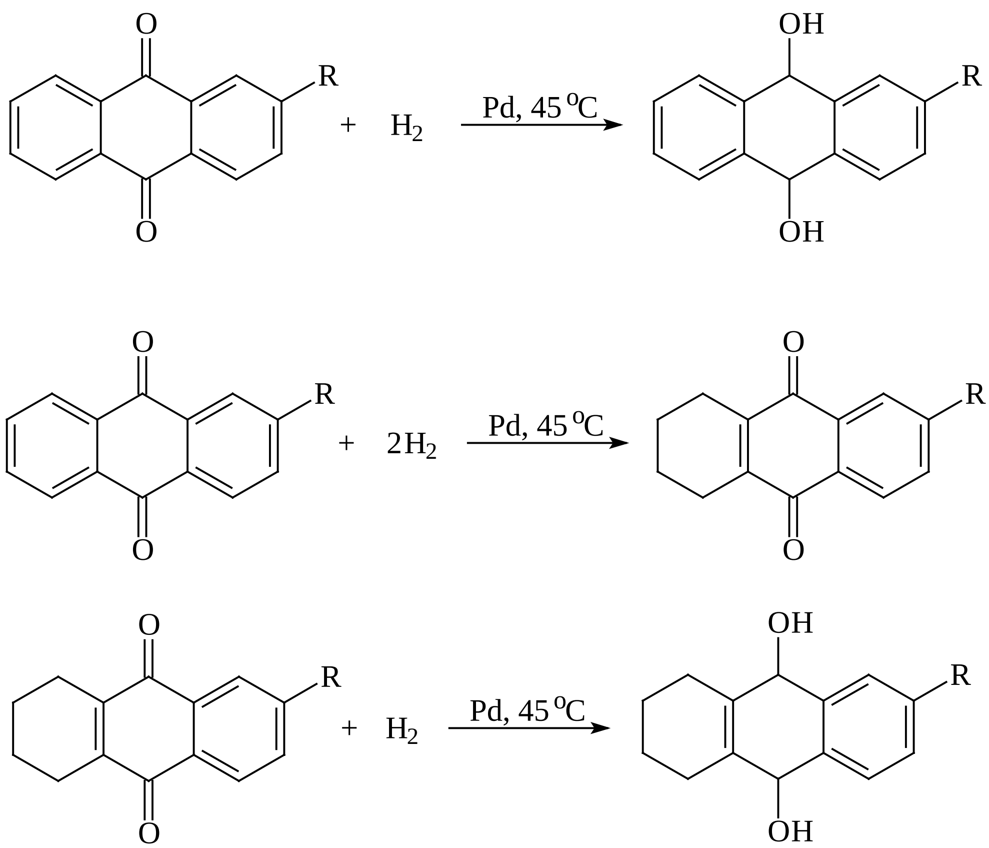
Hydrogen peroxide is manufactured using the anthraquinone process. This process is a cyclic operation where the alkyl anthraquinone is reused. The Synthesis Loop consists of sequential hydrogenation, filtration, oxidation and extraction stages (**Figure 1**). A number of ancillary processes are also involved.

Step 1 - Hydrogenation

An alkyl anthraquinone is dissolved in two solvents, one nonpolar and the other polar. Collectively the anthraquinone and solvents are called the working solution. This working solution is recycled.

The working solution containing the dissolved anthraquinone is hydrogenated using hydrogen gas in a slurry-type hydrogenator using alumina loaded with a small amount of palladium catalyst. Temperature is controlled to around 45^{o}C and the reactor is agitated to ensure good mixing of catalyst with working solution and hydrogen. During hydrogenation the alkylanthraquinone is converted to both the alkylanthrahydroquinone and the tetrahydroalkyl-anthrahydroquinone, although productionof the tetra-form of the quinone is preferred because it can be more easily hydrogenated.

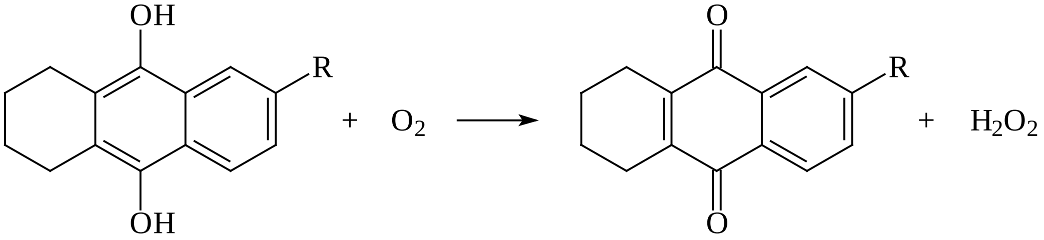
The hydrogenation stage is carefully controlled to avoid over-hydrogenation of the anthraquinone rings. Basicity and moisture content are important for optimum catalyst and activity.



Tetra-form *rapid* *Tetra-hydro-form*

Step 2 - Filtration
The working solution that now contains hydrogenated anthraquinone is then filtered to remove any trace levels of catalyst. If the catalyst is not removed then it will decompose the hydrogen peroxide in later stages, reducing yields and causing potential hazards.

Step 3 - Oxidation
The working solution is oxidised by blowing air through it. The tetrahydroalkylanthrahydro-quinone is oxidised, forming hydrogen peroxide in an organic phase. No catalyst is used and hence this step is often referred to as auto-oxidation.



Step 4 - H_2O_2 Extraction
Since the hydrogen peroxide is present in an organic phase and the product is required in aqueous phase, demineralised water is added to the top of a 35 metre high liquid-liquid extraction column. The water flows down the column over perforated trays while the working solution is pumped up the column. The extractor design and operation ensures a maximum contact of water with the working solution.

The water reaches the bottom of the extractor and contains 25-35% w/w crude hydrogen peroxide, whilst the working solution that leaves the top of the extractor is free of hydrogen peroxide and is pumped back to the hydrogenator. This working solution now contains the original alklyanthraquinone and tetrahydroalkylanthraquinone.

The crude hydrogen peroxide is subsequently purified and vacuum distilled to concentrations of up to 70% w/w. This concentrated product is stabilised against unwanted decomposition by adding proprietary stabilisers and then pumped to product storage tanks for final testing.

UTILITIES

The Synthesis Loop and peroxide processing stages are dependent on a number of ancillary processes.

Hydrogen Plant
This plant processes natural gas through a steam reforming stage and subsequent high temperature shift catalytic stage to produce high purity hydrogen gas. The gas is finally purified in a pressure swing absorber before being used by the hydrogenator. Details of this process can be found in the manufacture of methanol.

Demineralised Water
High purity water is used to feed the extractor, concentrator as well as the package boiler. Conventional degassing followed by cation and anion exchange beds is used to purify town water for use in the peroxide process.

Package Boiler
A small boiler generates steam for use in concentrating crude peroxide from 25-35% to 35-70%

Waste Gas System
The oxidiser can produce an exit gas containing trace levels of solvents. The solvent-entrained gas is fed to a bed of activated carbon where the solvents are absorbed onto the carbon. The activated carbon is purged with nitrogen gas and the solvent is stripped off and recovered for reuse in the synthesis loop.

Calciner Systems
A calciner is used to regenerate spent catalyst on a periodic basis. The catalyst is removed from the regenerators, washed and then roasted to remove any other organics that might be present. These organics, if not removed, will block the catalytic sites on the catalyst and lower its activity.

Fire System
The hydrogen peroxide manufacturing process uses natural gas, hydrogen and organic solvents, all of which are highly flammable. The site is equipped with a deluge system with foam injection. In addition, the local fire brigade has been provided with a foam tender.

Working Solution Regeneration
Hydrogenation generates not only peroxide-producing anthrahydroquinones but also some by-products. These by-products include anthraquinone species that can be converted back to useful quinones by regeneration. During the regeneration process, a side-stream of working solution is fed through a bed of dehydrogenation catalyst. The regeneration converts epoxidised anthraquinones and tetrahydroanthraquinones to their corresponding anthraquinones.

ROLE OF THE LABORATORY

The purpose of the laboratory is to provide information on the process performance and to carry out quality control testing of hydrogen peroxide. Proprietary equipment is used to measure the synthesis loop operation at each stage of the process. This information is used by operations personnel to control the loop.

Utility testing is carried out in support of on-line process instrumentation.

ENVIRONMENTAL IMPLICATIONS

The process is inherently very friendly to the environment. The major sources of waste are liquid wastes from decant water cooling tower blowdown and demineralisation plant wash water. Both of these effluents are pH adjusted before being pumped to the Morrinsville waste water treatment plant. Their benign nature and the presence of part per million levels of peroxide make them easy to treat.

Gaseous emissions of solvents are minimised through the waste gas system and by having solvent storage tanks vented to activated carbon scrubbers. Liquid solvent waste is incinerated as necessary.

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