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Extraction of Byproducts of Hydrogen Peroxide Working Solution Using Solvent

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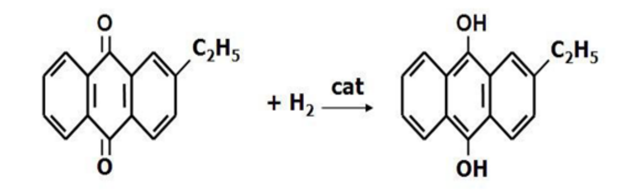
Abstract: Working solution comprising anthraquinone and its derivatives, used for preparation of hydrogen peroxide, leads to the formation of byproducts. These byproducts contain highly complex mixture of degradation products, which cannot take active part in the production of hydrogen peroxide, and cause higher viscosity and density of working solution. The low viscosity is important for mechanical reasons in cycling of the working solution through the equipment and density must be substantially different from the density of the water hydrogen peroxide solution resulting from water extraction of the hydrogen peroxide from the organic phase, in order to facilitate the extraction. The degradation products must be extracted from the working solution to prevent deteriorating the crude hydrogen peroxide color, smell, dissolved organic compounds and increase in density and viscosity of the working solution. A decrease in surface tension of the working solution promotes the formation of an emulsion during extraction degradation products decrease the activity and life time of the hydrogenation catalyst. Regeneration of the working solution for bringing it back to the good health a solvent Tetra Butyl Urea (TBU) is added in degraded working solution in a different proportion.

Keywords: Regeneration, Anthraquinone, Tetra Butyl Urea, Degradation.

1. Introduction

Widely used method for production of hydrogen peroxide is auto-oxidation process in which 2-ethyl-anthraquinone (EAQ) is dissolved in a carrier solvent such as Tri-Octyl Phosphate(TOP) and Tri methyl Benzene(TMB). This stream having hydrocarbon based carrier is known as "working solution". In Hydrogenation working Solution reacts with hydrogen & under goes in to the reduction reaction in the presence a Palladium (Pd) acting as a catalyst at temperature and pressure [2][3][8].



2-EAQ (Quinone) 2-EAHQ (Hydroquinone)

In hydrogenation reaction there are many secondary reactions which also occur during hydrogenation step. Hydrogenated working solution formed in hydrogenation is subsequently oxidized with air and converted back in to its quinine form with the simultaneous production of Hydrogen Peroxide [8].

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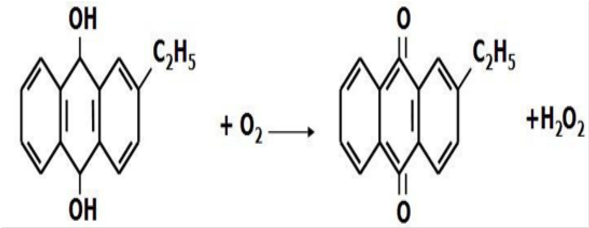


Hydroquinone Quinone

The quinone (2-EAQ) re-produced in the oxidation step is returned back to the hydro-generator for restart up of the cyclic process for proceeding the hydrogenation and oxidation steps for the formation of hydrogen peroxide [4][8].

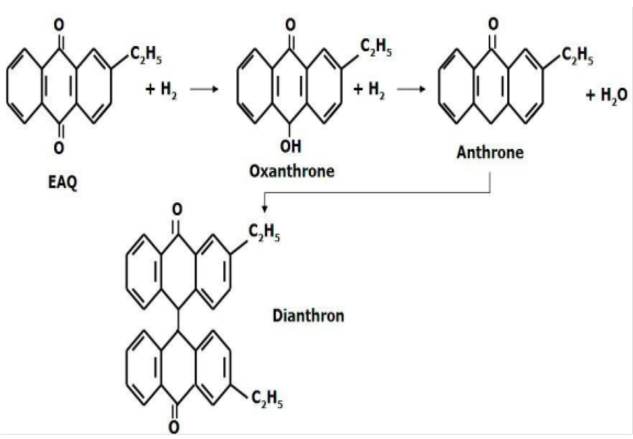
Side reactions in the hydrogenation and oxidation steps particularly during the catalytic hydrogenation step, the working solution is gradually converted to degradation products which are undesirable by-products are classified as non-effective anthraquinones, do not transformed between quinones to hydroquinone's and cannot produce the hydrogen peroxide[8]. Byproducts must have to remove from working solution to prevent hydrogen peroxide deterioration like smell, color, dissolved organic compounds,rise in working solution viscosity and density, Low viscosity is important for mechanical reasons and density must be differ from that of water [12]. Byproducts promote emulsion formation because of decrease in surface tension of working solution. Decrease in life and activity of palladium catalyst used in hydrogenation reactor [26].

The rate of formation of these degradation products increases as the temperature of the working solution during hydrogenation and oxidization steps are increased. Further these byproducts formation sharply increases at the level of hydrogenation as the proportion of the working solution per pass through the system increases (Depth of Hydrogenation) [16][17].

By-products formed by auto-oxidation process are known as Oxanthron, Anthron, Dianthron, Octahydroethyl antharquinone, Epoxide [8]. These byproducts are inert for auto oxidation process and lead to loss of active quinone. Some of them are regenerated to active quinone [23][24].

Hydrogenation by Products

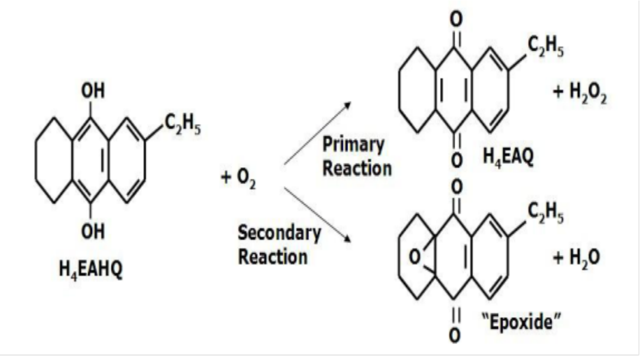
Oxanthrone is formed during hydrogenation and further hydrogenation leads to formation of anthrone, dianthrone formation which is inert and cannot be regenerated



With the increase in depth of hydrogenation 2-ethylo-octahydroquinone is formed in all tetra system, which is decomposition of active quinone and inert products [25].

Oxidation By-Products

Oxidation of tetra results in the formation of epoxides which cannot take part in the formation of hydrogen peroxide but regenerate to active tetra. A high epoxy anthraquinone generated in the oxidation process, which working together with floccus, makes catalyst activity decreased, and also the activity of activated alumina decreased. The capacity and quality of production stay on an unstable condition [25].



2. Process Description

Solvent System in AO Process

The solvent of working solution must have the capability to keep dissolved all the materials formed during hydrogenation, oxidation and must be appropriate for extraction process as well. Quinones and hydroquinone's formed during oxidation and hydrogenation respectively have different solubility tendency therefore it is the essentially required to have quinine solvent as well as hydroquinone solvent in the working solution , therefore it is necessary to use a solvent mixture for hydrogen peroxide production. Quinones are readily dissolved in non-polar organic aromatic solvents while hydroquinone is well dissolved in polar organic solvents like alcohols and esters [23][26].

The criteria for choosing solvent and preparing solvent mixtures:

a) Good solubility of both Quinone and hydroquinone.

b) Good stability in the hydrogenator and oxidizer.

c) Low solubility in water and aqueous hydrogen peroxide solutions.

d) Sufficiently higher density than water to ensure separation of the two phases during extraction.

e) Low volatility, i.e., high boiling point and flash point.

f) High distribution coefficient for hydrogen peroxide in the

g) Solvent-water system.

h) Low toxicity.

The Quinone Solvents used are as follows:

Benzene**,** Methylnaphthalene**,** Tert-Butylbenzene Trimethylebenzene(TMB)**,** Tert-Butylbenzene**,** Polyalkaylated benzene. Hydroquinone Solvents Alkyl Phosphate (TOP), Nonyl Alcohols, N, N Dialkylcarbonamides Tetra-Alkyl Ureas**.** Solvent Mixtures Polyalkylated benzene and alkyl phosphates (TMB&TOP), Polyalkylated benzene and tetra alkyl urea (TMB &TBU), Methylnaphthalene and Nonylalcohols, Trim ethyl benzene and alkylcyclohexanol esters [8][18].

3. Experimental Detail

Chemicals and Reagents:

Addition of Tetra-Butyl Urea in degraded working solution. Degraded working solution is collected after the steam treatment of the hydrogenation reactor having palladium catalyst. Tetra-Butyl Urea used has following properties.

Ingredients	**Amount in %**
Appearance	colorless Liquid
Dibutylamine	= 0.03%
Water content	= 0.03%
Density/cc @25	= 0.876-0.878
Color (APHA)	= 15
Cl	= 0.08ppm
Water, %	= less than 0.05
Sulfur, ppm	= less than 10.0
Purity, GC Area %	= 99.55

Results and discussions:

Working solution sludge is collected from hydrogenation reactor during steam treatment of reactor. Analyze the performance of given working solution viscosity, density, solubility of anthraquinone and hydroanthraquinone of working solution with addition of Tetra-Butyl Urea. Also with the addition of Tetra-Butyl Urea (TBU) in working solution will increase the hydrogenation efficiency of working solution (HWS) and extraction. Results are tabulated below:

Sr. #	***Test***	***Analysis***				
	Sample	**Working Solution**	1-A	2-A*	3-A*	4-A*
01	**Quantity of sludge**	Nil	1.00%	2.00%	2.5 %	3.5 %
02	**Quantity of TBU**	Nil	nil	1.00%	2.5 %	5.00%
03	**Density at 25ºC**	0.9269 g/cm³	0.930 g/cm³	0.9295 g/cm³	0.9290 g/cm³	0.9285 g/cm³
03	**Viscosity/40ºC**	1.4388 cp	1.4682 cp	1.4848 CP	1.4721 cp	1.4920 cp
04	**Solubility**	Soluble	suspension	Slight hazy	Soluble	Clearsoluble
04	**Appearance**	Orange yellow	Orange yellow	Hazy Orange yellow	Hazy Orange yellow	Clear Orange yellow
05	**HWS efficiency**	5.64 g/L	5.71 g/L	5.80 g/L	5.75 g/L	6.01 g/L
06	**EAQ**	72.00	72.60 g/L	73.01g/L	72.10g/L	71.50g/L
07	**H4EAQ**	69.00	69.80 g/L	70.00 g/L	68.20 g/L	68.20g/L
08	**Total EAQ**	**141.00g/L**	**142.40 g/L**	**143.01 g/L**	**140.30 g/L**	**139.70g/L**
09	**TMB %**	76.85	76.40	75.60	74.25	73.10
10	**TOP %**	23.05	22.10	22.90	22.25	20.90
11	**M.C %**	0.10 %	1.5 %	0.5 %	1.0%	1.0 %

Solvent tetra butyl urea (TBU) impacts on the viscosity, density, partition coefficient of hydrogen peroxide , solubility of AQ and HAQ of working solution (WS), the hydrogenation reaction activity of Pd-catalyst, and the extraction of hydrogen peroxide from working solution deeply studied. Results show that the addition of TBU in working solution is more effective for the production of hydrogen peroxide by using anthraquinone process because itincrease the hydrogen peroxide throughput and the hydrogen peroxide content in the extract, and decrease content of hydrogen peroxide in the extraction raffinate.

4. Conclusions

- Different quantities of sludge have been used but a favorable ratio is 1~3.5 % in the working solution.
- Different volumes of Tetra butyl Urea (TBU) have been used in experimental work and the best suitable quantity is 3~5% of the total sludge amount.
- With the addition of Tetra Butyl Urea (TBU), sludge or byproducts become active part of the working solution which can contribute in the main reaction and prevents the formation of side reactions.
- If sludge is added to the working solution, it will become hazy and remain un-dissolved so addition of Tetra Butyl Urea (TBU) in different proportions is carried out.
- The same percentage amount of Tetra butyl Urea (TBU) used in the Sludge or byproducts, the sludge dissolved completely and remains in liquid form even at room temperature.
- Excess of TBU should be added to avoid the formation of high viscous sludge or by products.

Tetra butyl Urea (TBU) will not only be helpful in increasing the span of steam treatment but also dissolve the sludge which will be adsorbed at the surface of Pd-catalyst that result in lowering hydrogenation efficiency, it means the productivity will also increase.

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