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Synthesis of 2-Ethylhydroanthraquinone for the Production of Hydrogen Peroxide in a Catalytic Slurry Reactor: Design Case

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Abstract

The demand of hydrogen peroxide in the international market is increasing because of its one of the most environment friendly chemical feature which is available in different grades with a wide range of applications. According to the demand in international market 3000kt/year is being produced by a traditional autoxidation method which is known as 2-ethylanthraquinone process. The purpose of this research is to design a catalytic slurry reactor which give maximum efficiency of hydrogenation reaction for this purpose we perform a list of experiments inthe synthesis of 2-ethylhydroanthraquinone for the hydrogen peroxide production in a catalytic slurry reactor in the lab. Catalyst is available in the spherical form and some useful data is collected some from experiment and some from literature and a design of slurry type catalytic hydrogenator is present in this paper.

Keywords: Hydrogen peroxide, 2-Ethylanthraquinone, catalyst, slurry reactor.

Introduction

Hydrogen peroxide (H_2O_2) in widely used in almost all industrial areas, particularly in chemical industry and environment protection. One of the most important feature of the hydrogen peroxide is that is usage does not yields any secondary pollution and it has a wide range of applications as rocket propulsion fuel, paper making, chemical synthesis, environmental protection, food processing, medical sterilization and other fields. It is the only one germicidal agent composed of hydrogen and oxygen[1].

2-Ethylanthraquinone (2-EAQ) is a key component of anthraquinone process for the production of hydrogen peroxide, pharmaceuticals, and many other useful chemicals. With the increasing demands of hydrogen peroxide in the international market it needs to increase the production of 2-ethylanthraquinone (2-eaq)[2].

Slurry reactors are three phase reactors, meaning that they can be react solids, liquids and gases simultaneously. They can operate in either semi batch or continuous mode[3]. In this well-established Anthraquinone process for the production of hydrogen peroxide first of all the key component 2-ethylanthraquinone is hydrogenated in a catalytic slurry reactor which produce 2-ethylhydroanthraquinone and the further air oxidation of 2-ethylhydroanthraquinone yields hydrogen peroxide along with the regeneration of the key component 2-ethylanthraquinone. We use palladium-alumina supported catalyst in the spherical form is used in this research[4].

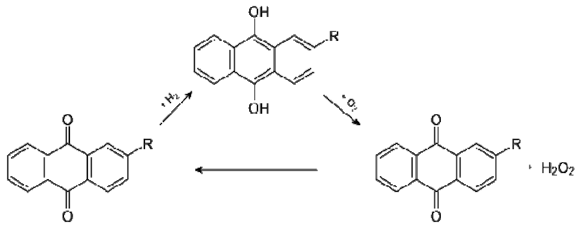
Previous research shows that when we use palladium alumina-silica catalyst then results shows that activation energy increases as the particle diameter of the catalyst which is available in the spherical is decreases[5].

The hydrogenation of 2-ethylanthraquinone in a catalytic reactor that the reaction rate is very high and the mass transfer layers are come into existences due to three phase catalytic reaction. we calculate the gas-liquid and liquid-solid co-efficient are calculated[6].

Reaction Mechanism

Previous research shows that the hydrogenation of 2-ethylanthraquinone is zero order reaction with respect to hydrogen and 1st order reaction with respect to the 2-ethylanthraquinone[7-10]. The reaction on silica-alumina supported palladium catalysts PD/AL-SI (pd 2%) is very fast. previous research on the 2-ethylanthraquinone hydrogenation demonstrate that when we use hydrogen as a key component it follows zero order kinetics and when we use 2-ethylanthraquinone as a key component it follows the 1st order kinetics[11].

A 2-ethylhydroanthraquinone (2-EHAQ) which is generated before from the corresponding 2-ethylanthraquinone (2-EAQ) by catalytic hydrogenation with silica-alumina supported palladium catalysts pd/al-si (pd 2%) and the organic phase react under formation of the anthraquinone and hydrogen peroxide[12].



Design Calculations

We select a slurry type semi batch reactor for this research

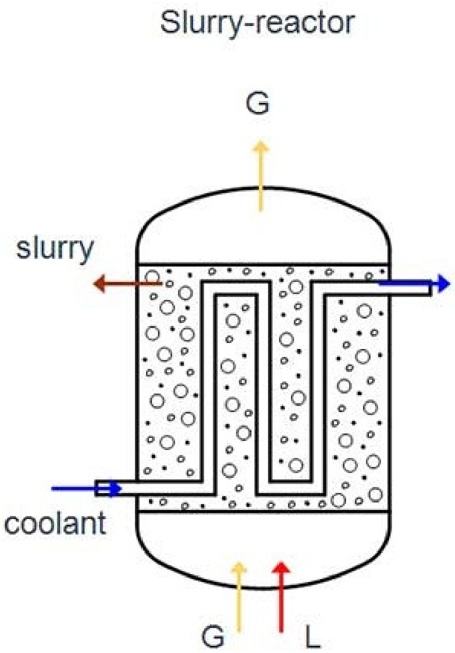


Figure-1
Following catalysts can be used: Raney Nickel catalyst Palladium–alumina catalyst, Chromium Nickel catalyst

The selected catalyst is Palladium–alumina catalyst. The properties of the selected catalyst are given in table-1

Table-1
Mass Transfer Resistances

Name	5% Palladium-Alumina
Catalyst Particle Diameter d_p	25×10^{-6} m
Catalyst Density ρ_p	1500 Kg/m^3
Catalyst Loading W_S	0.0001 $Kg_{Cat}\ Kg_{Liquid}^{-1}$

The Mass Transfer Resistance is given by this relation[13].

$$C' = \frac{H}{P_{H_2} K_{g_L} a_{g_L}} \quad (1)$$

Also we know that: $1/W_s = 1/0.0001 = 10000$, For 5% palladium-alumina catalyst, $1/w_s = 10000 \times 0.05$
so: $1/w_s = 500$ and for 1000 rpm, from graph[13]. We find $c' = 0.032\ m^3\ mole^{-1}$ sec. Also: Henry constant for hydrogen = h = $1.2821\ m^3\ mole^{-1}$ atm. Partial pressure of hydrogen gas = p_{h2} = 1.2 atm. Put all of these values in above equation we get

$$0.032 = \frac{1.2821}{1.2 \times K_{g_L} a_{g_L}}$$

$$K_{g_L} a_{g_L} = \frac{1.2821}{1.2 \times 0.032}$$

$$K_{g_L} a_{g_L} = \frac{1.2821}{0.0384}$$

$$K_{g_L} a_{g_L} = 33.388\ sec^{-1}$$

Specific Surface Area: The specific surface area of catalyst is given by this relation[13].

$$a_s = w_s \left(\frac{6}{d_p}\right)\left(\frac{\rho_L}{\rho_p}\right) \quad (2)$$

As we know that: catalyst loading = w_s = 0.0001 $kg_{cat}\ kg_{liquid}^{-1}$, catalyst particle diameter = $d_p = 25\times10^{-6}$ m
density of ethyl-anthraquinone = ρ_L = 1231 kg/m^3,
catalyst density = ρ_p = 1500 kg/m^3

Put all of these values in above equation we get

$$a_s = 0.0001\left(\frac{6}{25\times10^{-6}}\right)\left(\frac{1231}{1500}\right)$$

$$a_s = \left(\frac{0.7386}{37500\times10^{-6}}\right)$$

$$a_s = 0.0000196 \times 10^{-6}$$

$$a_s = 19.6\ m^2{}_{Catalyst} m^3{}_{Liquid}$$

Thiele Modulus: Thiele Modulus is given by the formula[13].

$$\emptyset_s = L\sqrt{\frac{k\,\rho_p}{D_{eff.}}} \quad (3)$$

As we know that[14]: $L = R/3 = d_p/6 = 25\times10^{-6}/6 = 4.1666\times10^{-6}$
Rate Constant[14] = k = $3.2\times10^{-6}\ m^3\ Kg^{-1}\ sec.^{-1}$

Now also we know that[15]: $D_{H_2} = 1.05\times10^{-2}\exp^{\left(\frac{-1520}{T}\right)}$

Reaction Temperature = T = 60 C° = 333.15 K

So put the value in the above equation in order to calculate the diffusivity of hydrogen gas

$$D_{H_2} = 1.05 \times 10^{-2} \exp^{\left(\frac{-1520}{333.15}\right)}$$

$$D_{H_2} = 1.05 \times 10^{-2} \exp^{(-4.5625)}$$

$$D_{H_2} = 1.05 \times 10^{-2} \times 0.01$$

$$D_{H_2} = 0.0105 \times 10^{-2} cm^2 sec^{-1}$$

or

$$D_{H_2} = 0.0105 \times 10^{-6} m^2 sec^{-1}$$

Now put all of these values in the above equation in order to calculate the Thiele Modulus we get

$$\emptyset_s = 4.1666 \times 10^{-6} \sqrt{\frac{3.2 \times 10^{-6} \times 1500}{0.0105 \times 10^{-6}}}$$

$$\emptyset_s = 4.1666 \times 10^{-6} \sqrt{\frac{1500 \times 3.2}{0.0105}}$$

$$\emptyset_s = 4.1666 \times 10^{-6} \sqrt{457142.8571}$$

$$\emptyset_s = 4.1666 \times 10^{-6} \times 676.1234$$

$$\emptyset_s = 2817.135 \times 10^{-6}$$

$$\emptyset_s = 0.0028$$

Effectiveness Factor: The effectiveness factor is given by the formula[13].

$$\varepsilon = \frac{\tanh \emptyset_s}{\emptyset_s} \quad (4)$$

Put the value of thiele modulus in above equation in order to calculate the effectiveness factor of catalyst.

$$\varepsilon = \frac{\tanh 0.0088}{0.0088}$$

$$\varepsilon = 1.00$$

Rate of Reaction: Basis = 1 hour Operation, The Rate of Reaction is given by the Formula[16].

$$r_{EHAQ} = 65.68 \exp^{\left(\frac{-17.041}{R \times T}\right)} P_{H_2} \quad (5)$$

Where: General gas constant = R = 8.314 J $mole^{-1}$ $K^{-1,}$ Partial pressure of hydrogen gas = P_{H2} = 1.2 atm, reaction temperature = T = 60 C^o = 333.15 K, Put all these values in above equation in order to calculate the rate of reaction we get

$$r_{EHAQ} = 65.68 \exp^{\left(\frac{-17.041}{8.314 \times 333.15}\right)1.2}$$

$$r_{EHAQ} = 65.68 \exp^{\left(\frac{-20.4492}{82778.80}\right)}$$

$$r_{EHAQ} = 65.68 \exp^{-0.00735}$$

$$r_{EHAQ} = 65.68 \times 0.9926$$

$$r_{EHAQ} = 65.1939 \text{ mole } m^{-3} hr^{-1}$$

Or

$$r_{EHAQ} = 0.01810 \text{ mole } m^{-3} sec^{-1}$$

Volume of Reactor: The volume of reactor is given by the formula[14].

$$\frac{V_r}{F_{A_o}} = \frac{X_A}{-r_A} \quad (6)$$

We want to design our Reactor for 80% Conversion so.

Conversion = X_A = 80% = 0.8

Hydrogen Flow Rate = V_o = 2 L/min = 0.0000333 m^3/sec.

Initial concentration of ethyl-anthraquinone = C_{Ao}= 2.795×10^{-4} mole/cm^3 = 2.795×10^2 mole/cm^3 = 2.795 mole/m^3

As we know that

Molar feed rate = F_{Ao} = C_{Ao} × V_o = 0.0000333×2.795 = 0.0093 mole/sec.

Now put the values in the above equation in order to calculate the volume of reactor we get.

$$\frac{V_r}{0.0093} = \frac{0.8}{0.01810}$$

$$V_r = \frac{0.8}{0.01810} \times 0.0093$$

$$V_r = \frac{0.00744}{0.01810}$$

$$V_r = \frac{0.00744}{0.01810}$$

$$V_r = 0.411 m^3$$

Area of Cooling Jacket: The Area of Jacket which is in the form of Annulus can be calculated by this formula[17].

$$A_J = \pi(R^2 - r^2) \quad (7)$$

Also we know that.

$$V = \pi r^2 h \quad (8)$$

For reactor the rule of thumb is.

L/D = 3

L = 3D

Put in volume formula we get

$V = \pi r^2 3D$

Put D = 2r we get

$V = \pi r^2 6r$

$V = 6\pi r^3$

Put the values we get.

$0.411 = 6 \times 3.14 \times r^3$

$0.411 = 18.84 \times r^3$

$r^3 = \frac{0.411}{18.84}$

$r^3 = 0.0218$

$r = \sqrt[3]{0.0218}$

$r = 0.2793$ m

Let the inner diameter of outer pipe is: R = 0.5 m

Put in the above equation to fine out the area of jacket we get.

$A_J = 3.14(0.5^2 - 0.2793^2)$

$A_J = 3.14(0.25 - 0.078)$

$A_J = 3.14 \times 0.172$

$A_J = 0.54008$ m

As we know that:

$$Q_J = U_j A_j (T_R - T_J) \quad (9)$$

Where: Overall heat transfer co-efficient[18] = U_J = 65 Btu/hr.ft^2.^{o}F (for cooling water and organics), area of jacket = a_j= 0.54008 m, water entering temperature = T_{J1} = 301K, water leaving temperature = t_{j2} = 312k, average temperature = T_J = $(T_{J1} + T_{J2})/2$ = (301 + 312)/2 = 306k, reaction temperature = T_R = 60 c^o = 333.15 K

Put the value in above equation we get

$Q_J = 65 \times 0.54008(333.15 - 306)$

$Q_J = 35.1052(27.15)$

$Q_J = 953.10618 \frac{Btu}{hr}$

Now as we know that

$$Q_J = mC_P(T_{J2} - T_{J1}) \quad (10)$$

Put the values we get

$953.10618 = m \times 4.18(312 - 301)$

$953.10618 = m \times 45.98$

$m = \frac{953.10618}{45.98}$

$m = 20.728 \frac{Kg}{hr}$

Material of Construction: The selection criteria for the reactor construction material are tensile strength, temperature conditions, corrosion resistance, cost.

Because of better tensile strength, useful at temperature greater than 700F, good corrosion resistance and cheaper we select stainless steel (ss) as a reactor construction material[19].

Specification Sheet

Hydrogenation efficiency increase with the increase in the pressure anddecrease with the increase in liquid hourly space velocity (LHSV)[20].

Table-2
Effect of Pressure and LHSV

Reactor Name	**Slurry Stirred Semi Batch Reactor**
Mass Transfer Resistance	$33.388\ sec^{-1}$
Specific Surface Area	$19.6\ m^2{}_{Catalyst} m^3{}_{Liquid}$
Thiele Modulus	0.0028
Effectiveness Factor	1.00
Rate of Reaction	$0.01810\ molem^{-3}sec^{-1}$
Volume of Reactor	$0.411m^3$
Area of Jacket	0.54008 m
Flow Rate Through Jacket	20.728 Kg/hr
Material of Construction	Stainless Steel

Results and Discussion

We find a reactor size of 0.411m^3 for 80% conversion of the hydrogenation reaction at 60c^o at atmospheric pressure. Which the optimized reactor size with construction material stainless steel (SS) and catalyst silica-alumina supported palladium catalysts Pd/Al-Si (Pd 2%).

Conclusion

In this research we conclude that we got maximum conversion of 2-Ethylanthraquinone in to 2-Ethylhydroanthraquinone with the optimized reactor size of 0.411m^3 in the presence of Palladium Alumina-Silica (Pd 2%) supported catalyst in a Slurry Reactor. Due to three phase chemical reaction we recommend Slurry Reactor with the catalyst in spherical form having effectiveness factor 1. Due to multiphase chemical reaction Gas-Liquid and Liquid-Solid Mass Transfer layers are also come into existences which are measured accurately.

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