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CASE STUDY: DESIGN AND SIMULATION OF ADIPIC ACID PLANT

Sreenivas Matla*, Assistant Professor, Dept. of Chemical Engineering and Petroleum Engineering, UCEK, JNTUK, Kakinada, Andhra Pradesh, India
Aparna Kurru, Business analyst, Emerson automation solutions, Hyderabad
Pampana Anil Kumar, Assistant Professor, Dept. of Chemical Engineering and Petroleum Engineering, UCEK, JNTUK, Kakinada, Andhra Pradesh, India
K. Baby Jyothsna, Assistant Professor, Dept. of Chemical Engineering and Petroleum Engineering, UCEK, JNTUK, Kakinada, Andhra Pradesh, India
J. A. Suhasini, Assistant Professor, Dept. of Chemical Engineering and Petroleum Engineering, UCEK, JNTUK, Kakinada, Andhra Pradesh, India
P. Varsha, Assistant Professor, Dept. of Chemical Engineering and Petroleum Engineering, UCEK, JNTUK, Kakinada, Andhra Pradesh, India

Abstract:
This paper deals with the Design and Simulation of Adipic Acid Plant. The adipic acid is mainly used to produce nylon, industrially important as raw material for the textile industry. For the process to be clean and environmentally friendly, the chemicals Like H_2O_2 as an oxidant and sodium tungstate as a catalyst were used instead of HNO_3 due to emission of N_2O gas which is one of the hazardous gases for environment. Different parameters like molar ratio of catalyst and reactants, concentration of hydrogen per oxide, molarity of acid, temperature, and residence time were optimized to obtain high yield of adipic acid. Cyclohexanone is oxidized to adipic acid and water produced as the main by-product. The units which we designed includes a heat exchanger, reactor, decanter, crystallizer, separator and dryer. HAZOP study was conducted on the heat exchanger. Economic feasibility, efficiency and operability were the basis for the design of the units mentioned above. In the end, we estimated the capital cost for the production process and discussed its profitability.
***Key words*:** Adipic Acid, Nylon 6,6, Cyclohexane, Hydrogen peroxide

1. Introduction:

Adipic acid (hexane dioic acid/ 1,4-butanedicarboxylic acid) is a white crystalline solid with a melting point of 153°C[1]. From a commercial viewpoint, it is the most important of all the aliphatic dicarboxylic acids, with a worldwide annual production of about 1.8 million metric tons. Its primary use is in the manufacture of nylon-6, the polyamide formed by its reaction with 1,6-hexamethylenediaamine[2]. This polymer, discovered by W. H. Carothers of the Du Pont Company in the early 1930s, has grown to be one of the most important materials employed in the manufacture of synthetic fibers. Although the later introduction of polyesters, acrylic, polyolefin and other polyamide fibers has reduced the share of the total market commanded by nylon6,6 its versatility has provided a healthy growth rate over the past three decades for adipic acid[3]. This coupled with the high- quality standards demanded for polymerization and processing into fibers, has led to other applications for adipic acid in plasticizers, resins, plastics, foams, and also as a food acidulate [4].

1.1 *Domestic and Global Market Analysis of Adipic Acid:*

05 October 2015 - Fast-growing economies, mainly in China and India, have significantly increased global demand for adipic acid over the past 10 years [5]. Adipic acid production is growing in the Asia-

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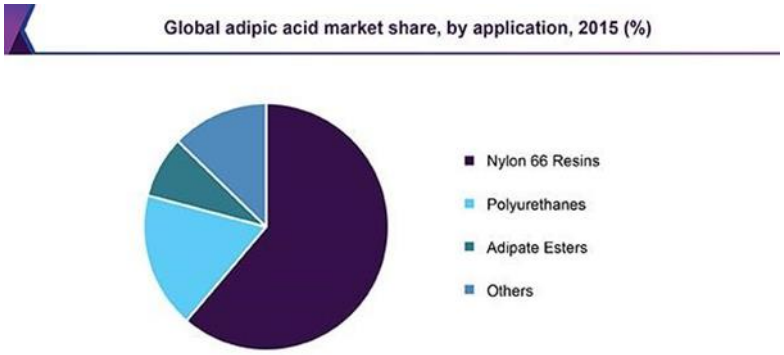

Figure 1: Global Adipic Acid Market Share

Pacific region as startups and small companies enter the market, BCC Research said in a new report [6]. The global market for IP Adipic Acid should reach $ 6.6 billion and $7.7 billion in 2015 and 2020, respectively, reflecting a five-year (2015-2020) compound annual growth rate (CAGR) of 3.2% [7]. The global adipic acid market, the largest and fastest growing end-user application for the automotive industry, is expected to reach approximately $2.6 billion by 2020, up from $ 2.1 billion in 2015 and a five-year CAGR of 4.2%. The market for the electrical and electronics industry, the second largest end-user application, should register a five-year CAGR of 2.7%, bringing the total market value to 11.1 billion by 2020 [8].

1.2 Review of Literature:

The production of Adipic Acids world-wide have also many methods. Some of the methods are given below:

- Synthesis of Adipic Acid Via The Nitric Acid Oxidation of Cyclohexanol in a Two Step Batch Process
- Clean Synthesis of Adipic Acid by direct Oxidation of Cyclohexene with H_2O_2
- Green Catalytic Oxidation of Cyclohexanone to Adipic Acid
- Influence of Reaction Conditions on Product distribution of Cyclohexene to Adipic Acid from H_2O_2
- Dual catalytic function of the task specific ionic liquid. Green oxidation of Cyclohexene to Adipic Acid using 30% H_2O_2
- Hydrothermal synthesis of WO_3 nano rods and their performance in the adsorption of Rhodamine
- Dawson-type poly oxometalates as green catalyst for Adipic Acid synthesis

2. Process Description:

The process selected is synthesis of Adipic Acid by direct combination of cyclohexene with Hydrogen peroxide H_2O_2 using Sodium Tungstate. Sodium tungstate dihydrate is a hydrated sodium salt of tungstic acid. It participates as a catalyst in the preparation of various epoxides. Various crystallographic properties of sodium tungstate dehydrate have been analyzed. It combines with Hydrogen peroxide for the oxidation of secondary amines to nitrones. Hydrogen peroxide is a colorless liquid that is widely used as an oxidizer and bleaching agent. Hydrogen peroxide decomposes over time to water and oxygen. Heat, ultraviolet light, and contaminants accelerate its decomposition, so it should be stored in cool, dark places. Noroyi reported a practical method of oxidation cyclohexene with 30% hydrogen peroxide in presence of small amounts of Na_2WO_4 and $[CH_3(n\text{-}C8H17)_3N]$ HSO_4 as a phase transfer catalyst. A novel clean per oxy tungstate-organic complex catalyst was also used to catalyze oxidation of cyclohexene by 30% hydrogen peroxide to produce adipic acid at a high yield (Ma et al., 2001). Long chain carbon alkyl ammonium sulphate was used to substitute the expensive phrase transfer catalyst to produce adipic acid and obtained a yield of 81.7% (Gong et al., 2000)[9].

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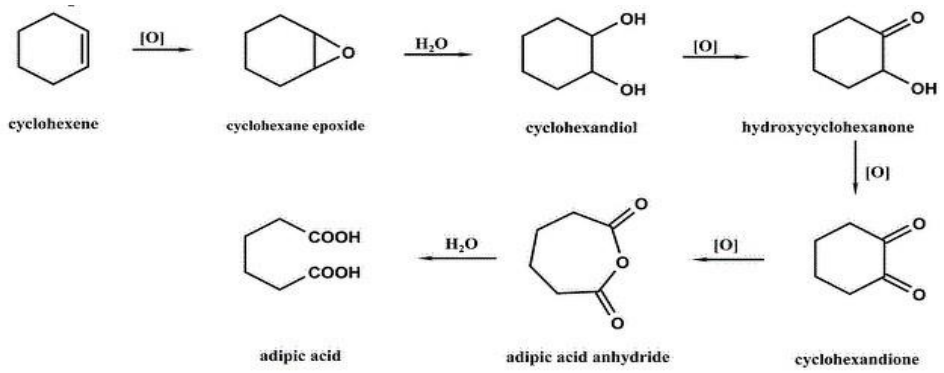
The process selection is based on the yield and environmental condition basis. It is an environment friendly process with highest yield of 95%. The process is operated at 1 atm pressure and 90^0C temperature. Hydrogen peroxide is used as oxidant while sodium tungstate as a catalyst. The catalyst is used to boast the reaction kinetics. The residence time for the process is 20 Hrs. The residence time is provided to give the contact time of the reactants and to get maximum yield [10].



The process is operated at 90°C temperature. The cyclohexene is firstly oxidized to form epoxide which is not a stable epoxide and reacted with H_2O to form ketone cyclohexandiol. This ketone on further oxidation is converted into adipic anhydride which on form adipic acid by combination of water generated during the reaction.

2.1 Process Flow diagram:

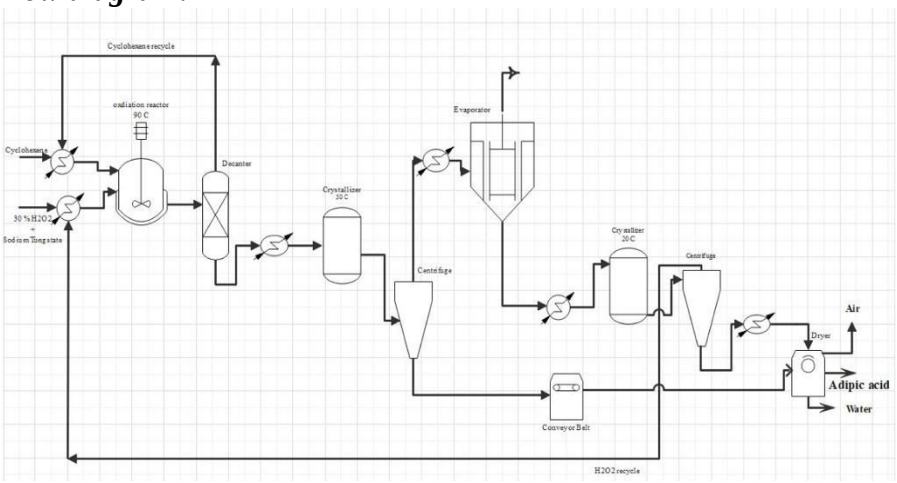


Figure 2: Process flow diagram

2.2 Material & Energy balances:

We have selected the capacity of plant 4500000 kg/year, No. of working days = 300 days,
The reaction conditions are: Temperature= 90°C, Pressure= 1 atm, Residence time /Cycle time=20 hr

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Overall conversion at these conditions =95%, **Reaction**: $C_6H_{10} + 4H_2O_2 \rightarrow C_6H_{10}O_4 + 4H_2O$

Table 1: Material Balances for components

Components	Input (kg/day)	Output (kg/day)
Cyclohexene	7288.82	364.44
Hydrogen peroxide	12088.77	604.44
Water	14933.19	21013.126
Adipic acid	-	12328.767
Total	34310.77	34310.77

2.3 Energy Balance:

The general form, $\mathbf{C_p = A + (B*T) + (C*T^2) + (D*T^3)}$, $\mathbf{Q = m*Cp*\Delta T}$, $\mathbf{Q = m*\lambda}$

Table 2: Energy Balances for components

Equipment	Energy Input (KJ/day)	
	Components	Energy Given
Heat Exchanger 1	0	160000
Heat Exchanger 2	0	3715376.72
Reactor	38157.24	1236946.65
Heat Exchanger 3	0	3653422.93
Crystallizer 1	4668842.13	2798582.11
Heat Exchanger 4	0	13171726.80
Evaporator	2301819.48	2361795.72
Heat Exchanger 5	0	321490.67
Crystallizer 2	508165.70	270879.90
Heat Exchanger 6	0	65036.28
Dryer	1006785.13	1667513.35

3. Specific Equipment Design for Reactor:

Since the process is all about the production of adipic acid through green pathway using hydrogen peroxide as an oxidizing agent. Following is the reaction occurs during the process: $C_6H_{10} + 4H_2O_2 \rightarrow C_6H_{10}O_4 + 4H_2O$

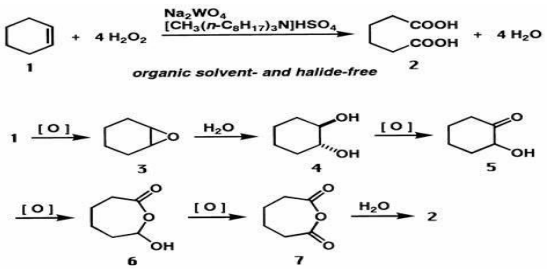

Table 3: Specification sheet of reactor

Design Specification Sheet	
Identification	
Name of Equipment	Continuous Stirred Tank Reactor
Type	Fixed bed catalyst reactor
Function	To allow the oxidation of cyclohexene in the presence of hydrogen peroxide
Number of units	1
Capacity (kg/day)	4.5 million
Operation	Oxidation
BASIC DESIGN DATA	
Pressure	1 atm
Temperature	368 k
Space time	24 hr
Conversion	95% N/A
Rotational speed of stir	1400 rpm
REACTOR DESIGN	
Rate constant	0.0459 hr-1
Reactor volume	3086.46 L
Reactor length	1.81 m
Reactor diameter	1.39 m
CATALYST BED	
Weight of catalyst	482.64 kg
Density of catalyst	1.84 kg/L
Volume of catalyst	262.30 L
Porosity of catalyst	0.65 unit less
Bed volume	749.43 L
Length of bed	0.495 m

4. Analytical Method:

The analytical procedures for food-grade adipic acid are described in Food Chemical Codex. Assay is by direct titration. Melting point is determined by the capillary melting point method using the Thomas-Hoover apparatus or equivalent. Arsenic is determined by the silver diethyldithiocarbamate procedure. Heavy metals (as Pb) are determined turbidimetrically as the sulfide. Ash is determined gravimetrically as the residue remaining after ashing 100 g of adipic acid at 850 ºC in a platinum dish. Waste is determined titrimetrically by the Karl Fisher method.

Other methods not specifically for food-grade adipic acid include iron in the ash by the colorimetric thioglycolic acid method and copper by chloroform extraction of the diethyldithiocarbamate copper complex from an aqueous ammoniacal solution. Organic nitrogen compounds (NH3 salts, amides, nitriles) are determined by distilling NH3 from an alkaline solution of adipic acid and titrating the distillate. Nitrates can be obtained in the same procedure by addition of Devarda's alloy to the

distillation pot after organic nitrogen is removed and continuing the distillation. APHA color of adipic acid is measured on 20 g of adipic acid in 100 mL of methanol solution against APHA standards. Silicone and hydrocarbon oils are determined by chloroform by extraction from an aqueous solution of diammonium adipate. After a back-extraction with aqueous caustic, the oils are separated chromatographically on solicit acid and measured by infrared spectroscopy.
Acidic impurities can be determined by gas chromatography of their methyl or trimethylsilyl esters. Levels as low as 10 ppm may be detected if adipic acid is first concentrated by crystallization from chlorobenzene. Chromatography determination of the esters has also become the method of choice for determining adipic acid in oxidation mixtures, synthetic fatty acid mixtures, and synthetic polyamides.

5. Conclusion:
Adipic Acid is very rare in nature, but is made mostly around world. Its primary application is in the production of nylon 6 6 polyamide. Different processes for its production are described. Combination of cyclohexene with hydrogen peroxide using sodium tungstate is selected for production. The material and energy balances are made to produce 4500000 kg/yr of Adipic Acid. Specific equipment design for the rector.

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