Scientific Journal of Impact Factor (SJIF): 5.71

e-ISSN (O): 2348-4470
p-ISSN (P): 2348-6406

International Journal of Advance Engineering and Research Development

Volume 5, Issue 04, April -2018

CATALYTIC HYDROGENATION OF AROMATIC NITRILES, STUDY FOR COST REDUCTION: A REVIEW

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Abstract-- *In the present process manufacturing of Benzylamine through catalytic hydrogenation of aromatic nitriles. In these reactions Polyamines are formed as by-products. Costing of the final product is severely affected by formations of polyamines. In present investigation the engineering aspects of manufacturing Benzylamines with minimal formation of polyamines is studied.*

Keywords: *Benzylamines, polyamines, catalytic hydrogenation, Quality control assurance, engineering aspects.*

I. INTRODUCTION

Benzylamine is a chemical compound with structural formula $C_6H_5CH_2NH_2$ .It is composed of a benzyl group, $C_6H_5CH_2$, attached to an amine functional group, NH_2. It was first produced by Rudolf Leuckart in the reaction of benzaldehyde with formamide in a process now known as the Leuckart reaction. Nitrile is any organic compound that has a −C≡N functional group The prefix cyano- is used interchangeably with the term nitrile in industrial literature. Benzylamine can be produced by several methods, the main industrial route being the reaction of benzyl chloride and ammonia. It is also produced by the reduction of benzonitrile and reductive amination of benzaldehyde over Raney nickel and the most effective way to produce benzyl amines are through catalytic hydrogenation of aromatic nitriles. Benzyl amines is the key product formed in present review paper Polyamines are positively charged nitrogenous compounds derived from amino acids It is an organic compound consisting of 2 or more amino groups (-NH2). Polyamines are synthesized in cells and play essential role in the proliferation and development of mammalian cells. They are a collective form of putrescine (PUT), spermidine (SPD) and spermine (SPM). In addition, polyamines have been shown to exert antioxidant activity anti-allergenic effect and suppression on glycation process. Recently, there are increasing interests on the research of polyamines. Polyamines are also important modulators of a variety of ion channels, including AMP Areceptors and NMDA receptors. They block inward-rectifier potassium channels so that the currents of the channels are inwardly rectified, thereby the cellular energy, i.e. K+ ion gradient across the cell membrane, is conserved. In addition, polyamine participate in initiating the expression of SOS response of Colicin E7 operon and down-regulate proteins that are essential for colicin E7 uptake, thus conferring a survival advantage on colicin-producing E. coli under stress conditions. In present investigation polyamines are a by-product and they severely affects the purity of benzyl amines formed and also increases the cost of the product formed.

II. LITERATURE REVIEW

2.1 Catalytic Hydrogenation and Nitrile Hydrogenation:

Catalytic Hydrogenations are of outmost importance in organic synthesis and play a key role in the production of numerous bulk products and intermediates in the chemical industry. From an ecologic point of view, reductions using molecular hydrogen as reducing agent represent one of the most efficient and atom economical transformations. In general, heterogeneous catalysts are well established in the hydrogenation of non-demanding polar functional groups, which often takes place at high temperatures and/or pressures. Complementary, the development of well-defined homogeneous complexes which allow for selective reduction under milder conditions constitutes a cutting-edge endeavor in modern catalyst design. In this context, the introduction of bifunctional metal ligand catalysis by Noyori for the catalytic hydrogenation of carbonyl compounds represents a breakthrough. Since then, significant progress has been made in this field using mainly noble metal complexes, namely ruthenium, iridium, and rhodium. However, in terms of sustainability such precious metals ought to be replaced by inexpensive and widely abundant first row base metals. After having some potential manganese catalysts in hand, we started to investigate their behavior in the hydrogenation of nitriles, ketones and aldehydes. Based on the recent interest in the selective reduction of carboxylic acid derivatives, 23 our initial attempts focused on the hydrogenation of benzonitrile as benchmark substrate.

2.2 Research Methodology:
The hydrogenation reactions were carried out in a 500 mL stirred autoclave (BuchiGlasUster). An automated gas flow controller (BPC1202) allowed the delivery of inert (N2, BOC, 99.999% purity) and active (H2, BOC, ≥99.995% purity) gases to be delivered directly to the reactor via a gas reservoir. Reactions were heated by silicon oilpassed around the reactor via a heating circulator (Julabo F25). The hydrogen uptake provided a direct indication of reaction rate and hydrogen consumption. The reactor was charged with the catalyst (0.5 g), then the sol-vent (300 mL, methanol) and the reactor was purged with inert gas (N_2). The catalyst/solvent mixture was heated and stirred at 300 rpm for 1 h under a constant flow of hydrogen in order to reduce the catalyst. Meanwhile, the nitrile substrate (17–23 mmol) was dissolved in 50 mL of solvent and degassed under a constant flow of helium. Once reaction pressure (4 bar g) was obtained, the reaction mixture was stirred at 800 rpm and samples taken periodically via an outlet valve throughout the course of the reaction. An agitation rate of 800 rpm corresponded to a mid-point of the plateau region of a plot of hydrogenation rate vs. agitation rate, where increased agitation speeds yield no improvement in hydrogenation rate. In this way, the reaction system was determined to be free from diffusion limitations and to be under kinetic control. All reactions were performed at least induplicate, with the profiles presented here being representative of the replicate measurements.

2.3 Hydrogenation Kinetics:
The hydrogenation kinetics was carried out by using platinum oxide in acetic acid and these are generally a first-order in the pressure of hydrogen and zero-order in the concentration of the aromatic compound. Zero-order indicates that the organic materials are strongly adsorbed to the catalytic surface. The rates of the hydrogenations are generally observed by following the pressure decrease in a constant volume system. The rates of the hydrogenations of alkyl benzenes catalyzed by platinum oxide in acetic acid at temperatures below 80°C and pressures below 4 atmospheres are proportional to the pH of the system, the amount of catalyst when the catalyst was present in low concentrations and the agitation rate when the concentration of the catalyst was high. In alkyl benzene reductions it was observed that the reaction course and the nature of the products are influenced by substituents which prevent the flatwise adsorption of the aromatic ring onto the catalytic surface. The rate of hydrogenation decreased with an increase in the number of substituents and the symmetry of substitution had an influence on the reaction rate.

III. GENERAL SETUPS

The Following things are required to for the manufacturing process of Benzylamines. These are just the general procedure as complete process was not disclosed by the industry. Glass Reactor with distillation setup:

- Autoclave
- Scada controlled setup
- Auto heating and cooling
- Temperature regulator
- Pressure and flow measuring devices

3.1 Experimental Setup:
Generally, the manufacturing process involves hydrogenation of benzonitrile derivatives. As a nitrile group is acetylinic function (A CN triple bond), the reduction takes place in two steps, and there is an enough scope for undergoing polyamine formation. This polyamine formation can be avoided by use of few solvents, Change in catalyst and hydrogen pressure.
Three families of Benzonitrile are selected to achieve the product are:

- Alkyl benzonitriles
- Halo benzo nitriles(Fluoro and Bromobenzonitriles)
- Alkoxy benzonitriles

The manufacturing process would be carried out in 25 lit Stainless Steel –Autoclave machine with heating and Supervisory control and data acquisition (**SCADA**) controlled process, loading and discharge.
Other depended facilities which are required are

- Auto cooling system
- Auto temperature and pressure control
- RPM and Flow Measuring Devices

PARAMETERS	MIN	MAX
TEMPERATURE	180^{0}C	225^{0}C
HYDROGEN PRESSURE (AUTOCLAVE)	15psi	18psi
STERILIZATION TEMPERATURE	121^{0}C	138^{0}C
STERILIZATION TIME	15mins	20mins
TIME (AUTOCLAVE)	6hrs	8hrs
UNWRAPPED ITEMS TEMPERATURE	132^{0}C	135^{0}C
TOTAL REACTION TIME	12hrs	13hrs

Fig 3.1 Parameters with ranges

3.2 Industrial Autoclave:

Autoclaves provide a physical method for disinfection and sterilization. They work with a combination of steam, pressure and time. Autoclaves operate at high temperature and pressure in order to kill microorganisms and spores.

Industrial autoclaves are pressure vessels used to process parts and materials which require exposure to elevated pressure and temperature. The manufacture of high performance components from advanced composites often requires autoclave processing. The selection of the materials from which the autoclave is fabricated turns entirely upon the application. For steam autoclaves, carbon steel is used, but a corrosion allowance is added to the calculated thickness. This accommodates the rusting that occurs with repeated cycles of exposure to steam, water, and air. Implicit in this is the need to monitor the loss of metal and decommission the vessel when excessive thickness loss has occurred. For temperatures of up to 650 °F (343 °C), no adjustment needs to be made in calculating vessel wall thickness.

3.3 Scada Controlled Process:

The key attribute of a SCADA system is its ability to perform a supervisory operation over a variety of other proprietary devices. The accompanying diagram is a general model which shows functional manufacturing levels using computerized control.

- Level 0 contains the field devices such as flow and temperature sensors, and final control elements, such as control valves.
- Level 1 contains the industrialized input/output (I/O) modules, and their associated distributed electronic processors.
- Level 2 contains the supervisory computers, which collate information from processor nodes on the system, and provide the operator control screens.
- Level 3 is the production control level, which does not directly control the process, but is concerned with monitoring production and targets.
- Level 4 is the production scheduling level.

IV. COST REDUCTION

Cost plays a very important role in the manufacturing process of any product. It defines the overall demand for the product benzyl amine is slightly expensive product as compared due to its complicated manufacturing process. It involves various steps as mentioned. Benzyl amine is very in demand product and is used in minimal quantity in any of its application. Due to formation of polyamines these Benzylamines concentration decreases due to which the yield is less. Hence cost of the product increases and it's difficult to cope up with the market so, the minimal formation of byproduct decreases the cost there by increasing the demand.

V. MARKET STUDY

5.1 Benzylamine Market: Market Segmentation

The Benzylamine market is segmented into four parts based on the industry type, application type, distribution channels, and geography.

5.1.1 Based on the industry type the Benzylamine market is segmented into:

- Agriculture
- Pest Control
- Chemicals
- Paint & Coatings Industry
- Automotive & Transportation Coatings
- Industrial coatings
- Others

5.1.2 Based on the application type the Benzylamine market is segmented into:

- Chemical Manufacturing
- Manufacturing of paints and lacquers
- Manufacturing of pesticide, fertilizer
- Manufacturing of pharmaceuticals
- Others

5.1.3 Based on the type of distribution channels Benzylamine market is segmented into:

- Internet Retailing
- Mass Retailers
- Direct Selling
- Others

5.2 Benzylamine Market: Regional Outlook

Regarding geography, Benzylamine market has been categorized into seven key regions including North America, Western Europe, Eastern Europe, APEJ, Japan, Latin America, and the Middle East & Africa. Benzylamine market is expected to register healthy CAGR during the forecast period. Asia-Pacific represents the significantly high market share and grow with comparatively high CAGR in forecast period. North America is experiencing the rapid increase in the production capacity of Benzylamine as demand for Benzylamine for wide range of end-user in the region is rising at faster pace. Key factors driving the growth of Benzylamine oil market in the region include growing chemical industry, increasing infrastructure across the globe as demand of benzylamine in paints and lacquers is booming at faster pace. The benzylamine market is projected to register healthy growth due rising consumption Benzylamine in various industry for production of their end user products such as in pharmaceutical for manufacturing medicine. Benzylamine market for Asia Pacific is also expected to witness rapid growth during the forecast period primarily attributed to the growth of chemical industry, and increasing production of the product type Especially in China and India. In China, demand of benzylamine is booming due to its usage as raw materials of solvent, alkyl alkanol amines, and ingredients of rocket fuels. With the total production of 2900 tones approximately annually in the market. Fine Orgokem manufactures and supplies 350 tons annually which includes both of the amines class.

5.3 Benzylamine Market: Drivers & Restraints

The major factors driving the growth of benzylamine market is growing demand of Benzylamine in wide range of application such as manufacturing paints and lacquers, pesticide, fertilizer, pharmaceuticals, and others. Moreover, growing chemical industry results to development of new technology for the manufacturing of benzylamine to meet its demand across the globe. Demand of benzylamine is rising, as benzylamine is versatile valuable intermediate for various applications and intermediate and building block in a variety of end-user industry like for the production of active pharma ingredients (APIs) and crop protection agents. In addition benzylamine is used as a masked source of ammonia, meanwhile after N-alkylation, the benzyl group can be separated by hydrogenolysis. Therefore, it is also major source for the derivation of other chemical compound. On the other hand, the major factor restraining the growth of benzylamine market are government regulation and its strong reactional property.

5.4 Feasibility Study:
The major objective of this project is to minimize the formation of Polyamines to its maximum which are formed as byproducts which alter the Costing of the final product (Benzylamine and derivatives) is severely affected. In present investigation the engineering aspects of manufacturing Benzylamines with minimal formation of polyamines is studied. As the chemical aspects for Benzylamines will be studied in detail in this project it is also important to investigate the engineering aspects so as to enable various technological information its engineering methods and future improvements in its technology.

5.5 Need and Significance:
As china is more dominant to the current market for this manufacturing process of benzyl amines hence the cost for the current market for this product is maximum for India as well as the globe. Hence various pharmaceutical company as well as other companies across the globe prefer India for the same. There are only 5-7 manufactures in India who manufacture these specialty product for the globe in large scale which includes Fine Orgokem pvt ltd. So it is needed to manufacture benzyl amines in India for the significant current market in India as well as across the globe.

VI. CONCLUSION

Hence manufacturing of benzyl amines is studies through catalytic hydrogenation of aromatic nitriles. The result of the manufacturing process is conducted and a statistical Output after evaluation of various parameters Utilized is drawn and Purity of 98.56% is achieved**.**

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