PROCESS STUDIES IN A MULTIPHASE REACTOR: *KETAZINE PRODUCTION FROM HYDROGEN PEROXIDE AND AMMONIA*

by

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submitted

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to the

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Dedicated to

... My Dearest

Father, Mother, Husband & Daughter

CERTIFICATE

This is to certify that the thesis entitled, **'PROCESS STUDIES IN A MULTIPHASE REACTOR: Ketazine production from hydrogen peroxide and ammonia'** being submitted by **Ms. Raminder Kaur** to the Indian Institute of Technology, Delhi for award of Doctor of Philosophy is a record of bonafide research work carried out by her under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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ABSTRACT

Abstract

Multiphase reactors play an important role in the development of new processes useful for industrial applications. In general, fine chemicals, agrochemicals, dyestuffs, textile auxiliaries, polymer industries etc all rely on multiphase reactors. The subject of multiphase reactions encompasses a vast field comprising different technological contexts, a broad range of engineering disciplines and a multitude of different analytical approaches. These reactors can be operated in gas-liquid, gas-liquid-solid and gas-liquid-liquid reactions. Some of the important commercial applications of these reactors are hydrogenation of unsaturated oils, hydrodesulphurization of petroleum feedstock, hydro cracking, pollution control and polymer-bound catalysis etc. In chemical industries, commonly available reactors for reactions and multiphase contacting include:

- Stirred Tank Reactors
- Trickle Bed Reactors
- Slurry Bubble Columns
- Plate Columns
- Packed Towers
- Jet/ Loop Reactors

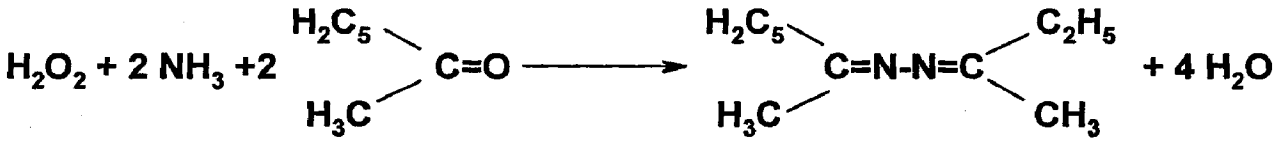
Abstract

Many studies have been carried out to study the behavior and mechanism of gas-liquid-liquid reaction systems in the past decade, but still many fields are virtually neglected and need a lot of attention. The kinetics studies for the formation of methyl ethyl ketazine, a typical gas-liquid-liquid reaction, with highly complex mechanism, can be quoted as a very good example to carry out research. It is fascinating to note that the system initially consist of only two phases, i.e. reactants gas (ammonia) and liquid (mixture of: 46% aqueous hydrogen peroxide, 70% solution of the catalyst acetamide in DM water, and methyl ethyl ketone, all present in a single phase). Although methyl ethyl ketone is organic in nature, it has good solubility in the aqueous mixture of hydrogen peroxide and catalyst acetamide. After the formation of product, due to low miscibility of ketazine in aqueous phase, the system becomes a gas-liquid-liquid system, thus contains three phases: reactant gas phase, lighter organic phase containing the main product i.e., ketazine (and unreacted ketone that got transferred from the single phase present initially to organic layer formed during the course of the reaction) and heavier aqueous phase containing regenerated catalyst and water formed during the reaction. In the present study, the kinetics studies for ketazine preparation have been carried out.

Ketazine is an intermediate in the formation of hydrazine hydrate that is one of the most versatile chemicals finding use in a wide spectrum of applications such as rocket fuel, energy source in fuel cell, blowing agent in plastic industry, in synthesis of organic nitrogen compounds, and in making herbicides and pesticides for agricultural use. Various commercial processes for the manufacture of hydrazine are: Raschig process; Urea process; Bayer process and Peroxide or ketazine process. Peroxide process has

many advantages as compared to the other processes i.e. no salt by-product, high yield, low energy consumption and no requirement of effluent treatment. Also the relative low cost of chemicals makes it more attractive. In peroxide process, hydrogen peroxide is used as an oxidizing agent to oxidize ammonia (NH_3). The reaction is carried out in the presence of methyl ethyl ketone (MEK) at atmospheric pressure and 50^0C. The hydrogen peroxide is activated by acetamide.

Overall reaction for the methyl ethyl ketazine formation, as reported by Kirk and Othmer, 2004 is:



This methyl ethyl ketazine is then hydrolyzed under pressure (0.8-10Mpa) and gives concentrated hydrazine hydrate. The ketazine is distinguished by a much greater stability to oxidation so that it can be produced much more economically than hydrazine. Most hydrazine now a day is produced by peroxide or ketazine process.

In view of the importance of hydrazine and the advantages of eco-friendly peroxide process, and, as ketazine being an important intermediate for hydrazine hydrate, many studies have been carried out for the formation of ketazine using different catalyst systems or the production of hydrazine hydrate through ketazine route, mainly including patents (Schirmann et al., 1976; Eichenhofer and Schliebs, 1976 ; Maekawa and Kume,

1979; Kuriyama et. al, 1983; Schirmann and Tellier, 1993; Kuriyama et al., 1997, Schirmann 2002, 2003, Suresh et al.,2005 and Wang et al.,2006).

The formation of methyl ethyl ketazine is a gas-liquid-liquid reaction with very complicated mechanism. In the reaction, two processes i.e. diffusion of ammonia into the reaction mixture and consumption of peroxide and ammonia by chemical reaction, compete. Moreover, after the phase splitting takes place, the reaction is affected by the transfer of MEK between organic and aqueous phase. The net effect observed is a combination of all these processes. The available literature gives no pertinent information on kinetics studies for methyl ethyl ketazine formation, which is imperative for the commercialization of such a process. The present study is undertaken with an objective to study the effect of various operational parameters on the formation of ketazine. As formation of ketazine from hydrogen peroxide and ammonia is a typical gas-liquid-liquid reaction, it has been carried out in a multiphase reactor system. The experimental data can be good fitted with the rate expression:

$$C_B = k_1 t - \frac{k_1}{k_2}(1 - e^{-k_2 t}) \text{ for } 0 < t < \frac{x_0}{k_1}$$

Where, k_1 and k_2 are the rate constants. From the experimental observations, the reaction for the methyl ethyl ketazine formation from hydrogen peroxide and ammonia is found to be dominated by the mass transfer. The experimental data is in good agreement with the derived model for the ketazine formation at 60^0C and is satisfactory at 40^0C and 50^0C.

From the experimental studies, the desired experimental parameters for carrying out the formation of methyl ethyl ketazine from hydrogen peroxide and ammonia are concluded in Table A1.

Table A1: Parameters for the formation of methyl ethyl ketazine through ketazine process

Parameters	**Value**
Agitation	600 rpm
Ammonia to Peroxide Ratio	3.0
MEK to Peroxide Ratio	4.0
Temperature	60^0C
Catalyst to Peroxide Ratio	2.5

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