

Alternative Route for Synthesis of Urea-Formaldehyde Resin & Its Kinetic Study

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Abstract: Urea-formaldehyde resin is a clear thermosetting synthetic resin used in various ways as textiles, adhesives, surface-coatings, molding resins, laminating resins. It is made by condensing urea with formaldehyde in presence of a catalyst under controlled conditions of heat; pH and molar ratios. Urea formaldehyde resin is in class of strong, odorless, colorless, water soluble and transparent type resins. Conventional urea-formaldehyde resin production is done by using acid catalyst. In this paper a new route for production of urea-formaldehyde resin by using ion exchange resin has been suggested and its kinetic study has been developed. A lab scale production of urea formaldehyde resin has been carried out. Comparison of both processes shows that percentage free formaldehyde present in the product is quite less by using ion exchange resin due to which odor problem is greatly reduced. Formaldehyde affects people in various ways. When present in the air at levels at or above 0.1 ppm, acute health effects can occur including watery eyes; burning sensations in the eyes, nose and throat; nausea; coughing; chest tightness; wheezing; skin rashes; and other irritating effects. Formaldehyde has caused cancer in laboratory animals and may cause cancer in humans; there is no known threshold level below which there is no threat of cancer. The risk depends upon amount and duration of exposure. The new route suggested for the manufacture of urea formaldehyde will not only reduce the hazardous effects of formaldehyde but will also improve the product quality.

Keywords: Urea-formaldehyde Resin, Catalyst, Resin, kinetics, amino resins, Ion exchange Resin.

I. INTRODUCTION

UF resins are based on a manifold reaction of two monomers, urea and formaldehyde. By using different reaction and preparation conditions, a more or less innumerable variety of condensed structures is possible. In the application stage, UF resins are still soluble or dispersed in water. They also can be supplied in the form of spray-dried water-soluble powders. Such structures consist of linear or branched polymeric molecules of various molecular masses. After hardening, UF resins form insoluble three-dimensional networks of thermosetting duromers. Urea-formaldehyde resins are widely used in industry as binders for the production of bonded wood products, particularly particle board, plywood, and various boards. They are usually employed as colloidal aqueous solutions having 60-70% solids content, the solids content being the percentage weight left when a 2 g sample of the resin is heated at atmospheric pressure at 120°

C. for 3 hours. The resins themselves are complex mixtures of various condensation products, ranging from simple methylolated urea's to fairly high molecular weight materials, and the precise properties of any particular resin will depend upon its F: U molar ratio (i.e. the ratio of formaldehyde to urea when used in its manufacture), the type and proportion of the various linkages within the resin structure, and the proportions of high and low molecular weight material. These last two factors are dependent upon the precise manufacturing method that is used. It was first synthesized in 1884 by Hölzer, who was working with Bernhard Tollens. In 1919, Hanns John (1891–1942) of Prague, Czechoslovakia Urea-formaldehyde resin is a clear thermosetting synthetic resin used in various ways as textiles, adhesives, surface-coatings, molding resins, laminating resins. It is made by condensing urea with formaldehyde in presence of a catalyst under controlled conditions of heat; pH and molar ratios. Urea formaldehyde resin is in class of strong, odorless, colorless, water soluble and transparent type resins. obtained the first patent for urea-formaldehyde resin.

II. REACTION MECHANISM

The first step in preparation is an addition reaction between the amide groups on urea or melamine and formaldehyde to form methylol compounds shown in figure 1. These reactions, which are reversible, occur readily at room temperature under neutral to form alkaline conditions. Urea to formaldehyde reaction forms monomethylol and dimethylol compounds.

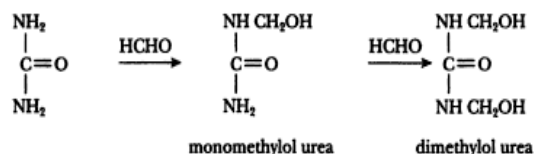


Fig. 1. Addition of Formaldehyde to Urea and Melamine

Methylol compounds can be isolated and characterized, but are difficult to obtain in pure form due to their instability. The addition products can polymerize via a condensation reaction mechanism, reaction taking place between two methylol groups or a methylol group and an active hydrogen atom shown in figure 2.

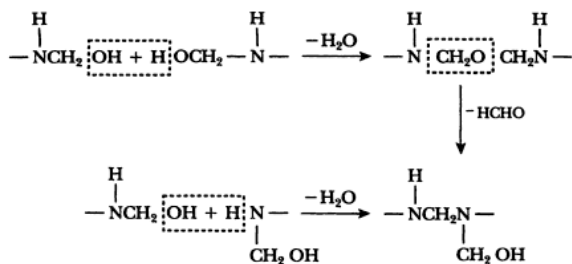


Fig. 2. Condensation of Methylol Groups

The reaction will be accelerated by heat and acid, and under these conditions, the methylene ether linkage will normally rearrange to form the more stable methylene bridge. Complete polymerization of dimethylol urea will lead to the theoretical structure shown in figure 3.

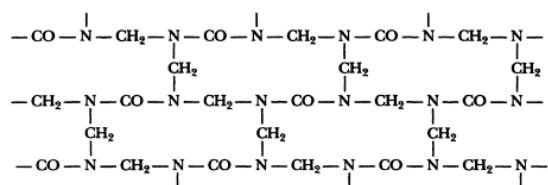


Fig. 3. Cross-Linked Urea Formaldehyde Resin

III. CONVENTIONAL MANUFACTURING PROCESS

Conventional process produces the urea formaldehyde using polycondensation reaction. Raw material butanol and formaline is fed to reactor which forms an acidic solution. According to the pH obtained for this solution, the 10% NaOH is added to neutralise the solution. Formaline used contains 37% of formaldehyde solution. Urea is being added to the neutralised solution and temperature is raised to 60°C-65°C. Once the temperature between 60-65°C is achieved the heating is closed for 90 minutes and again the temperature is raised to 70°C-85°C without any heating apparatus. Meanwhile toluene is added with the application of continuous heating in receiver to separate butanol-water system. Toluene is used as a solvent for separation purpose. The butanol water solution is fed to the condenser where the polycondensation reaction takes place. Reaction produces monomethylol and dimethylol urea as an intermediate product according to the residence time given in the condenser. Basically condenser will separate butanol and water. Once the reflux is started, catalyst (Phthalic anhydride + oxalic acid + butanol) is added in the mixture. Based on quantity of water recovered butanol and catalyst is added in the mixture and temperature is noted down. To avoid the formation of white milky fluid, another catalyst (butanol + phosphoric acid) is added. When water is completely removed, the reflux will stop which will ultimately separate the butanol. Viscosity is measured when the recovery of butanol is started. Particular range of viscosity will produce the required quality of urea formaldehyde. Finally the urea formaldehyde is analysed by measuring

properties like viscosity, acid value, solid content, solubility, Colour etc.

IV. ALTERNATIVE ROUTE FOR SYNTHESIS OF UREA-FORMALDEHYDE RESIN

The new route decreases the free formaldehyde in the process by replacing the conventional catalyst with the new catalyst. The conventional process uses the acid catalyst which is replaced by ion-exchange resin catalyst in new route. The new route is the same as that of conventional one but the only change is associated with the catalyst. The acid catalyst is added in three parts throughout the process in gap of particular time specified but the ion exchange catalyst is added only once in the process. This decreases the labour cost to the plant. New catalyst added can be recovered back from the process and can also be regenerated back to the original one.

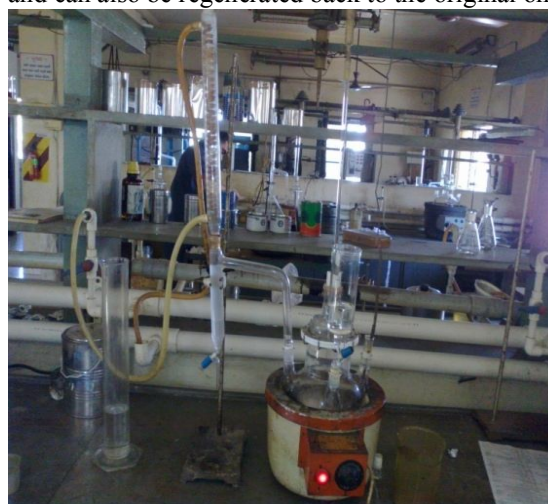


Fig. 4. Setup for Urea Formaldehyde Resin Production

V. KINETIC STUDY

For kinetic study of urea-formaldehyde resin, samples were taken at different time intervals and the concentrations were found out from limiting reactant by % free formaldehyde measured. For kinetics of urea-formaldehyde differential method of analysis is used.

$$C_A = N_A / V$$

$$-r_A = (-dC_A / dt) = k C_A^n$$

Table 1 Concentration-Time Data

Time (min)	Weight	% Free formaldehyde	concentration C_A (mol/lit)
0	-	-	4.57
120	2.239	4.96	1.323
180	2.389	3.324	0.8864
240	0.844	2.41	0.643
300	0.587	1.948	0.5195
360	2.258	0.4924	0.131

In differential method of analysis

1. Plot the C_A vs t data, and draw a curve to represent the data.

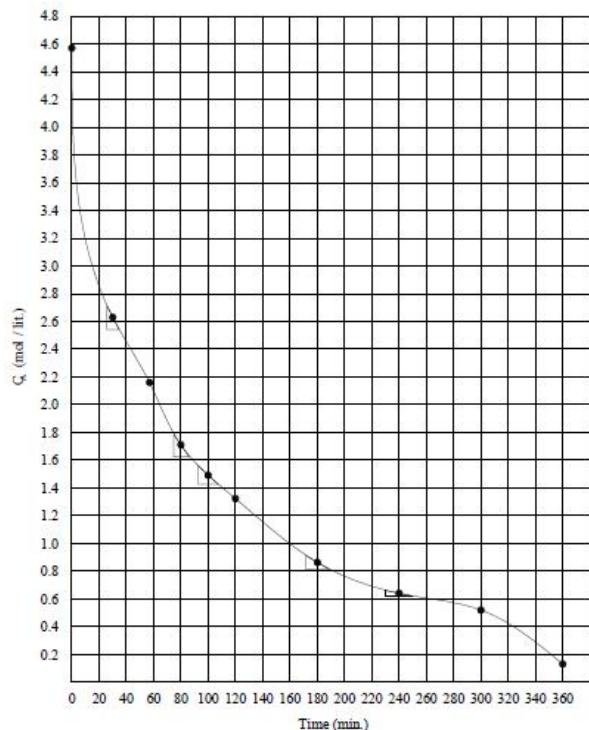


Fig. 5. Concentration VS time

As time increases the concentration of urea-formaldehyde resin decreases because as the formation of monomethylol, dimethylol and polycondensation reaction takes place.

2. Determine the slopes of this curve at suitably selected concentration values. These slopes $dC_A/dt = r_A$ are the rates of reaction at these compositions.

3. Now search for a rate expression to represent this r_A vs C_A data by testing an n^{th} order form kC_A^n by taking logarithms of this rate equation. $y = mx + c$ is compared with $\log(-r_A) = \log(-dC_A/dt) = \log_{10}k + n \log_{10}C_A$.

Table 2 Evaluation of Order of Reaction

Concentration (C_A)(mol/lit)	$(-dC_A/dt)$	$\log(-dC_A/dt)$	$\log C_A$
2.63	0.019	-1.72125	0.419956
1.71	0.0142	-1.84771	0.232996
1.49	0.00903	-2.04412	0.173186
0.86	0.0058	-2.23665	-0.0655
0.64	0.00203	-2.69224	-0.19382

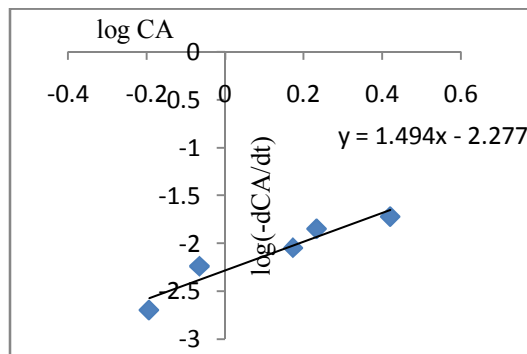


Fig. 6. Estimation of order and rate constant of the reaction

VI. COMPARISON OF BOTH ROUTES

Based on the experiment performed using both acid catalyst and ion exchange resin catalyst for the production of Urea-formaldehyde resin, the following differences can be seen as shown in the table below:

Table 3 Comparison of Acid Catalyst & Ion Exchange Resin Catalyst

Catalyst	Acid Catalyst	Ion Exchange Resin
Quantity of urea-formaldehyde resin(g)	1545	1580
Recovered butanol(g)	680	825
Viscosity(poise)	20	19
Acid value(mg KOH/g)	1.4042	0.9203
Solubility with MTO	Infinite	Infinite
Solubility with mix- xylene	1:3	1:5
% solid content	64.11	65.11
%free formaldehyde	0.8913	0.4813

Comparing both processes we can say that % free formaldehyde is quite less by urea-formaldehyde using Ion exchange resin catalyst due to that odour problem not occurs. Formaldehyde affects people in various ways. The risk depends upon amount and duration of exposure. As per government regulations have forced amino resin producers to produce higher solid resins to reduce the level of volatile organic compounds emitted by paints.

VII. RESULTS & DISCUSSION

Effect of change in catalyst weight

By changing the amount of ion exchange resin catalyst and seeing the effect of rate constant, quantity, %free formaldehyde and order of reaction. We changed catalyst weight in gm. as 50, 40, 30, 20, and 10 respectively. By changing the amount of catalyst weight the order of reaction is getting 2^{nd} order, quantity and quality of urea-formaldehyde also increases and % free formaldehyde which getting is decreases that reduces the hazardous effect of urea-formaldehyde resin.

Table 4 Effect of Change in Catalyst Weight

Amount of catalyst (g)	Order of reaction (n)	Rate constant (k)	Quantity of urea-formaldehyde resin(g)	% free formaldehyde
50	2	0.005	1980	0.4924
40	2	0.0166	1990	0.4711
30	2	0.013	2055	0.4407
20	2	0.0107	2105	0.3971
10	2	0.0276	2130	0.378

VIII. CONCLUSION

It can be concluded that the application of new route in place of conventional one can reduce the hazard to a large extent. The new route requires one time investment of catalyst as it can be regenerated back to its original state to use it back in the same process also it increase the quantity and quality of product as well. The new route is costlier than the conventional process but the hazard associated with the process is decreased. Cost is immaterial with respect to the hazards to mankind. By studying the kinetics of urea-formaldehyde resin using a new route suggests that reaction is of 2nd order.

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