Catalytic Depolymerization of Polyurethene Using Zinc and Lead

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Abstract: *Neutral hydrolytic depolymerization of the Polyurethane (PU) Foam waste was done using 0.5 L high pressure autoclave at temperatures of $150^0, 180^0, 200^0$ and 240^0 C, the autogenious pressures of 75, 160, 220 and 480 psi and time intervals of 30, 45, 60 and 90 minutes. Extent of depolymerization of polyurathene was studied by measuring the amine value of the product. Optimum amount of catalysts such as zinc acetate and lead acetate was found to be 1g. Zinc acetate was more effective catalyst than lead acetate for the depolymerization of PU foam reaction. On the basis of amine value and residual weight of the depolymerized product, the velocity constant was obtained and found to be in order of 10^{-3} min^{-1}; and the reaction was found to be first order. The energy of activation and frequency factor obtained by Arrhenius plot were 36.86 kJ mole $^{-1}$ and 1.349×10^2 min^{-1} respectively. The enthalpy of activation at 150^0C, 180^0C, 200^0C, and 240^0C was recorded as 43.89, 44.39, 44.72 and 45.37 kJmole^{-1} respectively. The entropy of activation at the respective temperatures was recorded as 10.37×10^{-2}, 9.79×10^{-2}, 9.45×10^{-2} and 8.84×10^{-2} kJ mole^{-1}.*

Keywords: *Energy of Activation, Depolymerization, Kinetics, Free Energy of Activation*

1. INTRODUCTION

Hydrolysis, glycolysis and aminolysis are well known processes used for depolymerization of PU in to amines and polyols. Polyurethane on hydrolysis produces primary polyols, carbon dioxide and the amine of conjugate isocynate. Depolymerization of PU foam by alcoholysis uses alcohol as the cracking agent. Alcoholysis and hydrolysis proceed in similar way, having slight difference in chemical reaction. Different rout is responsible for getting entirely different products. As polyurethane production increases, the amount of PU waste also increases. Traditional methods of destroying this waste are not particularly acceptable. Burning of polyurethane waste sends oxides of nitrogen, hydrocyanic acid, carbon dioxide and other toxic compounds in the atmosphere. When it is buried, it is broken down by action of water to give urea. This process causes pollution of air and water in environment. The most effective method of polyurethane waste processing is glycolysis, based on thermo-chemical interaction between polyurethane and hydroxyl containing compounds[1-2]. Literature survey indicates, glycolysis process can be used to resolve the disposal problems of PU waste and with obtaining high quality of polyols. Kouji et al[3] have indicated the method to design a comfort path of PU recycling. The degradation of polyurethane foam was carried out with diethylene glycol as a solvent and sodium hydroxide as the catalyst[4]. In the present work PU waste was depolymerized by neutral hydrolytic process in presence of zinc acetate and lead acetate as catalysts. The amount of catalyst was optimized.

2. EXPERIMENTAL

5 g PU foam, 300 ml water and catalyst of definite amount were charged in the reaction vessel. The reaction was carried out for 60 minutes at temperature 180^0C by varying the amount of catalysts from 0.4-1.2 g. Further the reaction was carried out using optimized amount of catalyst by varying the temperature from 150^0, 180^0, 200^0 and 240^0 C for the reaction time of 30, 45, 60 and 90 minutes. After the specified reaction time the vessel was cooled suddenly by circulating cold water through the inner coil. The vessel was opened by removing collar of reactor of high-pressure autoclave. Obtained product was cooled to room temperature. The reactant was filtered using Whatman filter paper. Amine values were determined using one gram of depolymerized

product by AOCS method

$$\text{Amine value} = \frac{\text{Equivalence point x N x 56.1}}{W}$$

W = Weight of sample in gram.

N = Exact Normality of HCl

The depolymerized product was taken for recovery of value added product. It was recovered by adding potassium hydroxide into depolymerized product. The recovered salt was characterized by recording FTIR spectra on Hyper FTIR of SHIMANDZU make.

3. RESULTS AND DISCUSSION

3.1. Optimization of Catalysts Concentration for Depolymerization of PU Foam

Depolymerization of PU foam waste was studied using lead acetate and zinc acetate as catalysts. Both the catalysts were taken from 0.4 g to 1.2 g using, 5 g of PU foam waste in 300 ml water at temperature of 180^0C and autogenious pressure of 160 psi for reaction time of 60 minutes. Results show an increase in percent conversion of PU foam waste with increase in amount of the catalysts,100% and 71% PU foam was found to be depolymerized by taking 1g of zinc acetate and lead acetate respectively. Further increase in amount of catalyst results decrease in percent conversion in case of lead acetate (Figure 1). Hence the optimized amount of catalyst for the depolymerization reaction is found to be 1 g for both zinc acetate and lead acetate. Decrease in percent conversion beyond optimized amount is might be due to occurring of reverse reaction at higher concentration of catalyst.
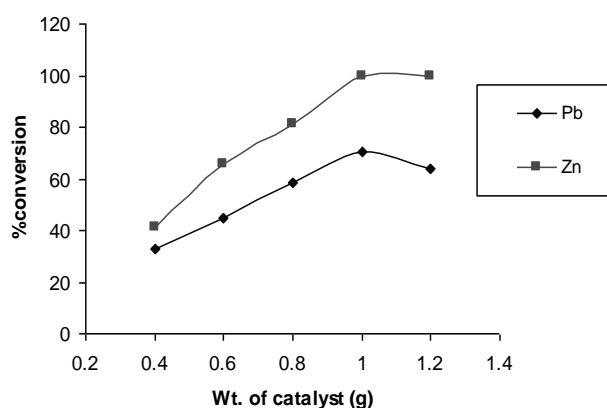

Fig1. *Depolymerization of PU foam waste with catalysts at180^0 C and 160 psi autogenious pressure for the reaction time 60 minutes.*

To measure the depolymerization value of PU foam waste, amine value of depolymerized product was determined (Figure 2). Behavior of the figure 2 is exactly same as that of figure 1. It shows an increase in amine value with increase in concentration of catalyst up to 1g and thereafter there is slight decrease in amine value for both the catalysts. It is also evident from this figure that the optimum weight of catalyst for depolymerization of 5 g PU foam waste is 1 g.
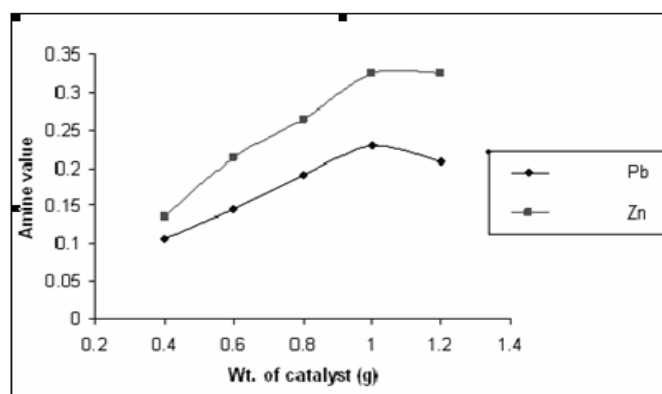

Fig2. *Effect of catalyst on depolymerization of PU foam waste at 180^{0}C by measuring the amine value.*

Figure 3 shows the results of amine values of depolymerized PU foam with increasing reaction time from 30 minute to 90 minute at 1 g of optimized amount of catalyst at 180^0C temperature and at autogenious pressure of 160 psi . The amine values increase with increase in time from 30-90 minute of reaction time in case of zinc acetate and uncatalysed reaction. The increments in amine value are recorded as 0.2246 for 30 minute reaction time and 0.3358 for 90 minute reaction time for zinc acetate. These values are highest for respective reaction times of lead acetate and uncatalysed reactions. It is worthy to mention that the lead acetate shows increase in amine value up to 0.3011 for 60 minute and thereafter it decreases to 0.2884 for 90 minutes of the reaction time. But it is also evident that zinc acetate catalyst is an effective catalyst for the depolymerization of PU foam waste, as the amine value is always greater at any instant as compared to that of lead acetate and without catalyst. Hence in this study we have undertaken the optimized amount (1 g) of zinc acetate catalyst for all the depolymerization reactions.
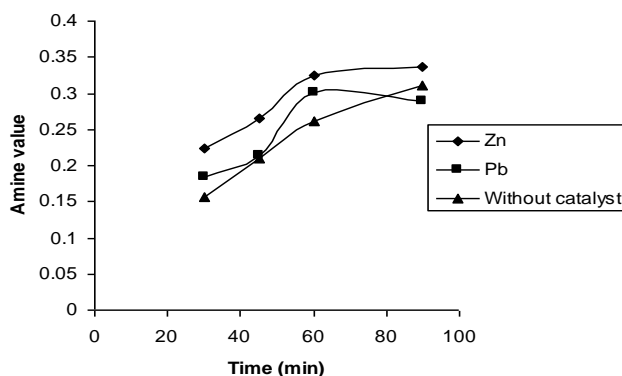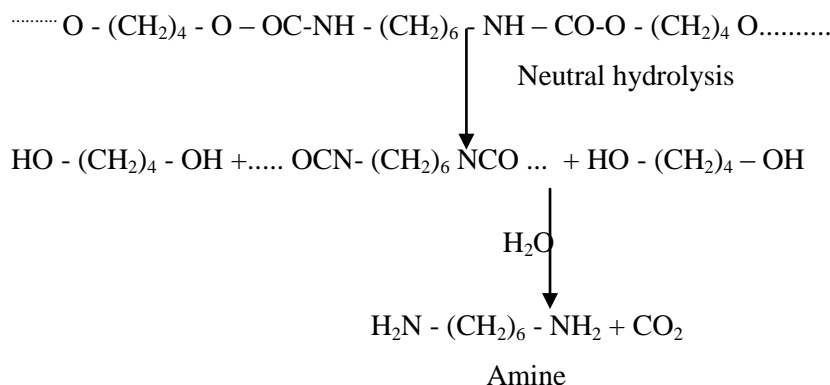

Fig3. *Effect of reaction time on depolymerization of PU foam waste with and without catalysts at 180^0C reaction temperature.*

3.2. Kinetics of Depolymerization of PU Foam Waste

PU foam on depolymerization breaks into fragments of NCO groups. The rate of depolymerization depends on number of NCO groups produced.

The NCO-groups produced in depolymerization reaction react with water to form amine; hence, rate of depolymerization is decided by measuring amine value at various time intervals.

The mechanism of the reaction can be represented as,

········ O - $(CH_2)_4$ - O – OC-NH - $(CH_2)_6$ ⌐ NH – CO-O - $(CH_2)_4$ O..........

Neutral hydrolysis

HO - $(CH_2)_4$ - OH +..... OCN- $(CH_2)_6$ NCO ... + HO - $(CH_2)_4$ – OH

H_2O

H_2N - $(CH_2)_6$ - NH_2 + CO_2

Amine

The rate of depolymerization was determined by measuring the amine value of the reaction product as well as residual weight of the PU foam waste. Amine value at zero time measures amine groups available at zero time. Similarly the amine value at $t = \infty$ is a measurement of total amine groups present after the completion of reaction. The first order kinetic model proposed by auothers[5] was found to be fit for our study using different catalyst,

k = 1/ t [- ℓn (1-Amine value)]   (1)

Equation (1) was used to calculate the velocity constant of depolymerization of PU foam on the basis of measurement of amine value. The values obtained for velocity constant at temperature 180^0C and at autogenious pressures of 160 psi were plotted against the weight of the catalysts. Figure 4 shows velocity constants, which are obtained maximum (6.56 x10^{-3} and 4.36 x10^{-3} for

zinc acetate and lead acetate respectively) for 1 g of the catalysts. The values of velocity constants are recorded as 6.56 x10 $^{-3}$ and 3.88 x10^{-3} for zinc acetate and lead acetate at 1.2 g of catalysts. Thus it can be concluded that below optimum amount of the catalysts the reaction is slow in case of both the catalysts, and above the optimum amount the reverse reaction is there in case of lead acetate.
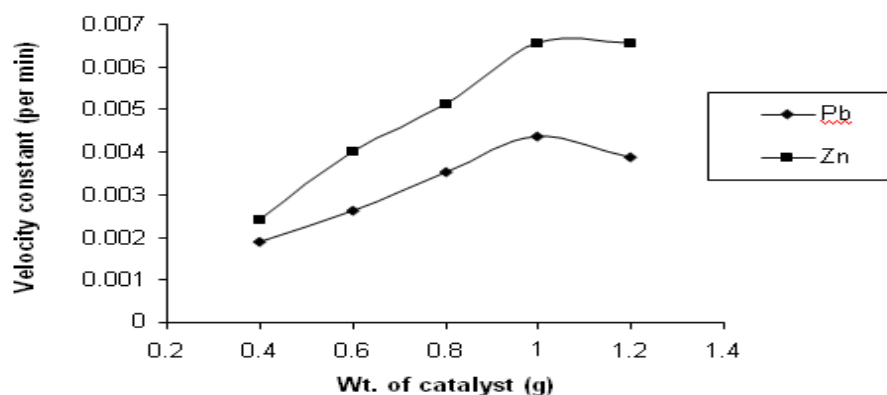

Fig4. *Effect of amount of catalyst on velocity constants (min $^{-1}$) for depolymerization of PU foam waste at 180^{0}C*

Velocity constants of the depolymerization reactions are also determined by using residual weight left after the complete reaction by equation as given below,

$$k = \frac{2.303}{t} \log \frac{C_o}{C_t} \tag{2}$$

Where $[C]_O$ is the concentration of the reactant at time $t = 0$ and $[C]_t$ is the concentration of the reactant at time t. It is observed that the velocity constants obtained by equation (1) and (2) are identical and are of the order of 10^{-3} min.$^{-1}$

Figure 5 shows an increment in the velocity constant with temperature at all the time intervals. An increase in velocity constants of the reactions is due to higher kinetic energy of the molecule obtained by thermal agitation. However, as reaction time increases the velocity constant decreases. The velocity constants increase for the 30 minutes reaction time but subsequently, at 45, 60 and 90 minutes, these values decrease successively for all respective temperatures, since the product of the reaction was not removed. It might be due to a Le-Chatelier effect [6].
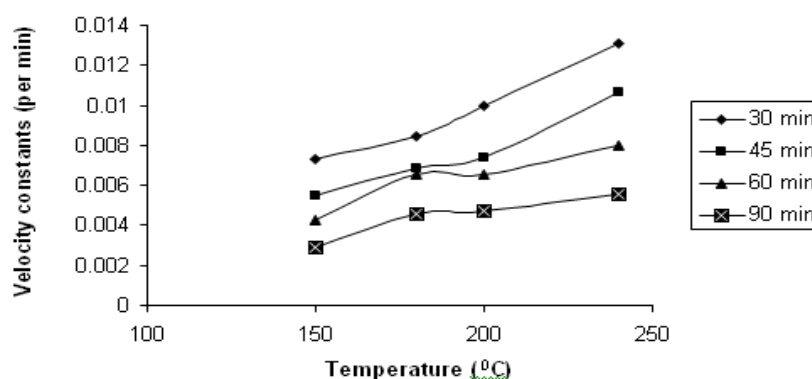

Fig5. *Effect of temperatures on velocity constants at different reaction time interval using optimized zinc acetate catalyst.*

The amine value at 150^0 C remains almost constant (0.22) at various time intervals. Figure (6). While variation in amine value increases up to 0.32 with time at 180^0 C and 200^0 C. Further the amine values remain almost constant at these temperatures. The degree of depolymerization is significant at 240^0 C. Initially up till 45 minutes reaction time, amine value gradually increases to 0.38 and thereafter it remains constant.
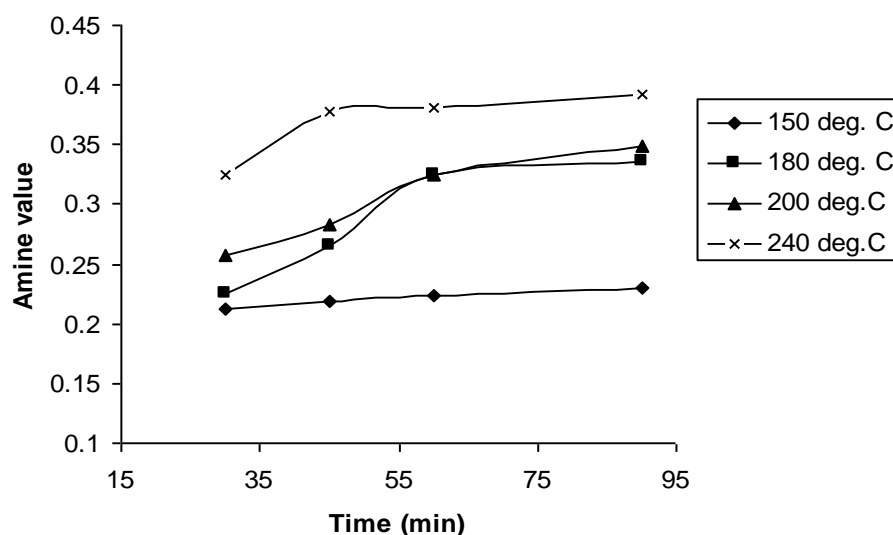
Fig6. *Effect of reaction time for depolymerization on amine value at different temperatures using optimized zinc acetate catalyst*

As per the reaction mechanism shown earlier, each chain scission utilizes one water molecule to form one each of amine and glycol end groups. Therefore, the progress of the reaction was studied by measuring concentrations of amine groups after the definite reaction time.

The rate of amine end group formation may be expressed as ,

$$d[-NH_2] / dt = k [PU][water] – k' [-NH_2] [OH] \tag{3}$$

Therefore, the equilibrium constant Ke is given as,

$$Ke = k / k' \tag{4}$$

Where, k = the rate constant of forward reaction (depolymerization),

k' = the rate of reverse reaction (condensation),

[PU] = concentration of polyurethane foam,

[Water] = concentration of water,

$[-NH_2]$ = concentration of amine end group,

[OH] = concentration of hydroxyl end group

Equations 4 was used to calculate rate constant of reverse reaction and hence the equilibrium constants were determined. The results of comparative study of velocity constants with and without catalyst of depolymerization reaction at temperatures $100^0, 150^0, 180^0, 200^0,$ and 240^0 C and at autogenious pressure were studied by Mishra et al[6]. The values of velocity constants obtained by measuring residual weight and amine values were found to be identical and these are in order of 10^{-3} min^{-1}. It indicates that the mathematical first order kinetics model proposed by Mishra et al[6] is justified.

3.3. Thermodynamics of Depolymerization of PU Foam Waste

Arrhenius plot was used to elucidate the activation energy. The energy of activation for depolymerization of PU foam waste was obtained by studying the depolymerization reaction at the temperatures ranging from 150^0 C to 240^0 C. The Arrhenius plot was drawn using the values of ln k versus 1/T. The slope of Arrhenius plot was found to be 4433.6 unit which was used to calculate the energy of activation. The energy of activation for depolymerization of PU foam waste was calculated as 36.86 kJ mole^{-1} (Figure 7). The intercept of Arrhenius plot is 4.9046 units, which is used to determine the frequency factor of the reaction, and it is found to be 1.349×10^2 min^{-1}. It shows that reactant molecules collide with each other with the frequency 1.349×10^2 min^{-1}.
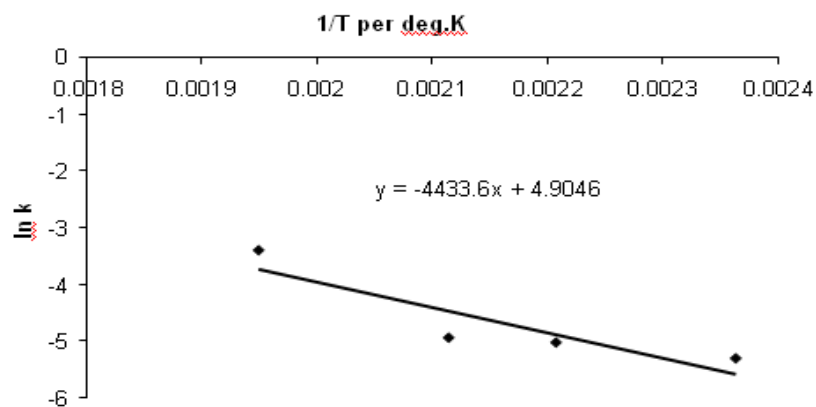
Fig7. *Arrhenius plot of variation of velocity constant (ln k) versus reciprocal of absolute temperature (1/T)*

4. CONCLUSION

The enthalpy of activation at various temperatures was obtained using the equation[7] $\Delta H = E_a + 2RT$. The minimum value of ΔH (43.89 kJ mole^{-1}) was recorded for 150^0C reaction temperature, while maximum (45.37 kJ mole^{-1}) for 240^0 C; on recording the entropy, the values are vice versa. It is evident from the values that as temperature increases, enthalpy of activation increases while entropy of activation decreases. The decrease in entropy with increase in temperature is due to higher rate of depolymerization so that conversion of PU foam waste obtained at early time.

Kinetic and thermodynamic parameters such as velocity constant for forward reaction (k), velocity constant for reverse reaction (k'), thermodynamic equilibrium constant (Ke) and Gibbs free energy (ΔG) at temperature 180^0C and for 60 minutes reaction time are summarized in Table1. Results show that as the amount of the catalyst increases the Gibbs free energy of activation also increases up to 1 g of catalyst. Hence this amount is an optimum amount for depolymerization of PU foam waste. Same behavior is observed for zinc acetate catalyst, however the values of k, k'and ΔG can not be evaluated since residual weight was not available due to complete disappearance of the reactant. However in case of lead acetate, the value of Ke is recorded in decreasing order from 32.38 to 5.99 for 0.4 to 1.0 g .Thereafter the value of Ke increases up to 7.58 for 1.2 g of lead acetate catalyst. Likewise value of ΔG increases up to 1 g of catalyst and further decreases for 1.2 g of lead acetate. Thus it is concluded that reversible reaction becomes more pronounced beyond 1 g of lead acetate as catalyst.

Table1. *Kinetic and Thermodynamic parameters for depolymerization of PU foam waste at 180^0 C using different catalysts.*

Weight (g)	Lead acetate catalyst				Zinc acetate catalyst			
	k x10^{-3} min^{-1}	k ' x10^{-4} min^{-1}	Ke	-Δ G kJ mole^{-1}	k x10^{-3} min^{-1}	k ' x10^{-4} min^{-1}	Ke	-ΔG kJ mole^{-1}
0.4	1.878	0.57	32.38	13.097	2.71	1.393	19.45	11.177
0.6	2.627	1.572	16.71	10.605	4.31	6.019	7.16	7.413
0.8	3.527	3.799	9.28	8.390	5.316	11.210	4.38	5.562
1.0	4.356	7.262	5.998	6.746	-	-	-	-
1.2	3.878	5.110	7.586	7.631	-	-	-	-

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