The Nature of Acid-Catalyzed Acetalization Reaction of 1,2-Propylene Glycol and Acetaldehyde

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Abstract – We investigated catalytic activity of ion-exchange resins in acetalization of 1,2-propylene glycol with acetaldehyde. The impacts of reaction variables, such as temperature, reaction time, catalyst loading and feedstock composition, on the conversion of 1,2-propylene glycol were measured. The life of the catalyst was also studied. Furthermore, the reaction kinetics of 1,2-propylene glycol acetalization was studied. It was found that reaction rate followed the first-order kinetics to acetaldehyde and 1,2-propylene glycol, respectively. Therefore, overall acetalization reaction should follow the second-order reaction kinetics, expressed as $r = kC_A^{nA}C_B^{nB} = 19.74e^{\frac{-6650}{T}}C_A^1C_B^1$.

Key words: 1,2-propylene Glycol, 2,4-dimethyl-1,3-dioxolane, Ion-exchange Resin, Polyhydroxy Compounds, Acetalization

1. Introduction

Polyhydroxy compounds such as 1,2-propylene glycol (PG) and ethylene glycol are important chemical intermediates widely used in producing polyester, surfactant, lubricant, and adhesives [1-5]. PG is difficult and expensive to recover from aqueous solution because of its high boiling point and affinity with water. Reactive distillation was reported to be applied to PG purification [6]. In the reactive distillation column where an acid catalyst is present, PG reacts reversibly with acetaldehyde to form 2,4-dimethyl-1,3-dioxolane. The reaction is known as an acetalization reaction. The reaction pathway involves protonation of acetaldehyde followed by the addition of nucleophilic PG molecule to the carbonyl group to form an intermediate, which is hemiacetal. In the presence of an acid catalyst, etherification reaction occurs within hemiacetal molecule to form 2,4-dimethyl-1,3-dioxolane and water [7]. The reaction equation is shown in Scheme 1.

The acidic function on solid acid catalyst is important in activating PG molecule to facilitate acetalization reaction. Ion-exchange resins are very effective in catalyzing acetal formation [8,9]. The use of heterogeneous ion-exchange resin catalysts offers many advantages over homogeneous acidic catalyst. Dhale *et al.* studied the recovery of
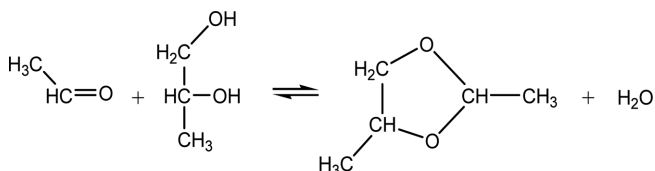
Scheme 1. Reaction equation of PG and acetaldehyde.

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1,2-propylene glycol from water via acetal formation using ion-exchange resins as catalysts in reactive distillation [6]. Acid-catalyzed acetalization is used to obtain intermediates or final compounds. In the past few decades, most of the studies reported in the literature for acetalization reactions focused on analyzing and comparing the activity of the solid catalysts [10]. However, in a recent trend, researchers directed their attention to the acidic macroporous resin to protect the environment. Acetaldehyde and 1,2-propylene glycol can be recovered and purified via the reverse hydrolysis reaction. High yield of 2,4-dimethyl-1,3-dioxolane can be obtained in the equilibrium limited reaction by removing the products [11]. Although there have been several studies describing the recovery of aqueous glycol solution via reactive extraction and reactive distillation [12-14], systematic experimental data, especially kinetic modeling work, have not been reported.

This study presents a comprehensive investigation on the formation of acetals via reaction between PG and acetaldehyde using an ion-exchange resin catalyst. The objective of this research was to measure the catalytic activity of ion-exchange resin catalysts in PG acetalization under various reaction conditions and to determine the optimal conditions for the formation of acetals. The specific objective was to elucidate equilibrium reaction and kinetics of the acetalization reaction [15]. The experimental data obtained from this research serves as a basis for the design of commercial reactive distillation column for acetalization reaction of polyhydroxy compounds [16].

2. Experimental Section

2-1. Apparatus and Procedure

Analytical grade PG and acetaldehyde (40 wt% solution) were used in all experiments. The ion-exchanged resin, D072, was purchased from the Chemical Plant of Nankai University, Tianjin, China. The physical properties of the resin D072 are listed in Table 1. The strong

Table 1. The basic properties of D072

Type	D072
The structure of resin	Styrene-DVB
Functional group	-SO$_3^-$
Ion-exchange capacity (mmol/g)	≥4.2
Granularity (0.315~1.25 mm)	≥95
The highest temperature (°C)	Na 120
PH range	1~14
The factory form	Na
Foreign reference product	Amberlyst-15; Diaion HPK-16

acidic ion-exchange resin possesses high ion exchange rate. The resin framework consists of an irregular, macromolecular and three-dimensional network of hydrocarbon chains. The matrix carries sulfonic acid -SO$_3$H as a functional group on the surface.

The reaction temperature, reaction time, catalyst loading and acetaldehyde/PG volume ratio were variables measured in catalytic performance test and kinetic study. After the reaction, the catalyst was separated by centrifugation. A typical experiment procedure was as follows: 100 ml acetaldehyde, 40 ml PG (acetaldehyde/PG volume ratio=2.5:1) and 3.5 g D072 (25 g/L) were used in a 250 ml glass reactor, respectively. Experiments were under ambient pressure in a constant temperature bath at 288 K with a stirring speed of 150 rpm.

Small amount of sample (0.2 micron liter) was drawn at 30 minutes time interval for GC analysis.

2-2. Analytical Method

The PG was analyzed by GC (Ling Hua 9890A gas chromatograph equipped with FID detector and an SE-54 capillary column, 50 m × 0.32 mm × 2.0 μm). Column temperature was programmed to maintain at 333 K for 5.5 min initially, then increased to 473 K at the rate of 298 K/min. The concentration of PG was determined by using the internal standard method. Tetrahydrofuran was chosen as an internal standard for GC calibration. The PG conversion was calculated by using the following formula:

$$\Phi = [(C_0 - C_t) / C_0] \times 100\%$$

where C_0 is the initial concentration of PG and C_t is the concentration of PG at a reaction time of t.

3. Results and Discussion

3-1. The Impact of Reaction Variables on PG Acetalization

PG acetalization is an equilibrium-limited reaction; therefore, some reaction variables affect the time and extent to reach equilibrium state. The dependence of PG conversion on key reaction variables was investigated. These reaction variables include temperature, reaction time, catalyst loading and the acetaldehyde/PG volume ratio.

The effect of reaction temperature on PG conversion over Resin D072 catalyst is illustrated in Fig. 1(a). By raising temperature from 273 K to 288 K, PG conversion significantly increases, reaching maximum conversion of 90.3±0.3% at 288 K. PG conversion starts to

decline when temperature is continually increased. Below 288 K, PG acetalization reaction is a kinetically controlled region, i.e., forward reaction rate is faster than reverse reaction rate and reaction is not in equilibrium state. When reaction temperature is increased to approach 288 K, the reverse reaction rate is increased at a faster pace to equal the forward reaction rate; then equilibrium state is reached. When reaction temperature is further increased beyond 288 K, the reverse reaction rate is greater than the forward reaction rate, PG conversion decreases, shifting equilibrium to the left; therefore, a downward PG conversion curve is observed. PG acetalization is an exothermic reaction. Thermodynamically, an increase in reaction temperature favors reverse reaction. Experimental results shown in Fig. 1(a) indicate that at a reaction temperature greater than 288 K, PG acetalization reaction is in equilibrium controlled region.

The impact of reaction time on PG conversion is shown Fig. 1(b). Initially, PG conversion increases sharply, then starts to level off as the reaction proceeds. At 180 min, PG conversion reaches 90.3±0.3% and remains at this level as the reaction continues. This indicates that the reaction has reached equilibrium under the experimental conditions. The ion-exchange resin catalysts are essential for PG acetalization to yield 2,4-dimethyl-1,3-dioxolane. The effect of catalyst loading on PG conversion was studied. Resin D072 catalyst was used and each experiment was at 288 K, 3 hours reaction time with acetaldehyde/PG volume ratio being 2.5:1. As shown in Fig. 1(c), PG conversion increases as catalyst loading is increased from 10 g/L to 25 g/L. The increase in reaction rate can be attributed to the increase in the total number of acid sites available for acetalization. Nevertheless, further increase in the catalyst loading beyond 30 g/L does not show any significant enhancement in PG conversion. Therefore, the optimal catalyst loading is determined to be 25 g/L for the PG acetalization reaction. The increase in PG conversion with the increase in the amount of catalyst loading is associated with the number of available active sites for acetalization of PG.

PG acetalization with acetaldehyde is an equilibrium limited reaction. To maximize PG conversion, an excess amount of acetaldehyde is necessary to shift equilibrium to the right. The effect of acetaldehyde/PG volume ratio on PG conversion was studied under the conditions of 288 K, catalyst loading of 25 g/L and 3 hours reaction time. The acetaldehyde/PG volume ratio was varied from 0.5:1 to 3.5:1. The relationship between acetaldehyde/PG volume ratio and PG conversion is shown in Fig. 1(d). When acetaldehyde/PG volume ratio is increased from 0.5:1 to 2.5:1, PG conversion increases and reaches a maximum of 90.3±0.3%, after which a steep decrease in PG conversion is observed. The upward PG conversion curve at acetaldehyde/PG volume ratio less than 2.5:1 can be explained by the shift of equilibrium to the direction that favors acetal formation because of the increase in acetaldehyde concentration. However, because acetaldehyde is introduced as 40% water solution, further increase in acetaldehyde/PG volume ratio actually leads to a decrease in PG concentration; the equilibrium can shift to the left that favors hydrolysis of 2,4-dimethyl-1,3-dioxolane, so a downward PG conversion curve is observed.
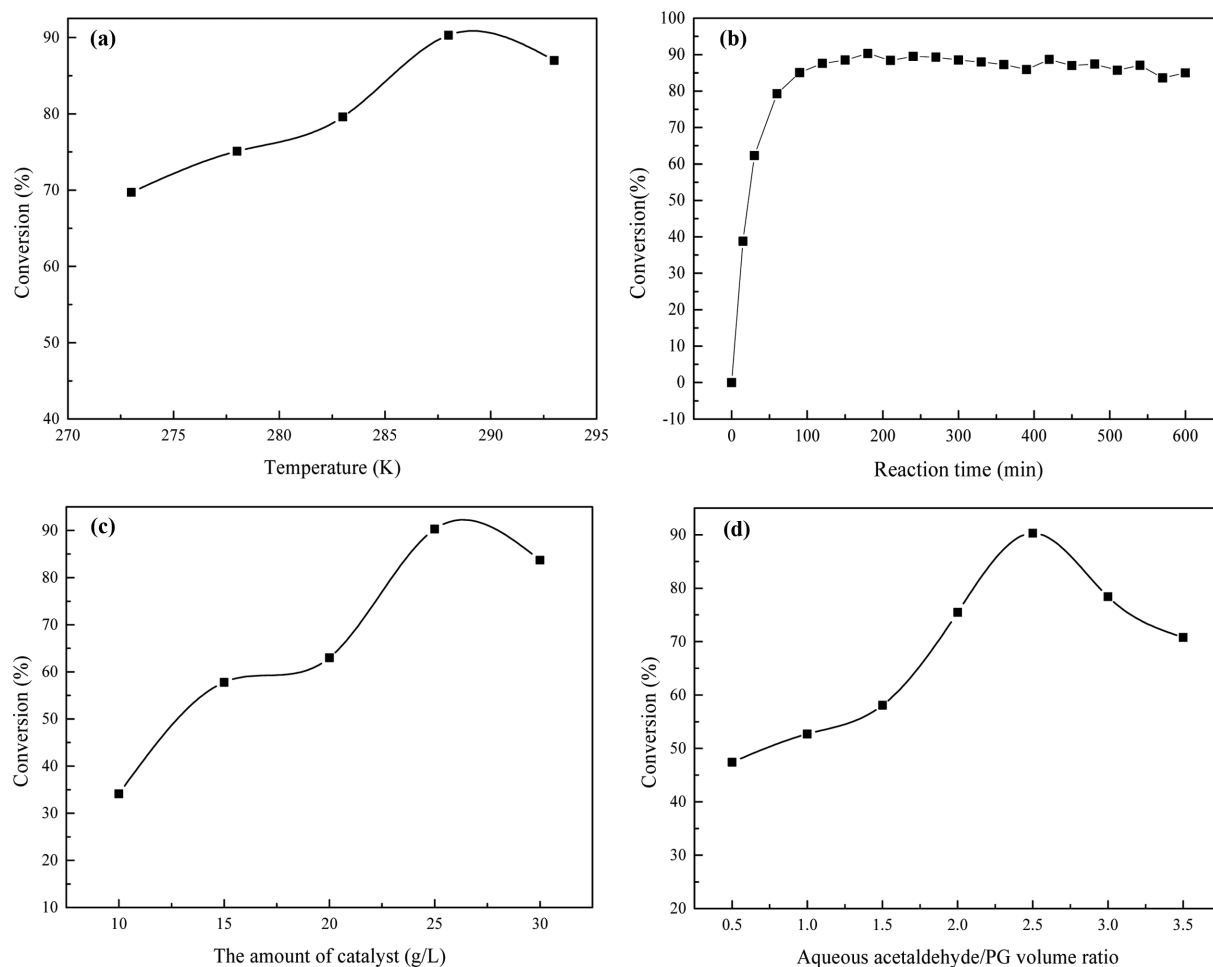
Fig. 1. Effects of reaction variables on PG acetalization over Resin D072 catalyst. (a) effect of temperature (catalyst loading=25 g/L, reaction time=3 hours, acetaldehyde/PG volume ratio=2.5:1), (b) effect of reaction time (T=288 K, catalyst loading=25 g/L, acetaldehyde/PG volume ratio=2.5:1), (c) effect of catalyst loading (T=288 K, reaction time=3 hours, acetaldehyde/PG volume ratio=2.5:1), (d) effect of acetaldehyde/PG volume ratio (T=288 K, catalyst loading=25 g/L reaction time=3 hours).

3-2. Catalyst Life Test

The ion-exchange resin catalysts deactivate over time in acetalization of polyhydroxy compounds. After a certain period of time-on-stream operation, catalytic performance may not satisfy economic requirements from the manufacturing point of view. There is a need to determine how many cycles the catalyst can be used in batch reaction.

To establish the reusability guideline for commercial application, after each test, the catalyst was recovered and tested for the subsequent acetalization of PG. Before the start of the subsequent test, the reclaimed catalyst was washed with solvent for several times and dried in an oven at 328 K. Each testing cycle was under the same reaction conditions.

As illustrated in Fig. 2, during the first six cycles of the test, catalytic activity measured by PG conversion decreased from 90.3±0.3% to 67.7±0.3%, probably due to the loss of the number of functional group. The deactivation rate appears to be linear at the beginning but not catastrophic. The deactivation rate slows down after four cycles of test. Although the deactivation mechanism and regeneration are not the focus of this study, we hypothesize that the deactivation is
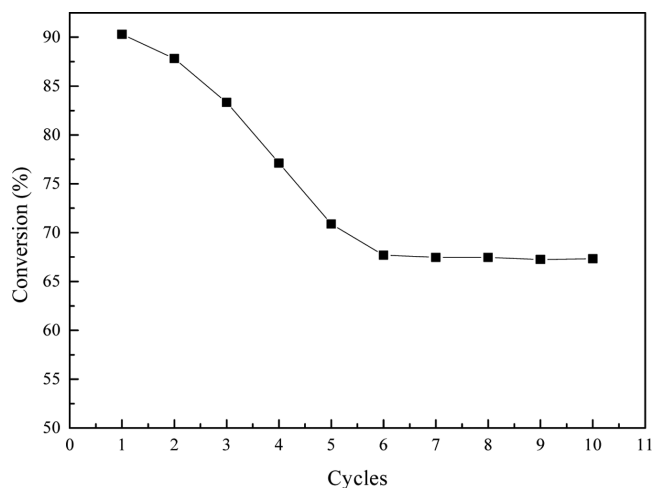

Fig. 2. Performance of ion-exchange Resin D072 catalyst in repeated cycle test (Resin D072 loading=25 g/L, T=288 K, reaction time= 3 hours, acetaldehyde/PG volume ratio=2.5:1).

caused by forming strong bonding between the acid sites and polymeric intermediates. Moreover, the agitator in the batch reactor can

also cause mechanical damage of the resin [17,18]. At the same time, we speculate that some of certain substances in the reaction process occupied the active site of catalyst, leading to decreased catalytic efficiency. To prove this conjecture, we used a 4% aqueous hydrochloric acid washing the catalyst, which has been used ten times. When the washed catalyst was put into use again, we found that PG conversion rate could be raised to 80±0.3%. This phenomenon demonstrates our inference very well. However, the material to occupy the center position of the catalyst activity requires further studies.

3-3. Reaction Kinetics

Determining the reaction orders of the kinetics is important in the design of a reactive distillation column for acetalization of polyhydroxy compounds. Guemez *et al.* [19,20] studied kinetics of acetalization reaction between glycerol and n-butyraldehyde. However, the kinetics for the acetalization of PG with acetaldehyde has not been published yet. In the kinetic study, the reaction mixture of PG and acetaldehyde was charged to a batch reactor. PG and acetaldehyde conversions were measured as reaction proceeded. Fig. 3 shows the conversion of acetaldehyde as a function of time. ExpDec1 equation in Origin 9 was fitted to the data?which can be expressed as:

$$y = y_0 + A_1 e^{-x/t1}$$

Among them, $-1/t_1$ is the first order reaction rate constant. Non-linear regression calculation was carried out for the kinetic modeling work. The results indicated that the reaction was first order for acetaldehyde.

Similarly, the conversion of PG as a function of time was measured according to the method described above. The result indicated that reaction was first-order for PG as well. Therefore, overall reaction follows second-order kinetics, which can be expressed as:

$$r = kC_A^1 C_B^1$$

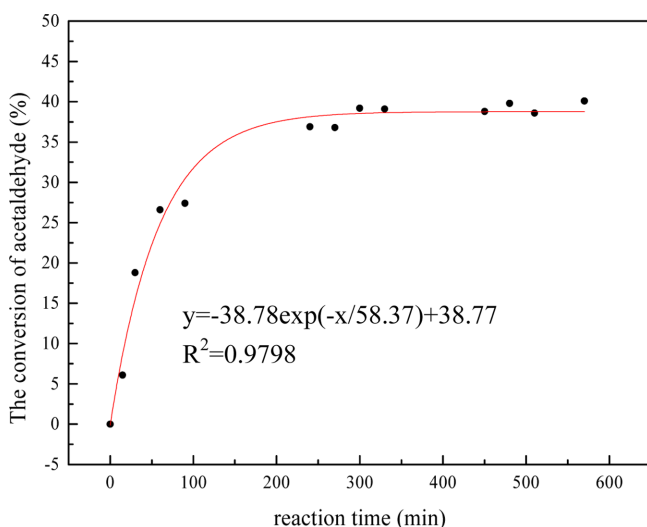where r is reaction rate and k is an Arrhenius factor defined as:

Fig. 3. The conversion of acetaldehyde as a function of time (Resin D072 loading=25 g/L, T=288 K, acetaldehyde/PG volume ratio =2.5:1).
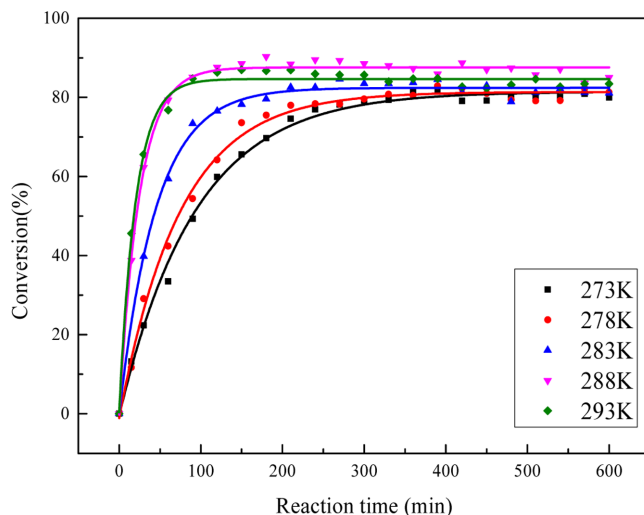
Fig. 4. The conversion of PG as a function of time at different temperature.

Table 2. The influence of reaction temperature on kinetic rate constants for PG acetalization

T/K	k/min^{-1}
273	0.01075
278	0.01351
283	0.02222
288	0.04000
293	0.05000

$$k = A_0 e^{\frac{Ea}{RT}}$$

The values of preexponential factor A_0 and activation energy E_a were determined experimentally. PG conversion was measured at different temperature varying from 273 K to 293 K. As illustrated in Fig. 4, the reaction rate increases with temperature. Non-linear regression calculation was conducted to obtain the reaction rate constant k at each temperature. The result listed in Table 2 shows the apparent rate constant k increases with reaction temperature.

To the temperature of the reaction, five sets of different reaction temperature were used in the experiment. The results (Fig. 4) show that as the reaction temperature increases, the reaction time is reduced to reach equilibrium. This phenomenon followed the endothermic reaction theory. When the reaction time exceeds 300 min, all reactions have reached equilibrium. After equilibrium is reached, under a different temperature, the conversion rate of PG has no significant change. However, when the reaction temperature reaches equilibrium at 293 K, the conversion rate of PG is lower than 288 K. Therefore, we conclude that the best reaction temperature is 288 K.

The Arrhenius plot is illustrated in Fig. 5 where the apparent rate constant is plotted against 1/RT. A_0 and E_a are obtained from the intercept and slope shown in Fig. 5. Therefore, the reaction kinetics equation for PG aldolization can be expressed as: $r = kC_A^{nA}C_B^{nB} = 19.74e^{\frac{-6650}{T}}C_A^1 C_B^1$ [21].
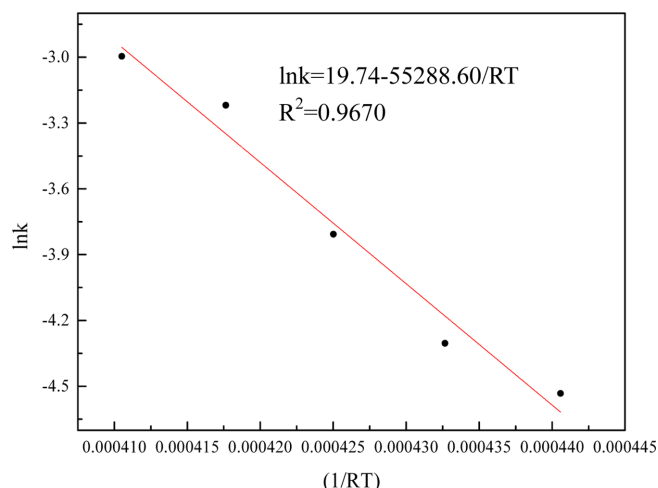
Fig. 5. Arrhenius plot for acetylation of PG with acetaldehyde.

4. Conclusions

This study not merely demonstrates that the resin based catalyst is capable of catalyzing 1,2-Propylene Glycol acetalization. It goes beyond the catalytic performance study by exploring the reaction kinetics that occurred on the catalyst. These experimental results have helped us to gain insights into the mechanism on the formation of acetals via reverse acetalization reaction over ion-exchange resin catalysts. The experimental data can be used as a basis for the design of commercial reactive distillation column and for the simulation of acetalization of polyhydroxy compounds with aldehyde to produce acetals.

Acknowledgment

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