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# Improving Hydrolytic Stability of POE Lubricants by the Addition of Acid Catchers

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## ABSTRACT

The kinetic and thermodynamics of the reaction of acid catcher (AC) with acid and the reaction of POE with water to form acids are determined.

The data obtained will be used to model the reaction of POE, AC and water in a refrigeration system. To simplify the modeling of reactions, pure single acid POE and single component epoxide type AC were studied. The parameters obtained from this study will be used to model reactions in a refrigeration system. The study illustrates the use of Acid Catcher to improve the hydrolytic stability of ester lubricants containing both branched and linear type of acids.

## INTRODUCTION

The lubricants of choice for use with hydrofluorocarbon (HFC) refrigerants are polyol esters (POE) due to their good miscibility properties, thermal and hydrolytic stability. The chemistry can be selected to provide a useful range of viscosities.

The chemical stability of polyol esters is due to the neopentyl carbon backbone of the polyol shown in Figure 1. With benefit of steric hindrance on the alcohol, the hydrolytic stability of these esters in the presence of water is excellent. However, hydrolysis is still a concern. The acid formed by hydrolysis act as catalysts for faster hydrolysis and acids formed may react with metals to form metallic salts. The salts that are formed have the potential for forming insoluble residues, which could lead to expansion device blockage. Improved hydrolytic stability is needed for refrigeration lubricants.

Chemical modification of the ester can reduce the rate of hydrolysis. Esters with carbon atom substitution on the *alpha*-carbon atom of the acid are slower to hydrolyze than esters synthesized with linear acids. Esters made from acids with double substitution on the *alpha*-carbon atom are even slower to hydrolyze. However, there are very few *alpha*-substituted acids commercially available. This limits the range of properties attainable.

Davis, et al. (1994) showed the catalytic effect of acid on the hydrolysis of esters. Therefore, the means of achieving improved hydrolytic stability of POE refrigeration lubricants is to remove the acid as it is formed. Sasaki (Sasaki, et al., 1981) disclosed a lubricant formulation containing at least one epoxy compound. The epoxy compound was used to stabilize the polyglycol lubricant from acid promoted decomposition.

## EXPERIMENTAL

The polyol esters pentaerythritol-tetra heptanoate, pentaerythritol-tetra 2-ethyl-hexanoate and pentaerythritol-tetra 3,5,5 trimethyl-hexanoate were obtained from Mobil Chemical. Heptanoic acid, 2-ethyl hexanoic acid was obtained from Aldrich Chemical Company. 3,5,5 trimethylhexanoic acid was obtained from Exxon and neodecanoyl glycidyl ester (E10) was obtained from Shell Chemical. Water used was HPLC grade. BFSTA with 1% TMSCI was obtained from Pierce Chemical. An HP 5971 Gas Chromatograph-Mass Selective Detector was used to analyze the reactants and products.

All reactions were carried out in sealed, evacuated glass ampoules using the technique described in ASHRAE 97. The concentration of acid was determined using the methods described in ASTM 974-95. Gas Chromatography-Mass Spectrometry performed the analysis of the reactants and products after derivatization to form trimethylsilyl derivatives of acids and alcohols to improve the chromatographic profiles and mass spectrometric intensity.

Thermodynamic heats of formation were calculated using MOPAC-97 using the AM1 quantum mechanical properties dataset.

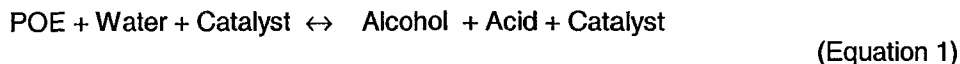
## RESULTS AND DISCUSSION

Neodecanoyl glycidyl ester (E10) (Figure 2) was studied after evaluation several epoxide compounds because it reacted at a temperature which are consistent with the operating conditions of refrigeration systems (100 to 200°C). The reaction of E10 with acid is shown in Figure 3 and with water in Figure 4.

Theoretical enthalpy of reaction was calculated using MOPAC with AM1 (Austin Model 1) potential functions. Table 1 shows the enthalpy of reaction for ring opening by hydration and acid. Diethyl ether is an acyclic ether and is used for reference. The large enthalpy of reaction (-40.8 kcal/mole) for the 3-atom ring epoxide structure indicates that the ring opening is a favored reaction. The heat of formation of the ester compound on ring opening is -30.1 kcal/mole. The 1-isomer of the ester formed by reaction with acid is more stable than the 2-isomer by 5.0 kcal/mole. All of the compounds shown in figures 3 and 4 are expected to form.

Reactions were carried out at high concentrations of acid with E10 to obtain the reaction products. Reactions carried out at high E10 concentration lead to polymerization of the E10 to polyglycol type compounds. Thus, all reactions with E10 were carried out at one weight percent E10 in order to prevent polymerization.

Davis, et al. modeled and quantified the catalytic effect of acid on the hydrolysis of esters. As acid is the product of hydrolysis, the rate of hydrolysis increases as the amount of acid increases. The rate of hydrolysis then decreases as one of the reactants, water, is completely consumed. The effect is called "autocatalytic kinetics" and the formation of acid follows a sigmoidal curve as is shown in Figure 5. These data can be modeled by the following mechanism,



The rate equation is simplified by assuming that the equilibrium shown is far to the left the reverse reaction is so small that it is not a factor. Then the formation of acid can be written as

$$[\text{Acid}]_t = ([\text{Water}]_0 + [\text{acid}]_0) / (1 + ([\text{Water}]_0 / [\text{acid}]_0) * \exp(-([\text{Water}]_0 + [\text{acid}]_0) + [\text{POE}]_0 * k * t)), \quad (\text{Equation 2})$$

k is the third order rate constant, t is the time and the terms in brackets are the molar concentration of the compounds. The catalyst is both the initial acid concentration plus the acid added by reaction for equation 2. The rate constant, K, is evaluated by curve fitting.

The effect of temperature is on the reaction is also shown in Figure 5. The reaction rate, k, increases with temperature. Figure 6 shows a plot of the rate constant versus the inverse of the absolute temperature for nC7-pentaerythritol ester over the temperature range 100 to 200°C. The relationship is linear indicating the mechanism is consistent over the entire range of temperatures.

Table 2 summarizes the results for the pentaerythritol ester evaluated. The data agree with the data of Davis (Davis et al. 1994).

**Table 2**  
**Thermodynamic and kinetic parameter for pentaerythritol ester hydrolysis**

Ester	k, lt/mol-sec at 150°C	$\Delta H_{\text{activation}}$ , kcal/mole
PE-(nC7) <sub>4</sub>	$1.71 \times 10^{-5}$	11.8
PE-(2EH) <sub>4</sub>	$2.89 \times 10^{-6}$	10.8
PE-(355C9) <sub>4</sub>	$2.03 \times 10^{-5}$	12.5

Figure 7 shows the plot of acid formed versus time for the three esters studied. The effect of alpha branching (PE-2EH) is seen in the lower rate constant.

In the above mechanism described by Equations 1 and 2, if the initial acid concentration is zero,  $[\text{acid}]_0=0$ , the hydrolysis cannot take place. This is a simplification of a complex reaction. The rate of hydrolysis without catalysis is assumed to be at least 1000 times slower than the rate with catalyst present. Thus, if the acid concentration can be kept very low then the hydrolysis of ester will be very slow. The use of acid catcher will improve the hydrolytic stability of the polyol ester by trapping acids as they are formed. Figure 8 shows the effect of acid catcher on the rate of hydrolysis.

Preliminary analysis of the reactions of acid, water and acid catcher show that all of the components are detectable by gas chromatography-mass spectrometry. The chromatographic analysis of reactants and products is shown in Figure 9. Figure 7A shows the chromatographic profile of E10. The isomers of neodecanoic acid give rise to multiple peaks in the chromatogram. Each of the reaction products shown in figures 3 and 4 are detectable as shown in 7B, 7C and 7D. The diester of E10 was unexpected and was found in reactions of E10 with acid alone. Glycerin and free neodecanoic acid, hydrolysis product of E10 were not detected.

## CONCLUSIONS

- The addition of acid catcher to an ester lubricant significantly improves the hydrolytic stability by removing acids as they are formed.
- The ester portion of the acid catcher does not hydrolyze at the experimental conditions used (100 to 200°C).

## REFERENCES

- Sundaresan, S. G., "Evaluation of lubricants for R410A/R407C applications in scroll compressors", 1998 International Compressor Engineering Conference at Purdue, 1998
- Davis, K. E., Jolley, S. T. and Shanklin, J. R., "Hydrolytic stability of polyol ester refrigeration lubricants", 1994 International CFC and Halon Alternatives Conference, Baltimore, 1994
- Sasaki, U, Tsunemi, M., Yamada, K., and Morikawa, Y., "Refrigeration lubricating oil compositions", US Patent 4,267,064, 1981

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Table 1  
Heat of Formation and Heats of Reactions for Various Model Compounds

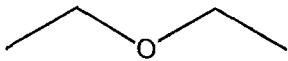
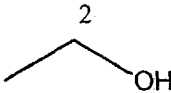
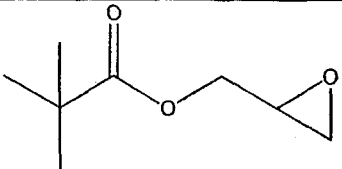
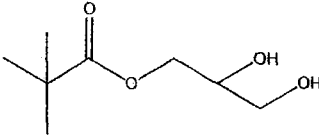
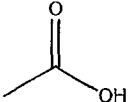
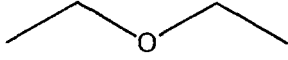
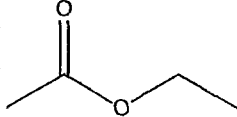

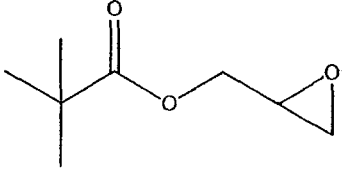
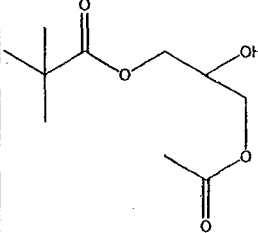
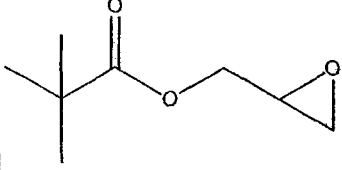
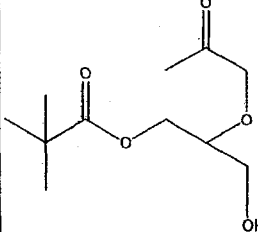
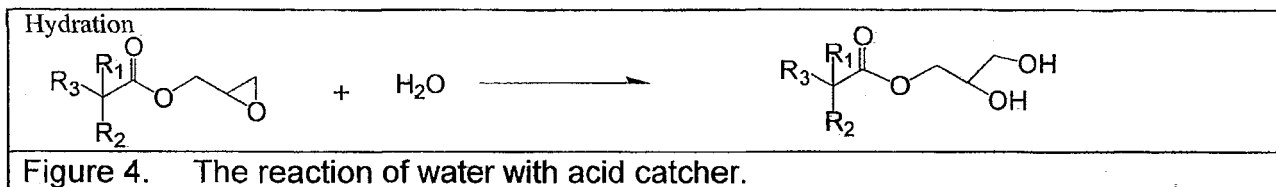
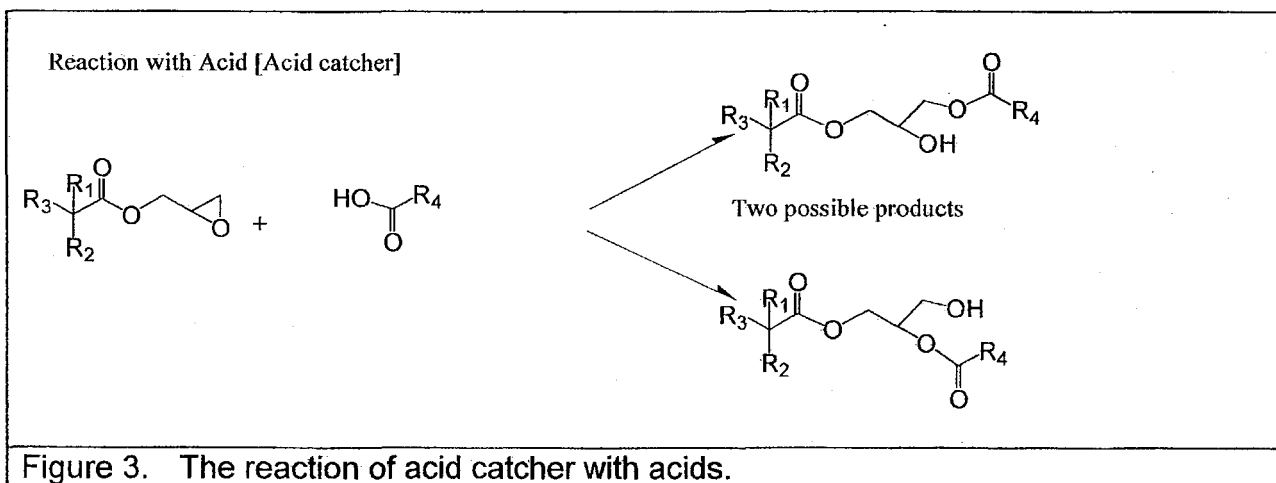
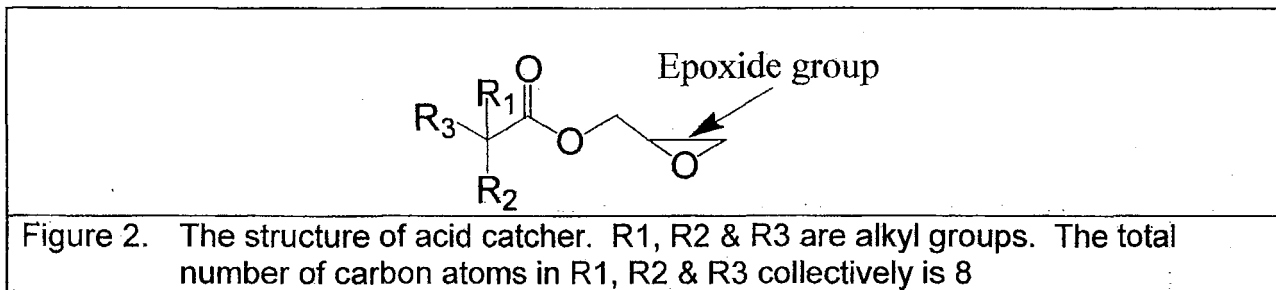
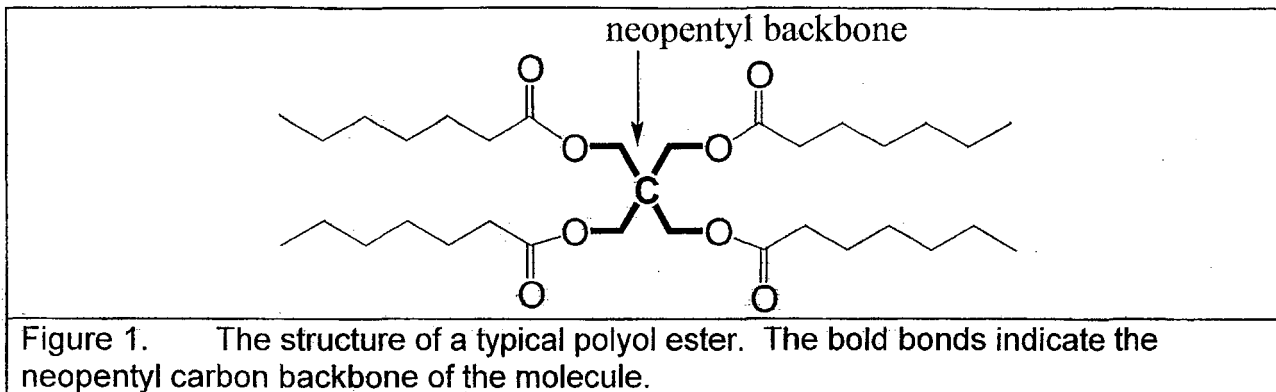
Reactants	Products		Heat of Reaction
Hydration reaction	$\Delta H_f$ , kcal/mole		kcal/mole
H <sub>2</sub> O	-59.3		
	-64.4	-128.5	 2 -4.8
	-110.9	-211.0	 -40.8
Acid trapping Reaction			
	-103.0		
	-64.4	-102.3	 and -64.3  +0.8
	-110.9	-244.0	 -30.1
	-110.9	239.0	 -25.1

Table 2  
Thermodynamic and kinetic parameter for pentaerythritol ester hydrolysis

Ester	k, lt/mol-sec at 150°C	$\Delta H_{\text{activation}}$ , kcal/mole
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PE-(355C9) <sub>4</sub>	2.03x10 <sup>-5</sup>	12.5



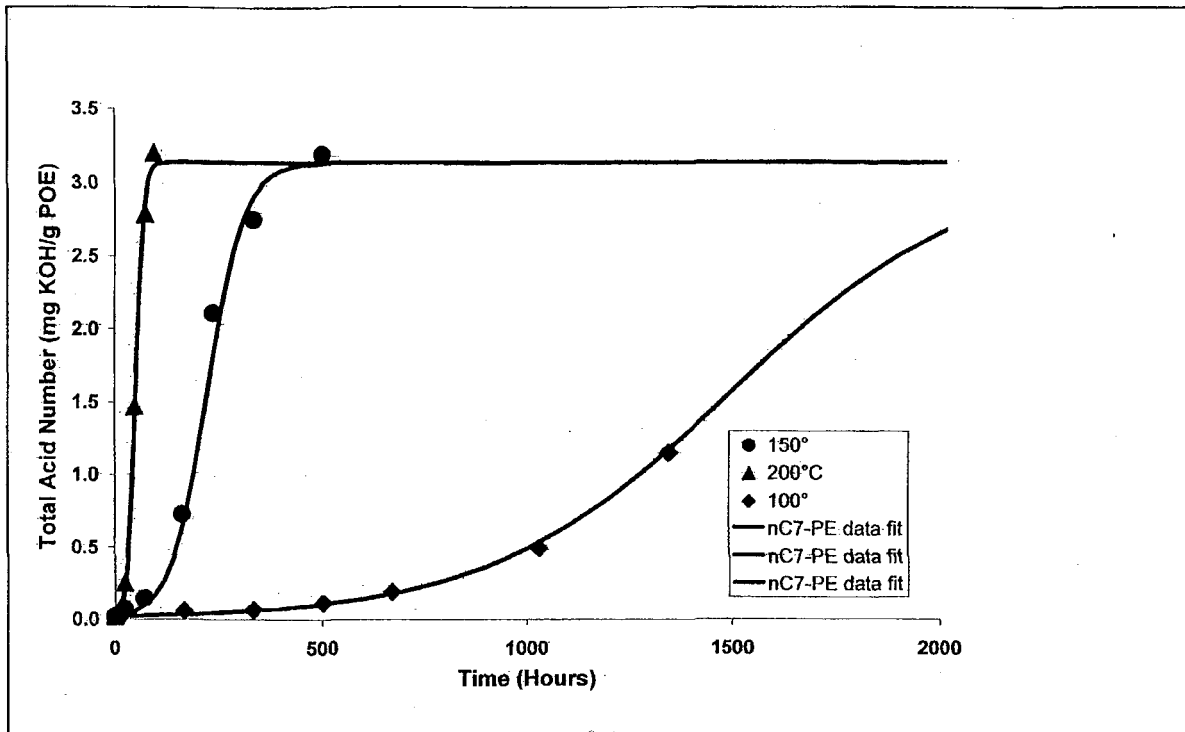


Figure 5 The formation of acid as a function of time at various temperatures. The sigmoidal nature of the curve are as expected from an "autocatalytic" reaction

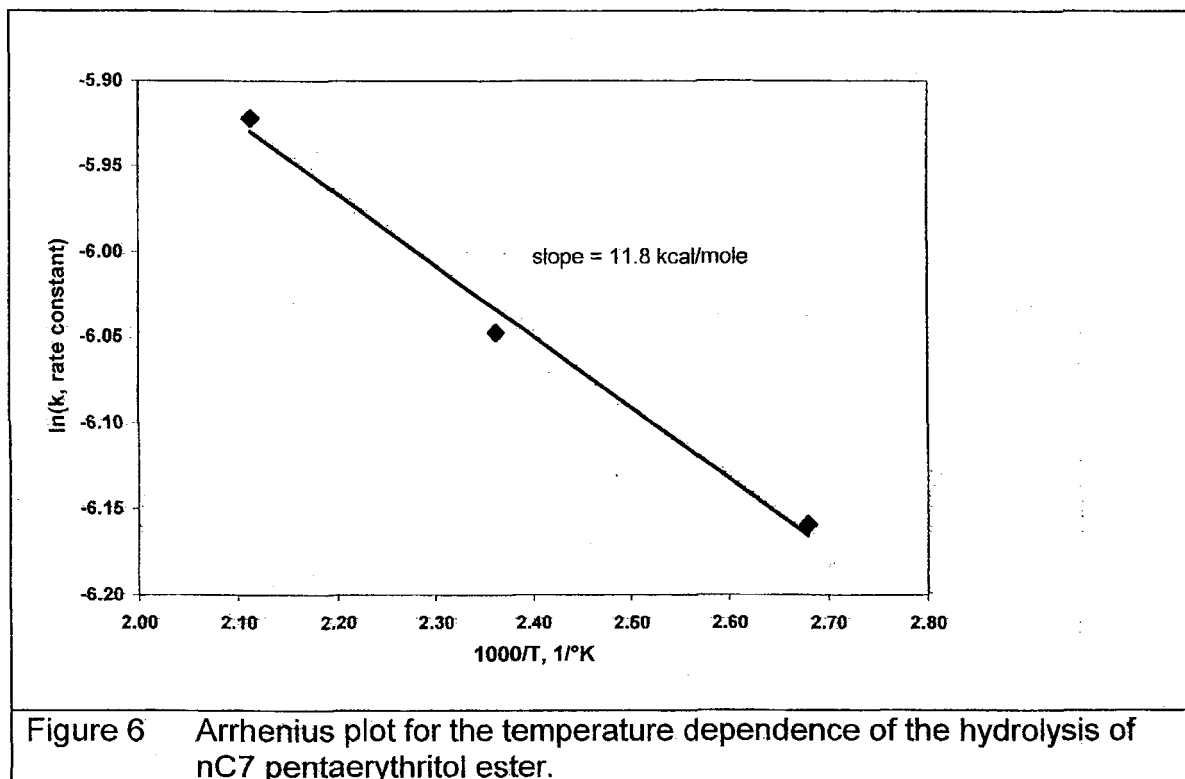


Figure 6 Arrhenius plot for the temperature dependence of the hydrolysis of nC7 pentaerythritol ester.

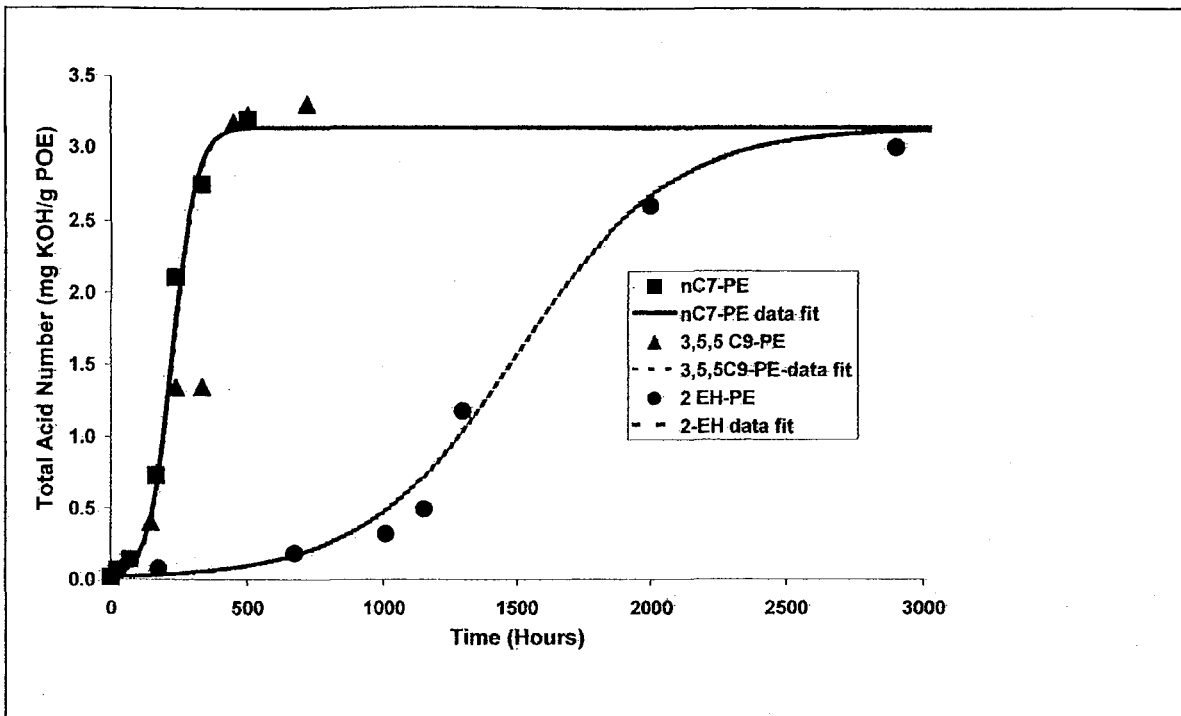


Figure 7 The kinetic curve for the production of acid from ■ linear acid polyol ester, ▲ a branched acid polyol ester and ● an alpha branched polyol ester. The amount of water for each sample was 1000 mg/kg and the temperature of reaction was 150°C

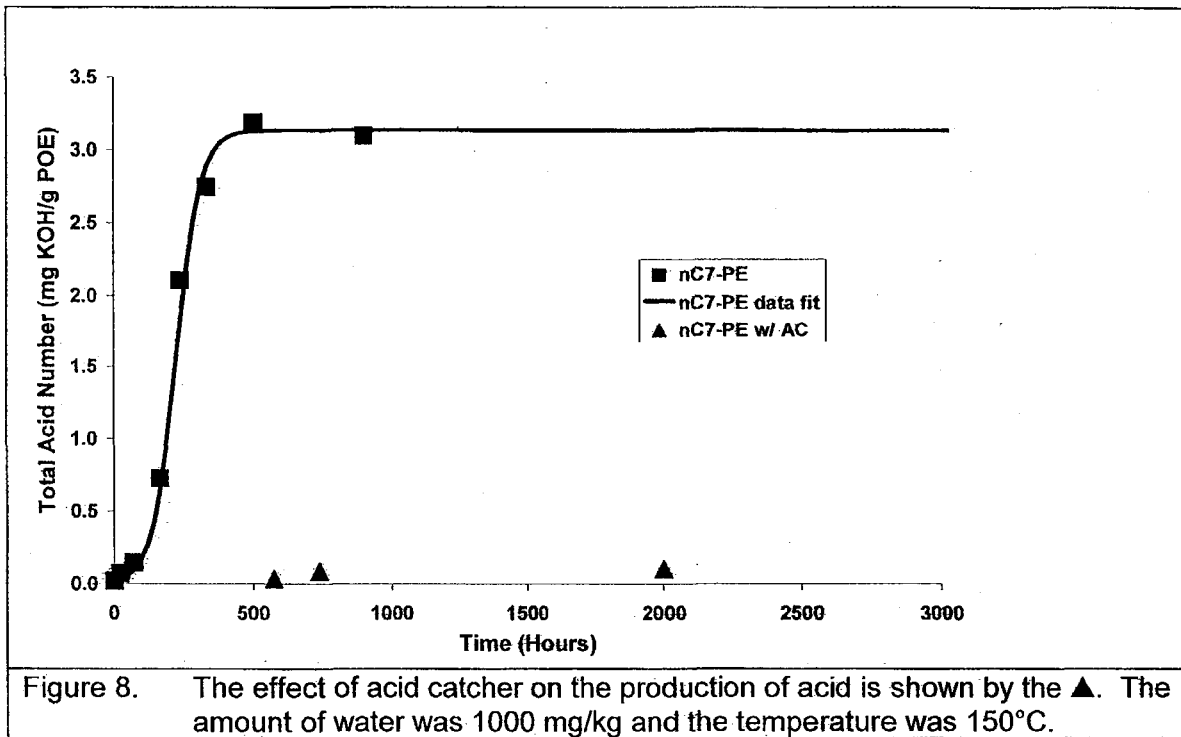


Figure 8. The effect of acid catcher on the production of acid is shown by the ▲. The amount of water was 1000 mg/kg and the temperature was 150°C.



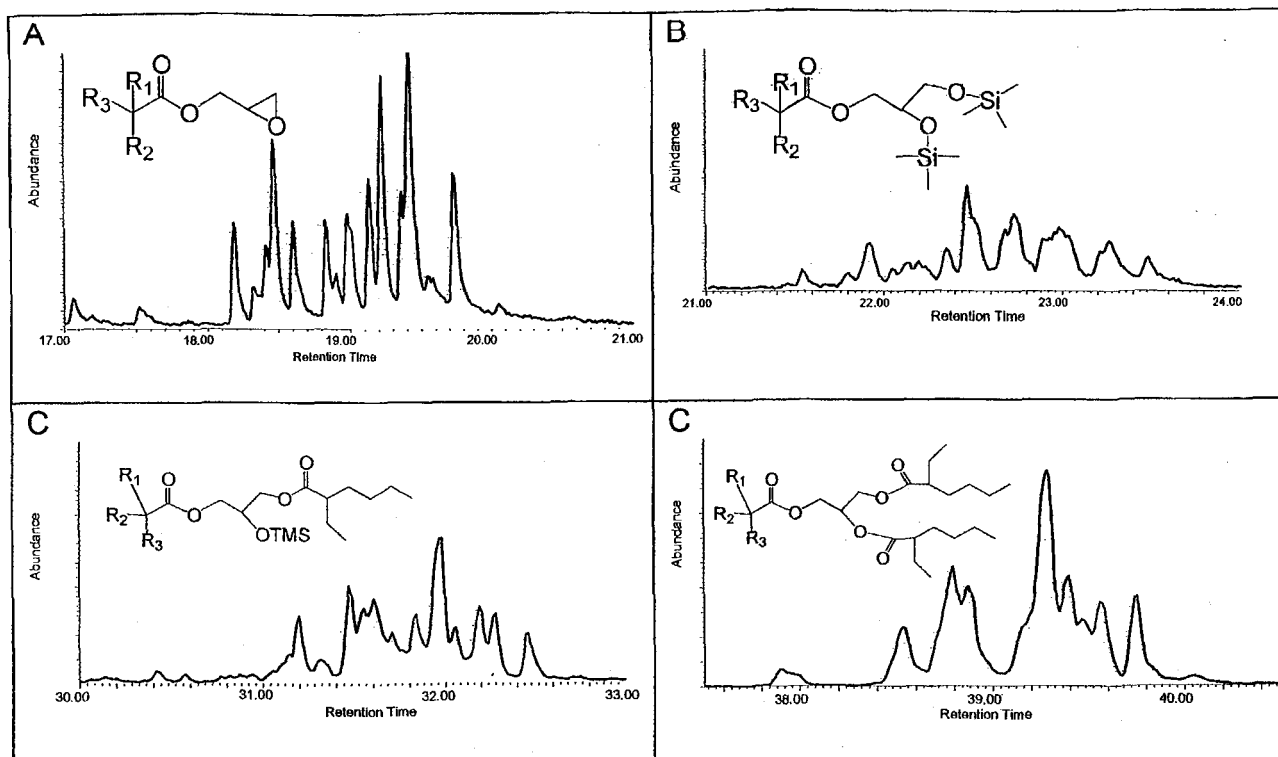


Figure 9 Chromatograms of the reactants and products of the acid catcher reactions. A. The acid catcher, E10. Showing at least 18 compounds. B. The trimethyl silane (TMS) derivative of the hydration product of the acid catcher. C. The TMS derivative of the 1-isomer of E10 reaction product with acid. D. E10 reacted with two molecules of acid. The retention times of each group of isomeric compounds are well separated to allow for integration of each peak group. The acid shown is 2-ethyl hexanoic.