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THE UNIVERSITY OF ALBERTA

THE CATALYTIC DEHYDRATION
AND ESTERIFICATION OF ETHANOL

BY

© ROLAND L. H. SCHECH

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled THE CATALYTIC DEHYDRATION AND ESTERIFICATION OF ETHANOL submitted by Roland L. H. Schech, B. Sc., in partial fulfilment of the requirements for the degree of Master of Science.

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Date: April 20, 1977.

ABSTRACT

Control studies involving chemical reaction systems have generally been of a theoretical nature. Even the theoretical work has tended to involve control of rather simple reaction schemes and published experimental studies of reaction control have usually been conducted on even simpler reactions. The objective of this thesis project was to design and construct a reactor system which could be used to study a chemical reaction scheme of moderate complexity from a control viewpoint.

The reactions chosen involve the simultaneous vapour phase dehydration of ethanol to form water and diethyl ether and the esterification of ethanol and acetic acid to form water and ethyl acetate. These reactions are catalyzed by an ion exchange resin.

The experimental system includes gas chromatographic composition analysis of the five components in the reaction network described above. The reactor system is based on a recycle reactor with a differential catalyst bed. The system can be run as a batch type reactor or as a differential recycle reactor. The temperature of the catalyst bed, which is the major variable influencing reaction rate, can be controlled very precisely. The catalyst bed temperature can be accurately manipulated as a function of time and this feature of accurate temperature programming should prove useful in future control studies.

Rate data for these two reactions were measured using the

differential recycle mode of operation. These data were taken at temperatures between 110°C and 135°C and over a wide range of compositions. The data were used to develop kinetic models based on Langmuir-Hinshelwood mechanisms. It was also confirmed that contact with acetic acid deactivated the resin catalyst and this phenomenon was studied and taken into account in the analysis of the esterification reaction rates. Expressions for the rates of the two reactions were obtained.

The experimental equipment proved to be useful for the kinetic studies. Experimental reactor control studies can also be carried out using the equipment constructed during this investigation.

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Recognition is due the late G. S. Robertson for his contribution in designing the differential reactor portion of the equipment.

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CHAPTER ONE

INTRODUCTION

The overall purpose of this project was to construct an experimental system for the study of various reactor control schemes involving chemical reactions of moderate complexity. In addition it was hoped that experimental kinetic studies could be carried out to obtain kinetic reaction models and that preliminary control studies could be conducted to prepare for future control projects involving the same equipment.

Previous studies of experimental reactor control have generally involved very simple reaction schemes (e.g. first order, irreversible, liquid phase). It was desirable to find a chemical reaction system which was nontrivial (i.e. somewhat closer to industrial reactions than a first order homogeneous irreversible reaction) but for which some kinetic studies had been carried out. In addition the reaction system had to be one where the conversion and rate could be manipulated (i.e. the reaction system had to be "controllable"). This latter criterion was the basis for choosing heterogeneous catalytic reactions and for the decision to construct a differential bed reactor with a recycle loop. The compact nature of the catalyst bed allowed one to control the bed temperature (and hence the reaction temperature) which is a major variable influencing the rates of chemical reactions.

The reaction scheme chosen involved the dehydration of ethanol to form water and diethyl ether (equation 1.1) and the esterification of acetic acid and ethanol to form water and ethyl acetate (equation 1.2). In the vapour phase these reactions proceed at appreciable rates in the presence of an ion exchange resin catalyst at temperatures between 90°C and 140°C. This reaction system was chosen because a large amount of good kinetic and thermodynamic data was available for the dehydration reaction (8, 5, 7, 15, 21) and some work had been done for the esterification reaction (3).

$$2\ C_2H_5OH(g) = H_2O(g) + (C_2H_5)_2O(g) \qquad (1.1)$$

$$C_2H_5OH(g) + CH_3COOH(g) = CH_3COOC_2H_5(g) + H_2O(g) \qquad (1.2)$$

At higher temperatures the following dehydration reactions become more significant.

$$C_2H_5OH(g) = H_2O(g) + C_2H_4(g) \qquad (1.3)$$

$$(C_2H_5)_2O(g) = \quad + H_2O(g) \qquad (1.4)$$

The increased rates of reactions (1.3 and 1.4) at higher temperatures and the ion exchange resin catalysts decompose at temperatures above 150°C accounted for the 140°C upper limit on the temperature employed. The lower limit of 90°C was dictated by the reactants used to remain in the vapour phase.

The equipment was designed so that various control strategies involving reactions 1.1 and 1.2 could be studied experimentally. It was necessary to have an accurate model of the reaction system as a prerequisite for control studies. Examples of control studies which could be undertaken are those involving optimal temperature path schemes to maximize conversion for a batch system in a given amount of time (14) and selectivity studies involving two reaction paths.

In the case of reaction 1.1 a good rate model (21) was available and this was modified slightly to account for the different type of ion exchange resin catalyst used in this study. Some work (3) had been done for the esterification reaction but it was necessary to determine a reasonable model for this reaction. Contact with acetic acid vapours also deactivated the catalyst and this phenomenon had to be investigated and defined qualitatively.

The thesis research included an investigation of kinetic models for the reaction system described above. The reactor system constructed for this project was used to measure experimental rates. The equipment was designed for isothermal temperature control (or "programmed" temperature control) of the differential catalyst bed through which reactants were cycled and was intended for future control and optimization investigations.

CHAPTER TWO

MEASUREMENT OF EXPERIMENTAL RATES AND THEORETICAL REACTION MODELS

2.1 Measurement of Reaction Rates

In order to test proposed rate functions it is necessary to experimentally measure reaction rates. The most suitable reactors for measuring reaction rates are continuous stirred tank reactors (CSTR) or differential reactors because rates are obtained directly. If batch or tubular reactors are used, differentiation of experimental data is required to obtain reaction rates. For heterogeneously catalysed reactions, CSTR behavior is obtained either by using a Carberry type reactor or a recycle reactor. In this work a recycle reactor was employed.

The design equation for a CSTR reactor (or a recycle reactor) for stoichoimetric simple reactions subject to steady state mass balance conditions is

$$r = \frac{r_i}{\nu_i} = \frac{F_{i,in}}{\nu_i G} X_i \qquad (2.1)$$

where

$$F_{i,in} = \text{feed rate of reactant } i$$

$$X_i = \text{fractional conversion} \qquad (2.2)$$

$$X_i \quad \frac{F_{i,in} - F_{i,out}}{F_{i,in}}$$

G = mass of catalyst in reactor

r = normalized reaction rate

r_i = rate of reaction of compound i

ν_i = stoichiometric coefficient

(<0 for reactants, >0 for products)

The fractional conversion can also be expressed in terms of a product by using the following substitution:

$$(F_{p,out} - F_{p,in})/\nu_p = (F_{i,out} - F_{i,in})/\nu_i \qquad (2.3)$$

where F_p is the molar flow rate of the product compound. Measurement of the fractional conversion allows direct calculation of the rate of reaction.

In order to use these experimentally determined values of the reaction rate function it is necessary to establish that the measured reaction rates are intrinsic rates, i.e. not influenced by heat and mass transfer effects. The effects of heat and mass transfer for the system used in the present work are discussed in Appendix A.

2.2 Rate Functions for the Dehydration Reaction

The kinetics of heterogeneous catalytic reaction 1,1 have been extensively studied over a ten year period by Kabel and coworkers. Kabel (8) investigated the adsorption phenomenon, kinetics and equilibrium constant at 120°C (and other temperatures).

The equilibrium values of reactions 1.1 and 1.2 as a function of temperature were studied by Hawes and Kabel (5). Mullarkey (15) studied the kinetics of reaction 1.1 at 90°C and Stula (21) explored the kinetics at 140°C. The result of all the aforementioned studies was that the steady state rate of the dehydration of ethanol over Dowex 50-X8 ion exchange resin was described according to the Langmuir-Hinshelwood dual site model (surface reaction is the rate controlling step) in the form of the following equation.

$$r = \frac{k_s K_A^2 (P_A^2 - \frac{P_W P_E}{K_1})}{(1 + K_A P_A + K_W P_W)^2} \qquad (2.4)$$

In equation 2.4 K_A and K_W are the adsorption constants for ethanol and water, P_A, P_W and P_E are the partial pressures of ethanol, water and ether. K_1 and k_s are the equilibrium and specific rate constants respectively. The experiments of Kabel and coworkers were performed under conditions such that there were no internal or external mass transfer limitations (i.e. equation 2.4 is an intrinsic rate function). The work was carried out using a fixed bed reactor.

The temperature dependence of the equilibrium constant was described by Hawes and Kabel (5) as

$$\ln K_1 = 1842/T - 1.446 \qquad (2.5)$$

The temperature (T[=]K) relationships of k_s, K_A and K_W were presented by Stula (21) as

$$k_s \quad 1.028 \times 10^{10} e^{-103.3/R_g T} \text{ (moles/(min g cat.))} \quad (2.6)$$

$$K_A \quad 1.9552 \times 10^{-7} e^{39.42/R_g T} \text{ (kPa}^{-1}\text{)} \quad (2.7)$$

$$K_W \quad 1.0595 \times 10^{-9} e^{58.7/R_g T} \text{ (kPa}^{-1}\text{)} \quad (2.8)$$

Thus knowing the temperature and the partial pressures of the three components involved in the dehydration reaction, it is possible to predict a reaction rate according to equation 2.4. The units of the activation and adsorption energies are kJ/mole (R_g = 8.31 x 10^{-3} kJ/mole K).

Apecetche and Cunningham (1) have also studied the ethanol dehydration reaction over an ion exchange resin. The resin used in their experiments was not the same as that used by Kabel but the study is comparable in any case. The Langmuir-Hinshelwood mechanism which these workers chose to describe their results was the reaction between two ethanol molecules adsorbed on one active center. This can be expressed according to equation 2.9.

$$r_1 = \frac{k_s K_A^* \left(P_A^2 - \frac{P_W P_E}{K_1}\right)}{(1 + K_A^* P_A^2 + K_W P_W)^2} \quad (2.9)$$

In the work of Apecetche and Cunningham (1) there was an ether adsorption term in the denominator of equation 2.9 but this term was small (relative to the other terms in the denominator) and was ignored for the purposes of evaluating equation 2.9 as a potential kinetic model for the dehydration reaction. At 100°C the

following values for the fitted parameters in equation 2.9, were reported in reference (1). The specific rate constant is k_s = 7.1 x 10^{-5} moles/(min g cat.), K_A^* = 3.6 x 10^{-4} kPa^{-2} and K_W = 0.106 kPa^{-1}. The approximate temperature dependence of k_s as used in equation 2.9 can be described according to equation 2.10.

$$k_s = 5.392 \times 10^{12} e^{-120.5/R_g T} \text{ (mol/(min g cat.))} \qquad (2.10)$$

The temperature correlations for K_A^* and K_W were not reported. The reported activation energy was 120.5 kJ/mole as opposed to 103.3 kJ/mole from equation 2.6. Apecetche and Cunningham (1) only made reference to the early work of Kabel (8) and did not compare their results with the later work of Kabel's group (10, 11, 5).

Lapidus and Peterson (12) analyzed the results of Kabel (8) and proposed the pseudo-homogeneous model presented in equation 2.11.

$$r_1 = k_s^* \left(P_A^2 - \frac{P_W P_E}{K_1} \right) \qquad (2.11)$$

Although these authors apparently did not consider all the data available (see Kabel (9)), it would be of interest to evaluate the predictive abilities of this pseudo-homogeneous rate expression. The value of the constant k_s^* was reported to be approximately (1.4 ± 0.15) x 10^{-8} moles/(kPa^2 min g cat.) at a temperature of 120°C.

2.3 Rate functions for the esterification Reaction

Dewan (3) proposed an esterification reaction model which involved the adsorption of water, ethanol and ethyl acetate. Acetic acid monomer (it was assumed that the acid monomer and dimer were in equilibrium) was postulated to adsorb on the sites which had water adsorbed on them. The contribution of the water partial pressure was adjusted empirically. The model was written as follows.

$$r_2 = \frac{k_{s2} K_{AM} K_A K_W P_W^S \left(P_M P_A - \frac{P_C P_W}{K_2}\right)}{\left(1 + K_A P_A + K_W P_W + K_C P_C\right)^2} \qquad (2.12)$$

In the expression presented in equation 2.12 K_{AM} and K_C are the adsorption constants for the acetic acid monomer-water complex and the ethyl acetate respectively. P_M and P_C are the partial pressures of the acetic acid monomer and ethyl acetate. The constant k_{s2} is the specific rate constant and the exponent S is an arbitrary constant. The equation is applicable to rates corrected for fresh catalyst. The esterification equilibrium constant K_2 is a function of temperature according to either equation 2.13a or 2.13b depending upon which dimerization constants are employed (see Hawes and Kabel (5)).

$$\log_{10} K_2 = 649/T + 0.012 \qquad (2.13a)$$

$$\log_{10} K_2 = 724/T - 0.127 \qquad (2.13b)$$

The model represented by 2.12 did not fit the experimental rate data of Dewan very accurately. This may have been due to problems in accounting for catalyst deactivation (3) or an incorrect rate function and, therefore, the applicability of the model described by equation 2.12 is in doubt.

Yeramian et al. (27) investigated the esterification reaction involving isopropanol and acetic acid over an ion exchange resin. No catalyst deactivation problems were reported. The surface reaction controlling Langmuir-Hinshelwood model proposed in the work was expressed as follows.

$$r_3 = \frac{k_{s3} K_I K_B P_I P_B}{(1 + K_I P_I + K_B P_B + K_J P_J + K_W P_W)^2} \qquad (2.14)$$

The subscripts I, J and B refer to isopropanol, isopropylacetate and acetic acid respectively. The reaction studied was similar to reaction 2.2 and the proposed model is analagous to equation 2.12, with the exception of the water terms in the numerator of 2.12. A standard Langmuir-Hinshelwood model similar to equation 2.14 may provide adequate description of the experimental esterification data.

The adsorption work of Kabel (8) showed that the adsorption of acetic acid and ethyl acetate on ion exchange resins is very limited in the absence of water. Thus one can speculate that the adsorption of acetic acid is dependent upon the presence of water or ethanol on catalytic sites. The additional complexity of having acetic acid exist in two states for the purposes of the kinetic model may not be justified by the accuracy of the experimental data.

Therefore it is postulated that only the "presence" of acetic acid (in any state) is important and that this is reasonably represented by assuming that acetic acid acts as an ideal gas like all the other components involved. The following models are based on the assumption that the surface reaction is the rate controlling step.

One way of adjusting the rate expression to account for the water/ethanol dependence would be to multiply the rate equation by the fraction of catalytic sites occupied by water and ethanol. The fractional coverage of sites by ethanol and water, $\mathcal{Z}$, can be expressed as follows (assuming that only water and ethanol are adsorbed directly on catalytic sites).

$$\mathcal{Z} = \frac{K_A P_A + K_W P_W}{(1 + K_A P_A + K_W P_W)} \qquad (2.15)$$

The standard Langmuir-Hinshelwood model is presented as equation 2.16 and the modified expression is given as equation 2.17.

$$r_2 = \frac{k_{s2} K_A K_B (P_A P_B - P_C P_W / K_2)}{(1 + K_A P_A + K_B P_B + K_C P_C + K_W P_W)^2} \qquad (2.16)$$

$$r_2 = \frac{\mathcal{Z} k_{s2} K_A K_B (P_A P_B - P_C P_W / K_2)}{(1 + K_A P_A + K_B P_B + K_C P_C + K_W P_W)^2} \qquad (2.17)$$

The above models involve only 3 constants which cannot be determined from dehydration studies (K_B, K_C and k_{s2}) and may provide a relatively simple way to account for the lack of adsorption of acetic acid and ethylacetate in the absence of water or ethanol. The constants K_B and K_C could be regarded as pseudo-adsorption

constants.

The following kinetic expressions are derived in Appendix B. The only compounds adsorbed directly on the catalyst sites are presumed to be water and ethanol. Acetic acid and ethyl acetate only adsorb on catalytic sites already covered with water or ethanol. The first mechanism proposed involves acetic acid forming an adsorbed complex on a site with ethanol adsorbed on it. This complex then reacts to form the reaction products. The model can be described as follows.

$$r_2 = \frac{K_4 K_A (P_A P_B - P_C P_W / K_2)}{(1 + K_A P_A + K_W P_W)} \qquad (2.18)$$

The second model involves acetic acid forming a complex on a site with a water molecule adsorbed. This acid-water complex then undergoes a reaction with ethanol adsorbed on an adjacent site to form the reaction products.

$$r_2 = \frac{k_5 K_A (K_W P_W)[P_A P_B - P_C P_W / K_2]}{(1 + K_A P_A + K_W P_W)^2} \qquad (2.19)$$

The models represented by 2.18 and 2.19 can be combined to form a composite model.

CHAPTER THREE

EXPERIMENTAL EQUIPMENT

3.1 Introduction

A schematic diagram of the experimental equipment is presented in Figure 3.1. In addition a schematic diagram of the temperature measurement and control equipment is given in Figure 3.2. Also presented is a photograph of the major equipment components as they were set up for the various runs (see Figure 3.3). The main parts of the equipment were the feed system, the circulation system, the gas chromatograph, the loop exit section and the reactor. The circulation pump and most of the system tubing and other equipment were contained in a heated, insulated oven to maintain the reactants in the vapour phase. The system components are described below.

3.2 Feed System

The feed mixtures were pumped into the reactor loop using two Sage Syringe Pumps (model 355, serial #16028 and model 352, serial #18955). Normally only one feed pump was used and the feed was contained in one syringe (dehydration runs) or two syringes on one pump (esterification runs) but for some of the esterification runs both feed pumps were used. The liquid feed mixtures were contained in a Hamilton gas tight syringe (50 ml size #1050). The approximate ranges of liquid injection rates which could be obtained

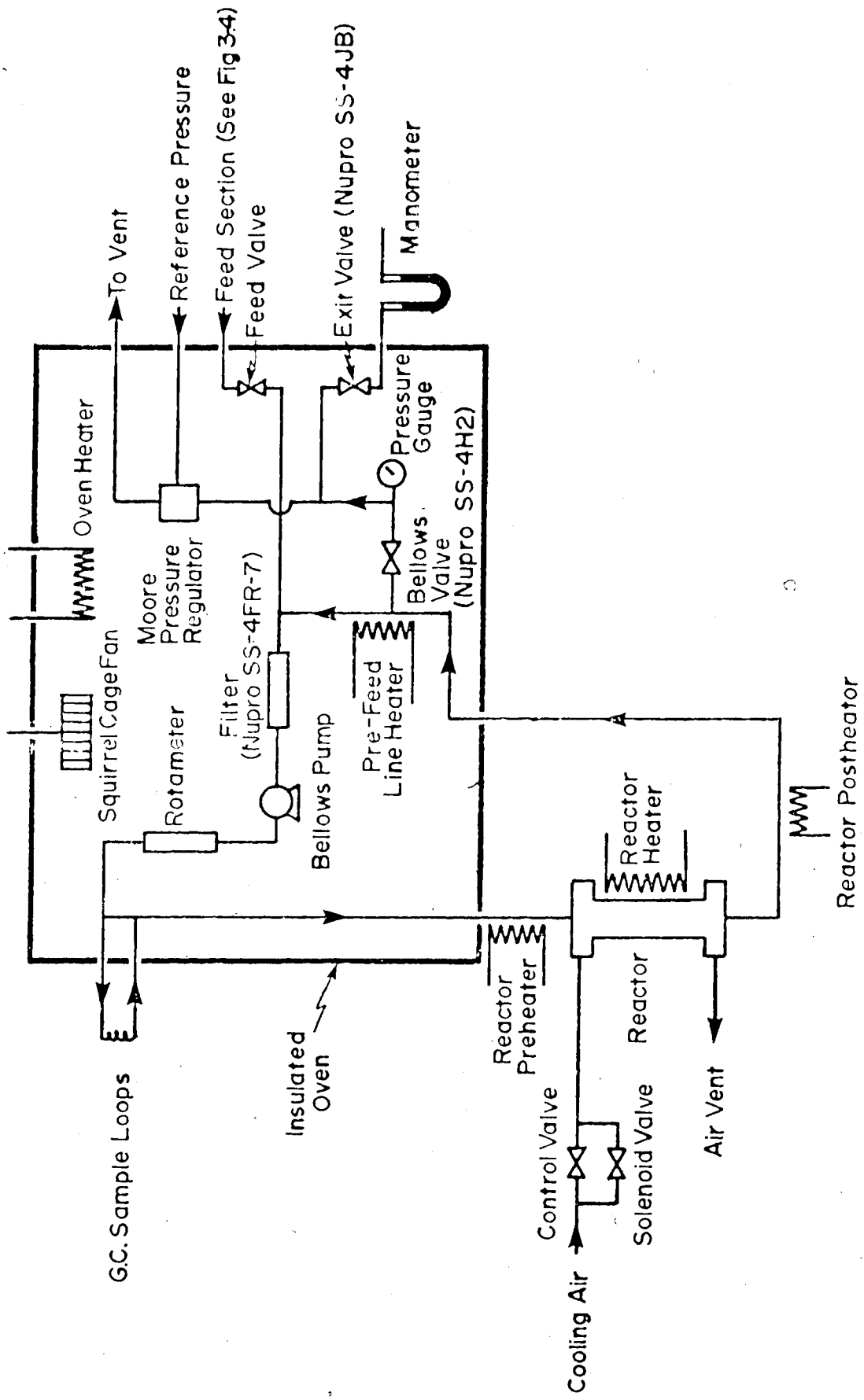

FIGURE 3.1: SCHEMATIC DIAGRAM OF EXPERIMENTAL EQUIPMENT

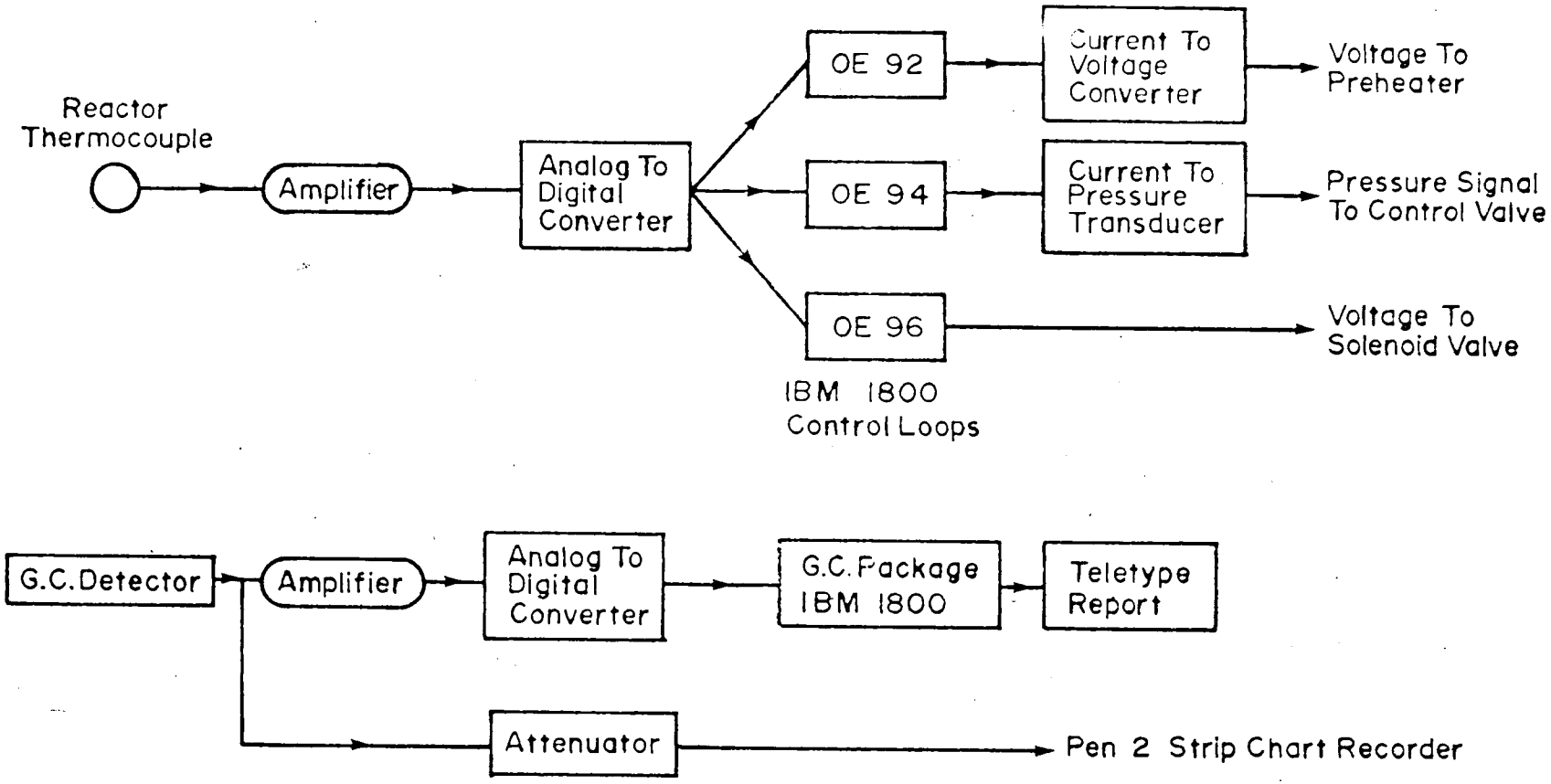

FIGURE 3.2: COMPOSITION AND TEMPERATURE MEASUREMENT

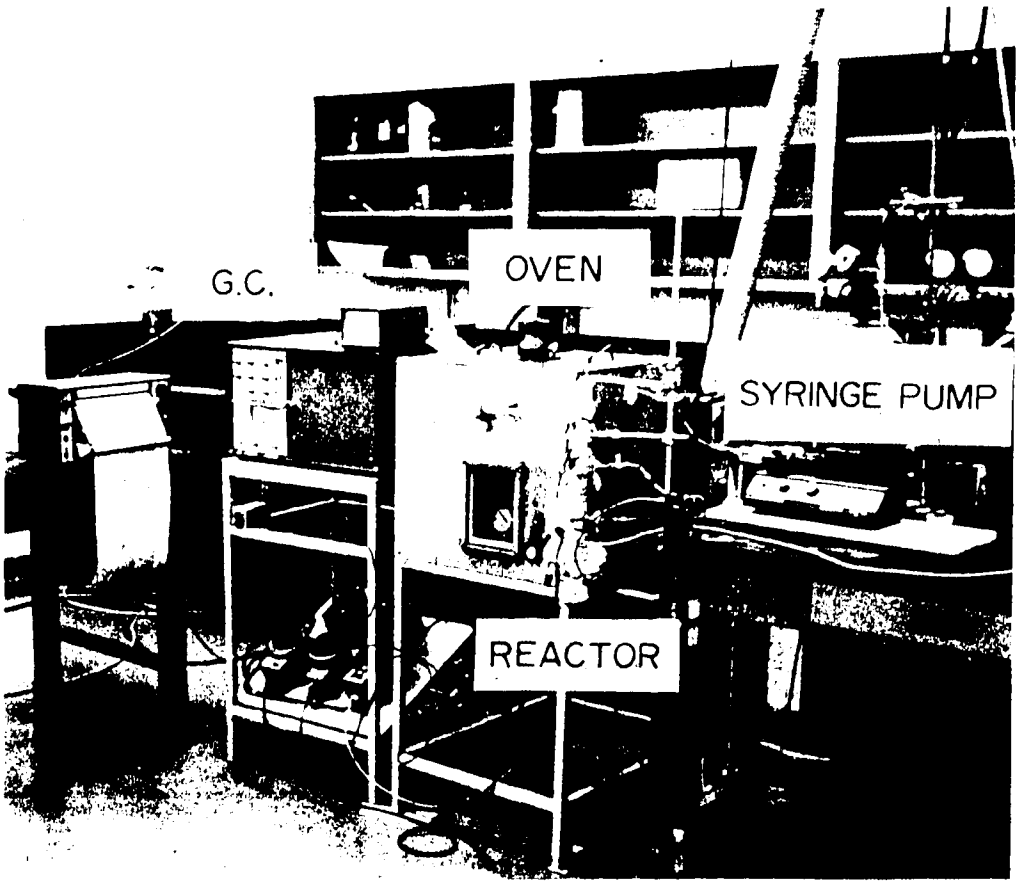

FIGURE 3.3: PHOTOGRAPH OF EXPERIMENTAL EQUIPMENT

were 0.003 to 50 ml/min (model 355) and 0.003 to 1.0 ml/min (model 352). The syringe pump and the syringe were calibrated as a unit (see Experimental Procedures).

A needle equipped with a Lur Lock was silver soldered into a short piece of 1/16 inch outside diameter (O.D.) 316 stainless steel (SS) tubing. The tubing with the Lur Lock was connected to the syringe. This tubing was connected to another piece of 1/16 inch O.D. tubing which led into the oven. The 3 foot section of feed tubing inside the oven was wrapped with copper wire to enhance heat transfer to the feed and vaporize the feed liquid as quickly as possible. A small block (1/2 inch x 1 inch x 2 inches) of aluminum was cut in half and grooved so that it could be clamped around the feed tubing just inside the oven. This was wrapped with fibreglass tape and with Nichrome resistance wire (connected across a Variac) and the whole block was loosely covered with insulation. If required, this "block" heater was used to provide supplementary heat for the feed stream.

A thermocouple was attached to the feed tubing inside the oven and this section was wrapped with insulation. Thus the outside wall temperature of the feed vaporization coil was monitored. The feed tubing joined the feed tee via a Nupro SS-2JB valve. In the feed tee (illustrated in Figure 3.4) the reactants were directed to the bottom of a modified 1/4 inch Swaglok tee. Any unvaporized liquids entrained in the feed contacted the hot wall of the feed tee, thus reducing the possibility of entrained liquids being circulated in the loop. A supplementary pre-feed line heater was available to

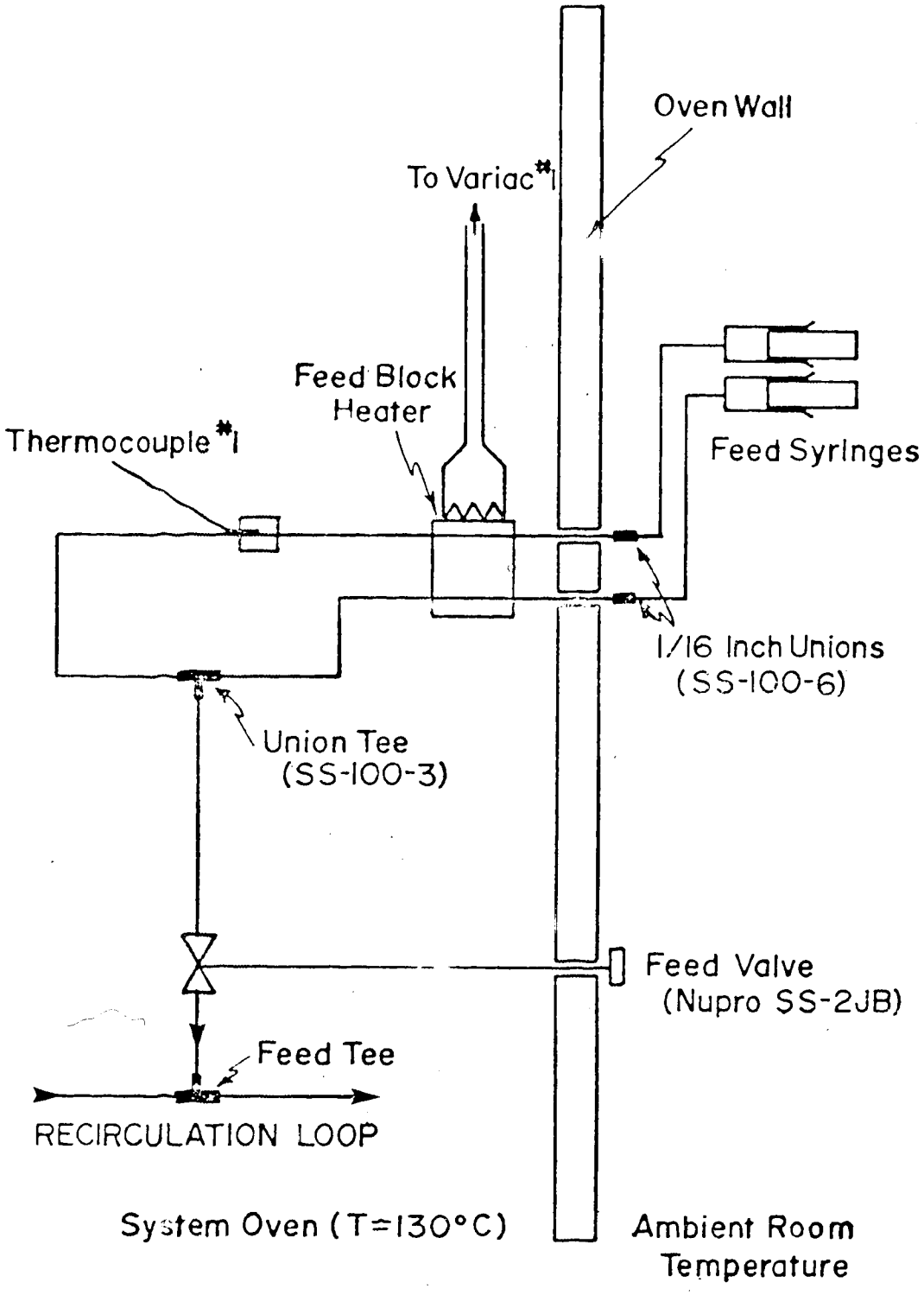

FIGURE 3.4: SCHEMATIC DIAGRAM OF FEED SYSTEM

heat the circulating vapours upstream of the feed inlet but it was not necessary to use this heater with the above feed configuration.

The system could be purged with nitrogen gas by connecting a pressure regulated nitrogen bottle to the inlet in place of the feed syringe pump. The tubing was purged before shutdown so that when the reactor system cooled there were no condensable (at room temperature) vapours in the system.

3.3 Circulation System

The oven, which contained most of the circulation loop, was constructed of sheet metal on an angle iron frame with outside dimensions of approximately 56 cm long by 51 cm wide by 53 cm in height. This was insulated on the inside with aluminum backed fibreglass duct type insulation (foil side in) approximately 2.5 cm thick (a product of Fibreglass Canada Ltd.). Attached to the removable oven lid was a 500 watt rod type resistance heater which was formed and positioned such that a squirrel cage-type fan circulated air across it. The fan was driven by a small electric motor mounted on top of the lid, i.e. outside the oven, and attached to the fan by a shaft which extended through the lid and insulation. The oven temperature was regulated at any desired value up to about 180°C by setting the voltage to the oven heater via a Variac. The time required to heat the oven from a cold start to operating temperature of ≈130°C was approximately 1.5 hours.

The majority of the tubing for the flow loop was 1/4 inch O.D. 316 SS for the section of the loop inside the oven. Starting around the loop from the feed tee, the flow was directed through a

sintered stainless steel 7 micron filter (Nupro SS-4FR-7) located at the inlet of the circulating pump, a Metal Bellows Co. 118-HT bellows pump.[1] The outside wall temperature of the pump was measured with a thermocouple (T.C. #2) taped to its back wall. The pump was driven by a 1 horsepower direct current motor equipped with a variable speed controller. The pump drive shaft extended through the oven wall and was connected to the motor shaft with a flexible coupling. From the exit side of the pump the loop continued on to a Fisher & Porter Co. rotameter (serial #7503B2015) equipped with a stainless steel float (tube No. FP-1/4-20-G-5/84). The rotameter was fixed at the front of the oven so that it could be viewed through a Pyrex window mounted in the oven wall.

From the rotameter the circulating vapours flowed to the gas sample bypass section. At this point a slip stream of the circulating vapours was sent to the gas sample valve where a sample could be taken. This slip stream was returned to the main flow loop. The lines to and from the sample valve were separated in the main loop by a short section of 1/8 inch O.D. tubing. In this restriction a small plug with a 0.050 inch I.D. hole was fitted. A small pressure drop was thus established in this section of the circulation loop and a gas flow rate of 60-100 ml/min (at S.T.P.) of the slip stream

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[1] Originally a carbon vane centrifugal pump was used but carbon dust was given off and coated the walls of the system tubing. This catalysed the reaction and adsorbed large quantities of reactants. The carbon vane pump is not suitable for applications of this type where hydrocarbons are present.

was maintained through the gas sample valve. Further details concerning the sample loop are given in the gas chromatograph analysis section. Another restrictive plug was installed just upstream of the filter. These two plugs helped damp out pressure fluctuations caused by the rapidly cycling positive displacement circulation pump.

After the sample loop section of tubing the loop led to a bulkhead union which in turn directed the flow out through the oven wall to the reactor section (this part of the equipment will be discussed in a subsequent section). After entering the oven downstream of the reactor, the flow was directed into a tee where a portion of the gas stream could leave the loop (depending on mode of operation) through a Nupro SS-4H2 Bellows valve. The majority of the stream flowed up through the pre-feed line heater (available to preheat the system vapours before injection of the feed stream) and back to the feed tee.

3.4 Sample Analysis Equipment

The sample loop was connected to a heated 18719A gas sample valve on a Hewlett-Packard 5710A gas chromatograph (G.C.). Tubing (1/16 inch O.D. 316 SS) connecting the sample valve to the flow loop was insulated and heated with Nichrome resistance wire (voltage regulated through Variac #5) to prevent condensation of sample in the section between the oven and the G.C. sample valve. The attenuated output of the G.C. detector was connected to one pen of a Hewlett-Packard 7100B strip chart recorder. The unattenuated signal was amplified (see Appendix C for details regarding the reason for

amplification) by a Hewlett-Packard 2470A amplifier and the amplified signal was monitored using the G.C. Package (16) on the I.B.M. 1800 computer. A more complete description of the G.C. analysis system is presented in Appendix C.

3.5 Loop Exit Section

The product stream left the circulatory loop through a Nupro bellows valve. A pressure gauge mounted in this section gave an indication of the system pressure in the loop. A Moore pressure regulator and a second exit port with a manual Nupro SS-4JB valve at its exit were also connected downstream of the bellows valve (see Figure 3.1). By sending a reference pressure to the pressure regulator the pressure in the system could be maintained at this desired pressure so long as the gas flow rate through the regulator was not excessive (i.e. ~500 ml/min). System pressure could also be measured by connecting a manometer to the auxiliary exit port (allowing for more accurate pressure measurements).

3.6 Reactor Section

The reactor tube, preheater and postheater sections were all made of 316 SS. The reactor section outside the oven had a preheat section (200 watts at 120v) to bring the gases flowing through the catalyst bed to the setpoint temperature. The voltage was manipulated using a current to voltage converter whose input signal (4 to 20 mA range) was set by the direct digital control (DDC) program (2) on the I.B.M. 1800 computer. Iron constantan thermocouples were situated in the reactor just above and below the

catalyst bed. These thermocouples were calibrated against a platinum resistance thermometer (see Appendix D) and could measure the temperature to within ±0.1°C. The thermocouples were sheathed in stainless steel and connected to the reactor through Conax thermocouple plugs (Cat. No. MTC-062-AA). The catalyst charges rested on a stainless steel screen and inside a sleeve of teflon (see Figure 3.1). Cooling air flowed through a spiral channel machined into the central section of the external wall of the reactor tube. An aluminum "jacket" was fitted over this portion of the reactor tube and Nichrome resistance wire wrapped around the outside of the jacket was used to heat the reactor section. The resistance wire was "cemented" permanently with zirconium cement and this was covered with a 1 cm layer of fiberglass insulation.

Air from the 550kPa (gauge) building supply system could flow downward along the reactor tube through the external channel to provide cooling. This air flow was regulated via a control valve or a solenoid valve. The temperature in the catalyst bed was regulated by adjusting the air flow through the cooling jacket or by adjusting the voltage to the reactor preheater. The thermocouple output (referenced to an ice bath) was amplified 300 times (Hewlett-Packard 2470A amplifier) and connected to the I.B.M. 1800 computer.

The section of tubing connecting the reactor exit to the oven was heated and insulated to prevent condensation of some of the circulating fluids.

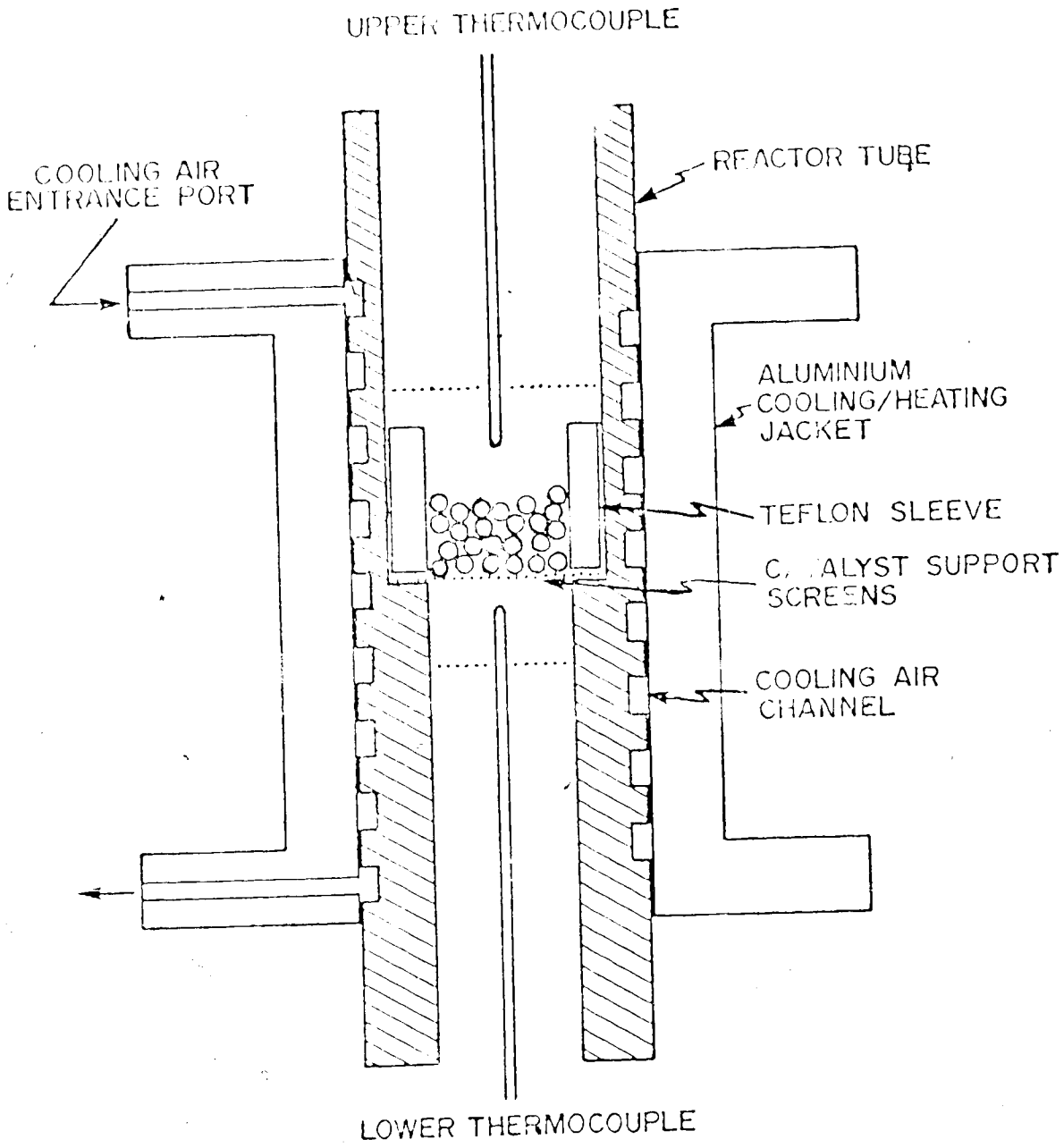

FIGURE 3.5: SCHEMATIC DIAGRAM OF THE REACTOR

3.7 Reagents and Catalyst

The catalyst used was obtained through representatives of the Dow Canada Ltd. offices in Calgary. Dowex Ion Exchange Resin HGR-W (H^+ form) lot no. MM 0865-.. , B-10 was used. The size was 20-50 mesh and the exchange capacity was 4.8 milliequivalents of cation exchange capacity per gram of dry resin. Other details are as described in a publication of the Dow Chemical Company (20).

The ethyl alcohol was obtained from the Chemistry Stores at the University of Alberta. Chromatographic analysis of each batch indicated that the only significant impurity was water. Reagent grade acetic acid and ethyl acetate were purchased from the Fisher Scientific Company. Double distilled laboratory water was used and gas chromatographic analysis did not indicate the presence of any impurities. The ethyl ether was labeled as analytical reagent and supplied by Mallinckrodt Canada Ltd. All the constituent components of the feed mixtures were analysed for composition. The final composition of feed mixtures was arrived at by correcting for the foreign components found. The only significant impurities in each of the five liquids described above were internal (i.e. only one or more of the components: water, ethanol, ether, ethyl acetate or acetic acid).

The Porapak gas chromatograph column packing materials were made by Waters Associates. Porapak Q-S, R, S and T (all 80-100 mesh) were used in the preparation of G.C. columns during this work.

3.8 General Equipment Information

3.8.1 System Volume

The volume of the circulation loop was determined to be 126 cm^3 + 2 cm^3. This was an "average" figure arrived at with the circulation pump in operation. A vessel of known volume at a higher pressure was attached to the system (which was at atmospheric pressure). The valve between the system and the known volume was opened and by measuring the pressure of the combined volume it was possible to calculate the volume of the reactor system.

3.8.2 Mode of Operation and Recirculation Rate

The equipment could be run as a batch reactor or as a continuous differential recycle reactor. In either case the recirculation rate was approximately 10 l/min (vapour at any temperature and pressure).

3.8.3 Temperature Control

The temperature of the catalyst bed was accurately controlled and hence the temperature at which the reaction was taking place could be easily manipulated. Using the electrical preheater and air cooling it was possible to heat the catalyst section at a rate of about 20°C/min and to cool this section at a rate of about 14°C/min. The temperature control capability was such that the temperature was within (and stayed within) 0.2°C of a new setpoint 7 min after a 20°C setpoint change (90°C - 150°C range of operation) and at a constant setpoint the controlled temperature varied less than ±0.1°C.

CHAPTER FOUR

EXPERIMENTAL PROCEDURES

4.1 Catalyst Preparation

A portion of the ion exchange resin was set aside in air for at least 5 days on a stainless steel mesh. The reason for this procedure was to reduce problems in pouring moist catalyst and to prevent any mass changes during the weighing of catalyst charges. The catalyst was loosely covered with a sheet of paper to prevent contamination by dust. Thus the moisture content of the resin attained equilibrium with the air and no weight losses were encountered when weighing individual catalyst charges. Catalyst charges were then prepared with raw weights that ranged between 0.1 and 0.7 g. The moisture content of the batch (at the time individual charges were prepared) was determined via the procedure described below.

A larger portion of the catalyst was weighed into a glass vial for bone dry weight determination. A glass wool plug was inserted into the neck of the vial and it was placed in a vacuum oven ($\approx$0.3kPa) at about 120^{o}C for two or three days. After removal from the oven the glass wool plug was taken out and the moisture content of the catalyst batch could be determined from the weight loss. It should be noted that if the vacuum dried resin was returned to the oven for another day, the additional weight change was

negligible. No weight change was observed during the time required to weigh the fine dry samples. All weights were determined to the nearest 0.0001 g on a Mettler H10w balance. Details concerning the individual catalyst charges prepared during the course of this work are presented in Appendix E.

4.2 Syringe Pump Calibration

Calibration curves were determined for all pump and syringe combinations. Distilled water was used as the calibration fluid. The calibration points for the two syringes fell on the same lines (i.e. the syringes were so similar that they were interchangeable).

Each calibration point was determined as follows. A 10 millilitre flask with a ground glass stopper was weighed empty. Water was injected into the flask by a syringe pump equipped with a needle. From the elapsed time and the weight of water injected a volumetric flow rate (given the density of H_2O) was calculated. Since the flow rates involved were quite low and some very low flow rate calibrations required up to 3 hours, precautions had to be taken to ensure that evaporation of water from the receiving flask did not prejudice the calibration curve. The injection needle was bent and inserted through a small cork stopper which had another needle through it to act as a vent. Thus when the timing was started the flask was lifted so that the cork blocked the neck of the receiving flask. In addition, for the model 355 calibration the receiving flask (which was inside a 250 ml beaker) was cooled by surrounding it with air which had been sent through tubing coiled in an ice bath. The temperature inside

the beaker was thus maintained at about 14°C and the relative humidity inside the stoppered calibration flask was increased, ensuring a low evaporation rate. Detailed calibration data are presented in Appendix F. The very linear nature of the calibration curves suggests that evaporation of water during calibration points was minimal. The calibration curves were within 2 per cent (at higher flow rates) of the approximate values suggested by the manufacturer. (The suggested values are nominal values for a given size of syringe.)

4.3 Thermocouple Calibrations and Temperature Measurement

The iron-constantin thermocouple which was the basis for temperature measurement and control of the reactor catalyst bed was calibrated against a platinum resistance thermometer over the range of 100 to 140°C. Other details regarding the calibration points are presented in Appendix D. During system operation compressed air was bubbled slowly through the ice bath used and the resulting agitation helped maintain the reference temperature constant. During steady-state, temperature-controlled operation, the reactor temperature varied less than ±0.1°C.

The thermocouple output was amplified 300 times to reduce error caused by digitization of the signal in the I.B.M. 1800 computer. This amplification factor was very steady. Spot checks showed that the temperature calculated using the amplified signal and the temperature calculated from the signal before amplification (measured by a Leeds and Northrup millivolt potentiometer Cat. No. 8686) differed by less than the temperature variation during

steady state temperature controlled operation.

Another consideration in the accuracy of the temperature measurement was the effect of the gas temperature gradient in the reactor tube on the temperature measurement (i.e. differences between thermocouple and gas temperature due to conduction along the thermocouple). Theoretical analysis (see Appendix D) of heat conduction and convection along the thermocouple indicated that the temperature measured by the thermocouple was no more than $0.2^{o}C$ different than the actual gas temperature. This was a very conservative estimate and the actual maximum temperature difference was probably less than $0.1^{o}C$.

The catalyst bed itself could have an actual length up to about 4 cm (for dehydration kinetic runs) and it was possible that a temperature gradient could exist along the catalyst bed. During kinetic runs any potential gradients were minimized by adjusting the reactor section heating and cooling so that the measured temperatures above and below the catalyst bed were matched. Measurements of the temperature along the reactor tube (above and below the Teflon sleeve) under simulated kinetic run conditions indicated (see Appendix D) that the section of reactor tube inside the Teflon sleeve was essentially isothermal.

There were four other thermocouples in the system. These were used to measure the wall temperature of the feed line, the pump temperature, the temperature just below the catalyst section of the reactor and the temperature of the post heater section between the reactor and the oven. These readings could all be displayed on the

strip chart recorder (through a 4 way switch). Thus the Variacs regulating the heating for these various sections of the system could be adjusted to get the desired temperatures.

4.4 Preparation of Feed Mixtures

In the preparation of liquid mixtures the components were always added to the sampl bottle in approximate order of increasing volatility (order of addition water, acetic acid, ethanol, ethyl acetate, ether). The ethanol used for making up the mixtures was kept in a refrigerator at -2°C prior to its addition and the diethylether was stored in the freezer section of the refrigerator at about -20°C. This was done to reduce weight changes due to evaporation during the blending and weighing of liquid mixtures and also to minimize the effect of the homogeneous liquid phase esterification reaction (equation 1.2) when ethanol and acid were both present in the feed.

The required weight fraction of a mixture was calculated from the mole fraction of that mixture. This, together with the liquid density of the components involved and the total expected sample weight (normally 50 to 100 grams), was used to calculate the required volume of each constituent which would yield the desired mixture. The compositions of mixtures were such that they were outside the ranges of immiscible compositions (immiscible compositions can exist for ethanol, ether, water mixtures or for ethanol, ethyl acetate, water mixtures).

The calculated volumes of the constituent liquids were then added to the sample bottle and the weight difference before and after

the addition of each component gave the weight of that component in the mixture. Liquid components were added with 10 ml and 50 ml pipettes which were cleaned with wash ethanol and thoroughly dried before use for each different component. Weights were determined to the nearest 0.0001 g.

After all the required components were added and capped sample bottles were stored in the refrigerator prior to use. The feed syringe (barrel only) was chilled in the refrigerator for 10 to 15 minutes before the chilled liquid mixtures were added. The feed syringe was equipped with a section of 1/16 inch (O.D.) tubing and this was blocked off with a rubber plug to stop the flow of liquid out the nozzle during the course of filling the syringe. The liquid sample bottle was vigorously shaken before the cap was removed and liquid mixture was poured into the chilled syringe barrel. The plunger was then inserted into the syringe, the syringe was inverted and the air pocket was forced out through the feed tubing (in a fume cabinet). The syringe was carried to the equipment and the feed mixtures were ready to be injected.

For the G.C. calibration feed mixtures the exact feed rate did not have to be known, therefore it was not necessary to allow the liquid in the feed syringe to reach room temperature (the density of the feed [used to calculate feed rate] was known at this temperature but the esterification reaction rate was also increased). In the case of dehydration runs there was no danger of a homogeneous reaction and the syringe was kept at room temperature for a sufficient amount of time to allow the feed liquid to reach room

temperature before the final steady state data were taken. For the esterification reaction the equipment was modified to allow the use of two syringes and the ethanol and acetic acid could be segregated.

The density of the feed liquids was determined experimentally by using a pycnometer. Determination of the weight of liquid which would fill the known volume vessel allowed one to calculate the liquid density. For some feed mixtures (water-ethanol) density-composition tables were available. The experimental density was always within 0.002 g/cm^3 of tabulated density. Therefore this was an accurate means of measuring liquid density.

4.5 Operation and Calibration of the Gas Chromatograph

4.5.1 Gas Chromatograph Operation

A Hewlett-Packard 5710A gas chromatograph was used to carry out the analysis. The following chromatograph column and operating conditions were used to separate water, ethanol, diethyl ethe ethyl acetate and acetic acid.

Columns: The two columns (A & B) were identical composite columns 4 feet long and made up of three sections. A 1/2 foot section of Porapak S was connected to a 3 foot section of Porapak R and the last section contained 1/2 foot of Porapak Q-S. The column tubing was 1/8 inch diameter 316 stainless steel seamless tubing (thinwall; 0.020 inch wall thickness). Connections between column segments were with standard Swagelok unions.

Column Temperature: The analysis was carried out with the columns at 185°C (i.e. isothermal G.C. oven temperature).

Carrier and Reference Gas Supply Pressure: Helium was used as the carrier gas. The upstream supply pressure was regulated at 60 psig.

Carrier and Reference Gas Flow Rate: The flow rate through each of the columns was regulated at about 45 ml/min at ambient

conditions (25°C, 93.5 kPa). This was equivalent to a flow rate of about 38 ml/min at S.T.P.

Detector: The detector temperature was controlled at 250°C and the bridge current sensitivity setting was 4 (~150 milliamperes).

Gas Sample Valve: A two loop Hewlett-Packard 18 719A gas sample valve was used to inject vapour samples.

Gas Sample Valve Temperature: The controller for the heated gas sample valve was set for 200°C.

Gas Sample Volume: Loops of sample volume 0.25 ml were used.

Liquid Injection Port Temperature: For liquid sample injections the injection port temperature was controlled at 150°C.

Liquid Sample Size: Liquid samples ranged in volume from 1.0 to 1.5 microlitres.

Additional details of the analysis, including a typical chromatogram, are given in Appendix C.

The gas sample valve was operated at 10°C intervals when heating the valve from 150°C to 200°C to insure that the Teflon parts did not seize up. The gas sample volume used for the experiments was 1/4 ml. Sample loops with volumes of 1/2 ml and 1/8 ml were also tried but the larger sample size resulted in increased fusion of component peaks while the smaller volume did not result in sufficient response for accurate analysis for low concentration components.

The carrier gas flow rate was measured with a bubble meter. Spot checks indicated that the carrier gas flow rate through the column remained constant over long periods of time given a constant regulated supply pressure. At the inlet of the gas chromatograph the gas passed through a drying tube containing molecular sieve 5A which reduced the moisture content of the helium.

The molecular sieve material had to be regenerated periodically (heated overnight at 300°C every 6 - 8 months) to insure that prolonged contact with excessive water (in the helium) did not degenerate the chromatograph columns.

The short term (i.e. overnight) shutdown of the G.C. system involved a reduction of the helium supply pressure to about 20 psig. The detector controller remained at 250°C with the sensitivity (brige current) off and all other temperature controllers turned off. Normally during start up of the G.C. in preparation for a run the oven was operated at 200°C while the detector output stabilized (about 2 hours).

4.5.2 Calibration with Gas Samples

Getting consistent, reproducible gas samples for analysis proved to be more difficult than at first imagined. Initially the samples were fed (via the syringe pump) into some connecting tubing in the heated oven and then directly into the sample valve. This resulted in widely fluctuating detected peak areas for repeated injections. Apparently the different components in the samples were not being vaporized in a steady manner. The feed was being vaporized in slugs and a particular injection might involve a sample rich in the lower boiling point components while another injection might be rich in the higher boiling point components.

This problem was solved by feeding the liquid mixtures into the circulation loop in the hot oven while the circulation pump was running. The vaporized sample was thus circulated in a smaller volume loop (the sample section was connected directly to the feed

tee with the loop exit just before the feed tee) with no catalyst present. This procedure resulted in reproducible peak areas.

The response factors for the components were defined relative to the ethanol (ETOH) response factor of 1.56 (4,18) according to equation 4.1.

$$RF_i = 1.56\ (A_i/A_{ETOH})/(x_i/x_{ETOH}) \qquad (4.1)$$

(A_i/A_{ETOH}) being the peak area ratio and (x_i/x_{ETOH}) the mass ratio. Response factors for the other compounds were calculated from analysis of mixtures of known composition. It was necessary to use different response factors for the two sample valve loops to give consistent results but for each loop only one set of response factors was used. Just as the liquid phase response factors are different from those obtained with vapour phase samples, there is no reason to presume that the response factors for two different gas sample loops should be identical. In fact the peak shapes for identical samples analyzed with the two different loops are different. The differences could be caused by the restricted nature of the small (≈1/32 inch internal diameter) sample loop tubing resulting in slightly different sample sizes and sample injection pulses which are unique to each loop. The response factors for all components are given in Table 4.1. Plots of the response factors versus the mass ratios are presented in Appendix C.

The ethanol and ether peaks tended to be fused to some extent (more so for gas samples) and the area calculation procedure used produced a change in the ether response factor when the area

TABLE 4.1

RESPONSE FACTORS

Component	Liquid Sample	Vapour Samples Loop 1	Vapour Samples Loop 2	Literature Value (4,18)
Water	1.83	2.07 (2.2)[1]	1.87	1.82
Ethanol	1.56	1.56	1.56	1.56
Ether	.47	1.37	..	1.49
Ethyl acetate	1.29	1.29	1.30	1.27
Acetic Acid	1.22	1.24	1.20	-

[1] See Section C.3, Appendix C

ratio of ether/ethanol was less than about 0.2. The peak area calculation procedure used for all other components resulted in a calculated ether area that was too high for samples of lower ether composition. The area calculation option in the G.C. program which was used for the ether peak drew a base line between a point in the region between the ethanol and ether peaks and the end of the ether peak (16).

The ether response factor for loops 1 and 2 was adjusted according to equations C.1 and C.2 (Appendix C) for smaller area fractions of ether/ethanol.

Given these response factors one could calculate compositions according to equation 4.2.

$$x_i = \frac{(A_i/RF_i)}{\sum_{k=1}^{n} \frac{A_k}{RF_k}} \qquad (4.2)$$

The composition calculated from the analysis of known feed mixtures for a number of samples is presented in Appendix C. Calculated compositions were consistent with the known compositions.

4.5.3 Injection with Liquid Samples

Liquid phase samples were injected into column B. A number of component mixtures were used to determine response factors for liquid samples. Response factors were calculated according to equation 4.1 and these were close to the literature values (4,18) (see Table 4.1). Analysis of liquid samples was carried out to calculate the fraction of impurities in the components which were blended (see section 3.7) to get the feed mixtures.

4.6 Insertion and Removal of Catalyst Charges

Prior to the filling of the reactor with catalyst, a 40 mesh stainless steel screen was positioned so that it rested on the ledge along the reactor tube (see Figure 3.4). Another stainless steel screen (~100 mesh size) was set in place above the 40 mesh screen. Two lengths of Teflon sleeve were then positioned on the screens. The lower one was 3 cm long and the upper one was 2 cm in length. These sleeves were made so that their internal diameter was equal to the I.D. of the reactor tube below the ledge and their outside diameter was such that they fit tightly into the upper section of the reactor tube. Two metal rods which had diameters close to that of the reactor tube above and below the ledge respectively were used to position and remove the screens and sleeves.

The catalyst was then poured into the reactor. This

operation was carried out by inserting a glass funnel with a long stem into the reactor tube. The catalyst charge was then poured from a vial into the funnel. A problem was encountered at this point because the catalyst beads tend to adhere to the glass walls of the funnel tube. To overcome this situation it was necessary to heat the reactor section and preheater to a moderate temperature ($50^{o}C$ - $70^{o}C$). The upper section of the funnel, which extended beyond the preheater section, was heated using a portable fan heater. The adhesion between the glass and the catalyst beads was reduced at higher temperatures so that the catalyst spheres flowed into the reactor tube. While the above procedure was useful for getting the catalyst into the reactor, it may have been responsible for some catalyst deactivation (in the case of some batches of catalyst) because of overheating of the catalyst during the insertion into the reactor. An improved procedure for filling the reactor with catalyst was employed in loading charge #6 of Batch 2. For this charge a long-stem funnel was fashioned out of paper and it was not necessary to heat the reactor tube since the catalyst did not stick to the paper.

The catalyst removal procedure involved using a metal rod to raise the entire catalyst section 1 or 2 cm. A small (1/16 inch diameter) rod was then inserted from above and pushed through the catalyst particles to tilt the screen discs below the sleeve section. The particles flowed out and were caught in a beaker (u[illegible] and put in labelled vials) at the bottom of the [illegible] he[illegible]reens and sleeves were then

pushed out of the top of the apparatus and the clear reactor tube could be cleaned thoroughly in preparation for the next charge of catalyst.

4.7 Operation of Equipment

4.7.1 Equipment Startup

In preparation for starting the circulation pump and the injection of feed the following operations were performed on the system components listed below.

G.C. System: This equipment was set to its normal operating state as described in section 4.5.1. In addition it was necessary to turn the G.C. signal amplifier on and to make sure that the G.C. analysis program on the IBM 1800 was operational. When the G.C. output had stabilized the baseline was set. The detector output at a G.C. attenuation of 1 was adjusted with the zero adjustment until it corresponded with the output at an attenuation of ∞.

Strip Chart Recorder: The recorder was turned on at a low chart speed (≈2 inches per hour) with the upper (red) pen set at a span of 0.10 mV. This pen was used to record the output from thermocouples 1 through 4. The span on the lower (black) pen was set at 1mV and this recorder channel was connected to the attenuated output of the G.C. detector.

Reactor System Oven: The squirrel cage fan on the lid of the oven was started and a full 120 V was sent to the oven heater via Variac #2. The oven temperature was monitored during startup and when the output signal from thermocouple (T.C.) #2 reached 7mV (≈131^{o}C) the Variac was adjusted to its "normal" run setting of ≈80%.

Ice Baths: The two vacuum flasks were filled with ice and water so that the liquid water level was near the top of the bottles. One bath served as a reference temperature for the thermocouples connected to the strip chart recorder. The other bath was the reference for the thermocouple measuring the reactor temperature. The cold junction of this thermocouple was strapped to an air tube and the assembly was immersed in the ice-filled vacuum flask so that the mixture was agitated by the bubbling of air.

Temperature Control Loops: The reactor thermocouple amplifier was turned on and the two P D.C. loops (2) (these loops perform the function of conventional controllers) controlling temperature

were made "operable manual" so that the reactor temperature could be measured and printed out when requested. Loop OE92 controlled the reactor preheater while loop OE94 controlled the flow of cooling air through the reactor cooling jacket.

Interheater between the Oven and the G.C. Sample Valve: The Nichrome resistance wire which was wound around the insulated section of sample tubing which carried a slipstream (of reactor vapours) to and from the G.C. sample valve was supplied with a voltage of about 14V via Variac #5. This insured that there was no condensation of reactants in this section of tubing.

Reactor Postheater: The reactor postheater was composed of Nichrome resistance wire wound around a long copper tube (covered with insulating tape) which was in turn wound around the section of tubing leading from the reactor back to the oven. The voltage across this section was about 70V (via Variac #4) during startup. As the temperature of this section (as monitored by T.C. #4) reached about 130°C the voltage was reduced to it's "normal" run setting of ~57V.

Feed Block Heater: The voltage sent to the feed heater was regulated via Variac #1. This was set at 6% to 10% depending on the feed flow rate. It was not necessary to use this block heater until just before the feed was started.

As the temperature of various system components approached the "run" values (this normally took 1 to 1.5 hours), the cooling air was set to its "normal" value (30% output on OE94). The reactor heater was set to about 50% (via Variac #3) and the voltage to the preheater was set to a medium value (or manual). When the reactor temperature approached 80°C the circulation pump (speed setting 8) and the feed pump (note: exit bellows valve and feed valve open), at some moderate setting (e.g. 100% setting at 1.00 range), were started. The feed during startup was usually pure ethanol or some ethanol-water, ethanol-ether mixture. This was to prevent any condensation problems which might have been caused by the presence of higher boiling point components. As the reactor temperature rose towards the desired setpoint value the preheater

controller (loop OE92) was set to the automatic control mode. The system was thus set for the start of any desired run. Additional details regarding experimental procedures are presented in Appendix G.

1.7.2 Procedures During a Run

During experimental kinetic rate runs the following procedures described below were carried out.

Recording DDC Loops: During control studies the DDC loops should be checked and recorded at the beginning of each series of runs. A listing of the control loops is presented in Appendix G. For this work the DDC package was used for simple temperature control only and the state of the loops was not recorded for each run.

Changing and Controlling Reactor Temperature: For temperature controlled operation the reactor setpoint temperature could be changed by adjusting loop OE92 through the teletype keyboard. For any desired reactor temperature, the temperature just below the catalyst bed (measured via T.C. #3) was adjusted (by manipulating Variac #3) so that the temperature above and below the catalyst bed were matched.

Changing and Setting Feed Rate: The feed syringes were connected to the system with Swagelok unions located just outside the oven. When only one syringe was used the second feed port was blocked off. The desired feed rates were set manually to the required values on the syringe pumps. Because the feed rates were sometimes quite low the feed valve was only opened about 1/4 turn. In this way the feed pumps were always working against a positive pressure and there was no opportunity for the fluctuating pressure in the circulation loop to affect the feed rate (this was possible with more volatile feed compositions). The exit section bellows valve was also choked back to about 1/4 turn open to help stabilize exit pressure.

Taking Gas Samples: The procedure for taking and analysing a vapour sample involved the following steps. The chart speed on the recorder was increased to 1, 1/2 or 1/5 inches per minute. The IBM 1800 interrupt button connecting the unattenuated, amplified G.C. signal to the computer was pressed and when the interrupt light came on the sample valve was switched. The appropriate attenuation was set for each peak (on the G.C. panel) and injection number was recorded on the strip chart output and on the teletype output when the sample report was printed. At least 6 to 8 samples were taken once

the experimental product analysis for each run had stabilized. Runs were carried out over at least a one hour time interval but some low flow rate dehydration runs took 4, 5 or more hours to reach steady state.

Reading Atmospheric Pressure: During each run (normally towards the end of the run) the barometric pressure was measured using a Cenco barometer (cat #76878) located in Room 404 of the Chemical-Mineral Engineering Building at the U of A. This room was across the hall from the area in which the experiments were being carried out. Atmospheric pressure varied between 92 and 95 kPa.

The output signals from the four thermocouples were checked by using the 4 way switch. The temperature normally recorded was the indicated temperature from thermocouple #3 just below the catalyst bed. The other three temperatures did not vary to any great extent with all the equipment operating at steady state and they were only recorded once or twice during each run.

4.7.3 Shutdown of the Equipment

The shutdown procedures at the end of an experimental run are described below.

Feed System: If the feed contained any acetic acid, the circulation loop was flushed by feeding ethanol or an ethanol mixture (not containing any acid) for 5 or 10 minutes at a relatively high feed rate (e.g. 100% setting at 1/100 range). The feed was shut off and the nitrogen was connected to the feed port. The nitrogen was used subsequently to flush the system (see nitrogen purge).

G.C. System: The G.C. signal amplifier was turned off and all other parameters were set as described at the end of section 4.5.1.

Temperature Controllers: The DDC loops for temperature control were placed into the operable manual mode. After the shutdown procedure was completed they were placed in the non-operable mode and the reactor thermocouple signal amplifier was turned off.

System Heaters: The voltage to all heaters (including the preheater) was set to zero. The oven and other insulated

portions of the system cooled slowly (≈2 hrs. to reach 30°C) therefore there was no danger of any condensation during the rest of the shutdown procedure.

Nitrogen Purge: As the temperature of the reactor approached 80°C the feed valve was opened wide and nitrogen gas (at a regulated pressure of ≈2 psig) was fed into the circulation tubing for 4 or 5 minutes. This prevented any condensation during the remainder of the cooling phase.

Circulation Pump: After the nitrogen purge the circulation pump was turned off and the oven fan was also stopped.

Catalyst Bed Cooling: The air flow through the reactor cooling jacket was increased to its maximum value for ≈5 min. and the catalyst bed temperature quickly dropped towards room temperature. The cooling air flow was then stopped.

Thermocouple Cold Junctions: The two cold junctions were removed from the ice baths. The iron-constantin thermocouples tended to corrode very quickly when left in water for extended periods of time.

Strip Chart Recorder: The pens were lifted from the recorder paper and the recorder was turned off.

After a spot check to insure that motors, pumps, heaters, amplifiers, G.C. detector current and recorder were all off the equipment was in a safe shutdown state.

CHAPTER FIVE

RESULTS FOR THE DEHYDRATION REACTION

5.1 Introduction

The dehydration reaction runs were carried out at three temperatures (110, 120 and 130^{o}C) over a period of about 4 months. The reactor pressure during experimental runs was atmospheric, which varied between 92 kPa and 95 kPa. Five different feed mixtures were used during the dehydration runs. Experimental runs performed without any catalyst in the reactor showed that no dehydration of ethanol occurred in the absence of catalyst (the temperature and feed rate were similar to those used during actual runs). Repeat runs made after 20 to 40 hours of operation with the same catalyst charge reproduced the original runs very well. Contacting the catalyst with water, ethanol and ether vapours did not result in any catalyst deactivation.

5.2 Consistency of Dehydration Data

The dehydration runs used to determine the kinetic constants for the dehydration reaction are summarized in Table 5.1. The compositions of the feed mixtures which were used during the dehydration runs are presented in Appendix H. Results for each run are summarized in Appendix I. Also included in Appendix I are runs which were less reliable for a number of reasons. The method used to calculate the dehydration rates is included in Appendix I

TABLE 5.1

DEHYDRATION REACTION RUNS

Run	T (°C)	Feed	Feed Rate[1] / Cat. Mass x10[3]	Conversion (%)	Rate[1] x10[4]	
III-1	110.0	ETOH[2]	0.825	4.89	0.403	
III-4	110.0	ETOH	0.325	9.69	0.315	
IV-1	135.0	ETOH	2.480	7.31	1.810	
IV-2	135.0	ETOH	1.100	14.11	1.550	
IV-3	135.0	ETOH	1.653	10.36	1.710	
IV-4	135.0	ETOH	0.823	17.27	1.420	
V-1	120.0	ETOH	0.826	8.30	0.685	
VI-1	135.0	ETOH	0.677	20.12	1.360	
VII-1	135.0	ETOH	0.679	20.77	1.410	
VII-2	135.0	ETOH	0.405	29.13	1.180	
VII-3	135.0	ETOH	1.096	14.70	1.610	
VII-4	135.0	ETOH[2]	0.682	20.85	1.420	
VIII-1	135.0	XXXI[2]	0.820	14.23	0.898	
VIII-2	135.0	XXXI	0.322	27.60	0.685	
VIII-3	135.0	XXXI	1.315	9.66	0.978	
IX-1	120.0	XXXI	0.985	4.93	0.374	
X-1	110.0	XXXI	0.322	4.55	0.113	
XI-1	135.0	XXXII[2]	0.582	24.93	1.140	
XII-1	135.0	ETOH	1.051	15.05	1.580[3]	
XII-2A	135.0	ETOH	1.127	14.13	1.590	(1.483)[4]
XII-3	135.0	ETOH	2.275	8.01	1.820	(1.698)[4]
XII-4	135.0	ETOH	0.554	24.20	1.340	(1.250)[4]
XII-5	135.0	ETOH	1.706	9.92	1.690	(1.576)[4]
XII-6	135.0	ETOH	1.131	13.99	1.580	(1.474)[4]
XII-7	135.0	ETOH	1.253	13.18	1.650	(1.386)[4]
XII-8	135.0	ETOH	1.375	12.16	1.670	(1.281)[4]
XIV-1	110.0	ETOH	0.556	6.61	0.367	(0.342)[4]
XIV-2	110.0	ETOH	0.287	11.54	0.331	(0.309)[4]
XVII-2	135.0	ETOH	1.495	11.45	1.710	
XVII-3	135.0	ETOH	0.889	17.57	1.560	

[1] Units are (mole/min g cat.)).

[2] Feed ETOH contained ~0.15 mole % water, feed XXXI was 23.05% water and feed XXXII was 0.11% water and 21.43% diethyl ether. Feed compositions are listed in Table H.1.

[3] The rates for run series XII and XIV were all adjusted to account for initial deactivation of the catalyst batch used.

[4] Rates before adjustment for catalyst deactivation due to exposure to acetic acid during E series runs.

along with a sample calculation.

One way of presenting the rate data is to plot the dehydration rate against the conversion (at one temperature and pressure). The data for a fixed feed composition should fall on a smooth curve. As the overall space velocity (feed rate/mass of catalyst) approaches ∞, the rate is equal to the rate for a fluid with a composition identical to the feed composition. In the ideal case as the space velocity approaches zero, the conversion approaches a value at which the composition of the reacting mixture is equal to the equilibirum composition.

The dehydration rate data were plotted at three different temperatures and are presented in Figures 5.1 to 5.3. The solid lines indicate the calculated curve using the final dehydration model as described in equation 2.4 (see Section 5.4). The rate as a function of conversion was calculated from the temperature, pressure (assumed to be 93.5 kPa) and the composition corresponding to various values of the conversion.

There is little doubt that the large amount of data at $135^{o}C$ is more reliable than the limited data at lower temperatures. Thus any model which fits the isothermal rate data at the higher temperature is probably a reasonable model for the dehydration reaction throughout the temperature range of interest. The rate at lower temperatures is much lower than the rate at $135^{o}C$ resulting in less accurate data. Hence the fit of the model will be poorer for the lower temperatures.

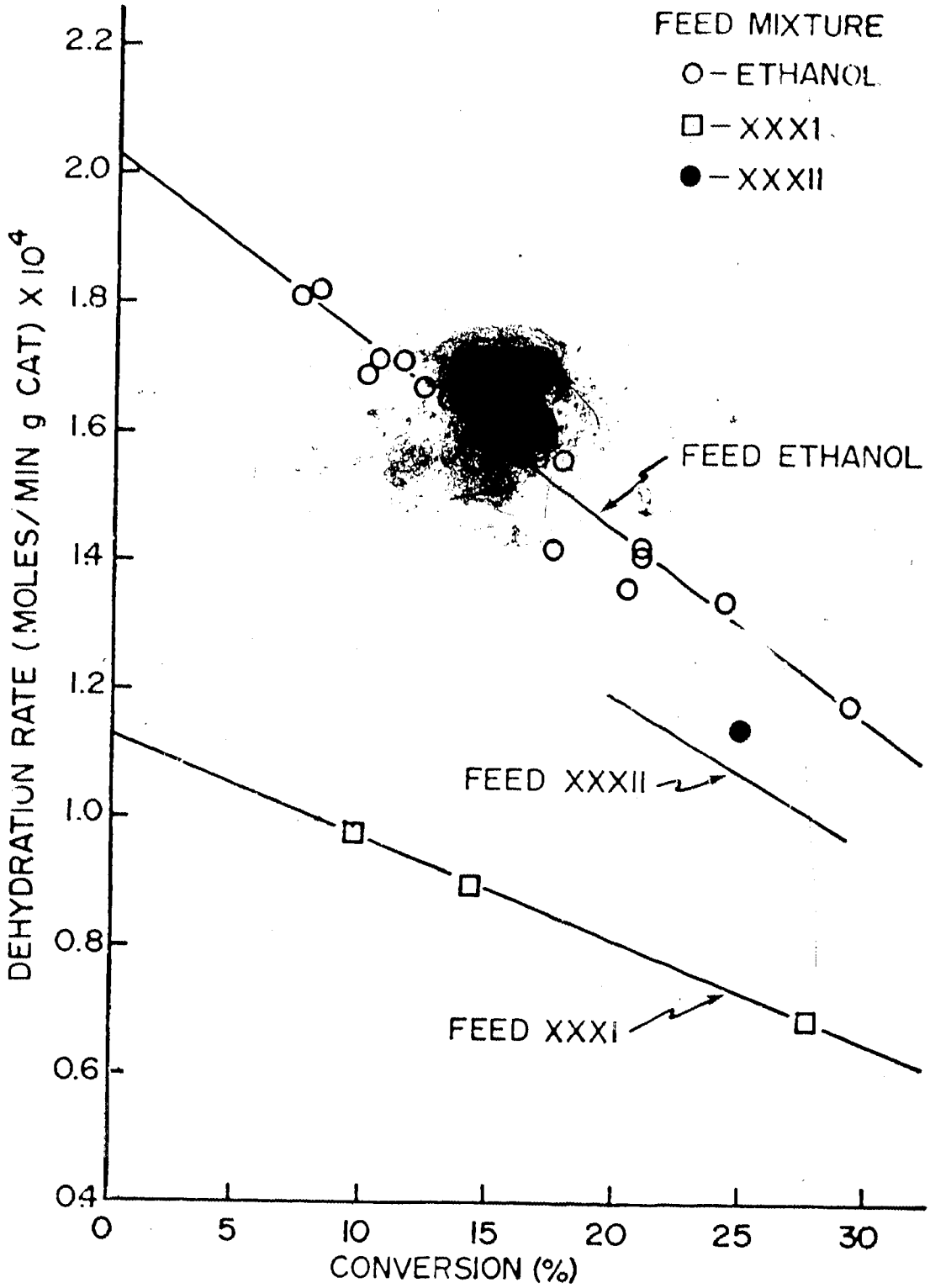

FIGURE 5.1: DEHYDRATION RATES VS CONVERSION AT 135 °C

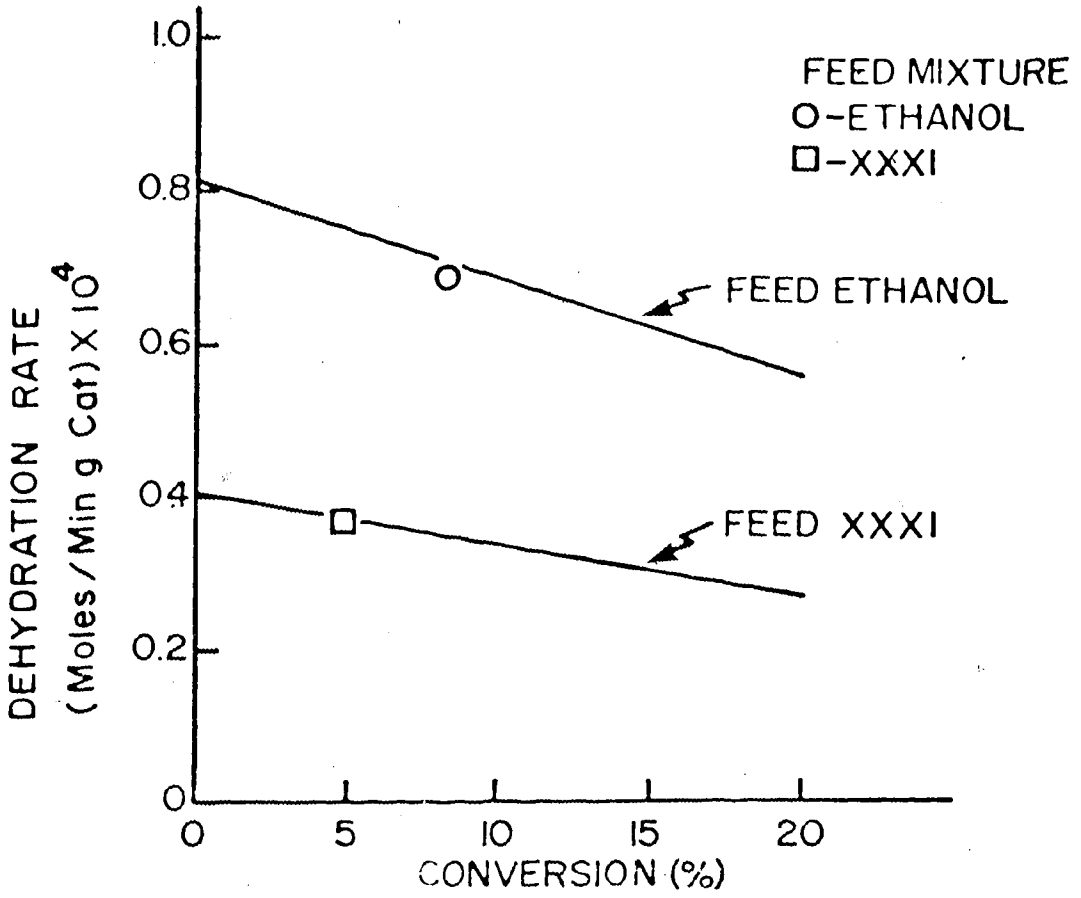

FIGURE 5.2: DEHYDRATION RATES VS CONVERSION AT 120° C

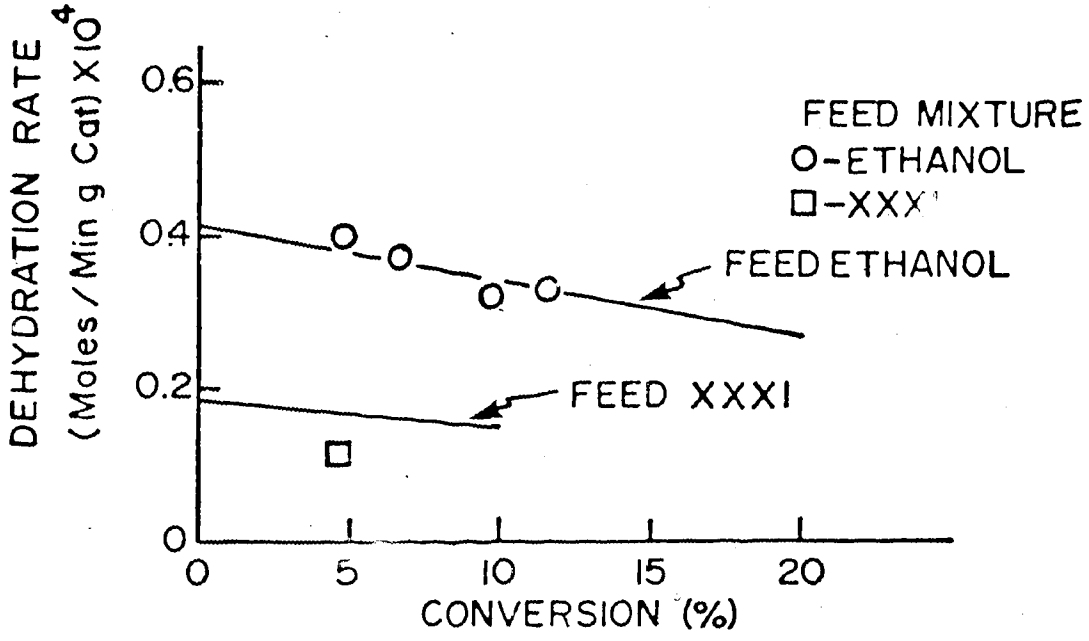

FIGURE 5.3 : DEHYDRATION RATES VS CONVERSION AT 110° C

5.3 Modeling of the Dehydration Rate Data

The dehydration run conditions were used to generate predicted rates according to equation 2.4. The constants in this model were calculated according to equations 2.5 to 2.8. These constants were taken from the work of Kabel and coworkers (5, 8, 15, 21) and were developed from data using a resin similar to the one used in this work. The activity of the two resins may be different, due to differences in acid site concentrations and surface area. The experimentally measured rates from this investigation are compared to the rates predicted by the model of Kabel, using the rate and adsorption constants presented by Stula (21) (given as equations 2.6 to 2.8), by plotting the ratio of experimental rates to the predicted rates. The experimental and predicted rates are tabulated according to temperature and feed composition in Table 5.2.

The ratio of rates (experimental/predicted) is plotted versus the composition of water (in the reactor product) in Figure 5.4. If the predicted temperature dependence of k_s is correct (equation 2.6) and the values of K_A and K_W are as described by equation 2.7 and 2.8, the plot presented in Figure 5.4 should be a horizontal line. The linear, non-horizontal lines shown were the relationships estimated by eye for the data at each temperature. By extrapolating these lines to 0 mole % water, the ratio of rates in the absence of water can be calculated. These water-free ratios are approximately 0.74, 0.68 and 0.82 at 135, 120 and 110°C respectively.

TABLE 5.2

EXPERIMENTAL AND PREDICTED[1] DEHYDRATION RATES

Feed	Run	T (°C)	Rate (moles/(min g cat.)) Experimental	Predicted	Rate Ratio (Experimental / Predicted)
ETOH	IV-1	135.0	1.81	2.394	0.755
ETOH	IV-2	135.0	1.55	2.103	0.736
ETOH	IV-3	135.0	1.71	2.245	0.761
ETOH	IV-4	135.0	1.42	1.946	0.729
ETOH	VI-1	135.0	1.36	1.835	.41
ETOH	VI	135.0	1.41	1.791	0.787
ETOH	VII-2	135.0	1.18	1.475	0.800
ETOH	VII-3	135.0	1.61	2.061	0.781
ETOH	VII-4	135	1.42	1.800	0.789
ETOH	XII-1	135.0	1.58	2.056	0.768
ETOH	XII-2A	135.0	1.59	2.084	0.763
ETOH	XII-3	135.0	1.82	2.337	0.778
ETOH	XII-4	135.0	1.34	1.664	0.805
ETOH	XII-5	135.0	1.69	2.251	.750
ETOH	XII-6	135.0	1.58	2.087	56
ETOH	XII-7	135.0	1.65	2.099	.786
ETOH	XII-8	135.0	1.67	2.135	0.782
ETOH	XVII-2	135.0	1.71	2.213	0.772
ETOH	XVII-3	135.0	1.56	1.933	0.806
XXXI	VIII-1	135.0	0.898	1.046	0.858
XXXI	VIII-2	135.0	0.685	0.762	0.899
XXXI	VIII-3	135.0	0.978	1.139	0.858
XXXI	XI-1	135.0	1.14	1.400	0.814
ETOH	V-1	120.0	0.685	0.929	0.737
XXXI	IX-1	120.0	0.374	0.433	0.862
ETOH	III-2	110.0	0.403	0.493	0.818
ETOH	III-4	110.0	0.315	0.438	0.718
ETOH	XIV-1	110.0	0.367	0.467	0.786
ETOH	XIV-2	110.0	0.331	0.418	0.791
XXXI	X-1	110.0	0.113	0.191	0.592

[1] From equations 2.4 to 2.8.

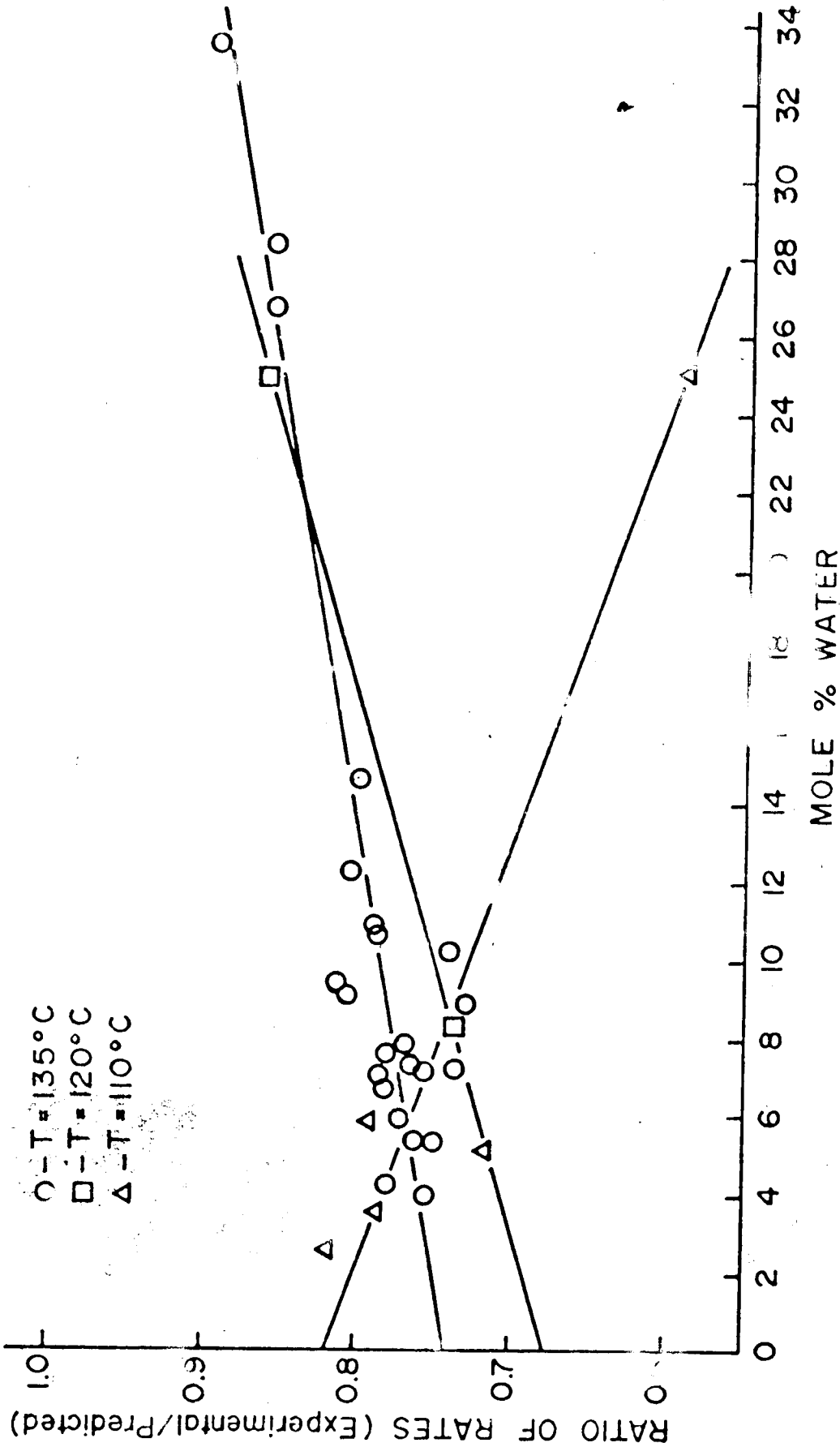

FIGURE 5.4: PLOT OF RATIO OF EXPERIMENTAL / PREDICTED RATES VERSUS MOLE % WATER

Since there is no apparent trend in the extrapolated rate ratios, a reasonable approximation is that the data at all temperatures extrapolated to the same water-free ratio. The rate expression in the absence of water, given by equation 5.1 (see equation 2.4, $P_W = 0$), need only be multiplied by a constant to properly model the rate data.

$$r_{1i} = \frac{k_s K_A^2 P_A^2}{(1 + K_A P_A)^2} \qquad (5.1)$$

Another explanation is that k_s and K_A compensate for one another in a way that $r_{1i} = cr_1$ where c is a constant with both k_s and K_a functions of temperature. This latter explanation is not very plausible. A better explanation is that K_A is modeled accurately by equation 2.7 and that the temperature dependence of k_s is described by equation 2.6.

By using the data at three different temperatures, it was possible to calculate the kinetic parameters k_s, K_A and K_W. The calculations are performed in Appendix J and the results are summarized in Table 5.3. The estimated adsorption constants at 135°C are within about 10% of the values calculated from equations 2.7 and 2.8. This suggests that the model represented by these equations is a reasonable one.

The data were fit in various ways by using a non-linear fitting scheme (11, 13). Kinetic parameters for the three different dehydration models represented by equations 2.4, 2.9 and 2.11 were

TABLE 5.3

ESTIMATED KINETIC PARAMETERS

T	Values Estimated from Data (see Appendix J) (Predicted from Equations 5 to 2.8) $k_s \times 10^4$	$K_A \times$	$K_W \times 10^2$	K_1
(^oC)	(moles/min g cat.))	(1/kPa)	(1/kPa)	
110	0.754 (0.844)	5.25[1] (4.59)	9.87[1] (10.58)	- (28.83)
120	1.15 (1.93)	3.83[1] (3.35)	6.18[1] (6.63)	- (25.51)
135	4.18 (6.15)	2.46 (2.15)	3.19 (3.42)	- (21.48)

[1] Calculated by using the value at 135^{o}C and assuming the temperature dependence of equations 2.7 and 2.8 to be correct.

found and the results of the calculations are summarized in Table 5.4. The MRD, (mean residual deviation) is the mean % deviation of the estimated and experimental values (i.e. [predicted-experimental]/experimental x 100). The TAD (total average deviation is the average of the absolute values of the percentage deviations. The non-linear fitting program (11) minimizes the sum of the squares (SQS) of the difference between the predicted and experimental values. The values of the fitting parameters required to minimize the SQS fitting index are generally not identical to those which would minimize the TAD index. In fitting the dehydration rate data the reaction equilibrium constant was not considered to be a parameter for fitting but was assigned a value according to equation 2.5.

The pseudo-homogeneous model (equation 2.11) was eliminated on the basis of the high TAD (5.13%, more than twice as large as the deviation of the best models) and the fact that the deviation of the ether-ethanol feed run (Run XI-1) was over 30% (an order of magnitude higher than the deviation of the same run for the best cases). Equation 2.9 provided a reasonable fit but was worse than the best fitting cases using equation 2.4. The slightly poorer fit of the Apecetche and Cunningham model and the fact the adsorption constants K_A^* and K_W as presented in the original paper (1) did not show consistent trends with temperature precluded the use of equation 2.9 as the best model. The Kabel model (8) represented by equation 2.4 modelled the data with the least deviation. In fact the fit was equally good when the parameters were fitted in two different ways. These cases are presented in Table 5.4 and can be described as follows:

1. Fitting only k_s and K_W and using K_A as described by equation 2.7 resulted in a TAD of 1.87%.

2. Fitting all three parameters yielded a TAD of 1.88%.

Thus at 135°C, equation 2.4 was able to represent the rate data within 2% on the average.

The results at 110°C and 120°C were sparse and less reliable than the data at 135°C. Since K_A and the modified k_s adequately represent the data in the absence of water, one reasonable way to fit lower temperature data was to adjust k_s by multiplying the results of equation 2.6 x 0.74, using K_A as described by equation 2.7 and modifying the water adsorption constant such that the heat of

TABLE 5.4

RESULTS OF FITTING WITH DEHYDRATION MODELS

Model Equation #	Constants not fitted	Estimated Value (Initial Guesses) $k_s \times 10^4$ ( )[1]	$K_W \times 10^2$ (1/kPa)	$K_A, K_A^* \times 10^2$ (1/kPa, 1/kPa^2)	Fitting Indices MRD (%)	TAD |%|
2.4	K_A	4.54 (4.31)	2.54 (3.19)	-	-0.05	1.87
2.4	K_A, K_W	4.76 (4.31)	-	-	-1.35	3.69
2.4	K_W	3.82 (4.31)	-	2.84 (2.46)	-0.07	1.94
2.4	-	4.16 (4.31)	2.19 (3.19)	2.45 (2.46)	-0.03	1.88
2.4	$k_s = 0.74 k_s$	-	2.54 (3.19)	2.15 (2.46)	-0.05	1.88
2.11	-	2.51×10^{-3} (0.0319)	-	-	-0.80	5.13
2.9	-	7.90 (0.001)	1.58 (3.19)	9.09×10^{-3} (0.01)	-0.17	2.34

[1] Units as required.

adsorption could change but the adsorption constant remained at about 0.0254 kPa^{-1} at 135.0°C. This was the method by which an expression for K_A was obtained.

5.4 Final Model for the Dehydration Reaction

The final dehydration model (see equation 2.4) used K_A and K_1 as given by equations 2.7 and 2.5 and the value of k_s from equation 2.6 multiplied by a constant of 0.74. The revised expressions for k_s and K_W are given below.

$$k_s = 7.6072 \times 10^{9} e^{-103.29/R_g T} \text{ (moles/(min g cat.))} \qquad (5.2)$$

$$K_W = 2.4902 \times 10^{-10} e^{62.56/R_g T} \text{ } (kPa^{-1}) \qquad (5.3)$$

The ability of this final dehydration model to fit the data is summarized in Table 5.5 for a number of different cases. The rates calculated using the model described above are shown as the solid lines on Figures 5.1 to 5.3. It can be seen that this model describes the experimental results quite well.

TABLE 5.5

SUMMARY OF FITTING FOR DEHYDRATION DATA

Data Set	Data Points	Fitting Indices	
		MRD	TAD
	#	(%)	(%)
Data at 135.0°C, Table 5.2	23	+0.16	1.85
Data at 110.0°C, and 120.0°C, Table 5.2	7	+2.04	8.96

CHAPTER SIX

ESTERIFICATION RESULTS

6.1 Introduction

The rate of reaction for the formation of ethyl acetate and water from acetic acid and ethanol was greater than the rate of ethanol dehydration. The esterification reaction also proceeds in the liquid phase and therefore the acetic acid and ethanol had to be fed from separate syringes. Another problem was the adsorption and or condensation of acetic acid somewhere in the system (the sintered filter element and the ceramic spacers in the thermocouple plugs were considered the most likely places). This resulted in the formation of esterification products even when no acetic acid was fed into the system but this "adsorption" effect was small when compared to the catalysed reaction rate.

The vapour-phase esterification reaction proceeded to some extent in the absence of catalyst. The "homogeneous" reaction phenomenon had to be investigated. In addition to the problem of homogeneous reaction, the acetic acid also deactivated the catalyst and the experimental rates had to be adjusted to account for the deactivation.

6.2 Esterification Rate for the Blank Reactor

Several runs were performed without any catalyst in the reactor and these are presented in Appendix K. The rate of

esterification in the absence of catalyst (r_{2h}) can be adequately represented by equation 6.1.

$$r_{2h} = k_{2h} P_A P_B \qquad (6.1)$$

The "homogeneous" esterification constant (k_{2h}) is described by equation K.2 (Appendix K).

This rate is in the order of 1/100 of the catalysed rate and considering other experimental errors, no adjustment to the experiment rates was made for this "homogeneous" reaction. After 10 hours of batch operation only about 30% of the original ethanol was converted (feed = 51% ETOH, 46% HOAC).

6.3 Catalyst Deactivation

The activity of the catalyst decreased upon contact with acetic acid. The relationship between contact time and the extent of deactivation was determined by doing repeat dehydration runs during the series of esterification runs. The details of this procedure are presented in Appendix L. Any reduction in dehydration rate was caused by contact with acetic acid (or ethyl acetate). The deactivation ratio (R_d) was defined as the "effective" catalyst mass divided by the actual catalyst mass (cf. Appendix L). Thus one had a means of determining the "effective" amount of catalyst, knowing the original mass of catalyst and the time of exposure to acetic acid.

The equation for the deactivation ratio of acetic acid was a linear expression.

$$R_d = 1-0.002803t \qquad (6.2)$$

Here the time of contact t has units of hours. After 100 hours in contact with acetic acid a charge would have approximately 70% of the activity of fresh catalyst.

6.4 Consistency of Esterification Rate Data

All esterification runs are tabulated in Table 6.1. Feed compositions are presented in Table H.1 (Appendix H). The runs were carried out at 3 different temperatures, 120°C, 125°C and 135°C. Details concerning the calculation of rates and the results of each run are presented in Appendix M. The rates for runs at each temperature were plotted on rate versus conversion plots and, as explained in section 5.2, all points for one type of feed at the same temperature and pressure should fall on the same curve. The conversion was always taken to be the conversion of ethanol to ester. Figures 6.1 through 6.5 show the esterification data at the three temperatures. The solid curves on these plots represent the rate-conversion relationship predicted using the final esterification model including the correction for catalyst deactivation (equation 6.3 using the kinetic constants given in Section 6.6). In general the esterification data are more scattered than the dehydration data (cf. Figure 5.1), but there are definite trends. All the esterification runs were considered for evaluation of the kinetic models.

6.5 Kinetic Model for the Esterification Reaction

For the purpose of evaluating kinetic models for the esterification reaction (as described in Section 2.3), the data was divided into three sets. Set 1 consisted of all data at 135°C

TABLE 6.1

ESTERIFICATION REACTION RUNS

Run	(°C)	Feed[3]	Feed Rate Mass of cat. ( )[1]x10[3]	Ethanol Conversion Via Reaction 1.2 (%)	Ethanol Conversion Via Reaction 1.1 (%)	Esterification Rate Adjusted[2] ( )[1]x10[4]	Esterification Rate Unadjusted ( )[1]x10[4]	Dehydration Rate Adjusted[2] ( )x10[4]	Dehydration Rate Unadjusted ( )[1]x10[4]
-1	125.0	XXI	1.76	40.16	2.81	4.64	4.61	0.32	0.32
I-2	125.0	XXI	17.70	16.78	0.63	19.40	19.23	0.73	0.72
I-3	125.0	XXI	60.43	6.38	-	25.20	24.95	-	-
II-1	125.0	XXI	3.58	32.03	2.50	7.50	7.39	0.58	0.57
II-2	135.0	XXI	3.59	27.97	3.56	6.57	6.46	0.23	0.82
[illegible]1	135.0	H.1.8[3]	11.56	4.06	1.91	4.21	4.16	1.98	1.95
[illegible]-2	135.0	H.1.9	11.23	52.78	-	11.40	11.16	-	-
EI-3	135.0	H.1.10	2.32	56.62	1.70	6.18	5.97	0.18	0.18
EI-4	135.0	H.1.11	45.07	11.25	0.36	24.70	23.78	0.81	0.78
EII-1	120.0	H.1.11	45.41	18.82	-	41.60	39.93	-	-
EII-2	120.0	H.1.8	12.01	6.10	0.88	6.56	6.24	0.94	0.90
EII-3	120.0	H.1.9	11.64	66.51	-	14.90	14.09	-	-
EII-4	120.0	H.1.10	40	65.87	0.46	7.45	6.94	0.05	0.04
EIII-1	135.0	H.1.12	28	17.31	9.75	19.10	17.68	0.83	0.76
EIII-2	135.0	H.1.12	.88	33.81	1.21	13.20	11.98	0.47	0.43
EIII-3	135.0	H.1.12	47.51	8.12	-	19.10	17.21	-	-
EIII-4	135.0	H.1.12	4.06	44.70	1.87	9.00	7.91	0.37	0.33
EIII-5	135.0	H.1.12	74.56	5.79	-	21.40	18.70	-	-
EIII-6	135.0	H.1.12	12.50	27.13	1.13	16.80	14.44	0.70	0.60
EIII-7	135.0	H.1.12	102.13	3.77	-	19.10	16.34	-	-
EIII-8	135.0	H.1.12	15.69	19.81	0.83	15.40	12.94	0.65	0.54
EIII-9	135.0	H.1.12	26.88	16.30	0.62	21.7	16.65	0.83	0.64
EIV-1	135.0	H.1.13	16.52	20.35	0.82	15.40	12.87	0.62	0.52
EIV-2	135.0	H.1.13	53.58	8.84	-	21.70	18.04	-	-
EIV-3	135.0	H.1.13	9.07	30.58	1.05	12.70	10.44	0.44	0.36

continued..

TABLE 6.1

ESTERIFICATION REACTION RUNS
(continued)

Run	(°C)	Feed	Feed Rate Mass of cat. ( )[1]x10[3]	Ethanol Conversion Via Reaction 1.2 (%)	1.1 (%)	Esterification Rate Adjusted[2] ( )[1]x10[4]	Unadjusted ( )[1]x10[4]	Dehydration Rate Adjusted[2] ( )[1]x10[4]	Unadjusted ( )[1]x10[4]
EV-1	120.0	H.1.13	9.15	43.40	-	18.20	14.84	-	-
EV-2	120.0	H.1.13	17.19	32.13	-	25.30	20.31	-	-
EV-3	120.0	H.1.13	55.73	16.18	-	41.30	33.04	-	-
EVI-1	120.0	H.1.12	53.80	16.70	-	44.50	35.41	-	-
EVI-2	120.0	H.1.12	9.09	44.84	-	20.20	15.90	-	-
EVI-3	120.0	H.1.12	17.19	33.25	-	28.30	21.81	-	-
EVII-1	135.0	H.1.12	17.52	22.82	0.88	19.80	19.68	0.77	0.76

[1]Units are moles/(min g cat.)

[2]Adjusted to account for catalyst deactivation due to contact with acetic acid.

[3]See Table H.1 (Appendix H) for feed compositions.

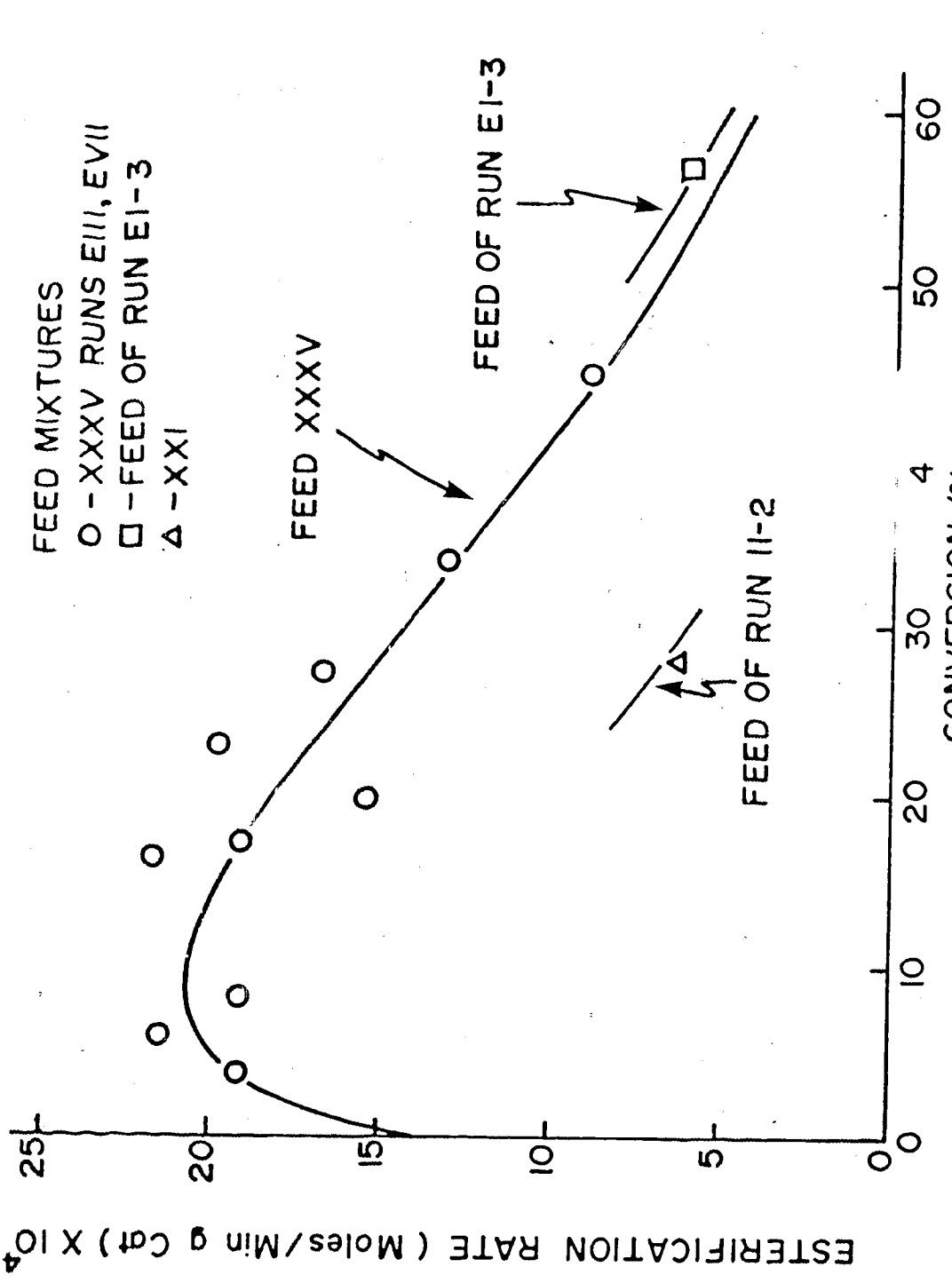

FIGURE 6.1: ESTERIFICATION RATES VS CONVERSION AT 135°C

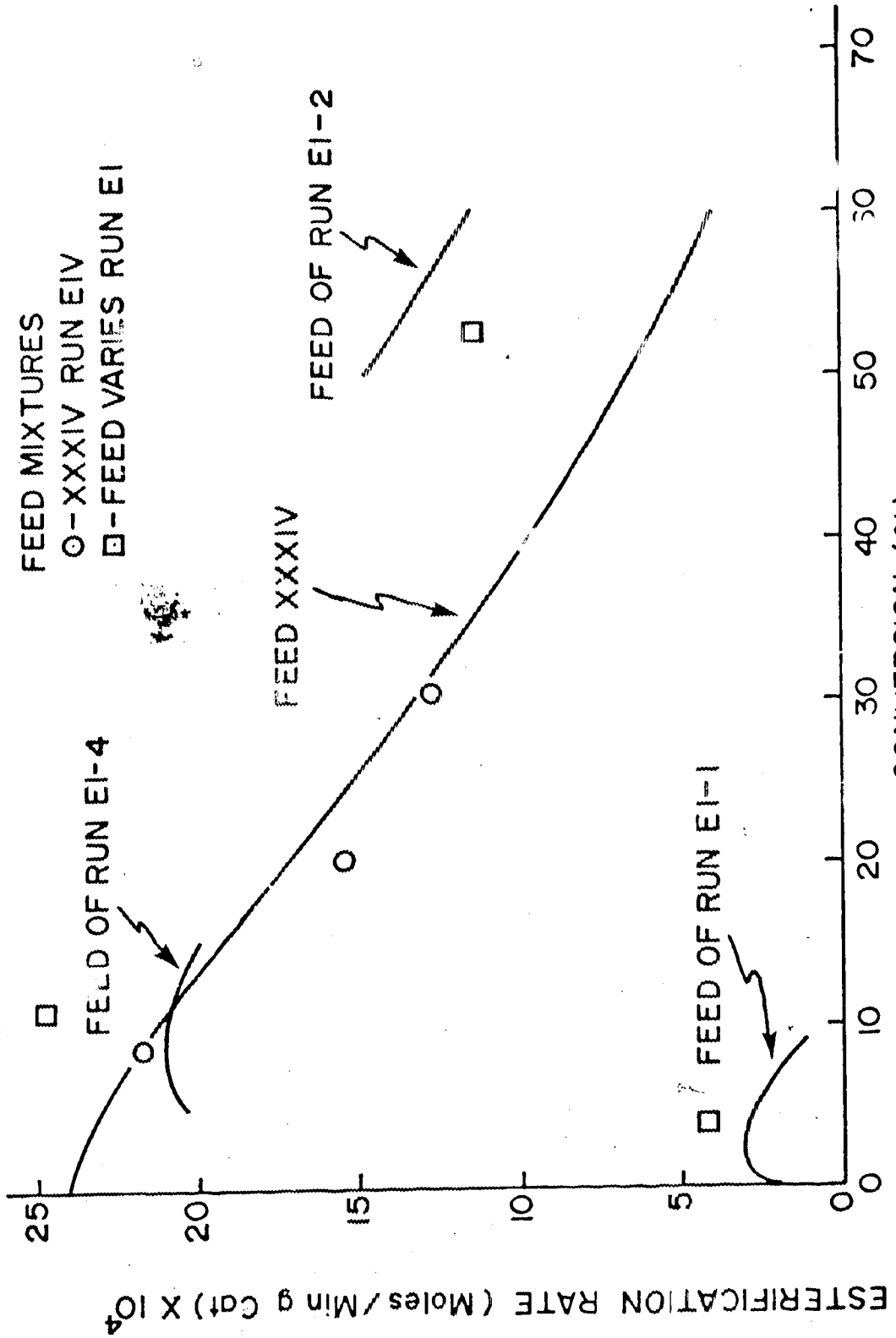

FIGURE 6.2: ESTERIFICATION RATES VS CONVERSION AT 135° C

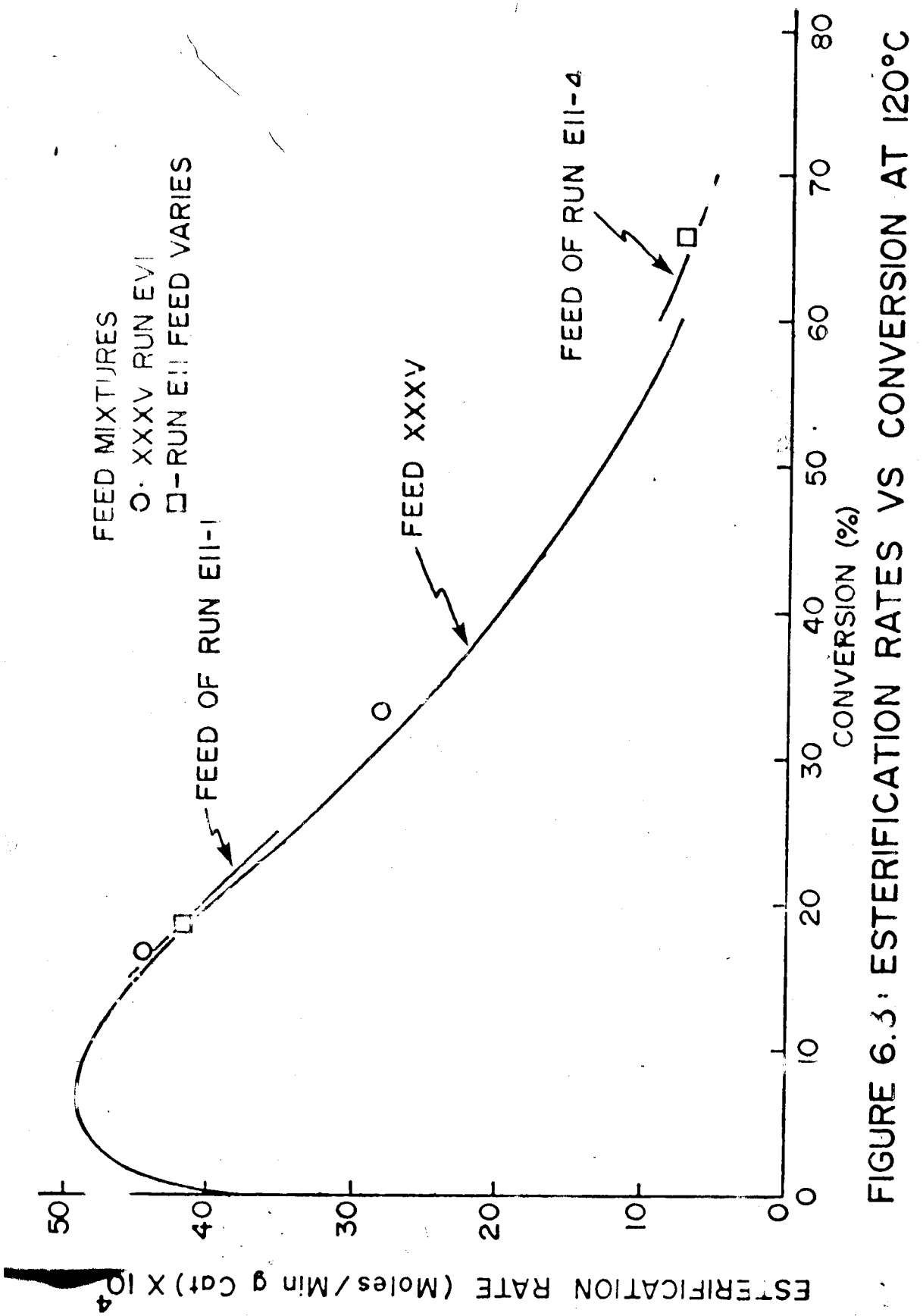

FIGURE 6.3: ESTERIFICATION RATES VS CONVERSION AT 120°C

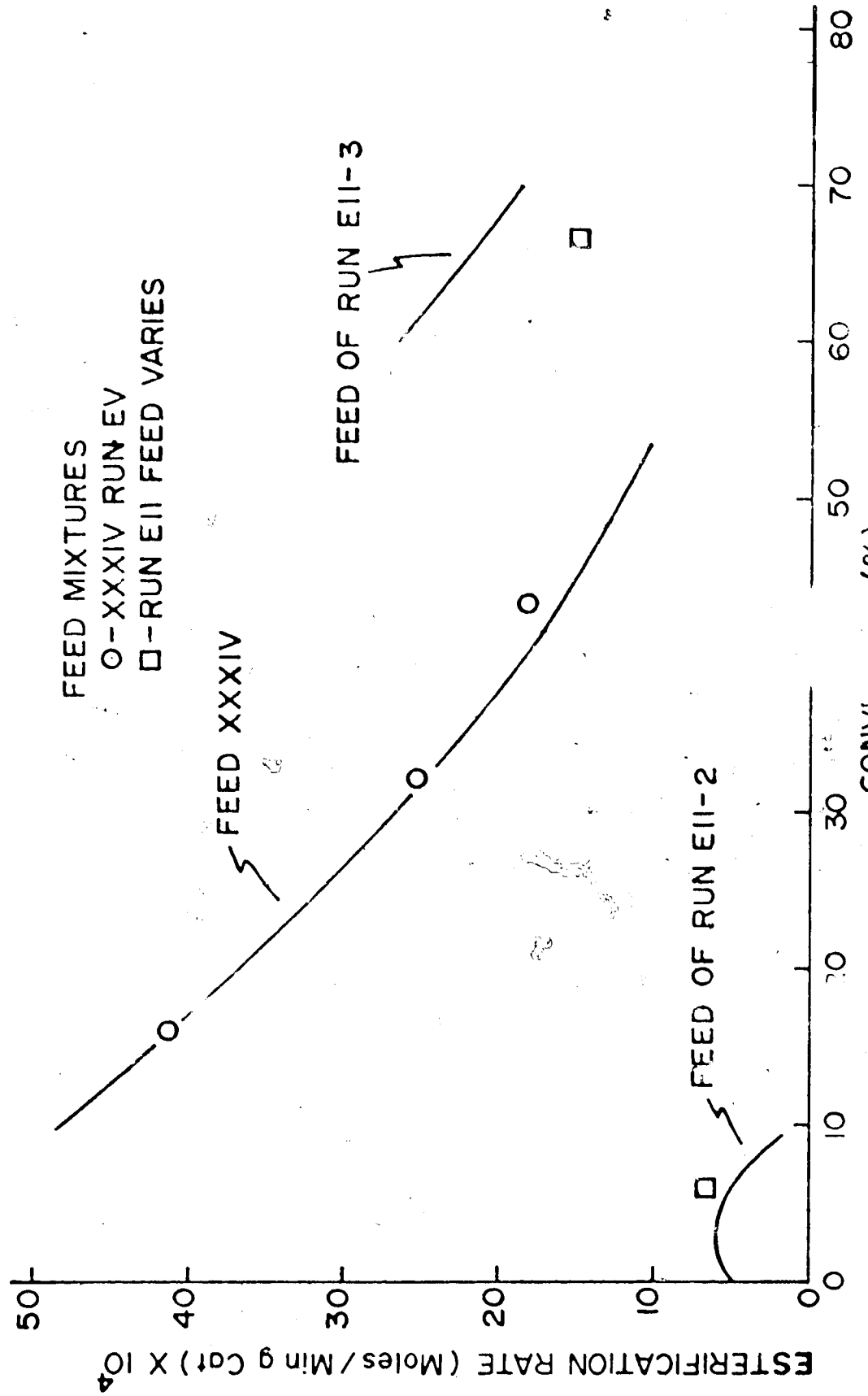

FIGURE 6.4: ESTERIFICATION RATES VS CONVERSION AT 120°C

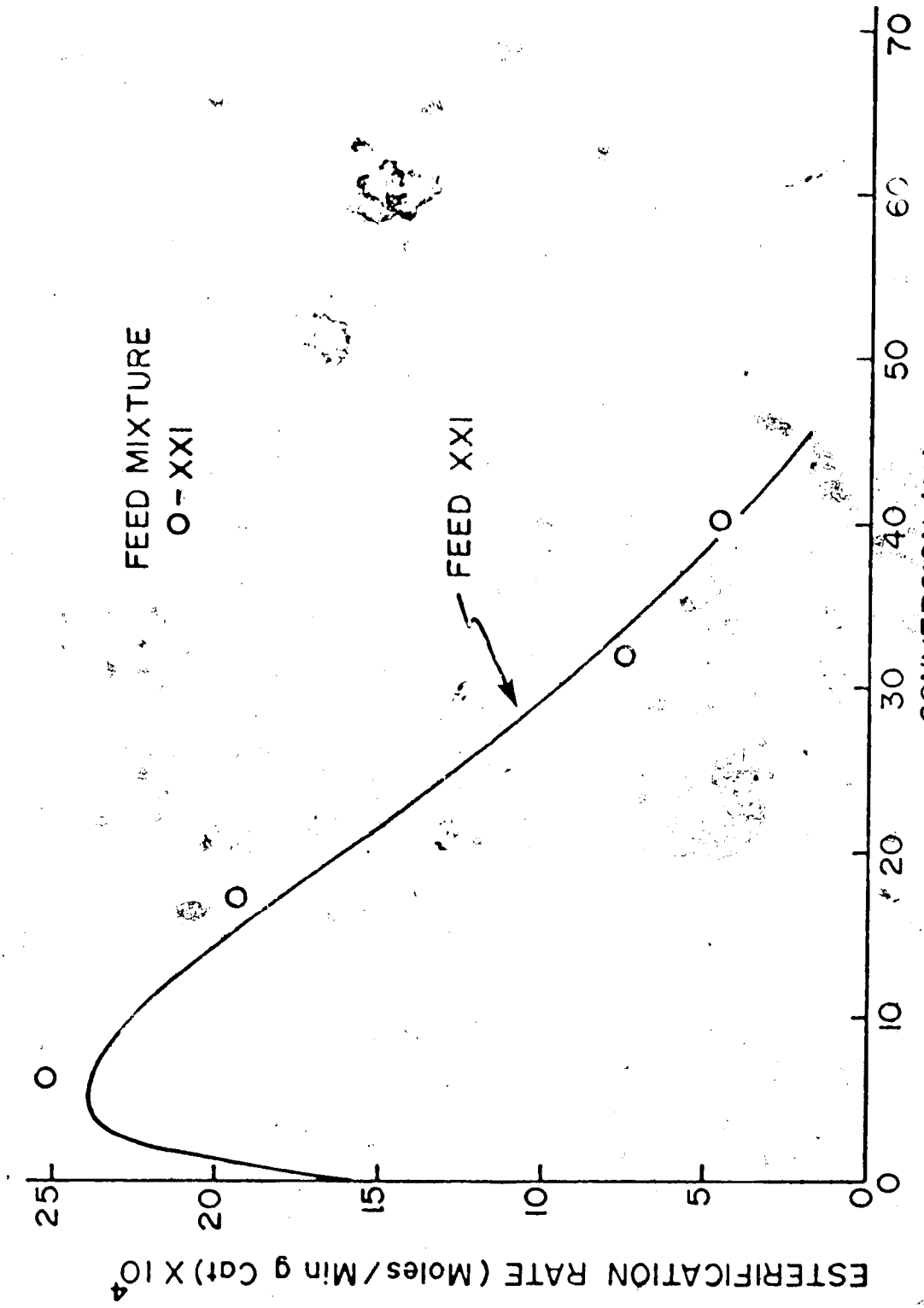

FIGURE 6.5: ESTERIFICATION RATES VS CONVERSION AT 125°C

while set 2 was composed of all 120°C runs and set 3 of all the remaining runs at 125°C. For these evaluations K_A was calculated using equation 2.7 while K_W was calculated using equation 5.7. The equilibrium constant K_2 was described by equation 2.13a. For fitting purposes the partial pressures were calculated using the ideal gas law. The model described by equation 2.12 was rewritten as follows.

$$r_2 = \frac{k_{s2}K_AK_WP_W^2(P_AP_B - P_CP_W/K_2)}{(1 + K_AP_A + K_WP_W + K_CC)^2} \qquad (6.3)$$

A code for the parameters used in fitting the rate data to the esterification models of Section 2.3 is given in Table 6.2. The models of equations 2.18 and 2.19 were combined.

TABLE 6.2

ESTERIFICATION FITTING PARAMETERS

Model	Fitting Constants #1	#2	#3
6.3	k_{s2}	K_C	s
2.16, 2.17	$k_{s2}K_B$	K_B	K_C
2.18, 2.19	k_4	k_5	-

6.6 Final Model for the Esterification Reaction

The two best kinetic models from Section 6.5 were evaluated for all the data at the 3 temperatures. The results are summarized in Table 6.4. The constant K_A was calculated using equation 2.7 and K_W was calculated according to equation 5.2. The other kinetic

TABLE 6.3

RESULTS OF FITTING WITH ESTERIFICATION MODELS

Model Equation #	Data Set	Fitting Constant #1 ( )[1]	#2 ( )[1]	#3 ( )[1]	Fitting Indices SQS[1] x10^8	MRD (%)	TAD (|%|)
6.3	1	69.67	0.012	0.272	53.2	-0.12	9.39
	2	69.38	0.037	0.354	31.4	-1.45	8.23
2.16	1	3.78	0.013	0.0	104.7	-0.40	11.90
	2	9.21	0.012	0.003	19.9	1.90	6.14
2.17	1	4.69	0.0	0.0	138.0	-4.81	13.77
	2	10.41	0.0	0.0	23.1	-0.59	5.03
2.18	1	1.17	-	-	126.2	-3.47	12.70
	2	2.41	-	-	17.2	1.97	6.04
2.18,2.19	1	0.961	2.16×10^{4}	-	73.4	2.50	12.46
	2	2.25	0.753×10^{4}	-	12.3	.67	5.72

[1] Units as required.

TABLE 6.4

SUMMARY OF FITTING FOR ESTERIFICATION DATA

Model	Data Set	Fitting Indices SQS x10^8	MRD (%)	TAD (|%|)
6.3	All	88.6	-0.36	8.58
6.6	All	106.3	4.17	10.99

parameters for model 6.3 were calculated according to the following equations.

$$k_{s2} = 2.654 \times 10^{-6} e^{26.12/R_g T} \text{ moles/(min kPa g cat.)} \qquad (6.4)$$

$$K_C = 2.831 \times 10^{-68.3/R_g T} \text{ kPa}^{-1} \qquad (6.5)$$

The value of s was set at 0.3.

The combined model (equation 2.18 and 2.19) is given as equation 6.6.

$$r_2 = \left| \frac{K_4 K_A}{(1 + K_A P_A + K_W P_W)} + \frac{K_5 K_A K_W P_W}{(1 + K_A P_A + K_W P_W)^2} \right| (P_A P_B - P_C P_W / K_2) \qquad (6.6)$$

The parameters k_4 and k_5 are calculated using the following equations

$$k_4 = 1.629 \times 10^{-14} e^{76.25/R_g T} \text{ moles/(min kPa g cat.)} \qquad (6.7)$$

$$k_5 = 1.546 \times 10^{8} e^{-92.32/R_g T} \text{ moles/(min kPa g cat.)} \qquad (6.8)$$

The esterification model of equation 6.3 provides a better fit of the data than the model of equation 6.6. The model described by equation 6.3, using the parameters k_{s2}, K_C, and K_W as explained above, was used to calculate predicted rate-conversion curves and these predictions are shown as the solid curves on Figures 6.1 through 6.5. Some of the points which were not fit very well (e.g. Runs EI-1, EI-2, EII-2 and EII-3) had feeds with a high fraction of one reactant. The lower rates for these extreme conditions were

still fit satisfactorily.

The esterification rate based on fresh catalyst is multiplied by the deactivation ratio to get the actual rate. Thus the actual esterification rate, taking the deactivation effect of contact with acetic acid into account, can be predicted.

CHAPTER

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The final experimental system, as designed and constructed during the course of work, was useful in obtaining kinetic data for the dehydration and esterification reactions. In particular the composition analysis via gas chromatograph was accurate and rapid (five component mixtures could be analyzed in five minutes). Since the compositions of all the components were actually measured, mass balance checks were possible to give an indication of when steady state operation was achieved and one could infer the accuracy of the rate data based on these balances. Problems encountered concerning the computerized peak analysis were solved by amplifying the G.C. detector signal.

The temperature control and temperature programming ability of the experimental system was a unique feature which will be useful for the investigation of other control and kinetic objectives.

The rate model of Kabel (8) was found to be accurate for the catalytic dehydration of ethanol. The rate model of Dewan (3) for the esterification reaction was also found to be a reasonable model. Several alternative kinetic models for the two reactions were found to yield poorer agreement with the experimental data. Thus the results of this investigation tend to support the conclusions

of Kabel and co-workers at Pennsylvania State University regarding the kinetics of the dehydration and esterification reactions in the vapour phase over an ion exchange resin.

The two reactions described above were found to be poor candidates for future control studies involving the selectivity of these reactions. Given the normal range of compositions used during this study, the esterification rate was about an order of magnitude larger than the dehydration rate. There is a possibility that the selectivity could be investigated if the feeds were composed of 90 mole % ethanol, but under these conditions measurement errors would be increased relative to absolute compositions and this would result in more scattered data.

7.2 Recommendations

The possibility of using other reactions systems and or catalysts should be investigated to determine if selectivity type studies could be carried out using the equipment constructed during this project. One reaction which could prove to be compatible with the ethanol-acetic acid esterification reaction would be the isopropanol-acetic acid reaction discussed in Section 2.3. There might be problems due to the large number of chemical species which would be involved but this system of reactions merits investigation.

Future control studies will require the installation of an automatic sampling system. The compositions could then be automatically sampled and recorded, relieving the operator of a sometimes tedious chore.

Another reactor section should be constructed so that kinetic and control studies of slower reactions could be conducted with greater accuracy. One possible alternate reactor section would involve replacing the reactor tube, preheater section and reactor cooling/heating jacket with another section of similar design but where the internal diameter of the stainless steel reactor tube would be a minimum of 1.5 cm. Catalyst baskets made of Teflon could be built so that the catalyst charges could be loaded externally and then the entire jacket section could be lowered into the reactor tube. The effective internal diameter of the proposed reactor could be changed by using cylindrical Teflon sleeves of appropriate internal and external diameters. With this configuration, the superficial gas velocity through the catalyst bed could be adjusted as required. The catalyst support screens would only contact the Teflon sleeving.

The reactor section proposed above would provide the flexibility of using large or small charges of catalyst and could be built so that it would be interchangeable with the present reactor section. Given the capability of using larger catalyst charges, the tubing configuration could be altered to run the reactor as a one pass fixed bed reactor.

Consideration should be given to replacement of the existing single chamber bellows pump with a dual chamber model with a larger capacity. The dual chamber type pump should also tend to reduce pressure fluctuations in the circulation loop.

Since the operator found it necessary to wear ear protection

throughout the experimentation period, the reactor system should be moved to a quieter location or the noisy equipment next to the reactor system, in its present location, should be shut down.

NOMENCLATURE

a) Alphabetic

A	Cross sectional thermocouple area
A_i	G.C. peak area of component i
A_{R1}, A_{R2}	Ether/ethanol peak area ratios for loop 1 and loop 2 samples
b1, b2, b3, b4, b5	Reverse rate constants in the Langmuir-Hinshelwood model
C1, C2, C3, C4	Constants for heat transfer solution along thermocouple
f1, f2, f3, f4, f5	Forward rate constants in the Langmuir-Hinshelwood model
F_i	Feed rate of component i
h, h_L	Convective heat transfer coefficients
G	Catalyst Mass
H	Enthalpy
J_1, J_2	Gas temperature profile constants
J	Constant for heat transfer solution
k_{2h}, k_4, k_5	Constants for esterification reaction models
k_s, k_s^*	Constants for ethanol dehydration reaction
k_{s2}, k_{s3}	Constants for esterification reaction models
K_A, K_A^*	Adsorption constants for ethanol
K_B, K_C, K_W	Adsorption constants for acetic acid, ethyl acetate and water

K_I, K_J	Adsorption constants for Isopropanol and Isopropyl acetate
L	Length of thermocouple used during the solution of the temperature profile
M	Constant for heat transfer solution
p	Circumference of thermocouple
P	Total pressure
P_A, P_B, P_C, P_E	Partial pressures of ethanol, acetic acid, ethyl acetate and diethyl ether
P_I, P_J, P_W	Partial pressures of isopropanol, isopropyl acetate and water
q_x, q_{x+dx}	Heat flux into and out of a differential segment dx
r, r_1	Rate of reaction and/or rate of dehydration reaction
r_{1i}	Rate of dehydration in the absence of water
r_2	Rate of ethanol-acetic acid esterification
r_{2h}	Homogeneous Esterification rate
r_3	Rate of isopropanol-acetic acid esterification
r_i	Rate of reaction of component i
R_1, R_2	Ratios of dehydration rates
R_d	Deactivation ratio
R_g	Gas constant (8.31×10^{03} kJ/mole K)
RF_1, RF_2	Loop 1, loop 2 ether response factors
RF_i	Response factor of component i
s	Esterification model water exponent

S	Catalyst site
t	Time
T	Normally temperature in degrees Kelvin
T_0	Initial thermocouple temperature
Te	Effective thermocouple temperature
Tg, Tg_0	Gas temperature and initial gas temperature
x_i	Mass fraction of component i
X_1	Conversion of ethanol to ether
X_2	Conversion of ethanol to ethyl acetate
X_3	Conversion of acetic acid to ethyl acetate
X_i	Fractional conversion of component i
Y_A, Y_E, Y_W	Mole fractions of ethanol, ether and water
Z	Fraction of catalytic sites covered by ethanol or water

b) Greek

υ	Stoichiometric coefficient
Δ	Change operator out-in
	Time constant

Abbreviations

ADC	Analog to digital converter
DDC	Direct digital control
ET_2O	Ether (diethyl ether)
ETAC	Ethyl acetate
ETOH	Ethanol
G.C.	Gas Chromatograph
HOAC	Acetic acid

MRD	Mean residual deviation
O.D.	Outside diameter
SQS	Sum of the squares
SS	Stainless steel
TAD	Total absolute deviation

Roman Numerals

I	1
II	2
III	3
IV	4
V	5
IX	9
X	10
XIV	14
XV	15
XIX	19
XX	20
XXX	30
XL	40
L	50
C	100
D	500
M	1000

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APPENDIX A

HEAT AND MASS TRANSFER LIMITATIONS

A recycle reactor was used in order to minimize external heat and mass transfer limitations. The recycle rate used was ~150 cm^3/s. This corresponds to a superficial velocity of ~750 cm/s. This superficial velocity is ~10 times greater than the largest value employed by Kabel (8) in his fixed bed experiments and hence it is unlikely that external transport effects are significant in the present work.

An approximate estimation of the maximum external concentration and temperature gradients using the method of Smith (19) was done. The calculations indicated that the reactant concentration at the catalyst surface was ~0.2% lower than the concentration in the bulk phase. It was also found that the external catalyst particle temperature was less than $0.2^{o}C$ higher than the bulk phase temperature. The above values were calculated by assuming a reaction rate greater than the largest esterification rates observed and employing conservative estimates of physical properties. Therefore, the maximum gradients described above are probably still an order of magnitude higher than the actual gradients.

The small size of the catalyst particles (<0.1 cm in diameter) and the fact that the reactions studied had low heats

of reaction (e.g., ΔH for esterification is approximately -20 kJ/mole) suggests that individual pellets were unlikely to have internal temperature gradients. Regarding diffusion limitations, Herrman (6) in previous work with a similar catalyst found the ethanol esterification rate to be independent of catalyst particle size. In Kabel's (8) work there was never any indication of internal mass transfer limitations.

APPENDIX B

ESTERIFICATION MODELS

The Langmuir-Hinshelwood models described by equations 2.18 and 2.19 are derived in this appendix. The symbol S refers to an active surface site and A, B, C and W refer to molecules of ethanol, acetic acid, ethyl acetate and water, respectively. It is postulated that only water and ethanol adsorb on the surface sites and that acetic acid and ethyl acetate only adsorb on sites on which water or ethanol are already adsorbed. For both models the surface reaction was taken to be the rate controlling step. For the single site model (equation 2.18) the following series of equations apply.

$$A + S \underset{b1}{\overset{f1}{\rightleftharpoons}} A\text{-}S \qquad (B.1)$$

$$A\text{-}S + B \underset{b2}{\overset{f2}{\rightleftharpoons}} AB\text{-}S \qquad (B.2)$$

$$AB\text{-}S \underset{b3}{\overset{f3}{\rightleftharpoons}} WC\text{-}S \qquad (B.3)$$

$$WC\text{-}S \underset{b4}{\overset{f4}{\rightleftharpoons}} W\text{-}S + C \qquad (B\text{-}4)$$

$$W\text{-}S \underset{b5}{\overset{f5}{\rightleftharpoons}} W + S \qquad (B.5)$$

With the assumption that the surfact reaction (equation B.3) is rate controlling, the following equation is written. The square brackets denote concentration.

$$r_2 = f3[AB\text{-}S] - b3\,[WC\text{-}S] \qquad (B.6)$$

Given that the rates of reaction for reactions B.1, B.2, B.4 and B.5 are much faster than the rate for reaction B.3 the equalities presented below hold.

$$[A\text{-}S] = (f1/b1)[A][S] \qquad (B.7)$$

$$[AB\text{-}S] = (f2/b2)[B][A\text{-}S] \qquad (B.8)$$

$$[WC\text{-}S] = (b4/f4)[W\text{-}S][C]$$
$$= (b4b5/f4f5)[W][C][S] \qquad (B.9)$$

$$[W\text{-}S] = (b5/f5)[W][S] \qquad (B.10)$$

Substituting the equalities presented above into equation B.6 yields the following expression.

$$r_2 = (f3(f1f2/b1b2)[A][B] - b3(b4b5/f4f5)[W][C])[S] \qquad (B.11)$$

Taking L to be the total number of surface sites the following equations are written.

$$L = [S] + [A\text{-}S] + [W\text{-}S] \qquad (B.12)$$

$$S = \frac{1}{(1 + [(f1/b1)[A] + (b5/f5)[W]]^2} \qquad (B.13)$$

Substituting equations B.13 into B.11 and combining the constant L with f3 and b3 yields the expression for r_2 (in terms of partial pressures and the nomenclature of Section 2.3).

$$r_2 = \frac{k_4 K_A (P_A P_B - P_C P_W / K_2)}{(1 + K_A P_A + K_W P_W)^2} \qquad (B.14)$$

The derivation of equation 2.19 uses a similar methodology. The derivation differs because the model involves the reaction of acetic acid adsorbed on water reacting with an adsorbed ethanol molecule. The final modified dual site model is given below.

$$r_2 = \frac{k_5 K_A K_W P_W (P_A P_B - P_C P_W / K_2)}{(1 + K_A P_A + K_W P_W)^2} \qquad (B.15)$$

The two surface sites involved result in the squared denominator term and the role of the adsorbed water accounts for the $K_W P_W$ term in the numerator.

APPENDIX

GAS CHROMATOGRAPHIC COMPOSITION ANALYSIS

C.1 Peak Detection and Area Measurement

The signal which results when the separated components of a sample pass through the thermal conductivity detector is sent to a strip chart recorder and also to the IBM 1800 computer via an analog to digital converter (ADC) (cf. Figure 3.2). The computer program which analyzes the G.C. output and determines the peak areas is described elsewhere (16). One problem with the computer analysis of G.C. peaks was that the analysis of smaller peaks was erratic. This was true even though these peaks appeared to be reproducable based on examination of the strip chart recorder output for a number of identical samples.

During this investigation it was found that the problem was not due to the G.C. program but rather it was due to the fact that smaller peaks were "lost" in the digitization or created when the detector signals were digitized in the ADC. This problem is illustrated by looking at the computer interpretation of two small peaks. The same two peaks were analyzed by the computer under three different amplification conditions.

The detector signal was amplified by factors of 1, 10 and 30 for the two small peaks. The first peak maximum was 0.07 mV while the second had a maximum of 0.007 mV (these maximums were

relative to the baseline detector signal). The digitized G.C. signal for the three amplification factors is shown in Figure C.1. It can be seen that at the lowest amplification factor the second peak is "lost" in the ADC digitization noise. The effect of increased amplification of the G.C. signal was to "lift" this second peak out of the ADC noise along the baseline. The explanation for the improvement with signal amplification is that the specification for the ADC at the lowest range (0 - 10 mV) is for measurement accuracy equivalent to ±0.03 mV. This is true even when a very steady signal (e.g. dead short or a resistor) is sent to the ADC. At an amplification factor of 30 the second peak maximum is 0.21 mV and at this level maximum digitization error at less than 0.03 mV does not obliterate the peak signal.

The actual logic of determining peak area involves the use of the first derivative of the G.C. signal. The first derivatives of the G.C. outputs shown in Figure C.1 are presented in Figure C.2. To register the start of a peak the derivative must reach and stay beyond an upper deadband value for a specified time interval. In the case of amplication factor 1 it is difficult to pick out the second peak based on the first derivative criterion stated above. For higher amplification factors, the second peak can be easily picked out by examining the peak derivatives (see Figure C.2).

The actual specification of G.C. jobs which set the parameters required to detect chromatographic peaks is described by Nagy (16). In this study two jobs were used during the kinetic work. The first, as summarized in Table C.1, was used to analyze

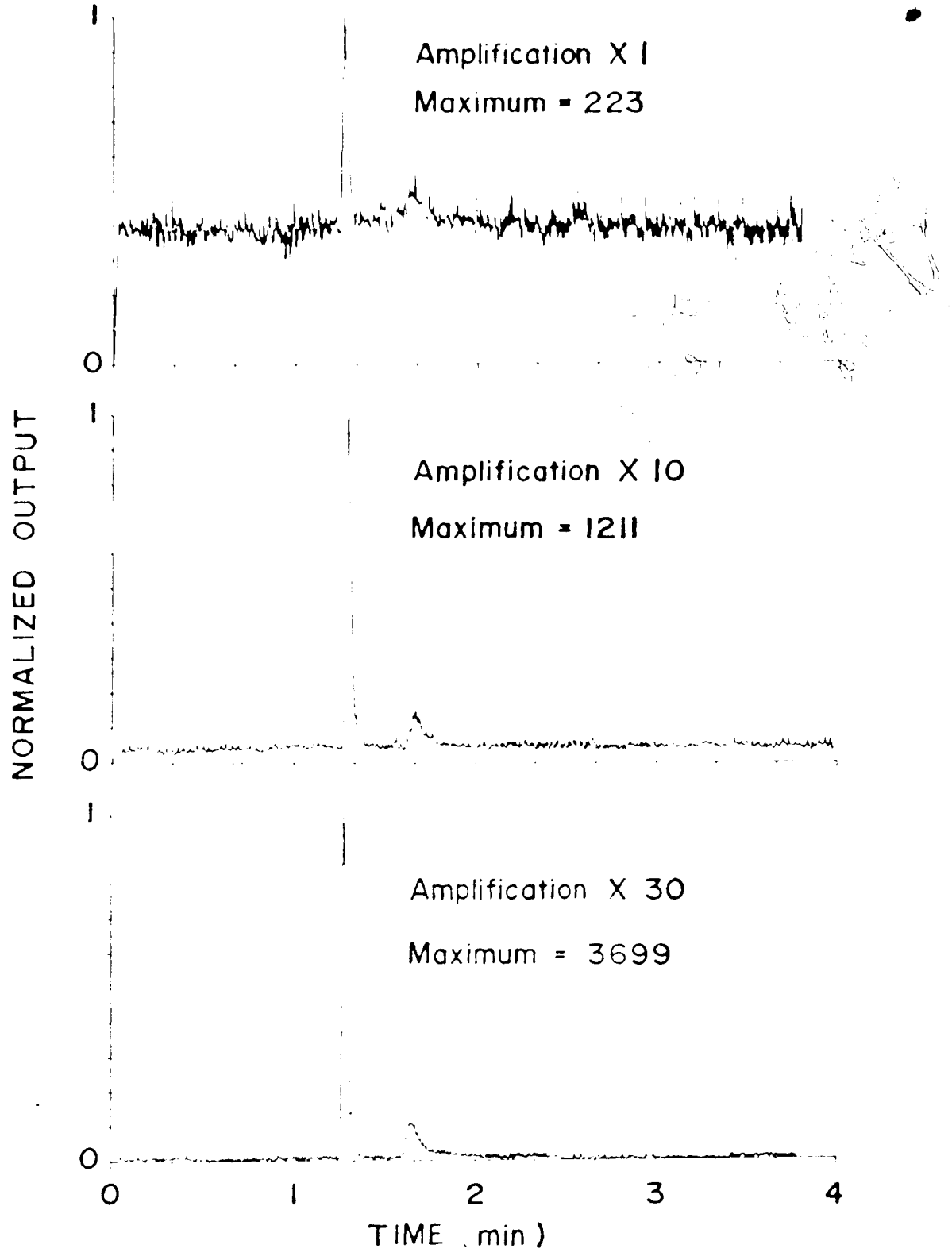


FIGURE C.1: AMPLIFIED G.C. OUTPUT

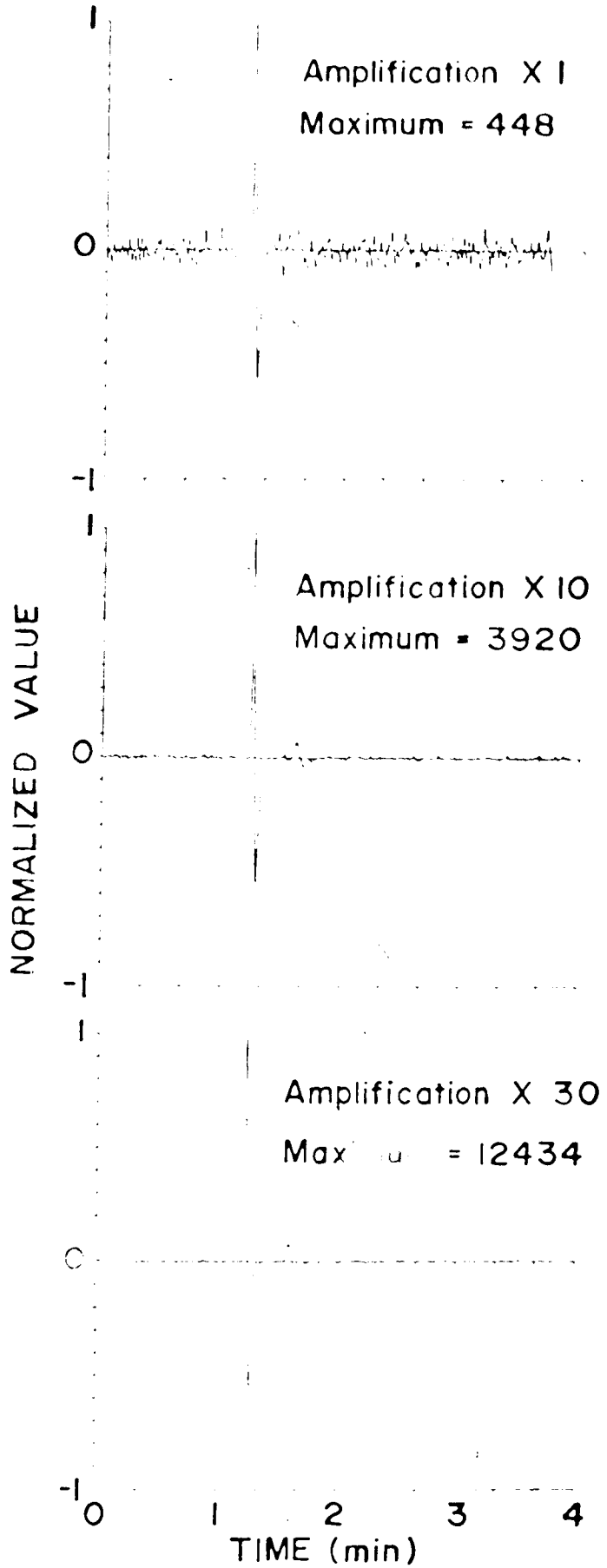


FIGURE C.2 : DERIVATIVES OF AMPLIFIED G.C. OUTPUT

TABLE C.1

G.C. JOB 94

** GAS CHROMATOGRAPH FOR FITTING **

[illegible]	94	CALCULATION OPTION =	7
CC NUMBER =	9	TOTAL PEAKS =	6

[illegible] = 90
[illegible] CONST. = 100.

* REFERENCE PEAK DATA *

[illegible] PEAK	37.
[illegible] PEAK	55.
[illegible] PEAK	0.
[illegible] PEAK	0.

* TEMP RAMP DATA *

COM TEMP	RAMP TIME	CONST TEMP TIME	FACTOR	TYPE	COMPONENT
15.	19.	0.	.100	1	N2
19.	37.	0.	2.321	1	H2O
37.	55.	0.	1.394	1	ETOH
55.	100.	0.	0.358	4	ET2O

COMPONENT	NUMBER	PEAKS	PEAK	PEAKS	TREST	UNITS
N2	1	0	0	0	0	MOL%
H2O	2	0	0	0	0	MOL%
ETOH	3	0	0	0	0	MOL%
ET2O	4	3	0	0	0	MOL%

* PARAMETER AND CONTROL ACTION DATA *

PARAMETER ACTIONS

ACTION	TIME	SYSTEM	PETS	PEAKS	ERROR	SLOPE	INTRO	ISSET	ISAVE	IEXPZ
0	AB	11	[illegible]	150	-100	5	8	2	3	
5	AB	1	[illegible]	150	-50	3	3	2	3	
10	AB	0	8895	150	-10	4	4	2	3	
20	AB	0	8895	150	-100	4	4	2	3	
30	AB	0	8895	150	-100	4	4	2	3	

MOL ACTIONS

00 MOL ACTIONS SPECIFIED

JOB COMPLETE

TABLE C.2

G.C. JOB 98

** [illegible] **

RUN NUMBER =	9[illegible]	CALCULATION OPTION	1
GC NUMBER =	9	TOTAL PEAKS =	10

FINISH TIME = 230
NORMALIZATION CONST. = 100.

* REFERENCE PEAK DATA *

LOW TIME OF REF PEAK	37.
HIGH TIME OF REF PEAK	55.
CONCENTRATION OF REF PEAK	0.
RESPONSE FACTOR OF REF PEAK	0.

* TIME BAND DATA *

LOW TIME	HIGH TIME	CONC FOR STND	FACTOR	ITYPE	COMPONENT
6.	17.	0.	0.000	1	N2
19.	37.	0.	[illegible].971		H2O
37.	55.	0.	1.394		ETOH
55.	100.	0.	0.958		ET2O
100.	135.	0.	0.[illegible]4	1	ETAC
135.	230.	0.	1.[illegible]	1	HOAC

COMPONENT	SOCPID	IPLUS	IPNF	IACID	IDCEI	UNITS
N2	1	0	0	0	0	MOL%
H2O	2	0	0	0	0	MOL%
ETOH	3	0	0	0	0	MOL%
ET2O	4	0	0	[illegible]	0	MOL%
ETAC	5	0	0	[illegible]	0	MOL%
HOAC	6	0	0	[illegible]	0	MOL%

* PARAMETER AND CONTROL ACTION DATA *

PARAMETER ACTIONS

ACTION TIME	AMODE	ISTS	IRATE	IHIGH	ILOW	IHARD	ISOFT	IEXP1	IEXP2
0	AB	11	1[illegible]PPS	150	-100	8	8	2	3
5	AB	1	16PPS	150	-50	3	3	2	3
19	AB	0	[illegible]PPS	150	-10	4	4	2	3
39	AB	0	4PPS	150	-100	4	4	2	3
96	AB	0	4PPS	15	-10	10	10	2	3
140	AB	0	4PPS	50	-50	6	6	2	3
225	BL	20	4PPS	50	-50	6	6	2	3
230	BL	[illegible]	4PPS	50	-50	6	6	2	3

ECO ACTIONS

NO ECO ACTIONS SPECIFIED

JOB COMPLETE

for water, ethanol and ether. Table C.2 presents the computer summary of the G.C. job which was used to analyze for the five component mixtures.

C.2 Column Development

The original G.C. column was composed of 6 feet of Porapak Q-S and 9 inches of Porapak T. All columns were constructed of 1/8 inch O.D. 0.02 inch wall thickness 316 stainless steel. This column provided a good separation of peaks for five component mixtures but was deactivated due to excess water in the He supply. Subsequent to that time the He supply line was equipped with a drying section (the drying agent was mole sieve 5A which was regenerated at 6 month intervals by overnight heating at 300°C). At this point another column consisting of 5.5 feet of Porapak Q-S and 15 inches of Porapak T was fabricated. This column also yielded good separation but the acetic acid peak tended to tail into the ethyl acetate peak (for this column the acid peak was the fourth peak). A better column was needed.

The final column was composed of 6 inches of Porapak S, followed by 3 feet of Porapak R and the remainder of Porapak Q-S. The operating conditions have been described in section 4.5.1. The column never showed any sign of deterioration and could withstand high temperature G.C. oven operation. At higher temperatures the column was cleared of any accumulated heavy ends (maximum safe temperature for the column packing was 250°C). The big advantage of this column was that the acetic acid peak, which tailed the most, was eluted last. The development of the final G.C. column

involved the testing of about 50 different column combinations, roughly 500 G.C. oven temperature - carrier gas flow rater - column combinations and several thousand sample injections.

A typical G.C. output is shown in Figure C.3. The first peak after the sample injection is a nitrogen or air peak. This was present to varying degrees in most G.C. outputs but was so small that it was ignored when compositions were calculated. During some kinetic runs a small ethylene peak was detected between the nitrogen and the water peaks. If present at all, this peak was even smaller than the nitrogen peak. The ethanol peak tailed into the ether peak (illustrated by the dramatic rise upon changing the attenuation from 16 to 1) and this was the cause of problems in peak area determination for certain ethanol/ether area ratios (see Section 4.5.2 and Section C.3 of the appendix). In general, the peak separation for the final G.C. column was good.

C.3 Calibration of the G.C.

The G.C. was calibrated by sampling mixtures of known composition. The area ratios for the components (relative to the ethanol reference component) were then calculated for a number of injections and the response factors were calculated according to equation 4.1. The water, diethyl ether, ethyl acetate and acetic acid response factors for the calibration mixtures are tabulated in Tables C.3 through C.6. The compositions of the calibration mixtures are listed in Table H.2. The response factors for the four components given above are plotted as a function of the mass ratios (relative to ethanol) in Figures C.4 through C.7. The

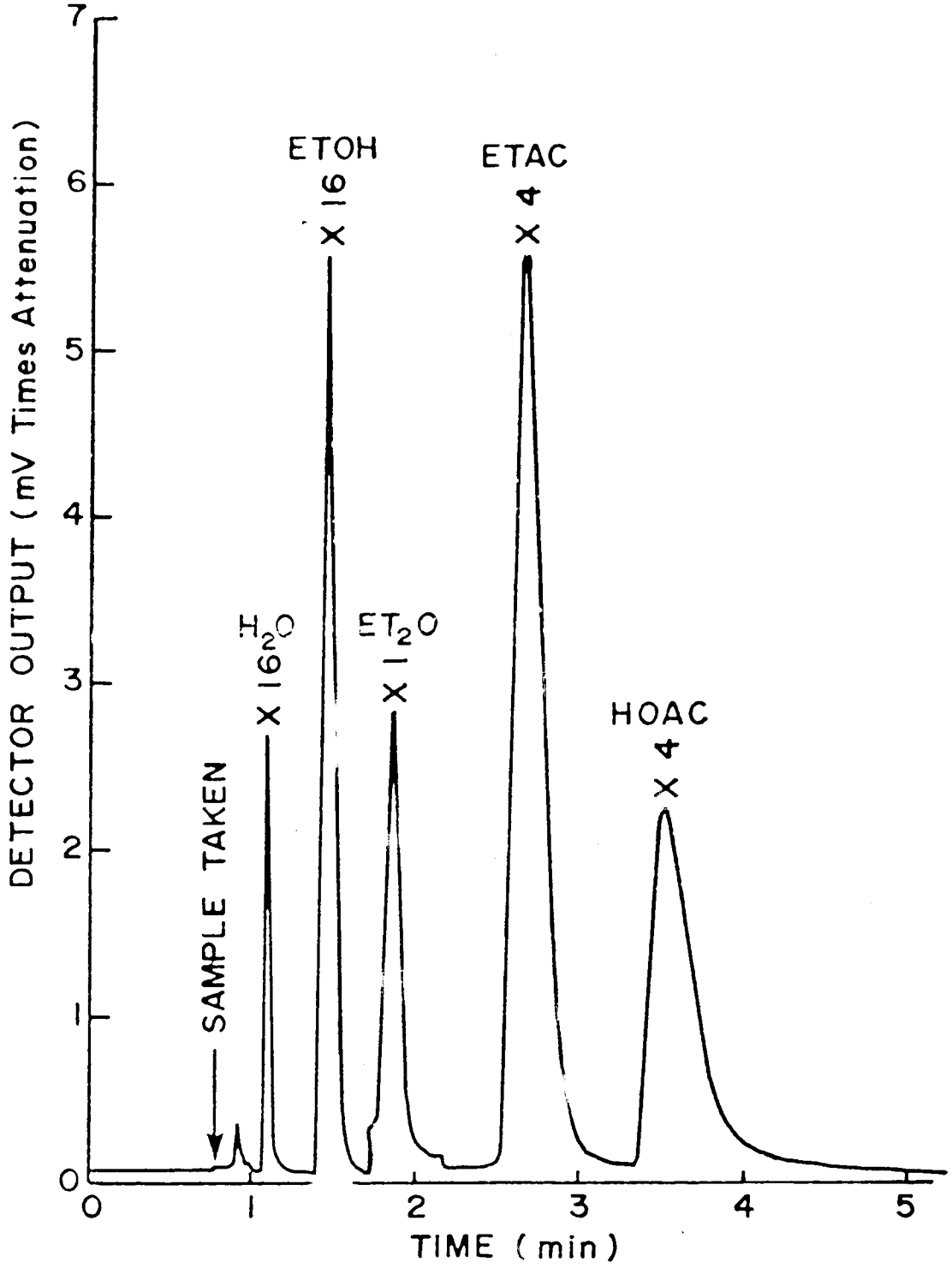


FIGURE C.3 : TYPICAL G.C. OUTPUT CHART

TABLE C.3

RESPONSE FACTOR CALIBRATION POINTS FOR WATER

Mixture #	Mass Ratio (H_2O/ETOH)	Sample Loop[1]	Area Ratio (H_2O/ETOH)	Response Factors Low	Average	High
VIII	0.03084	1	0.0430	2.172	2.175	2.178
		2	0.0380	1.917	1.924	1.936
IX	0.1169	1	0.1681	2.231	2.242	2.249
		2	0.1500	1.990	2.001	2.012
X	0.2957	1	0.4116	2.148	2.171	2.199
		2	0.3724	1.952	1.964	1.983
XI	0.6414	1	0.7943	1.914	1.931	1.965
		2	0.7364	1.741	1.791	1.834
XII	0.01409	1	0.02057	2.263	2.276	2.285
		2	0.01670	1.794	1.848	1.885
XIII	0.3127	1	0.4137	2.043	2.063	2.078
		2	0.3749	1.843	1.870	1.893
XIV	0.2900	1	0.3911	2.100	2.103	2.108
		2	0.3482	1.852	1.872	1.889
XV	0.0421	1	0.0581	2.133	2.154	2.179
		2	0.0504	1.836	1.865	1.882
XVI	0.2266	1	0.2952	2.002	2.032	2.046
		2	0.2718	1.858	1.871	1.881
XVII	0.1444	1	0.1869	1.992	2.019	2.044
		2	0.1731	1.864	1.869	1.874
XVIII	0.01163	1	0.01647	2.127	2.209	2.309
		2	0.01319	1.729	1.769	1.798
XIX	0.04033	1	0.05372	2.071	2.078	2.082
		2	0.04772	1.826	1.845	1.862
XX	0.3974	1	0.5301	2.029	2.080	2.132
		2	0.4637	1.769	1.820	1.877
I	0.05952	L	0.07075	1.837	1.854	1.872
II	0.9436	L	1.083	1.752	1.79	1.83
III	2.899	L	3.342	1.774	1.799	1.847

[1] 1 = gas sample loop 1, 2 = gas sample loop 2, L = liquid sample.

TABLE C.4

RESPONSE FACTOR CALIBRATION POINTS FOR ETHER

Mixture #	Mass Ratio (ET_2O/ETOH)	Sample Loop	Area Ratio (ET_2O/ETOH)	Response Factors Low	Average	High
VIII	0.1039	1	0.08551	1.269	1.283	1.305
		2	0.08941	1.319	1.342	1.376
IX	0.4227	1	0.3678	1.343	1.357	1.372
		2	0.3833	1.388	1.414	1.428
X	0.9921	1	0.8798	1.364	1.376	1.397
		2	0.9071	1.396	1.419	1.430
XI	2.632	1	2.324	1.370	1.377	1.384
		2	2.446	1.436	1.449	1.473
XII	0.03847	1	0.02841	1.138	1.152	1.166
		2	0.03065	1.233	1.243	1.259
XIII	1.956	1	1.699	1.341	1.354	1.371
		2	1.763	1.392	1.405	1.413
XIV	2.916	1	2.532	1.345	1.354	1.363
		2	2.649	1.412	1.417	1.420
XV	0.05828	1	0.0482	1.273	1.290	1.303
		2	0.0487	1.286	1.303	1.313
XVI	0.1304	1	0.1132	1.334	1.353	1.371
		2	0.1140	1.347	1.363	1.389
XVII	0.3094	1	0.2746	1.379	1.384	1.389
		2	0.2770	1.380	1.396	1.406
XVIII	0.1282	1	0.1110	1.343	1.350	1.357
		2	0.117	1.344	1.359	1.377
XIX	0.02589	1	0.01901	1.138	1.145	1.150
		2	0.01925	1.151	1.160	1.166
XX	25.59	1	23.24	1.389	1.416	1.439
		2	23.69	1.433	1.444	1.458
XXIII	0.0286	1	0.0134	0.704	0.730	0.751
		2	0.0141	0.744	0.771	0.789
XXIV	0.00909	1	0.00474	0.794	0.813	0.828
		2	0.00502	0.833	0.862	0.879
XXV	0.01058	1	0.00603	0.880	0.889	0.905
		2	0.00669	0.976	0.986	0.997
XXVII	0.03185	1	0.02318	1.124	1.135	1.145
		2	0.02487	1.192	1.218	1.236

continued

TABLE C.4 (continued)

RESPONSE FACTOR CALIBRATION POINTS FOR ETHER

Mixture #	Mass Ratio (ET_2O/ETOH)	Sample Loop[1]	Area Ratio (ET_2O/ETOH)	Response Factors Low	Average	High
XXIX	0.0255	1	0.0172	1.015	1.051	1.084
		2	0.0189	1.135	1.159	1.182
XXX	0.0147	1	0.0083	0.85	0.881	0.900
		2	0.0096	1.001	1.023	1.053
I	0.05239	L	0.05126	1.412	1.417	1.424
II	0.8824	L	0.8193	1.447	1.449	1.45
III	2.67	L	2.45	1.517	1.526	1.54

[1] 1 = gas sample loop 1, 2 = gas sample loop 2, L = liquid sample.

TABLE C.5

RESPONSE FACTOR CALIBRATION POINTS FOR ETHYL ACETATE

Mixture #	Mass Ratio (ETAC/ETOH)	Sample Loop[1]	Area Ratio (ETAC/ETOH)	Response Factors Low	Average	High
XV	0.1407	1	0.1171	1.295	1.298	1.301
		2	0.1178	1.303	1.306	1.307
XVI	0.9404	1	0.7719	1.270	1.280	1.291
		2	0.7821	1.287	1.297	1.305
XVII	0.35	1	0.2978	1.284	1.290	1.299
		2	0.2997	1.291	1.299	1.303
XVIII	0.8126	1	0.6753	1.291	1.296	1.300
		2	0.6821	1.303	1.309	1.318
XIX	0.1323	1	0.1100	1.291	1.296	1.300
		2	0.1109	1.305	1.307	1.311
XX	1.[illegible]3	1	1.557	1.258	1.280	1.298
		2	1.596	1.291	1.312	1.320
XXV		1	1.665	1.262	1.271	1.277
		2	1.70[illegible]	1.301	1.301	1.303
XXVII		1	1.666	1.277	1.281	1.283
		2	1.689	1.296	1.299	1.305
I	060[illegible]	[illegible]	0.05116	1.019	1.325	1.339
II	0.8409		0.6955	1.276	1.29	1.295
III	2.873		341	1.268	1.271	1.273

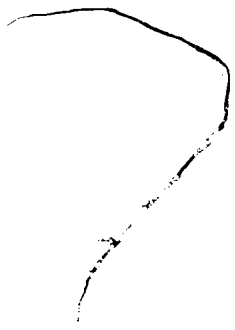
[1] 1 = gas sample loop 1, 2 = sample loop 2, L = liquid sample.

TABLE C.5

RESPONSE FACTOR CALIBRATION POINTS FOR ACETIC ACID

Mixture #	Mass Ratio (HOAC/ETOH)	Sample Loop[1]	Area Ratio (HOAC/ETOH)	Response Factors Low	Average	High
XV	0.2076	1	0.1685	1.250	1.266	1.285
		2	0.1634	1.202	1.228	1.253
XVI	1.136	1	0.9380	1.244	1.287	1.351
		2	0.9232	1.221	1.267	1.317
XVII	0.1829	1	0.1447	1.216	1.234	1.256
		2	0.1414	1.186	1.205	1.222
XVIII	0.05634	1	0.04388	1.143	1.198	1.253
		2	0.04272	1.137	1.182	1.267
XIX	0.05354	1	0.04029	1.147	1.173	1.186
		2	0.03885	1.117	1.132	1.158
XX	1.085	1	0.8708	1.218	1.251	1.272
		2	0.8284	1.156	1.191	1.219
I	0.0571	L	0.0406	0.059	1.110	1.129
II	0.9652	L	0.7521	1.181	1.216	1.228
III	2.901	L	2.262	1.209	1.216	1.221

[1] 1 = gas sample loop 1, 2 - gas sample loop 2, L = liquid sample.



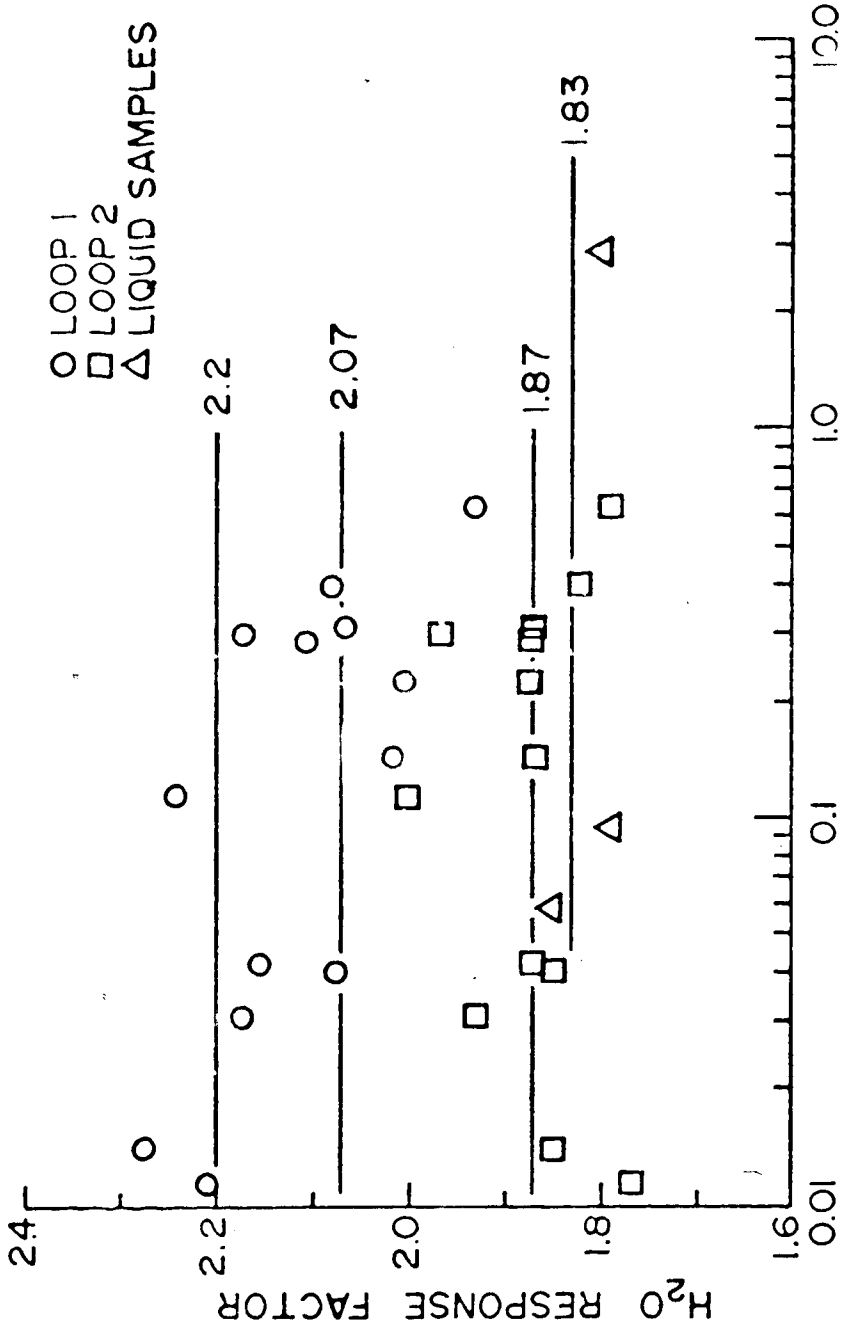


FIGURE C.4: RESPONSE FACTOR CALIBRATION PLOT FOR WATER

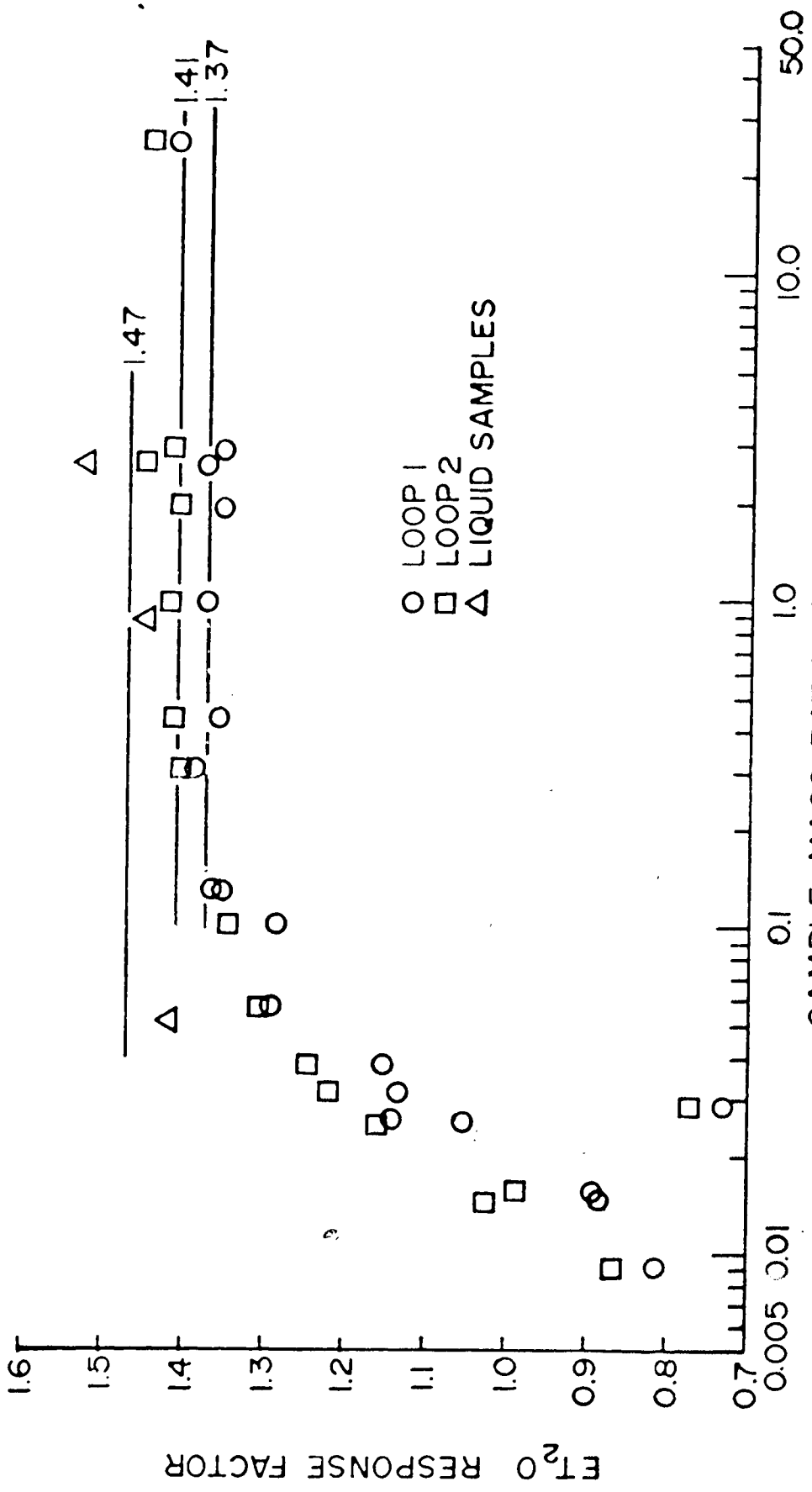


FIGURE C.5: RESPONSE FACTOR CALIBRATION PLOT FOR ETHER

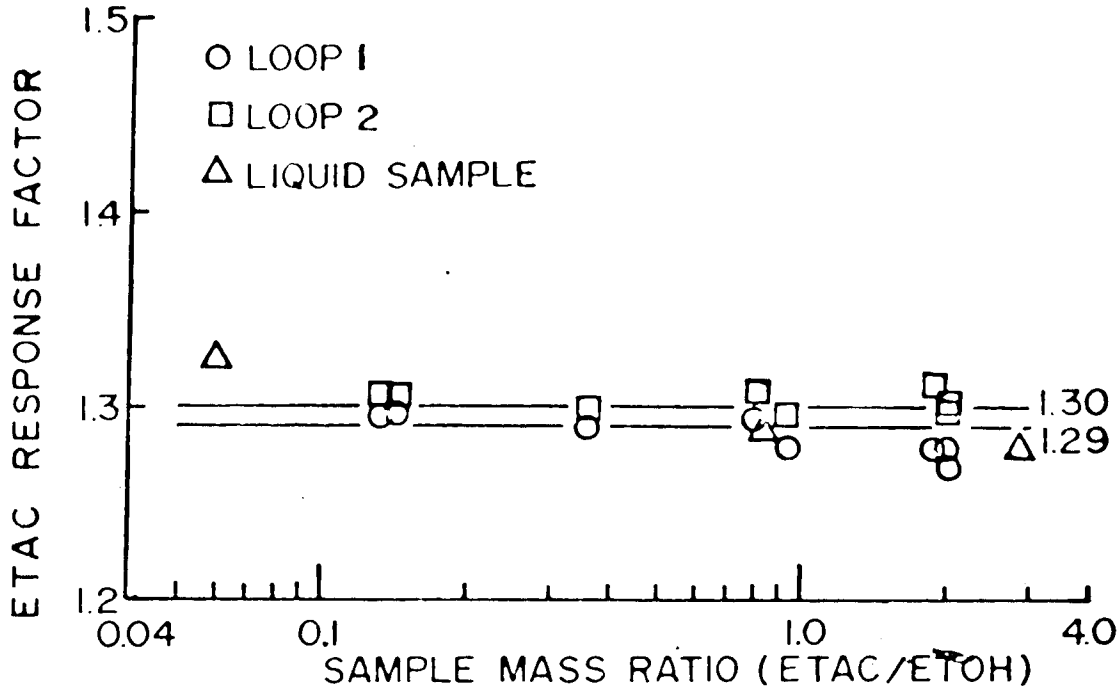


FIGURE C.6: RESPONSE FACTOR CALIBRATION PLOT FOR ETHYL ACETATE

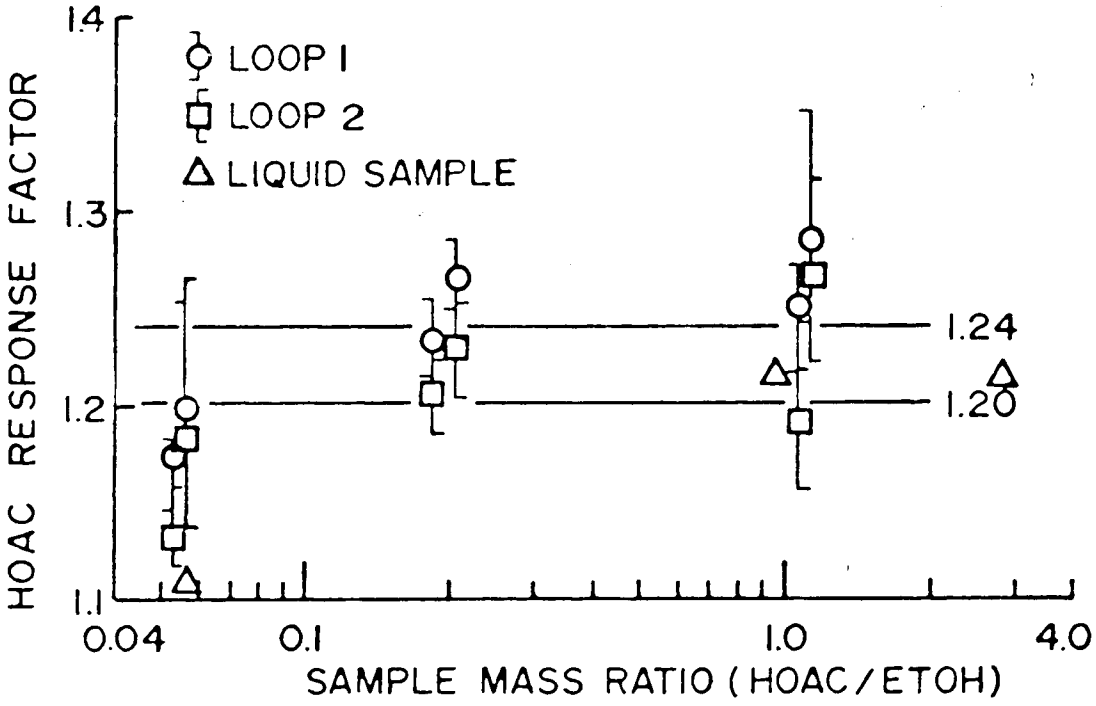


FIGURE C.7: RESPONSE FACTOR CALIBRATION PLOT FOR ACETIC ACID

captions "Loop 1" and "loop 2" are in reference to gas sample injections via these gas sample loops. This method of plotting the response factors tends to emphasize any scatter in the response factor data. It is then possible to determine what the best average response factors are. The final response factors presented in Table 4.1 were arrived at by examining mass ratio versus response factor plots.

For water the loop 1 gas sample calibration points tended to be more scattered than the loop 2 points. Water mass balances during kinetic runs (see Appendix I) indicated that the loop 1 water response factor of value of 2.2 resulted in better agreement with the balances calculated for loop 2 samples. Thus the water response factor was set at 2.2 (a better value for low water/ethanol mass ratios) for the kinetic runs. The value 2.07 was probably better at higher mass ratios but during kinetic runs the mass ratios were normally quite low (the molecular weight of water is less than half that of any other component and therefore the water/ethanol mass ratios were much lower than the molar ratios).

The ether response factors plotted in Figure C.5 appeared to drop off at lower mass ratios. This was caused by the way in which the area was calculated for the ether peak (the ether peak started on the shoulder of the ethanol peak). As discussed in section 4.5.2, if another area calculation procedure was used the response factors would have curved up rather than down for lower ether/ethanol mass ratios. The response factor versus area ratio plot is shown in Figure C.8. The calibration points at the lower ether/ethanol area

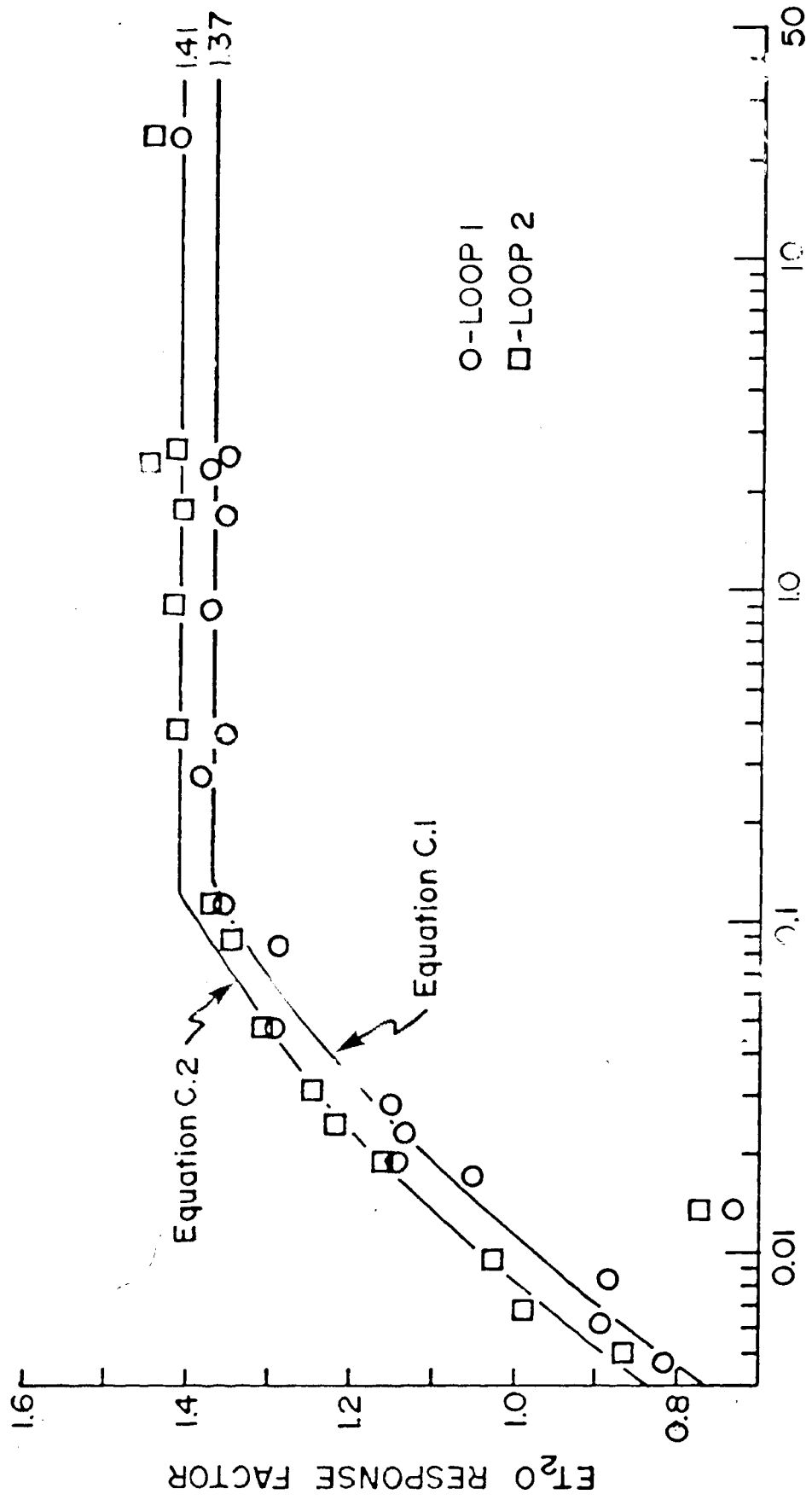


FIGURE C.8: ETHER RESPONSE FACTOR VERSUS AREA RATIO

ratios (area ratios less than about 0.1) were fit to polynomial equations. The loop 1 and loop 2 ether response factors at low area ratios were calculated according to the best fit equations C.1 and C.2.

$$RF_1 = -0.0235(\ln A_{R1})^2 + 0.0072(\ln A_{R1}) + 1.48 \qquad (C.1)$$

$$RF_2 = -0.0274(\ln A_{R2})^2 - 0.1043(\ln A_{R2}) + 1.298 \qquad (C.2)$$

In equations C.1 and C.2 the peak area ratios for loops 1 and 2 are A_{R1} and A_{R2}.

The response factors were used to analyze the G.C. results for the compositions of the calibration mixtures. Equation 4.2 was used to calculate the compositions based on mass functions and these were converted to a molar basis. Tables C.7 through C.12 list the composition analysis for six calibration mixtures. The analysis for a number of samples, the average analysis and the [illegible] are tabulated. Odd sample numbers indicate gas samples and even sample numbers are for loop 2 gas samples. It can be seen that the calculated compositions are quite close to the actual values.

TABLE C.7

CALCULATED COMPOSITIONS FOR CALIBRATION

MIXTURE XV

SAMPLE #	PRODUCT ANALYSIS MOLE % COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
5	7.70	72.52	2.71	5.37	11.67
7	7.57	72.54	2.69	5.36	11.81
9	7.59	72.37	2.72	5.36	11.93
11	7.59	72.46	2.71	5.37	11.85
6	7.79	72.43	2.64	5.35	11.77
8	7.66	72.51	2.60	5.36	11.85
10	7.79	72.44	2.62	5.35	11.78
12	7.77	72.22	2.65	5.32	12.01
	7.68	72.44	2.67	5.36	11.83
FEED	7.81	72.64	2.63	5.34	11.56

TABLE C.8

CALCULATED COMPOSITIONS FOR CALIBRATION

MIXTURE XVI

SAMPLE	PRODUCT ANALYSIS MOLE % COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
1	18.00	33.48	2.73	16.40	29.36
21	17.63	32.76	2.61	15.86	31.11
23	17.60	33.10	2.65	16.07	30.55
[illegible]	17.80	33.19	2.71	16.33	29.95
25	18.89	32.81	2.69	16.17	29.40
22	18.95	32.51	2.61	15.87	30.03
24	18.77	32.36	2.61	15.89	30.35
26	18.89	32.5[illegible]	2.64	15.97	29.93
	18.31	32.85	2.66	16.07	30.09
FEED	19.15	33.07	2.68	16.26	28.81

TABLE C.9

CALCULATED COMPOSITIONS FOR CALIBRATION

MIXTURE XVII

PRODUCT SAMPLE #	ANALYSIS MOLE % COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
33	18.01	53.85	10.49	10.11	7.53
35	19.72	58.04	11.24	10.98	0.00
37	18.13	53.72	10.43	10.07	7.63
39	18.38	53.58	10.45	10.16	7.42
32	19.52	53.04	10.08	9.99	7.35
34	19.56	52.87	10.08	9.92	7.55
36	19.49	52.91	10.15	9.98	7.44
38	19.57	53.02	9.98	9.91	7.50
	19.05	53.88	10.36	10.14	6.55
FEED	19.53	52.91	10.17	9.95	7.42

TABLE C.10

CALCULATED COMPOSITION FOR CALIBRATION

MIXTURE XVIII

PRODUCT SAMPLE #	SIS MOLE % COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
19	1.95	63.20	5.03	27.04	2.76
21	1.86	63.41	5.04	27.03	2.63
23	1.97	63.35	5.03	27.03	2.59
27	1.84	63.47	5.01	26.99	2.66
20	1.74	63.33	5.11	27.21	2.59
22	1.78	63.48	5.03	27.05	2.63
24	1.78	63.37	5.05	27.09	2.69
28	1.80	63.08	5.05	27.18	2.87
	1.84	63.34	5.04	27.08	2.68
FEED	1.88	63.39	5.05	26.92	2.73

TABLE C.11

CALCULATED COMPOSITIONS FOR CALIBRATION

MIXTURE XIX

PRODUCT SAMPLE #	ANALYSIS MOLE % COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
5	7.93	81.79	1.37	5.70	3.18
7	7.98	81.83	1.37	5.69	3.10
9	7.97	81.79	1.36	5.66	3.20
11	7.96	81.74	1.37	5.70	3.20
8	8.36	81.49	1.30	5.67	3.16
10	8.35	81.45	1.30	5.65	22
12	8.33	81.51	1.30	5.66	17
14	8.26	81.62	1.29	5.67	3.14
	8.14	81.65	1.33	5.67	3.17
FEED	8.38	81.34	1.30	5.62	3.33

TABLE C.12

CALCULATED COMPOSITIONS FOR CALIBRATION

MIXTURE XX

PRODUCT SAMPLE #	ANALYSIS MOLE % COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
27	4.65	4.91	81.36	4.88	4.18
29	4.60	4.91	81.41	4.86	4.19
31	4.67	4.93	81.37	4.87	4.13
33	4.87	4.95	81.16	4.87	4.12
26	4.89	4.95	81.02	4.99	4.12
28	4.90	4.99	80.91	4.98	4.20
30	4.95	4.99	80.91	5.01	4.12
34	4.91	4.97	80.90	5.00	4.20
	4.81	4.95	81.13	4.93	4.16
FEED	5.14	5.06	80.55	5.02	4.21

APPENDIX D

TEMPERATURE MEASUREMENT

D.1 Thermocouple Calibration

The temperature of the catalyst bed was measured with an iron-constantan thermocouple (#74-14) which was referenced to an ice bath cold junction. The thermocouple was calibrated against a platinum resistance thermometer over the temperature range of interest. The temperature was calculated from the thermocouple output by using the least-squares best fit line obtained from the calibration points. The calibration points, the temperature calculated using the linear fit and the temperature calculated from standard tables for iron-constantan thermocouples (17) are presented in Table D.1.

The relationship between thermocouple output and temperature was found to be expressed by the following equation.

$$\text{Temperature } (^{o}C) = 18.205 \times \text{Output (mV)} + 4.1 \qquad (D.1)$$

The average deviation of calculated versus actual temperature was $0.06^{o}C$, hence the linear output-temperature relationship was accurate over the temperature range of interest.

D.2 Temperature Profile, Reactor Tube

The Teflon sleeve (see Figure 3.5) was installed in the reactor tube to limit longitudinal temperature gradients in the catalyst bed. Measurement of the temperature profile above the

TABLE D.1

TEMPERATURE MEASUREMENT CALIBRATION

Actual Temperature (^{o}C)	Thermocouple Output (mV)	Calculated Temperature (Equation D.1) (^{o}C)	Temperature From Tables (^{o}C)
102.61	5.405	102.52	102.53
102.76	5.420	102.79	102.80
112.47	5.952	112.47	112.56
112.59	5.960	112.62	112.71
122.46	6.503	122.51	122.64
122.71	6.516	122.75	122.87
122.61	6.510	122.64	122.76
132.72	7.066	132.76	132.89
132.68	7.064	132.72	132.85
132.48	7.042	132.33	132.45
142.56	7.603	142.55	142.65

catalyst support screens showed that the temperature was isothermal within the sleeve section. The measurements were carried out by moving the thermocouple in the reactor tube above the support screens under conditions similar to normal run conditions. Five centimetres of sleeve were in the reactor tube and the longitudinal temperature profile is presented in Table D.2.

TABLE D.2

LONGITUDINAL TEMPERATURE PROFILE

Distance Above Screen (cm)	Measured Temperature (^{o}C)
3.0	136.0
4.0	136.0
5.0	136.0
6.0	136.7
7.0	138.0
8.0	138.5
9.0	139.2
10.0	140.4
11.0	139.8

D.3 Heat Conduction

Heat conduction along the thermocouple can cause the measured temperature to be different from the actual gas temperature. One can determine the temperature difference at the end of the thermocouple by setting up a heat balance and solving the resulting differential equation. The gas temperature is changing along the thermocouple. The scheme is presented in Figure D.1.

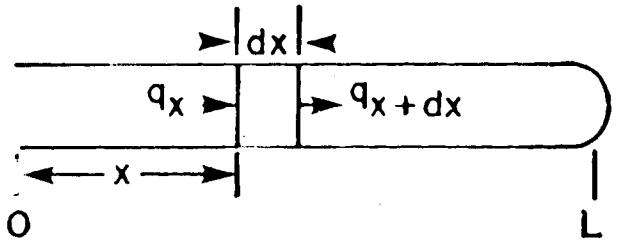


FIGURE D.1: HEAT TRANSFER ALONG THE THERMOCOUPLE

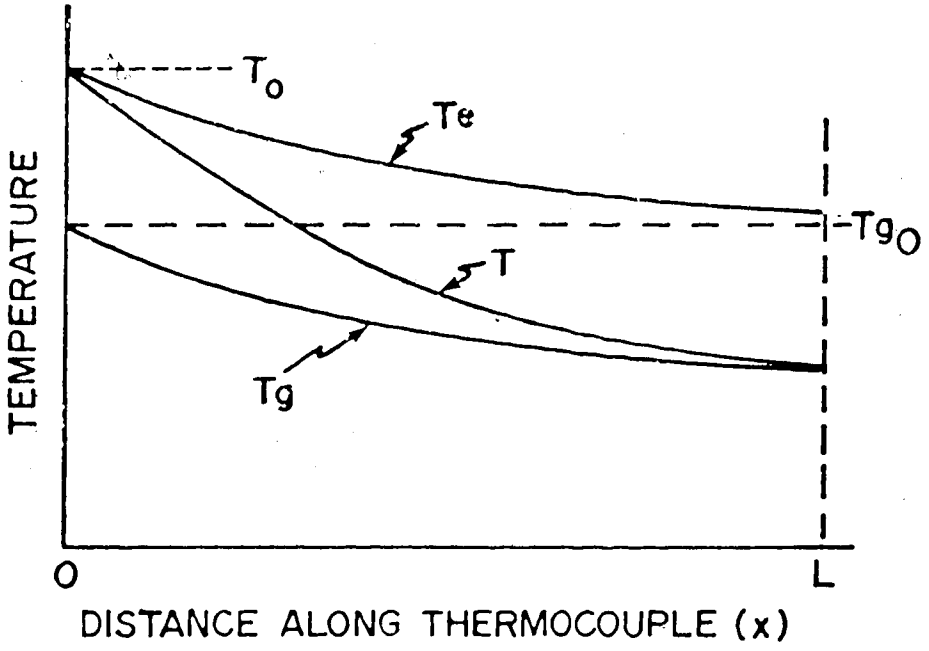


FIGURE D.2: TEMPERATURE PROFILES ALONG THE THERMOCOUPLE

The temperature of the gas surrounding the thermocouple is also a function of the distance along the reactor tube. The temperature profiles are presented in Figure D.2. Referri g to Figure D.1., the heat conducted into the differential element dx minus the heat conducted out is equal to the heat lost by convection.

$$q_x - q_{x+dx} = hp(T - Tg)dx \qquad (D.2)$$

Equation D.2 can be rewritten in the following form.

$$-kA \left.\frac{dT}{dx}\right|_x + kA \left.\frac{dT}{dx}\right|_{x+dx} = hp(T - Tg)dx \qquad (D.3)$$

Here k = thermal conductivity ıg the thermocouple

A = cross sectional area of the thermocouple available for heat transfer

h = convective heat transfer coefficient

p = circumference of the thermocouple

The temperature in equation D.3 can be replaced with an effective temperature, Te, which is defined according to equation D.4.

$$Te = T + (Tg_0 - Tg) \qquad (D.4)$$

Sub ituting this definition of temperature into equation D.3 and rearranging results in the following equation

$$kA \left[\left(\frac{dTe}{dx} + \frac{dTg}{dx}\right)\right|_{x+dx} - \left.\left(\frac{dTe}{dx} + \frac{dTg}{dx}\right)\right|_x] = hp(Te - Tg_0)dx \qquad (D.5)$$

With $M^2 = hp/kA$, equation D.5 can be expressed as follows.

$$\frac{d^2Te}{dx^2} + \frac{d^2Tg}{dx} = M^2(Te - Tg_0) \qquad (D.6)$$

One can now assume a temperature profile for the gas stream to be an exponential temperature drop and the first and second derivatives of the gas temperature can be defined.

$$Tg = T_g + J_1 e^{-J_2 x} \qquad (D.7)$$

$$\frac{dTg}{dx} = J_1 J_w e^{-J_2 x} \qquad (D.8)$$

$$\frac{d^2Tg}{dx^2} = J_1 J_2^2 e^{-J_2 x} \qquad (D.9)$$

Letting $Y = Te - Tg_0 = T - Tg$ equation D.6 is written according to the following equation.

$$\frac{d^2Y}{dx^2} - M^2(Y) = -J_1 J_2^2 e^{-J_2 x} \qquad (D.10)$$

The particular solution of D.10 is $Yp = \bar{J}\, e^{-J_2 x}$ where $\bar{J} = -J_1 J_2^2/(J_2^2 - M^2)$. The general solution is

$$Yg = C1e^{Mx} + C2e^{-Mx} \qquad (D.11)$$

Therefore the solution of equation D.10 is as follows.

$$Y = C1e^{Mx} + C2e^{-Mx} + Je^{J_2 x} \qquad (D.12)$$

The two boundary conditions given below apply

$$\text{at } x = 0 \text{ , } Y = T_0 - Tg_0$$

$$\text{at } x = l \text{ , } -k \left.\frac{dT}{dx}\right|_{x=L} = h_L(T_L - Tg_L)$$

Here h_L is the convective heat transfer coefficient and the subscript l refer to temperatures at the end of the thermocouple.

One can then solve for C_1 and C_2.

$$C1 = \frac{[-(T_0-Tg_0)(C3-1)e^{-ML}]+[\bar{J}(C3-1)e^{-ML}]-[(C3\bar{J}-C4)e^{-J_2L}]}{2(\cosh ML + C3\sinh ML)} \tag{D.13}$$

$$C2 = \frac{[(T_0-Tg_0)(C3+1)e^{ML}]+[\bar{J}(C3+1)e^{ML}]+[(C3\bar{J}-C4)e^{-J_2L}]}{2(\cosh ML + C3\sinh ML)} \tag{D.14}$$

where T_0 = thermocouple temperature at x = o

$C3 = h/kM$

$C4 = J_2\bar{J}/M$

If the second derivative of the gas temperature is zero (in this case when $J_2 = 0$), the solution corresponds to the solution for heat transfer from an extended fin of uniform cross-section (10) (Note: the temperature substitution of equation D.4 still holds). The solution for the simpler problem (10) is

$$Y = \frac{(T - Tg)(\cosh M(L-x) + C3\sinh M(l-x))}{\cosh ML + C3\sinh ML} \tag{D.15}$$

The temperature profiles for a number of combinations of heat transfer parameters and gas temperature profiles were calculated. One such case is explained here. The thermocouple section was taken to be 4 cm long and the gas temperature drop was set at 9.5°C over the interval (the gas temperature profile was calculated according to equation D.7). At the start of the interval the temperature of the thermocouple was assumed to be 10°C higher than the gas temperature. The following parameters were used for the calculations:

$$k = 62.4 \text{ kJ/m K hr}$$

$$A = 1.98 \times 10^{-6} \text{ m}^2$$

$$h = 614 \text{ kJ/m}^2 \text{ K hr}$$

$$h_L = 205 \text{ kJ/m}^2 \text{ K hr}$$

$$p = 4.99 \times 10^{-3} \text{ m}$$

With the above assumptions and parameters the temperature difference $(T_L - Tg_L)$ at the tip of the thermocouple was calculated to be 0.23°C using equation D.12. Using equation D.15 the calculated temperature difference was 0.03°C.

The calculation described above was conservative for a number of reasons. One assumption was that the thermal conductivity of the entire cross-sectional area was equal to that of stainless steel. In fact a large portion of the thermocouple probe is insulation which is covered with a stainless steel sheath and thus the actual thermal conductivity is less than the value used (as $k \to 0$, $T \to Tg$). The gas temperature drop along the section of thermocouple was assumed to be 9.5°C but it was actually

approximately $3^{o}C$ (4 cm temperature drop = 139.2 - 136.0 = $3.2^{o}C$, see Table D.2). With a smaller gas temperature drop (and a nearly linear profile) the calculated thermocouple tip temperature would approach the gas temperature even closer than was indicated in the example calculation. Thus the temperature indicated by the thermocouple (as measured at the tip) is probably within $0.1^{o}C$ of the actual gas temperature during normal operation of the system.

APPENDIX E

CATALYST CHARGES

The purpose of this appendix is to provide details concerning the actual amounts of catalyst used for the experimental runs. The individual charges listed in Tables E.1 and E.2 were prepared from Dowex HGR-W (H+) cation exchange resin according to the procedures presented in section 4.1. The long term storage of the catalyst in individual capped vials did not cause any deterioration of the catalyst. The results of later dehydration runs (with catalyst stored for over 2 months) are consistant with earlier runs using different catalyst charges.

Table E.3 is a listing of the runs carried out with various charges of catalyst. The physical colour of the catalyst after contact with acetic acid was different from the colour of the fresh catalyst (golden yellow). Charges of catalyst exposed only to ethanol and dehydration products retained the colour of the fresh catalyst. Catalyst exposed to high temperatures ($>150^{o}C$) for extended periods of time became black and did not regain the colour of fresh resin.

TABLE I

BATCH 1 CATALYST CHARGES

Charge Number	Vial Mass Net/Gross (g)	Total Charge Mass (g)
1	9.7064 9.4936	0.2128
2	9.3052 9.1457	0.1595
3	9.3521 9.1844	0.1677
4	9.4632 9.1362	0.3270
5	9.4571 9.3304	0.1267
6	9.2231 9.1551	0.0680
7	9.9508 9.4708	0.4800

Moisture determination for Batch 1 charges

Mass of vial empty - 19.7800
Mass before vacuum heating - 21.3515
Mass after vacuum heating - 20.9733

$$\text{Bone dry fraction of total mass} = \frac{\text{mass of bone dry catalyst}}{\text{mass of "wet" catalyst}}$$

$$= \frac{(20.9733-19.7800)\ g}{(21.3515-19.7800)\ g}$$

$$= \frac{1.1933}{1.5715} = 0.759$$

$$\approx 76\%$$

TABLE E.2

BATCH 2 CATALYST CHARGES

Charge Number	Vial Mass Net/Gross (g)	Total Charge Mass (g)
1	5.4428 4.7765	0.6663
2	4.9742 4.7350	0.2392
3	4.9542 4.6782	0.2760
4	5.3389 4.6767	0.6622
5	5.2878 4.8545	0.4333
6	5.1350 4.8336	0.3014

Moisture determination for Batch 2 charges

Mass of vial empty - 19.7840 g
Mass before vacuum heating - 21.4338 g
Mass after vacuum heating - 21.1003 g

$$\text{Bone dry fraction of total mass} = \frac{\text{mass of bone dry catalyst}}{\text{mass of "wet" catalyst}}$$

$$= \frac{(21.1003-19.7840)\ g}{(21.4338-19.7840)\ g}$$

$$= \frac{1.3163}{1.6498} = 0.798$$

$$\simeq 80.0\%$$

TABLE E.

CATALYST CHARGES USED FOR EXPERIMENTAL RUNS

Charge	Catalyst Batch	Runs
4	1	I, II
1 and 7	1	III, IV, V
1	2	VI
4	2	VII, VIII, IX, X, XI
3	2	XII, XIII, XIV, XV, XVI EI through EVI
6	2	XVII, EVII

APPENDIX F

SYRINGE PUMP CALIBRATIONS

The calibration points for various combinations of pumps, ranges and syringes are listed in Table F.1. The experimental method used for calibrating the pumps is given in section 4.2. For the calibration points the density of water was between 0.997 and 0.998 gcm^{-3} at the ambient temperature during calibrations.

The two syringes used were so similar that calibration points from each fell on the same line. Hence the syringes were essentially interchargeable.

The experimental points (the three calibration lists of Table F.1) were fit to straight lines (Equations F.1 to F.6 Table F.2) with least-squares fitting routines. The equations of the resulting lines along with the standard deviations of the fitting are presented in Table F.2. The calibration points and the fitting lines are plotted in Figures F.1, F.2 and F.3

The calibration did not change with time. This is substantiated by the fact that some of the calibration points (Table F.1: e.g. the last 50%/1000 point and the last two 1/100 range points) were taken over 6 months later than previous points in the same columns.

TABLE F.1

SYRINGE PUMP CALIBRATION POINTS

Pump 355 Range 1/1000		Pump 355 Range 1/100		Pump 352 Range 50 ml	
Setting (%)	Flow Rate (ml/min)	Setting (%)	Flow Rate (ml/min)	Setting (ml/hr)[1]	Flow Rate (ml/min)
Syringe #1		Syringe #1		Syringe #2	
10.	0.00857	50.	0.4267	0.60	0.01113
20.	0.0166	20.	0.1620	0.15	0.003011
4.	0.00322	70.	0.6030	0.30	0.005108
30.	0.0255	10.	0.0774	2.0	0.0346
7.	0.005488	10.	0.07935	1.0	0.01784
40.	0.03486	80.	0.6798	6.0	0.10623
15.	0.01257	30.	0.2524	4.0	0.07104
50.	0.042205	90.	0.7738	15.0	0.259
25.	0.02183	40.	0.33325		
60.	0.05047	60.	0.5172		
35.	0.0299				
70.	0.05997	Syringe #2			
39.	0.0324				
80.	0.06944	25.	0.2109		
24.	0.0195	75.	0.6433		
90.	0.0761				
45.	0.03678				
100.	0.0841				
55.	0.0458				
65	0.0532				
75	0.0625				
65	0.05622				
85	0.07268				
95	0.08046				
50.	0.04256				

[1] nominal value

TABLE F.2

CALIBRATION LINES FOR SYRINGE PUMPS

Fitting Equation[1] $Y_c = a_0 + a_1 X$, n points

Calibration Pump #, Range	Number Of Points	a_0	a_1	Equation Number	Standard Deviation $(\Sigma(Y-Y_c)^2)^{1/2}/n$	Total Average Deviation (%) $[\Sigma\lvert\frac{Y-Y_c}{Y}(100)\rvert]/n$
355, 1/1000	25	0.0	0.0008462	F.1	0.000787	2.02
355, 1/1000	25	-0.000218	0.00084955	F.2	0.000779	1.78
355, 1/100	12	0.0	0.008546	F.3	0.00551	2.70
355, 1/100	12	-0.00891	0.0086892	F.4	0.00324	0.85
352, 50	8	0.0	0.017354	F.5	0.00110	3.71
352, 50	8	-0.000759	0.017277	F.6	0.000925	4.31

[1]Here X has the units of the setting value and a_0 and a_1 have units such that the result is in ml/min.

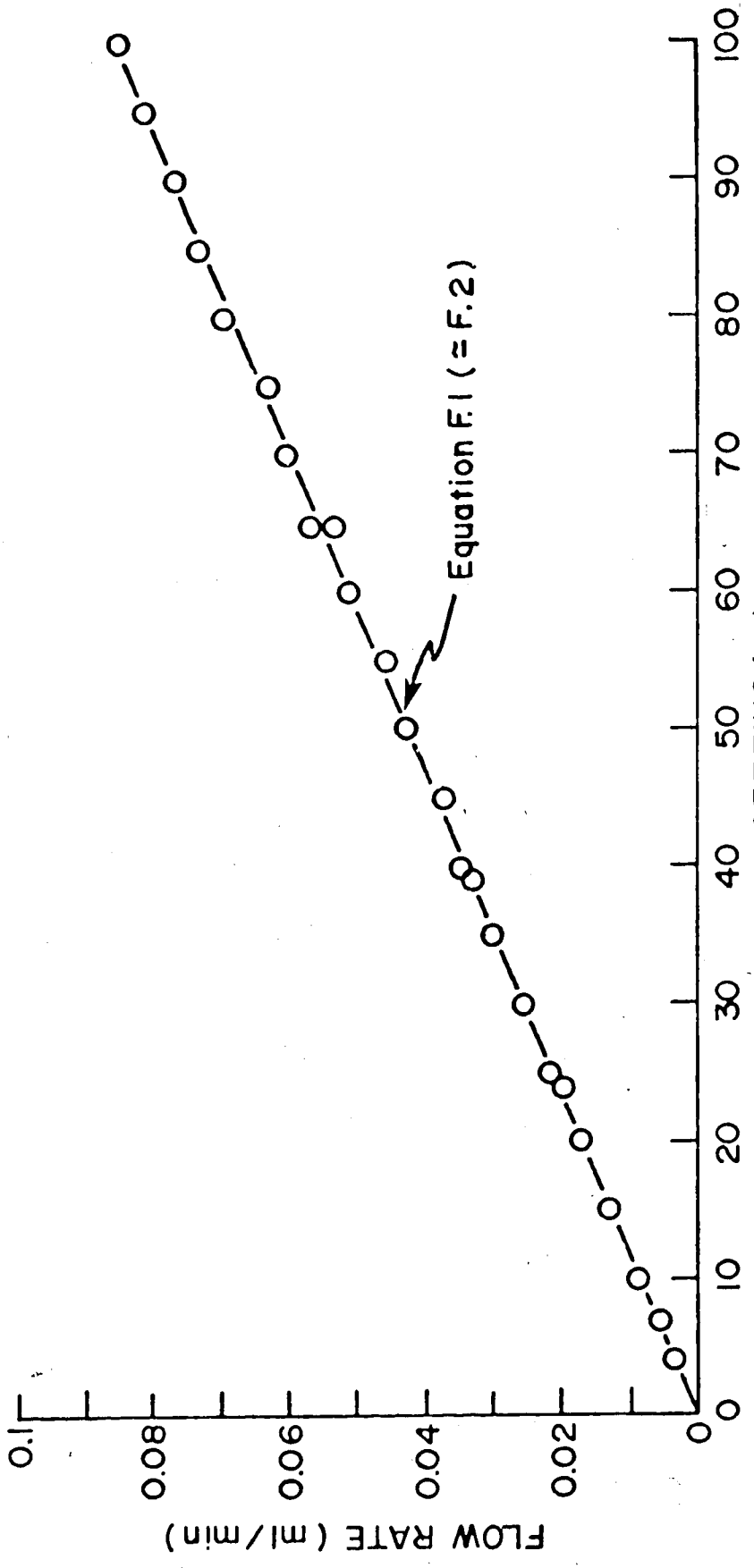


FIGURE F.1: CALIBRATION POINTS MODEL 355 PUMP, RANGE 1/1000

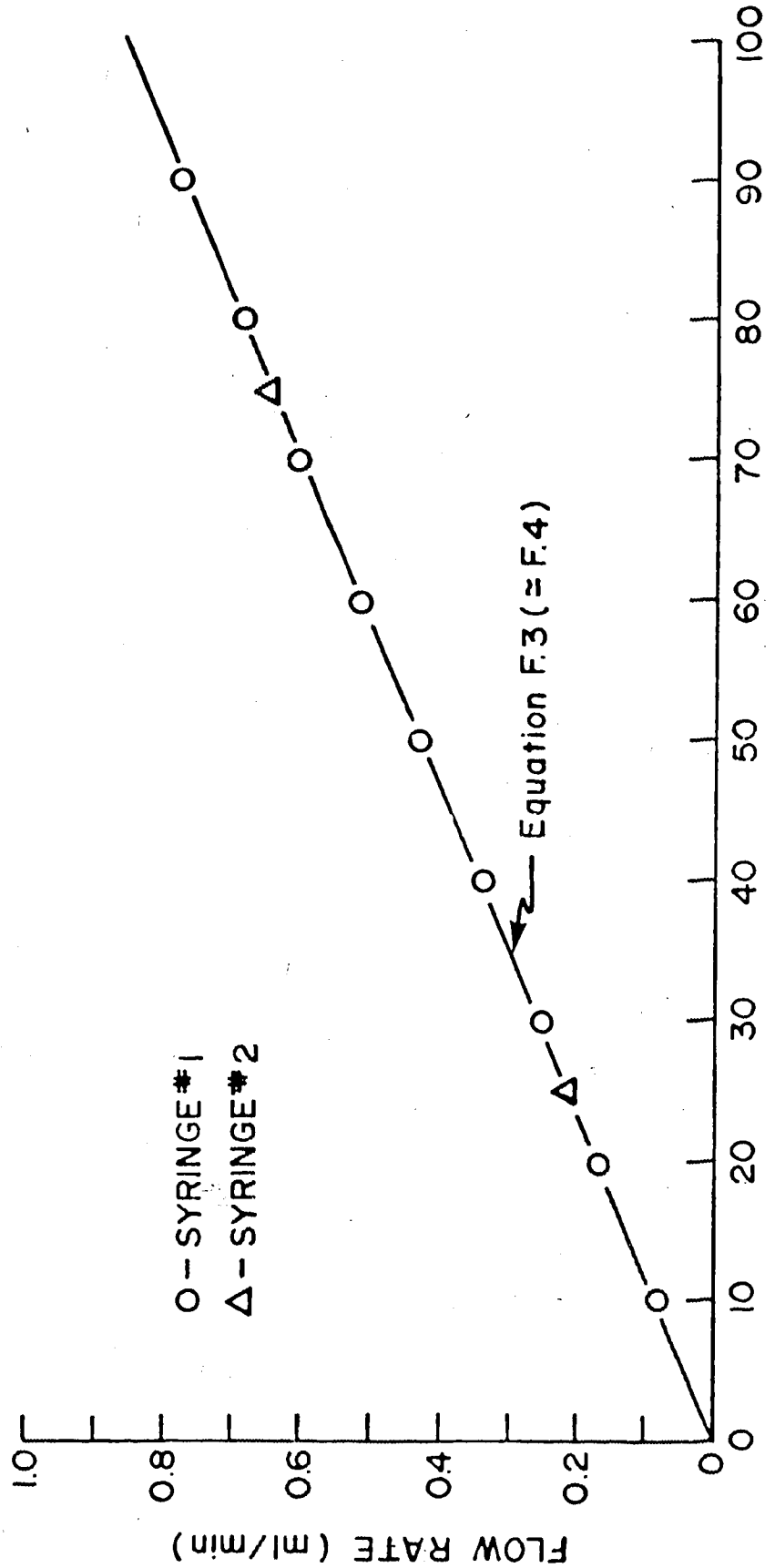


FIGURE F.2: CALIBRATION POINTS MODEL 355 PUMP, RANGE 1/100

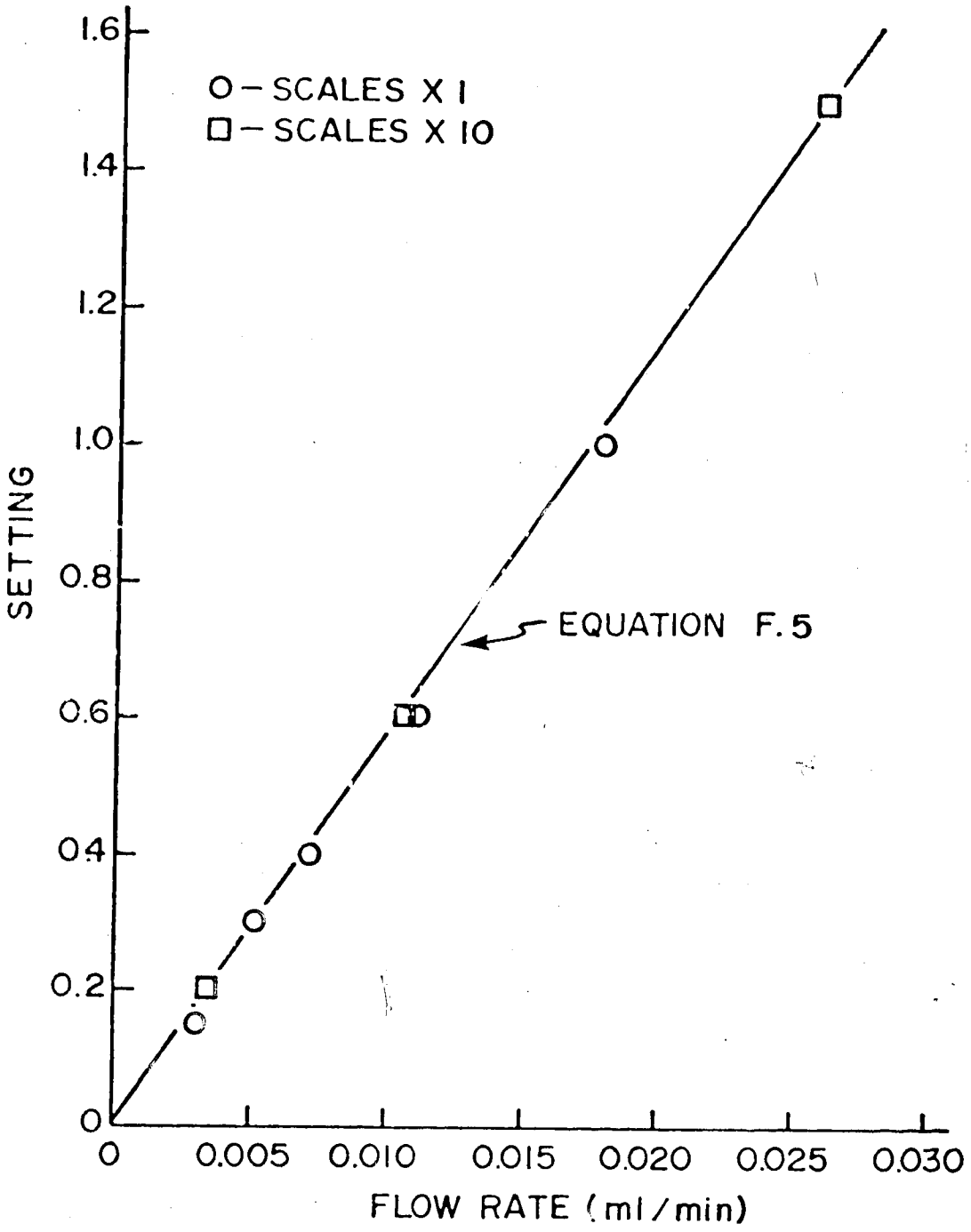


FIGURE F.3: CALIBRATION POINTS
MODEL 353 PUMP, 50ml RANGE

APPENDIX G

EQUIPMENT OPERATION

This appendix is supplemental to the information presented in Chapter Four. Normal operation during kinetic runs involved setting the voltage inputs to the system heaters as described in Section 4.7.1. Some of the system heaters were not designed for voltages beyond certain maximums. These maximum heater inputs are given in Table G.1.

TABLE G.1

MAXIMUM VOLTAGE SETTINGS FOR HEATERS

Heater Description	Variac Normally Used	Maximum Input (V)
Feed Block Heater	1	20
Oven Heater	2	120
Reactor Heater	3	0
Reactor Postheater	4	0
Interheater (Oven-G.C.)	5	20
Pre-Feed Line Heater	-	40

Good temperature control of the catalyst bed section of the reactor was achieved when DDC loop OE92, which controlled the preheater, was run as a proportional plus integral action controller and DDC loop OE94 regulating the cooling air control valve was in

the proportion control mode only (during kinetic runs loop 0E94 was used in the manual mode of operation with a constant output of about 30%). At the setpoint temperature the control signal from loop 0E94 was normally set at 30%. DDC loop 0E96 controlled the solenoid valve on the cooling air line but this on/off controller was not normally used. The solenoid valve was available for the implementation of large, quick drops in reactor temperature. The DDC loops used during this work are presented in Table G.2. An explanation of the information summarized in these loop records is available elsewhere (2).

Included in Table G.2 are 3 other DDC loops which were not used during kinetic runs but which were designed and used during the course of this work. Loop 0E01 is a reverse data acquisition loop which was used to send a programmed setpoint to temperature control loop 0E92. Loops 0E02 and 0E03 are data acq-isition loops which were available to record the setpoint temperature and measured temperature from loop 0E92.

Actual operation of the equipment during kinetic runs involved sending the signal from the upper reactor thermocouple (referenced to an ice bath) to analog input point 173 for digitization. The digitized measurement signal was then used by DDC loop 0E92 (loops 0E94 and 0E96 also used the same measurement signal) as the measured temperature for control purposes and this temperature could be printed out on the teletype upon request. The detector signal from the G.C. was digitized via analog input point 160 and this information was available for use by the G.C. package on the IBM 1800 computer.

TABLE G.2

DDC LOOPS

LOOP RECORD 0E92

0E92	7218	100E	00AD	0000	A0C0	1784	0029	3738	3739
7FFF	7FFF	0440	7FFF	0000	0440	1D70	0000	0440	146A
19E8	0340	0000	19B4	5200	0014	08C0			

LOOP RECORD 0E94

0E94	7218	200E	00AD	0000	A0C0	1784	0029	3738	3739
7FFF	7FFF	1440	7FFF	0000	1440	4000	0A3D	1440	1078
2663	0300	0000	0A3D	0000	0000	0380			

LOOP RECORD 0E96

0E96	7D17	100E	00AD	0000	A0C0	1784	0029	2E20	3301
7FFF	7FFF	1440	7FFF	0000	1440	0000	0300	1440	0719
0000	1040	0000							

LOOP RECORD 0E01

0E01	0915	200C	0E92	090C	4AE4	4AF1	4AFB	4B08	4B14
4B1F	4B2C	4B38	4B43	4B50	4B5C	4B67	4B73	4B80	4B8B
4B97									

LOOP RECORD 0E02

0E02	0620	4003	0E92	000E	06AE	810A	3739	3739	3739
3739	3739	3739	3739	3739	3739	3739	3739	3739	3739
37	3739	3739	3739	3739	3739	3739	3739	3739	3739
37	3739								

LOOP RECORD 0E03

0E03	0620	4000	0E92	000C	06AE	810A	3740	3740	3740
3740	373C	3744	3744	3748	3746	3740	3742	3742	3740
373	373C	3736	3736	373C	3740	3740	373A	3740	373A
374	744								

One problem encountered during this work was that sometimes the DDC loops controlling the reactor temperature received an erroneous, low temperature measurement signal for a brief period of time. This occurred during level steady state temperature controlled operation (as monitored by the lower reactor thermocouple) and the resulting control action caused the catalyst bed temperature to rise quickly. By the time the measurement signal to the control loop returned to its corrected value the catalyst batch was heated beyond its maximum operating temperature. The cause of these brief lapses in temperature measurement were never determined (one possible cause was interference from the pilot plant evaporator unit located next to the reactor system) but the problem was overcome by limiting the control signal which could be sent to the current to voltage converter. The input of heat via the reactor preheater was thus limited to a specified maximum.

Another problem encountered during operation of the equipment was interference with the G.C. detector signal (this signal was sent to the computer). Sharp drops in the G.C. signal were caused by the operation of a constant temperature bath which was used in conjunction with adjacent equipment. This temperature bath was then plugged into a different set of electrical outlet boxes and the problem did not recur.

APPENDIX H

FEED AND G. C. CALIBRATION MIXTURES

Feed mixtures of various compositions were prepared for use during reaction studies and G. C. calibration. The feed preparation procedure was described in Section 4.4. Table H.1 lists the compositions of the various feed mixtures used for kinetic studies. Some of the compositions listed were not actually prepared but were the calculated feed compositions when two feed syringes were used. Table H.2 lists the compositions of mixtures used for G. C. calibration.

TABLE H.1

FEED MIXTURES

Code H.I.	Feed Mixture or Runs for Calculated Feed[1]	Mole % H_2O	ETOH	ET_2O	HOAC	Densit (g/ml)
1	ETOH	0.153	99.847	-	-	0.791
2	HOAC	0.83	-	-	99.17	1.044
3	XXI	0.43	65.28	-	34.28	0.878
4	XXXI	23.05	76.95	-	-	0.817
5	XXXII	0.13	78.44	21.43	-	0.766
6	XXXIII	0.14	75.18	24.68	-	0.762
7	XXXIV	11.33	88.67	-	-	0.800
8	EI-1, EII-2	0.2..	89.44	-	10.32	-
9	EI-2, EII-3	0.69	19.23	-	80.06	-
10	EI-3, EII-4	0.51	46.91	-	52.54	-
11	EI-4, EII-1	0.49	48.67	-	50.82	-
12	EIII, EVI, EVII[2]	0.49	49.50	-	49.99	-
13	EIV, EV	6.24	45.78	-	47.47	-
14	XXXV[2]					

[1]Calculated from the rate and compositions of two syringes.

[2]H.I.12 and XXXV are identical feeds.

TABLE H.2

G. C. CALIBRATION MIXTURES

Calibration Mixtu	Mass % H_2O	ETOH	ET_2O	ETAC	HOAC
I	4.842	81.348	4.260	4.901	4.645
II	20.370	21.588	19.049	18.153	20.837
III	23.429	8.083	21.812	23.223	2.901
VIII	2.71	88.12	9.15	-	-
IX	2.59	64.94	27.45	-	-
X	12.90	43.61	43.49	-	-
XI	15.01	23.40	61.59	-	-
XII	1.34	95.01	3.65	-	-
XIII	9.57	30.58	59.85	-	-
XIV	6.90	23.77	69.33	-	-
XV	2.906	69.024	4.023	9.716	14.331
XVI	6.599	29.121	3.800	27.387	33.093
XVII	7.235	50.079	15.495	18.028	9.163
XVIII	0.579	49.780	6.384	40.452	2.805
XIX	3.221	79.865	2.068	10.570	4.276
XX	1.326	3.336	85.385	6.333	3.620
XXIII	0.059	97.160	2.781	-	-
XXIV	0.059	99.041	0.900	-	-
XXV	0.089	32.686	0.346	66.792	0.087
XXVII	0.089	32.620	1.039	66.166	0.086
XXIX	0.058	97.46	2.482	-	-
XXX	0.059	98.496	1.445	-	-
H_2O	100.00	-	-	-	-
ETOH	0.06	99.94	-	-	-
ET_2O	0.01	0.01	99.83	0.15	-
ETAC	0.105	0.147	-	99.618	0.13
HOAC	0.25	-	-	-	99.75

APPENDIX I

DEHYDRATION RUNS

A summary of all the dehydration runs is presented in this appendix. Information about each run is given in tabular form (Tables I.1 through I.41). Multiple samples were taken for each steady state kinetic run and these are given to show the degree of reproducibility. The compositions do not necessarily add up to 100% since the computer which produced the tables truncates when printing out values.

Each table includes the run number, the date on which the run was conducted, temperature, pressure and the catalyst mass (bone dry). In cases where the catalyst was exposed to acetic acid, the effective mass of the catalyst is also given (see Appendix L). The details of the syringe pump setting and calculated feed rate are listed. The product analysis for each sample, the average product analysis and the feed composition are then presented.

Given the information explained in the above paragraph it was possible to calculate conversions and rates. The following sample calculation is for Run VII-4 (Table I.16). The basis is 100 moles of f[illegible] symbol Δ followed by a component refers to the moles [illegible] ponent in the product minus the moles of the component [illegible] ion is calculated in the following way.

$$X_1 = 2(\Delta ET_2O)100/ETOH,in$$

$$= 2(10.41-0.0)100/99.84 = 20.85\% \qquad (I.1)$$

The dehydration rate is now calculated by using equation 2.3.

$$r_1 = 3.62\times10^{-4}(0.9984)(0.2085)/0.5297$$

$$= 1.42\times10^{-4} \text{ moles/(min g cat.)} \qquad (I.2)$$

This rate is based on the reactor operating at steady state and an indication of the reliability of the data is a "mass" balance. One form of the mass balance is to calculate the moles of ethanol from the product composition and conversion and compare this to the amount of ethanol in the feed. The calculation is as follows:

$$ETOH,e = 2(\Delta ET_2O) + ETOH,out$$

$$= 2(10.41-0.0) + 78.63 = 99.45 \text{ moles} \qquad (I.3)$$

The symbol e designates the estimated value. The "excess ethanol" is then calculated in the equation given below

$$\text{Excess Ethanol} = (ETOH,e-ETOH,in)100/ETOH,in$$

$$= (99.45-99.84)100/99.84 = 0.39\% \qquad (I.4)$$

In the same way the "excess water" is calculated by comparing the actual product water composition with the estimated composition

$$H_2O,e = (\Delta ET_2O) + H_2O, in$$

$$= (10.41-0.0) \quad 0.15 = 10.56 \text{ moles} \qquad (I.5)$$

Therefore the "excess water" is

$$\text{Excess Water} = (H_2O,\text{out}-H_2O,e)100/H_2O,e$$

$$= (10.95-10.56)100/10.56 = 3.7\% \qquad (I.6)$$

Another way to evaluate the consistency of the product analysis is to estimate the moles of hydrogen, oxygen and carbon in the product (on the basis of 100 moles feed) and compare with the number of moles of these elements in the feed. The moles of hydrogen, oxygen and water in the feed for Run VII-4 are given below.

$$H,in = 2(H_2O,in)+6(ETOH,in)+10(ET_2O,in)$$

$$= 2(0.15)+6(99.84)+10(0.0)$$

$$= 599.34 \qquad (I.7)$$

$$O,in = 1(H_2O,in)+1(ETOH,in)+1(ET_2O,in)$$

$$= 1(0.15)+1(99.84)+1(0.0)$$

$$= 99.99 \qquad (I.8)$$

$$C,in = 0(H_2O,in)+2(ETOH,in)+4(ET_2O,in)$$

$$= 0+2(99.84)+4(0.0)$$

$$= 199.68$$

In an analagous fashion the moles of each of these elements in the product can be calculated.

$$H,out = 2(10.95)+6(78.63)+10(10.41)$$

$$= 597.78 \qquad (I.10)$$

$$O,out = 1(10.95)+1(78.63)+1(10.41)$$
$$= 99.99 \qquad (I.11)$$

$$C,out = 0+2(78.63)+4(10.41)$$
$$= 198.90 \qquad (I.12)$$

The hydrogen, water and carbon balance in Table I.16 are calculated below.

$$\text{Hydrogen Balance} = (\Delta H)100/H,in$$
$$= (-1.56)100/599.34 = 0.26\% \qquad (I.13)$$

$$\text{Oxygen Balance} = (\Delta O)100/O,in$$
$$= (0.0)100/99.99 = 0.00\% \qquad (I.14)$$

$$\text{Carbon Balance} = (\Delta C)100/C,in$$
$$= (-0.78)100/199.68 = -0.39\% \qquad (I.15)$$

A number of dehydration runs were less reliable for a variety of reasons. These "rejected" runs, although excluded from the analysis carried out in Chapter Five, are included in this appendix and are listed in Table I.42 along with an explanation of why they were not used. The final dehydration model fit the rate data for the 11 rejected runs with a TAD of 14.73%; thus even for the less reliable results the model yielded a reasonable prediction of the rate.

TABLE I.1

EXPERIMENTAL RUN III- 1
DATE CONDUCTED 10/ 5/76

RUN TEMPERATURE- 110.0 DEG.C
RUN PRESSURE- 701.6 MMHG =0.9206 ATM = 93.2 KPA
CATALYST MASS - 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	100.00	1/1000	0.8473E-01	0.6702E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.1458E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
14	0.94	98.39	0.66
15	0.99	98.36	0.63
16	0.96	98.37	0.65
17	0.95	98.37	0.66
18	0.97	98.38	0.63
19	1.04	98.27	0.67
20	0.95	98.41	0.63
21	0.92	98.46	0.61
22	0.91	98.45	0.62
23	0.94	98.41	0.63
24	0.98	98.37	0.63
25	1.01	98.31	0.66
26	0.96	98.35	0.67
	0.96	98.38	0.64
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	1.29	3.587

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.16 %	21.03 %	
HYDROGEN	OXYGEN	CARBON
-0.11 %	-0.00 %	-0.16 %

TABLE I.2

EXPERIMENTAL RUN III- 2
DATE CONDUCTED 10/ 5/76

RUN TEMPERATURE= 110.0 DEG.C
RUN PRESSURE= 701.6 MMHG =0.9206 ATM = 93.2 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/1000	0.2526E-01	0.1998E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.4349E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
37	2.50	95.14	2.35
38	2.54	94.92	2.53
39	2.59	94.95	2.44
40	2.53	94.94	2.52
41	2.59	94.96	2.44
42	2.58	94.91	2.49
43	2.64	94.88	2.46
44	2.59	94.94	2.45
45	2.63	95.04	2.31
46	2.60	94.93	2.45
47	2.67	94.94	2.38
48	2.61	94.92	2.45
	2.59	94.96	2.44
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	4.89	4.036

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.00 %	0.04 %	
HYDROGEN	OXYGEN	CARBON
0.00 %	-0.01 %	0.00 %

TABLE I.3

EXPERIMENTAL RUN III- 3
DATE CONDUCTED 10/ 5/76

RUN TEMPERATURE= 110.0 DEG.C
RUN PRESSURE= 701.6 MMHG =0.9206 ATM = 93.2 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	50.00	1/1000	0.4225E-01	0.3342E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.7273E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
59	1.82	96.73	1.43
60	1.84	96.71	1.44
61	1.80	96.82	1.36
62	1.80	96.70	1.49
63	1.85	96.66	1.47
64	1.80	96.71	1.47
65	1.77	96.72	1.50
66	1.81	96.66	1.51
	1.81	96.72	1.46
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	2.93	4.048

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.19 %	12.19 %	
HYDROGEN	OXYGEN	CARBON
-0.13 %	-0.00 %	-0.19 %

TABLE I.4

EXPERIMENTAL RUN III- 4
DATE CONDUCTED 10/ 6/76

RUN TEMPERATURE= 110.0 DEG.C
RUN PRESSURE= 709.5 MMHG =0.9310 ATM = 94.3 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	12.00	1/1000	0.99761-02	0.7891E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.1717E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
54	5.13	89.94	4.91
55	5.05	90.21	4.72
56	5.15	89.81	5.02
57	5.02	90.18	4.79
58	5.18	89.92	4.88
59	5.09	90.22	4.68
60	5.18	89.94	4.87
	5.12	90.03	4.84
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	9.69	3.158

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.12 %	2.55 %	
HYDROGEN	OXYGEN	CARBON
-0.08 %	-0.00 %	-0.12 %

TABLE I.5

EXPERIMENTAL RUN IV- 1
DATE CONDUCTED 10/ 6/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 709.5 MMHG =0.9310 ATM = 94.3 KPA
CATALYST MASS - 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	90.00	1/1000	0.7624E-01	0.6030E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.1312E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
82	4.07	92.17	3.74
83	3.97	92.41	3.61
84	4.07	92.22	3.69
85	3.89	92.61	3.49
86	4.07	92.22	3.70
	4.01	92.33	3.65
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	7.31	1.819

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.21 %	5.61 %	
HYDROGEN	OXYGEN	CARBON
-0.14 %	-0.00 %	-0.21 %

TABLE I.6

EXPERIMENTAL RUN IV- 2
DATE CONDUCTED 10/ 6/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 709.5 MMHG =0.9310 ATM = 94.3 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	40.00	1/1000	0.3376E-01	0.2670E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.5811E-03 MOLE/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	
1	6.96	86.29	6.73
2	7.45	85.28	7.25
3	7.11	86.03	6.84
4	7.40	85.35	.23
5	7.13	86.00	.85
6	7.56	85.09	7.34
7	7.23	85.70	7.05
	7.26	85.68	7.04
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	14.11	1.355

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.06 %	0.97 %	
HYDROGEN	OXYGEN	CARBON
-0.04 %	-0.00 %	0.06 %

TABLE I.7

EXPERIMENTAL RUN IV- 3
DATE CONDUCTED 10/ 7/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 699.5 MMHG =0.9178 ATM = 93.0 KPA
CATALYST MASS - 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	60.00	1/1000	0.5075E-01	0.4014E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.8735E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
13	5.34	89.54	5.11
14	5.46	89.27	5.25
15	5.34	89.51	5.13
16	5.51	89.12	5.35
17	5.24	89.73	5.01
18	5.50	89.27	5.22
19	5.36	89.61	5.02
20	5.51	89.21	5.26
21	5.31	89.56	5.12
22	5.47	89.31	5.21
	5.40	89.41	5.17
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	10.36	1.716

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.08 %	1.55 %	
HYDROGEN	OXYGEN	CARBON
-0.05 %	-0.00 %	-0.08 %

TABLE I.8

EXPERIMENTAL RUN IV- 4
DATE CONDUCTED 10/ 7/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 699.1 MMHG =0.9173 ATM = 92.9 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/1000	0.2536E-01	0.1998E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOL
TOTAL FEED RATE = 0.4349E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
40	8.88	82.71	8.40
41	8.64	82.83	8.51
42	9.10	82.15	8.74
43	8.67	82.70	8.62
44	9.10	82.05	8.84
	8.88	82.49	8.62
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	17.27	1.424

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.10 %	1.20 %	
HYDROGEN	OXYGEN	CARBON
-0.07 %	-0.00 %	-0.10 %

TABLE I.9

EXPERIMENTAL RUN IV- 5
DATE CONDUCTED 10/13/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 693.3 MMHG = 0.0097 ATM = 92.1 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	40.00	1/1000	0.376E-01	0.267OE-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.5811E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
59	60	86.99	6.39
60	79	86.74	6.45
61	6.22	87.87	5.90
62	6.72	86.81	6.46
63	6.50	87.28	6.20
64	6.68	86.84	6.46
	6.59	87.09	6.31
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	12.65	1.394

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.12 %	1.89 %	
HYDROGEN	OXYGEN	CARBON
-0.08 %	-0.00 %	-0.12 %

TABLE I.10

EXPERIMENTAL RUN V- 1
DATE CONDUCTED 10/12/76

RUN TEMPERATURE - 120.0 DEG.C
RUN PRESSURE - 706.9 MMHG =0.9276 ATM 93.9 KPA
CATALYST MASS - 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/1000	0.2526E-01	0.1998E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.4349E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
21	4.16	91.69	4.13
22	4.29	91.52	4.17
23	4.22	91.71	4.05
25	4.30	91.57	4.11
26	4.34	91.21	4.43
27	4.28	91.56	4.15
28	4.42	91.32	4.25
29	4.26	91.79	3.94
30	4.30	91.62	4.06
	29	91.56	4.14
FEED	5	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	8.30	6.851

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.00 %	-0.13 %	
HYDROGEN	OXYGEN	CARBON
0.00 %	-0.00 %	0.00 %

TABLE I.11

EXPERIMENTAL RUN V- 2
DATE CONDUCTED ... 10/13/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE= 693.3 MMHG =0.9097 ATM = 92.1 KPA
CATALYST MASS = 0.5265 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DEN G/ML
1	ETOH	45.00	1/1000	0.3801E-01	0.3006E-01	

AVERAGE MOL. WT = 46.95 G/MOLE
TOTAL FEED RATE = 0.6542E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
40	2.89	94.38	2.71
41	2.90	94.45	2.63
42	3.01	94.19	2.78
43	3.01	94.13	2.85
44	3.02	94.08	2.89
45	3.00	94.23	2.76
46	3.05	94.14	2.80
	2.98	94.23	2.77
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	5.56	6.902

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.05 %	1.99 %	
HYDROGEN	OXYGEN	CARBON
-0.03 %	-0.00 %	-0.05 %

TABLE I.12

EXPERIMENTAL RUN VI- 1
DATE CONDUCTED 10/25/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 702.4 MMHG =0.9[illegible] ATM 93.3 KPA
CATALYST MASS - 0.5330 G

SYRINGE #		RATE	RANGE	G/MIN	DENSITY G/ML
1	ETOH	25.00	1/1000 0.21[illegible]-01	0.1662E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.3618E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
25	9.95	80.10	9.94
26	10.42	79.39	10.17
27	10.06	79.95	9.97
28	10.39	79.72	9.88
29	.21	79.67	10.11
30	10.56	79.32	10.11
31	10.11	79.89	9.99
32	10.57	79.24	10.17
	10.28	79.66	10.04
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	20.12	1.363

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.08 %	0.86 %	
HYDROGEN	OXYGEN	CARBON
-0.05 %	-0.00 %	-0.08 %

TABLE I.13

EXPERIMENTAL RUN VII- 1
DATE CONDUCTED 10/27/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 694.5 MMHG =0.9113 ATM = 92.3 KPA
CATALYST MASS = 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	25.00	1/1000	0.2102E-01	0.1662E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.3618E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
15	10.56	79.02	10.40
16	10.90	78.72	10.37
17	10.33	79.54	10.11
18	10.94	78.84	10.21
19	10.35	79.20	10.43
20	10.83	78.90	10.26
21	10.52	78.82	10.65
23	10.53	79.12	10.34
24	10.98	78.45	10.55
	10.66	78.96	10.37
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	20.77	1.416

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.13 %	1.31 %	
HYDROGEN	OXYGEN	CARBON
-0.09 %	-0.00 %	-0.13 %

TABLE I.14

EXPERIMENTAL RUN VII- 2
DATE CONDUCTED 10/27/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE = 694.5 MMHG =0.9113 ATM = 92.3 KPA
CATALYST MASS = 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY * G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.2155E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
66	14.95	70.34	14.70
67	14.19	71.21	14.58
68	14.92	70.33	14.73
69	14.03	71.61	14.35
70	15.04	70.49	14.45
71	14.36	71.24	14.38
72	14.98	70.47	14.54
73	14.46	71.21	14.32
74	14.92	70.25	14.82
	14.65	70.80	14.54
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	29.13	1.183

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.04 %	-0.30 %	
HYDROGEN	OXYGEN	CARBON
0.02 %	-0.00 %	0.04 %

TABLE I.15

EXPERIMENTAL RUN VII- 3
DATE CONDUCTED 11/ 1/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 703.6 MMHG 0.9232 ATM = 93.5 KPA
CATALYST MASS = 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	40.00	1/1000	0.3376E-01	0.2670E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.5811E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
13	7.54	85.16	7.29
14	7.73	84.77	7.48
15	7.53	85.25	7.20
16	7.76	84.86	7.37
	7.64	85.01	7.33
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	14.70	1.610

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.15 %	2.04 %	
HYDROGEN	OXYGEN	CARBON
-0.10 %	-0.00 %	-0.15 %

TABLE I.16

EXPERIMENTAL RUN VII- 4
DATE CONDUCTED 11/11/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 709.8 MMHG =0.9314 ATM = 94.3 KPA
CATALYST MASS - 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	25.00	1/1000	0.2102E-01	0.1662E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.3618E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
26	10.99	78.40	10.59
27	11.03	78.54	10.41
28	10.83	78.84	10.32
29	11.14	78.42	10.43
30	10.99	78.72	10.27
31	10.97	78.70	10.32
32	10.80	78.88	10.30
33	11.00	78.56	10.43
34	10.82	78.57	10.60
	10.95	78.63	10.41
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	20.85	1.422

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.39 %	3.72 %	
HYDROGEN	OXYGEN	CARBON
-0.26 %	-0.00 %	-0.39 %

TABLE I.17

EXPERIMENTAL RUN VIII- 1
DATE CONDUCTED 11/ 2/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 713.3 MMHG =0.9360 ATM = 94.8 KPA
CATALYST MASS = 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXI	25.00	1/1000	0.2102E-01	0.1717E-01	0.817

AVERAGE MOL. WT = 39.54 G/MOLE
TOTAL FEED RATE = 0.4342E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
23	27.51	67.16	5.31
24	28.92	65.54	5.53
25	27.75	66.72	5.51
26	28.91	65.49	5.58
27	27.68	66.90	5.41
28	29.03	65.36	5.59
29	27.84	66.84	5.31
30	29.18	65.25	5.55
	28.35	66.16	5.47
FEED	23.05	76.94	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	14.23	8.982

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.22 %	-0.60 %	
HYDROGEN	OXYGEN	CARBON
0.13 %	-0.00 %	0.22 %

TABLE I.18

EXPERIMENTAL RUN VIII- 2
DATE CONDUCTED 11/ 2/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 712.5 MMHG =0.9350 ATM = 94.7 KPA
CATALYST MASS = 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXI	10.00	1/1000	0.8277E-02	0.6762E-02	0.817

AVERAGE MOL. WT = 39.54 G/MOLE
TOTAL FEED RATE = 0.1710E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
64	33.70	55.50	10.78
66	33.26	55.99	10.74
68	33.58	55.86	10.55
70	33.61	55.98	10.39
	33.54	55.83	10.62
FEED	23.05	76.94	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	27.60	6.856

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.16 %	-0.37 %	
HYDROGEN	OXYGEN	CARBON
0.10 %	-0.30 %	0.16 %

TABLE I.19

EXPERIMENTAL RUN VIII-3
DATE CONDUCTED 11/ 3/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 706.5 MMHG =0.9271 ATM = 93.9 KPA
CATALYST MASS - 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXI	40.00	1/1000	0.3376E-01	0.2758E-01	0.817

AVERAGE MOL. WT = 39.54 G/MOLE
TOTAL FEED RATE = 0.6975E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
11	26.14	70.29	3.55
12	26.91	69.39	3.68
13	26.10	70.18	3.71
14	27.08	69.25	3.66
15	26.18	70.06	3.75
16	27.28	68.80	3.90
17	26.37	69.93	3.69
18	27.57	68.67	3.75
19	26.32	70.00	3.67
20	27.25	68.96	3.78
	26.72	69.55	3.71
FEED	23.05	76.94	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G .)
DEHYDRATION	9.66	9.7

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.05 %	-0.15 %	
HYDROGEN	OXYGEN	CARBON
0.03 %	-0.00 %	0.05 %

TABLE I.20

EXPERIMENTAL RUN IX- 1
DATE CONDUCTED 11/ 4/76

RUN TEMPERATURE- 120.0 DEG.C
RUN PRESSURE- 700.1 MMHG =0.9186 ATM = 93.0 KPA
CATALYST MASS - 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXI	30.00	1/1000	0.2526E-01	0.2064E-01	0.817

AVERAGE MOL. WT = 39.54 G/MOLE
TOTAL FEED RATE = 0.5220E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
23	24.46	73.64	1.89
24	25.40	72.71	1.87
25	24.58	73.55	1.85
26	25.23	72.83	1.93
27	24.47	73.63	1.89
28	25.24	72.85	1.89
29	24.08	73.91	2.00
30	25.20	72.93	1.85
	24.83	73.26	1.90
FEED	23.06	76.94	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	4.93	3.745

BALANCES

EXCESS ETHANOL 0.14 %
EXCESS WATER -0.45 %
HYDROGEN 0.08 %
OXYGEN -0.00 %
CARBON 0.14 %

TABLE I.21

EXPERIMENTAL RUN X - 1
DATE CONDUCTED 11/10/76

RUN TEMPERATURE- 110.0 DEG.C
RUN PRESSURE- 713.0 MMHG =0.9356 ATM = 94.8 KPA
CATALYST MASS - 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXI	10.00	1/1000	0.8277E-02	0.6762E-02	0.817

AVERAGE MOL. WT = 39.54 G/MOLE
TOTAL FEED RATE = 0.1710E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
33	24.67	73.59	1.73
34	25.48	72.77	1.74
35	24.65	73.59	1.75
36	25.78	72.46	1.74
37	24.44	73.75	1.80
38	25.30	.95	1.74
	25.05	73.18	1.75
FEED	23.05	76.94	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	4.55	1.132

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.32 %	1.02 %	
HYDROGEN	OXYGEN	CARBON
-0.19 %	-0.00 %	-0.32 %

TABLE I.22

EXPERIMENTAL RUN XI- 1
DATE CONDUCTED 11/15/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 701.0 MMHG =0.9198 ATM = 93.2 KPA
CATALYST MASS - 0.5297 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSI G/M
1	XXXII	25.00	1/1000	0.2102E-01	0.1610E-01	0..

AVERAGE MOL. WT = 51.96 G/MOLE
TOTAL FEED RATE = 0.3098E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
13	8.97	59.78	31.24
14	9.53	59.48	30.98
15	9.36	59.55	31.08
16	9.60	59.19	31.19
17	9.36	58.87	31.76
18	9.63	59.35	31.01
	9.41	59.37	31.21
FEED	0.11	78.45	21.43

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	24.93	1.143

BALANCES

EXCE ETHANOL	EXCESS WATER	
0.61 %	-4.79 %	
HYDROGEN	OXYGEN	CARBON
0.28 %	-0.00 %	0.39 %

TABLE I.23

EXPERIMENTAL RUN XII- 1
[illegible] CONDUCTED 12/ 3/76

RUN TEMPERATURE 135.0 DEG.C
RUN PRESSURE 709.7 MMHG = 0.9313 ATM = [illegible].3 KPA
CATALYST MASS = 0.2040 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE 0.2155E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
8	8.16	84.21	7.[illegible]
9	7.51	84.33	7
10	8.06	84.46	7.46
11	7.35	85.32	7.32
12	8.04	84.56	7.38
13	7.[illegible]	84.78	7.66
14	8.08	84.44	7.47
15	7.71	84.77	7.51
16	8.10	84.35	7.54
	7.84	84.63	7.51
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE 10**4 MOLES/ (ML-G CAT.-)
DEHYDRATION	1[illegible].05	[illegible].588

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.17 %	2.29 %	
HYDROGEN	OXYGEN	CARBON
-0.11 %	-0.00 %	-0.17 %

TABLE I.24

EXPERIMENTAL RUN XII-2A
DATE CONDUCTED 12/ 9/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 702.8 MMHG =0.9222 ATM = 93.4 KPA
CATALYST MASS = 0.2046 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.2155E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
13	7.07	85.90	7.02
14	7.57	85.21	7.21
15	7.06	85.98	6.94
16	7.43	85.59	6.97
17	7.12	85.97	6.89
18	7.43	85.34	7.22
19	7.42	85.49	7.08
20	7.55	85.29	7.14
21	7.24	85.80	6.94
22	7.57	85.32	7.09
	7.35	85.59	7.05
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	14.13	1.598

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.14 %	1.95 %	
HYDROGEN	OXYGEN	CARBON
-0.09 %	-0.00 %	-0.14 %

TABLE I.25

EXPERIMENTAL RUN XII - 3
DATE CONDUCTED 12/13/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 694.4 MMHG =0.9111 ATM = 92.3 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00 1/1000	0.2526E-01	0.1998E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.4349E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
3	4.17	91.79	4.02
4	4.14	91.84	4.00
5	4.13	91.96	3.89
6	4.28	91.77	3.93
7	4.29	91.65	4.04
8	4.35	91.61	4.03
9	4.25	91.61	4.13
10	4.38	91.53	4.07
11	4.12	91.91	3.95
12	4.35	91.59	4.05
13	4.17	91.93	3.89
14	4.26	91.78	3.94
	4.24	91.75	4.00
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	8.01	1.829

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.09 %	2.21 %	
HYDROGEN	OXYGEN	CARBON
-0.06 %	-0.00 %	-0.09 %

TABLE I.26

EXPERIMENTAL RUN XII- 4
DATE CONDUCTED 12/13/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 697.1 MMHG =0.9147 ATM = 92.6 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	7.50	1/1000	0.6153E-02	0.4867E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.1059E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
18	11.58	76.47	11.94
19	12.27	75.32	12.40
21	12.42	75.23	12.34
23	11.95	75.75	12.29
24	12.86	75.01	12.12
25	12.32	75.57	12.10
26	12.60	75.51	11.88
27	12.22	75.86	11.90
28	12.40	75.86	11.73
	12.29	75.62	12.08
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	24.20	1.345

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.05 %	0.51 %	
HYDROGEN	OXYGEN	CARBON
-0.03 %	-0.00 %	-0.05 %

TABLE I.27

EXPERIMENTAL RUN XII-5
DATE CONDUCTED 12/13/76

RUN TEMPERATURE= [illegible].0 DEG.C
RUN PRESSURE= 7.1 MMHG =0.9147 ATM [illegible].6 KPA
CATALYST MASS = 2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS 1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	22.50	1/1000	0.1889E-01	0.1494E-01	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.3252E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
33	5.27	89.89	4.83
34	5.27	89.85	4.86
35	5.19	89.80	4.99
36	5.40	89.51	5.07
37	5.18	89.86	4.94
38	5.46	89.47	5.05
39	5.20	89.90	4.88
40	5.43	89.57	4.99
	5.30	89.73	4.95
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONV %EN	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	9.92	1.694

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.19 %	3.80 %	
HYDROGEN	OXYGEN	CARBON
-0.12 %	-0.00 %	-0.19 %

TABLE I.28

EXPERIMENTAL RUN XII-6
DATE CONDUCTED 12/20/76

RUN TEMPERATURE 135.0 DEG.C
RUN PRESSURE = 699.0 MMHG =0.9172 ATM = 92.9 KPA
CATALYST MASS = 0.2060 G DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	t	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 46.98 G/MOLE
TOTAL FEED RATE = 0.2109E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
7	7.14	85.91	6.93
8	7.22	85.72	7.05
9	7.12	86.14	6.72
10	7.11	85.86	7.02
11	7.11	86.02	6.86
12	7.30	85.18	7.31
	7.20	85.81	6.98
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	13.99	1.983

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.06 %	0.91 %	
HYDROGEN	OXYGEN	CARBON
-0.04 %	-0.00 %	-0.06 %

TABLE I.29

EXPERIMENTAL RUN XII- 7
DATE CONDUCTED 12/22/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 697.9 MMHG =0.9157 ATM = 92.7 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.840
EFFECTIVE MASS = 0.1714 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.2156E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
7	7.19	86.17	6.63
8	7.43	85.84	6.71
10	7.33	86.07	6.59
11	6.88	86.69	6.42
13	6.94	86.62	6.43
15	6.94	86.41	6.65
16	7.13	86.30	6.56
	7.13	86.29	6.58
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	13.18	1.656

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.38 %	5.72 %	
HYDROGEN	OXYGEN	CARBON
2.25 %	-0.00 %	-0.38 %

TABLE I.30

EXPERIMENTAL RUN XII-8
DATE CONDUCTED 12/24/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 698.9 MMHG [illegible] 92.9 KPA
CATALYST MASS = 0.2040 G [illegible] ATION RATIO=0.767
EFFECTIVE MASS = 0.1565 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.125E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.2155E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
11	6.68	87.19	6.13
[illegible]	7.10	86.79	6.09
[illegible]	6.70	87.15	6.14
[illegible]	7.13	86.65	6.21
[illegible]	6.52	87.38	6.08
16	6.89	86.96	6.13
17	6.37	87.82	5.79
18	6.70	87.31	5.98
	6.76	87.16	6.07
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	12.16	1.612

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.53 %	8.63 %	
HYDROGEN	OXYGEN	CARBON
-0.35 %	-0.00 %	-0.53 %

TABLE I.31

EXPERIMENTAL RUN XIII-1
DATE CONDUCTED 12/ 9/76

RUN TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 700.5 MMHG =0.9192 ATM = 93.1 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791

AVERAGE MOL. WT = 46.96 G/MOLE
TOTAL FEED RATE = 0.2155E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
33	4.01	92.19	3.78
34	4.05	92.14	3.79
35	3.96	92.23	3.79
36	4.01	92.18	3.79
37	4.00	92.26	3.73
38	3.90	92.35	[illegible]
	3.99	92.22	3.77
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	7.56	8.555

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.06 %	1.68 %	
HYDROGEN	OXYGEN	CARBON
-0.04 %	-0.00 %	-0.06 %

TABLE I.32

EXPERIMENTAL RUN XIII- 2
DATE CONDUCTED 12/ 0/7(

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE= 693.2 MMHG =0.9096 ATM = 92.1 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	7.50	1/1000	0.6153E-02	0.4867E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.1059E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
21	7.14	85.91	6.94
22	7.46	85.44	7.09
23	7.32	85.84	6.82
24	7.42	85.58	6.99
25	7.37	85.74	6.88
26	7.46	85.40	7.13
	7.36	85.65	6.97
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	13.97	7.768

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.23 %	3.31 %	
HYDROGEN	OXYGEN	CARBON
-0.15 %	-0.00 %	-0.23 %

TABLE I.33

EXPERIMENTAL RUN XIV- 1
DATE CONDUCTED 12/10/76

RUN TEMPERATURE= 110.0 DEG.C
RUN PRESSURE= 693.5 MMHG =0.9100 ATM = 92.2 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	7.50	1/1000	0.6153E-02	0.4867E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.1059E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
1	3.50	93.15	3.34
2	3.72	92.86	3.41
3	3.69	92.98	3.32
4	3.73	92.89	3.37
5	3.70	93.08	3.21
6	3.71	92.99	3.29
7	3.53	93.24	3.21
8	3.65	93.08	3.25
	3.65	93.03	3.30
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	6.61	3.677

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.20 %	5.85 %	
HYDROGEN	OXYGEN	CARBON
-0.13 %	-0.09 %	-0.20 %

TABLE I.34

EXPERIMENTAL RUN XIV- 2
DATE CONDUCTED 12/14/76

RUN TEMPERATURE= 110.0 DEG.C
RUN PRESSURE= 695.6 MMHG =0.9127 ATM = 92.4 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	DE	4.00	1/1000	0.3180E 02	0.2515E-02	0.791

AVERAGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.5473E-04 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
1	5.75	88.56	5.67
2	5.92	88.22	5.86
3	5.93	88.31	5.74
4	5.89	88.22	5.87
5	5.93	88.44	5.61
6	5.94	88.22	5.82
	5.89	88.33	5.76
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	11.54	3.317

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.01 %	-0.30 %	
HYDROGEN	OXYGEN	CARBON
0.01 %	-0.00 %	0.01 %

TABLE I.35

EXPERIMENTAL RUN XV- 1
DATE CONDUCTED 12/14/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 696.5 MMHG =0.9139 ATM = 92.6 KPA
CATALYST MASS - 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS - 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIII	22.50	1/1000	0.1889E-01	0.1439E-01	0.762

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.2723E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
23	4.62	66.36	29.01
24	4.48	66.58	28.92
25	4.53	66.51	28.94
26	4.66	66.64	28.69
27	4.51	66.58	28.89
28	4.29	66.97	28.72
29	4.28	66.96	28.75
30	4.28	66.98	28.72
31	4.33	66.59	29.07
32	4.41	66.75	28.83
	4.44	66.69	28.85
FEED	0.14	75.17	24.67

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	11.12	1.197

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.15 %	2.69 %	
HYDROGEN	OXYGEN	CARBON
-0.06 %	-0.00 %	-0.09 %

TABLE I.36

EXPERIMENTAL RUN XV- 2
DATE CONDUCTED 12/15/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 693.3 MMHG =0.9097 ATM = 92.1 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.932
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIII	15.00	1/1000	0.1252E-01	0.9544E-02	0.762

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.1805E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
7	5.80	64.05	30.13
9	5.88	64.24	29.86
10	5.81	63.69	30.49
11	5.8[illegible]	63.94	30.18
13	5.8[illegible]	63.68	30.42
14	5.8[illegible]	63.65	30.49
15	5.62	64.27	30.10
16	5.81	64.15	30.03
	5.81	63.96	30.21
FEED	0.14	75.17	24.67

	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
[illegible] DEHYDRATION	14.74	1.051

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.17 %	2.39 %	
HYDROGEN	OXYGEN	CARBON
-0.07 %	-0.00 %	-0.10 %

TABLE I.37

EXPERIMENTAL RUN XVI - 1
DATE COMPLETED 12/12/76

RUN [illegible] = 110.0 DEG.C
[illegible] 603.5 MMHG 0.9100 ATM 12.2 KPA
CALIBRATION GAS 0.7060 G % ACTIVATION RATE 32
[illegible] MASS 0.1900 G

CARBON #	FEED RATE	PSIG	ML/MIN	G/MIN	DENSITY G/ML
1	XCEL	[illegible] 0.1/1000	.1253E-01	0.[illegible]E-0[illegible]	0.762

[illegible] = 5.5% G/MOLE
[illegible] 0.[illegible] MOLES/MIN

PRODUCT ANALYSIS MOLE %

CARBON #	COMPONENTS ETOH	ETOH	ET2O
10	1.94	71.45	26.59
16	1.98	71.34	26.67
15	2.19	70.88	26.92
16	2.33	71.05	26.62
17	2.08	71.19	26.72
	2.05	71.19	26.74
FEED	0.14	75.17	24.67

REACTION	ETHANOL CONVERSION %	K *10**5 - LES/ (MINUS CAT.)
DEHYDRATION	5.50	3.929

BALANCES

EXCESS ETHANOL 0.21 %
HYDROGEN 0.09 %

EXCESS WATER -7.13 %
OXYGEN -3.00 %

CARBON 0.12 %

TABLE I.38

EXPERIMENTAL RUN XVI - 2
DATE CONDUCTED 12/17/76

[illegible] TEMPERATURE = 110.0 DEG.C
FEED PRESSURE = 697.3 MMHG 0.9150 ATM 92.7 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO 0.93
EFFECTIVE MASS = 0.1902 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIII	6.00	1/100	0.3379E-02	0.3718E-02	0.762

AVERAGE MOL. WT = 52.96 G/MOLE
TOTAL FEED RATE 0.7052E-04 MOLES/MIN

PRODUCT ANALYSIS, MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
23	4.78	66.25	28.[illegible]
25	4.74	64.81	29.42
27	4.74	64.56	29.69
29	4.65	65.03	29.31
29	4.73	64.69	29.57
31	4.[illegible]	64.07	29.16
33	4.[illegible]	64.09	29.20
	4.73	64.93	29.33
FEED	0.14	75.17	24.67

REACTION	%ETHANOL CONVERSION %	RATE*10**5 MOLES/ (MIN*G CAT.)
DEHYDRATION	12.39	3.442

BALANCES

EXCESS ETHANOL	EXCESS WATER	
0.09 %	-1.21 %	
HYDROGEN	OXYGEN	RBON
0.04 %	-0.00 %	05 %

TABLE I.39

EXPERIMENTAL RUN XVII-1
DATE CONDUCTED 12/28/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 99.1 MMHG 0.9252 ATM 93.7 KPA
CATALYST MASS = 0.2911 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9407E-02	0.791

AVERAGE MOL. WT = 46.8 G/MOLE
TOTAL FEED RATE = .2155E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	EOH	ET2O
16	10.28	80.32	9.39
17	10.01	79.91	10.07
18	10.44	79.41	9.94
1	9.80	80.08	10.11
2	10.6	79.54	9.79
21	10.09	79.86	10.04
22	10.40	79.67	9.91
23	9.85	80.29	9.74
4	10.49	79.79	9.70
25	9.80	80.71	9.48
26	10.44	80.06	9.48
27	9.98	80.41	9.61
28	10.33	80.23	9.42
	10.22	80.02	9.74
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ MIN*G CAT.)
DEHYDRATION	9.52	1.743

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.32 %	3.32 %	
HYDROGEN	OXYGEN	CARBON
-0.21 %	-0.00 %	-0.32 %

TABLE I.40

EXPERIMENTAL RUN XVII-2
DATE CONDUCTED 12/30/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 708.5 MMHG = 0.9297 ATM = 94.2 KPA
CATALYST MASS = 0.2411 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	25.0	1/	0.2102E-01	0.1662E-01	0.791

AVERAGE MOL. WT = 45. /MOLE
TOTAL FEED RATE = 0.3618E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
1	5.80	88.51	5.67
2	6.20	87.96	5.82
3	5.75	88.66	5.58
4	6.22	87.94	5.82
5	6.04	88.03	5.91
6	6.32	87.75	5.91
7	5.64	88.92	5.42
8	6.35	88.20	5.74
9	5.74	88.67	5.58
10	6.10	88.22	5.66
11	5.87	88.41	5.70
12	6.12	88.10	5.77
	5.99	88.28	5.72
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	11.45	1.716

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.11 %	2.00 %	
HYDROGEN	OXYGEN	CARBON
-0.07 %	-0.00 %	-0.11 %

TABLE I.41

EXPERIMENTAL RUN XVII-3
DATE CONDUCTED 2/ 3/77

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 703.8 MMHG = 0.9235 ATM = 93.5 KPA
CATALYST MASS = 0.2411 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	141000	0.1252E-01	0.9907E-02	0.791

AVE AGE MOL. WT = 45.95 G/MOLE
TOTAL FEED RATE = 0.2156E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O
16	9.26	81.86	8.86
17	8.95	82.39	8.[illegible]
18	9.30	81.90	8.[illegible]
19	8.79	82.55	8.64
20	8.40	81.83	8.76
21	8.99	82.17	8.83
22	9.52	81.61	8.85
	9.17	82.04	8.77
FEED	0.15	99.84	0.00

REACTION	ETHANOL CONVERSION %	E*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	17.57	1.568

BALANCES

EXCESS ETHANOL	EXCESS WATER	
-0.25 %	2.79 %	
HYDROGEN	OXYGEN	CARBON
-0.16 %	-0.00 %	-0.25 %

TABLE I.42

REJECTED DEHYDRATION RUNS

Runs	Reasons for Omission
III-1, III-3	Low conversion runs; the water balance was not good and it was suspected that the data was taken under unsteady state conditions.
IV-5, V-2	Thermal deactivation of the catalyst charge due to overheating.
XIII-1, XIII-2	Low feed rate, low conversion runs which were inconsistent with other similar runs.
XV-1, XV-2	Low conversion runs, inconsistent with another, more accurate run which used a similar feed.
XVI-1, XVI-2	Low conversion, low feed rate runs, inconsistent with other runs at the same temperature.
XVII-1	An incorrect reading of the pump setting or high initial catalyst activity.

APPENDIX J

ESTIMATED KINETIC PARAMETERS FOR THE DEHYDRATION REACTION

The purpose of this appendix is to calculate kinetic parameters for the dehydration reaction based on the information available from the set of runs presented in Table 5.1. In the following analysis the pressure (P) is assumed to be 93.5 kPa. The information used in the calculations at the three different temperatures is presented in Table J.1. The dehydration model of equation 2.4 is used, neglecting the reverse terms. Y_W, Y_A and Y_E are the water, ethanol and ether mole fractions.

TABLE J.1

RATE DATA

^oC	j	$r_{1,j} \times 10^4$ moles/(min g cat.)	Description	Composition (mole fraction) Y_{Wj}	Y_{Aj}	Y_{Ej}
135.0	1	2.03	ethanol feed[1] 0.0% conversion	≈0.0	1.000	0.0
135.0	2	1.18	Run VII-2	0.1465	0.708	0.1454
135.0	3	0.685	Run VIII-2	0.3354	0.5583	0.1062
120.0	4	0.69	Run V-1	0.0429	0.9156	0.0414
110.0	5	0.32	Run III-4	0.0512	0.9003	0.0484

[1] Extrapolated Value at zero conversion (see Figure 5.1).

Three equations can be written using the data at 135°C.

$$r_{1,1} = \frac{k_s(K_A P Y_{A1})^2}{[1 + K_A P Y_{A1}]^2} \qquad (J.1)$$

$$r_{1,2} = \frac{k_s(K_A P Y_{A2})^2}{[1 + (K_A P Y_{A2}) + (K_W P Y_{W2})]^2} \qquad (J.2)$$

$$r_{1,3} = \frac{k_s(K_A P Y_{A3})^2}{[1 + (K_A P Y_{A3}) + (K_W P Y_{W3})]^2} \qquad (J.3)$$

Dividing J.1 by J.2 and J.1 by J.3 results in the following two equations in two unknowns (K_A and K_W).

$$R_1 = (r_{1,1}/r_{1,2})^{0.5}$$

$$= \frac{(Y_{A1}/Y_{A2})[1 + (K_A P Y_{A2}) + (K_W P Y_{W2})]}{[1 + (K_A P Y_{A1})]} \qquad (J.4)$$

Since the square roots of ratios were being compared to solve for the kinetic data, the points presented in Table J.1 were chosen to have the widest spread of rates to improve the accuracy of the solutions.

$$R_2 = (r_{1,1}/r_{1,3})^{0.5}$$

$$= \frac{(Y_{A1}/Y_{A3})[1 + (K_A P Y_{A3}) + (K_W P Y_{W3})]}{(1 + (K_A P Y_{A1}))} \qquad (J.5)$$

Equations J.4 and J.5 can be rewritten in the following manner.

$$K_A = \frac{[1 - (R_1 Y_{A2}/Y_{A1})]/P}{Y_{A2}(R_1 - 1)} + \frac{Y_{W2}K_W}{Y_{A2}(R_1 - 1)} \qquad (J.6)$$

$$K_A = \frac{[1 + (R_2 Y_{A3}/Y_{A1})]/P}{Y_{A3}(R_2 - 1)} + \frac{Y_{W3}K_W}{Y_{A3}(R_2 - 1)} \qquad (J.7)$$

Entering the appropriate values from Table J.1 results in $K_A = 0.0246$ kPa^{-1} and $K_W = 0.0319$ kPa^{-1}. The value of K_A can now be used in equation J.1 to solve for k_s.

$$k_s = \frac{r_{1,1}[1 + (K_A P Y_{A1})]^2}{(K_A P Y_{A1})^2} \text{ moles/(min g cat.)} \qquad (J.8)$$

The value of k_s is thus 4.18×10^{-4} moles/(min g cat.).

For the data at 120°C the following equation can be written.

$$r_{1,4} = \frac{k_s (K_A P Y_{A4})^2}{[1 + (K_A P Y_{A4}) + (K_W P Y_{W4})]^2} \qquad (J.9)$$

Assuming that K_A and K_W at 120°C are in the same ratio to the values calculated from equations 2.6 and 2.7 as the values at 135°C were, one can calculate K_A and K_W at the lower temperature. Thus K_A and K_W at 120°C are 0.0383 kPa^{-1} and 0.0618 kPa^{-1}, respectively and substituting these values into J.9 yields k_s (120°C) = 1.15×10^{-4} mole/(min g cat.).

An equation similar to J.9 can be written at 110°C.

$$r_{1,5} = \frac{k_s (K_A P Y_{A5})^2}{[1 + (K_A P Y_{A5}) + (K_W P Y_{W5})]^2} \qquad (J.10)$$

In a manner analagous to the procedure described in the previous paragraph one can calculate K_A and K_W at 110°C. Using the values of the calculated adsorption constants (K_A = 0.0525 kPa^{-1}, K_W = 0.0987 kPa^{-1}) the value of k_s can be solved from equation J.10. The result is k_s (110°C) = 0.754x10^{-4} moles/(min g cat.).

The results of this appendix are summarized in Table 5.3. The rate data at 135°C was known to be more accurate than data at other temperatures and the adsorption constants (K_A and K_W) are quite close to the values predicted by equations 2.7 and 2.8. These results tend to confirm that the kinetic model of Kabel (8) is applicable for this reaction system.

APPENDIX K

BLANK RUNS

A number of runs were carried out without any catalyst in the reactor. These runs are summarized in Tables K.1 through K.7. The calculation procedure is discussed in Appendix M.

For the series of blank runs the reactor temperature was varied and the feed rate and composition were also changed. The set of Runs B-2, B-2A, B-2B and B-2C were conducted while the temperatures of other portions of the flow loop (e.g. oven, feed block heater, reactor postheater) were varied. Generally the esterification rate was low and did not change appreciably with varying conditions. The blank rates were fit to a "homogeneous" model of the following form.

$$r_{2h} = k_{2h} P_A P_B \qquad (K.1)$$

The constant k_{2h} was found for all the blank runs. The resulting value of k_{2h} is given in the following equation. The total pressure was assumed to be 93.5 kPa.

$$k_{2h} = (1.5 \pm 0.5) \times 10^{-9} \text{ moles}/(\text{min kPa}^2) \qquad (K.2)$$

If one takes a hypothetical case of a 50/50 ethanol-acetic acid feed and assumes that the catalyst charge is 0.2 g, then the calculated "homogeneous" esterification rate would be 1.5×10^{-9}

$(3.5^2)(0.25)/0.2 = 1.6\times10^{-5}$ moles/(min g cat.). This rate is about two orders of magnitude lower than the esterification rates presented in Table 6.1. Therefore the effect of the "homogeneous" rate on the experimental catalystic esterification rate was neglected.

After Run B-4 (see Table K.7) the feed of ethanol and acetic acid was stopped and the system feed value and circulation loop exit valve were closed. Under these batch conditions the progress of the esterification reaction was monitored for ten hours. The feed was assumed to be the average product composition of Run B-4 and the batch conversion as a function of time is shown in Figure K.1. Even after 10 hours of batch operation the conversion of ethanol was only about 30%. This indicates a low "homogeneous" esterification rate and gives further justification for neglecting the homogeneous reaction rate in the analysis of the heterogeneous catalyzed reaction rate.

TABLE K.1

EXPERIMENTAL RUN B - 1
DATE CONDUCTED 11/30/76

REF TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 709.6 MMHG = 0.9311 ATM 94.3 KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/1000	0.25 [illegible]	0.1992E-01	0.791
2	HOAC	0.20	50	0.3470E-02	0.3623E-02	1.054

AVERAGE MOL. WT = 47.63 G/MOLE
TOTAL FEED RATE = 1.4956E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
26	0.66	86.62	0.00	0.35	12.35
22	0.65	86.32	0.00	0.31	12.71
23	0.65	87.78	0.00	0.25	11.30
24	0.67	86.84	0.00	0.29	12.19
36	0.62	85.69	0.00	0.37	13.30
37	0.85	86.20	0.13	0.44	12.37
38	0.60	87.13	0.00	0.38	11.87
40	0.64	86.54	0.00	0.29	12.53
44	0.52	87.59	0.00	0.32	11.55
45	0.68	87.45	0.00	0.33	11.52
	0.64	86.82	0.01	0.33	12.18
FEED	0.23	87.61	0.00	0.00	12.15

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.03	0.131
ESTERIFICATION	2.76	0.38	1.665
TOTAL	2.76	0.41	1.796

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.48 %	10.28 %	3.05 %
HYDROGEN	OXYGEN	CARBON
-0.16 %	0.33 %	-0.05 %

TABLE K.2

EXPERIMENTAL RUN B- 2
DATE CONDUCTED 12/ 1/76

RUN TEMPERATURE= 135.0 DEG.C
RUN [illegible] SLOPE = 23.5 PSIG 0.0231 ATM [illegible] KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/1000	0.25258-01	0.19948-01	0.791
2	HOAC	0.40	5:1	0.63248-02	0.75978-02	1.044

AVERAGE MOL. WT = 49.34 G/MOLE
TOTAL FEED RATE = 0.55648-03 MOLES/MIN

PRODUCT ANALYSES MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
4	0.58	74.18	0.00	0.30	24.92
5	0.78	74.60	0.00	0.34	24.26
6	0.68	73.41	0.00	0.40	[illegible]9
7	[illegible].30	73.53	0.00	0.34	[illegible]
9	0.90	76.[illegible]1	0.00	0.32	[illegible]
10	0.69	75.99	0.00	0.32	[illegible]8
	0.74	74.62	0.00	0.34	24.29
FEED	0.30	78.04	0.00	0.00	21.65

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	1.58	0.43	1.904
TOTAL	1.58	0.43	1.904

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-3.94 %	1[illegible].63 %	13.7[illegible] %
HYDROGEN	OXYGEN	CARBON
-1.14 %	2.44 %	-0.0[illegible] %

TABLE K.3

EXPERIMENTAL RUN # B-2A
DATE CONDUCTED 1/7 1/76

REACTION TEMPERATURE = 150.0 DEG.C
RUN PRESSURE = 203.5 MMHG = 0.2731 ATM = 27.5 KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	50.00 TO 100.00	0.2526E-01	0.1965E-01	0.791
2	HOAC	1.00 TO 50.00	0.2576E-02	0.2676E-02	1.044

AVERAGE MOL. WT = 46.06 = MOLE
TOTAL FEED RATE = 0.4266E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
11	0.76	76.56	0.00	0.33	22.32
12	0.78	75.69	0.00	0.37	23.14
13	0.75	76.18	0.00	0.36	22.69
14	0.80	75.22	0.00	0.37	23.60
15	0.72	78.21	0.00	0.38	20.67
16	0.56	77.10	0.00	0.26	22.07
17	0.69	76.66	0.00	0.29	22.34
18	0.78	77.02	0.00	0.47	21.73
19	0.83	78.64	0.00	0.45	20.68
20	0.76	75.82	0.00	0.46	22.96
	0.74	76.65	0.00	0.37	22.22
FEED	0.30	78.04	0.00	0.00	21.65

REACTION	ACID CONVERSION %	ETH OL CONVE	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	1.74	0.48	2.108
TOTAL	1.74	0.48	2.108

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID.ESTER
-1.29 %	0.47 %	4.38 %
HYDROGEN	OXYGEN	CARBON
-0.38 %	0.73 %	-0.06 %

TABLE K.4

EXPERIMENTAL RUN B-28
DATE CONDUCTED 12/ 1/76

RUN TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 703.5 MMHG 0.9231 ATM = 93.5 KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	1.00	1/1000	0.2526E-01	0.1998E-01	0.791
2	HOAC	.40	50	0.6941E-02	0.7247E-02	1.044

AVERAGE MOL. WT = 48.94 G/MOLE
TOTAL FEED RATE = 0.5564E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
21	0.84	75.81	0.00	0.45	22.88
22	0.77	75.33	0.00	0.42	23.46
23	0.89	76.86	0.00	0.47	21.76
24	0.85	75.48	0.00	0.53	23.12
	0.84	75.87	0.00	0.47	22.81
FEED	0.30	78.04	0.00	0.00	21.65

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	2.18	0.60	2.628
TOTAL	2.18	0.60	2.628

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-2.17 %	8.98 %	7.52 %
HYDROGEN	OXYGEN	CARBON
-0.63 %	1.33 %	-0.06 %

TABLE K.5

EXPERIMENTAL RUN B-2C
DATE CONDUCTED 12/ 1/76

RUN TEMPERATURE = 135.0 DEG.C
RUN PRESSURE = 703.5 MMHG = 0.9231 ATM = 93.5 KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	50 30 1/1000	0.2526E-01	0.1998E-01	0.791
2	HOAC	0.40 50	0.6941E-02	0.7247E-02	1.044

AVERAGE MOL. WT = 48.94 G/MOLE
TOTAL FEED RATE = 0.5564E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
27	0.91	75.00	0.00	0.51	23.56
28	0.69	75.63	0.00	0.37	23.29
	0.80	75.32	0.00	0.44	23.43
FEED	0.30	78.04	0.00	0.00	21.65

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	2.05	0.57	2.479
TOTAL	2.05	0.57	2.479

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-2.92 %	7.05 %	10.26 %
HYDROGEN	OXYGEN	CARBON
-0.84 %	1.82 %	-0.05 %

TABLE K.6

EXPERIMENTAL RUN B-33
DATE CONDUCTED 12/ 1/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 703.5 MMHG =0.9231 ATM = 93.5 KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	20.00	1/10	0.	0.13?6E-01	0.791
2	HOAC	0.40	50	0.6941E-02	0.7247E-02	1.044

AVERAGE MOL. WT = 50.01 G/MOLE
TOTAL FEED RATE = 0.4101E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
30	0.82	72.39	0.00	0.43	26.34
31	1.00	72.36	0.00	0.45	26.17
32	0.81	72.03	0.00	0.46	26.68
33	0.85	70.70	0.00	0.45	27.98
34	0.79	69.58	0.00	0.44	29.16
35	0.93	71.16	0.00	0.43	27.40
36	0.82	66.25	0.00	0.49	32.42
37	1.01	66.28	0.00	0.51	32.18
38	0.97	65.66	0.00	0.57	32.78
39	1.01	68.52	0.00	0.53	29.91
	0.91	69.49	0.00	0.48	29.10
FEED	0.35	70.27	0.00	0.00	29.37

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	1.63	0.68	1.973
TOTAL	1.63	0.68	1.973

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.41 %	9.16 %	0.74 %
HYDROGEN	OXYGEN	CARBON
-0.13 %	0.16 %	-0.07 %

TABLE K.7

EXPERIMENTAL RUN B- 4
DATE CONDUCTED 12/ 2/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 704.2 MMHG =0.9240 ATM [illegible] KPA
CATALYST MASS = 1.0000 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	20.00	1/1000	0.1677E-01	0.1326E-01	0.791
2	HOAC	0.80	50	0.1388E-01	0.1449E-01	1.044

AVERAGE MOL. WT = 52.21 G/MOLE
TOTAL FEED RATE = 0.5316E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
5	1.19	52.22	0.00	0.63	45.93
6	1.25	50.05	0.00	0.73	47.95
7	1.16	52.57	0.00	0.63	45.62
8	1.29	51.21	0.00	0.66	46.82
9	1.16	51.56	0.00	0.62	46.64
10	1.39	55.63	0.00	0.68	42.28
11	1.24	50.35	0.00	0.63	47.75
12	1.25	49.21	0.00	0.66	48.86
	1.24	51.60	0.00	0.66	46.48
FEED	0.46	54.21	0.00	0.00	45.32

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**6 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	1.45	1.21	3.510
TOTAL	1.45	1.21	3.510

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-3.59 %	11.13 %	4.02 %
HYDROGEN	OXYGEN	CARBON
-0.81 %	1.25 %	-0.12 %

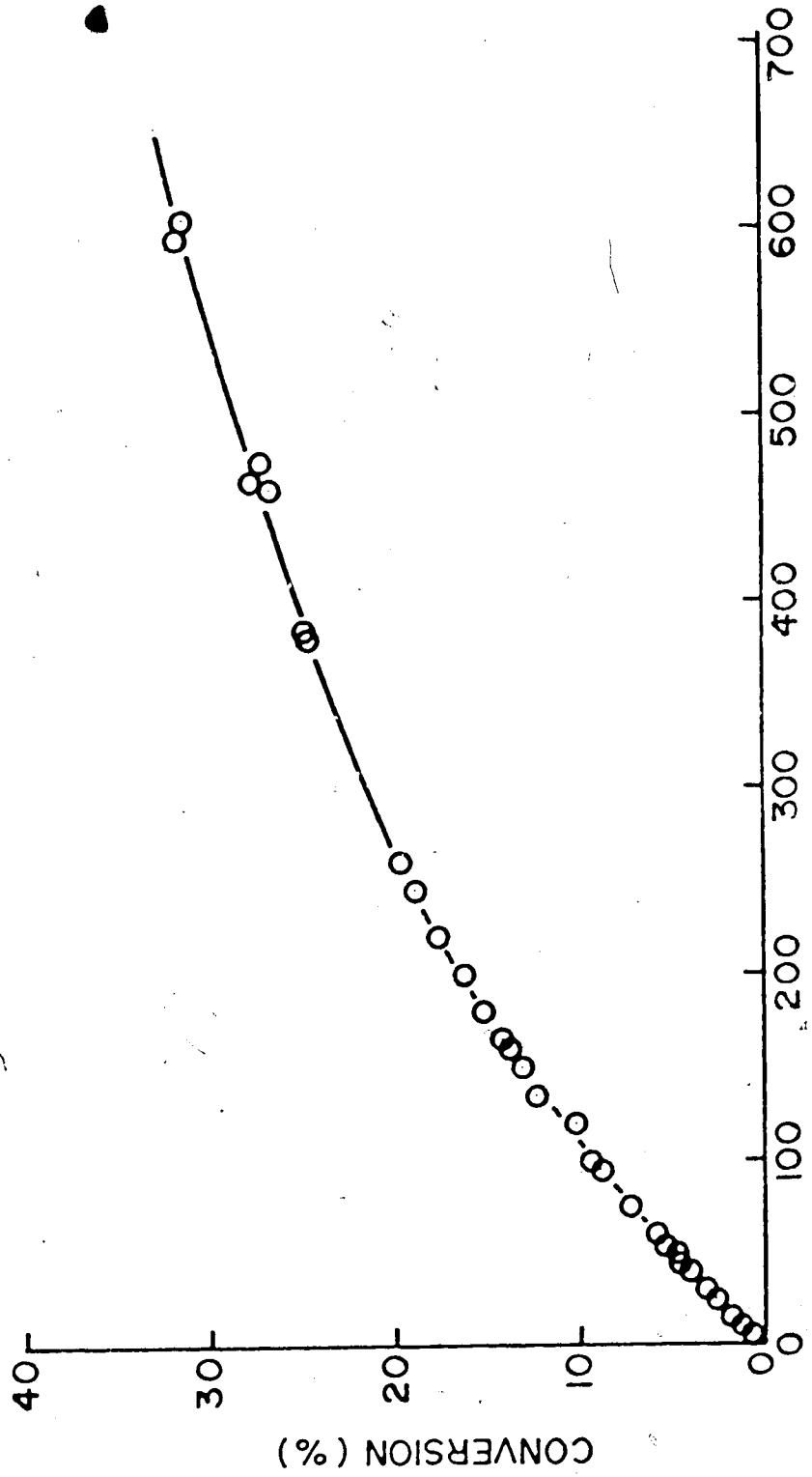


FIGURE K.I: BATCH ESTERIFICATION RUN WITHOUT CATALYST

APPENDIX L

CATALYST DEACTIVATION

No catalyst deactivation was observed during dehydration runs but exposure to acetic acid (or ethyl acetate) caused a decrease in catalyst activity. It was necessary to know the effect of catalyst deactivation on reaction rates so the rates could be adjusted and compared on the basis of fresh catalyst.

The catalyst batch used for Runs XII-1 through XVI-2 and Runs EVI-1 through EVI-3 (see Tables E.2 and E.3, charge #3 batch 2) was deactivated by two different mechanisms. In loading this batch into the reactor it is probable that a certain amount of deactivation occurred as a result of overheating. (See Section 4.4). In Figure 5.1 the point for unadjusted Run XII-1 fell about 10% below the line of ethanol feed points. The rates for the runs affected were corrected for this heat deactivation by reducing the total charge mass from 2550 g to 2550 g.

During the time when acetic acid runs were being carried out, attempted repeat runs of Run [illegible] taken after 24, 57 and 83 hours of exposure to acetic [illegible] work with the dehydration reaction it was known that [illegible] was not deactivated due to exposure to the [illegible] used in dehydration. It was possible to conduct dehydration runs after many (>20) hours of operation

The unadjusted points for Runs XII-2A through XII-8 were plotted on Figure L.1. On this rate versus conversion plot the points fall well below the expected ethanol feed line (at 135°C). A deactivation ratio is defined such that when the actual amount of catalyst is multiplied by the ratio the adjusted rate falls on the line. The deactivation ratios as a function of the exposure time to acetic acid are tabulated in Table L.1.

TABLE L.1

DEACTIVATION RATIOS

Run	Deactivation Ratio	Exposure Time (hours)
XII-2A, XII-6	0.919	24
XII-7	0.845	57
XII-8	0.768	83

The rate of reaction adjusted for fresh catalyst is the experimental rate divided by the deactivation ratio.

The deactivation data was fit to two functions. The first involved a linear decay in catalyst activity.

$$R_d = 1 - 0.002803t \qquad (L.1)$$

The deactivation ratio is R_d and t is the number of hours the catalyst is exposed to acetic acid. The second fitting equation involves an exponential decay expressed as follows.

$$R_d = e^{-t/\tau} \qquad (L.2)$$

The value of the time constant τ is about 320 hours. Both equations fit the deactivation data to approximately the same accuracy, therefore the simpler linear equation (1.1) was used.

The deactivation ratio as a function of time is shown in Figure L.2.

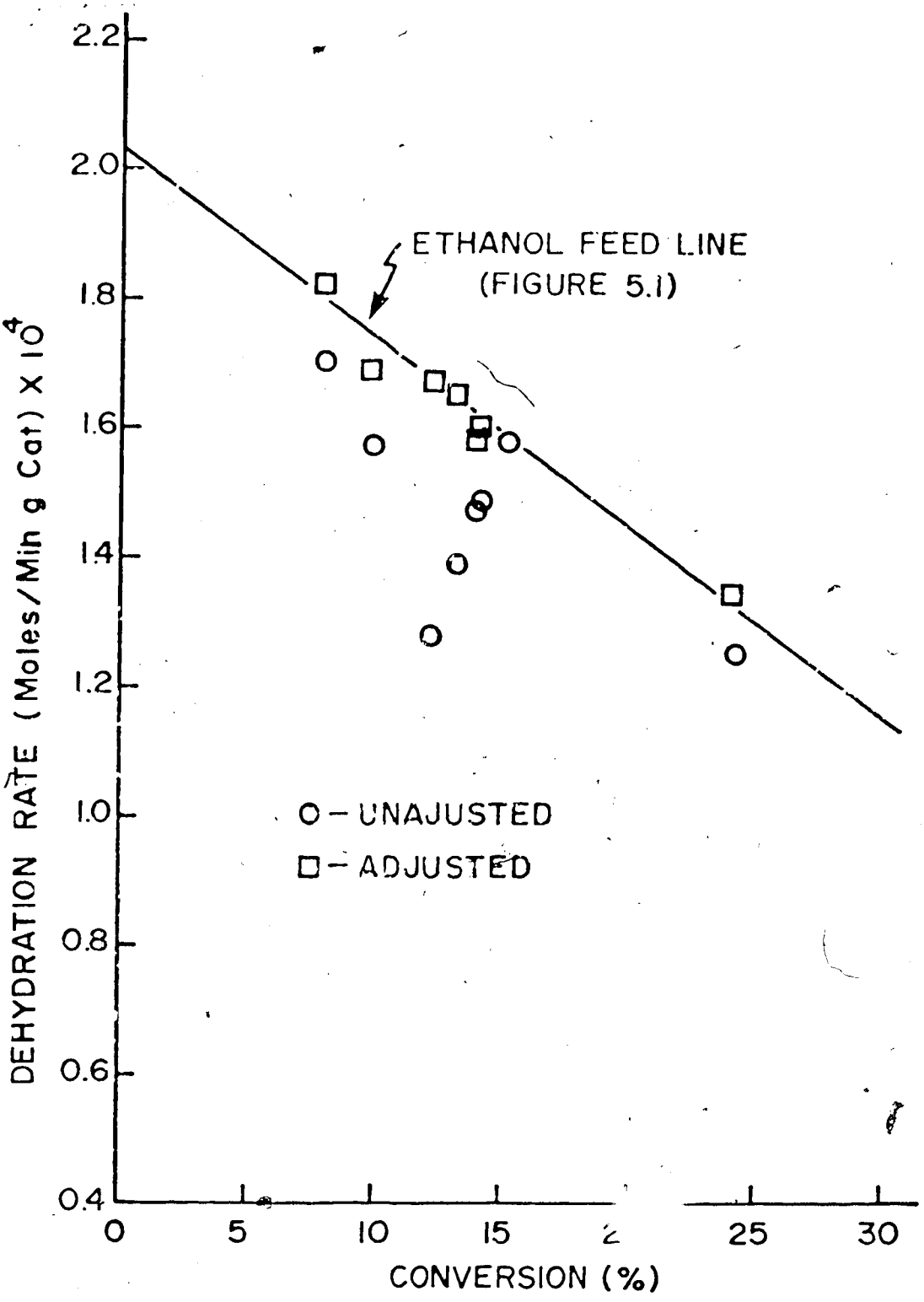


FIGURE L.I: DEHYDRATION RATES VS CONVFRSION FOR RUN XII

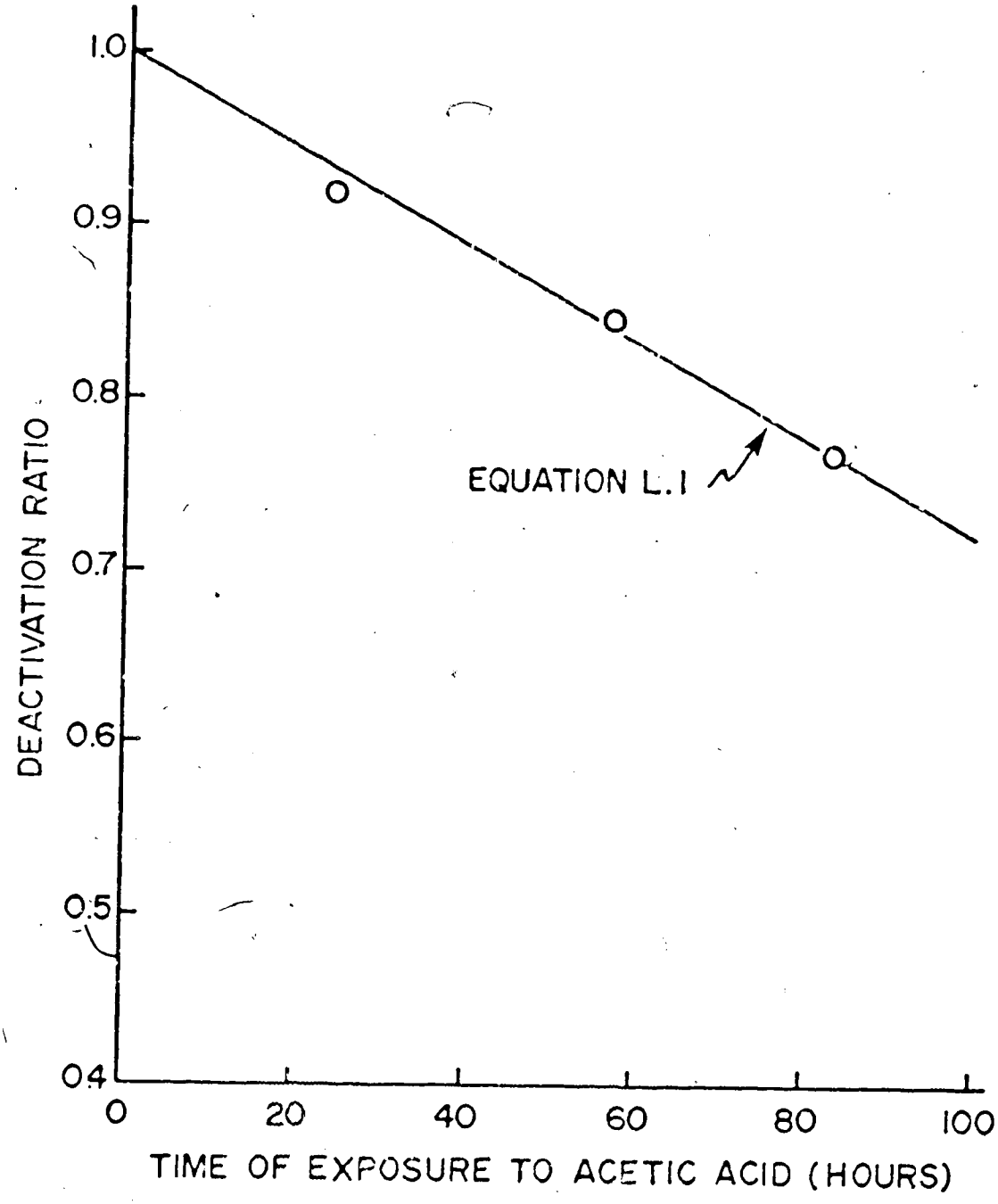


FIGURE L.2: CATALYST DEACTIVATION

APPENDIX M

ESTERIFICATION RUNS

This appendix contains a summary of all the esterification runs. These are presented in tabular form (Tables M.1 through M.32) and a sample calculation for one of the runs is given below.

The calculation is for Run EIII-8, Table M.21. The first five lines of the table state the table number, run number, date of the experiment, the temperature and the pressure (the pressure reading in mm Hg is corrected for temperature and latitude by subtracting 1.9 mm). The catalyst mass and effective mass are given next. The relationship between these two masses and the deactivation ratio is presented in Appendix L.

Given the rate settings for the syringes the feed rates can be calculated (see Appendix F) and knowing the composition of each feed mixture (given in Appendix H) the overall feed composition and feed rate can be calculated. The product analysis for each sample, the average analysis and the feed composition are then presented.

Given the above information it is possible to calculate the conversion and rates. The basis is 100 moles of feed and in the subsequent equations the symbol Δ followed by a component refers to the moles of that component in the product minus the moles of the component in the feed. The conversions are calculated as follows:

X_1 2(DET$_2$O)100/ETOH,in

2(0.20-0.0)100/49.50 0.8% (M.1)

X_2 (DETAC)100/ETOH,in

(9.81-0.0)100/49.50 19.83% (M.2)

X_3 (DETAC)100/HOAC,in

(9.81-0.0)100/49.93 19.63% (M.3)

X_1 is the conversion of ethanol to ether and X_2 is the conversion of ethanol to ester. X_3 is the conversion of acetic acid to ester.

The ethanol feed rate is calculated as follows.

$$F_{ETOH} = (\text{Total Feed Rate})(\text{ETOH,in}/100)$$
$$= 2.71\times10^{-3}(49.50/100)$$
$$= 1.34\times10^{-3} \text{ (moles/min)} \quad (M.4)$$

The dehydration and esterification rates are now calculated using equation 2.3.

$$r_1 = \frac{(F_{ETOH})(X_1/100)}{(\text{g cat.})R_d}$$

$$= \frac{(1.34\times10^{-3})0.008}{(0.204)0.340}$$

$$= 0.65\times10^{-4} \text{ (moles/(min g cat.))} \quad (M.5)$$

$$r_2 = \frac{(F_{ETOH})(X_2/100)}{(\text{g cat.})R_d}$$

$$= \frac{(1.34\times10^{-3})0.1983}{(0.204)0.340}$$

$$= 15.50\times10^{-4} \text{ (moles/(min g cat.))} \quad (M.6)$$

The first form of the "excess" balance (discussed in Appendix I) is presented below. The symbol e refers to the estimated number of moles for a particular component. The estimated amounts of ethanol, water and acetic acid-ester are calculated as follows:

$$\text{ETOH,e} = 2(\text{ETOH,out} - \text{ETOH,in}) + (\text{ETAC} - \text{ETOH,out}) + \text{ETOH,in}$$

$$2(0.70-0.0) + (9.8 - 0.0) + 38.56$$

$$48.77 \text{ moles} \qquad \text{(M.7)}$$

$$H_2O,e = 2(H_2O,out - H_2O,in) + ETAC + H_2O,in$$

$$= 0.2 + 9.81 + 0.49 = 10.50 \text{ moles} \qquad \text{(M.8)}$$

$$\text{HOAC-ETAC,e} = \text{ETAC,out} + \text{HOAC,out}$$

$$9.81 + 41.48 = 51.29 \text{ moles} \qquad \text{(M.9)}$$

The "excess ethanol", "excess water" and "excess acetic acid-ester" are calculated according to the equations given below.

$$\text{Excess Ethanol} = (\text{ETOH,e-ETOH,in})100/\text{ETOH,in}$$

$$= (48.77-49.50)100/49.50$$

$$= -1.42\% \qquad \text{(M.10)}$$

$$\text{Excess Water} = (H_2O,out-H_2O,e)100/H_2O.e$$

$$= (9.81-10.50)100/10.50$$

$$= -6.68\% \qquad \text{(M.11)}$$

$$\text{Excess Acis-Ester} = \frac{[\text{HOAC,ETAC,e-(HOAC,in+ETAC,in)}]100}{\text{(HOAC,in + ETAC, in)}}$$

$$= (51.29-49.99)100/49.99$$

$$= +2.61\% \qquad \text{(M.12)}$$

The second form of the mass balance involved comparing the number of moles of hydrogen, oxygen and carbon with the number of moles of these elements in the product (on the basis of 100 moles of feed). The moles of the three elements in the feed for Run 1-1-8 are calculated in the equation given below.

$$H,in = 2(H_2O,in) + 6(EtOH,in) + 10(Et_2O) + 8(EtAc,in) + 4(HOAc,in)$$
$$= 2(0.12) + 6(49.50) + 10(0) + 8(0) + 4(49.99)$$
$$= 497.94 \text{ moles} \quad (M.13)$$

$$O,in = 1(H_2O,in) + 1(EtOH,in) + 1(Et_2O) + 2(EtOH,in) + 2(HOAc,in)$$
$$= 1(0.49) + 1(49.50) + 1(0.0) + 2(0.0) + 2(49.99)$$
$$= 149.97 \text{ moles} \quad (M.14)$$

$$C,in = 0(H_2O,in) + 2(EtOH,in) + 4(Et_2O,in) + 4(EtAc,in) + 2(HOAc,in)$$
$$= 0(0.49) + 2(39.60) + 4(0.0) + 2(49.99)$$
$$= 198.98 \text{ moles} \quad (M.15)$$

In an analogous fashion the moles of each of these elements in the product can be calculated.

$$H,out = 6(38.56) + 10(0.2) + 8(9.81) + 4(41.48)$$
$$\text{moles} \quad (M.16)$$

$$O,out = 1(9.91) + 1(38.56) + 1(0.2) + 2(9.81) + 2(41.48$$
$$= 151.25 \text{ moles} \quad (M.17)$$

$$C,out = 0(9.91) + 2(38.56) + 4(0.2) + 4(9.81) + 2(41.48)$$
$$= 200.12 \text{ moles} \quad (M.18)$$

The hydrogen, oxygen and carbon balances in Table M.21 are calculated below.

$$\text{Hydrogen Balance} = (\Delta H)100/H,\text{in}$$

$$= (-0.36)100/497.94 = -0.05\% \qquad \text{(M.19)}$$

$$\text{Oxygen Balance} = (\Delta O)100/O,\text{in}$$

$$= (1.28)100/149.97 = 0.85\% \qquad \text{(M.20)}$$

$$\text{Carbon Balance} = (\Delta C)100/C,\text{in}$$

$$= (1.14)100/198.98 = 0.57\% \qquad \text{(M.21)}$$

Due to round off errors the numbers given above do not correspond exactly to those presented in Table M.21 for Run EIII-8.

TABLE M.1

EXPERIMENTAL RUN I- 1
DATE CONDUCTED 9/ 2/76

RUN TEMPERATURE= 125.0 DEG.C
RUN PRESSURE= 698.3 MMHG =0.9163 ATM = 92.8 KPA
CATALYST MASS = 0.2485 G ,DEACTIVATION RATIO=0.994
EFFECTIVE MASS = 0.2471 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXI	30.00	1/1000	0.2526E-01	0.2218E-01	0.878

AVERAGE MOL. WT = 50.67 G/MOLE
TOTAL FEED RATE = 0.4377E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
14	25.94	37.42	1.04	25.48	10.09
16	27.21	35.79	0.99	26.88	9.10
18	27.02	36.69	0.92	26.36	9.00
19	26.38	37.53	0.92	26.14	9.00
20	26.74	37.38	0.85	25.78	9.24
21	26.31	37.36	0.89	26.16	9.25
22	27.13	36.60	0.83	26.30	9.11
23	27.12	36.51	0.89	26.67	8.78
	26.73	36.91	0.91	26.22	9.19
FEED	0.43	65.28	0.00	0.00	34.28

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	2.81	0.325
ESTERIFICATION	76.49	40.17	4.645
TOTAL	76.49	42.99	4.971

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.45 %	-3.04 %	3.32 %
HYDROG	OXYGEN	CARBON
0.20 %	0.84 %	0.84 %

TABLE M.2

EXPERIMENTAL RUN I- 2
DATE CONDUCTED 9/ 2/76

RUN TEMPERATURE= 125.0 DEG.C
RUN PRESSURE= 698.3 MMHG =0.9163 ATM = 92.8 KPA
CATALYST MASS = 0.2485 G ,DEACTIVATION RATIO=0.991
EFFECTIVE MASS = 0.2464 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXI	30.00	1/ 100	0.2517E 00	0.2210E 00	0.878

AVERAGE MOL. WT = 50.67 G/MOLE
TOTAL FEED RATE = 0.4361E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
26	11.65	52.73	0.19	10.85	24.55
27	11.78	53.22	0.20	11.14	23.63
28	11.42	53.39	0.21	10.99	23.97
29	11.54	53.36	0.20	10.95	23.92
30	11.20	53.18	0.20	10.84	24.56
31	10.89	53.44	0.21	11.01	24.42
	11.41	53.22	0.20	10.96	24.17
FEED	0.43	65.28	0.00	0.00	34.28

REACTION	ACID CONVERSION %	HANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.63	0.735
ESTERIFICATION	31.98	16.80	19.412
TOTAL	31.9	17.43	20.148

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.02 %	-1.61 %	2.50 %
HYDROGEN	OXYGEN	CARBON
-0.18 %	0.63 %	0.18 %

TABLE M.3

EXPERIMENTAL RUN I-,3
DATE CONDUCTED 9/ 2/76

RUN TEMPERATURE= 125.0 DEG.C
RUN PRESSURE= 698.3 MMHG =0.9163 ATM = 92.8 KPA
CATALYST MASS = 0.2485 G ,DEACTIVATION RATIO=0.990
EFFECTIVE MASS = 0.2460 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXI	100.00	1/ 100	0.8600E 00	0.7550E 00	0.878

AVERAGE MOL. WT = 50.67 G/MOLE
TOTAL FEED RATE = 0.1489E-01 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
34	4.71	59.90	0.00	4.34	31.04
35	4.95	60.76	0.00	4.18	30.09
36	4.49	59.47	0.00	4.03	31.99
37	4.60	60.07	0.00	4.13	31.18
	4.69	60.05	0.00	4.17	31.08
FEED	0.43	65.28	0.00	0.00	34.28

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	12.18	6.39	25.293
TOTAL	12.18	6.39	25.293

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.61 %	1.79 %	2.82 %
HYDROGEN	OXYGEN	CARBON
-0.42 %	0.72 %	-0.08 %

TABLE M.4

EXPERIMENTAL RUN II- 1
DATE CONDUCTED 9/13/76

RUN TEMPERATURE- 125.0 DEG.C
RUN PRESSURE- 702.6 MMHG =0.9219 ATM = 93.4 KPA
CATALYST MASS - 0.2485 G ,DEACTIVATION RATIO=0.995
EFFECTIVE MASS - 0.2450 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXI	60.00	1/1000	0.5075E-01	0.4456E-01	0.878

AVERAGE MOL. WT = 50.67 G/MOLE
TOTAL FEED RATE = 0.8793E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
9	20.55	43.94	0.84	20.55	14.10
10	21.07	43.21	0.81	20.86	14.02
11	20.90	43.65	0.83	20.85	13.74
12	21.22	43.31	0.78	20.78	13.88
13	21.15	43.18	0.84	21.14	13.66
14	21.80	42.75	0.80	21.37	13.25
15	20.94	43.30	0.79	20.79	14.16
	21.09	43.34	0.81	20.91	13.83
FEED	0.43	65.28	0.00	0.00	34.28

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	2.50	0.587
ESTERIFICATION	60.98	32.03	7.503
TOTAL	60.98	34.53	8.090

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
0.92 %	-4.80 %	1.33 %
HYDROGEN	OXYGEN	CARBON
0.63 %	0.34 %	1.06 %

TABLE M.5

EXPERIMENTAL RUN II- 2
DATE CONDUCTED 9/13/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 702.6 MMHG =0.9219 ATM = 93.4 KPA
CATALYST MASS = 0.2485 G ,DEACTIVATION RATIO=0.983
EFFECTIVE MASS = 0.2443 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXI	60.00	1/1000	0.5075E-01	0.4456E-01	0.878

AVERAGE MOL. WT = 50.67 G/MOLE
TOTAL FEED RATE = 0.8793E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
19	19.67	44.45	1.09	18.38	16.38
20	19.77	44.53	1.07	18.08	16.53
21	19.77	44.22	1.16	18.55	16.28
22	19.72	44.43	1.12	18.20	16.50
23	19.40	44.92	1.19	18.30	16.17
24	19.47	44.98	1.14	18.18	16.20
27	19.24	44.52	1.25	18.52	16.45
28	19.68	44.56	1.20	18.28	16.25
29	19.00	45.09	1.21	17.93	16.74
30	19.57	44.43	1.17	18.13	16.67
	19.53	44.61	1.16	18.26	16.42
FEED	0.43	65.28	0.00	0.00	34.28

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	3.56	0.838
ESTERIFICATION	53.25	27.97	6.571
TOTAL	53.25	31.54	7.409

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.11 %	-1.61 %	1.15 %
HYDROGEN	OXYGEN	CARBON
0.09 %	0.29 %	0.32 %

TABLE M.6

EXPERIMENTAL RUN EI- 1
DATE CONDUCTED 12/ 6/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 699.3 MMHG =0.9176 ATM = 92.9 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.988
EFFECTIVE MASS = 0.2017 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/ 100	0.1214E 00	0.9604E-01	0.791
2	HOAC	0.80	50	0.1388E-01	0.1449E-01	1.044

AVERAGE MOL. WT = 47.38 G/MOLE
TOTAL FEED RATE = 0.2332E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
9	4.60	84.48	0.89	3.84	6.17
10	4.48	85.30	0.78	3.44	5.97
11	4.56	84.51	0.91	3.69	6.30
12	4.62	84.39	0.82	3.59	6.55
	4.57	84.67	0.85	3.64	6.25
FEED	0.22	89.44	0.00	0.00	10.32

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	1.91	1.980
ESTERIFICATION	35.29	4.07	4.216
TOTAL	35.29	5.99	6.197

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
0.65 %	-3.12 %	-4.17 %
HYDROGEN	OXYGEN	CARBON
0.25 %	-0.39 %	0.15 %

TABLE M.7

EXPERIMENTAL RUN EI- 2
DATE CONDUCTED 12/ 6/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 701.9 MMHG =0.9210 ATM = 93.3 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.979
EFFECTIVE MASS = 0.1998 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/1000	0.2526E-01	0.1998E-01	0.791
2	HOAC	6.00	50	0.1041E 00	0.1087E 00	1.044

AVERAGE MOL. WT = 57.01 G/MOLE
TOTAL FEED RATE = 0.2257E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
21	10.53	7.95	0.00	10.18	71.32
22	11.25	8.01	0.00	10.68	70.04
23	10.51	8.12	0.00	9.98	71.37
24	10.76	6.16	0.00	10.20	72.86
25	10.32	7.50	0.00	10.08	72.07
26	10.66	7.00	0.00	9.75	72.57
	10.67	7.46	0.00	10.15	71.70
FEED	0.69	19.23	0.00	0.00	80.06

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	12.67	52.76	11.466
TOTAL	12.67	52.76	11.466

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-8.44 %	-1.57 %	2.24 %
HYDROGEN	OXYGEN	CARBON
-0.66 %	0.99 %	0.17 %

TABLE M.8

EXPERIMENTAL RUN FI- 3
DATE CONDUCTED 12/ 6/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 704.9 MMHG =0.9250 ATM = 93.7 KPA
CATALYST MASS - 0.2040 G ,DEACTIVATION RATIO=0.966
EFFECTIVE MASS - 0.1971 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN,	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791
2	HOAC	0.80	50	0.1398E-01	0.1449E-01	1.044

AVERAGE MOL. WT = 53.21 G/MOLE
TOTAL FEED RATE = 0.4585E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
30	27.22	17.94	0.45	27.03	27.34
31	25.28	18.10	0.38	27.00	29.21
32	26.88	19.25	0.35	26.12	27.37
33	25.08	19.41	0.40	26.95	28.13
34	27.22	18.11	0.38	26.04	28.23
35	25.71	19.84	0.41	27.05	26.97
36	27.04	18.67	0.40	25.89	27.98
	26.35	18.76	0.40	26.58	27.89
FEED	0.51	46.94	0.00	0.00	52.54

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	1.70	0.186
ESTERIFICATION	50.59	56.63	6.184
TOTAL	50.59	58.34	6.370

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.67 %	-4.10 %	3.68 %
HYDROGEN	OXYGEN	CARBON
0.14 %	1.26 %	1.15 %

TABLE M.9

EXPERIMENTAL RUN EI- 4
DATE CONDUCTED 12/ 6/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 704.9 MMHG =0.9250 ATM = 93.7 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.963
EFFECTIVE MASS = 0.1964 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/ 100	0.2517E 00	0.1991E 00	0.791
2	HOAC	15.00	50	0.2603E 00	0.2717E 00	1.044

AVERAGE MOL. WT = 52.97 G/MOLE
TOTAL FEED RATE = 0.8889E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
37	5.88	44.31	0.07	5.59	44.13
39	6.15	43.30	0.09	5.61	44.83
40	6.05	43.13	0.10	5.46	45.23
41	5.91	42.16	0.08	5.58	46.24
42	6.04	42.26	0.09	5.45	46.13
43	6.02	43.38	0.08	5.47	45.02
44	6.10	40.26	0.08	5.34	48.19
45	5.88	42.49	0.08	5.46	46.06
46	5.95	42.49	0.09	5.32	46.12
	6.00	42.64	0.08	5.48	45.77
FEED	0.49	48.67	0.00	0.00	50.82

REACTION	~~ACID~~ CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.36	0.811
ESTERIFICATION	10.78	11.25	24.796
TOTAL	10.78	11.62	25.608

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.74 %	-1.07 %	0.84 %
HYDROGEN	OXYGEN	CARBON
-0.12 %	0.28 %	0.06 %

TABLE M.10

EXPERIMENTAL RUN FII- 1
DATE CONDUCTED 12/ 6/76

RUN TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 704.9 MMHG =0.9250 ATM = 93.7 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.959
EFFECTIVE MASS = 0.1958 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/ 100	0.2517E 00	0.1991E 00	0.791
2	HOAC	15.00	50	0.2603E 00	0.2717E 00	1.044

AVERAGE MOL. WT = 52.97 G/MOLE
TOTAL FEED RATE = 0.8889E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
48	9.37	39.22	0.00	8.85	42.54
49	9.38	40.12	0.00	9.01	41.46
50	9.51	39.19	0.00	8.99	42.28
51	8.89	39.26	0.00	9.18	42.65
52	9.69	37.74	0.00	9.25	43.30
53	9.43	37.75	0.00	9.62	43.19
54	9.68	38.32	0.00	9.22	42.76
	9.42	38.80	0.00	9.16	42.60
FEED	0.49	48.67	0.00	0.00	50.82

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	18.03	18.82	41.602
TOTAL	18.03	18.82	41.602

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.44 %	-2.38 %	1.84 %
HYDROGEN	OXYGEN	CARBON
-0.18 %	0.62 %	0.23 %

TABLE M.11

EXPERIMENTAL RUN FII-2
DATE CONDUCTED 12/ 7/76

RUN TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 701.7 MMHG =0.9207 ATM = 93.2 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.951
EFFECTIVE MASS = 0.1941 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/ 100	0.1214E 00	0.9604E-01	0.791
2	HOAC	0.80	50	0.1388E-01	0.1449E-01	1.044

AVERAGE MOL. WT = 47.38 G/MOLE
TOTAL FEED RATE = 0.2332E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
7	5.44	83.84	0.38	5.37	4.94
8	5.90	82.85	0.40	5.32	5.50
9	5.82	82.63	0.42	5.76	5.35
10	5.90	82.86	0.36	5.29	5.57
11	5.81	83.00	0.39	5.46	5.32
12	6.08	82.17	0.39	5.51	5.83
13	5.71	83.13	0.39	5.50	5.26
	5.81	82.92	0.39	5.46	5.39
FEED	0.22	89.44	0.00	0.00	10.32

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.88	0.949
ESTERIFICATION	52.88	6.10	6.565
TOTAL	52.88	6.98	7.514

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.29 %	-4.32 %	5.16 %
HYDROGEN	OXYGEN	CARBON
-0.00 %	0.48 %	0.26 %

TABLE M.12

'PERIMENTAL RUN EII- 3
ATE CONDUCTED 1' ' 7776

RUN TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 701.0 MMHG =0. ATM = 93.2 KPA
CATALYST MASS = 0.2040 G .DE IVATION RATIO=0.945
EFFECTIVE MASS = 0.1929 G

SYRINGE #	FEED	RATE	RANGE	ML/MI	G/MIN	DENSITY G/I
1	ETOH	10.00	1/1000	0.7526E-01	0.1998E-01	0.791
2	HOAC	6.00	50	0.1041E 00	0.1087E 00	1.044

AVERAGE MOL. WT = 57.01 G/MOLE
TOTAL FEED RATE = 0.22'7E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
16	13.74	5.51	0.00	12.79	67.95
17	12.46	5.29	0.00	12.89	69.34
18	13.56	5.57	0.00	12.5	68.32
19	12.69	6.28	0.00	12.85	68.16
2	13.50	5.14	0.00	12.77	68.57
21	12.64	5.77	0.00	13.18	68.39
22	13.41	5.33	0.00	12.71	68.52
23	12.75	5.56	0.00	13.02	68.65
24	13.24	5.13	0.00	12.41	69.20
	13.11	5.51	0.00	12.79	68.57
FEED	0.69	19.23	0.00	0.00	80.06

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	15.98	66.52	14.971
TOTAL	15.98	66.52	14.971

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-4.81 %	-2.76 %	1.63 %
HYDROGEN	OXYGEN	CARBON
-0.24 %	0.72 %	0.38 %

TABLE M.13

EXPERIMENTAL RUN EII- 4
DATE CONDUCTED 12/ 7/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE= 698.5 MMHG =0.9165 ATM 92.8 KPA
CATALYST MASS = 0.2040 G ,DEACTIVAT RATIO=0.931
EFFECTIVE MASS = 0.1901 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/1000	0.1252E-01	0.9907E-02	0.791
2	HOAC	0.80	50	0.1388E-01	0.1449E-01	1.044

AVERAGE MOL. WT = 53.21 G/MOLE
TOTAL FEED RATE = 0.4585E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
26	31.55	15.73	0.10	30.90	21.69
27	29.03	15.61	0.11	31.45	23.77
28	31.00	14.44	0.10	29.88	24.56
29	29.29	15.41	0.11	31.65	23.51
30	30.87	14.72	0.09	30.34	23.95
31	29.15	15.80	0.11	31.30	23.62
	30.15	15.28	0.10	30.92	23.52
FEED	0.51	46.94	0.00	0.00	52.54

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.46	0.052
ESTERIFICATION	58.84	65.87	7.459
TOTAL	58.84	66.34	7.511

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.08 %	-4.31 %	3.61 %
HYDROGEN	OXYGEN	CARBON
0.35 %	1.24 %	1.39 %

TABLE M.14

EXPERIMENTAL RUN EIII- 1
DATE CONDUCTED 12/[illegible]/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 698.2 MMHG =0.9161 ATM = 92.8 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.925
EFFECTIVE MASS = 0.1888 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/ 100	0.1214E 00	0.9604E-01	0.791
2	HOAC	15.00	1/ 100	0.1214E 00	0.1267E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.4215E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
20	8.92	39.21	0.17	8.35	43.33
22	8.72	38.89	0.18	8.02	44.18
23	8.20	41.40	0.18	8.72	41.47
24	9.01	39.09	0.16	8.33	43.39
25	8.91	41.64	0.20	8.20	40.42
26	9.43	41.93	0.19	9.17	39.26
	8.86	40.36	0.18	8.57	42.01
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.75	0.830
ESTERIFICATION	17.14	17.31	19.129
TOTAL	17.14	18.06	19.959

BALANCES

EXCESS ETHANOL	EXC WATER	EXCESS ACID,ESTER
-0.40 %	-4.02 %	1.16 %
HYDROGEN	OXYGEN	CARBON
0.07 %	0.38 %	0.38 %

TABLE M.15

EXPERIMENTAL RUN EIII- 2
DATE CONDUCTED 12/20/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 697.7 MMHG =0.9155 ATM = 92.7 KPA
CATALYST MASS - 0.2040 G ,DEACTIVATION RATIO=0.908
EFFECTIVE MASS - 0.1852 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	50.00	1/1000	0.4225E-01	0.3342E-01	0.791
2	HOAC	50.00	1/1000	0.4225E-01	0.4411E-01	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.1466E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
34	16.94	32.96	0.31	16.46	33.31
35	15.31	33.41	0.34	16.10	34.81
37	16.05	33.33	0.35	16.70	33.55
39	15.91	33.45	0.38	16.98	33.26
41	15.78	33.43	0.09	17.46	33.21
	16.00	33.31	0.29	16.74	33.63
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	1.21	0.475
ESTERIFICATION	33.49	33.82	13.261
TOTAL	33.49	35.03	13.736

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
2.33 %	-8.71 %	0.75 %
HYDROGEN	OXYGEN	CARBON
1.08 %	0.25 %	1.54 %

TABLE M.16

EXPERIMENTAL RUN EIII-3
DATE CONDUCTED 12/20/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 698.3 MMHG =0.9163 ATM = 92.8 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.901
EFFECTIVE MASS = 0.1838 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/ 100	0.2517E 00	0.1991E 00	0.791
2	HOAC	30.00	1/ 100	0.2517E 00	0.2628E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.8739E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
47	4.81	42.60	0.00	3.96	48.62
48	4.37	44.83	0.00	3.89	46.89
51	4.64	41.71	0.00	3.91	49.72
52	4.94	44.67	0.00	4.31	46.06
53	4.56	43.78	0.00	4.07	47.58
55	4.70	43.65	0.00	4.07	47.56
56	4.66	42.63	0.00	3.96	48.73
	4.67	43.41	0.00	4.02	47.88
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	8.05	8.13	19.157
TOTAL	8.05	8.13	19.157

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-4.16 %	.34 %	3.82 %
HYDROGEN	OXYGEN	CARBON
-0.88 %	1.27 %	-0.15 %

TABLE M.17

EXPERIMENTAL RUN EIII-4
DATE CONDUCTED 12/21/76

RUN TEMPERATURE= 155.0 DEG.C
RUN PRESSURE= 702.5 MMHG =0.9218 ATM = 93.4 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.879
EFFECTIVE MASS = 0.1794 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	25.00	1/1000	0.2102E-01	0.1662E-01	0.791
2	HOAC	25.00	1/1000	0.2102E-01	0.2194E-01	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.7296E-03 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
4	21.73	27.50	0.44	21.69	28.61
5	20.91	27.45	0.47	22.17	28.97
6	22.26	25.71	0.46	21.89	29.66
7	21.00	25.92	0.47	22.19	30.40
8	22.06	25.67	0.43	21.85	29.97
9	21.94	27.02	0.50	23.73	26.78
12	21.87	26.47	0.44	21.39	29.81
	21.68	26.53	0.46	22.13	29.17
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	1.87	0.376
ESTERIFICATION	44.26	44.70	9.002
TOTAL	44.26	46.58	9.378

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
0.18 %	-5.98 %	2.62 %
HYDROGEN	OXYGEN	CARBON
0.60 %	0.87 %	1.40 %

TABLE M.18

EXPERIMENTAL RUN EIII-5
DATE CONDUCTED 12/21/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE = 702.6 MMHG =0.9219 ATM = 93.4 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.873
EFFECTIVE MASS = 0.1782 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	45.00	1/ 100	0.3821E 00	0.3022E 00	0.791
2	HOAC	45.00	1/ 100	0.3821E 00	0.3989E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.1326E-01 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
15	3.38	43.88	0.00	2.86	49.85
16	3.69	47.72	0.00	3.15	45.42
17	3.35	45.94	0.00	2.88	47.81
20	3.26	45.05	0.00	2.75	48.93
22	3.26	43.87	0.00	2.74	50.12
25	3.51	46.55	0.00	2.90	47.02
26	3.27	45.71	0.00	2.82	48.17
	3.39	45.53	0.00	2.87	48.19
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	5.75	5.80	21.401
TOTAL	5.75	5.80	21.401

BALANCES

EXCESS ETHANOL -2.20 %
HYDROGEN -0.44 %

EXCESS WATER 0.67 %
OXYGEN 0.71 %

EXCESS ACID,ESTER 2.14 %
CARBON -0.02 %

TABLE M.19

EXPERIMENTAL RUN EIII-6
DATE CONDUCTED 12/21/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 703.4 MMHG =0.9230 ATM = 93.5 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.859
EFFECTIVE MASS = 0.1754 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	75.00	1/1000	0.6349E-01	0.5022E-01	0.791
2	HOAC	75.00	1/1000	0.6349E-01	0.6629E-01	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.2204E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
27	12.23	37.69	0.28	13.29	36.49
28	13.07	37.72	0.24	12.83	36.11
29	12.34	38.68	0.27	13.39	35.30
33	12.64	37.95	0.28	13.70	35.41
35	12.52	38.37	0.28	13.57	35.22
36	13.44	37.48	0.27	13.40	35.39
37	12.82	37.95	0.30	13.85	35.05
	12.72	37.98	0.27	13.43	35.57
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	1.13	0.703
ESTERIFICATION	26.87	27.14	16.884
TOTAL	26.87	28.27	17.587

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
4.99 %	-10.35 %	-1.98 %
HYDROGEN	OXYGEN	CARBON
1.58 %	-0.66 %	1.48 %

TABLE M.20

EXPERIMENTAL RUN EIII-7
DATE CONDUCTED 12/21/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 703.4 MMHG =0.9230 ATM = 93.5 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.855
EFFECTIVE MASS = 0.1745 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	60.00	1/ 100	0.5124E 00	0.4053E 00	0.791
2	HOAC	60.00	1/ 100	0.5124E 00	0.5349E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.1778E-01 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
42	2.45	42.93	0.00	1.83	52.76
46	2.48	47.76	0.00	2.08	47.66
48	2.43	47.17	0.00	1.98	48.41
49	2.34	43.44	0.00	1.60	52.60
	2.43	45.33	0.00	1.97	50.36
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	3.75	3.79	19.126
TOTAL	3.75	3.79	19.126

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-4.64 %	2.99 %	4.47 %
HYDROGEN	OXYGEN	CARBON
-0.94 %	1.49 %	-0.06 %

TABLE M.21

EXPERIMENTAL RUN EIII-8
DATE CONDUCTED 12/21/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 704.0 MMHG =0.9238 ATM = 93.6 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.840
EFFECTIVE MASS = 0.1715 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	10.00	1/ 100	0.7794E-01	0.6168E-01	0.791
2	HOAC	10.00	1/ 100	0.7798E-01	0.8141E-01	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.2707E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
57	9.75	38.56	0.20	10.05	41.40
58	10.52	38.54	0.22	10.24	40.46
59	9.71	38.01	0.19	9.93	42.14
60	10.23	37.44	0.20	9.52	42.59
61	9.36	40.26	0.20	9.33	40.83
	9.91	38.56	0.20	9.81	41.48
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN* CAT.)
DEHYDRATION	-	0.83	0.652
ESTERIFICATION	19.63	19.83	15.495
TOTAL	19.63	20.66	16.148

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.42 %	-5.68 %	2.61 %
HYDROGEN	OXYGEN	CARBON
-0.04 %	0.87 %	0.60 %

TABLE M.22

EXPERIMENTAL RUN FIII-9
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 698.3 MMHG =0.9163 ATM = 92.8 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.767
EFFECTIVE MASS = 0.1565 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/ 100	0.1214E 00	0.9604E-01	0.791
2	HOAC	15.00	1/ 100	0.1214E 00	0.1267E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.4215E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
83	8.06	40.69	0.15	8.11	42.97
84	9.17	39.80	0.15	8.30	42.55
85	8.08	40.57	0.13	8.00	43.20
86	8.54	39.61	0.15	7.96	43.71
87	8.25	40.64	0.15	8.25	42.70
88	8.64	40.65	0.17	7.96	42.56
89	8.07	40.37	0.15	8.21	43.17
90	8.41	38.21	0.16	7.77	45.43
	8.40	40.07	0.15	8.07	43.29
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.62	0.837
ESTERIFICATION	16.14	16.30	21.740
TOTAL	16.14	16.93	22.578

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-2.11 %	-3.59 %	2.72 %
HYDROGEN	OXYGEN	CARBON
-0.29 %	0.90 %	0.31 %

TABLE M.23

EXPERIMENTAL RUN FIV- 1
DATE CONDUCTED 12/22/76

RUN TEMPERATURE- 135.0 DEG.C
RUN PRESSURE- 698.3 MMHG =0.9163 ATM = 92.8 KPA
CATALYST MASS - 0.2040 G ,DEACTIVATION RATIO=0.836
EFFECTIVE MASS - 0.1705 G

SYRINGE #	FEED	RATE RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIV	10.00 1/ 100	0.7798E-01	0.6238E-01	0.800
2	HOAC	10.00 1/ 100	0.7798E-01	0.8141E-01	1.044

AVERAGE MOL. WT = 50.96 G/MOLE
TOTAL FEED RATE = 0.2821E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
24	15.19	34.69	0.18	9.01	40.90
25	15.07	35.57	0.21	9.68	39.45
26	15.32	34.51	0.18	9.08	40.89
27	14.74	35.69	0.20	9.43	39.92
28	15.72	34.16	0.19	9.29	40.63
29	14.90	35.37	0.18	9.32	40.60
30	15.62	33.61	0.16	9.28	41.30
31	14.65	35.22	0.18	9.52	40.40
32	15.61	34.83	0.17	9.27	40.10
	15.15	34.85	0.18	9.32	40.47
FEED	6.24	45.78	0.00	0.00	47.97

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G C.T.
DEHYDRATION	-	0.82	0.624
ESTERIFICATION	19.43	20.36	15.424
TOTAL	19.43	21.19	16.049

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-2.67 %	-3.76 %	3.79 %
HYDROGEN	OXYGEN	CARBON
-0.26 %	1.23 %	0.63 %

TABLE M.24

EXPERIMENTAL RUN EIV- 2
DATE CONDUCTED 12/22/76

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 697.8 MMHG =0.9156 ATM = 92.7 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.831
EFFECTIVE MASS = 0.1696 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIV	30.00	1/ 100	0.2517E 00	0.2014E 00	0.800
2	HOAC	30.00	1/ 100	0.2517E 00	0.2628E 00	1.044

AVERAGE MOL. WT = 50.96 G/MOLE
TOTAL FEED RATE = 0.9109E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
41	9.57	39.97	0.00	4.05	46.39
42	10.06	39.78	0.00	3.91	46.23
43	9.59	40.29	0.00	4.13	45.97
44	10.29	39.44	0.00	4.12	46.13
45	9.77	41.40	0.00	4.00	44.82
46	9.55	40.25	0.00	3.97	46.22
47	9.50	40.76	0.00	4.16	45.56
	9.76	40.27	0.00	4.05	45.90
FEED	6.24	45.78	0.00	0.00	47.97

REACTION	ACID CONVERSION %	ET ANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	8.44	8.85	21.756
TOTAL	8.44	8.85	21.756

BALANCE

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-3.17 %	-5.19 %	4.14 %
HYDROGEN	OXYGEN	CARBON
-0.38 %	1.34 %	0.57 %

TABLE M.25

EXPERIMENTAL RUN FIV- 3
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 139.0 DEG.C
RUN PRESSURE= 696.8 MMHG =0.9143 ATM = 92.6 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.822
EFFECTIVE MASS = 0.1676 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIV	50.00	1/1000	0.4225E-01	0.3380E-01	0.800
2	HOAC	50.00	1/1000	0.4225E-01	0.4411E-01	1.044

AVERAGE MOL. WT = 50.96 G/MOLE
TOTAL FEED RATE = 0.1528E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
3	18.62	30.79	0.18	13.84	36.54
4	19.69	29.80	0.23	13.42	36.84
5	19.43	31.87	0.27	14.64	33.77
6	20.18	30.52	0.25	14.05	34.98
7	19.23	31.20	0.29	15.12	34.13
8	19.92	30.83	0.22	13.72	35.28
9	18.75	31.65	0.24	13.76	35.58
10	19.86	30.22	0.22	13.41	36.26
	19.46	30.86	0.24	14.00	35.42
FEED	6.24	45.78	0.00	0.00	47.97

REACTION	ACID CONVERSION %	ESTER CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	1.05	0.441
ESTERIFICATION	29.18	30.58	12.766
TOTAL	29.18	31.64	13.208

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-0.94 %	-4.92 %	3.03 %
HYDROGEN	OXYGEN	CARBON
0.24 %	0.98 %	1.09 %

TABLE M.26

EXPERIMENTAL RUN EV- 1
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE = 696.4 MMHG =0.9134 ATM = 92.5 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.915
EFFECTIVE MASS = 0.1663 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXSIV	50.00	1/1000	0.4225E-01	0.3380E-01	0.800
	HOAC	50.00	1/1000	0.4225E-01	0.4411E-01	1.044

AVERAGE MOL. WT = 60.96 G/MOLE
TOTAL FEED RATE = 0.1538E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
20	26.14	25.15	0.00	19.83	28.81
21	24.16	26.43	0.00	20.64	28.75
22	24.69	24.39	0.00	19.37	31.53
23	24.36	26.48	0.00	20.86	28.28
24	24.82	24.45	0.00	18.61	32.11
25	23.86	25.36	0.00	19.41	31.39
26	26.07	25.17	0.00	20.35	28.39
	24.87	25.35	0.00	19.87	29.89
FEED	6.24	45.78	0.00	0.00	47.97

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	41.43	43.42	18.267
TOTAL	41.43	43.42	18.267

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
.19 %	-4.71 %	3.74 %
HYDROGEN	OXYGEN	CARBON
0.29 %	1.21 %	1.33 %

TABLE M.27

EXPERIMENTAL RUN EV- 2
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE = 696.0 MMHG =0.9132 ATM = 92.5 KPA
CATALYST MASS 0.2040 G ,DEACTIVATION RATIO=0.802
EFFECTIVE MASS 0.1638 G

SYRINGE #	FEED	RATE RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIV	10.00 1/ 100	0.7798E-01	0.6238E-01	0.800
2	HOAC	10.00 1/ 100	0.7798E-01	0.8141E-01	1.044

AVERAGE MOL. WT = 50.96 G/MOLE
TOTAL FEED RATE = 0.2821E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
36	21.09	29.99	0.00	14.33	34.58
37	19.08	29.71	0.00	14.45	36.74
39	19.42	30.83	0.00	14.76	34.97
40	21.29	30.14	0.00	15.08	33.47
41	19.68	31.62	0.00	15.12	33.56
42	20.78	29.45	0.00	14.55	35.20
	20.22	30.29	0.00	14.71	34.75
FEED	6.24	45.78	0.00	0.00	47.97

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	30.68	32.15	25.354
TOTAL	30.68	32.15	25.354

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.67 %	-3.50 %	3.13 %
HYDROGEN	OXYGEN	CARBON
-0.01 %	1.01 %	0.78 %

TABLE M.28

EXPERIMENTAL RUN EV- 3
DATE CONDUCTED 12/23/76

RUN TEMPERATURE = 120.0 DEG.C
RUN PRESSURE = 695.6 MMHG =0.9127 ATM = 92.4 KPA
CATALYST MASS - 0.2040 G ,DEACTIVATION RATIO=0.800
EFFECTIVE MASS - 0.1632 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	XXXIV	30.00	1/ 100	0.2517E 00	0.2014E 00	0.800
2	HOAC	30.00	1/ 100	0.2517E 00	0.2628E 00	1.044

AVERAGE MOL. WT = 50.96 G/MOLE
TOTAL FEED RATE = 0.9109E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ETOO	ETAC	HOAC
45	12.71	38.23	0.00	7.47	41.57
46	13.44	36.99	0.00	7.22	42.33
47	12.66	37.31	0.00	7.34	42.66
48	13.54	36.40	0.00	7.47	42.57
50	13.70	36.79	0.00	7.57	41.92
52	13.60	36.57	0.00	7.35	42.45
	13.28	37.05	0.00	7.41	42.25
FEED	6.24	45.78	0.00	0.00	47.97

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	15.44	16.18	41.352
TOTAL	15.44	16.18	41.352

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-2.87 %	-2.74 %	3.52 %
HYDROGEN	OXYGEN	CARBON
-0.39 %	14 %	0.40 %

TABLE M.29

EXPERIMENTAL RUN EVI- 1
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE= 695.5 MMHG =0.9126 ATM = 92.4 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.795
EFFECTIVE MASS = 0.1623 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	30.00	1/ 100	0.2517E 00	0.1991E 00	0.791
2	HOAC	30.00	1/ 100	0.2517E 00	0.2628E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.8739E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
55	8.50	39.92	0.00	8.32	43.24
56	8.88	39.68	0.00	8.26	43.15
58	8.64	39.41	0.00	8.05	43.88
59	8.34	40.87	0.00	8.40	42.38
60	8.53	39.00	0.00	8.13	44.33
61	8.35	40.04	0.00	8.29	43.31
62	8.54	39.22	0.00	7.86	44.36
63	8.31	39.30	0.00	8.32	44.05
64	9.47	41.07	0.00	8.80	40.63
	8.62	39.83	0.00	8.27	43.26
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	16.54	16.71	44.537
TOTAL	16.54	16.71	44.537

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-2.81 %	-1.63 %	3.07 %
HYDROGEN	OXYGEN	CARBON
-0.50 %	.02 %	0.14 %

TABLE M.30

EXPERIMENTAL RUN EVI-2
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE= 695.6 MMHG 0.9127 ATM = 92.4 KPA
CATALYST MASS.= 0.2040 G ,DEACTIVATION RATIO=0.787
EFFECTIVE MASS = 0.1606 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	50.00	1/1000	0.4225E-01	0.3342E-01	0.791
2	HOAC	50.00	1/1000	0.4225E-01	0.4411E-01	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.1466E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
67	20.87	28.22	0.00	22.65	28.25
68	22.35	27.35	0.00	21.46	28.82
	20.80	27.89	0.00	22.41	28.88
70	22.47	26.54	0.00	22.30	28.67
	62	27.50	0.00	22.20	28.66
FEED	49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	44.41	44.86	20.279
TOTAL	44.41	44.86	20.279

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
0.41 %	-4.65 %	1.74 %
HYDROGEN	OXYGEN	CARBON
0.51 %	0.58 %	1.08 %

TABLE M.31

EXPERIMENTAL RUN EVI- 3
DATE CONDUCTED 12/23/76

RUN TEMPERATURE= 120.0 DEG.C
RUN PRESSURE= 698.0 MMHG =0.9159 ATM = 92.8 KPA
CATALYST MASS = 0.2040 G ,DEACTIVATION RATIO=0.770
EFFECTIVE MASS = 0.1572 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	10.00	1/ 100	0.7798E-01	0.6168E-01	0.791
2	HOAC	10.00	1/ 100	0.7798E-01	0.8141E-01	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.2707E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
71	15.71	32.98	0.00	17.30	33.99
72	17.09	31.39	0.00	16.54	34.95
73	15.52	33.18	0.00	16.45	34.83
75	15.88	32.96	0.00	16.87	34.27
76	16.53	32.09	0.00	15.94	35.42
77	15.50	31.49	0.00	16.11	36.88
78	16.91	31.37	0.00	16.19	35.51
79	15.71	32.94	0.00	16.53	34.80
80	16.74	32.16	0.00	16.21	34.87
	16.18	32.28	0.00	16.46	35.06
FEED	0.45	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	-	-
ESTERIFICATION	32.93	33.25	28.338
TOTAL	32.93	33.25	28.338

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
-1.51 %	-4.50 %	3.05 %
HYDROGEN	OXYGEN	CARBON
0.0 %	1.01 %	0.78 %

TABLE M.32

EXPERIMENTAL RUN EVII- 1
DATE CONDUCTED 2/ 3/77

RUN TEMPERATURE= 135.0 DEG.C
RUN PRESSURE= 704.0 MMHG =0.9238 ATM = 93.6 KPA
CATALYST MASS = 0.2411 G ,DEACTIVATION RATIO=0.994
EFFECTIVE MASS = 0.2397 G

SYRINGE #	FEED	RATE	RANGE	ML/MIN	G/MIN	DENSITY G/ML
1	ETOH	15.00	1/ 100	0.1214E 00	0.9604E-01	0.791
2	HOAC	15.00	1/ 100	0.1214E 00	0.1267E 00	1.044

AVERAGE MOL. WT = 52.86 G/MOLE
TOTAL FEED RATE = 0.4215E-02 MOLES/MIN

PRODUCT ANALYSIS MOLE %

SAMPLE #	COMPONENTS H2O	ETOH	ET2O	ETAC	HOAC
27	11.46	38.39	0.23	10.90	38.99
28	11.77	36.66	0.21	11.02	40.31
29	11.97	39.19	0.22	11.62	36.97
30	12.19	36.95	0.21	11.08	39.54
31	11.57	37.98	0.21	11.83	38.38
33	11.58	38.22	0.22	11.50	38.44
34	11.71	37.11	0.19	11.12	39.85
	11.75	37.79	0.21	11.30	38.93
FEED	0.49	49.50	0.00	0.00	49.99

REACTION	ACID CONVERSION %	ETHANOL CONVERSION %	RATE*10**4 MOLES/ (MIN*G CAT.)
DEHYDRATION	-	0.88	0.770
ESTERIFICATION	22.60	22.82	19.869
TOTAL	22.60	23.71	20.640

BALANCES

EXCESS ETHANOL	EXCESS WATER	EXCESS ACID,ESTER
0.05 %	-2.08 %	0.46 %
HYDROGEN	OXYGEN	CARBON
0.11 %	0.15 %	0.26 %