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DECOMPOSITION OF DIACETONE ALCOHOL
IN PACKED BEDS OF ION EXCHANGE RESINS

BY

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AND

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ABSTRACT

A study was made of the rate of decomposition of diacetone alcohol by anion exchange resins in a packed bed under adiabatic and isothermal conditions. Two different resins were compared: a conventional type gel structure resin, Amberlite IRA-400, and a newly marketed macroreticular resin, Amberlyst A-26.

In a substrate with low water content, the rate of decomposition of diacetone alcohol by Amberlite IRA-400 was controlled by intraparticle diffusion. This was due to shrinkage of the polymer chain matrix of the resin. When dry diacetone alcohol feed was introduced the amount of decomposition was not measurable.

It was found that the macroreticular type resin, Amberlyst A-26 was considerably more effective as a catalyst due to its porous structure. Decreasing the water content of the feed actually increased the rate of decomposition. Amberlyst A-26 effectively catalyzed the decomposition of dry diacetone alcohol. Intraparticle diffusion does not control the rate of decomposition over the range of variables studied.

The equilibrium concentration at 25°C for this reaction,using the Amberlyst resin,was determined by extrapolating to zero space velocity the concentration of acetone in the effluent. The value obtained was 88.95 weight per cent acetone. This is in reasonable agreement with the value reported by Davis and Burrows (6) of 88.27%, who conducted the decomposition reaction at 25°C in an agitated batch system using

barium hydroxide as a catalytic agent. A value of the equilibrium constant of K = 18.65 was calculated from the Amberlyst equilibrium concentration data at 25°C.

An attempt was made to develop a mathematical model for the flow reaction in a packed bed, using the simplifying assumption that a single step controlled the overall rate. Equations have been derived for the following cases:

1) First order kinetic control unidirectional.
2) Bidirectional first order kinetic control.
3) Bidirectional reaction, first order for the decomposition and second order for the formation of diacetone alcohol.
4) Film diffusion control.
5) Intraparticle diffusion control.

It was found that none of the above reaction mechanisms involving diffusion and reaction kinetics could be reduced to a linear or non linear form and solved with the data obtained using Amberlyst A-26 at 25°C over the entire range of variable studied. Therefore, the simplifying assumption that a single step controls the overall rate does not seem to apply for the system studied.

The effect of film diffusion was studied by varying the superficial velocity while maintaining all other variables constant. The differences in superficial velocity did not affect the conversions obtained using Amberlyst A-26. It was concluded that film diffusion to and from the bulk of the fluid did not influence the rate of decomposition of diacetone alcohol for superficial velocities in the range of 0.001 to 0.014 feet per second. This study, as well as the entire investigation, was conducted in the laminar flow region of low Reynolds Numbers.

The first order kinetic equation for the unidirection reaction will fit the experimental data for conversions below 85%. Above 85% conversion, the effect of the reverse reaction becomes apparent. The rate constant for the decomposition of diacetone alcohol by Amberlyst A-26 resin at 25°C was calculated and found to be $k = 0.0194$ sec.$^{-1}$ which compares favorably with a value of $k = 0.0205$ sec.$^{-1}$ reported by Akerlof (1) using 0.1N KOH for first order kinetics at the same temperature of 25°C. Basinski and Narebska (2) reported a value of $k = 0.000535$ sec.$^{-1}$ for the decomposition reaction at 25°C using Amberlite IRA-400 in a batch system with an ethanol-water substrate.

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INTRODUCTION

There has been considerable interest in the use of ion exchange resins as catalysts for a number of organic reactions that are catalyzed by acids or bases. Ion exchange resins are synthetic polymers (macromolecules or polyelectrolytes) which, though insoluble, simulate or react much as acids or bases and can be considered as solid gel acids or bases.

There are several advantages of using ion exchange resins rather than the conventional acids or bases, the most important of which are:

1) The ease of separation of product and catalyst which, in the case of conventional acids or bases, involves neutralization and several physical separation techniques such as distillation, washing, decantation, centrifuging, etc.
2) The equipment required for an ion exchange operation is fairly simple and economical and the process can be run as a continuous flow operation.
3) The resin systems exhibit greater selectivities than conventional acids or bases with resultant reduction of side reactions along with improvement of yield and quality of product.
4) The resin can usually be used repeatedly without regeneration in batch processes or for long periods of time in a continuous flow process before regeneration becomes necessary.

5) The corrosion problems encountered with conventional acids and bases are usually non-existent for resins.

Several shortcomings and limitations exist in the use of ion exchange catalysts in non aqueous organic media. By far the most important is that the gel structure of the resin shrinks with loss of water to the organic process stream. This tends to inhibit diffusion through the compactly shrunken gel and in effect, creates unfavorable reaction kinetics. Another important shortcoming is in the case of resin regeneration by polar solvents. The resin beads will swell appreciably during regeneration,but will revert to a shrunken state with the reintroduction of non-polar solvent feed. The alternate swelling and shrinking provokes stresses that cause progressive cracking and breaking of the resin beads. This attrition of the resin increases the pressure drop through the bed, increases the loss of resin, and occasionally causes mechanical breakdown of associated equipment. Finally, the temperature limits for ion exchange resins are relatively low. The most common type used, the divinylbenzene styrene polymers, start to decompose at 100°C. In the specific case of quaternary ammonium anion exchange resins, a further limitation of 45 - 60°C exists due to the decomposition of the ammonium radical.

The introduction of macroreticular ion exchange resins that have physical pores much larger than the openings in the gel structure of normal resins seems to alleviate some of the previously mentioned

4) Decomposition in amino-acid buffered solutions. (17)
5) Decomposition in a batch system catalyzed by an anion exchange resin. (2)

The above listed areas are in chronological order with the latest work concluded in 1961. This was the investigation of Basinski and Narebska (2) who reported work carried out in a small scale batch system using Amberlite IRA-400 as reaction catalyst in an alcohol-water substrate.

The present work investigates the catalytic decomposition of diacetone alcohol in packed anion exchange resin beds using a continuous flow process. Aqueous and non-aqueous feeds were employed. The experimentation was conducted under adiabatic and isothermal conditions for the Amberlite IRA-400 gel resin and under isothermal conditions for the Amberlyst A-26 macroreticular resin.

disadvantages. The relative rates of diffusion to the active sites of the resin are much faster due to increased porosity and surface area. Macroreticular resins are much more resistant to osmotic shock induced by alternate swelling and shrinking; therefore, their rate of attrition is reduced.

Very little information or data is available concerning the relative performances of macroreticular and standard gel type resins. The purpose of this investigation is to examine the relative performances of a macroreticular resin Amberlyst A-26 and a conventional gel resin Amberlite IRA-400 with respect to the diacetone alcohol decomposition reaction and to extend the work carried out by previous investigators on this reaction.

$$\underset{\text{Diacetone Alcohol}}{(CH_3)_2COHCH_2COCH_3} \rightleftharpoons \underset{\text{Acetone}}{2CH_3COCH_3}$$

This reaction was chosen because it is fairly well known and has a well established kinetic mechanism.

Research work previously reported on the decomposition has been confined to the areas listed below:

1) Decomposition in a 10% aqueous solution using a hydroxide solution as catalyst in a batch system. (12)
2) Decomposition in alkali hydroxide-alkali salt solutions in a batch system. (1)
3) Decomposition in a non-aqueous batch system using dry powdered barium hydroxide as catalyst. (6)

THEORY

The Resins:

The anion exchange resins used in this study in the OH form can be considered very high molecular weight polybases in which the OH radicals are part of quaternary ammonium groups held together by a three dimensional hydrocarbon network produced by the polymerization of styrene and divinylbenzene. The degree of crosslinking of the polymer is dependent on the amount of divinylbenzene used in the copolymerization.

When the resins are in contact with water they behave like gels. They are capable of absorbing and retaining the water. The OH radicals become ionized and leave the polymer chain or matrix and are free to diffuse within the resin and to some extent to the water outside the resin. This absorption of water involves an increase in volume of the resin or swelling which is limited by the degree of crosslinking of the resin. The lower the degree of crosslinking of the resin, the more the resin can swell and the more the matrix expands to accommodate the water volume. This expansion of the matrix on swelling increases the space between coils of the polymer chain.

From the former paragraph it would seem desirable to use resins with very low degress of crosslinkage to obtain an expanded matrix that would offer very little resistance to diffusion and would increase the mobility and effectiveness of the OH radical. The degree of crosslinkage also affects the physical and chemical stability and the mechanical strength of the resin. Enough crosslinking must be provided to fulfill the requirements in this area.

In the particular case of the newly developed macroreticular resins due to a refinement in the polymerization technique, physical extra-gelular pores are left in the resin. Therefore, the free space in the resin is not limited by the degree of crosslinking and swelling of the resin. The access to the interior of the resin is guaranteed by the physical pores and the degree of crosslinkage can be increased to obtain better mechanical properties. This increased degree of crosslinkage means that macroreticular resins will be less free to swell and shrink than the conventional resins.

Swelling in Organic and Mixed Solvents

Liquids other than water can be sorbed by the resin and will also produce an increase in volume or swelling. The degree of swelling induced is in general a function of the affinity of the resin for the solvent. In general, the resins swell more with increased polarity of the solvent although some exceptions exist.

If a mixture of two liquids are used in the general case, the resin will sorb one more strongly than the other. In fact, the preference may be so strong that one of the liquids may be excluded altogether from the resin. It is possible,due to this preferential sorption,to maintain in the resin phase a liquid which is not present at all or only in very small quantities in the fluid in equilibrium with the resin. As a matter of fact, it is possible to have only water in the resin and only solvent in the fluid outside the resin if a solvent of extremely low polarity like kerosene is used.

In the case of diacetone alcohol and water the resin has a stronger affinity for water. If a water swollen resin is in contact with a stream of dry or low moisture diacetone alcohol and acetone, it will not lose all of its water. The resin willretain some of the water but it will sorb some diacetone alcohol and acetone.

The Catalytic Process

The catalytic effect on the diacetone alcohol decomposition by ion exchange resins should be considered homogeneous rather than hetergeneous catalysis inasmuch as the actual catalyst is the counter ion of the resin. The catalytic effect is due to the presence of OH ions in the intersticial liquid inside the resin gel.

It would be difficult to explain the fact that ion exchange resins and conventional acids or bases behave identically as catalysts. This is in direct contrast with the more common reaction in which the reaction occurs only at the catalyst surface. The following steps can then be postulated for a reaction catalyzed by an ion exchange resin:

1) The reactants must diffuse from the bulk of the fluid stream to the resin surface and into the resin phase.
2) A homogeneous catalytic reaction occurs in the resin gel.
3) The product must diffuse out of the resin and to the bulk of the fluid.

Film diffusion from the bulk of the fluid to ion exchange resins is not different from the general case and will not be discussed here in any detail. If this diffusion rate is fast enough and equilibrium is reached, the concentration at the resin interface will be essentially that of the bulk fluid.

The diffusion into the resin phase is actually a sorption process. The composition in the resin phase when equilibrium with the bulk fluid is reached may be different from the composition of the bulk fluid. The composition will be proportional and related by a distribution constant as in the general case of distribution of solutes between two immiscible solvents.

Kinetic Mechanism

The mechanism of the homogeneous catalytic decomposition of diacetone alcohol by bases is fairly well developed in the literature. The rate of decomposition of diacetone alcohol is a first order reaction with respect to the concentration of the diacetone alcohol. The catalysis mechanism, as defined by Frost and Pearson (7), involves the formation of an activated complex with the OH^-, decomposition of the activated complex and regeneration of the OH^- in three steps:

$$CH_3COCH_2COH(CH_3)_2 + OH^- \longleftrightarrow CH_3COCH_2C(CH_3)_2O^- + H_2O$$

$$CH_3COCH_2C(CH_3)_2O^- \longleftrightarrow (CH_3)_2\,CO + CH_3COCH_2^-$$

$$CH_3COCH_2^- + H_2O \longleftrightarrow (CH_3)_2\,CO + OH^-$$

Therefore, the concentration,or rather the activity of the OH^- radical in the phase where the reaction is taking place, will also affect the rate of decomposition of diacetone alcohol.

Summarizing, it can be said that the date of decomposition of diacetone alcohol is pseudo first order being proportional to the first power of the concentration of diacetone alcohol and the first power of the activity of the OH^- radical.

The reverse reaction, the formation of diacetone alcohol from acetone, would involve the same mechanism and the same statements made for the decomposition of diacetone alcohol are true also for the reverse reaction.

EXPERIMENTAL

Operating Procedures

Resin Properties	IRA-400	A-26
Maximum Operating Temperature	60°C	45°C
Density (backwashed and drained bed volume)	44#/ft^3	43#/ft^3
Moisture holding capacity	48%	64%
Effective Size	0.38 - .45 mm	0.45 - 0.55 mm
Experimental Exchange Capacity	4.1 ± 0.1	4.1 ± 0.1 meq/g Dry Resin

Diacetone Alcohol Feed	
Density at 25°C	0.938 gm/cc
Viscosity at 25°C	6.0 centipoises
Purity of feed supply	1.0 - 5.0% acetone 0.2 - 0.8% mesityl oxide

The variation in feed purity was due to two factors. First, the shipment of different material lots by the supplier and second, the slow but steady decomposition of the supply over a period of months while awaiting use.

The column containing the resin was put into operation no later than 24 hours after regeneration of fresh resin. This time factor allowed for minimum decomposition of unstable quaternary ammonium groups in the resin. The resin used in one series of runs was analyzed and discarded. Fresh resin was regenerated for each new series of runs. The system of regenerating fresh resin contributed to the consistency of the runs and held any possible effect of resin fouling to a minimum.

Adiabatic Operation This operation was carried out using both Amberlite IRA-400 and Amberlyst A-26 resins. At a feed temperature of 25°C the temperature difference between ambient and the column was small enough so that heat transfer to the bed was found to be negligible. Therefore, it was decided not to insulate the column in order to observe the bed at all times. Thermometers for control and measurement were placed in four areas of the system: in the feed reservoir, in the constant temperature water bath, in the column approximately two inches below the resin surface, and in the product outlet stream.

Diacetone alcohol was pumped from a glass carboy through a glass heat exchanger to the top of the packed column. The glass heat exchanger was suspended in a constant temperature water bath at 25°C. The pump employed for diacetone alcohol feed had a volumetric flow rate range of 15 to 100 cc per minute. When a predetermined flow rate was established, the resin bed was allowed to attain equilibrium with the feed. In this process the resin would lose water to the feed and absorb solvent from it.

At the equilibrium point the bed contracted to a volume dependent upon the aqueous content of the feed. This equilibrium point was established by three methods: the constancy of the bed height, the reproducibility of effluent composition as measured by successive G.L.C. analyses, and by Karl Fisher moisture determination on the product stream.

Experimental runs were carried out by limitation of the system variables to feed flow rate and feed moisture content.

In the first series of runs with variable flow rates, samples were taken at the apparent equilibrium points and analyzed by the gas chromatograph at 10 to 15 minute intervals until the results of three consecutive samples checked within 0.2 per cent. The feed flow rate was then changed to the next desired rate and the same criteria used to check the attainment of steady state. Reaction data pertaining to these series of Adiabatic runs are contained in Table 2 for Amberlite IRA-400 Resin and Table 4 for Amberlyst A-26 Resin.

In the second series of runs, the feed with the highest water content was processed first with subsequent sampling and analysis. This was followed by the addition of more concentrated feeds. This order of feed addition accomplished progressive dehydration of the catalyst bed until equilibrium with the driest feed was attained. Reaction data pertaining to these series of adiabatic runs are contained in Tables 1 and 3 for Amberlite IRA-400 and Amberlyst A-26 respectively.

Since the decomposition of diacetone alcohol is an endothermic reaction, the temperature gradient within the catalyst bed was of special interest. When steady state was attained, temperature measurements were made at two locations in the system. The first point was two inches below the bed surface and the second in the product stream. Measurements taken over the entire series of adiabatic experimentation revealed a maximum temperature gradient of 2°C within the bed. The resin bed was an efficient heat sink due to its large head capacity. Even though the temperature gradient within the bed was negligible at equilibrium conditions, the bed temperature was substantially lower than that of the feed.

Isothermal Operation Isothermal experimentation followed essentially the same mode of operation as the previously described adiabatic work. Reaction variables were limited to feed flow rate, column diameter, and weight of catalyst. Experimentation was confined to Amberlyst A-26 resin using dry diacetone alcohol feed.

Isothermal operation was obtained by jacketing three different diameter columns and recirculating water from the water bath through the jacket to maintain a bed reaction temperature of 25°C. The feed reservoir was also maintained at 25°C by immersion in a separate constant temperature bath. The same criteria described in the adiabatic section was used to establish that steady state was reached. The sampling and analyzation techniques were also the same as described in the adiabatic section.

At the conclusion of a series of isothermal or adiabatic runs, the column was drained and the resin in the column allowed to discharge by gravity. A representative sample was obtained for moisture determination and ion exchange capacity. A more detailed description of the four series of isothermal runs may be obtained from Tables 5 through 8.

Regeneration of Amberlite IRA-400 to Free Base Form

Amberlite IRA-400 is shipped in the chloride salt form and must be regenerated with a 5 per cent sodium hydroxide solution before advantage can be taken of its strong base catalytic properties. Due to the fact that the rate of flow during the regeneration and rinse steps has a marked effect on the final exchange capacity, it was necessary to standardize these rates and also the amount of sodium hydroxide so as to achieve minimum variation in ion exchange capacities from one run to another. Since all runs with IRA-400 resin were made with 510 grams (wet basis) of unregenerated resin, the regeneration procedure used was:

1) The wet unregenerated resin was weighed to ± 0.2 gram and added slowly but continuously as a slurry in deionized water to the column two-thirds filled with deionized water. The column was allowed to drain as needed to prevent overflow. The resin was supported by a one inch layer of 2 mm glass beads added on top of a plug of glass wool.
2) A prepared solution of 3.75 liters of 5% sodium hydroxide solution was pumped through the bed at a rate of 40 cc per minute.
3) The resin was then rinsed with deionized water pumped through the column at a rate of 150 cc per minute. The rinse was continued until 100 cc of the effluent solution was neutral to phenolphthalein upon the addition of two drops of N/10 HCL.

Regeneration of Amberlyst A-26 to Free Base Form

Amberlyst A-26 is also shipped in the chloride form and must be regenerated in a similar manner to Amberlite IRA-400. The only major difference in the regeneration procedure of Amberlyst A-26 was the rinse flow rate. A rinse flow rate of 40 cc per minute was used for the Amberlyst A-26 resin as per manufacturer's suggested procedure. (15) (16)

Isothermal runs were made using two different amounts of Amberlyst resin. In the experimental runs made with the standard 510 gram bed, Runs 10 through 21, a regenerant solution of 3.75 liters of 5% sodium hydroxide was used. When the bed size was reduced to 170 grams, in Runs 22 through 38, the amount of regenerant was reduced proportionally to 1.25 liters of 5% sodium hydroxide solution.

The previously mentioned standarized procedures resulted in exchange capacities of 4.1 ± 0.1 meq/gram dry resin for both Amberlite IRA-400 and Amberlyst A-26 resins.

Analytical Procedure for Composition of Feed and Product Streams

Three possible methods of analysis were surveyed:

1) Ultraviolet Spectrophotometry
2) Infrared Spectrophotometry
3) Gas Liquid Chromotography

The accuracy of the Ultraviolet Spectrophotometric method is limited considerably due to the fact that the absorbance peaks of acetone and diacetone alcohol are very close together. Diacetone alcohol peaks at 276-283 mu and acetone 270-273 mu depending on the solvent used. Therefore, background corrections would have been necessary. Mesityl oxide would have been very easy to measure. It has a very high abosrbance peak at a lower wave length. This compound would interfere with the measurement of acetone or diacetone alcohol even though it has a minimum in its U.V. spectra in the 270-280 region due to its extremely high absorbance.

Infrared Spectrophotometry is very convenient and useful for identification of organic compounds and qualitative work, but is not sensitive enough for fine quantitative analysis. It could not pick up small amounts of acetone in diacetone alcohol or vice versa. This was due to the fact that the compounds involved are closely related and have similar functional groups.

It was finally found that Gas Liquid Chromotography gave very accurate and reproducible results with a minimum of sample preparation and in a short period of time. The only disadvantage was that even though the actual time of analysis was less than ten minutes, the instrument required a period of several hours warm up time to reach equilibrium. The following is a list of equipment characteristics and operating conditions of the gas chromotograph:

Instrument	F & M Model 500 Gas Chromatograph.
Partition Column	
Liquid	Carbonwax 1540, 20% on Chromosorb

Solid Support	Chromosorb P 60-80 mesh
Length	4 Feet
Diameter	1/4 Inch

Operating Conditions

Column Temperature	80°C
Detector Block Temp.	80°C
Injection Port Temp.	100°C
Partition Gas	Helium
Gas Flow Rate, Column	80 cc/min.
Gas Flow Rate, Ref.	30 cc/min.
Detector Filament	150 milliamperes
Chart Speed	1 inch/min.
Sample Size	1 microliter
Attenuation	As needed to keep peaks on scale

The only sample preparation was drying over anhydrous sodium sulfate. A small amount of sample was shaken vigorously with the sodium sulfate and allowed to settle out for a few minutes. A one microliter Hamilton syringe was filled with the supernatant liquid and used to inject the sample into the column. Samples of known composition were analyzed with and without addition of anhydrous sodium sulfate. After allowing to stand for different periods of time, no change in sample composition could be detected.

Although the analysis could be postponed for two or three hours without any detectable change, samples were analyzed immediately.

The retention times obtained for the products involved at the conditions listed above were as follows:

Acetone	0.75 minutes
Mesityl Oxide	1.75 minutes
Diacetone Alcohol	5.25 minutes

The internal normalization method was used to calculate the composition from the chromatogram. The area under the respective peaks was obtained from the disc integrator tracing and converted to percentages. The weight percentages were calculated from the area percentages by the use of a calibration curve for acetone and diacetone alcohol. This calibration curve was plotted by preparing and analyzing known mixtures of pure spectro grade reagents. The amounts of mesityl oxide involved were so small that it was not desirable or necessary to use any calibration curve for this component. The area present under its respective peak was assumed identical to the weight per cent of mesityl oxide in the sample.

The reproducibility of the analytical method as outlined above was found to be ± 0.1% for identical samples run consecutively. The overall accuracy of the method was estimated to be ± 0.5% minimum, allowing for the error in the calibration and the reproducibility of instrument operating conditions from one day to the other.

Analytical Procedure For Resin, Feed and Product Moisture Contents

At the end of an experimental run, the resin is discharged from the column and a representative sample obtained. The Karl Fischer

Method which yields very accurate moisture determinations was employed for the resin system.

The resin sample was weighed in an analytical balance into standard Karl Fischer weighing bottles. The size of the sample varied from one to five grams depending on the expected moisture content. Twenty-five cc of a 3:1 chloroform methanol solution were pipetted into the bottle. Then 10 cc of standard Karl Fischer Reagent was added to the resin by means of burette. The resin solution was then titrated with a known water standard. The endpoint of this titration was ascertained by means of a color change and by potentiometric readings. For each experimental run at least two samples were titrated with the results expected to check within ± 0.1% of one another.

In addition to checking the moisture content of the resin at the conclusion of a series of experimental runs, the Karl Fischer Moisture Determination Method was used to measure the water contents of the feed and product. The moisture content of the product was especially important because it established the time the bed was initially in equilibrium with the feed and signaled the starting point of gas chromotography on the product. The moisture of the feed was determined in duplicate for each series of runs and the moisture of the product at least once for each experimental run.

Analytical Procedure for Ion Exchange Capacities of Resins

In order to check the regenerated resin for consistency of exchange capacity, samples of the resin were obtained prior to and after experimentation. After several series of runs the analysis of used resin was discontinued when it became apparent that the capacities before and after experimentation did not vary more than ± 0.1 milliequivalent per gram of dry resin.

For each series of runs an excess of ten grams of resin was regenerated to afford sufficient material for analytical purposes. Prior to experimentation a ten gram aliquote sample of resin was removed from the column. Five grams of this sample were weighed out on an analytical balance to three place accuracy and then tray dried at 100°C until constant weight was attained. The solid content of the aliquote sample was then calculated.

From the same ten gram aliquote, two - 2 gram samples were weighed with three place accuracy into separate Erlenmeyer flasks. Seventy-five cc of 0.1% phenolphthalein in 3A alcohol solution was added to each flask. The resin samples were titrated with 0.100 N HCl until the resin beads changed in color from red to normal amber. At this point the pH of the solution was checked on a Beckman pH Meter. When a pH of 7.5 ± 0.2 was attained, the volumetric titration was discontinued and an end point was established. The ion exchange capacity for each series of runs were calculated from the following formula:

$$\text{Meq/gm. dry regenerated resin} = \frac{(\text{Titration in cc})\ (\text{N of Acid})}{\text{Dry weight of titrated resin}}$$

CALCULATIONS

Equilibrium Constant

Conversions approaching equilibrium were obtained using 510 grams of Amberlyst A-26 as catalyst at 25°C and low flow rates. The composition at equilibrium conditions was calculated from stoichiometric considerations and the concentration of acetone extrapolated to zero space velocity in a concentration versus space velocity plot, Figure No. 7. Mole fractions of acetone and diacetone alcohol were calculated for the equilibrium composition. The equilibrium constant, K, was calculated using these mole fractions in the equation that follows:

$$(1) \qquad K = \frac{[C_A]^2}{[C_D]} = 18.65$$

Kinetic Mechanism

A rigorous treatment of the kinetics of the decomposition of diacetone alcohol, according to the mechanisms postulated in the theory, should include the effect of the hydroxyl ions in the rate according to the equation proposed by Frost and Pearson (7):

$$(2) \qquad r = k \; C_D \; C_{OH^-}$$

This approach could not be used when using ion exchange resins as catalyst because it is impossible to measure or calculate the activity or concentration of the hydroxyl ion inside the resin particles where the reaction is taking place. The alternative approach used was to carefully control the regeneration of the resin to obtain identical exchange capacities and assume that the resulting concentration and activity of the hydroxyl radical would remain constant. In that case, the concentration of the OH^- can be included in the rate constant and the equation for the rate decomposition can be written:

$$(3) \qquad r = k_D \, C_D$$

The same considerations are involved in obtaining a rate equation for the reverse reaction, the formation of diacetone alcohol from acetone.

Equation for First Order Decomposition

Helfferich (9) derived the following:

$$(4) \qquad C_D = C_D^{\circ} e^{\left(-k\lambda \frac{1-\beta}{v} z\right)}$$

The above equation was converted to the linear logarithmic form:

$$(5) \qquad \ln \frac{C_D}{C_D^{\circ}} = -k\lambda \frac{1-\beta}{v} z$$

A plot of $\ln C_D/C_D^{\circ}$ versus $z(1-\beta)/v$ was prepared, Figure No. 10. The value of β used was 0.4; this value was taken from the porosity correlations for packed beds as defined in Brown (4). From an inspection of Figure No. 10 it is apparent that this equation fits very well for conversions below 85%. The value of $k\lambda$ was calculated for each one of the eleven points where conversions were below 85%. Arithmetic average of the values obtained was:

$$k\lambda = 0.01342 \text{ sec}^{-1}$$

It was assumed that the molar distribution coefficients of diacetone alcohol and acetone are similar when compared against the molar distribution coefficient of water. The molar distribution coefficient of diacetone alcohol would then be equal to the weight fraction of solvent in the interstitial liquid. The value of λ obtained on this basis from Table 10 is $\lambda = 0.693$. This permitted us to calculate a value of k = 0.0194 sec.$^{-1}$ for Amberlyst A-26 at 25°C.

Internal Reaction Control: First Order Decomposition and First Order Reverse Reaction

The differential equation derived for this case is:

$$\frac{dC}{dz} = -k'_D C_D \frac{1-\beta}{v} + k'_A C_A \frac{1-\beta}{v} \tag{6}$$

The concentration of acetone was expressed in terms of the concentration of diacetone alcohol, and the rate constant of the reverse reaction substituted by K/k' . The equation was then integrated and the following expressions results:

$$\ln\left(2\frac{K}{k'_D} + k'_D\right)C_D - 2\frac{K}{k'_D}C^0_D = \frac{1-\beta}{v} z \left(2\frac{K}{k'_D} + k'_D\right) \tag{7}$$

An attempt was made to fit the above equation to the data using the value of k' obtained from Equation (3) for conversions below 85%, and a value of the equilibrium constant K assuming first order reverse reaction. The equation would not fit the experimental data.

Internal Reaction Control: First Order Decomposition-Second Order Reverse Reaction

The differential equation derived for this case is:

$$\frac{dC}{dz} = -k'_D C_D \frac{1-\beta}{v} z + k'_A C_A^2 \frac{1-\beta}{v} \tag{8}$$

The concentration of acetone was expressed in terms of the concentration of diacetone alcohol. The equation was then integrated and the following expressions result:

$$\text{(9a)} \qquad \frac{1}{\sqrt{b^2-4ac}} \ln \frac{2ax+b-\sqrt{b^2-4ac}}{2ax+b+\sqrt{b^2-4ac}} = \frac{1-\beta}{v} z \qquad \text{for } b^2 > 4ac$$

$$\text{(9b)} \qquad \frac{2}{\sqrt{4ac-b^2}} \tan^{-1} \frac{2ax+b}{\sqrt{4ac-b^2}} = \frac{1-\beta}{v} z \qquad \text{for } b^2 < 4ac$$

$$\text{(9c)} \qquad -\frac{2}{2ax+b} = \frac{1-\beta}{v} z \qquad \text{for } b^2 = 4ac$$

where $a = 4k'_A$

$b = -(k'_D + 4k'_A C^o_A + 8k'_A C^o_D)$

$c = (4C^o_D C^o_A + C^{o\,2}_A + 4C^{o\,2}_B)k'_A$

$x = C_D$

The value of $k'_D = 0.01342$ was used in the above equation. The k' was calculated from this value of k'_D and the equilibrium constant K calculated from the equilibrium composition. The equation did not fit the data.

Film Diffusion Control

The equation proposed by Helfferich (9) for film diffusion control is:

$$\text{(10)} \qquad C_D = C^o_D \, e^{\left(-3D \frac{1-\beta}{\delta v r_o} z\right)}$$

The film thickness δ was calculated from the equation proposed by Gilliland (8) and is as follows:

$$(11) \qquad \delta = 0.1\, r_o\, Re^{-0.84}$$

The proposed equation did not fit the data.

Intraparticle Diffusion Control

The equation for intraparticle diffusion given by Helfferich (9) is as follows:

$$(12) \qquad C_D = C_D^\circ\, e^{\left(-3k_s \frac{1-\beta}{v} z\right)}$$

It could not be made to fit the whole range of experimental data.

DISCUSSION OF RESULTS

Amberlite vs. Amberlyst

The gel type resin, Amberlite IRA-400, did not appreciably catalyze the decomposition reaction unless significant amount of water were present in the system. Runs performed with dry (0.3%), 2%, and 4% water in diacetone alcohol feed yielded corresponding equilibrium bed moistures of 6.4%, 18.9% and 24%. Significant conversions were not attained from these runs. Sizeable conversions were not achieved until a feed of 8% water in diacetone alcohol was introduced. The equilibrium moisture content of the resin using this feed was 31%. The conversion obtained with feed containing 8% moisture was found to be ten times greater than with feeds containing 4%.

The proposed explanation for the above results is related to the fact that the degree of swelling of the resin is proportional to its water content. This is shown in the graphs relating bed height to per cent water in the feed and in the resin. See Figures Nos. 2 and 3. Shrinkage and swelling of the bed is a result of shrinkage and expansion of the resin polymer chains.

The rate of diffusion of reactants and products in and out of the resin gel is dependent upon the free space or pores available. This free space decreases with gel shrinkage because of a corresponding decrease in distance between loops of the polymer spiral chain.

Therefore, it is proposed that at low bed water content, the rate of diffusion in and out of the gel is negligible and correspondingly small conversions are obtained at the gel surface. Intraparticle diffusion was found to be the rate controlling step when using low moisture feeds for the range of variables studied with Amberlite IRA-400.

The second resin studied, Amberlyst A-26, is a macroreticular ion exchange resin with discrete physical extra-gelular pores. This results in a slightly lower bulk density when compared to Amberlite IRA-400 and a given weight will yield a larger bed volume. The observed degree of shrinkage and swelling of the A-26 resin was much smaller than that of the IRA-400 resin due to its higher degree of crosslinkage.

Another interesting quality of Amberlyst A-26 was its tendency to retain a larger amount of water than IRA-400 when used with feed moisture streams containing 0.2 to 4.0 water.

The effectiveness of the A-26 resin as a catalyst did not decrease with corresponding decreases in resin water contents. In fact, due to the corresponding increase in the diacetone alcohol concentration in the feed, the conversion obtained with dry feed was larger than that obtained with moist feeds. As the concentration of water in the feed stream was increased the conversions obtained were progressively lower. This can be seen from Figure No. 4.

The smaller bed length and greater degree of shrinkage or the smaller percentage of water retained in the resins are not enough to explain the difference in conversions. For example, in experimental runs 3 and 11 where the water contents of the resins are approximately the same, conversions were 4.7% for Amberlite IRA-400 and 68.3% for Amberlyst A-26. In experimental runs 4 and 11 with identical bed lengths and greater resin water content in the IRA-400 run, the macroreticular resin catalyst achieved substantially higher conversions.

The higher conversions obtained with Amberlyst A-26 as compared to Amberlite IRA-400 under similar conditions can be explained by the fact that intraparticle diffusion is no longer the rate controlling step. Further evidence is the increased conversions obtained while decreasing the moisture content of the feed as opposed to the decreasing conversions obtained with the IRA-400 resin.

Equilibrium Constant

Conversions approaching equilibrium were obtained using low flow rates with Amberlyst A-26 resin. These runs were made under isothermal conditions at 25°C. The concentration of acetone in the product at equilibrium conditions was determined by extrapolating to zero space velocity in a concentration of acetone in the effluent versus space velocity plot. See Figure No. 7. The value obtained by this procedure was 88.95% acetone. A value of K = 18.65 was calculated from the extrapolated concentration of acetone and the concentration of diacetone alcohol from stoichimetric requirements.

The experimental value of the equilibrium concentration is in good agreement with the value reported by Davis and Burrows (6) of 88.27% acetone, who conducted the decomposition reaction in a batch system using barium hydroxide as a catalyst. An equilibrium concentration of 89.0% acetone was reported by Basinski and Nerebska (2), who used Amberlite IRA-400 in an ethanol-water substrate. The latter work was conducted in a batch system.

Rate Controlling Step

It is usually assumed in studying catalysis problems quantitatively that of the several rate processes involved one is much slower than the others and the overall process progresses at this rate while the faster ones proceed essentially at equilibrium conditions. Otherwise, the mathematical treatment is impossible. The different steps involved in this care have already been discussed in the theory section and are as follows:

1) Film diffusion of the reactants from the bulk of the fluid to the resin interface.
2) Intraparticle diffusion into the catalyst beads.
3) Chemical reaction catalyzed by the OH ions in the resin phase.
4) Intraparticle diffusion out to the resin interface.
5) Film diffusion to the bulk of the fluid.

Helfferich (9) has developed rate equations for the diffusion steps, and for the kinetic step in the particular case of a first order unidirectional decomposition. The authors of this thesis also developed the equations for the kinetic step for two more cases: bidirectional reaction, first order forward and reverse, and bidirectional reaction first order decomposition but second order reverse reaction.

An attempt was made to fit each one of the above equations to the experimental data contained with Amberlyst A-26 resin and dry diacetone alcohol feed at 25°C. Even the ones that could not be reduced to a linear form were tried by trial and error, but all the attempts were unsuccessful. None of the equations fit the experimental data over the entire range covered.

Film Diffusion

Three series of experimental runs were made using different diameter packed beds to study the effect of film diffusion on the rate of decomposition of diacetone alcohol by Amberlyst A-26 under isothermal conditions at 25°C. An identical amount of catalyst, 170 grams, from the same lot was used in all three cases, and the volumetric flow rate was varied over the same range, 15 to 100 cc per minute.

The space velocity and retention time are dependent only upon the amount of resin in the bed and the volumetric flow rate. They are not affected by the difference in diameter of the bed. The superficial velocity of the bulk of the fluid past the resin particle is a function of the volumetric flow and the cross section area of the bed. Therefore, at the same volumetric flow rates, the superficial velocity was greater for the smaller diameter bed and decreases with increase in cross sectional area when going to larger diameter beds.

The resistance to film diffusion should increase with lower superficial velocities due to lower Reynolds Numbers obtained which would result in an increased film thickness. The higher resistance to film diffusion should result in lower conversions when using larger diameter columns due to a decrease in the overall rate of the process. There was no difference in conversions obtained by changing the column diameters from 1-1/4 to 1 to 7/8 inch as can be seen from Figure No. 8. Therefore, for superficial velocities of 0.001 to 0.014 feet per second, film diffusion to and from the bulk of the' fluid was fast enough not to affect the rate of decomposition.

Rate Constant of the Decomposition Reaction

Although no satisfactory equation could be developed for the entire range of experimental data, it was found that the equation for the unidirectional decomposition of diacetone alcohol fitted the data for conversions below 85%. A rate constant of $k = 0.0194$ sec.$^{-1}$ was obtained by taking the average of the rate constants calculated from eleven experimental runs in this range and using a value of the molecular distribution constant $\lambda = 0.693$.

This rate constant compares very well with the value of $k \simeq 0.0205$ sec.$^{-1}$ obtained by Gosta Akerlof at 25°C (1) using potassium hydroxide in an 0.1N concentration as a catalyst. Basinski and Nerebska (2) reported a value of $k = 0.0005 \text{ sec.}^{-1}$ for the first order decomposition of diacetone alcohol at 25°C using Amberlite IRA-400 in a batch system with an ethanol-water substrate.

Catalyst Deactivation and Fouling

The exchange capacity of the resin was checked before and after several of the runs. No difference could be detected in exchange capacity after four gallons of diacetone alcohol had been processed through the 170 gram bed. This would mean that in this type of service the resin could be used for extended periods of time before regeneration would be needed.

Anion exchange resins are effective organic scavengers. They efficiently absorb high molecular weight organic materials. This was apparent in the experimental work on diacetone alcohol decomposition. The diacetone alcohol feed had a very light amber color due to the presence of some impurity. This impurity did not come out with the effluent but was retained in the resin, which darkened appreciably. Even though the resin color turned progressively from a light tan to a dark brown the performance did not change. The conversions obtained at the start of the run could be reproduced at the end and the exchange capacity did not decrease as already has been mentioned.

Mesityl Oxide Formation

The formation of mesityl oxide from acetone according to the equation:

$$\underset{\text{acetone}}{2\,CH_3\,COCH_3} \rightleftharpoons \underset{\text{mesityl oxide}}{(CH_3)_2C = CHCOCH_3} + \underset{\text{water}}{H_2O}$$

is also catalyzed by ion exchange resins in the OH form.

It was found that at 25°C. the amount of mesityl oxide formed was usually only a few tenths of a per cent except for a few runs where very high conversions to acetone were achieved and the amount of mesityl oxide formed increased up to 1.5%. Still these levels of mesityl oxide formation are too low to justify or permit a quantitative study and should not affect appreciably the decomposition of diacetone alcohol.

CONCLUSIONS

The decomposition of diacetone alcohol is catalyzed by anion exchange resins in the hydroxyl form. Both resins studied, the gel type Amberlite IRA-400 and the macroreticular type Amberlyst A-26 will effectively increase the decomposition in the water swollen state.

The introduction of dry diacetone alcohol to a packed bed of the gel type resin resulted in loss of nearly all its swelling water and in considerable contraction of the resin bed. The macroreticular resin, however, retained a larger proportion of its water content when dry feed was supplied to the bed and the observed decrease in bed height was also smaller.

The Amberlite IRA-400 resin will not effectively catalyze the decomposition of dry diacetone alcohol. In contact with dry diacetone alcohol it will lose its water content and shrink. Once the resin is no longer swollen the diffusion into the gel is virtually impossible and the decomposition reaction does not proceed at a measurable rate for non-aqueous media.

For feeds containing up to 10% moisture the rate controlling step for Amberlite IRA-400 is intraparticle diffusion. This is the result of increased resistance to diffusion within resin particles due to shrinkage of the polymer chain.

The Amberlyst A-26 resin was found to be much more effective as a catalyst than the Amberlite IRA-400 due to its porous structure. The rate of diffusion into the catalyst beads was much faster and the conversions obtained under similar conditions much higher. Amberlyst's effectiveness as a catalyst did not decrease upon loss of moisture to the diacetone alcohol, due to the fact that intraparticle diffusion is not limited by the swelling of the resin. This is due to the presence of physical pores available for diffusion in the Amberlyst structure. Intraparticle diffusion is not rate controlling for Amberlyst A-26.

The concentration of acetone at equilibrium conditions using Amberlyst A-26 at 25°C was 88.95%. This is in good agreement with the value of 88.27% obtained by Davis and Burrows (6) using barium hydroxide as catalyst, and the value of 89.0% of Basinski and Narebska (2) using Amberlite IRA-400 in a batch system. The equilibrium constant calculated from Amberlyst A-26 data was found to be $K = 18.65$.

The rate constant for the first order decomposition of diacetone alcohol was calculated from the experimental data obtained using Amberlyst A-26 at 25°C in the range of conversions below 85%. The value of the rate constant $k = 0.0194$ sec.$^{-1}$ was obtained by using a value of the distribution constant of diacetone alcohol between the bulk fluid and the resin of $\lambda = 0.693$. The value of the rate constant obtained compares very favorably with the value of $k = 0.0205$ sec.$^{-1}$ by Akerlof (1) using 0.1 N potassium hydroxide at 25°C. Basinski and Narebska (2) reported a value of $k = 0.000535$ sec.$^{-1}$ for the first order decomposition of diacetone alcohol in an ethanol-water substrate by Amberlite IRA-400.

The fact that the values for the equilibrium and rate constants using Amberlyst A-26 are similar to those obtained for inorganic bases support the conclusion that the resin can be considered essentially high molecular weight polybases in which the hydroxyl radicals are ionized and mobile within the polymer matrix. These hydroxyl ions in the resin matrix homogeneously catalyze the decomposition of the diacetone alcohol which has diffused into the resin.

An unsuccesful attempt was made to develop a mathematical equation to fit the whole range of data including the high conversions near the equilibrium point assuming that only one of the rate steps controlled the overall rate of decomposition.

The effect of film diffusion was studied by varying the superficial velocity while maintaining the other variables constant. This was accomplished using the same amount of resin in different diameter columns. The difference in superficial velocity did not affect the conversions obtained. It was concluded that film diffusion to and from the bulk of the fluid did not appreciably influence the rate of decomposition of diacetone alcohol by Amberlyst A-26 at 25°C over the range of superficial velocities between 0.001 to 0.014 feet per second.

It was found that the ion exchange capacity of the resin and its activity as a catalyst did not decrease during a series of experimental runs. Regeneration will be needed only after extended periods of operation in this service. Fouling will be more of a problem than the loss of activity. The resin absorbed a small amount of colored impurities present in the diacetone alcohol feed, as can be appreciated from the fact that the effluent from the bed was colorless, but the resin turned progressively darker during the runs.

The formation of mesityl oxide is also catalyzed by Amberlyst A-26. For the experimental conditions covered, the amounts formed were too small, in most cases, not even detectable except when large conversions to acetone were obtained. This indicates that mesityl oxide was formed from acetone rather than from diacetone alcohol.

SUGGESTIONS

A study of the effect of temperature on the rate of diacetone alcohol decomposition by Amberlyst A-26 would yield information helpful in understanding the mechanism of the overall process. This study would be limited to a narrow temperature range due to the decomposition of the active groups of the resin at temperatures above 45°C.

Different particle sizes of resin could be used as catalysts and the effect on the rate of decomposition observed. This information would be of great value in determining the effect of diffusion within the resin particles if narrow cuts of the same resin could be prepared over a wide enough range to get measurable differences in the rate of decomposition.

The rate of formation of diacetone alcohol using pure alcohol as feed could be studied in the same resin system as the decomposition reaction. A much stronger attempt could then be made at developing an equation covering the high range of conversion.

Quantitative information of sorption by ion exchange resins of different organic liquids in non-aqueous media is virtually non-existent. This results in a great handicap in trying to interpret and correlate experimental data. Work in this area would yield information of a general nature and its applicability and usefulness would not be limited to catalysis problems but would be a contribution to ion exchange technology in general.

Liquids other than water could be used to swell the resin, and the conversions obtained compared to those using water swollen resin. Methanol or ethanol would be good choices because in general strong base ion exchange resins swell more strongly with these than with water and their polarities are only slightly lower than water. Acetone would have the advantage of not having to introduce an extra component into the system and its polarity is similar to that of methanol and ethanol.

The formation of mesityl oxide could be studied at slightly higher temperatures where the conversions would be large enough to measure accurately. The temperature would be limited by decomposition of the quatenary ammonium groups of the resin above 45°C in Amberlyst A-26.

NOMENCLATURE

C_A°	Concentration of acetone in feed - moles/liter
C_D°	Concentration of diacetone alcohol in feed - miles/liter
C_A	Concentration of acetone - moles/liter
C_D	Concentration of diacetone alcohol - moles/liter
$[C_A]$	Concentration of acetone - mole fraction
$[C_D]$	Concentration of diacetone alcohol - mole fraction
D	Diffusion coefficient - $cm^2/sec.$
e	2.718
k	Reaction rate constant - $sec.^{-1}$
k_A	Reaction rate constant for diacetone alcohol formation - $sec.^{-1}$
k_D	Reaction rate constant for diacetone alcohol decomposition - $sec.^{-1}$
k'	Apparent reaction rate constant - $sec.^{-1}$
k_s	Apparent reaction rate constant for surface reaction - $sec.^{-1}$
K	Equilibrium constant - dimensionless
r_o	Particle radius of spherical ion exchanger beads - cm.
Re	Reynolds Number - dimensionless
v	Linear flow rate in column - cm/sec.
z	Bed length - cm.
β	Fractional void volume in bed - dimensionless
δ	Film thickness - cm.
λ	Molar distribution coefficient - dimensionless

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TABLE 1

Amberlite IRA-400 - Adiabatic - Constant Flow - 1 1/4" Column - 510 Gm. Bed

Experiment Number	1	2	3	4
Flow Rate-cc/min.	28	28	28	28
Superficial Velocity Ft/Sec. 10^{-3}	2.01	2.01	2.01	2.01
Retention Time-Sec.	513	531	642	760
Space Vel. - Sec. $^{-1}$ X 10^{-3}	1.143	1.143	1.143	1.143
% Water in Resin at Operating Cond.	6.4	18.9	24.0	31.0
Bed Height as Regenerated - Ft.	3.06	3.20	3.0	3.05
Bed Height at Operating Cond.-Ft.	1.72	1.78	2.15	2.55
Feed Composition				
% Diac. Alc.	98.9	98.9	98.8	98.2
% Acetone	0.9	0.9	1.0	1.6
% Mesityl O.	0.2	0.2	0.2	0.2
% Water	0.3	2.0	4.0	8.0
Product Composition				
% Diac. Alc.	98.9	98.1	95.1	49.7
% Acetone	0.9	1.7	4.7	50.0
% Mesityl O.	0.2	0.2	0.2	0.2
Conversion - Wt. %	Nil	0.8	3.7	49.4
Diac. Alc. in Feed Moles/100 gm.	0.852	0.852	0.850	0.846
Diac. Alc. in Prod. Moles/100 gm.	0.852	0.845	0.820	0.428
Conversion Miles/100 gm.	Nil	0.007	0.030	0.418

TABLE 2

Amberlite IRA-400 - Adiabatic - Constant Feed - 1 1/4" Column - 510 Gm. Bed

Experiment Number	5	6	7	8	9
Flow Rate-cc/min	22.5	44	55	80	100
Superficial Velocity Ft/Sec. 10^{-3}	1.62	3.07	3.96	6.12	7.19
Retention Time-Sec.	940	497	382	243	205
Space Vel. - Sec. $^{-1}$ X 10^{-3}	0.920	1.795	2.25	3.27	4.07
% Water in Resin at Operating Cond.	31.0	31.0	31.0	31.0	31.0
Bed Height as Regenerated - Ft.	3.05	3.05	3.05	3.05	3.05
Bed Height at Operating Cond.-Ft.	2.54	2.54	2.52	2.48	2.46
Feed Composition					
% Diac. Alc.	98.4	98.4	98.4	98.4	98.4
Acetone	1.6	1.6	1.6	1.6	1.6
% Mesityl O.	0.2	0.2	0.2	0.2	0.2
% Water	8.0	8.0	8.0	8.0	8.0
Product Composition					
% Diac. Alc.	48.9	58.7	62.2	68.4	70.2
% Acetone	50.9	41.1	37.6	31.4	29.6
% Mesityl O.	0.2	0.2	0.2	0.2	0.2
Conversion - Wt. %	50.2	40.1	36.6	30.3	28.5
Diac. Alc. in Feed Moles/100 gm.	0.848	0.848	0.848	0.848	0.848
Diac. Alc. in Prod. Moles/100 gm.	0.422	0.505	0.536	0.590	0.605
Conversion Moles/100 gm.	0.426	0.343	0.213	0.258	0.243

TABLE 3

Amberlyst A-26 Adiabatic - Constant Flow - 1 1/4" Column - 510 Gm. Bed

Experiment Number	10	11	12	13
Flow Rate - cc/min	28	28	28	28
Superficial Velocity Ft/Sec. 10^{-3}	2.01	2.01	2.01	2.01
Retention Time-Sec.	830	771	765	765
Space Vel. - Sec.$^{-1}$ X 10^{-3}	1.143	1.143	1.143	1.143
% Water in Resin at Operating Cond.	28.6	24.7	22.2	18.0
Bed Height as Regenerated - Ft.	3.25	3.33	3.33	3.33
Bed Height at Operating	2.78	2.58	2.56	2.56
Feed Composition				
% Diac. Alc.	98.0	98.0	98.0	98.0
% Acetone	1.8	1.8	1.8	1.8
% Mesityl O.	0.2	0.2	0.2	0.2
% Water	8.0	3.9	2.1	0.2
Product Composition				
% Diac. Alc.	35.6	34.1	32.3	30.8
% Acetone	64.2	65.7	67.5	69.0
% Mesityl O.	0.2	0.2	0.2	0.2
Conversion - Wt. %	63.6	65.2	67.0	68.5
Diac. Alc. in Feed Moles/100 gm.	.846	.846	.846	.846
Diac. Alc. in Prod. Moles/100 gm.	.307	.294	.278	.265
Conversion Moles/100 gm.	.539	.552	.568	.581

TABLE 4

Amberlyst A-26 - Adiabatic - Constant Feed - 1 1/4" Column - 510 Gm. Bed

Experiment Number	14	15	16	17	18
Flow Rate - cc/min	16	44	64	76	100
Superficial Velocity Ft/Sec. 10^{-3}	1.152	3.17	4.61	5.47	7.19
Retention Time-Sec.	1455	525	361	303	229
Space Vel. - Sec. $^{-1}$ X 10^{-3}	0.653	1.795	2.61	3.10	4.08
% Water in Resin at Operating Cond.	28.6	28.6	28.6	28.6	28.6
Bed Height as Regenerated - Ft.	3.25	3.25	3.25	3.25	3.25
Bed Height at Operating Cond.-Ft.	2.80	2.77	2.77	2.76	2.75
Feed Composition					
% Diac. Alc.	96.5	96.5	96.5	96.5	96.5
% Acetone	3.2	3.2	3.2	3.2	3.2
% Mesityl O.	0.3	0.3	0.3	0.3	0.3
% Water	8.0	8.0	8.0	8.0	8.0
Product Composition					
% Diac. Alc.	28.4	38.4	39.1	53.2	57.3
% Acetone	71.3	61.3	60.6	46.5	42.4
% Mesityl O.	0.3	0.3	0.3	0.3	0.3
Conversion - Wt. %	70.7	60.2	59.5	44.9	40.7
Diac. Alc. in Feed Moles/100 gm.	0.832	0.832	0.832	0.832	0.832
Diac. Alc. in Prod. Moles/100 gm.	0.245	0.331	0.337	0.458	0.494
Conversion Moles/100 gm.	0.587	0.501	0.495	0.374	0.338

TABLE 5

Amberlyst A-26 - Isothermal - Constant Feed - 1 1/4" Column - 510 Gm. Bed

Experiment Number	19	20	21
Flow - Rate - cc/min.	15	28	80
Superficial Velocity Ft/Sec. 10^{-3}	1.08	2.01	5.76
Retention Time-Sec.	1400	752	263
Space Vel. - $Sec.^{-1}$ X 10^{-3}	0.612	1.143	3.27
% Water in Resin at Operating Cond.	16.2	16.2	16.2
Bed Height as Regenerated - Ft.	3.33	3.33	3.33
Bed Height at Operating Cond.-Ft.	2.52	2.52	2.52
Feed Composition			
% Diac. Alc.	95.4	95.4	95.4
% Acetone	4.0	4.0	4.0
% Mesityl O.	0.6	0.6	0.6
% Water	0.2	0.2	0.2
Product Composition			
% Diac. Alc.	9.6	10.0	12.4
% Acetone	88.6	88.3	86.7
% Mesityl O.	1.8	1.7	0.9
Conversion - Wt. %	88.6	88.3	86.7
Diac. Alc. in Feed Moles/100 gm.	0.813	0.813	0.813
Diac. Alc. in Prod Moles/100 gm.	0.083	0.086	0.107
Conversion Moles/100 gm.	0.730	0.727	0.706

TABLE 6

Amberlyst A-26-Isothermal - Constant Feed - 1 1/4" Column - 170 Gm. Bed

Experiment Number	22	23	24	25	26
Flow - Rate - cc/min.	16	37	62	77	96
Superficial Velocity Ft/Sec. 10^{-3}	1.152	2.59	4.47	5.55	6.91
Retention Time-Sec.	500	222	129	103	83
Space Vel. - Sec.^{-1} X 10^{-3}	1.96	4.53	7.60	9.43	11.75
% Water in Resin at Operating Cond.	15.5	15.5	15.5	15.5	15.5
Bed Height as Regenerated - Ft.	1.25	1.25	1.25	1.25	1.25
Bed Height at Operating Cond.-Ft.	0.958	0.958	0.958	0.958	0.958
Feed Composition					
% Diac. Alc.	95.4	95.4	95.4	95.4	95.4
% Acetone	4.0	4.0	4.0	4.0	4.0
% Mesityl O.	0.6	0.6	0.6	0.6	0.6
% Water	0.2	0.2	0.2	0.2	0.2
Product Composition					
% Diac. Alc.	11.7	17.7	19.8	25.1	32.9
% Acetone	86.3	81.2	79.6	74.3	66.5
% Mesityl O.	2.0	1.1	0.6	0.6	0.6
Conversion - Wt. %	86.2	80.9	79.3	73.7	65.5
Diac. Alc. in Feed Moles/100 gm.	0.813	0.813	0.813	0.813	0.813
Diac. Alc. in Prod. Moles/100 gm.	0.101	0.153	0.171	0.217	0.284
Conversion Moles/100 gm.	0.712	0.660	0.642	0.596	0.529

TABLE 7

Amberlyst A-26 - Isothermal - Constant Feed - 1" Column - 170 Gm. Bed

Experiment Number	27	28	29	30	31	32
Flow Rate - cc/min	16	28	45	63	77	95
Superficial Velocity Ft/Sec. 10^{-3}	2.0	3.5	5.62	7.87	9.75	11.86
Retention Time-Sec.	387	221	138	99	80	65
Space Vel. - Sec.^{-1} X 10^{-3}	1.96	3.43	5.52	7.73	9.43	11.63
% Water in Resin at Operating Cond.	12.2	12.2	12.2	12.2	12.2	12.2
Bed Height as Regenerated - Ft.	1.80	1.80	1.80	1.80	1.80	1.80
Bed Height at Operating Cond.-Ft.	1.29	1.29	1.29	1.29	1.29	1.29
Feed Composition						
% Diac. Alc.	94.7	94.7	94.7	94.7	94.7	94.7
% Acetone	4.8	4.8	4.8	4.8	4.8	4.8
% Mesityl O.	0.5	0.5	0.5	0.5	0.5	0.5
% Water	0.2	0.2	0.2	0.2	0.2	0.2
Product Composition						
% Diac. Alc.	11.0	12.1	15.2	20.5	28.5	32.5
% Acetone	87.8	86.9	84.2	79.0	71.0	67.0
% Mesityl O.	1.2	1.0	0.6	0.5	0.5	0.5
Conversion - Wt. %	87.7	85.7	83.8	78.3	69.8	65.7
Diac. Ac. in Feed Moles/100 gm.	0.817	0.817	0.817	0.817	0.817	0.817
Diac. Alc. in Prod. Moles/100 gm.	0.095	0.104	0.131	0.177	0.245	0.280
Conversion Moles/100 gm.	0.722	0.712	0.686	0.640	0.572	0.537

TABLE 8

Amberlyst A-26 - Isothermal - Constant Feed - 7/8" Column - 170 Gm. Bed

Experiment Number	33	34	35	36	37	38
Flow Rate - cc/min.	15	30	49	65	79	97
Superficial Velocity Ft/Sec. 10^{-3}	2.16	4.32	7.06	9.37	11.38	13.95
Retention Time-Sec.	466	233	142	107	88	72
Space Vel.-Sec.$^{-1}$ X 10^{-3}	1.84	3.68	6.01	7.97	9.68	11.90
% Water in Resin at Operating Cond.	14.0	14.0	14.0	14.0	14.0	14.0
Bed Height as Regenerated - Ft.	2.41	2.41	2.41	2.41	2.41	2.41
Bed Height at Operating Cond.-Ft.	1.675	1.675	1.675	1.675	1.675	1.675
Feed Composition						
% Diac. Alc.	95.7	95.7	95.7	95.7	94.1	94.1
% Acetone	4.0	4.0	4.0	4.0	5.1	5.1
% Mesityl O.	0.3	0.3	0.3	0.3	0.8	0.8
% Water	0.2	0.2	0.2	0.2	0.2	0.2
Product Composition						
% Diac. Alc.	10.3	12.1	16.0	28.6	32.8	35.2
% Acetone	88.9	87.4	83.6	71.0	66.4	64.0
% Mesityl O.	0.8	0.5	0.4	0.4	0.8	0.8
Conversion - Wt. %	88.7	87.1	83.2	70.0	65.1	62.6
Diac. Alc. in Feed Moles/100 gm.	0.825	0.825	0.825	0.825	0.811	0.811
Diac. Alc. in Prod. Moles/100 gm.	0.089	0.104	0.138	0.247	0.283	0.303
Conversion Moles/100 gm.	0.736	0.721	0.687	0.578	0.528	0.508

TABLE 9

CALIBRATION OF F. AND M. GAS CHROMATOGRAPH

Known Mixtures	Actual % Acetone	Chromatograph Area - % Acetone
(1)	8.33	10.82
(2)	11.25	13.45
(3)	61.10	54.20
(4)	73.40	79.35
(5)	78.55	84.95
(6)	82.04	86.95
(7)	88.35	91.78
(8)	95.77	97.56

TABLE 10

ANALYSIS OF ION EXCHANGE RESIN

Experiment No.	19-21	22-26
Exchange capacity before run (milliequivalents per gram dry resin)	4.1	4.1
Exchange capacity after run (milliequivalents per gram dry resin)	4.1	4.2
% Volatile (wet basis)	52.0	51.5
% Water (wet basis)	16.2	15.5
% Solvent (wet basis)	35.8	36.0
Weight fraction of solvent in the interstitial liquid	0.689	0.698

TABLE 11

CALIBRATION OF FEED PUMP FLOW RATE

Make and Model:	Distillers Company Ltd., Marlin Pump, 0.864 cc/stroke, 400 psig. max. working pressure.
Motor:	Paralux, 1/15 H.P.

Pump Setting	Volumetric Flow Rate - 25°C
1.0	13.0 cc/min.
2.0	28.0
3.0	43.5
4.0	56.0
5.0	70.0
6.0	85.0
7.0	100.0

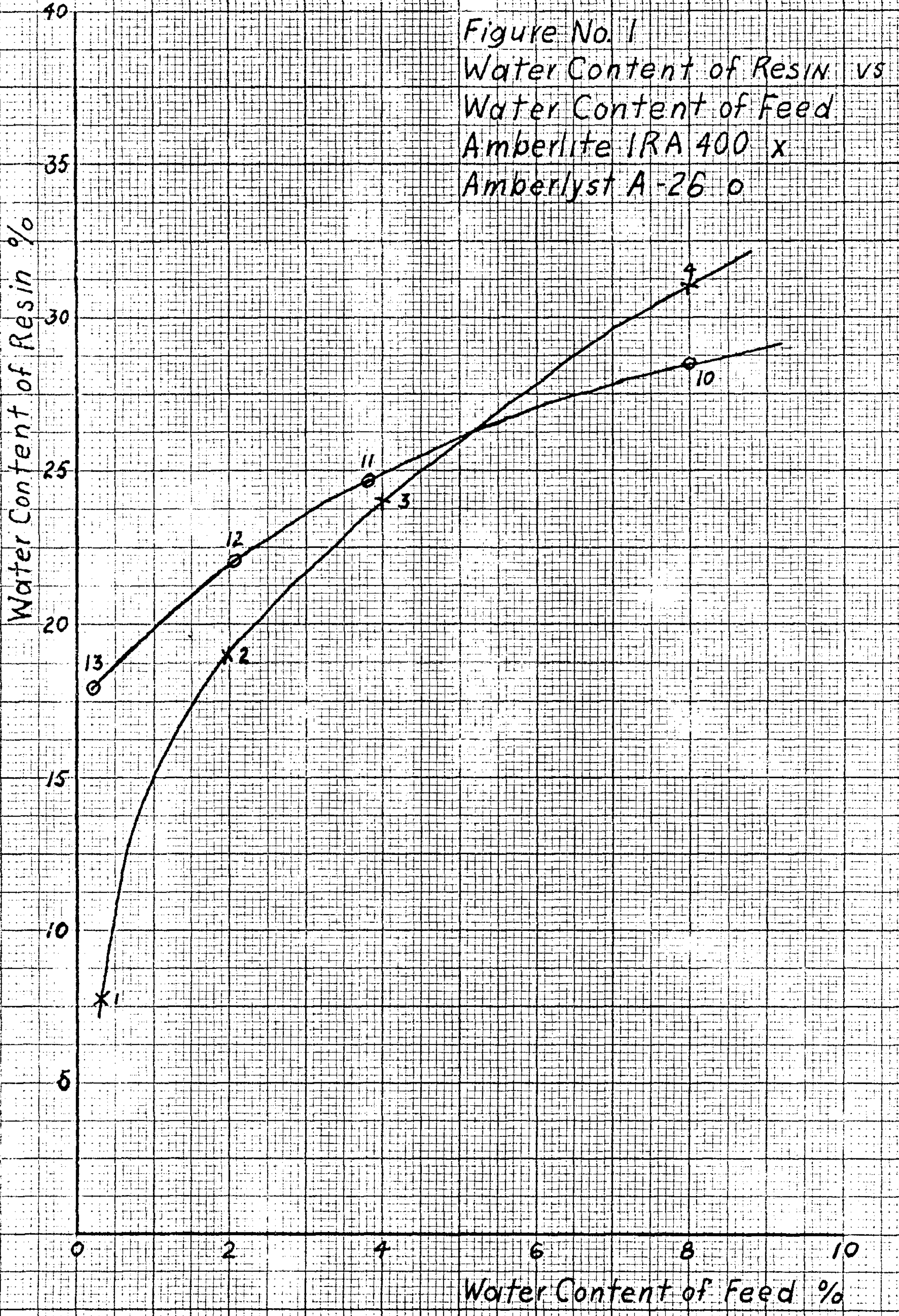

Figure No. 1
Water Content of Resin vs
Water Content of Feed

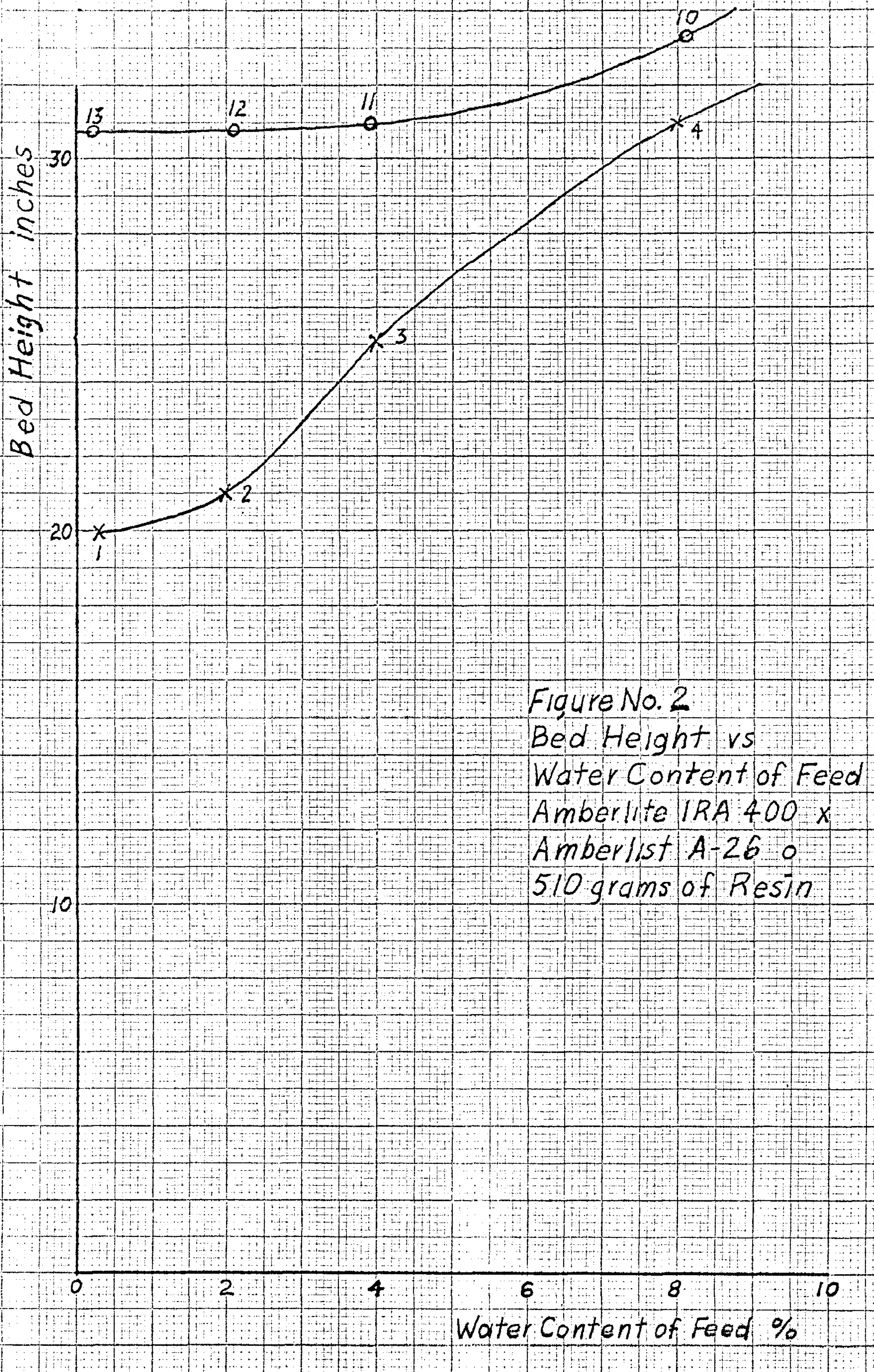

Figure No. 2
Bed Height vs
Water Content of Feed
Amberlite IRA 400 x
Amberlyst A-26 o
510 grams of Resin

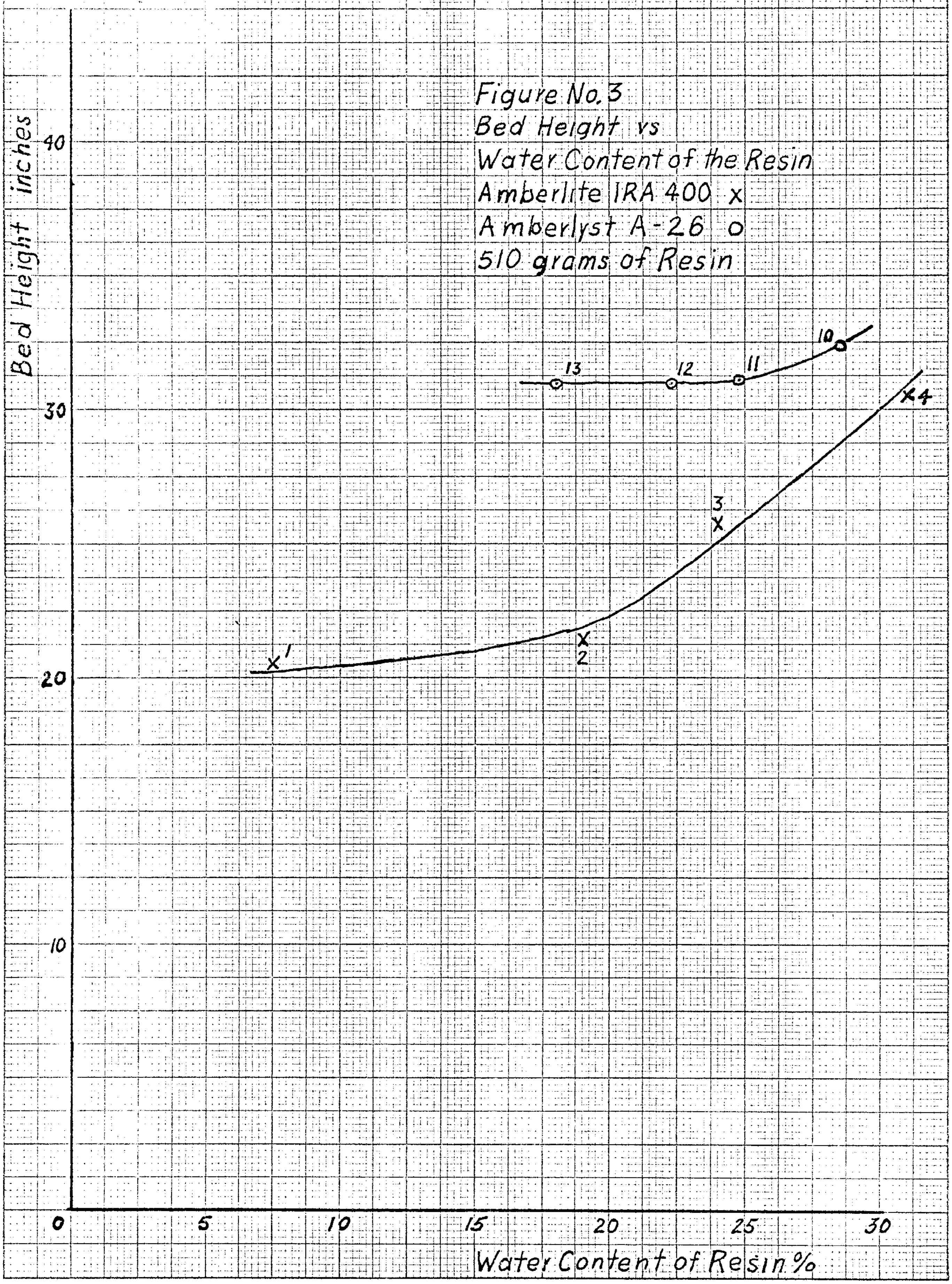

Figure No. 3
Bed Height vs
Water Content of the Resin
Amberlite IRA 400 x
Amberlyst A-26 o
510 grams of Resin
Bed Height inches
40
30
20
10
0
5
10
15
20
25
30
Water Content of Resin %
1
2
3
4
10
11
12
13

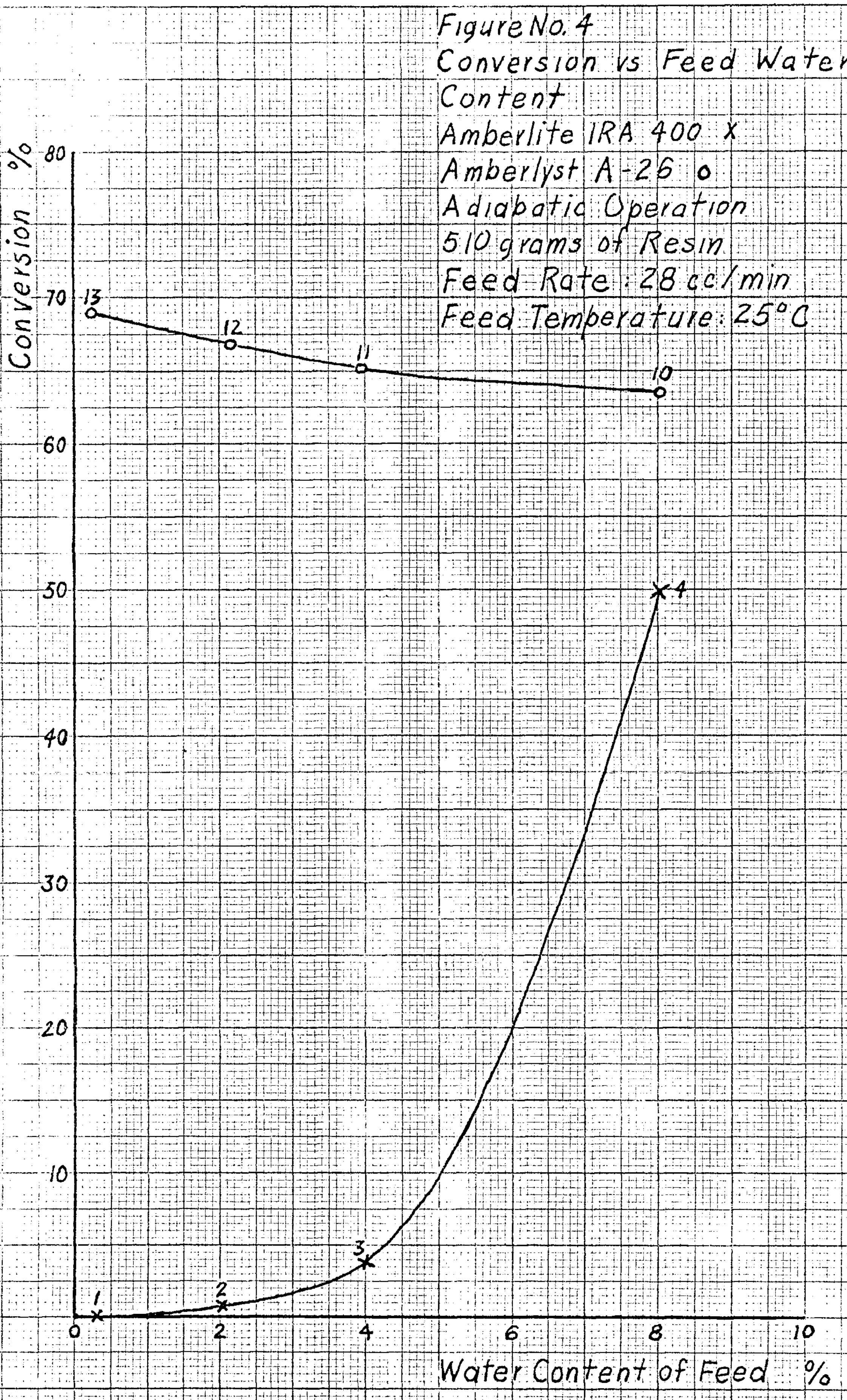

Figure No. 4
Conversion vs Feed Water Content
Amberlite IRA 400 x
Amberlyst A-26 o
Adiabatic Operation
510 grams of Resin
Feed Rate : 28 cc/min
Feed Temperature: 25°C

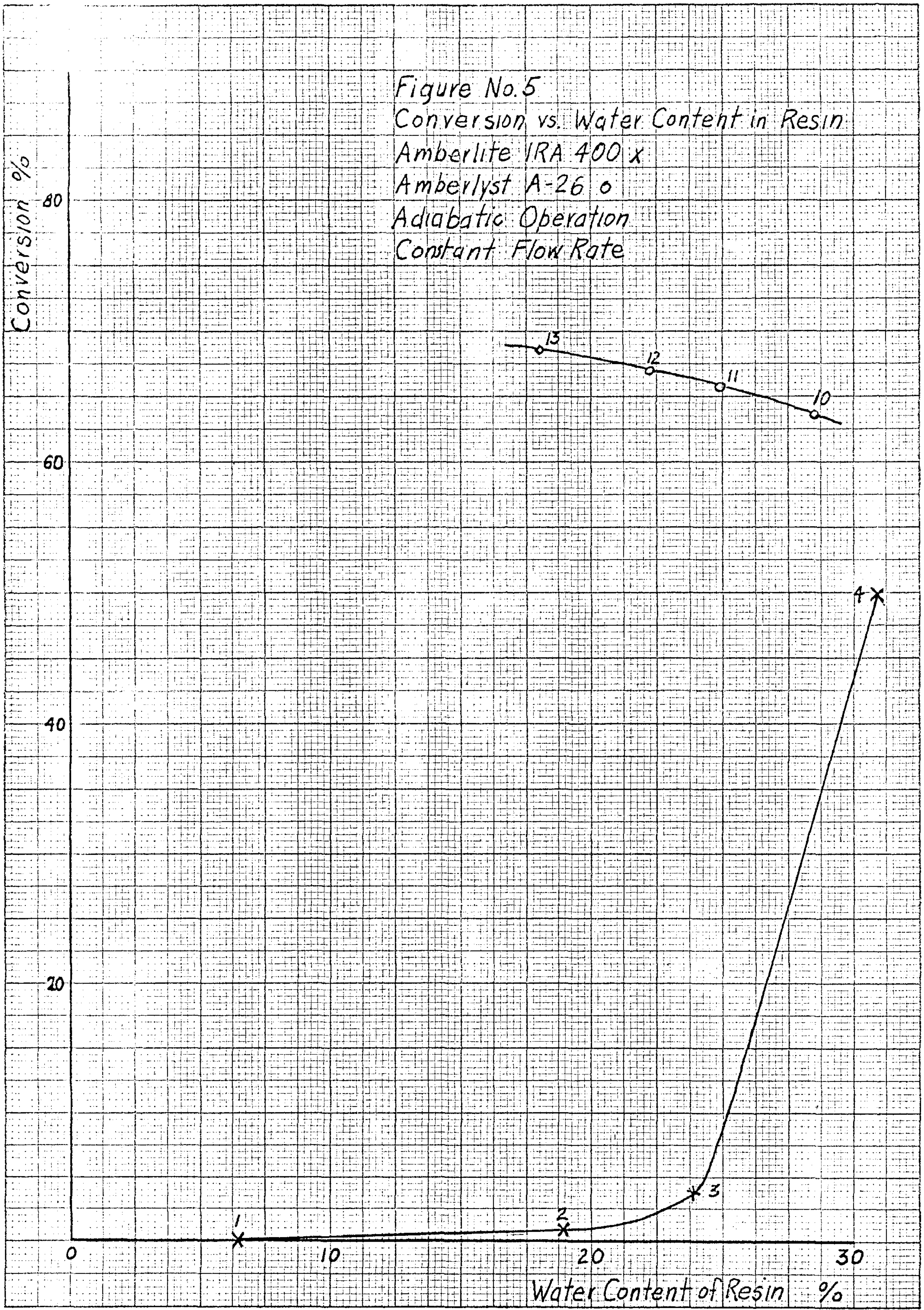

Figure No. 5
Conversion vs. Water Content in Resin
Amberlite IRA 400 x
Amberlyst A-26 o
Adiabatic Operation
Constant Flow Rate

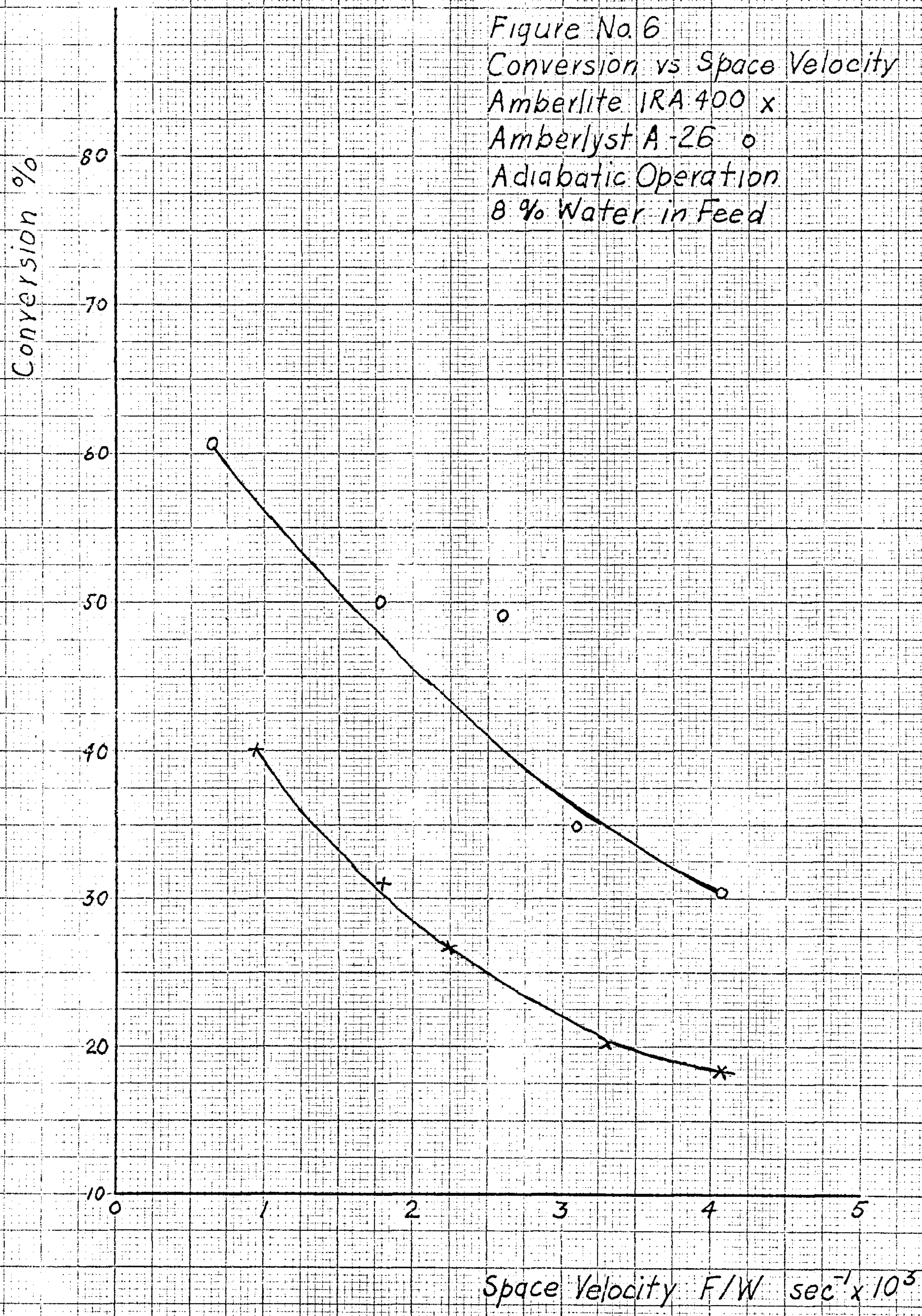

Figure No. 6
Conversion vs Space Velocity
Amberlite IRA 400 x
Amberlyst A-26 o
Adiabatic Operation
8 % Water in Feed

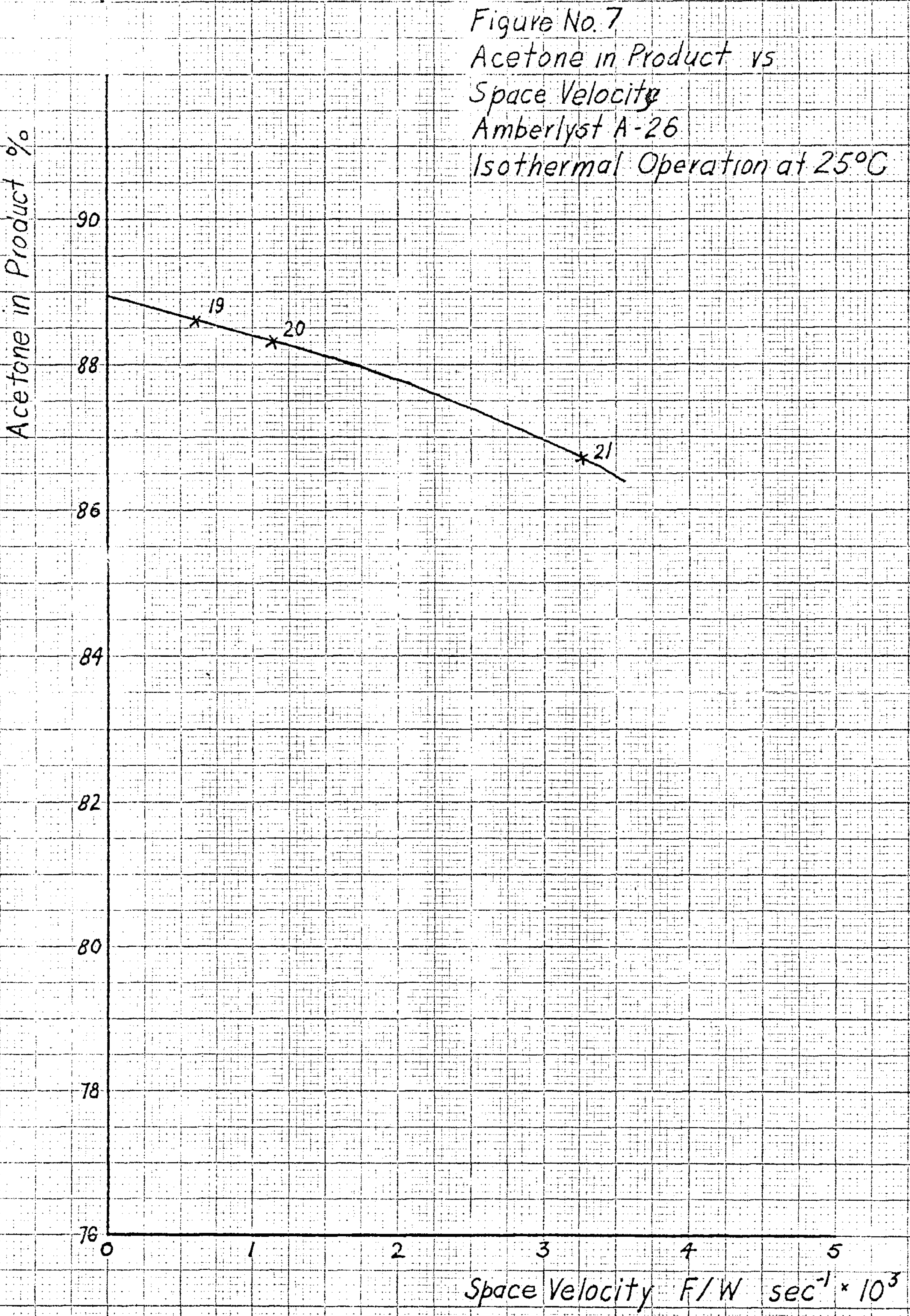

Figure No. 7
Acetone in Product vs
Space Velocity
Amberlyst A-26
Isothermal Operation at 25°C

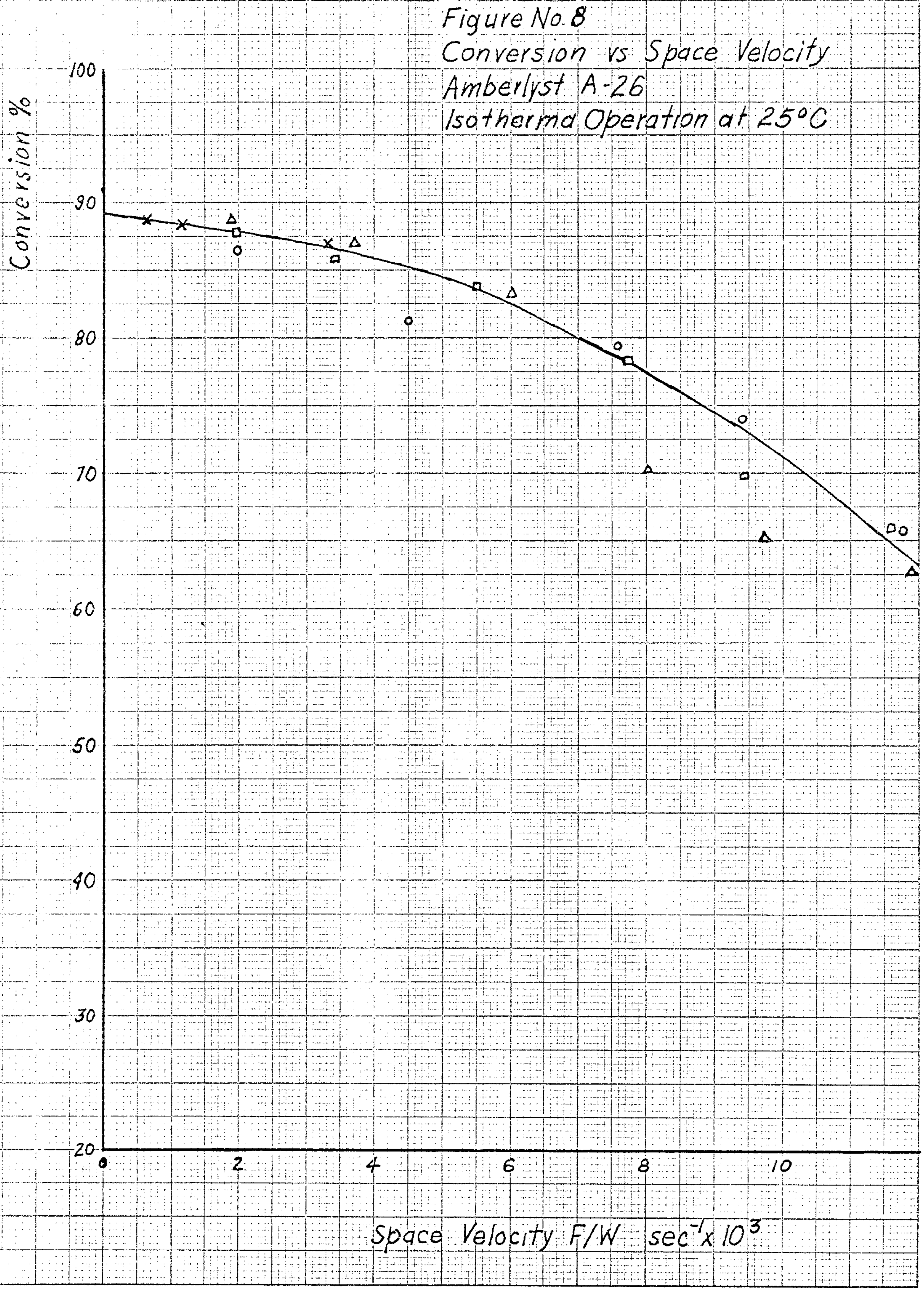

Figure No. 8
Conversion vs Space Velocity
Amberlyst A-26
Isotherma Operation at 25°C

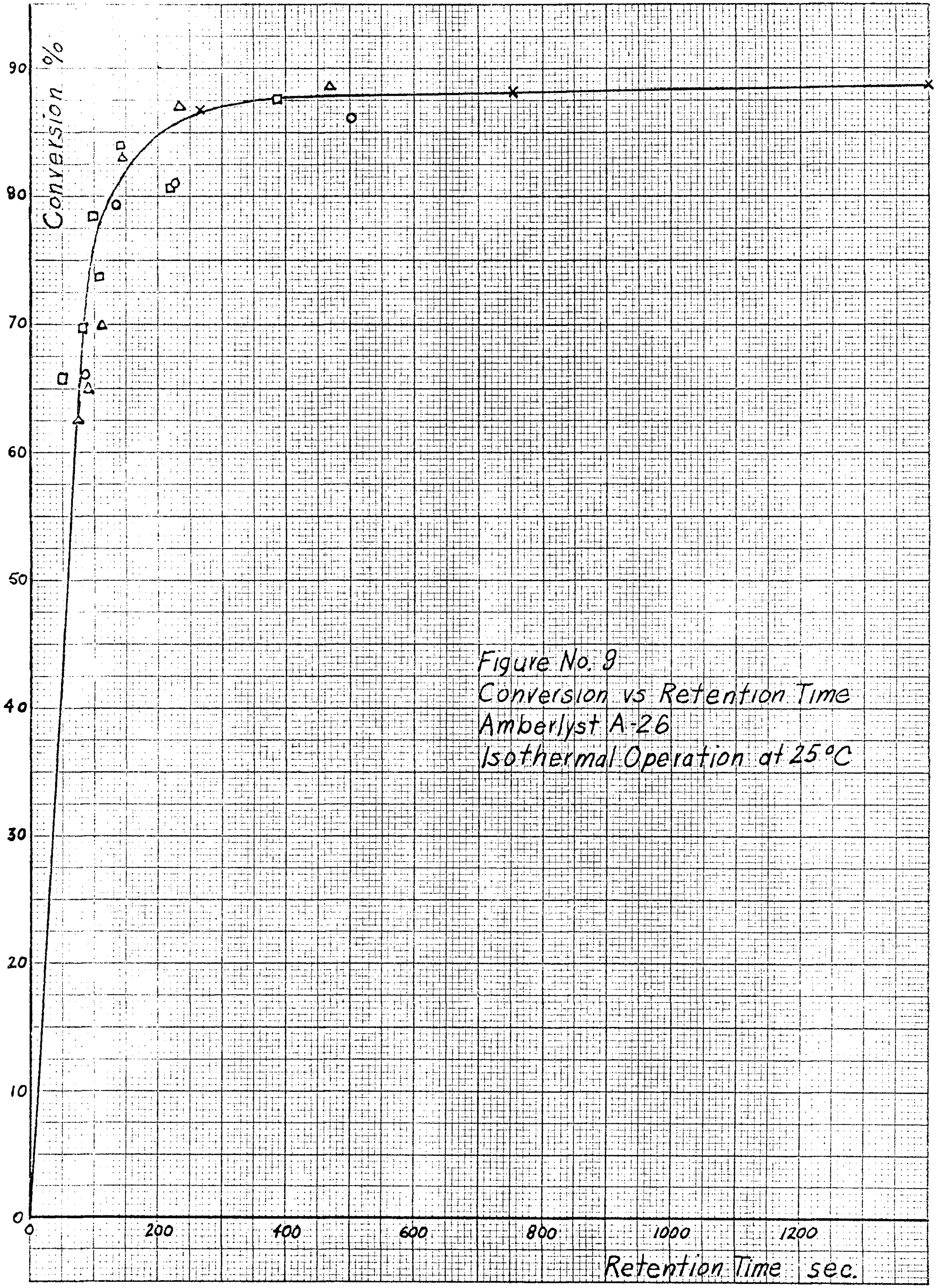

Figure No. 9
Conversion vs Retention Time
Amberlyst A-26
Isothermal Operation at 25°C

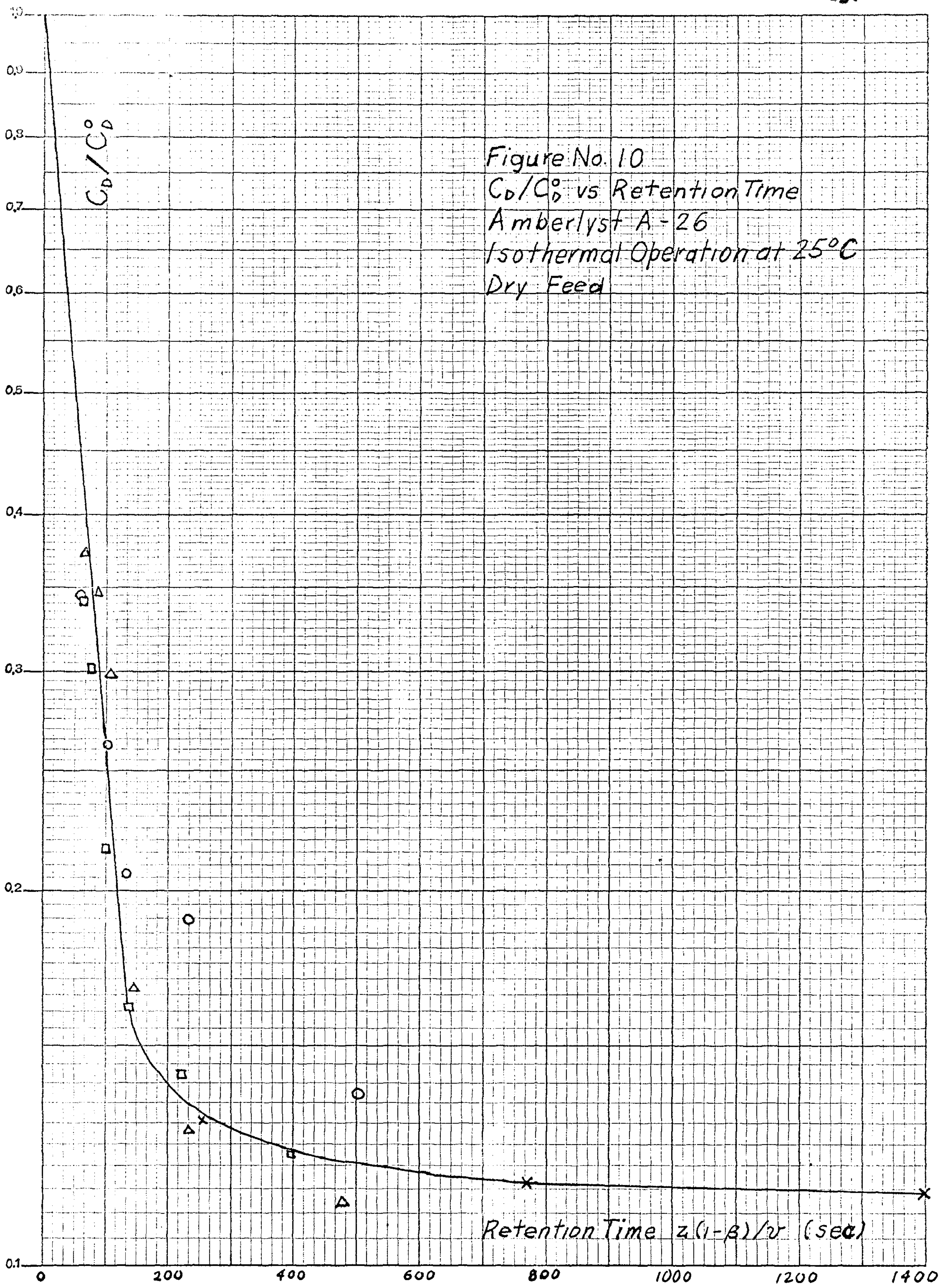

Figure No. 10
C_D/C_D° vs Retention Time
Amberlyst A-26
Isothermal Operation at 25°C
Dry Feed

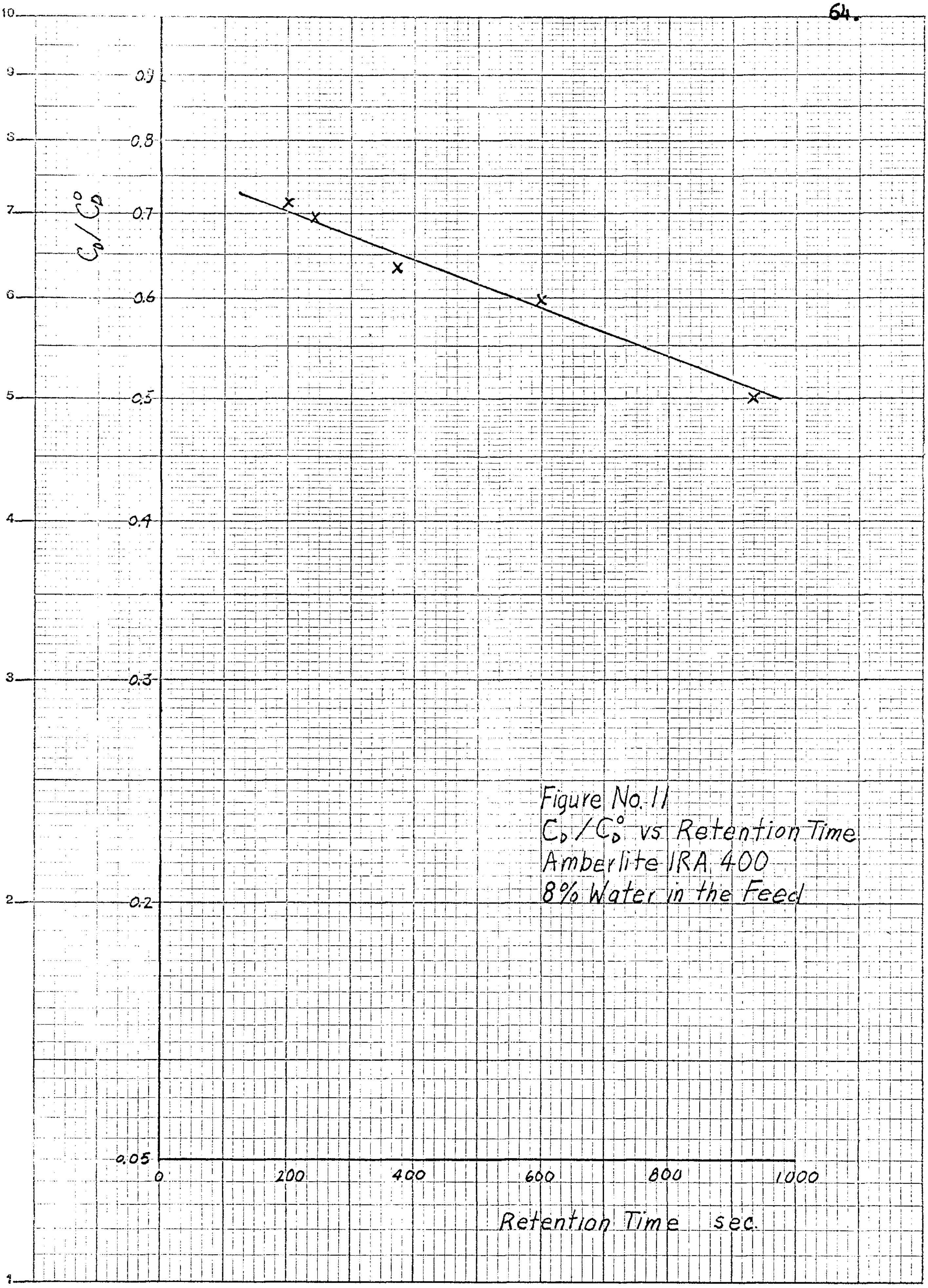

Figure No. 11
C_D/C_D^o vs Retention Time
Amberlite IRA 400
8% Water in the Feed

Figure No. 12
Calibration Curve of Gas
Chromatograph

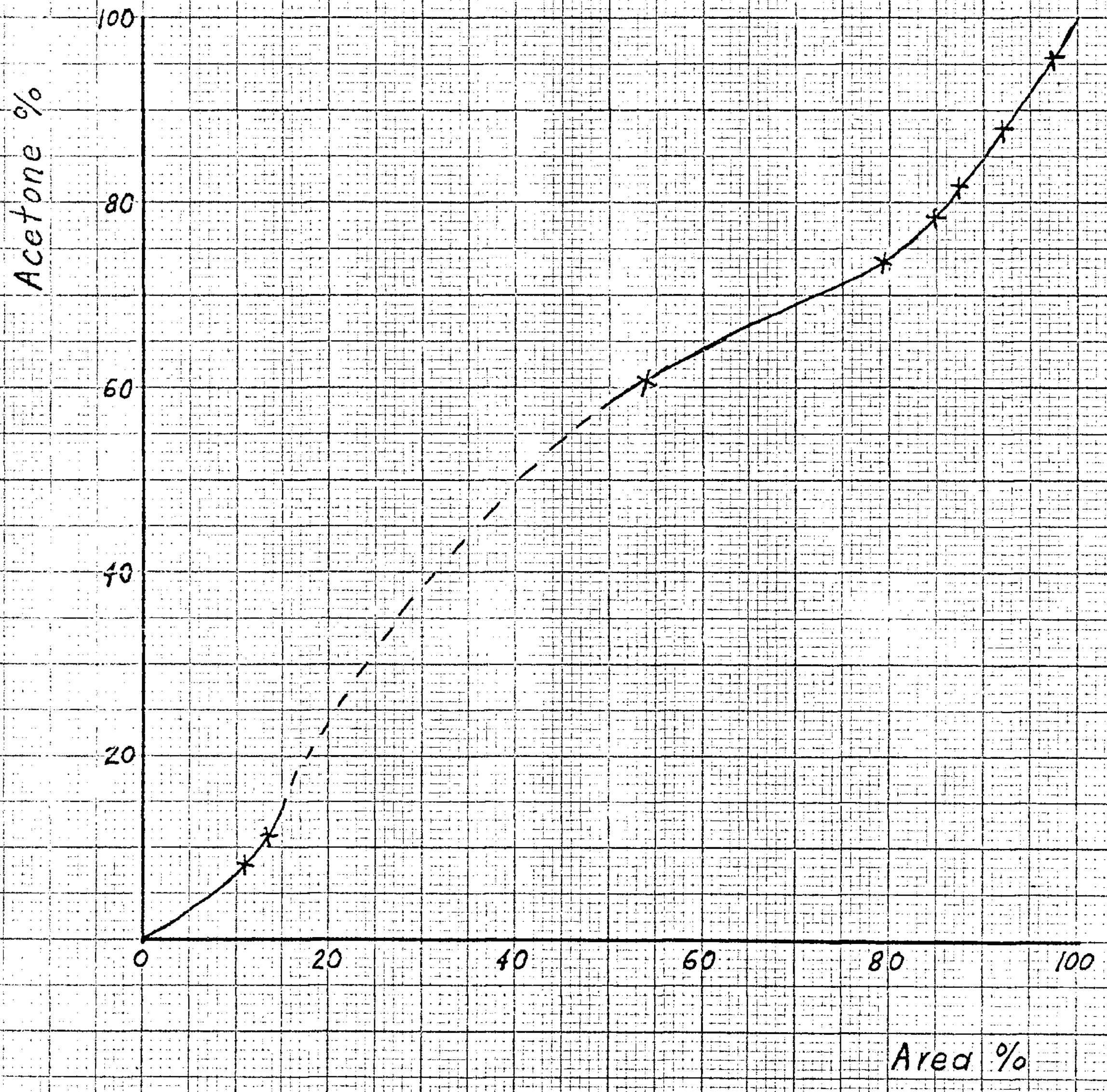

Figure No. 13
Calibration of DCL-M
Feed Pump

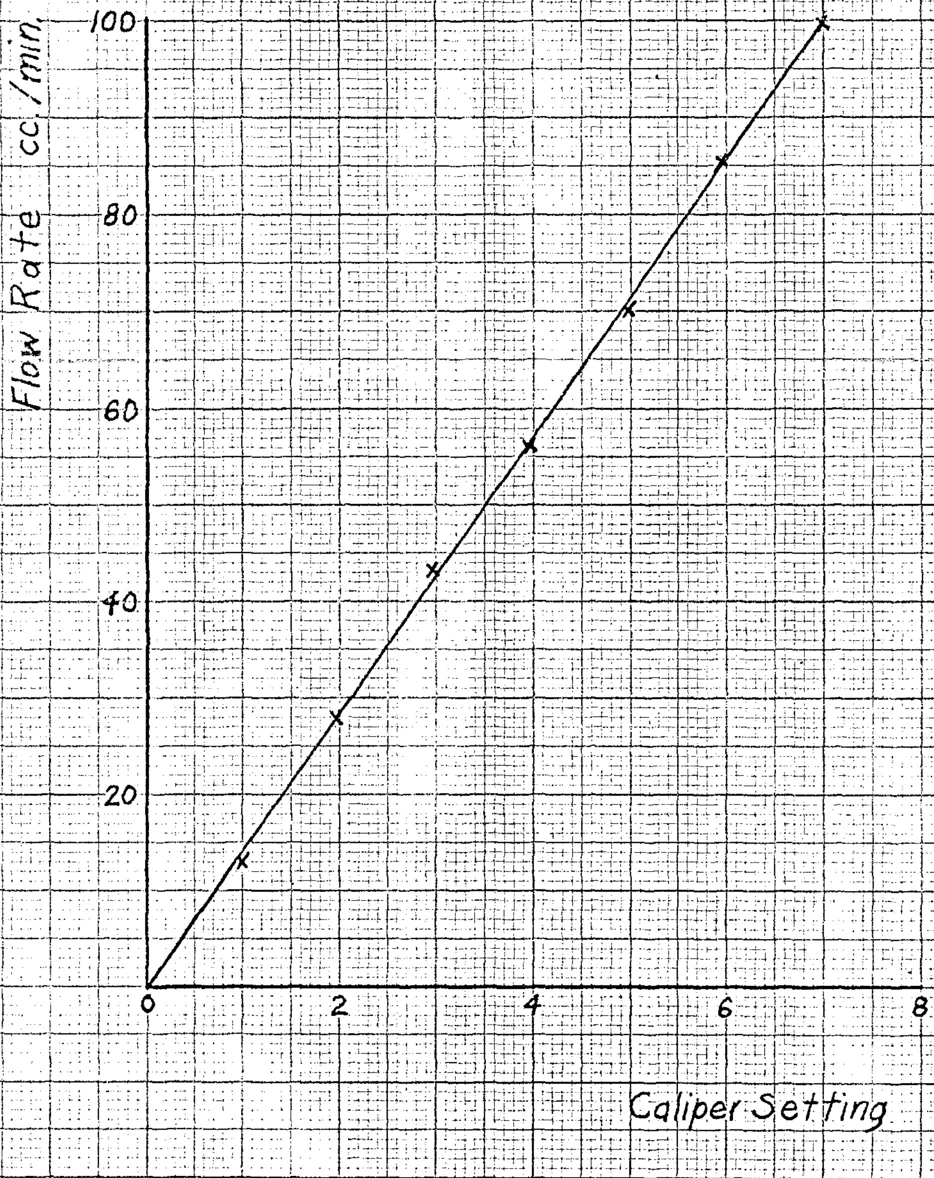

Figure No. 14
Diagram of Apparatus