

"PRODUCTION OF EDIBLE CARBOHYDRATES
FROM FORMALDEHYDE IN A SPACECRAFT"

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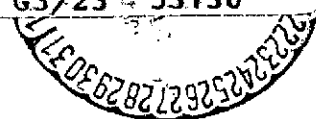
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pH Variations in the
Calcium Hydroxide Catalyzed
Formose Reaction

by

Tom John

A Master of Science Thesis

Supervised by

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ABSTRACT

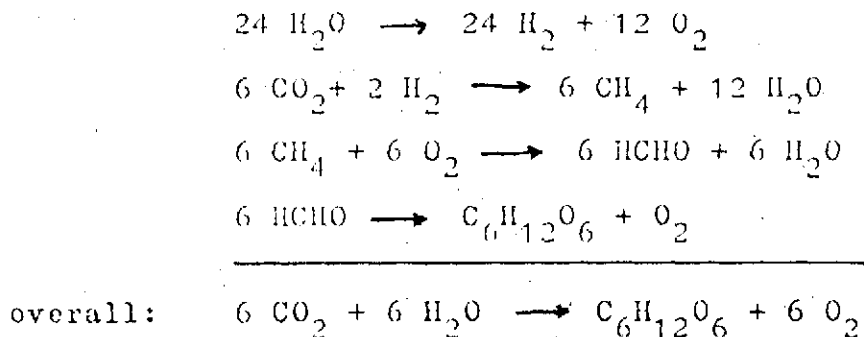
The study of the calcium hydroxide catalyzed condensation of formaldehyde was extended to a batch reactor system. pH decreases, often into the acid regime, were observed when using this basic catalyst. This observation was shown to be similar to results obtained by others who used less basic catalysts in the batch mode. Since the Cannizzaro and Formose reactions are both competitive and interdependent, the relative rates of these reactions are different in a batch reactor than in a continuous stirred tank reactor. This difference in relative rates is due to the fact that at any degree of advancement in the batch system the products have a "history" of previous products, pH, and dissolved catalyst. The CSTR, on the other hand, does not have this same history at any of its steady state operating points. The relative rate differences can be expected to yield a different nature of product sugars for the two types of reactors.

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I. INTRODUCTION

The formose reaction is a general term which refers to the self-condensation of formaldehyde in the presence of a catalyst to produce a complex mixture of sugars. The formation of monosaccharides from formaldehyde was first described by Butlerow¹ in 1861. Since his time, there has been intermittent study of the reaction, primarily to identify and characterize the various components of the product mixture.^{2,3,4,5}

Recently, the reaction has aroused the interest of both American and Russian researchers in the space program because of its potential as a route to food regeneration.^{6,7,8} It is possible that carbon dioxide and water, an astronaut's waste products, could be converted to usable food during extended space missions. The carbon dioxide can be hydrogenated to methane, then partially oxidized to formaldehyde, and finally converted to formose sugars:

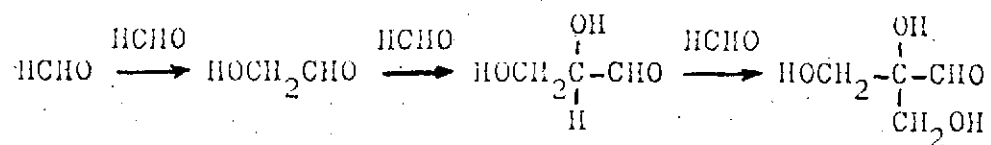


The final product of the formaldehyde condensation is a complex mixture of aldose and ketose sugars which range

from the 2-carbon glycoaldehyde through 6, 7, 8, and even higher carbon number species.⁹ Both straight chain and branched chain carbohydrates are formed, many of which are not found in nature. This formose "syrup", however, has been shown to be toxic when fed to animals.^{10,11} The toxicity appeared due to some of the sugar constituents, rather than to free or bound formaldehyde which might have been present in the syrup. Researchers have attempted to characterize the reaction mechanisms and to control both the diversity and concentration of the reaction products.^{5,12,13} Such control could lead to a more desirable reaction and higher yield of usable carbohydrates for the space program.

The reaction chemistry and sugar characterization of the formose reaction are detailed in a recent comprehensive review by Mizuno and Weiss¹⁴ and a brief summary is presented here.

The formose reaction is basically an aldol condensation:



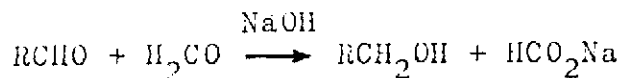
The first initiating step, that of formaldehyde with itself, is not a true aldol condensation since there is no α -hydrogen present, and is therefore difficult to rationalize. However, once this "induction period" is passed and a small quantity of glycoaldehyde has been formed by the first condensation, the reaction proceeds autocatalytically to produce the higher

formose sugars.

Study of the formose reaction is complicated by the presence of the interdependent Cannizzaro reaction which proceeds in situ with the formose reaction. In the Cannizzaro reaction, two aldehyde groups are transformed into the corresponding hydroxyl and carboxyl functions by (generally) aqueous or alcoholic alkali. The simplest example of this type of reaction involves two formaldehyde molecules yielding methyl alcohol and formic acid, and in general the reaction can be written:



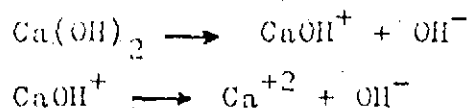
Dismutations of the same type but involving two unlike aldehyde molecules are classed as "Crossed" Cannizzaro reactions:



The ratio of the Cannizzaro reaction to the formose reaction is a function of the reaction conditions and of the catalyst used.¹⁵ The hydroxides of alkaline earth metals such as $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, certain alkali-metal hydroxides, and some heavy metal hydroxides catalyze the aldol (Formose) reaction. Tri- and tetra-valent rare-earth metal hydroxides¹⁶ and some organic bases¹⁷ were also shown to be effective. The Cannizzaro reaction is suppressed by

addition of low molecular weight alcohols but is activated by the hydroxides of alkaline earth and alkali metals, except for thallium hydroxides, in the order $\text{TlOH} < \text{Ca(OH)}_2 < \text{Ba(OH)}_2 < \text{NaOH} < \text{LiOH}$.^{14,15}

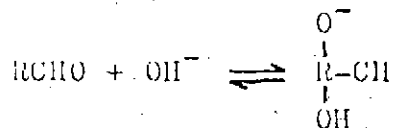
A series of recent studies which involved the use of a continuous stirred tank reactor (CSTR) and Ca(OH)_2 as a catalyst have enumerated more observations and peculiarities of the formose reaction. By using a CSTR, rates could be determined directly, and conversion could be held at any desired level, thus showing the dependence of the rate on catalyst and pH. From these studies, it was suggested that the decomplexing of products was the rate-limiting step for the formose reaction, and a kinetic expression similar to Langmuir-Hinshelwood equations was developed.^{18,19} Both the formose and the Cannizzaro reactions were shown to exhibit remarkable Ca(OH)_2 and pH sensitivities.²⁰ In an article by Weiss and John²¹ a unifying mechanism is developed to explain the peculiarities of the formose reaction. The mechanism involves the use of CaOH^+ produced by the dissociation of Ca(OH)_2 :



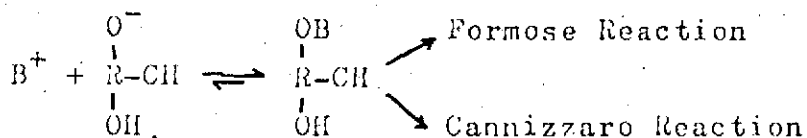
Generalized to any base, the first dissociation can be written:



The anionic form of any aldose can be formed by addition of the OH^- .²²

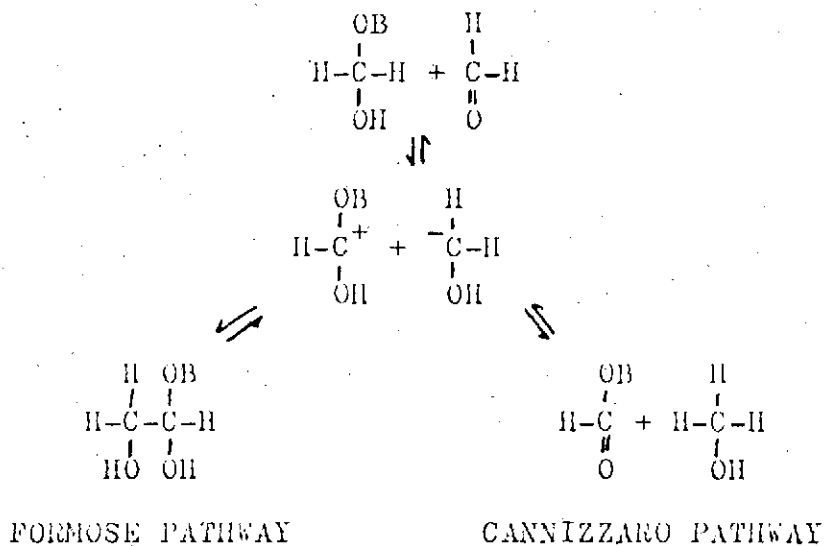


Combining these two reactions, one obtains the complexed form:¹³



This complexed form is suggested as the common intermediate for both the formose and the Cannizzaro reactions. Depending on the catalyst and the reaction conditions, the complex may undergo a metathesis (formose reaction) or a proton transfer (Cannizzaro reaction).

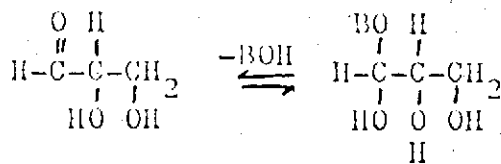
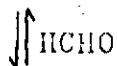
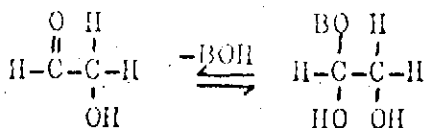
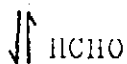
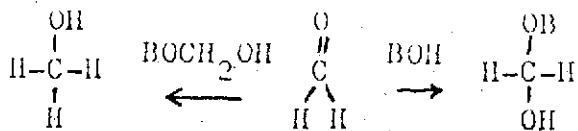
Specifically, for the case of the first self-condensation of formaldehyde, the mechanism would be as follows:



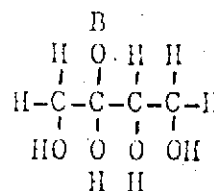
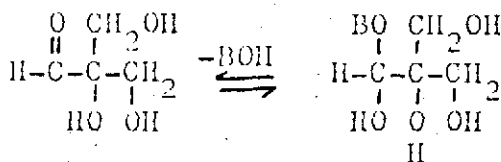
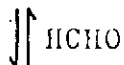
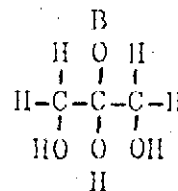
This mechanism allows for the initiation of the reaction, the pH sensitivity, and the catalyst selectivity as discussed in the article by Weiss and John. Coupled with the Lobry de Bruyn-van Eckenstein ketose-aldose shift, the mechanism leads to the building of both branched and straight chain carbohydrates of n-carbon numbers (see scheme on page 8).

The pH sensitivities of the formose reaction are not limited to the $\text{Ca}(\text{OH})_2$ system, and reaction conditions need not be highly basic for the condensation to proceed. Cairns-Smith²³ tested common minerals for their ability to catalyze the formose reaction and found that, under his experimental conditions (6g. of the mineral refluxed for 5 hours with 150ml of 0.13 M HCHO), those minerals which gave a solution pH in the range 6.5 - 8.0 were generally the most effective catalysts. Some Russian batch reactor studies which used rare earth metal hydroxides as catalysts for the formose reaction^{16,19} were reported to have initial pH values in the acid regime (4.5 - 6.5). The pH was then observed to drop lower as the reaction progressed. Greater conversion of formaldehyde through the Cannizzaro reaction pathway by the tetravalent $\text{Ce}(\text{OH})_4$ and $\text{Th}(\text{OH})_4$ catalysts was proposed as the reason for the greater decrease in the pH during the course of their reaction (final pH = 2.7). $\text{Sm}(\text{OH})_3$, $\text{Ho}(\text{OH})_3$, and $\text{Er}(\text{OH})_3$ were deemed as more selective in catalyzing the formose reaction; their final pH was in the range 3.8 - 4.5.

In a batch study utilizing PbO^{24} with 1/100 mole of benzoyl carbinol as a co-catalyst to reduce the induction

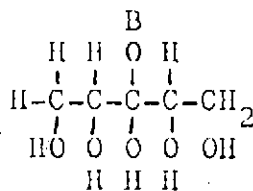


L.A.
shift

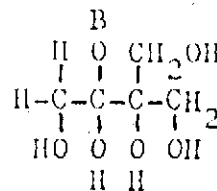


4-Carbon
Branched Chain

4-Carbon
Straight Chain



5-Carbon
Straight Chain



5-Carbon
Branched Chain

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Scheme I

period, an interesting pH effect was observed. The solution pH, initially in the range 7.5 - 8.0, increased, then decreased to pH 7.0 and lower. The decrease was more dramatic as the amount of initial PbO was reduced, and at 0.5g of PbO (with 100ml of 20% HCHO, 75°C), the pH dropped from an initial value of 7.1 to 5.5 at 80% conversion of HCHO. A later batch study of PbO²⁵ also showed initially acid pH values (4.5) which rose to the neutral range (6.5 - 7.5) after one hour of reaction, then dropped back into the acid range (5.0 - 6.0) at complete conversion. The authors consider the Cannizzaro reaction to be insignificant in this weakly acid medium. In this same study, the authors claim that addition of CH₃OH was shown not to greatly effect either the conversion rate or the pH of the corresponding solutions.

In their studies of calcium hydroxide in a stirred tank reactor, Tambawala and Weiss²⁰ have shown that the pH of the system decreased from 12 to 10 as the concentration of Ca(OH)₂ was increased. However, a minimum was reached, and the pH of the solution then increased as the calcium hydroxide concentration was further increased. This behavior mirrors the Cannizzaro rate and reflects the formation of acid products by that reaction. These authors have shown that the Cannizzaro rate increases to a maximum at near 50% formaldehyde conversion, then decreases through a minimum. Near complete conversion, the reaction again ascribes to a maximum due to the Cross Cannizzaro reaction.

In further studies on this same system²¹ the reaction

pH was forcibly varied by addition of either NaOH or formic acid to the reactor. Excessive amounts of either the acid or the base effectively quenched the total conversion reaction, clearly showing the sensitivity of both the Cannizzaro and formose reaction to pH. The article also shows the behavior of the pH passing through a minimum as a function of increasing $\text{Ca}(\text{OH})_2$ concentration. This minimum was shown to relate to the total rate maximum, again demonstrating the pH sensitivity and showing that the Cannizzaro rate is directly related to the total formaldehyde conversion rate.

The present study examines the relationship of reaction pH to total formaldehyde conversion under varying formaldehyde and calcium hydroxide concentrations.

II. EXPERIMENTAL

A. Description of Reactor

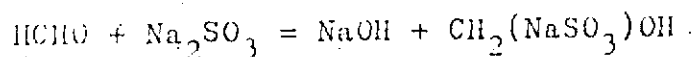
The batch reactor used throughout this study consisted of a 300ml Berzelius pyrex glass beaker (high rise) with a teflon cap which was gas tight. The beaker was immersed to the level of the cap in a Fisher Isotemp constant temperature bath. The temperature of the bath was held constant at 50°C. A two-bladed stirring impeller and baffle, a Sargent combination glass pH electrode,^{26,27} an iron-constantan thermocouple and a Swagelok fitting with a rubber septum penetrated the Teflon cap and were immersed in the reaction mixture. The apparatus is shown in Figure 1.

The pH of the mixture was monitored by a Coleman Metrion mark IV pH meter which was coupled to a Sargent chart recorder. The temperature difference between the water bath and the batch reactor contents was measured by the thermocouple. Liquid samples were withdrawn through the Swagelok septum with a syringe.

B. Quantitative Techniques

1. The Sodium Sulfite Test

The sodium sulfite test was used prior to each experiment to establish the initial formaldehyde concentration and to verify the accuracy of the gas chromatograph. This test makes use of the reaction:



The NaOH thus formed is on a one-to-one ratio with the formaldehyde initially present. This product is then back titrated to neutral to phenolphthalein by the addition of standardized HCl.

The sodium sulfite test is not specific for formaldehyde since any higher aldose or ketose can interfere with the results and give a reading which is falsely high.²⁸ Therefore, this method is more suitable for determination of formaldehyde concentration prior to reaction and is less suitable for following the concentration of formaldehyde as a function of time throughout the reaction.

2. Gas Chromatograph

A dual column gas chromatograph (Perkin-Elmer, model 900) which was equipped with a thermal conductivity detector and linear oven programming was used to follow the formaldehyde concentration throughout the course of the reaction. A single copper column (1/8 inch by 3 feet) filled with Carbosieve B (60 to 80 mesh) was used to separate the water, formaldehyde, and methanol components of the reaction mixture.²⁹ Experimental conditions were: Injector, 200°C; Manifold, 210°C; detector, 200°C @ 175 ma.; oven, 145°C to 185°C at 10°C/min; He flow, 20 cc/min @ 150°C.

The choice of temperature was made to provide optimum peak separation and sharpness and to reduce analysis time. The upper temperature of 185°C also prevented the polymerization of formaldehyde.²⁸ Samples were withdrawn from the reactor at approximately 10 minute intervals with an

automatic, adjustable syringe (Hamilton Co.). The injection port septum was replaced after every run to avoid inaccuracies due to septum leakage. A chart recorder (Leeds and Northrup) which was equipped with a Disc integrator was used to record the detector response. Chart speed was 3 inches/minute.

Relative response factors and retention times were determined by injection of 1) Formaldehyde and water; 2) Formaldehyde, water, and methanol; and 3) methanol and water of known concentrations which covered the experimental range. Formaldehyde concentrations were measured by the sodium sulfite test (see section B.1). Calculations were made as suggested in the Basic Chromatography Handbook.³⁰ A typical chromatogram is shown in figure 2, with retention times and DISC area values.

3. Computer Programs

To aid in compilation and analysis of data, several computer programs were developed. The main program used in this study is given in Appendix 1. For each experiment, the time of each sample injection and the peak areas for the water, formaldehyde, and methanol peaks, which were obtained from the DISC integrator, were entered into the disc memory of the WACCC PDP-10 computer (Digital Equipment Corp.). The main program retrieved the data of the desired experimental run and calculated the weight percents of water, formaldehyde, and methanol for each sample injection. A second section of the program calculated and printed the

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percent formaldehyde ($C_t/C_t = 0$) for each injection time. A sample output is given in Appendix 2A. In the third section of the program, the computer plotter (Cal. Comp., Inc.) was used to plot the percent formaldehyde vs. sample time. The Cal Comp. plotter connected each data point by a series of straight lines, as shown in Appendix 2B. A smooth curve was subsequently drawn through the plotted points.

C. Operating Procedure

Prior to each experiment, the column of the GC was baked out and the water bath was brought to temperature. The chromatograph was allowed to equilibrate for several hours and the septum was changed. A known quantity of paraformaldehyde (Baker Chemical Co., AR grade) was dissolved in distilled, deionized water by heating and vigorous stirring. After filtration, the concentration of the formaldehyde solution was determined by sodium sulfite titration (section B 1). More water was added to achieve the desired concentration of formaldehyde. Approximately 200ml of this formaldehyde solution was transferred to the batch reactor which was subsequently lowered into the water bath. The pH meter was calibrated with pH = 7.0 and 10.0 buffer solutions, the glass electrode was set into the teflon cap, and pH monitoring was begun.

When the thermocouple showed the temperatures of the bath and of the reactor fluid to be equal, the calcium hydroxide (Mallinckrodt, AR grade) was added to the solution

and the timer was started. The first sample was then injected into the GC and the time was noted. Samples were injected into the GC approximately every 10 minutes throughout the course of the reaction, until no measurable formaldehyde was observed at the highest sensitivity of the GC.

A total of 12 experiments were run. The formaldehyde concentration was varied from 0.327 M to 0.825 M, and the calcium hydroxide was varied from 0.028 M to 0.21 M. All experiments were conducted at 50° C.

III. RESULTS AND DISCUSSION

The data obtained from the experiments is presented in Table I. The most striking result of this study has been the demonstration of batch pH values in the acid regime using $\text{Ca}(\text{OH})_2$ as the sole catalyst. Figure 3 is a drawing of the recorder tracings for three experimental runs, MAY16, JUN06, and JUN10. In all three cases, as the calcium hydroxide was added, $t = 0$, the pH can be seen to jump dramatically upwards towards a value of 12, the value of a saturated calcium hydroxide solution. The pH then immediately drops down to acid values. Although all three curves stabilize at considerably different pH values, the initial behavior of the three is similar. The general relationships between pH vs. time and formaldehyde conversion vs. time for all the experimental runs are shown in figures 1 through 12 of Appendix 3. In these plots, the common occurrence of acid pH values that vary with conversion can be clearly seen.

The reported lack of reproducibility³¹ in batch studies was not a major problem here, although occasional discrepancies did occur. For example, compare the results for MAY06 and MAY08, figures 7 and 8 of Appendix 3. The initial conditions for MAY08 were: HCHO , 0.386 M; $\text{Ca}(\text{OH})_2$, 0.0343 M. For MAY06, the initial values were: HCHO , 0.363 M; $\text{Ca}(\text{OH})_2$, 0.0388 M. These values are in reasonably close agreement, yet the MAY08 experiment reached 100% conversion of HCHO in 110 minutes, while the MAY06 experiment achieved only 25% conversion in that same time.

It is difficult to speculate on the possible reasons for the lack of reproducibility. However, in a system as complex as this one with so many parameters affecting the reaction, slight discrepancies in ostensibly identical runs may cause widely different results. Perhaps the initial conditions are not enough alike, or these concentrations correspond to a more than usually sensitive regime on the rate response surface.

Since any change--obvious or otherwise--in a parameter that affects the rate of reaction (hence conversion) will directly affect the pH of the solution, it is more useful to plot the pH values against formaldehyde conversion, thus giving a plot which is more reproducible than plotting either of these parameters versus time. These plots are given in Appendix 4, figures 1 through 12, and are more internally consistent than the corresponding plots where time is the variable. Comparing figures 7 and 8 of Appendix 4, the plots for MAY06 and MAY08 discussed previously, it is obvious that the curves are indeed in much better agreement than in Appendix 3.

To analyze the dependence of pH on initial conditions, the plots of Appendix 4 were grouped into sets of constant formaldehyde concentration, with varying parameters of calcium hydroxide. These sets are presented in figures 4, 5, 6, and 7. In these plots, the dashed line at $\text{pH} = 12.5$ represents the pH of a saturated (0.018 Molar at 50°C) calcium hydroxide solution. This would be the line expected

with an infinite amount of $\text{Ca}(\text{OH})_2$ added to the reaction mixture such that the mixture was always saturated despite losses by Cannizzaro reaction and complexing by product sugars. Notice that as the $\text{Ca}(\text{OH})_2$ concentration is decreased, the corresponding pH-conversion curve of all the plots is also depressed; however, the curves apparently pass through a minimum, and then increase at still lower $\text{Ca}(\text{OH})_2$ concentrations. At 0.00 M $\text{Ca}(\text{OH})_2$, the pH would rise to that of a formaldehyde solution at 50°C , for example a pH of 9.0 for the case of 0.386 M formaldehyde.

Despite the danger in drawing conclusions from only three graphs of three curves each, it is interesting to speculate on the chemistry involved. One explanation is that a pH minimum is reached since, initially, the Cannizzaro rate is greater than the rate of dissolution of $\text{Ca}(\text{OH})_2$. As the reaction progresses, the rate of formose reaction becomes appreciable and a point will be reached at a lowered $\text{Ca}(\text{OH})_2$ concentration at which the Cannizzaro rate is small compared to that of the formose rate. At this point, the dissolution of $\text{Ca}(\text{OH})_2$ and the buffering action of calcium formate tend to return the pH of the mixture toward a value of 10.0, the pH of the $\text{Ca}(\text{OH})_2$ -formose complex.

A cross plot of pH at constant $\text{Ca}(\text{OH})_2$ and variable parameters of HCHO is presented in figure 8. Again, the indication of a minimum curve occurring as formaldehyde concentration is increased from zero (dashed line) cannot be overlooked; however, other explanations such as irreproduc-

ibility and analogies to similarly shaped curves of Cannizzaro rate versus total conversion rate cannot be ruled out either. More experimentation in this area is seen to be necessary before solid conclusions can be drawn.

It is important to note that no CH_3OH , the primary product of the Cannizzaro reaction (along with formic acid) was detected at any time. The minimum limit of methanol which was measurable by the gas chromatograph in this experimental configuration was approximately 0.02 wt% CH_3OH . The Cannizzaro reaction must therefore have been less than 10% of the total reaction to be unobservable. Yet the pH's were indeed acid, presumably due to the production of formic acid and the slightly acid sugars themselves. It follows that the rate of Cannizzaro reaction, although very small, is still greater than the rate of neutralization by dissolution of $\text{Ca}(\text{OH})_2$. Mizuno and Weiss¹⁴ indicate that batch studies of the formose reaction using various catalysts initially showed a drop in pH, exhibiting an induction period during which Cannizzaro reaction was the major reaction. Again, additional studies are indicated to verify and explain this conclusion.

It has been demonstrated^{14,24,32} that the addition of an organic co-catalyst at the start of the formose reaction shortens the induction time without affecting either the reaction rate or the catalyst selectivity. We should therefore be able to compare other published studies using other catalysts and organic co-catalysts to the present work.

Figure 9 is a plot taken from pH vs. time and conversion vs. time graphs by Langenbeck²⁴ in which lead oxide was used as a catalyst. This plot shows the variation of pH with conversion for four concentrations of PbO catalyst at constant formaldehyde concentration. The pH curves are seen to become progressively lower as the concentration of PbO is decreased, a result which is in agreement with the present $\text{Ca}(\text{OH})_2$ studies. No experimental minimum is reached; however, we can draw two additional theoretical curves on this graph, one at infinite PbO concentration and one at 0.00 Molar PbO as was done for the $\text{Ca}(\text{OH})_2$ system. A saturated PbO solution has a pH of approximately 9.0, and decreasing the PbO concentration towards zero would imply that a minimum pH must at some point be reached, since at exactly zero PbO concentration the pH must return to the pH of the formaldehyde solution alone. The PbO studies would then be consistent with the $\text{Ca}(\text{OH})_2$ studies reported here.

The results of a later Russian study²⁵ of PbO are shown in figure 10. In this article, pH-conversion values were not given, and although plots of pH vs. time data are not always desirable, these data do show that a lowering of the PbO (accompanied this time by a reduction in HCHO as well) did depress the pH curve. This can be compared to the aforementioned German study, in which plots of pH vs. time showed a similar shape. Of additional interest in the Russian article is the fact that increasing the CH_3OH concentration from 10% to 40% raises the pH-time curve about 0.5 pH unit. Addition

of methanol, as previously noted, hinders the Cannizzaro reaction. It would appear that this rate decrease is responsible for the increase in pH observed.

In figure 11, the effect of rare earth hydroxides having approximately equal ion radii are shown.¹⁹ It is claimed that the tetravalent Ce^{+4} and Th^{+4} allow more Cannizzaro reaction to proceed than do the more formose-selective Sm^{+3} , Ho^{+3} , and Er^{+3} ; and therefore have lower pH values.

Since the saturated solutions of these rare earth hydroxides and of PbO are basic, it is assumed that the reported pH at time zero is not the pre-reaction pH but rather shows the sudden drop in the pH of the solution immediately after the initiation of the reaction, a result similar to the calcium hydroxide data shown in figure 3 and Appendix 4.

Although the conversion versus pH curves for the PbO , rare earth hydroxides, and many of the calcium hydroxide experiments have very similar shapes, they cannot unfortunately be superimposed due to the differences in formaldehyde concentrations (6.67 M, 3.9 - 4.3 M, and 0.3 - 0.8 M, respectively). As figure 8 shows, interpolation over even a small concentration range may lead to entirely erroneous results, and no real conclusions should be drawn from these similarly shaped curves without further experimental verification.

The differences in pH behavior between batch and stirred tank reactors may be explained as follows:

In the CSTR, the rate of the Cannizzaro reaction is less than the rate of the $Ca(OH)_2$ dissolution, due in part to the

steady-state configuration of the reactor. Of course, in a CSTR there is no "induction period" per se, and operation is always at final conditions. In the stirred tank, the formaldehyde being added sees reaction products, both complexed and decomplexed, as well as the catalyst and more formaldehyde. These product sugars readily complex with the calcium hydroxide catalyst which is being fed to the reactor and provide a strong driving force for dissolution of the catalyst. The batch reactor experiences a different history. In the batch mode, the formaldehyde sees initially only itself and undissolved Ca(OH)_2 , plus the dissolved Ca(OH)_2 at its (low) saturation level. The calcium hydroxide would then have less of an initial driving force into solution in a batch configuration than in a stirred tank reactor held at appreciable conversion levels. It is possible then that the rate of Ca(OH)_2 dissolution, rather than the rate of product decomplexing, is the slowest step in the initiation of the batch formose reaction. Thus, by changing the type of reactor, we have also changed the rate limiting step of the reaction. It follows that there will be a far different selectivity in a batch reactor than in a CSTR, since the relative rates can vary with time in a batch reactor and are fixed in a stirred tank configuration.

This same argument can be used to explain in detail the pH behavior of the Ca(OH)_2 -CSTR experiments. Figure 12 is obtained from the article by Weiss and Tambawala.²⁰ The lower curve shows the relationship between Cannizzaro rate

and total formaldehyde conversion rate. At point a, both the Cannizzaro rate and the total rate are low. At this low conversion, the Cannizzaro is the major reaction, and there are effectively no formose sugars present to complex the $\text{Ca}(\text{OH})_2$ rapidly. The pH is low in a CSTR operated at low conversion since acids are being produced by Cannizzaro reaction that cannot be neutralized by undissolved $\text{Ca}(\text{OH})_2$. Under certain conditions of low conversion and low $\text{Ca}(\text{OH})_2$, Tambawala and Weiss obtained pH values as low as 9.5.

Progressing along the curve towards point b, the Cannizzaro rate and the total rate both increase. The increase in the absolute rate of the Cannizzaro reaction neutralizes the $\text{Ca}(\text{OH})_2$ and the pH of the solution is seen to decrease (upper curve).

At point b of figure 12, the Cannizzaro rate is at its maximum required by its stoichiometry. However, the total rate has also greatly increased, and HCHO disappearance by Cannizzaro reaction is $\sim 5\%$ of the formose rate at the same point. Large quantities of formose sugars are beginning to be produced which will aid in the dissolution of $\text{Ca}(\text{OH})_2$. As can be seen, this point also corresponds to the minimum value of pH. At point c of figure 12, the Cannizzaro rate has again fallen to a low value and the reaction is almost entirely formose condensation. Due to the excess of $\text{Ca}(\text{OH})_2$ and the lack of HCHO as complete conversion is approached, the Cannizzaro rate is now low in comparison to the rate of $\text{Ca}(\text{OH})_2$ dissolution. The pH curve then tends back towards

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higher values, and approaches the pH of the saturated solution and the formate complex.

Thus the explanation is consistent, and the stirred tank reactor is seen to demonstrate the same trends as the batch reactor. It does not show these trends to the same degree, however, for the reasons previously mentioned. For such a complex reaction, each step depends on the products present at that time. Therefore, the final result is dependent on the history of the reaction, its pH, and the products of the Cannizzaro and formose reactions. A stirred tank reactor will never experience this history, and the final results must be different.

It is often assumed³³ that, when there are no interactive effects (e.g. simple, parallel, or consecutive) in a set of reactions, a stirred tank reactor represents the conditions within the batch reactor at a given instant of time. A series of experiments, each at a given τ , will give a corresponding value for the rate of reaction directly. This ease of interpretation has made CSTR data of great value in reaction studies. However, the rate law obtained through CSTR data will not necessarily hold true for very complex systems. As this study has shown, if product compositions for the two reactors differ, interpretation of data must be confined to the reactor from which that data was obtained. The batch reaction responds on the cumulative history of all the parameters, while the CSTR is devoid of a history and is only an environment.

In this sense, one must consider complex reactions not as an immediate candidate for interpretation by CSTR studies, but as a set of either independent or interactive reactions. For independent processes, e.g. the simple, parallel, or consecutive reactions, the overall effects will be mathematically tractable, and the system can be analyzed in principle by studies in any reactor. For the interactive processes, however, the system must be studied in toto, since any artificial control of any of the parameters will affect all parameters. For this type of situation, results obtained in one reactor under varied conditions cannot be generalized for all reactors under any conditions. This suggests much more work is needed to develop rules of generality for sets of reactions.

An interesting future CSTR study would be to generate the catalyst in situ, using equivalent feed streams of calcium acetate and sodium hydroxide. The product diversity, monitored by TMS derivitization, as well as reaction rate could be studied under autonomic pH and forced pH conditions. In addition, monitoring of the effluent streams throughout startup and before steady state is reached could show unexpected dependencies and interactions otherwise hidden by the steady state operation. This information could then be compared to batch reactor studies in which the time-varying product distribution as well as pH had been determined.

Acknowledgements

This research was supported by the National Aeronautics and Space Administration, Grant Numbers NGR22-017-023 and NGR22-017-024, and by the National Science Foundation, Grant Number ENG 74-17599. The author wishes to thank all those whose suggestions or efforts aided in the completion of this project, especially Dr. A.H. Weiss and Dr. J.T. Kohler for their time and guidance. Special thanks go to Mr. T.Y. Lee and Mr. David Hayhurst.

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TABLE I

Experimental data

Temperature = 50°C.

| Date | HCHO Initial Molarity | Ca(OH) ₂ Molarity | Time (min.) | HCHO Conversion | pH |
|-------|-----------------------------|---------------------------------|----------------|--------------------|------|
| APR04 | .327 | 0.116 | 0.5 | .03 | 9.6 |
| | | | 8.5 | .18 | 6.3 |
| | | | 17.0 | .08 | 5.8 |
| | | | 28.5 | .24 | 4.5 |
| | | | 39.0 | .28 | 4.5 |
| | | | 49.0 | .46 | 5.0 |
| | | | 61.0 | .94 | 6.0 |
| | | | 71.0 | 1.00 | 10.5 |
| APR10 | .33 | 0.138 | 1.0 | 0.00 | 8.2 |
| | | | 12.0 | 0.00 | 3.5 |
| | | | 14.0 | 0.00 | 5.2 |
| | | | 24.0 | .01 | 6.0 |
| | | | 32.5 | .08 | 5.5 |
| | | | 43.5 | .15 | 7.0 |
| | | | 52.0 | .15 | 5.2 |
| | | | 61.5 | .47 | 3.4 |
| | | | 71.0 | .61 | 1.8 |
| | | | 81.0 | 1.00 | 9.6 |
| APR18 | .373 | 0.0960 | 1.0 | .02 | 9.6 |
| | | | 11.0 | .01 | 8.2 |
| | | | 19.0 | .04 | 8.4 |
| | | | 28.5 | .04 | 8.1 |
| | | | 40.0 | .01 | 7.2 |
| | | | 49.5 | .28 | 7.8 |
| | | | 58.0 | .56 | 8.4 |
| | | | 67.0 | .95 | 9.2 |
| | | | 75.0 | 1.00 | - |
| APR22 | .369 | 0.151 | 1.0 | 0.00 | 9.6 |
| | | | 9.5 | 0.00 | 9.8 |
| | | | 19.0 | 0.00 | 10.0 |
| | | | 28.5 | .12 | 10.2 |
| | | | 38.5 | .44 | 10.2 |
| | | | 48.0 | 1.00 | 11.0 |

TABLE I (cont.)

| | | | | | |
|-------|------|--------|-------|------|------|
| MAY09 | .386 | 0.21 | 1.5 | 0.00 | 4.6 |
| | | | 11.0 | .09 | 6.4 |
| | | | 20.5 | .04 | 7.7 |
| | | | 32.5 | .32 | 9.5 |
| | | | 40.0 | 1.00 | 10.5 |
| MAY16 | .458 | 0.05 | 2.0 | .07 | 9.5 |
| | | | 14.0 | .08 | 11.0 |
| | | | 25.5 | .14 | 11.0 |
| | | | 32.5 | .20 | 10.9 |
| | | | 42.0 | .22 | 10.8 |
| | | | 52.0 | .37 | 10.8 |
| | | | 62.0 | .35 | 10.7 |
| | | | 72.0 | .85 | 10.3 |
| | | | 82.0 | 1.00 | 9.0 |
| JUN06 | .422 | 0.0870 | 3.0 | 0.00 | 6.0 |
| | | | 14.0 | .04 | 5.8 |
| | | | 23.0 | .09 | 5.8 |
| | | | 32.5 | .25 | 6.0 |
| | | | 41.5 | 0.00 | 6.0 |
| | | | 51.0 | .12 | 6.0 |
| | | | 60.5 | .09 | 6.0 |
| | | | 72.0 | .26 | 8.0 |
| | | | 81.5 | .38 | 9.2 |
| | | | 92.0 | .90 | 9.5 |
| | | | 102.0 | 1.00 | - |
| JUN10 | .835 | 0.121 | 2.0 | .13 | 12.0 |
| | | | 12.0 | .11 | 3.4 |
| | | | 22.0 | .15 | 3.6 |
| | | | 32.0 | .26 | 3.7 |
| | | | 52.0 | .29 | 4.0 |
| | | | 62.0 | .27 | 3.6 |
| | | | 72.0 | .65 | 3.6 |
| | | | 80.0 | .99 | 6.0 |
| | | | 90.0 | 1.00 | - |

Figure 1

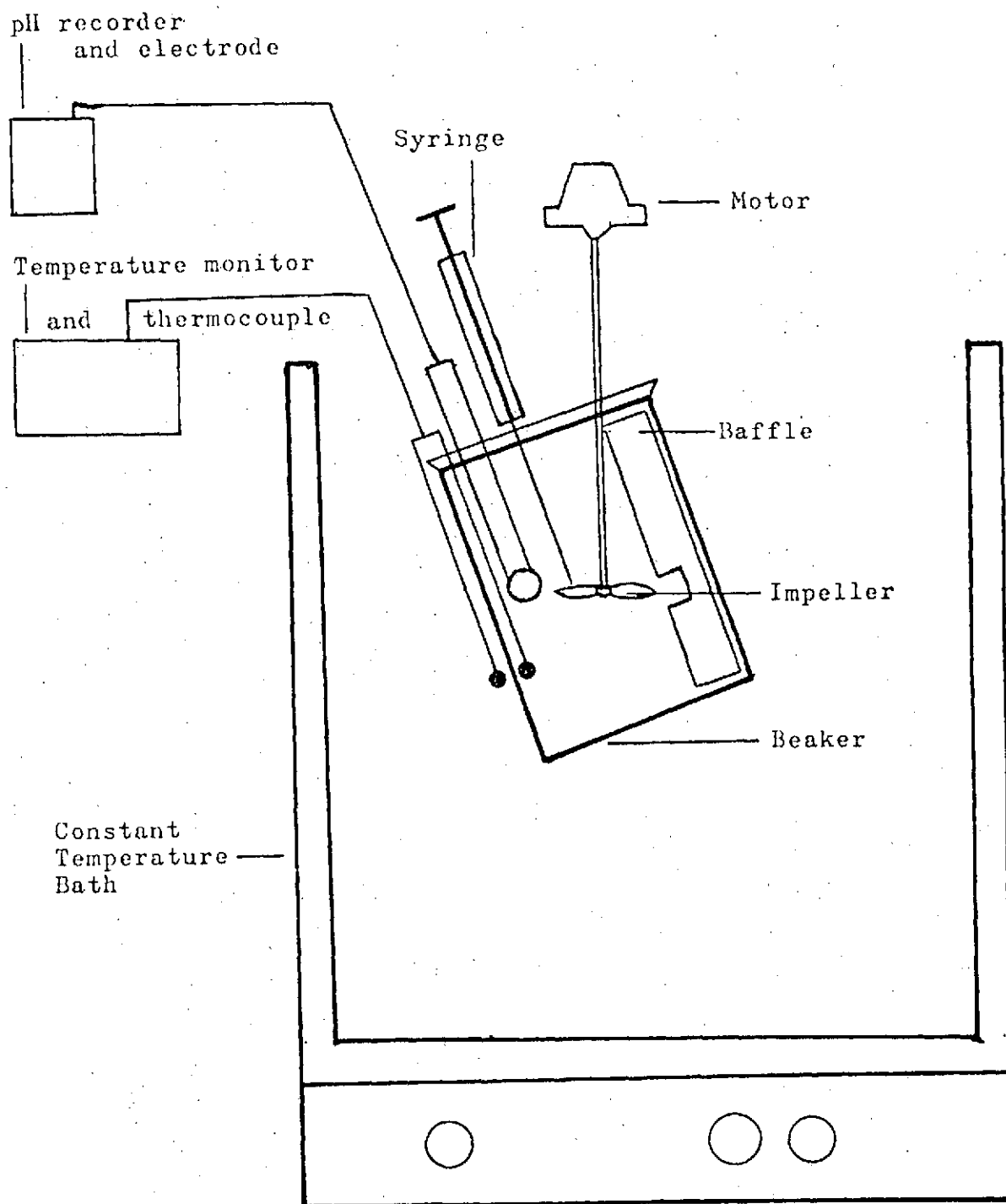
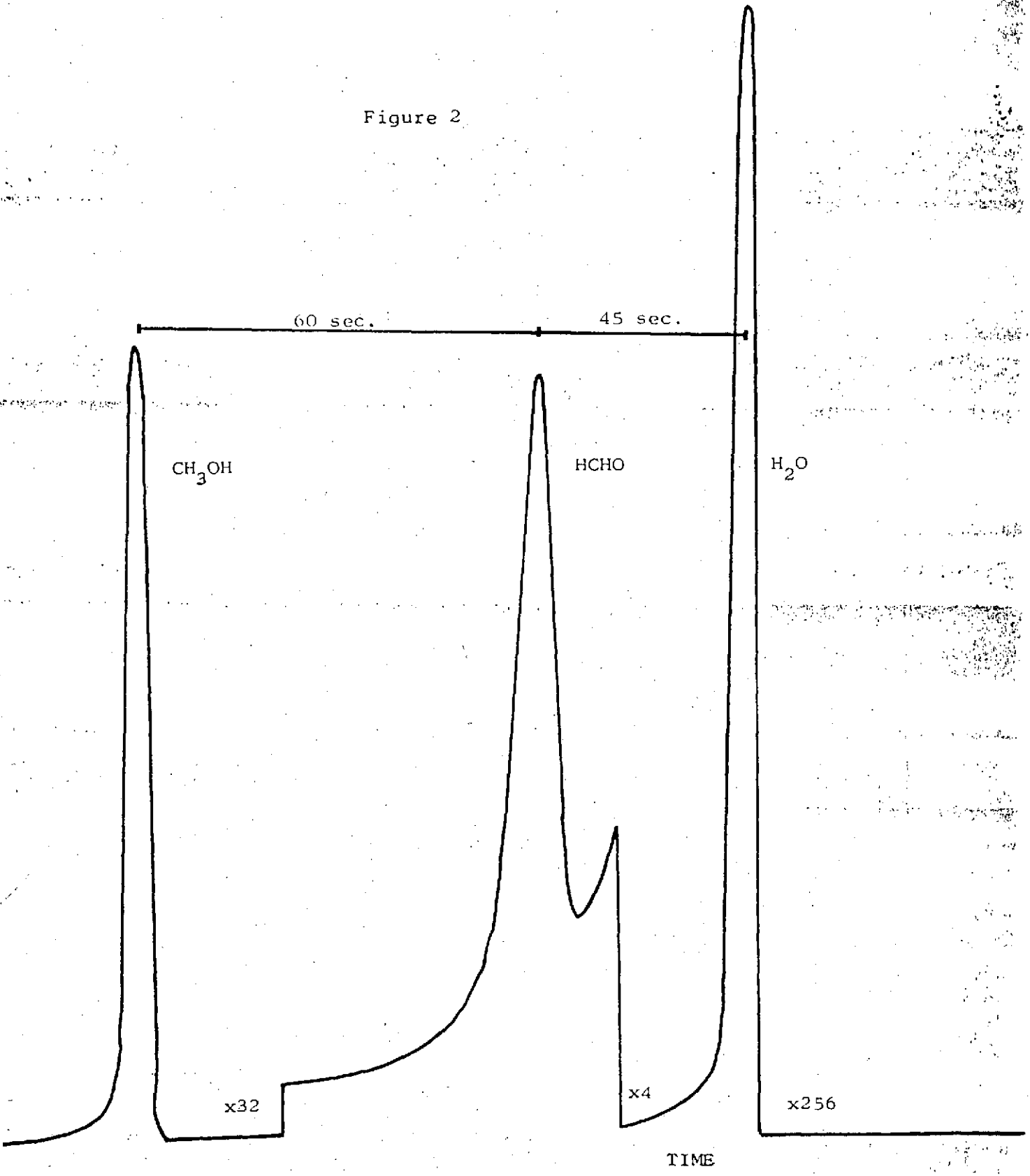


Figure 2



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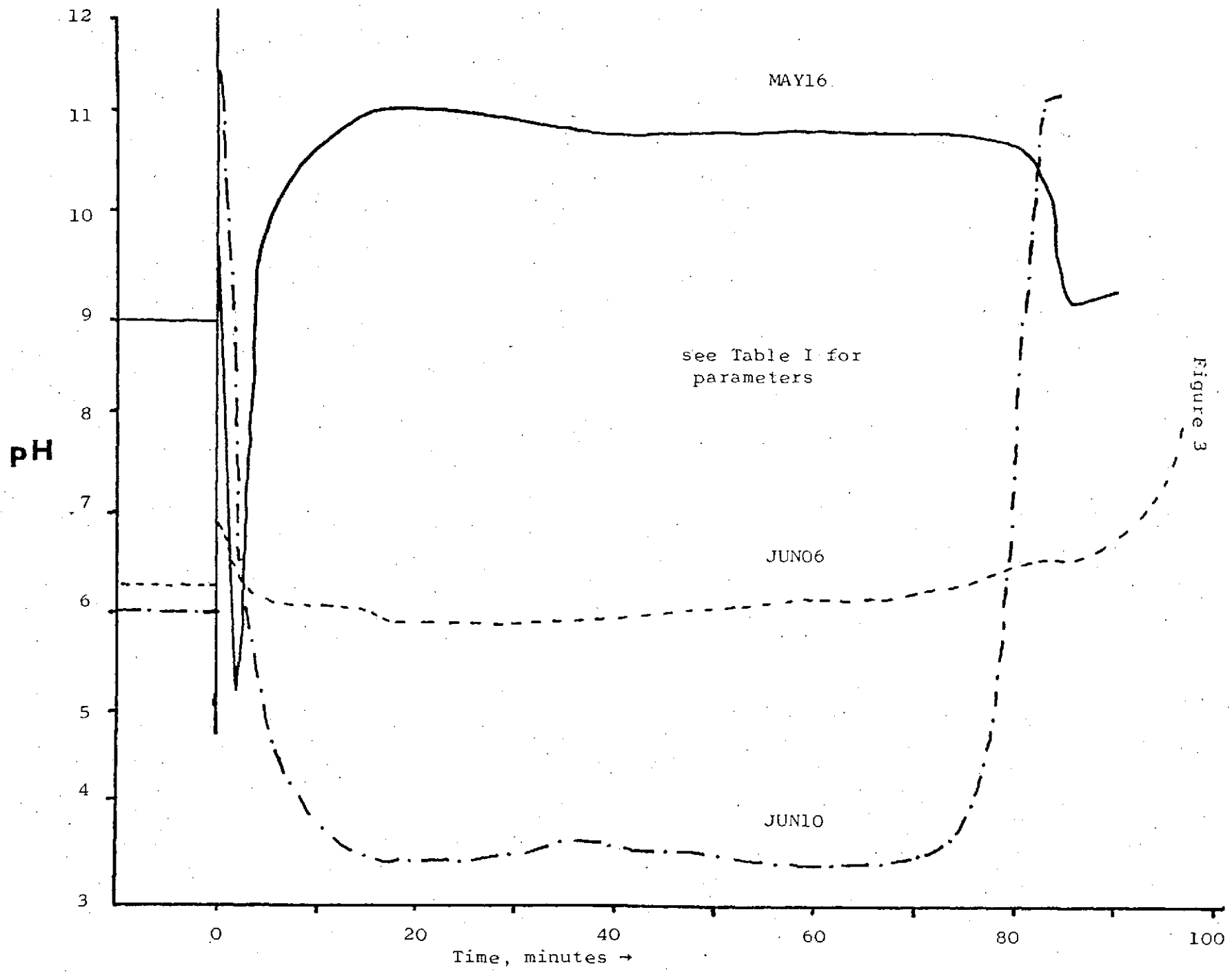
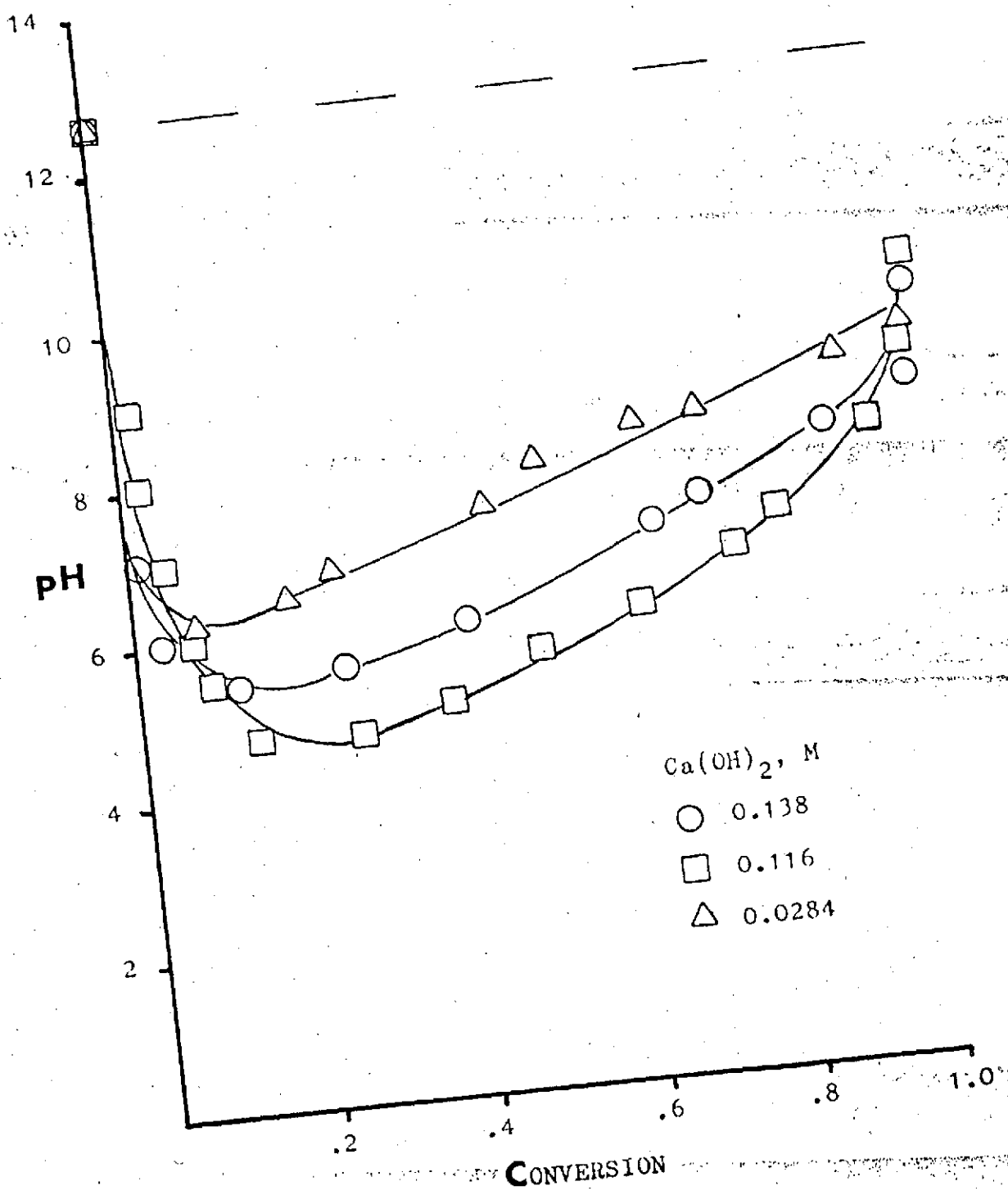


Figure 3

Figure 4.

HCHC = 0.33 ± 0.01 M

50° C.



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Figure 5

HCHO = 0.365 ± 0.01 M

50°C.

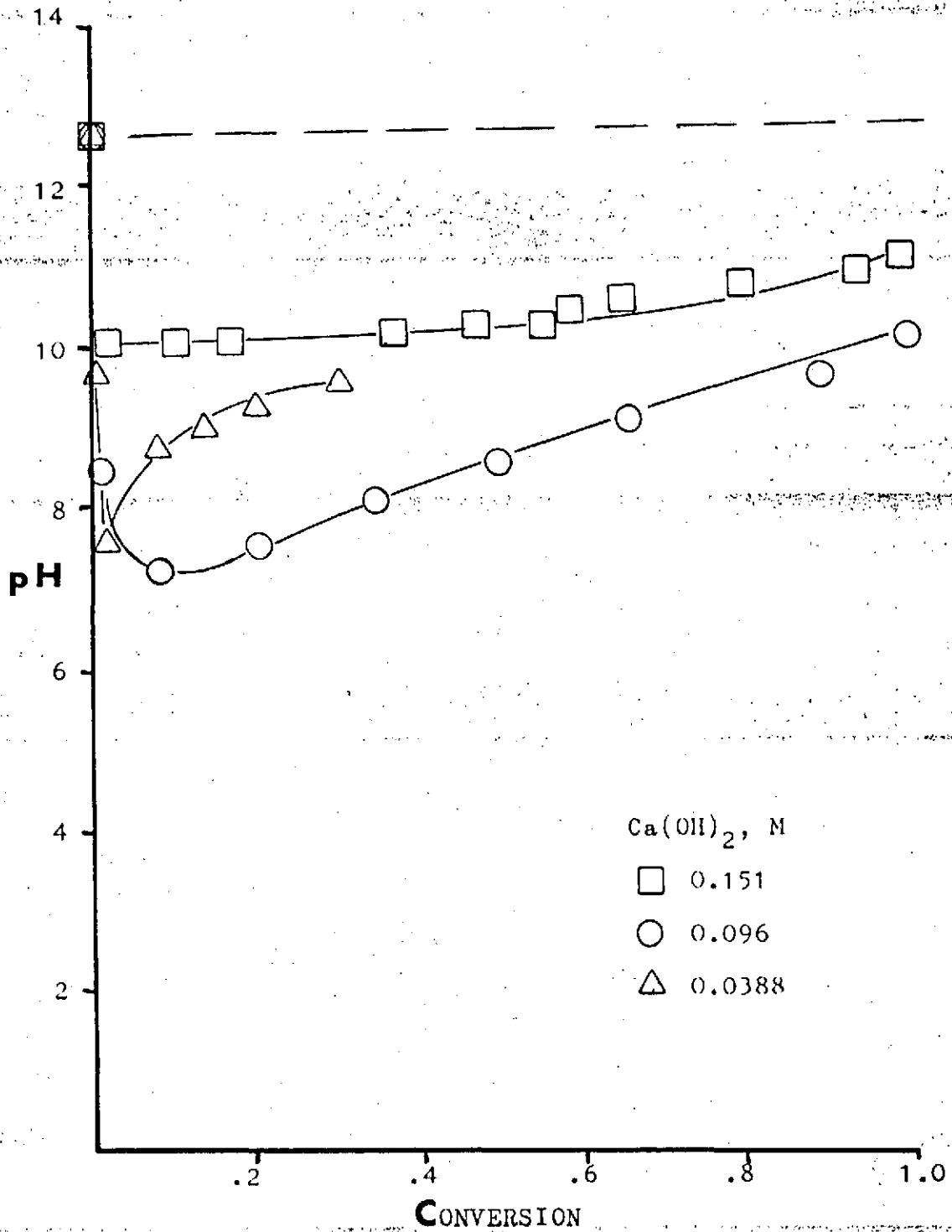


Figure 6

HCHO = 0.386 M

50°C.

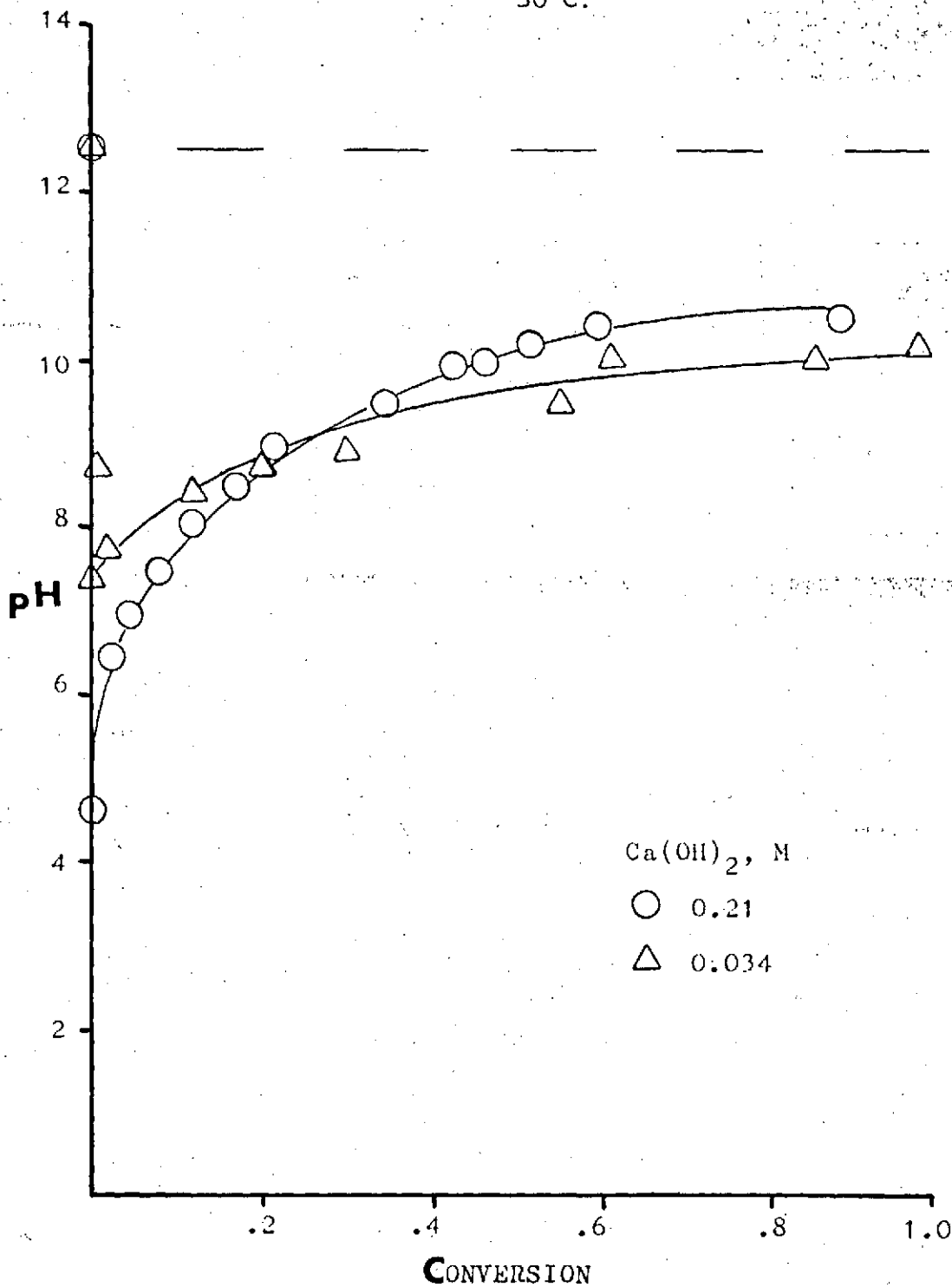
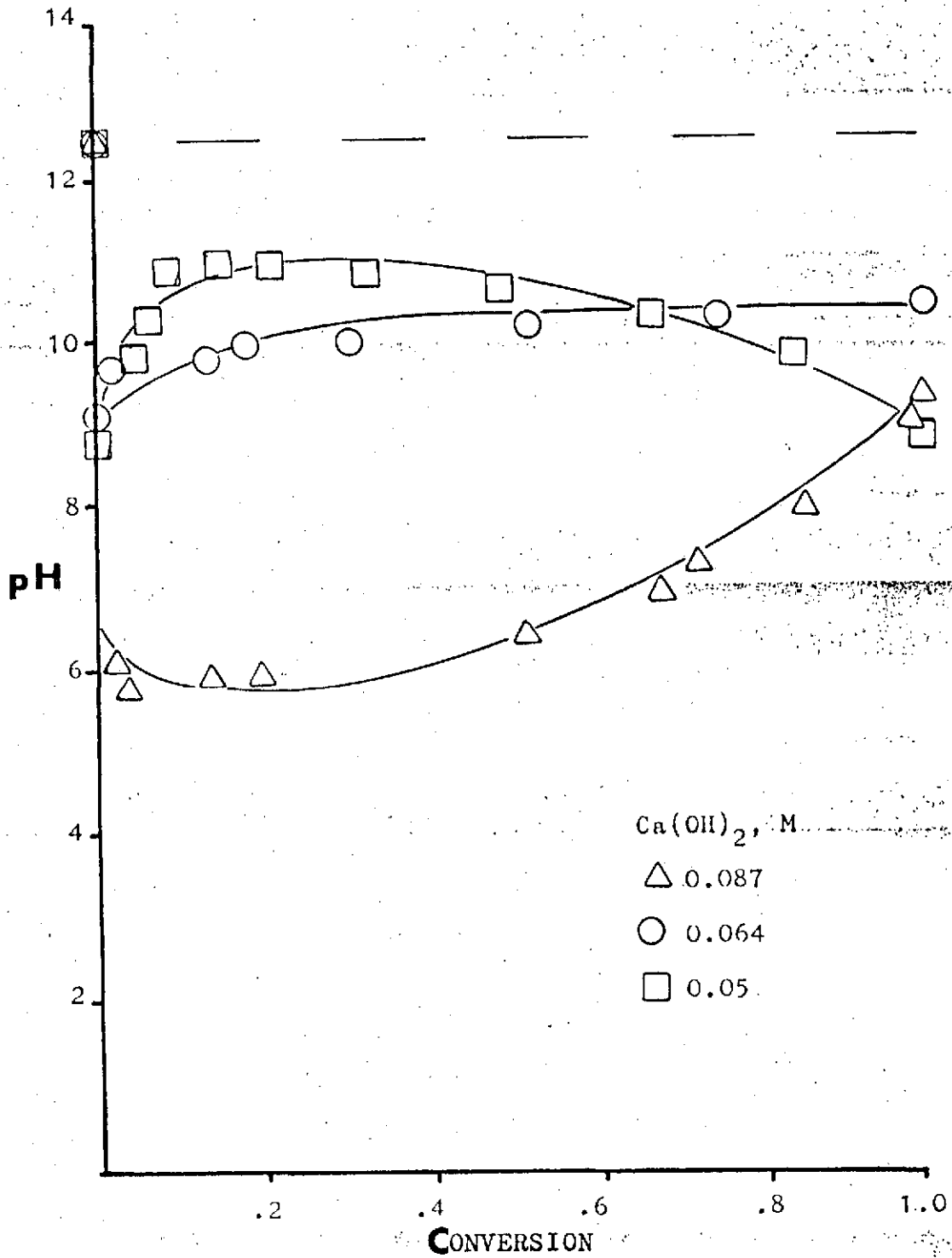


Figure 7

HCHO = 0.44 ± 0.02 M

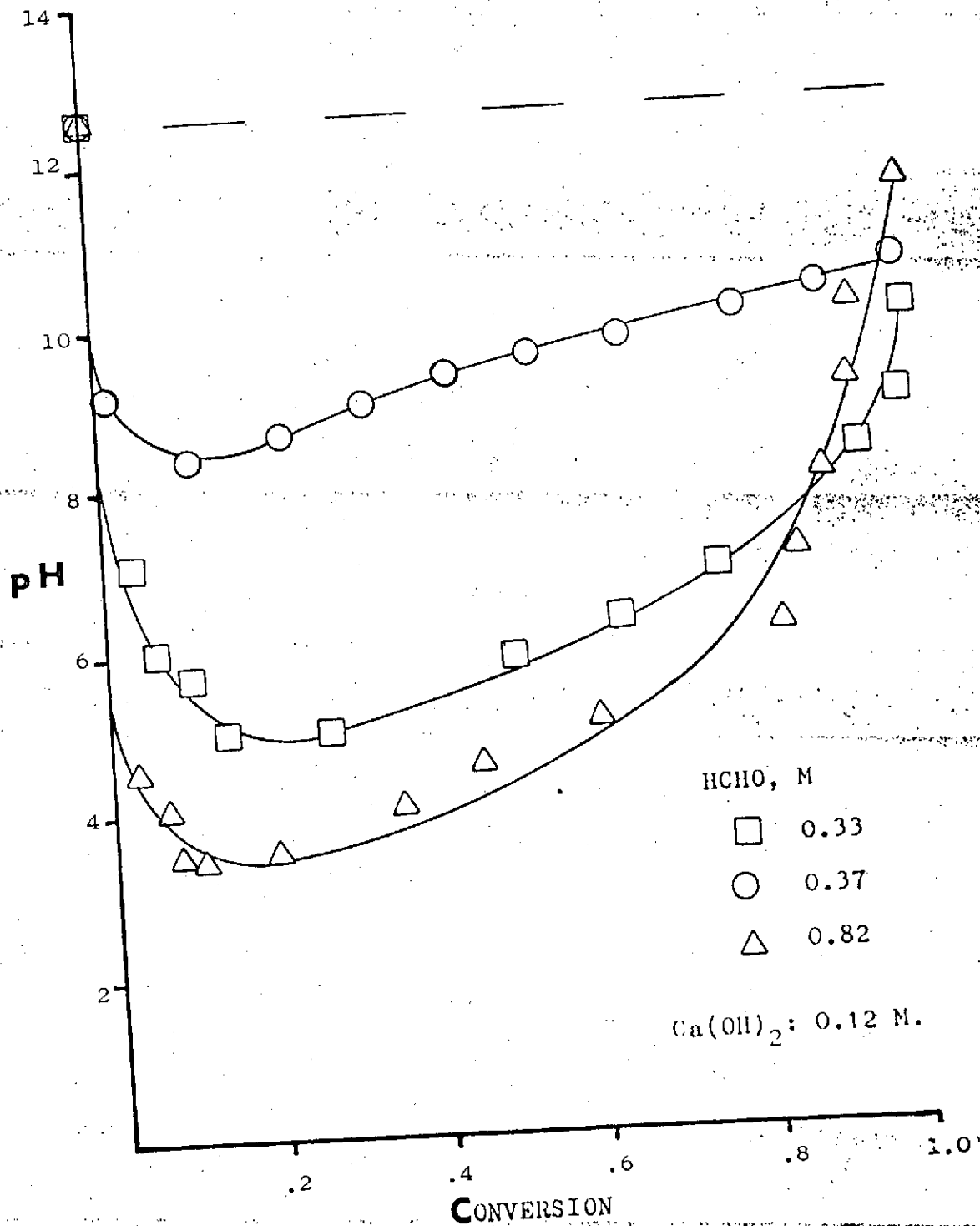
50° C.



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Figure 8

50°C.



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Figure 9

T = 75°C; 0.01 mole benzoyl carbinol

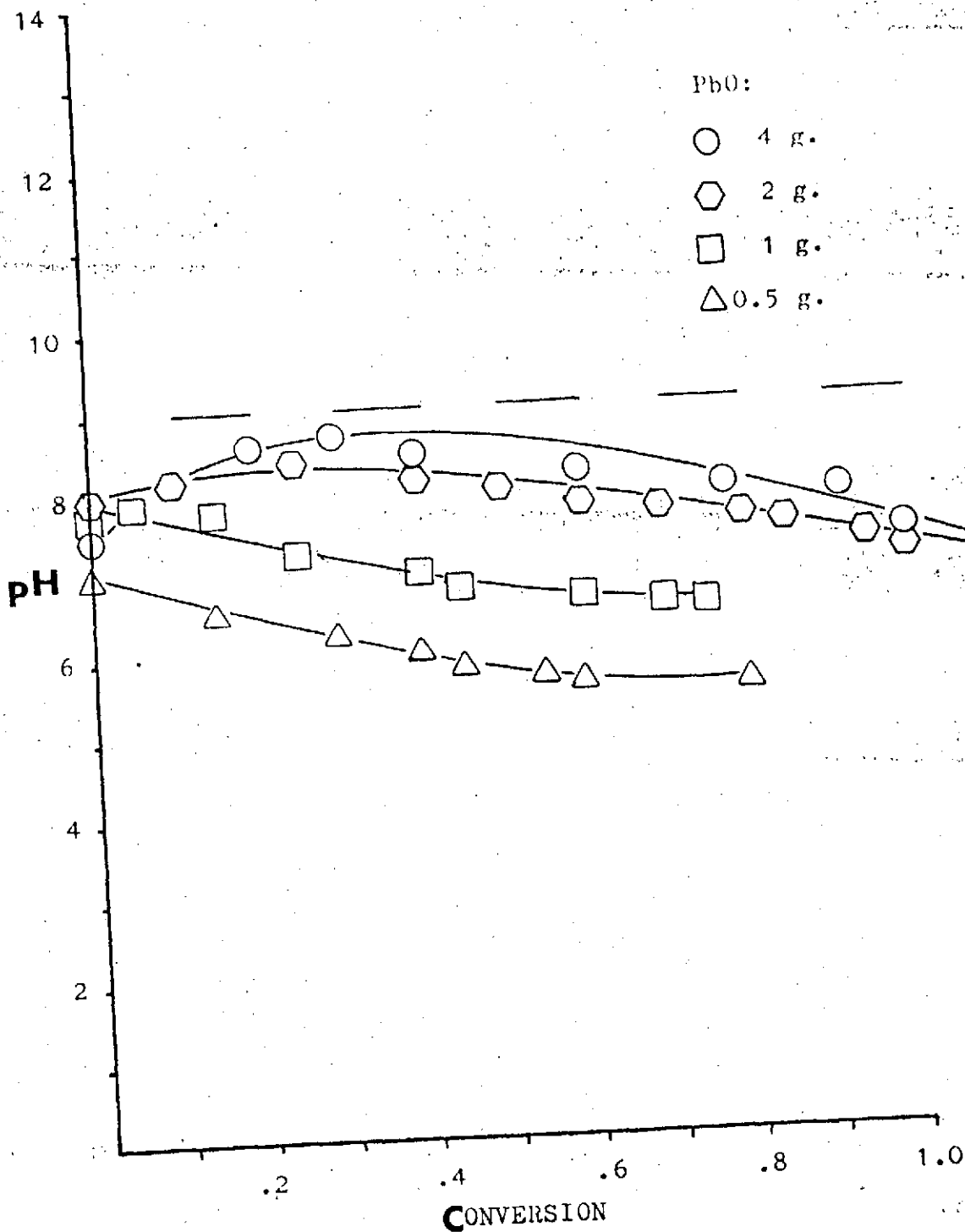
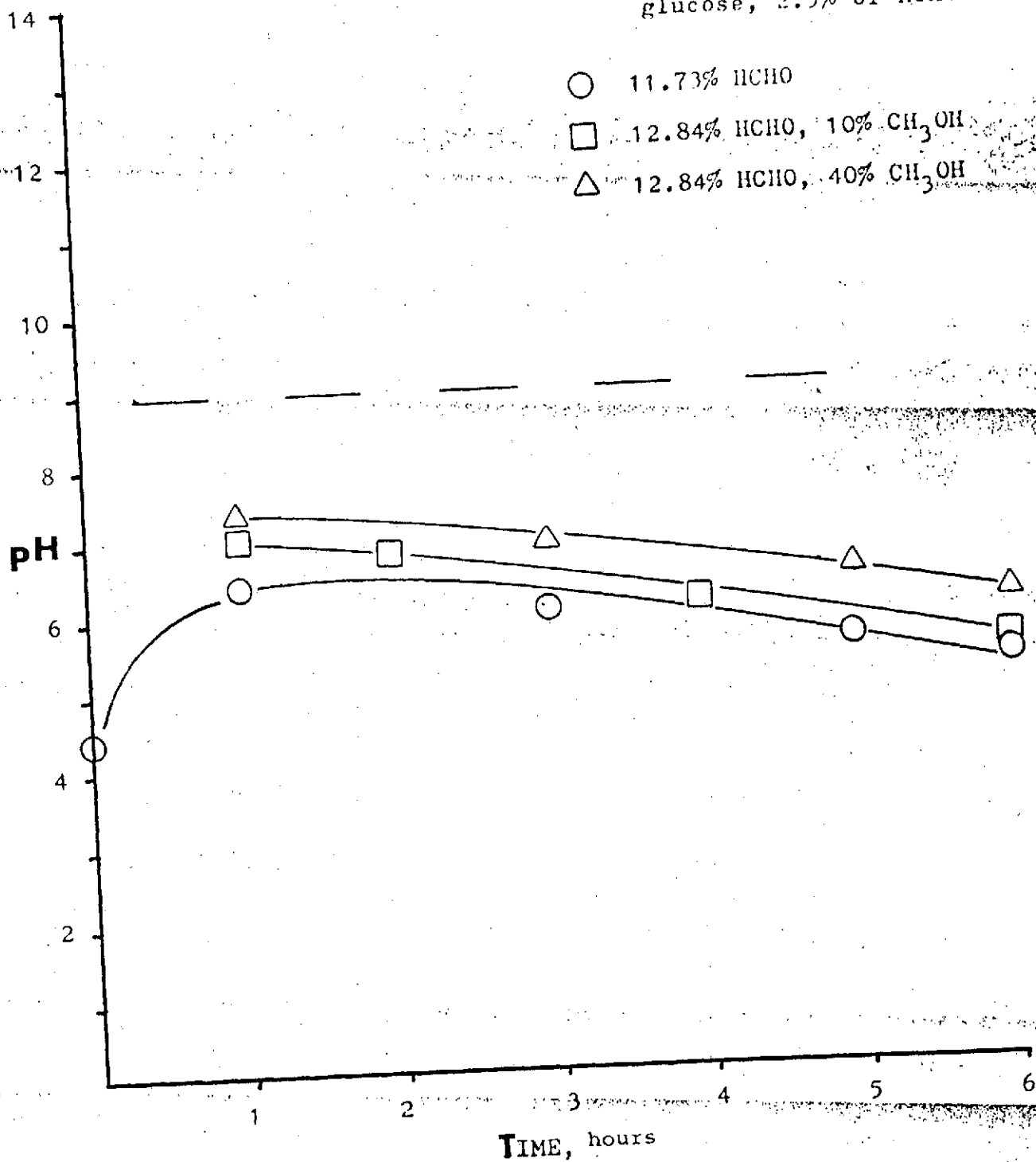


Figure 10

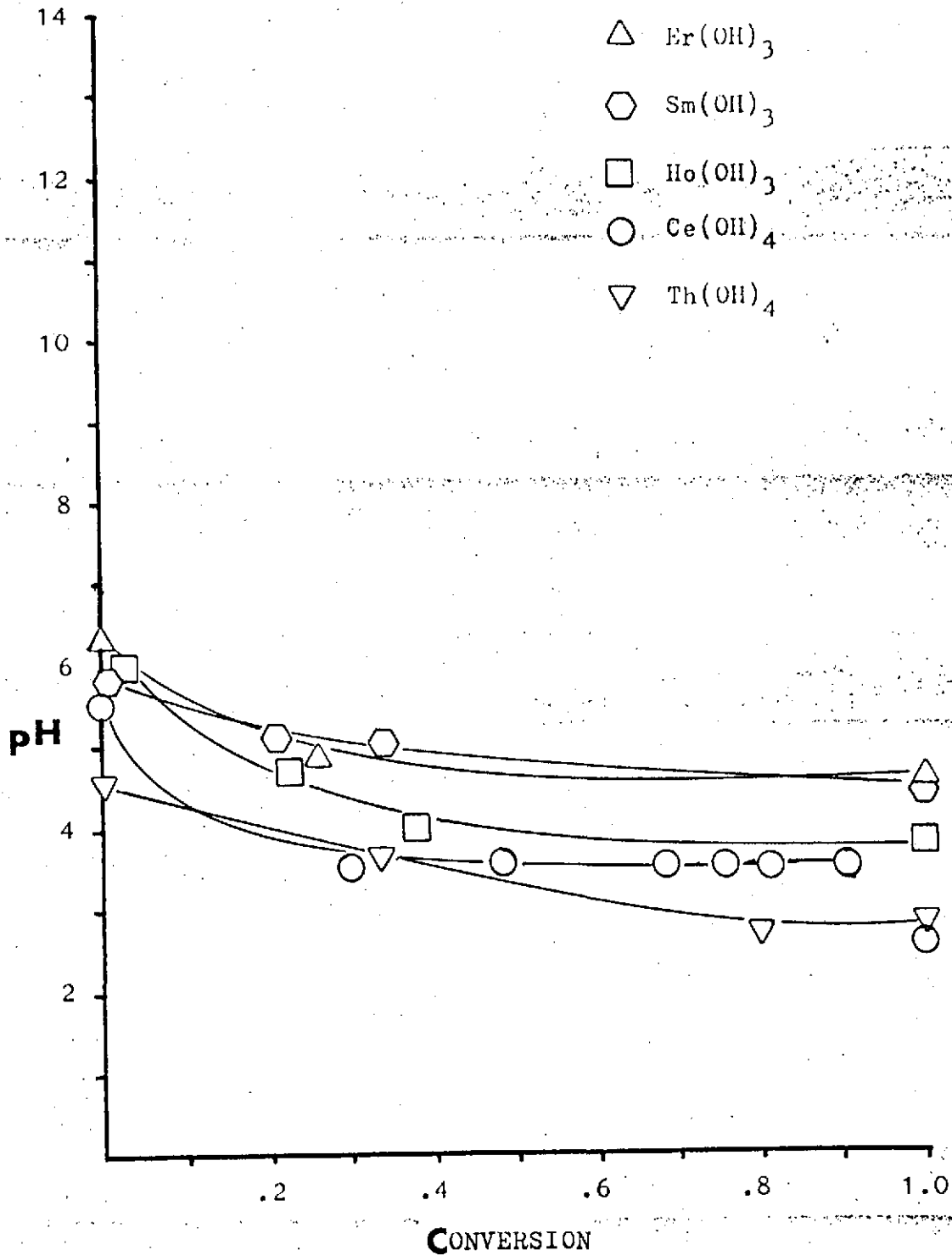
$T = 75^{\circ}\text{C}$; $\text{PbO}:\text{HCHO} = 1:10$
glucose, 2.5% of HCHO



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Figure 11

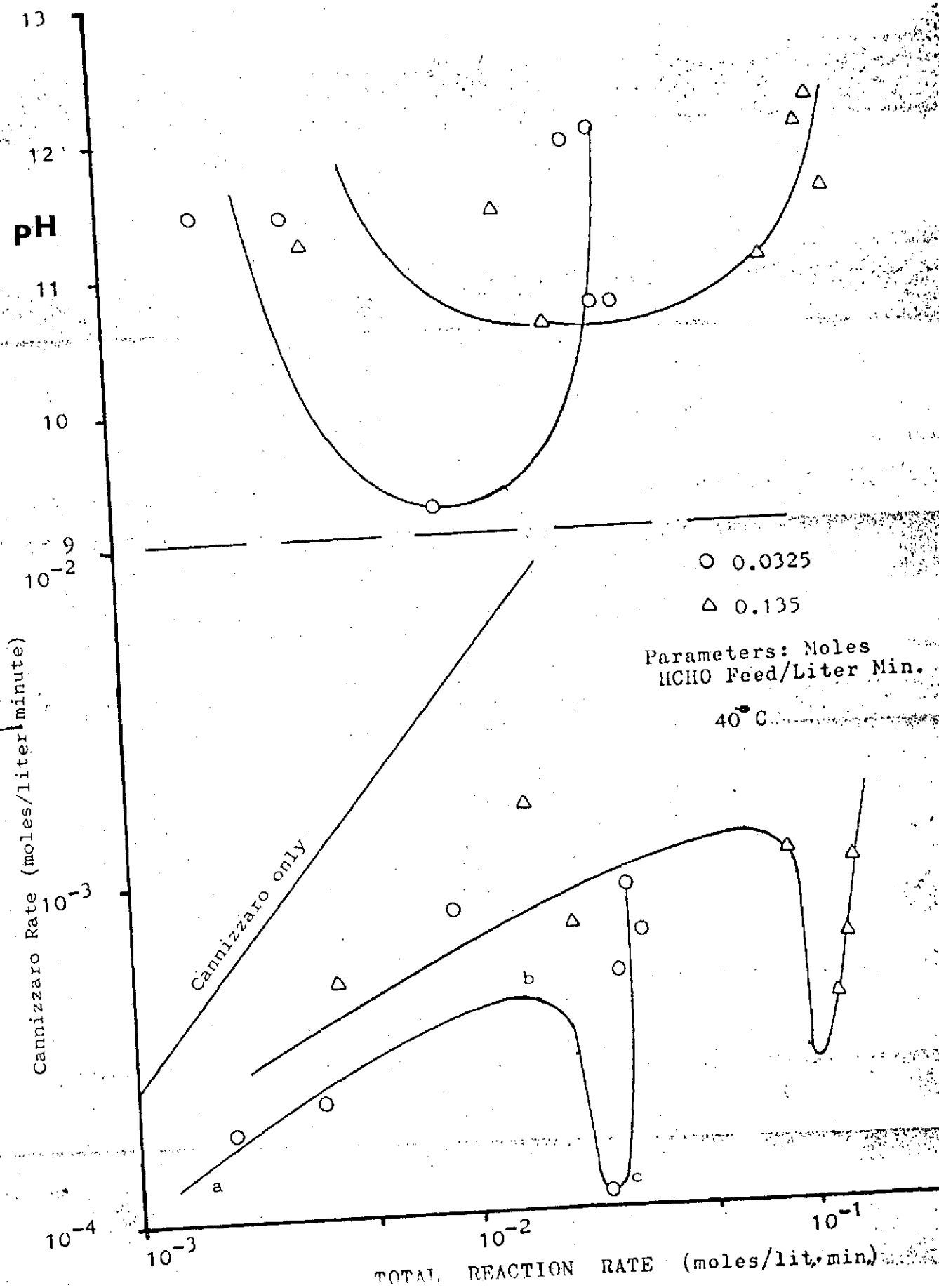
T = 110° C, P = 1.8 atm.



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Figure 12



Appendix 1

Computer Program

```
DOUBLE PRECISION NAME  
READ(5,100)NAME  
CALL IFIDE(20,NAME)  
FORMAT(A14)  
WRITE(21,101)NAME  
READ(20,12)CO  
READ(20,12)CAT  
FORMAT(1F)  
FORMAT(1I)  
READ(20,13)N  
J=N-4  
K=N-2
```

```
WRITE(5,10)CO  
WRITE(21,11)CO  
WRITE(5,50)CAT  
WRITE(21,50)CAT  
FORMAT(10X,'CAT POLARITY',F9.4)  
DIMENSION A(50),E(50),C(50),D(50),E(50)  
WRITE(5,11)J  
WRITE(21,11)J  
FORMAT(10X,'NUMBER OF POINTS IS',I4)  
FORMAT(10X,'WT PCNT HCHO INITIAL',F6.4)  
PRINT DATE,INITIAL CONDITIONS,NUM OF PTS
```

```
DO 35 I=3,N  
PRINT TIME AND PEAK AREAS  
READ(20,25)A(I),B(I),C(I),D(I)  
WRITE(21,25)A(I),B(I),C(I),D(I)  
FORMAT(4F)  
CALC AND PRINT WT. PCNTS
```

```
B(I)=B(I)*256.  
C(I)=C(I)*2.4*2.  
C(I)=D(I)*1.05*1.  
E(I)=B(I)+C(I)+D(I)  
B(I)=B(I)/E(I)  
C(I)=C(I)/E(I)  
D(I)=D(I)/E(I)  
CONTINUE  
DUMMY SCALING VARIABLES
```

```
A(1)=0.0  
A(2)=0.1  
C(1)=CO*1.5  
C(2)=CO  
WRITE(5,30)  
WRITE(21,30)  
FORMAT(10X,'TIME, WT PCNTS H2O, HCHO, CH3OH')  
WRITE(5X40) (A(I),B(I),C(I),D(I) I=3,K)  
WRITE(21,40) (A(I),B(I),C(I),D(I) I=3,K)  
FORMAT(10X,4F8.4)  
CONTINUE
```

```
DO 55 I=1,N  
NORMALIZE TO HCHO AND PRINT  
C(I)=C(I)/CO  
CONTINUE  
WRITE(5,50)  
FORMAT(10X,'TIME, WT PCNT HCHO/INITIAL')  
WRITE(21,50)  
WRITE(5,60) (A(I),C(I), I=1,N)  
WRITE(21,60) (A(I),C(I), I=3,K)  
WRITE(21,60) (A(I),C(I), I=3,K)  
WRITE(22,60) (A(I),C(I), I=3,K)  
FORMAT(4X,2F8.4)
```

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```
..PLOT RESULTS  
CALL PLOTS(1)  
CALL PLOT(1.0,1.0,3)  
CALL SYMBOL(1.2,1.0,2.25,NAME,0.0,10)  
CALL PLOT(3.0,3.0,3)  
CALL SCALE(A,N,5.0,XMIN,DX)  
CALL AXIS(3.0,3.0,4,TIME,4,5.0,0.0,XMIN,DX)  
CALL SCALE(C,N,5.0,YMIN,DY)  
CALL AXIS(3.0,3.0,4,HC/CO,4,5.0,90.0,YMIN,DY)  
CALL PLOT(3.0,3.0,-3)  
CALL LINE(A,C,N,1)  
STOP  
END
```

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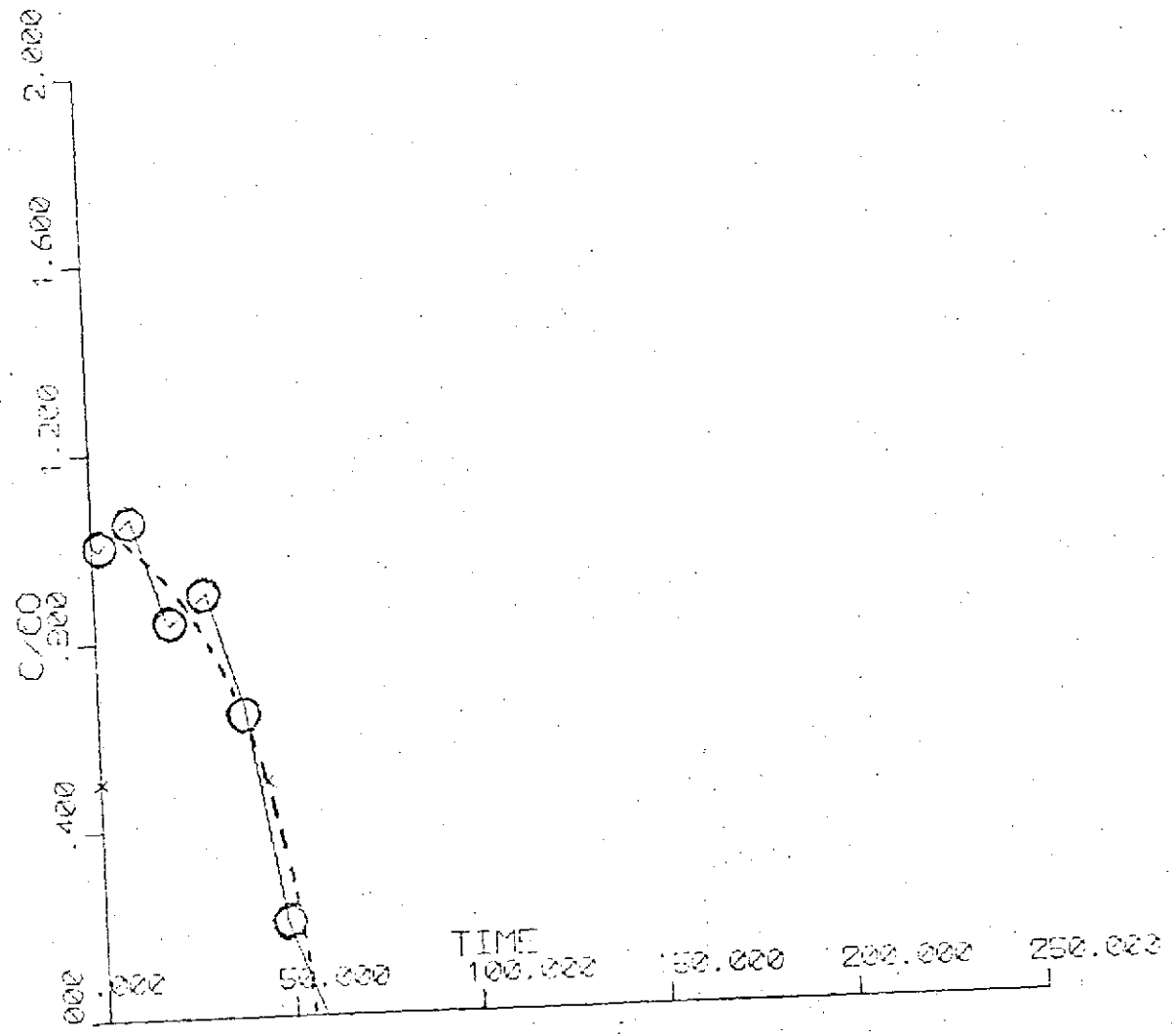
Appendix 2

Sample computer output

Sample computer graph

ISSN=9192 DSKA0.DATA.PLT[1000,11246]

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APR23.DAT

APR23.DAT

WT PNT HCHO INITIAL .2117

CAI MOLARITY .2100

NUMBER OF POINTS IS 4

| | | | |
|-------------|-----------|-----------|-----------|
| 1.5000000 | 1.9300000 | 1.2450000 | 0.0000000 |
| 11.0000000 | 1.9200000 | 1.1120000 | 0.0000000 |
| 20.5000000 | 1.7150000 | 1.0400000 | 0.0000000 |
| 32.5000000 | 1.7770000 | 0.7680000 | 0.0000000 |
| 40.0000000 | 1.8900000 | 0.0000000 | 0.0000000 |
| 220.0000000 | 1.8800000 | 0.0000000 | 0.0000000 |

TIME, WT PNTS H2O, HCHO, CH3OH

| | | | |
|----------|--------|--------|--------|
| 0.0000 | 0.0000 | 0.0176 | 0.0000 |
| 0.1000 | 0.8897 | 0.0117 | 0.0000 |
| 1.5000 | 0.9879 | 0.0121 | 0.0000 |
| 11.0000 | 0.9893 | 0.0107 | 0.0000 |
| 20.5000 | 0.9880 | 0.0112 | 0.0000 |
| 32.5000 | 0.9920 | 0.0080 | 0.0000 |
| 40.0000 | 1.0000 | 0.0000 | 0.0000 |
| 220.0000 | 1.0000 | 0.0000 | 0.0000 |

TIME, WT PNT HCHO/INITIAL

| | |
|----------|--------|
| 0.0000 | 0.3150 |
| 0.1000 | 0.2133 |
| 1.5000 | 0.2160 |
| 11.0000 | 0.1920 |
| 20.5000 | 0.2000 |
| 32.5000 | 0.1437 |
| 40.0000 | 0.0000 |
| 220.0000 | 0.0000 |

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Appendix 3

Figures 1 through 12

pH and conversion vs. time

Figure 1

APRO4

HCHO, 0.327 M; Ca(OH)₂, 0.116 M

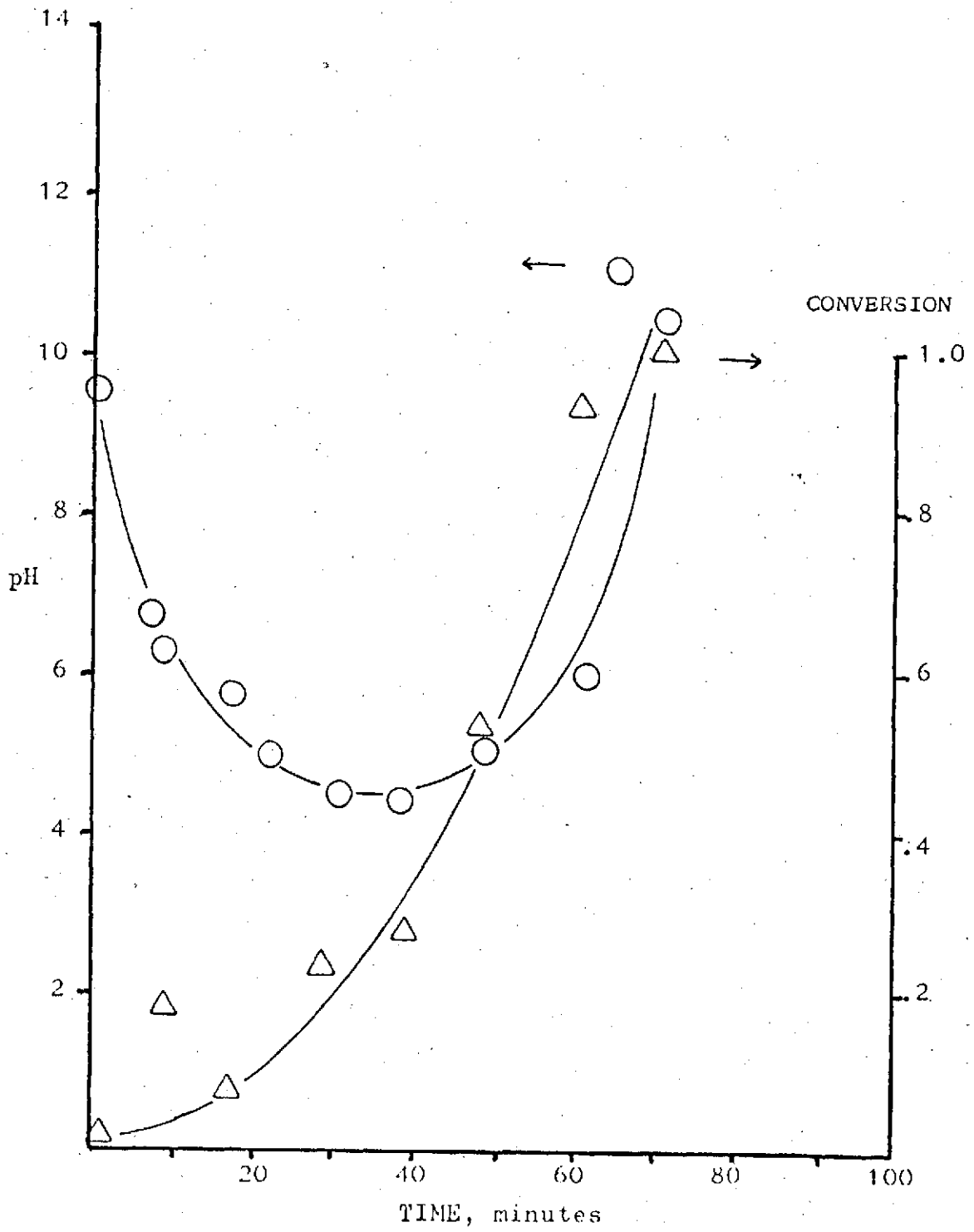


Figure 2

APR10

HCHO, 0.33 M; Ca(OH)₂, 0.138 M

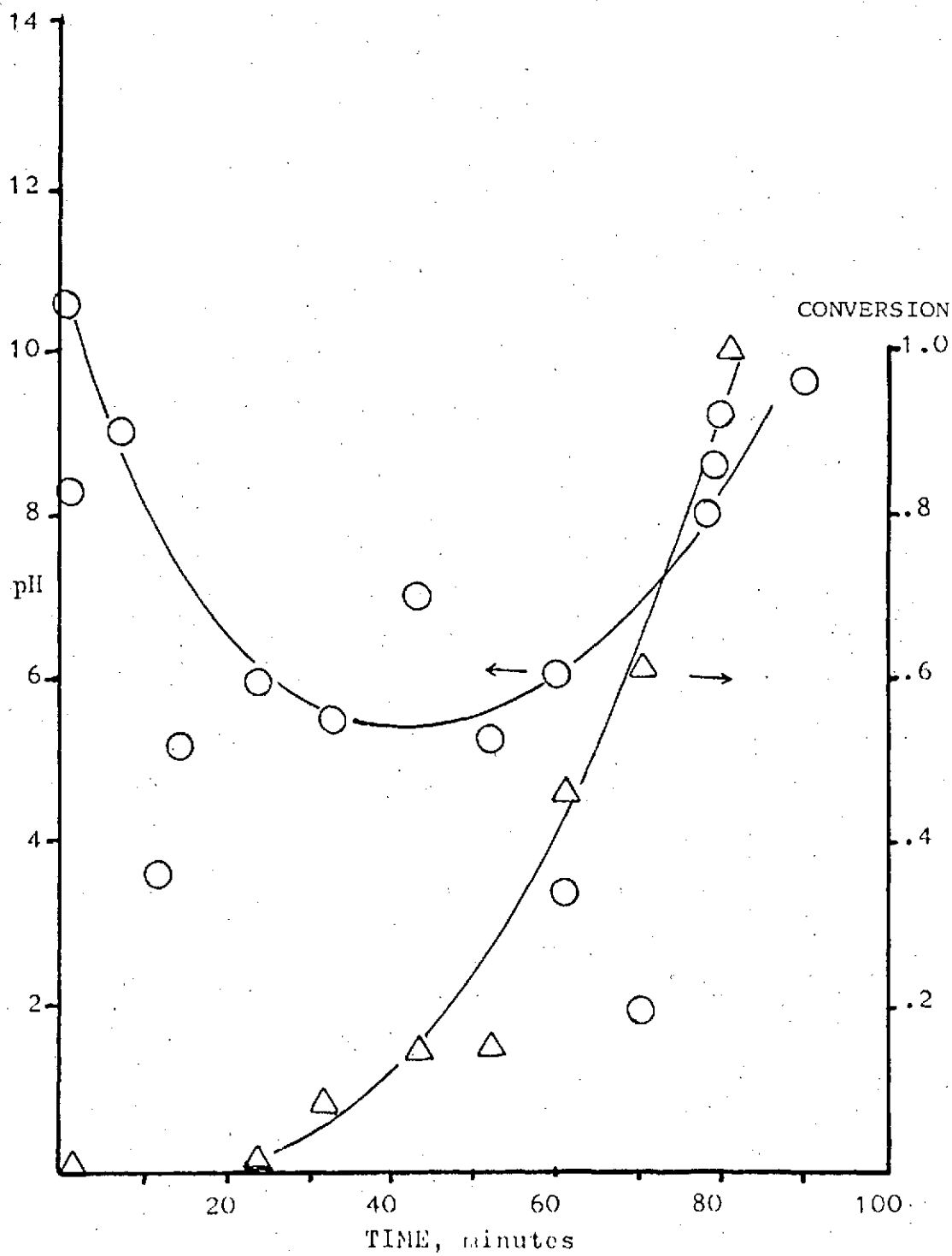


Figure 3

APR18

HCHO, 0.373 M; Ca(OH)₂, 0.096 M

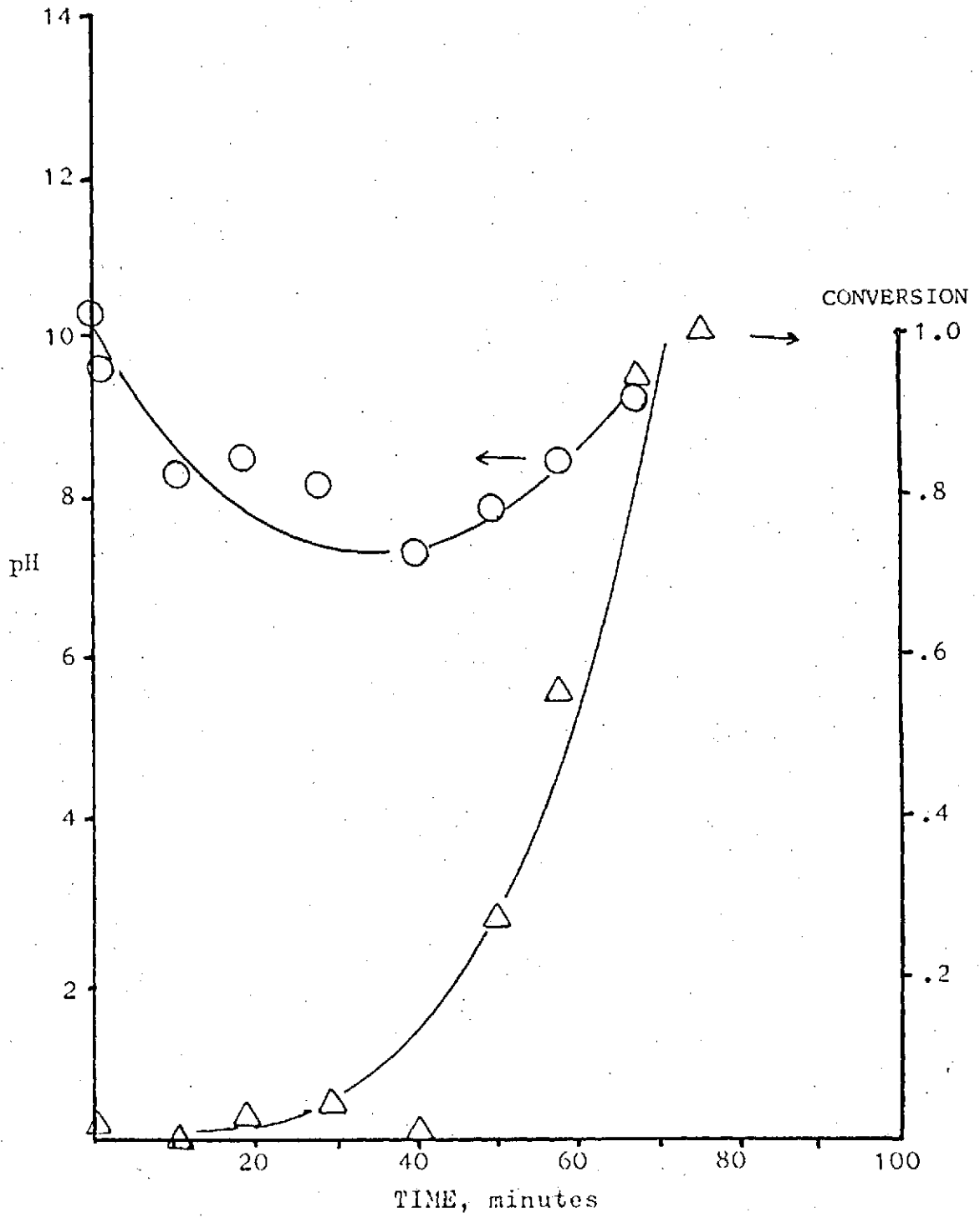


Figure 4

APR22

HCHO, 0.369 M; Ca(OH)₂, 0.151 M

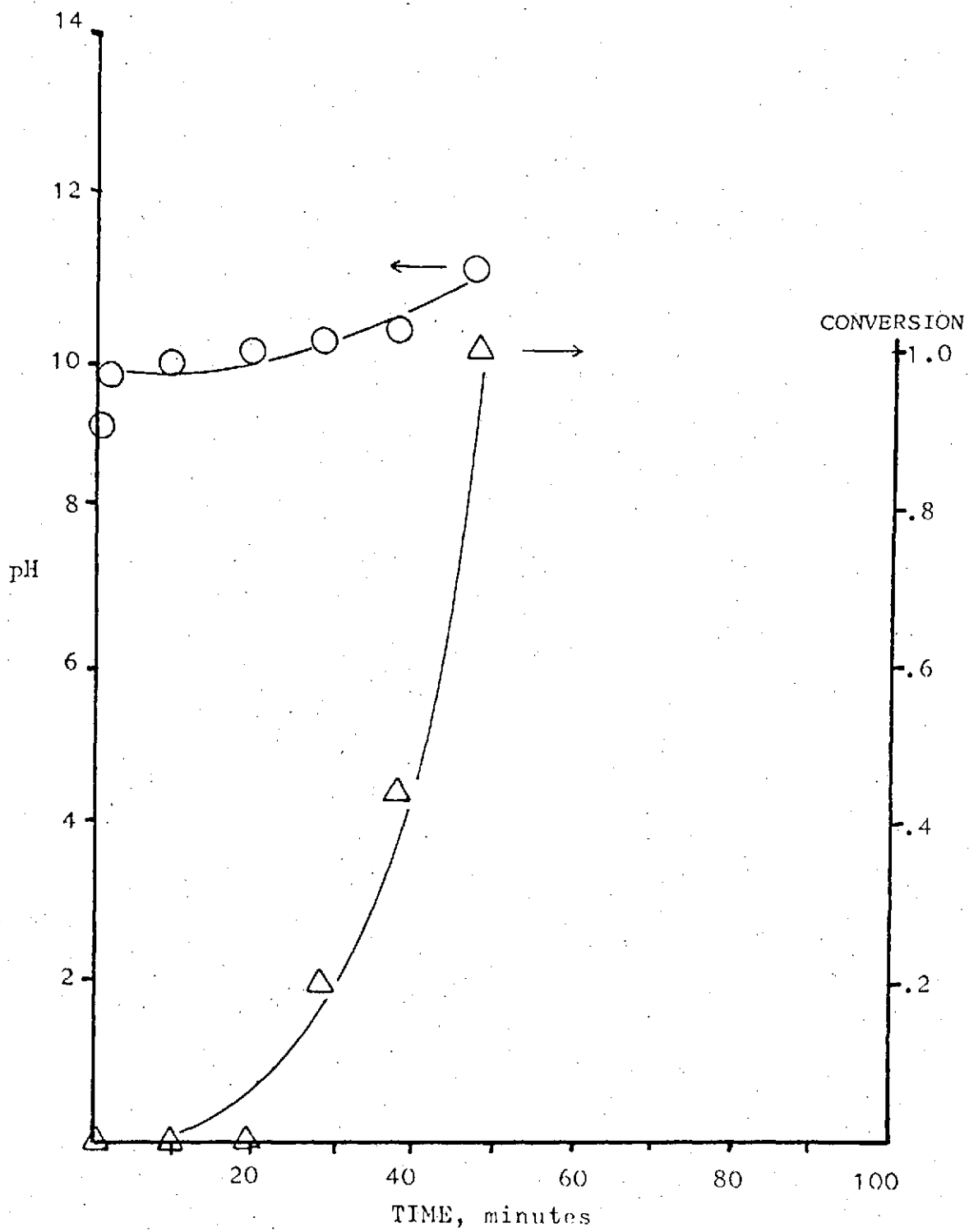


Figure 5

APR23

HCHO, 0.443 M; Ca(OH)₂, 0.064 M

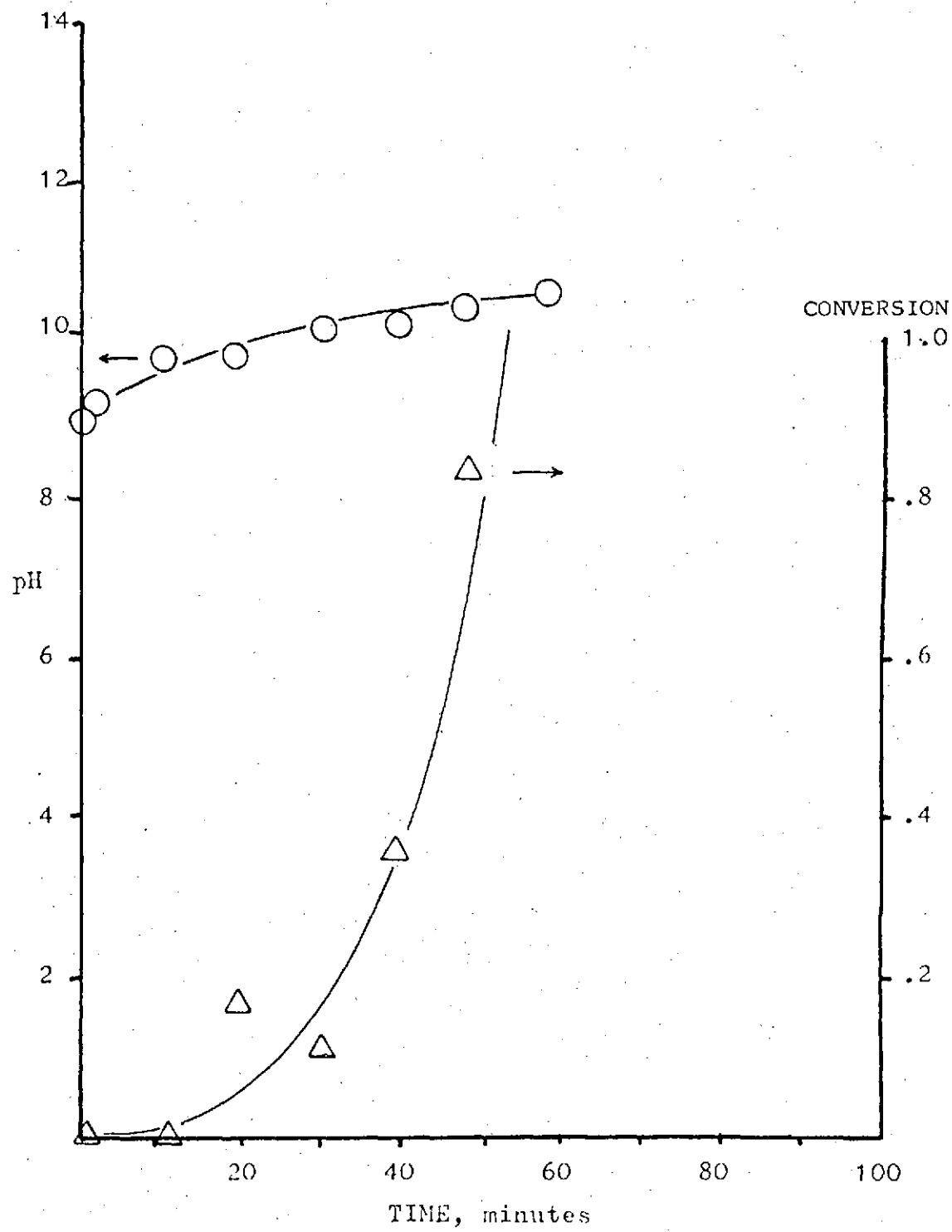


Figure 6

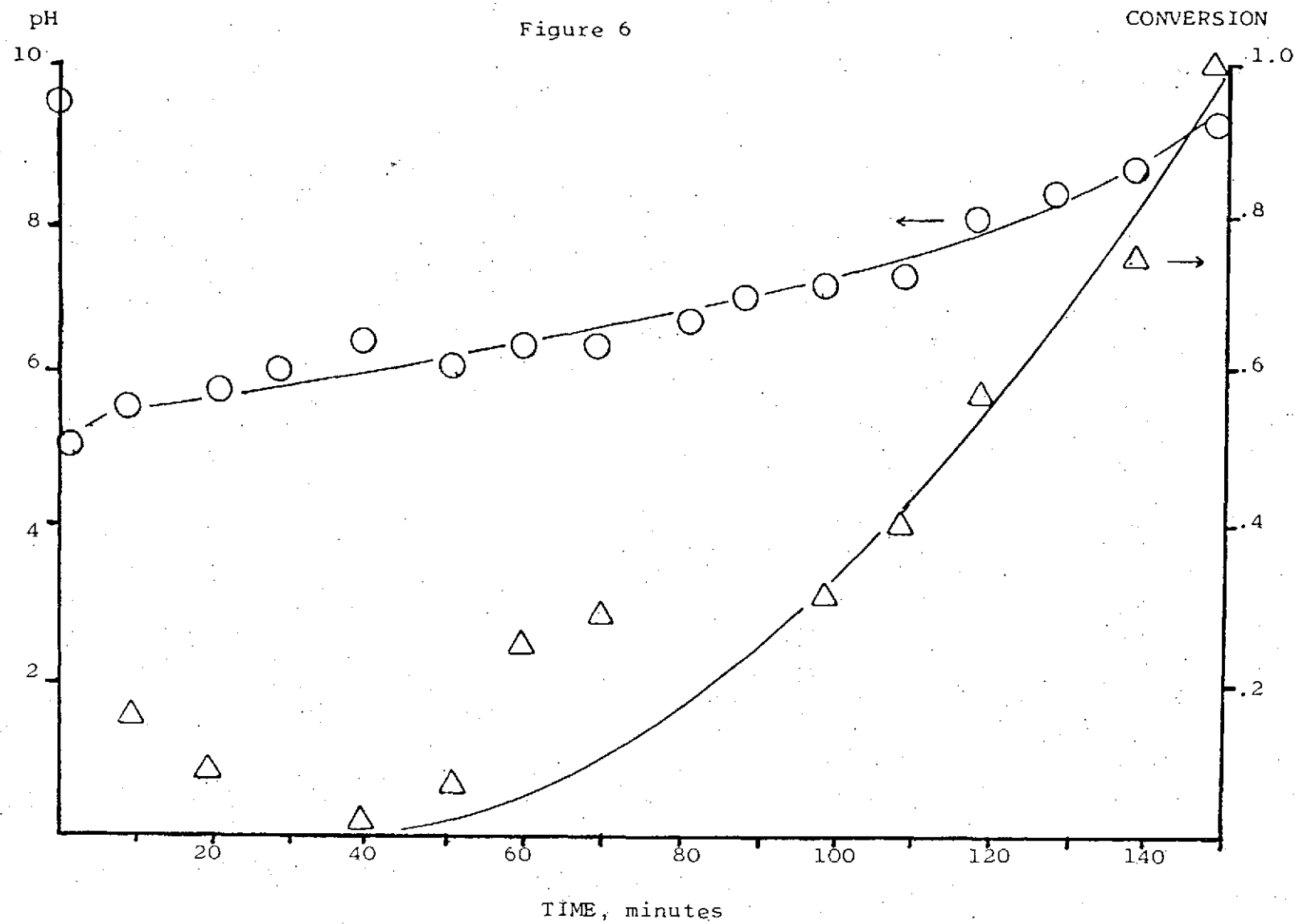


Figure 7

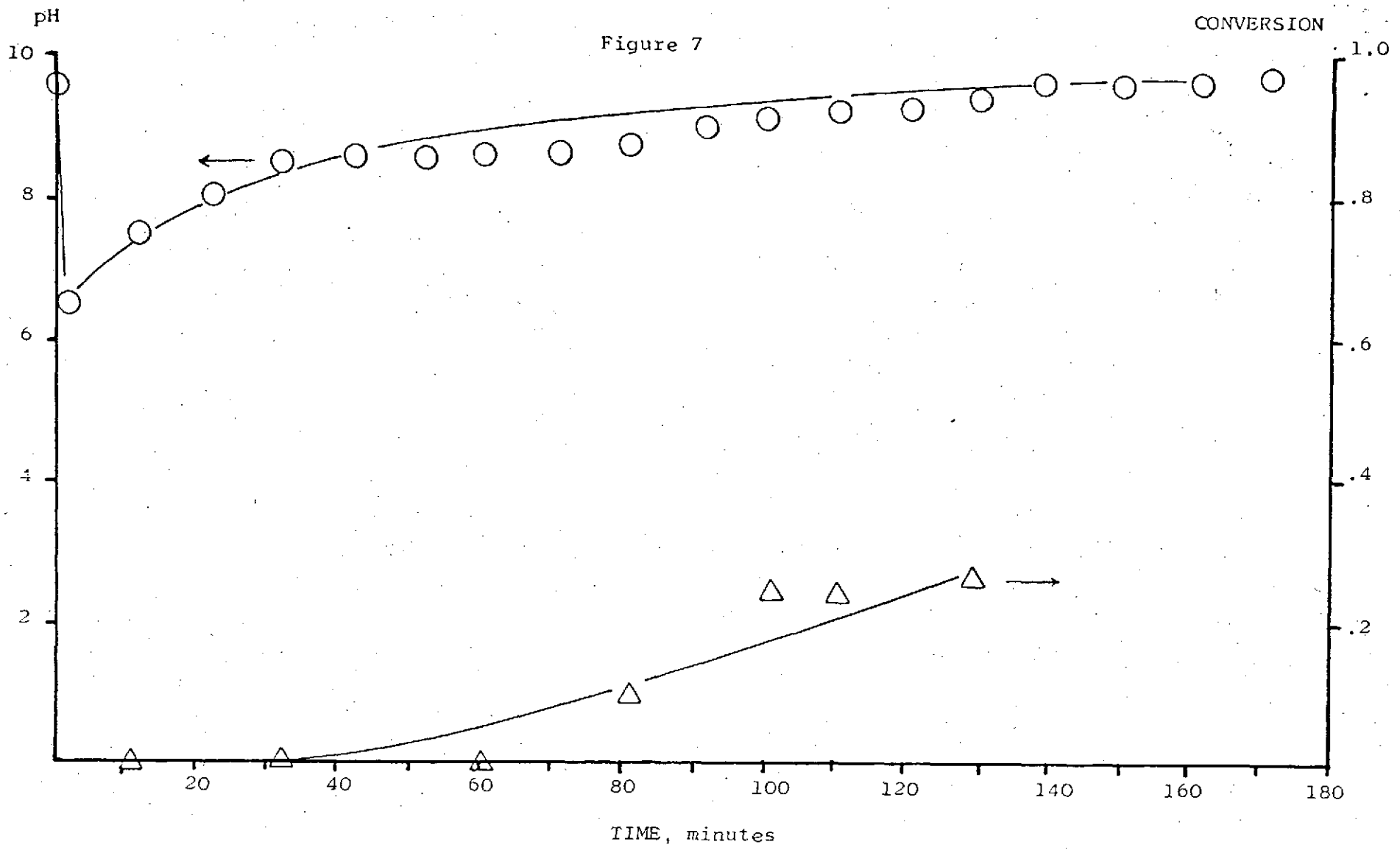


Figure 8 MAYOS HCHO, 0.386 M; Ca(OH)₂, 0.0343 M

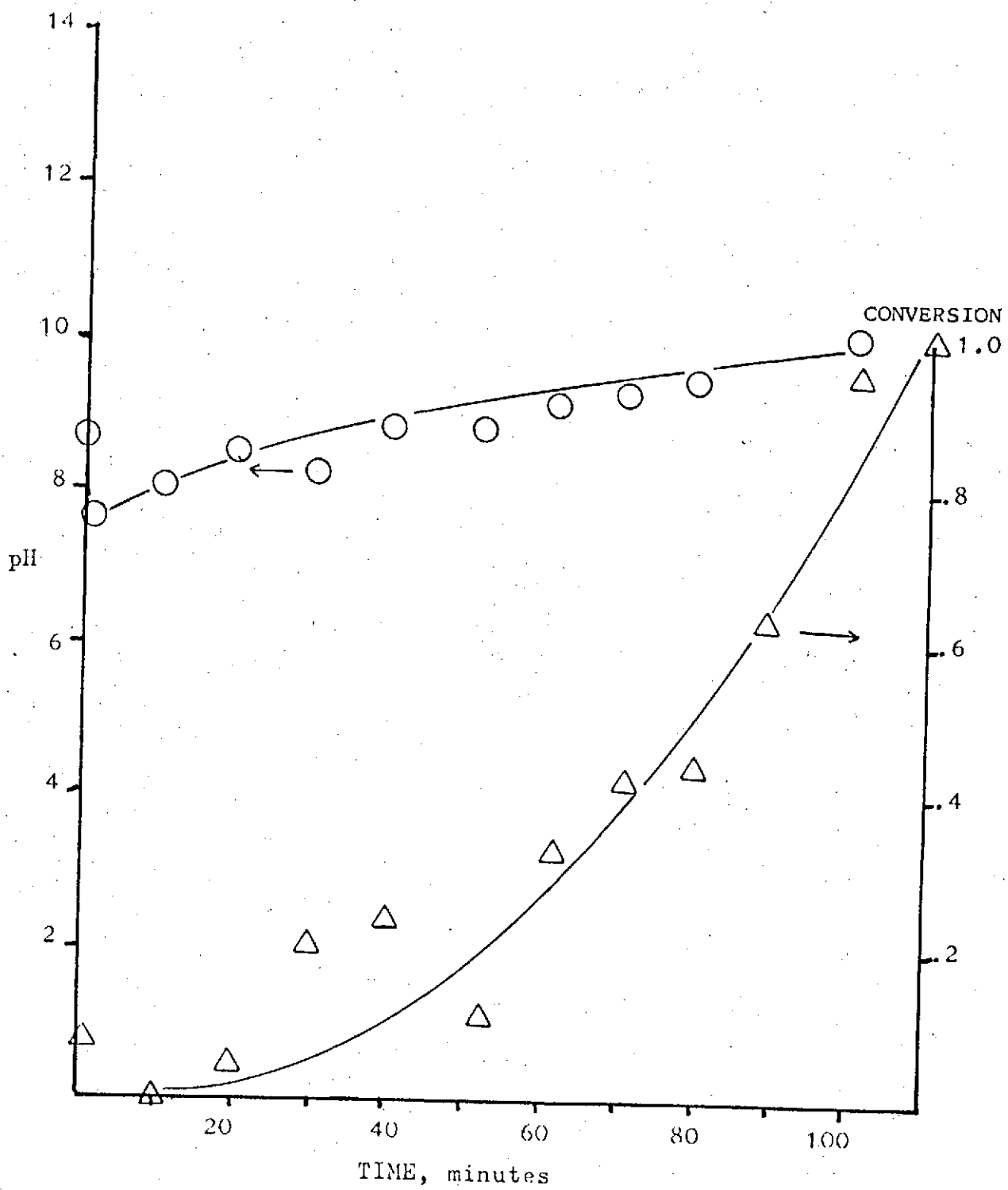


Figure 9

MAY09

HCHO, 0.386 M; Ca(OH)₂, 0.21 M

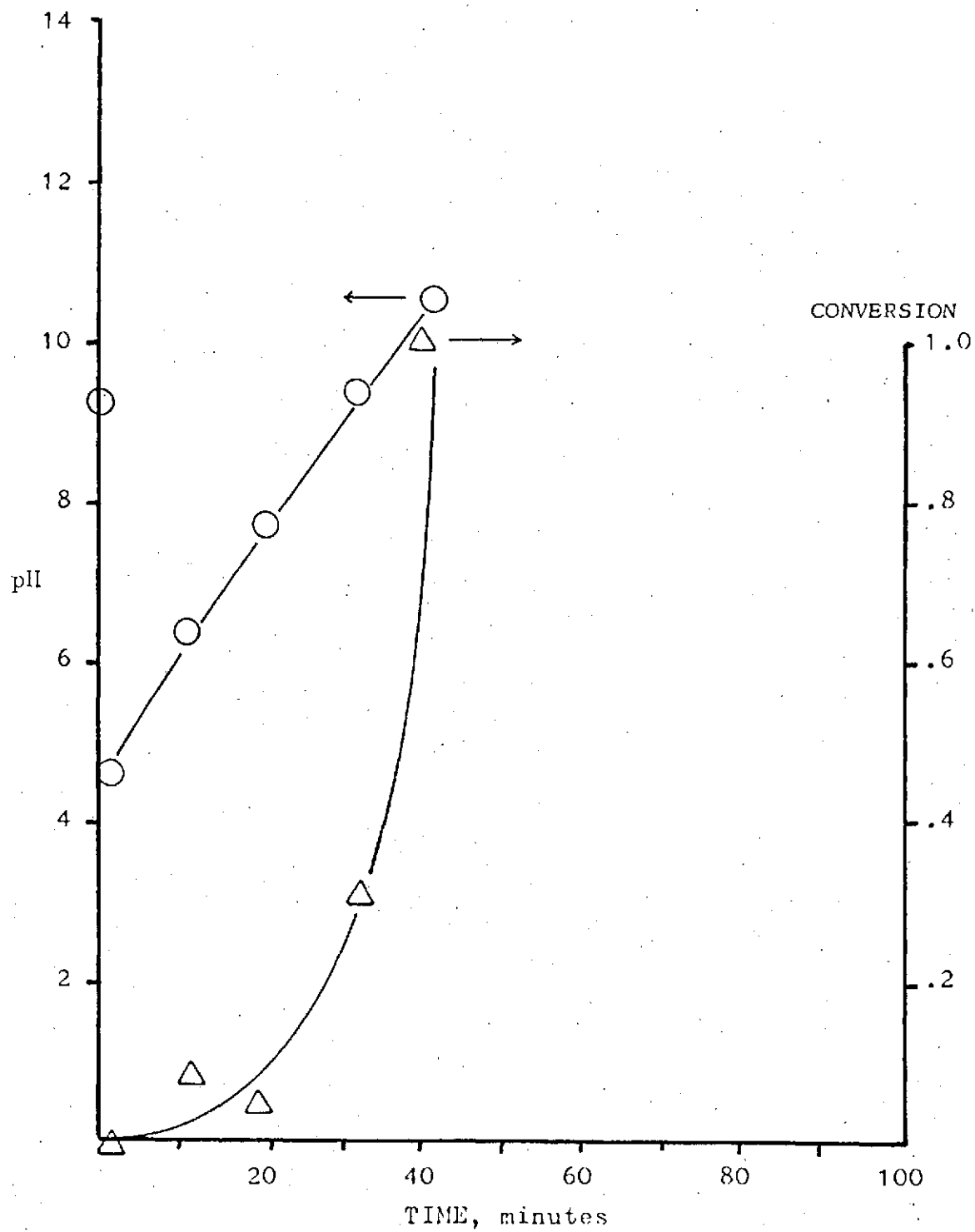


Figure 10

MAY16

HCHO, 0.458 M; Ca(OH)₂, 0.05 M

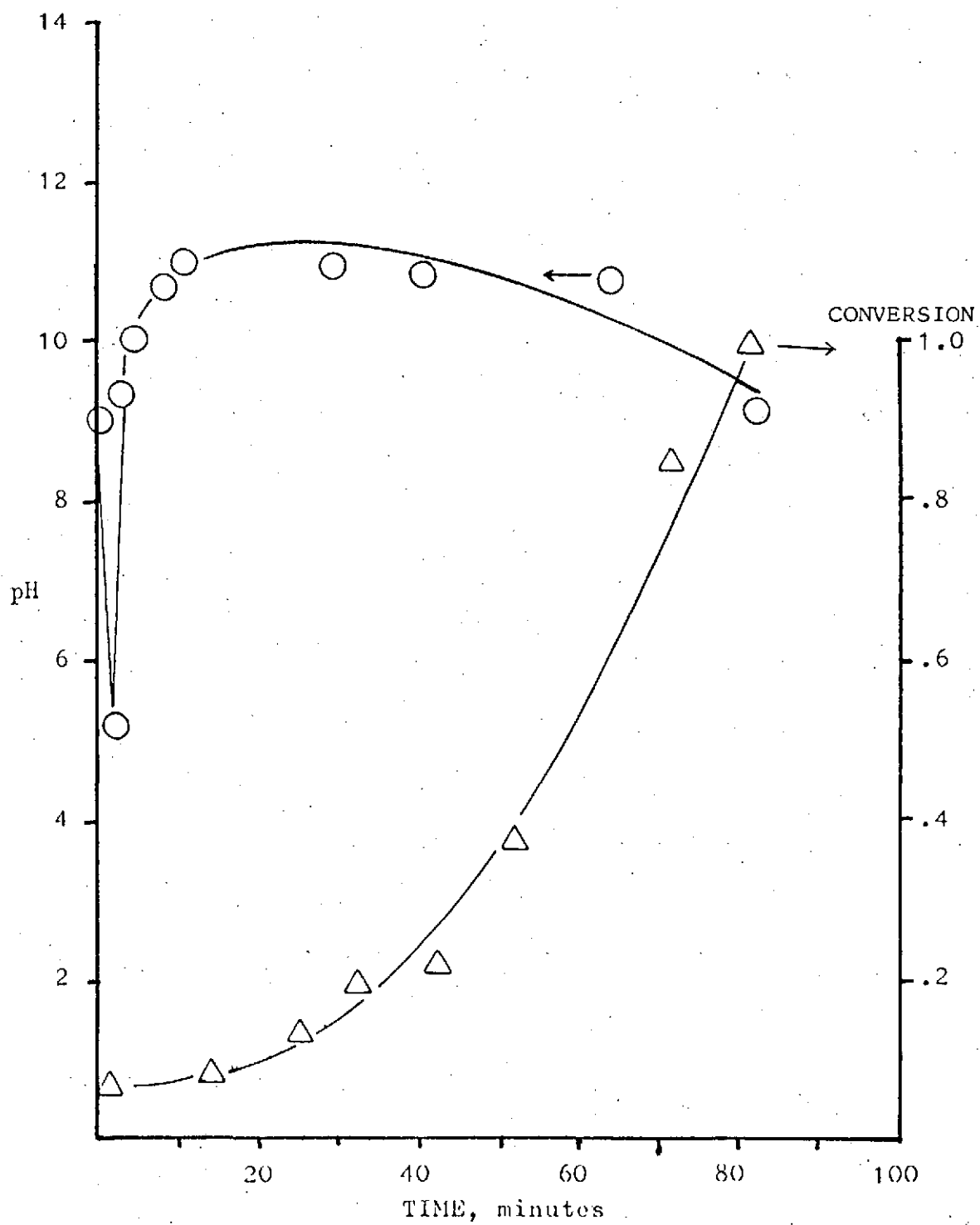


Figure 11

JUN06

HCHO, 0.422 M; Ca(OH)₂, 0.087 M

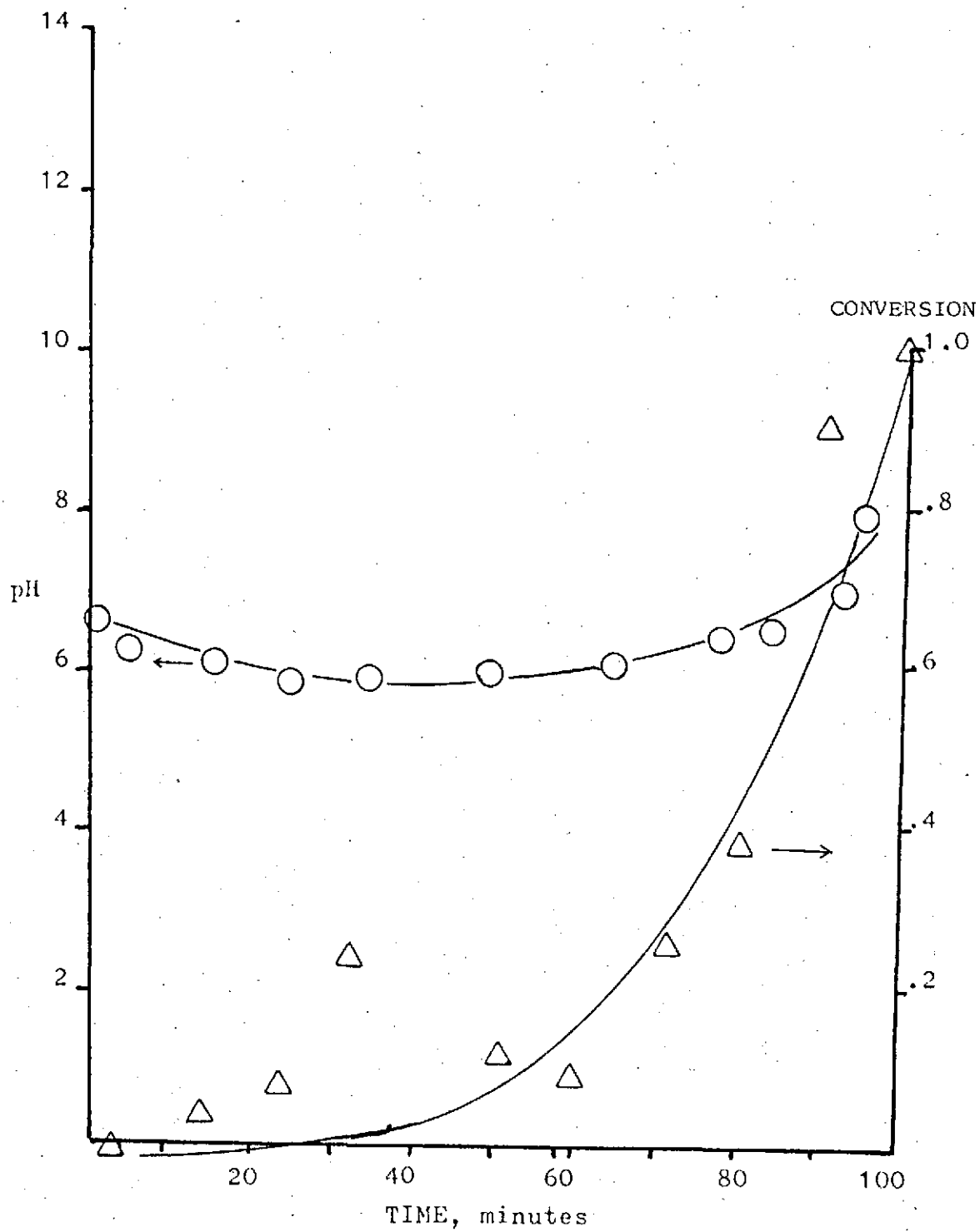
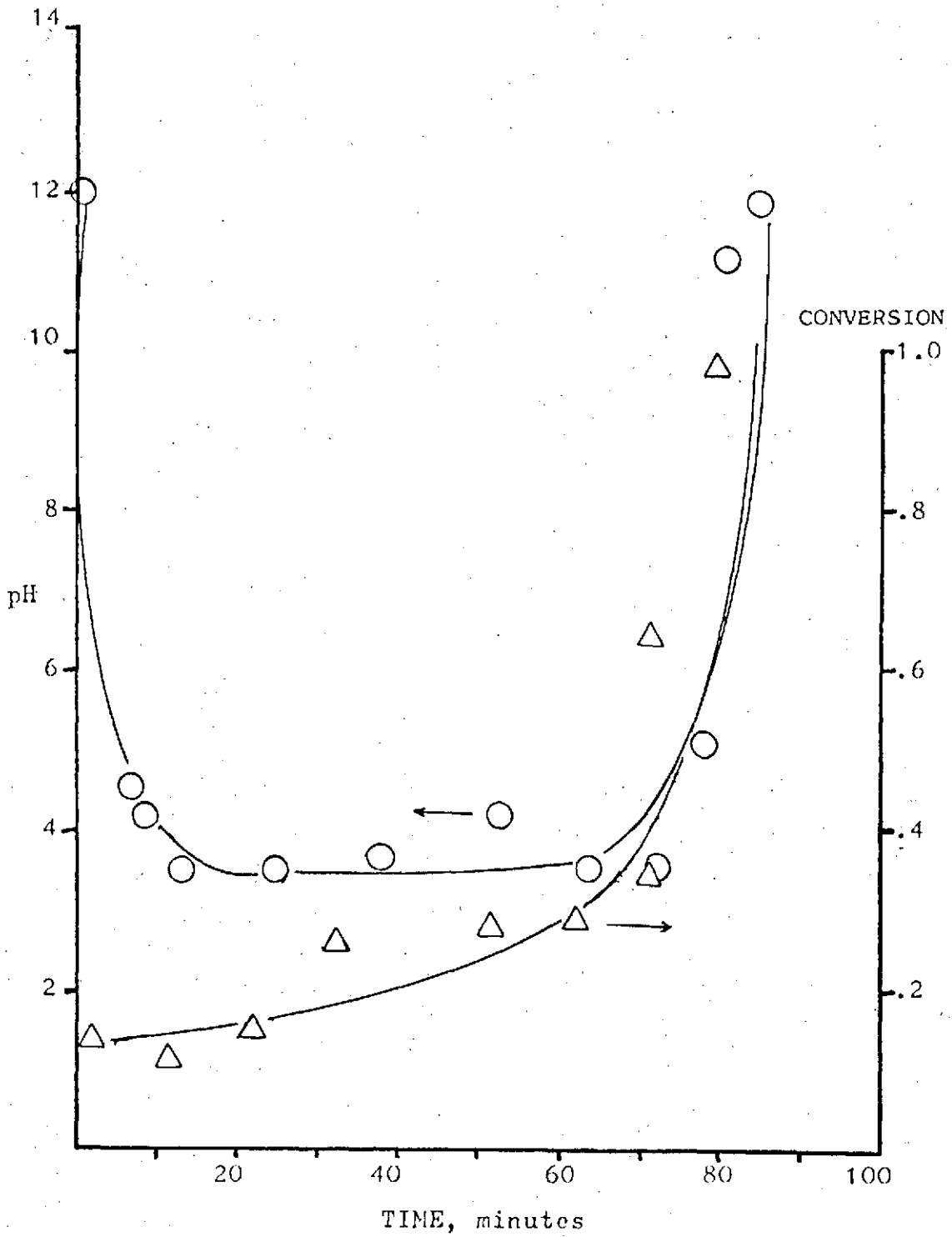


Figure 12 JUN10 HCHO, 0.825 M; Ca(OH)₂, 0.121 M



Appendix 4

Figures 1 through 12

pH vs. conversion

Figure 1 APRO4 HCHO = 0.327 M, Ca(OH)₂ = 0.116 M

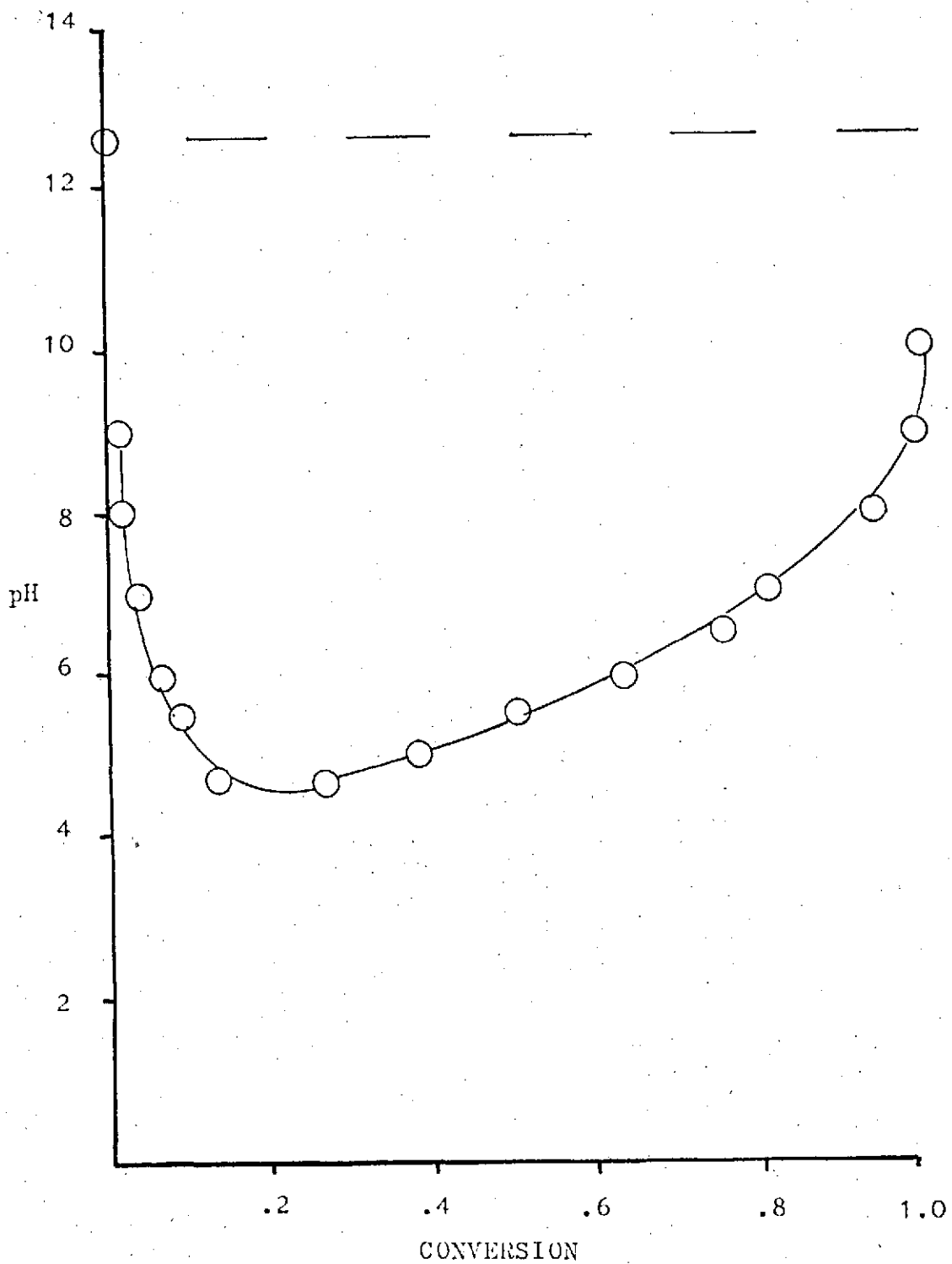


Figure 2 APR10 HCHO = 0.330 M, Ca(OH)₂ = 0.138 M

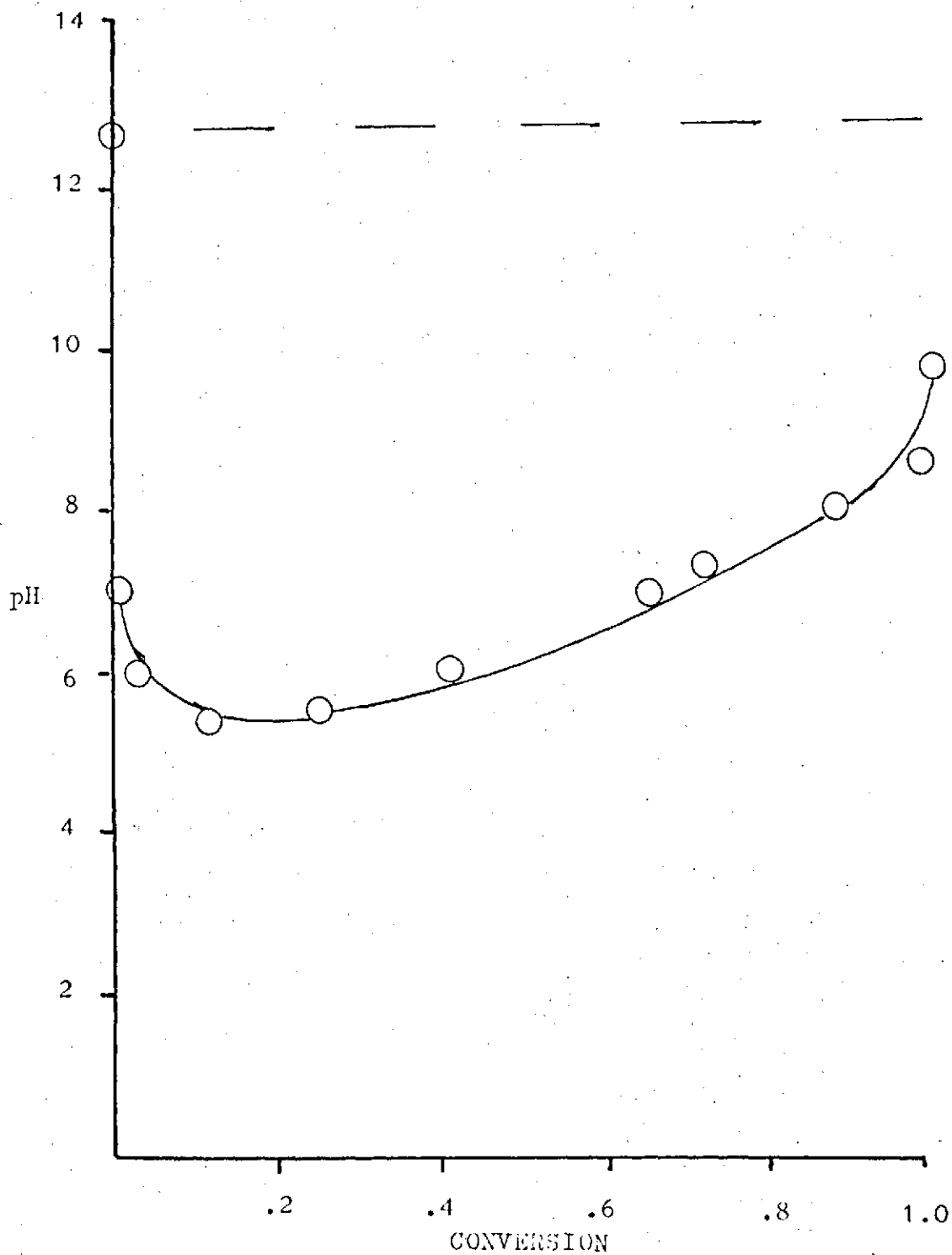


Figure 3

APR18

HCHO= 0.373 M, Ca(OH)₂= 0.096 M

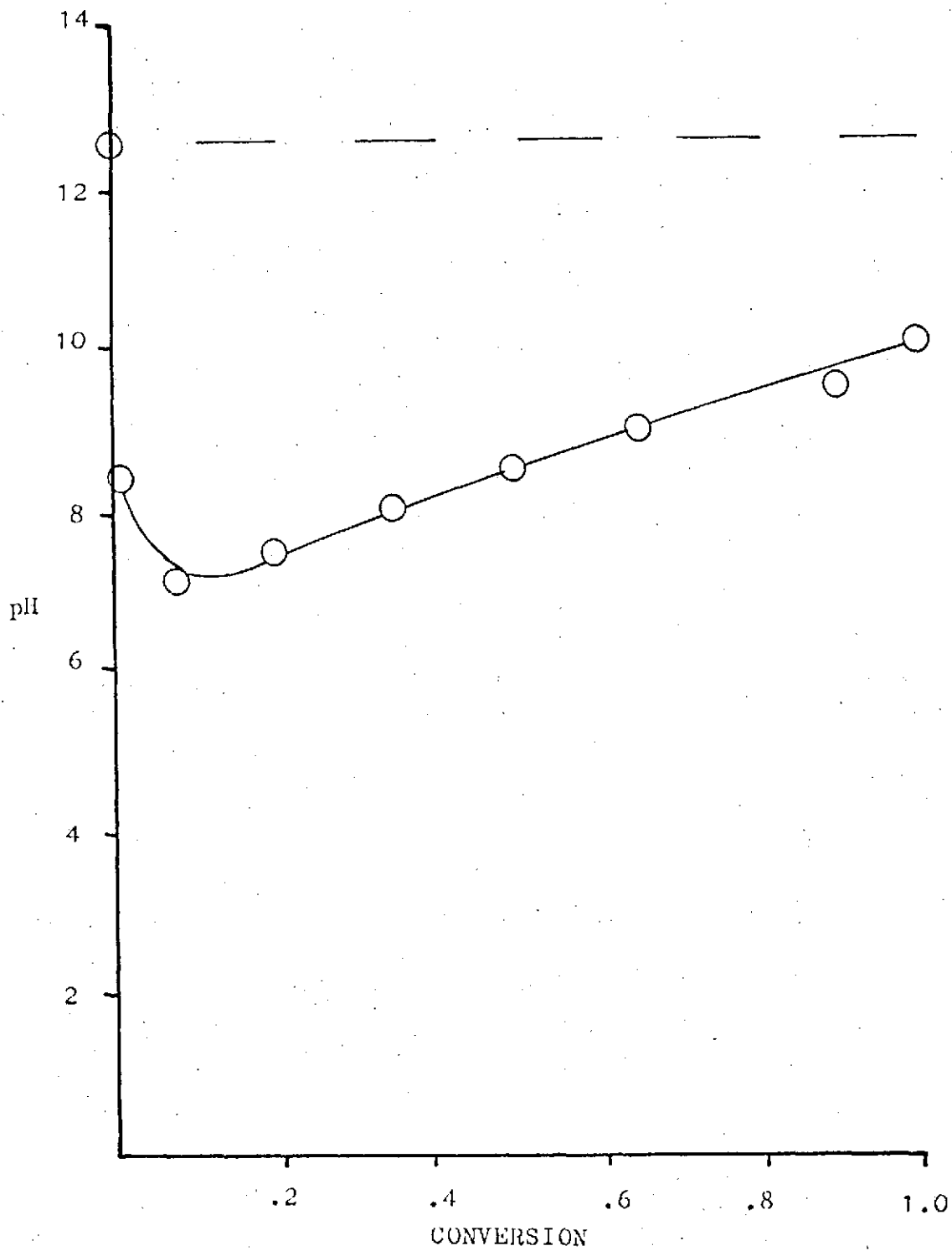


Figure 4 APR22 $\text{HCHO} = 0.369 \text{ M}$, $\text{Ca}(\text{OH})_2 = 0.151 \text{ M}$

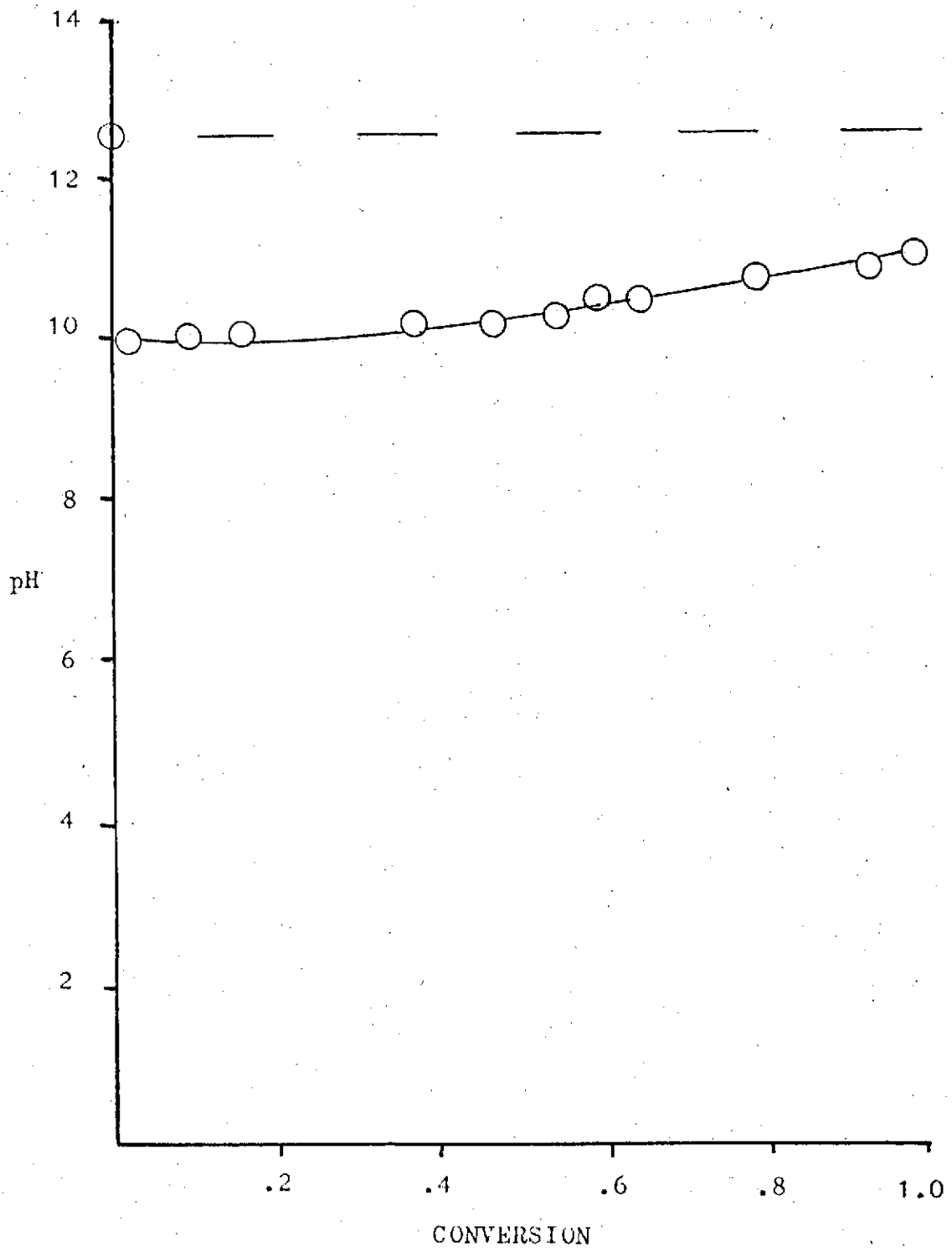


Figure 5

APR23

HCHO = 0.443 M, Ca(OH)₂ = 0.064 M

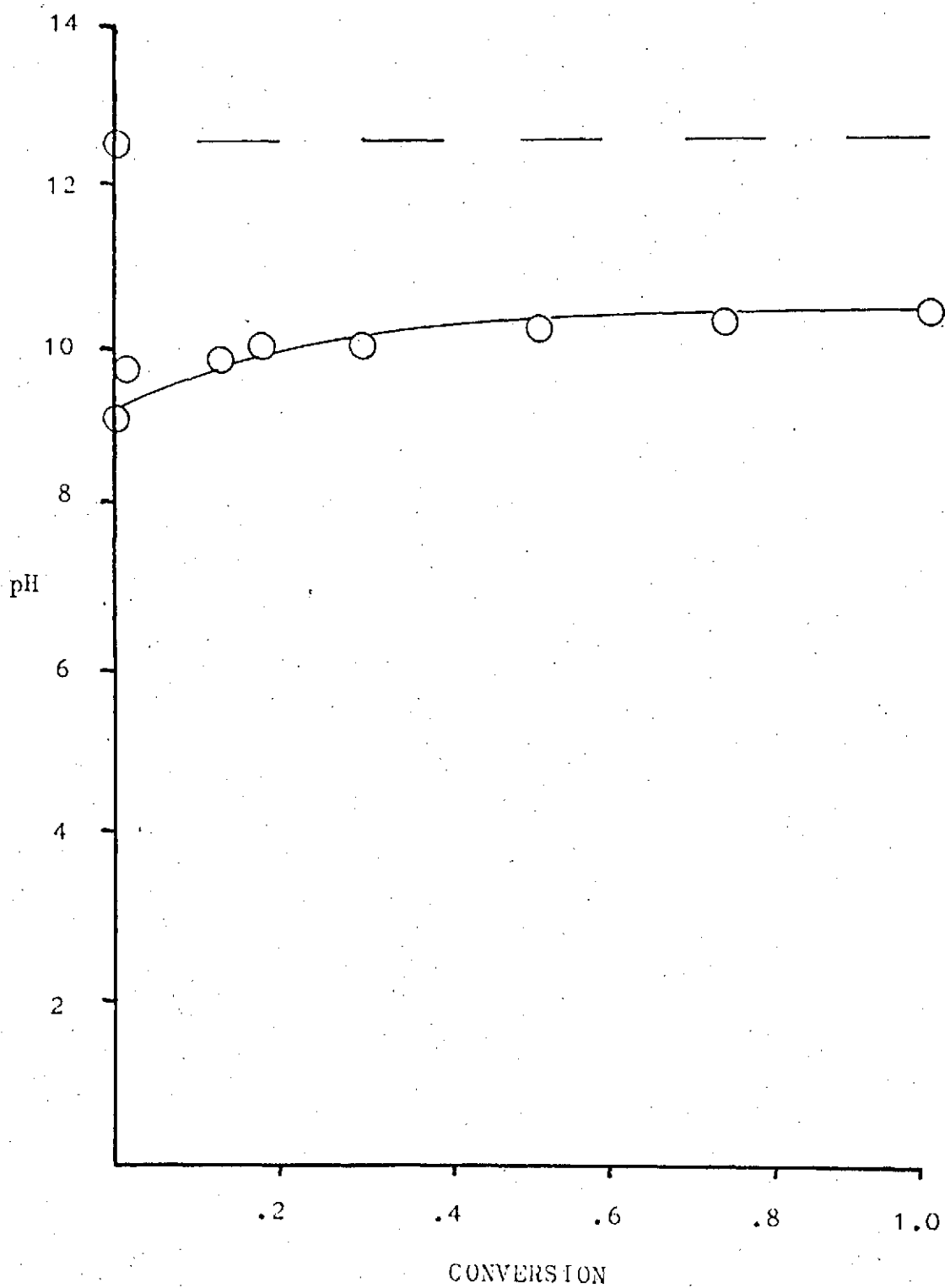


Figure 6

MAY02

HCHO = 0.34 M, Ca(OH)₂ = 0.0284 M

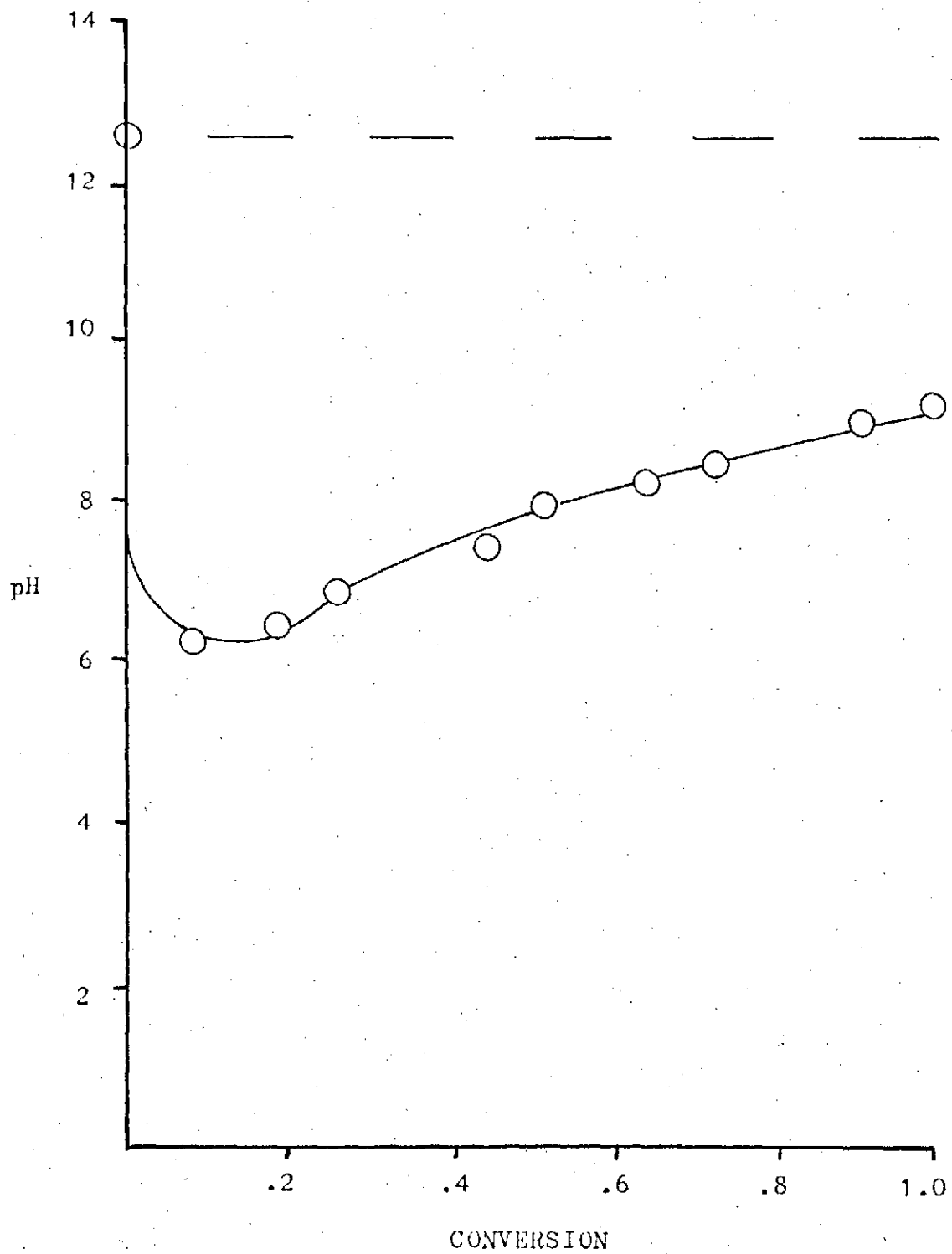


Figure 7 MAY06 HCHO = 0.363 M, Ca(OH)₂ = 0.0388 M

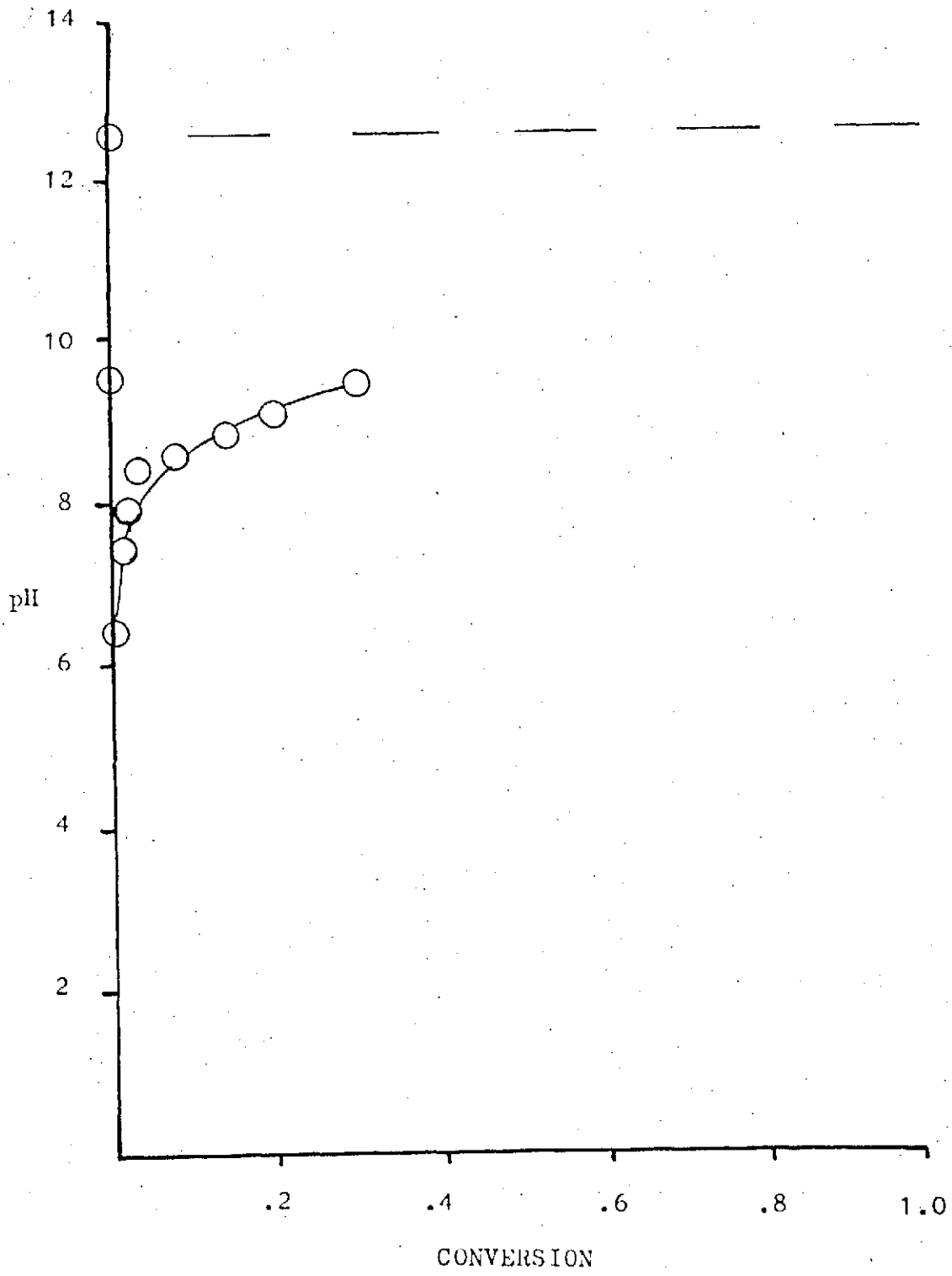


Figure 8

MAY08

HCHO = 0.386 M, $\text{Ca}(\text{OH})_2 = 0.034 \text{ M}$

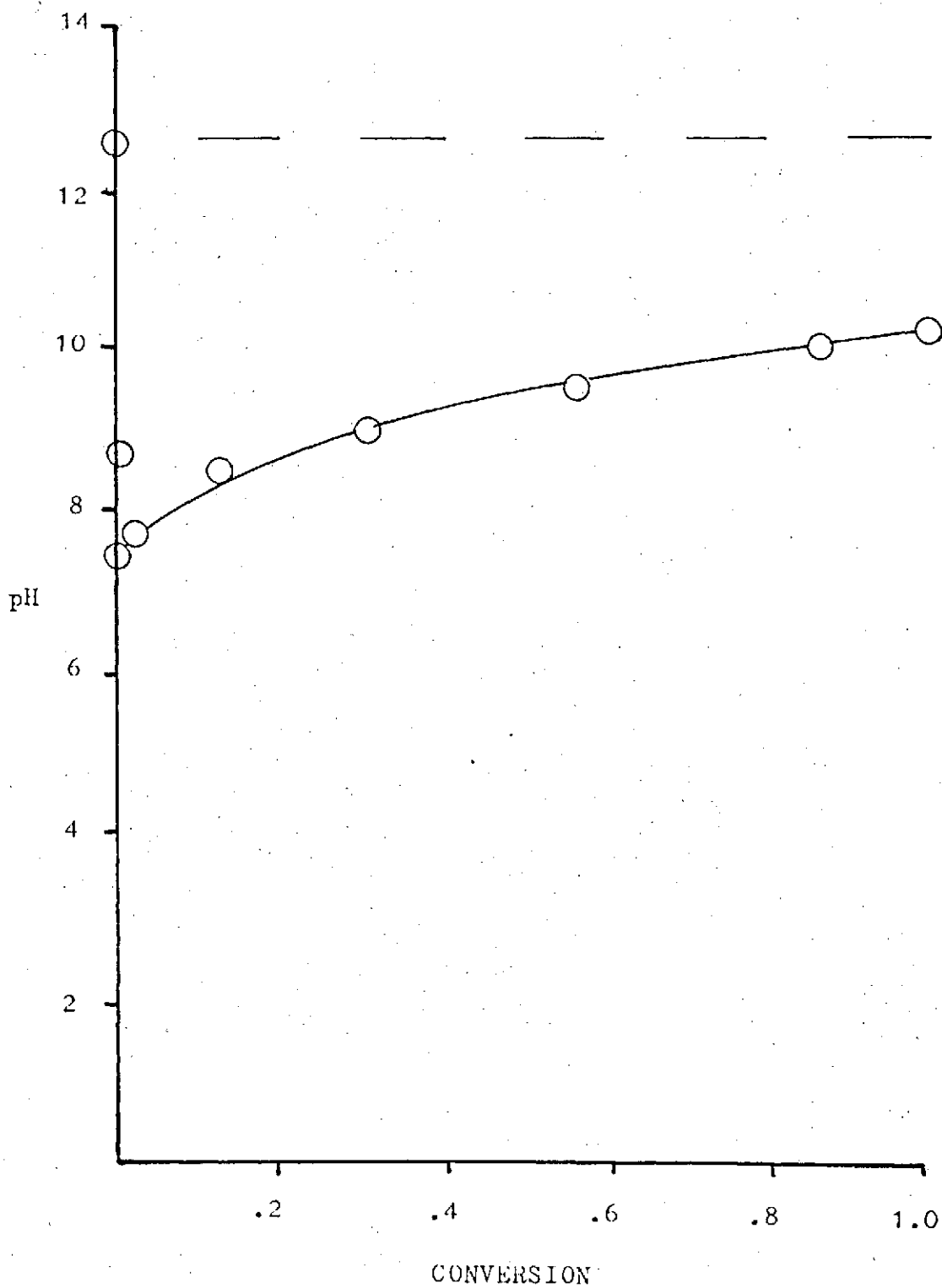


Figure 9 MAY09 HCHO = 0.386 M, Ca(OH)₂ = 0.21 M

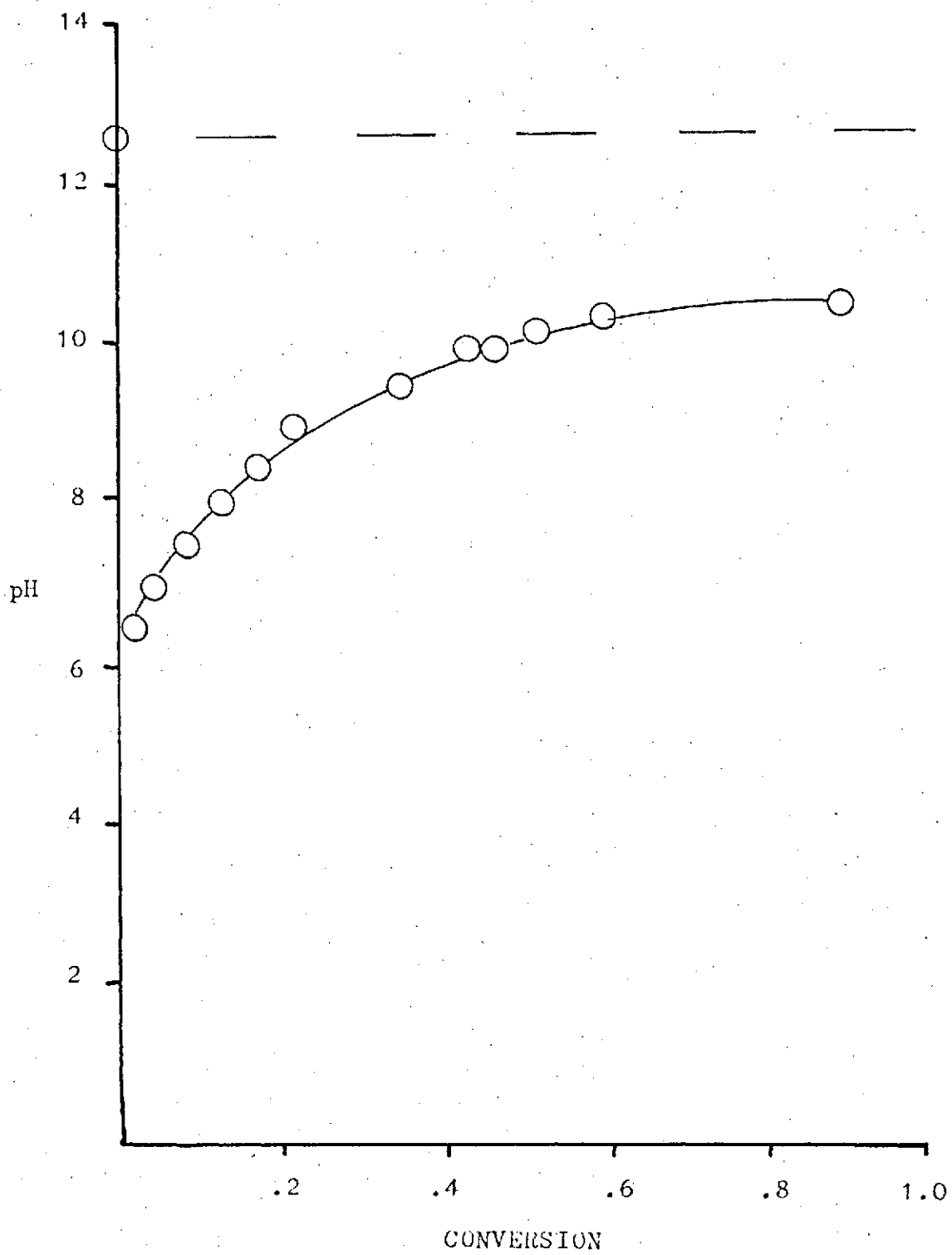


Figure 10

MAY16

HCHO = 0.458 M, Ca(OH)₂ = 0.05 M

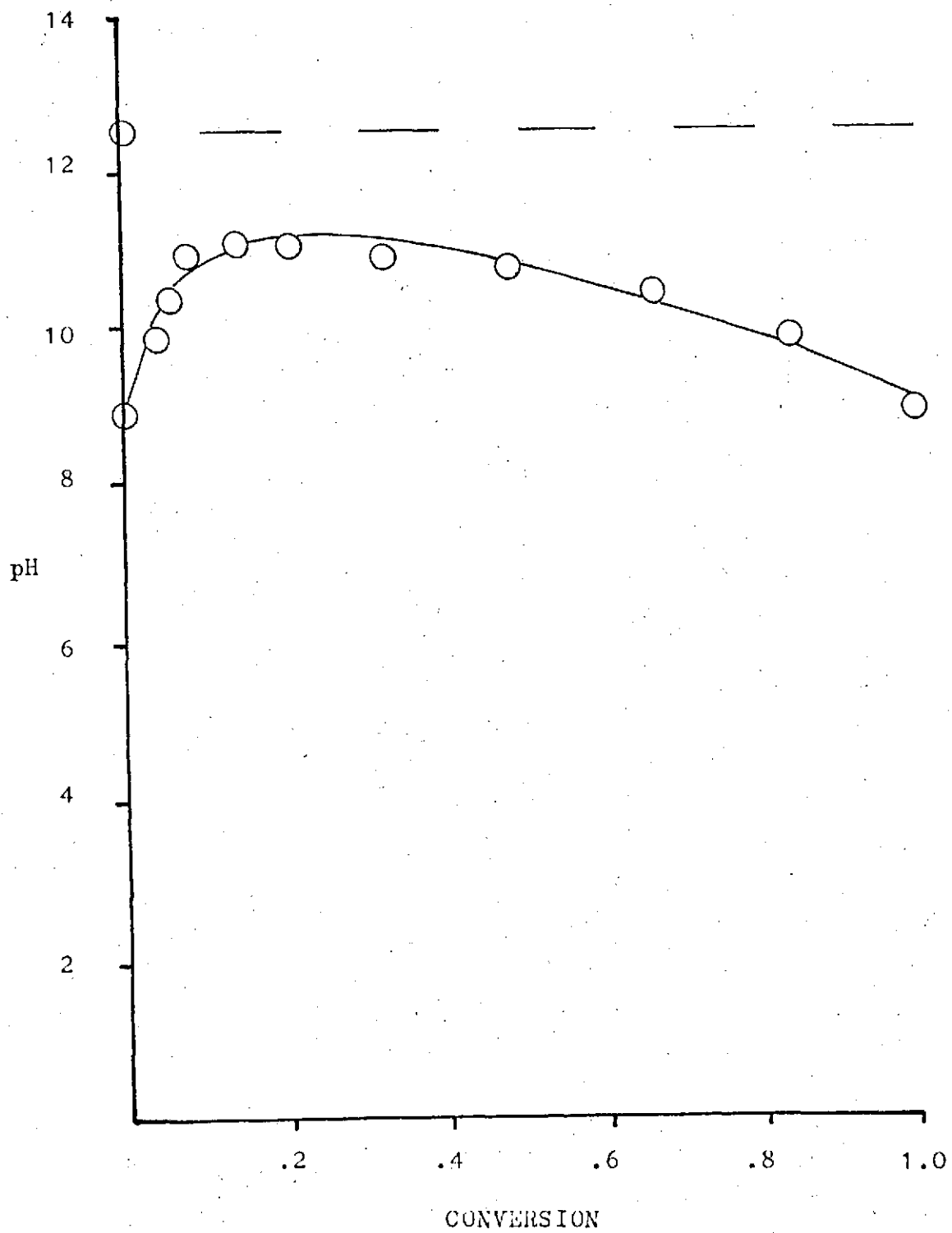


Figure 11 JUN06 HCHO= 0.422 M, Ca(OH)₂= 0.087 M

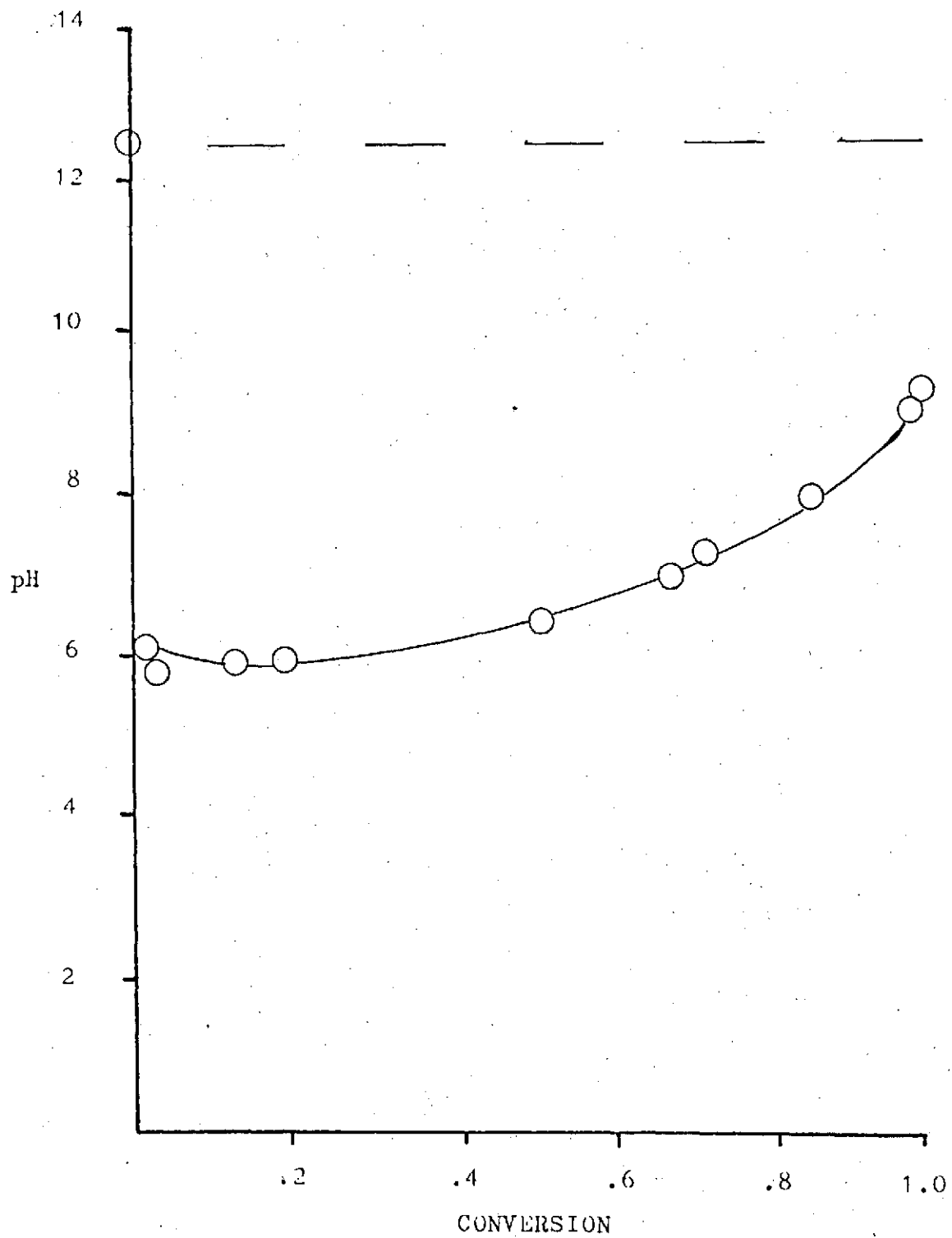


Figure 12

JUN10

HCHO = 0.825 M, Ca(OH)₂ = 0.12 M

