"PRODUCTION OF EDIBLE CARBOHYDRATES

FROM FORMALDEHYDE IN A SPACECRAFT"

by

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pH Variations in the

Calcium Hydroxide Catalyzed

Formose Reaction

by

Tom John

A Master of Science Thesis

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Table of Contents

List of Tables and Figures

ABSTRACT

The study of the calcium hydroxide catalyzed conden-
sation 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.

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 Butlerow[1] 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:

$$24 \ H_2O \longrightarrow 24 \ H_2 + 12 \ O_2$$
$$6 \ CO_2 + 2 \ H_2 \longrightarrow 6 \ CH_4 + 12 \ H_2O$$
$$6 \ CH_4 + 6 \ O_2 \longrightarrow 6 \ HCHO + 6 \ H_2O$$
$$6 \ HCHO \longrightarrow C_6H_{12}O_6 + O_2$$

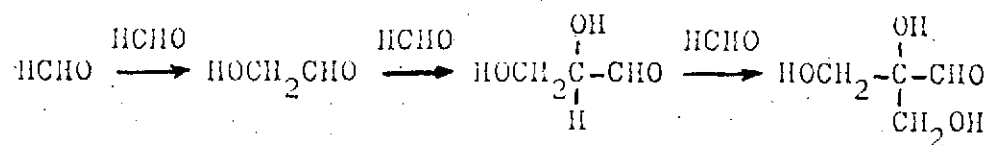overall: $$6 \ CO_2 + 6 \ H_2O \longrightarrow C_6H_{12}O_6 + 6 \ O_2$$
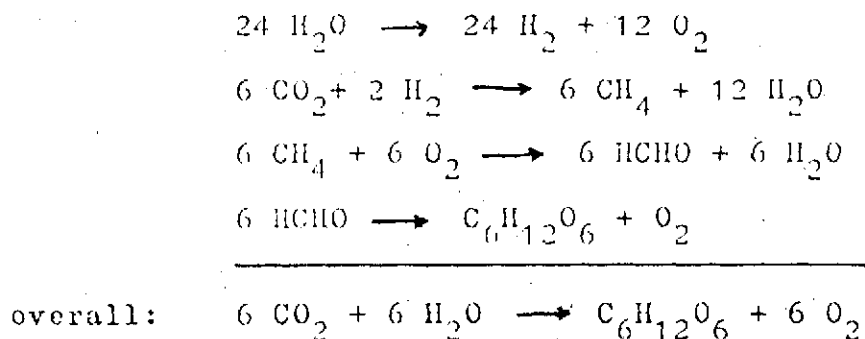
The final product of the formaldehyde condensation is a complex mixture of aldose and ketose sugars which range

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 tox-
icity 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 char-
acterize 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 Weiss[14] and a brief summary is presented
here.

The formose reaction is basically an aldol condensation:

$$HCHO \xrightarrow{HCHO} HOCH_2CHO \xrightarrow{HCHO} HOCH_2\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CHO \xrightarrow{HCHO} HOCH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_2OH}{|}}{C}}-CHO$$

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:

$$4\ RCHO + Ca(OH)_2 \longrightarrow 2\ RCH_2OH + Ca(OOCR)_2$$

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

$$RCHO + H_2CO \xrightarrow{\text{NaOH}} RCH_2OH + HCO_2Na$$
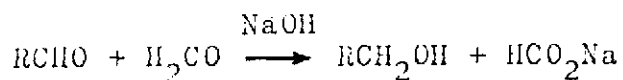
The ratio of the Cannizzaro reaction to the formose reaction is a function of the reaction conditions and of the catalyst used.[15] The hydroxides of alkaline earth metals such as $Ba(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$, $Sr(OH)_2$, certain alkali-metal hydroxides, and some heavy metal hydroxides catalyze the aldol (Formose) reaction. Tri- and tetra-valent rare-earth metal hydroxides[16] and some organic bases[17] 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 $TlOH < Ca(OH)_2$
$< Ba(OH)_2 < NaOH < LiOH.$[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 John[21] 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
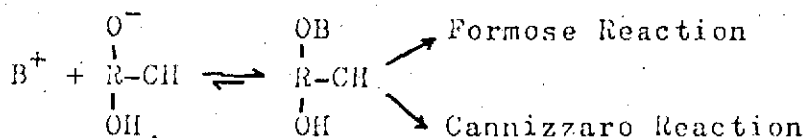$Ca(OH)_2$:

$$Ca(OH)_2 \longrightarrow CaOH^+ + OH^-$$
$$CaOH^+ \longrightarrow Ca^{+2} + OH^-$$
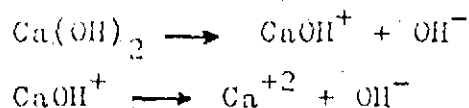
Generalized to any base, the first dissociation can be
written:

$$BOH \longrightarrow B^+ + OH^-$$

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

$$RCHO + OH^- \rightleftharpoons R-CH \begin{array}{c} O^- \\ | \\ | \\ OH \end{array}$$
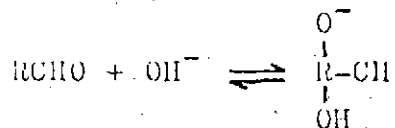
Combining these two reactions, one obtains the complexed form: [13]

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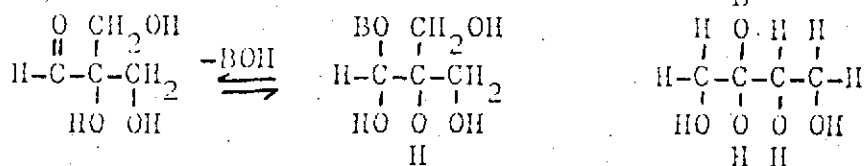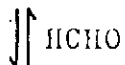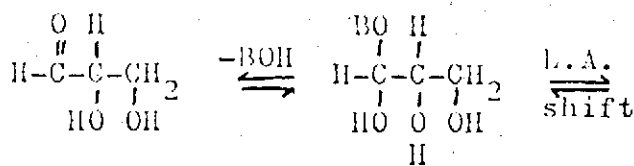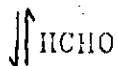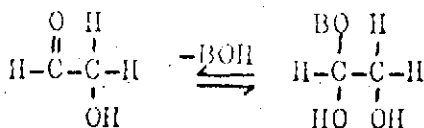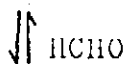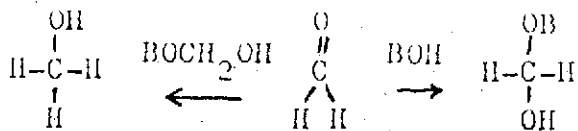
Specifically, for the case of the first self-condensation of formaldehyde, the mechanism would be as follows:

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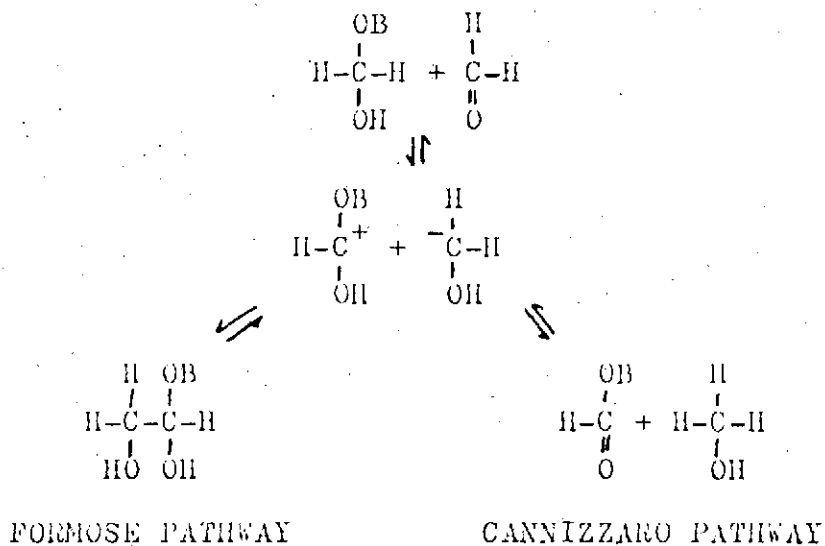
This mechanism allows for the initiation of the reaction, the pH sensitivity, and the catalyst selectivity as discussed in the article by Weiss and John. Coupled with the Lobry de Bruyn-van Eckenstein ketose-aldose shift, the mechanism leads to the building of both branched and straight chain carbohydrates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

The pH sensitivities of the formose reaction are not limited to the $Ca(OH)_2$ system, and reaction conditions need not be highly basic for the condensation to proceed. Cairns-Smith[23] 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 $Ce(OH)_4$ and $Th(OH)_4$ catalysts was proposed as the reason for the greater decrease in the pH during the course of their reaction (final pH = 2.7). $Sm(OH)_3$, $Ho(OH)_3$, and $Er(OH)_3$ 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

$$\text{H--C--H} \xleftarrow{\text{BOCH}_2\text{OH}} \overset{\text{O}}{\underset{\text{H H}}{\text{C}}} \xrightarrow{\text{BOH}} \text{H--C--H}$$

(structures with OH / OB groups)

$$\Updownarrow \text{HCHO}$$

$$\overset{\text{O H}}{\text{H--C--C--H}} \xrightleftharpoons{\text{--BOH}} \overset{\text{BO H}}{\text{H--C--C--H}}$$
$$\text{OH} \qquad \text{HO OH}$$

$$\Updownarrow \text{HCHO}$$

$$\overset{\text{O H}}{\text{H--C--C--CH}_2} \xrightleftharpoons{\text{--BOH}} \overset{\text{BO H}}{\text{H--C--C--CH}_2} \xrightleftharpoons[\text{shift}]{\text{L.A.}} \overset{\text{B}}{\text{H--C--C--C--H}}$$
$$\text{HO OH} \qquad\qquad \text{HO O OH} \qquad\qquad \text{HO O OH}$$

$$\Updownarrow \text{HCHO} \qquad\qquad\qquad\qquad \Updownarrow \text{HCHO}$$

$$\overset{\text{O CH}_2\text{OH}}{\text{H--C--C--CH}_2} \xrightleftharpoons{\text{--BOH}} \overset{\text{BO CH}_2\text{OH}}{\text{H--C--C--CH}_2} \qquad \overset{\text{B}}{\text{H--C--C--C--C--H}}$$
$$\text{HO OH} \qquad\qquad \text{HO O OH} \qquad\qquad \text{HO O O OH}$$

4-Carbon Branched Chain	4-Carbon Straight Chain
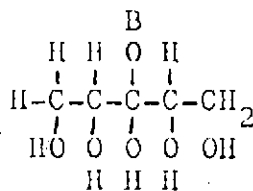
$$\Downarrow\!\!\!/ \text{HCHO} \qquad\qquad \Updownarrow \text{HCHO}$$

$$\overset{\text{B}}{\text{H--C--C--C--C--CH}_2}$$
$$\text{HO O O O OH}$$

5-Carbon
Straight Chain

$$\overset{\text{B}}{\text{H--C--C--C--CH}_2}$$
$$\text{HO O O OH}$$
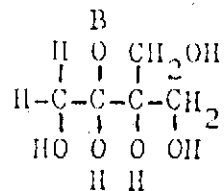
5-Carbon
Branched Chain

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 PbO[25] 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 CH_3OH 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 Weiss[20] 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 system[21] 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 $Ca(OH)_2$ 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:

$$HCHO + Na_2SO_3 = NaOH + CH_2(NaSO_3)OH$$
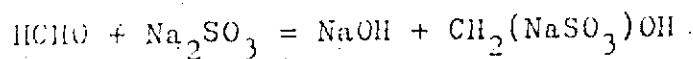
The NaOH thus formed is on a one-to-one ratio with the formaldehyde initially present. This product is then back titrated to neutral to phenolphthlein by the addition of standardized HCl.

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 programing 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 inaccur-
acies 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 de-
termined by injection of 1) Formaldehyde and water; 2) Form-
aldehyde, 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 exper-
imental 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

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 paraformal-
dehyde (Baker Chemical Co., AR grade) was dissolved in dis-
tilled, 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 solu-
tions, 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 hy-
droxide (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 $Ca(OH)_2$ 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 hydrox-
ide was added, t = 0, the pH can be seen to jump dramatically
upwards towards a value of 12, the value of a saturated cal-
cium 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 be-
tween 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 reproducibility[31] 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; $Ca(OH)_2$,
0.0343 M. For MAY06, the initial values were: HCHO, 0.363 M;
$Ca(OH)_2$, 0.0388 M. These values are in reasonably close
aggrement, 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 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 $Ca(OH)_2$ 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 $Ca(OH)_2$ concentration is de-
creased, 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
$Ca(OH)_2$ concentrations. At 0.00 M $Ca(OH)_2$, the pH would
rise to that of a formaldehyde solution at $50°C$, for ex-
ample 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 Canni-
zzaro rate is greater than the rate of dissolution of $Ca(OH)_2$.
As the reaction progresses, the rate of formose reaction be-
comes appreciable and a point will be reached at a lowered
$Ca(OH)_2$ concentration at which the Cannizzaro rate is small
compared to that of the formose rate. At this point, the
dissolution of $Ca(OH)_2$ 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 $Ca(OH)_2$-formose complex.

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

ibility and analogies to similarly shaped curves of Canni-
zzaro 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 experi-
mental 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
$Ca(OH)_2$. Mizuno and Weiss[14] 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 there-
fore 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 Langenbeck[24] 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 $Ca(OH)_2$ 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 $Ca(OH)_2$ 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 $Ca(OH)_2$ studies reported here.

The results of a later Russian study[25] 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 res-
ponsible 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 hy-
droxides 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 ex-
periments have very similar shapes, they cannot unfortunately
be superimposed due to the differences in formaldehyde concen-
trations (6.67 M, 3.9 - 4.3 M, and 0.3 - 0.8 M, respectivly).
As figure 8 shows, interpolation over even a small concen-
tration 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 $Ca(OH)_2$ 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 $Ca(OH)_2$. Under certain conditions of low conversion and low $Ca(OH)_2$, 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 $Ca(OH)_2$ 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 ~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 $Ca(OH)_2$. 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 $Ca(OH)_2$ and the lack of HCHO as complete conversion is approached, the Cannizzaro rate is now low in comparison to the rate of $Ca(OH)_2$ dissolution. The pH curve then tends back towards

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 assumed[33] that, when there are no inter-
active effects (e.g. simple, parallel, or consecutive) in a
set of reactions, a stirred tank reactor represents the condi-
tions 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 para-
meters, 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 develope 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

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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
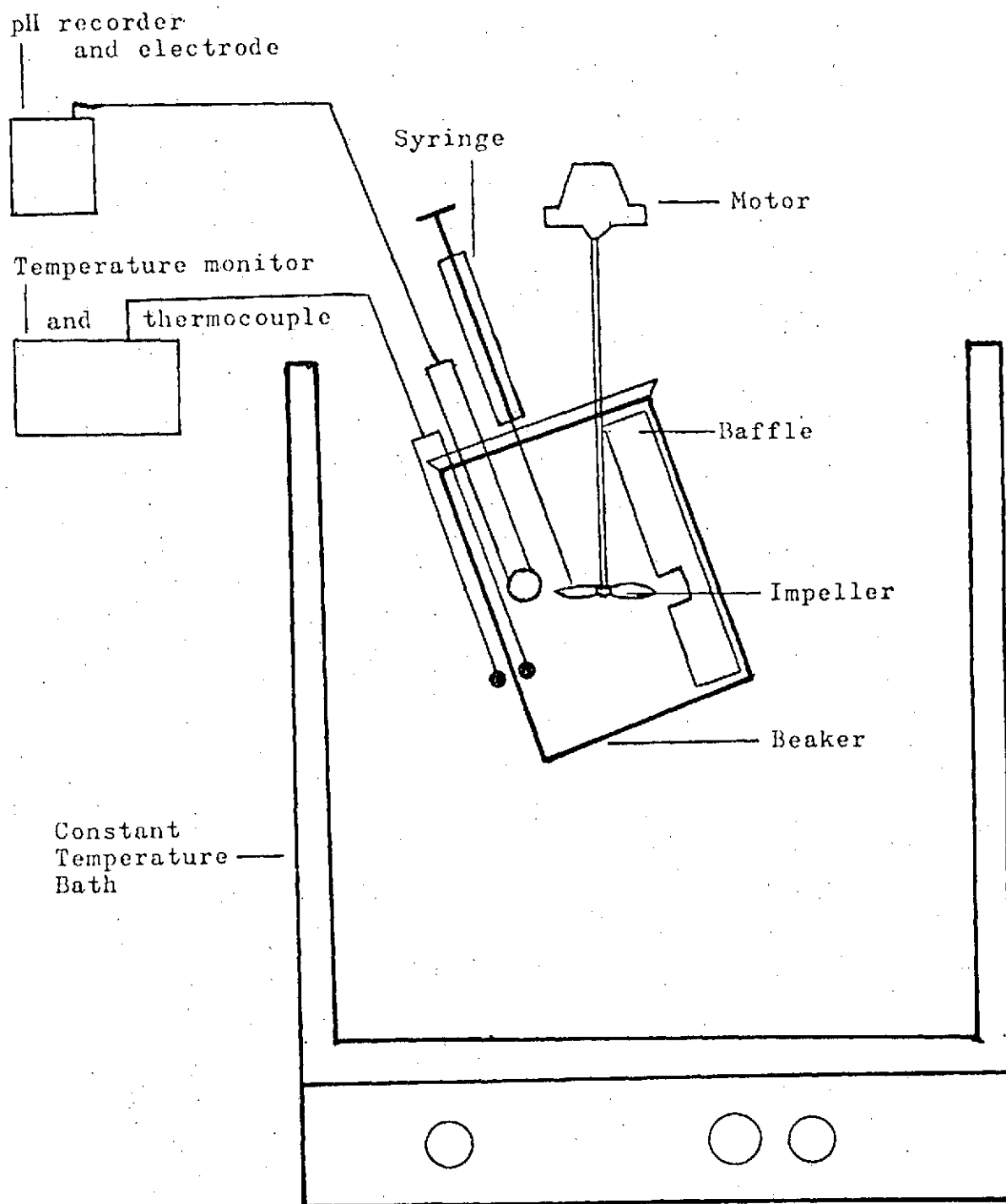
Figure 2
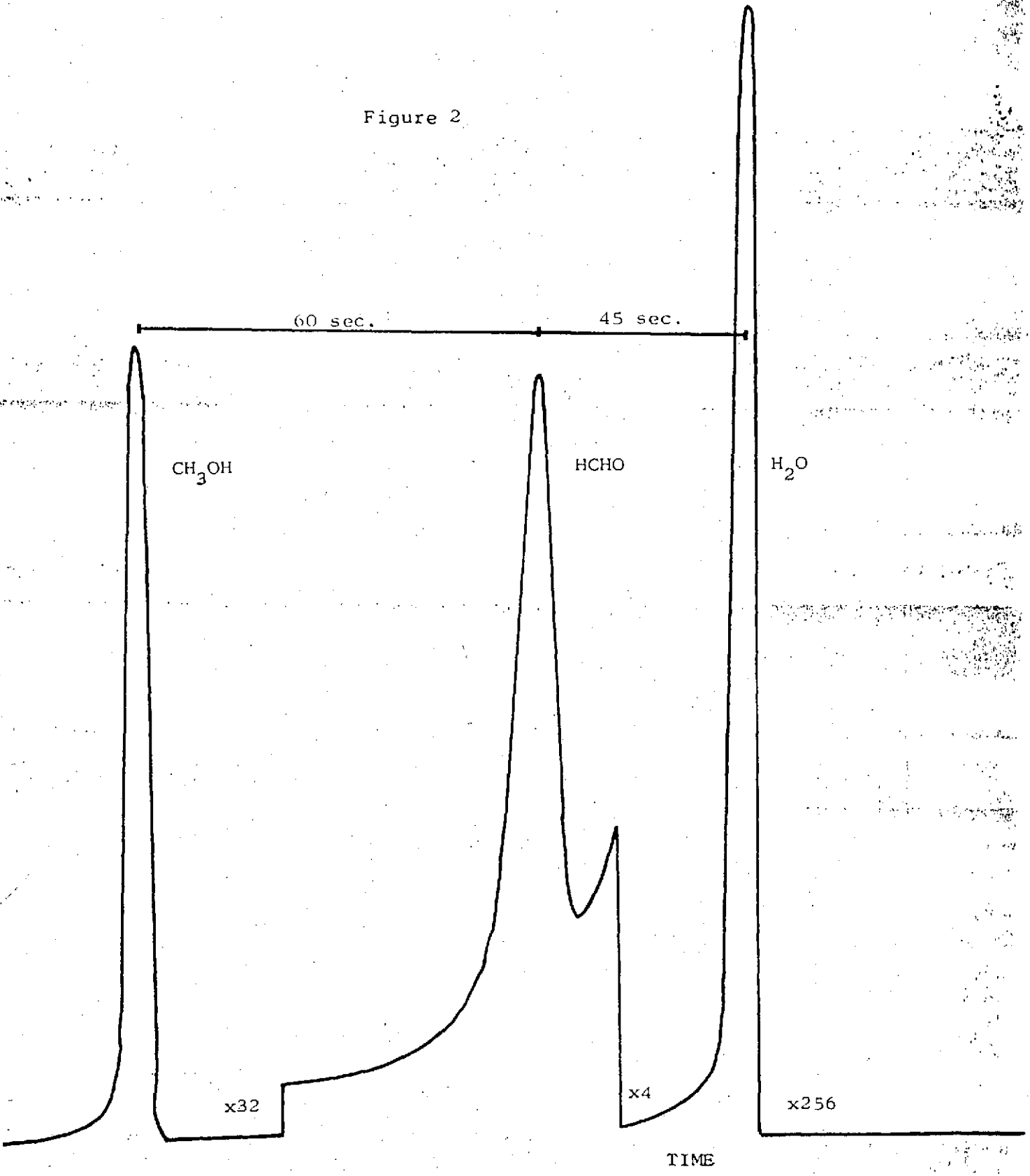
CH$_3$OH   HCHO   H$_2$O

60 sec.

45 sec.

x32   x4   x256

TIME

Figure 3

MAY16

see Table I for
parameters

JUN06

JUN10

pH

Time, minutes →
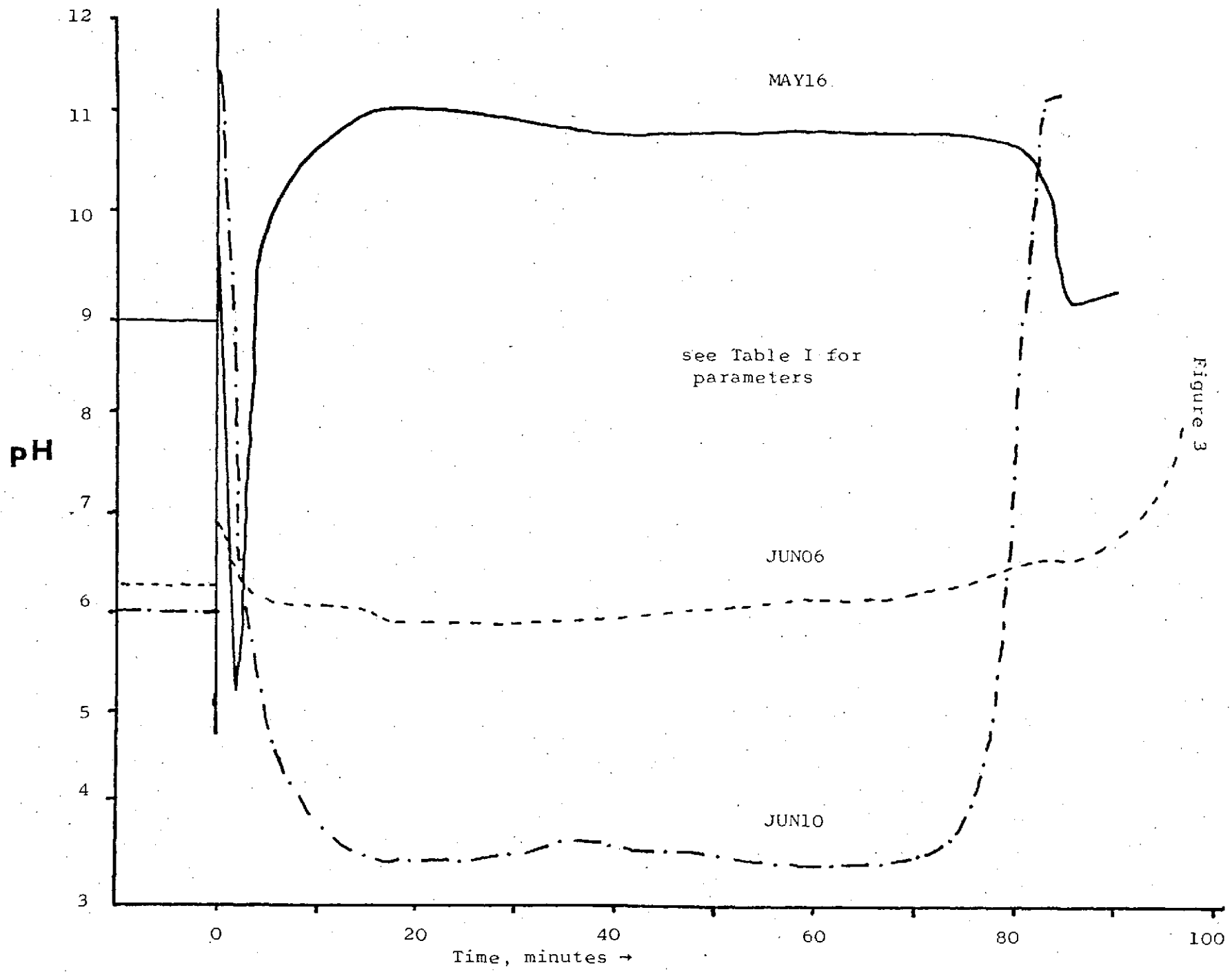
Figure 4

HCHC = 0.33 ± 0.01 M

50° C.

Ca(OH)$_2$, M
○ 0.138
□ 0.116
△ 0.0284

PH

CONVERSION
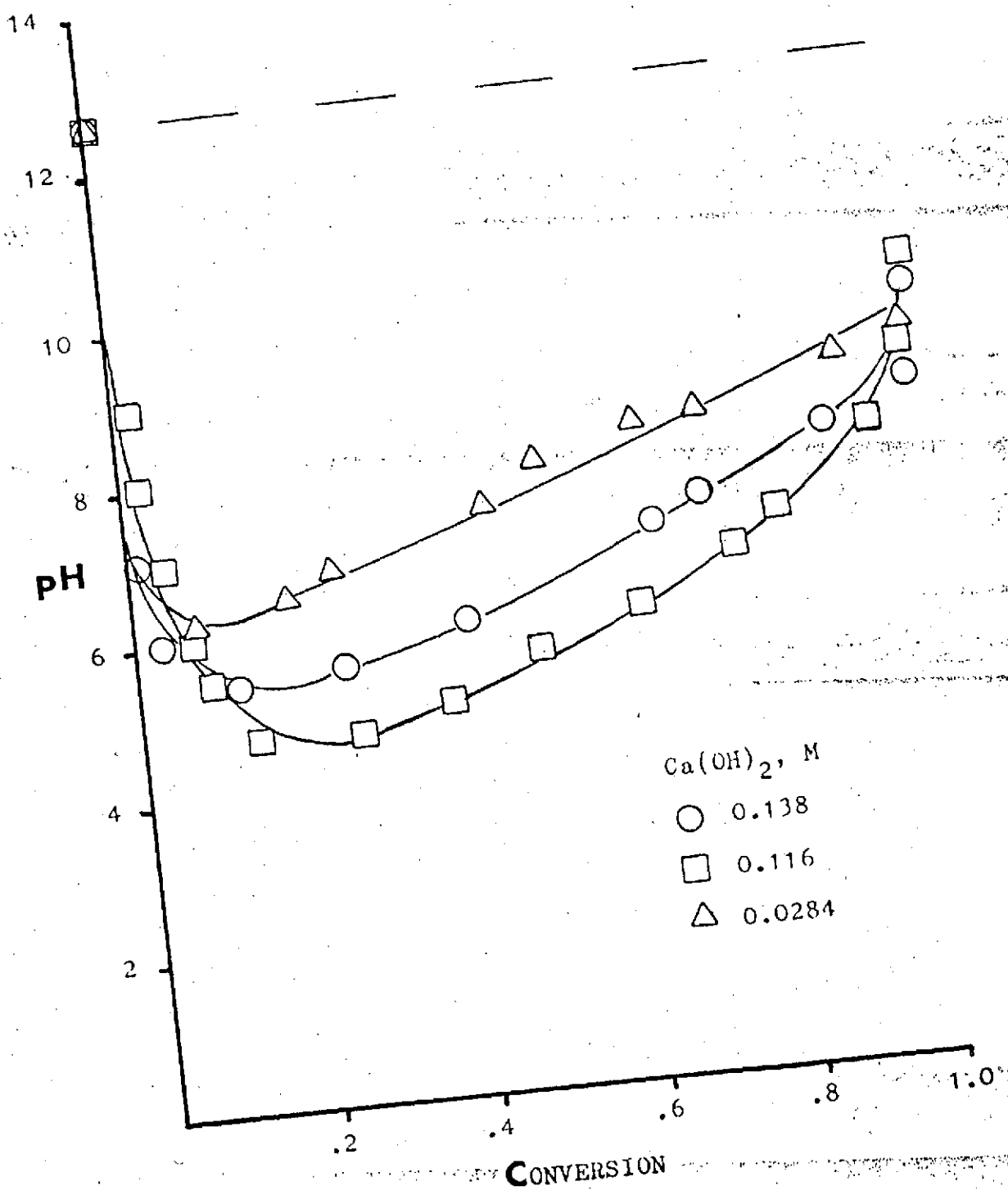
Figure 5

$HCHO = 0.365 \neq 0.01$ M

$50°C.$

pH vs CONVERSION

Ca(OH)$_2$, M
□ 0.151
○ 0.096
△ 0.0388
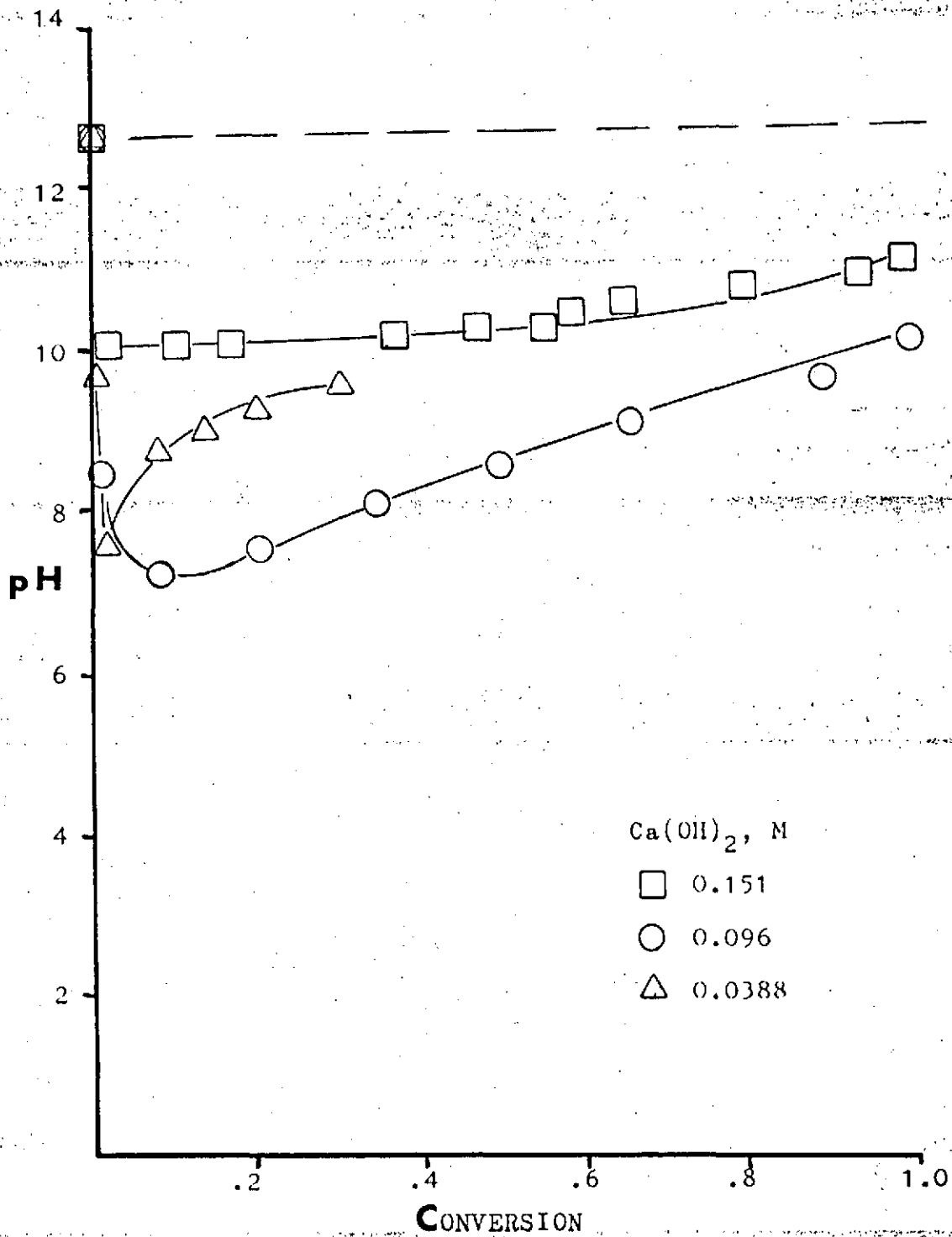
Figure 6

HCHO = 0.386 M

50°C.

pH vs Conversion

Ca(OH)$_2$, M
○ 0.21
△ 0.034
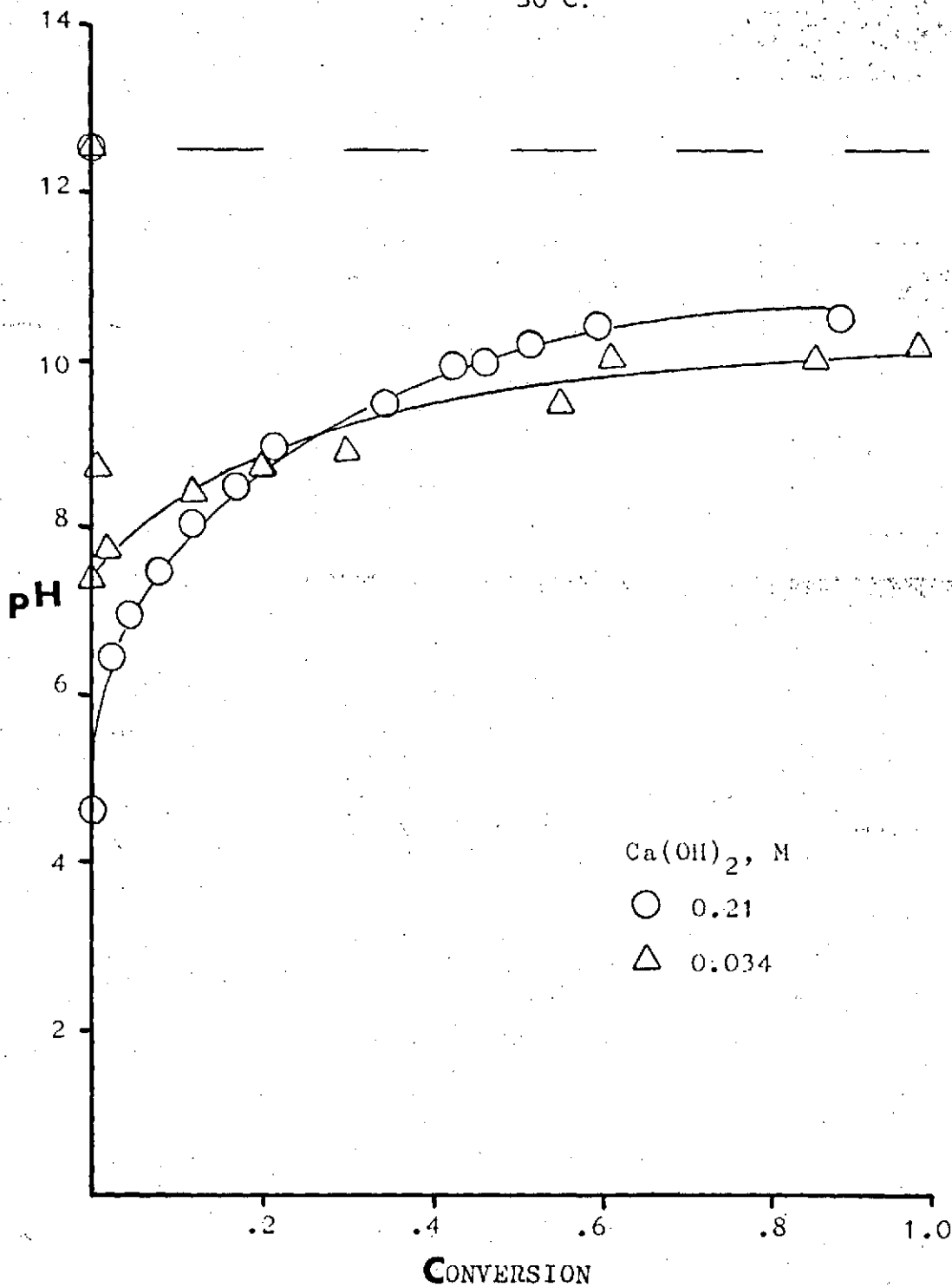
Figure 7

HCHO = 0.44 ± 0.02 M

50° C.
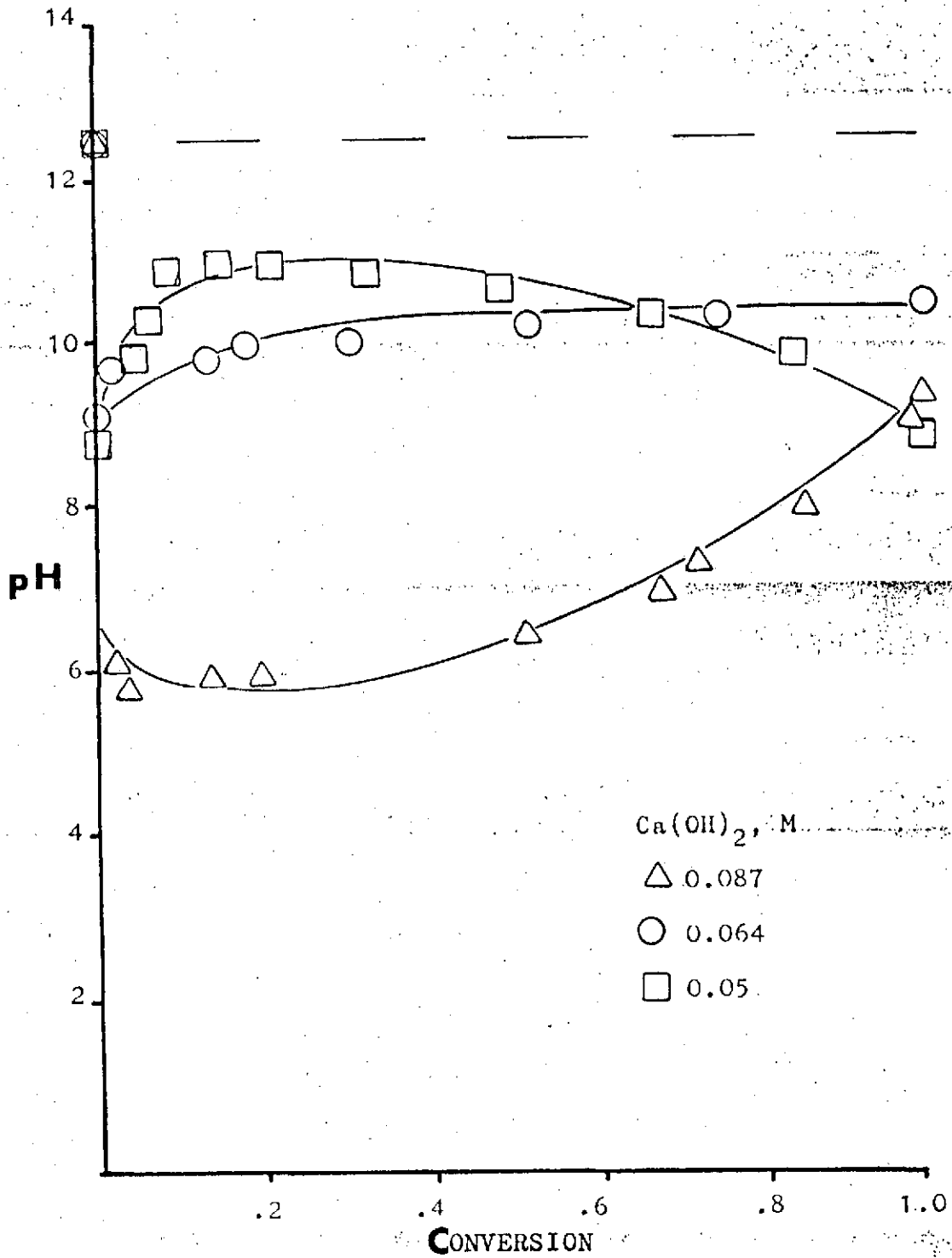
Ca(OH)$_2$, M

△ 0.087

○ 0.064

□ 0.05

pH

CONVERSION

Figure 8

50°C.

pH

CONVERSION

HCHO, M

□ 0.33

○ 0.37

△ 0.82

Ca(OH)$_2$: 0.12 M.
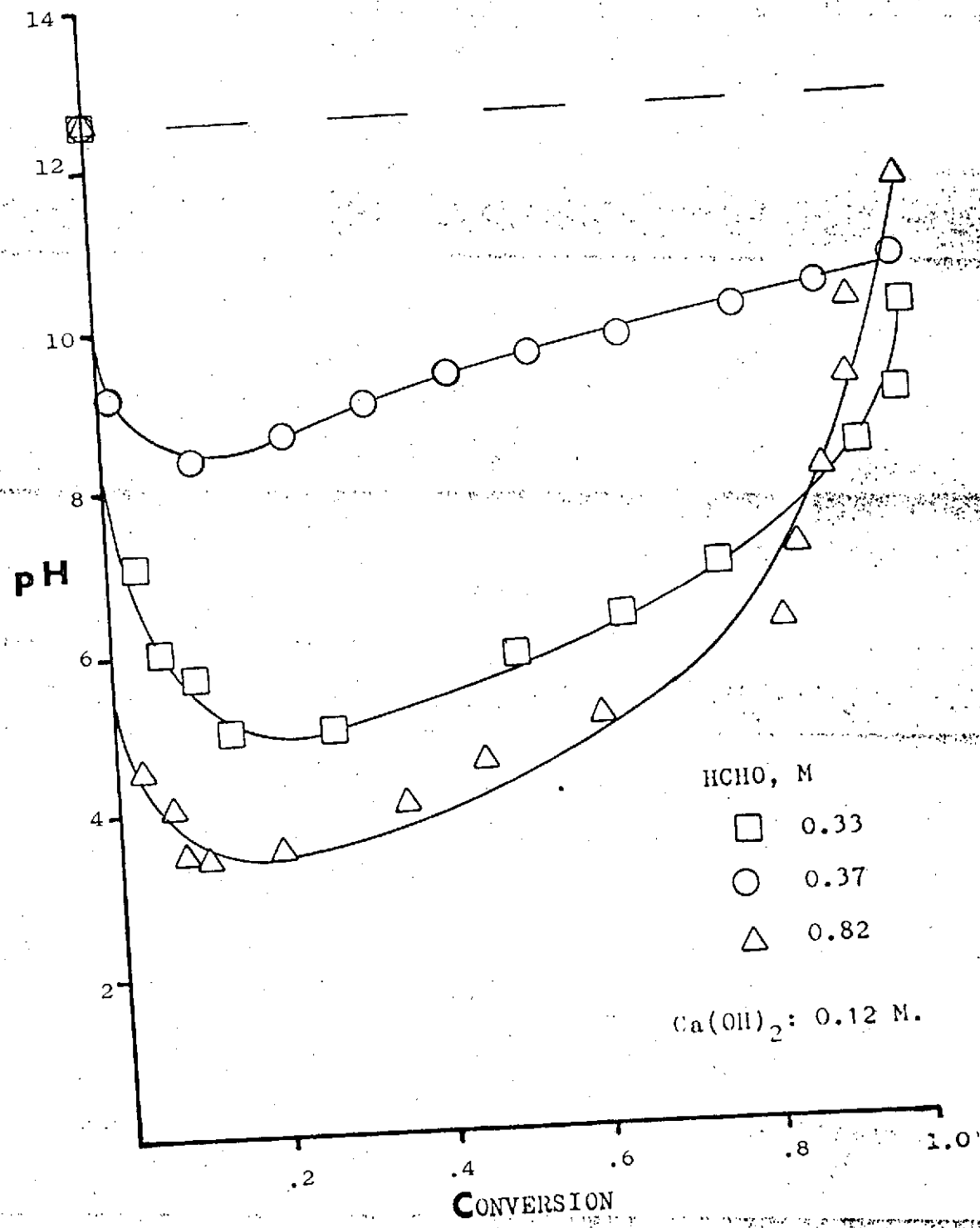
Figure 9

T = 75°C; 0.01 mole benzoyl carbinol
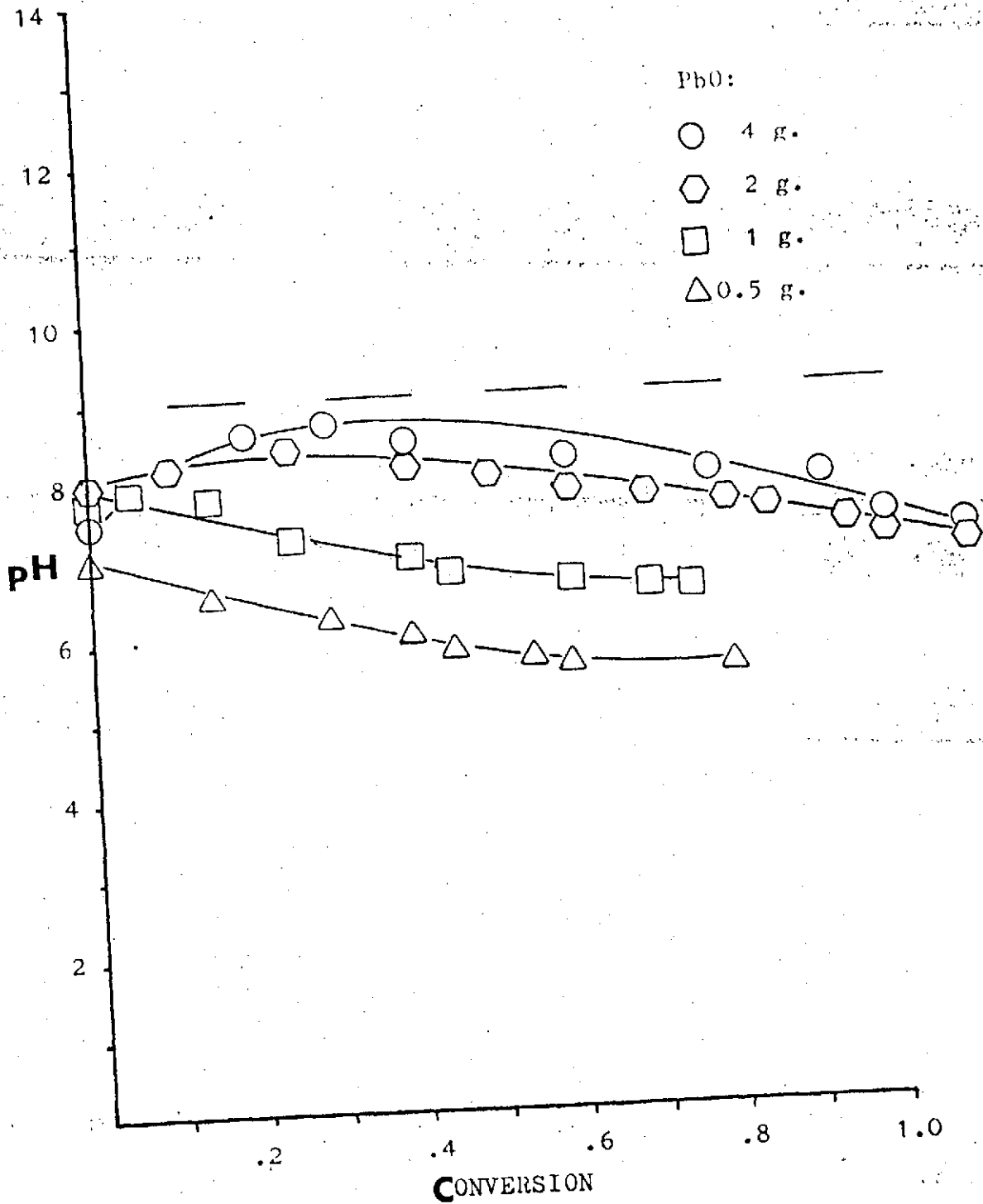
Figure 10

$T = 75°C$; $PbO:HCHO = 1:10$

glucose, 2.5% of HCHO
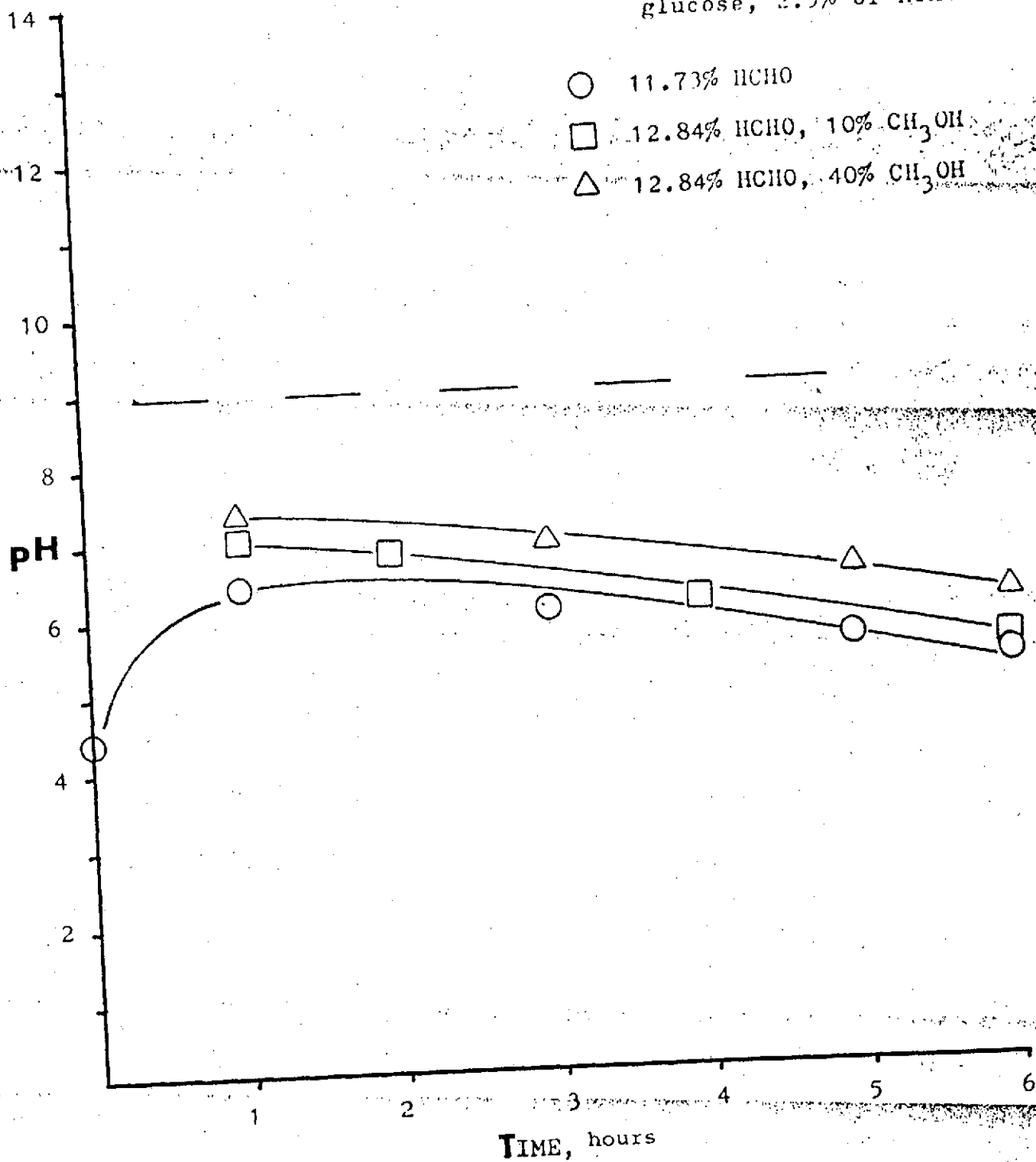
○   11.73% HCHO

□   12.84% HCHO, 10% CH_3OH

△   12.84% HCHO, 40% CH_3OH

Figure 11

$T = 110^\circ C$, $P = 1.8$ atm.
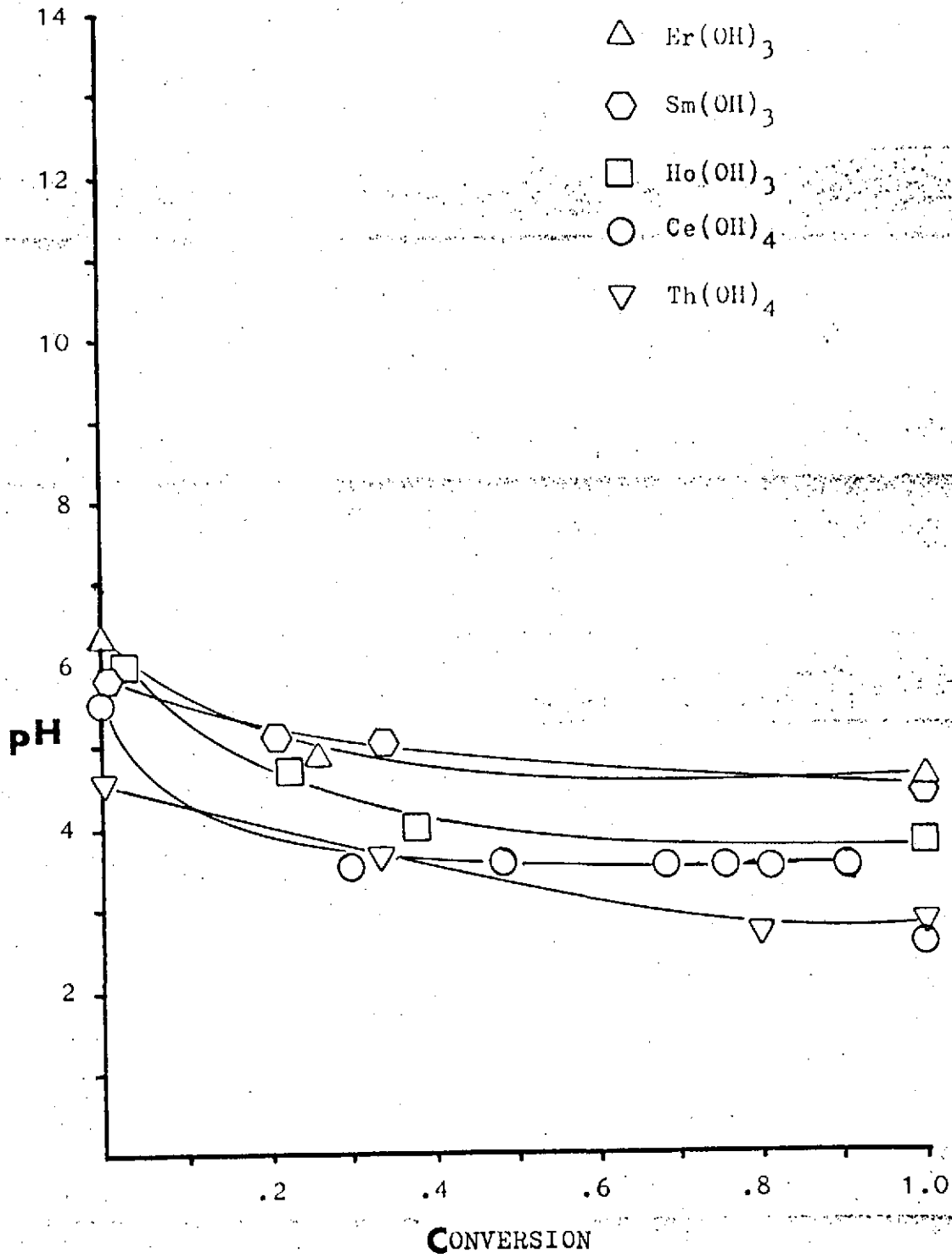
△ $Er(OH)_3$

⬡ $Sm(OH)_3$

□ $Ho(OH)_3$

◯ $Ce(OH)_4$

▽ $Th(OH)_4$

pH

2

.2   .4   .6   .8   1.0

CONVERSION

Figure 12

pH

Cannizzaro Rate (moles/liter minute)

Cannizzaro only

○ 0.0325

△ 0.135

Parameters: Moles
HCHO Feed/Liter Min.

40° C

a

b

c

TOTAL REACTION RATE (moles/lit. min.)
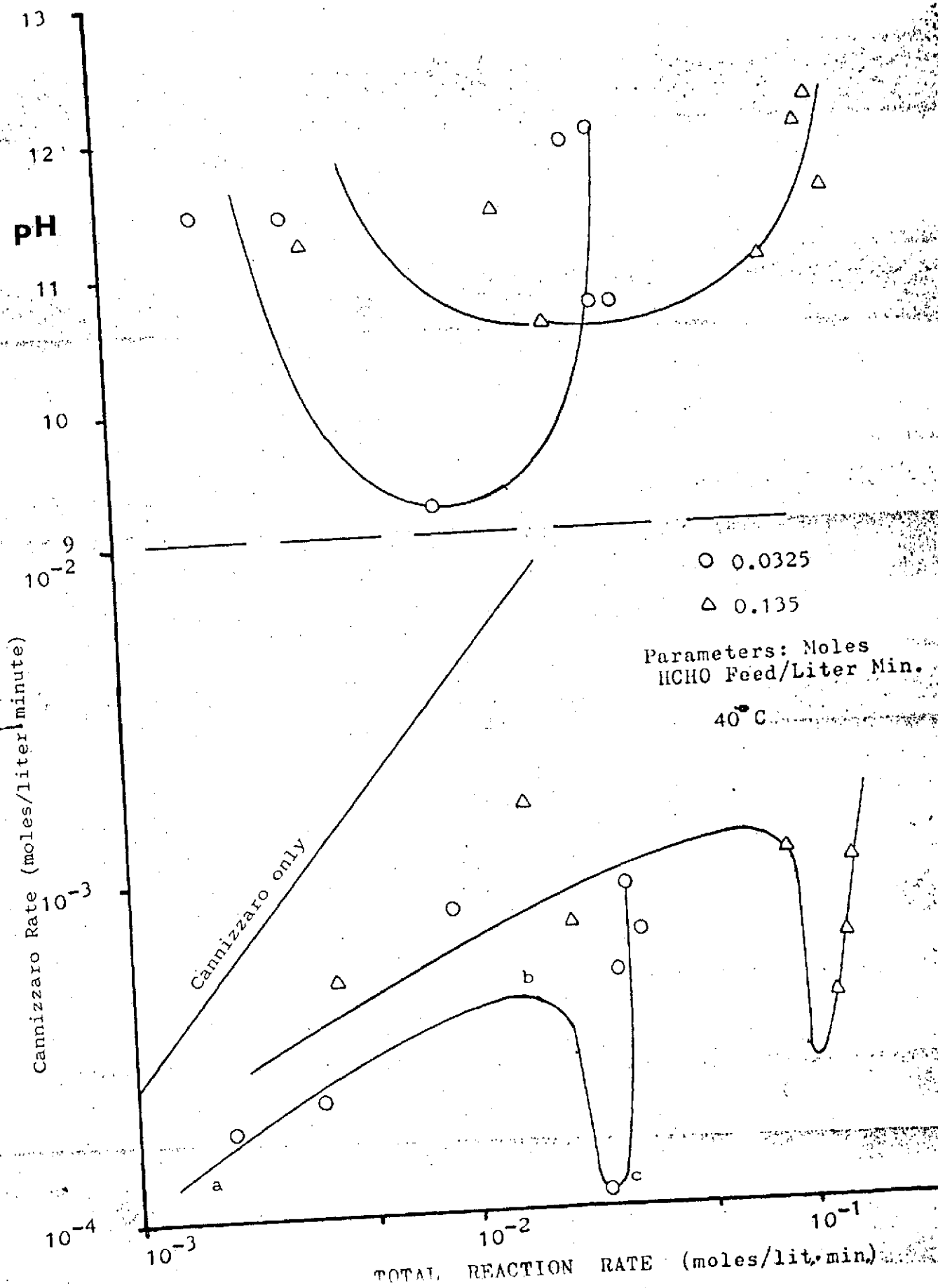
Appendix 1

Computer Program

```
            DOUBLE PRECISION NAME
            READ(5,100)NAME
            CALL IFILE(20,NAME)
            FORMAT(A14)
            WRITE(21,100)NAME
            READ(20,12)CO
            READ(20,12)CAT
            FORMAT(1F)
 12         FORMAT(1I)
 13         READ(20,13)N
            J=N-4
            K=N-2
            WRITE(5,13)CO
            WRITE(21,1)CO
            WRITE(5,50)CAT
            WRITE(21,50)CAT
            FORMAT(10X,'CAT MOLARITY',F9.4)
 50         DIMENSION A(50),B(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)
 11    C    PRINT DATE,INITIAL CONDITIONS,NUM OF PTS
 10         DO 35 I=3,N
       C    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)
 25         FORMAT(4F)
       C    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)
 35         CONTINUE
       C    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)
 30         WRITE(21,40) (A(I),B(I),C(I),D(I) I=3,K)
            FORMAT (10X,4F8.4)
 40         CONTINUE
 45         DO 55 I=1,N
       C    NORMALIZE TO HCHO AND PRINT
            C(I)=C(I)/CO
 55         CONTINUE
            WRITE(5,58)
            FORMAT(12X,'TIME, WT PCNT HCHO/INITIAL')
 58         WRITE(21,58)
            WRITE(5,60)(A(I),C(I), I=1,N)
            WRITE(21,60)(A(I),C(I), I=3,K)
            WRITE(22,60)(A(I),C(I), I=3,K)
            FORMAT(4X,2F8.4)
 60
```

```
C     PLOT RESULTS
C
      CALL PLOTS(1)
      CALL PLOT(1.0,1.0,3)
      CALL SYMBOL(1.0,1.0,0.25,NAME,0.0,10)
      CALL PLOT(3.0,3.0,3)
      CALL SCALE(A,N,5.0,XMIN,DX)
      CALL AXIS(3.0,3.0,4HTIME,4,5.0,0.0,XMIN,DX)
      CALL SCALE(C,N,5.0,YMIN,DY)
      CALL AXIS(3.0,3.0,4HC/CO,4,5.0,90.0,YMIN,DY)
      CALL PLOT(3.0,3.0,-3)
      CALL LINE(A,C,N,1)
      STOP
      END
```

Appendix 2

Sample computer output

Sample computer graph

APR23.DAT

[SN=9192 DSKA0.DATA.PLT[1000,11246]
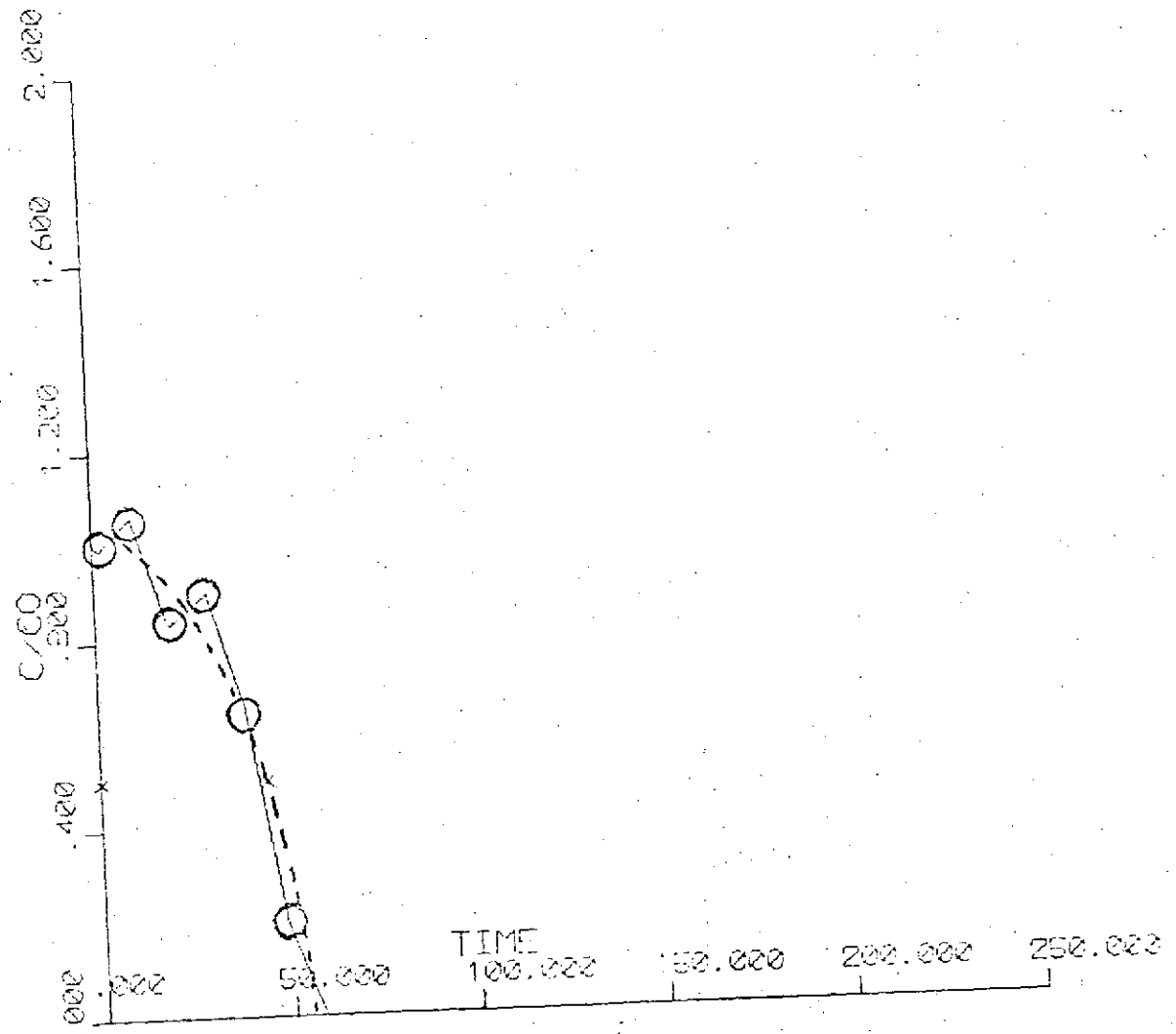
APR23.DAT

```
WT PCNT HCHO INITIAL .2117
CAT MOLARITY .2100
NUMBER OF POINTS IS    4
   1.5000000        1.9370000        1.2453000       .0.0200000
  11.0000000        1.9200000        1.1120000        0.0000000
  20.5000000        1.7150000        1.0400000        0.0000000
  32.5000000        1.7770002        0.7680000        0.0000000
  40.0000000        1.7900000        0.0000000        0.0000000
 220.0000000        1.4570000        0.0000000        0.0000000
    TIME,WT PCNTS H2O,HCHO,CH3OH
     0.0000    0.0002    0.0176    0.0000
     0.1000    0.3332    0.0117    0.0000
     1.5000    0.9379    0.0121    0.0000
    11.0000    0.9893    0.0107    0.0000
    20.5000    0.9888    0.0112    0.0000
    32.5000    0.9920    0.0088    0.0000
    40.0000    1.0000    0.0000    0.0000
   220.0000    1.4700    0.0000    0.0000
    TIME, WT PCNT HCHO/INITIAL
    0.0000    0.3152
    0.1000    0.2100
    1.5000    0.2160
   11.0000    0.1920
   20.5000    0.2009
   32.5000    0.1437
   40.0000    0.0000
  220.0000    0.0000
```

Appendix 3

Figures 1 through 12

pH and conversion vs. time

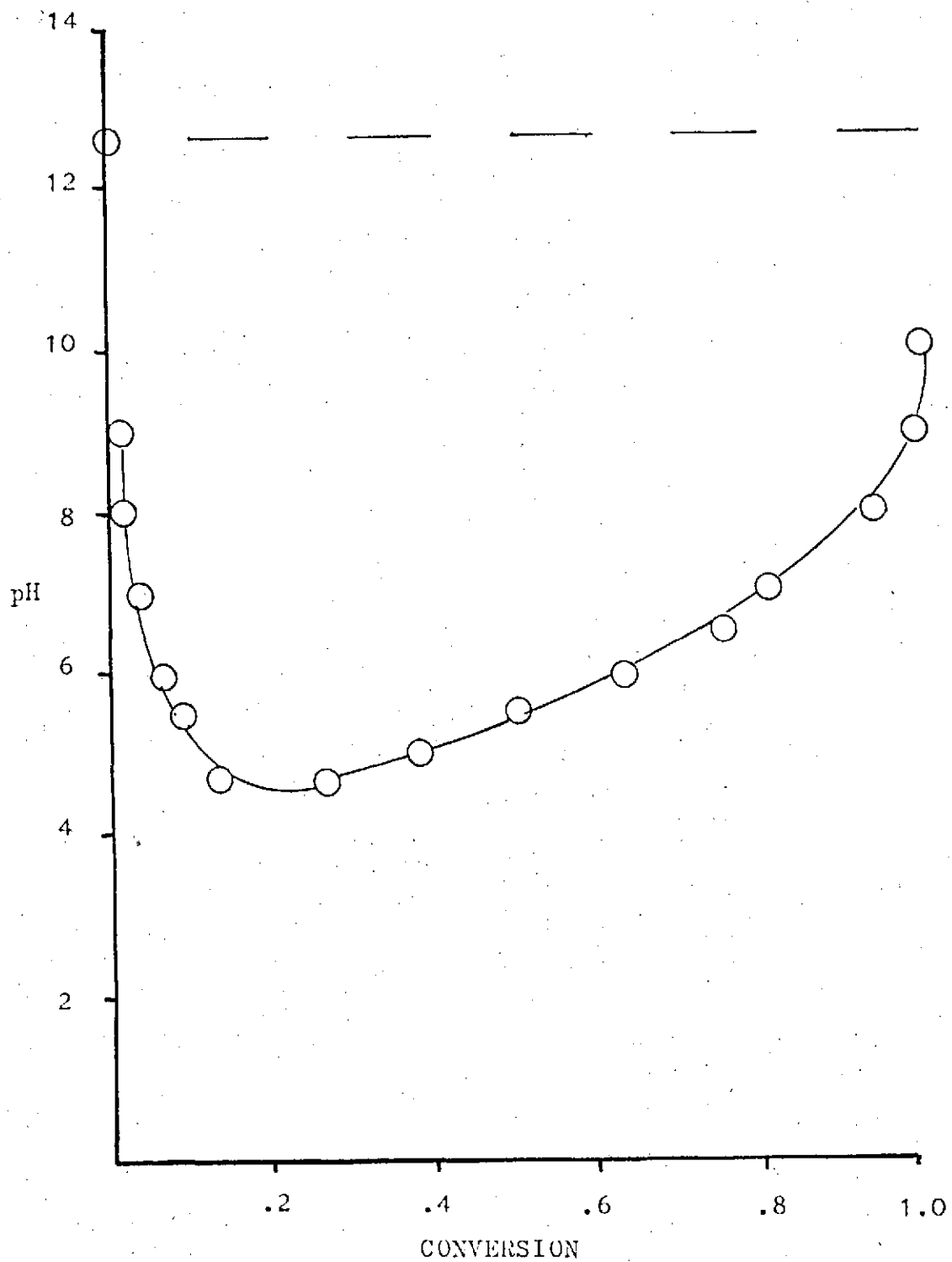Figure 1   APR04   HCHO, 0.327 M; Ca(OH)$_2$, 0.116 M

Figure 2 APR10 HCHO,0.33 M; Ca(OH)$_2$,0.138 M
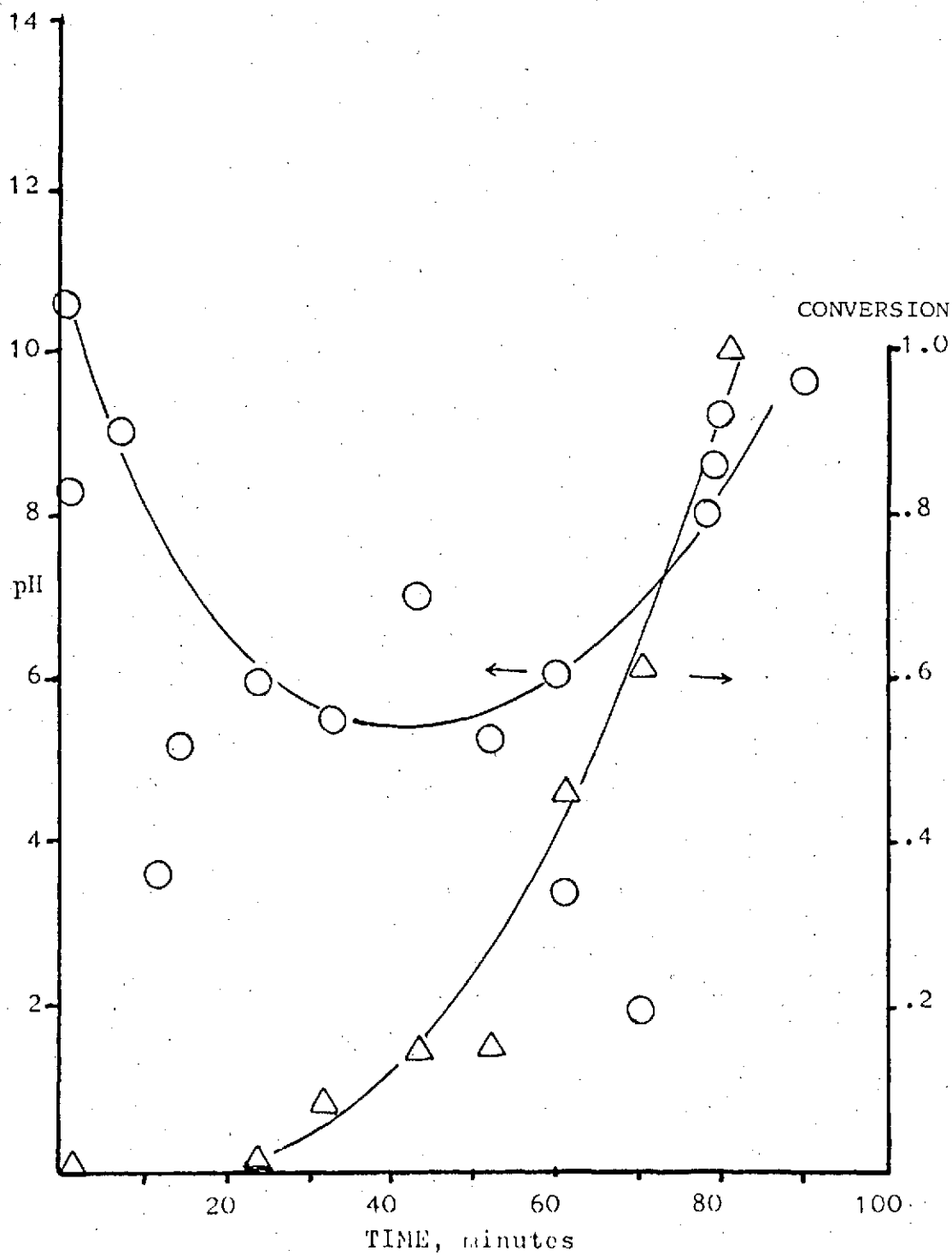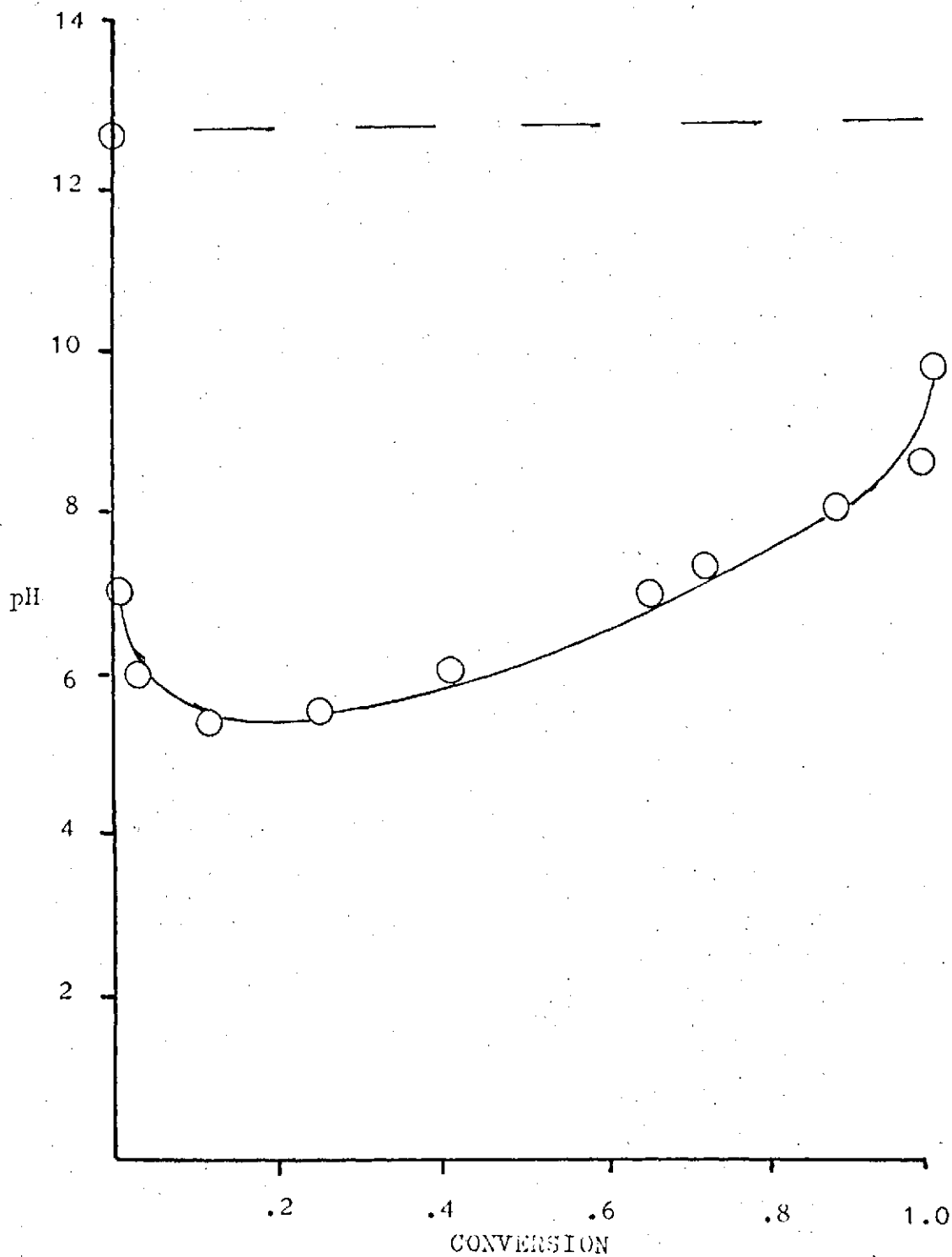
Figure 3   APR18   HCHO,0.373 M; Ca(OH)$_2$,0.096 M
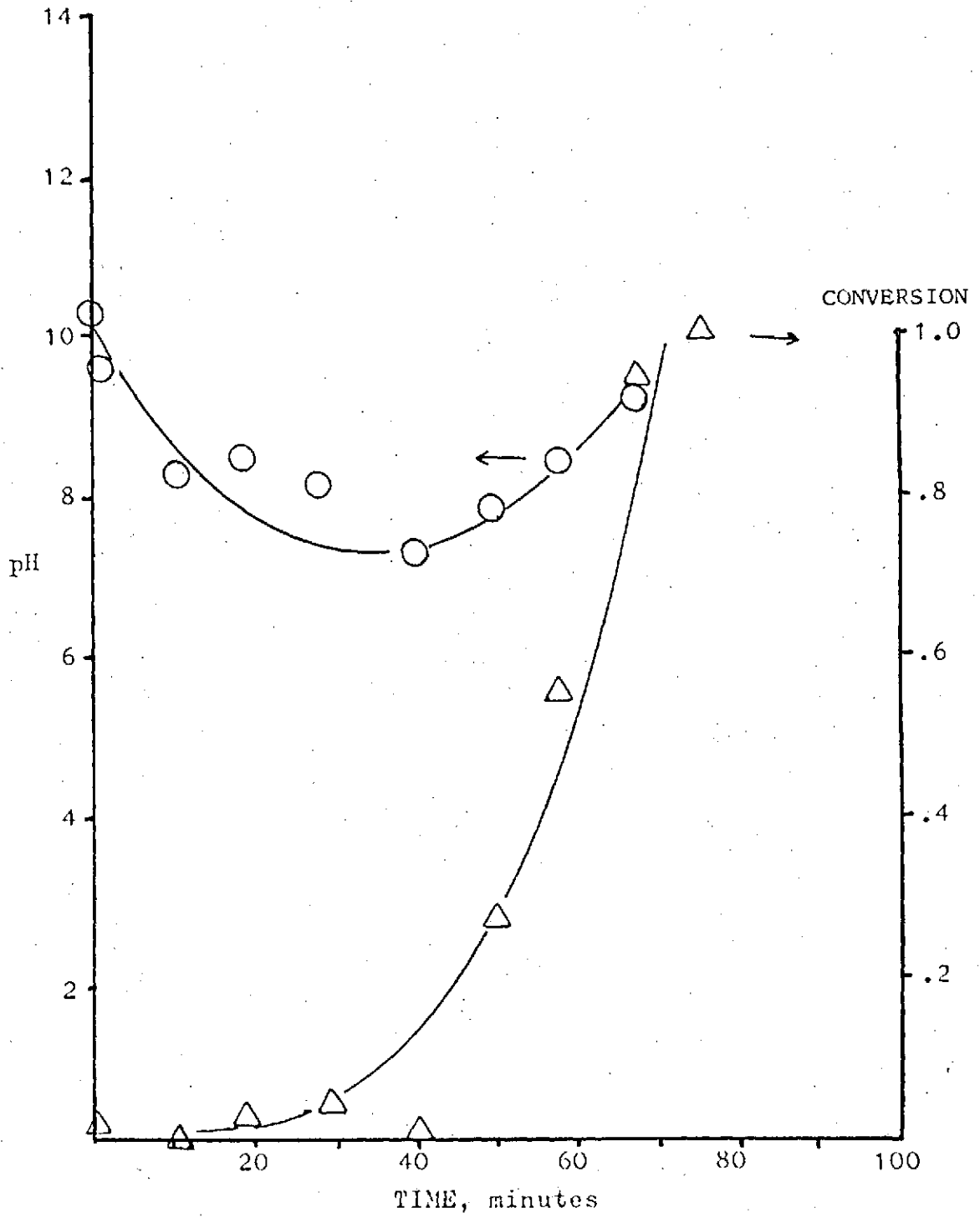
Figure 4   APR22   HCHO, 0.369 M; Ca(OH)$_2$, 0.151 M
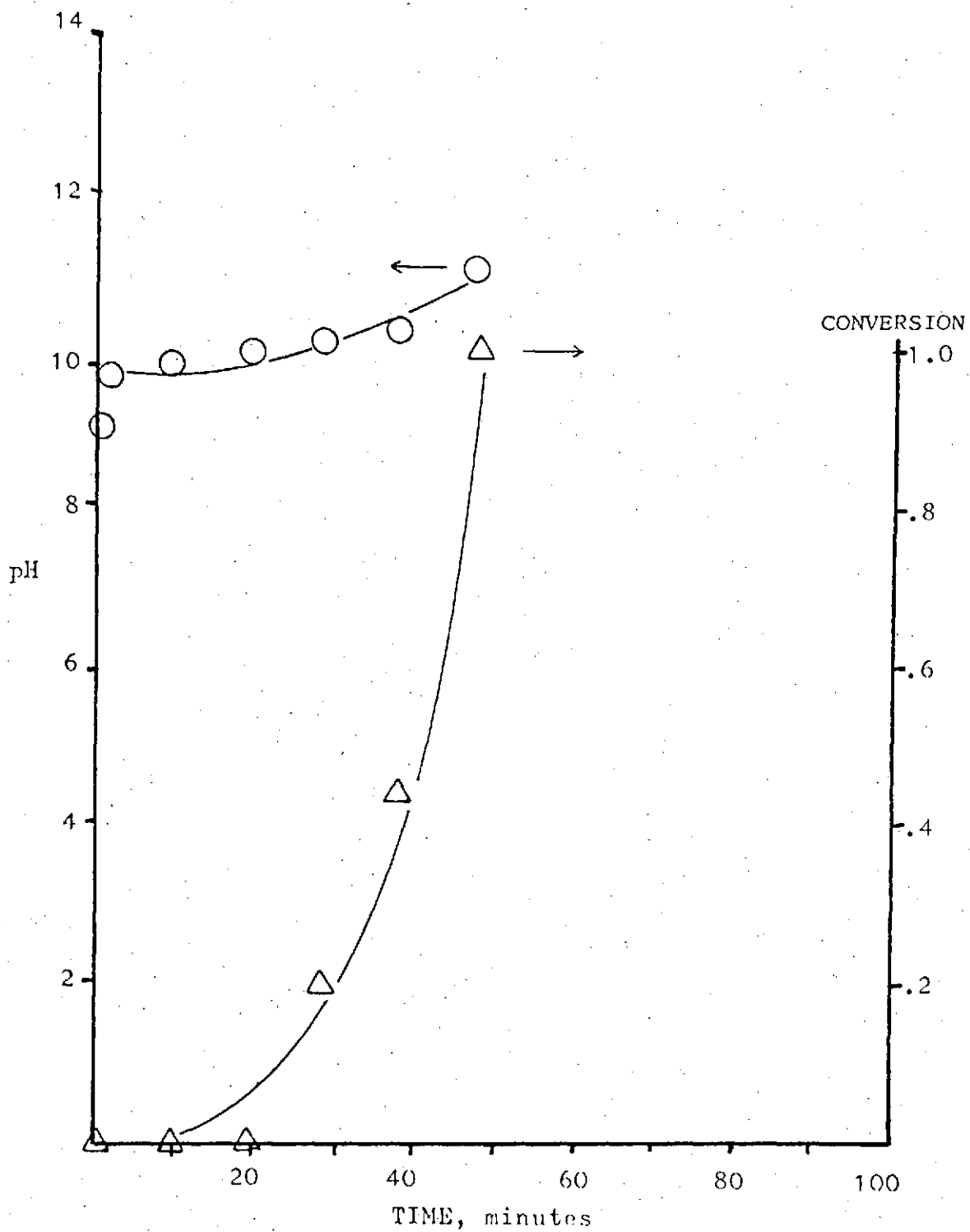
Figure 5   APR23   HCHO, 0.443 M; Ca(OH)$_2$, 0.064 M
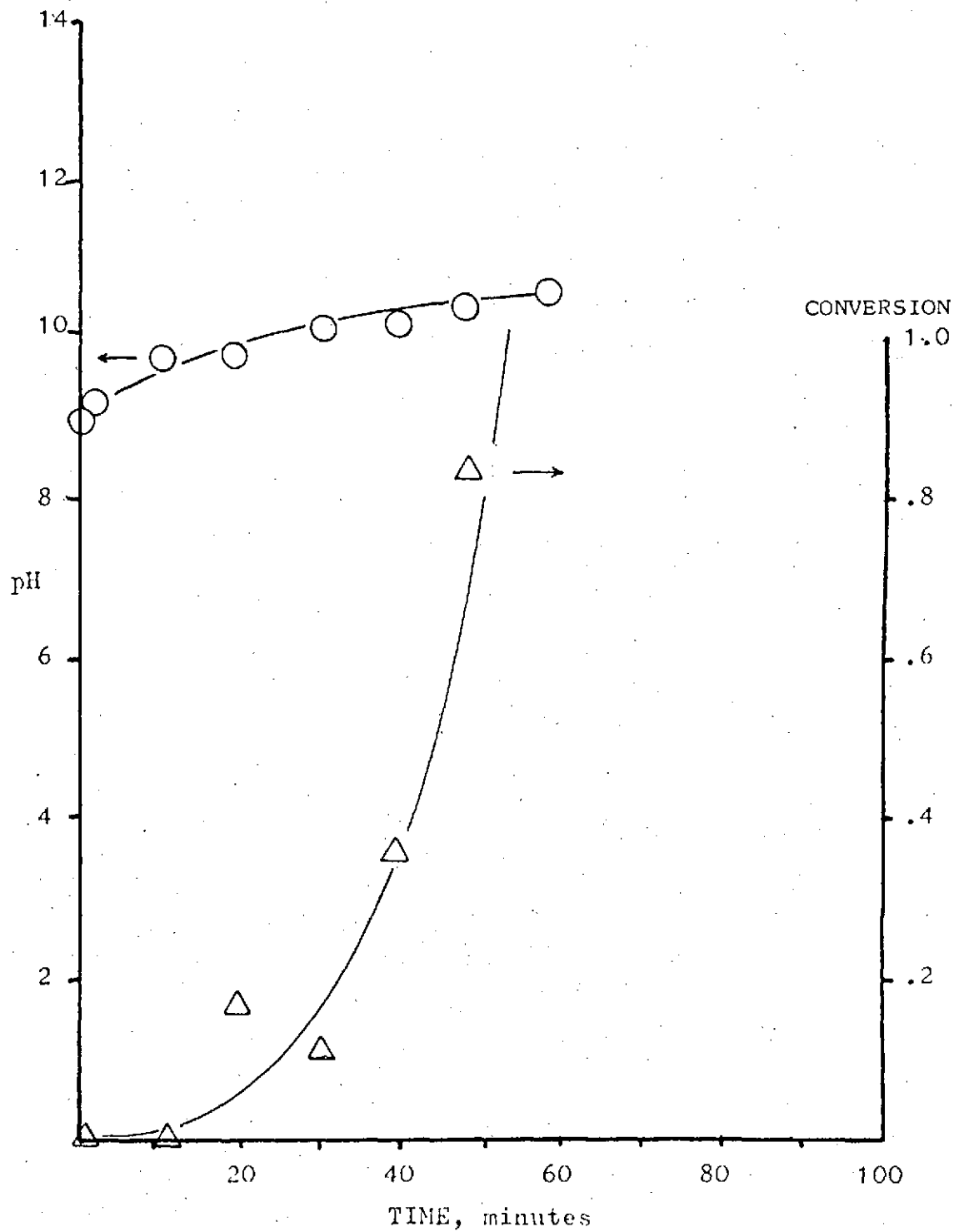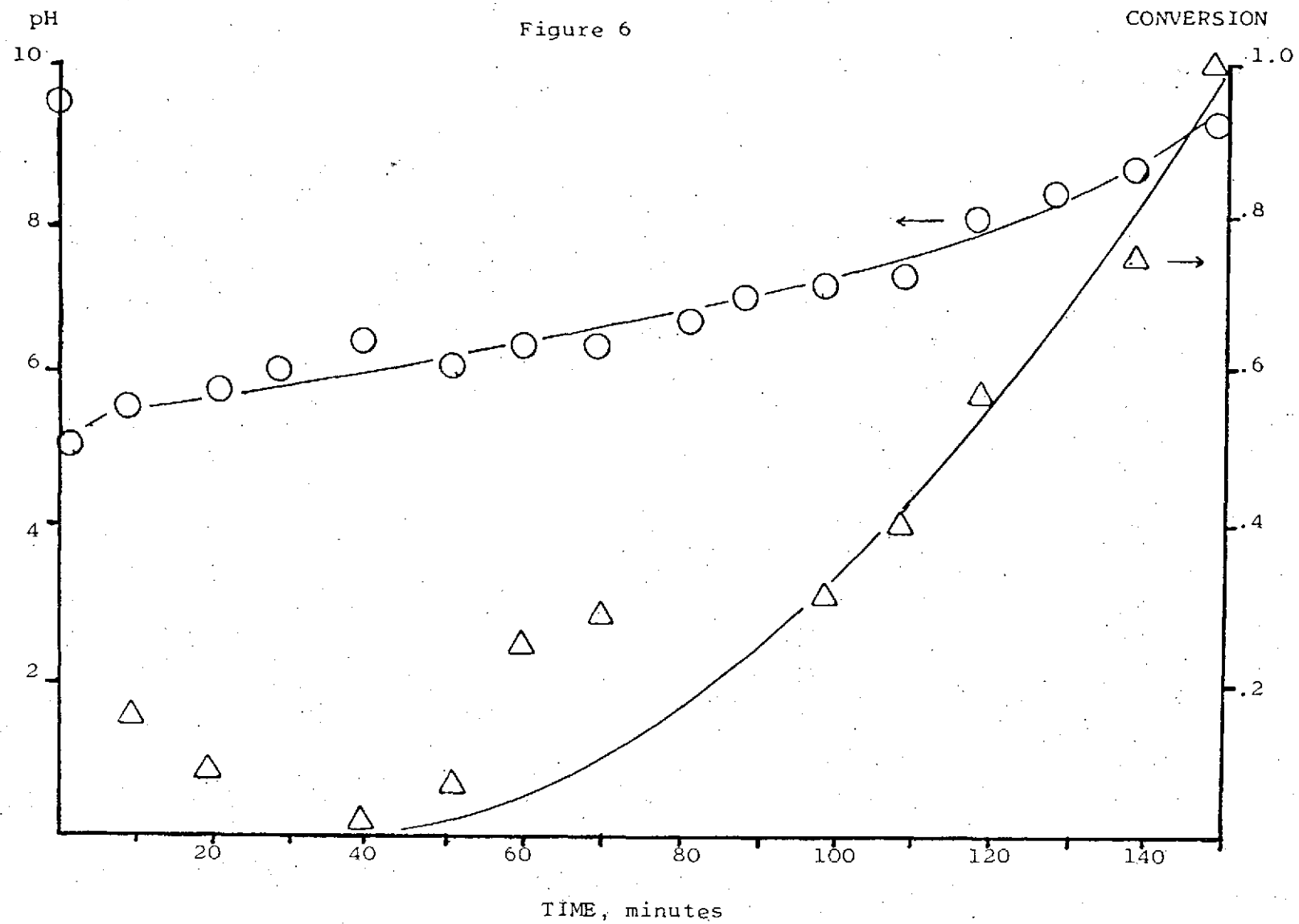
Figure 6

Figure 7
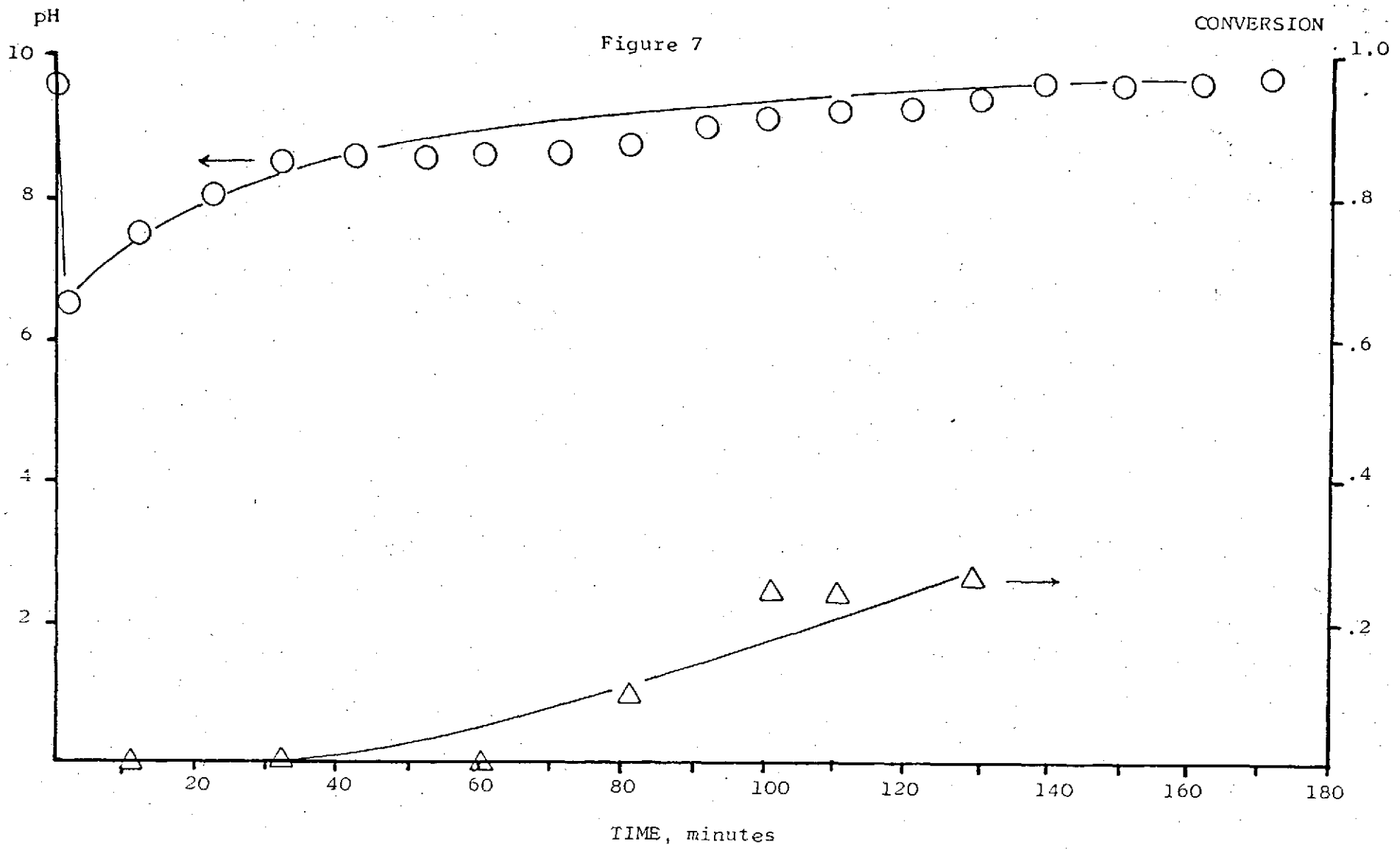
Figure 8   MAY08   HCHO, 0.386 M; Ca(OH)$_2$, 0.0343 M
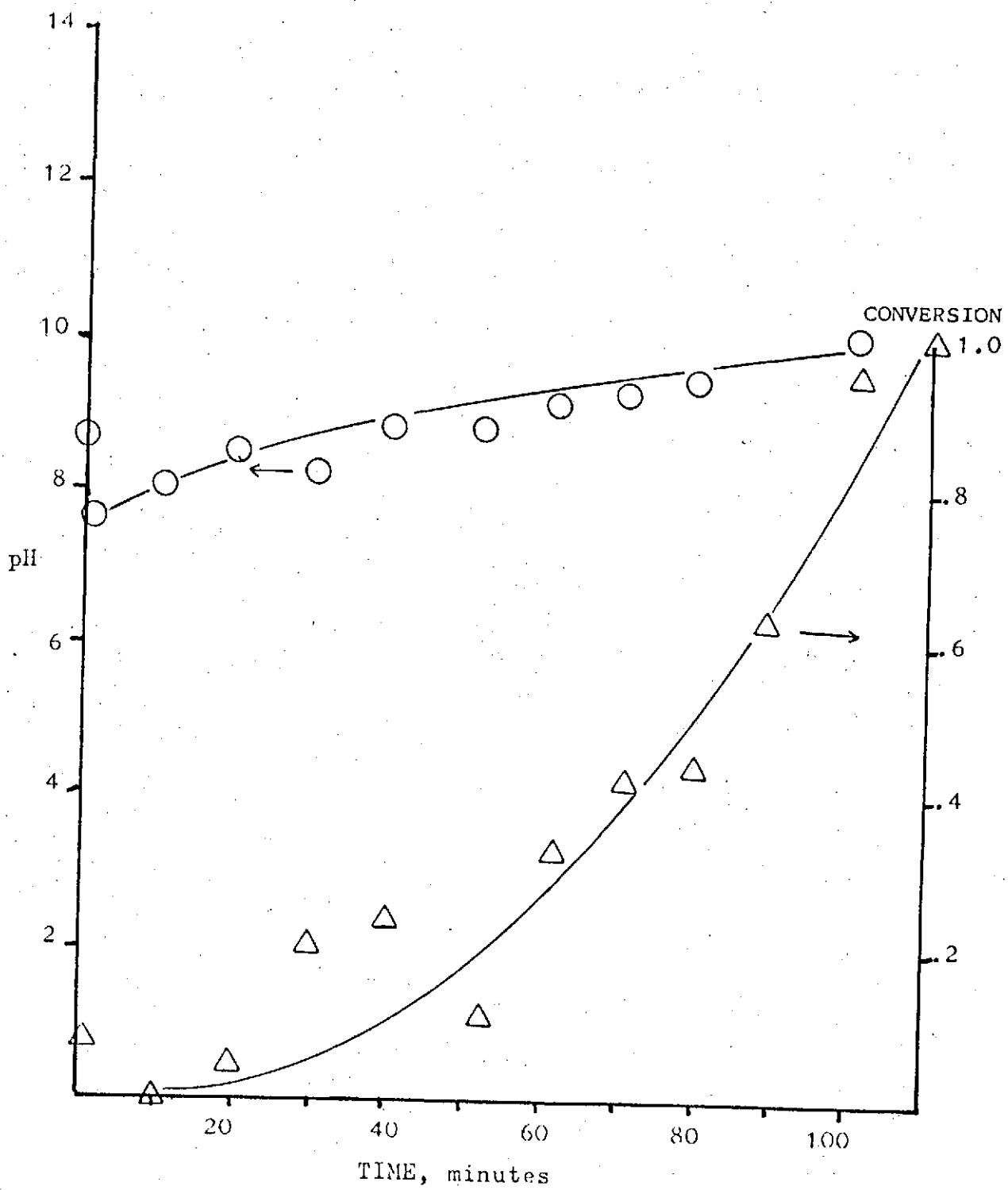
Figure 9   MAYO9   HCHO, 0.386 M; Ca(OH)$_2$, 0.21 M

Figure 10　　MAY16　　HCHO,0.458 M; Ca(OH)$_2$,0.05 M

Figure 11   JUNO6   HCHO, 0.422 M; Ca(OH)$_2$, 0.087 M

Figure 12   JUN10   HCHO,0.825 M; Ca(OH)$_2$,0.121 M
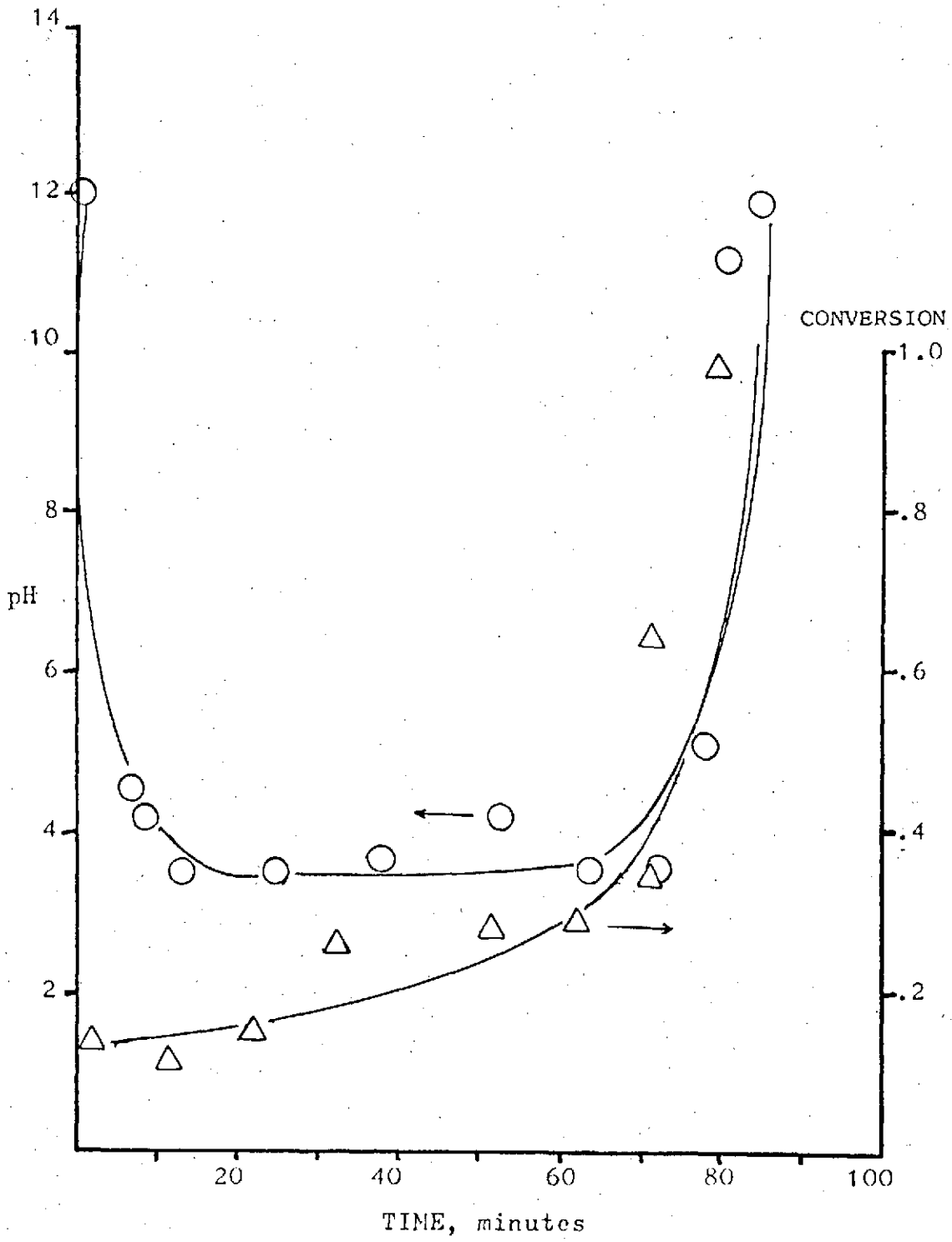
Appendix 4

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
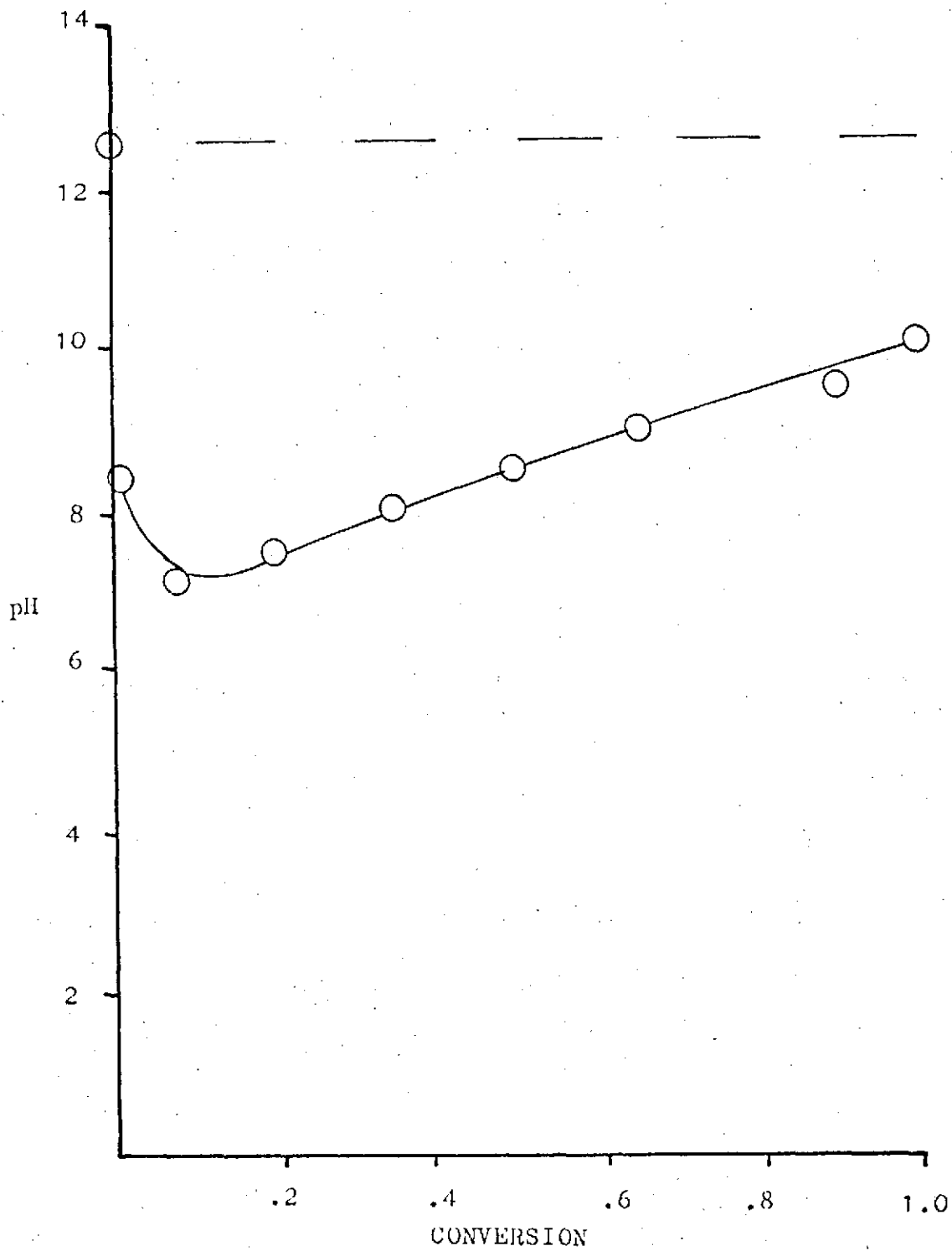
Figure 4   APR22   HCHO = 0.369 M, Ca (OH)$_2$ = 0.151 M
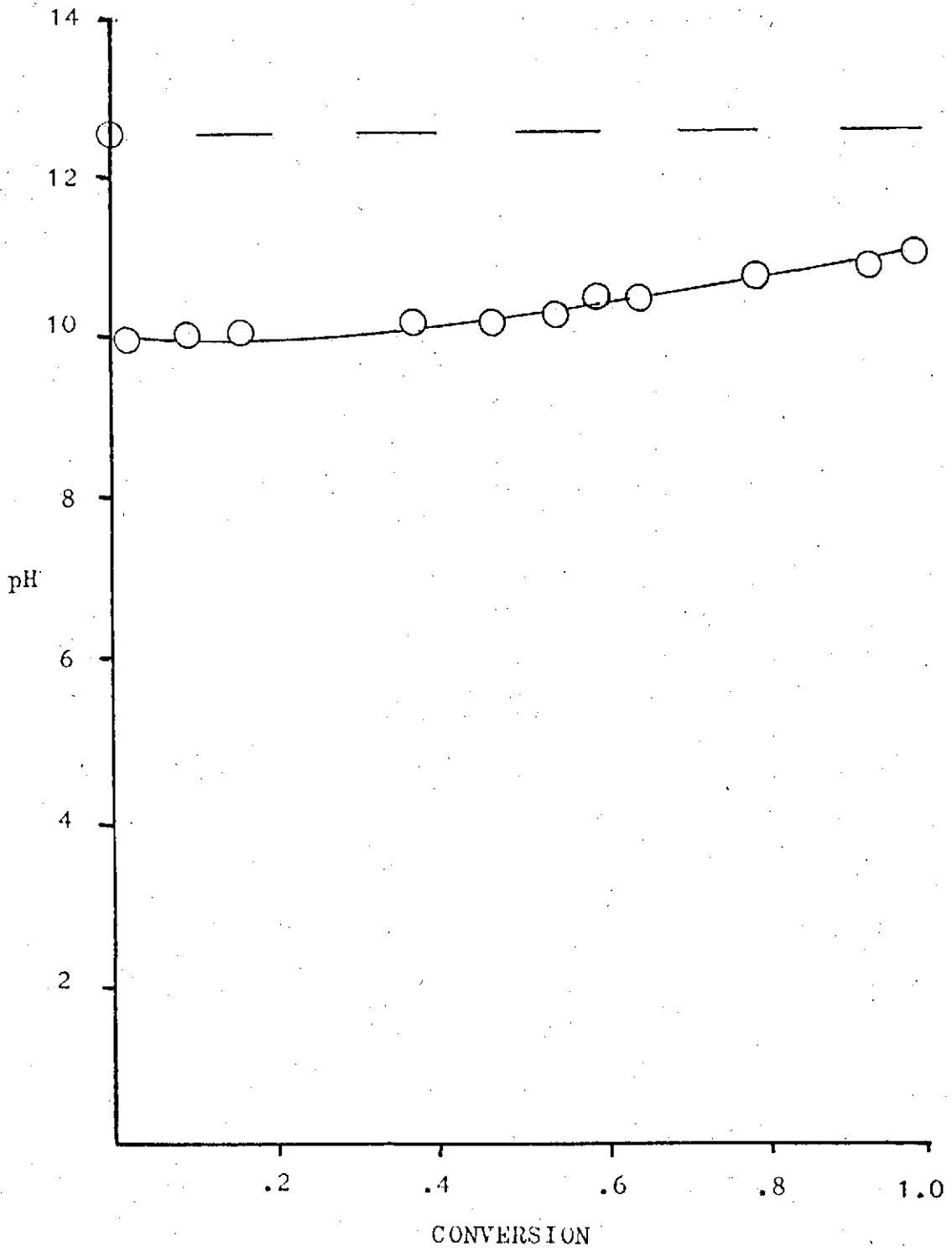
Figure 5   APR23   HCHO = 0.443 M, Ca(OH)$_2$ = 0.064 M
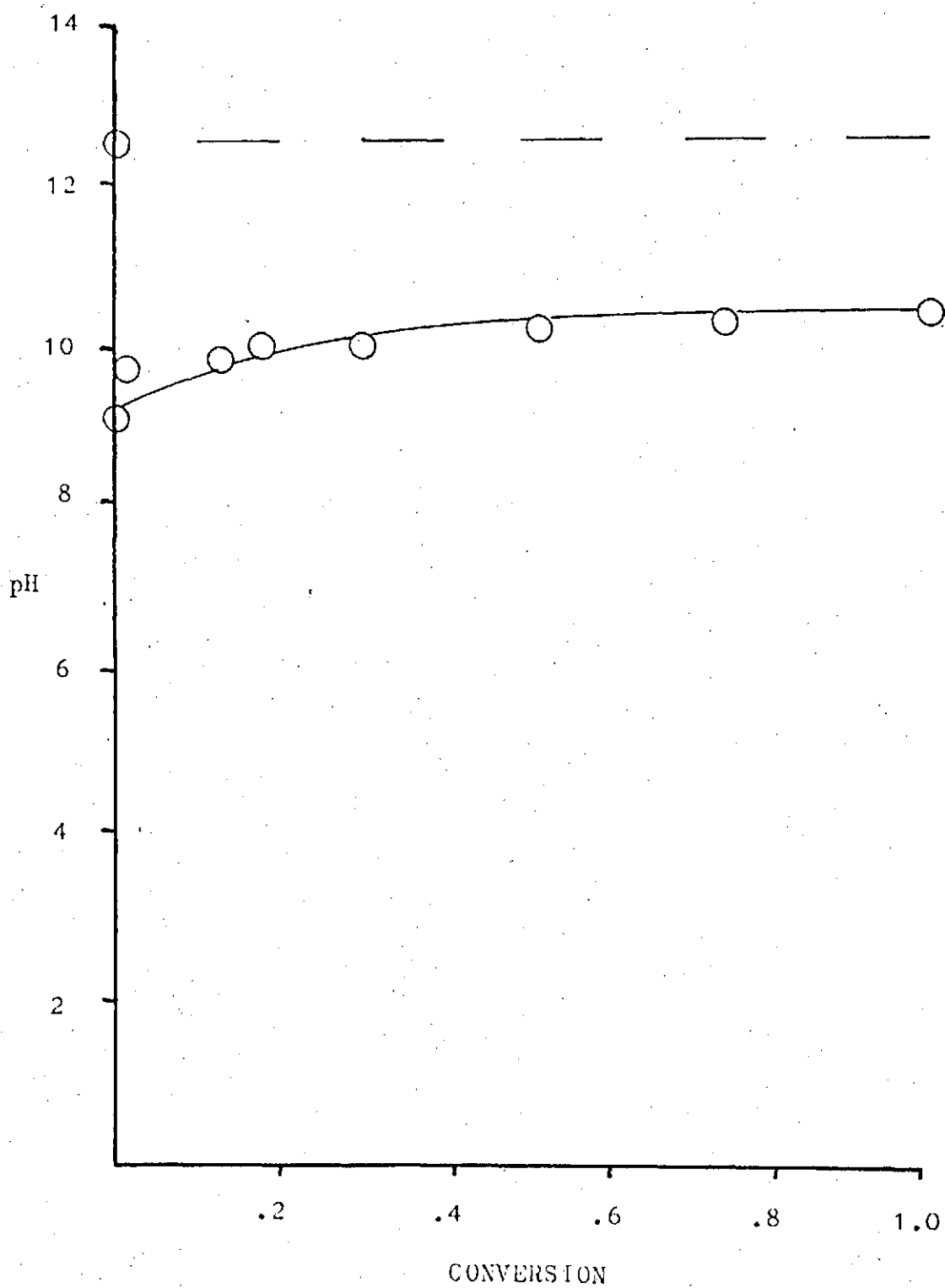
Figure 6　　　MAY02　　　HCHO = 0.34 M, Ca(OH)$_2$ = 0.0284 M
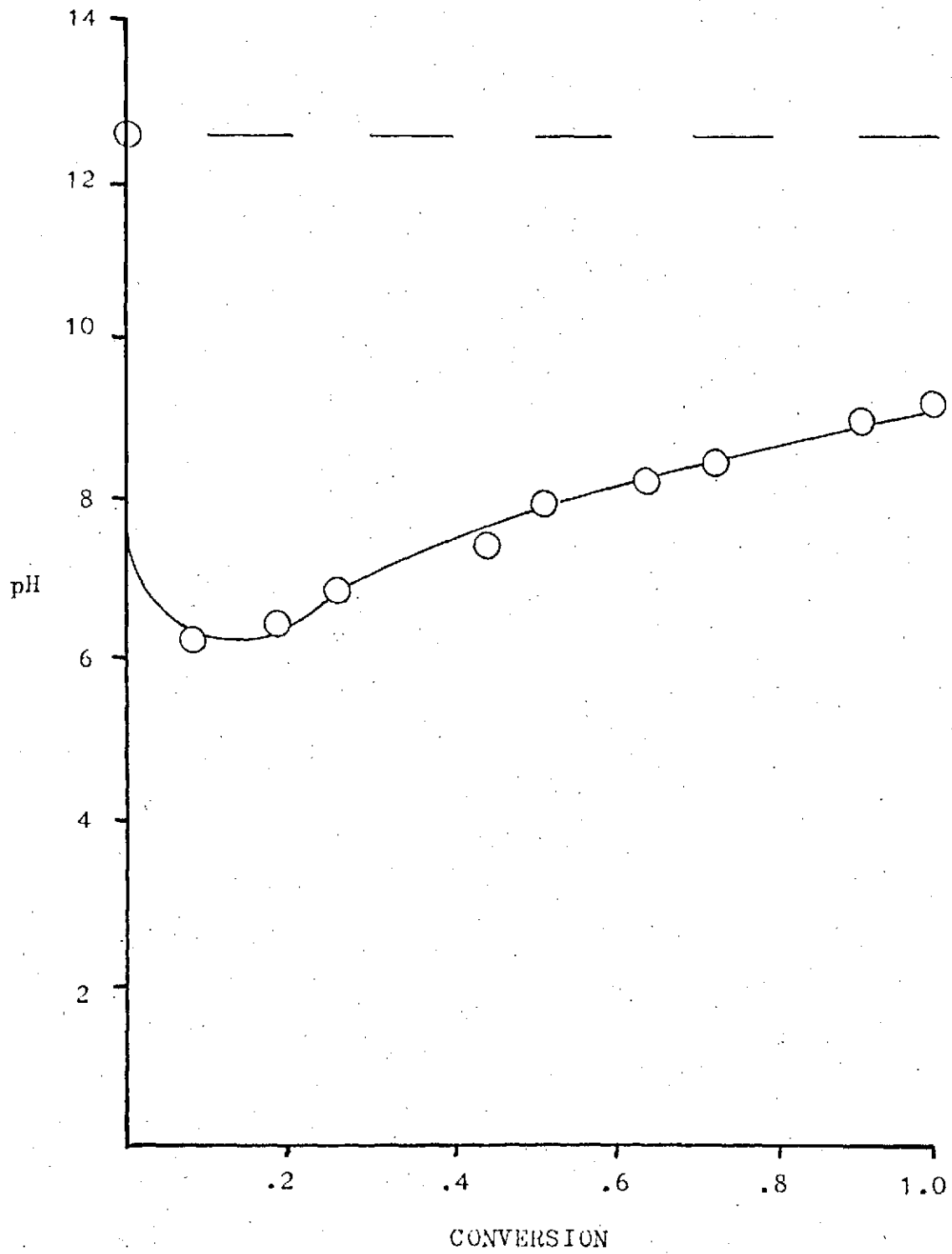
Figure 7   MAYO6   HCHO = 0.363 M, Ca(OH)$_2$ = 0.0388 M
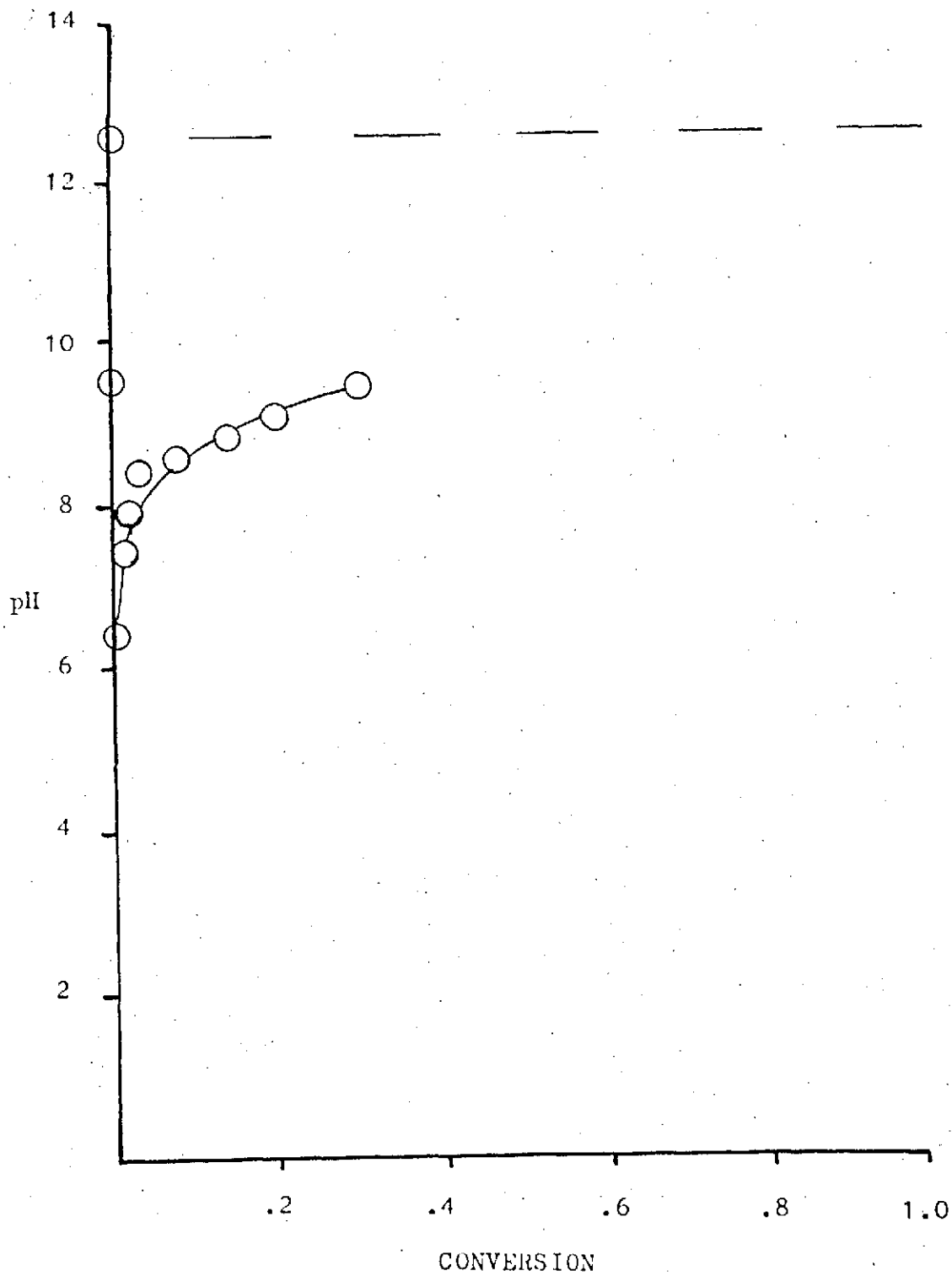
Figure 8   MAY08 $HCHO = 0.386$ M, $Ca(OH)_2 = 0.034$ M
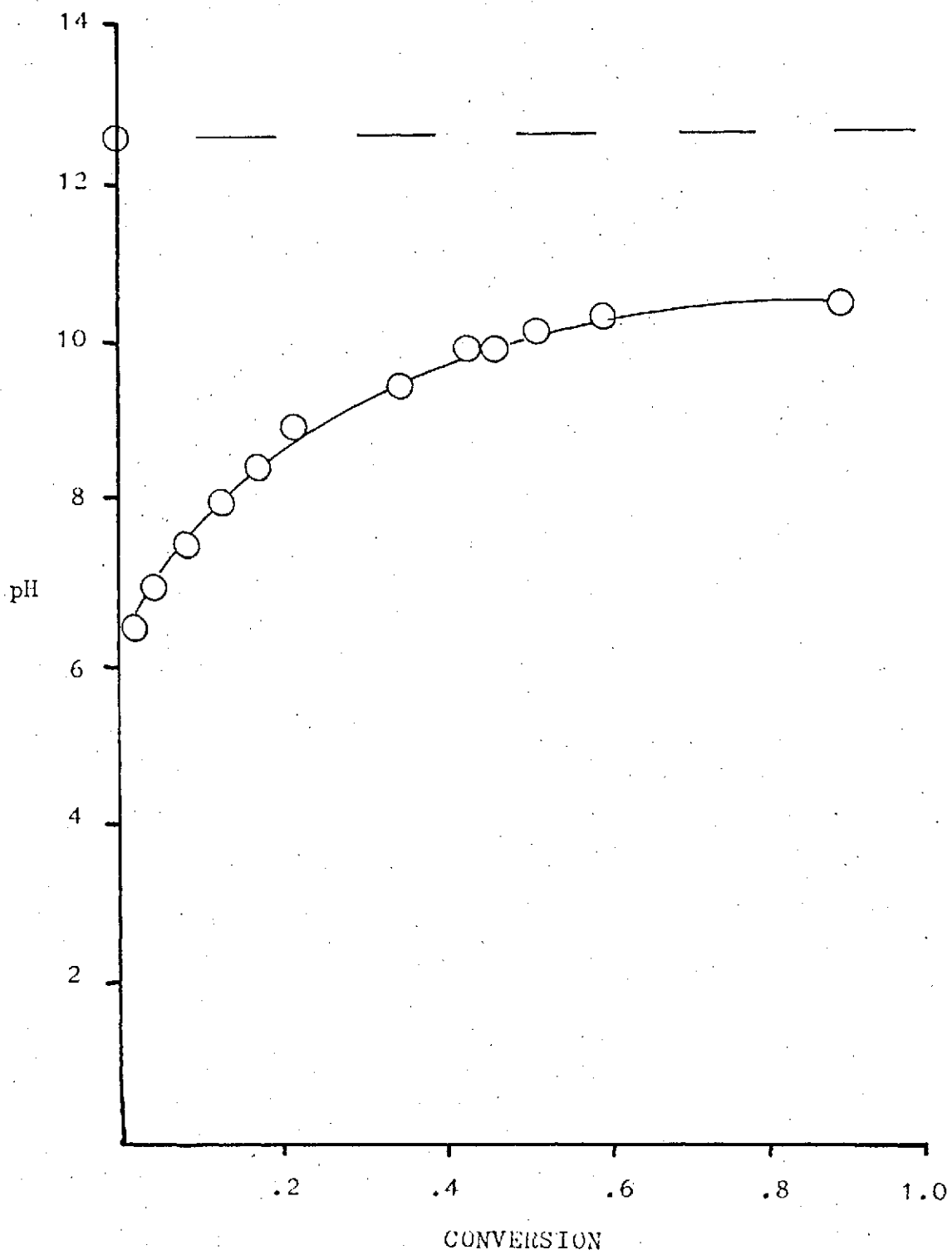
Figure 9   MAYO9   HCHO = 0.386 M, Ca(OH)$_2$= 0.21 M

pH

CONVERSION

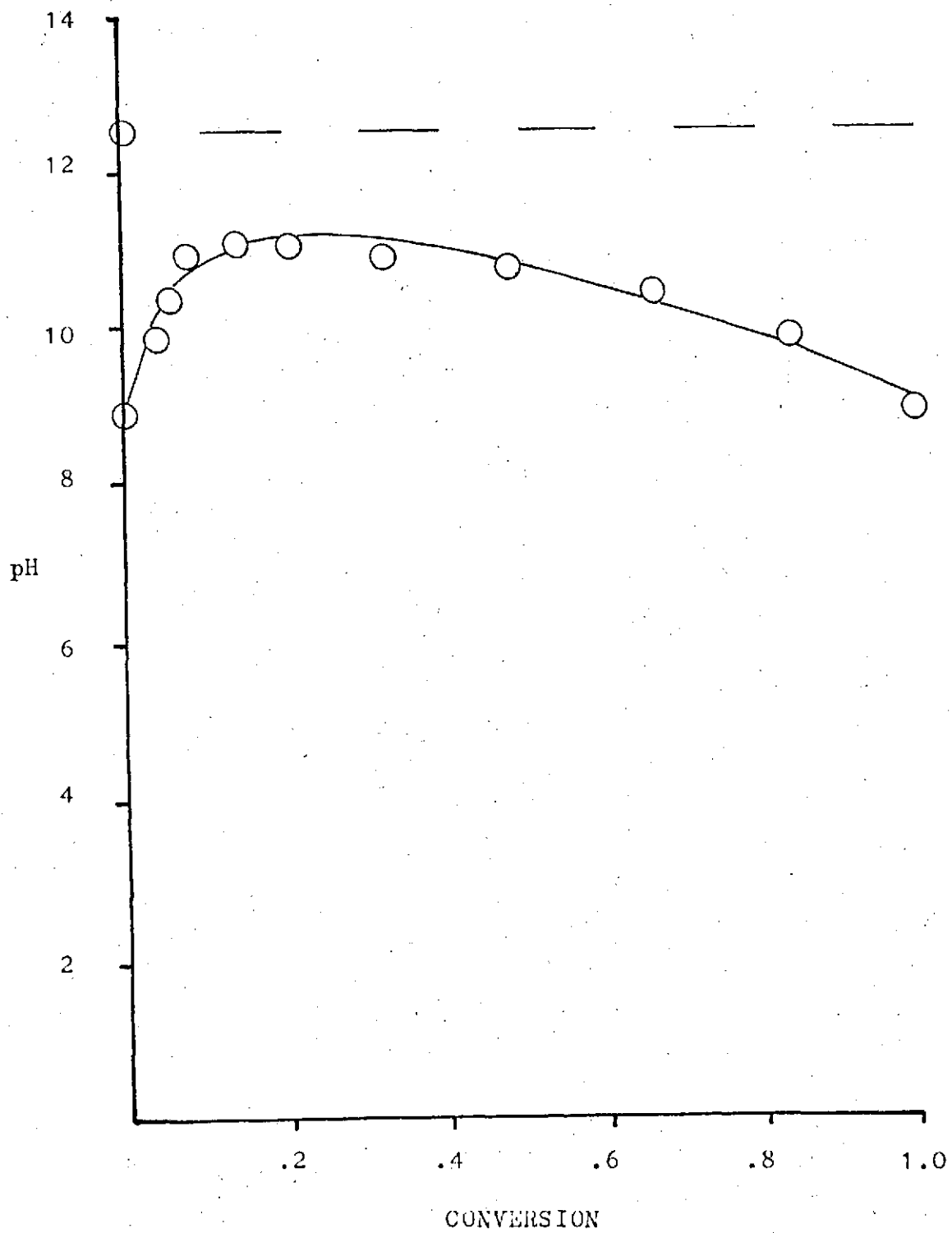Figure 10   MAY16   HCHO = 0.458 M, Ca(OH)$_2$= 0.05 M

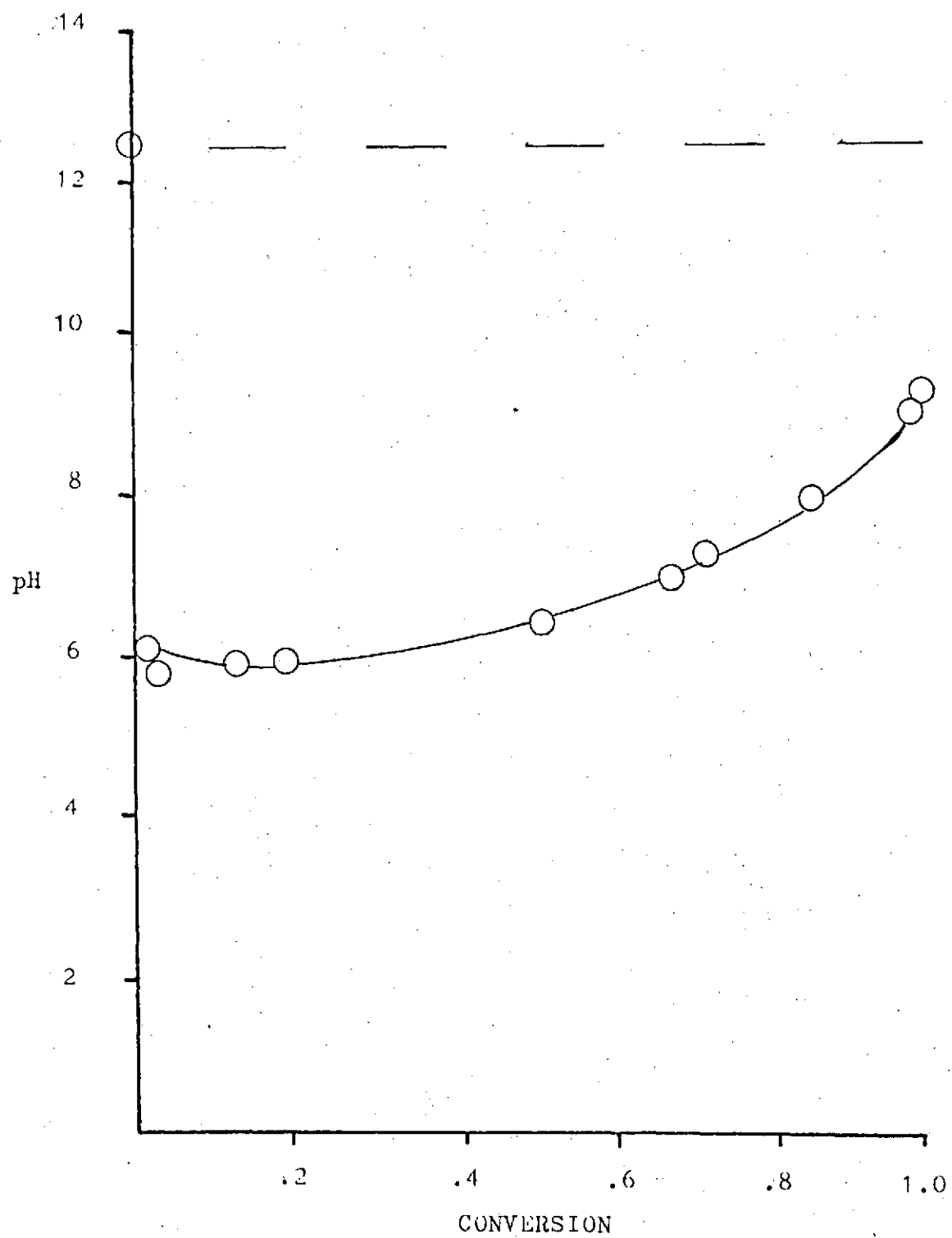Figure 11   JUN06   HCHO= 0.422 M, Ca(OH)$_2$= 0.087 M

Figure 12   JUN10   HCHO = 0.825 M, Ca(OH)$_2$ = 0.12 M