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CATALYSTS AND SUPPORTS FOR CONVERSION OF LACTIC ACID TO ACRYLIC ACID AND 2,3-PENTANEDIONE

By

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ABSTRACT

CATALYSTS AND SUPPORTS FOR CONVERSION OF
LACTIC ACID TO ACRYLIC ACID AND 2,3-PENTANEDIONE

By

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Reactions of vapor-phase lactic acid over various supports and supported catalysts were studied to maximize the production of acrylic acid and 2,3-pentanedione. A 34 wt% aqueous lactic acid solution was vaporized and passed over a catalyst bed which was positioned in a vertical, down-flow packed bed reactor. Condensible product analysis was accomplished with a Varian 3700 Gas Chromatograph with FID detection, while non-condensibles were analyzed with a Varian 3300 Gas Chromatograph which used thermal conductivity for detection.

Extensive catalyst/support microporosity causes lactic acid cracking and increases acetaldehyde production, and thus should be avoided. The XOC 005 silica support impregnated with Na_2HAsO_4 gave a 2,3-pentanedione yield of 23.3% with 67.5% selectivity at 300°C. The best acrylic acid yield (22.7%) was found with the same support impregnated with $NaNO_3$ at a reaction temperature of 350°C. Although these are promising results, much more work is necessary for this project to produce a marketable system.

This work is dedicated to my mother, Mrs. Myrna Langford, and to my loving and supportive family.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Dennis J. Miller for his support and guidance throughout the course of this project; Dr. James E. Jackson, for his suggestions and comments; Mr. Garry C. Gunter, for access to his data, methods and knowledge of the subject matter; and Mr. Johnathan P. Grow and Mr. Timothy Carlson, for their work with calcium hydroxyapatite.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION AND BACKGROUND

Lactic acid (2-hydroxy-propanoic acid) is an optically active molecule that is used as a food additive and in textile production (1). It has been traditionally used in limited quantities (40-50 MM lb/yr) at a price of 0.60 to 1.00 $/lb but it is undergoing a surge in production via efficient starch-based fermentation processes (1). This is giving lactic acid potential applications in biodegradable polylactide polymers (2). The new production technologies have a decreased cost associated with them which suggests that lactic acid could become a major biomass-based feedstock in the near future. The projected production capacity and cost for 1996 are 300+ MM lb/yr and 0.25 to 0.35 $/lb, respectively.

Lactic acid's structure allows it to exist in various forms. The lactic acid molecule has an asymmetric carbon atom, therefore it is capable of existing as the d- or l-forms. Both forms of lactic acid form esters and salts readily.

Reactions of vapor-phase lactic acid over various supports and supported catalysts are the focus of this study. The primary pathways of lactic acid conversion are shown in Figure 1.1: pathways to acrylic acid and to 2,3-pentanedione are the desired routes of reaction. Lactic acid conversion to

Primary Catalytic Reaction Pathways of Lactic Acid

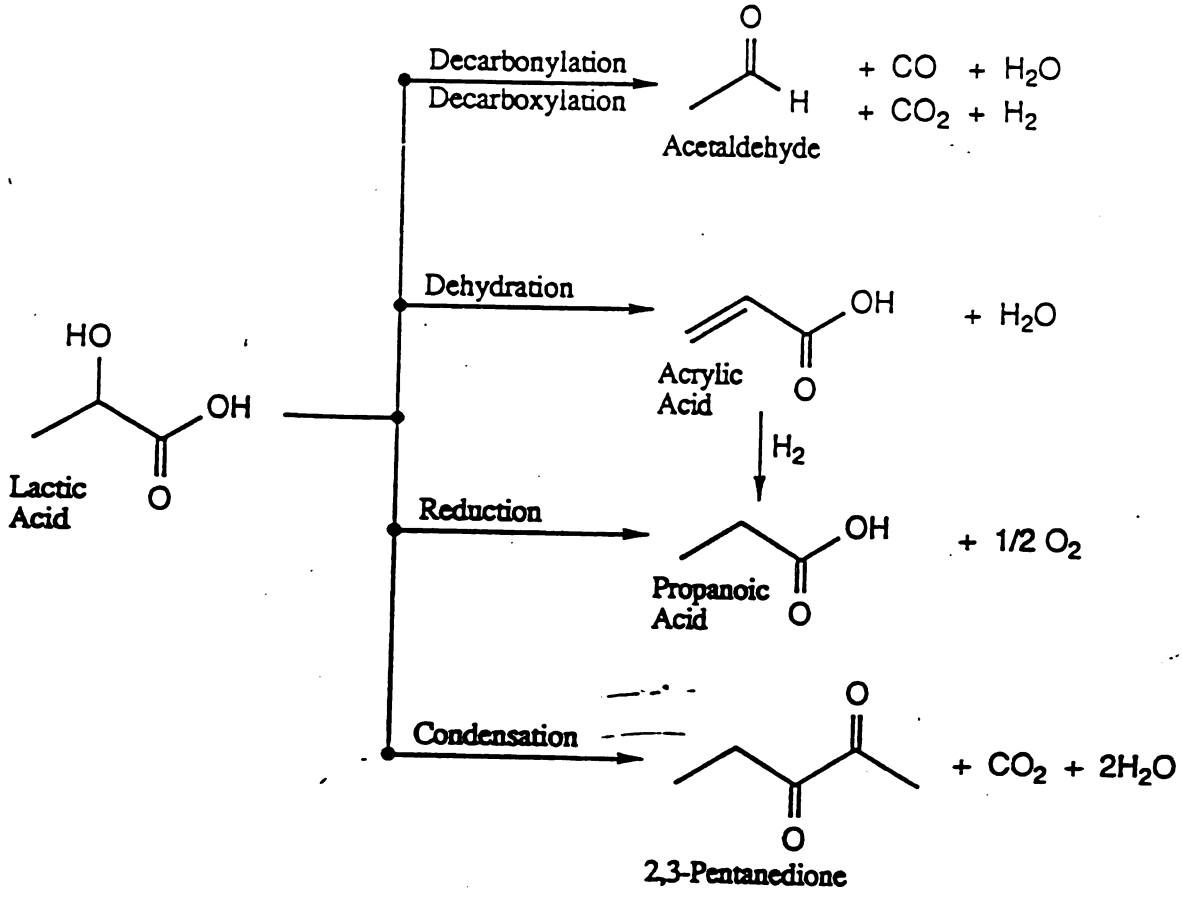

Figure 1.1 - Lactic Acid Conversion Pathways

acrylic acid is accomplished through direct dehydration, which has long been of interest as a potential route to polymers from biomass. However, selectivity to this pathway has not been high enough to make commercialization feasible. Current demand for acrylic acid is approximately 2 x 10^9 lb/yr with major applications being polyacrylate esters, superabsorbing polymers and detergents (2).

Lactic acid conversion to 2,3-pentanedione is achieved by condensation, and was first observed in our laboratory at Michigan State University. Carbon dioxide and water are also produced by this pathway. 2,3-Pentanedione is a high-value fine chemical ($70/kg) that is currently produced in limited quantities (4000 kg/yr) through a multistep chemical synthesis or via recovery from dairy waste. Its primary use is as a flavoring ingredient but it has potential for applications as a feedstock (3), solvent (4), fuel additive, or photoinitiator for chain reactions (5).

There are also major reaction pathways for lactic acid which are undesirable. Formation of acetaldehyde occurs through decarbonylation or decarboxylation of lactic acid. Decarbonylation also forms carbon monoxide and water while decarboxylation forms carbon dioxide and hydrogen. Acetaldehyde is presently produced inexpensively (0.45 $/lb) from petroleum. Reduction of lactic acid produces propanoic acid. Propanoic acid can also be formed by hydrogenation of acrylic acid. Again these methods of production do not hold much promise, as propanoic acid is produced more efficiently

and inexpensively from petroleum.

Secondary pathways, which in some reactions produced major products, were also found in lactic acid conversion. Those which are known include pathways to acetic acid, acetone, hydroxyacetone, methyl acetate and ethanol.

Most lactic acid conversion studies have focused on the dehydration reaction pathway to acrylic acid. Holmen (6) reported conversion over phosphate and sulfate catalysts in 1958. Acrylic acid yields of 68% were achieved over Na_2SO_4 at 400°C. Paparizos et al. (7) used ammonium lactate as a feed at 340°C and 4.2s residence time over NH_3-treated $AlPO_4$ and reported a 61% yield of acrylic acid. Silica-supported NaH_2PO_4 buffered with $NaHCO_3$ was used by Sawicki (8) who reported an acrylic acid yield of 58% with a selectivity of 65% at 350°C.

Lactic acid reaction studies have produced major products other than acrylic acid. Odell et al. (9) contacted lactic acid with Pt complexes in aqueous solution at 200-250°C and found large yields of propanoic acid and 3-hydroxypropanoic acid and only small amounts (<5%) of acrylic acid. Propanoic acid, in absolute yields of 65% at 350°C, was made in another study via lactic acid conversion over a mixed metal oxide catalyst (10). Formation of both cyclic and acyclic lactic acid dimers over silica aerogel at low temperatures was reported by Sholin (11).

Formation of lactic acid esters usually occurs during processes which include lactic acid. Concentrating lactic acid aqueous solutions by distillation removes water but at

the same time produces lactic acid esters. Lactyllactic acid ($CH_3CHOHCOOCH(CH_3)COOH$) is the first esterification product but higher linear esters, that is, trimeric, tetrameric and polymeric lactic acid, are formed as the dehydration proceeds (12). Esterification of lactic acid has also been shown to form cyclic compounds such as glycolide and lactide (12).

Pyrolysis of lactic acid and other aliphatic α-hydroxy acids has been reported to produce an aldehyde (or ketone), carbon monoxide, and water (12). Lactic acid mono-esters also decompose into aldehydes and CO when heated. The hydroxy esters undergo auto-alcoholysis under suitable conditions. For example, when heated in a closed vessel at 250°C for 7 to 8 hours, ethyl lactate yields lactide and ethyl lactyllactate (12).

Mok, Antal and Jones (13) published a study of the reaction pathways of lactic acid in supercritical water in 1989. In the study, three primary reaction pathways were described. The first is acid catalyzed decarbonylation which yields acetaldehyde, CO and water. Second, the decarboxylation pathway yields acetaldehyde, CO_2 and water. Finally, dehydration produces acrylic acid and water. Acetic acid and acetone are further reaction products of acetaldehyde while hydrogenation of acrylic acid produces propanoic acid and decarboxylation of acrylic acid produces ethene. Effects of solvent concentration, temperature, pressure, and acid catalysts are described in the paper, for each pathway.

McCrackin and Lira (14) investigated the conversion of

lactic acid in supercritical water in a specially designed reactor. They found that aging their Hastelloy C-276 reactor for approximately 70 hours at reaction conditions increased the yields of acrylic acid by decreasing the alternate pathway conversions. They found a maximum acrylic acid selectivity of 58% at a residence time of 70 seconds and a temperature of 360°C. The maximum acrylic acid selectivity was obtained with a 0.40 M lactic acid solution containing small amounts (< 0.01 M) of phosphate salts.

The acrylic acid yields reported in the literature look very promising; if our lactic acid study could improve the results, then our process could be used to produce acrylic acid inexpensively. Also, the discovery of the condensation product, 2,3-pentanedione, has given our research group an added incentive to continue lactic acid studies. An inexpensive method for producing the diketone would be very profitable. The results reported in this thesis describe catalyst and support screening studies directed at achieving high yields and selectivity to 2,3-pentanedione and acrylic acid from lactic acid.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 MATERIALS

For reaction, the lactic acid feed solution (Purac, 88 wt% in solution) was diluted to 34 wt% prior to being fed to the reactor. High purity (99.99%) helium gas obtained from AGA Gas was used as the carrier. High purity acrylic acid, 2,3-pentanedione, propanoic acid, acetaldehyde, hydroxyacetone, and other chemicals were used as calibration standards.

2.2 CATALYST PREPARATION

Various materials were tested as catalyst supports (Table 2.1) and catalysts (Table 2.2). Among the catalysts studied first was biomineral-derived calcium hydroxyapatite, seen as a potentially inexpensive phosphate catalyst. This catalyst was prepared by calcination of bovine teeth in air to remove organic matter, then was crushed to a suitable size before reaction.

Other catalysts tested consist mostly of sodium salts which were supported on carbon and/or silica supports. The sodium salt catalysts were generally prepared using the following procedure: First, a quantity of the support to be

Table 2.1 - Supports Studied

CARBON	OTHERS
Strem Activated Carbon	1 mm Glass beads
Activated Cherry Pits	Silica gel
Charred Cherry Pits	XOA 400 Silica
Alltech Carbograph 1	XOB 030 Silica
Alltech Carbograph 2	XOC 005 Silica

Table 2.2 - Catalysts Studied

CATALYST	SUPPORTS TESTED ON
Na_3PO_4	Cherry, Cherry Char, XOC 005
NaOH	XOC 005 Silica
$NaNO_3$	XOC 005 Silica
Na_2HAsO_4	XOC 005 Silica
$Ca_{10}(PO_4)_6(OH)_2$	None

impregnated was weighed. Then, 0.001 gmol of salt per gram of support was dissolved in a small amount of reverse osmosis water. The support was then added to this solution and heated on a hot plate until nearly dry. Finally, the support was placed overnight in a vacuum oven which was heated to 100°C to finish the drying process.

Catalyst supports were studied in detail and the performance of each was evaluated for comparison. Carbon supports (see Table 2.1) included activated cherry pits, charred cherry pits, an activated carbon from Strem and two carbons from Alltech. Silica supports included a silica gel, and three silicas obtained from Anspec. Glass beads (1 mm) were also tested in the reactor.

2.3 REACTOR CONFIGURATION

The reactor system used for all studies was a vertical, down-flow packed bed reactor equipped with a quartz insert (Figure 2.1). The reactor was chosen to exist in a vertical position because of advantages over a horizontal orientation. The horizontal configuration produced coking in the catalyst bed and poor product recovery as a result of incomplete lactic acid vaporization.

The body of the reactor consists of a 316 Stainless Steel tube 19.5" long, 1.25" OD and 0.55" ID. The body is mounted on a wooden stand to make the system portable. A flange closure at the bottom of the reactor is sealed, after catalyst

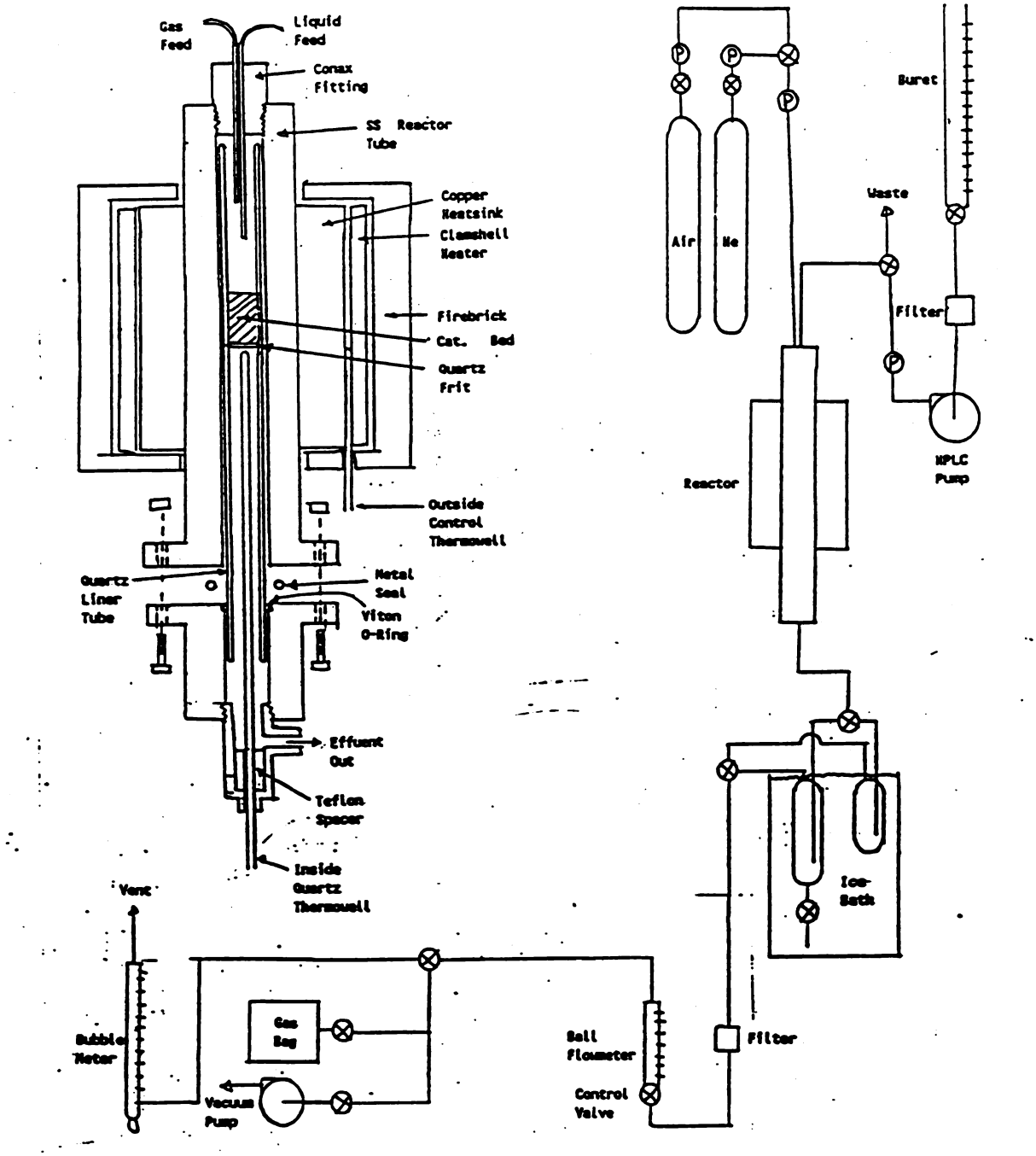

Figure 2.1 - Reactor system

loading, by a spring-loaded metal seal (Helicoflex). This closure facilitates internal access. The reactor system is designed to hold pressure up to 5 MPa at a temperature of 500°C. A quartz liner tube which contains the catalyst is inserted into the reactor from the bottom and sealed to the flange to prevent gas bypass. The quartz-lined interior was used because a metal interior enhanced the undesirable reaction pathways to acetaldehyde and propanoic acid. The liner tube is 19" long x 0.50" OD and contains a coarse quartz frit fused to the tube 9" from one end. The catalyst sits on this frit during reaction. An internal quartz thermocouple well extends from the reactor flange to just below the support frit to measure reaction temperature.

A clamshell electric heater controlled by an Omega series CN-2010 programmable temperature controller is used to heat the high-temperature zone of the reactor. The heater is controlled by an external control thermocouple and can achieve a temperature of 600°C. A copper heat sink (6.5" long x 0.5" thick) surrounds the reaction zone to minimize temperature gradients. During a reaction, the catalyst bed temperature is measured by the internal thermocouple. The reactor temperature setpoint is adjusted to achieve the desired catalyst bed reaction temperature.

Flexible heat tapes are used on each end of the reactor. The heat tape upstream of the reactor is used to preheat the lactic acid feed to more readily allow feed vaporization. The downstream heat tape is used mostly to prohibit reaction

products from condensing before reaching the collection system. The heat tapes were consistently held at 190°C during system operation.

Stainless steel liquid and gas feed tubes (0.062" OD) enter the reactor from the top through a Conax fitting and extend well inside the quartz liner tube. The liquid feed tube extends further into the liner than the helium feed tube; the liquid feed vapor cannot escape through the top of the liner because the helium stream forces it to flow down towards the catalyst bed. An Eldex HPLC metering pump is used to pump the liquid feed solution; high purity helium is used to flush the reactor and to dilute the feed during reaction.

2.4 PRODUCT COLLECTION

During reaction, reactants and products travel through the catalyst bed, the quartz frit, and then out the bottom of the reactor. The effluent then passes through a 10 ml stainless steel trap placed in an ice bath. This trap collects all condensible products. Noncondensible products flow through a metering valve and a flowmeter and are collected in a gas bag. Liquid and gas products were collected for a specified time (20-40 min for liquid and 10-25 min for gas) during steady state operation of the reactor. Volumes of liquid product collected and gas product collected were measured in order to calculate flow rates and to perform overall mass balance calculations. Liquid product volumes

were usually 2-7 ml and gas volumes were usually 200-500 ml. During transient periods of system operation, liquid products were condensed in an 80 ml waste trap and gas products were sent to a fume hood.

2.5 PRODUCT ANALYSIS

Condensible products were analyzed with a Varian 3700 Gas Chromatograph with FID detection. A 4% Carbowax 80/100 carbopack B-DA glass column was used in the GC. Liquid product GC preparation included filtering the condensed effluent to remove particulates using disposable syringe filters. Also, the liquid product was mixed with a solution containing 2-propanol as an internal standard and oxalic acid as a column conditioner. One microliter samples were injected directly onto the column while leaving the syringe in the injector for one minute. This assured complete lactic acid vaporization and resulted in reproducible, linear calibration curves for lactic acid. As mentioned earlier, the major products analyzed were found to be acetaldehyde, 2,3-pentanedione, propanoic acid, and acrylic acid. Reactions involving sodium salts on silica supports produced hydroxyacetone as an additional major product. Secondary products include ethanol, acetone, acetic acid, methyl acetate, and several unknowns. These minor products are reported as "Other" in the results. Product yields are calculated from product-to-internal standard peak areas and

detector response factors, and are reported as molar percentages based on theoretical lactic acid conversion. Figure 2.2 shows a typical chromatogram. Product identification was conducted by matching of residence time with standards, by gas chromatography/mass spectroscopy, and by ^1H NMR.

A Supelco Spherocarb column in a Varian 3300 Gas Chromatograph was used to analyze gas samples. This instrument uses thermal conductivity for detection. The gas products analyzed were CO, CO_2 and methane. Yields of CO and CO_2 are reported on the same basis as liquid products (mole of gas per mole of lactic acid fed).

Catalyst dimensions, peak areas from GC runs, liquid and gas product volumes, feed flow rates and concentration are entered into a spreadsheet program designed to calculate residence times, product yields as a percentage of theoretical, selectivities as percentages of products formed, and the overall carbon mass balance for the experiment.

2.6 TYPICAL PROCEDURE

Each reaction experiment contains some of the same operating procedures. For instance, in each experiment, catalyst is loaded into the reactor and tested at several increasing reaction temperatures (usually 280, 300, 320 and 350°C). The catalyst is first heated in a helium flow until reaction temperature is reached. Then a relatively high

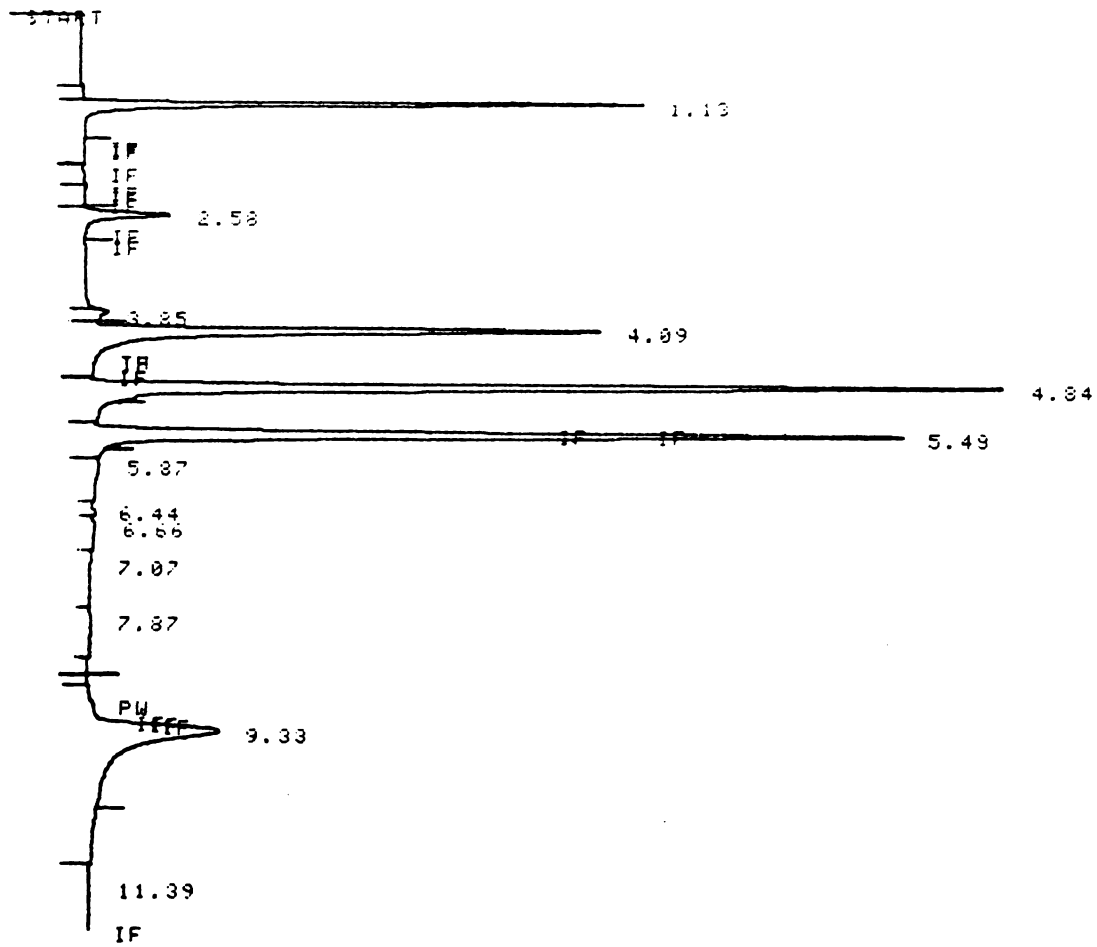

Figure 2.2 - Typical GC Chromatogram

lactic acid feed flow (0.5 ml/min) is started and run for approximately 15 minutes in order to coat the reactor walls and catalyst bed with lactic feed vapor. Next, helium and lactic feed flows are adjusted to desired setpoints and held there until steady state operation of the system is achieved. When this occurs, product collection is conducted by directing the reactor effluent to the product collection vessel and gas bag for a specified period of time. Usually, this time is dictated by the amount of material which has been fed to the reactor, and should be long enough to collect at least 2.0 ml of liquid product. When collection is complete, the reactor is operated with product flows again directed towards waste streams and the process is then repeated at each temperature to be tested. Most experiments were conducted at either "short" or "long" residence time; a compilation of the two sets of experimental conditions is given in Table 2.3.

Table 2.3 - Normal Operating Parameters

PARAMETER	SHORT RESIDENCE (2s)	LONG RESIDENCE (6-7s)
REACTOR PRESSURE	60 psig	60 psig
LIQUID FLOW RATE	0.20 ml/min	0.05 ml/min
HELIUM FLOW RATE	40 ml/min	10 ml/min
CATALYST BED LENGTH	2-3"	2-3"
CATALYST/SUPPORT	1-3 grams	1-3 grams
LIQUID COLLECTION	35 min.	40 min.
LIQUID PRODUCT VOLUME	7 ml	2 ml
GAS COLLECTION TIME	700 s	1300 s
GAS PRODUCT VOLUME	460 ml	220 ml

CHAPTER 3

BIOMINERAL-DERIVED CALCIUM HYDROXYAPATITE

3.1 INTRODUCTION

When 2,3-pentanedione was found to be a major lactic acid reaction product, an investigation was done to determine the demand for such a compound. We found that the diketone is an expensive specialty compound that is often used as a flavoring agent. A process which would produce the diketone "naturally" could increase its market value. In an attempt to produce the diketone in a natural process, we searched for a catalyst which would be considered "natural", and decided to try biomineral-derived calcium hydroxyapatite. Bovine teeth were selected as our source of calcium hydroxyapatite because they are readily available and are an inexpensive source of the hydroxyapatite.

The catalytic use of chemically synthesized calcium hydroxyapatite has been documented in the literature. Hydroxyapatite has been prepared by titration of concentrated H_3PO_4 into saturated $Ca(OH)_2$ by Bett, Christner and Hall (15). Misono and Hall (16) have shown that hydroxyapatites enhance hydrolysis, dehydration, dehydrogenation, and condensation reactions as well as many others.

3.2 CALCIUM HYDROXYAPATITE PROPERTIES

Biological systems such as teeth and bones are constructed of hydroxyapatite and as such bovine teeth were used in our studies as a source of the catalyst. The ideal unit cell of hydroxyapatite is of the form $Ca_{10}(PO_4)_6(OH)_2$ where the Ca:P ratio is 1.67. In biological systems the ratio is closer to 1.5 which results in the tricalcium phosphate compound (17). This low ratio is due to CO_3 substitution, for some hydroxyapatite phosphate groups, in various lattice positions. The lower ratio of calcium to phosphate results in high chemical reactivity. Also, the small crystal size of this hydroxyapatite (220 x 65Å) leads to high reactivity (18).

3.3 CATALYST PREPARATION

For our studies, cow's teeth were crushed and then calcined at various temperatures in order to burn off all organic matter; the calcined teeth constituted our catalyst supply. The calcination temperature study consisted of sample calcination at 300, 400, 500, 600, 700 and 800°C before reaction. Catalysts were calcined at 325°C for the particle size study. Calcination was done in a horizontal heated quartz cylinder under a steady air flow. An Omega Temperature Controller ramped the temperature up to calcination point and held it there for four hours before ramp down. The flow of air through the cylinder was maintained at approximately 1

Table 3.1 - Calcium Hydroxyapatite Properties

TEMPERATURE (°C)	SOAK TIME (h)	SIZE (mesh)	BET SURFACE AREA (m^2/g)	AVERAGE WEIGHT LOSS (%)
300	5	10X16	140.2	19.48
400	5	10X16	82.5	16.55
500	4	10X16	38.8	16.75
600	4	10X16	28.5	21.37
700	1	10X16	12.2	20.54
800	1	10X16	6.2	22.10
325	12	10X16	72.9	19.22
325	12	16X30	84.4	18.07
325	12	30X60	65.1	16.17
325	12	60X100	53.7	12.12

L/min in order to carry the organic matter to a collection vessel. Approximately 15 grams were calcined for each run; the catalyst was distributed equally in five ceramic boats which rested in the quartz chamber. Weight loss results during calcination are listed in Table 3.1.

3.4 CATALYST CHARACTERIZATION

Total surface area was measured for each catalyst sample by the nitrogen BET method. Surface area results are listed in Table 3.1. As can be seen, there is a twenty-fold difference in surface areas between the sample calcined at 300°C and the one calcined at 800°C. There does not seem to be a trend in surface area with particle size since the highest surface area is found with the intermediate particle size.

Mercury porosimetry was performed on each calcium hydroxyapatite sample in order to obtain a pore size distribution. Pore size results are found in Figure 3.1. Complete pore size distributions can be found in the Appendix. Each catalyst sample shows the same general behavior; there are three sizes ranges which contain the majority of pores. Calcination seems to have no affect on the largest two pore sizes. However, the smallest pore size seems to become larger as the calcination temperature is increased, thus explaining the reduction in surface area. An increase in small pores, which is the case at the lower calcination temperatures,

AVERAGE PORE SIZE - HYDROXYAPATITE

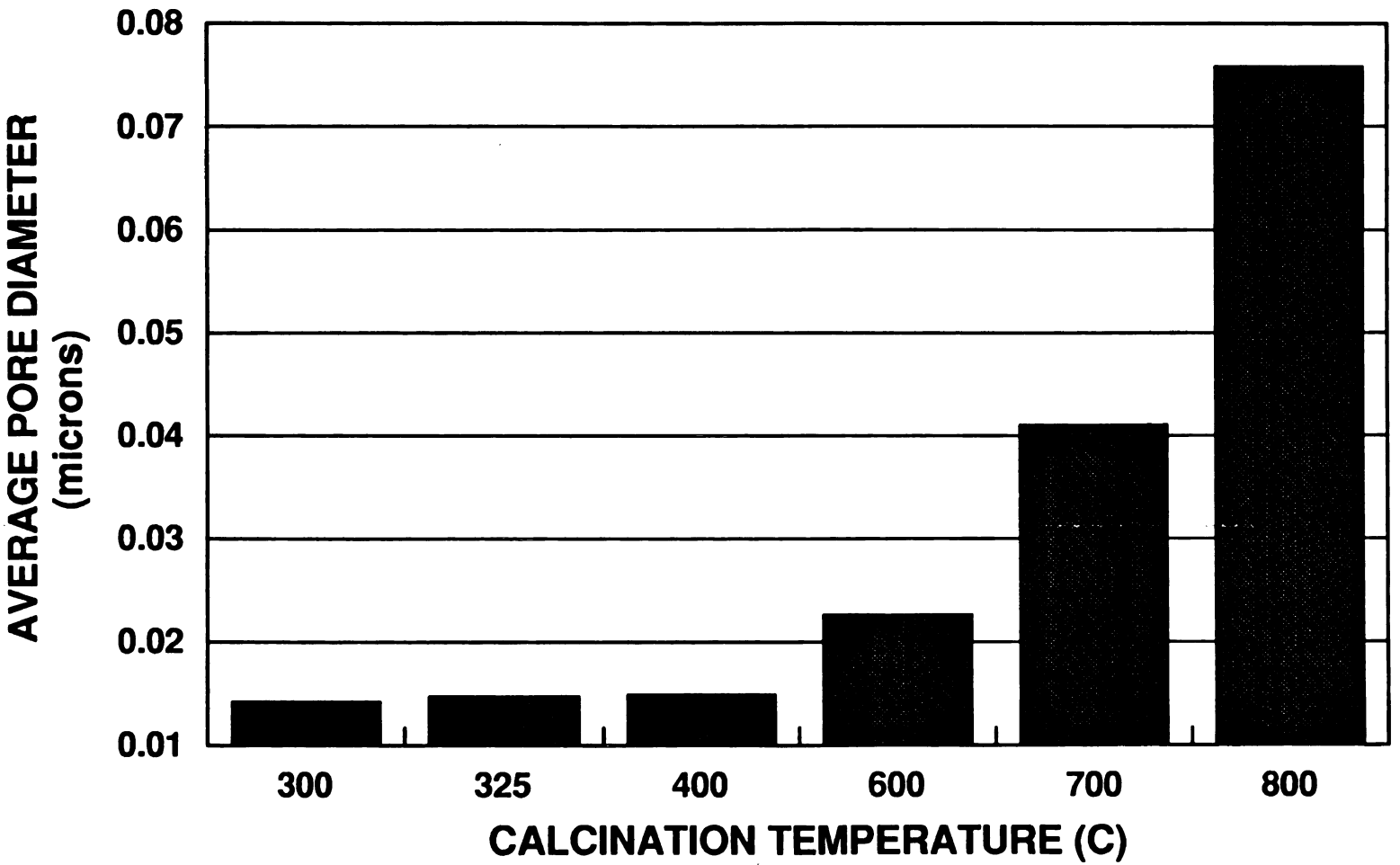

Figure 3.1 - Average Pore Size vs. Calcination Temperature for Calcium Hydroxyapatite

usually means more surface area.

Relative acidity of the various bovine samples was also studied in order to better understand how acidity affects catalyst performance. The following method was used to calculate the relative acidity of the samples. First, the sample was ground with a mortar and pestle into a powder. A solution containing the powder and KCl was then prepared along with a solution containing KCl only. Equal amounts of the two solutions were then boiled under reflux for two hours, cooled to room temperature, and the pH of each solution was measured. The delta pH, or the difference in pH between the blank solution and the solution containing the sample, was computed. When negative, this number signifies a solution more acidic than the blank, and when positive, less acidic than the blank. The delta pH's of the various samples are listed in figures 3.2 and 3.3. The noticeable trend shows that the samples calcined at the lower temperatures are more acidic than those calcined at the higher temperatures. There is no noticeable trend with particle size.

3.5 EFFECTS OF CALCINATION TEMPERATURE

Two separate reaction studies were conducted with biomineral-derived calcium hydroxyapatite. The first study was designed to determine how trends in product yields, selectivity, and activity are affected by calcination temperature. The second study examined various particle sizes

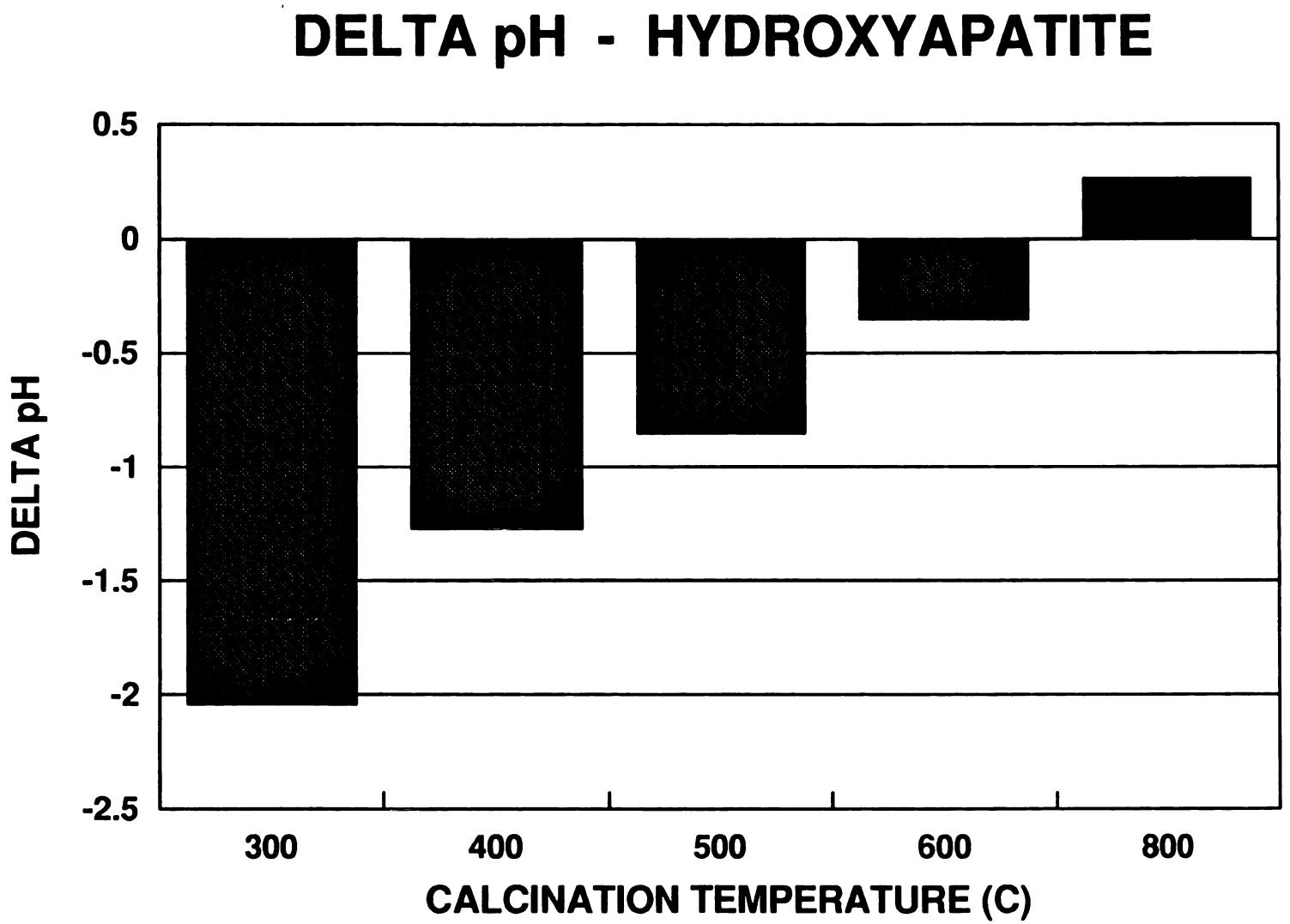

Figure 3.2 - Delta pH vs. Calcination Temperature for the Calcium Hydroxyapatite

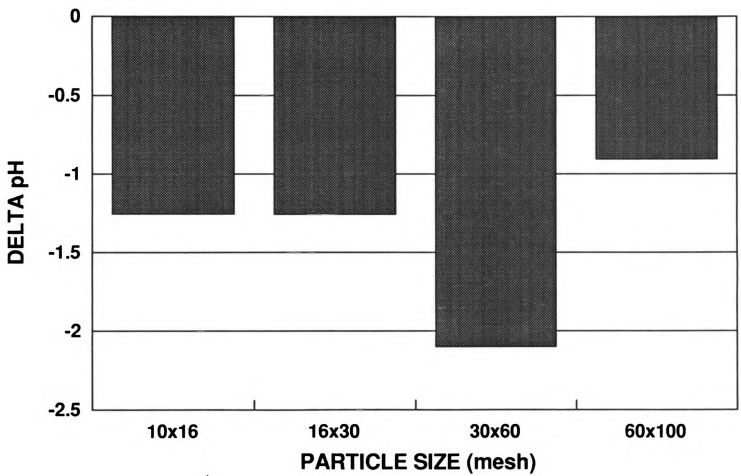

Figure 3.3 - Delta pH vs. Particle Size for the Calcium Hydroxyapatite

of the calcium hydroxyapatite and how they affect catalyst performance. The catalysts were tested in the reactor at usual operating conditions (see Table 2.3) with a liquid feed rate of approximately 0.05 ml/min and a He flow rate of approximately 10 ml/min. A 34 wt% lactic acid feed concentration was used in each run. Reaction temperatures were usually 280, 300 and 320°C. The results of the calcination temperature study at 300°C and 320°C are shown in Tables 3.2 and 3.3. The absolute product yields and product selectivities (parentheses) are shown for each liquid product. A more complete compilation of reaction results can be found in the Appendix.

The results show various trends in selectivities towards the lactic acid reaction pathways based on calcination temperature. For instance, 2,3-pentanedione selectivity increases with increasing calcination temperature. A reaction temperature of 300°C produces higher 2,3-pentanedione selectivities than 320°C. Yields of the diketone seem to go through a minimum at a calcination temperature of 500°C. These yields are relatively low (0.5% - 3.0%) when compared to some of the other reaction products. Reaction temperature (300°C or 320°C) for these samples does not seem to affect diketone yields. The highest 2,3-pentanedione selectivity for these runs was found to be 25.6% at 300°C from a sample calcined at 700°C. Figures 3.4 to 3.9 show the product yield distributions at each reaction temperature for the various calcination temperature reactions.

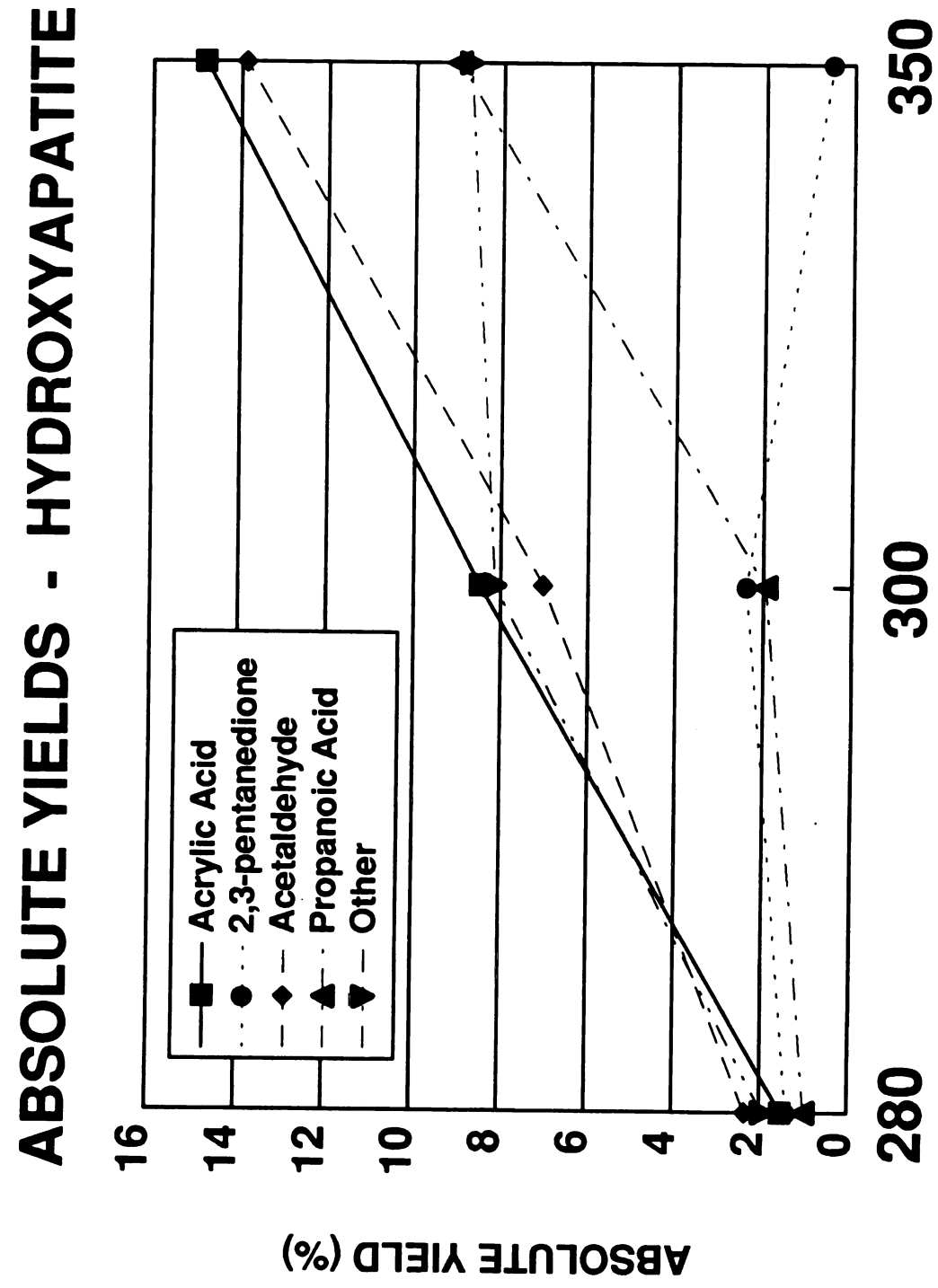

Figure 3.4 - Absolute Product Yields vs. Temperature for the Calcium Hydroxyapatite calcined at 300C

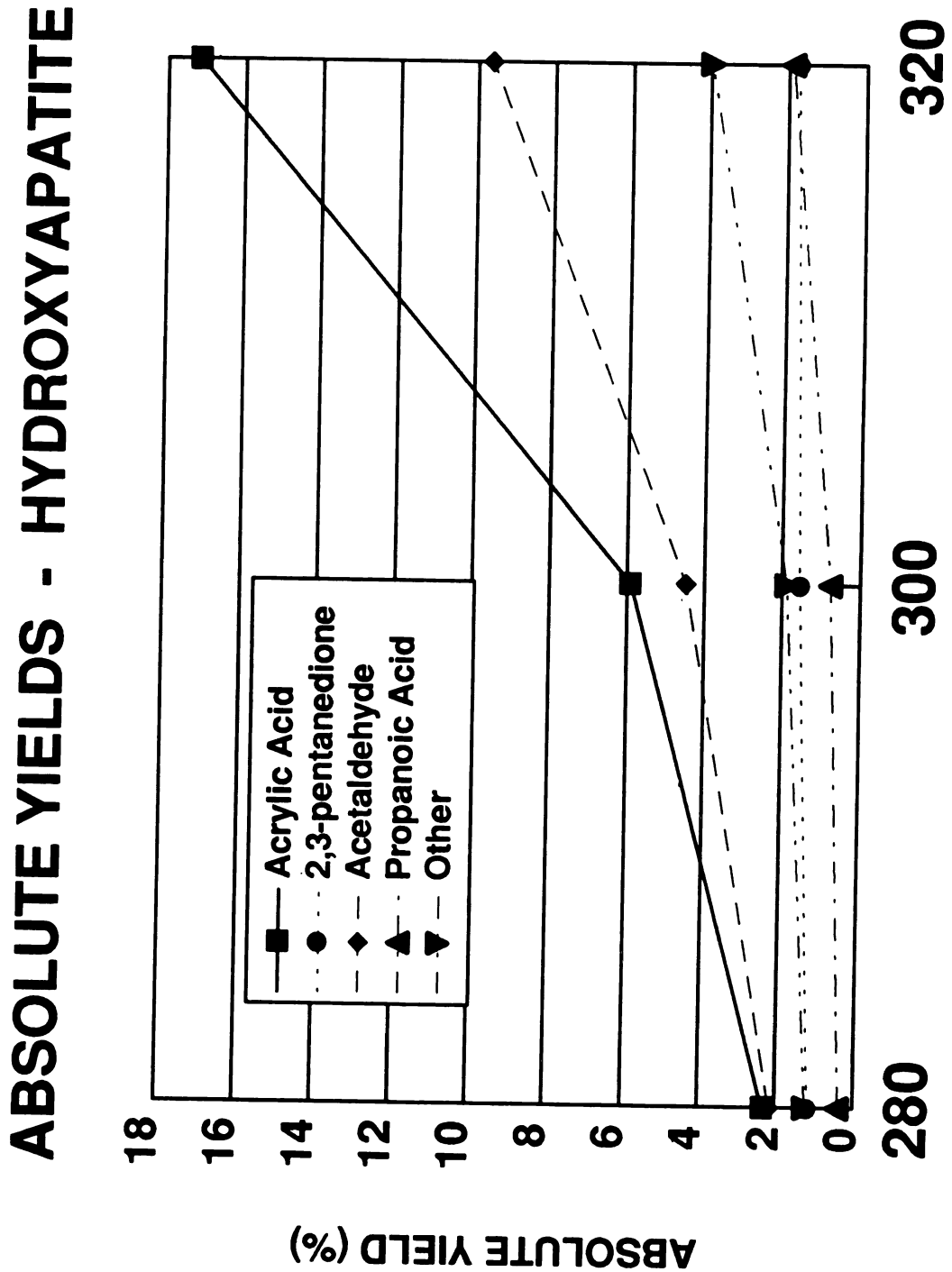

Figure 3.5 - Absolute Product Yields vs. Temperature for the Calcium Hydroxyapatite calcined at 400C

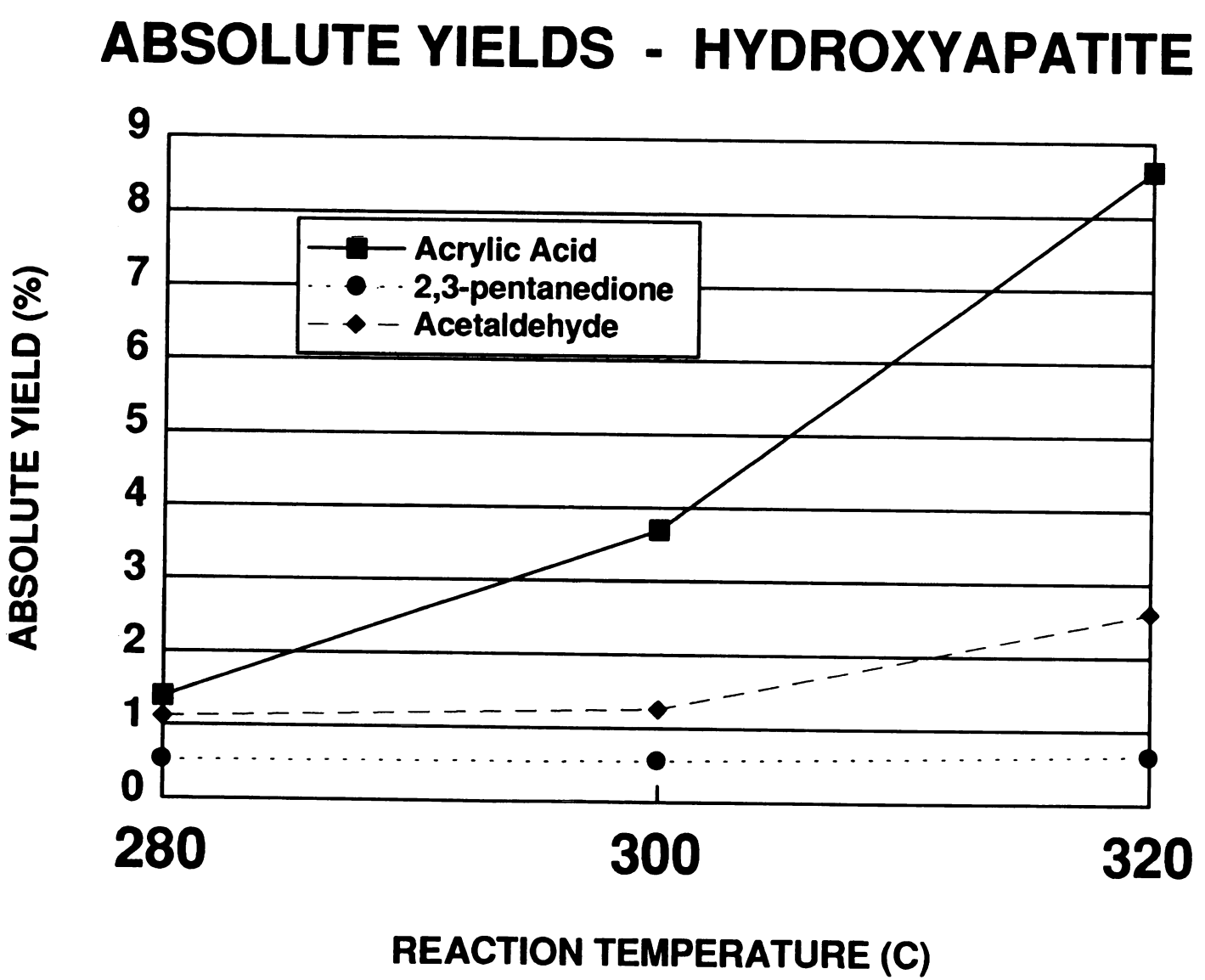

Figure 3.6 - Absolute Product Yields vs. Temperature for the Calcium Hydroxyapatite calcined at 500C

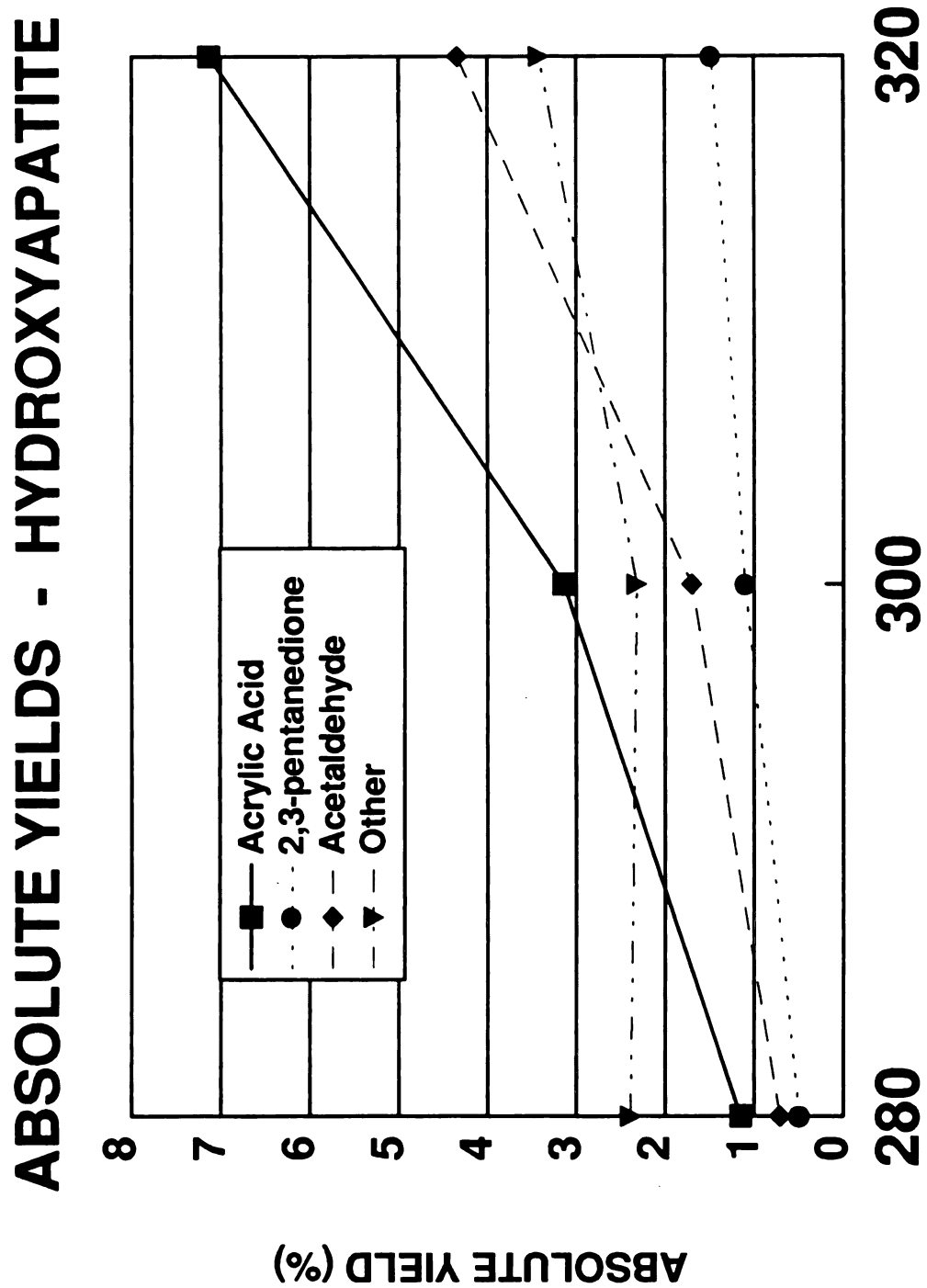

Figure 3.7 - Absolute Product Yields vs. Temperature for the Calcium Hydroxyapatite calcined at 600C

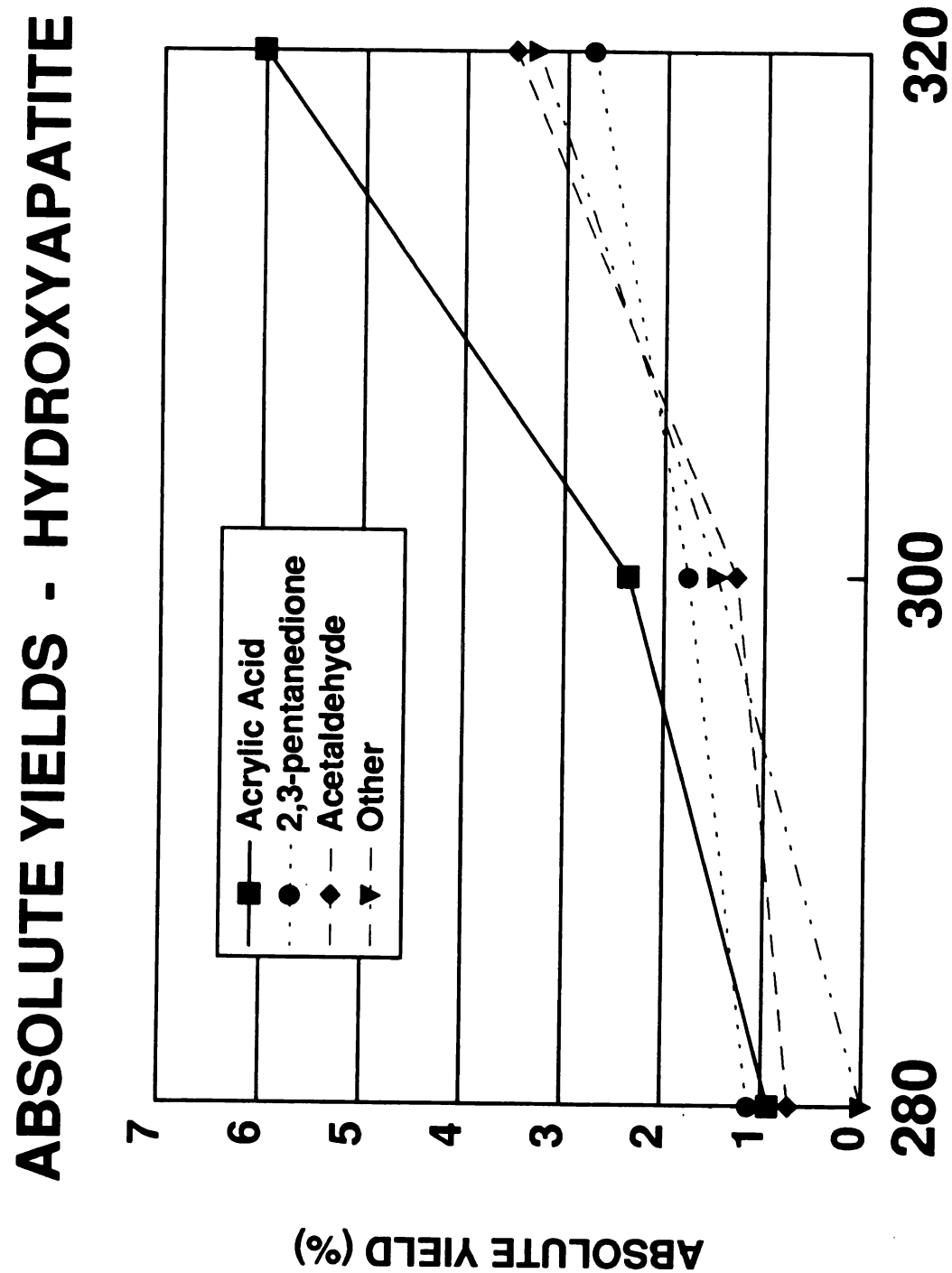

Figure 3.8 - Absolute Product Yields vs. Temperature for the Calcium Hydroxyapatite calcined at 700C

ABSOLUTE YIELDS - HYDROXYAPATITE

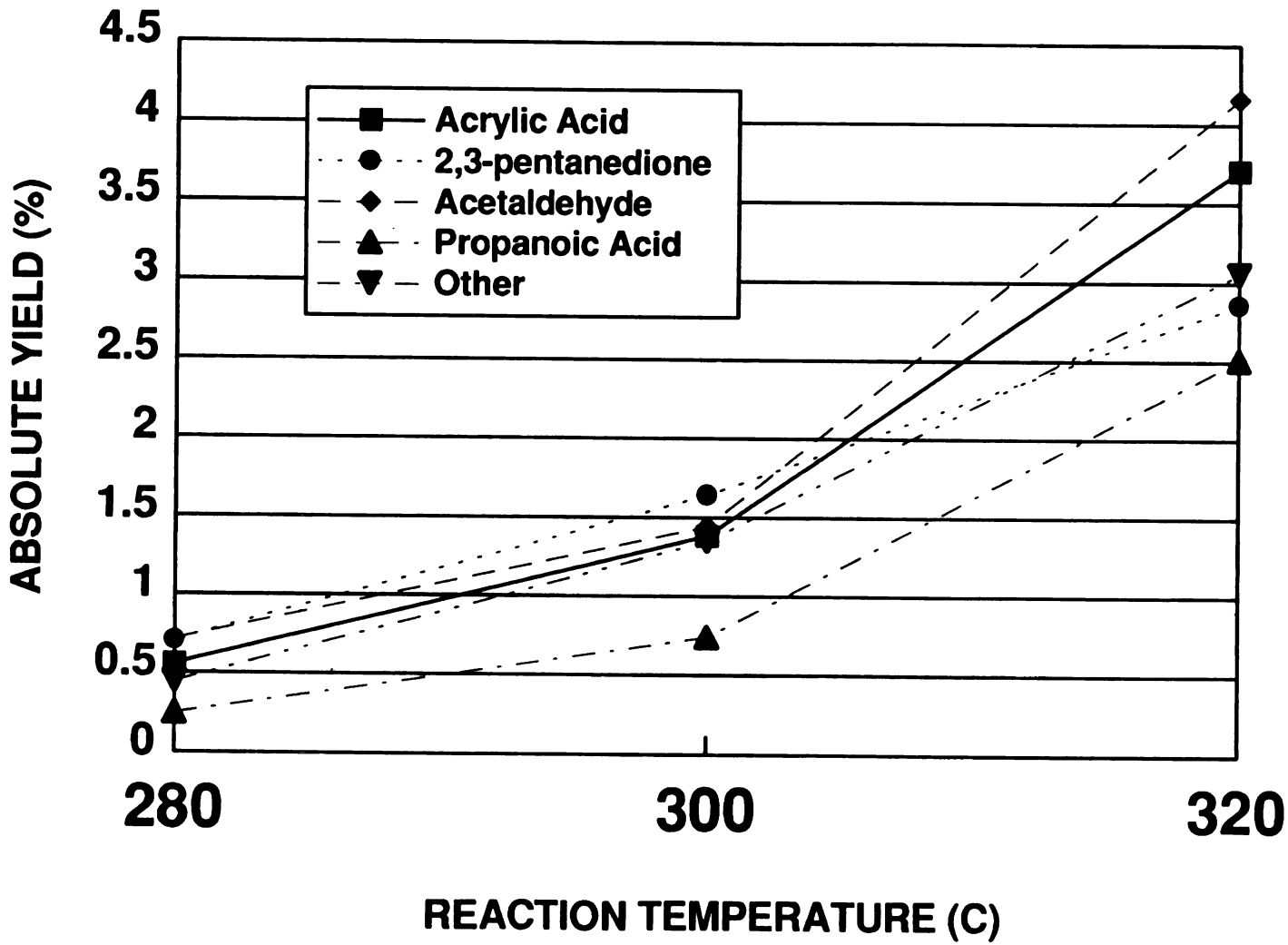

Figure 3.9 - Absolute Product Yields vs. Temperature for the Calcium Hydroxyapatite calcined at 800C

Table 3.2 - Calcium Hydroxyapatite Results at 300°C

CALCINATION TEMP(°C)	300	400	500	600	700	800
ACRYLIC ACID	8.47 (30.3)	5.91 (40.5)	3.70 (54.6)	3.14 (38.1)	2.36 (34.4)	1.38 (21.1)
2,3-PENTANEDIONE	2.38 (8.5)	1.55 (10.6)	0.56 (8.3)	1.10 (13.3)	1.76 (25.6)	1.64 (25)
ACETALDEHYDE	7.03 (25.2)	4.48 (30.7)	1.26 (18.6)	1.70 (20.6)	1.28 (18.6)	1.44 (22)
PROPANOIC ACID	1.94 (6.9)	0.76 (5.2)	0.19 (2.8)	0.18 (2.2)	0.25 (3.6)	0.74 (11.3)
OTHER	8.13 (29.1)	1.89 (13)	1.07 (15.8)	2.13 (25.8)	1.22 (17.8)	1.35 (20.6)
CARBON MONOXIDE	0.87	2.20	1.02	1.84	1.16	0.73
CARBON DIOXIDE	2.81	2.18	0.71	2.38	3.27	0.81
CONVERSION	35.81	19.32	19.82	11.33	10.93	9.68
CARBON RECOVERY (%)	98.69	94.85	86.93	97.21	96.70	96.52
SURFACE AREA (m^2/g)	140.2	82.5	38.8	28.5	12.2	6.2
DELTA pH	-2.042	-1.273	-0.854	-0.352	-	0.263

Table 3.3 - Calcium Hydroxyapatite Results at 320°C

CALCINATION TEMPERATURE (°C)	300*	400	500	600	700	800
ACRYLIC ACID	14.80 (31.5)	17.15 (49.9)	8.62 (63.3)	7.13 (43.5)	6.01 (38.7)	3.71 (22.8)
2,3-PENTANEDIONE	0.47(1)	1.73 (5)	0.66 (4.8)	1.48 (9)	2.73 (17.6)	2.86 (17.5)
ACETALDEHYDE	13.88 (29.6)	9.63 (28)	2.60 (19.1)	4.34 (26.4)	3.51 (22.6)	4.16 (25.5)
PROPANOIC ACID	9.01 (19.2)	1.88 (5.5)	0.30 (2.2)	0.40 (2.4)	0.57 (3.7)	2.51 (15.4)
OTHER	8.76 (18.7)	3.97 (11.6)	1.43 (10.5)	3.03 (18.5)	2.72 (17.5)	3.06 (18.8)
CARBON MONOXIDE	4.31	4.69	1.89	4.45	2.10	2.14
CARBON DIOXIDE	5.95	4.15	3.46	3.87	4.41	4.31
CONVERSION	77.60	43.07	43.52	37.95	35.18	31.98
CARBON RECOVERY (%)	69.75	91.42	70.81	79.04	80.78	84.44
SURFACE AREA (m^2/g)	140.2	82.5	38.8	28.5	12.2	6.2
DELTA pH	-2.042	-1.273	-0.854	-0.352	-	0.263

* Reaction Temperature 350°C

Acrylic acid yields and selectivities are higher than those of 2,3-pentanedione for this set of runs. The yields of acrylic acid decrease as calcination temperature increases, while the selectivities go through a maximum at a calcination temperature of 500°C. A reaction temperature of 320°C produces higher yields and selectivities than 300°C. The best yield of acrylic acid was 17.15% at a reaction temperature of 320°C and a calcination temperature of 400°C. The best selectivity towards acrylic acid of 63.3% occurred at 320°C and a calcination temperature of 500°C.

Acetaldehyde production is unwanted and therefore low yields and selectivities are desirable. However, in this set of runs acetaldehyde was produced in considerable amounts. Although yields of acetaldehyde were only 1-14%, the selectivities were 18-35% at all reaction and calcination temperatures. Acetaldehyde yields decrease as calcination temperature increases but the reaction conversion also decreases thereby stabilizing the selectivity towards this product.

Propanoic acid is produced only in minor quantities. Yields are low, except at high reaction temperatures (350°C), ranging from 0.15% to 1.95% at reaction temperatures of 300°C and 320°C. Selectivities at 300 and 320°C range from 2-15% but most are under 6%. The 800°C calcination temperature gives selectivities of 11.3% and 15.4% at 300°C and 320°C, respectively. The catalyst calcined at 300°C and tested at

350°C gave a yield of propanoic acid of 9% and a selectivity of 19%.

Other known products found in these reactions are acetic acid and hydroxyacetone. The yields of these products decreases as calcination temperature increases while the selectivities seem to increase somewhat. Yields at 300 and 320°C range from 1-8% and selectivities from 10-26%.

Gas product analysis found carbon monoxide and carbon dioxide in varying amounts. No strong trends were found for CO and CO_2 yields; yields of both gases increase with increasing reaction temperature and range from 0.7-6.0%.

The surface areas of these catalysts range from 140.2 m^2/g at a calcination temperature of 300°C to 6.2 m^2/g at a calcination temperature of 800°C. The lower surface area materials have fewer reaction sites, therefore, one would expect the reaction conversions to be lower for the lower surface area materials. This happens to be the case as conversions do decrease as calcination temperature increases. At the reaction temperature of 300°C, conversions descend from 35.8% to 9.7% as calcination temperature increases to 800°C. At 320°C, conversions decrease from 43.1% to 32.0%.

An interesting feature of these samples is the fact that delta pH values increase with reaction temperature. This means that material calcined at the higher temperatures are less acidic than those which were calcined at lower temperatures. Lower acidity of samples calcined at the higher temperatures could help explain the increasing selectivity of

the 2,3-pentanedione pathway, which apparently is favored at more basic catalyst conditions.

3.6 PARTICLE SIZE STUDY

The second catalytic study conducted with the biomineral hydroxyapatite was a particle size study. The effect of particle size on catalyst performance was examined in the study, with the goal of finding an optimum particle size. Different particle sizes of a catalyst often can have different physical characteristics, such as pore structure, packing ability, etc., which may affect performance.

Three different catalyst mesh sizes were selected for testing: 10 x 16, 16 x 30, and 30 x 60 mesh sizes. The bovine teeth were calcined at 325°C following the procedure given previously. Calcination weight loss data is in Table 3.1. The calcined teeth were then crushed and sized with sieves. The experimental runs were performed at normal reaction conditions with a 34 wt% lactic acid feed and liquid and helium flowrates of 0.05 ml/min and 10 ml/min, respectively. The reaction temperatures studied were 280, 300 and 320°C. Key results of the particle size study at 300 and 320°C are found in Table 3.4; a complete compilation of results can be found in the Appendix.

Yield and selectivities of 2,3-pentanedione increase as the particle size decreases. This suggests that the smaller particle size favors the diketone production. Figures 3.10,

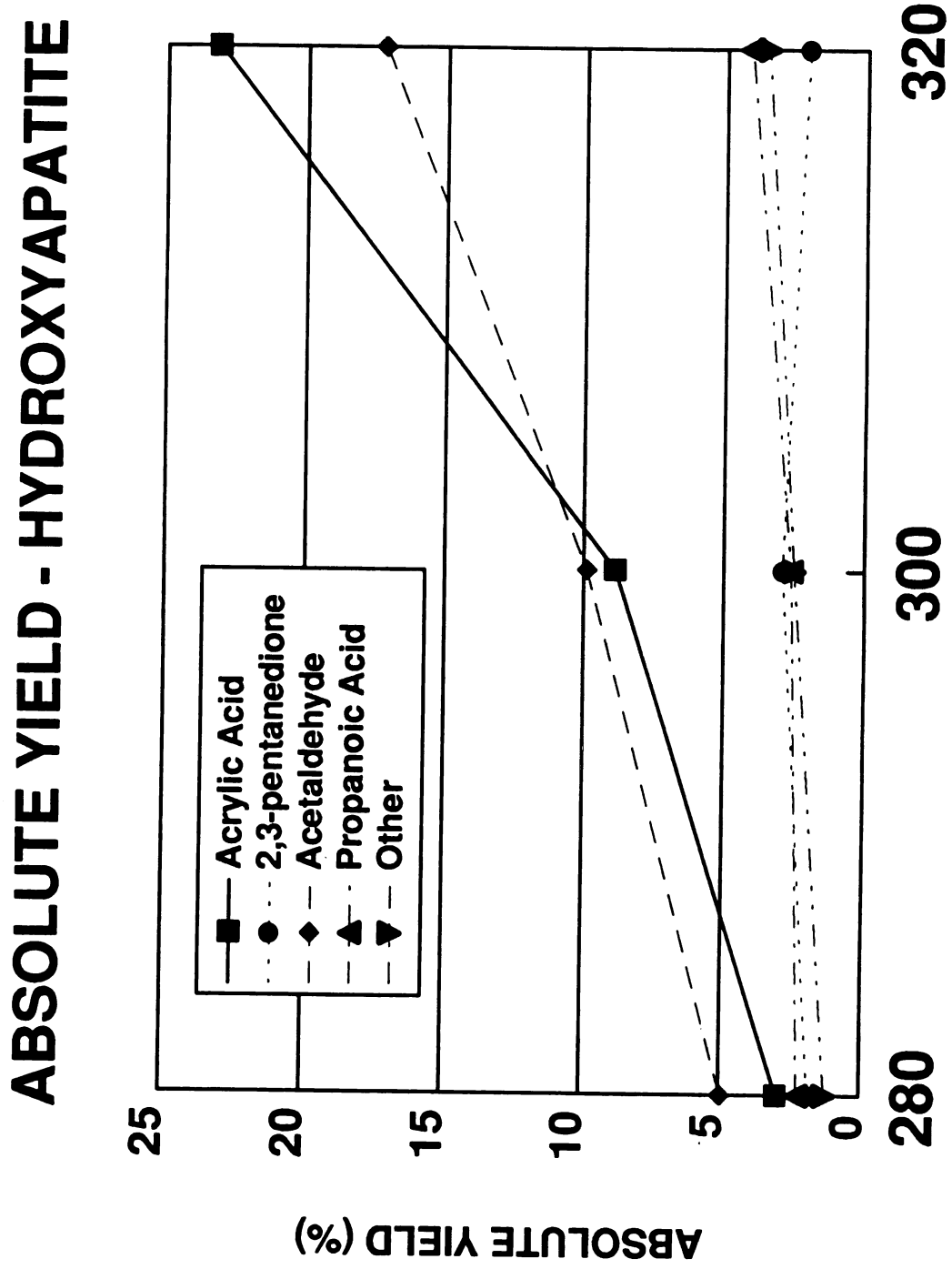

Figure 3.10 - Absolute Product Yields vs. Temperature for the 10 x 16 mesh Hydroxyapatite

ABSOLUTE YIELDS - HYDROXYAPATITE

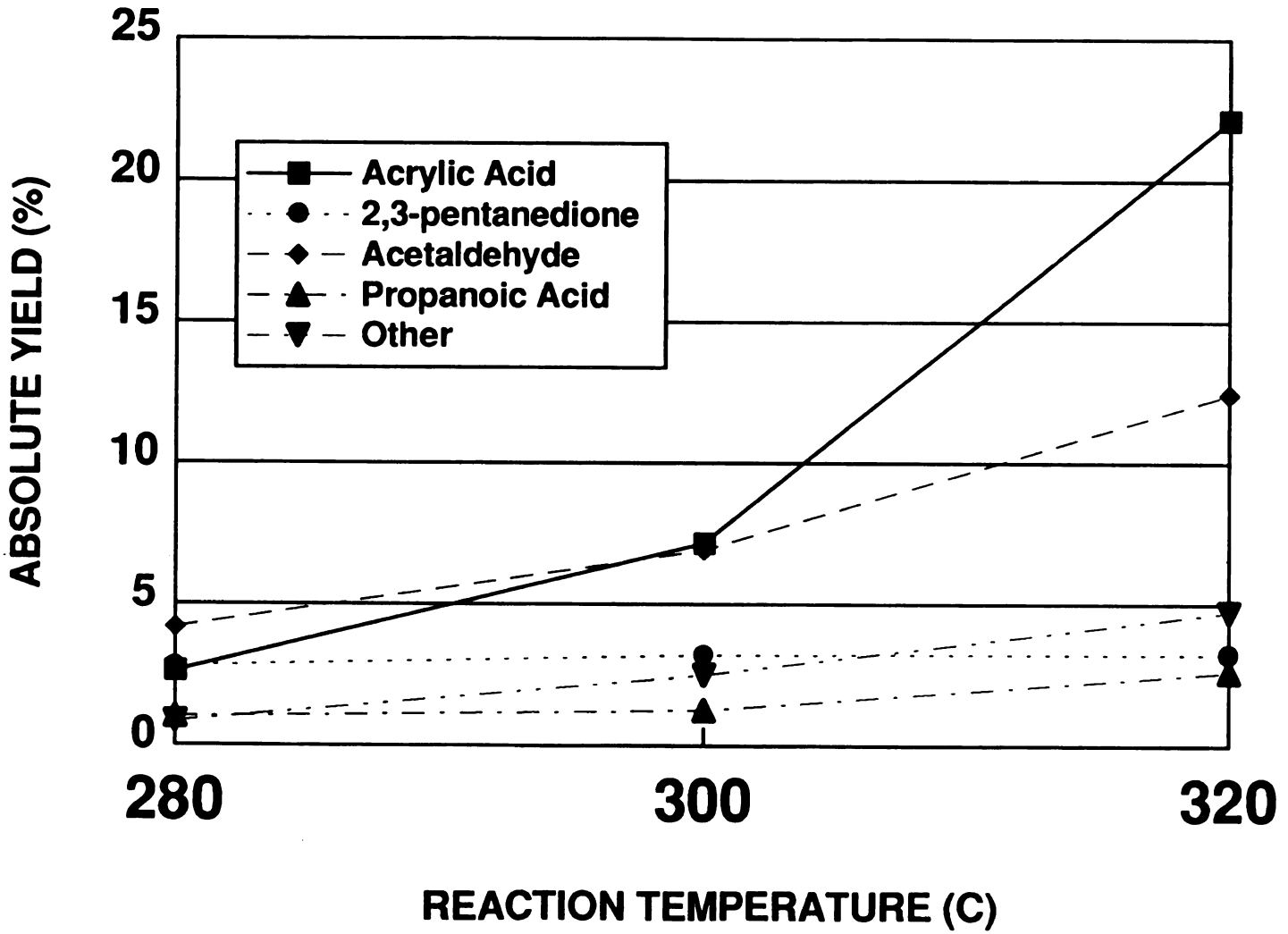

Figure 3.11 - Absolute Product Yields vs. Temperature for the 16 x 30 mesh Calcium Hydroxyapatite

ABSOLUTE YIELDS - HYDROXYAPATITE

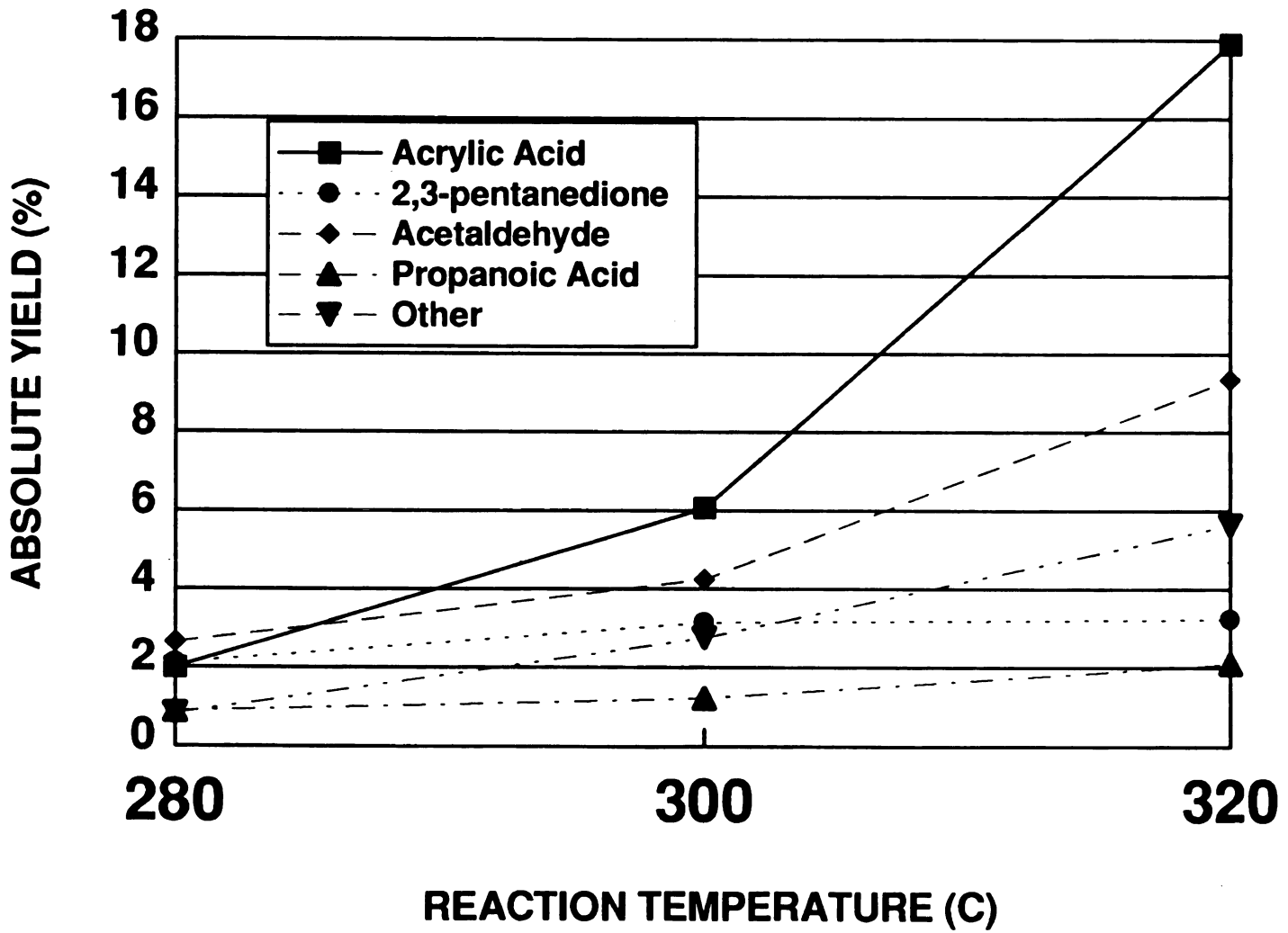

Figure 3.12 - Absolute Product Yields vs. Temperature for the 30 x 60 mesh Calcium Hydroxyapatite

3.11 and 3.12 show the product yield distributions for the 10 x 16, 16 x 30 and 30 x 60 mesh size reaction studies. At a reaction temperature of 300°C and a particle size of 30 x 60 mesh, a 3.15% yield of the diketone is achieved at a selectivity of 18.1%. Although the yield of 2,3-pentanedione is slightly higher at a reaction temperature of 320°C, selectivity falls off to 8.5% at the 30 x 60 mesh size.

Acrylic acid production at all particle sizes is significant in that it is the product found in the greatest abundance in practically every test. As particle size decreases, acrylic yield decreases slightly although selectivity towards this product remains constant. A reaction temperature of 320°C gives the greatest yields of acrylic acid (18-23%). The selectivity towards acrylic is quite high (46-49%) at a reaction temperature of 320°C. Particle size does not seem to have a significant affect on acrylic acid production.

Acetaldehyde production (yield and selectivity) decreases as the catalyst particle size decreases. This trend coincides with the aformentioned opposite trend of 2,3-pentanedione. These results, coupled with the stability of acrylic acid production, suggest that small catalyst particle sizes give more favorable results. However, even at the smallest particle size (30 x 60 mesh), acetaldehyde formation is appreciable. At a reaction temperature of 300°C, the yield of acetaldehyde is 4.24% which corresponds to a selectivity of 24.3%. At 320°C, acetaldehyde yields are higher but the

Table 3.4 - Calcium Hydroxyapatite Particle Size Results

REACTION TEMP (°C)	300			320		
PARTICLE SIZE	10 X 16	16 X 30	30 X 60	10 X 16	16 X 30	30 X 60
ACRYLIC ACID	8.87 (33.2)	7.16 (34)	6.06 (34.8)	23.14 (46.2)	22.15 (49.1)	17.9 (46.8)
2,3-PENTANEDIONE	2.90 (10.8)	3.20 (15.2)	3.15 (18.1)	2.05 (4.1)	3.23 (7.2)	3.23 (8.5)
ACETALDEHYDE	9.88 (37)	6.92 (32.9)	4.24 (24.3)	17.22 (34.4)	12.44 (27.6)	9.35 (24.5)
PROPANOIC ACID	2.59 (9.7)	1.25 (5.9)	1.22 (7)	4.11 (8.2)	2.60 (5.8)	2.10 (5.5)
OTHER	2.49 (9.3)	2.50 (11.9)	2.76 (15.8)	3.52 (7)	4.73 (10.5)	5.64 (14.8)
CARBON MONOXIDE	2.72	10.11	2.67	8.73	7.75	3.39
CARBON DIOXIDE	4.40	9.46	4.81	8.42	8.33	4.67
CONVERSION	34.83	23.59	29.77	74.32	51.22	48.95
CARBON RECOVERY (%)	105.56	106.86	99.62	86.34	103.40	97.68
SURFACE AREA (m^2/g)	72.90	84.40	65.06	72.90	84.40	65.06
DELTA pH	-1.26	-1.26	-2.10	-1.26	-1.26	-2.10

selectivity towards this product is relatively constant.

Yield of propanoic acid at each reaction temperature decreases as the catalyst size decreases, which also supports the conclusion that the smaller mesh size is most desirable. Selectivities of propanoic acid vary from 5 to 10% based on reaction conditions but they do not seem to follow a trend with catalyst size. The 320°C reaction temperature gives yields which are approximately twice those of the 300°C reaction temperature while selectivities at each reaction temperature are relatively constant.

Yields of the other reaction products do not follow any strong trends with particle size, but selectivities of the other products seem to increase as the catalyst particle size decreases. These minor products consist primarily of ethanol, acetic acid, and hydroxyacetone. Reaction temperature has little affect, if any, on the selectivity of these products. The greatest combined yields and selectivities are found with the smallest particle size and are approximately 6% and 15%, respectively.

Gas product analysis shows formation of only carbon monoxide and carbon dioxide from reaction. The ratio, CO:CO2, in most cases is close to unity and there seems to be no particle size based trend in the ratio. Gas yields range from 2-10%.

Lactic acid conversion decreases with particle size with one exception at a reaction temperature of 300°C and a particle size of 16 x 30 mesh. Conversion, in each test,

increases with reaction temperature which is a very normal result. The highest conversion of 74.3% is found at a reaction temperature of 320°C and a particle size of 10 x 16 mesh. Reaction temperatures higher than 320°C were not tested in this study. The lowest conversion of 17.65% was found at a reaction temperature of 280°C and a 30 x 60 mesh particle size.

The mass balances for the particle size study were excellent in relative terms. Carbon recoveries ranged from 86 to 106% with only one figure greater than 10% loss.

CHAPTER 4

CARBON SUPPORTS

An attempt was made to identify a carbon support which would produce very little acetaldehyde and propanoic acid when lactic acid was passed over it. If such a carbon was found, we planned to impregnate it with catalyst and react lactic over the supported catalyst. Five carbon supports were chosen for study; they are shown in Table 4.1. The Table also shows the total surface areas of the carbons as well as other physical properties. As can be seen, a huge contrast in surface area exists between the carbons, from 1600 m^2/g to 5 m^2/g.

Aside from sizing the carbon particles there was little support preparation. The Strem activated carbon was ground to 10 x 16 mesh for reaction and calcined at 800°C for one hour. The particle sizes for the other carbons are given in Table 4.1. All reactions were completed following the long residence time reaction parameters given in Table 2.3. Complete carbon support results can be found in the Appendix.

4.1 STREM ACTIVATED CARBON

The first carbon support studied was Strem activated carbon. Figure 4.1 shows the product yields versus reaction temperature for Strem activated carbon. The product

ABSOLUTE YIELD - STREM ACTIVATED CARBON

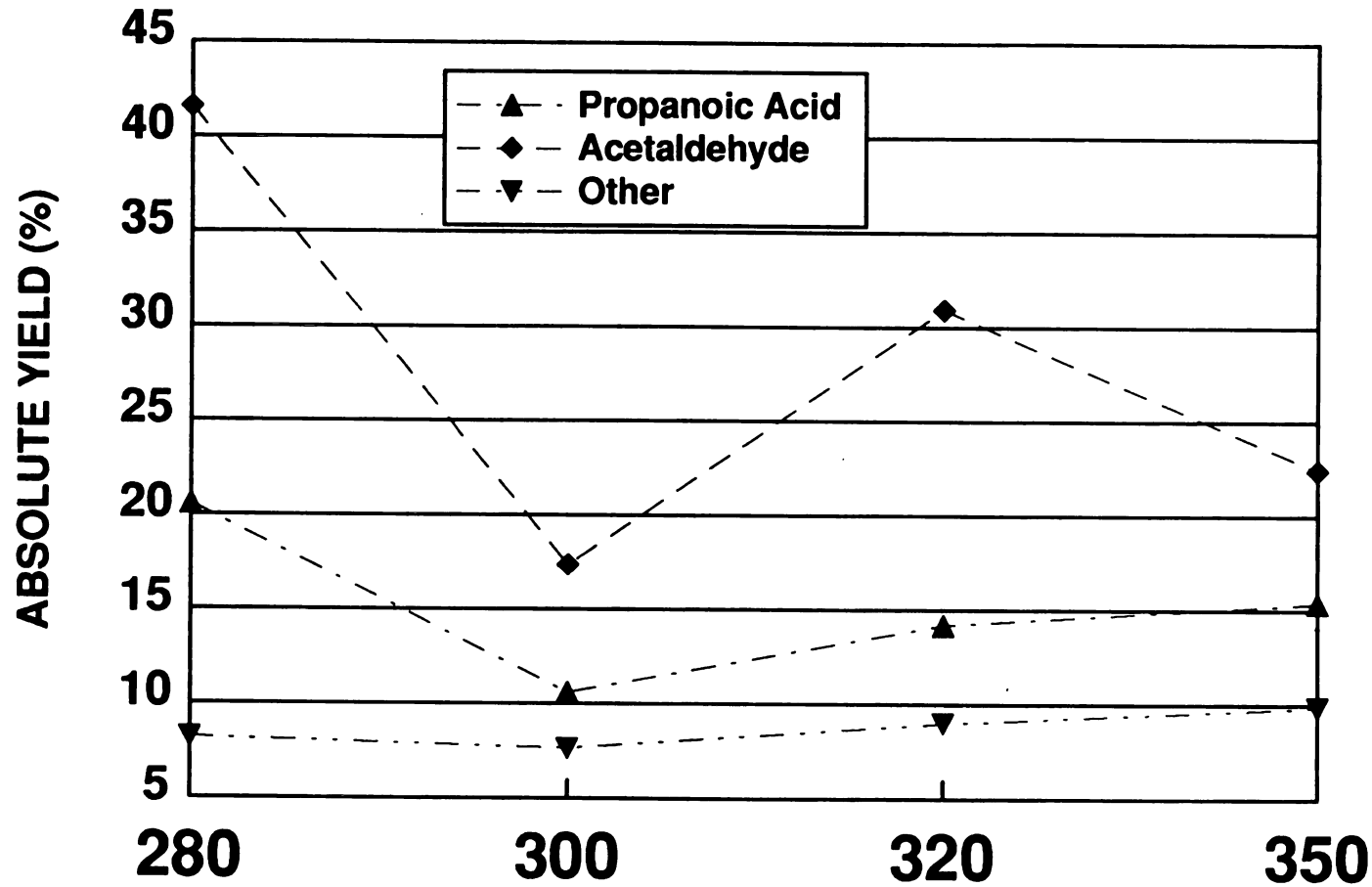

Figure 4.1 - Absolute Product Yields vs. Temperature for the Strem Activated Carbon

distribution is dominated by acetaldehyde and propanoic acid. Yields of 2,3-pentanedione and acrylic acid were found to be less than 1% at all temperatures tested. The other liquid reaction products, ethanol, acetic acid and hydroxyacetone, were also minor, and combined, accounted for combined yields of only 5-10%. Gas product analysis showed that production of CO and CO_2 was prominent, with a CO:CO_2 yield ratio near unity or slightly greater than unity in all cases.

The activity of the Strem carbon was high at all temperatures. At 280°C, the conversion was 82.4%; it increased to 99.9% at 375°C. The large surface area of this carbon may have contributed to its high activity. High surface area materials usually have more reaction sites than lower surface area materials. Even more important in this case, however, the microporosity of the carbon may cause the condensation and cracking of lactic acid to acetaldehyde.

The carbon error at 280°C was only 2.3% for the Strem carbon, which means that 97.7% of the original carbon in the lactic acid feed was recovered. The error became much larger at higher temperatures. At 300, 320 and 350°C the carbon recoveries were 63.2, 69.9 and 67.8%, respectively. The low recoveries indicate that less carbon was recovered than that which was fed through the reactor, suggesting that cracking is important. The most favorable results are found at 300°C but this is also where the largest mass balance error (63.2% carbon recovery) occurs. Here only 64% of the carbon fed during reaction is recovered. The result of this large error

Table 4.1 - Carbon Reaction Parameters

SUBSTRATE	PARTICLE SIZE (mesh)	SURFACE AREA (m^2/g)	REACTION TEMPS. (°C)	SAMPLE SIZE (g)
STREM ACTIVATED CARBON	10 x 16	1600#	280, 300, 320, 350, 375	2.1
STREM w/NA_3PO_4	10 x 16	1600#	230, 250, 280, 300, 320, 350	1.8
ACTIVATED CHERRY CARBON	10 x 30	1000#	280, 300, 320	2.1
CHARRED CHERRY CARBON	10 x 16	40*	280, 300, 320, 350	2.3
CHARRED CHERRY w/NA_3PO_4	10 x 16	40*	280, 300, 320, 350	1.9
CARBOGRAPH 1	60 x 100	80*	280, 300, 320, 350	2.0
CARBOGRAPH 2	60 x 100	10	280, 300, 320, 350	3.1

- Measured by CO_2 adsorption at 298K, 26.2 A/molecule CO_2

* - N_2 BET area

is the appearance of lower yields. Even at this temperature, however, product selectivity greatly favors acetaldehyde and propanoic acid (see Figure 4.2).

Overall, the Strem carbon did not show much promise as a support. It was very active, but the high activity was directed to the wrong reaction products. Acetaldehyde and propanoic acid yields were too high and selectivity towards the desired products was practically non-existant.

The Strem carbon was impregnated with Na_3PO_4 in order to determine if the salt could affect the poor support performance in a positive manner. Impregnation with the trisodium phosphate consisted of placing 0.0025 gmol of $Na_3PO_4 \cdot 12H_2O$ per gram of support on the support.

The long residence time reaction parameters were utilized for the experimental run. Figure 4.3 shows the yield distribution for the Na_3PO_4/Strem carbon catalyst. Again, acetaldehyde and propanoic acid yields were very high and desired product yields were low. Gas analysis showed that the $CO:CO_2$ yield ratio was approximately 0.5 throughout the experimental run. This is different from the ratio of about 1.0 found with the support alone. As this was one of the few differences in the Strem carbon versus Na_3PO_4/Strem carbon results, we concluded that Na_3PO_4 did not seem to affect the reaction performance of the Strem carbon in a positive manner.

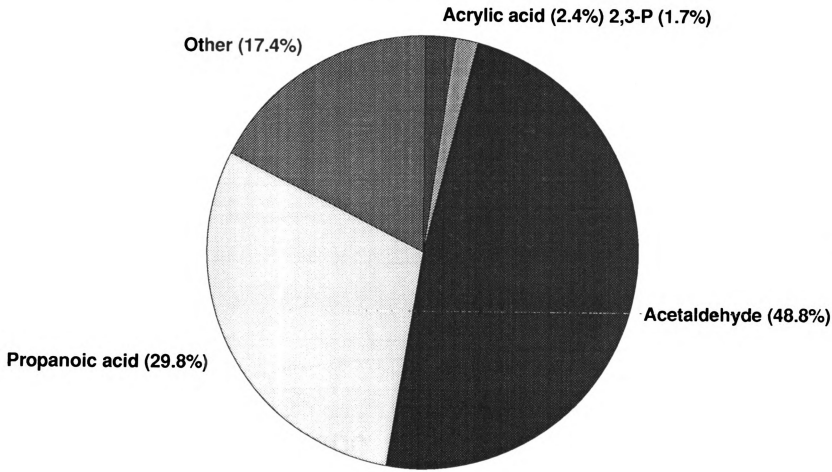

Figure 4.2 - Product Selectivities for the Strem Activated Carbon - REACTION TEMPERATURE 300C

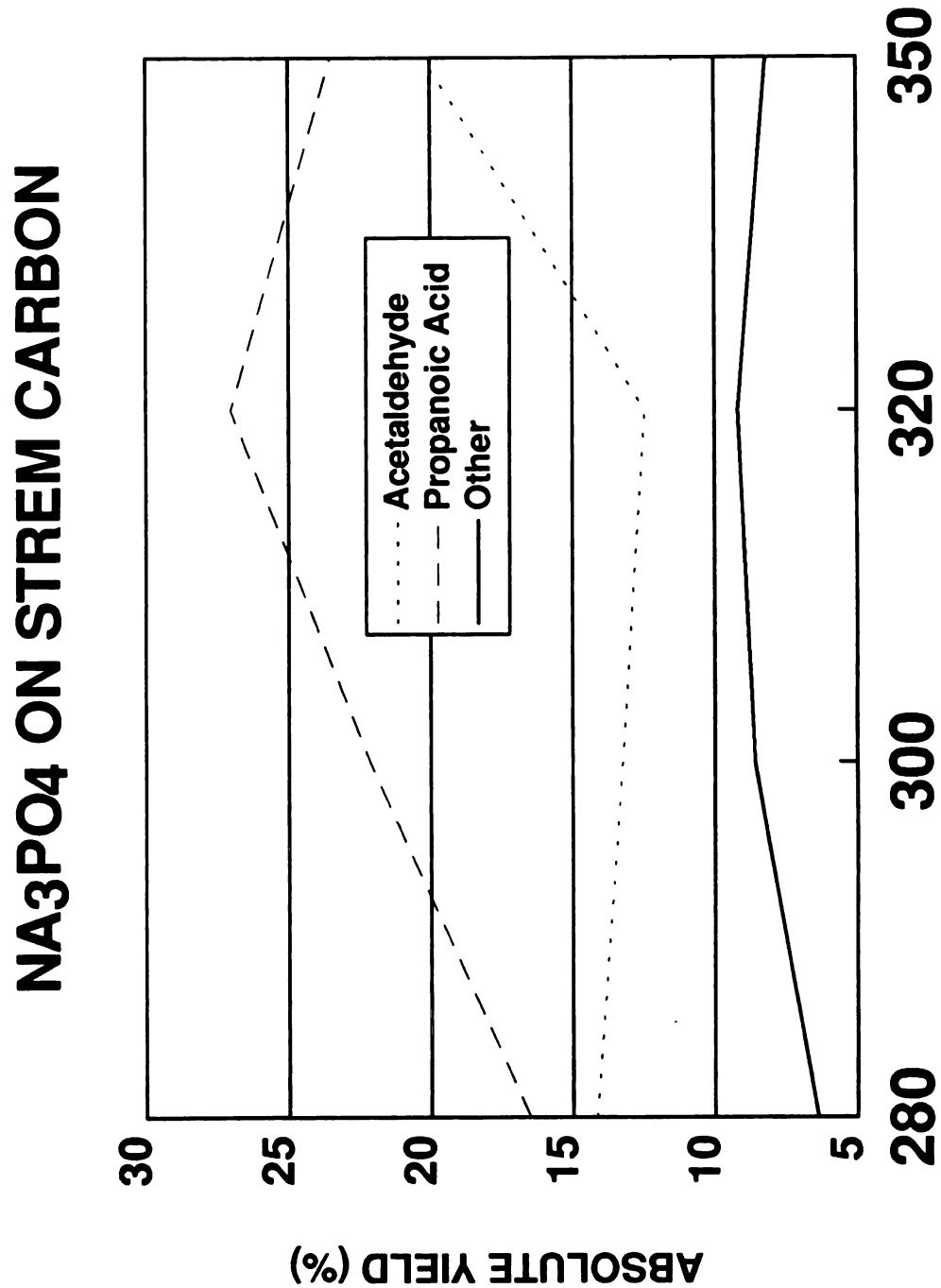

Figure 4.3 - Absolute Product Yields vs. Temperature for Na_3PO_4 on the Strem Carbon

4.2 CHERRY-DERIVED CARBON

The next carbon studied was an activated cherry pit carbon with a surface area of approximately 1000 m^2/g. The activated carbon was prepared by steam activation of charred cherry pits at 800°C for two hours as part of another ongoing research project. We expected high conversions as seen in the high surface area Strem carbon, and observed conversions averaging 85% over all temperatures.

Figure 4.4 shows the product yields at the temperatures of reaction. Acetaldehyde dominates the product mixture, (23-35% yield), with propanoic acid yield ranging from 6-8%. Acrylic acid and 2,3-pentanedione yields were less than 1% at all temperatures. Acetic acid constituted the largest portion of the minor product yields (1.6-2.3%). Selectivity to acetaldehyde was even greater than that found in the Strem carbon. The gas analysis showed a $CO:CO_2$ yield ratio which decreased from 2.5 at 280°C to 1.5 at 320°C. Carbon monoxide yields were large in comparison to previous values (see Tables 4.2 and 4.3).

Cherry carbon mass balances were not very good. At 280°C, 82.7% of the carbon was recovered and at 300 and 320°C this figure was approximately 70%.

ABSOLUTE YIELD - ACTIVATED CHERRY CARBON

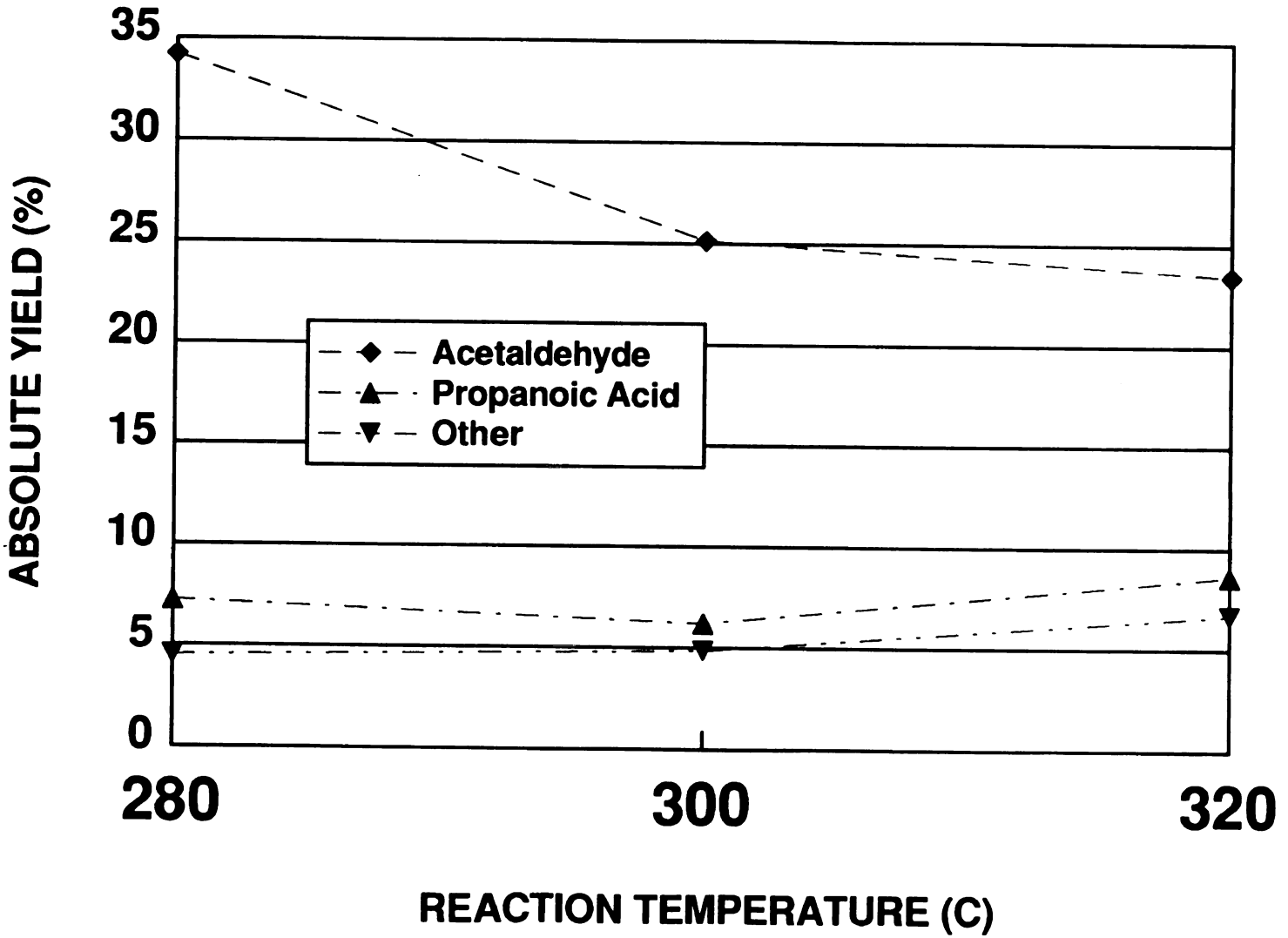

Figure 4.4 - Absolute Product Yields vs. Temperature for the Activated Cherry Carbon

4.3 CHARRED CHERRY PITS

To avoid the possible deleterious effects of microporosity in activated carbons, low surface area (40 m^2/g) charred cherry pits were studied. These were expected to show less activity than the higher surface area materials. Reaction conditions are shown in Table 4.1.

Figure 4.5 shows the liquid product yields from lactic acid reaction over the charred cherry pits. Acetaldehyde production is suppressed when compared with previous carbons; yields are consistently under 10% at all reaction temperatures. At 320°C the acetaldehyde yield is only 5%; this yield increases to 9% at 350°C. The yield of propanoic acid is at 4% at 300°C but approaches 15% at 350°C. Propanoic acid is the favored liquid product at the higher reaction temperatures.

Yields of 2,3-pentanedione are modest but much greater than with any other carbons. The diketone yield peaks at 8% (300°C - 320°C) and falls off to 3% at 350°C. Acrylic acid yield is also small but it does reach 6% at 320°C. The other liquid products of reaction consist mainly of hydroxyacetone and acetic acid.

Gas analysis showed little CO production and a great deal of CO_2 production. The CO:CO_2 yield ratio ranges from 1:3 to 1:20 at different reaction temperatures. This could be in some way a result of the low surface area of this material.

Conversions after accounting for the mass balance errors

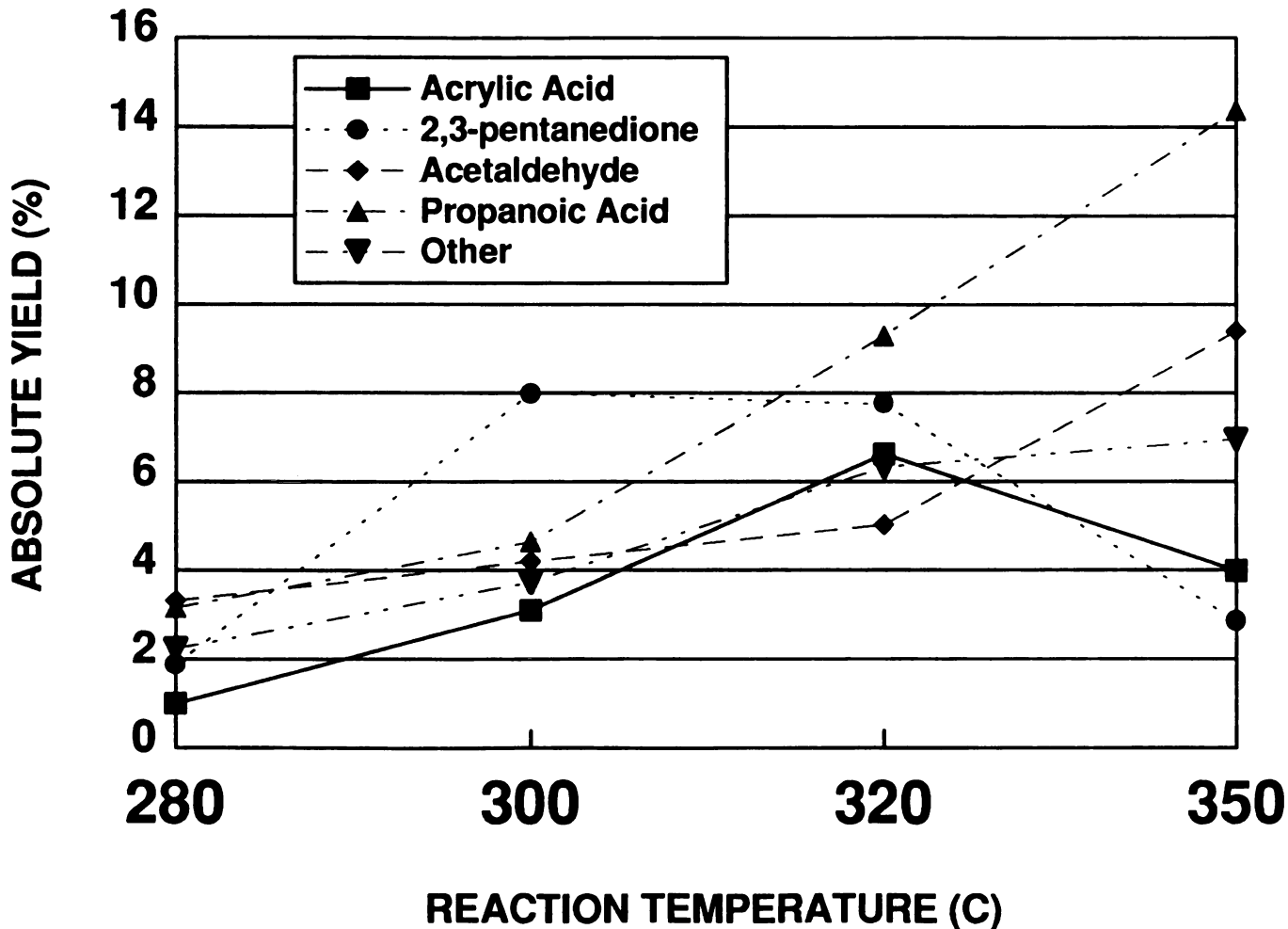

Figure 4.5 - Absolute Product Yields vs. Temperature for the Charred Cherry Pits

are 23, 34, 55 and 64% at 280, 300, 320 and 350°C, respectively. The conversions at low temperatures are less than those of previous carbons. The mass balances again are not very good, ranging from 95.1% carbon recovery to 66.6% recovery at 280°C. At 280°C, the 66.7% carbon recovered led to a huge conversion error. The calculated conversion was 58.3% but this includes the 33.3% of carbon that was not collected.

The promising product yields and suppressed acetaldehyde formation led us to impregnate the charred cherry pit support with Na_3PO_4 to determine if reaction performance could be improved. The previously mentioned impregnation method was used except the amount of salt placed on the surface was 0.001 gmol salt per gram of support.

Figure 4.6 shows the product yield results for the Na_3PO_4/charred cherry pit catalyst. The most noticeable difference between the catalyst and the support alone is in the acrylic acid yields. Over the support alone, acrylic acid yield barely reached 6%, but with trisodium phosphate added, the yield of acrylic approached 13% at 320°C. At 300°C, the acrylic acid yield was almost 7% where before it was only 3%. The yield of 2,3-pentanedione did not change much, and the same plateau behavior (9% at 320°C) was seen in this catalyst.

Propanoic acid yield was somewhat suppressed by the introduction of trisodium phosphate. With the support alone, at 350°C, the propanoic yield approached 15%. With the catalyst added, this yield was 11%. Production of

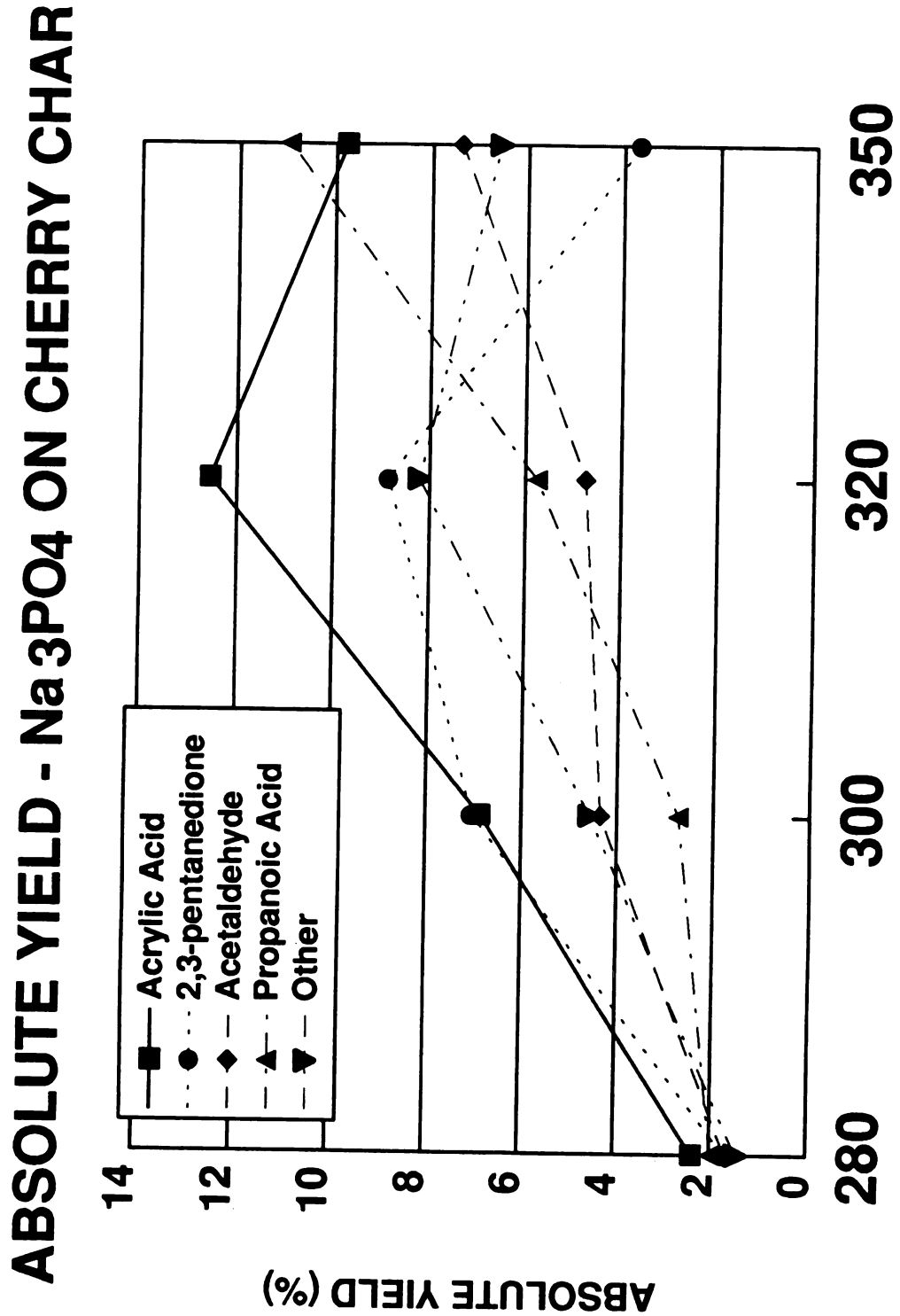

Figure 4.6 - Absolute Product Yields vs. Temperature for Na_3PO_4 on Charred Cherry Pits

acetaldehyde was for the most part constant and remained low except at the highest temperature.

The ratio of CO to CO_2 yields was again much less than unity and ranged from 1:6 to 1:13. CO_2 yields were generally higher than those found when testing the support alone.

Conversions accounting for mass balance errors were 25, 49, 64 and 67% at 280, 300, 320 and 350°C, respectively. These conversions are slightly higher than those calculated from the charred cherry pits only. The mass balances are better than those found using the support alone, ranging from 85.4% carbon recovery to 74.7% recovery. Over 80% of the carbon was recovered at every temperature except 350°C.

4.5 CARBOGRAPH CARBONS

Two carbon samples were purchased from Alltech, Carbograph 1 and Carbograph 2, for lactic acid reaction. The first of these, Carbograph 1, was determined to have a surface area of 80 m^2/g and a 60 x 80 mesh particle size. Particles were spherical and black. The experimental run was conducted using the parameters listed in Table 4.1.

Figure 4.7 shows the liquid product yields for all reaction temperatures. Acetaldehyde yields dwarf all other liquid products, even though at lower temperatures, the support activity is quite low. At 280°C, the acetaldehyde yield is less than 4%, but it reaches its high (18%) at 350°C. Propanoic acid yield ranged from 1% at 280°C to 8% at 350°C.

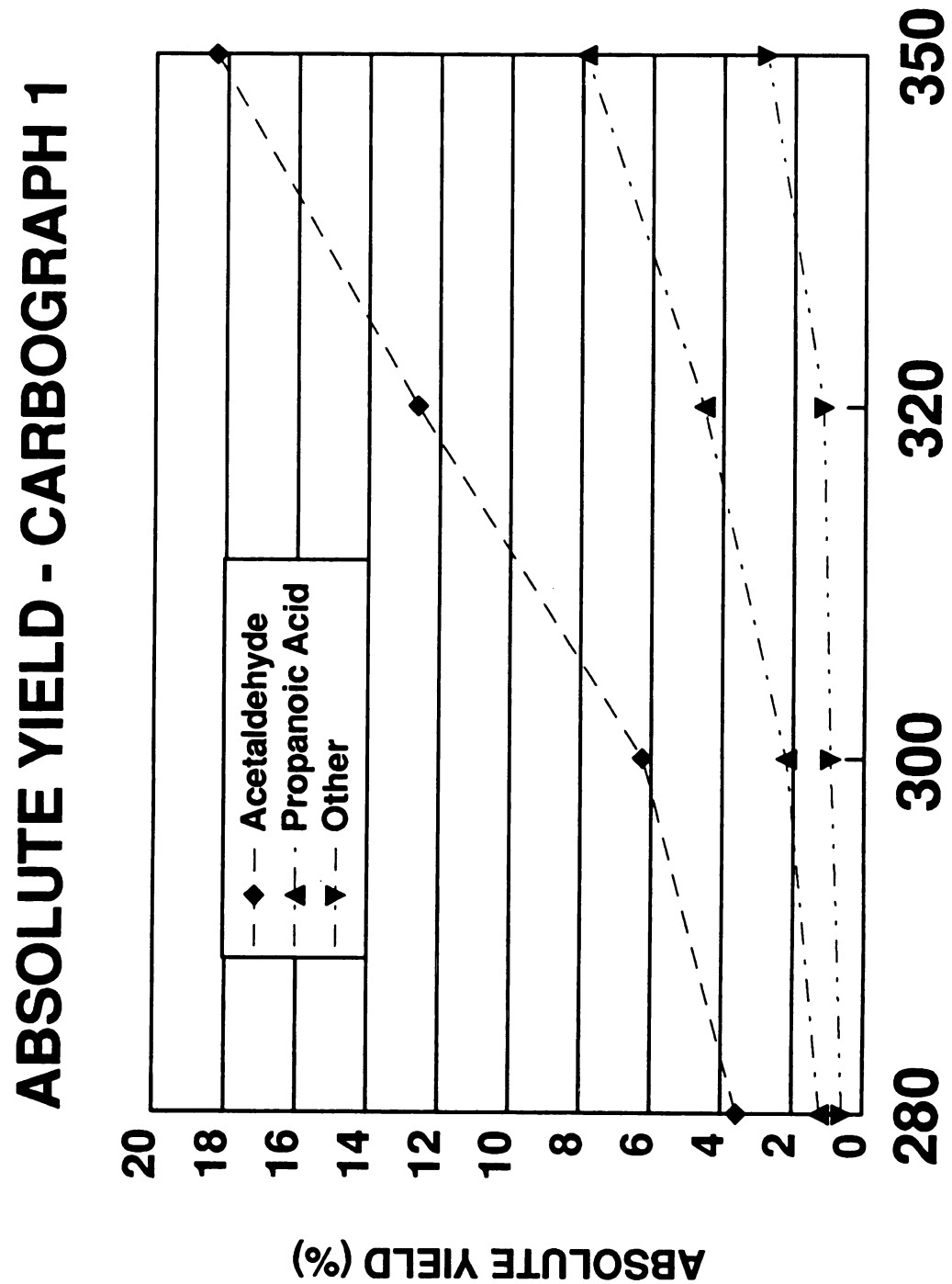

Figure 4.7 - Absolute Product Yields vs. Temperature for Carbograph 1

All other liquid products only combined to produce a 3% yield at 350°C. Yields of 2,3-pentanedione and acrylic acid are less than 1% at all reaction temperatures.

Gas product analysis shows a $CO:CO_2$ yield ratio which starts off at 8 at 280°C and then decreases to 0.5 at 350°C.

Conversions of lactic acid, with the carbon error accounted for, were 13, 26, 37, and 47% at 280, 300, 320 and 350°C. This particular carbon was less active than previous carbons. The carbon mass balances were generally good with carbon recoveries of 104.2, 107.8, 91.7 and 73.8% at 280, 300, 320 and 350°C.

The last carbon support to be tested was Carbograph 2, a 10 m^2/g carbon with spherical 60 x 80 mesh particles. The reaction was performed using reaction conditions listed in Table 4.1.

Product yields at the various reaction temperatures are shown in Figure 4.8. Results are similar to those for Carbograph 1. Support activity is very low at the lower temperatures and the only liquid products present at appreciable levels are acetaldehyde and propanoic acid. Acetaldehyde yield once again dominates the product mixture even though it only rises over 5% at 350°C. Propanoic acid yields remain under 3% until 350°C where the yield is 10%. Yields of 2,3-pentanedione and acrylic acid are less than 1% at each reaction temperature. Acetic acid and hydroxyacetone are formed to a small extent at 350°C.

Carbograph 2 is very similar to most of the other carbons

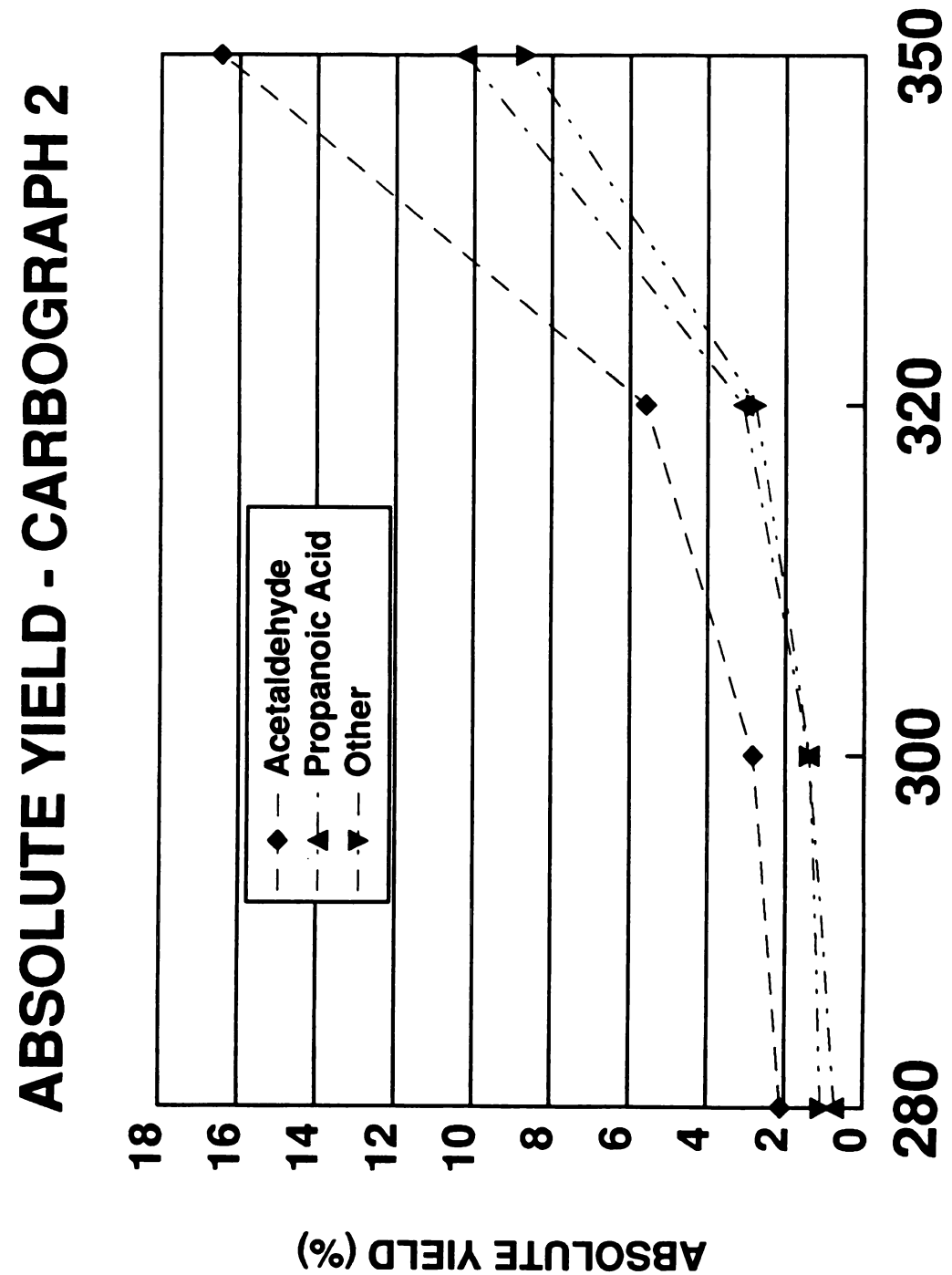

Figure 4.8 - Absolute Product Yields vs. Temperature for Carbograph 2

in terms of support selectivity. Figure 4.9 shows the product selectivity of Carbograph 2 at 300°C. Two-thirds of all liquid products formed in the reaction are acetaldehyde. Propanoic acid contributes 23% and all other liquid products combine to form 10% of the product mixture.

Just as seen in the gas analysis of Carbograph 1, the $CO:CO_2$ yield ratio for Carbograph 2 dropped with the reaction temperature. At 280°C and 300°C, the ratio was slightly greater than unity; then at 320°C the ratio decreased to 0.6 and at 350°C it was 0.3. Yields of CO and CO_2 were much less than those observed for Carbograph 1 and were generally the lowest of any of the carbon supports which were tested.

Lactic acid conversions were lower than conversions witnessed with other carbons, due probably to the low surface area (10 m^2/g) Correcting for mass balance error, conversions were 9, 10, 28 and 53% at 280, 300, 320 and 350°C, respectively. Carbon mass balance errors were not bad as recovery was greater than 86% at all reaction temperatures.

4.5 SUMMARY

As a whole, the carbon supports did not do a very good job. The production of and selectivity to acetaldehyde was large for all of the supports except the charred cherry pits and Carbograph 2. Desired product formation was low in most cases. We were not looking for a large formation of products in a support, but instead a support which suppressed the

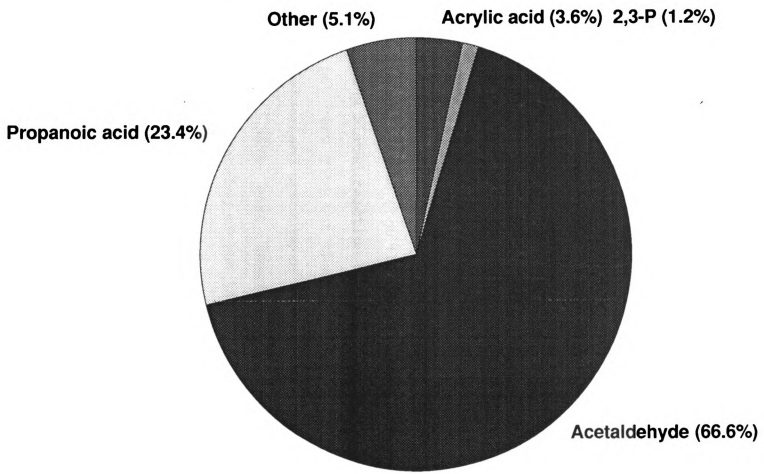

Figure 4.9 - Product Selectivities for Carbograph 2 - REACTION TEMPERATURE 300C

formation of acetaldehyde and propanoic acid. The charred cherry pits did a far superior job than any of the other carbon supports as far as product selectivity is concerned. However, there was some production of acetaldehyde and propanoic acid and at a reaction temperature of 350°C, they were by far the most selectively produced liquid products. All carbon supports were characterized by an increasing tendency towards acetaldehyde production at high temperatures.

Tables 4.2 and 4.3 show the reaction results for all carbon supports at 300 and 320°C, respectively. The reaction yields and selectivities to liquid products (parentheses) can be compared easily. Conversions can be seen to increase with temperature and with support surface areas.

Tables 4.2 and 4.3 also show the mass balance results for the supports at the listed reaction conditions. Overall, mass balances were not very good but there were no huge material losses. Condensation and cracking of the lactic acid over the carbons seems to have been important due to support microporostiy. This cracking of the lactic acid probably led to the poor mass balances. The two Carbographs had the best mass balances probably due to a less microporous structure.

Table 4.2 - Carbon Support Results for 300°C

SUBSTRATE	STREM CARBON	CHERRY	CHERRY CHAR	CARBOGRAPH 1	CARBOGRAPH 2
ACRYLIC ACID	0.84 (2.4)	0.64 (1.8)	3.10 (13.1)	0.34 (3.6)	0.96 (17.1)
2,3-PENTANEDIONE	0.61 (1.7)	0.54 (1.5)	7.99 (33.8)	0.12 (1.3)	0.07 (1.3)
ACETALDEHYDE	17.37 (48.8)	25.15 (69.4)	4.19 (17.7)	6.25 (66.6)	2.84 (50.5)
PROPANOIC ACID	10.60 (29.8)	6.20 (17.1)	4.64 (19.6)	2.19 (23.4)	1.40 (24.8)
ACETOL	0.0	0.32 (.9)	2.53 (10.7)	0.0	0.0
OTHER	6.20 (17.4)	3.38 (9.3)	1.20 (5.1)	0.48 (5.1)	0.36 (6.4)
CO	27.43	45.86	1.01	18.60	3.72
CO_2	20.65	16.97	19.54	6.90	3.05
CONVERSION (%)	85.86	86.26	38.51	18.08	23.73
CARBON RECOVERY (%)	63.25	68.02	95.09	107.76	86.35

Table 4.3 - Carbon Support Results for 320°C

SUBSTRATE	STREM CARBON	CHERRY	CHARRED CHERRY	CARBOGRAPH 1	CARBOGRAPH 2
ACRYLIC ACID	0.40 (.7)	0.83 (2.1)	6.62 (18.9)	0.74 (4.1)	0.49 (4.3)
2,3-PENTANEDIONE	0.27 (.5)	0.55 (1.4)	7.76 (22.2)	0.17 (.9)	0.17 (1.5)
ACETALDEHYDE	30.93 (57.1)	23.49 (60.5)	5.02 (14.3)	12.62 (68.8)	5.59 (48.8)
PROPANOIC ACID	14.19 (26.2)	8.62 (22.2)	9.30 (26.6)	4.54 (30.3)	3.10 (27.0)
ACETOL	0.0	0.82 (2.1)	5.03 (14.4)	0.0	1.31 (11.4)
OTHER	8.34 (15.4)	4.50 (11.6)	1.29 (3.7)	0.27 (1.5)	0.80 (7.0)
CO	29.33	27.66	4.04	14.78	5.96
CO_2	24.37	19.71	32.75	16.00	9.63
CONVERSION (%)	94.67	84.00	75.46	45.51	41.00
CARBON RECOVERY (%)	69.88	69.55	77.14	91.74	86.80

CHAPTER 5

SILICA SUPPORTS

In the course of our catalyst/support search, various silica containing supports were studied. These supports are listed in Table 5.1 along with some physical properties including reaction particle size and surface area. A large surface area range was chosen; therefore, we expected widely varying reaction activity results. All supports were run using the long residence time operating parameters.

5.1 GLASS BEADS

Glass beads (1 mm diameter) were the first support to be studied. The very low (< 1 m^2/g) surface area of the beads seemed to suggest that there would be little activity as lactic acid was passed over them. Figure 5.1 shows the absolute yield data for the liquid products obtained from the glass beads experimental run. There was not much reaction, even at the highest reaction temperature, 320°C. All major reaction products (acrylic acid, 2,3-pentanedione, acetaldehyde, and propanoic acid) were produced in small quantities. All yields of these products are between 0.5 - 2.5% at all reaction temperatures. Although product yields are very small, there is a noticeable trend of product yields increasing with reaction temperature. Selectivity to acrylic

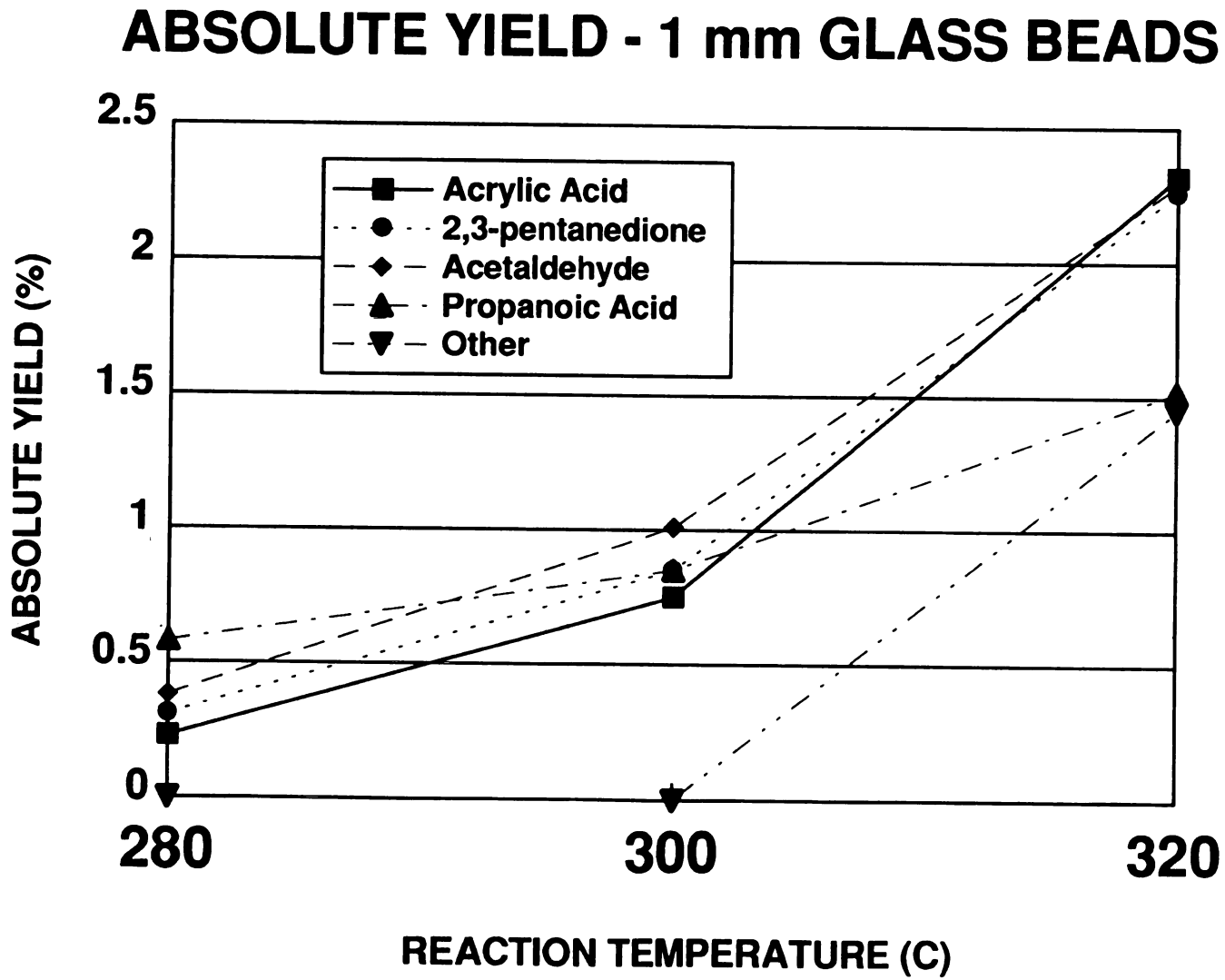

Figure 5.1 - Absolute Product Yields vs. Temperature for 1mm Glass Beads

acid, acetaldehyde, and 2,3-pentanedione remain constant (20 - 25%) throughout the run. The low acetaldehyde and propanoic acid yields are a positive feature of this support.

Very little liquid product formation was accompanied by very little gas product formation. Carbon monoxide and carbon dioxide yields were less than 3% at all reaction temperatures, and CO:CO_2 yield ratios were approximately 1:4 for all temperatures.

Table 5.1 - Reaction Parameters for Silica Supports

SUPPORT	PARTICLE SIZE	REACTION TEMPERATURES (°C)	RESIDENCE TIME CONDITIONS	SURFACE AREA (m^2/g)
GLASS BEADS	1 mm diam.	280, 300, 320	LONG	<1
SILICA GEL	10 x 16 mesh	280, 300, 320, 350	LONG	301
XOA 400	80 x 100 mesh	280, 300, 320, 350	LONG	400
XOB 030	80 x 100 mesh	280, 300, 320, 350	LONG	31
XOC 005	80 x 100 mesh	280, 300, 320, 350	LONG	14

Lactic acid conversions were low for the entire run with conversions of 6.2, 8.0 and 15.5% at 280, 300 and 320°C, respectively. Mass balances for each temperature are excellent with carbon recoveries of 101, 98 and 104% at the three reaction temperatures. The good mass balances could be a result of no lactic acid cracking taking place due to very little sample microporosity.

5.2 SILICA GEL

A highly pure silica gel support was chosen to be studied next. The uncalcined gel's surface area was found by nitrogen BET to be 301 m^2/g (Table 5.1). In addition to the original silica gel sample, a sample calcined at 900°C, overnight, was also studied and a calcination temperature versus surface area study was conducted. The results of the surface area study are listed in Table 5.2.

Figure 5.2 shows the liquid product yield data for the silica gel study. This relatively high surface area material exhibits high activity, especially at the higher reaction temperatures. Acetaldehyde dominates all other liquid products in terms of product yield and selectivity. Acetaldehyde yield reaches 53% at 350°C and the reaction selectivity towards acetaldehyde is approximately 80% at this temperature. Product selectivity towards acetaldehyde does not fall below 80% at any of the reaction temperatures. Propanoic acid yield is between 1-5% at all temperatures and

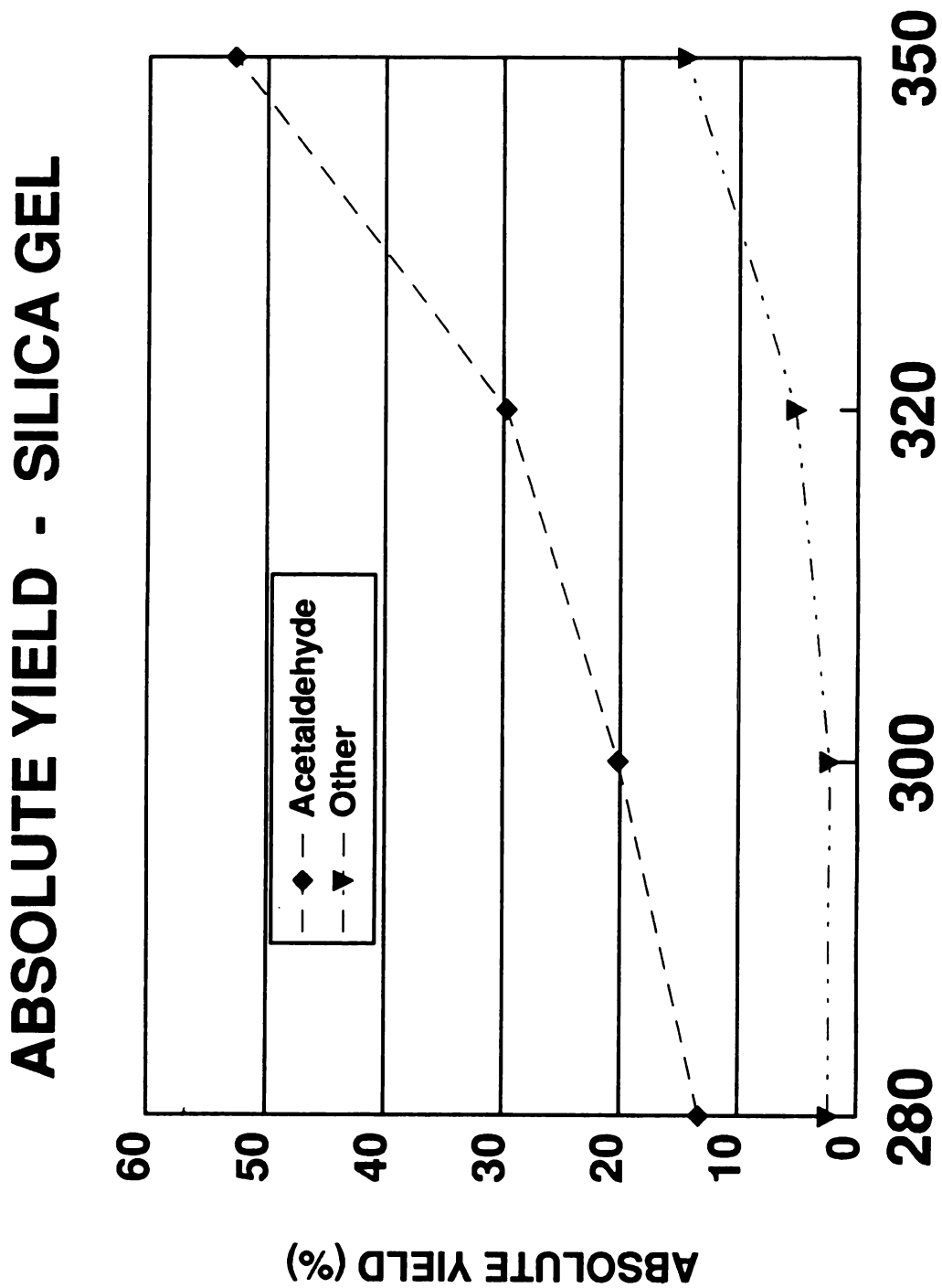

Figure 5.2 - Absolute Product Yields vs. Temperature for Silica Gel

acrylic acid and 2,3-pentanedione yields are also consistently less than 5%.

Carbon monoxide production is far greater than that of carbon dioxide at all reaction temperatures; $CO:CO_2$ yield ratios range from 4:1 at 350°C to 17:1 at 300°C. Yields of both gas products increase with temperature.

Conversions corrected for carbon error were 22, 26, 36 and 63% at 280, 300, 320, and 350°C, respectively. Mass balances for this study were not bad as over 75% of the carbon initially passed over the support was recovered at each temperature. Carbon errors were again lowest at the lower reaction temperatures with recoveries of 88 and 94% at 280 and 300°C.

Table 5.2 - Calcination Temperature vs. Surface Area

CALCINATION TEMPERATURE (°C)	SAMPLE WEIGHT (g)	SURFACE AREA (m^2/g)
ROOM TEMPERATURE	0.33	301
340	0.12	274
540	0.31	308
900	0.21	232

The silica gel was calcined in a Thermolyne 1300 furnace at several temperatures and nitrogen BET was performed on each

sample for surface area determination. We were attempting to decrease the materials microporosity by calcination in hopes that it would decrease acetaldehyde production. Table 5.2 shows the surface area results and one can see that there is little difference in surface areas as a function of calcination temperature for the silica gel. However, the surface area is slightly lower for the material calcined at 900°C. We expected to see decreased activity for this support and possibly some suppression of the acetaldehyde reaction pathway.

Figure 5.3 shows the liquid product yield results for the silica gel material calcined at 900°C. Reaction parameters for this study are listed in Table 5.1. Acetaldehyde production, again, is far greater than any other liquid product. Acetaldehyde yield reaches its peak of 38% at 320°C. Propanoic acid only reaches a yield of 8% at 350°C. Acrylic acid and 2,3-pentanedione yields are low at each temperature and other liquid products are present in very small quantities.

The gas product yields are similar to those seen in the uncalcined silica gel. Carbon monoxide production is greater than that of carbon dioxide at all reaction temperatures. The CO:CO_2 ratio ranges from approximately 7:1 at 300°C to 2:1 at 350°C. As seen before, CO_2 production becomes closer to CO production at higher temperatures.

Lactic acid conversions are 21, 30, 53 and 57% at 280, 300, 320, and 350°C, respectively, which is similar to the

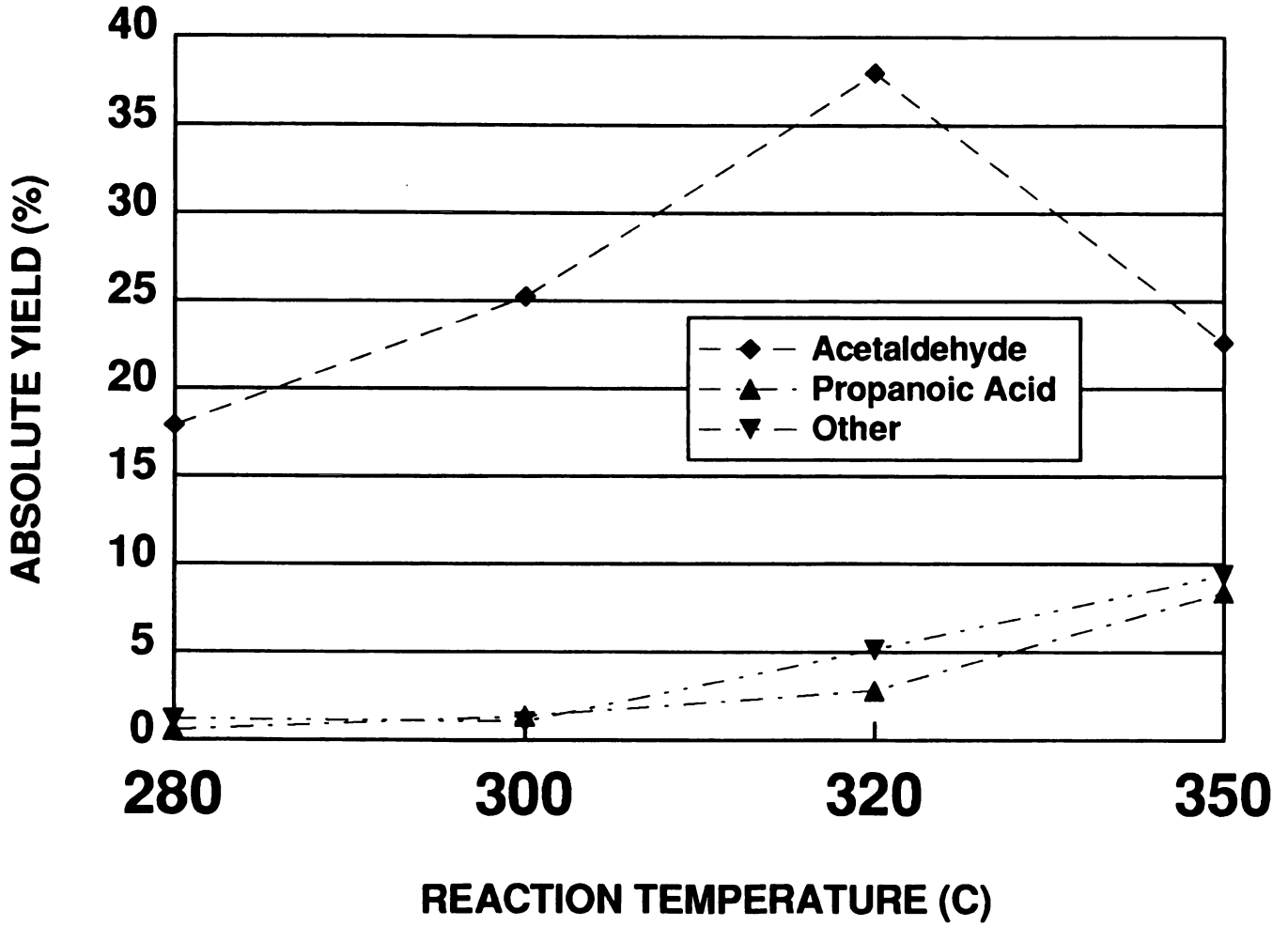

Figure 5.3 - Absolute Product Yields vs. Temperature for Calcined Silica Gel

uncalcined material. Mass balances are poor for this particular study; only at 320°C was more than 75% of the original carbon recovered. The largest carbon error occurred at 280°C where only 66% of the carbon in the lactic acid feed was recovered.

5.3 SPHEROSIL SUPPORTS

The first of the three Spherosil silica supports to be studied was the high surface area (400 m^2/g) XOA 400 sample. Because of its high surface area, it was expected that this support would show greater activity than the others. The Spherosil samples were tested using the parameters listed in Table 5.1. All the Spherosil samples were smaller particles (80 x 100 mesh) than any of the other silica supports.

Figure 5.4 shows the liquid product yield results for the XOA 400 silica support. Acetaldehyde production dwarfs all other liquid products at each reaction temperature. There is, however, a peculiar trend as the acetaldehyde yield decreases at each temperature. Acetaldehyde yield reaches its peak of 67% at 280°C and decreases to 34% at 350°C. Propanoic acid yield begins very slowly (0.5% at 280°C) but reaches 7% at 350°C. Acrylic acid and 2,3-pentanedione yields remain less than 1% at all reaction temperatures. Other liquid products are only present in extremely small quantities.

Gas analysis shows a great deal of carbon monoxide production which decreases with increasing reaction

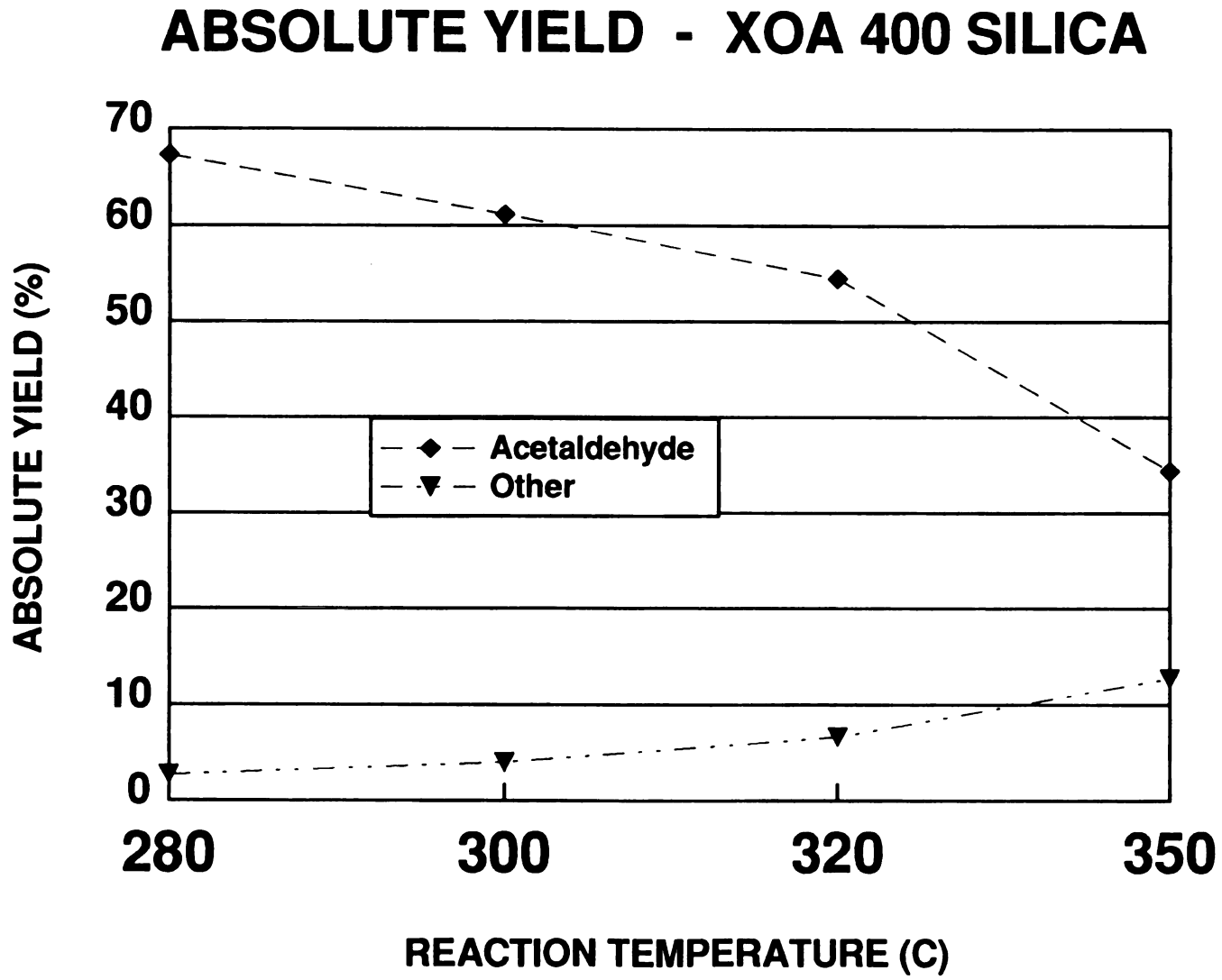

Figure 5.4 - Absolute Product Yields vs. Temperature for the XOA 400 silica

temperature and increasing carbon dioxide production. $CO:CO_2$ yield ratio ranges from 30:1 at 280°C to approximately unity at 350°C.

Lactic acid conversions were 45, 80, 68 and 63% at 280, 300, 320 and 350°C. These figures seem odd, especially at 300°C where it seems that the conversion is much higher than it should be. A possible cause for the error in conversions could be a very poor mass balance. Carbon recoveries were 120, 92, 72 and 67% at 280, 300, 320 and 350°C, respectively. At least part of the mass balance errors could be attributed to condensation and cracking of the lactic acid which also would account for the high acetaldehyde production.

The second Spherosil silica support to be studied was XOB 030, which was found to have a 31 m^2/g surface area. The material was tested using the parameters listed in Table 5.1. There were expectations of less activity and suppressed acetaldehyde production due to the lower surface area and probable decrease in microporosity compared to the XOA 400 support.

Figure 5.5 shows the liquid product yield results for the XOB 030 support. Again, acetaldehyde yield is much greater than all other liquid products. Yield trends exhibit the normal behavior, increasing with reaction temperature. Acetaldehyde yield ranges from 8% at 280°C to 37% at 350°C while propanoic acid yield ranges from 1% to 11% at the same temperatures. Acrylic acid and 2,3-pentanedione yields do not rise above 5% at any reaction temperature and other liquid

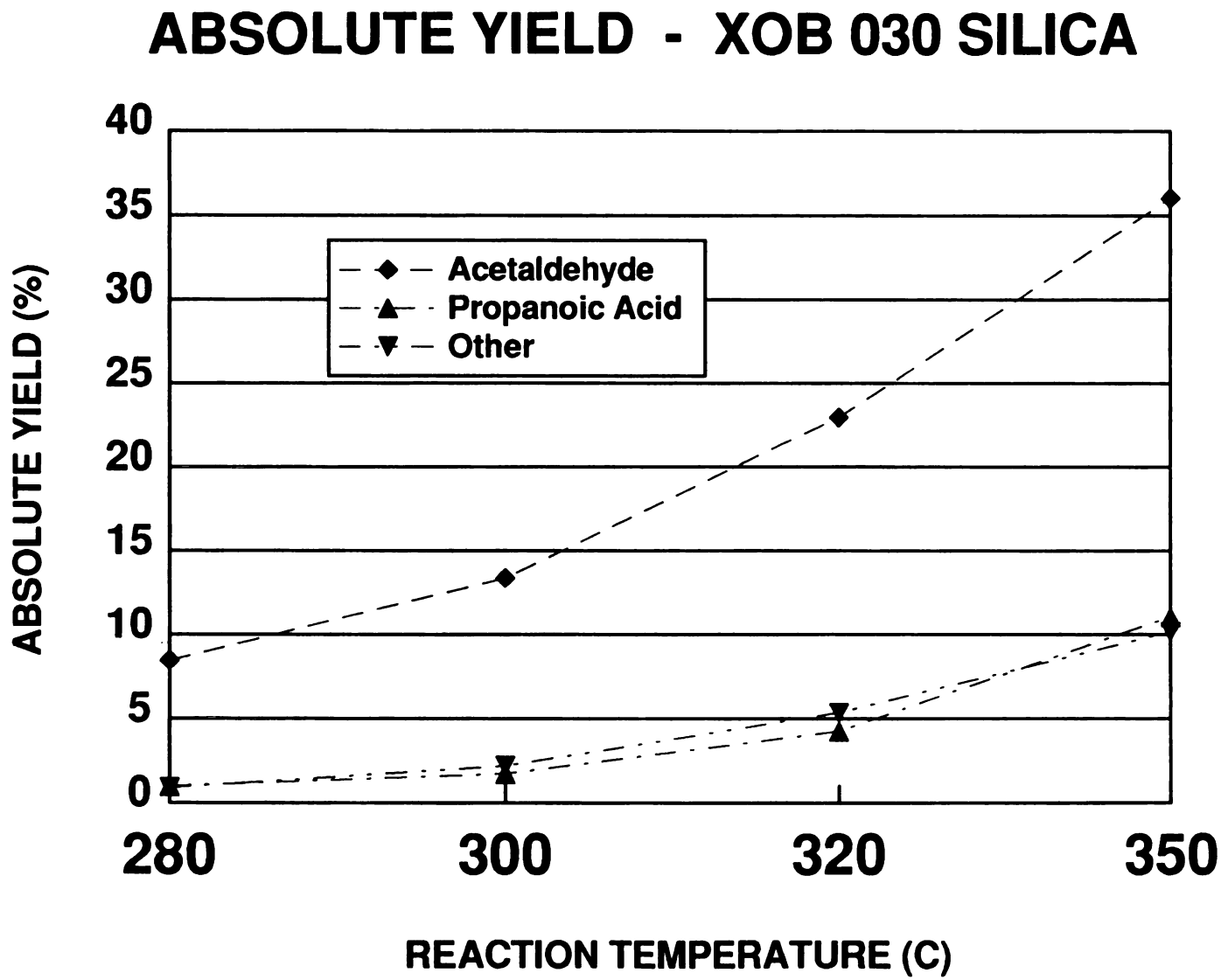

Figure 5.5 - Absolute Product Yields vs. Temperature for the XOB 030 silica

products are present only in very small quantities.

Gas product analysis once again shows greater carbon monoxide production than carbon dioxide. Production of both gas products is lower than for the XOA 400 support. The $CO:CO_2$ yield ratio ranges from 6:1 at 280°C to 1.6:1 at 350°C. This again shows CO_2 production catching the CO production at higher temperatures although yields of both gas products increase with reaction temperature.

Lactic acid conversions are 16, 26, 37, and 65% at 280, 300, 320 and 350°C, and are much more normal than those found for the XOA 400 support. Mass balances were better with recoveries exceeding 75% at all temperatures except 320°C where only 73% of the carbon was recovered. There still is present a loss of carbon which implies that condensation and cracking may still be important here.

The last Spherosil support to be studied was the XOC 005 sample which has the lowest surface area (14 m^2/g) of the three samples. The support was tested using the parameters listed in Table 5.1. Again, it was predicted that the lower surface area material would show less activity and would suppress acetaldehyde production.

Figure 5.6 shows the liquid product yields for the XOC 005 support. Acetaldehyde yield is again the most dominant product although it is less abundant than in the previous two studies. Acetaldehyde yield starts at 4.7% at 280°C and only reaches a high of 13.7% at 350°C. The suppressed acetaldehyde yield is accompanied by suppressed yields of all other liquid

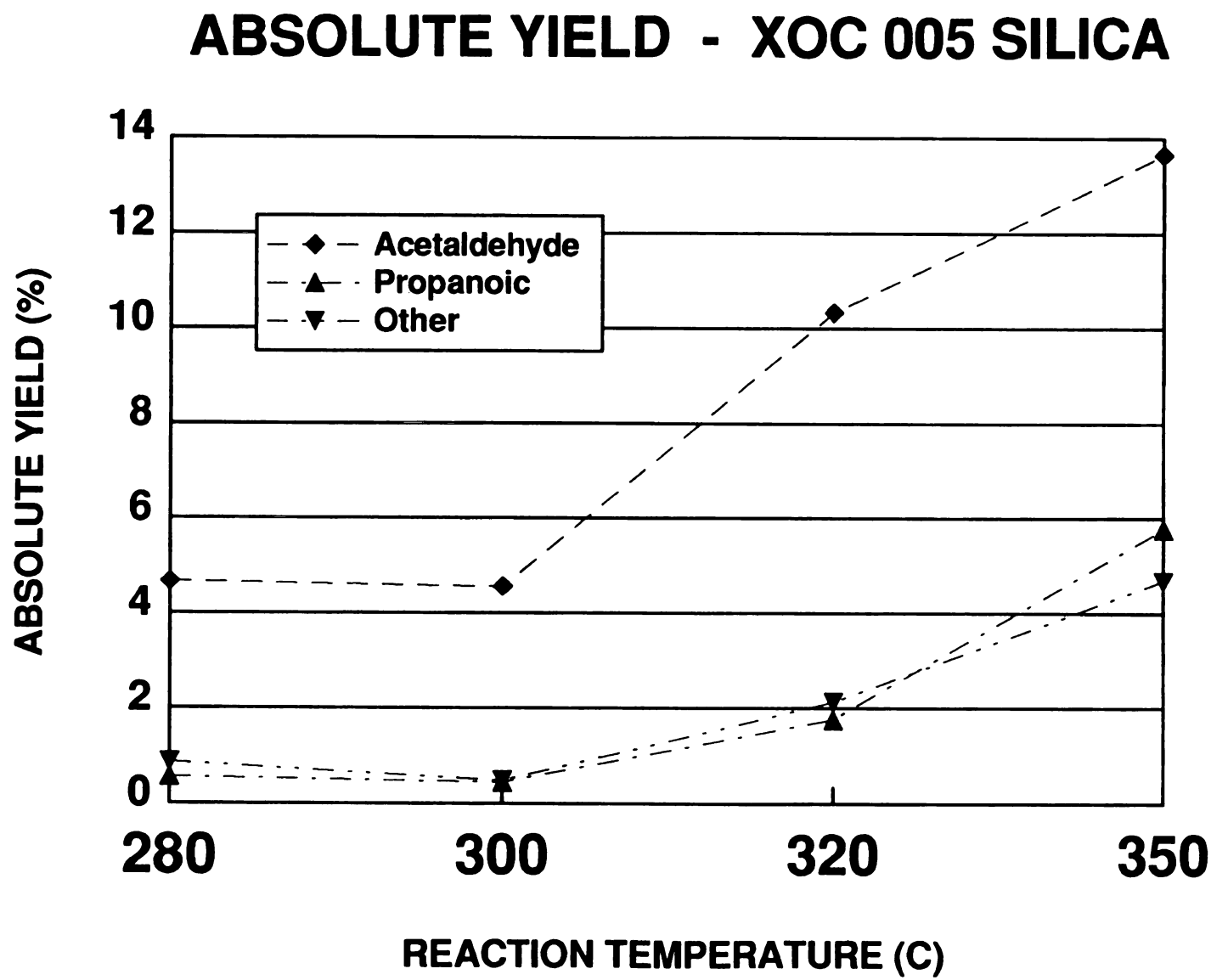

Figure 5.6 - Absolute Product Yields vs. Temperature for the XOC 005 silica

products including propanoic acid, which ranges from a yield of 0.6% at 280°C to 5.8% at 350°C. Acrylic acid and 2,3-pentanedione yields are less than 2% at all reaction temperatures. Other liquid products are present in extremely small quantities.

Gas product analysis shows the same general trend of greater carbon monoxide production than carbon dioxide with CO_2 production increasing faster with reaction temperature. $CO:CO_2$ ratios range from 3:1 at 300°C to slightly less than unity at 350°C. Yields of both gases are lower than those of the previous two Spherosil samples.

Lactic acid conversions were 12, 14, 20 and 40% at 280, 300, 320, and 350°C and are lower than the other two Spherosil supports, as expected. Mass balances are good at the lower reaction temperatures but are very poor at the higher temperatures. Carbon recoveries range from 108% at 280°C to only 53% at 350°C.

Table 5.3 shows summarized results for the three Spherosil silicas at 300 and 320°C. The absolute product yields are shown along with the product selectivities in parentheses. The XOC 005 support shows the lowest acetaldehyde production and the best results even though the product distribution still greatly favors acetaldehyde on a relative basis. It is the suppression of acetaldehyde yield that is most significant, however, and this feature is the cause behind more studies being done with this support.

Table 5.3 - Spherosil Silica Results at 300 and 320°C

TEMPERATURE (°C)	300			320		
SUBSTRATE	XOA 400	XOB 030	XOC 005	XOA 400	XOB 030	XOC 005
ACRYLIC ACID	0.33 (0.5)	1.04 (6)	0.27 (4.9)	0.80 (1.3)	2.73 (8.4)	0.79 (5.6)
2,3-PENTANEDIONE	0.26 (0.4)	0.84 (4.9)	0.22 (4)	0.31 (0.5)	1.93 (5.9)	0.68 (4.8)
ACETALDEHYDE	61.12 (93.8)	13.36 (77.4)	4.56 (82.9)	54.5 (89.1)	22.95 (70.5)	10.33 (72.6)
PROPANOIC ACID	1.03 (1.6)	1.71 (9.9)	0.45 (8.2)	2.74 (4.5)	4.25 (13.1)	1.77 (12.4)
OTHER	1.39 (2.1)	0.31 (1.8)	0	2.27 (3.7)	0.68 (2.1)	0.65 (4.6)
CO	74.6	15.7	3.5	51.9	18.8	7.9
CO_2	7.1	3.2	0.9	14.1	5.8	4.0
CONVERSION (%)	88.23	37.61	18.91	96.08	63.50	52.46
CARBON RECOVERY (%)	91.69	88.43	94.75	71.86	73.30	67.94

CHAPTER 6

CATALYST SURVEY

The Spherosil XOC 005 silica support was used in a catalyst survey which was intended to produce a superior catalyst/support combination. It was decided that the catalyst search would employ the short residence time operating parameters. The catalysts which were chosen are sodium salts and are listed along with their physical properties in Table 6.1. It was assumed that the XOC 005 support surface area of 14 m^2/g remained approximately constant after impregnation with the various salts.

Preparation of the catalysts was basically identical in all cases. A loading of 0.001 mol catalyst per gram of support was chosen for each study and impregnation was carried out using the methods described earlier (Chapter 4).

Figures 6.1 - 6.5 show the liquid product yields for the XOC 005 support and each catalyst studied. The support alone showed very little activity at the lower temperatures and even at 350°C, the acetaldehyde yield is only 9% with all other liquid products combining for a 2.3% yield. Acrylic acid, 2,3-pentanedione and propanoic acid yields are less than 1% at each temperature. Lactic acid conversions are 4, 6, 10 and 20% at 280, 300, 320 and 350°C when the carbon errors are accounted for and mass balances are fair with carbon recoveries of 85, 102, 105 and 82%. Gas product formation is

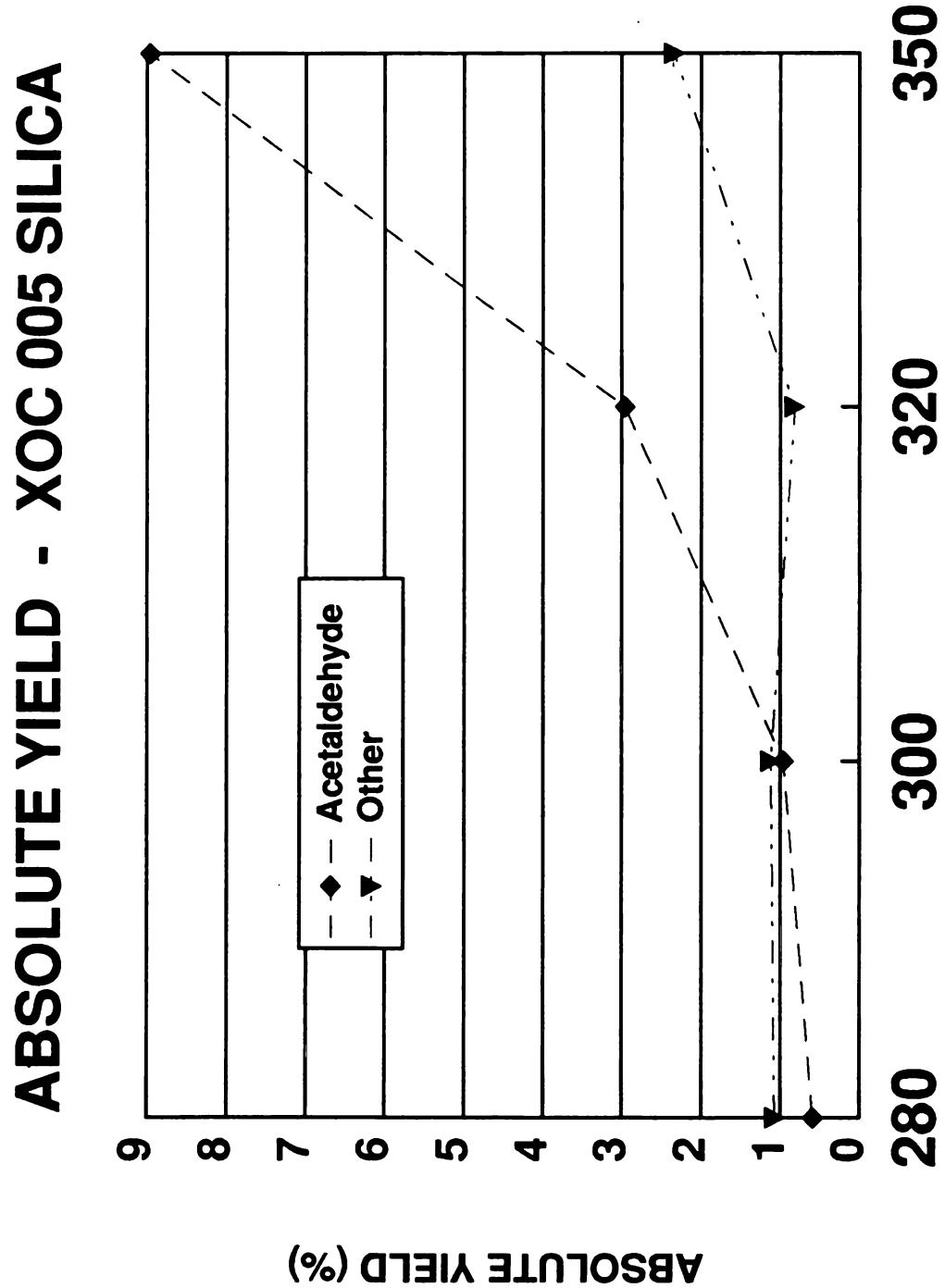

Figure 6.1 - Absolute Product Yields vs. Temperature for the XOC 005 silica

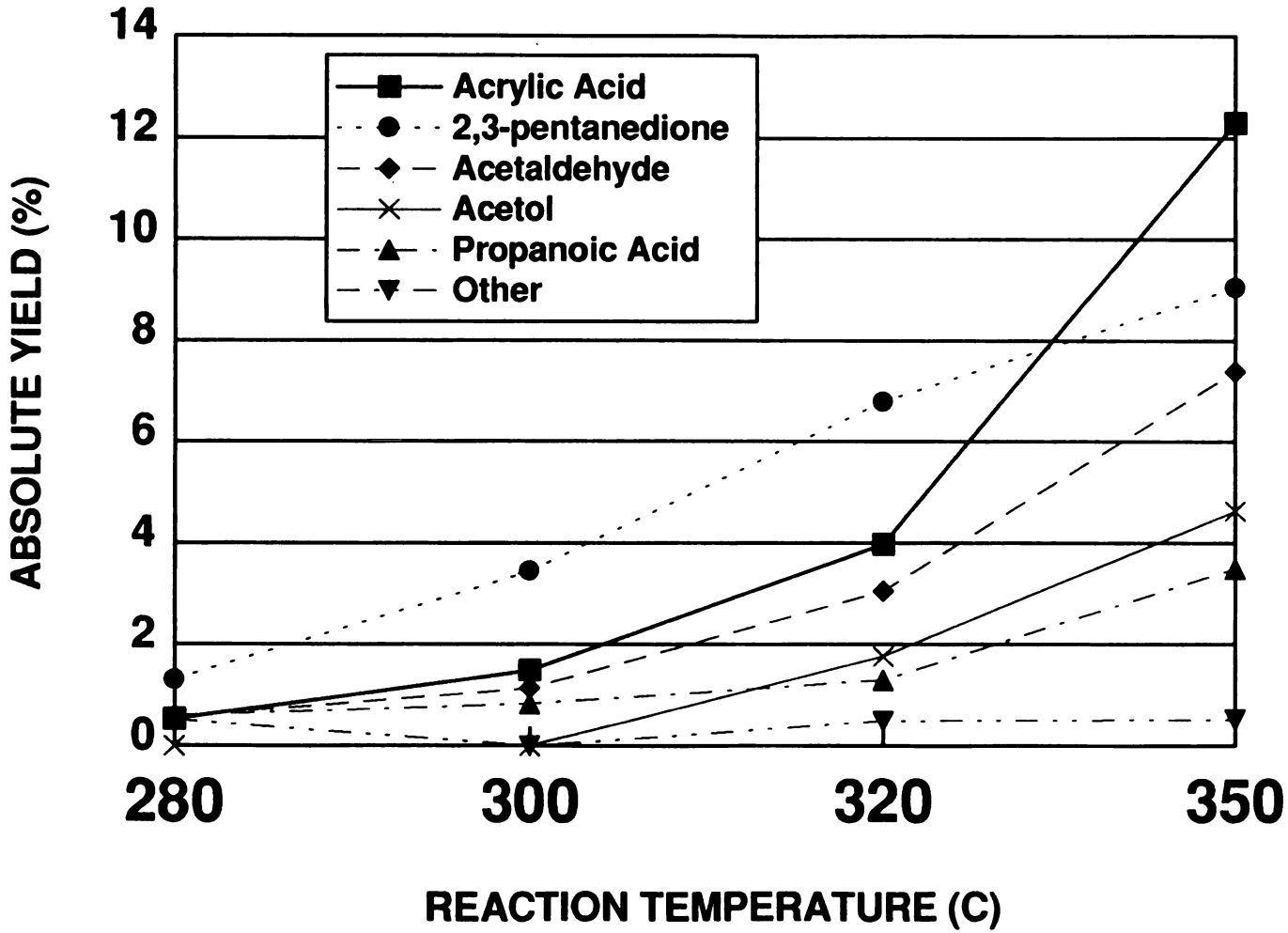

Figure 6.2 - Absolute Product Yields vs. Temperature for NaOH on XOC 005 silica

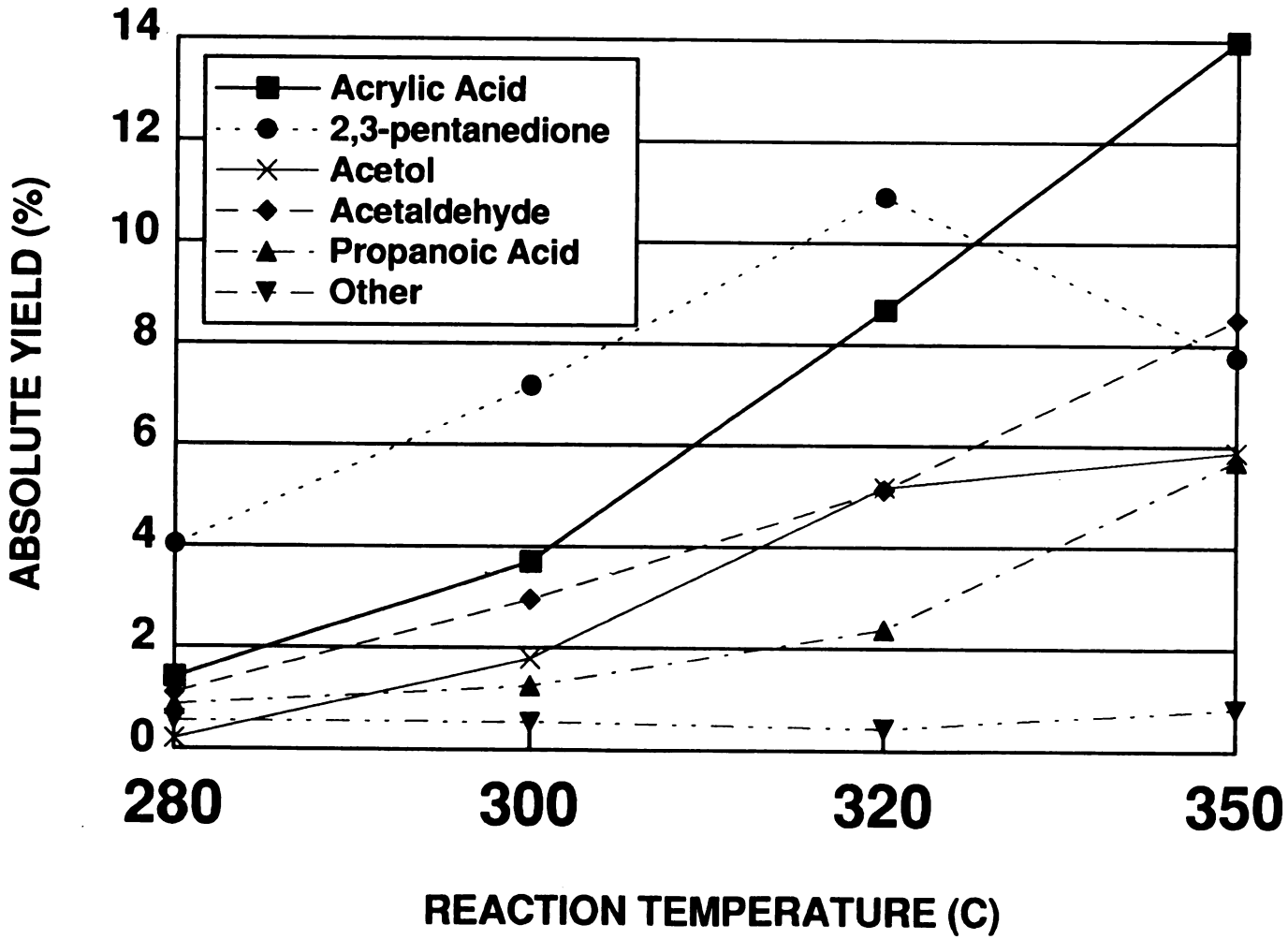

Figure 6.3 - Absolute Product Yields vs. Temperature for Na_3PO_4 on the XOC 005 silica

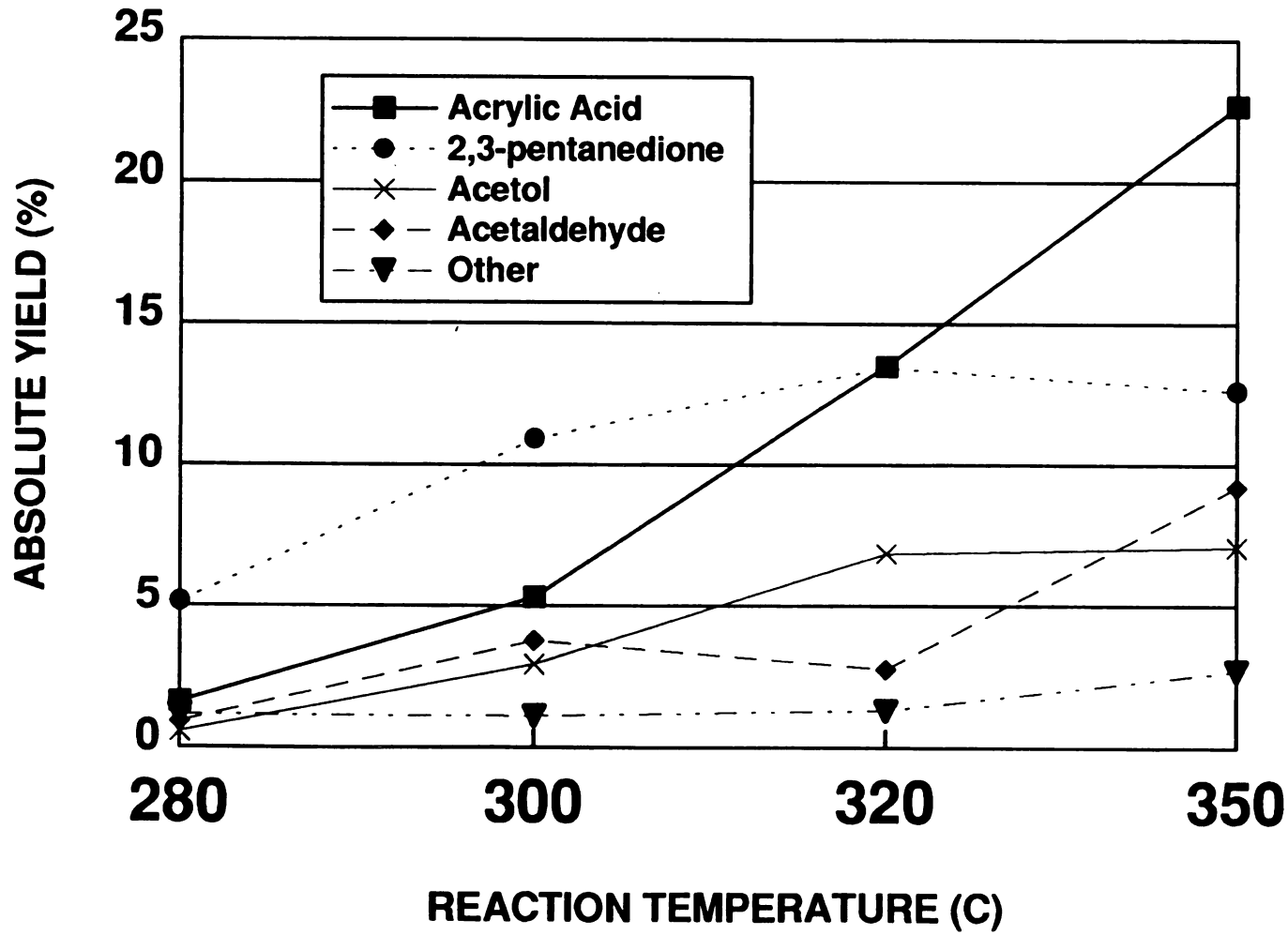

Figure 6.4 - Absolute Product Yields vs. Temperature for $NaNO_3$ on the XOC 005 silica

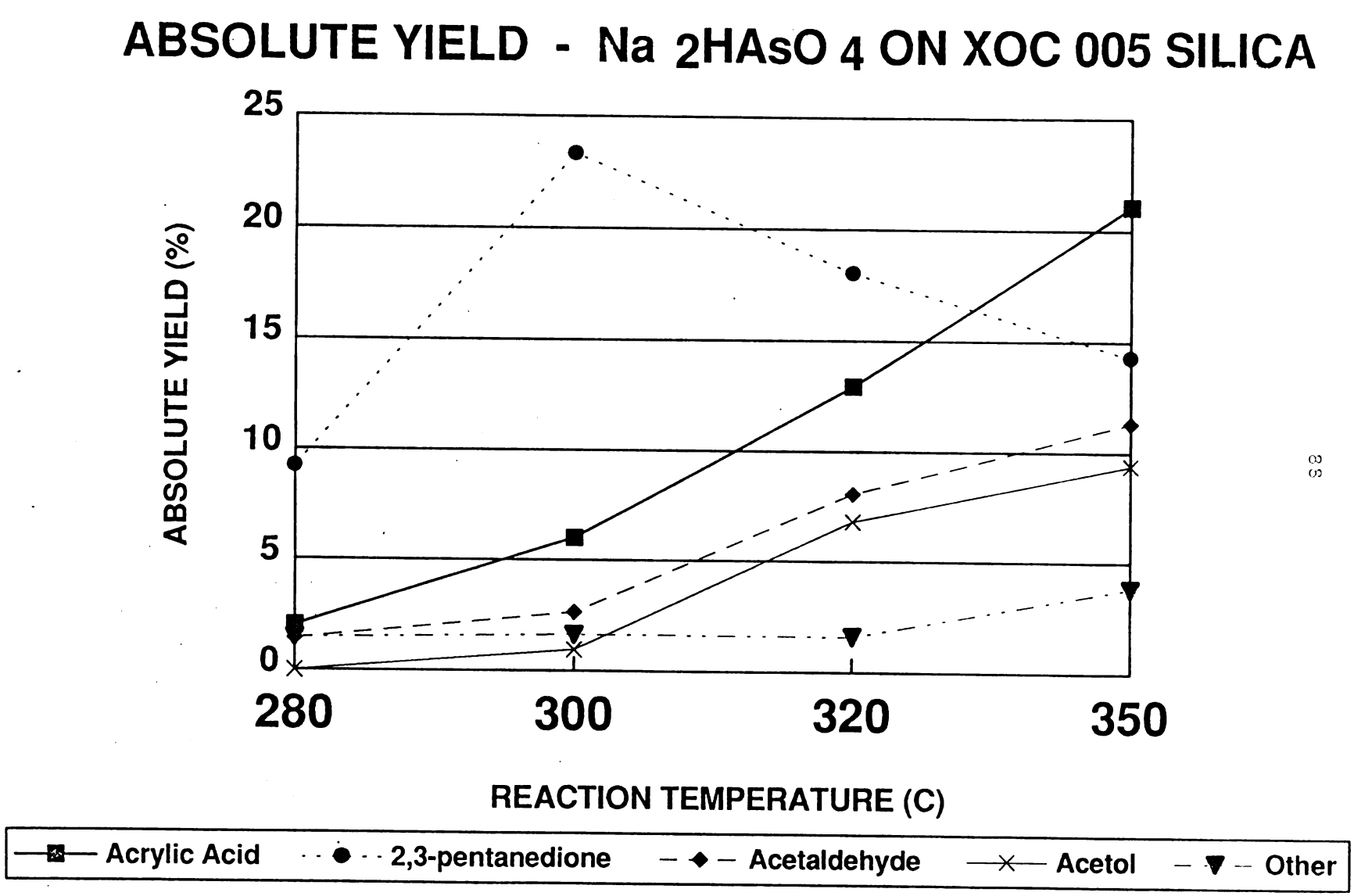

Figure 6.5 - Absolute Yields vs. Temperature for Na_2HAsO_4 on the XOC 005 silica

low and favors CO, especially at the higher temperatures. The suppression of acetaldehyde production is a very positive result from this study and it was predicted that a catalyst impregnated version of the support would give good selectivity results. Tables 6.2 - 6.5 show the important results obtained from the catalyst survey.

Table 6.1 - Catalyst Reaction Parameters

CATALYST	SURFACE AREA (m2/g)	PARTICLE SIZE (mesh)	REACTION TEMPERATURES (°C)	RESIDENCE TIME CONDITIONS
SUPPORT	14	80 x 100	280, 300, 320, 350	SHORT
NaOH	14	80 x 100	280, 300, 320, 350	SHORT
Na_3PO_4	14	80 x 100	280, 300, 320, 350	SHORT
$NaNO_3$	14	80 x 100	280, 300, 320, 350	SHORT
Na_2HAsO_4	14	80 x 100	280, 300, 320, 350	SHORT

In an attempt to make the support more basic, a study was done using sodium hydroxide as a catalyst. This catalyst/support was moderately active and gave good carbon

recoveries. However, at the lower temperatures, there was not much conversion as all product yields were less than 4% at 300°C. At the higher temperatures, acetaldehyde yield begins to pick up and it becomes a major product.

The study done using trisodium phosphate as a catalyst gave even more positive results. Acetaldehyde production remained the same (1-8% yield) but acrylic acid and 2,3-pentanedione yields were higher than previously seen. Hydroxyacetone is seen as a major product with yields approaching 6% at 350°C. Propanoic acid is also important at the higher temperatures with yields reaching 6%. Mass balances for this study were not very good with carbon recoveries of 105, 75, 73 and 65% at 280, 300, 320 and 350°C, respectively. Selectivities of 26.5% and 33.3% for acrylic acid and 2,3-pentanedione were found (Figure 6.6). Gas product analysis shows a carbon dioxide production far greater than carbon monoxide production.

Sodium nitrate was studied as a possible catalyst and gave good results. Acetaldehyde yields were low again (1-9%) and only surpassed 4% at the highest temperature (350°C). Acrylic acid, hydroxyacetone and 2,3-pentanedione were the major products at the lower temperatures and Figure 6.7 shows the selectivity towards products at 320°C. Conversions and mass balances were not bad for this study. Again, gas production was moderate and favored carbon dioxide over carbon monoxide.

Sodium arsenate results are superior to any of the other

SELECTIVITY TO PRODUCTS

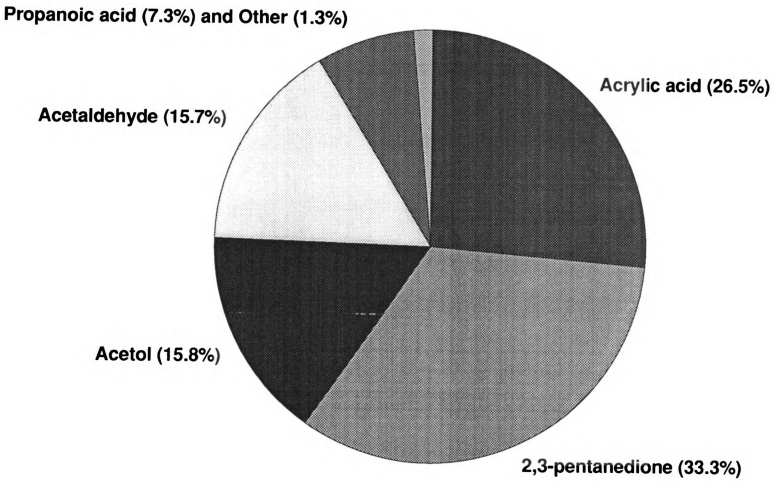

Figure 6.6 - Product Selectivity of Na_3PO_4 on XOC 005 silica - REACTION TEMPERATURE 320C

SELECTIVITY TO PRODUCTS

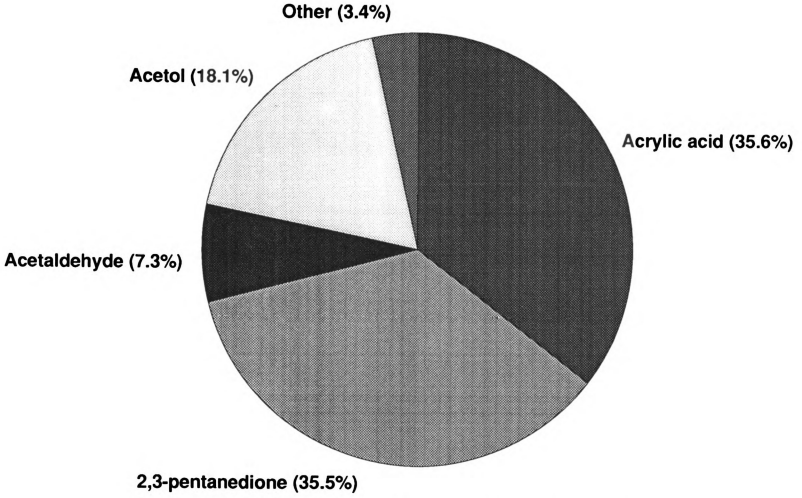

Figure 6.7 - Product Selectivity of $NaNO_3$ on XOC 005 silica - REACTION TEMPERATURE 320C

catalysts as far as 2,3-pentanedione production is concerned. Also, acetaldehyde production is suppressed at the lower temperatures. Yield of 2,3-pentanedione reaches a peak of 23% at 300°C while acetaldehyde yield is less than 3%. Figure 6.8 shows the selectivity to products at 300°C. Conversions were fairly high for this study (20 - 71%). Although the results for the Na_2HAsO_4 were very good, the commercial potential for arsenate catalysts is not good as arsenic is a very dangerous substance.

SELECTIVITY TO PRODUCTS

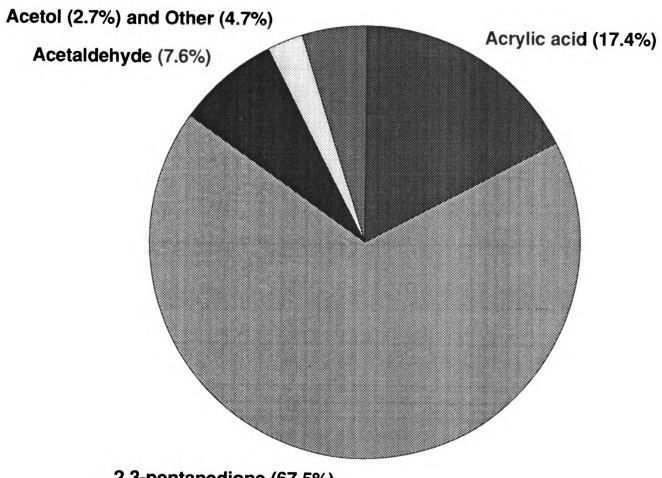

Figure 6.8 - Product Selectivity of Na_2HAsO_4 on XOC 005 silica - REACTION TEMPERATURE 300C

Table 6.2 - Catalyst Survey Results at 280°C

SUBSTRATE	SUPPORT	NaOH	Na_3PO_4	$NaNO_3$	Na_2HAsO_4
ACRYLIC ACID	0.22 (13.5)	0.53 (15.1)	1.41 (17.2)	1.61 (17.1)	2.02 (14.3)
2,3-PENTANEDIONE	0.03 (2)	1.31 (36.9)	4.02 (49.3)	5.15 (54.9)	9.24 (65.2)
ACETALDEHYDE	0.59 (35.5)	0.58 (16.3)	1.1 (13.5)	0.91 (9.7)	1.44 (10.1)
PROPANOIC ACID	0.38 (22.7)	0.6 (17)	0.87 (10.7)	0.63 (6.7)	0.83 (5.8)
HYDROXYACETONE	0	0	0.2 (2.4)	0.56 (5.9)	0
OTHER	0.44 (26.3)	0.52 (14.8)	0.57 (6.9)	0.54 (5.7)	0.65 (4.6)
CO	0.52	0.55	0.88	0.96	1.57
CO_2	0.46	1.2	3.48	4.32	11.27
CONVERSION (%)	18.84	14.9	7.65	17.22	41.08
CARBON RECOVERY (%)	85.21	91.51	104.98	96.19	78.66

Table 6.3 - Catalyst Survey Results at 300°C

SUBSTRATE	SUPPORT	NaOH	Na_3PO_4	$NaNO_3$	Na_2HAsO_4
ACRYLIC ACID	0.21 (10.1)	1.49 (21.6)	3.7 (21.3)	5.31 (22.1)	6.01 (17.4)
2,3-PENTANEDIONE	0.14 (6.6)	3.45 (50)	7.16 (41.1)	10.91 (45.4)	23.34 (67.5)
ACETALDEHYDE	0.96 (46)	1.34 (16.5)	2.96 (17)	3.77 (15.7)	2.64 (7.6)
PROPANOIC ACID	0.38 (18.4)	0.83 (12)	1.26 (7.2)	0.8 (3.3)	1.14 (3.3)
HYDROXYACETONE	0	0	1.79 (10.3)	2.93 (12.2)	0.95 (2.8)
OTHER	0.39 (18.8)	0	0.54 (3.1)	0.32 (1.3)	0.49 (1.4)
CO	1.28	1.05	1.41	1.81	1.76
CO_2	0.68	3.68	7.63	12.24	16.76
CONVERSION (%)	4.06	21.05	47.71	37.94	44.17
CARBON RECOVERY (%)	102.68	89.95	75.63	93.57	94.88

Table 6.4 - Catalyst Survey Results at 320°C

SUBSTRATE	SUPPORT	NaOH	Na_3PO_4	$NaNO_3$	Na_2HAsO_4
ACRYLIC ACID	0.29 (7.6)	3.97 (22.9)	8.68 (26.6)	13.49 (35.6)	12.92 (27.2)
2,3-PENTANEDIONE	0.20 (5.2)	6.79 (39.1)	10.90 (33.3)	13.44 (35.5)	8.07 (17)
ACETALDEHYDE	2.96 (78.3)	3.05 (17.6)	5.13 (15.7)	2.76 (7.3)	1.10 (2.3)
PROPANOIC ACID	0.34 (8.9)	1.30 (7.5)	2.38 (7.3)	0.92 (2.4)	6.81 (14.4)
HYDROXYACETONE	0	1.76 (10.1)	5.18 (15.8)	6.87 (18.1)	0.5 (1.1)
OTHER	0	0.49 (2.8)	0.44 (1.3)	0.38 (1.1)	0.5 (1.1)
CO	4.72	1.51	3.00	2.30	2.52
CO_2	1.31	8.40	15.59	17.76	25.65
CONVERSION (%)	5.15	23.40	66.48	63.94	77.04
CARBON RECOVERY (%)	105.5	101.3	72.67	80.32	77.37

Table 6.5 - Catalyst Survey Results at 350°C

SUBSTRATE	SUPPORT	NaOH	Na_3PO_4	$NaNO_3$	Na_2HAsO_4
ACRYLIC ACID	0.93 (8.3)	12.3 (32.9)	13.98 (32.7)	22.69 (41.8)	21.06 (35.2)
2,3-PENTANEDIONE	0.64 (5.7)	9.05 (24.2)	7.76 (18.2)	12.6 (23.21)	14.28 (23.8)
ACETALDEHYDE	8.96 (79.3)	7.39 (19.8)	8.51 (19.9)	9.2 (17)	11.3 (18.9)
PROPANOIC ACID	0.76 (6.8)	3.49 (9.3)	5.72 (13.4)	1.8 (3.3)	2.04 (3.4)
HYDROXYACETONE	0	4.63 (12.4)	5.89 (13.8)	7.08 (13)	9.41 (15.7)
OTHER	0	0.52 (1.4)	0.82 (1.9)	0.9 (1.7)	1.78 (3)
CO	19.61	4.05	6.17	6.01	5.41
CO_2	2.8	20	28.52	31.89	33.71
CONVERSION (%)	38.95	65.8	90.63	91.94	92.96
CARBON RECOVERY (%)	81.82	80.94	64.15	73.05	78.23

CHAPTER 7

DISCUSSION AND CONCLUSIONS

During lactic acid reaction studies, there were various experiments conducted in order to verify that the methods used for data analysis were correct and that the best possible results were obtained.

7.1 MASS BALANCE CONSIDERATIONS

The concentration of feedstock lactic acid was a concern early in our studies. The assay from Purac for lactic acid concentration was 88 wt%. This concentrated solution was diluted with reverse osmosis (RO) water to 34 wt% lactic acid for each experimental run. As any error in lactic feed concentration would result in poor mass balances and incorrect product yields, two attempts were made to determine the actual lactic acid concentration.

An attempt was made to determine the lactic acid concentration by means of pH analysis. The dissociation constant (Ka) of lactic at 25°C is approximately 1.37×10^{-4}. Concentrated Purac and Aldrich lactic acid solutions were diluted by factors of 10, 100 and 1000 to arrive at reasonable pH ranges. A Fisher Scientific Accumet 950 pH/ion meter was used to obtain data. Table 7.1 shows the results of the pH tests. It can be easily seen that these data are not very

reliable. The two lactic acid samples remained close in pH but they give results which are very different from the correct concentration, although the values at the 100-fold dilution are close. The reason for the scatter is unknown.

The second method used to determine the lactic acid concentration was a carbon/hydrogen/nitrogen (CHN) test performed on a feed sample by the Michigan Biotechnology Institute. The sample was an 88 wt% lactic acid sample diluted to 34 wt%. The CHN results gave a carbon assay of 13.06 wt% carbon, which translates to a 32.7 wt% lactic acid solution. A 34 wt% lactic acid solution contains 13.60 wt% carbon. The error here is approximately 4%, which is too small to cause a large mass balance error. It was decided that the lactic acid feed concentration was close to 34 wt%.

Table 7.1 - Lactic Acid pH Results

DILUTION	LACTIC ACID WT%		pH CALCULATED LACTIC WT%	
	PURAC LACTIC	ALDRICH LACTIC	PURAC LACTIC	ALDRICH LACTIC
10	8.8	8.5	10.58	14.99
100	0.88	0.85	0.74	0.83
1000	0.088	0.085	0.042	0.047

Gas chromatograph response factors were calculated for all known reaction products using standards diluted to various

concentrations. These response factors are used to determine product concentrations based on the GC peak area for particular products. The old response factors were calculated in solutions which contained only one reaction product and the internal standard. This was not a correct representation of a product mixture, therefore, it was decided to combine various products to simulate product mixtures. It was necessary to recalculate the response factors for acrylic acid, 2,3-pentanedione, propanoic acid, hydroxyacetone, acetic

Table 7.2 - Response Factors

SUBSTANCE	OLD RESPONSE	NEW RESPONSE
Acetaldehyde	1.58	1.59
Acetic acid	2.08	1.95
Acetol	2.94	2.12
Acetone	1.07	0.98
Acrylic acid	1.34	1.22
Ethanol	1.37	1.10
Lactic acid	4.79	5.17
2,3-pentanedione	0.99	1.14
Propanoic acid	1.21	1.11

acid, acetaldehyde, acetone, ethanol and lactic acid in a mixture. This check was performed in order to ensure that we

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were obtaining the best possible mass balances on the system. Again, 2-propanol was used as the internal standard. Table 7.2 shows the results of the response factor check. The response factors listed in the table are a ratio of the product GC area to the internal standard GC area.

Most of the new response factors changed somewhere between 10 and 15%. To explain what this means in terms of product analysis, consider acrylic acid as an example. The new response factor is approximately 10% lower than the old. A concentration or yield calculated with the old response factor for acrylic acid would be 10% higher than with the new. The new response factors are probably more reliable than the old factors because solutions containing all reaction products together are similar to our reaction product mixtures.

In order to determine if our analysis procedure was correct, we attempted to recreate a reaction product by adding known quantities of products to a lactic acid solution. Our rationale for doing this was to determine if the mass balance would be correct if a known product solution was run through the system. This test consisted of creating a reaction product solution, from standards, which simulated the product from one of our experimental runs. This liquid pseudo-product was run through the gas chromatograph and analyzed. Gas product concentrations were calculated based on the liquid product concentrations and a lactic acid feed concentration was calculated based on the total carbon content of the pseudo-liquid and gas products.

Two previous runs were simulated; they were the 280°C and 320°C runs of Na_2HAsO_4 supported on Spherosil XOC 005. Only the major reaction products were simulated (acetaldehyde, acrylic acid, 2,3-pentanedione, hydroxyacetone and lactic acid). Table 7.3 shows the results of our study. The run at 320°C was performed twice due to the unacceptable carbon error found in the first run due to incorrect product concentration calculations. Hydroxyacetone was not included as a product for the second run. If our analysis procedure is exact, we would expect all GC calculated concentrations to be correct and there would be no carbon mass balance errors. One of the larger contributors to the carbon error is probably the lactic acid GC peak. Lactic acid is not very volatile and therefore, may be held up in our GC column. Since our conversion calculation is based on this peak, any errors would result in a carbon balance error. Carbon balance errors of 1-10% are very common and can be considered to be within experimental limits. Overall, this test went well and it suggests that our methods of data analysis are adequate for the scope of our studies.

Mass balance closure has been a problem in the past and a great deal of time was spent minimizing this problem. Overall, mass balances improved very much over the course of the study. Recovery of 85 to 105% of the carbon introduced to the reactor has become the normal expectation of our system at reaction temperatures below 320°C. However, there are exceptions to this general rule. For instance, in many

Table 7.3 - Pseudo-Run Results

RESULTS	280°C NaHAsO4	320°C NaHAsO4 (1)	320°C NaHAsO4 (2)
ACRYLIC ACID YIELD (%)	3.46	12.36	20.48
2,3-PENTANEDIONE YIELD (%)	11.04	18.21	34.53
ACETALDEHYDE YIELD (%)	2.56	11.02	14.44
ACETOL YIELD (%)	0.85	13.63	0.00
CONVERSION (%)	24.48	74.18	71.51
% CARBON ERROR	-3.74	-16.09	-7.83

experimental runs, a trend can be seen which implies that mass balances become worse as the reaction conversion increases and Table 7.4 shows this trend very well. The example used here is a $NaNO_3$/silica catalyst run under short residence time

Table 7.4 - Carbon Error Trends

TEMPERATURE (C)	CONVERSION (%)	CARBON ERROR (%)
280	17.22	3.82
300	37.94	6.43
320	63.94	19.68
350	91.94	26.95

operating conditions (Table 1.3). High reaction temperatures usually exhibit the greatest mass balance errors. The elevated mass balance errors are probably a result of a process or processes which more readily occur at higher reaction temperatures.

7.2 MECHANISTIC CONSIDERATIONS

The microporosity of the supports used during our study seems to have been very important in determining product

selectivity and mass balance closure. Supports that possessed a more microporous structure seemed to form selectively more acetaldehyde and these supports also gave the poorest carbon recoveries. These are findings which seem to suggest that lactic acid cracking is taking place. For our studies, supports which do not exhibit extensive microporosity are recommended.

Experimental runs produced carbon monoxide and carbon dioxide gas reaction products. As Figure 1.1 depicts, CO_2 is produced in the decarboxylation and condensation reactions of lactic acid while CO is produced in its decarbonylation. Production of CO, in our studies, is theoretically accompanied by acetaldehyde production. CO_2 can be accompanied by the production of acetaldehyde through decarboxylation or 2,3-pentanedione through condensation. In theory, the $CO:CO_2$ ratio shows the selectivity of the reaction towards the decarbonylation pathway versus the decarboxylation/ condensation pathways. Of these, only the condensation reaction mechanism is desired, therefore, $CO:CO_2$ ratios should be less than one for good results, although the decarboxylation pathway proves that a small ratio may not always produce desired results.

7.3 CONCLUSIONS

Our studies produced a large quantity of data that contained very useful information. Although we have not yet

achieved a system which could produce 2,3-pentanedione and/or acrylic acid in high enough yields to warrant industry production, we have gone a long way in narrowing our search for a catalyst/support combination. Our study with the biomineral-derived calcium hydroxyapatite was first to show us the suppression of acetaldehyde due to a less microporous catalyst/support structure. The calcium hydroxyapatite runs with the material which had been calcined at higher temperatures showed this supression. This high calcination reduced the materials microporosity. We found also, however, that the production of the desired products was suppressed over the material calcined at the higher temperatures. Desired product yields over the calcium hydroxyapatite were not high enough to continue experimentation with them.

The carbon supports, with the exception of the charred cherry pits, showed high product selectivity towards acetaldehyde. Suppression of the acetaldehyde yield occurred over the charred cherry pits and also over Carbograph 2. Both of these materials have low surface areas and probably have little microporosity. The reaction product distribution of the charred cherry carbon was unlike the other carbon supports. Acrylic acid, hydroxyacetone, and 2,3-pentanedione yields were very competitive with acetaldehyde and propanoic acid yields. The char has approximately 4% ash content, which might have catalyzed the acrylic acid and/or 2,3-pentanedione formation.

The silica supports showed the same trend in acetaldehyde

suppression. Those supports with the lower surface areas and suspected lower microporosity suppressed the production of acetaldehyde. The Spherosil XOC 005 gave the most promising results (Chapter 5) and was used for a catalyst screening. The best results were achieved by impregnating the XOC 005 silica with Na_2HAsO_4 (Chapter 6) but it was decided to discontinue use of this catalyst due to its extreme poisonous properties. The $NaNO_3$/XOC 005 catalyst did a very good job suppressing acetaldehyde production and also showed good selectivity towards the desired products. It is recommended that a more in-depth study be done with this catalyst/support combination. This could consist of varying reaction parameters such as the loading, residence time, reactor pressure, etc.

A more complete catalyst study would be necessary in order to determine how successful our experiments were. A look at more sodium compounds and possibly calcium compounds would definitely expand our knowledge of the chemistry and may improve our results. Improvements to the reactor system would also make experiments easier to conduct. On-line reaction product analysis could minimize the time between experiments and also would give insight on catalyst deactivation. An improved liquid feed mechanism and preheated zone would ensure lactic acid vaporization prior to catalyst contact which may have been a problem during our present studies.

Overall, our study was successful and informative but there is a lot of work left to do in order to make our method

of lactic acid conversion to 2,3-pentanedione and/or acrylic acid marketable.

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APPENDIX

PORE SIZE DISTRIBUTION - HYDROXYAPATITE

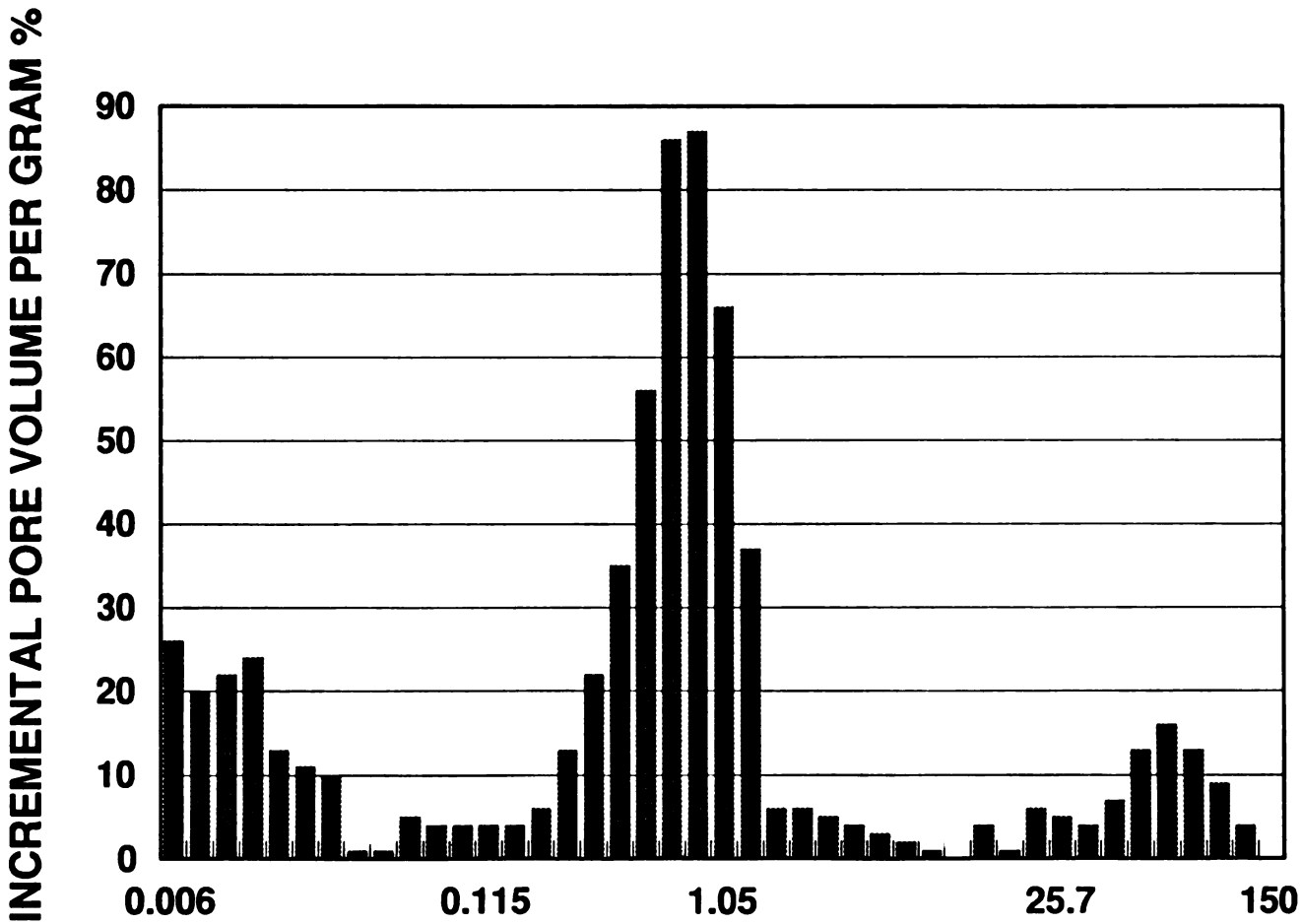

Figure A.1 - Pore Distribution 300C

PORE SIZE DISTRIBUTION - HYDROXYAPATITE

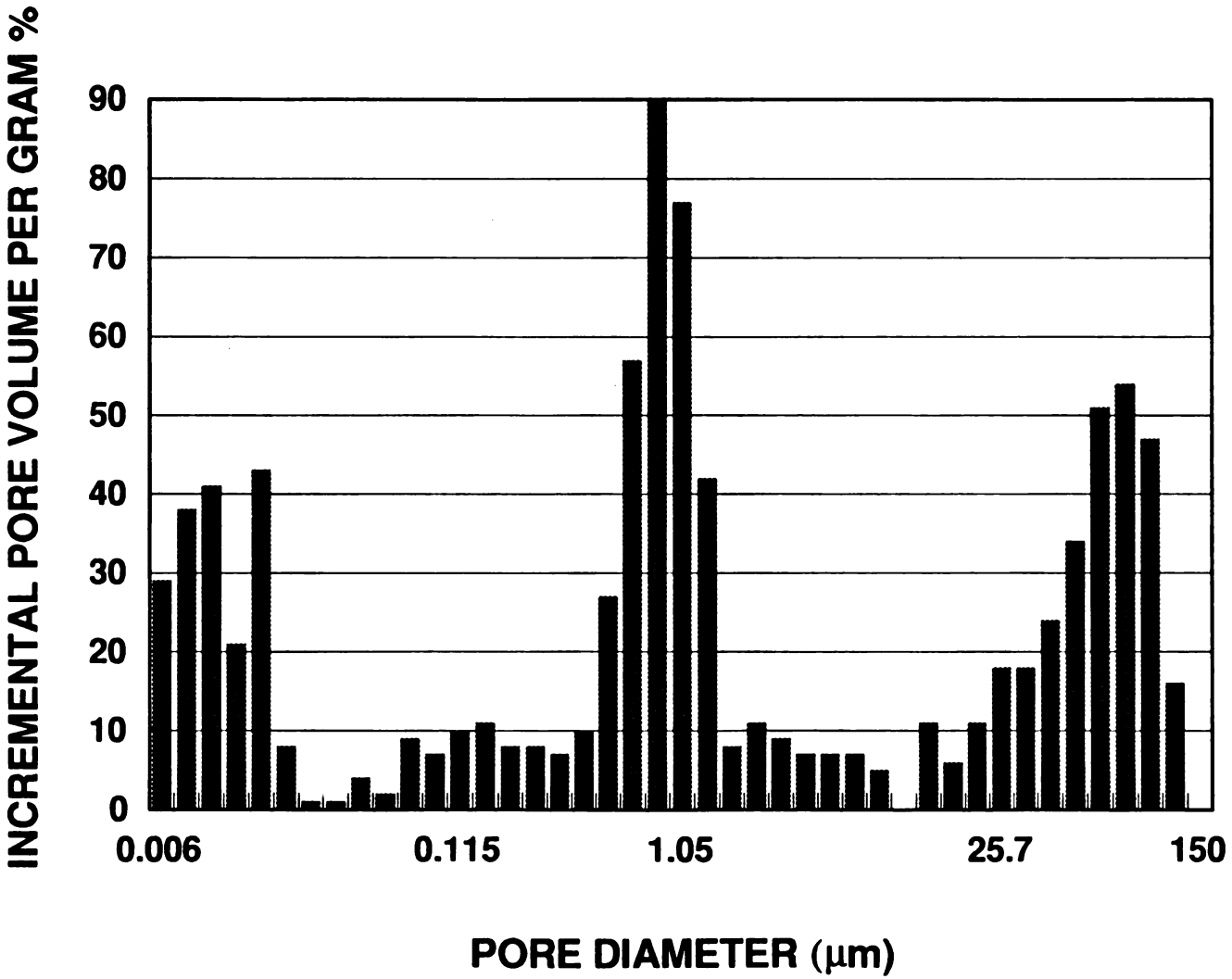

Figure A.2 - Pore Distribution 325C

PORE SIZE DISTRIBUTION - HYDROXYAPATITE

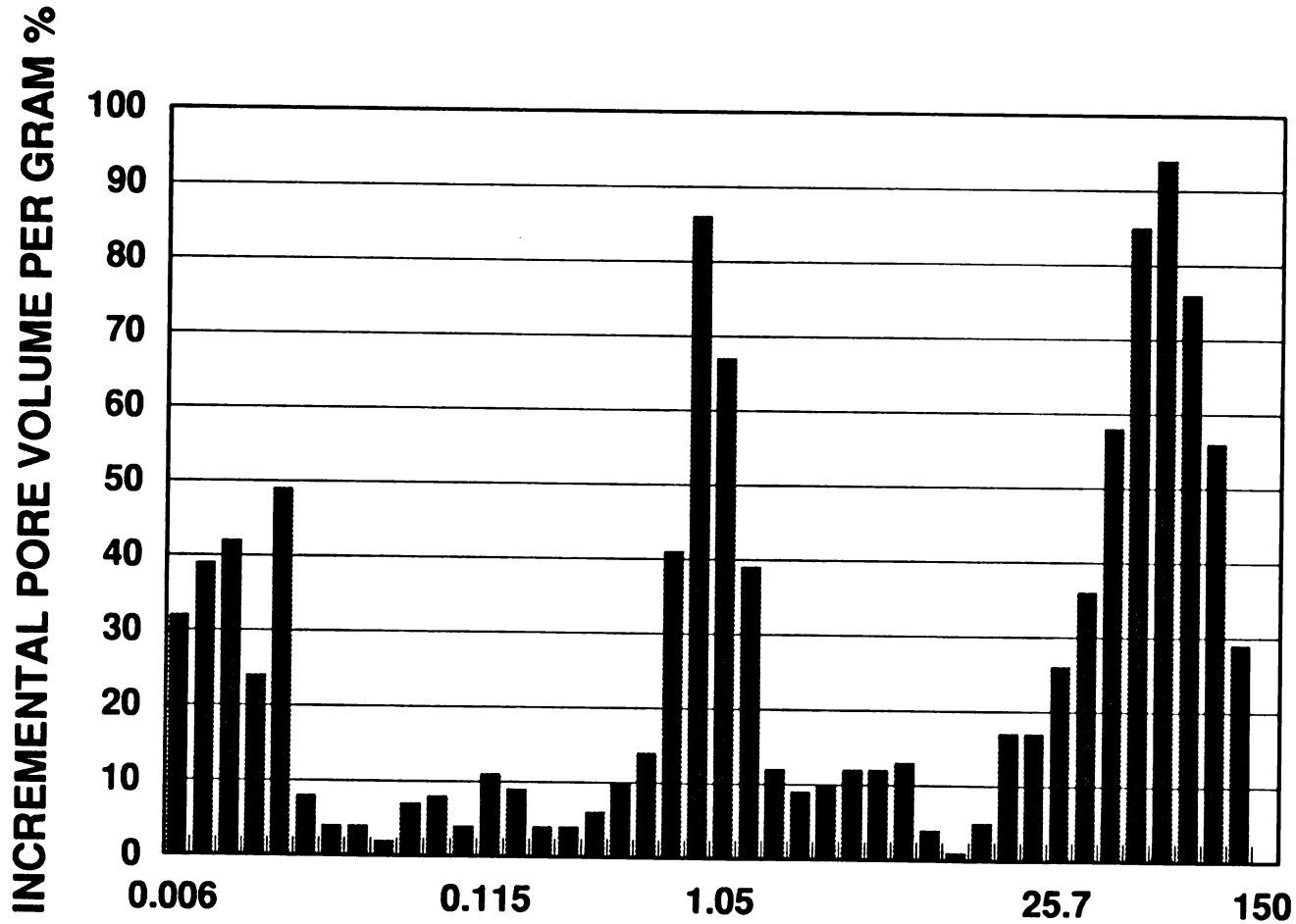

Figure A.3 - Pore Distribution 400C

PORE SIZE DISTRIBUTION - HYDROXYAPATITE

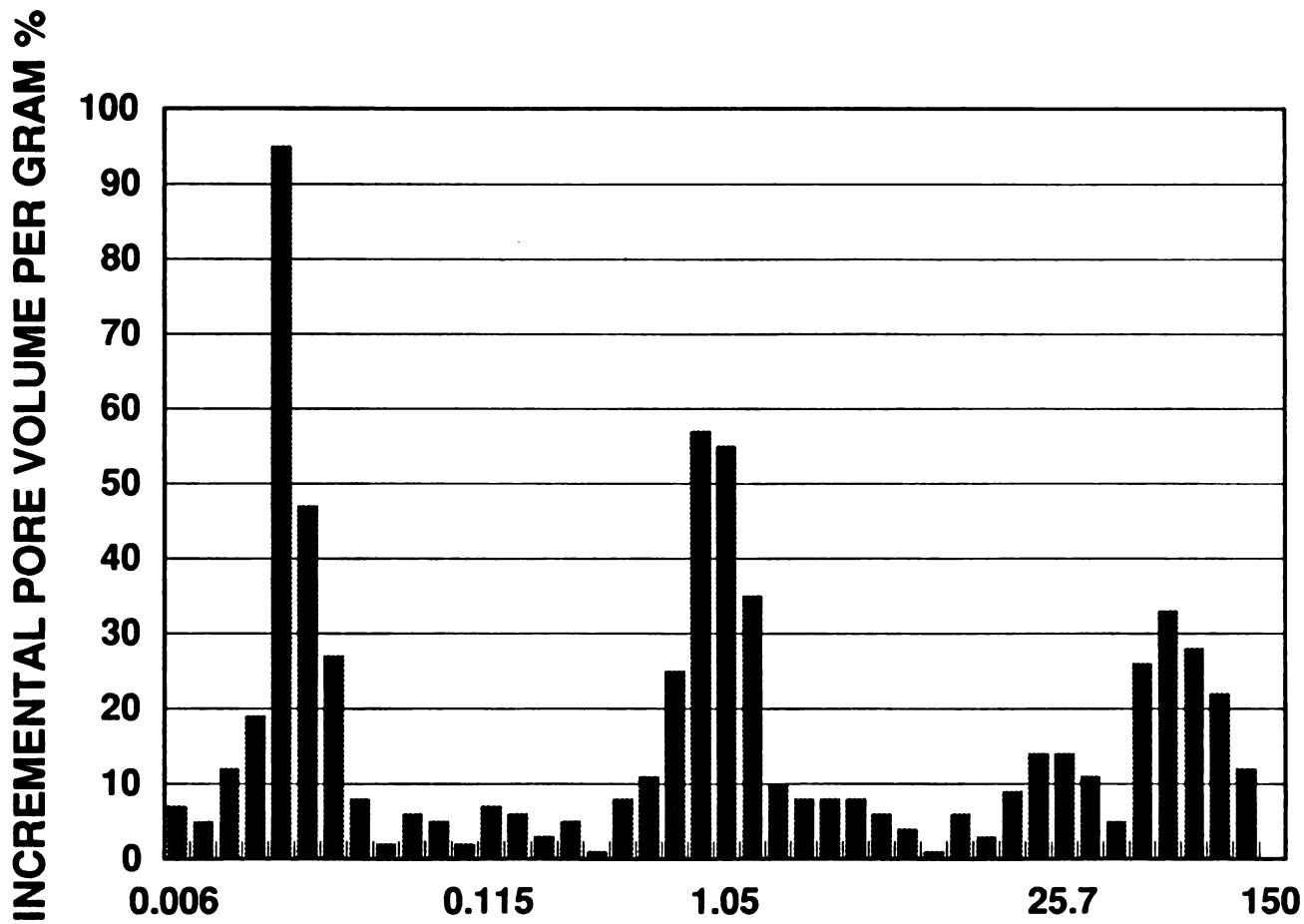

Figure A.4 - Pore Distribution 600C

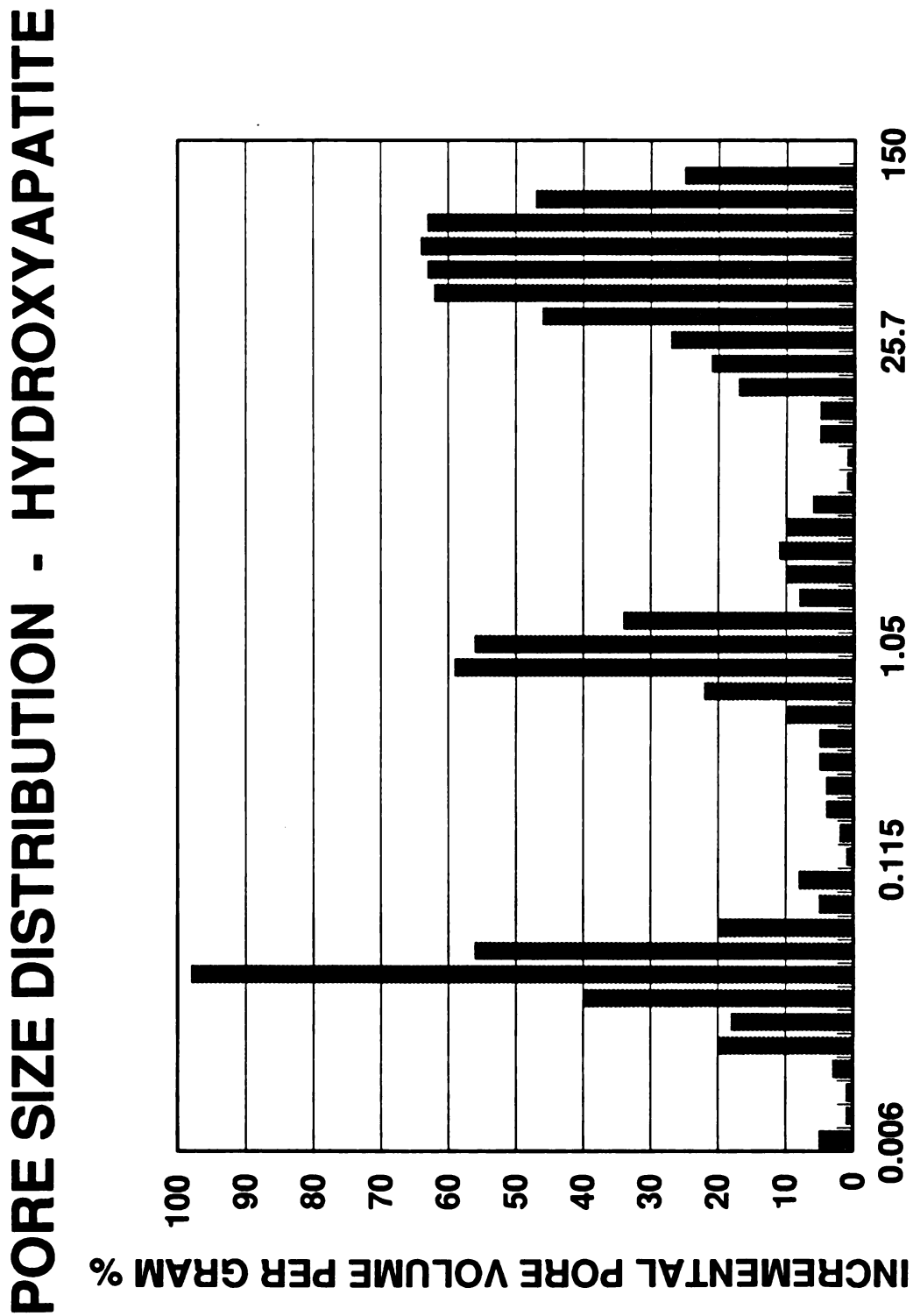

Figure A.5 - Pore Distribution 700C

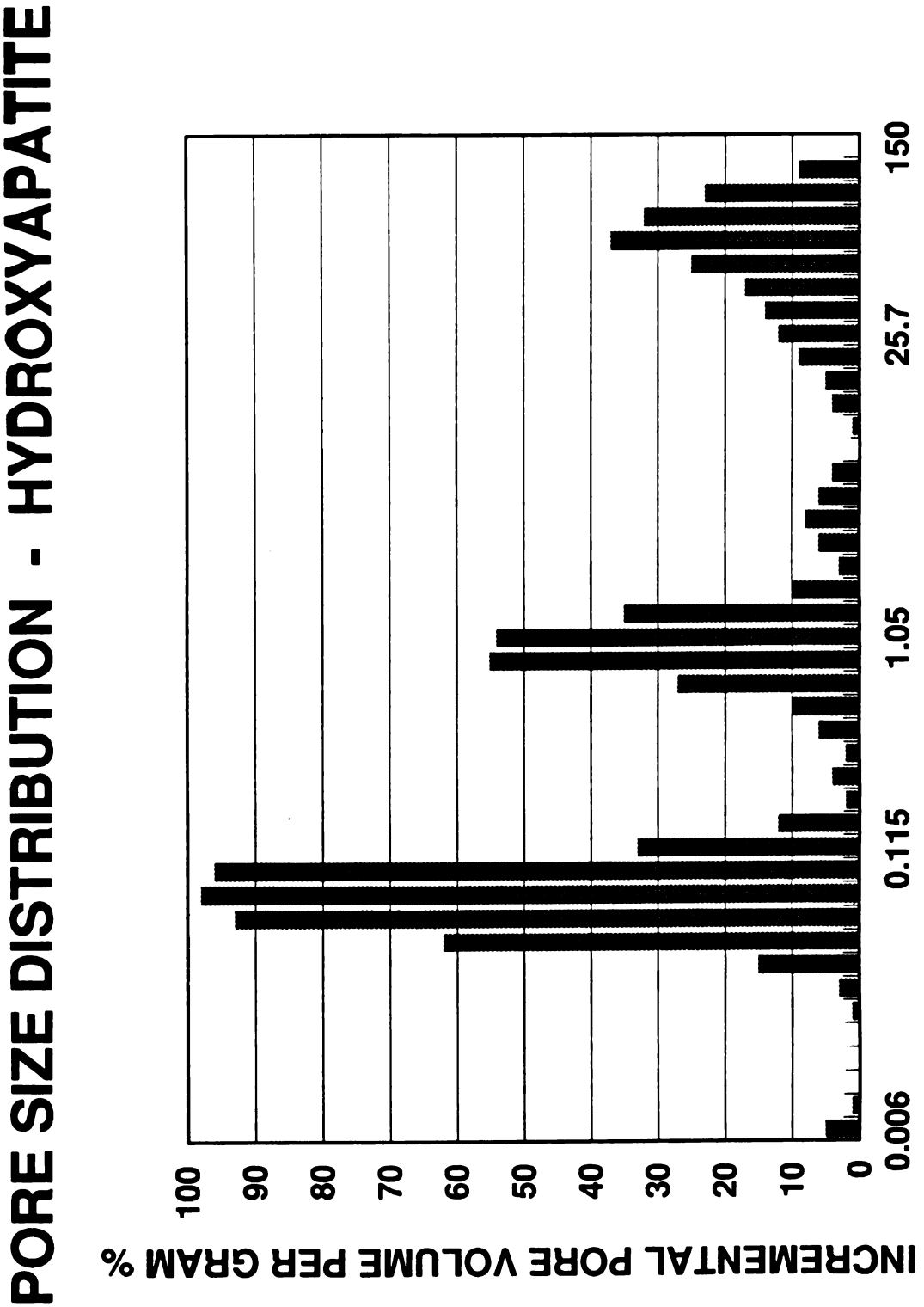

Figure A.6 - Pore Distribution 800C

Table A.1 - Results for Calcium Hydroxyapatite calcined at 300°C

	A	B	C	D	E	F	G
127	REPORT						
128			Date	05/01/92	05/01/92	05/01/92	05/01/92
129			Update	06/02/93	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	350.000	280.000
132			RT(s)	7.320	7.378	7.374	7.709
133			Err(%C)	-19.196	-1.312	-30.248	-25.497
134			Conv(BOF)	31.285	35.809	77.602	72.126
135			Yld BOF(%)				
136			Acryl	1.522	8.469	14.795	2.068
137			Prop	1.000	1.939	9.013	4.406
138			23P	1.403	2.381	.468	3.998
139			Acetal	2.341	7.027	13.875	26.143
140			Oth	1.943	8.129	8.762	3.827
141			Unknown	4.763	9.670	4.181	14.351
142			Unacct	18.314	-1.806	26.507	17.334
143			CO*	.390	.870	4.308	4.536
144			CO2*	1.951	2.805	5.946	4.012
145			Yld BOC(%)				
146			Acryl	4.863	23.650	19.066	2.867
147			Prop	3.195	5.414	11.614	6.109
148			23P	4.485	6.650	.603	5.542
149			Acetal	7.484	19.625	17.880	36.246
150			Oth	6.211	22.701	11.291	5.305
151			Unknown	15.223	27.003	5.388	19.897
152			Unacct	58.538	-5.042	34.158	24.033
153			CO*	1.247	2.429	5.552	6.289
154			CO2*	6.237	7.833	7.662	5.563
155			AcrPth	8.058	29.064	30.680	8.976
156			Acr/Pth	60.352	81.374	62.144	31.942

Table A.2 - Results for Calcium Hydroxyapatite calcined at 400°C

	A	B	C	D	E	F	G
127	REPORT						
128			Date	05/14/92	05/14/92	05/14/92	05/14/92
129			Update	06/02/93	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000	280.000
132			RT(s)	4.416	4.385	4.261	4.501
133			Err(%C)	-13.393	-5.148	-8.583	-13.295
134			Conv(BOF)	20.493	19.319	43.073	19.706
135			Yld BOF(%)				
136			Acryl	2.325	5.909	17.152	2.801
137			Prop	.394	.762	1.880	.447
138			23P	1.181	1.550	1.729	.637
139			Acetal	2.161	4.483	9.627	1.155
140			Oth	1.237	1.894	3.970	1.196
141			Unknown	.000	.000	1.063	.000
142			Unacct	13.196	4.721	7.651	13.470
143			CO*	.621	2.196	4.690	.552
144			CO2*	2.054	2.180	4.152	1.825
145			Yld BOC(%)				
146			Acryl	11.346	30.587	39.822	14.215
147			Prop	1.921	3.944	4.364	2.267
148			23P	5.763	8.023	4.015	3.233
149			Acetal	10.543	23.203	22.350	5.862
150			Oth	6.036	9.804	9.218	6.068
151			Unknown	.000	.000	2.468	.000
152			Unacct	64.390	24.440	17.764	68.355
153			CO*	3.030	11.367	10.889	2.801
154			CO2*	10.021	11.282	9.640	9.263
155			AcrPth	13.267	34.531	44.186	16.482
156			Acr/Pth	85.520	88.578	90.123	86.244

Table A.3 - Results for Calcium Hydroxyapatite calcined at 500°C

	A	B	C	D	E	F	G
127	REPORT						
128			Date	05/18/92	05/18/92	05/18/92	05/18/92
129			Update	06/02/93	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000	280.000
132			RT(s)	5.544	5.304	5.069	5.450
133			Err(%C)	-.658	-13.073	-29.191	-6.437
134			Conv(BOF)	3.645	19.820	43.516	10.459
135			Yld BOF(%)				
136			Acryl	1.389	3.701	8.621	2.074
137			Prop	.000	.191	.300	.000
138			23P	.529	.562	.656	.327
139			Acetal	1.106	1.261	2.599	.575
140			Oth	.000	1.071	1.434	.000
141			Unknown	.000	.000	.000	.000
142			Unacct	.621	13.035	29.906	7.483
143			CO*	.583	1.022	1.885	.591
144			CO2*	.675	.705	3.461	3.282
145			Yld BOC(%)				
146			Acryl	38.110	18.675	19.811	19.834
147			Prop	.000	.962	.690	.000
148			23P	14.515	2.835	1.508	3.126
149			Acetal	30.346	6.361	5.972	5.498
150			Oth	.000	5.402	3.295	.000
151			Unknown	.000	.000	.000	.000
152			Unacct	17.029	65.765	68.723	71.542
153			CO*	15.993	5.157	4.333	5.653
154			CO2*	18.514	3.557	7.953	31.384
155			AcrPth	38.110	19.637	20.501	19.834
156			Acr/Pth	100.000	95.100	96.634	100.000

Table A.4 - Results for Calcium Hydroxyapatite calcined at 600°C

	A	B	C	D	E	F	G
127	REPORT						
128			Date	05/28/92	05/28/92	05/28/92	05/28/92
129			Update	06/02/93	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000	280.000
132			RT(s)	5.476	5.447	5.237	5.500
133			Err(%C)	3.245	-2.790	-20.961	-3.398
134			Conv(BOF)	1.046	11.327	37.950	7.870
135			Yld BOF(%)				
136			Acryl	1.154	3.142	7.130	2.017
137			Prop	.000	.182	.396	.000
138			23P	.487	1.103	1.478	.546
139			Acetal	.710	1.702	4.335	.638
140			Oth	2.386	2.133	3.027	1.219
141			Unknown	.000	.000	.000	.000
142			Unacct	-3.691	3.066	21.584	3.450
143			CO*	.936	1.841	4.454	.798
144			CO2*	1.064	2.379	3.865	.908
145			Yld BOC(%)				
146			Acryl	110.309	27.737	18.788	25.625
147			Prop	.000	1.603	1.043	.000
148			23P	46.541	9.736	3.894	6.942
149			Acetal	67.874	15.030	11.424	8.113
150			Oth	228.077	18.827	7.977	15.484
151			Unknown	.000	.000	.000	.000
152			Unacct	-352.801	27.067	56.874	43.836
153			CO*	89.479	16.252	11.738	10.144
154			CO2*	101.719	21.001	10.185	11.531
155			AcrPth	110.309	29.341	19.831	25.625
156			Acr/Pth	100.000	94.535	94.742	100.000

Table A.5 - Results for Calcium Hydroxyapatite calcined at 700°C

	A	B	C	D	E	F	G
127	REPORT						
128			Date	05/19/92	05/19/92	05/19/92	05/19/92
129			Update	06/02/93	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000	280.000
132			RT(s)	5.199	5.255	5.255	5.533
133			Err(%C)	2.705	-3.303	-19.216	-6.457
134			Conv(BOF)	.355	10.928	35.177	10.076
135			Yld BOF(%)				
136			Acryl	.929	2.361	6.006	1.275
137			Prop	.000	.249	.569	.000
138			23P	1.132	1.756	2.726	.911
139			Acetal	.729	1.280	3.513	.406
140			Oth	.000	1.221	2.716	.672
141			Unknown	.000	.000	.000	.000
142			Unacct	-2.435	4.062	19.648	6.810
143			CO*	.779	1.163	2.098	.712
144			CO2*	1.326	3.271	4.407	1.210
145			Yld BOC(%)				
146			Acryl	261.600	21.605	17.073	12.657
147			Prop	.000	2.279	1.616	.000
148			23P	318.469	16.070	7.751	9.043
149			Acetal	205.194	11.710	9.985	4.034
150			Oth	.000	11.169	7.722	6.673
151			Unknown	.000	.000	.000	.000
152			Unacct	-685.263	37.167	55.853	67.593
153			CO*	219.336	10.642	5.963	7.062
154			CO2*	373.062	29.935	12.527	12.011
155			AcrPth	261.600	23.884	18.690	12.657
156			Acr/Pth	100.000	90.457	91.353	100.000

Table A.6 - Results for Calcium Hydroxyapatite calcined at 800°C

	A	B	C	D	E	F	G
127	REPORT						
128			Date	05/08/92	05/08/92	05/08/92	05/08/92
129			Update	10/25/92	10/25/92	10/25/92	10/25/92
130			Cat.	Teeth	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000	280.000
132			RT(s)	5.042	4.941	4.731	4.944
133			Err(%C)	-1.727	-3.476	-15.560	-7.369
134			Conv(BOF)	4.447	9.678	31.976	11.185
135			Yld BOF(%)				
136			Acryl	.557	1.378	3.714	.725
137			Prop	.252	.742	2.511	.605
138			23P	.706	1.643	2.855	.757
139			Acetal	.718	1.443	4.159	1.146
140			Oth	.446	1.351	3.059	.634
141			Unknown	.000	.000	.000	.000
142			Unacct	1.769	3.121	15.678	7.319
143			CO*	.762	.727	2.139	.636
144			CO2*	.882	.811	4.308	.737
145			Yld BOC(%)				
146			Acryl	12.519	14.243	11.615	6.478
147			Prop	5.673	7.667	7.854	5.412
148			23P	15.872	16.978	8.928	6.765
149			Acetal	16.137	14.908	13.007	10.244
150			Oth	10.020	13.959	9.567	5.668
151			Unknown	.000	.000	.000	.000
152			Unacct	39.779	32.246	49.030	65.434
153			CO*	17.125	7.514	6.689	5.689
154			CO2*	19.834	8.377	13.474	6.589
155			AcrPth	18.192	21.910	19.469	11.890
156			Acr/Pth	68.817	65.007	59.660	54.481

Table A.7 - Results for Calcium Hydroxyapatite 10 x 16 mesh particle size

	A	B	C	D	E	F
127	REPORT					
128			Date	09/16/92	09/16/92	09/16/92
129			Update	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000
132			RT(s)	6.679	6.406	6.232
133			Err(%C)	.278	5.556	-13.657
134			Conv(BOF)	24.517	34.829	74.316
135			Yld BOF(%)			
136			Acryl	2.960	8.865	23.140
137			Prop	2.211	2.589	4.106
138			23P	1.847	2.903	2.050
139			Acetal	4.959	9.883	17.222
140			Oth	1.245	2.487	3.519
141			Unknown	12.913	15.698	12.166
142			Unacct	-1.619	-7.596	12.112
143			CO*	1.106	2.720	8.729
144			CO2*	2.023	4.402	8.422
145			Yld BOC(%)			
146			Acryl	12.074	25.454	31.138
147			Prop	9.020	7.434	5.525
148			23P	7.534	8.335	2.758
149			Acetal	20.228	28.377	23.174
150			Oth	5.079	7.140	4.735
151			Unknown	52.670	45.070	16.371
152			Unacct	-6.605	-21.810	16.299
153			CO*	4.510	7.810	11.746
154			CO2*	8.253	12.637	11.332
155			AcrPth	21.094	32.888	36.663
156			Acr/Pth	57.238	77.395	84.930

Table A.8 - Results for Calcium Hydroxyapatite
16 x 30 mesh particle size

	A	B	C	D	E	F
127	REPORT					
128			Date	9/22/92	9/22/92	9/22/92
129			Update	06/02/93	06/02/93	06/02/93
130			Cat.	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000
132			RT(s)	5.629	5.781	5.500
133			Err(%C)	-9.447	6.864	3.397
134			Conv(BOF)	28.935	23.591	51.219
135			Yld BOF(%)			
136			Acryl	2.627	7.164	22.146
137			Prop	1.016	1.251	2.597
138			23P	2.800	3.197	3.230
139			Acetal	4.180	6.917	12.443
140			Oth	.860	2.496	4.725
141			Unknown	8.613	6.243	9.840
142			Unacct	8.840	-3.678	-3.762
143			CO*	1.415	10.112	7.745
144			CO2*	3.616	9.455	8.330
145			Yld BOC(%)			
146			Acryl	9.078	30.368	43.237
147			Prop	3.512	5.305	5.070
148			23P	9.677	13.553	6.307
149			Acetal	14.445	29.319	24.294
150			Oth	2.972	10.582	9.224
151			Unknown	29.766	26.464	19.212
152			Unacct	30.550	-15.591	-7.344
153			CO*	4.890	42.865	15.121
154			CO2*	12.496	40.080	16.263
155			AcrPth	12.590	35.673	48.307
156			Acr/Pth	72.106	85.130	89.505

Table A.9 - Results for Calcium Hydroxyapatite
30 x 60 mesh particle size

	A	B	C	D	E	F
127	REPORT					
128			Date	9/29/92	9/29/92	9/29/92
129			Update	10/20/92	10/20/92	10/20/92
130			Cat.	Teeth	Teeth	Teeth
131			T(C)	280.000	300.000	320.000
132			RT(s)	5.150	5.486	5.378
133			Err(%C)	-1.525	-.376	-2.324
134			Conv(BOF)	17.653	29.767	48.946
135			Yld BOF(%)			
136			Acryl	1.998	6.062	17.900
137			Prop	.887	1.215	2.099
138			23P	2.117	3.147	3.234
139			Acetal	2.654	4.242	9.348
140			Oth	.841	2.761	5.638
141			Unknown	8.023	12.027	10.262
142			Unacct	1.134	.312	.466
143			CO*	1.063	2.671	3.386
144			CO2*	2.335	4.809	4.673
145			Yld BOC(%)			
146			Acryl	11.317	20.366	36.570
147			Prop	5.023	4.082	4.288
148			23P	11.991	10.573	6.608
149			Acetal	15.031	14.251	19.098
150			Oth	4.762	9.276	11.519
151			Unknown	45.451	40.405	20.965
152			Unacct	6.425	1.047	.952
153			CO*	6.024	8.972	6.917
154			CO2*	13.229	16.155	9.547
155			AcrPth	16.340	24.448	40.858
156			Acr/Pth	69.259	83.303	89.506

Table A.10 - Results for Strem Activated Carbon

	A	B	C	D	E	F	G
127	REPORT						
128			Date	11/17/92	11/17/92	11/17/92	11/17/92
129			Update	02/17/93	02/17/93	02/17/93	02/17/93
130			Cat.	Carbon	Carbon	Carbon	Carbon
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	6.202	5.980	5.829	5.500
133			Err(%C)	-2.249	-36.755	-30.120	-32.155
134			Conv(BOF)	82.437	85.861	94.672	94.571
135			Yld BOF(%)				
136			Acryl	.279	.840	.399	.397
137			Prop	20.593	10.599	14.186	15.383
138			23P	.000	.606	.274	.251
139			Acetal	41.588	17.366	30.925	22.427
140			Oth	7.940	6.199	8.341	9.210
141			Unknown	8.239	5.686	6.373	6.962
142			Unacct	3.799	44.566	34.174	39.942
143			CO*	33.805	27.427	29.325	30.844
144			CO2*	21.364	20.649	24.370	28.167
145			Yld BOC(%)				
146			Acryl	.338	.978	.421	.420
147			Prop	24.980	12.344	14.985	16.266
148			23P	.000	.706	.289	.266
149			Acetal	50.448	20.226	32.666	23.714
150			Oth	9.631	7.220	8.810	9.738
151			Unknown	9.994	6.623	6.732	7.361
152			Unacct	4.608	51.904	36.097	42.234
153			CO*	41.007	31.943	30.975	32.615
154			CO2*	25.916	24.049	25.742	29.784
155			AcrPth	25.318	13.322	15.406	16.686
156			Acr/Pth	1.337	7.340	2.734	2.517

Table A.11 - Results for Na_3PO_4 on Strem Carbon

	A	B	C	D	E	F	G
127	REPORT						
128			Date	11/24/92	11/24/92	11/24/92	11/24/92
129			Update	12/02/92	12/02/92	12/02/92	12/02/92
130			Cat.	Na3PO4	Na3PO4	Na3PO4	Na3PO4
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	5.837	5.578	5.774	5.484
133			Err(%C)	-1.769	-13.749	-21.358	-26.961
134			Conv(BOF)	52.812	77.881	87.422	96.306
135			Yld BOF(%)				
136			Acryl	.872	1.386	1.363	.244
137			Prop	16.486	22.132	27.027	23.510
138			23P	.114	.142	.315	.290
139			Acetal	14.159	13.234	12.459	20.253
140			Oth	5.382	7.063	7.496	7.635
141			Unknown	8.825	8.854	7.957	6.626
142			Unacct	6.973	25.071	30.806	37.749
143			CO*	12.439	20.144	15.727	23.221
144			CO2*	21.619	33.306	33.400	40.154
145			Yld BOC(%)				
146			Acryl	1.651	1.779	1.559	.253
147			Prop	31.217	28.417	30.915	24.412
148			23P	.216	.183	.361	.301
149			Acetal	26.811	16.992	14.252	21.030
150			Oth	10.191	9.068	8.574	7.928
151			Unknown	16.710	11.369	9.102	6.880
152			Unacct	13.204	32.191	35.238	39.197
153			CO*	23.554	25.865	17.989	24.111
154			CO2*	40.937	42.765	38.205	41.694
155			AcrPth	32.868	30.196	32.474	24.665
156			Acr/Pth	5.023	5.891	4.799	1.026

Table A.12 - Results for the Activated Cherry Carbon

	A	B	C	D	E	F
127	REPORT					
128			Date	1/14/93	1/14/93	1/14/93
129			Update	02/17/93	02/17/93	02/17/93
130			Cat.	cherry	cherry	cherry
131			T(C)	280.000	300.000	320.000
132			RT(s)	6.033	5.864	5.539
133			Err(%C)	-17.324	-31.981	-30.454
134			Conv(BOF)	83.370	86.262	83.999
135			Yld BOF(%)			
136			Acryl	.437	.635	.826
137			Prop	7.253	6.199	8.622
138			23P	.781	.541	.554
139			Acetal	34.219	25.145	23.494
140			Oth	3.320	3.694	5.321
141			Unknown	8.233	7.136	8.893
142			Unacct	29.127	42.913	36.289
143			CO*	52.287	45.859	27.656
144			CO2*	22.097	16.971	19.708
145			Yld BOC(%)			
146			Acryl	.524	.737	.984
147			Prop	8.699	7.186	10.264
148			23P	.936	.627	.660
149			Acetal	41.045	29.150	27.969
150			Oth	3.983	4.282	6.335
151			Unknown	9.875	8.272	10.587
152			Unacct	34.938	49.747	43.201
153			CO*	62.717	53.163	32.924
154			CO2*	26.504	19.674	23.463
155			AcrPth	9.223	7.922	11.248
156			Acr/Pth	5.681	9.297	8.747

Table A.13 - Results for the Charred Cherry Pits

	A	B	C	D	E	F	G
127	REPORT						
128			Date	01/26/93	01/26/93	01/26/93	01/26/93
129			Update	02/17/93	02/17/93	02/17/93	02/17/93
130			Cat.	Carbon	Carbon	Carbon	Carbon
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	5.610	5.499	5.432	5.152
133			Err(%C)	-33.255	-4.911	-22.859	-28.797
134			Conv(BOF)	58.199	38.509	75.455	92.511
135			Yld BOF(%)				
136			Acryl	.995	3.099	6.615	3.976
137			Prop	3.156	4.638	9.303	14.365
138			23P	1.868	7.987	7.763	2.851
139			Acetal	3.310	4.191	5.016	9.401
140			Oth	2.227	3.725	6.325	6.954
141			Unknown	8.274	6.374	8.866	14.893
142			Unacct	38.368	8.494	31.567	40.071
143			CO*	5.353	1.011	4.037	8.124
144			CO2*	16.458	19.541	32.749	41.387
145			Yld BOC(%)				
146			Acryl	1.710	8.048	8.766	4.298
147			Prop	5.423	12.045	12.329	15.528
148			23P	3.210	20.741	10.288	3.081
149			Acetal	5.688	10.883	6.648	10.162
150			Oth	3.827	9.674	8.382	7.517
151			Unknown	14.216	16.552	11.750	16.099
152			Unacct	65.925	22.057	41.836	43.315
153			CO*	9.199	2.626	5.350	8.782
154			CO2*	28.278	50.745	43.402	44.737
155			AcrPth	7.134	20.093	21.095	19.826
156			Acr/Pth	23.976	40.055	41.556	21.679

Table A.14 - Results for Na_3PO_4 on the Cherry Char

	A	B	C	D	E	F	G
127	REPORT						
128			Date	02/04/93	02/04/93	02/04/93	02/04/93
129			Update	02/05/93	02/05/93	02/05/93	02/05/93
130			Cat.	Na3PO4	Na3PO4	Na3PO4	Na3PO4
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	8.212	8.030	7.881	7.666
133			Err(%C)	-19.095	-14.590	-16.433	-25.271
134			Conv(BOF)	44.344	63.099	80.475	92.298
135			Yld BOF(%)				
136			Acryl	2.382	6.856	12.542	9.768
137			Prop	1.991	2.715	5.750	10.958
138			23P	1.688	7.041	8.847	3.661
139			Acetal	1.689	4.351	4.741	7.380
140			Oth	1.461	4.577	8.212	6.574
141			Unknown	13.818	16.273	8.809	11.018
142			Unacct	21.315	21.286	31.573	42.938
143			CO*	.836	2.787	7.780	9.740
144			CO2*	8.814	26.195	47.833	54.896
145			Yld BOC(%)				
146			Acryl	5.371	10.866	15.585	10.583
147			Prop	4.491	4.302	7.146	11.873
148			23P	3.806	11.158	10.994	3.966
149			Acetal	3.808	6.895	5.891	7.996
150			Oth	3.296	7.254	10.204	7.123
151			Unknown	31.161	25.790	10.947	11.938
152			Unacct	48.067	33.734	39.233	46.521
153			CO*	1.886	4.417	9.667	10.553
154			CO2*	19.876	41.514	59.438	59.477
155			AcrPth	9.862	15.168	22.731	22.456
156			Acr/Pth	54.464	71.636	68.564	47.128

Table A.15 - Results for Carbograph 1

	A	B	C	D	E	F	G
127	REPORT						
128			Date	02/22/93	02/22/93	02/22/93	02/22/93
129			Update	02/26/93	02/26/93	02/26/93	02/26/93
130			Cat.	carbo 1	carbo 1	carbo 1	carbo 1
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	7.329	7.135	6.967	6.789
133			Err(%C)	-.961	2.440	-12.784	-29.800
134			Conv(BOF)	13.296	22.118	48.196	75.012
135			Yld BOF(%)				
136			Acryl	.247	.324	.706	.848
137			Prop	1.152	2.085	4.319	7.511
138			23P	.000	.112	.157	.392
139			Acetal	3.373	5.938	11.993	17.400
140			Oth	.297	.459	.252	1.399
141			Unknown	2.538	9.712	12.341	5.684
142			Unacct	5.689	3.488	18.428	41.779
143			CO*	16.113	17.676	14.051	18.966
144			CO2*	1.742	6.560	15.206	36.095
145			Yld BOC(%)				
146			Acryl	1.856	1.466	1.465	1.131
147			Prop	8.662	9.428	8.961	10.013
148			23P	.000	.505	.326	.523
149			Acetal	25.368	26.849	24.883	23.196
150			Oth	2.233	2.073	.523	1.865
151			Unknown	19.092	43.910	25.606	7.577
152			Unacct	42.788	15.770	38.236	55.696
153			CO*	121.188	79.916	29.153	25.284
154			CO2*	13.101	29.660	31.551	48.118
155			AcrPth	10.518	10.894	10.426	11.144
156			Acr/Pth	17.647	13.454	14.051	10.146

Table A.16 - Results for Carbograph 2

	A	B	C	D	E	F	G
127	REPORT						
128			Date	03/03/93	03/03/93	03/03/93	03/03/93
129			Update	03/10/93	03/10/93	03/10/93	03/10/93
130			Cat.	carbo 2	carbo 2	carbo 2	carbo 2
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	6.170	5.926	5.802	5.604
133			Err(%C)	5.516	-13.649	-13.205	-7.728
134			Conv(BOF)	3.528	23.726	40.988	60.507
135			Yld BOF(%)				
136			Acryl	.540	.961	.492	.832
137			Prop	.723	1.396	3.101	10.218
138			23P	.045	.072	.167	.644
139			Acetal	2.109	2.840	5.594	16.470
140			Oth	.498	.360	2.113	7.213
141			Unknown	4.057	3.273	13.283	11.311
142			Unacct	-4.445	14.825	16.239	13.819
143			CO*	2.993	3.717	5.957	10.195
144			CO2*	2.848	3.047	9.627	27.739
145			Yld BOC(%)				
146			Acryl	15.307	4.049	1.199	1.376
147			Prop	20.504	5.883	7.566	16.887
148			23P	1.272	.304	.406	1.064
149			Acetal	59.777	11.972	13.648	27.219
150			Oth	14.122	1.516	5.155	11.921
151			Unknown	115.003	13.795	32.407	18.694
152			Unacct	-125.985	62.482	39.619	22.839
153			CO*	84.845	15.667	14.533	16.850
154			CO2*	80.734	12.843	23.488	45.844
155			AcrPth	35.811	9.932	8.765	18.262
156			Acr/Pth	42.745	40.765	13.682	7.533

Table A.17 - Results for the 1 mm diameter glass beads

	A	B	C	D	E	F
127	REPORT					
128			Date	10/08/92	10/08/92	10/08/92
129			Update	10/21/92	10/21/92	10/21/92
130			Cat.	Glass	Glass	Glass
131			T(C)	280.000	300.000	320.000
132			RT(s)	5.523	5.469	5.405
133			Err(%C)	1.242	-1.922	4.512
134			Conv(BOF)	5.094	10.054	11.048
135			Yld BOF(%)			
136			Acryl	.227	.753	2.316
137			Prop	.582	.850	1.518
138			23P	.314	.853	2.255
139			Acetal	.380	1.009	2.287
140			Oth	.000	.000	1.446
141			Unknown	4.633	4.446	5.607
142			Unacct	-1.042	2.143	-4.380
143			CO*	.252	.440	.868
144			CO2*	.886	1.658	2.942
145			Yld BOC(%)			
146			Acryl	4.447	7.492	20.959
147			Prop	11.426	8.457	13.735
148			23P	6.160	8.483	20.407
149			Acetal	7.466	10.034	20.703
150			Oth	.000	.000	13.090
151			Unknown	90.954	44.223	50.753
152			Unacct	-20.454	21.311	-39.648
153			CO*	4.953	4.380	7.861
154			CO2*	17.400	16.489	26.631
155			AcrPth	15.874	15.949	34.695
156			Acr/Pth	28.017	46.973	60.411

Table A.18 - Results for the Silica Gel

	A	B	C	D	E	F	G
127	REPORT						
128			Date	12/12/92	12/12/92	12/12/92	12/12/92
129			Update	02/17/93	02/17/93	02/17/93	02/17/93
130			Cat.	Silica	Silica	Silica	Silica
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	5.892	5.757	5.690	5.418
133			Err(%C)	-22.378	-17.386	-33.331	-31.731
134			Conv(BOF)	41.559	40.296	64.767	87.179
135			Yld BOF(%)				
136			Acryl	.340	.673	1.617	3.879
137			Prop	.894	.787	1.278	4.162
138			23P	.210	.362	.713	1.699
139			Acetal	11.736	17.808	26.247	46.516
140			Oth	.645	.234	.995	3.027
141			Unknown	4.217	3.258	2.481	2.994
142			Unacct	23.517	17.175	31.436	24.901
143			CO*	14.237	16.578	19.941	25.231
144			CO2*	1.667	1.011	2.277	5.101
145			Yld BOC(%)				
146			Acryl	.819	1.670	2.497	4.450
147			Prop	2.150	1.953	1.974	4.775
148			23P	.505	.898	1.101	1.949
149			Acetal	28.238	44.193	40.525	53.357
150			Oth	1.553	.580	1.537	3.472
151			Unknown	10.148	8.085	3.831	3.435
152			Unacct	56.587	42.621	48.537	28.563
153			CO*	34.256	41.140	30.788	28.941
154			CO2*	4.012	2.509	3.516	5.851
155			AcrPth	2.969	3.622	4.470	9.224
156			Acr/Pth	27.580	46.092	55.847	48.238

Table A.19 - Results for the Calcined Silica Gel

	A	B	C	D	E	F	G
127	REPORT						
128			Date	01/28/93	01/28/93	01/28/93	01/28/93
129			Update	02/17/93	02/17/93	02/17/93	02/17/93
130			Cat.	silica	silica	silica	silica
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	5.746	5.624	5.541	5.273
133			Err(%C)	-25.381	-19.787	.987	-28.712
134			Conv(BOF)	47.617	52.721	54.246	83.241
135			Yld BOF(%)				
136			Acryl	.329	.751	1.931	2.924
137			Prop	.544	1.345	2.808	8.388
138			23P	.423	.290	1.092	1.072
139			Acetal	17.901	25.234	37.964	22.634
140			Oth	.428	.000	2.115	5.385
141			Unknown	2.793	3.962	4.868	6.281
142			Unacct	25.200	21.139	3.468	36.556
143			CO*	15.010	25.116	45.133	32.500
144			CO2*	2.985	4.316	8.169	17.726
145			Yld BOC(%)				
146			Acryl	.692	1.425	3.559	3.512
147			Prop	1.143	2.551	5.176	10.076
148			23P	.887	.550	2.014	1.288
149			Acetal	37.593	47.862	69.985	27.191
150			Oth	.898	.000	3.899	6.469
151			Unknown	5.866	7.516	8.975	7.545
152			Unacct	52.922	40.095	6.393	43.917
153			CO*	31.523	47.639	83.200	39.043
154			CO2*	6.269	8.187	15.059	21.295
155			AcrPth	1.834	3.976	8.735	13.589
156			Acr/Pth	37.718	35.846	40.744	25.848

Table A.20 - Results for the XOA 400 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	03/06/93	03/06/93	03/06/93	03/06/93
129			Update	03/10/93	03/10/93	03/10/93	03/10/93
130			Cat.	XOA 400	XOA 400	XOA 400	XOA 400
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	8.386	7.522	7.350	7.031
133			Err(%C)	20.285	-8.311	-28.139	-33.151
134			Conv(BOF)	65.408	88.231	96.080	95.866
135			Yld BOF(%)				
136			Acryl	.155	.329	.803	.996
137			Prop	.549	1.034	2.744	7.121
138			23P	.183	.259	.305	.212
139			Acetal	67.334	61.121	54.504	34.407
140			Oth	1.809	2.422	2.824	4.426
141			Unknown	6.569	8.647	3.848	6.965
142			Unacct	-11.191	14.418	31.051	41.738
143			CO*	92.547	74.570	51.886	34.151
144			CO2*	3.252	7.081	14.128	29.996
145			Yld BOC(%)				
146			Acryl	.237	.373	.836	1.039
147			Prop	.839	1.172	2.856	7.428
148			23P	.280	.294	.317	.221
149			Acetal	102.945	69.274	56.728	35.891
150			Oth	2.766	2.745	2.940	4.617
151			Unknown	10.044	9.800	4.005	7.265
152			Unacct	-17.109	16.342	32.318	43.538
153			CO*	141.491	84.516	54.004	35.624
154			CO2*	4.971	8.025	14.705	31.290
155			AcrPth	1.076	1.545	3.693	8.468
156			Acr/Pth	22.007	24.133	22.646	12.275

Table A.21 - Results for the XOB 030 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	03/09/93	03/09/93	03/09/93	03/09/93
129			Update	03/10/93	03/10/93	03/10/93	03/10/93
130			Cat.	XOB 030	XOB 030	XOB 030	XOB 030
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	6.823	6.683	6.314	6.227
133			Err(%C)	2.455	-11.571	-26.696	-23.880
134			Conv(BOF)	13.715	37.613	63.496	88.779
135			Yld BOF(%)				
136			Acryl	.207	1.036	2.730	4.985
137			Prop	.974	1.706	4.247	11.041
138			23P	.335	.841	1.932	3.294
139			Acetal	8.462	13.356	22.950	36.013
140			Oth	.334	.308	.678	1.877
141			Unknown	3.693	7.163	4.339	6.694
142			Unacct	-.290	13.203	26.621	24.874
143			CO*	13.233	15.740	18.762	26.489
144			CO2*	2.226	3.240	5.831	16.424
145			Yld BOC(%)				
146			Acryl	1.507	2.755	4.299	5.615
147			Prop	7.103	4.536	6.688	12.437
148			23P	2.443	2.236	3.043	3.710
149			Acetal	61.704	35.508	36.144	40.565
150			Oth	2.436	.818	1.068	2.114
151			Unknown	26.924	19.045	6.833	7.541
152			Unacct	-2.117	35.102	41.925	28.018
153			CO*	96.488	41.847	29.548	29.838
154			CO2*	16.229	8.615	9.184	18.500
155			AcrPth	8.610	7.291	10.987	18.052
156			Acr/Pth	17.506	37.790	39.127	31.105

Table A.22 - Results for the XOC 005 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	03/12/93	03/12/93	03/12/93	03/12/93
129			Update	03/12/93	03/12/93	03/12/93	03/12/93
130			Cat.	XOC 005	XOC 005	XOC 005	XOC 005
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	6.585	6.268	6.072	5.917
133			Err(%C)	8.261	-5.251	-32.060	-46.973
134			Conv(BOF)	4.686	18.911	52.456	86.818
135			Yld BOF(%)				
136			Acryl	.252	.267	.794	1.682
137			Prop	.559	.453	1.767	5.782
138			23P	.099	.219	.683	1.341
139			Acetal	4.666	4.564	10.326	13.650
140			Oth	.517	.000	.649	1.654
141			Unknown	3.069	8.252	5.986	7.323
142			Unacct	-4.476	5.156	32.251	55.387
143			CO*	9.081	3.455	7.939	18.262
144			CO2*	7.507	.934	3.952	23.246
145			Yld BOC(%)				
146			Acryl	5.379	1.412	1.513	1.937
147			Prop	11.925	2.396	3.369	6.660
148			23P	2.103	1.158	1.303	1.545
149			Acetal	99.586	24.136	19.685	15.722
150			Oth	11.028	.000	1.236	1.905
151			Unknown	65.502	43.637	11.412	8.435
152			Unacct	-95.523	27.262	61.483	63.796
153			CO*	193.794	18.267	15.135	21.034
154			CO2*	160.206	4.937	7.533	26.776
155			AcrPth	17.304	3.808	4.881	8.597
156			Acr/Pth	31.085	37.086	30.990	22.531

Table A.23 - Results for the XOC 005 Silica (short residence time)

	A	B	C	D	E	F	G
127	REPORT						
128			Date	04/06/93	04/06/93	04/06/93	04/06/93
129			Update	04/07/93	04/07/93	04/07/93	04/07/93
130			Cat.	XOC 005	XOC 005	XOC 005	XOC 005
131			T(C)	280	300	320	350
132			RT(s)	1.991	1.933	1.905	1.816
133			Err(%C)	-14.793	2.680	5.500	-18.181
134			Conv(BOF)	18.838	4.056	5.150	38.954
135			Yld BOF(%				
136			Acryl	.224	.210	.288	.934
137			Prop	.377	.381	.336	.763
138			23P	.033	.138	.197	.644
139			Acetal	.588	.956	2.964	8.962
140			Oth	.436	.391	.000	.000
141			Unknown	2.407	4.479	5.877	5.097
142			Unacct	14.772	-2.501	-4.510	22.555
143			CO*	.521	1.280	4.721	19.608
144			CO2*	.458	.675	1.309	2.799
145			Yld BOC(%				
146			Acryl	1.191	5.190	5.589	2.397
147			Prop	2.004	9.391	6.518	1.958
148			23P	.176	3.406	3.821	1.653
149			Acetal	3.119	23.582	57.539	23.005
150			Oth	2.316	9.647	.000	.000
151			Unknown	12.777	110.448	114.099	13.084
152			Unacct	78.418	-61.664	-87.566	57.902
153			CO*	2.767	31.564	91.661	50.337
154			CO2*	2.430	16.635	25.424	7.185
155			AcrPth	3.194	14.581	12.107	4.355
156			Acr/Pth	37.271	35.595	46.164	55.037

Table A.24 - Results for NaOH on the XOC 005 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	03/30/93	03/30/93	03/30/93	03/30/93
129			Update	04/01/93	04/01/93	04/01/93	04/01/93
130			Cat.	NaOH	NaOH	NaOH	NaOH
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	1.589	1.545	1.512	1.461
133			Err(%C)	-8.491	-10.052	1.298	-19.063
134			Conv(BOF)	14.902	21.051	23.403	65.804
135			Yld BOF(%)				
136			Acryl	.534	1.488	3.969	12.304
137			Prop	.602	.827	1.302	3.494
138			23P	1.306	3.446	6.786	9.046
139			Acetal	.578	1.135	3.053	7.390
140			Oth	.524	.000	2.249	5.149
141			Unknown	2.870	3.480	6.864	5.692
142			Unacct	8.488	10.675	-.820	22.730
143			CO*	.547	1.048	1.510	4.047
144			CO2*	1.200	3.681	8.398	19.996
145			Yld BOC(%)				
146			Acryl	3.584	7.071	16.961	18.697
147			Prop	4.038	3.930	5.561	5.310
148			23P	8.761	16.367	28.998	13.746
149			Acetal	3.881	5.390	13.045	11.230
150			Oth	3.516	.000	9.609	7.825
151			Unknown	19.260	16.531	29.331	8.650
152			Unacct	56.961	50.710	-3.506	34.542
153			CO*	3.669	4.977	6.451	6.150
154			CO2*	8.056	17.485	35.884	30.387
155			AcrPth	7.621	11.001	22.522	24.008
156			Acr/Pth	47.021	64.275	75.307	77.881

Table A.25 - Results for Na_3PO_4 on the XOC 005 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	03/25/93	03/25/93	03/25/93	03/25/93
129			Update	03/25/93	03/25/93	03/25/93	03/25/93
130			Cat.	Na3PO4	Na3PO4	Na3PO4	Na3PO4
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	1.987	1.901	1.863	1.784
133			Err(%C)	4.982	-24.371	-27.332	-35.850
134			Conv(BOF)	7.647	47.708	66.484	90.630
135			Yld BOF(%)				
136			Acryl	1.407	3.701	8.684	13.978
137			Prop	.870	1.255	2.378	5.721
138			23P	4.021	7.161	10.896	7.760
139			Acetal	1.103	2.963	5.134	8.513
140			Oth	.761	2.325	5.611	6.710
141			Unknown	4.242	5.277	4.058	5.113
142			Unacct	-4.757	25.025	29.722	42.836
143			CO*	.880	1.409	2.997	6.174
144			CO2*	3.476	7.633	15.590	28.522
145			Yld BOC(%)				
146			Acryl	18.399	7.757	13.062	15.423
147			Prop	11.383	2.631	3.577	6.312
148			23P	52.581	15.010	16.389	8.562
149			Acetal	14.417	6.211	7.722	9.393
150			Oth	9.955	4.874	8.440	7.404
151			Unknown	55.466	11.061	6.103	5.641
152			Unacct	-62.201	52.456	44.706	47.265
153			CO*	11.501	2.954	4.507	6.813
154			CO2*	45.459	16.000	23.449	31.471
155			AcrPth	29.783	10.388	16.639	21.735
156			Acr/Pth	61.779	74.671	78.503	70.957

Table A.26 - Results for $NaNO_3$ on the XOC 005 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	04/08/93	04/08/93	04/08/93	04/08/93
129			Update	04/08/93	04/08/93	04/08/93	04/08/93
130			Cat.	NaNO3	NaNO3	NaNO3	NaNO3
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	2.130	2.082	2.065	1.957
133			Err(%C)	-3.815	-6.427	-19.677	-26.952
134			Conv(BOF)	17.220	37.944	63.942	91.938
135			Yld BOF(%)				
136			Acryl	1.605	5.307	13.485	22.689
137			Prop	.627	.795	.915	1.804
138			23P	5.146	10.914	13.435	12.603
139			Acetal	.910	3.765	2.759	9.204
140			Oth	1.093	3.246	7.249	7.983
141			Unknown	3.604	5.985	3.148	3.712
142			Unacct	4.236	7.931	22.951	33.944
143			CO*	.957	1.807	2.297	6.008
144			CO2*	4.321	12.242	17.757	31.885
145			Yld BOC(%)				
146			Acryl	9.321	13.988	21.090	24.678
147			Prop	3.640	2.096	1.431	1.962
148			23P	29.882	28.764	21.011	13.708
149			Acetal	5.286	9.923	4.315	10.011
150			Oth	6.345	8.555	11.336	8.683
151			Unknown	20.930	15.772	4.924	4.037
152			Unacct	24.596	20.902	35.894	36.921
153			CO*	5.555	4.761	3.593	6.535
154			CO2*	25.095	32.262	27.770	34.681
155			AcrPth	12.961	16.084	22.520	26.640
156			Acr/Pth	71.914	86.967	93.648	92.636

Table A.27 - Results for Na_2HAsO_4 on the XOC 005 Silica

	A	B	C	D	E	F	G
127	REPORT						
128			Date	04/01/93	04/01/93	04/01/93	04/01/93
129			Update	04/07/93	04/07/93	04/07/93	04/07/93
130			Cat.	Na2HAsO4	Na2HAsO4	Na2HAsO4	Na2HAsO4
131			T(C)	280.000	300.000	320.000	350.000
132			RT(s)	2.014	1.965	1.918	1.837
133			Err(%C)	-21.345	-5.121	-22.626	-21.775
134			Conv(BOF)	41.084	44.174	77.041	92.955
135			Yld BOF(%)				
136			Acryl	2.023	6.012	12.917	21.057
137			Prop	.826	1.144	1.097	2.042
138			23P	9.235	23.343	18.043	14.275
139			Acetal	1.438	2.638	8.071	11.298
140			Oth	.647	1.441	7.312	11.191
141			Unknown	3.619	3.375	3.584	5.187
142			Unacct	23.296	6.221	26.017	27.905
143			CO*	1.571	1.757	2.517	5.409
144			CO2*	11.273	16.755	25.648	33.710
145			Yld BOC(%)				
146			Acryl	4.924	13.609	16.766	22.653
147			Prop	2.011	2.590	1.424	2.196
148			23P	22.480	52.844	23.420	15.357
149			Acetal	3.500	5.971	10.476	12.154
150			Oth	1.574	3.262	9.491	12.039
151			Unknown	8.808	7.641	4.653	5.580
152			Unacct	56.704	14.083	33.770	30.020
153			CO*	3.825	3.977	3.267	5.819
154			CO2*	27.438	37.930	33.291	36.265
155			AcrPth	6.935	16.199	18.190	24.849
156			Acr/Pth	71.008	84.013	92.172	91.162