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The Conversion of Lactic Acid to
Acrylic Acid in Near-Critical Water

presented by
Perry Joseph McCrackin

has been accepted towards fulfillment
of the requirements for
M.S. degree in Chem. Engr.

Major professor

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ABSTRACT
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IN NEAR-CRITICAL WATER

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A THESIS
The reactor and sampling system was designed and optimized to provide consistent and reproducible data with low maintenance costs. The primary conditions affecting the conversion to acrylic acid were investigated including temperature, pressure, pH, reactor wall effects, and homogeneous catalyst. Data obtained from these primary experiments were used to determine the most favorable conditions for the degree of conversion. The results of the lactic acid conversion reactions compared favorably with literature data concerning supercritical reactions of lactic acid. The passivation of the reactor walls was found to be a significant factor in the pyrolysis pathways and therefore, increasing the acrylic acid yields.

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ABSTRACT

To my wife, Michelle, and my parents, Edna and Adam

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An experimental plug-flow reactor was designed and constructed to provide conditions under which the reaction could be studied. Gas and liquid samples were analyzed using gas chromatography and high performance liquid chromatography, respectively. Equilibrium conversions of the three main reaction pathways and of the secondary reaction were determined using a commercially available computer program and estimated thermodynamic criteria. The model used to determine fugacities of the components was the Peng-Robinson equation of state.

The reactor and sampling system was designed and optimized to provide consistent and reproducible data with low maintenance costs. The primary conditions affecting the conversion to acrylic acid were investigated including temperature, pH, reactor wall effects, and homogeneous catalysts. These results obtained from these primary experimental runs were thoroughly analyzed including the use of overall reaction rates to determine the most favorable conditions. The results of the lactic acid conversion reactions compared favorably with previous literature data concerning supercritical reactions of lactic acid. The passification of the reactor walls was found to be very important in decreasing the pyrolysis pathways and therefore, increasing the acrylic acid yields.

ACKNOWLEDGEMENTS

To my wife, Michelle, and my parents, John and Alice.

The author wishes to thank the following people for their contributions to this research:

Brad Kech, Environmental Engineering Graduate Student, for his initial reactor design and for "volunteering" to perform the early experiments. Especially appreciated were his wiring expertise and his brewing knowledge.

Dr. Carl Lira, Associate Professor of Chemical Engineering, for his unending approaches to process control and his dedication to the College of Engineering.

Dr. Dennis J. Miller, Associate Professor of Chemical Engineering, for his useful suggestions.

Dr. Ned E. Jackson, Associate Professor of Chemistry, for the use of his technical background, and for the little reminder me of why I did not continue my career in chemistry.

Bharath Rangarajan, Graduate Fellow, Rameshwar Subramanian, Mike Bly and Gary White, Chemical Engineering students and lab mates, for their never ending support, counsel, and companionship.

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production of useful materials. The effect of these functionalities (hydrogen bonding) on adjacent molecules lends itself to the high boiling point.

CHAPTER I

INTRODUCTION

With the increasing consumption of non-renewable resources such as coal, oil, and natural gas by developed nations and the increasing political instability in major oil-producing countries, there is an urgent need to develop technology to produce energy, fuels, and chemical feedstocks from renewable domestic resources. Feasibility studies must be undertaken to determine which bio-materials can economically exploited to yield the most potential. The reaction identified as a possible candidate for this area is the conversion of lactic acid to acrylic acid. This identified reaction is actually the second step of the desired renewable resource-to-useful chemical specie. The first step, which is not investigated in this work, is the conversion of a bio-material to an intermediate (the intermediate being the lactic acid). The second step is the conversion of lactic acid to the structurally similar acrylic acid.

Lactic acid (alpha-hydroxy-propionic acid) is a commercial fine chemical used in food and medical applications which is readily available from many renewable resources via fermentation of biomass (corn, cheese whey and plant residue). It is also produced commercially using an organic synthesis route from hydrogen cyanide and acetaldehyde. Lactic acid is a hygroscopic viscous material with a molecular weight of 90.08 grams. The melting point of the pure material is 18 °C and the boiling point, at 12 mm of pressure, is 119 °C. At room pressure lactic acid degrades before it can attain enough energy to vaporize. The lactic acid's unique arrangement contains a hydroxyl and a carboxylic acid, which lends its usefulness as a chemical feedstock, since it can participate in reactions characteristic of each functionality. The proximity of these groups on successive carbons, though, is detrimental to the

production of useful materials. The effect of these functionalities (hydrogen bonding) on adjacent molecules lends itself to the high boiling point.

Lactic acid's attractiveness as a chemical feedstock is enhanced by the nearly unlimited sources for the biomass, which are renewable domestic resources. It can be produced in abundance and with advancing biotechnology, cheaper methods are being developed which can utilize the large amounts of biomass that is treated as waste. If corn grain is utilized as a source for the lactic acid and thirty two pounds of starch is available from each bushel of corn (56 lbs) of which there is an 85% conversion to lactic acid, the potential lactic acid stocks based on a yearly corn production of eight billion bushels would be approximately 220 billion pounds. Currently the cost of producing lactic acid is between 35 and 40 ¢/lb.

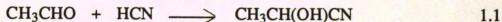
One of the earliest investigations into the production of lactic acid is by Pelouze and Guy-Lussac using the newly discovered and fledgling fermentation process of using calf rennet membrane to convert sugar to lactic acid in the late 1830's (Benninga, 1990). Boutron and Fremy expanded the lactic acid fermentation feedstocks to the use of malt sprouts and milk/lactose solutions as the starting material (Boutron and Fremy, 1841).

Medicinal uses of lactic acid are the first primary reasons for the development of a reliable source of pure lactic acid. Iron lactate was introduced and promoted as a treatment for anemia and chlorosis. It was recommended because it was found that the body contained lactic acid and was thought to be easily assimilated (Schnieder, 1975). For the next 40 years Pasteur and Von Liebig investigated how the fermentation process was initiated and how it was sustained in the production of lactic acid. Fermentation knowledge was developed thanks to Pasteur and Von Liebig both of whom followed the Bensch recipe for the production of lactic acid.

The first commercial production of lactic acid was developed by the Avery Lactate Company, established in Littleton, Massachusetts, using a refined fermentation process developed from the crude Bensch process patented by Charles Avery (1880, 1881). Great care was taken to preserve the bacteria used to ferment the corn meal, to

provide optimal conditions for the formation of lactic acid, and to suppress the butyric acid formation by using pure cultures. Only a small amount of the foul tasting butyric acid was needed to give the food-grade lactic acid product a bad taste. Several improvements over the Bensch process were noted, especially the use of cultured bacteria. The uses for the commercial lactic acid were as a baking powder substitute, as a vinegar substitute, and as a tart drink additive for the fledgling soft drink industry (Benninga, 1990). Later in the late 19th century, a new use for lactic acid turned up in the clothing industry as a mordanting agent for the fixation of dyes on silk and wool. The turn of the century brought another use in the tanning industry in the deliming and bating operations of the hides as a replacement for sulfuric acid. This developed into the use of lactic acid as a tanning agent. Total U.S. production of the lactic acid in the 1930's was 3500 tons.

With the advent of supermarkets and once a week shopping after World War II, calcium stearoyl lactylate was discovered to act as a conditioner in bread to prevent staleness (Thompson and Buddemeyer, 1951). Lactic acid is the primary ingredient in the additive and with this huge market potential, the Monsanto corporation committed to building a new plant to make purer lactic acid synthetically from hydrogen cyanide (a by-product of Monsanto's acrylonitrile production) and acetaldehyde in 1962 (Benninga, 1990). The reaction (shown below) is a two step process with lactonitrile as an intermediate.



With the new synthetic process in production, which produced a superior quality product to the fermentation product, many small manufacturers of lactic acid discontinued the fermentation production of lactic acid. Table 1.1 shows the production figures for lactic acid in 1962, 1972, 1982 and 1989 (estimated). The amount of

lactic acid produced by fermentation decreased steadily from nearly 100% in 1962 to 53% in 1982 (no figures available for 1989).

One purpose of the recent research centering around lactic acid is to dehydrate the lactic acid to acrylic acid. Acrylic acid is an important monomer used to make a variety of polymers used in latexes, coatings, etc. and as an intermediate for the formations of acrylate polymers used in the formation of polymers with many industrial and consumer applications.

Table 1.1. Production of Lactic Acid and Lactates (1000 tons/y).

	1962	1972	1982
Synthetic	0.3	8.3	12.3
Fermentation	11.0	11.1	13.9
Total	11.3	19.4	26.2
Yearly Growth (%/y)	--	5.5	3.0
% by Fermentation	97.0	57.0	53.0

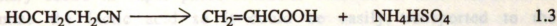
The first acrylic acid was made by the oxidation of propylene oxide back to 1843. Redtenbacher oxidized ethyl alcohol with chromic acid of sulfur oxide and isolated an acid which he called "acrylic acid". But he did not obtain acrylic acid from the oxidation of propylene oxide. Others (Lusk, 1867) found that methyl acrylate was a solid by heating or exposing the liquid to air. He also showed the solid's insolubility in acids, alkalis, and bases. Commercial exploitation of the acrylic acid was not until its success to the early development of a process for the acrylic acid monomer from ethylene oxide or ethyl acrylate by Bauer (1921, 1931). The esters of acrylic acid are obtained by refluxing the appropriate alcohol with the acryboxylic acid in the presence of an acid catalyst. The earliest polymerizations of acrylate polymers were initiated by thermal or photochemical initiators. Later chemical initiators (peroxides) were developed which were widely accepted. The first uses for the polymers were as coatings and in adhesive applications. Currently acrylic acid and its derivatives are manufactured at the rate of 2×10^9 lb/yr from petroleum sources via several reactions. (Sawicki, 1988)

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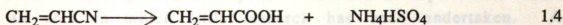
One purpose of the recent research centering around lactic acid is to dehydrate the lactic acid to acrylic acid. Acrylic acid is an important monomer used to make a variety of polymers used in latexes, coatings, etc; and as an intermediate for the formations of acrylate esters also used in the formation of polymers with many industrial and consumer applications. The availability of an extensive group of monomeric materials offer the possibility of tailor-made products with a wide range of physical properties adaptable to the requirements of many different applications. Despite their variety in composition and physical form, the acrylate polymers share the common qualities of film clarity, brilliance, and outstanding resistance to many chemical agents, aging, and degradation by light (Luskin, 1970).

The history of acrylic acid goes back to 1843, Redtenbacher oxidized acrolein with an aqueous slurry of silver oxide and isolated an acid which was named acrylic acid. Beilstein obtained acrylic acid from the distillation of the salts of hydracrylic acid as did several others (Luskin, 1970). More importantly for the future developments of polymeric materials, Kahlbaum (1863) found that methyl acrylate formed a clear, colorless, solid by heating or exposing the monomer to sunlight. He also showed the solid's insolubility in most solvents, acids, and bases. Commercial exploitation of the acrylates owed much of its success to the early development of a practical synthesis of the acrylic acid monomer from ethylene oxide, or ethylene chlorohydrin by Bauer (1921, 1931). The esters of acrylic acid are obtained by refluxing the appropriate alcohol with the carboxylic acid in the presence of an acid catalyst. The earliest polymerizations of acrylate polymers were initiated by thermal or photochemical initiators. Later chemical initiators (peroxides) were developed which were widely accepted. The first uses for the polymers were as coatings and in adhesive applications. Currently acrylic acid and its derivatives are manufactured at the rate of 2×10^9 lb/yr from petroleum sources via several reactions. (Sawicki, 1988)

form. Acrylic acid is produced commercially by several producers, including Union Carbide, through the conversion of ethylene cyanohydrin to acrylic acid by treatment with sulfuric acid and steam (Luskin, 1970).



Another method of formation is the conversion of acrylonitrile to acrylic acid.



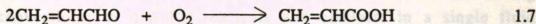
The Reppe process uses acetylene, carbon monoxide, and water in the presence of nickel or other carbonyl forming metal catalyst.



Acrylic acid can be produced from the preparation of ketene and formaldehyde via B-propiolactone.



The oxidation of acrolein over bismuth Phosphomolybdate is another increasingly popular method.



The synthesis of acrylic acid from lactic acid is an alternative method to the established routes listed above, but it fulfills the motivation of finding renewable resources as chemical feedstock. Previous research work shows the lactic acid does catalytically dehydrate to form acrylic acid in appreciable amounts in vapor phase reactions (Sawicki, 1988; Paparizos, 1988). But, at these elevated temperatures and relatively low pressures, the lactic acid will primarily decompose into acetaldehyde, carbon monoxide and carbon dioxide. Additional reformation reactions can take place

forming a variety of chemical species. Since lactic acid degrades before it boils at room pressure, the tendency for the lactic acid to form degradation products first before it has a chance to form useful products would be more prevalent in vapor phase reactions. The primary desire in vapor phase reactions with lactic acid would be to atomize the lactic acid so it could be easily transported to the reaction site before degradation occurs.

More recently, Mok, Antal and Jones (1989), have shown acrylic acid formation occurs in supercritical water with small amounts of homogeneous catalysts. Reactions in supercritical fluids is an area in which little research has been undertaken. A supercritical fluid is a solvent which is at a temperature above its critical temperature (T_c) and a pressure above its critical pressure (P_c). McHugh and Krukoni (1986) describes several established industrial applications utilizing supercritical fluids mainly in separations technology (i.e. coffee decaffeination with supercritical CO_2 ; edible-oils extraction with supercritical CO_2 ; separation of isomers with supercritical CO_2 ; etc). Although there are very few examples where supercritical fluid is used as a reaction media in an industrial process, the polymerization of propylene in supercritical propylene is one.

The supercritical fluid as a reaction medium either actively participates in the reaction or functions as the solvent medium for the reactants, catalysts and products. With supercritical fluid it may be possible to increase the selectivity of a reaction while maintaining high conversions, to dissolve reactants and catalysts in a single fluid phase and carry out the reaction homogeneously, and to capitalize on the solvent characteristics of the supercritical fluid to separate the product species from the reactants, catalyst, and unwanted by-products. Reaction rates may also be enhanced while the process is operating in the mixture's critical region as a result of the potentially favorable effect of applied hydrostatic pressure. The selectivities and reaction rates may be enhanced because of the large negative partial molar volumes of the product species in dilute reaction mixtures operating near the supercritical point of the pure solvent.

The goal of this work is to determine the feasibility of dehydrating lactic acid in near-supercritical water. Additional information such as the use of heterogeneous and homogeneous catalysts in near-supercritical media were investigated. Much of the data is compared with previous results obtained in both supercritical mediums and vapor-phase. Relative reaction rate data is determined for several conditions and compared to determine the best conditions

Supercritical Fluid Properties

The critical region of a pure component is shown in Figure 2.1. A supercritical phase is unlike normal gas, liquid or solid. It is essentially a gas which has been heated above its critical temperature and compressed above its critical pressure. The resulting phase is a very dense gas. Table 2.1 lists the critical temperatures and pressures for a number of gases and liquids (McHugh & Krukonis, 1986).

Supercritical fluids exhibit a wide variation of solvent characteristics that can be adjusted by simply changing the temperature or pressure of the system. Figure 2.2 shows an example of this characteristic with a solid/supercritical ethylene system (McHugh & Krukonis, 1986). The solubility of a solid in a gas is extremely low at low temperatures and pressures. At a temperature of 27 °C, the solubility of solid naphthalene increases dramatically to 500 mg/g as the pressure is increased to 50 atm. The solubility of solid naphthalene is over 100 percent above 100 atm. When the temperature is increased to 33 °C, the effect is even larger.

Several other factors about the supercritical fluid an interesting reaction media. The density of supercritical fluids tend to be fairly close to density of liquid, which provides a denser reaction media and higher concentrations of reactant per volume of reactor. The density can be changed dramatically by changing the pressure or temperature slightly. The viscosities of supercritical fluids lie in between gas and liquid phases.

Advantages and Disadvantages of Reactions in Supercritical Fluids

Through the use of supercritical fluids, it may be possible to reduce the operating temperature of a typical pyrolysis reaction.

CHAPTER II

LITERATURE REVIEW:

Supercritical Fluid Properties:

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Table 2.1. Critical Constants for Various Compounds.

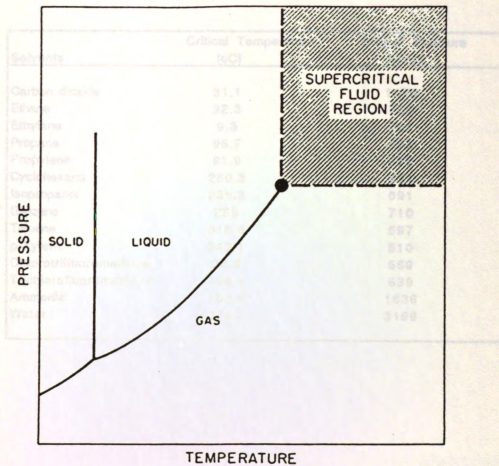


Figure 2.1. Pressure-Temperature Diagram for a Pure Component (McHugh and Krukonis, 1986).

Table 2.1. Critical Constants for Various Compounds.

Solvents	Critical Temperature (°C)	Critical Pressure (psi)
Carbon dioxide	31.1	1070
Ethane	32.3	709
Ethylene	9.3	731
Propane	96.7	616
Propylene	91.9	670
Cyclohexane	280.3	591
Isopropanol	235.2	691
Benzene	289	710
Toluene	318.6	597
p-Xylene	343.1	510
Chlorotrifluoromethane	28.9	569
Trichlorofluoromethane	198.1	639
Ammonia	132.5	1636
Water	374.2	3199

Figure 2.2. Solubility of 2,3-Dinitro-Naphthalene in Supercritical Ethylene (McClure et al., 1990).

The carbon formation that occurs at high temperature in pyrolysis reactions can be reduced. Koll and Metzger (1978) report the use of supercritical acetone as the reaction media for the thermal degradation of cellulose in a flow reactor. Normal degradation of cellulose occurring in vacuum is rate limiting due to poor heat transfer and the primary product's yield, glucosan, is 28%. The supercritical pyrolysis reaction yields 38% glucosan with minimal carbon build up. The authors note that at lower temperatures,

when heterogeneous catalytic reactions are involved, the use of supercritical fluids can be used to regenerate the catalyst and regain the activity. This can be done either by adjusting the temperature or pressure to return the fluid to a supercritical state or by carrying out the reaction under supercritical conditions. Tillscher, Wolf, and Schuler (1984) describe an example of a supercritical reaction medium regeneration power with the catalytical isomerization of α -methyl- α -ethyl- α -butyrate which had been poisoned by the different catalyst. They were able to regain the original activity each time.

The change in viscosity of the fluid may have an effect on the product distribution of a reaction (McHugh and Krukons, 1986). The solvent viscosity also affects the homopolymerization of the cis-1,4-butadiene monomer. The authors note that the rate of polymerization decreases as the pressure of the CO_2 decreases. Some shift can be expected due to density changes in the fluid, but the sharp decrease at 40 °C is largely due to the large decrease in viscosity as the CO_2 pressure is reduced in Figure 2.4.

The facilitation of product removal is another advantage of supercritical reaction media. In a recent patent, Modell (1982) describes the efficient utilization of supercritical water as a reaction media to oxidize organic wastes which would normally have to be separated from the wastewater stream and then incinerated or recycled, if possible. This results in decreased cost in terms of

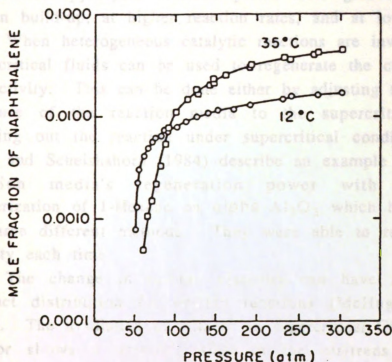


Figure 2.2. Solubility Behavior of Solid Naphthalene in Supercritical Ethylene (McHugh and Krukons, 1986).

The carbon formation that occurs at high temperature in pyrolysis reactions can be reduced. Koll and Metzger (1978) report the use of supercritical acetone as the reaction media for the thermal degradation of cellulose in a flow reactor. Normal degradation of cellulose occurring in vacuum is rate limiting due to poor heat transfer and the primary product's yield, glucosan, is 28%. The supercritical pyrolysis reaction yields 38% glucosan with minimal carbon build-up, at higher reaction rates, and at lower temperatures.

When heterogeneous catalytic reactions are involved, the use of supercritical fluids can be used to regenerate the catalyst and regain the activity. This can be done either by adjusting the temperature or pressure of the reaction media to the supercritical state or by carrying out the reaction under supercritical conditions. Tiltcher, Wolf and Schelshshorn (1984) describe an example of a supercritical reaction media's regeneration power with the catalytical isomerization of 1-Hexene on $\alpha\text{-Al}_2\text{O}_3$ which had been poisoned by three different methods. They were able to regain the original activity each time.

The change in solvent viscosity can have an effect on the product distribution for certain reactions (McHugh and Krukonis, 1986). The irradiation of stilbene in supercritical CO_2 through a flow reactor shows a dramatic shift in the cis/trans ratio when the viscosity of the solvent is changed (Squires, Venier and Aida, 1983). As the solvent viscosity increases the photoisomerization of the cis isomer is inhibited while the trans isomer is increased. Figure 2.3 shows the dramatic shift in the cis/trans ratio as the pressure of the supercritical CO_2 is decreased. Some shift can be expected due to density changed of the CO_2 , but the sharp decrease at 40 °C is largely due to the large decrease in viscosity as the CO_2 pressure is reduced in Figure 2.4.

The facilitation of product removal is another advantage of supercritical reaction media. In a recent patent, Modell (1982) describes the efficient utilization of supercritical water as a reaction media to oxidize organic wastes which would normally have to separated from the wastewater stream and then incinerated or recycled, if possible. This results in decreased cost in terms of

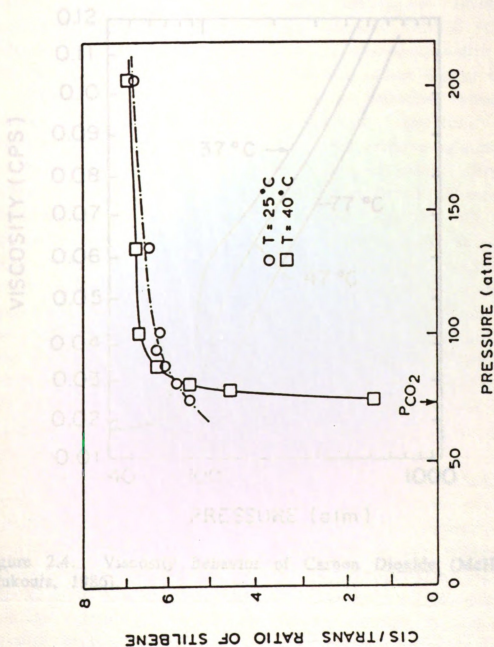


Figure 2.3. Transient Product Distribution of the Cis/Trans Isomer Obtained when Stilbene is Irradiated in Supercritical Carbon Dioxide at 40 °C and 136 Atmospheres (Squires, Venier and Aida, 1983).

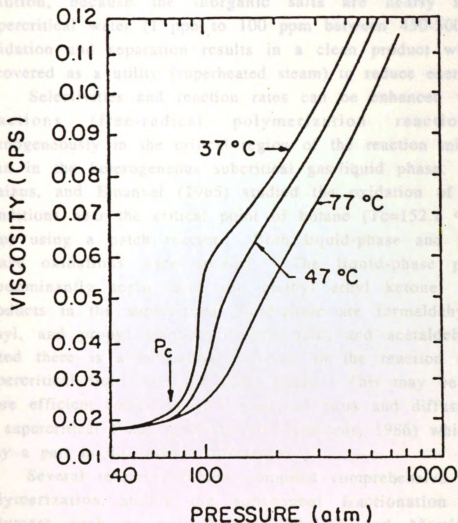
equipment and energy requirements. Total oxidation can be achieved by adding stoichiometric amounts of oxygen to the wastewater because the reaction mixture is completely miscible in the mixture's critical region. Inorganic salts present in the wastewater stream, are easily separated and removed from the solution, because the inorganic salts are nearly insoluble in supercritical CO_2 . Separation results in a clear product which can be recovered as a utility (superheated steam) and reduce energy costs.

Several studies and reaction rates are enhanced when certain reactions (free-radical polymerization reactions) occur homogeneously in the reaction mixture, rather than in a two-phase system. Bilyunberg, Matus, and Mortimer (1975) studied the reaction of n-butane at conditions near the critical point ($T_c=152^\circ\text{C}$, $P_c=37.5$ atm) using a batch reactor. They found that the reaction rates in the liquid-phase and supercritical-phase are similar, whereas the products in the supercritical phase are formaldehyde, methyl, ethyl, and acetaldehyde. They noted that the reaction rates in the supercritical phase may be due to the more efficient mixing and diffusion of such, in supercritical CO_2 (Mortimer, 1986) which may also play a role.

Several studies have been reported on the polymerization of various monomers in supercritical CO_2 (Mortimer, 1970), polystyrene (Mortimer, 1970), and polyacrylonitrile (Mortimer, 1970).

Figure 2.4. Viscosity Behavior of Carbon Dioxide (McHugh and Krukonis, 1986).

Several studies have been reported on the polymerization of various monomers in supercritical CO_2 (Mortimer, 1970), polystyrene (Mortimer, 1970), and polyacrylonitrile (Mortimer, 1970). After the reaction is finished the system pressure is reduced in a step-wise manner to precipitate the crystalline polymers from the non-crystalline forms and the non-crystalline forms or amorphous forms from the lower molecular weight oligomers, catalyst and residual monomers.



equipment and energy requirements. Total oxidation can be achieved by adding stoichiometric amounts of oxygen to the wastewater because the reaction mixture is completely miscible in the mixture's critical region. Inorganic salts present in the wastewater stream, are easily separated and removed from the solution, because the inorganic salts are nearly insoluble in supercritical water (1 ppb to 100 ppm between 450-500 °C). This oxidation and separation results in a clean product which can be recovered as a utility (superheated steam) to reduce energy costs.

Selectivities and reaction rates can be enhanced when certain reactions (free-radical polymerization reactions) occur homogeneously in the critical region of the reaction mixture, rather than in the heterogeneous subcritical gas-liquid phase. Blyumberg, Maizus, and Emanuel (1965) studied the oxidation of n-butane at conditions near the critical point of butane ($T_c=152.1$ °C, $P_c=37.5$ atm) using a batch reactor. Both liquid-phase and supercritical-phase oxidations were studied. The liquid-phase products are predominantly acetic acid and methyl ethyl ketone, whereas the products in the supercritical fluid-phase are formaldehyde, methyl, ethyl, and propyl alcohols, formic acid, and acetaldehyde. They noted there is a substantial increase in the reaction rates in the supercritical fluid over the liquid-phase. This may be due to the more efficient formation of free-radical pairs and diffusion of such, in supercritical fluids (McHugh and Krukonis, 1986) which may also play a part in the product differences.

Several researchers have compiled comprehensive data on the polymerization and/or the subsequent fractionation of various polymers such as polyethylene (Ehrlich and Mortimer, 1970), polystyrene (Jentoft and Gouw, 1969, 1970) and polypropylene (Cottle, 1966) in supercritical fluids. The supercritical fluid can be used as both the reactant and the solvent (ethylene, propylene). After the reaction is finished the system pressure is reduced in a step-wise manner to precipitate the crystalline polymers from the non-crystalline forms and the non-crystalline forms or amorphous forms from the lower molecular weight oligomers, catalyst and residual monomers.

For more detailed descriptions and examples of reactions in supercritical fluids refer to Krase and Lawrence, 1946 - (polyethylene polymerization); Ehrlich, 1965; Ehrlich and Pittilo, 1960; Ehrlich and Kurpen, 1963 - (polyethylene polymerization); Baumgartner, 1983 - (tertiary-butyl-hydroperoxide formation); Kramer and Leder, 1975 - (isomerization of paraffinic hydrocarbons); and Bhise, 1983 - (production of ethylene glycol in CO_2).

Related Reactions in Supercritical Fluids

Disadvantages

Although the advantages outweigh the disadvantages, the disadvantages are significant. With the need to operate under high pressure, this can mean a significant cost for processing equipment which can handle the supercritical pressures (> 5000 psi for SC water). With many reactions, a significant amount of heat is required to sustain the reaction which along with the pressure requirement can double or triple the wall thickness of a room temperature reactor (Anon., 1972).

Reactor Wall Effects

In a paper by Torry, Kaminsky, Klein, and Klotz (1991), the effect of salt concentration on the rate of hydrolysis of dibenzyl ether (DBE) and benzyl phenyl amine (BPA) in supercritical water is studied. Torry et al. found that the addition of salts to the reaction mixture increases the hydrolysis rate at low salt concentrations, while having no effect on the competing pyrolysis reaction rate. As the salt concentration is increased, the hydrolysis rate peaks and then approaches the reaction rate observed in the absence of salts.

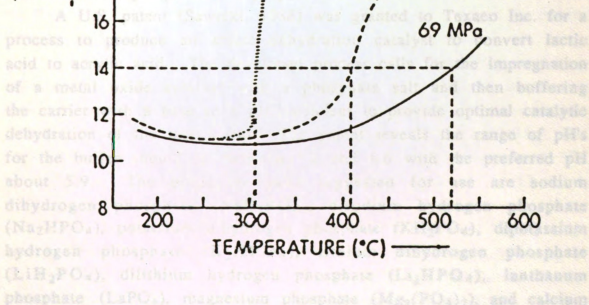
Although the importance of ion effects on the reaction rates and pathways is important, the fact that Torry et al. noticed there was a difference in the pyrolysis reaction rate between old and new reactors, has the most relevance to this work and will be shown later in the experimental/discussion chapters. Since the potential for corrosion by supercritical water and supercritical water/salt solution to interfere with rates of pyrolysis and hydrolysis is rather high, Torry and co-workers conducted DBE hydrolysis reactions in both stainless steel and titanium reactors. No differences in reaction rates

were noted between the two types of reactors, but the yield of pyrolysis products was an order of magnitude greater in the new stainless steel reactors than in the used stainless steel and titanium reactors. They note that this is due to passification of active wall sites during the reaction and that the hydrolysis reaction, the reaction of interest, is not affected by the passification.

Related Reactions in Supercritical Fluids

Dehydration reactions in supercritical water have proved possible in a paper by Ramayya et al (1987). Several successful dehydration reactions are investigated in the paper including ethanol to ethylene, n-propanol to propene, and glycerol to acrolein. Ramayya et al. (1987) reports high yields of ethylene could be obtained from 1.0 M ethanol solutions in supercritical water at 5000 psi and 385 °C. When small amounts of sulfuric acid (< 0.05 M) are used as a catalyst, yields were in the range of 80-90% with a high of 97%. Conversion was in the range of 30-40 percent with catalyst. Propanol dehydration was not as successful with yields typically in the 30-50% range with a high of 64% under the same conditions. Dilute sulfuric acid (0.005 M) selectively catalyzes the dehydration of glycerol to acrolein between 300 and 350 °C at 5000 psi, with yields typically near 100%.

Ramayya et al. also shows the selectivity of supercritical reaction fluids on the glycerol reaction. Acetaldehyde is produced as a by-product of the dehydration reaction in a ratio of 1.0:5.5 molar ratio of yields, acetaldehyde to acrolein. In gas-phase pyrolysis of glycerol in steam, a ratio of 1.0:1.0 molar ratio of yields, is obtained. The high pressures and the dense reaction fluid provides a shift in reaction pathways. The ability of the supercritical water to remain a protic solvent well beyond its critical pressure is also beneficial for ionic chemical reactions. In Figure 2.5 the ion products at three different pressures are plotted versus temperature. Dramatic differences are shown for the three pressures; at 2000 psi water remains a protic solvent up to 300 °C, this increases to approximately 410 °C at 5000 psi, and well over 500 °C at 10000 psi. An additional paper by Zulfugarov et al. (1984) provides insight into alcohol



dehydrations using gallosilicate and alumogermanate zeolites as heterogeneous catalysts.

Odell and Earlam, (1985) report the homogeneously catalyzed reactions of lactic acid by group VIII metal complexes in aqueous solutions between 220 and 250 °C. Several group VIII metal complexes are examined as catalysts including, $[\text{PtH}(\text{PEt}_3)_3]^+$, PdCl_2 , $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$, and $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$. Reactions catalyzed with $[\text{PtH}(\text{PEt}_3)_3]^+$ show rather poor molar yields of acrylic acid, typically less than 2 percent, yet the molar yields of propanoic acid are in the range of 40 to 50 mol percent with selectivities in the area of 70 percent. The researchers theorized that acrylic acid is evidently forming as an intermediate to the propanoic acid, and then subsequently hydrogenated to the propanoic acid by the group VIII metal catalyst. This is proven by placing acrylic acid in aqueous solution with the same metal catalyst and reacting at 180 °C for two hours. The major product is propanoic acid.

A U.S. patent (Sawicki, 1988) was granted to Texaco Inc. for a process to produce an acidic dehydration catalyst to convert lactic acid to acrylic acid. The developed process calls for the impregnation of a metal oxide catalyst with a phosphate salt and then buffering the carrier with a base to a pH sufficient to provide optimal catalytic dehydration of the lactic acid. The patent reveals the range of pH's for the buffer should be between 5.2 and 6.6 with the preferred pH about 5.9. The phosphate salts suggested for use are sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), lithium dihydrogen phosphate (LiH_2PO_4), dilithium hydrogen phosphate (Li_2HPO_4), lanthanum phosphate (LaPO_4), magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2$), and calcium dihydrogen phosphate (CaH_2PO_4). The preferred phosphate is listed as the sodium dihydrogen phosphate (NaH_2PO_4).

The Texaco patent described the preparation of phosphate-type catalysts for use in the vapor phase conversion of lactic acid at temperatures between 200 and 400 °C at atmospheric pressure. The reported yields are typically in the range of 40 mol % with a high of 58 mol %. Their selectivities are generally in the 40's with a high of

65 mol %. The best yields and selectivities occurred with catalysts prepared with basic solutions.

A European patent application (Paperizos 1985) involves the catalytic conversion of lactic acid and ammonium lactate to acrylic acid in a vapor phase reaction. The catalyst used in these reactions involves a base treated, calcined aluminum phosphate solid. The calcination process requires a temperature of between 450 and 550 °C, while the dehydration reaction occurs at temperatures listed between 320 and 375 °C with a contact time of two to four seconds.

Several examples are given in the application with the highest yield of acrylic acid being reported as 61 mol % for an example which is completely reacted. Typically they are below 40%. Several reactions show very good ratios of acrylic acid to propionic acid, as high as ten to one, while others are very poor. Paperizos shows that when the catalyst is not treated with base prior to use, the products are mainly acetaldehyde and propionic acid. Additional information on the use phosphates as catalysts can be found in a paper by Pellet, Coughlin, Shamshoum and Rabo (1988)

Previous work (Mok, Antal, and Jones 1989) dealing with the dehydration of lactic acid to acrylic acid in supercritical water fell short of promising results, but much knowledge of the reaction network of lactic acid in supercritical water is discovered. Mok and co-workers performed most of the reactions at a temperature of 385 °C and 5000 psi with a initial lactic acid concentration of 0.1 M and a residence time of approximately 30 seconds.

They found in the presence of small amounts of strong acid catalyst, H_2SO_4 , or base, NaOH, lactic acid (0.1 M) exists primarily in its free acid form and the reaction is fast and produces mainly acetaldehyde and carbon monoxide in equal proportions. This reaction is identified as the first pathway. Water is also determined to be produced in this pathway to balance the equation. The reaction is shown in Figure 2.6 and will be referred to as pathway 1 or the decarbonylation pathway:

As the pH of the reactant solution is increased, Mok, et al. found the rate of conversion decreases, accompanying a major shift in the product distribution. The relative amounts of carbon

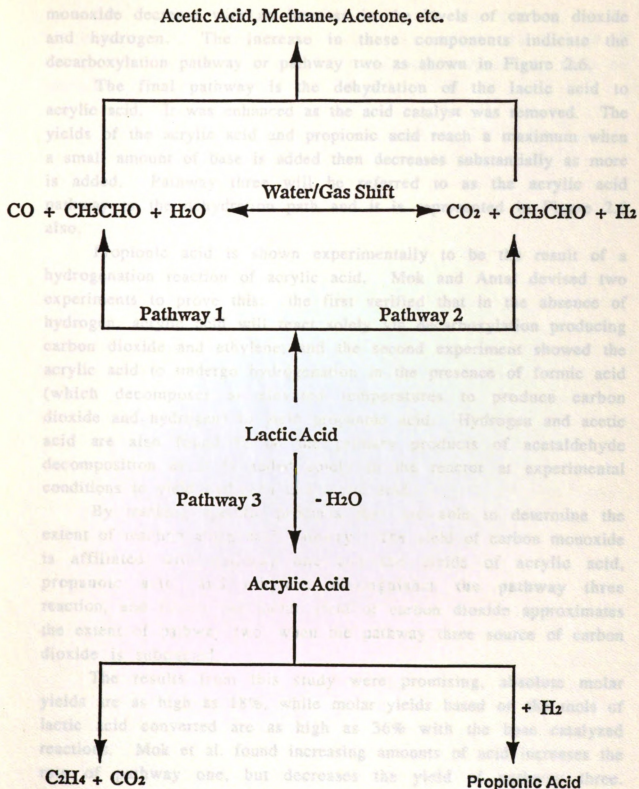


Figure 2.6. Reaction Network for Lactic Acid Conversion in Supercritical Water as Proposed by Mok et al. (1989).

monoxide decrease with an increase in the levels of carbon dioxide and hydrogen. The increase in these components indicate the decarboxylation pathway or pathway two as shown in Figure 2.6. The final pathway is the dehydration of the lactic acid to acrylic acid. It was enhanced as the acid catalyst was removed. The yields of the acrylic acid and propionic acid reach a maximum when a small amount of base is added then decreases substantially as more is added. Pathway three will be referred to as the acrylic acid pathway or the dehydration path and it is represented in Figure 2.6 also.

Propionic acid is shown experimentally to be the result of a hydrogenation reaction of acrylic acid. Mok and Antal devised two experiments to prove this: the first verified that in the absence of hydrogen, acrylic acid will react solely via decarboxylation producing carbon dioxide and ethylene; and the second experiment showed the acrylic acid to undergo hydrogenation in the presence of formic acid (which decomposes at elevated temperatures to produce carbon dioxide and hydrogen) to yield propanoic acid. Hydrogen and acetic acid are also found to be the primary products of acetaldehyde decomposition as it is added solely to the reactor at experimental conditions to yield hydrogen and acetic acid.

By tracking specific products they are able to determine the extent of reaction along each pathway. The yield of carbon monoxide is affiliated with pathway one and the yields of acrylic acid, propanoic acid, and ethylene distinguishes the pathway three reaction, and finally the molar yield of carbon dioxide approximates the extent of pathway two, when the pathway three source of carbon dioxide is subtracted.

The results from this study were promising, absolute molar yields are as high as 18%, while molar yields based on the mols of lactic acid converted are as high as 36% with the base catalyzed reactions. Mok et al. found increasing amounts of acid increases the rate of pathway one, but decreases the yield of pathway three. Increasing the basic catalyst initially increases the rate of pathway three, but additional amounts suppresses the dehydration pathway along with pathway one. Pathway two is found to be unresponsive

to either catalyst. Their work investigates the role of reactor temperature on the pathways and yields. They found the rates of all three pathways to increase with increasing temperature, with no particular pathway favored.

CHAPTER III

EQUILIBRIUM CONVERSIONS OF THE PRIMARY PRODUCTS OF THE REACTION OF LACTIC ACID IN SUPERCRITICAL WATER

Discussion

With this investigation into the dehydration of lactic acid to acrylic acid, there are two questions which need to be answered: first, it is necessary to determine if the dehydration reaction is feasible at supercritical conditions and secondly, to what extent can the reaction be taken. Obviously, the literature (Mek et al., 1989) yields an insight into the first question, which is decisively positive. The second question is rather difficult to answer, given the conditions in which the reaction takes place. The equilibrium conversion of a particular species is determined to be one minus the mol fraction of the particular species left at the point in which the reactants and products are in equilibrium. This equilibrium is a state of minimum Gibbs free energy.

$$G = \sum_i \nu_i \mu_i = \sum_i \nu_i (G_i^0 + RT \ln \frac{[i]}{[i]^0}) \rightarrow 0 \quad (3.1)$$

Where ν denotes the stoichiometric coefficient of species (positive for products; negative for reactants) and G_i^0 denotes the Gibbs free energy of formation for each species. The $[i]^0$ term is the species mol fractions taken to the power of its stoichiometric coefficient.

It is desirable to determine for this particular reaction the equilibrium conversion to acrylic acid. Mek et al. (1989) showed that at least 18 percent equilibrium conversion to acrylic acid could be attained with the three main pathways and the various side/secondary reactions shown in Figure 2.6. This is promising but additional information is needed to determine whether the conversion of lactic acid to acrylic acid is feasible from a research

and economic standpoint. That is the purpose of this chapter, to determine the equilibrium conversions of the reactions of lactic acid in supercritical water, from a thermodynamic standpoint. Knowing the equilibrium conversion

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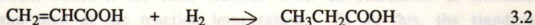
$$(-\sum_i \nu_i \Delta G_{fi})/RT = \sum_i \ln (f/f^0)^{\nu_i} = 0 \quad 3.1$$

Where ν denotes the stoichiometric coefficient of species (positive for products, negative for reactants) and ΔG_f denotes the Gibbs free energy of formation for each species. The $(f/f^0)^{\nu_i}$ term is the species mol fractions taken to the power of its stoichiometric coefficient.

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and economic standpoint. That is the purpose of this chapter, to determine the equilibrium conversions of the reactions of lactic acid in supercritical water, from a thermodynamic standpoint. Knowing the equilibrium conversions allows for confidence that the stated research has a purpose.

With lactic acid's unique characteristic of bearing a hydroxyl group and a carboxylic group in close proximity to each other, the lactic acid has many advantages as a chemical feedstock, because it can participate in reactions characteristic of each functionality. Under various conditions, this characteristic also lends the lactic acid to react in a multitude of ways, yielding various products. A single lactic acid reaction pathway is difficult to obtain. The primary purpose of the recent research centering around lactic acid is to dehydrate the lactic acid to acrylic acid, a useful monomer. Mok et al. (1989) discovered because of the proximity to the carboxyl group, the selective dehydration of the alpha-hydroxyl is very difficult. Additional reactions were found to take place forming a variety of chemical species. Mok and co-worker's research is described in the chapter 2 in the literature review section. The lactic acid can undergo self-polymerization to form a variety of esters. At elevated temperatures and relatively low pressures, the lactic acid will primarily decompose into acetaldehyde and several gases. There are two pathways for the degradation of lactic acid: Pathway one produces acetaldehyde, water, and carbon monoxide; and the second pathway produces acetaldehyde, hydrogen, and carbon dioxide. Pathway three denotes the acrylic acid formation. Reactions one through three are the main pathways under which lactic acid will react in supercritical water as indicated by Mok et al. These reactions will be the focus of the analysis for equilibrium constants and conversions along with secondary reactions which convert the desirable product acrylic acid to its decomposition products. The main secondary reaction (reaction 4) to be examined will be the following:



There are other secondary reactions but this reaction leads to the highest conversion of unwanted by-products via the acrylic acid. Other secondary products produced from the acrylic acid are ethylene and carbon dioxide. The longer the reactant material is kept in the reactor (residence time), the more reactions influence the product mixture as indicated by Mok et al. Other free radical reactions further break down the by-products into appreciable amounts of acetic acid, acetone, methane, ethane, and other undefined materials.

At the conditions of the reaction the products, reactants, and solvent will have much different fugacities than at atmospheric conditions. But at the same time, since the concentration of the lactic acid is 0.4 M the fugacity of the lactic acid will not vary much, because the molarity of the water is around 50 M. The products will also be reasonably close to infinite dilution. The fugacities of the products/reactants/solvent will not change much from zero to 100 % conversion.

In order to calculate the equilibrium conversion in a straight forward manner, the equilibrium conversions for each of the three primary reactions and the secondary reaction were calculated independently using the fugacities of the components (reactants, products, solvent) involved. Later the equilibrium conversions were compared relative to each other and then these results are compared to the conversions in the Mok et al. paper. Otherwise the reactions would have to be taken as ideal, neglecting the fugacities, and the defining the conversion in terms of the reaction equilibrium conversions of all four reactions, simultaneously. The latter method was dropped in favor of the former method, because more useful data could be obtained and compared under more realistic conditions.

Procedure

In order to calculate the equilibrium conversions the equilibrium constant for each reaction must be calculated at standard state and then at the reaction temperature. To do this, the standard state free energies of formation (ΔG_f°) and heats of formation (ΔH_f°)

for each constituent in the reaction phase must be known. The equation used to calculate the equilibrium constant at standard state is:

$$K_a(T) = \exp((-\sum v_i \Delta G_f^\circ)/RT) \quad 3.3$$

In this equation the v represents the stoichiometric amounts in each reaction equation, R is the gas constant, T is the standard state temperature of 25 °C. The summation of the free energies of formation can be replaced by the free energy of the reaction in question. Equation 3.4 is used to determine the equilibrium constant at elevated temperatures and uses the heats of formation:

$$\ln(K_a(T_2)/K_a(T_1)) = ((\sum v_i \Delta H_f^\circ(T_1))/RT^2) \partial T \quad 3.4$$

In this equation the summation can be replaced by the standard state heat of reaction (ΔH°_{rxn}). If the heats of formation of the chemical species in the reaction are independent of temperature the above equation can be integrated easily to:

$$\ln(K_a(T_2)/K_a(T_1)) = (\sum v_i \Delta H_f^\circ(T_1)/R)(1/T_2 - 1/T_1) \quad 3.5$$

The equilibrium constants for each reaction and the heats of formation and free energies of formation for each specie is listed in Tables 3.2 and 3.1, respectively. If the heat of formation was dependent on temperature then the summation of the heat capacities of the reaction species should be included in the equation to account for the differences incurred in the equilibrium constants. When the equilibrium constants are in the range of 1.0 then the heat capacity differences (ΔC_p 's) have a large influence on the calculated constant, but at higher constant values the significance of the ΔC_p 's decreases greatly and the equilibrium constant can be approximated by the above equation. The equilibrium constants for the reactions discussed here, all have constants which are much greater than one, justify the use of the above equation for the calculation of the higher temperature equilibrium constant.

Table 3.1. Heats of Formation and Free Energy of Formation Values of Lactic Acid Reaction Species.

Species	ΔH_f @ 25 C	ΔG_f @ 25 C	Reference
Lactic Acid	-144.7	121.2	Miller, 1989
Acrylic Acid	-79.6	68.8	Miller, 1989
H ₂ O	-57.8	-54.635	Sandler, 1989
Acetaldehyde	-39.76	-31.81	Miller, 1989
Carbon Dioxide	-94.052	-94.26	Sandler, 1989
Hydrogen	0	0	Weast, 1982
Carbon Monoxide	-26.416	-32.808	Sandler, 1989
Propionic Acid	-108.75	-88.27	Sandler, 1989

Table 3.2. Equilibrium Constants for the Lactic Acid Reaction Pathways.

Reaction # 1 LA - AC + H2O + CO		
Temp - 298 K	3730	
Temp - 633 K	20600	
Reaction #2 LA - AC + H2 + CO2		
Temp - 298 K	0.0373	
Temp - 633 K	1.12 X 10^8	
Reaction #3 LA - AA + H2O		
Temp - 298 K	43.6	
Temp - 633 K	725	
Reaction #4 AA + H2 - PA		
Temp - 298 K	1.91 X 10^14	
Temp - 633 K	1.91 X 10^14	

In Table 3.1 the heats of formation and free energies of formation of each chemical specie were obtained from the sources listed. The constants are for each specie in the vapor state. This is for two reasons: the first is to make sure all the values for each specie are consistent, the second reason is the reaction conditions under supercritical water tend to mimic a vapor phase more than a liquid phase. All values listed are found in the literature, except for the values for lactic acid and acrylic acid. The values for these two materials are only for the liquid state. When the values for liquid and vapor states of similar specie were compared, the difference was found to be the heat of vaporization. The vapor state values for the two materials calculated in a similar fashion were used. These values were then compared favorably to the group contribution method used in the software program called Unifac (Sandler, 1989).

As can be seen from the equilibrium constants listed in Table 3.2, the constants are all dependent upon the temperature except for reaction 4; the hydrogenation of acrylic acid. It is temperature independent, but it is a very high value in the range of 10^{14} , meaning that the hydrogenation reaction goes essentially to completion. The acrylic acid formation pathway (reaction 3) has a reasonably large constant at 725 at a temperature of 633 K, but the competing reactions have higher constant values at 20600 and 112×10^8 for reactions 1 & 2, respectively.

In order to calculate an equilibrium conversion for each of the reactions, the equilibrium constant must be set equal to the concentrations of products divided by the concentration of the reactants all in terms of X; the conversion. Reaction three is shown at standard state at atmospheric pressure:

$$K_a(633 \text{ K}) = [\text{mol frac of AA}][\text{mol frac. of H}_2\text{O}]/[\text{mol frac of LA}] \quad 3.6$$

At elevated pressures the fugacity of the components must be taken into account along with the pressure of the reaction conditions. The above equation then becomes:

$$K_a(633 \text{ K}) = Y_{AA}\phi_{AA}P Y_{\text{H}_2\text{O}}\phi_{\text{H}_2\text{O}}P/Y_{\text{LA}}\phi_{\text{LA}}P \quad 3.7$$

Where Y is the mol fraction of the component, ϕ is the fugacity coefficient of the component, and P is the pressure of the reaction.

The reactions and their mol fraction calculations are shown in Table 3.3. The initial concentration of lactic acid used is 0.4 mols per liter of solution. The concentration of water initially is calculated by dividing the remaining mass of material by the molecular weight of water to yield 50.55 mols of water per liter of solution.

The method used to calculate the fugacities of the components in the reaction mixture was a packaged computer program called VLMU (Sandler, 1989) written in basic language which prompts the user for information on the quantity of the materials and the critical constants. Most of the critical constants could be found for the species used, but for acrylic acid, lactic acid, propanoic acid, and acetaldehyde some or all the constants had to be estimated by Lyderson's group contribution method which is explained in Perry's Chemical Engineer's Handbook (Perry, 1989). This group contribution method needs only the boiling point temperature as an input and then factors are assigned to specific groups contained in the molecule. These factors are combined in specific equations to calculate the individual constants. The estimated values are accurate to within two percent except for compounds which contain multiple polar groups such as the materials used here. The values for the boiling temperatures are found easily except for the value for lactic acid, which does not boil at atmospheric pressure, but rather it decomposes. The boiling temperature of the lactic acid at 10 mm of Hg is found and it is extrapolated to 760 mm using the Clausius-Clapeyron equation. The equations and calculations for the critical constants appear in Appendix C and the critical constants for the species are listed in Table 3.4.

The actual and estimated values for the critical constants are entered into the basic program to obtain fugacities for the components of interest. Reaction fugacities are calculated first by entering the critical constants and the mol fraction of the reactants/solvents. Since the conversion is not known guessed values of conversion are used to estimate the mol fractions for the

Table 3.3. Mol Fractions of Lactic Acid Reaction Species for the Individual Pathways.

Reaction 1 LA - AC + H₂O + CO

Component	Initial Conc.	Final Conc.	Mol Fraction
LA	0.4	0.4 - X	$(0.4 - X)/50.951 + 2X$
AC	0	X	$X/50.951 + 2X$
CO	0	X	$X/50.951 + 2X$
H ₂ O	50.551	50.551 + X	$(50.551 + X)/50.951 + 2X$
TOTAL		50.951 + 2X	

Reaction 2 LA - AC + H₂ + CO₂

Component	Initial Conc.	Final Conc.	Mol Fraction
LA	0.4	0.4 - X	$(0.4 - X)/50.951 + 2X$
AC	0	X	$X/50.951 + 2X$
CO ₂	0	X	$X/50.951 + 2X$
H ₂	0	X	$X/50.951 + 2X$
H ₂ O	50.551	50.551	$50.551/50.951 + 2X$
TOTAL		50.951 + 2X	

Reaction 3 LA - AA + H₂O

Component	Initial Conc.	Final Conc.	Mol Fraction
LA	0.4	0.4 - X	$(0.4 - X)/50.951 + X$
AA	0	X	$X/50.951 + X$
H ₂ O	50.551	50.551 + X	$(50.551 + X)/50.951 + X$
TOTAL		50.951 + X	

Reaction 4 AA + H₂ - PA

Component	Initial Conc.	Final Conc.	Mol Fraction
AA	X1	X1 - X	$(X1 - X)/50.951 + X1 + X2 + X$
H ₂	X2	X2 - X	$(X2 - X)/50.951 + X1 + X2 + X$
PA	0	X	$X/50.951 + X1 + X2 + X$
H ₂ O	50.551	50.551	$50.551/50.951 + X1 + X2 + X$
TOTAL		50.951 + X1 + X2 + X	

Table 3.4. Critical Constants for Reactants and Products.

COMPONENT	Pc(bar)	Tc(K)	Eccentric Factor	T-boil(K)
Lactic Acid	58.84	637.4	-0.5319	463
Acrylic Acid	55.81	611.9	-0.5105	412
Water	220.5	647.3	0.344	373.2
Acetaldehyde	54.71	461	0.25617	294
Carbon Dioxide	73.76	304.2	0.225	194.7
Hydrogen	12.97	33.2	-0.22	20.4
Carbon Monoxide	34.96	132.9	0.049	81.7
Propanoic Acid	53	612.5	0.5098	412.3

Results

Using the information in the literature of reaction three at a temperature of 450 K and a pressure of 33 bar, the decomposition of lactic acid to acrylic acid is assumed by reversing the appropriate mol fractions in terms of X , the compressed fugacities of the components, and inserting in the system into the equilibrium conversion equation. The algebra for each reaction conversion was solved on a spread sheet. The final equation for reaction three was in terms of a quadratic equation, which was easily solved using the quadratic formula to obtain the conversion in terms of mol fraction of acrylic acid. The calculated equilibrium conversion is 21 percent.

For reaction one the final equilibrium equation reduces down to a cubic equation in terms of conversion. The equation is solved by iteration between 0 and 0.4 to obtain the final conversion of 31

components. These first estimates of the fugacities for the components in the reaction mixture are inserted into the equilibrium conversion equation along with the pressures at which the reaction would be taking place to obtain the first estimate for the conversion. This estimate is then used to obtain new fugacities from the program and then in turn, these fugacities are used to find the new conversion values and then the process repeats until the value converges. The value obtained for the equilibrium conversion is the conversion of the reaction if it was the only reaction occurring at the time in the reactor. This is an ideal condition and it is a simplified solution to the designated problem, otherwise, to solve for the conversion involving three competing reactions and a major secondary reaction, would require a very complex numerical analytical technique. The results obtained in this chapter for each reaction can be compared to each other in a relative manner to estimate the actual conversions to the individual components. These results can be used to calculate the maximum possible conversion of the lactic acid to products under the stated conditions, if unnecessary side reactions can be reduced or blocked completely by kinetic effects. The calculation of the reaction equilibrium constants and conversions appear in Appendix C along with the final fugacities of the individual components.

Results

Using the above procedure the conversion of reaction three at a temperature of 633 K and a pressure of 313 bar, the dehydration of lactic acid to acrylic acid, is estimated by inserting the appropriate mol fractions in terms of X , the computed fugacities of the components, and pressure of the system into the equilibrium conversion equation. The solutions for each reaction conversion was solved on a spread sheet. The final equation for reaction three was in terms of a quadratic equation, which was easily solved using the quadratic formula to obtain the conversion in terms of mol fraction of acrylic acid. The calculated equilibrium conversion is 85 percent.

For reaction one the final equilibrium equation reduces down to a cubic equation in terms of conversion. This equation is solved by iteration between 0 and 0.4 to obtain the final conversion of 57

percent. The solution for reaction two is solved the same way and this results in a conversion of greater than 99 percent.

The secondary reaction, the hydrogenation of acrylic acid to propanoic acid, was estimated by arbitrarily choosing equal mol fractions of hydrogen and acrylic acid at 0.15 mols and using the same trial and error approach to calculate the estimated fugacities of acrylic acid, propanoic acid, and hydrogen. The final equilibrium equation in quadratic form is solved with the quadratic equation. This corresponds to a conversion of 41 percent of the acrylic to propanoic acid assuming there is equimolar amounts of reactants.

When a starting concentration of 0.1 M lactic acid was used the equilibrium conversion to acrylic acid increased only slightly to 85.5%. The changes in the reactant concentration does not have a significant effect on the formation of acrylic acid. When the temperature is varied in the analysis to obtain different equilibrium constants at the same 0.1 M reactant concentration, the equilibrium conversion increases with decreasing reaction temperature up to 90% at 310 °C. These results are shown in Figure 3.1. At a reaction temperature of 400 °C and a pressure of 313 bar the conversion drops to 84% as shown on the graph. The analysis at these concentrations and temperatures were performed to obtain an idea where Mok et al. stood in their investigation. These results show that Mok et al. (1989) were far from obtaining equilibrium conversion of the acrylic acid. The highest non-catalyzed conversion to acrylic acid is 18% (exp. #14). If the reaction pathway equilibrium conversions can be compared to each other in a relative manner the yields obtained by Mok are reasonable.

The reason that the first reaction equilibrium conversion does not go to completion, as determined from the results found here, is the equilibrium equation contains a squared pressure term in the product terms and these terms also contain a large fugacity value for carbon monoxide in reaction one. From the results we can see the three primary reactions are all temperature dependent and exothermic as the equilibrium constant increases with increasing temperature.

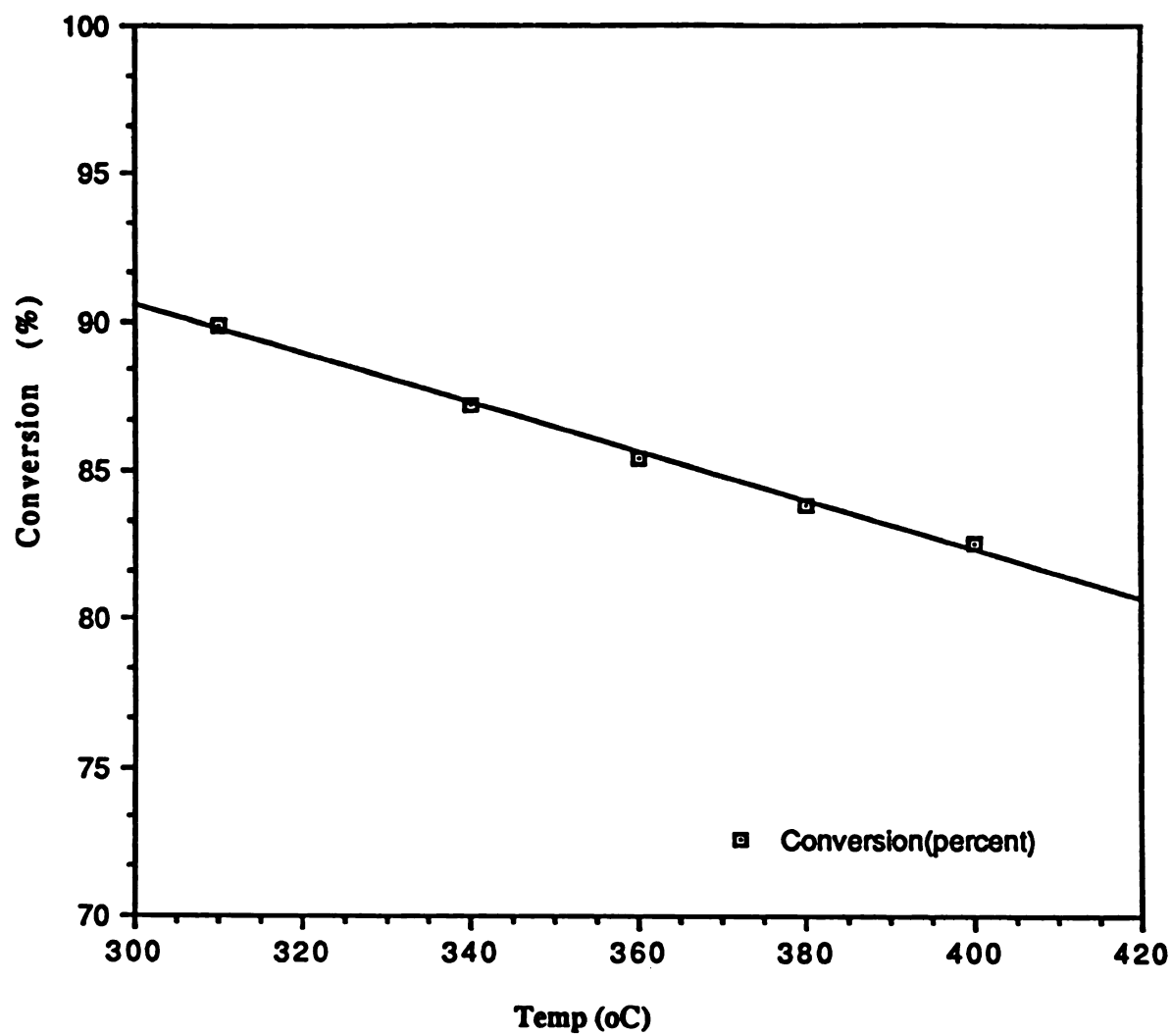


Figure 3.1. The Effect of Temperature on the Equilibrium Conversion of Lactic Acid to Acrylic Acid.

There were several assumptions made in the analysis of the equilibrium conversions. The first assumption was that the concentrations of the lactic acid and products at any time in the reactor were low enough to stay in solution and, therefore, the system would be homogeneous. This is very reasonable since the lactic acid is at a concentration of 0.4 M and the products would also be lower in concentration than the lactic acid. If the concentrations were higher, the solubility of the product gases in supercritical water may be exceeded and there may be two phases in the reactor promoting the conversion of lactic acid via reactions one and two. The second assumption made in the analysis was in the fugacity calculation for the products and reactants. In the computer program for calculation of fugacity coefficients it was assumed that the mixing coefficients were zero since, it would be unlikely to find the values for the unusual mixtures listed in the literature. Although these are not expected to be zero, the approximation was made to facilitate calculations.

CHAPTER IV

EXPERIMENTAL DESIGN

The experimental design of the supercritical/near-critical reactor is divided into four sections; the feed or pumping section, the reactor design section, the sampling section, and the heater/oven configuration section. Each design section is important to the accuracy of the data obtained and great care was taken in the selection and construction of the apparatus. Figures 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8 show the experimental apparatus in detail and should be referred to during the following text. Figure 4.1 is a simplified schematic of the overall design shown for clarification purposes.

Feed Section (Figure 4.2)

In this section the feed solution is introduced into the reactor. The lactic acid feed solution is kept in a two-liter glass flask equipped with a glass frit sparger and a spout at the bottom to provide gravity feed to a 100 ml buret. The feed solution is sparged with argon gas supplied to the sparger via Tygon® tubing. A cylinder of argon gas supplied by Michigan Welding Supply (99.95%) is the source of the sparge gas. The argon gas flow is controlled by a cylinder regulator supplied by Airco Welding Supply Division (model # 580 CGA) and a needle valve located inline to the sparger. A flow indicator is also located inline to the sparger. A one-liter bottom feed flask contains HPLC grade water. Both flasks feed through Tygon® tubing into a 100 ml buret equipped with a side-arm inlet located at the bottom near the valve. A glass tee two inches from the inlet connects the two feed flasks to the buret. Pinch clamps are used to control the flow of the individual flasks. The outlets of the feed flasks are approximately 15 inches above the pump.

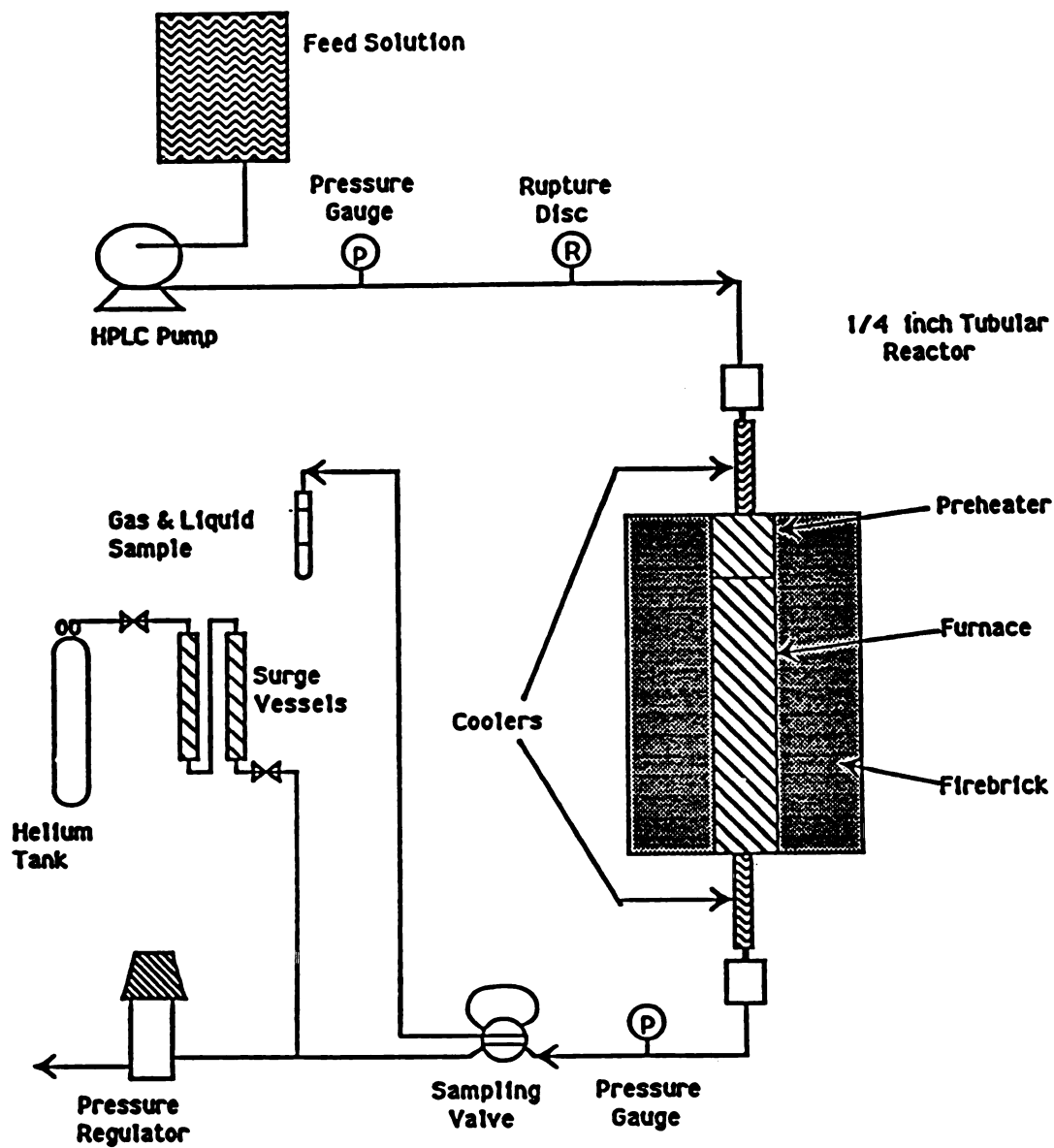


Figure 4.1. Schematic of High Pressure Experimental Apparatus.

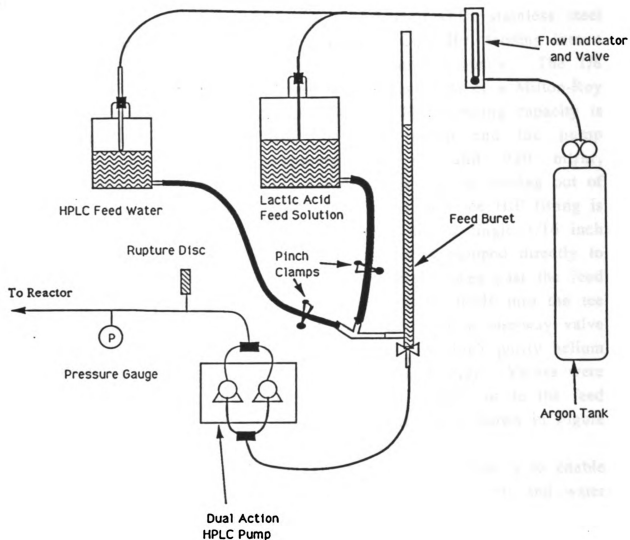


Figure 4.2. Schematic of Feed and Pumping Section of Experimental Apparatus.

The buret opening was approximately 4 inches above the pump. The solution is fed through the buret valve into 1/4 inch O.D. Tygon® tubing which is connected to 1/8 inch O.D. stainless steel tubing, supplied by High Pressure Equipment Co (HIP), feeding into a stainless steel tee fitting supplied by the same company. The 1/8 inch O.D. outlets of the tee fitting feed into each side of a Milton-Roy Duplex Minipump® model number 34540. The pumping capacity is controlled by separate controls on each pump and the pump minimum and maximum capacity was 46 and 920 ml/hr, respectively. The 1/16 inch O.D. stainless steel tubing coming out of the pump is manufactured by HIP. A stainless steel tee HIP fitting is used to combine the outputs from the pump into a single 1/16 inch O.D. stainless steel tubing. The feed solution is pumped directly to the reactor inlet. A HIP tee is located several inches past the feed junction. A 1/16 inch O.D. stainless steel tubing feeds into the tee from the helium source through a needle valve and a one-way valve supplied by HIP model number 15-41AF1-T. The high purity helium (> 99.995%) was supplied by Michigan Welding Supply. Valves were used to divert the helium to either the surge vessels or to the feed line. The helium section and surge vessel diagram is shown in Figure 4.3 and is described in the sampling section.

The purpose of the helium source in the feed line is to enable the reactor and sampling valves to be purged of reactants and water after use to prevent corrosion. A rupture disc fitting is located inline between the reactor and the pump. The rupture fitting and disc is supplied by HIP. The Oseco Co. 316 stainless steel 1/4 inch rupture disc has a rating of 5075 psi. The part number is H-0617-01. An Ashcraft 10,000 psi pressure gauge is mounted inline, 10 inches from the pump, through a HIP 1/16 inch O.D. tee.

Reactor Section

The reactor is shown in detail in Figure 4.4 for reference. The reactor was composed of a 1/4 inch O.D. 1/8 inch I.D. Hastelloy C-276 reactor from Autoclave Engineers Group in Erie, Pa. The reactor is 30 inches long with 10,000 psi 1/4 inch tee fittings mounted on each end so the run of the fitting is inline with the reactor. Through the

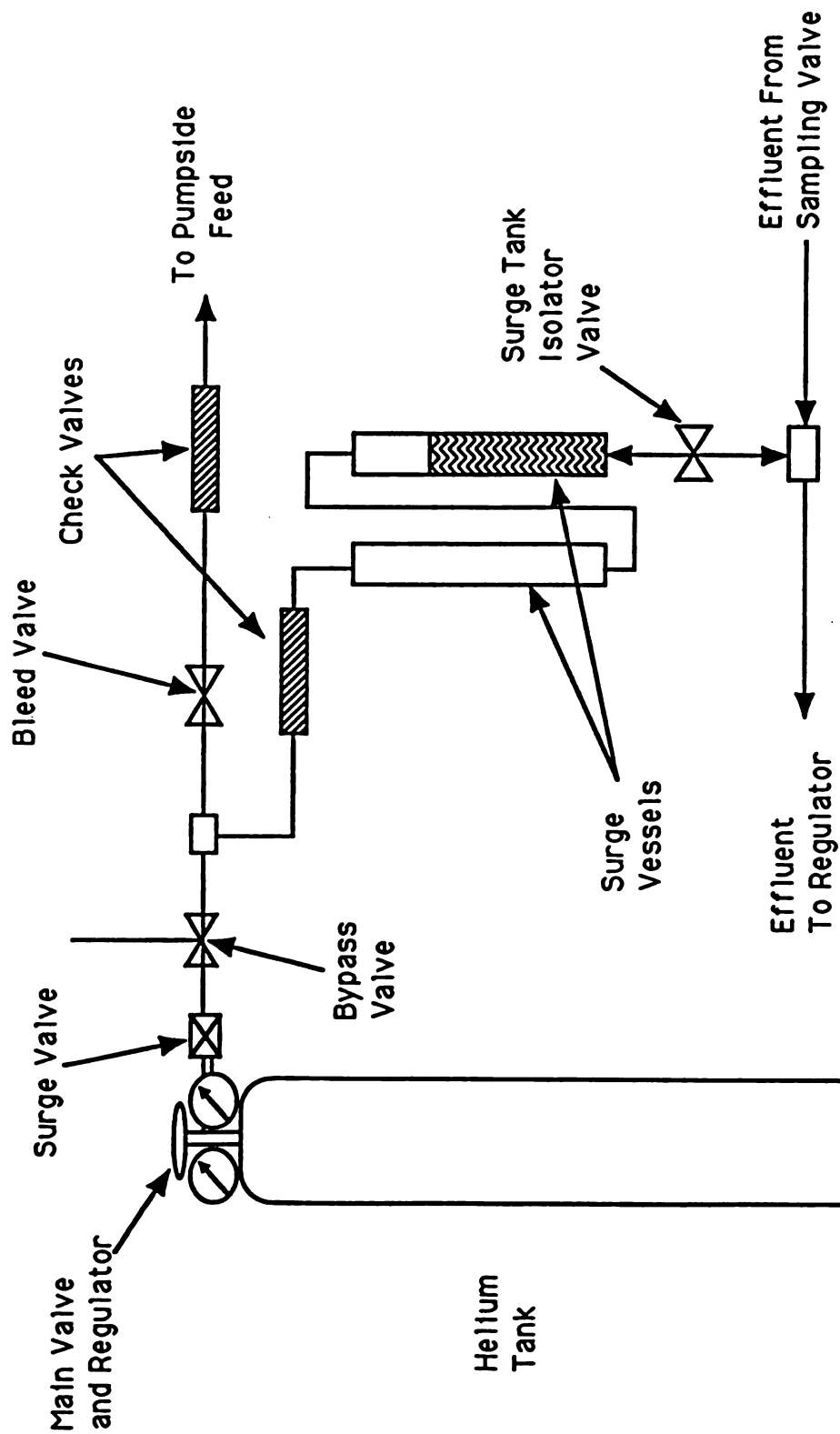


Figure 4.3. Schematic of Pressure Dampener Section of Experimental Apparatus.

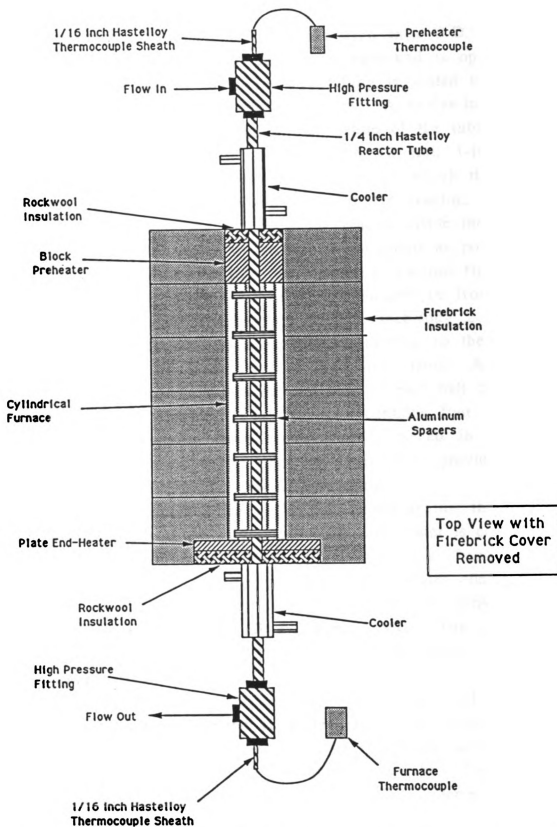


Figure 4.4. Schematic of Reactor and Heater Sections of Experimental Apparatus.

inside of the 1/4 inch reactor is placed a 1/16 inch O.D. Hastelloy tube which extends through both fittings so each end is open to the atmosphere. Each end of the 1/16 inch tubing is sealed to the 1/4 inch tee fitting with 1/16 inch adapter fittings. A twelve-inch-long 1 inch I.D. cylindrical furnace encloses the middle of the tubing. The reactor is supported inside the furnace with 12 flat, 1-inch-round spacers with 1/4 inch holes in the middle through which the reactor is supported. The spacers not only support the reactor, they also prevent convection along the length of the reactor inside the furnace. The spacers maintain as close to isothermal conditions as possible.

A preheater is used to heat the incoming reaction fluid up to the desired operating temperature and it is located in front of the furnace. The preheater is composed of a 2 inch-long 2-1/2 inch-diameter aluminum cylinder split in half length-wise so the cylinder can be clamped onto the reactor with a large hose clamp. A 1/4 inch diameter groove is machined into the flat side of each half to provide good contact to the reactor. The preheater contains four 3/8 inch-diameter cartridge heaters from Grainger Inc. placed in 3/8 inch holes drilled in the block. The holes are designed to provide a snug fit for the heaters to provide optimal heat transfer.

A heater is located at the outlet end butted against the furnace to control heat losses at the outlet end. The end heater is constructed from two four-inch-square brass plates with a bead heater sandwiched between the two plates. The entire heater configuration is enclosed in firebrick with a rating of 2000 °C provided by Industrial Firebrick Warehouse (Grand Rapids, MI). The end heater and the preheater are covered with rockwool insulation where the firebrick could not be used.

At each end of the reactor, 1/2 inch before and after the furnace, coolers are constructed from 1/4 inch O.D. brass tees, 1/2 inch Tygon® tubing, and hose clamps. The run of the brass tees are drilled out to 3/8 inch O.D. to fit over the reactor tube. Two tees per cooler are used and a four inch section of the Tygon® tubing is positioned between them and clamped to the threaded end of the tee. The outside ends of the tees are locked to the reactor with the 1/4 inch fittings. Copper tubing is used to connect the coolers to the

lab water through a King Industries GPM model flow meter. At the outlet end of the reactor, a stainless steel five micron Parker T-Filter from Forberg Scientific, Inc. protects the sensitive sampling valve and back pressure regulator from particulate damage.

Sampling Section

The sampling section is shown in Figure 4.5 for reference. From the reactor and filter, a 1/16 inch stainless steel tubing carries the reactor effluent to the six-port sample switching valve manufactured by Valco Instruments Company, model number C6W. The load position and the sample position are shown in Figures 4.6 a & b, respectively. To port number one on the the sampling valve is fitted a HIP needle valve (valve 3, Figure 4.5) and a 16 gauge female syringe fitting. Port number two is connected via 1/16 inch tubing to a HIP needle valve (valve 2, Figure 4.5) and then to a 16 gauge needle.

When the sample valve is rotated to the sample position, Figure 4.6a, the needle valve is opened at port two to allow material from the loop flow into the evacuated test-tube. When the equilibrium pressure reading is taken, the needle valve at port one is opened to equalize the pressure in the test-tube and to flush the remaining liquid from the loop. Port three and six contains the 1.303 ml sample loop constructed from approximately 16 inches of 1/8 inch O.D. stainless steel tubing and two 1/8 to 1/16 inch reducer fittings manufactured by HIP. Port four is the inlet from the reactor and port five is the outlet.

In the load position Figure 4.6.b, the effluent flows into port four out of port three to the sample loop into port six and then out of port five under operating pressure. To obtain a sample, the valve is rotated to sample position and the reactor effluent flows into port four and out of port five. The gas and liquid sample flows into port three from the sample loop and out port two to the test-tube. A more detailed description of the sampling procedure appears in Chapter 5.

The test-tube pressure and volume is measured in the set-up shown in Figure 4.5. A Welch Duo-Seal vacuum pump model # 1400

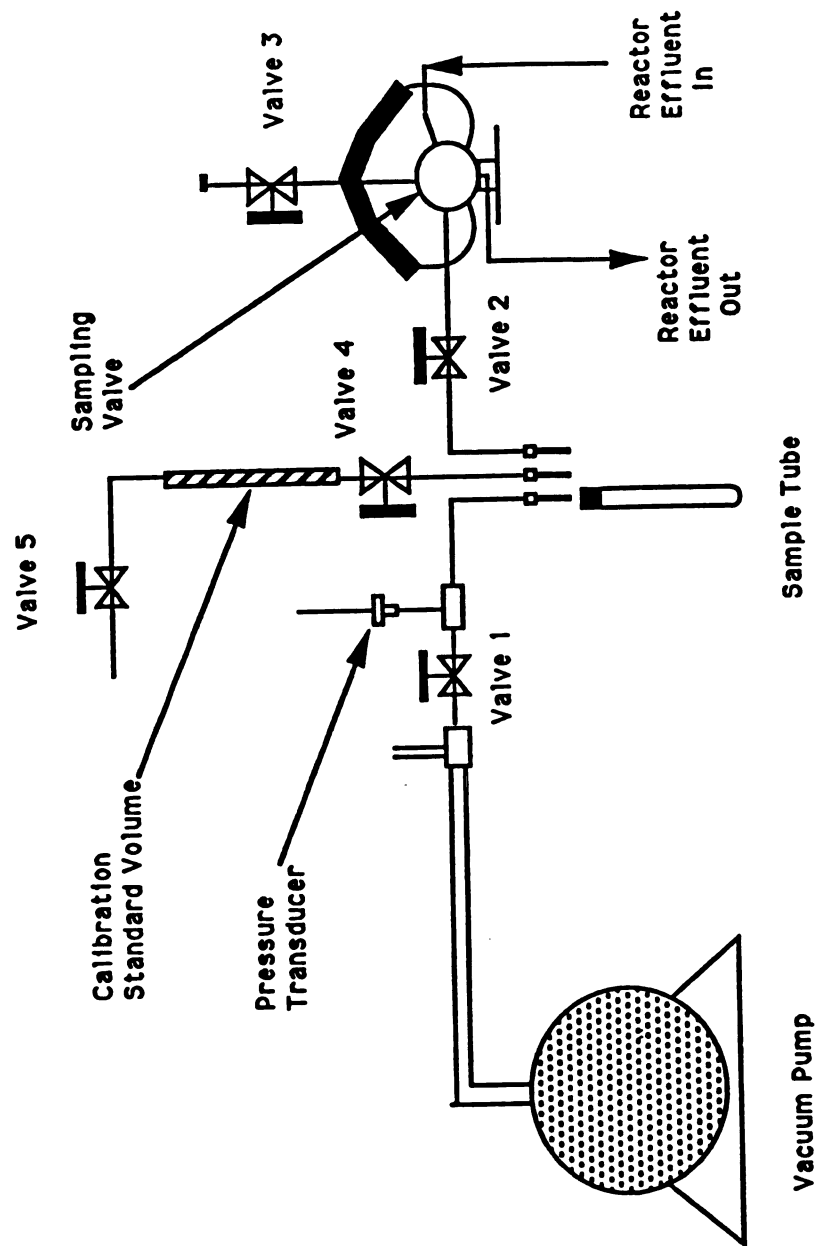
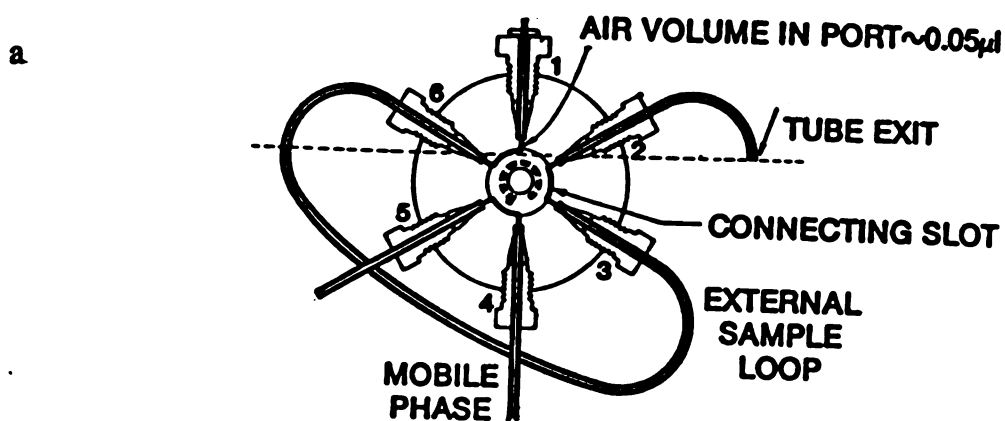


Figure 4.5. Schematic of Sampling Section of Experimental Apparatus.



VALVE IS VIEWED FROM SPRING END.
LOAD TO INJECT IS A COUNTERCLOCKWISE ROTATION.

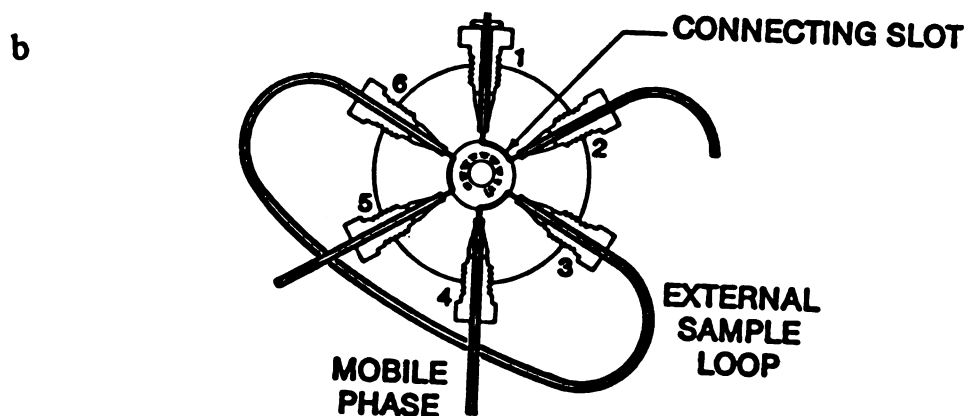


Figure 4.6. Schematic of Sampling Valve Operation in Sampling Section.

is connected, via heavy duty vacuum hose, to a glass three-way valve. One end of the valve opens to the atmosphere and the other is connected to 1/4 inch copper tubing via vacuum tubing. A 1/4 to 1/16 inch reducer leads into a HIP needle valve (valve 1) which leads to a tee fitting. One end of the tee fitting leads to a 1/4 inch Omega pressure transducer, the other end leads to 16 gauge needle which is inserted through the rubber stopper of a sample test-tube. The pressure transducer is connected to a Fluke model 73 multimeter through a Michigan State University shop-built converter. The sample tubes were Vacutainer® brand evacuated 10 and 20 ml glass tubes fitted with rubber stoppers. The collection tube are used to collect blood samples, therefore they are exceptionally clean.

A 20 inch length of copper tubing, 1/2 inch in diameter, contains a needle valve on each end. One end is open to the atmosphere and the other end is fitted with a 1/2 to 1/16 inch reducer. The 1/16 reducer is fitted with a 6 inch piece of 1/16 O.D. stainless steel tubing. A 16-gauge needle is connected to the tubing with finger-tight connectors. This tubing is used for the determination of the sample tube volumes, which vary in volume.

The reactor effluent passes from the sampling valve to a Tescom model number 26-3220-24 backpressure regulator through 1/16 inch stainless steel tubing in Figure 4.1. Two HIP tee fittings are connected inline between the sampling valve and the backpressure regulator. One is used as a pressure source to a HEISE digital pressure indicator, accurate to ± 1 psi, and the other is connected to two six-inch long 1/2-inch i.d. stainless steel vessels in series shown in Figure 4.3. The opposite end of the vessels is connected through a one-way valve, manufactured by HIP model number 15-41AF1-T, to a helium tank equipped with a regulator. The helium was provided by Michigan Welding Supply with a purity of 99.995%. The tank flow was controlled with a Harris regulator model number 87-1500. The stainless steel vessels are pressurized with helium and control pressure fluctuations during operation. The one-way valve ensures that no reactor effluent can be transferred to the tank. A three-way valve is located between the regulator and

the one-way valve to bleed off helium during shut-down. The vessels are isolated from the reactor effluent through a needle valve located inline.

From the outlet of the backpressure regulator, the effluent passes through 1/16 inch stainless steel tubing to the top of a 50 ml glass buret sealed with a rubber stopper. The tubing extends into the buret about 10 inches. Another 1/16 inch stainless steel tubing extending one-inch into the buret through the rubber stopper is connected to a sparger suspended in water. The sparger acts to dissolve volatile gases into the liquid and also as a gauge to determine the amount of gas evolving from the reaction. The gas is then released to a fume hood. The liquid effluent is collected in a flask below the buret and periodically the valve at the bottom of the buret is closed and the reactant flowrate is calculated by measuring the amount of liquid collected in a specified time. The liquid effluent is collected as waste and disposed of properly.

Heater Section

The schematic for the wiring of the furnace is shown in Figure 4.7. The furnace temperature is regulated with an Omega CN9111 miniature microprocessor temperature controller. The controller switches a variac, set at the maximum voltage (87.5 volts/ 73% variac setting) which the furnace could handle, on or off. The variac is then wired directly to the furnace. The thermocouple in the outlet end of the furnace provides input for the temperature controller. Overloads are prevented in the system with fuses in the variac and also in the miniature controller. A on/off switch provides current to the microprocessor and the variac.

The outlet end-heater and the preheater are wired together through one on/off switch as shown in Figure 4.8. Individual Omega temperature controllers (model CN9122) are used as before except Omega solid-state relay switches (model SSR 240 D25) are positioned between the temperature controller and the variac. This is done to prevent the temperature controllers from burning out from the frequent cycling occurring with the end-heater and preheater operation. The resistance of the bead heater is 2.5 ohms per foot and

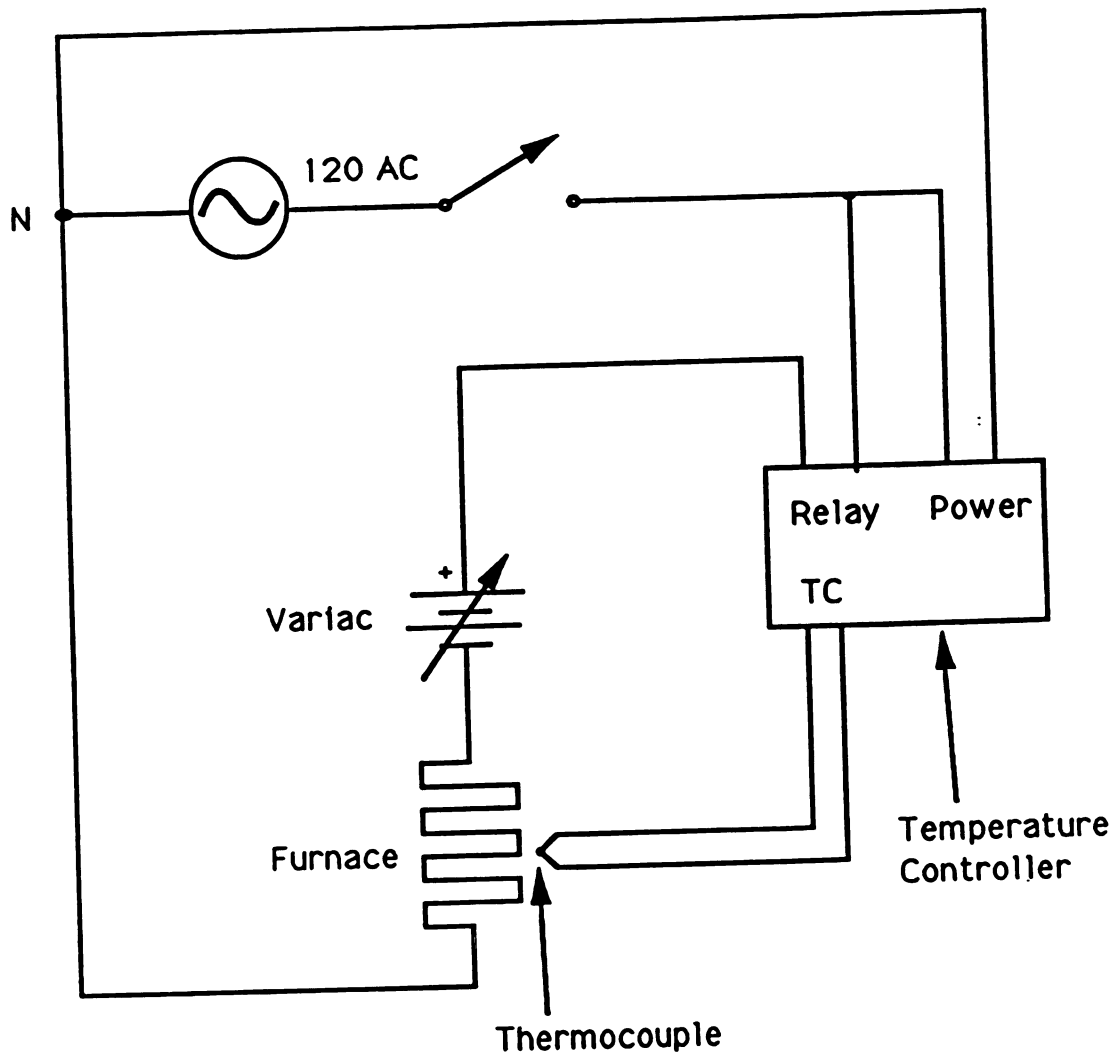


Figure 4.7. Schematic of Furnace Heater Wiring in Heater Section.

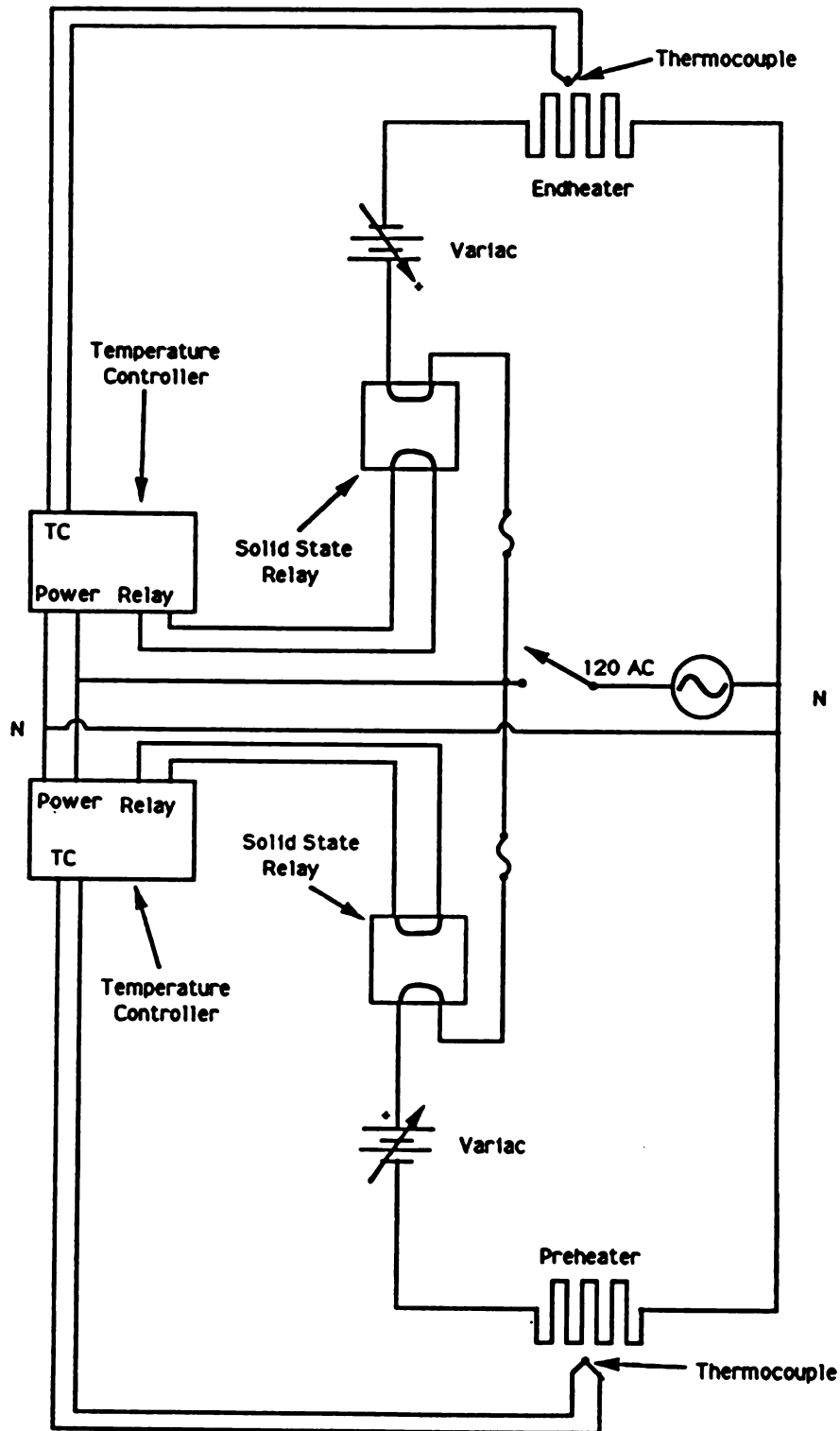


Figure 4.8. Schematic of End Heater and Pre-Heater Wiring in Heater Section.

2.8 feet of wire is used. The variac setting for the end-heater is limited to 22 percent or 25.9 volts. The variac setting for the preheater is not limited to the design of the cartridge heaters and it is arbitrarily set at 60 percent. The wiring of the preheater and end-heater is essentially the same as the wiring for the furnace.

CHAPTER V

EXPERIMENTAL PLAN

Preparation

1. The lactic acid feed solution was accurately prepared by weighing the lactic acid to four significant figures and then quantitatively transferring the liquid to a volumetric flask. HPLC analytical grade water was added to fill remaining volume. If a water soluble catalyst was to be used, approximately half of the water would be added to the flask before the catalyst was added, then the remaining water was added. An accuracy of ± 1 percent was attained in the weight of the lactic acid and catalyst and in the volume measurement.

2. A stirbar was added to the flask and then the solution was allowed to stir for at least 20 minutes on a magnetic stirrer.

3. Once the solution was well mixed, it was placed into a vented 2 liter flask equipped with a bottom port and argon sparger. The solution was sparged 30 minutes before use and then during the experiment to remove residual oxygen which may enhance the reactions. The sparge rate was set at approximately 90 mls/min as indicated from the flowmeter.

4. A similar one liter flask was filled with HPLC analytical grade water and sparged 30 minutes before use with argon.

5. The furnace heater and firebrick oven cover was carefully placed over the reactor tube and snugly fitted to the bottom firebrick section.

6. The water to the condensers was turned on to a steady flowrate of approximately one liter per minute. If the flowrate was too slow, the excess heat from the heat exchanger could be determined by feeling the outlet lines

7. The pinch clamp to the HPLC analytical grade water reservoir was opened to allow the water to fill the feed buret (see Figure 4.2). The buret valve was also opened at this time and the feed pump was started at a rate 10 to 15 times higher than the operating flowrate.

8. When the feed solution primed the entire system, as evidenced by the solution flowing into the product buret, the pressure regulator was slowly turned to increase pressure in the system to approximately 2500 psi as read from the Heise pressure gauge.

9. The bypass valve was turned so the surge tank side will be pressurized and the bleed valve was turned off as shown in Figure 4.3. With the helium surge valve off, the helium tank main valve was opened and the regulator was adjusted to yield 1600 psi of helium output pressure. The tank main valve was closed and then the helium surge valve was opened. with the surge tank isolator valve completely closed. The tank main valve is opened again for a few seconds to equilibrate the surge tanks to 1600 psi. This process allows the tanks to build up pressure gradually and also prevents full pressure from being applied to the system with a valve unexpectedly open.

10. The surge tank isolator valve was opened slowly to expose the system to the surge suppressor tanks. The momentary drop in pressure was followed by a slow increase up to the previously attained system pressure. The backpressure regulator was gradually adjusted up to the operating pressure over a ten minute time period. Once the surge tanks were employed, the pressure was maintained +- 15 psi.

11. During the final pressure buildup the main switches to the outlets and the variacs were turned on. The setpoints for the preheater and the furnace were set at the desired operating temperature of the reactor and the setpoint for the outlet end heater was set at approximately 280 °C. The variacs were set at the desired voltage output. The temperature was held to within ± 3 degrees Celsius

12. After the operating pressure had been reached and the temperatures of the furnace and preheater had equilibrated, the pinch clamp to the HPLC water was applied so the water remaining in the buret would be used (see feed section Figure 4.2). When the buret was nearly empty, the feed solution pinch clamp was opened and approximately 10 mls of feed solution was added to the buret then the pinch clamp was closed. As the buret was emptied a second time the process was repeated again. After the second 10 mls of feed solution was used, the pinch clamp was released, completely filling the buret with feed solution.

13. The appropriate feed rate was adjusted at the HPLC pump. The feed rate was calculated from the reactor effluent in a buret graduated in tenths of a ml. A quantity of liquid was collected for a period of at least ten minutes and no more than twenty minutes. The HPLC pump was adjusted accordingly. The process was repeated as needed. The flow rate was accurate to within ± 2 percent.

Sampling Procedure: (refer to Figures 4.5 and 4.6)

1. When the system had attained equilibrium for at least 30 minutes, a gas and liquid sample was collected in 10 or 20 ml evacuated blood collection test tubes equipped with rubber stoppers.

2. The test tubes were initially evacuated to 10 percent of atmospheric pressure with a vacuum pump through a 16 gauge needle inserted into the stopper. The pressure in the test tubes was measured with a pressure transducer which was connected to a

voltmeter (not shown) to measure the voltage changes. These voltages were interpreted as pressures by calibrating the voltages to pressures. The volumes were determined with a Basic computer program incorporating the calibrations (see Appendix B).

3. The evacuated test tube was connected to the pressure transducer and a calibrated standard volume of air at atmospheric pressure through a 16 gauge needle. The known volume was accessible through a needle valve (valve 4). The voltmeter readings were recorded before and after the valve was opened. The standard volume was removed and replaced with a 16 gauge needle connected to the outlet port of the sampling valve.

4. The tube was once again evacuated to approximately 10 percent of atmospheric pressure. With both needle valves (valves 2 & 3) closed to the outlet ports of the sampling valve, the sampling valve was rotated from the load position to the sample position. The needle valve (valve 2) between the sample valve and the evacuated test tube is opened slowly to pull the liquid and gas sample from the sample loop into the test tube. The voltmeter readings were recorded both before sampling and after equilibrium has been reached after sampling

5. The needle valve (valve 3) on the upper end of the outlet port of the sampling valve was opened slowly to flush the remaining fluid from the sample loop and to bring the test tube up to atmospheric pressure.

6. The 16 gauge needle connections were then removed from the test tube and the test tube was placed aside for later analysis. .

7. A 4 ml volume of HPLC water was flushed through the sample loop from valve 3 with the aid of a syringe and syringe fitting. When the sample loop was completely filled with water (as determined by the amount of water left in the syringe) the valve was switched over to load, so the filled sample loop would not drop the operating

system pressure as it was switched over. The water remaining in the tubing and valves was removed by forcing air through valve 3 via the syringe. This was performed until no more water flowed from the 16 gauge needle. Valves 2 & 3 on the outlet ports were then closed. The sampling apparatus was now ready for the next sample. The gas/liquid samples were saved for analytical examination by Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC).

Sample Analysis:

1. The first step in the analysis was to determine the relative composition of the gas phase with Gas Chromatography (GC). Immediately after the sample was collected, a volume (between 0.2 mls and 1.0 mls) of the gas sample was removed from the sample tube with a gas syringe and injected into a Perkin-Elmer model 8500 equipped with a 80/100 mesh Spherocarb™ column supplied by Alltech Associates, Inc. The gas analysis was performed immediately, to reduce uptake of carbon dioxide to the liquid phase, if the analysis was performed within 10 minutes of collection, the loss would be less than 2 percent. The column reproducibly separated carbon dioxide, carbon monoxide, methane and ethylene very well. For more details on the gas chromatograph used, type of column and the calibration performed refer to Appendix A

2. The next step in the analysis was to determine the composition of the liquid phase and the quantity of the components in the sample. This was done by High Performance Liquid Chromatography (HPLC). The HPLC unit is a Waters 600 solvent delivery system equipped with a Waters 490 refractive index detector. The column used was a Hypersil C-18 10 micron column supplied by Alltech Associates. HPLC grade water (Baker HPLC-grade) buffered with 0.1 molar K_2HPO_4 (Baker Analyzed) was used as the carrier solvent. The solvent was adjusted to a pH of 4.2 with H_3PO_4 and a flowrate of 2.0 ml/min. The component calibration and details on the HPLC system used appears in Appendix A.

CHAPTER VI

RESULTS AND DISCUSSION

From the beginning of this project many design changes were incorporated to improve the performance of the reactor. Initially the reactor set-up was similar to Figure 6.1. The reactor was equipped with the furnace and two end heaters instead of a preheater and one end heater as illustrated in Figure 4.4. Only one firebrick lengthwise, parallel to the reactor was used to cover each half of the furnace. The thermocouples controlling the heaters were located inside the reactor, exposed to the supercritical fluid. The 1/16 inch thermocouples were placed inside from each end of the reactor. Initial experimental runs failed to accomplish the desired reactor temperature needed for supercritical conditions. The heat loss through the firebrick walls was excessive. The idea behind the changes was to make the reactor as isothermal as possible by incorporating thicker insulated walls and using firebrick with a higher insulating value. The lengthwise firebrick design was replaced with firebrick, set on edge, perpendicular with the furnace, with a 2 inch half-moon piece cut out to accommodate the 2 inch diameter furnace. This worked much better as the reactor temperature was attained quickly and with minimal heat loss. Outside firebrick temperatures were on the order of 45 - 50 °C when the reactor temperature is 400 °C and the flowrate is 1.0 ml/minute. The furnace controller's output is on 10 - 20 percent of the time when the reactor has attained steady-state, indicating slow heat loss.

The first series of experiments after the reactor change was to evaluate zeolite-type catalysts as lactic acid dehydration catalysts. The reactor was packed with zeolite Y-82 type catalyst particles between the sizes of 16 and 32 mesh. The reactor was filled between the end heaters along the full length of the furnace (12

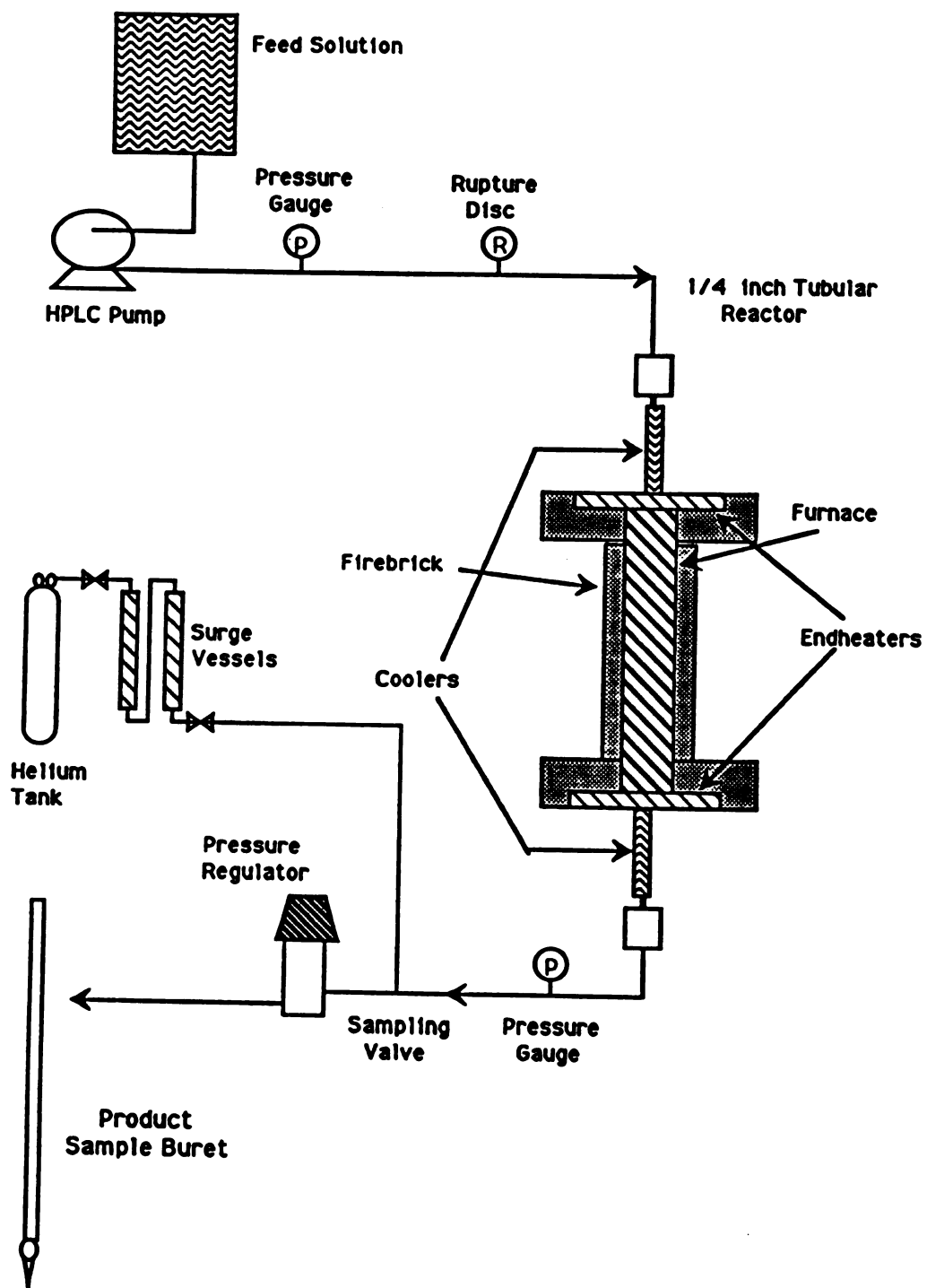


Figure 6.1. Schematic of Preliminary Reactor Design.

inches). The residence times were estimated by determining the void volume in the reactor using the estimated size of the particles. The reactor temperatures were controlled using a thermocouple at the end of the reactor. Several runs were executed for a total of 10 hours of reactor operation. After completion of the studies the reactor was removed and the zeolite catalyst was removed. Only 16 percent of the original amount of catalyst was recovered. The remaining catalyst was dissolved by the supercritical fluid. Literature sources support the increased solubility for silica in supercritical water as shown in Figure 6.2 by Kennedy (1950), but no data was found dealing directly with zeolites. Several sources for solubilities of inorganic compounds in supercritical or high temperature water exist including Marshall (1968, 1975), Cobble (1966) and Franck (1968). A general tutorial on the solubilities of solids in supercritical water can be found in a paper by Lira (1987). The reaction results varied over a period of time, because the catalyst was eluting. Initial results also indicate the use of zeolite-type catalyst was not worth pursuing because of the low amount of acrylic acid produced.

Several series of runs were performed with the thermocouples placed inside of the reactor itself. The end plate heater was controlled by a stainless steel thermocouple in the inlet end extending 1.5 inches into the reactor furnace zone. This plate heater was used a preheater just before the furnace. A stainless steel thermocouple in the outlet end controlled the furnace and it extended about 1.5 inches into the reactor furnace. After several runs the thermocouples which extended into the supercritical reaction zone dissolved readily in an area 1/2 inch long, about one inch from the end of the thermocouple. The very ends of the thermocouple were black and pitted but not dissolved. The concentration corrosion was apparently in a area between the supercritical fluid and the reactant liquid at high pressure. More on this type of corrosion is described by Metcalf (1973). To solve the problem, different types of thermocouples were used (i.e. Inconel) without success, although the 316 stainless steel performed better than Inconel. More resistant-type thermocouples (i.e. Hastelloy)

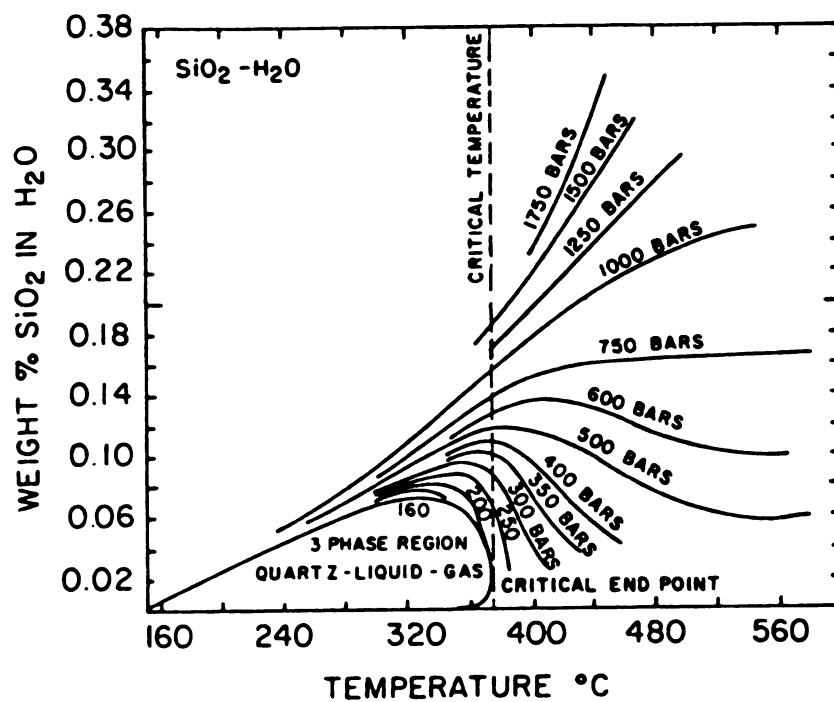


Figure 6.2. Solubility of Solid Silica in Supercritical Water (Kennedy, 1950).

were expensive because they had to be custom-made and a minimum order was required, therefore they were not used. The solution was to move the thermocouples to the outside of the reactor into the furnace zone. An experimental run was executed to determine the furnace and end heater temperatures required to maintain 400 °C in the reactor at constant flowrate of 1.0 ml/minute. The runs were performed with 1.0 M lactic acid solution and not water because the exothermic reaction lactic acid undergoes contributes heat to the reactant solution. The thermocouple controlling the furnace was placed four inches into the furnace approximately 1/4 inch from the reactor equidistant between the outer reactor wall and furnace. The thermocouple controlling the end heater was placed just inside the preheater at the beginning of the furnace equidistant from the furnace and reactor.

After several runs it was evident that the existing set-up did not adequately heat the incoming fluid quickly enough to provide a large enough reactor zone and, hence, long enough residence times. There was not enough heat input at the inlet end to bring the fluid up to operating temperature fast enough. This could result in a large error in the data because of the large product contribution from the reactions occurring between room temperature and the operating temperature in the preheat zone. The shorter the preheat zone the more reliable and fundamentally sound the reactor data will be. With this in mind a new preheater was designed to replace the end heater. The new end heater was designed to direct a large amount of heat to the incoming fluid in short zone. It was also designed with enough mass to resist small temperature fluctuations. Two half-moon shaped aluminum blocks were constructed, which are two inches long with a diameter of two inches. The pieces were clamped onto the reactor in front of the furnace and heated with one inch long cartridge heaters inserted into holes bored into the ends. The holes provided a snug fit for the cartridge heaters. The diagram of the preheater position is shown in Figure 4.4. The heaters were interfaced with the same temperature controller and variac as was used on the previous end heater. With the new design, the inlet end cooler was shifted 2 inches away from the furnace to allow room for

the new preheater. The firebrick insulation was redesigned by adding a few more bricks to accommodate the new preheater. A thermocouple well was drilled into one half of the block between the cartridge heaters and the reactor. A thermocouple inserted into this hole, initially provided temperature information for cartridge heater control. The set point was determined as in previous trials.

Poor reactor temperature control and lack of setpoint data for the reaction at different flow rates and at varying pressures and temperatures led to the need for better reaction temperature control via better reactor temperature data. Inconel thermocouples, 16 inches long, were used to read the temperatures in the reactor. These were inserted from each end into the preheater zone and furnace zone. After several runs these thermocouples were found to perform worse than the stainless steel thermocouples. This led to the final design change. A 1/16 inch Hastelloy tube was inserted through the reactor so both ends extended through the fittings on the outlet and inlet ends. The tubing was locked in place with HIP fittings. The inside of the 1/16 inch tube was exposed to the atmosphere and 24 inch long 0.02 inch diameter thermocouples were inserted into the reactor from each end. This solved two problems: first the fragile thermocouples would be protected from the harsh corrosive environment and second the thermocouples could be moved along the whole length of the reactor to obtain a temperature profile.

An analysis of the reactor temperature profile over the length of the preheater and furnace zones was performed at a controller setpoint of 360 °C. A tabulation of these results appears in Table 6.1. A summation of these results appears in Figure 6.3. The temperature is fairly consistent over a 11-inch long area in the furnace, not varying more than +/- three degrees Celsius over the length. The temperature rises sharply and decreases sharply as indicated from the figure. This result gives confidence that the results presented in this thesis are characteristic of the temperatures stated. The fast temperature rise and drop leaves very little time for reaction to occur at temperatures other than the stated reactor temperature.

Table 6.1. Reactor Temperature Profile Data.

Relative Length - Inlet (inches)	Temperature (°C)
0	188
1	302
2	347
3	359
4	363
5	364
6	363
7	362
8	362
9	362
10	362
11	362
12	361
13	356
14	335
15	268

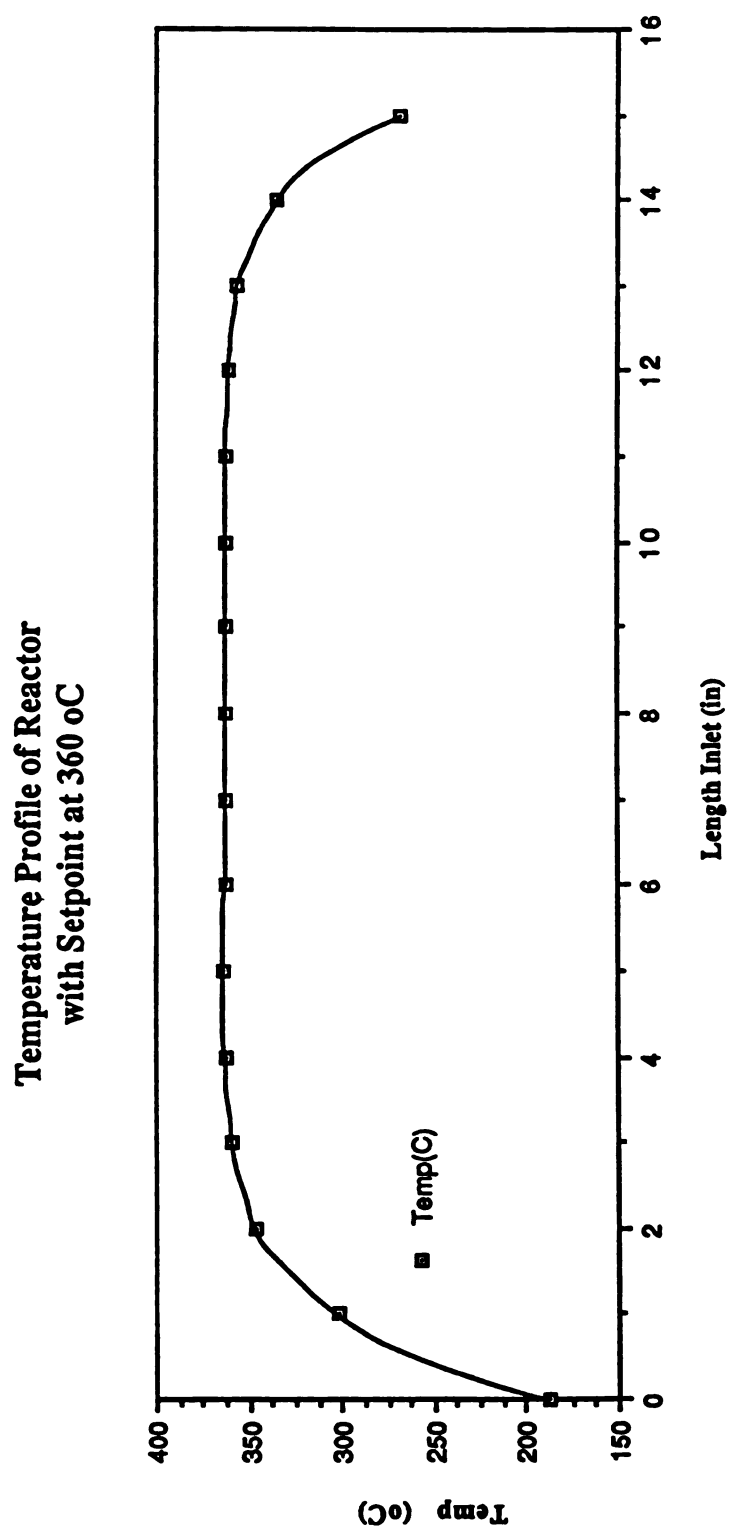


Figure 6.3. Temperature Profile of Reactor at Operating Temperature of 360 °C.

Results

Table 6.2 presents results of the studies. The reaction products are tabulated on a basis of grams obtained per liter of reactant solution. The water produced in the reaction is calculated from the total mols of lactic acid reacted via pathway one and pathway three. The mols of carbon monoxide plus the mols of acrylic acid, propionic acid, and ethylene are equal to the mols of water produced. Hydrogen gas is a product of the pathway two reaction and it is produced in such small quantities that it is neglected in the overall mass balance. The column labelled 'Reaction Effluent g/L' is the sum of the mass of all reaction effluents per liter of feed solution. The molar yield, based on feed (BOF), is based on the mols of acrylic acid produced, divided by the theoretical mols of lactic acid fed into the reactor and the molar yield, based on conversion (BOC), is based on the mols of acrylic acid divided by the mols of lactic acid reacted to products (calculated from 'Reaction Effluent g/L' minus 'lactic acid').

The percentage of lactic acid reacting by pathway three is calculated by dividing the number of mols of lactic acid reacted via pathway three (acrylic + propionic + ethylene) by the mols of lactic acid reacted and is labelled 'Pathway III' in Table 6.2. The remaining percentage of lactic acid reacted is divided among the other two pathways based on the ratio of the mols of carbon monoxide and carbon dioxide produced (labelled 'Pathway I' and 'Pathway II', respectively). Carbon dioxide associated with ethylene formation is not included in the last calculation. The yields of certain products (acetic acid, methane, etc.) are neglected in the calculated yields because they are negligible in comparison to the specified pathways.

The column labelled 'Selectivity' is the mols of acrylic acid divided by the mols of lactic acid reacted to other products. The column labelled 'Selectivity/Pathway III' is the mols of lactic acid reacted via pathway three divided by the mols of lactic acid reacted via pathway one and two. The values of selectivity range from zero for no formation of acrylic acid to infinity for complete conversion to

Table 6.2. Experimental Data.

Run	Acetaldehyde	Methane + Acetic acid	Propionic Acid	Acrylic Acid	Lactic Acid	Carbon Monoxide	Carbon Dioxide	Ethylene	Water	Reaction Effluent g/l
1	1.0	0.01	0.2	1.2	32.6	1.08	0.21	0.00	1.03	37.3
2	1.1	0.01	0.1	1.4	31.5	1.22	0.37	0.01	1.17	37.0
3	1.7	0.01	0.1	1.9	29.8	1.53	0.48	0.02	1.49	37.0
4	2.2	0.01	0.2	2.4	28.5	1.72	0.61	0.02	1.76	37.4
5	2.5	0.01	0.2	2.6	26.9	1.95	0.74	0.03	1.96	36.9
6	2.6	0.01	0.2	2.7	26.3	2.03	0.79	0.04	2.08	37.1
7	3.1	0.01	0.3	3.1	24.5	2.11	0.88	0.04	2.23	36.3
8	0.7	0.00	0.0	2.3	34.9	0.92	0.07	0.01	1.18	40.2
9	1.9	0.01	0.1	2.1	32.5	1.48	0.17	0.02	1.51	39.8
10	2.2	0.03	0.1	2.4	31.2	1.73	0.18	0.03	1.74	39.8
11	2.3	0.04	0.1	2.8	29.7	1.88	0.22	0.04	1.97	39.2
12	3.0	0.05	0.1	3.4	27.4	2.29	0.31	0.05	2.37	39.0
13	3.5	0.06	0.2	4.3	19.4	3.08	1.18	0.29	3.30	35.4
14	1.9	0.03	0.0	4.3	24.8	1.55	0.66	0.19	2.20	35.6
15	0.8	0.01	0.0	2.5	31.5	0.86	0.23	0.05	1.09	36.9
16	0.4	0.01	0.0	1.1	34.4	0.28	0.09	0.02	0.46	36.7
17	0.2	0.00	0.0	0.5	35.2	0.23	0.05	0.01	0.28	36.5
18	3.6	0.11	0.2	4.4	19.8	2.69	1.25	0.35	3.10	35.5
19	2.6	0.09	0.0	2.8	27.7	2.09	0.25	0.07	2.08	37.6
20	1.4	0.03	0.0	2.9	29.5	0.97	0.45	0.15	1.46	36.9
21	1.2	0.04	0.0	3.2	31.2	1.03	0.34	0.08	1.51	36.6
22	1.4	0.04	0.1	3.2	30.8	1.08	0.34	0.13	1.60	36.6
23	1.2	0.07	0.1	3.2	30.4	0.97	0.44	0.15	1.55	36.0
24	0.7	0.03	0.0	3.1	29.4	0.76	0.69	0.20	1.40	36.3
25	3.7	0.01	0.1	3.6	24.3	2.49	0.45	0.04	2.54	37.2
26	2.2	0.01	0.2	3.0	26.3	1.72	0.77	0.05	1.93	36.2
27	1.5	0.07	0.3	3.1	27.2	0.94	1.17	0.05	1.49	35.8
28	0.9	0.15	0.2	1.6	32.2	0.38	0.98	0.06	0.75	37.3
29	1.2	0.22	0.2	2.3	30.4	0.51	1.02	0.12	1.04	37.0
30	1.1	0.00	0.0	2.0	31.1	0.76	0.73	0.06	1.04	36.8

Table 6.2. (Continued)

Run	Molar yield BOC	Molar yield BOF	Conv. %	C Bal. %	Temp. (°C)	Pressure (psi)	Residence time - s	Catalyst	Selectivity Pathway III	Path I %	Path II %	Path III %
1	32.1	4.17	13.0	103	360	4550	27	blank	0.66	56.8	6.9	36.3
2	33.0	4.95	15.0	101	360	4500	42	blank	0.74	53.8	10.2	36.2
3	31.9	6.42	20.1	102	360	4550	53	blank	0.61	54.7	10.5	34.8
4	33.8	8.34	24.7	103	360	4500	67	blank	0.62	51.9	11.3	36.8
5	32.4	8.94	27.6	101	360	4540	81	blank	0.59	52.2	12.1	35.7
6	31.9	9.52	29.9	102	360	4500	94	blank	0.55	51.9	12.3	35.8
7	33.1	10.84	32.7	100	360	4470	117	blank	0.56	50.1	12.7	37.2
8	54.2	8.09	49.8	112	360	4550	20	blank	1.39	44.7	1.8	53.6
9	39.5	7.39	36.5	110	360	4647	39	blank	0.65	60.6	3.5	35.9
10	38.2	8.32	35.6	109	360	4509	50	blank	0.62	61.7	3.1	35.2
11	36.8	9.75	37.2	108	360	4605	63	blank	0.68	59.5	3.3	37.3
12	36.6	11.82	36.8	107	360	4520	83	blank	0.65	59.6	3.8	36.6
13	44.2	15.01	34.0	96	400	4550	54	0.02 M Na ₂ HPO ₄	0.64	49.5	9.1	41.4
14	30.0	14.68	49.5	98	360	4550	56	0.02 M Na ₂ HPO ₄	1.18	37.2	7.2	55.5
15	15.0	9.77	56.5	102	360	4530	55	0.02 M Na ₂ HPO ₄	1.69	32.5	5.6	61.9
16	6.4	3.67	57.0	102	340	4670	56	0.02 M Na ₂ HPO ₄	1.45	34.8	5.5	59.7
17	3.7	1.82	49.4	101	320	4620	54	0.02 M Na ₂ HPO ₄	1.28	43.8	5.5	50.6
18	43.6	15.34	35.2	97	400	4618	54	0.02 M Na ₂ HPO ₄	0.61	46.5	9.8	43.7
19	27.5	9.60	34.9	104	360	4640	81	blank	0.62	62.9	2.8	34.3
20	20.7	10.23	49.4	102	360	4640	81	0.04 M Na ₂ HPO ₄	1.05	40.4	5.6	54.0
21	20.5	11.12	54.4	106	360	4640	81	0.004 M Na ₂ HPO ₄	1.47	41.3	5.4	53.3
22	21.8	11.18	51.3	107	360	4640	81	0.008 M Na ₂ HPO ₄	1.20	41.9	3.5	54.6
23	21.2	11.22	52.9	105	360	4640	81	0.02 M Na ₂ HPO ₄	1.31	38.4	5.0	56.6
24	19.2	10.81	56.3	100	360	4640	81	0.08 M Na ₂ HPO ₄	1.82	31.3	10.0	58.7
25	35.7	12.48	34.9	103	360	4655	82	blank	0.58	57.5	6.0	36.5
26	27.3	10.44	38.2	99	360	4759	82	pH 2.20 w/NaOH	0.77	45.7	12.1	42.2
27	24.1	10.76	44.6	99	360	4733	82	pH 2.74 w/NaOH	1.01	27.9	21.0	51.1
28	14.0	6.70	40.8	103	360	4660	82	pH 3.43 w/NaOH	0.83	20.0	30.4	49.6
29	18.5	7.97	43.2	102	360	4660	82	pH 3.09 w/NaOH	0.83	21.9	24.6	53.5
30	15.9	7.02	44.0	102	360	4650	82	pH 2.45 w/NaOH	1.00	33.4	18.7	47.9

Table 6.2. (Continued)

Run	Acetaldehyde	Methane + Acetic acid	Propionic Acid	Acrylic Acid	Lactic Acid	Carbon Monoxide	Carbon Dioxide	Ethylene	Water	Reaction Effluent g/l
31	1.9	0.01	0.1	2.0	28.1	1.86	0.35	0.03	1.75	36.1
32	4.0	0.02	0.1	2.4	24.7	2.84	0.19	0.03	2.47	36.7
33	4.7	0.02	0.0	2.2	22.4	3.61	0.17	0.04	2.90	36.0
34	6.4	0.01	0.0	2.3	18.8	4.63	0.17	0.04	3.56	35.9
35	8.7	0.01	0.0	2.3	14.6	5.74	0.33	0.03	4.28	35.9
36	0.9	1.87	0.0	2.7	31.4	1.28	0.23	0.03	1.51	39.9
37	3.4	2.77	0.1	1.2	24.2	1.92	0.54	0.09	1.62	35.9
38	1.3	1.87	0.2	2.1	30.4	1.15	0.29	0.03	1.32	38.5
39	5.4	0.6	1.3	0.0	25.7	0.06	4.74	0.01	0.37	38.1
40	1.1	0.00	0.0	1.1	33.5	0.45	0.40	0.02	0.58	37.1
41	1.3	0.00	0.0	1.7	32.6	0.50	0.56	0.03	0.75	37.4
42	1.7	0.01	0.2	2.0	31.2	0.62	0.81	0.05	0.98	37.6
43	2.0	0.01	0.3	2.4	29.7	0.67	1.07	0.07	1.15	37.4
44	2.2	0.01	0.5	2.4	28.0	0.72	1.24	0.10	1.26	36.4
45	0.7	0.00	0.0	1.2	33.7	0.40	0.10	0.01	0.58	36.7
46	0.6	0.00	0.0	1.4	33.2	0.53	0.16	0.02	0.69	36.5
47	0.7	0.00	0.0	2.0	32.8	0.61	0.19	0.03	0.92	37.3
48	0.7	0.00	0.0	2.3	32.2	0.77	0.30	0.05	1.09	37.3
49	1.1	0.00	0.0	3.0	31.2	0.89	0.41	0.08	1.38	38.1
50	1.2	0.01	0.0	3.3	30.7	0.93	0.47	0.10	1.51	38.2
51	1.1	0.01	0.1	3.7	29.4	1.03	0.57	0.16	1.70	37.8
52	1.0	0.00	0.0	2.8	31.8	0.66	0.63	0.07	1.17	38.1
53	0.8	0.07	0.0	2.7	31.9	0.65	0.53	0.08	1.14	38.0
54	1.0	0.01	0.0	2.8	31.4	0.64	0.47	0.10	1.18	37.7
55	0.9	0.01	0.0	3.1	30.8	0.74	0.49	0.13	1.34	37.7

Table 6.2. (Continued)

Run	Molar yield BOC	Molar yield BOF	Conv. %	C Bal. %	Temp. (°C)	Pressure (psl)	Residence time - s	Catalyst	Selectivity Pathway III	Path I %	Path II %	Path III %
31	31.64	7.00	22.3	99	360	4502	59	Blank	0.61	59.3	6.4	34.3
32	25.13	8.40	33.4	101	360	4610	58	0.02 M H ₃ PO ₄	0.36	70.6	2.5	26.9
33	20.49	7.80	37.9	99	360	4630	58	0.04 M H ₃ PO ₄	0.29	76.8	1.8	21.5
34	16.58	7.80	47.2	99	360	4580	58	0.08 M H ₃ PO ₄	0.21	81.3	1.5	17.3
35	13.23	7.80	59.1	99	360	4598	58	0.16 M H ₃ PO ₄	0.16	83.5	2.8	13.7
36	56.2	9.34	16.6	103	360	4630	76	pH 2.8/ H ₃ PO ₄	1.45	27.9	8.0	64.2
37	36.9	4.17	33.4	100	360	4640	76	pH 2.8/ HNO ₃	0.15	9.7	75.5	14.9
38	36.7	7.22	17.6	101	360	4660	76	pH 2.8/ H ₂ SO ₄	0.82	21.7	28.6	49.7
39	0.0	0.00	34.5	107	360	4600	76	pH 2.8/ Molybdate	0.00	1.7	85.2	13.2
40	10.2	3.93	38.7	103	360	4354	27	pH 2.70 w/NaOH	0.62	39.0	20.6	40.3
41	13.3	5.77	43.3	104	360	4360	40	pH 2.70 w/NaOH	0.75	32.6	22.1	45.3
42	17.7	6.83	38.6	104	360	4350	58	pH 2.70 w/NaOH	0.62	30.5	24.0	45.5
43	21.3	8.28	38.9	104	360	4362	67	pH 2.70 w/NaOH	0.63	27.4	25.9	46.7
44	23.5	8.37	35.6	101	360	4340	62	pH 2.70 w/NaOH	0.55	26.7	26.6	46.7
45	8.3	4.31	51.7	102	360	4660	23	0.04 M Na ₂ HPO ₄	1.09	42.5	5.3	52.3
46	9.2	4.68	50.8	101	360	4603	31	0.04 M Na ₂ HPO ₄	1.38	40.4	6.8	52.8
47	12.4	7.06	56.9	103	360	4570	43	0.04 M Na ₂ HPO ₄	1.66	35.2	6.0	58.8
48	14.4	7.83	54.5	103	360	4710	53	0.04 M Na ₂ HPO ₄	1.74	35.2	7.1	57.7
49	19.2	10.34	54.0	105	360	4660	66	0.04 M Na ₂ HPO ₄	1.42	33.7	7.7	58.7
50	21.0	11.61	55.2	106	360	4662	80	0.04 M Na ₂ HPO ₄	1.48	32.0	8.0	59.9
51	23.2	12.69	54.6	104	360	4635	89	0.04 M Na ₂ HPO ₄	1.51	30.2	7.6	62.2
52	55.0	9.65	17.6	105	360	4648	81	pH 2.8-0.08 M PO ₄	1.52	26.7	14.3	59.0
53	56.2	9.36	16.7	105	360	4620	79	pH 2.8-0.04 M PO ₄	1.63	27.6	12.2	60.2
54	56.4	9.72	17.2	104	360	4660	81	pH 2.8-0.08 M PO ₄	1.47	27.6	10.3	62.1
55	57.6	10.69	16.5	104	360	4660	81	pH 2.8-0.16 M PO ₄	1.71	27.1	8.5	64.4

acrylic acid. Therefore the selectivity is a highly sensitive indicator of the acrylic acid formation.

The aging of the Hastelloy C-276 reactor has a dramatic effect on the pathways displayed in Figure 2.6. During initial studies there was noticed a dramatic shift in carbon monoxide and carbon dioxide yields as the reactor aged. To explore the aging phenomena, data was collected for a reactor in the first four hours of use and again after 70 hours of use when virtually no further changes in pathways were detected. The aging phenomena was followed by using gas chromatography to determine the ratio of carbon monoxide to carbon dioxide. The aging was determined to be complete when the ratio remained nearly constant. The data for comparison were collected during two three-hour periods where the residence time was varied between 30 and 120 seconds at 360 °C and 310 bar.

Figure 6.4 shows a comparison of the absolute yield of carbon dioxide and carbon monoxide for the two data sets (runs 1-7 and 8-12). The carbon dioxide yield decreases with aging while the carbon monoxide yield is largely unaffected. Figure 6.5 shows the acrylic acid pathway is not significantly affected as evidenced by the molar yield based on feed (BOF), but the overall acrylic acid yield benefits due to less reaction along competing pathways resulting in a higher yield, based on conversion (BOC). Other reactors have been aged in the laboratory in the presence and absence of phosphate salts (discussed later) with nearly identical results. All aging was performed in the presence of lactic acid under flow conditions of 310 bar and 360 °C. Torry et al. (1991), as discussed in chapter three, noticed there is a difference in the pyrolysis reaction rate between old and new reactors in supercritical reactions. Since the potential for corrosion by supercritical water and supercritical water/salt solution to interfere with rates of pyrolysis and hydrolysis is rather high, Torry and co-workers conducted dibenzyl ether hydrolysis reactions in both stainless steel and titanium reactors. No differences in hydrolysis reaction rates were noted between the two types of reactors, but the yield of pyrolysis products was an order of magnitude greater in the new stainless steel reactors than in the used stainless steel and titanium reactors. Torry and co-workers

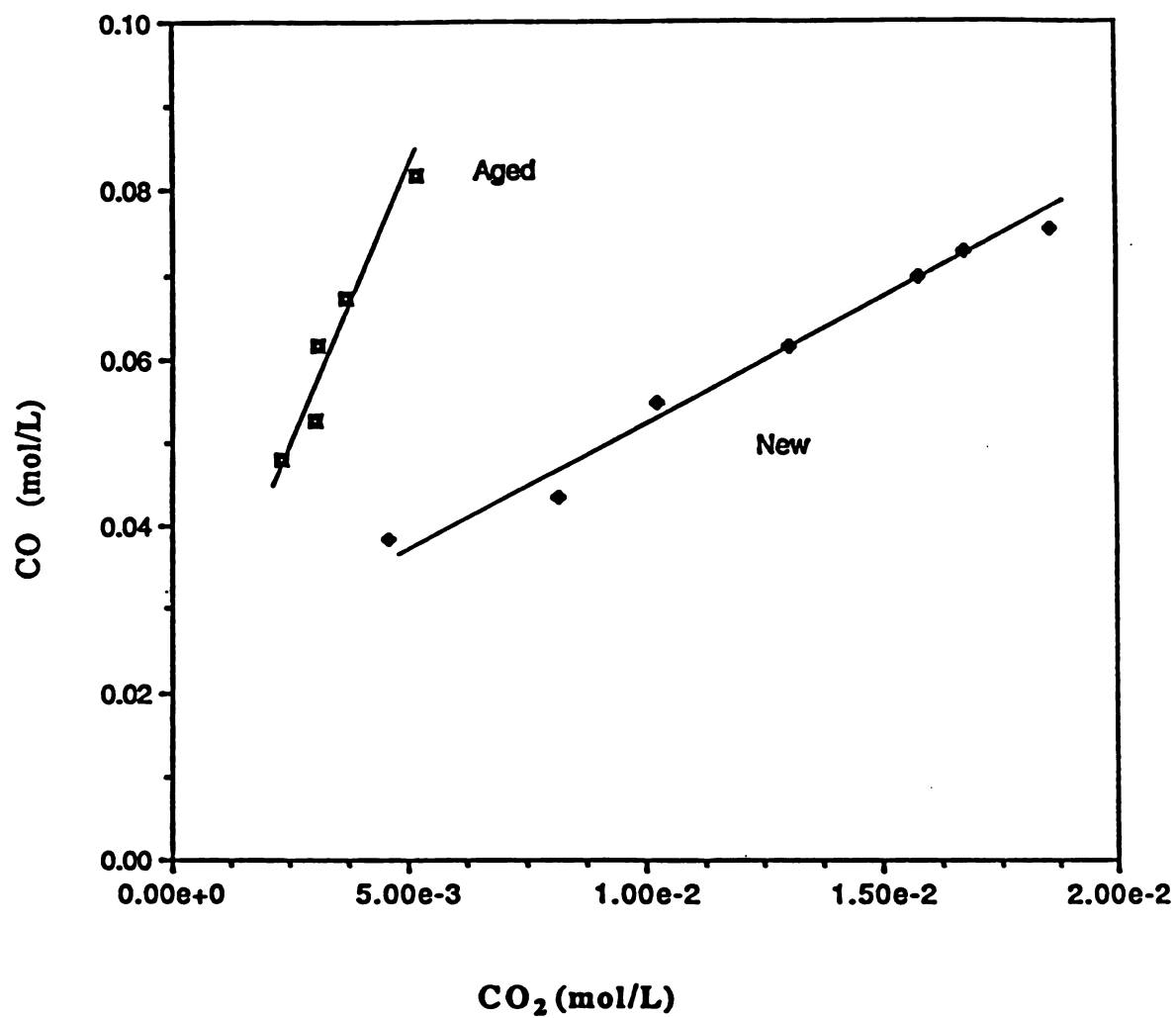


Figure 6.4. Absolute Yields of CO and CO₂ Obtained at Various Residence Times in a New Reactor and a Reactor Aged over 70 Hours.

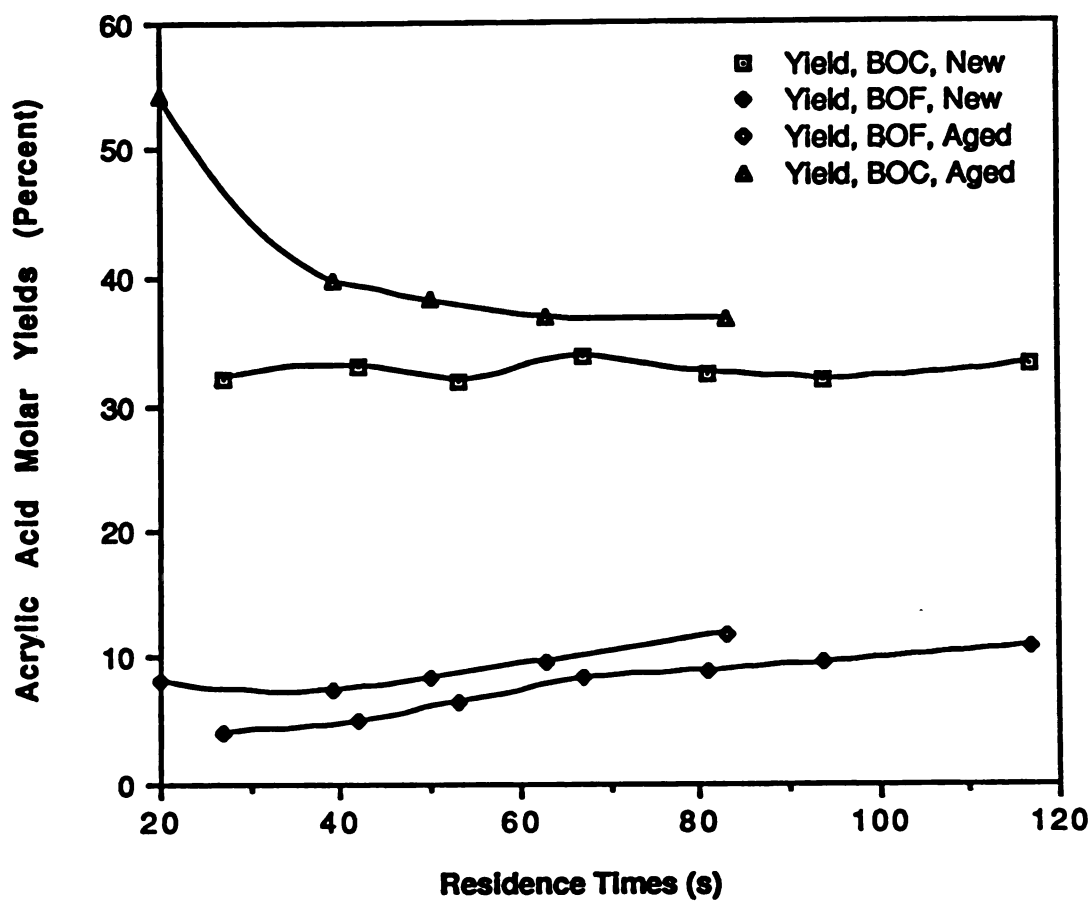


Figure 6.5. The Effect of Reactor Aging on Acrylic Acid Yields.

propose that this is due to passification of active wall sites during the reaction and that the hydrolysis reaction, the reaction of interest, is not affected by the passification.

Figure 6.6 shows the effect of reactor temperature on the reaction pathways and on the acrylic acid molar yields (runs 13-17). A temperature of 360 °C provides maximum yields of acrylic acid. Carbon monoxide is minimized while the carbon dioxide yield does not change appreciably. The shift in the pathway yields over the temperature range is a result of two effects: 1) the decrease in the density of the reaction fluid as the temperature increases, promoting more gaseous products, and 2) the increase in temperature from 320 to 400 °C. Figure 6.7 shows the selectivity of acrylic acid and of pathway three. Acrylic acid and pathway three selectivity peaks at 360 °C with values of 2.0 and 1.6, respectively. The selectivity values tend to deviate as the temperature is increased from 320 °C, indicating higher conversions of secondary reaction products, i.e. propionic acid and ethylene. All remaining experiments were conducted at 360 °C.

Based on previous literature sources which suggest that phosphate salts may provide catalytic dehydration effects on hydroxy acids, homogeneous phosphates salts (Na_2HPO_4) were added to the reactant mixture to determine their effect at supercritical conditions. Varying levels of the phosphate salt were added to the reactant solution up to 20% of the lactic acid on a molar basis. The pH at room temperature of the buffered reaction solutions varied from a value of 2.0 for the blank run without phosphate up to 3.0 for the 0.08 M experiment. Figure 6.8 shows the most noticeable effects from the phosphate salt addition (runs 19-24), which are the abrupt changes in the acrylic acid and carbon monoxide pathways from a small addition of the salt. Additional amounts of phosphate salt over 0.02 mols per liter did not have significant effects on the reaction pathways.

The effect of the phosphate salts was thoroughly investigated. The effect of the differing anionic phosphates was determined to be insignificant in terms of the type of salt used, i.e. sodium phosphate monobasic (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4) and

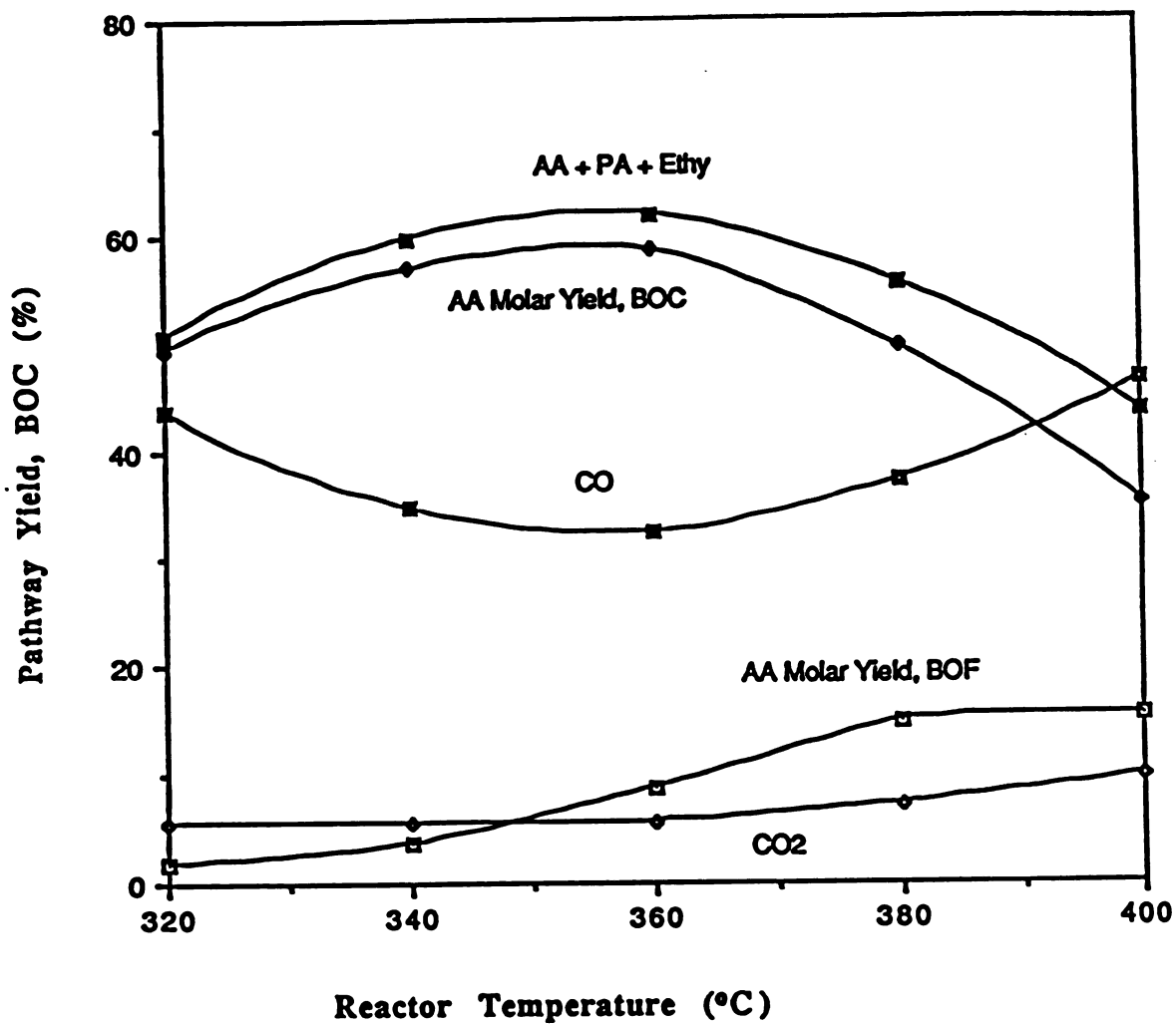


Figure 6.6. Acrylic Acid (AA) Molar Yields and Pathway Distributions for Lactic Acid Reactions at Various Temperatures Catalyzed with 0.02 M Na_2HPO_4 (PA - Propionic Acid, Ethy - Ethylene).

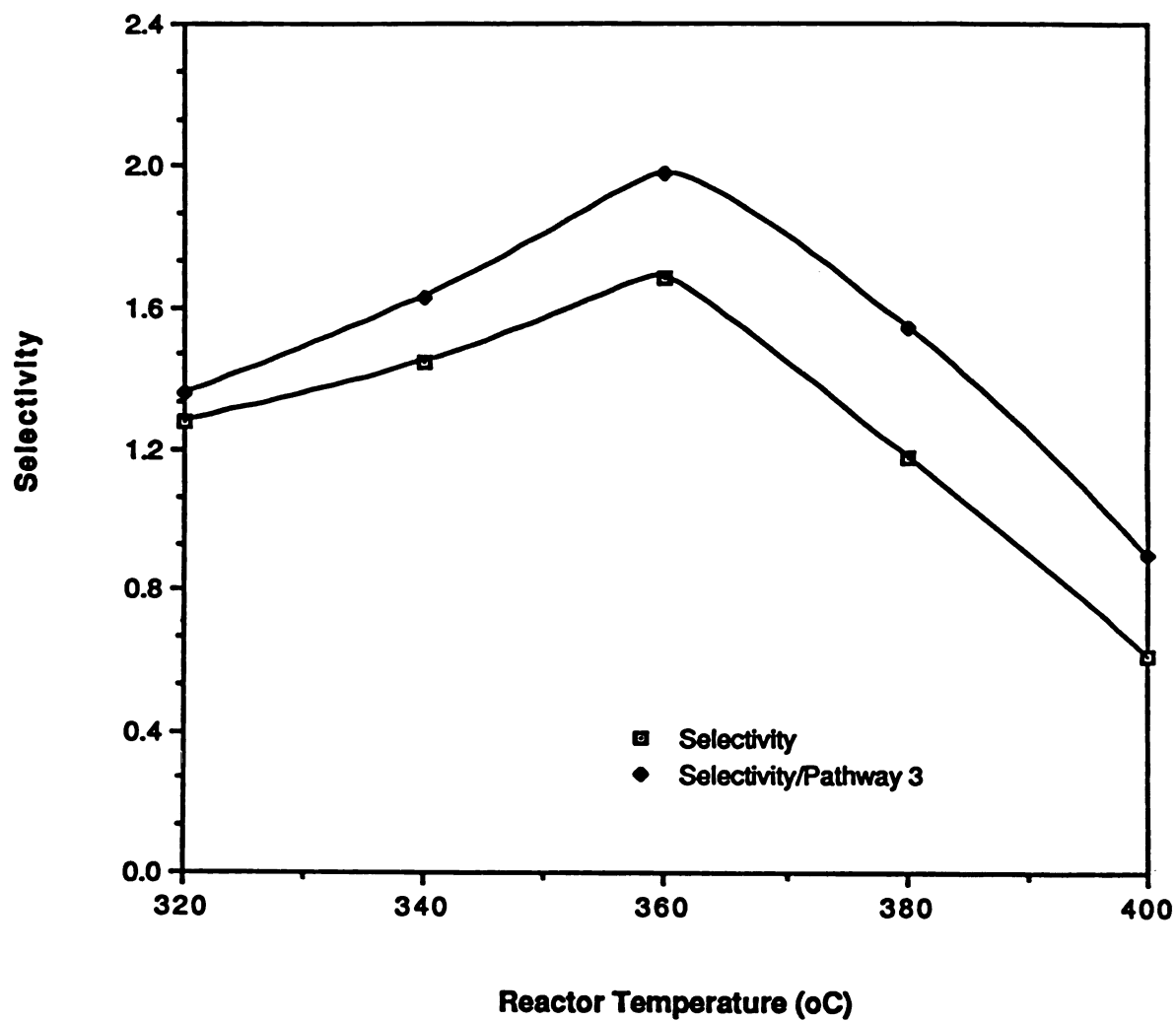


Figure 6.7. Selectivity and Selectivity via Pathway Three for Lactic Acid Reactions at Various Temperatures Catalyzed with 0.02 M Na_2HPO_4 .

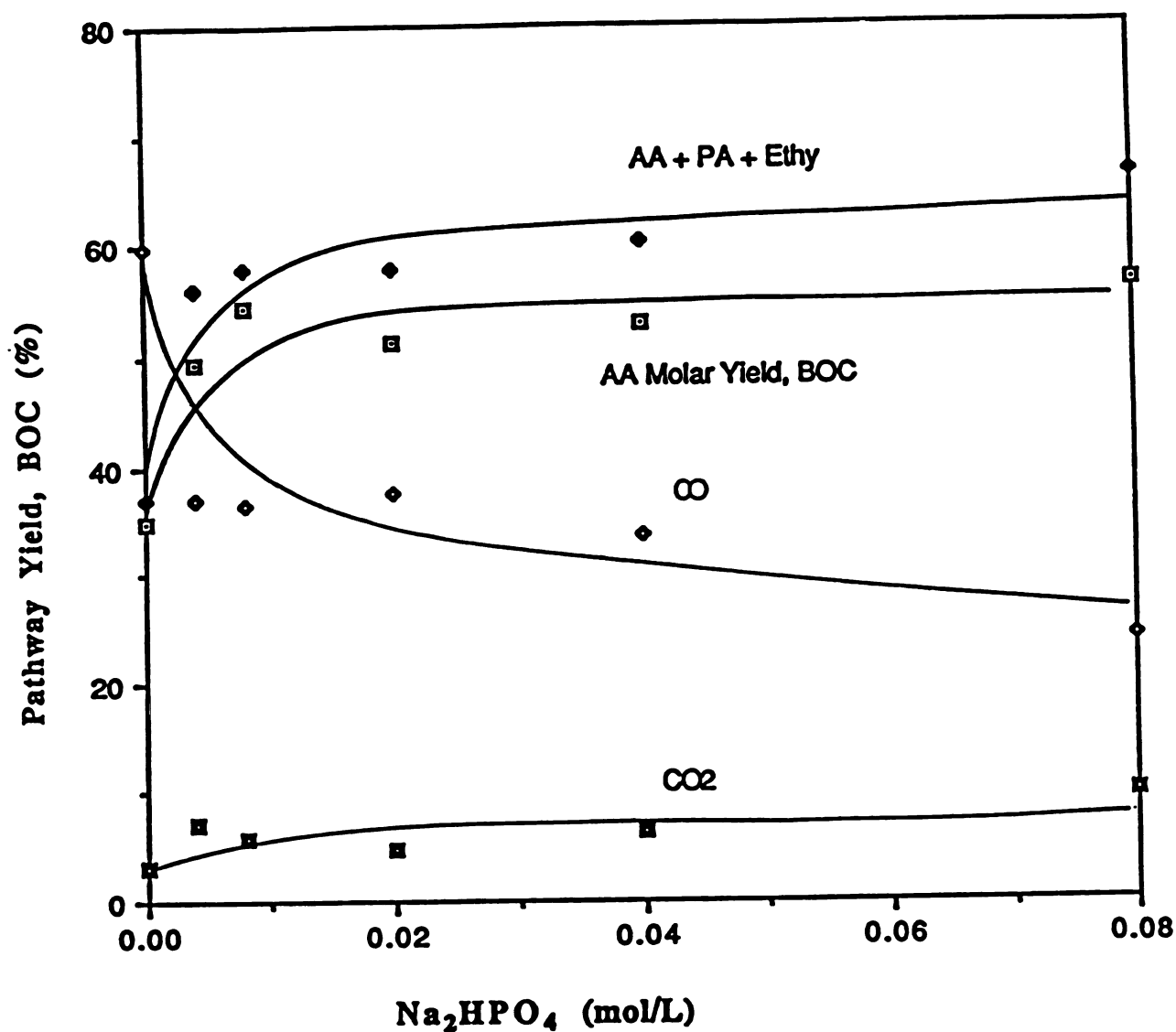


Figure 6.8. The Effect of Phosphate Concentration on Pathway Distribution and Acrylic Acid Molar Yield.

sodium phosphate tribasic (Na_3PO_4). What did make a difference in the product distribution was noted to be the effect of anion to shift the pH of the starting solution. This is because of the pK_a 's of the different sodium phosphates are all higher than the pH of the 0.4 M lactic acid solution. The result of adding small amounts of any of the sodium phosphate forms to the reactant solution is the complex interaction of the resulting phosphoric acid in equilibrium with the monobasic form of sodium phosphate, which is also in equilibrium with the lactic acid and the deionized lactic acid. The pH of the reactant solutions catalyzed with phosphate salts did not reach above 3.0. The pH of a 0.4 M lactic acid solution is approximately 2.0. Although not shown here, the cation of the phosphate salt did not have any noticeable influence on the reaction. A variety of phosphates were used with cations including calcium, magnesium, barium and lithium (See Appendix D).

This dependence of the reaction on pH led to a more thorough investigation on its effect on the reactant solution. The effect of the pH on the product distribution is shown in Figure 6.9 for an aged reactor (runs 25-30). The pH is increased with NaOH to compare with the pH changes occurring in the phosphate runs. The pH of the solutions are measured at room temperature before the runs. Although the pH of the reactant solution will be different at supercritical conditions due to changes in the ion product (Ramaya, 1989), the effect of such is not investigated in this work and we will refer to the pH of the reactant solution at room temperature as a reference point. The molar yield of acrylic acid increases to a value of about 43% then it starts to decrease because of increased reaction along the secondary pathway (propionic acid, ethylene and carbon dioxide). The carbon monoxide pathway decreases steadily while the carbon dioxide pathway increases. The general trend for the increase in pH of the reactant solution is to increase the acrylic acid pathway including secondary products. Differences over the same pH range are noted in the reaction pathways and acrylic acid yields when using phosphate salt rather than the base. The acrylic acid yield is higher when phosphate salt is used (56% compared with

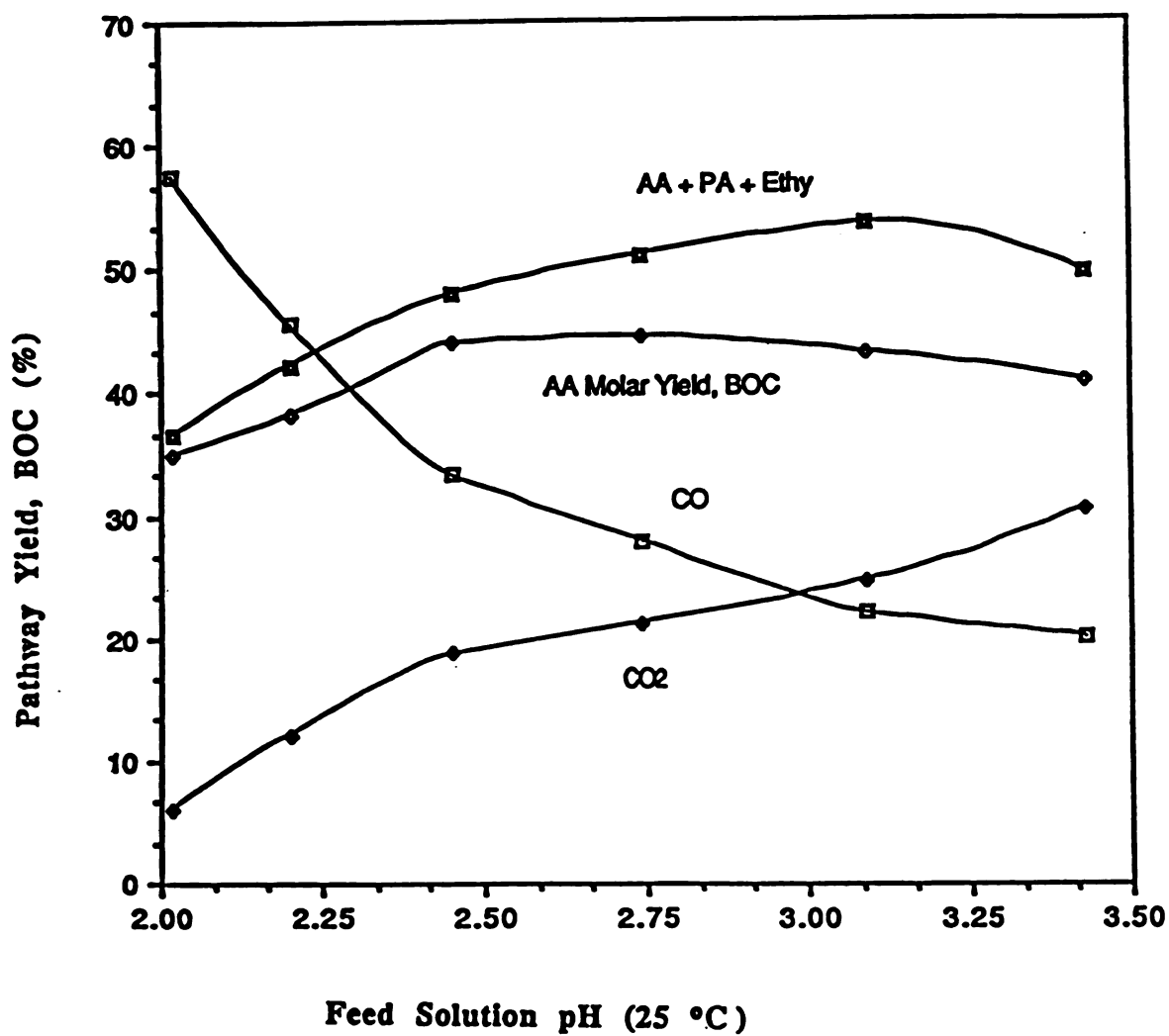


Figure 6.9. The Effect of NaOH on Pathway Distribution and Acrylic Acid Molar Yield.

44%). Pathway two is considerably smaller when phosphate salt is used rather than base.

With the pH on the reactant solution a strong influence on the product distribution, a series of experiments were performed using H_3PO_4 as the phosphate source (runs 52-55). The pH of the reactant solution was then adjusted with NaOH to a constant value of 2.80 for all experiments to determine how much affect the phosphate ion has on the reaction. The results of this experiment appear in Figure 6.8. The base case experiment was eliminated because the results of which were inconsistent with previous blank runs. When the results of this experiment are compared with the phosphate runs with no pH adjustment in Figure 6.8, the results look very similar. What is noticed is pathway one is fairly steady in Figure 6.10 indicating there is no influence on the pathway. Pathway two yields are higher and pathway three yields steadily increase at the same phosphate levels in Figure 6.10 as compared with Figure 6.8. With the addition of 0.06 molar Na_2HPO_4 to the lactic acid solution a pH of 2.80 results. Therefore, the values for 0.06 molar phosphate are compared for the two experiments in Figures 6.8 and 6.10. The pathway percentages compare well, indicating consistency in the results between the runs. But, when these results at pH 2.80 are compared to Figure 6.9, which shows the results of only using NaOH as the catalyst, there are two big differences noted in the pathways; 1) the acrylic acid pathway is 10% lower (62% compared to 52% in Figure 6.9), 2) the decarboxylation reaction is higher when using only NaOH (10% compared to 21% in Figure 6.9).

The opposite effect of the hydronium ion increase in the reactant solution is also investigated to compare with Mok and co-workers (1989). The differences between previous studies and this experiment are the use of an aged reactor and phosphoric acid in this study compared with a relatively new reactor and sulfuric acid as the catalyst in the Mok experiments. Figure 6.11 shows the considerable increase in the total lactic acid conversion using an acid catalyst, while the acrylic acid yield (BOF) remains fairly steady (runs 31-35). The addition of phosphoric acid does not bring an immediate effect on the acrylic acid pathway as the phosphate salt

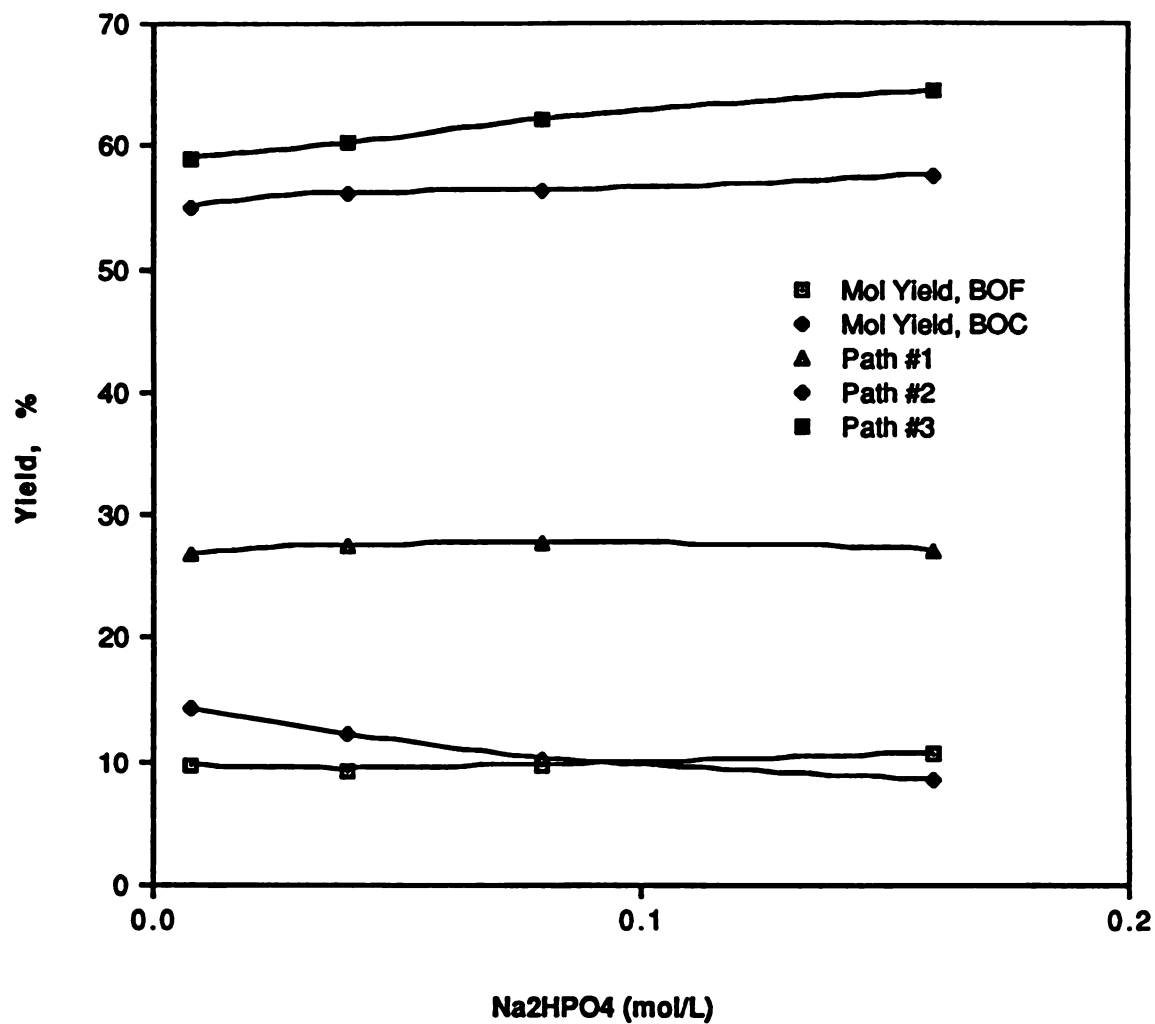


Figure 6.10. The Effect of Phosphate Concentration at a Constant pH of 2.8 (25 °C) on Pathway Distribution and Acrylic Acid Molar Yield.

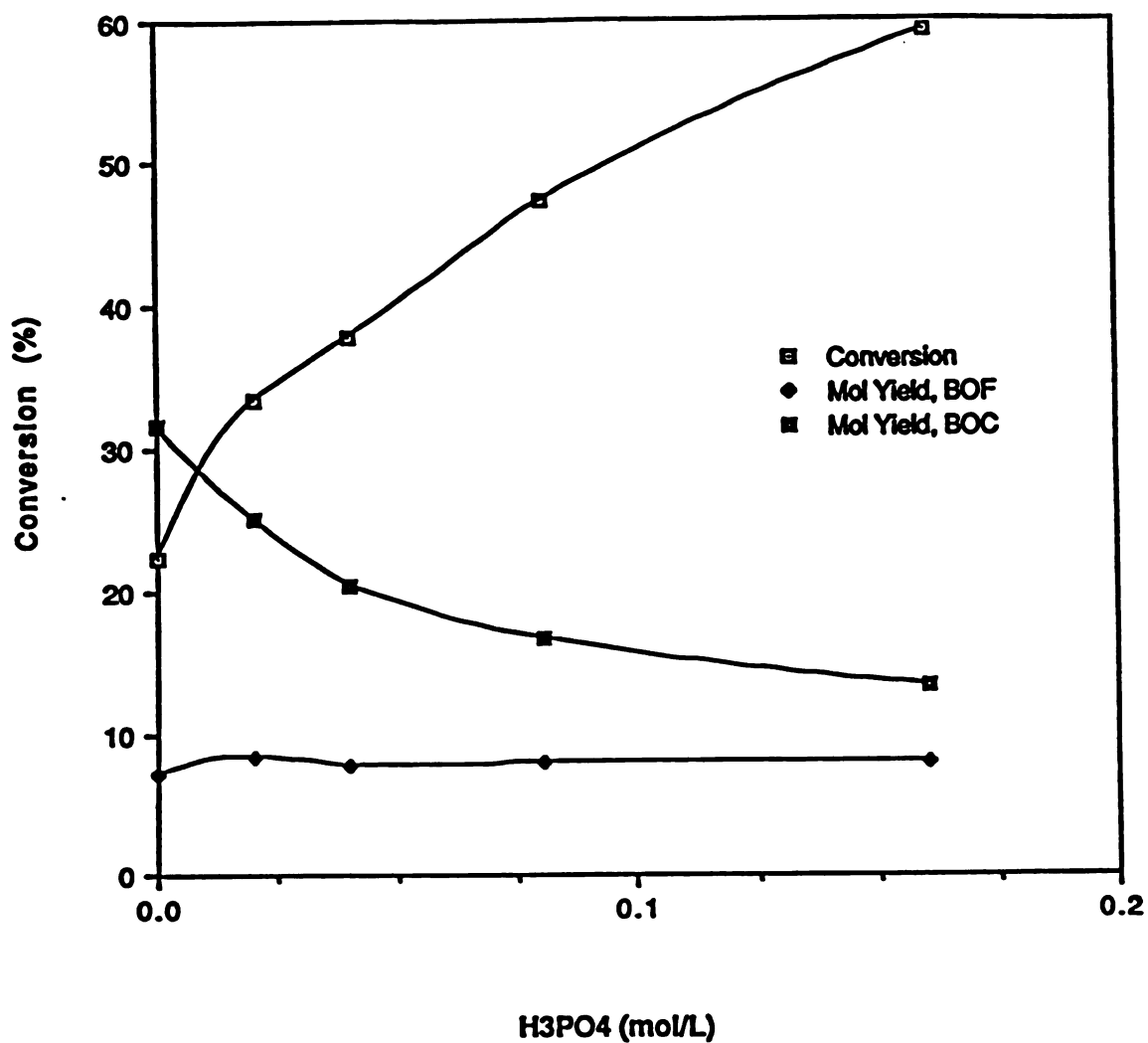


Figure 6.11. The Effect of Phosphoric Acid Concentration on Conversion and Acrylic Acid Molar Yields.

does in the previous experiments, as shown in Figure 6.8. The more dramatic effect with the phosphate salt addition may be due to complex formation of the carboxylic acid with the salt or deprotonization of the carboxylic acid. Phosphoric acid actually decreases the molar yield of acrylic acid, BOC as shown in 6.12, because of the large increase in conversion. The decarbonylation pathway increases significantly from 60% to and then levels off at 80% with increasing amounts of acid catalyst. The selectivity and selectivity via pathway three is plotted in Figure 6.13 for the same series of runs and it shows the dramatic decrease in selectivity with increasing amounts of acid catalyst.

The purpose of runs 36-39 were to determine what effect different anion salts had on the lactic acid reactions. The catalysts used were phosphoric acid (H_3PO_4), nitric acid (HNO_3), sulfuric acid (H_2SO_4) and diammonium molybdate tetrahydrate ($(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$). These runs were prepared in the following manner: 0.04 mols of the catalyst was added to each liter of reactant solution and the pH was adjusted with NaOH up to 2.80 to correspond to the pH of previous phosphate salt (Na_2HPO_4) catalyzed runs. Only 0.02 mols of the diammonium molybdate tetrahydrate was used due to its large molecular weight. The phosphate catalyzed run was similar to previous phosphate runs and the sulfate catalyzed runs were similar except acrylic acid was obtained at lower yields and the decarboxylation pathway was increased a great deal from 7.8% to 28.6%. This increase in the carbon dioxide may not be accurate because the huge amount of carbon dioxide produced in the previous run may not have been completely removed (along with the previous catalyst) from the reactor, but a minimum of 30 minutes is allowed between runs and the carbon balance was only off by 1.4% for the sulfuric acid run indicating the results may be accurate. The nitrate catalyzed run was completely different from the phosphate as only half as much of the acrylic acid was produced and a large amount of carbon dioxide was produced resulting in a conversion which was double the phosphate and sulfate catalyzed runs. The pathway two percentage was greater than 75% which is very high for the lactic

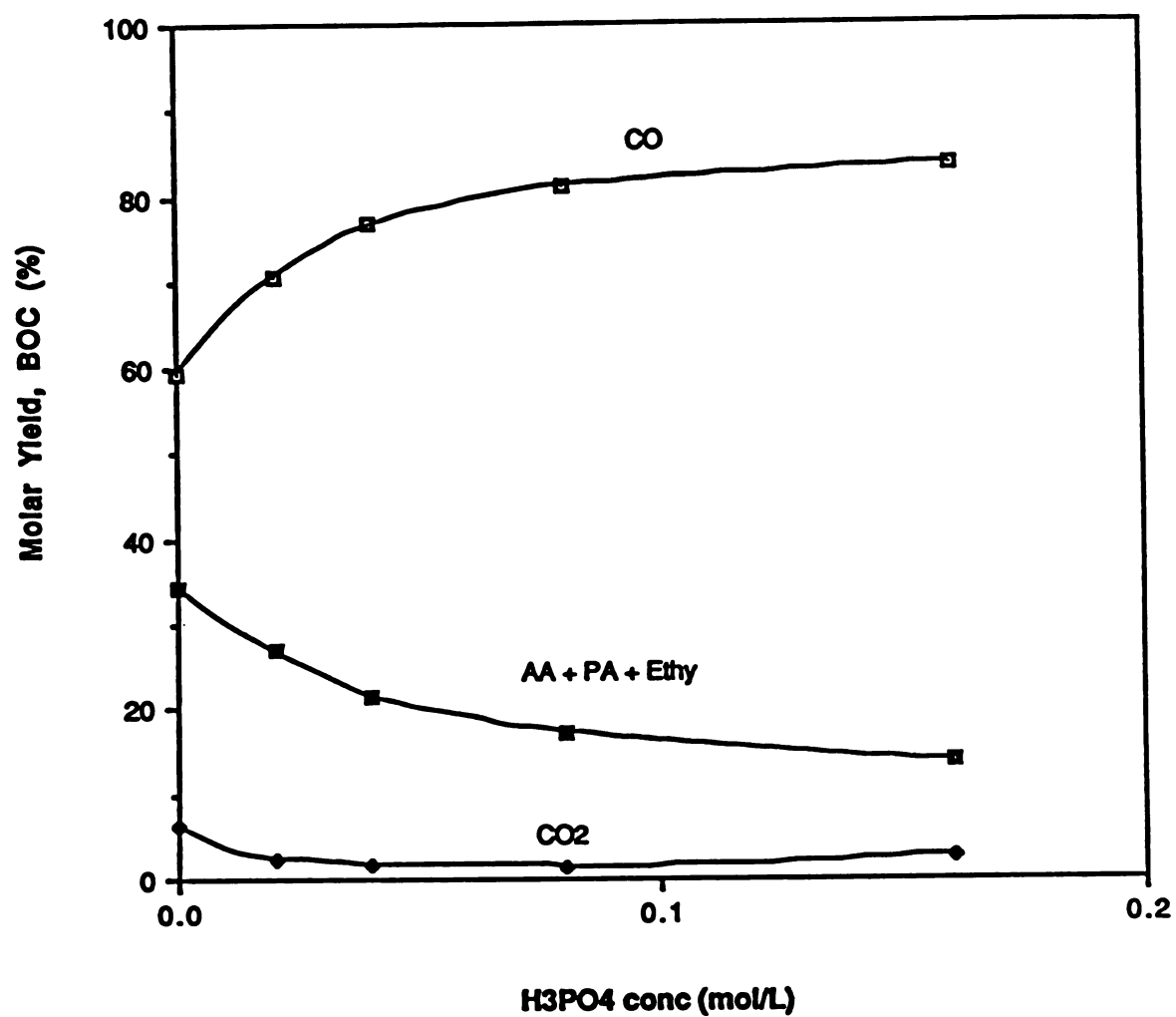


Figure 6.12. The Effect on Phosphoric Acid Concentration on Pathway Distribution.

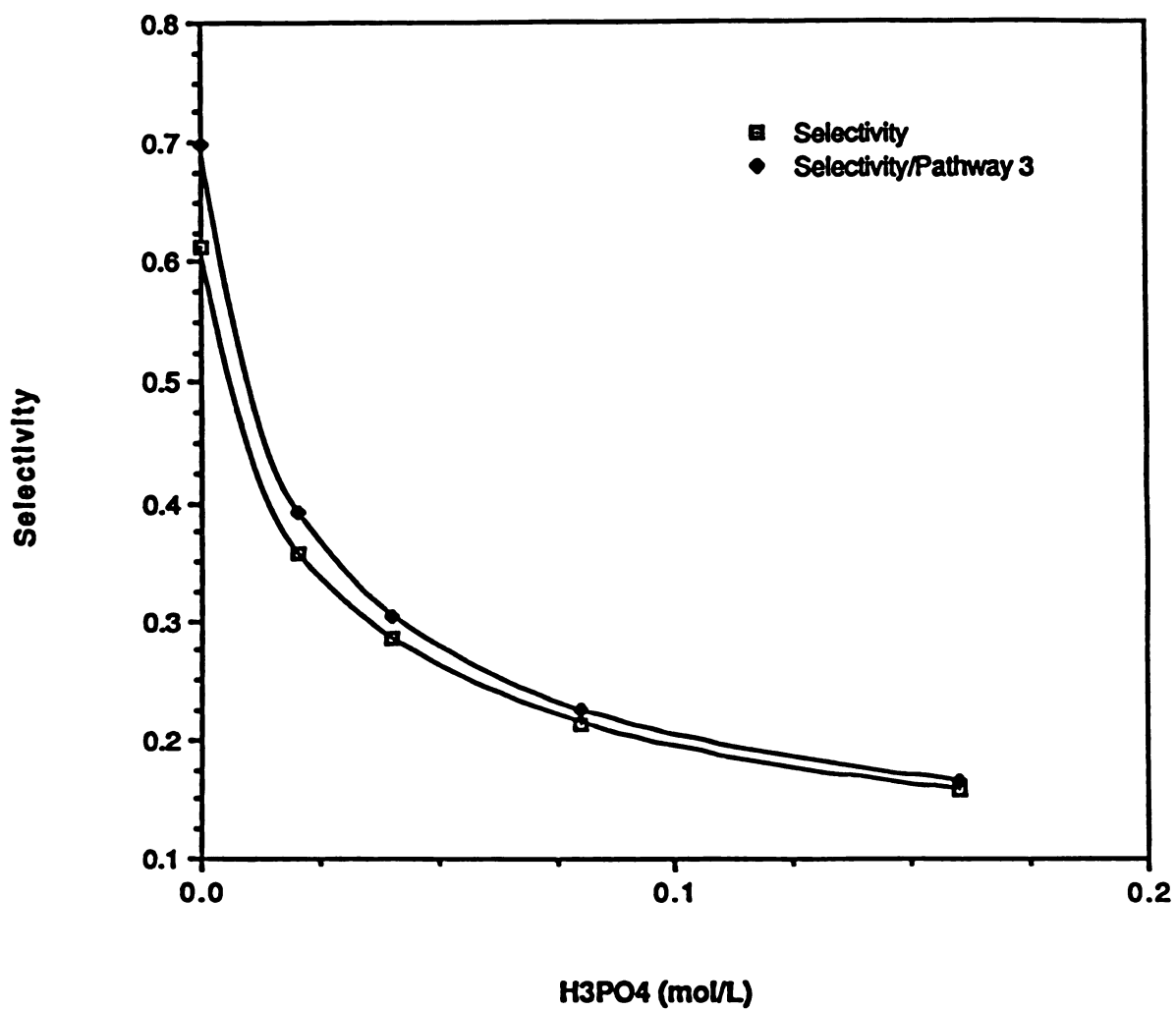


Figure 6.13. Selectivity and Selectivity via Pathway Three for Lactic Acid Reactions Catalyzed with Phosphoric Acid.

acid reactions and the selectivity was less than 0.200. The last run was catalyzed with a molybdate salt which acted in a similar manner to the nitrate catalyst, but a larger amount of carbon dioxide was produced and almost no carbon monoxide was found. What was unusual with the experiment was there was no acrylic acid detected and a comparatively large amount of propionic acid was found indicating the acrylic acid was formed but was immediately hydrogenated to the corresponding carboxylic acid. It is very unusual to see the large production of carbon dioxide from the supercritical reaction of lactic acid as the highest previous pathway levels were no more than 30%. It should be noted that as soon as the sample was taken for this experiment the reactor became plugged, because the molybdate salt solubility decreased significantly in supercritical fluids. Therefore during the collection of the sample in the sample loop, the concentration of the salt was not the starting the concentration.

Kinetic Studies

To investigate effects of catalysts and reactor age, we performed global kinetic studies. This series of runs was to determine reaction order and the rate constant of the three main reactions and the overall reaction rate of the lactic acid. The reaction rate of the lactic acid was assumed to be first order since it mimics a decomposition pathway. This rate equation is

$$-\tau_{LA} = -dC_{LA}/dt = k_0 C_{LA} \quad 6.1$$

which upon integration yields

$$-\ln(C_{LA}/C_{LA0}) = k_0 t = (k_1 + k_2 + k_3)t \quad 6.2$$

where C_{LA} denotes the molar concentration of lactic acid remaining after reacting, C_{LA0} denotes the concentration of lactic acid initially and k_0 is the overall reaction constant for lactic acid. The plots for the overall lactic acid reaction rate appears in Figure 6.14 and appears to follow the first order assumption rather well, although the

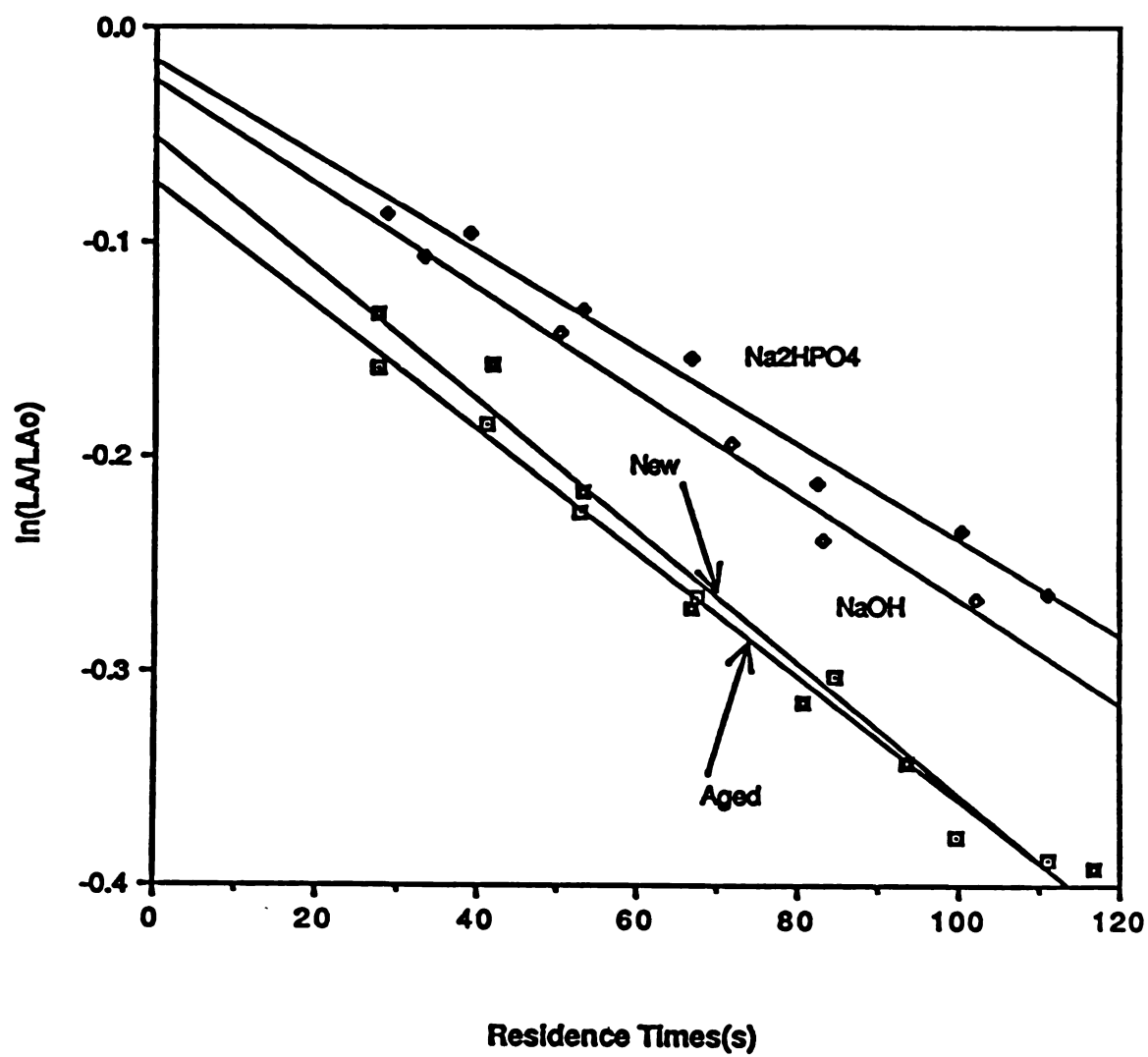


Figure 6.14. First Order Rate Constant Determination for Lactic Acid.

intercepts do not extrapolate through the point (0,0). There may be several reasons for this, such as undetermined impurities in the lactic acid, reaction pathways other than the three described here etc., but none were verified. Although the data are consistent with this model, the equipment permitted only up to 25% conversion at 360 °C, and more data must be obtained at higher conversion to verify this assumption. Kinetic data are obtained for four different reaction conditions: 1) no catalyst (runs 8-12), 2) NaOH @ pH 2.70 (runs 40-44), 3) 0.04 M Na₂HPO₄ @ pH 2.70 (runs 45-51), 4) new reactor (runs 1-7). The NaOH and phosphate runs are in an aged reactor and the aged, new and NaOH series are without phosphate catalysts.

Each reaction series was performed at various residences by adjusting the flowrate through the reactor. The estimated density of the reaction fluid was assumed to be that of water at the specified temperatures and pressures, since the concentrations of the other components were rather low. The density for water at 360 °C and 4600 psi is obtained from A.S.M.E. steam tables (Meyer, 1983). The residence times varied from approximately 20 seconds to as much as 120 seconds. The determination of the rate constant for lactic acid is obtained from the plot of the natural log of the lactic acid conversion versus the residence times shown in Figure 6.14. The slope of the lines are the overall rate constants k_o for lactic acid. These rate constants are presented in Table 6.3. The rate constants show the addition of phosphates and NaOH to the reactant mixture suppresses the reaction of lactic acid as does the aging of the reactor.

Normally, from the same series of experimental runs, the reaction rates for the three main parallel reactions ($k_1 + k_2 + k_3$) can be determined from the overall reaction rates and from the concentration of a identifiable product from the particular pathway. Carbon monoxide is associated with pathway one, carbon dioxide is associated with pathway two, and acrylic acid is associated with pathway three. These equations are represented as follows:

$$r_{CO} = dC_{CO}/dt = k_1 C_{LA} \quad 6.3$$

$$r_{CO_2} = dC_{CO_2}/dt = k_2 C_{LA} \quad 6.4$$

$$r_{AA} = dC_{AA}/dt = k_3 C_{LA} \quad 6.5$$

Equation 6.3 is divided by 6.4 and integrated to yield.

$$C_{CO} - C_{CO_0} / C_{CO_2} - C_{CO_2_0} = k_1/k_2 \quad 6.6$$

Equation 6.3 is divided by 6.5 and integrated in a likewise manner to yield.

$$C_{CO} - C_{CO_0} / C_{AA} - C_{AA_0} = k_1/k_3 \quad 6.7$$

The subscript o indicates an initial concentration, which for all pathway components is zero. Thus a plot of C_{CO} versus C_{CO_2} yields a line with a slope of k_1/k_2 and a plot of C_{CO} versus C_{AA} yields k_1/k_3 . Knowing these values and the overall rate constant from equation 6.2 the individual rate constants can be found.

The actual reaction rate analysis for this project is determined in a similar manner listed above and yields the most reliable results. Again, first order reactions were assumed. Secondary reaction products are included in the pathway calculations, but are assumed to have no effect on the first reaction step. We therefore assume lactic acid reacts irreversibly along the three primary pathways. The carbon monoxide and carbon dioxide yields are combined for comparison with the acrylic acid pathway because the potential water-gas shift involved between pathway one and two products prevents the use of the individual pathway data. The resulting rate equation is the combination of equations to yield:

$$r_{(CO_2 + CO)} = dC_{(CO_2 + CO)}/dt = k_{(1 + 2)} C_{LA} \quad 6.8$$

resulting in

$$C_{(CO_2 + CO)} - C_{(CO_2 + CO)_0} / C_{AA} - C_{AA_0} = k_{(1 + 2)}/k_3 \quad 6.9$$

Which is plotted and evaluated for rate constants in the manner described above. It should be noted that the sum of mols of carbon dioxide and carbon monoxide does not equal the mols of acetaldehyde as it should if only the three reaction pathways are present and there are no other reactions. Also, a plot of pathway three yield versus the sum of pathway one and two yields does not extrapolate linearly through (0,0) with varying residence times. There may be several explanations such as the possibility of contamination in the reactant solution or other reaction pathways, but none could be verified. The plots of the concentrations of acrylic acid versus the sum of carbon dioxide and carbon monoxide concentrations are shown in Figure 6.15, which is $k_{(1+2)}/k_3$.

Considerable difference is noted between the use of the aged and new reactor as is between the use of NaOH and Na_2HPO_4 . The rate constants are listed in order of performance from worst case to best case and appear in Table 6.3. The rate constants of the acrylic acid pathway remain nearly constant increasing only slightly while the combined rate constants for carbon monoxide and carbon dioxide decrease significantly by one-half from the worst to the best case.

The addition of salts to supercritical reactions are also studied by Torry et al. (1991). They investigated the effect of salt concentration (NaCl) on the rate of hydrolysis of dibenzyl ether and benzyl phenyl amine in supercritical water. Torry finds that the addition of salts to the reaction mixture increases the hydrolysis rate, while having no effect on the competing pyrolysis reaction rate. As the salt concentration is increased, the hydrolysis rate peaks and then approaches the reaction rate observed in the absence of salts. Mok et al. (1989) studied effects of NaCl addition to lactic acid reactions in supercritical water. They found that all three pathways were catalyzed. A beneficial effect was noted in our work with the addition of phosphate salts (Na_2HPO_4) but there are differences when compared to previous work. The concentrations of the reactant and of the salt in Torry's work are considerably higher than the concentrations used in this work. The reactant molar concentrations are 1-1/2 to 2-1/2 times the level used in our experiments. The ratio of mols of salt to mols of reactant used by Torry et al. are as

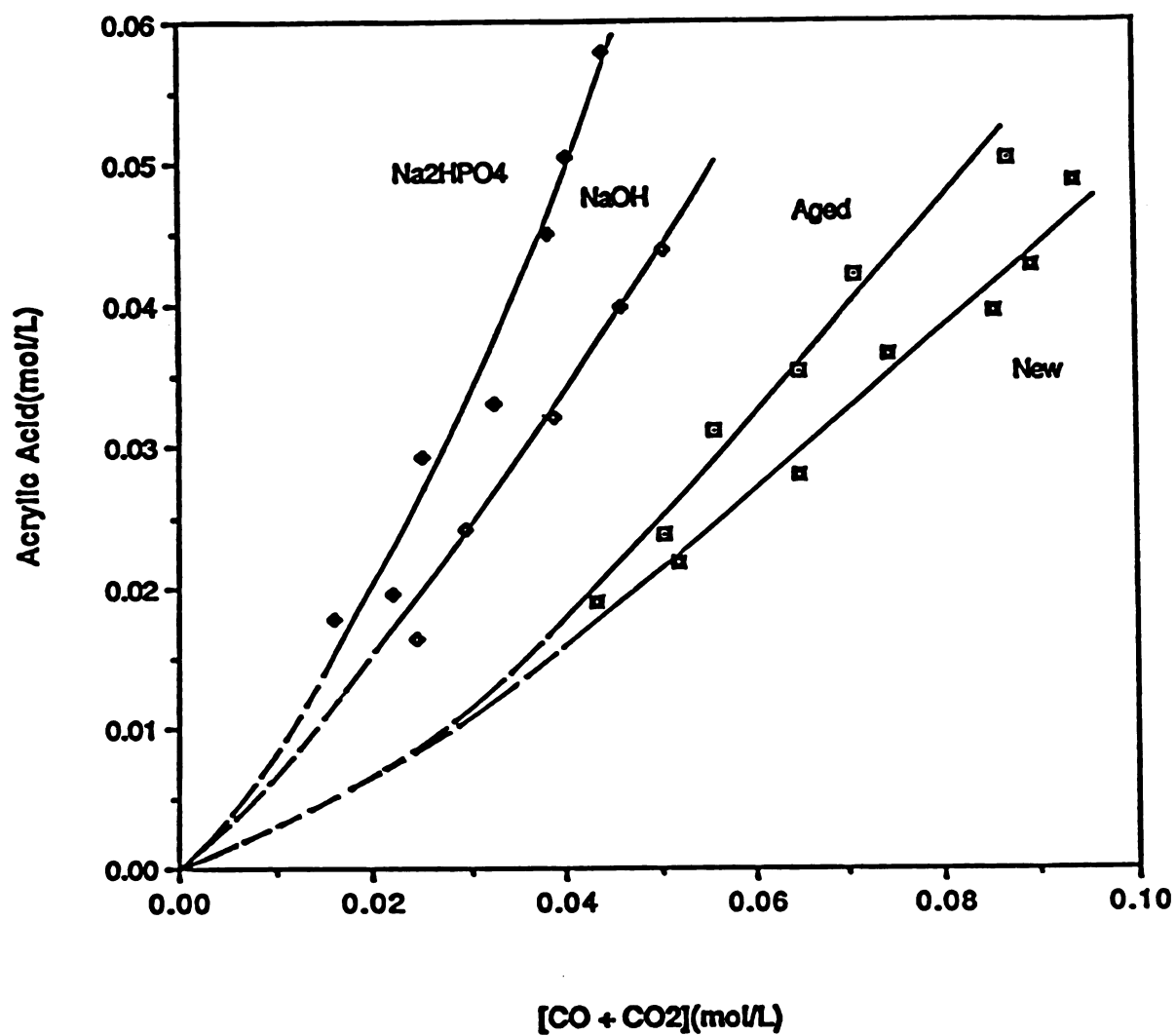


Figure 6.15. Relative First Order Reaction Rates for Lactic Acid Pathways at Several Conditions.

Table 6.3. First Order Rate Constants for Lactic Acid Reactions in Supercritical Water.

	Overall Rate	Product Pathways	
	k(/s) Lactic Acid	k(/s) CO + CO ₂	k(/s) AA + PA + Ethy
New	0.0031	0.0020	0.0011
Aged	0.0028	0.0017	0.0012
NaOH	0.0024	0.0012	0.0012
Na₂HPO₄	0.0022	0.00091	0.0013

high as 6.25:1.0. The ratios used in this work are no higher than 0.20:1.0. Torry et al. emphasizes the hydrolysis reaction in supercritical water is catalyzed by the addition of salt, while we have shown the addition of phosphate salts (Na_2HPO_4) does not catalyze the dehydration reaction, but suppresses the competing reactions (see Table 6.2), thereby increasing the acrylic acid yield. Mok et al. (1989) used 1.0 M NaCl and a ratio of salt to lactic acid of 10.0:1.0.

Error Analysis

The accuracy of the instruments used in the analysis of the compositions of the liquid and vapor streams are listed below.

Table 6.4. Accuracy of Equipment Used in Experiments

Instrument	Accuracy
Heise Pressure Gauge	+/- 5 psi
Temperature Controllers	+/- 2 °C
Electronic Balance	+/- 0.0005 g
Volumetric Flask	+/- 0.05 %
Sample Loop Volume	+/- 0.04 ml
Liquid Effluent Buret	+/- 0.02 ml
Timer	+/- 0.5 s
Sample Test-tube	+/- 0.6 ml
Voltmeter	+/- 0.1 mv
Gas Chromatograph	+/- 2%
HPLC	+/- 3%

Applying the above accuracy correlations to an error analysis calculation, the relative accuracy of the gaseous and liquid product components, effluent out, molar yields, conversion, residence times, selectivities and pathway percentages can be obtained. The error obtained for these values are listed below.

Table 6.5. Calculated Experimental Errors in Tabulated Values.

Value	% Error
Gaseous Product	+/- 10.1
Liquid Product	+/- 6.5
Reaction Effluent	+/- 6.9
Molar Yield, BOC (Highest Conv.)	+/- 10.9
Molar Yield, BOF (Highest Yield of AA)	+/- 3.1
Conversion (Highest Conv.)	+/- 7.3
Selectivities	+/- 13.9
Pathway Percentages	+/- 10.5
Residence Times	+/- 1.2 seconds

The errors calculated are meant to be worst case scenarios and the actual errors are reflected in the carbon balance calculated in Table 6.2. Most of the carbon balances are within 7% but as the operator techniques and analysis improved the carbon balances differences decreased to within 4% as indicated in the last 20 experiments listed in Table 6.2. Other sources of error not included in the error analysis include:

1. Not reaching the equilibrium state of the reaction. There could be two scenarios for this condition: first, the reactor might not be up to the reaction temperature or secondly, the sample loop may not be completely purged of the of the HPLC water from the previous sample. This would result in lower conversions, lower yields and lower carbon balance. Possible sources of error for this may be too high of flowrates or not allowing enough time between runs for the system to be flushed
2. Higher conversions of the lactic acid, causes the effluent in the sample loop to become two phase, which results in

surges in the gaseous components which will throw the analysis off a great deal. The causes may be from using reactant solutions greater than 0.4 M concentration.

3. An error in the calibration of the sample test-tube volume will increase the error of the gas phase components more than the liquid phase components, but the gas components are only about 1/3 of the total product distribution based on mols. This may be caused by leaks in the calibration tubing and the standard volume.
4. Other components in the lactic acid solution may affect the products and their distribution. A small amount of a residual fermentation product may be incorporated into the reaction scheme, but no other products were detected with HPLC standard analysis of the starting material

CHAPTER VII

CONCLUSIONS

The conversion of lactic acid in supercritical and near-supercritical water was determined and optimized at several conditions. A pressure of approximately 4600 psi was used for the experiments along with a reactant concentration of 0.4 M lactic acid. A high pressure continuous flow reactor was designed and optimized to provide reaction conditions which result in consistent and reproducible data. Analysis techniques were also developed to analyze the gas phase on a gas chromatograph and the liquid phase on a high pressure gas chromatograph.

The product and pathway distributions were determined at 360 °C and 4600 psi for the lactic acid conversion using several catalysts including Na_2HPO_4 , NaOH , H_3PO_4 and other inorganic acids. The results of which compared favorably to previous literature reports dealing with the conversion of lactic acid to acrylic acid (Mok, 1989; Sawicki, 1988; Odell and Earlam, 1985; Paperizos, Shaw and Dolhyj, 1985)

Reaction rates were determined for lactic acid using a first order analogy for the overall reaction rate and also for the individual pathway reaction rates. Rates were determined for the lactic acid reactions in aged reactors, new reactors, and in aged reactors with phosphate (Na_2HPO_4) catalyst and with NaOH as the catalyst. The following conclusions were reached from this investigation:

1. Aging the Hastelloy C-276 reactor approximately 70 hours at reaction conditions increases the yields of acrylic acid by decreasing the alternate pathway conversions. This may be due to passification

of reactive wall sites. The use of phosphate salts may also prevent corrosion of the surface sites (Romig, 1954) although the aging of the reactor was not affected by the use or absence of phosphate salts.

2. Maximum acrylic acid yield based on the conversion of 0.40 M lactic acid feed at a residence time of 70 seconds occurs at a temperature of 360 °C.

3. Small amounts (<0.01 M) of phosphate salts (i.e. Na_2HPO_4) added to the 0.40 M reactant solution raise the pH (25 °C) and increase acrylic acid yields from 35% to greater than 57% BOC of lactic acid (run 55).

4. The addition of NaOH to the reactant solution raises the pH (25 °C) but acrylic acid yields are maximized at less than 45% BOC of lactic acid. The NaOH acts in a similar manner to Na_2HPO_4 except the decarboxylation pathway is increased as the concentration is increased.

5. The addition of H_3PO_4 to the reactant solution dramatically increases conversion and decarbonylation, and decreases acrylic acid yield, BOC. The decrease in pH of the reactant solution resulting from the addition of the acid catalyst was compared to the results obtained from Mok et al., 1989. Mok et al. used sulfuric acid as the catalyst and the results of his experiments were very similar to the pathway distributions obtained in this experiment (i.e. large decarbonylation increase).

6. Application of first order kinetic models show that 0.04 M Na_2HPO_4 provides a small enhancement of the rate constant for acrylic acid production, but more dramatic suppression of the rate constants for the competing decarbonylation, decarboxylation and secondary reactions.

CHAPTER VIII

RECOMMENDATIONS

The following recommendations are made for future experimental work and investigation:

1. Eliminate the process of measuring the vacuum sample tube volume with the calibrated pressure transducer and a known volume. Too many errors are incorporated into the system resulting in an unreliable determination of the mols of gas obtained in the sample tube. The tedious process can be replaced by simply obtaining response factors for the gases from the gas chromatograph after injecting a known volume of sample gas. After the gas/liquid sample has been obtained in the evacuated test-tube, the remaining vacuum can be eliminated by introducing air into the sample tube. A known volume can be injected into the GC and the reaction gas concentrations can be found from the calibrations. The volume of the sample tube can be assumed to be a constant in order to determine the mols of gas evolved in each sample. The volume of the test-tubes can be found by filling the tubes with water and weighing the tube before and after the water is added. The volume can be found easily from knowing the density of water at the temperature of the lab.

2. Investigate the reactions of other materials under supercritical conditions, such as the dehydration of alcohols to their corresponding alkenes (Ramayya, 1987), or the supercritical degradation of glucose/cellulose (Koll and Metzger, 1978; Miller and

Saunders, 1987 & 1987), or the supercritical degradation of wastewater (Modell, 1978)

3. Develop a better HPLC analysis technique (i.e. column or software) to analyze for components which overlap and are difficult to integrate. These include the acetic acid and acetaldehyde peaks which overlap a great deal mainly because the acetaldehyde peak is very broad. The implementation of newer software (Maxima 820 Version 3.3/Waters) may help the integration of peak data.

4. Remove the Milton-Roy HPLC pump from the feed section as shown in Figure 4.2 and replace it with a higher pressure, lower volume pump to investigate the reaction of lactic acid at longer residence times to obtain better kinetic data and at higher pressures to possibly suppress side reactions.

5. Investigate the use of other solvents which will facilitate the dehydration reaction and offer lower temperature reactions at reduced pressures i.e. methanol.

APPENDICES

APPENDIX A

CHROMATAGRAPHIC ANALYSIS

The analysis of the liquid and gas phases of the experimental samples were performed using a gas chromatograph for the gas phase and a high performance liquid chromatograph for the liquid phase of the sample.

Gas Chromatograph:

A Perkin-Elmer, model 8500 gas chromatograph equipped with a hot wire thermal conductivity detector, was used for the gas phase analysis. The column used in the analysis was manufactured by Analabs catalog number GCA-012. The packing was 80/100 mesh spherical carbon molecular sieves called Sphero carb. The calibrations were determined based on a relationship of volume or mols of gas versus peak area. Known volumes of a gas standard mixture were injected using a 2 milliliter gas syringe marked in 0.05 milliliter graduations. The results were plotted as the response area versus mols of component. The plot is shown in Figure A.1. A summary of the chromatographic conditions is presented in Table A.1. The tabulated data is presented in Table A.2.

Table A.1. Gas Chromatographic Conditions for the Analysis of the Gas Phase in the Experimental Samples.

Carrier Gas	Helium
Carrier Gas Flow Rate cm ³ /min	
Column A	40
Column B	40
Carrier Gas Pressure, psig	5.5

Table A.1 (Continued)

Temperature Operation Mode	Ramp
Stage 1	
Oven Temperature, °C	40
Isothermal Time, min	3.0
Ramp Rate, deg C/min	30.0
Stage 2	
Oven Temperature, °C	90
Isothermal Time, min	1.0
Ramp Rate, deg C/min	20.0
Stage 3	
Oven Temperature, °C	220
Isothermal Time, min	2.0
Injection Port Temperature, °C	220
Detector Temperature, °C	270
Detector Area Sensitivity	50
Detector Range	Low
Detector Base Sensitivity	4
Detector Attenuation	64
Skim Sensitivity	0
Area/Height Rejection	0

High Performance Liquid Chromatograph:

A Waters 600 solvent delivery system equipped with a model 410 refractive index detector was used for liquid phase analysis of the experimental samples. Data from the analysis was interpreted with a Waters WIRC software program version 1.0 on a IBM XT. The data was transferred through a Waters System Interface Module (SIM). The column used in the analysis was manufactured by Alltech Associates. The Econosil® column contained a C-18 silicon bonded phase which was 10 microns in size. The column was 240 mm long by 4.6 mm in diameter and its catalog number was 60086. The column was protected with cartridge columns of the same composition. The solvent was 0.1 molar K_2HPO_4 in HPLC grade water

Table A.2. Gas Chromatograph Calibration Data for Gas Phase Reaction Products.

Compound	Nitrogen	Oxygen	Carbon Monoxide	Methane	Carbon Dioxide	Ethylene
Vol %/mol %	5.01	5.02	5.01	4.10	5.01	1.00
Mols/ml sample	2.04E-06	2.05E-06	2.23E-06	1.83E-06	2.23E-06	4.46E-07
Response Area	12.58	16.52	14.38	9.61	16.92	6.60
mmols	0.0150	0.0151	0.0150	0.0123	0.0150	0.0000
Response Area	24.81	32.20	29.94	19.29	34.07	10.54
mmols	0.0301	0.0301	0.0301	0.0246	0.0301	0.0000
Response Area	37.81	47.07	44.20	29.03	52.46	13.92
mmols	0.0451	0.0452	0.0451	0.0369	0.0451	0.0000
Response Area	43.01	70.00	59.24	37.97	68.80	17.21
mmols	0.0601	0.0602	0.0601	0.0492	0.0601	0.0000

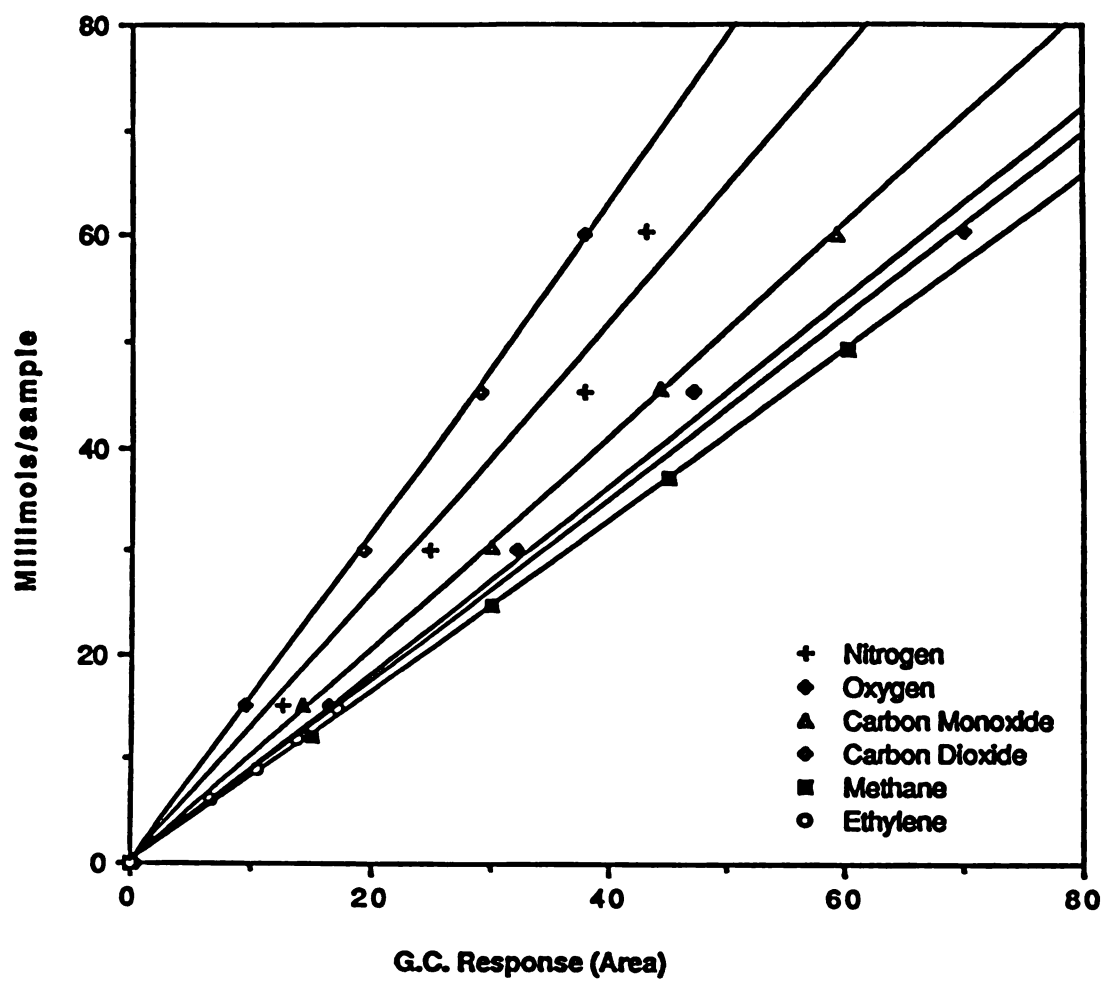


Figure A.1. Gas Phase Component Calibration for Gas Chromatography.

acidified to pH 4.20 with H_3PO_4 . Table A.3 lists specific conditions used in the analysis.

The HPLC was calibrated with known amounts of the identified main components of the lactic acid reactions. The component amounts were calibrated with the peak area response. A plot of the peak areas versus amounts appear in Figure A.2. A summary of the response data appears in Table A.4. The lactic acid used in the calibrations samples was heated at 75-80 °C for 12 hours prior to use because the lactic acid naturally occurs as the free acid and lactate oligomers which is a combination of two lactic acid molecules minus water. Heating the lactic acid prior to use hydrolyzes the lactate to lactic acid, otherwise the response factor for lactic acid will not be consistent. The calibration samples were mixed in a volumetric flask and diluted as needed. The solvent used in the calibration sample was taken directly from the HPLC reservoir to avoid interference of large solvent peaks in the calibrations.

Table A.3. High Performance Liquid Chromatography Conditions for Liquid Phase Reaction Products using an Econosil® C-18 Column.

Solvent Flow	
Flowrate, ml/min	2.0
Data Acquisition, min	10.0
Data Rate, points/sec	5.00
Integration Sensitivity	
Coarse, $\mu\text{v}/\text{sec}$	18.62
Fine, $\mu\text{v}/\text{sec}^2$	3.773
Skim Ratio	8.000
Component Retention Times, min.	
Lactic Acid	2.62
Acetic Acid	3.45
Acetaldehyde	3.80
Acrylic Acid	5.10
Propionic Acid	7.60

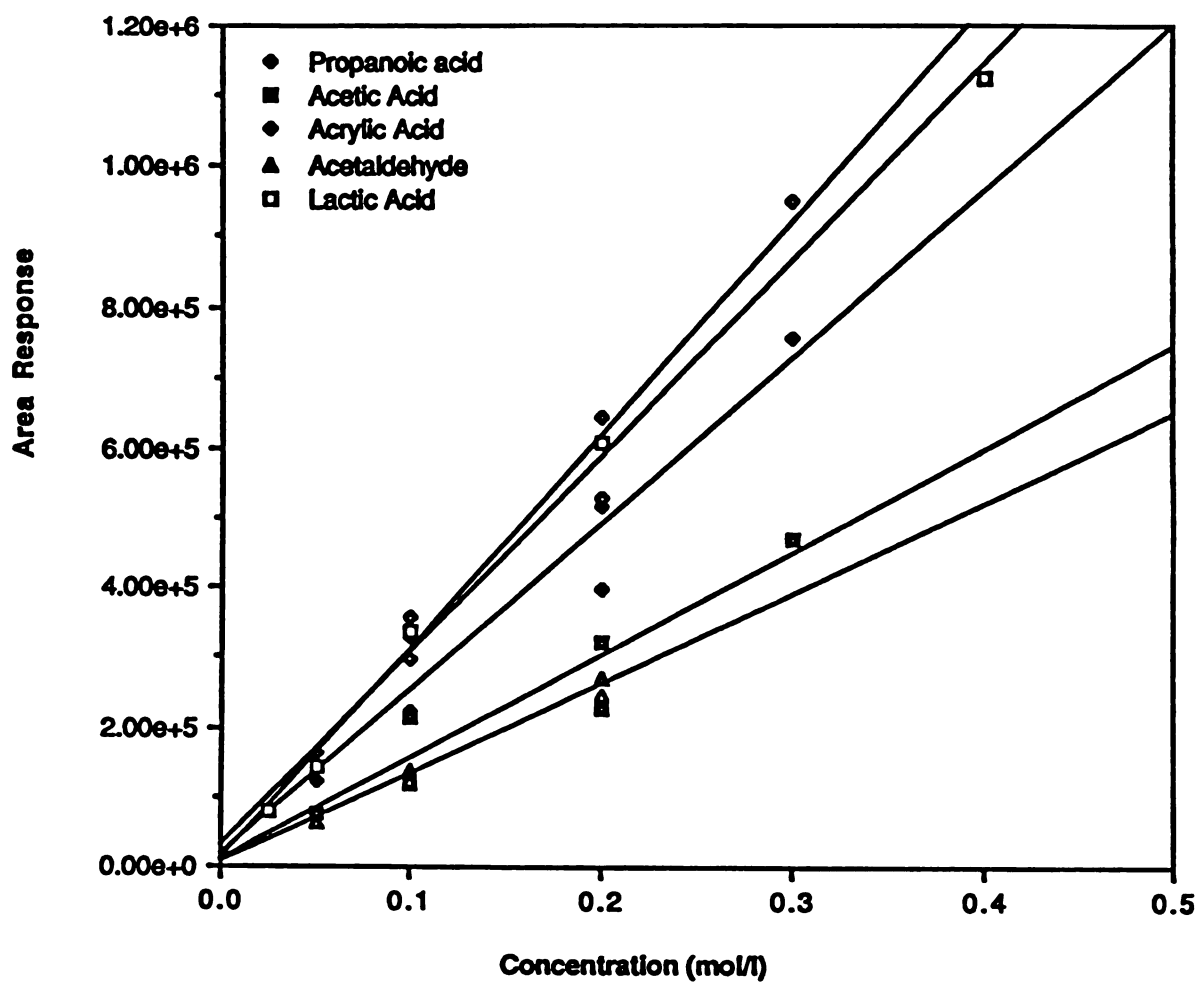


Figure A.2. Liquid Phase Component Calibration for High Pressure Liquid Chromatography.

Table A.4. High Performance Liquid Chromatography Calibration Data for Liquid Phase Reaction Products.

Concentration mol/L	Response Area				
	Lactic Acid	Propanoic Acid	Acetic Acid	Acrylic Acid	Acetaldehyde
0.025	7.90E+04				
0.05	1.44E+05	1.22E+05	7.68E+04	1.61E+05	6.44E+04
0.1	3.37E+05	3.28E+05	2.14E+05	3.56E+05	1.23E+05
0.1	2.18E+05	2.24E+05	1.19E+05	3.00E+05	1.40E+05
0.2	6.07E+05	5.18E+05	3.21E+05	6.45E+05	2.44E+05
0.2	4.57E+05	3.97E+05	2.25E+05	5.30E+05	2.72E+05
0.3	6.56E+05	7.54E+05	4.69E+05	9.50E+05	
0.4	1.12E+06				

APPENDIX B

Transducer Calibration and Sample Tube Calculation

The calibration of the transducer involved the use of a highly accurate vacuum meter which was connected to a vacuum source (i.e. vacuum pump) and the transducer through a sample tube. A full vacuum was applied to the tube and the reading on the voltmeter was recorded along with the reading from the vacuum meter. The results of the calibration appear in Table B.1 and the calibration plot appears in Figure B.1. A basic computer program was developed to determine the volume of the test tube based on the voltmeter readings before and after the evacuated test-tube was exposed to a known volume of air. The basic program follows:

Basic Computer Program to Calculate the Volume of Sample Tubes

```
REM Program to Calculate the sample tube volume
REM T=atmospheric temperature(K)
REM P=atmospheric pressure(mm Hg)
REM R=62400 mm Hg * ml/gmol * K
REM VA=initial air volume to be added to tube in ml
REM NA=moles of air to be added to tube
REM VT=approximate volume of tube in ml
REM VP=volume of pressure transducer tubing in ml
REM VB=volume of tubing past valves in ml
REM VV=total volume of valve system in ml
REM Define constant values
Let R=62400!
Let VA=13.527
Let VT=13.068
Let VP=1.18317
```

```

Let VB=0.74043
Let VV=14.26743#
  REM  Input of atmospheric conditions
Print "Input atmospheric temperature in Celsius"
Input T
Let T=T + 273.15
Print "Input atmospheric pressure in mm Hg"
Input P
  REM  Calculation of # of moles in the tube initially
Let NA=P * VA/(B * T)
Print "Input initial pressure of tube in mV"
Input P1
Let P1=P - ( -6.37252 * P1 + 751.7791#)
Let V1=VT + VP + VB
Let N1=P1 * V1/(R * T)
  REM  Calculation of the tube volume
Let N2=NA + N1
Print "Input the final pressure of the tube in mV"
Input P2
Let P2=P - ( -6.37252 * P2 + 751.7791)
Let V2 = N2 * R * T/P2
Let VTUBE=V2 - VV - VP
Let VTUBE=VTUBE + 0.11845 * VTUBE
Print "The tube volume is"; VTUBE
Print "Do you want to go again?"
Input A$
If A$="Y" then 270 else 440
END

```

Table B.1. Sample Tube/Transducer Calibration Data.

Multimeter Reading (mv)	Vacuum (mm Hg)	Vacuum minus Atmospheric Pressure	Difference divided by Atmospheric	Tube Pressure (psia)
1.9	738.12	-2.88	0.00	0.06
4.5	713.99	-27.01	-0.04	0.54
9.7	688.59	-52.41	-0.07	1.04
14.1	663.19	-77.81	-0.11	1.54
18	637.79	-103.21	-0.14	2.05
22	612.39	-128.61	-0.17	2.55
26.2	586.99	-154.01	-0.21	3.06
30.2	561.59	-179.41	-0.24	3.56
33.4	536.19	-204.81	-0.28	4.06
37.7	510.79	-230.21	-0.31	4.57
41.5	485.39	-255.61	-0.34	5.07
45.9	459.99	-281.01	-0.38	5.57
49.7	434.59	-306.41	-0.41	6.08
53	409.19	-331.81	-0.45	6.58
57.3	383.79	-357.21	-0.48	7.09
61.2	358.39	-382.61	-0.52	7.59
65.5	332.99	-408.01	-0.55	8.09
69.5	307.59	-433.41	-0.58	8.60
73.7	282.19	-458.81	-0.62	9.10
77.8	256.79	-484.21	-0.65	9.61
81.7	231.39	-509.61	-0.69	10.11
85.6	205.99	-535.01	-0.72	10.61
89.7	180.59	-560.41	-0.76	11.12
94	155.19	-585.81	-0.79	11.62
98	129.79	-611.21	-0.82	12.13
101.8	104.39	-636.61	-0.86	12.63
105.9	78.99	-662.01	-0.89	13.13
109.9	53.59	-687.41	-0.93	13.64
113.9	28.19	-712.81	-0.96	14.14
118	2.79	-738.21	-1.00	14.64
118.1	0	-741	-1.00	14.70

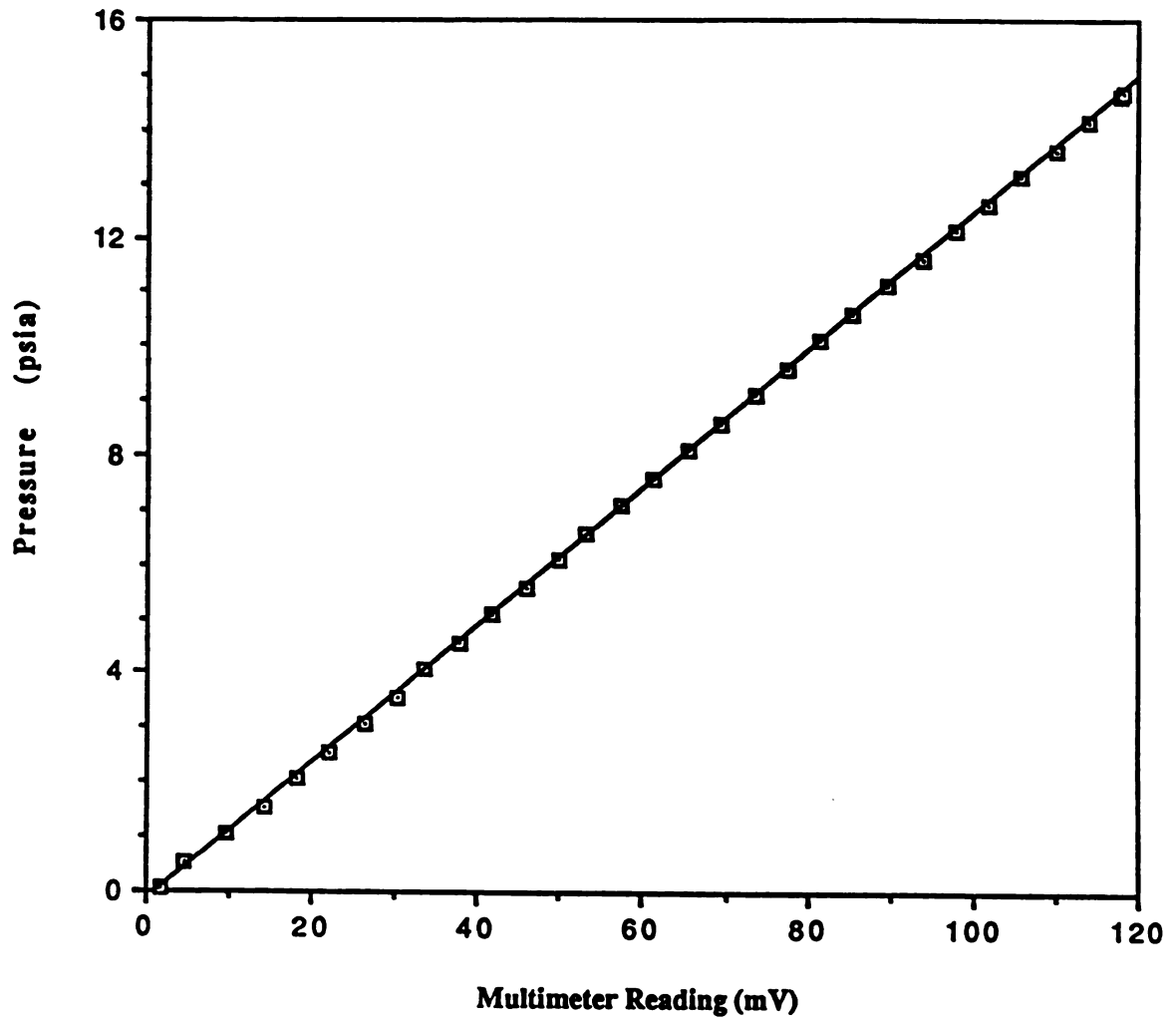


Figure B.1. Transducer/Multimeter Versus Sample Tube Pressure Calibration.

APPENDIX C

EQUILIBRIUM CONVERSION CALCULATIONS

For the determination of the equilibrium conversions for the three main reaction pathways of lactic acid in and the secondary hydrogenation reaction of acrylic acid in near-supercritical water, the critical constants of the species involved in each reaction are needed to determine the species' fugacities at the elevated temperatures and pressures. The critical constants are plugged into the VLMU basic program to determine the reaction mixture fugacities. The critical constants for most of the reaction species can be found in the literature, except for acrylic acid, lactic acid, propanoic acid, and acetaldehyde. For these materials, the constants were estimated using Lydersen's group contribution correlation found in Perry's Chemical Engineers' Handbook (1984). The group increments used in the calculations are found in Table 3-330 page 3-266 of Perry's.

The errors for the calculations are on the order of 2% for the critical temperature calculation for most chemical species except for multipolar groups, e.g., lactic acid, where the error is unknown. The error for the critical pressure calculation is less than 5% for most compounds again except for multipolar groups where it is unknown. The acentric factor (ω) calculation errors are dependent upon the errors of P_c and T_c used in the calculation.

The critical temperature equation appears below:

$$T_c = T_b / (0.567 + \sum \Delta T - (\sum \Delta T)^2) \quad C.1$$

Where T_b is boiling temperature of the specie and $\sum \Delta T$ is the sum of the functional group increments from Table 3-330 in Perry's (1984). The boiling point for lactic acid was estimated using Clausius-

Clapeyron (Sandler, 1989) and an estimated heat of vaporization (Miller, 1989).

The critical pressure equation appears below:

$$P_c = MW / (0.34 + \sum \Delta_p)^2 \quad C.2$$

Where MW is the molecular weight of the specie in question and $\sum \Delta_p$ is the sum of the functional group increments also from Table 3-330 in Perry's (1984).

The acentric factor calculation is as follows:

$$\omega = \frac{(-\ln P_c - 5.92714 + 6.09648 * \phi^{-1} + 1.28862 * \ln \phi - 0.169347 * \phi^6)}{15.2518 - 15.6875 * \phi^{-1} - 13.4721 * \ln \phi + 0.43577 * \phi^6} \quad C.3$$

Where P_c is the critical pressure of the component and ϕ is defined as the boiling temperature of the component divided by the critical temperature of the component.

The next step of the analysis incorporates the use of each separate reaction mixture's critical constants to find the fugacities of the reaction components including the reaction solvent, near-supercritical water. The fugacities depend on the concentration of the components in the reaction mixture, so the reaction conversion is first estimated and then the fugacities can be estimated from the estimated equilibrium concentrations. The fugacities are then plugged into the equilibrium conversion equation and solved for the lactic acid molar conversion (X). The first reaction pathway, the dehydration reaction, is represented below for an example:

$$K_a = y_{AA} f_{AA} P * y_{H_2O} f_{H_2O} P / y_{LA} f_{LA} P \quad C.4$$

The fugacity coefficient for each component is f and the mol fraction of the component is y . The pressure is denoted as P and is in terms of bar. The mol fractions of the individual components are represented by the equations in Table 3.3 labelled 'Mol Fraction', since the actual mol fractions are unknown at equilibrium. The conversion constants

K_a are listed in Table 3.2 and they are incorporated into the equation. The resulting equation is:

$$K_a = \frac{[X/50.951 + X] [(50.551 + X)/(50.951 + X)] f_{AA} f_{H_2O} P}{[0.4 + X]/[50.951 + X] f_{LA}} = 725 \quad C.5$$

The lactic acid molar conversion is represented by X . The equation, after cancelling terms, becomes:

$$f_{LA} (0.4 - X) (50.951 + X) 725 = (50.551 + X) X f_{AA} f_{H_2O} P \quad C.6$$

After multiplying through the result is a second order equation which is solved easily with the quadratic equation in a spreadsheet program after the estimated fugacities are entered into the equation. The calculated conversion is then compared with the conversion estimated to find the fugacities. If they are different, then the process is repeated until the molar conversions are the same. The quadratic equation is as follows:

$$X^2 (725 f_{LA} + f_{AA} f_{H_2O} P) + X (50.551 f_{AA} f_{H_2O} P + 36,650 f_{LA}) + 14,780 f_{LA} = 0 \quad C.7$$

Higher ordered equations were solved for X by iteration between 0.0 and 0.4 mols which represents the concentration of lactic acid after equilibrium.

APPENDIX D

PRELIMINARY EXPERIMENTAL WORK

There were several experiments that were not represented in the text of the thesis but have relevance to the work by providing support and a basis for the data provided in the figures. One of the first series of experiments determined the difference of performing the reaction at varying pressures. The two pressures used were 4600 psi and 3500 psi at a reactor temperature of 400 °C. The higher pressures consistently gave better results in terms of higher acrylic acid yields, selectivity and pathway yields. The conversion was also twice as much at the higher pressure, which is consistent with the data shown by Eckert (1972) that the higher pressure would increase the overall reaction rate of the lactic acid.

Different initial concentrations of lactic acid were used, from 0.2 M to 2.0 M, before the concentration of 0.4 M was used as the standard initial concentration for the experiments listed here. With concentrations lower than 0.2 M the subsequent liquid analysis was difficult to perform if the conversion was low. If the initial concentration was higher than 0.4 M the results could be very inconsistent especially when the conversion was fairly high (> 50%). The gas sample would vary in volume. This was probably due to phase separation when the reaction mixture was cooled.

Another type of reactor configuration was also investigated to determine the effect of increasing the reactor surface area on the lactic acid reactions because the aging phenomena showed an effect on the reaction and it was thought that the increased surface area would show a more dramatic effect on the pathways. The reactor zone was packed with small (1/16 inch by 1/32 inch) Hastelloy chips. The increased area did not have a noticeable effect on the reaction pathways, but it did increase the conversion significantly,

probably due to better heat transfer. Phosphoric acid-treated chips were also used with no significant product changes (Romig, 1954). This indicates the phosphated surface probably has no effect on the reaction.

The last significant preliminary result was the use of other phosphate salts and NaCl. The phosphate salts used were CaHPO_4 , BaHPO_4 and Li_3PO_4 . There were no significant differences between the use of the standard Na_2HPO_4 and the other phosphate salts at comparable pH's. When NaCl was used at the same ionic levels as the Na_2HPO_4 , the NaCl runs were lower in acrylic acid yield and lower in pathway three yield. Although, the conversion and the acrylic acid yield was higher than the blank run, which shows that there is an ionic effect on the reaction.

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