This is to certify that the

thesis entitled

CONDENSED PHASE CONVERSION OF LACTIC ACID TO
2,3-PENTANEDIONE

presented by

Rajesh Baskaran

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemical Engineering

Dennis J. Miller
Major professor

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CONDENSED PHASE CONVERSION OF LACTIC ACID TO 2,3-PENTANEDIONE

By

Rajesh Baskaran

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1998

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ABSTRACT

CONDENSED PHASE CONVERSION OF LACTIC ACID TO 2,3-PENTANEDIONE

By

Rajesh Baskaran

The continuous conversion of biomass derived lactic acid to 2,3-pentanedione in the homogenous condensed phase is achieved using alkali metal salt catalysts. Preliminary condensed phase studies were conducted in batch and semi-batch reactors. Various alkali metal catalysts were studied at different temperatures and catalyst concentrations. Cesium lactate was found to be the most effective catalyst. Of the several reactor configurations evaluated, the most efficient operation was achieved in a 50ml continuous stirred tank reactor equipped with an overflow tube for level control and a second port for vapor products. It was possible to maintain steady state conditions in the reactor for an extended period of time by operating the reactor at much lower temperatures (180-250°C) than in the vapor phase system. Analysis of condensable vapor products was done using GC.

Three variables were identified as key parameters affecting reactor performance - temperature, catalyst concentration in the continuous feed, and feed flow rate. The product yields of 2,3-pentanedione and acrylic acid, conversion, and selectivity obtained from the optimization experiments were fit to a quadratic model to generate contour plots of the product yields, conversion and selectivity. Highest 2,3-pentanedione yield of 20% was obtained at 240°C. Acrylic acid yields up to 15% were observed at high flow rates. Conversion of lactic acid increases with temperature and catalyst concentration, the selectivity to 2,3-pentanedione is highest at low flow rates. A kinetic model to describe the system was developed.

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This work is dedicated to my parents, Jayapal and Prithi Baskaran, and my brother Sanjay.

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Dr. Scranto

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ACKNOWLEDGEMENTS

I would like to thank Dr. Dennis Miller, my advisor, for his valuable guidance and constant encouragement during the course of this work. Dr. James Jackson was very helpful during numerous group meetings. I would also like to express my appreciation to Dr. Scranton for serving on my graduate committee.

Thanks to the members of Miller group - Man, Dushyant, Shubham, and Kirthi for being so helpful during my graduate work.

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INTRODUCTION

This research investigates the continuous conversion of biomass derived lactic acid to 2,3-pentanedione in the homogenous condensed phase using alkali lactate catalysts. Technological developments have made the use of corn derived lactic acid a viable feed stock alternative for the production of specialty chemicals (1). The catalytic conversion of lactic acid to 2,3-pentanedione in the vapor phase was discovered in our laboratory (2). Several studies were done to screen catalysts and supports for the vapor phase reaction (3,4). Preliminary condensed phase studies were conducted in batch and semi-batch reactors (5). Various alkali metal catalysts were studied at different temperatures and feed-to-catalyst ratios. Cesium lactate was found to be the most effective catalyst.

Lactic acid at high temperatures and at reaction conditions forms oligomers (6). This reduces the yield and eventually stops the reaction. The main challenge of this study was to minimize the side reaction of lactic acid to polylactic acid and increase the selectivity and reaction time. This involved evaluating various reactor configurations to find the one most suitable for the continuous conversion of lactic acid. Contour plots were used to identify trends in conversion, selectivity, and product yields. The last step was to develop a kinetic model.

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CHAPTER 1

BACKGROUND

1.1 Literature Review

1.1.1 Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is an optically active compound that displays a large range of reactions due to the presence of the carboxyl and hydroxyl functional groups. The Swedish chemist Scheele discovered lactic acid in 1780 (7). It occurs naturally and can be manufactured through fermentation of carbohydrates or chemical synthesis. It is also a metabolic intermediate in humans. It has been traditionally used as a food additive and in textile production. Currently it is an intermediate-volume specialty chemical with an annual production of 50,000 tons/yr. The major producers of lactic acid are Archer Daniels Midland, Cargill, A. E. Staley, and CCA biochem b.v. of the Netherlands. The development of separation technologies like electrodialysis with bipolar membranes, and extractive distillation integrated with fermentation (1) has lowered the cost of producing lactic acid. Consequently it is receiving increasing attention as an intermediate and raw material source.

The chemical synthesis of lactic acid produces only the racemic isomer of lactic acid. The process is based on a byproduct from acrylonitrile synthesis, lactonitrile. The base ca

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base catalyzed liquid phase reaction involves reacting hydrogen cyanide and acetaldehyde. The lactonitrile produced is distilled and hydrolyzed using a concentrated mineral acid like hydrochloric or sulfuric acid to produce lactic acid. The crude lactic acid produced is esterified to methyl lactate and recovered by distillation and hydrolysis with water under acid catalysts.

$$\begin{aligned}
CH_3CHO + HCN &\longrightarrow CH_3CHOHCN \\
CH_3CHOHCN + H_2O + 1/2\ H_2SO_4 &\longrightarrow CH_3CHOHCOOH + 1/2(NH_4)_2SO_4 \\
CH_3CHOHCOOH + CH_3OH &\longrightarrow CH_3CHOHCOOCH_3 + H_2O \\
CH_3CHOHCOOCH_3 + H_2O &\longrightarrow CH_3CHOHCOOH + CH_3OH
\end{aligned}$$

Figure 1.1: Chemical Synthesis of Lactic Acid.

Production of lactic acid from carbohydrate fermentation can yield the desired stereoisomer. Current commercial processes use homolactic organisms like *Lactobacillus delbrueckii, L. bulgaricus, L. leichmanii* (8,9,10). Selection of carbohydrate source depends on price, availability and purity. The fermentation process requires the use of excess calcium carbonate, to neutralize the acid and maintain the optimum pH for fermentation. The fermentation is a batch process requiring 4 to 6 days, and yields in excess of 90% (w/w), from a dextrose equivalent, are obtained. The broth containing the lactate is filtered to remove the cells, carbon treated, evaporated, and acidified with sulfuric acid to convert the salt to lactic acid and insoluble calcium lactate, which is then removed by filtration. The filtrate is further purified to food grade lactic

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acid by carbon columns and ion exchange. To produce heat stable lactic acid, the technical grade is esterified with methanol or ethanol. The ester is recovered by distillation, followed by hydrolysis, and evaporation. The alcohol recovered in the process is recycled.

The primary uses of lactic acid are in the food industry. It is used as a food acidulant/flavoring/pH-buffering agent or as an inhibitor of bacterial spoilage in several processed foods like soups, candy, bread, etc. Another application is as an emulsifying agent in foods such as bakery goods. Lactic acid finds use in the leather tanning industry for delining hides. Pharmaceutical and cosmetic applications include use in topical ointments, lotions, and biodegradable polymers for medical applications. The use of lactic acid and other 2-hydroxycarboxylic acids have been shown to alleviate or improve signs of skin, nail, and hair changes associated with intrinsic or extrinsic aging (11).

An increase in the demand for lactic acid is associated with its use as a feedstock for the manufacture of biodegradable polymers, oxygenated chemicals, and specialty chemicals. Polylactides are biodegradable thermoplastics. Lactic acid has both the hydroxyl and carbonyl group and can be directly converted to polyesters by condensation polymerization. The preferred route is the preliminary formation of dilactide by metal catalyzed selfesterification. Lactide does not undergo esterification and is readily converted to high molecular weight polymers by ring opening polymerization (12).

Extensive research has been done on the conversion of carboxylic acids to alcohols (13). The availability of cheap lactic acid has led to the possible commercial production of propylene glycol and ethylene glycol from lactic acid. Low-molecular-weight polymers of lactic acid can be used to produce devices for the controlled release of an

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of an active agent in medical applications (14). Such biodegradable polymers are used to construct the encapsulation matrix. The active agent can be released over a period of one week to several months. The release rate depends on several factors including polymer composition, molecular weight, surface to volume ratio, etc. Active agents include contraceptives, narcotic antagonists, anesthetics, anticancer agents, hormones, enzymes, vaccines, etc.

Table 1.1: Physical Properties of Aqueous Lactic Acid

Molecular structure	CH_3-CH(OH)-COOH
Molecular Weight	90
Appearance	Clear/light brown aqueous solution
Odor	Characteristic
Boiling point	230 °F (40% solution) 257 °F (90% solution)
Density	1.20-1.21 g/ml

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1.1.2 Reactions of Lactic Acid

The presence of two functional groups (hydroxyl and carbonyl) makes this molecule very reactive. The primary reaction pathways relevant to this study are listed in Figure 1.2.

1.1.2.1 Thermal Degradation

Lactic acid undergoes disintegration when oxidized. There are several possible decarboxylation products. In 1884, Beilstein and Wiegland observed the formation of pyruvic acid when a 2% solution of calcium lactate was treated with potassium permanganate (15). The acid was extracted with ethyl ether. The formation of oxalic acid, formic acid, and acetic acid as decomposition products has been demonstrated. The catalytic oxidation of lactic acid has produced a mixture of acetaldehyde, formic acid, acetic acid, and carbon dioxide (16). Oxidation of lactic acid using chromic acid in sulfuric acid yields oxalic acid and carbon dioxide (17).

1.1.2.2 Dehydration to Acrylic Acid

The demand for acrylic acid polymers has led to several studies for conversion of lactic acid to acrylic acid (18,19). Holmen claimed a process in which an acrylic acid yield of 68% was obtained at around 400°C using sulfate and phosphate catalysts (20). The formation of acrylic acid from lactic acid is also reported in supercritical water (21).

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The mechanism proposed for the dehydration of lactic acid to acrylic acid, without catalyst, involved the leaving of the α-hydroxyl group and the carboxyl hydrogen instead of hydrogen from the methyl group. This resulted in the formation of a lactone as an intermediate. The decarboxylation of lactic acid to acetaldehyde was identified as the major competing reaction. Gunter (22) and Langford (23) performed extensive conversion studies of lactic acid to acrylic acid over various sodium salts and supports. It was found that sodium metasilicate and bromate exhibit the highest selectivity toward the formation of acrylic acid.

1.1.2.3 Reduction to Propylene Glycol

Lautemann first reduced lactic acid to propanoic acid in 1860 using hydrogen iodide. (24). Catalytic reduction of lactic acid, using rhenium black at an average pressure of 258 atm. and average temperature of 150°C, gave a propylene glycol yield of 84% (25).

1.1.2.4 Condensation Reactions

Lactic acid undergoes condensation reactions, either with itself or other molecules, to form larger molecules. Several interesting reactions have been reported (26). Engelhardt (1849) reported that the dry distillation of lactic acid and copper (II) lactate resulted in the formation of lactoylllactic acid, dilactide, carbon dioxide and citraconic acid. Another example of this kind of reaction was reported in 1926 by

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Ipat'ev and Razuvaev. Sodium lactate was hydrogenated in the presence of water and a catalyst consisting of nickel oxide and clay at 70 atm. and 270°C for 12 hours. The products obtained were methylsuccinic acid (35% yield) and small amounts of propanoic acid, butyric acid, and 2-methyl butyric acid (27). The condensation of lactic acid in the presence of a base yields 2,3-pentanedione (28).

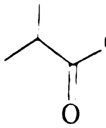

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Figure 1.2: F

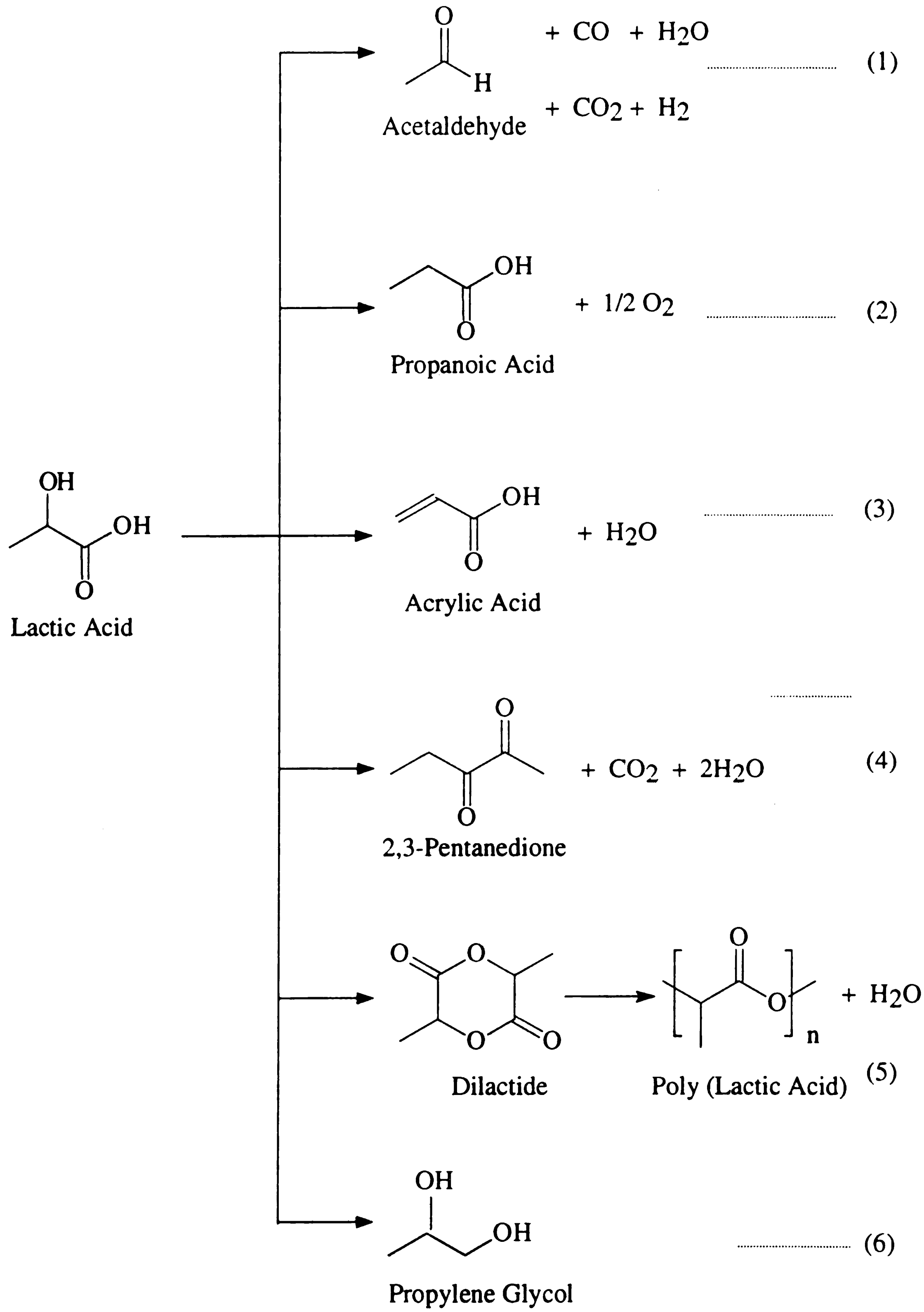

Figure 1.2: Reaction Pathways of Lactic Acid.

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1.1.3 2,3-Pentanedione.

2,3-Pentanedione (acetylpropionyl) is a high value fine chemical. At room temperature, it exists as a clear yellow liquid with a distinct buttery odor in dilute solutions. It is used as a butter flavoring agent and in coffee products to enhance aroma (29). It also has potential for use as a photopolymerization initiator and biodegradable solvent. If its cost is reduced, 2,3-pentanedione has possible use as a feedstock.

Currently, 2,3-pentanedione is produced in limited quantities (about 4000 kg/yr.) through a multi-step chemical synthesis (30) or by extraction from dairy waste. The natural form of 2,3-pentanedione costs \$60 - \$80 /lb, while the synthetic form costs \$50 - \$60 /lb (31). The formation of 2,3-pentanedione from lactic acid over supported catalysts in the vapor phase was discovered in our laboratory. Several studies were done to characterize the reaction and optimize the reaction conditions. Down stream applications, such as the use of 2,3-pentanedione as an intermediate for the manufacture of fine chemicals like duroquinone and pyrazine, were studied by Thiel (32).

2,3-Pentanedione undergoes self-condensation to form duroquinone in a basic environment with heating. The experimental procedure involved the drop wise addition of a dilute solution of 2,3-pentanedione (1 wt%) into a solution of NaOH. The separation of the product was done by liquid-liquid extraction using an immiscible organic solvent. Only low yields of 10% were obtained which makes this pathway unfavorable when compared to commercial methods (32). Duroquinones find applications as antioxidants, photosensitive materials, etc.

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2,3-Pentanedione also reacts with vicinal diamines(α,β-diamino) compounds like ethylenediamine and propylenediamine. The reaction was achieved by refluxing equimolar quantities in a solvent. The solvent chosen is usually the ether corresponding to the diamine. The dihydropyrazine formed was oxidized to the pyrazine using a copper II oxide and KOH catalyst (32).

Table 1.2: Physical Properties of 2,3-Pentanedione.

Molecular Weight	100.11 (g/mol)
Density	0.9565 g/ml
Boiling Point	108 °C
Refractive Index	1.4068

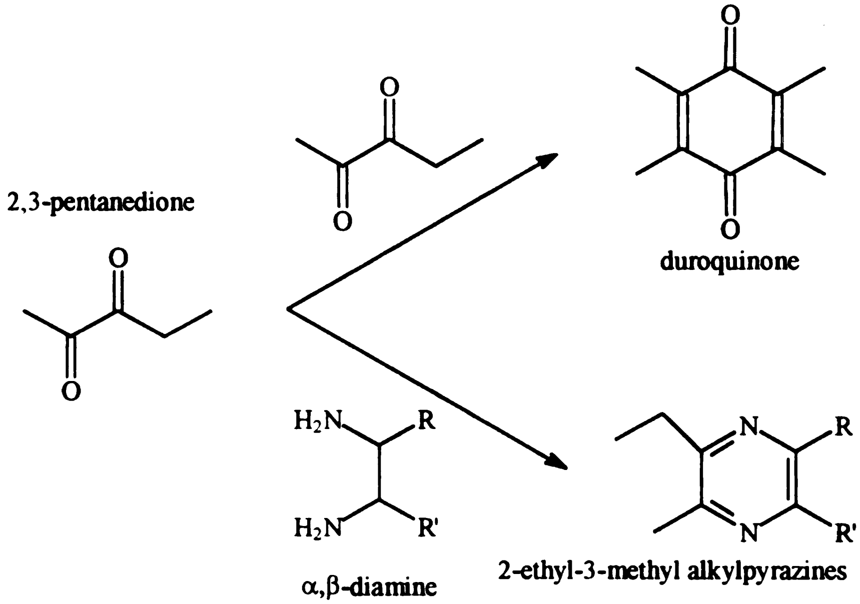

Figure 1.3: Reactions of 2,3-Pentanedione.

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1.1.4 Acrylic Acid

The annual worldwide production of acrylic acid is currently at 2 billion lb. Although the demand for acrylic acid is steadily growing, increased plant capacities have kept prices low. This growth can be attributed to the increasing demand for acrylic esters in water based coatings and adhesive applications. Acrylic acid is also used in the manufacture of superabsorbent polymers.

Of the four commercially viable processes for the manufacture of acrylic acid, the most dominant is the oxidation of propylene from steam crackers in refineries to acrolein. Acrolein is further oxidized to acrylic acid at high temperatures over a molybdenum-vanadium catalyst (33).

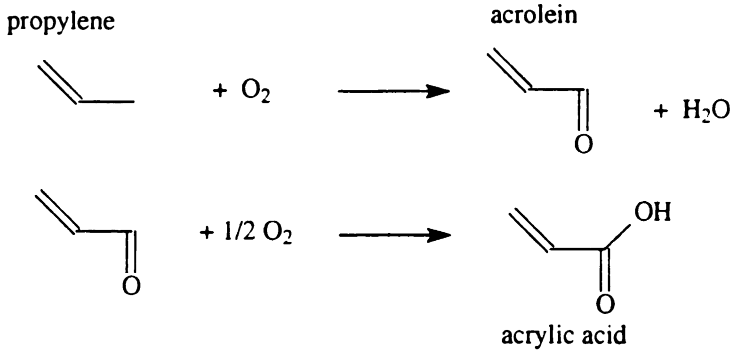

Figure 1.4: Oxidation of Propylene to Acrylic Acid.

Other processes include the treatment of ethylene oxide with hydrocyanic acid and then sulfuric acid. Hydrolysis of acrylonitrile is another possible pathway.

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1.1.5 Propanoic Acid

Propanoic acid (propionic acid) can be manufactured either by chemical synthesis or fermentation of carbohydrates. Synthetically, propanoic acid is produced exclusively by the oxidation of propionaldehyde, which is obtained by the catalytic hydroformylation of ethylene with carbon monoxide and hydrogen, under relatively high temperature and pressure (34). Propanoic acid is also produced from the fermentation of whey using *Propionibacterium acidipropionici* (35). This route is however not economically viable as compared to the synthetic route. The annual production of propanoic acid is around 400 million pounds worldwide, of which about 60% is consumed by the U. S. (36). Propanoic acid and its salts find use as animal feed and corn preservatives, mold inhibitors, herbicides, cellulosic plastics, and anti-arthritic drugs. Synthetic propanoic acid is priced around $0.41/lb, while natural propanoic acid is priced several times higher. This has led to the investigation of the possible conversion of byproduct acrylic acid to propanoic acid by hydrogenation, which would add further value to the conversion of lactic acid.

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1.2 Vapor Phase Conversion of Lactic Acid

The continuous formation of 2,3-pentanedione from lactic acid over supported catalysts in the vapor phase was discovered in our laboratory and several studies were done to characterize the reaction over different catalysts and to optimize the reaction conditions. Studies with various sodium salts showed that the best catalysts, for conversion of lactic acid to 2,3-pentanedione formation, were group IV and V oxides. Sodium arsenate gave the best 2,3-pentanedione yield of 25% at a temperature of 300°C and 0.5 MPa (37). Studies with sodium phosphates demonstrated that both conversion and selectivity toward 2,3-pentanedione increased with increasing basicity of the phosphates; in the order of Na_3PO_4 > Na_2HPO_4 > NaH_2PO_4. FTIR and ^{31}P-NMR spectroscopic studies of the phosphate catalysts, before and after lactic acid conversion, confirmed the formation of tetrasodium pyrophosphate and sodium lactate on Na_2HPO_4 and Na_3PO_4 catalyst surfaces after reaction (38). With NaH_2PO_4, sodium polyphosphates and sodium trimetaphosphate were observed with considerably less proton exchange between the phosphates and lactic acid. The conclusion drawn was that the presence of sodium lactate and/or pyrophosphate on the supported catalysts increased the catalytic activity toward the formation of 2,3-pentanedione.

In the vapor phase, lactic acid is converted to 2,3-pentanedione, acrylic acid, and acetaldehyde at 0.5 MPa over phosphate salts (3). Highest selectivity to 2,3-pentanedione is achieved at 280-300°C and long residence times, while selectivity to acrylic acid is best at 350°C and short residence times. The use of low surface area

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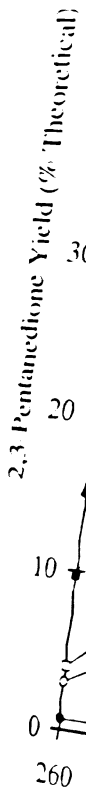
supports like silica was found to minimize undesirable side reactions to acetaldehyde and propanoic acid, which are favored over high surface area (microporous) or surface acidic materials.

Reaction conditions were also optimized for the formation of 2,3-pentanedione from lactic acid, over sodium salts supported on low surface area silica, at 300°C, 0.5 MPa, and 3 second residence time (39). Use of silica support with low surface acidity was recommended to lower the activity toward acetaldehyde formation. Figure 1.5 shows the percent theoretical yield of 2,3-pentanedione for the vapor phase conversion of lactic acid over different alkali salt catalysts.



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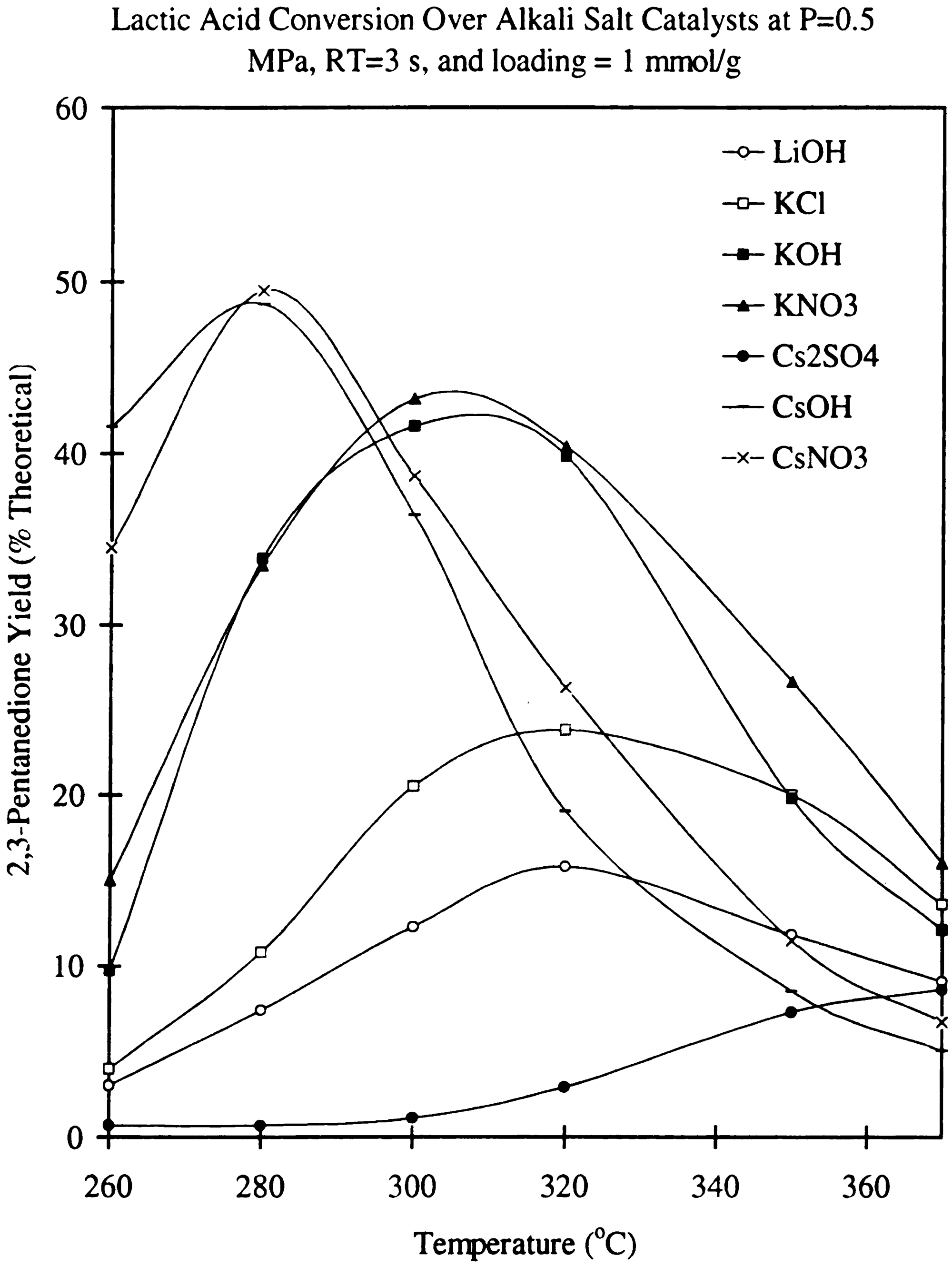

Figure 1.5: 2,3-Pentanedione Yields for Vapor Phase Conversion of Lactic Acid using Alkali Salt Catalysts (39).

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1.3 Mechanism

Craciun (40) proposed the mechanism of catalytic conversion of lactic acid to 2,3-pentanedione. The reaction takes place in the vapor phase over supported alkali metal phosphates, nitrates, and hydroxides and in the homogenous condensed phase using alkali metal salt catalysts (5). The mechanism was proposed for conversion of lactic acid to 2,3-pentanedione in the presence of supported base catalysts (MOH/SiO_2, where M = Na, K, Cs). The possible reaction intermediates are suggested by product analysis, variable temperature-mass spectroscopy (VT-MS), post reaction diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, deuterium labeling studies, and computational modeling using semi-empirical and *ab initio* molecular orbital calculations.

Under high temperature and buffered lactic acid/alkali lactate conditions, hydrogen bonds and ion pairing may stabilize the enolate or enol forms of lactic acid which then may attack a molecule of lactic acid at carbonyl. After the loss of water, the six carbon dihydroxy-ketocarboxylate (Intermediate I) loses CO_2 to form Intermediate II. Loss of hydroxide leads via Intermediate III and subsequent ketonization to 2,3-pentanedione (40).

Post reaction FTIR studies of the salt catalyzed vapor phase reaction have revealed that alkali lactate is the primary stable species found on the support during the reaction (3). The formation of 2,3-pentanedione and acrylic acid are strongly influenced by the ability of the sodium salt to form sodium lactate on the surface of the support;

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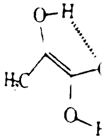

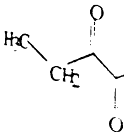

Figure 1.6:

further the rate of formation of sodium lactate depends on the accessibility of the salt to lactic acid. Maximum accessibility is expected for salts that form a molten or liquid film on the surface at reaction conditions (3). This hypothesis led to the development of the reaction of lactic acid to 2,3-pentanedione in the condensed phase.

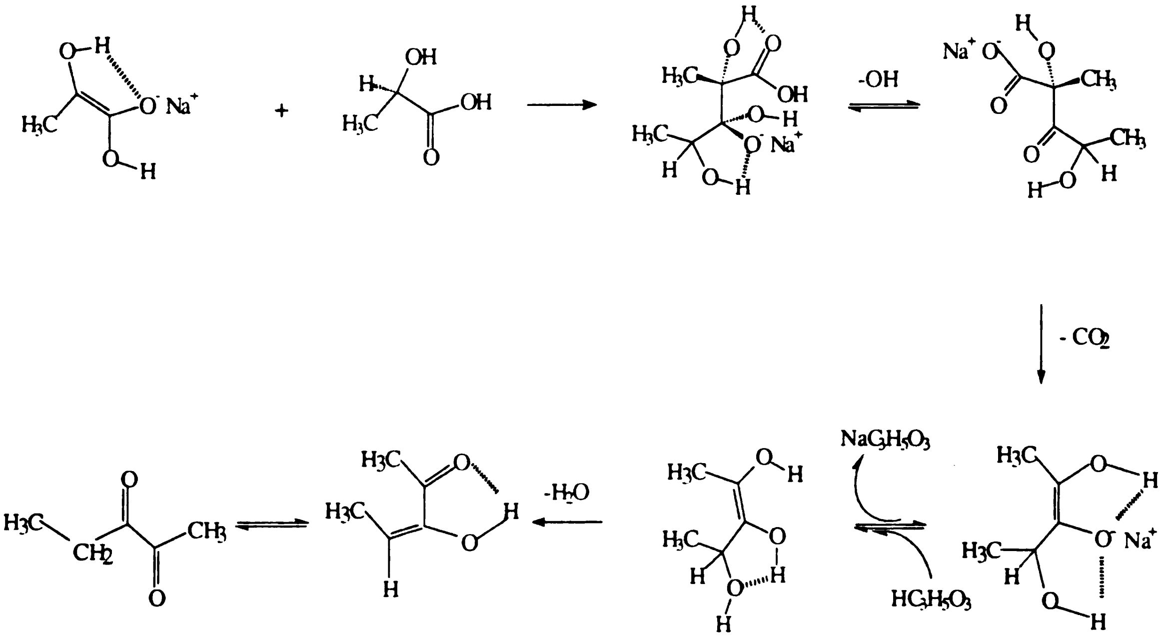

Figure 1.6: Reaction Mechanism.

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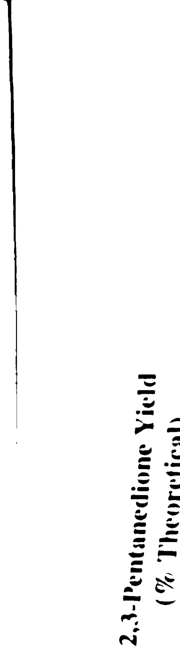
1.4 Rationale for Proposed Work

The initial experiments were done to determine the feasibility of the lactic acid to 2,3-pentanedione conversion in the condensed phase. After verifying the reaction in cold-finger type reaction flasks, efforts were made to characterize the reaction, to improve the reactor design, and screen different homogenous catalysts (5). Alkali metal salt catalysts were found most suitable for this reaction in a batch reactor.

Lactic acid was converted to 2,3-pentanedione in the homogenous condensed phase in a one step process. The feed lactic acid was mixed with the alkali lactate in a fixed initial ratio and heated to the reaction temperature using a ramping program. A carrier gas, like helium, was bubbled through the reaction mixture to remove the product formed. The reaction mixture was well stirred to keep the concentration and temperature constant throughout the reactor. The product gases were condensed using a water-cooled condenser and an ice trap.

The condensed phase conversion was found to be sensitive to several factors (5). These results were important in catalyst selection and determining the optimum operating conditions for the continuous reactor. Figure 1.7 shows the percent theoretical product yield obtained using different maximum temperature setpoints and for different alkali lactate catalysts. The yield was found to increase with increasing temperature up to 250°C; the yield dropped beyond this temperature. This drop in yield was accompanied with an increased formation of polylactides and char in the reactor.



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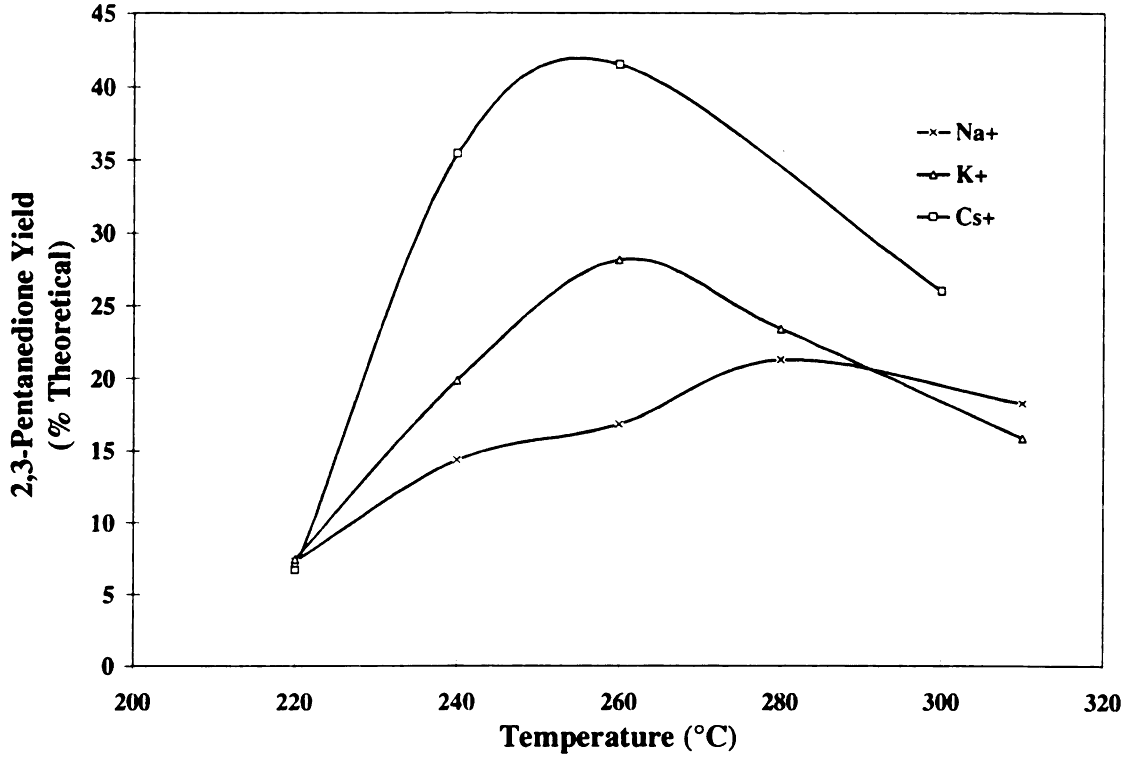

Figure 1.7: Effect of Temperature on 2,3-Pentanedione Yield in a Batch Reactor (5).

Figure 1.8 shows 2,3-pentanedione yield vs. initial ratio of the alkali lactate:lactic acid used. For each alkali lactate salt, the yield was a strong function of initial ratio of the alkali salt to free acid loaded in the reactor. Maximum yields of 2,3-pentanedione achieved were 20.5% of theoretical using sodium lactate/lactic acid mixture, 28.1% using potassium lactate/lactic acid mixtures, and 41.5% using cesium lactate/lactic acid mixtures. Clearly, for any given initial ratio of lactic acid to alkali lactate, the yield depends on the strength of the bases used. This is consistent with the results of the vapor phase studies. Thus, cesium lactate gave the highest yields of all the base used and was chosen for the continuous reactor optimization studies. The strength of the base affected the

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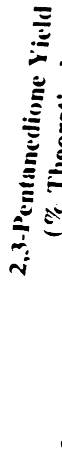

Figure 1.8:

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the 2,3-pentanedione yield. From Figure 1.8, we can further see that for any given temperature and catalyst concentration the highest yields were obtained from the catalyst prepared from the strongest base.

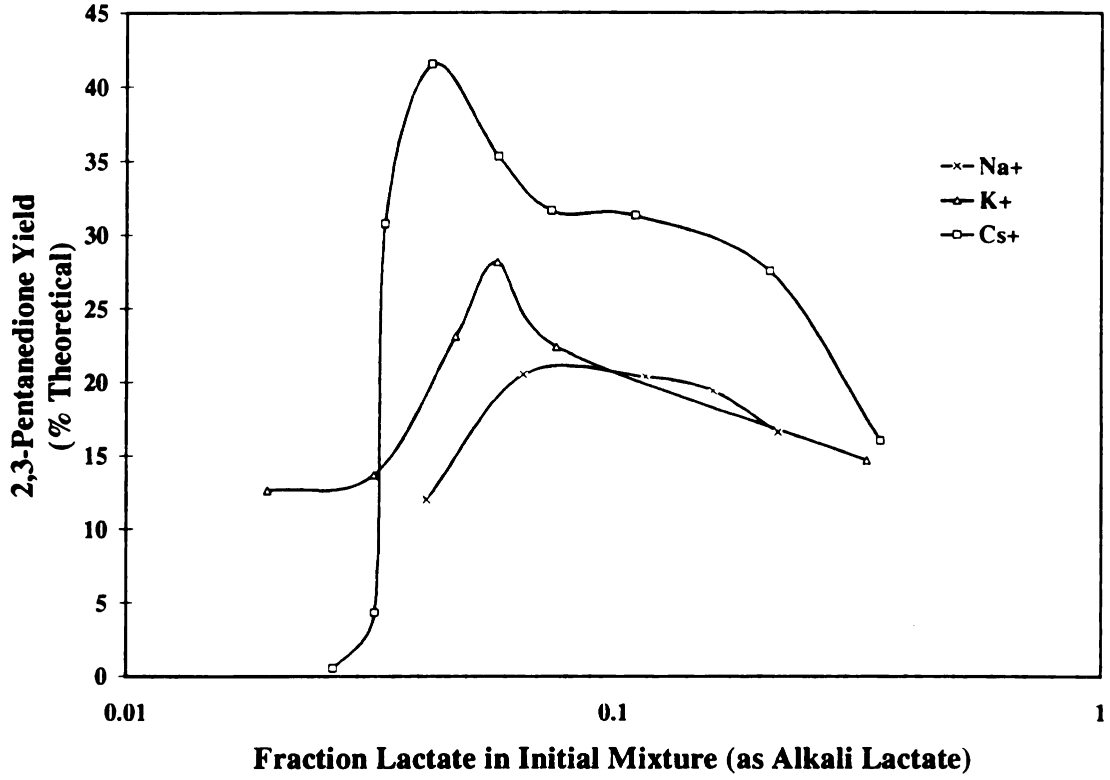

Figure 1.8: Effect of Initial Alkali Concentration on 2,3-Pentanedione Yield in a batch reactor (5).

The production of 2,3-pentanedione from the homogenous condensed phase represents an improvement over current vapor phase and petroleum based technologies. The condensed phase conversion has several advantages over these other technologies. Firstly, the alpha-diketone is produced in a single processing step in good yields and at a

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potentially low cost with the technical challenges of feed vaporization avoided. Secondly, the reaction proceeds without the use of supported catalysts, thereby facilitating uniform reaction, eliminating mass transport limitations and minimizing difficulties associated with catalyst deactivation. The reactions can be performed at lower temperatures and pressures. Further, the need to remove all nonvolatile residues from the feed prior to conversion may be circumvented and large amounts of feed can be processed. Ideally, of course this reaction should extend to other potential substitutes.

By choosing a continuous reaction system, it is hoped that the conditions favorable to the formation of 2,3-pentanedione can be maintained in the reactor for a longer period of time.

1.5 Research Objectives

The primary objective of this investigation was to demonstrate that the conversion of lactic acid to 2,3-pentanedione is possible in a steady state continuous reactor. The second objective was to identify process variables that affect the performance of the reactor and optimize the reaction conditions. The last goal was to study the kinetics of the reaction and propose a model to describe the system.

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CHAPTER 2

LACTIC ACID CONVERSION IN A CONTINUOUS REACTOR

2.1 Introduction

The condensed phase conversion of lactic acid using alkali lactate catalysts is a complex reaction and designing a continuous reactor presented several challenges. From the results of the batch experiments it was evident that the yield of 2,3-pentanedione was dependent on several reaction conditions, especially the temperature. The reactive nature of this molecule made it difficult to find operating conditions favorable to the formation of a single product. By conducting the reaction in a steady state continuous reactor it was possible to maintain the optimum conditions in the reactor for an extended period of time. This would minimize the production of polylactic acid in the reaction vessel allowing the reaction to proceed at a higher selectivity. Further, a continuous reactor would facilitate scaling up of the reactor system to a pilot plant.

2.2 Methods

2.2.1 Materials

Lactic acid used for all studies was supplied by Purac, Inc. as 88 wt.% aqueous solution. The cesium hydroxide used to prepare the alkali lactate catalysts was obtained fro

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from Aldrich as a 50% aqueous solution of 99% purity. The lactic acid was diluted to 34% or 50% with HPLC grade water for continuous studies. High temperature grease was used to seal the glass-to-glass joints in the reaction vessel. A high temperature melting point bath oil (SIGMA catalog # M-9389) was used in the oilbath for additional heating and also in the thermocouple well. The oil is a clear colorless silicone fluid and is stable to temperatures of 315°C. Chemicals used as GC standards are listed below.

Table 2.1: Chemicals Used as Gas Chromatography Standards.

Name	Supplier	Catalog #	Purity	CAS-Registry
2,3-Pentanedione	Aldrich	24,196-2	97%	600-14-6
Acrylic acid	Aldrich	14,723-0	99%	79-10-7
Propanoic acid	Aldrich	24,035-4	99%	79-09-4
Lactic acid	Purac	FCC grade	88%	79-33-4
Methyl ethyl ketone	Aldrich	27,069-5	99.5%	78-93-3
Acetaldehyde	Aldrich	11,007-8	99%	75-07-0
2-Propanol	Aldrich	27,0490-0	99.5%	67-63-0

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2.2.2 Catalyst Preparation

Catalysts were prepared as alkali lactate by the dropwise addition of stoichiometric amounts of the required base to lactic acid. This produced equimolar quantities of the alkali lactate and water. The cesium hydroxide solution used was 50% aqueous and 99% pure and the homogenous catalyst prepared contained 44.75% by weight of cesium lactate. To dissipate the large amount of heat generated, the addition was done in an ice bath, followed by stirring to ensure homogeneity. The final solution was stored under helium.

2.2.3 Reactor Description

Several reactor configurations were attempted before arriving at this reactor setup. Details of reactor development are given in Section 2.3.1. Initial semi-continuous runs were done in a 3-neck 100-ml round bottom flask. This was changed to a 50-ml cylindrical reaction flask and a four-neck flask head. Figure 2.1 shows the reaction apparatus for the continuous conversion of lactic acid in the condensed phase. The flask head had openings for the following connections: a central 19/38 joint for the introduction of carrier gas, two straight 14/20 joints to hold the feed inlet and thermocouple, and a 14/20 elbow for removal of product gases. The inlet for carrier gas was a glass tube of 6 mm ID. The tube extended below the liquid surface in the reactor. This caused the carrier gas to bubble through the reaction mixture.

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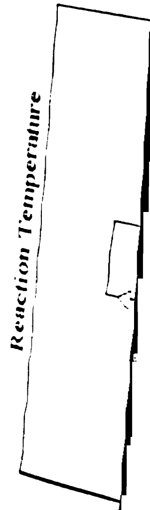
The continuous feed was pumped from a 125 ml Erlenmyer flask into the reaction vessel using a Watson Marlow (Model # 505-S) peristaltic pump, with 0.8 mm ID Viton® tubing. The reactor control thermocouple was placed in a 4 mm glass tube with a few drops of high temperature melting point bath oil. The reactor was heated using a heating tape 6 feet long and 0.5 inches wide. The heating of the reactor was controlled using an Omega CN 2011 programmable temperature controller. A second thermocouple was placed between the heating tape and the reactor to monitor the surface temperature of the reaction flask.

Additional heat was supplied to the reactor by placing it into a stirred oilbath filled with high temperature melting point bath oil. The reactor was insulated with glass wool and insulating firebricks to minimize heat loss. The reactor was supported over a stirrer hot plate, which heated the oilbath and also stirred the reactor and oilbath. The heating and stirring rates were controlled manually.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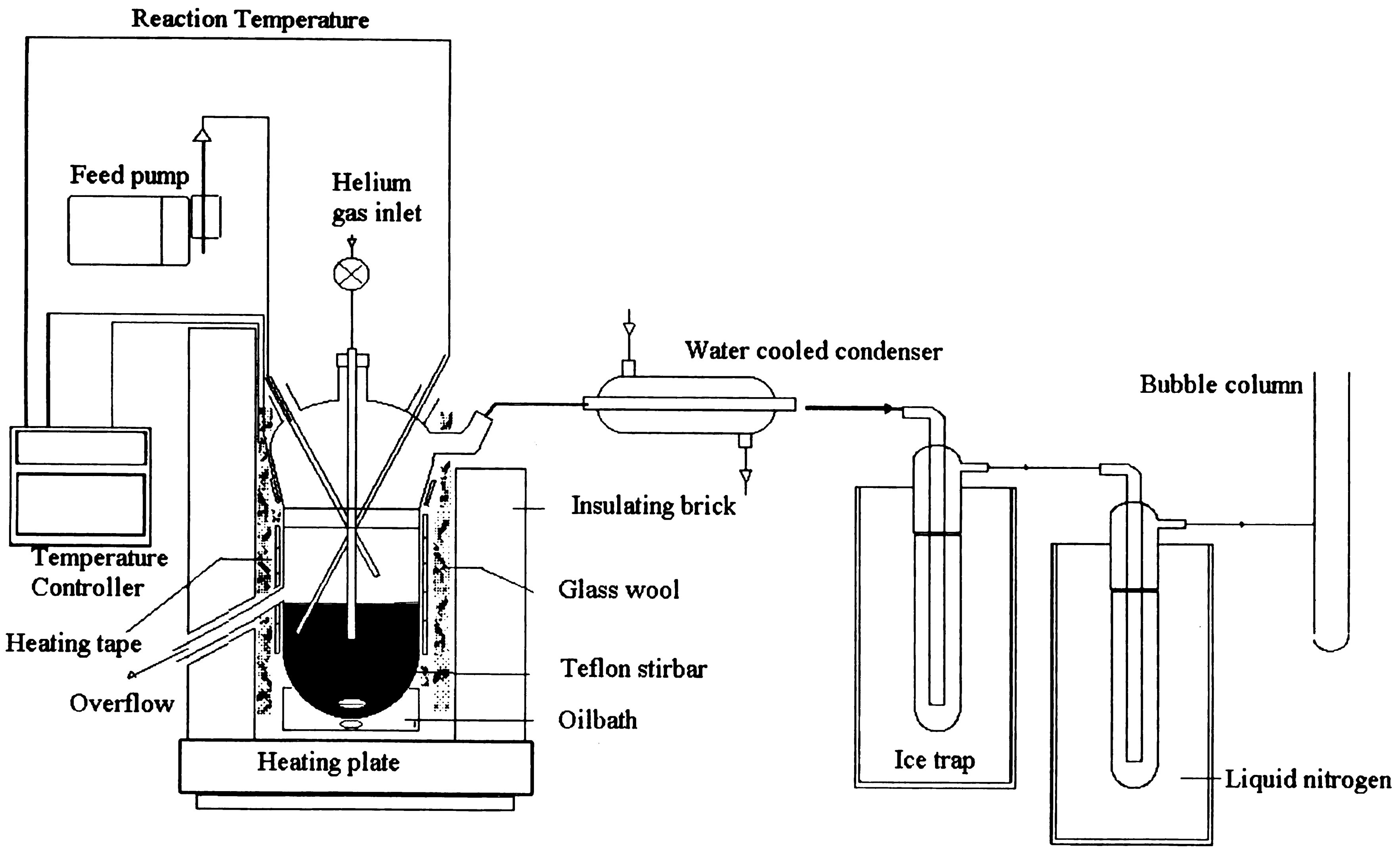

Figure 2.1: Reaction Apparatus for the Continuous Condensed Phase Conversion of Lactic Acid

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Figure 2.2:
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The reaction flask was equipped with an overflow tube (Figure 2.2) for continuous operation. The tube continuously removed liquid product from the reactor and also acted as a level control for the reactor, resulting in an effective reactor volume of 40 ml. The overflow tube was connected to a flask to collect the liquid overflow product. The overflow tube and the collection flask were heated with heating tape to prevent the liquid product, which contained oligomers of lactic acid, from cooling and blocking the tubing.

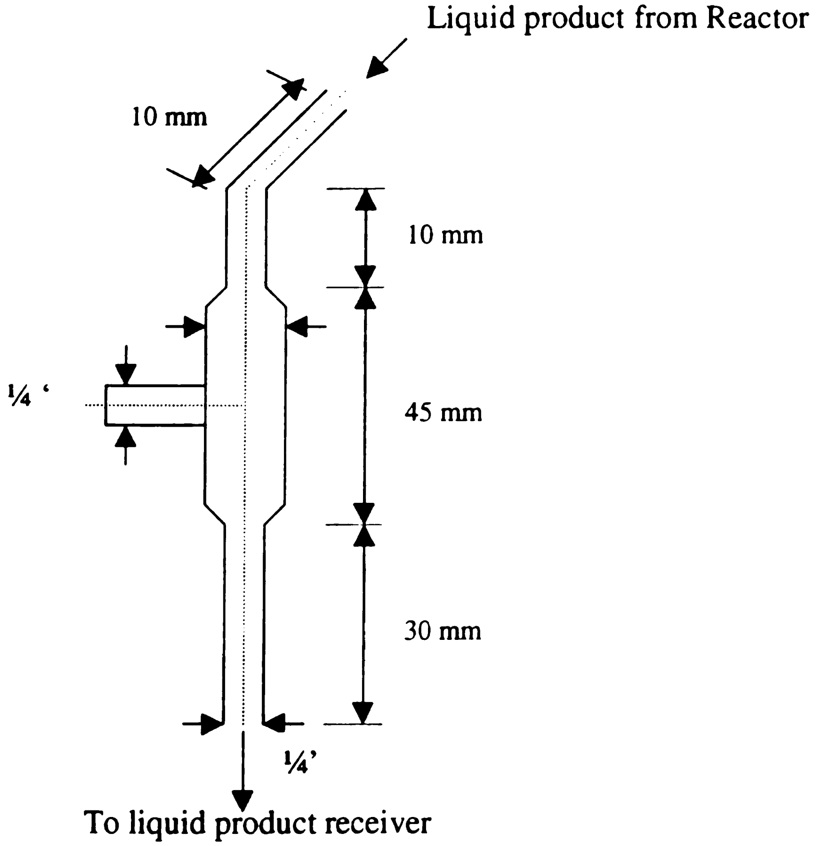

Figure 2.2: Overflow Tube to Remove Liquid Product in Continuous Operation of Reactor.

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The gases exiting the reactor consisted of the helium carrier gas, condensible vapor products including 2,3-pentanedione, acrylic acid, acetaldehyde, propanoic acid, some unreacted lactic acid, and product gases carbon monoxide and carbon dioxide. The gases were cooled and partially condensed using a water-cooled glass condenser. The water-cooled condenser was inclined so that any product condensed flowed down to the traps by gravity. The products were completely condensed and collected in a cold finger trap placed in ice.

The reaction apparatus for initial experiments included a second cold finger trap cooled by liquid nitrogen for product collection. This was later abandoned because some of the CO_2 would cool in the tubing and block the flow of the carrier gas. The amount of CO and CO_2 present in the product gases was determined for selected experiments using two Riken infra red gas analyzers (model 550 A) obtained from CEA instruments, Inc.

2.2.4 Experimental Procedure

The experimental procedure for the continuous reaction involved the following steps. First, the reactor flask and flask head were connected and high temperature grease was used to seal the joints. The reaction vessel was wrapped with heating tape and the fittings for feed inlet, carrier gas inlet, thermocouple, and product gas outlet were connected. The reaction vessel was placed into an oilbath that was filled with high temperature melting point bath oil to a depth of 0.5 inches. Next, the reactor was insulated with glass wool and insulating firebricks. The overflow tube and collection

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flask were wrapped with heating tape and connected to the reaction vessel. The reactor was then connected in series to the water-cooled condenser and product collection traps. The product collection traps were placed in Dewar flasks filled respectively with ice and liquid nitrogen.

The initial reactor charge consisting of 88 wt% lactic acid and cesium lactate catalyst. For most continuous experiments, the initial reactor charge consisted of 36 g of lactic acid and 8 g of cesium lactate catalyst. This corresponded to a lactic-to-lactate molar ratio of 22:1. The reaction mixture was weighed in a 100-ml beaker and poured into the reactor. The reaction mixture was stirred with a Teflon® stirbar. Carrier gas (helium) flow was started and stabilized at 50ml/min. A soap bubble column was used to measure the gas flow rate. The continuous feed of 50% aqueous lactic acid was prepared in batches of 100 g and the desired amount of cesium lactate catalyst was mixed with the feed solution and continuously fed to the reactor.

After completing the initial preparations, the heating of the reaction mixture was started using a ramping program similar to the batch reaction. Simultaneously, the heating of the overflow line and the oilbath was started. The reactor temperature was increased from room temperature to an intermediate setpoint of 130°C in 30 minutes. After the temperature reached 130°C, feed addition was begun using the peristaltic pump at a rate of 3 rpm, which corresponded to a flow rate of about 0.3 ml/min. The reaction temperature was maintained at 130°C for 20 minutes while the continuous feed flow rate was increased to the final flow rate of 0.5-1.5 ml/min. This increase in continuous feed flow rate was done manually at a rate of about 0.5 ml/min every minute. After the continuous feed flow rate had reached steady state, the reaction temperature was inc

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increased to the final reaction temperature setpoint in 40 minutes. Thus, steady state in temperature and continuous feed flow rate was reached an hour and 30 minutes after the reaction was started. To establish steady state, it was found necessary to increase the feed flow rate and temperature gradually, as described.

After the reaction mixture reached the steady state temperature, the product collection trap was changed to begin collection of steady state product. The product traps were weighed and the sample collected for analysis by gas chromatography (GC). The product collection traps were emptied and replaced periodically as the reaction proceeded. The product concentrations obtained from the GC analysis were entered into an EXCEL 7.0 spreadsheet to calculate product yields.

2.2.5 Reaction Conditions

Condensed phase conversion experiments were conducted at a range of reaction conditions. A typical ramping program for reaction temperature of the continuous reaction is given below.

$$25^\circ\text{C} \xrightarrow{\text{30 min}} 130^\circ\text{C} \xrightarrow{\text{20 min}} 130^\circ\text{C} \xrightarrow{\text{40 min.}} 240^\circ\text{C} \xrightarrow{\text{300 min.}} 240^\circ\text{C}$$

Quantifiable yields of 2,3-pentanedione were achieved using maximum reaction temperature setpoints of 200°C to 300°C. Helium gas flow rates of 25 to approximately 2000 ml/min were used in the batch reactor (5); best results had been achieved at 50 ml/min. This flow rate for the carrier gas was used in the continuous reactor studies.

2.2.6 Product Analysis

Product analysis was performed using a Varian Model 3700 gas chromatograph, connected to a Hewlett Packard Model 3394 integrator for determination of product concentrations. The chromatograph uses a flame ionization detector and a 2 mm I. D. x 2 m, 4% Carbowax 80/100 Carbopack B-DA glass column (Supelco). Samples were prepared for injection as a 1:1 mixture of product sample and internal standard. The internal standard used was a 10g/L aqueous solution of 2-propanol in a 0.06 M solution of oxalic acid. The oxalic acid was needed to condition the column. Samples that contain only an aqueous phase are mixed directly; biphasic and neat organic samples were diluted in a quantity of HPLC grade acetone or water adequate to produce a single phase. Dilution sizes were recorded and final concentrations from GC analysis were calculated accordingly. One microliter samples were injected for analysis.

Raw data from the chromatogram, along with feed and product masses, feed flow rates and reaction conditions were entered into an Excel spreadsheet to calculate product yields and selectivity. All product yields are calculated from the ratios of product/internal standard peak areas and detector response factors. Product yields are reported as a percentage of the theoretical yield based on the lactic acid fed to the reactor; product selectivity is the percentage of theoretical yield based on lactic acid consumed in the reactor. Product component identification was done in earlier studies (22,23,39) by residence time analysis, gas chromatography/ mass spectrometry (GC/MS), and ^{1}H and ^{13}C NMR spectroscopy.

Figure 2.3 shows a chromatogram of the condensed vapor product. The temperature program used for all gas chromatography analysis was-

$$100°C \xrightarrow{5°C/min.} 200°C \xrightarrow{6\ min.} 200°C$$

Using this program 2,3-pentanedione appears at a time of 9.5 minutes. Table 2.2 shows the response factor and retention time for major products.

Table 2.2: Retention Time and Response Factor for Product Analysis by Gas Chromatography.

Product	Response factor	Time (min)
Acetaldehyde	2.00	0.92
2-propanol (Internal Standard)	1.00	3.03
2,3-Pentanedione	1.14	9.42
Propanoic acid	1.60	11.03
Acrylic acid	1.98	12.77
Lactic acid	4.10	20.36

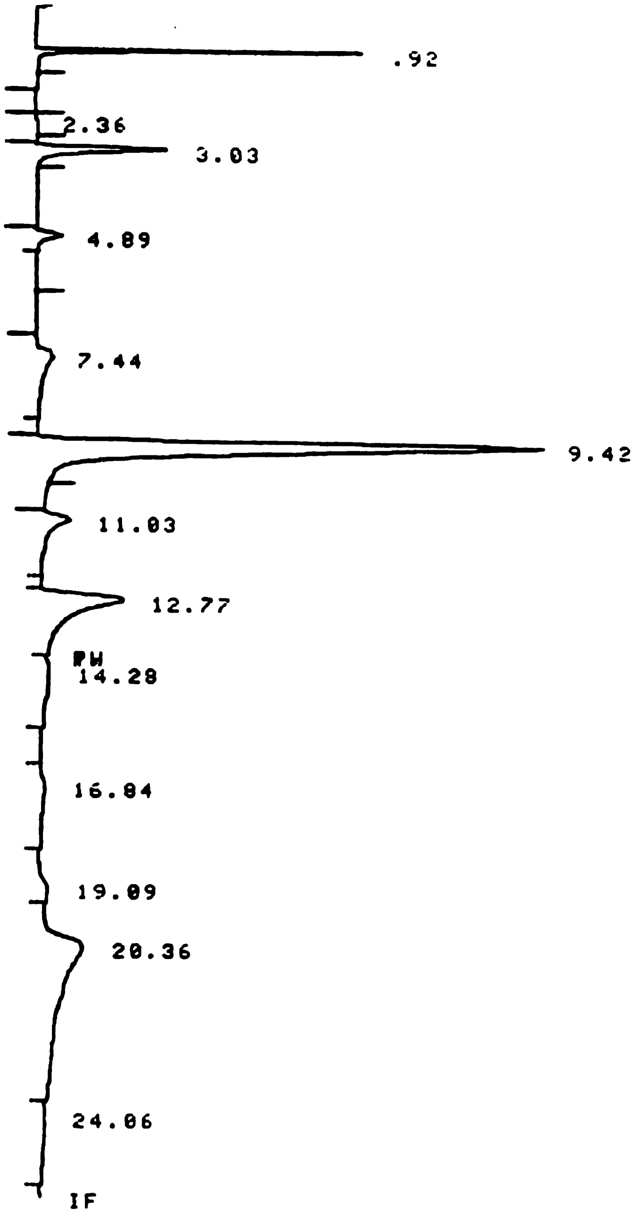


Figure 2.3: Gas Chromatogram of Condensed Vapor Products. (Numbers to the right of peaks indicate retention time in minutes)

2.3 Results and Discussion

Cesium lactate was chosen as the catalyst for continuous reactor studies as it gave the best yields in semi-batch studies. Several variables were identified as important in the optimization of the continuous reactor performance. Reaction temperature and catalyst concentration in the feed affected the performance of the reactor. It was found that operating the reactor at lower temperatures allowed the reaction time to be increased from one hour in semi-continuous operations to 24 hours in continuous operation. The lower reaction temperature (180-250°C) maintained in the reactor reduced the formation of tar and oligomers of lactic acid.

2.3.1 Development of Reactor Configuration for Continuous Operation

The reactor configuration had to be adjusted several times to facilitate the continuous processing of material. Initial semi-continuous condensed phase conversion was achieved using the same 100-ml 3-necked flask used in prior batch studies. A figure of this reaction apparatus is included in Appendix 1. Temperature control was difficult using this setup as the heating mantle could not supply the heat needed to maintain a steady state temperature with feed addition. Therefore, a smaller (25 ml) round bottom 3-neck flask was used to reduce the reaction volume and the heat requirement. This reactor produced the highest yields in both the semi-batch and continuous operation. In experiment 25C08, at a reaction temperature of 235°C and 35% lactic acid feed fed to the reactor at 0.1 ml/min, a 2,3-pentanedione yield of 48% was obtained over a run period of 4 hr.

These initial runs were categorized as semi-continuous because only condensible vapor products were being removed from the reactor. The level of the liquid reaction mixture in the reactor changed as the reaction progressed because of the accumulation of lactic acid in the reactor. The greater extent of oligomerization of lactic acid could be attributed to the long contact time. For true steady state operation, the reactor setup required the addition of an overflow tube to continuously remove the liquid phase from the reactor. This would reduce the residence time of lactic acid in the reactor and also act as an effective level control. This prevented the build up of lactic acid oligomers in the reactor and extended reaction time. The 50-ml reaction flask described in Section 2.2.3, allowed the modifications required for the continuous removal of liquid product from the reactor and also allowed the use of heating tape that provided better temperature control than the heating mantle used previously.

In experiment 50C19, addition of externally generated steam was used as a further heat source for the reaction. It was also theorized that the use of steam would continuously reverse the oligomerization of lactic acid. The addition of steam did not serve its purpose as it lowered the reaction temperature and the reaction temperature could not be maintained at 240°C. This was because the steam supply available in our laboratory was at 20 psi. For its possible use as a heat source the steam needed to be superheated. Instead, the additional heat load was supplied by placing the reactor to a depth of 0.5 inches in a stirred silicone oil bath heated by the stirrer-hot plate supporting the reactor. This proved an effective means of heating the bottom of the reactor.

Several schemes were tried to operate the reactor as a CSTR. One involved using another tubing in the peristaltic feed pump to remove the liquid from the reactor (Experiment 50C21). However, the small diameter tubing used for feed addition did not permit the free flow of the highly viscous liquid product and the removal tube became blocked after a period of time. This scheme was abandoned in favor of removing liquid from the reactor via an overflow tube using gravitational flow. It was found necessary to heat trace the overflow tube from the reaction vessel to the flask collecting the overflow. This lowered the viscosity of the liquid products enough to allow the smooth flow of the liquid product into a receiver.

Finally, glass beads were used in experiment 50C12 to increase the surface area for reaction, however the stirring of the reaction mixture with the Teflon stirbar was ineffective with the glass beads present, and the use of glass beads was thus abandoned.

2.3.2 Effect of Temperature and Catalyst Concentration in Feed

A typical temperature program used in the continuous condensed phase experiments is given below:

$$25^\circ\text{C} \xrightarrow{30'} 130^\circ\text{C} \xrightarrow{20'} 130^\circ\text{C} \xrightarrow{60'} 220^\circ\text{C} \xrightarrow{240'} 220^\circ\text{C}$$

In experiment 50C25, using an initial reactor charge of 36 g lactic acid and 8 g of cesium lactate, at a temperatures of 200^{0}C and a feed (50% aq lactic acid) flow rate of 0.55 ml/min, a conversion of 13% was obtained. The addition of feed was begun at a temperature of 160°C. Less amount of liquid product was recovered from the reactor, as the liquid level in the reactor did not reach the level of the overflow. In experiment

50C26, at similar reaction conditions, the feed addition was begun at a temperature of 130°C. The amount of liquid product collected increased three fold to 30 grams and the conversion increased to 19%. This showed that the establishment of a steady state in the feed flow and reaction temperature depends on the continuous removal of liquid product from the reactor. However a larger amount of acrylic acid was formed relative to 2,3-pentanedione. The low selectivity to 2,3-pentanedione of 24% could be attributed to the low catalyst concentration in the reaction mixture because of the absence of catalyst in the continuous feed. The method of feed addition described above was repeated in experiment 50C27 with catalyst in the continuous feed. At a temperature of 200°C, with a similar initial reactor charge, the selectivity increased to 36%. Table 2.3 summarizes the results of experiments 50C25, 50C26, and 50C27.

Table 2.3: Summary of Results for Experiment 50C25, 50C26, and 50C27.

	50C25	50C26	50C27
Date	2/11/98	2/21/98	2/24/98
Reaction temperature	200°C	200°C	200°C
Reaction time	2 hr 11 min	3 hr.	3 hr. 4 min
Initial reactor charge			
Lactic acid (g)	36.33	36.02	36.02
Cesium lactate (g)	8.022	8.004	8.001
Lactic-to-lactate mole ratio	21.7	21.8	21.8
Continuous feed			
Lactic acid (g)	99.9	171.1	176.1
Cesium lactate (g)/100 g of feed	0	0	3.75
Feed addition start	160°C	130°C	130°C
Feed time (min)	101	150	154
Feed flow rate (ml/min)	1.0	1.2	1.1
Total Vapor Product(g)	70.5	141.5	136.3
2,3-Pentanedione (g)	2.00	3.02	1.81
Acrylic acid (g)	2.74	7.53	1.56
Acetaldehyde (g)	2.08	3.25	1.75
Propanoic acid (g)	0.43	0.88	0.18
Liquid product-Overflow (g)	11.2	30.35	36.72
Conversion (%)	14.6	18.9	7.6
Selectivity(23P)	30.1	23.8	35.8
% Theoretical yield (23P)	4.3	4.5	2.7

In experiment 50C33, a series of product samples were taken as the reaction temperature was being increased. Table 2.4 shows the concentration of 2,3-pentanedione determined from gas chromatography for the product samples. As seen, the presence of 2,3-pentanedione was seen in the first sample taken at a temperature of 170°C. The start of 2,3-pentanedione production was also confirmed by observing yellow condensate on the walls of the glass condenser. The increase in 2,3-pentanedione concentrations reflects drying out of the initial reactor charge to lower the water content in the product.

Table 2.4: Variation of 2,3-Pentanedione Concentration in Condensible Vapor Product with Reaction Temperature.

Sample #	Time (min.)	Reaction Temp (°C)	2,3-pentanedione concentration (g/lt)
1	70	173	8.1
2	73	185	13.7
3	78	196	20.8
4	98	197	25.8
5	158	198	44.1

2.3.3 Effect of Feed Rate

One of the goals in the development of the continuous reactor was to establish steady state operation of the reactor. Initial continuous experiments were done using lactic acid feed concentrations of 34%. However, the large amounts of water present in this continuous feed increased the heat load on the reactor, and the steady state temperature could not be reached. For continuous operation, the feed lactic acid concentration was increased to 50%. This reduced the amount of water that needed to be evaporated and also increased the concentration of the product. The flow rate was increased from 0.1 ml/min to 0.5 ml/min in experiment 50C20. This permitted the level of liquid in the reactor to reach the level of the overflow faster and facilitated recovery of liquid product. Thus, given the reactor heating limitations, steady state in the reactor could only be established with higher feed flow rates and lactic acid concentrations.

2.3.4 Extended reaction

To determine if the reactor operated at steady state, an extended reaction (experiment 50C50) of 24 hours was done at 220°C. The catalyst loading used was 7.5g/100 g lactic acid feed at a feed flow rate of 1.1 ml/min. The lactic acid conversion was about 27% and the selectivity to 2,3-pentanedione was 37%. Overall yield of 2,3-pentanedione was 9.7% and the yield of acrylic acid was 10.1%. Over 1600g of 50% lactic acid along with 120g of cesium lactate catalyst was fed continuously to the reactor. This corresponded to a feed throughput of 43 reactor volumes. The total liquid product collected as overflow was 343g, which corresponded to 8.6 reactor volumes. The product collection traps used in this run were 500 ml Erlenmeyer flasks. Product concentrations and reaction temperatures were monitored to observe if there were any changes over time.

As seen in Figure 2.4, there was a little oscillation in the product concentrations measured by gas chromatography. Consistent production of 2,3-pentanedione was seen even at 24 hours, establishing that the condensed phase reaction was stable. The plot of reaction conditions vs. time shown in Figure 2.5 show that good control of temperature was maintained through the reaction. Figure 2.5 also shows the manner in which the flow rate of the feed was gradually ramped to the rate of 1.1 ml/min while keeping the temperature constant at an intermediate setpoint of 130°C. After the flow reached steady state, the temperature was ramped to the final set point of 220°C. Table 2.5 summarizes the results of this experiment.

Table 2.5: Summary of Results for Extended Reaction - Experiment 50C50.

Date	7/17/98
Reaction temperature	220°C
Reaction time	24 hr
Initial reactor charge	
Lactic acid (g)	36.10
Cesium lactate (g)	8.05
Lactic-to-lactate mole ratio	21.7
Continuous feed	
Lactic acid (g)	1600
Cesium lactate (g)	120
Feed addition start	130°C
Feed time (min)	1410
Feed flow rate (ml/min)	1.22
Product(grams)	
2,3-Pentanedione	46.3
Acrylic acid	69.5
Acetaldehyde	19.6
Propanoic acid	7.73
Liquid product (Overflow)(g)	343
Conversion	26.8
Selectivity(2,3P)	37.3
% Theoretical yield (2,3P)	9.7

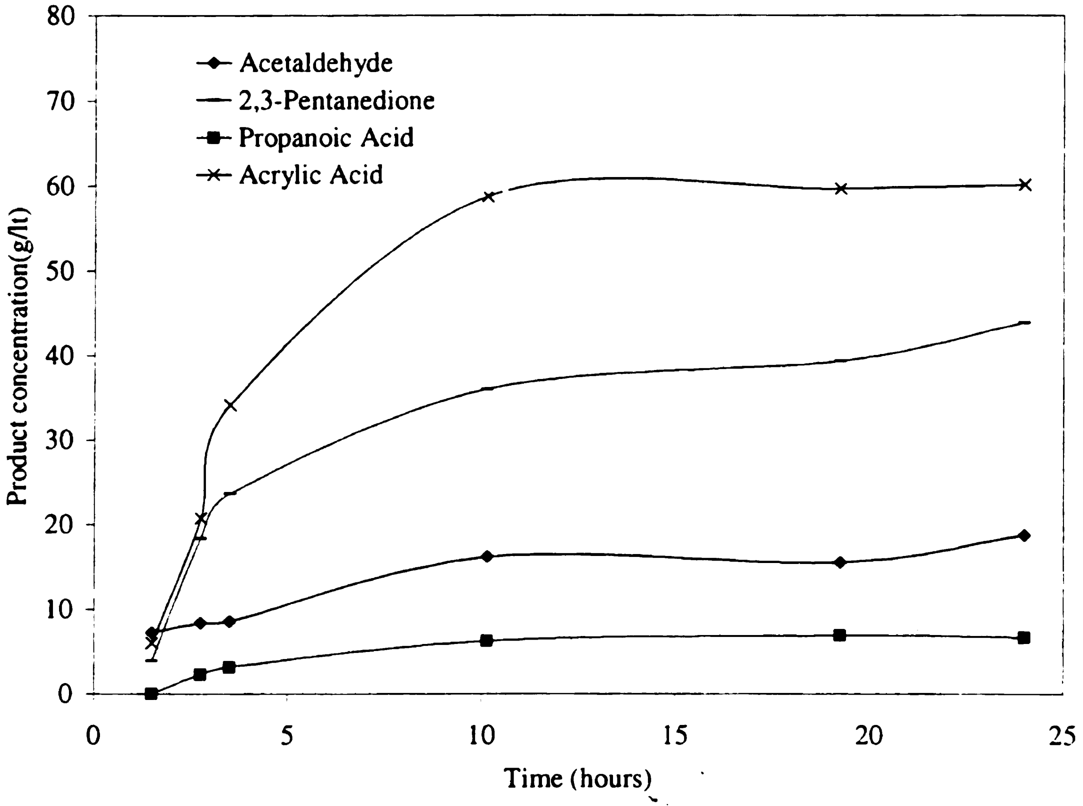


Figure 2.4: Plot of Product Concentrations vs. Time for Extended Reaction.

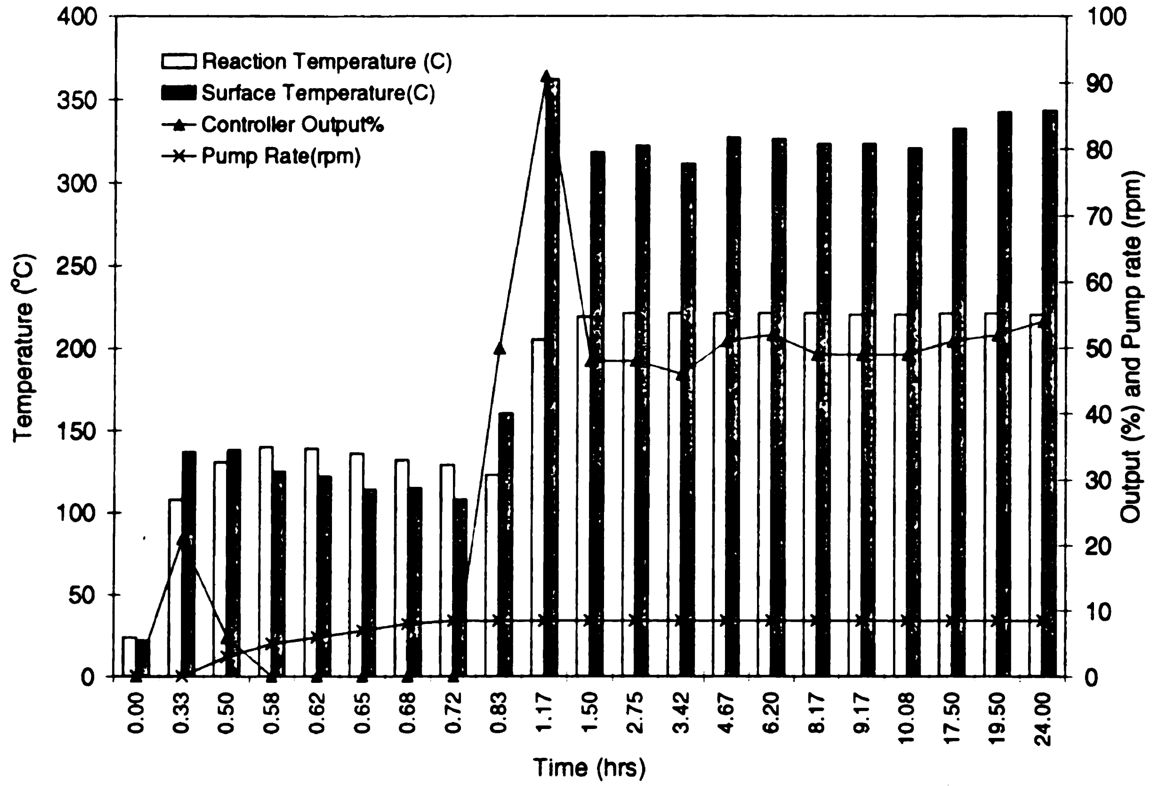


Figure 2.5: Plot of Reaction Conditions vs. Time for Extended Reaction.

2.3.5 Material Balances

2.3.5.1 Mass Balance

To verify the quality of reactions and analyses an overall mass balance was calculated for one experiment. Initial and final weights were measured to determine gain of weight of each component of the reaction apparatus. The weight gain was added to the mass of products collected. The reactor weight gain represents the amount of product remaining in the reactor. The effective volume of the reactor was about 40 ml. The density of the reactor residue, calculated by dividing the amount of reactor residue by the reactor volume, was approximately 1.1 g/lt. Table 2.6 shows the overall mass balance calculations. IR meters measured CO and CO_2 concentration in the exit gases. The gas yields were calculated and were added to the product mass. The results show that the mass balance closes accurately for this reaction.

Table 2.6: Mass Balance Calculations for Experiment 50C51.

Mass Balance

				Initial(g)	Final(g)	Gain
Initial charge	Lactic	36.07 g	Reactor	266.13	309.76	43.63 g
	Cesium Lactate	8.05 g	Thermocouple	10.44	10.51	0.07 g
Continuous Feed	Lactic	400 g	Feed Tube	12.97	13.01	0.04 g
	Cesium Lactate	30 g	Gas Inlet	25.95	26.60	0.65 g
			Condenser	96.51	96.73	0.22 g
			Tubing #1	81.72	82.13	0.41 g
			Tubing #2	36.84	36.87	0.03 g
			Total Product(g)			318.31 g
			Overflow (g)			108.43 g
			CO and CO_2 (g)			6.99 g
IN	Total Mass	474.127 g	**OUT**	Total	Mass	478.79 g
					Gain	4.66 g
					% Recovered	100.98

2.3.5.2 Carbon Balance

The carbon balance calculations for experiment 50C51 is shown in Table 2.7. To account for all the carbon in the system, CHN analysis of reactor residue, liquid product, and vapor product was done. The CHN analysis was done at the Department of Civil and Environmental Engineering at Michigan State University. Carbon enters the reactor as lactic acid or cesium lactate catalyst. The initial reactor charge consists of 36 g of 88% lactic acid supplied by Purac, Inc. and 8 g of cesium lactate catalyst prepared by mixing equimolar amounts of cesium hydroxide and lactic acid. The 88% lactic acid was diluted to 50% for continuous feed using HPLC grade water. The amount of cesium lactate catalyst in the continuous feed was 7.5g/100 g of feed. The carbon balance closes very satisfactorily to within 3.5%.

The weight percentage of carbon, both in the reactor residue and the liquid product, was about 38%. This is a validation of the steady state and also shows that the reactor is well mixed.

Table 2.7: Carbon Balance Calculations for Experiment 50C51

Carbon Balance					
In				**Out**	
Initial reactor charge	grams	moles	g carbon	Reactor residue (g)	44.4
Lactic Acid (88%)	36.08	0.35	12.69	%C from CHN analysis	38.98%
Cesium Lactate	8.05	0.016	0.58	Total carbon (g)	17.30
Continuous feed				Liquid product (g)	108.43
Lactic Acid (50%)	400	2.22	79.93	%C from CHN analysis	38.12%
Cesium Lactate	30	0.061	2.17	Total carbon (g)	41.33
				Vapor Product (g)	318.97
				%C from CHN analysis	12.56%
				Total carbon (g)	40.063
Total Carbon (g)			**95.38**	**Total Carbon (g)**	**98.70**
				Difference %	-3.49

2.3.5.3 Hydrogen Balance

The CHN analysis data used for the calculating the carbon balance was further used to calculate the hydrogen balance. These balances are not as accurate as they take into account the large amounts of water in the system. Table 2.8 shows the hydrogen balance calculations for experiment 50C51.

Table 2.8: Hydrogen Balance Calculations for Experiment 50C51.

Hydrogen Balance **In**				**Out**	
Initial reactor charge	grams	moles	g hydrogen	Reactor residue (g)	44.4
Lactic Acid (88%)	36.07	0.35	2.117	%H from CHN analysis	4.80%
Cesium Lactate(44%)	8.05	0.016	0.081	Total hydrogen (g)	2.13
Water(acid + catalyst)	8.78	0.48	0.976	Liquid product (g)	108.43
				%H from CHN analysis	6.42%
Continuous feed				Total hydrogen (g)	6.96
Lactic Acid(50%)	400	2.22	13.32	Vapor Product (g)	318.97
Cesium Lactate(44%)	30	0.06	0.30	%H from CHN analysis	8.40%
Water(acid + catalyst)	216.5	12.03	24.06	Total hydrogen (g)	26.79
Total hydrogen (g)			**40.86**	**Total hydrogen (g)**	**35.88**
				Difference %	12.18

2.3.5.4 Comparison of Product Analyses

CHN analysis was done on condensed vapor product samples for several reactions. Experiment 50C42 was conducted at 240°C, 50C46 at 220°C, and 50C51 at 200°C. Table 2.9 shows the comparison between the carbon and hydrogen content determined from GC and CHN analysis of the condensed vapor product. The carbon content determined is similar from these two techniques. It should be noted that the concentration of lactic acid determined from gas chromatography has an error of ±14%. This could account for the higher carbon % obtained from GC.

Table 2.9: Comparison of Product Analysis by GC and CHN Analysis.

	50C42 P4		**50C46 P4**		**50C51 P4**	
LIQ GC	g/lt	mol/lt	g/lt	mol/lt	g/lt	mol/lt
Acetaldehyde	42.4	0.96	15.1	0.34	3.3	0.08
2,3-Pentanedione	64.3	0.64	27.0	0.27	19.9	0.2
Propanoic acid	10.9	0.15	4.2	0.06	10.2	0.14
Acrylic acid	71.9	0.99	42.9	0.60	97.0	1.36
Lactic acid	203.	2.26	378.1	4.20	215.9	2.4
Water (difference)	605.1	33.61	531.8	29.55	652.3	36.24
	CHN	GC	*CHN*	GC	*CHN*	GC
Carbon %	*15.46*	18.54	*14.43*	19.96	*12.56*	15.43
Hydrogen %	*8.54*	9.49	*8.56*	9.07	*8.40*	9.51
Oxygen	*75.05*	71.97	*76.32*	70.97	*78.38*	75.06
		100.00		100.00		100.00

2.3.6 CO and CO_2 Production

The accuracy of the reaction procedure and product analysis can be checked by the comparison of carbon dioxide and carbon monoxide yields obtained by gas analysis using IR meters to theoretical yields. The moles of product formed at steady state were calculated from the product concentration obtained from Gas Chromatography. Dividing by reaction time gave the average rate of formation of each product in units of moles/sec.

Figure 1.2 shows the reactions of lactic acid. From reaction (1) we can see that for every mole of acetaldehyde formed either one mole of carbon monoxide or one mole of carbon dioxide is formed. Further, for every molecule of 2,3-pentanedione formed one mole of CO_2 is formed. While the reaction temperature was at steady state, 7.31g of 2,3-pentanedione was formed. This corresponded to an average CO_2 production rate of 5.15 $\times 10^{-6}$ mol/sec.

Table 2.10 shows the calculation of CO and CO_2 flow rates. The amount of CO and CO_2 in the vapor product was calculated from the percentage compositions determined from the IR meters. The total gas flow rate was 55 ml/min. Average percentage of CO and CO_2 observed was 7.7 % and 22.6 % respectively. This corresponded to a flow rate of 3.17 x10^{-6} mol/sec for CO and 9.24 x10^{-6} mol/sec for CO_2. By equating the theoretical CO formation from acetaldehyde to the CO flow rates obtained from the IR meter, the CO_2 formed from the conversion of lactic acid to acetaldehyde (6.34 x10^{-6} mol/sec) can be determined by difference. Adding the amount of CO_2 produced from the formation of 2,3-pentanedione from lactic acid (5.15 x10^{-6} mol/sec) gave the CO_2 production from the two reactions (1.15 x10^{-5} mol/sec). This is comparable to the total flow rate of CO_2 detected by the IR meter (9.24 x10^{-6}).

Table 2.10: Comparison of Measured CO and CO_2 Flow to Theoretical Flow Rates Estimated from Steady State Product Concentrations.

Theoretical Rate					**From CO and CO_2 meters**		
			CO	CO_2			
	moles	moles/sec	moles/sec	moles/sec		CO	CO_2
From 2,3P	0.073	5.15 x10^{-6}	0	5.15 x10^{-6}	Avg %	7.7	22.6
Acetaldehyde	0.134	9.51 x10^{-6}	3.17 x10^{-6}	6.34 x10^{-6}	moles/sec	3.17 x10^{-6}	**9.24 x10^{-6}**
Total			3.17 x10^{-6}	**1.15 x10^{-5}**			

CHAPTER 3

OPTIMIZATION AND KINETIC ANALYSIS

3.1 Optimization of Operating Conditions

After the design of the continuous reactor system was completed, a study to find the optimum operating conditions was conducted. Three variables were identified as key parameters affecting reactor performance - temperature (x_1), feed flow rate (x_2) and catalyst concentration in the continuous feed (x_3). Optimization involved varying these three different variables at three different values. This would require 27 experiments. However, using a two level, three-parameter factorial design designated as a "Box-Benkhen" design (41), the number of experiments was reduced to 15.

3.1.1 Box-Benkhen design of Experiments

Implementation of the Box-Benkhen experimental design involved identifying "boundary values" (maxima and minima) for each of the independent variables, and then conducting experiments in the factor space defined by the boundary values. The range of these experiments can be described by a cube, the coordinates of the corners representing the range of the variables. Figure 3.1 shows a schematic representation of the Box-Benkhen design of experiments. The center of the cube (0,0,0) is the base set of the conditions. Twelve experiments were conducted at coordinates corresponding to the centers of the cube edges and three at the base conditions. These experiments were conducted in a random order to prevent any systematic error. The reaction conditions are listed in Table 3.1.

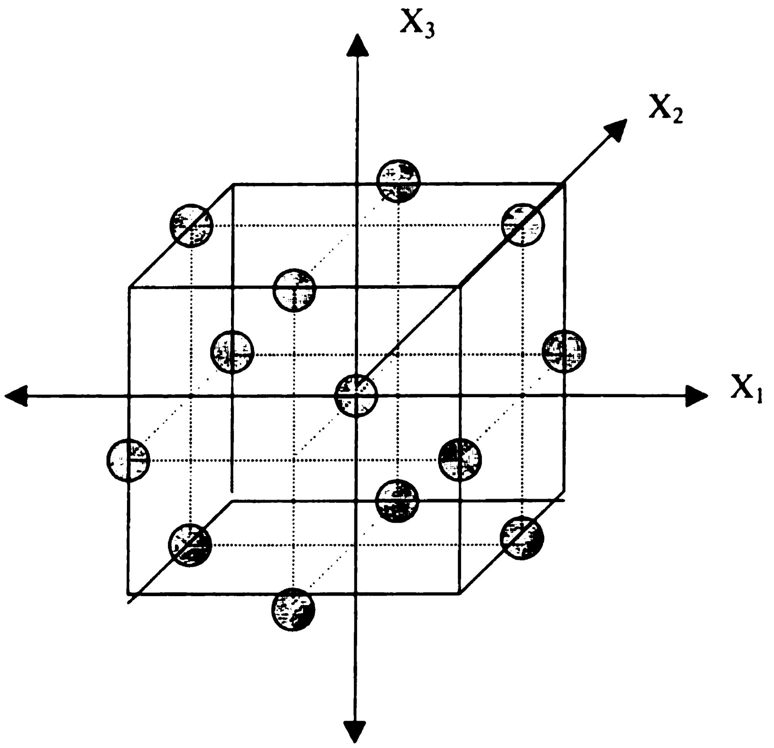


Figure 3.1: Schematic Representation of Box-Benkhen Design.

Table 3.1: Box-Benkhen Design Values.

		Box-Benkhen design Values		
Parameter	Range	-1	0	1
Temperature (°C)	200 – 240	200	220	240
Flow Rate (ml/min)	0.6 - 1.5	0.6	1.1	1.5
Catalyst Concentration [a]	5 – 10	5	7.5	10

[a] catalyst concentration in continuous feed - g cesium lactate/100 g of 50% aqueous lactic acid feed

3.1.2 Experimental Method

All reactions were carried out in the 50 ml reaction flask described in Section 2.2.3 and were started at the same initial conditions. The initial reactor charge consisted of 36 g of lactic acid and 8 g of cesium lactate catalyst, which corresponded to a lactic-to-lactate molar ratio of 22:1. While the continuous feed used in all the experiments was a 50% aqueous solution of lactic acid, the catalyst concentration in the continuous feed was varied. The catalyst used was the 1:1 molar cesium lactate prepared as described in Section 2.2.2. The protocol for the temperature ramp and feed addition described in Section 2.2.4 was implemented consistently in the entire set of experiments.

The reaction was started at room temperature and the reaction mixture was heated to 130°C, and maintained at 130°C for 30 minutes while the feed addition was started. The feed rate was started at about 0.3 ml/min and gradually increased to the steady state feed rate (0.5 –1.5 ml/min.). The length of the experiments varied from 5 to 7 hours. An extended reaction of 24 hours was also conducted to verify the establishment of steady state in the reactor system. The results of these experiments are listed in Table 3.2.

The product concentrations were determined using gas chromatography. The lactic acid used as initial reactor charge was included in the calculation of the yields of 2,3-pentanedione and acrylic acid that are reported. The product concentrations used in the kinetic analysis were calculated by taking an average of the steady state product concentrations determined by gas chromatography.

Table 3.2: Results of Optimization Experiments.

ID	Temp (^oC)	Flow (ml/min)	Cat Conc. [a]	Time (hr)	Conv.[b] %	Select. [c] %	Yield 2,3P [d] %	Yield Acrylic [e] %
50C37	200	1.21	10	7	16.7	32.4	5.2	6.1
50C38	220	0.69	5	7	10.1	34.8	3.4	3.6
50C39	220	0.63	10	6	32.2	47.6	14.8	8.5
50C40	200	0.65	7.5	6	17.7	51.1	8.8	4.6
50C41	220	1.13	7.5	6	25	28.9	7	7.8
50C42	240	1.48	7.5	5	36.6	35	12.4	12.8
50C43	240	1.12	10	6	47.2	42.3	19.2	7.7
50C44	240	0.71	7.5	5	23.5	60.7	13.2	5.0
50C45	220	1.18	7.5	6	15.4	51.8	7.8	4.0
50C46	220	1.49	5	5	15.2	36.7	5.4	5.1
50C47	240	1.13	5	5	31.5	43.9	13.5	7.8
50C48	220	1.47	10	5	26.6	34.2	8.8	10.0
50C49	200	1.18	5	6	13.7	35.6	4.8	5.0
50C50	220	1.22	7.5	24	26.8	37.3	9.7	10.2
50C51	200	1.45	7.5	5	33.4	21.7	6.46	14.9

[a] Catalyst concentration in continuous feed g cesium lactate/100 g of feed (50% aqueous lactic acid)

[b] Conversion = (moles lactic acid converted / moles lactic acid fed)*100

[c] Selectivity = (moles lactic acid converted to 2,3P/ moles lactic acid converted) *100

[d] % theoretical yield 2,3-pentanedione = (grams 2,3P formed / grams 2,3P formed if all lactic acid fed was converted to 2,3P)*100

[e] % theoretical yield acrylic acid = (grams acrylic formed / grams acrylic formed if all lactic acid fed was converted to acrylic)*100

3.1.3 Results and Discussion

The product yields of 2,3-pentanedione and acrylic acid, conversion, and selectivity obtained from these experiments were fit into a quadratic model of the form

$$Y=b_0 + b_1x_1 + b_2x_2 +b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 +b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2,$$

where x_1, x_2, and x_3 are the three independent variables temperature, the feed flow rate, and catalyst concentration in the continuous feed. The coefficients b_i and b_{ij} were determined using the regression analysis tool in Microsoft Excel 7.0.

The regression was repeated after discounting experiment 50C45. This greatly improved the fit and much higher R^2 values were obtained for regression of acrylic acid yields and conversion. The results of the regression analysis are listed in Table 3.3 to 3.6. The corrected coefficients reported are the results of the regression analysis after discounting experiment 50C45. A R^2 value of 0.91 was obtained for the regression of 2,3-pentanedione yield. The R^2 value for lactic acid conversion was 0.71. A confidence level of 0.95 was used for all regressions.

Table 3.3: Regression Statistics and Coefficients for 2,3-Pentanedione Yield.

	2,3-Pentanedione yield	Corrected
Multiple R	0.95	0.95
R Square	0.91	0.91
Adjusted R Square	0.74	0.70
Standard Error	2.25	2.51
Observations	15	14

	Coefficients	
Intercept	283.05	270.69
x_1	-2.67	-2.57
x_2	1.76	2.85
x_3	-1.78	-1.55
x_1*x_2	0.10	0.10
x_1*x_3	0.02	0.02
x_2*x_3	-2.22	-2.23
x_1*x_1	0.01	0.01
x_2*x_2	-4.19	-4.79
x_3*x_3	0.03	0.02

Table 3.4: Regression Statistics and Coefficients for Conversion of Lactic Acid.

	Conversion of lactic acid	Corrected
Multiple R	0.85	0.87
R Square	0.72	0.75
Adjusted R Square	0.20	0.19
Standard Error	9.12	9.22
Observations	15	14

	Coefficients	
Intercept	718.8	473.0
x_1	-6.75	-4.74
x_2	16.13	37.72
x_3	-4.52	0.05
x_1*x_2	0.07	0.09
x_1*x_3	0.06	0.06
x_2*x_3	-3.20	-3.43
x_1*x_1	0.01	0.01
x_2*x_2	0.59	-11.37
x_3*x_3	-0.15	-0.42

Table 3.5: Regression Statistics and Coefficients for 2,3-Pentanedione Selectivity.

	Reaction selectivity	Corrected
Multiple R	0.77	0.86
R Square	0.60	0.74
Adjusted R Square	-0.13	0.14
Standard Error	10.65	9.06
Observations	15	14

	Coefficients	
Intercept	150.8	588.5
x_1	-1.52	-5.10
x_2	-0.58	-39.03
x_3	10.74	2.59
x_1*x_2	0.09	0.04
x_1*x_3	0.00	0.00
x_2*x_3	-3.76	-3.35
x_1*x_1	0.00	0.01
x_2*x_2	-4.98	16.31
x_3*x_3	-0.39	0.09

Table 3.6: Regression Statistics and Coefficients for Acrylic Acid Yield.

	Acrylic acid yield	Corrected
Multiple R	0.75	0.80
R Square	0.56	0.64
Adjusted R Square	-0.23	-0.18
Standard Error	3.66	3.56
Observations	15	14

	Coefficients	
Intercept	93.4	-21.4
x_1	-1.04	-0.10
x_2	-1.74	8.34
x_3	5.47	7.61
x_1*x_2	-0.07	-0.06
x_1*x_3	0.00	0.00
x_2*x_3	-0.14	-0.25
x_1*x_1	0.00	0.00
x_2*x_2	11.79	6.21
x_3*x_3	-0.26	-0.39

The regression coefficients obtained were used to generate contour plots of the product yields, conversion, and selectivity. These plots helped identify trends in reactor performance as reaction parameters are varied relative to each other. The contour plots were extremely important in interpreting the results of the experiments, as trends may be difficult to spot when varying three parameters. It is important to note that the trends identified are only valid for the factor space defined by the Box-Benkhen design.

3.1.3.1 2,3-Pentanedione Yield

Figure 3.2 shows the contour plot for the yield of 2,3-pentanedione at a temperature of 220°C. As expected, the yield increased as the concentration of catalyst in the feed was increased. At low catalyst concentrations, 2,3-pentandione yield increased as feed flow rate was increased. Experiments 50C38 and 50C46 were conducted at 220°C and feed catalyst concentrations of 5 g Cs Lactate/100g of feed. Yield of 2,3-pentanedione increased from 3.4% at a flow rate of 0.6 ml/min to 5.4% at a flow rate of 1.5 ml/min.

This trend was reversed at higher catalyst concentrations. Experiments 50C39 and 50C48 were conducted at 220°C and feed catalyst concentration of 10 g Cs Lactate/100g of feed. A yield of 14.8% was obtained at a feed flow rate of 0.6 ml/min and a lower yield of 8.8% was obtained at a flow rate of 1.5 ml/min. This lowering in yields at high flow rates can be explained by the lower residence time in the reactor. More feed lactic acid may be flowing out unreacted as liquid product.

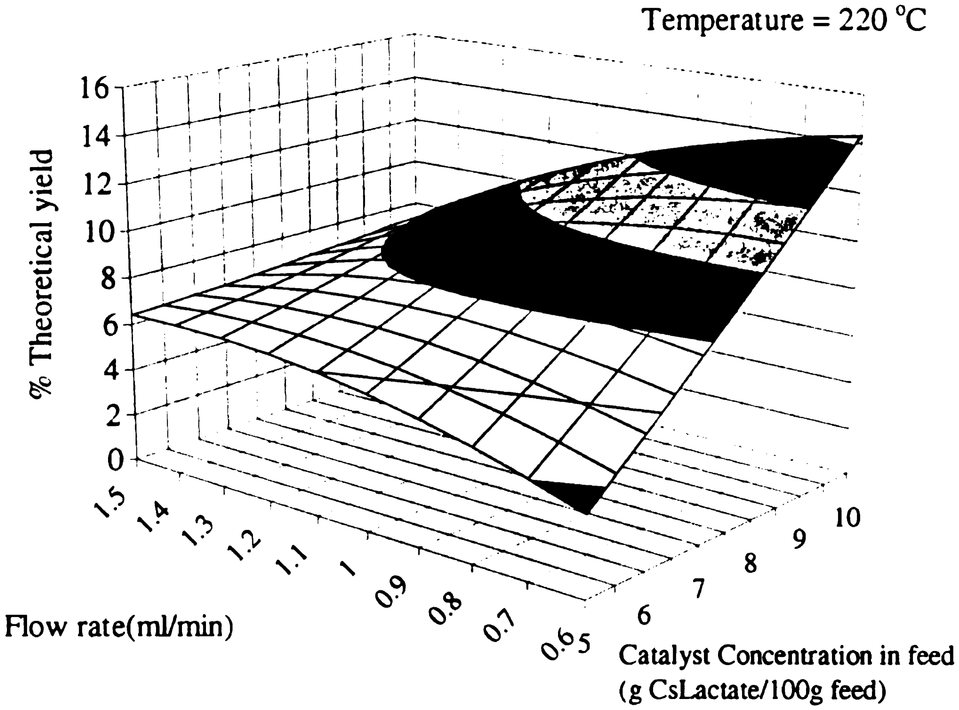


Figure 3.2: Contour Plot of 2,3-Pentanedione Yield at 220°C.

Figure 3.3 shows the variation in 2,3-pentanedione yields at a feed flow rate of 0.6 ml/min. For a given catalyst concentration, the yield increased with increase in temperature. Experiments 50C40 and 50C44 were conducted at a catalyst concentration of 7.5 g Cs Lactate/100 g of feed and a feed flow rate of 0.6 ml/min. As reaction temperature was increased from 200°C to 240°C, the yield of 2,3-pentanedione increased from 8.8% to 13.2%.

Similarly, at any temperature, the yield increased with increase in catalyst concentration in the feed. Experiments 50C38 and 50C39 were conducted at a temperature 220°C and a feed flow rate of 0.6 ml/min. Yield of 2,3-pentanedione increased from 3.4% to 14.8%, as the catalyst concentration was increased from 5 to 10 g Cs Lactate/100 g of feed.

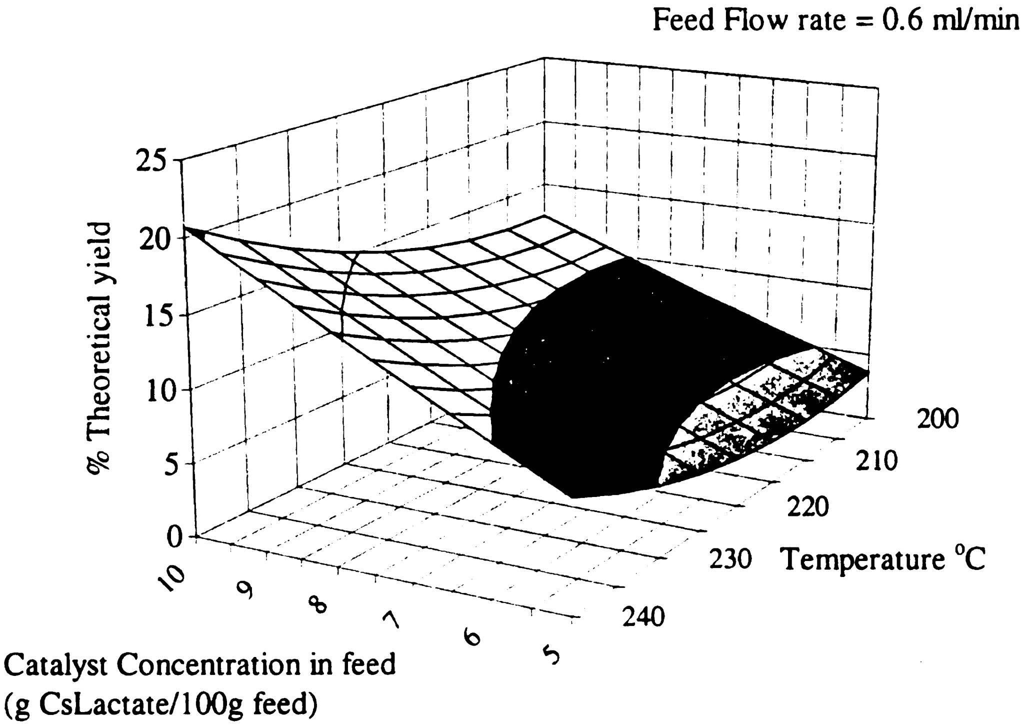


Figure 3.3: Contour Plot of 2,3-Pentanedione Yield at Flow Rate of 0.6 ml/min.

3.1.3.2 Acrylic Acid Yield

Figure 3.4 shows the contour plot of acrylic acid yield at a temperature of 240°C. The plot is in the shape of a saddle. The yield of acrylic acid increased with increase in flow rate for any given temperature and catalyst concentration. This trend continued even as the temperature was increased. Experiments 50C42 and 50C44 were conducted at a temperature of 240°C and 7.5 g Cs Lactate/100g of feed. The yield of acrylic acid increased from 5% to 12.8%, as the flow rate was increased from 0.6 ml/min to 1.5 ml/min. Clearly, the formation of acrylic acid was favored by shorter residence times.

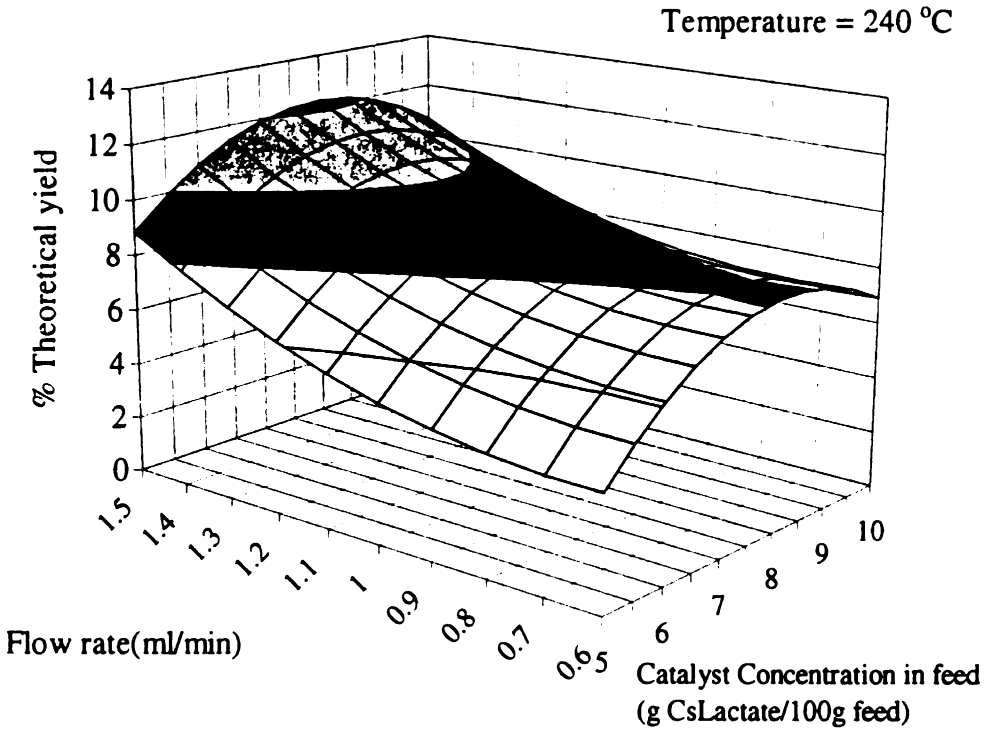


Figure 3.4: Contour Plot of Acrylic Acid Yield at 240°C.

The effect of temperature on acrylic acid yield can be seen in Figure 3.5, the contour plot for the yield of acrylic acid at a feed flow rate of 1.1 ml/min. At a given catalyst concentration, the yield of acrylic acid increased with increase in temperature. Experiments 50C37 and 50C43 were conducted at a flow rate of 1.1 ml/min and catalyst concentration of 10 g Cs Lactate/100 g of feed. The yield of acrylic acid increased from 6.1% at 200°C to 7.7% at 240°C.

A similar trend was seen at a lower catalyst concentration of 5 g cesium lactate/100g of feed. The yield for acrylic acid increased from 5.6% to 7.8% when reaction temperature was increased from 200°C (Experiment 50C49) to 240°C (Experiment 50C47).

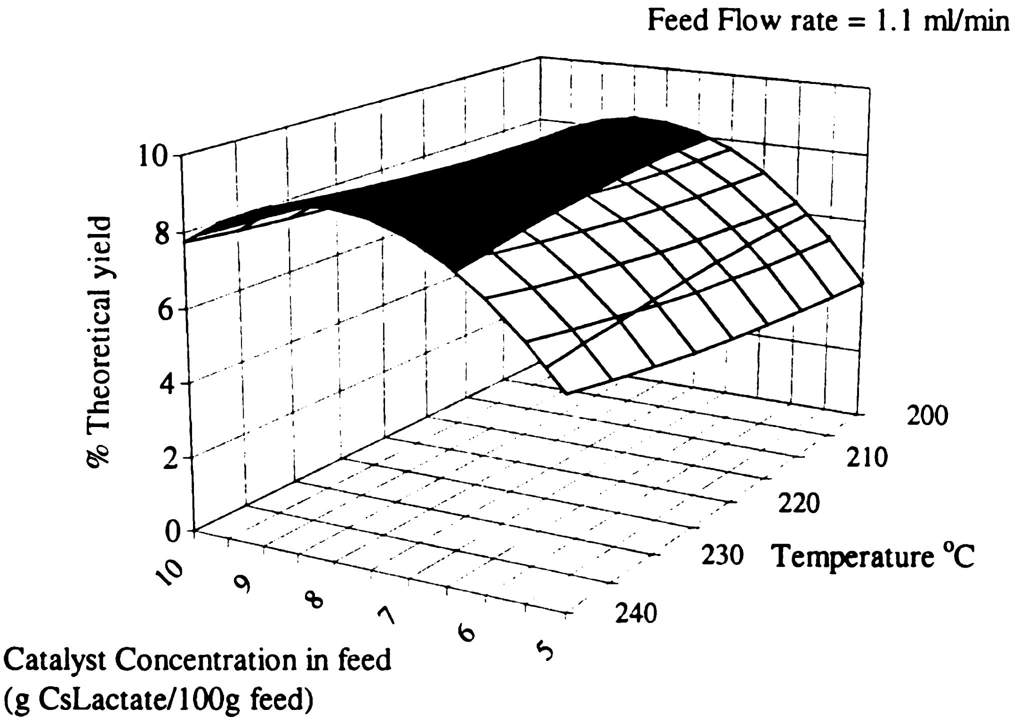


Figure 3.5: Contour plot of Acrylic Acid Yield at a Flow Fate of 1.1 ml/min.

3.1.3.3 Conversion of lactic acid

The conversion of lactic acid was computed from the fraction of lactic acid converted to condensible vapor products. No attempt was made to account for the lactic acid converted to polylactic acid by intermolecular esterification. It was assumed that the formation of oligomers of lactic acid was reversible by hydrolysis, and unreacted feed recovered as liquid product could be reprocessed.

Figure 3.6 shows the contour plot for conversion of lactic acid at a temperature of 240°C. At a given flow rate, the conversion increased as the catalyst concentration in the feed increased. Experiments 50C38 and 50C39 were conducted at 220°C and a feed flow rate of 0.6 ml/min. The conversion increased from 10.1% to 32.2% when the catalyst concentration was changed from 5 g to 10 g Cs Lactate/100 g of feed.

Figure 3.6 shows that for a given catalyst concentration, the conversion increased as flow rate was increased. Experiments 50C40 and 50C51 were conducted at 200°C and a catalyst concentration of 7.5g Cs Lactate/100 g of feed. As the flow rate was increased from 0.6 ml/min to 1.5 ml/min, the conversion increased from 17.7% to 33.4%. Similarly, experiments 50C44 and 50C42 were conducted at 240°C and a catalyst concentration of 7.5 g Cs Lactate/100 g of feed. The conversion increased from 23.5% to 36.6% as the flow rate was increased from 0.6 to 1.5 ml/min.

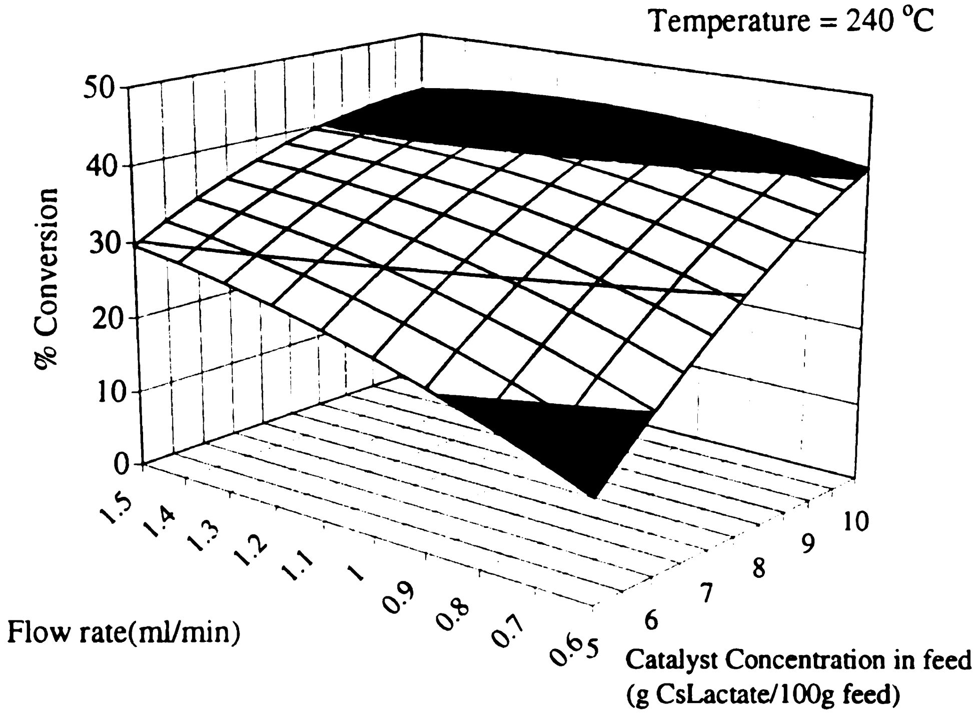


Figure 3.6: Contour plot of Lactic Acid Conversion at 240°C.

Figure 3.7 shows the contour plot for lactic acid conversion at a flow rate of 1.1 ml/min. As expected, the conversion increased with temperature. Experiments 50C37 and 50C43 were conducted at a flow rate of 1.1 ml/min and a catalyst concentration of 10 g Cs Lactate/100 g of feed. The conversion almost tripled from 16.7% to 47.2% as the reaction temperature was increased from 200°C to 240°C.

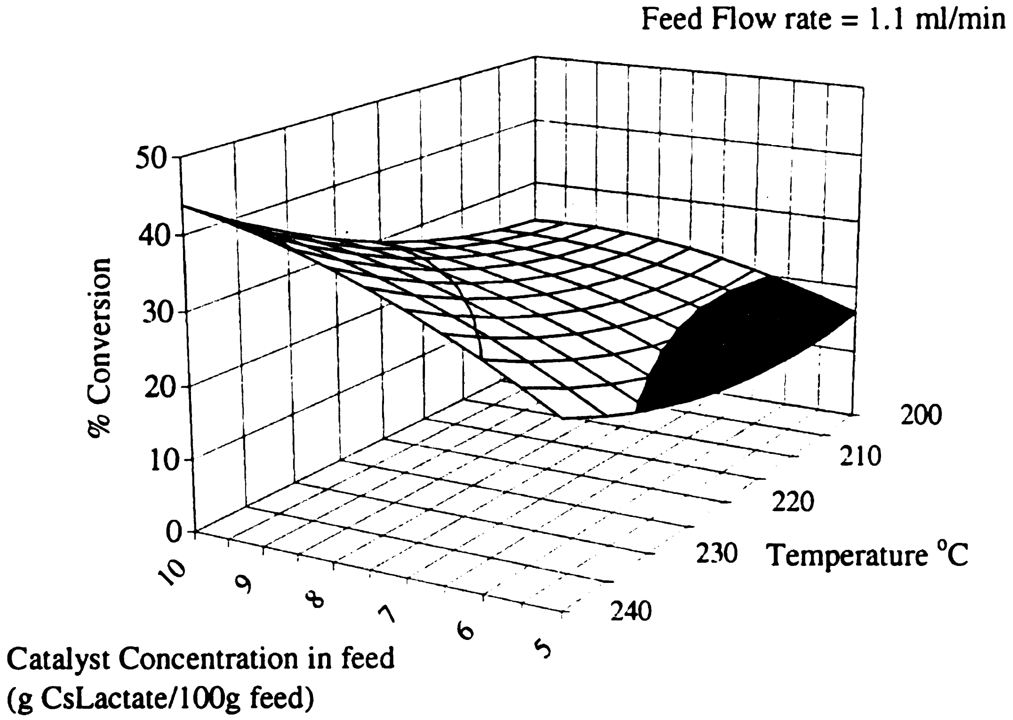


Figure 3.7: Contour Plot of Lactic Acid Conversion at a Flow Rate of 1.1 ml/min.

3.1.3.4 Selectivity

The effect of reaction conditions on the yields of 2,3-pentanedione and acrylic acid has been shown in Section 3.1.3.1 and 3.1.3.2. Figure 3.8 shows that the conversion of lactic acid is most selective to the formation of 2,3-pentanedione at high temperatures and low flow rates. The highest selectivity of 60% was obtained for Experiment 50C44. The reaction was conducted at 240°C, at a feed flow rate of 0.6 ml/min and a catalyst concentration of 7.5 g Cs Lactate/100 g of feed.

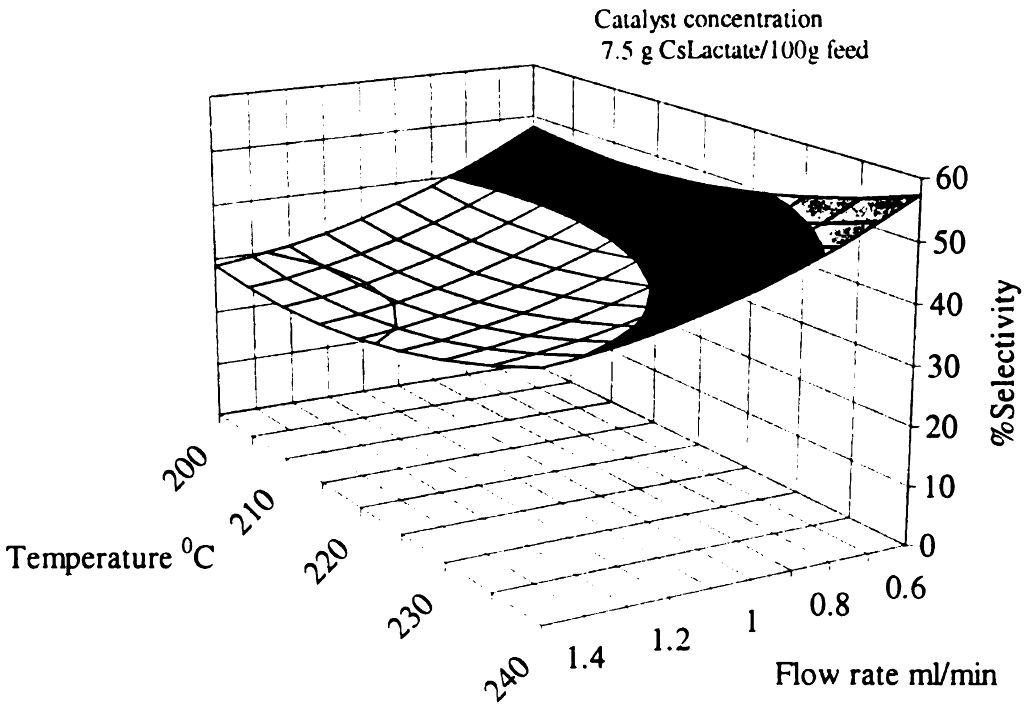
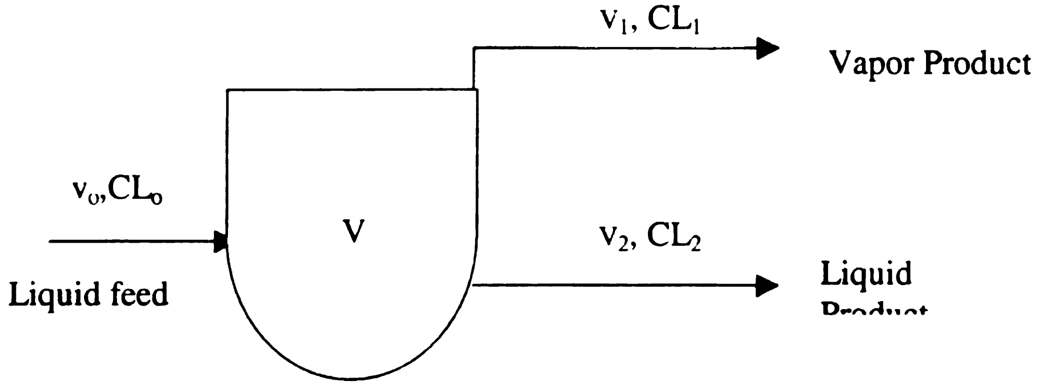


Figure 3.8: Contour Plot for Selectivity to 2,3-Pentanedione Formation at a Catalyst Concentration of 7.5g Cs Lactate/100g of feed.

3.2 Kinetic Analysis

3.2.1 Continuous Stirred Tank Reactor

The reactor was modeled as a continuous stirred tank reactor, as shown in Figure 3.9. Stream (0), liquid feed, a homogenous mixture of 50% aqueous lactic acid and cesium lactate catalyst, was fed to the reactor. The reactor was heated and well stirred. The reaction apparatus is described in Section 2.2.3. The product leaves the reactor in two streams; stream (1) consisted of the condensable vapor product including, 2,3-pentanedione, acrylic acid, propanoic acid, and acetaldehyde. Stream (2), liquid product, contained unreacted lactic acid, lactic acid oligomers, cesium lactate catalyst, and water. Product concentrations were determined by gas chromatography. It was assumed that no condensable vapor product was present in the liquid product stream. Gas chromatography on diluted samples of the liquid product has validated this assumption.



V = Volume of Reactor (lt.)
v_i = Volumetric flow rate (lt./sec)
CL_i= Concentration of Lactic Acid (mol/lt.)
CP_i= Concentration of 2,3 Pentanedione (mol/lt.)
CA_i= Concentration of Acrylic Acid (mol/lt.)
CB_i= Concentration of Acetaldehyde (mol/lt.)
CCs_i= Concentration of Cesium Lactate (mol/lt.)

i=0 Inlet
i=1 Vapor Product
i=2 Liquid Product (Overflow)

Figure 3.9: Schematic Representation of Reactor Model.

3.2.2 Reaction System

The primary reactions taking place in the reactor are listed below in Figure 3.10. Reaction 1, the thermal decomposition of lactic acid to acetaldehyde was modeled as a first order reaction. The condensation of lactic acid to 2,3-pentanedione in the presence alkali lactate was modeled as a second order reaction, with first order dependence on the concentrations of lactic acid and cesium lactate. The formation of acrylic acid from lactic acid was a first order reaction. The reaction system also included first order decomposition reactions for acrylic acid and 2,3-pentanedione. However, the results of vapor phase studies showed that the decomposition of 2,3-pentanedione was not significant at the reaction temperatures used in the condensed phase experiments (3). Therefore, the decomposition of 2,3-pentanedione was listed as a possible reaction pathway but not included in the calculations. Each reaction was assumed to be irreversible with a rate constant k_i $i = 1 - 5$.

Lactic acid → Acetaldehyde + Products ... (1)
Lactic acid + (Cesium) Lactate → 2,3-Pentanedione ... (2)
Lactic acid → Acrylic acid ... (3)
Acrylic acid → Products ... (4)
2,3-Pentanedione → Products ... (5)

Figure 3.10: Primary Reactions.

3.2.3 Method

The steady state molar balance for each species is given by the general expression-

$$\text{Moles in} = \text{Moles out} + \text{Disappearance by reaction} \qquad (3.1)$$

Using the rate equations for each reaction and molar balances, an expression for the steady state exit concentration of each species was obtained. These expressions are listed below. The flow rates of the two product streams, v_1 and v_2, were calculated by dividing the amount of product collected by total collection time.

Acetaldehyde (mol/lt), $$CB_1 = \frac{k_1 * CL_2 * V}{v_1} \qquad (3.2)$$

2,3-pentanedione (mol/lt), $$CP_1 = \frac{k_2 * CL_2 * CCs_2 * V}{v_1 + k_5 V} \qquad (3.3)$$

Acrylic acid (mol/lt), $$CA_1 = \frac{k_3 * CL_2 * V}{v_1 + k_4 V} \qquad (3.4)$$

The formation of decomposition products of acrylic acid was modeled by a first order rate expression. The concentration of acrylic acid was adjusted to represent the concentration inside the reactor, as it was assumed that the decomposition reaction took place in the condensed phase.

$$\text{Decomposition products of acrylic acid} = \frac{k_4 * CA_1 * V}{(v_1 + v_2)} \qquad (3.5)$$

The expressions for product concentration were entered into an Excel spreadsheet. Using the Solver function, the exit concentrations were calculated by simultaneously varying k_1 through k_4, minimizing the sum-of-squares residuals for conversion and species exit concentration reactions at a given temperature. The concentration residual was the difference of the concentration predicted by the model from the average steady state product concentration measured by gas chromatography. This process was repeated for the reaction data at two other temperatures.

3.2.4 Lactic Acid Concentration

The lactic acid concentration used to compute the product concentrations in the above expressions was very important to the success of the model. Since there was no way to accurately measure the lactic acid concentration inside the reactor at steady state, the reactor model was used to find the lactic acid concentration theoretically.

Figure 3.9 shows a schematic of reactor model A. This method involved using the lactic acid concentration in the liquid product for the kinetic analysis. The concentration of lactic acid was calculated by doing a water balance over the system. Knowing the amount of water in the liquid product and the density, the amount of lactic acid was calculated by difference. The concentration calculated cannot be used directly because literature suggests that lactic acid exists in equilibrium with its intermolecular esters. Moreover, an initial attempt of using the concentration of lactic acid in the liquid feed (CL_2) to predict product concentrations did not fit the experimental data. The results of this model are listed in Appendix D. It was clear that an estimate of the amount of free lactic acid in the reactor, that was available for chemical reaction, was needed.

Alén and Sjöström (42) determined the amount of lactic acid that is converted to its linear and cyclic dimer, trimer etc. upon heating. The results of their experiments are listed in Appendix B. The amount of dimer present in the solution remained constant after about 6 hours of heating. This was assumed to be the equilibrium distribution for the reversible reaction of lactic acid to its linear dimer, lactyl lactic acid. The concentration data at 100°C and 125°C was used to calculate equilibrium constants and the heat of formation of the dimer. The equilibrium constant at reaction temperature was calculated using van't Hoff's relation. Next, the amount of free lactic acid was calculated using estimates of the water and lactic acid present in the liquid product. These calculations are summarized in Table 3.7.

Table 3.7: Estimate of Free Lactic Acid in the Reactor Using Reaction Data of Alén and Sjöström (42).

Exp #	Coordinates	$Water_2$		CL_2		Free Lactic acid	
		(g/lt)	(mol/lt)	(g/lt)	(mol/lt)	(mol/lt)	% of CL_2
50C37	(-1,0,1)	357.9	19.9	930.7	10.3	8.06	78.0
50C40	(-1,-1,0)	458.9	25.5	880.0	9.7	7.99	81.8
50C49	(-1,0,-1)	510.5	28.4	812.5	9.0	7.57	83.9
50C51	(-1,1,0)	389.6	21.6	1018.0	11.3	8.81	77.9
50C38	(0,-1,-1)	279.9	15.5	1037.4	11.5	7.58	65.7
50C39	(0,-1,1)	184.8	10.3	1093.6	12.1	7.22	59.4
50C41	(0,0,0)	160.0	8.9	1161.7	12.9	7.34	56.9
50C45	(0,0,0)	1065.5	59.2	310.6	3.44	3.24	93.8
50C46	(0,1,-1)	577.9	32.1	757.7	8.41	6.75	80.2
50C48	(0,1,1)	668.7	37.1	688.9	7.64	6.36	83.2
50C50	(0,0,0)	555.6	30.9	827.1	9.18	7.22	78.6
50C42	(1,1,0)	351.4	19.5	937.1	10.40	6.57	63.2
50C43	(1,0,1)	556.2	30.9	799.2	8.87	6.43	72.5
50C44	(1,-1,0)	742.9	41.3	664.8	7.38	5.84	79.1
50C47	(1,0,-1)	770.9	42.8	593.2	6.59	5.34	81.1

Similarly, the steady state concentration of the catalyst inside the reactor was not known. However, as the catalyst concentration in the feed is known, and assuming all the catalyst entering the system at steady state leaves the reactor as liquid product, we can compute the steady state catalyst concentration in the reactor by the formula

$$CCs_2 = \frac{v_0 * CCs_0}{v_2} \tag{3.6}$$

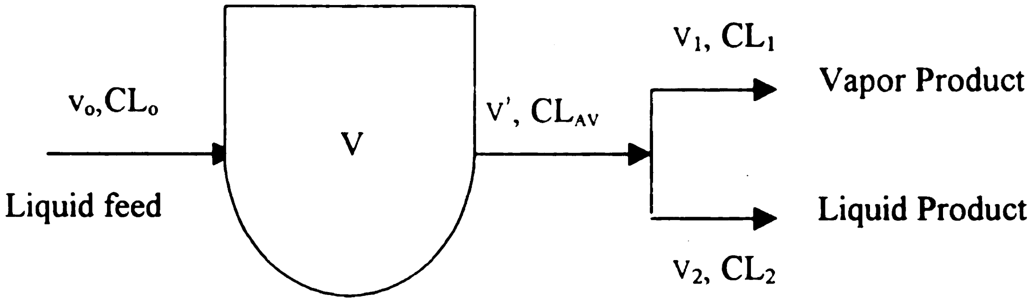


Figure 3.11: Schematic Representation of Alternate Reactor Model.

Another scheme examined is shown in Figure 3.11. At steady state, the concentration of lactic acid inside the reactor will be the same as CL_{av}. CL_{av} can be calculated from the average of the concentration of lactic acid in the two product streams. CL_1, the concentration of lactic acid in the condensed product, was obtained from gas chromatography and CL_2 is obtained from an overall component balance for lactic acid. The amount of lactic acid in the liquid product is the difference between the amount of lactic acid fed to the reactor (CL_0) and the amount of lactic acid that is converted to condensable vapor product. The lactic acid present in the vapor product, (CL_1) is also accounted for. From the component balance for lactic acid:

$$CL_2 = \frac{v_0 * CL_0 - v_1(CL_1 + 2 * CP_1 + CA_1 + CB_1)}{v_2} \tag{3.7}$$

Thus, CL_{av} can be calculated from the expression below.

$$CL_{av} = \frac{v_1 CL_1 + v_2 CL_2}{v_1 + v_2} \tag{3.8}$$

The results of this model are listed in Appendix C.

3.2.5 Results

The rate constants for reactions 1-4 obtained from the EXCEL solver routine for the kinetic analysis are listed in Table 3.8. After obtaining rate constants at three temperatures, an Arrhenius plot (ln k_i vs. 1/T) was made to determine the activation energy and preexponential factor.

Table 3.8: Rate Constants at Different Reaction Temperatures.

T(K)	473.15	493.15	513.15
k1 (sec^{-1})	1.03E-05	1.35E-05	3.88E-05
k2 (liter mol^{-1} sec^{-1})	1.65E-05	2.18E-05	3.80E-05
k3 (sec^{-1})	4.61E-05	4.84E-05	7.34E-05
k4 (sec^{-1})	2.91E-04	2.96E-04	3.43E-04

Figure 3.12 –3.15 show the Arrhenius plots for k_1, k_2, k_3, and k_4 respectively. The kinetic constants shown in Table 3.9 were calculated from the line fit of the rate constants. Slope of the line equals $-E_a/R$, where E_a is the activation energy of the reaction and R, the gas constant. The intercept of the line fit equals the natural logarithm of the preexponential factor.

Table 3.9: Kinetic Constants Calculated from Arrhenius Plots.

Reaction	Preexponential factor (k_{io})	Activation energy(J/mol)
Lactic acid $\longrightarrow$ Acetaldehyde + Products	1.83E+02 sec^{-1}	66177.4
Lactic acid + (Cs)Lactate $\longrightarrow$ 2,3-P	6.26E-01 liter mol^{-1} sec^{-1}	41620.8
Lactic acid $\longrightarrow$ Acrylic acid	3.01E-02 sec^{-1}	25616.1
Acrylic acid $\longrightarrow$ Products	6.80E-03 sec^{-1}	12310.2

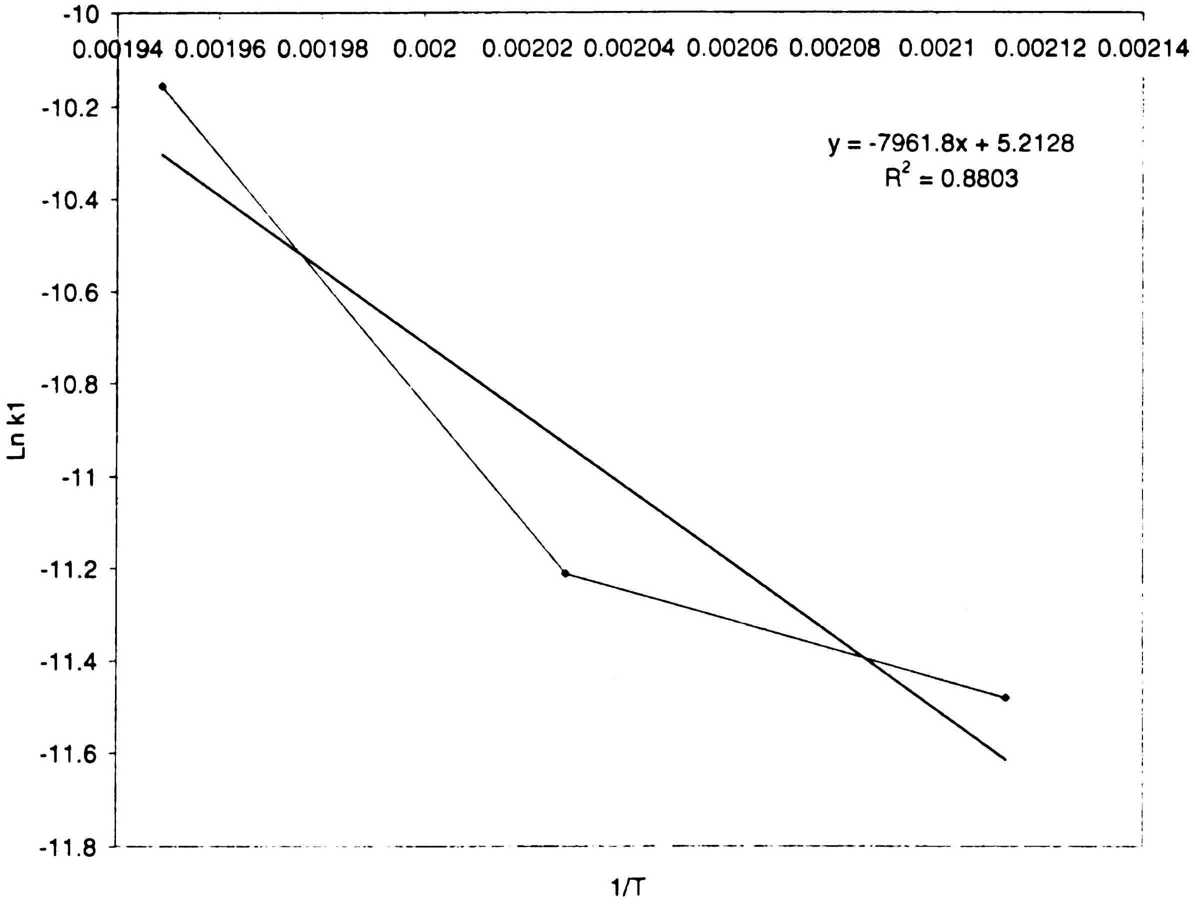


Figure 3.12: Arrhenius Plot for Reaction 1.

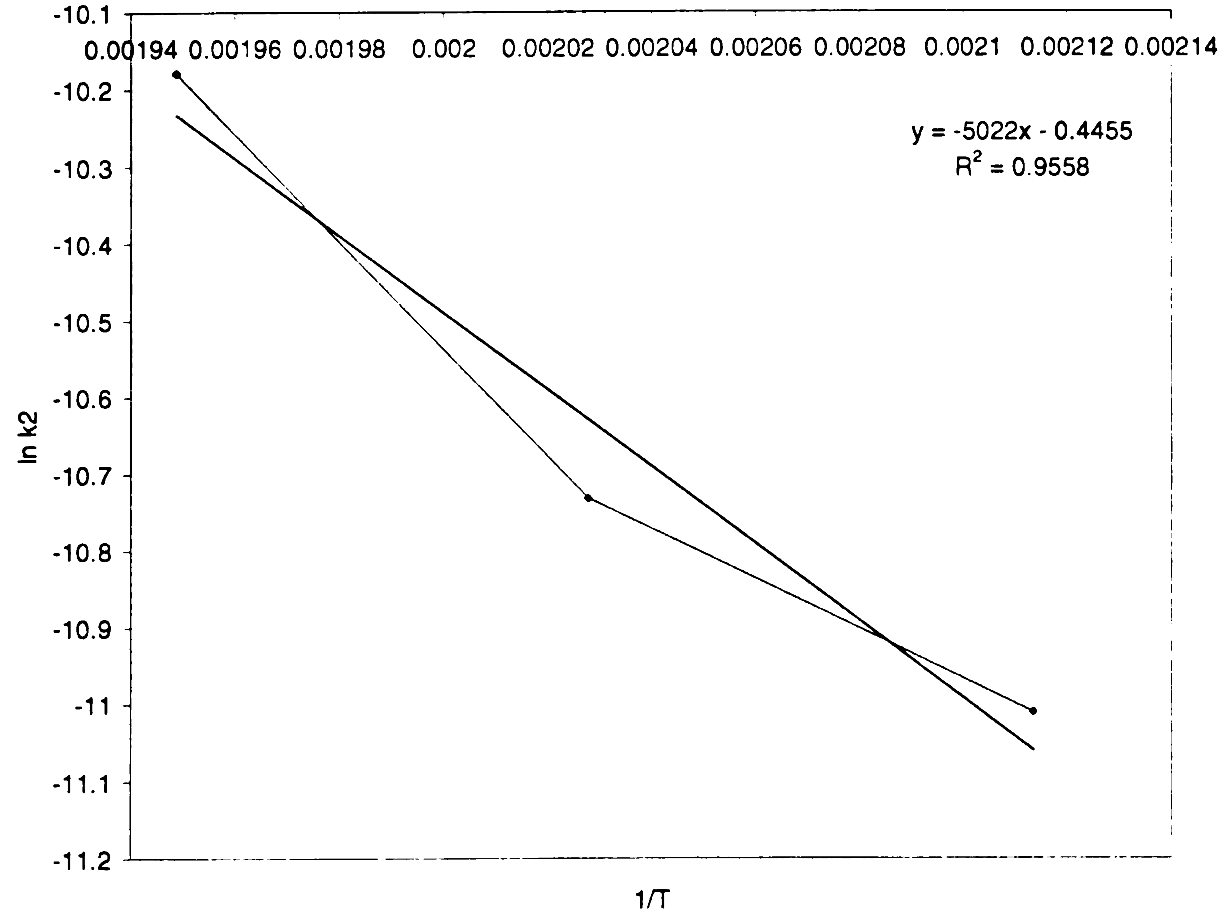


Figure 3.13: Arrhenius Plot for Reaction 2.

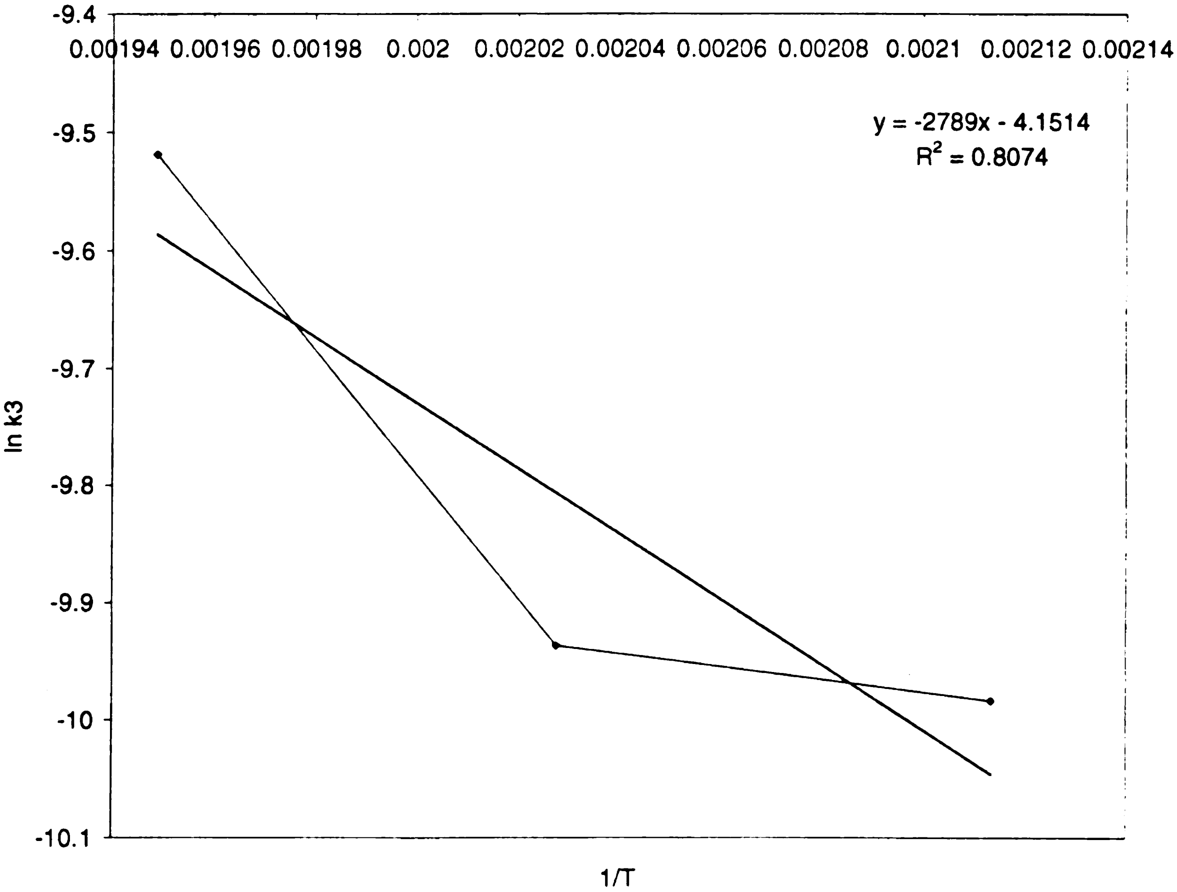


Figure 3.14: Arrhenius Plot for Reaction 3.

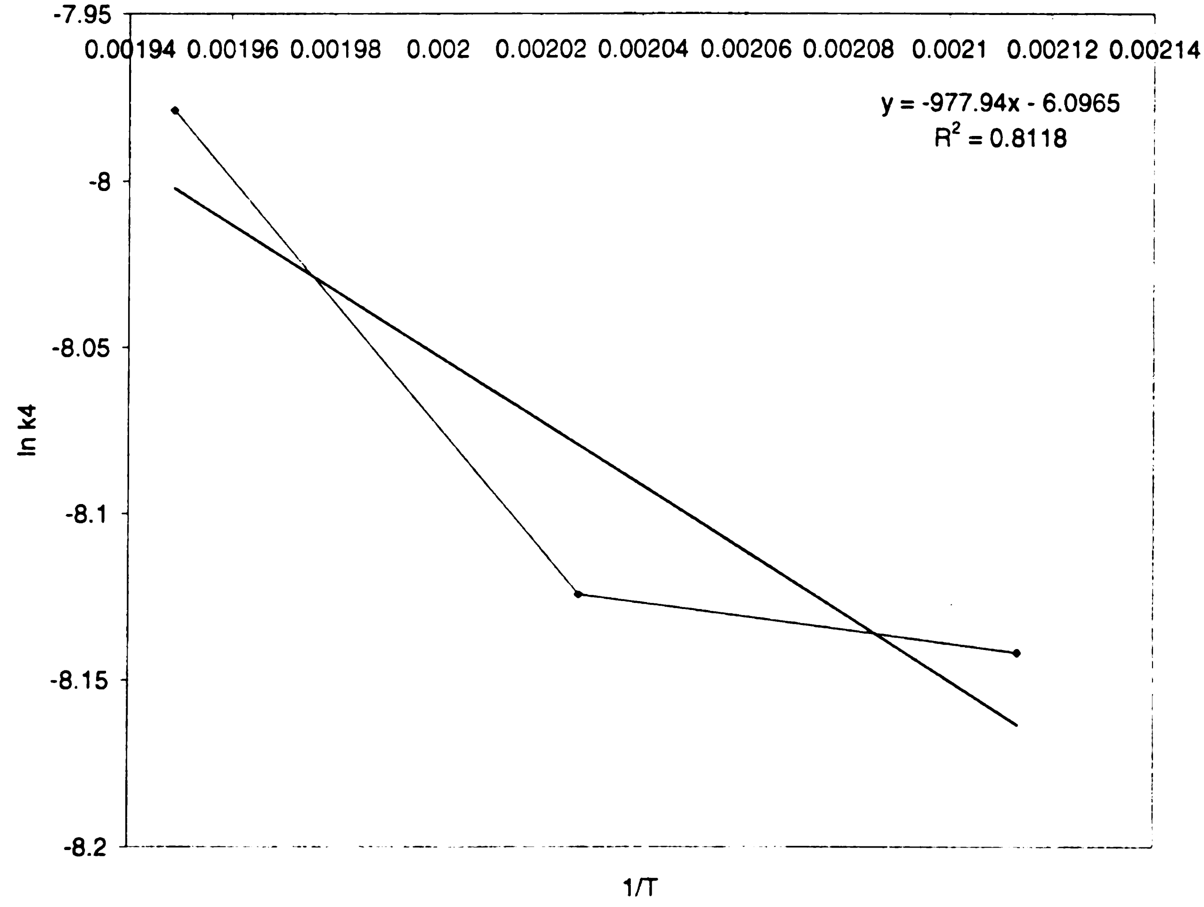


Figure 3.15: Arrhenius Plot for Reaction 4.

3.2.6 Discussion

The kinetic model proposed for the condensed phase conversion did not predict the concentration of products as accurately as hoped. The kinetic model reported was reached after trying several reaction schemes. It is not possible to discuss the results of the different possible combinations attempted. The kinetic model reported best represented the reaction data collected. The experimental data used to calculate the kinetic constants were reasonably accurate as the different balances shown in Section 2.3.5 close favorably.

Table 3.10 shows a summary of the results of the kinetic analysis. The difference in the predicted and experimental concentrations could be explained by the fact only four reactions were included in the model. Several other competing reactions may be taking place, such as the formation of coke from lactic acid, the formation of propanoic acid etc. For simplicity, the reactor was assumed to be an ideal reactor, nevertheless certain non-ideal behavior such as short-circuiting of feed was possible.

Most importantly, the concentration of lactic acid inside the reactor at reaction conditions was very difficult to measure or estimate. The extent of polymerization of lactic acid was also not known. So, various component balances and equilibrium data were used to get a reasonable estimate of the free lactic acid concentration at reaction conditions.

Table 3.10: Comparison of Predicted Product Concentration and Experimental Concentration.

		Concentrations predicted (mol/lt)			*Experimental concentrations(mol/lt)*			*Error%*		
Exp #	Coordinate	2,3P	Acrylic	Acetaldehyde	2,3P	Acrylic	Acetaldehyde	2,3P	Acrylic	Acetaldehyde
50C37	(-1,0,1)	0.247	0.542	0.202	0.247	0.561	0.342	0.0	3.4	40.9
50C40	(-1,-1,0)	0.426	0.702	0.346	0.469	0.416	0.231	9.2	68.8	49.5
50C49	(-1,0,-1)	0.243	0.504	0.187	0.244	0.476	0.215	0.6	5.9	13.3
50C51	(-1,1,0)	0.227	0.564	0.203	0.274	1.221	0.505	17.3	53.8	59.9
50C38	(0,-1,-1)	0.724	0.836	0.717	0.222	0.465	0.299	225.5	79.8	139.6
50C39	(0,-1,1)	0.663	0.770	0.626	0.726	0.696	0.473	8.7	10.7	32.5
50C41	(0,0,0)	0.379	0.603	0.364	0.357	0.713	0.635	6.4	15.3	42.6
50C45	(0,0,0)	0.338	0.249	0.143	0.330	0.327	0.193	2.3	23.8	26.0
50C46	(0,1,-1)	0.299	0.484	0.263	0.256	0.507	0.325	16.6	4.6	19.0
50C48	(0,1,1)	0.283	0.442	0.236	0.393	0.858	0.433	28.0	48.5	45.6
50C50	(0,0,0)	0.361	0.578	0.341	0.336	0.697	0.302	7.7	17.2	13.0
50C42	(1,1,0)	0.379	0.518	0.411	0.640	1.011	1.004	40.8	48.7	59.0
50C43	(1,0,1)	0.498	0.595	0.529	0.787	0.666	1.164	36.6	10.8	54.6
50C44	(1,-1,0)	0.874	0.707	0.842	0.760	0.428	0.425	15.0	65.1	98.2
50C47	(1,0,-1)	0.509	0.499	0.448	0.613	0.664	0.531	17.0	24.8	15.5
							Average error %	28.8	32.1	47.3
					[a] Average error at reaction temperatures		200°C	6.8	33.0	40.9
							220°C	11.6	20.0	29.8
							240°C	27.3	37.4	56.8

[a] Average error reported does not include concentrations predicted for experiment #50C41

The concentration of 2,3-pentanedione at low temperatures was predicted more accurately. This could be because at low temperatures the conversion of lactic acid was low and competing side reactions were at a minimum. Also, the self-polymerization of lactic acid was limited. Table 3.11 shows the results of an F-Test on the 2,3-pentanedione concentrations predicted from the kinetic model. A confidence level of 95% was used in this test. The F-Test used is part of the Data Analysis tools in Microsoft EXCEL.

Table 3.11: Results of F-Test on 2,3-Pentanedione Concentrations Predicted.

	Predicted Concentration	Experimental Concentration
Mean	0.429	0.443
Variance	0.037	0.042
Observations	15	15
df	14	14
F	0.872	
P(F<=f) one-tail	0.400	
F Critical one-tail	0.402	

The predicted concentrations of acetaldehyde and acrylic acid were comparatively more accurate at low temperatures. A higher concentration of acrylic acid was predicted for experiments conducted at low feed flow rates. It is possible that acrylic acid decomposes by a pathway not listed in the reaction system. Another possible explanation is that in these experiments the concentrations of lactic acid and cesium lactate in the reactor did not reached steady state values. Table 3.12 shows the results of the F-test for the acrylic acid concentrations predicted by the kinetic model. Again, a confidence level of 95% was used in this test.

Table 3.12: Results of F-Test on Acrylic Acid Concentrations Predicted.

	Predicted Concentration	Experimental Concentration
Mean	0.573	0.647
Variance	0.0206	0.0577
Observations	15	15
df	14	14
F	0.357	
P(F<=f) one-tail	0.032	
F Critical one-tail	0.402	

The kinetic model predicted higher acetaldehyde concentrations for experiments conducted at low flow rates. Table 3.13 shows the result of the F-Test on concentrations predicted from the kinetic model.

Table 3.13: Results of F-Test on Acetaldehyde Concentrations Predicted.

	Predicted Concentration	Experimental Concentration
Mean	0.390	0.471
Variance	0.0434	0.0782
Observations	15	15
df	14	14
F	0.554	
P(F<=f) one-tail	0.141	
F Critical one-tail	0.402	

CHAPTER 4

SUMMARY AND RECOMMENDATIONS

4.1 Summary

This work has shown that the condensed phase conversion of lactic acid, in the presence of alkali lactate catalyst, can be conducted in a continuous reactor to yield 2,3-pentanedione, acrylic acid, acetaldehyde and propanoic acid. The reactive nature of lactic acid, especially its ability to form intramolecular esters and oligomers, makes the design and operation of a continuous reactor challenging. By operating the reactor at steady state, it is possible to maintain conditions in the reactor favorable to the formation of a single product for a longer period of time. To run the reactor in a continuous mode, it is necessary to continuously remove liquid product from the reactor using an overflow tube. Further, high feed flow rates and feed concentrations are required to establish steady state in the reactor. The reactor was operated at a steady state temperature of 220°C, feed flow rate of 1.1 ml/min, and catalyst concentration of 7.5 g cesium lactate/100g of 50 % aqueous lactic acid feed for over 24 hours, proving the stability of the catalyst and the reaction system.

The performance of the reactor depends mainly on three parameters, reaction temperature, feed flow rate, and catalyst concentration. The highest 2,3-pentanedione yield of 19% was obtained at a temperature of 240°C. The reaction was most selective to the formation of 2,3-pentanedione at low feed flow rates. Increase in feed catalyst

concentration increases the yield of 2,3-pentanedione. The formation of acrylic acid is favored at high feed flow rates. The highest yield of acrylic acid obtained was 15 %.

The kinetic model developed predicted the concentrations of product accurately only at low temperatures and high feed flow rates. The increase in percentage error for higher reaction temperature suggests that reaction pathways not included in the model may be occurring. The accuracy of the kinetic model can be increased if a precise estimate of free lactic acid concentration in the reactor is available.

4.2 Recommendations

The optimization of 2,3-pentanedione formation from lactic acid in the condensed phase is mostly complete. Cesium lactate is the best catalyst for this reaction. A greater yield of 2,3-pentanedione is possible by choosing a higher feed catalyst concentration than that selected as maxima for the optimization study. The reaction temperature for continuous operation should be around 240°C, higher temperature will lead to excessive formation of char and oligomers in the reactor.

Further work needs to be done to investigate the possibility of converting byproduct acrylic acid to propanoic acid. This reaction can be either done after the products are condensed or by possibly hydrogenating acrylic acid as it is formed in the reactor. The recycle of liquid product, which contains lactic acid and cesium lactate catalyst, to the reactor after dilution and hydrolysis is another option to increase the yield of the reaction.

APPENDICES

Appendix A

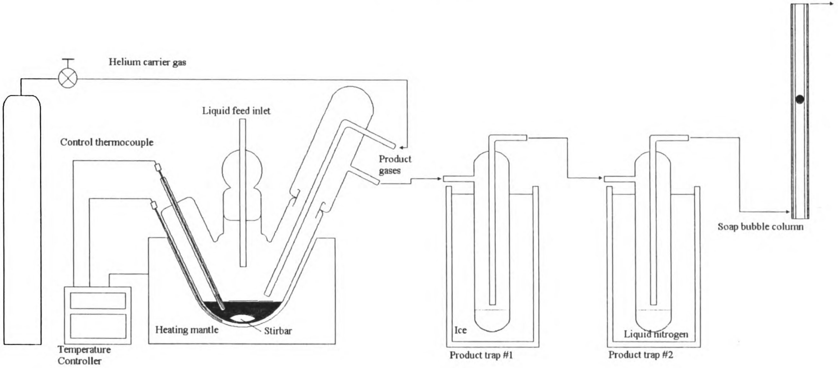


Figure A1: Reaction Apparatus for Semi-Continuous Conversion of Lactic Acid.

Appendix B

Table B1: Conversion of Lactic Acid on Heating [a] (42).

Time/hr.	Lactic Acid	Dimer	Lactide	Lactide	Trimer
100°C					
1	85.5	14.5	-	-	-
2	78.4	20.9	-	-	-
4	72.3	27.2	-	-	+
6	66.5	30.2	+	+	2.4
125°C					
1	74.6	24.4	-	-	-
2	67.4	31.1	+	+	0.7
4	55.1	36.1	0.7	1.5	6.2
6	49.8	36.7	1.3	2.6	8.9

[a] Figures are given as % of the total observed.

Appendix C

Table C1: Comparison of Predicted Product Concentration and Experimental Concentration for Kinetic Model B.

		Concentrations predicted (mol/lt)			*Experimental concentrations(mol/lt)*			*Error%*		
Exp #	Coordinate	2,3P	Acrylic	Acetaldehyde	2,3P	Acrylic	Acetaldehyde	2,3P	Acrylic	Acetaldehyde
50C37	(-1,0,1)	0.257	0.539	0.206	0.247	0.561	0.342	4.1	3.9	39.7
50C40	(-1,-1,0)	0.443	0.672	0.338	0.469	0.416	0.231	5.6	61.7	46.0
50C49	(-1,0,-1)	0.252	0.549	0.208	0.244	0.476	0.215	3.4	15.3	3.3
50C51	(-1,1,0)	0.236	0.448	0.165	0.274	1.220	0.505	14.0	63.3	67.3
50C38	(0,-1,-1)	0.803	0.912	0.748	0.222	0.465	0.299	261.3	96.1	150.2
50C39	(0,-1,1)	0.736	0.631	0.491	0.726	0.696	0.473	1.4	9.4	3.9
50C41	(0,0,0)	0.421	0.558	0.324	0.357	0.713	0.635	18.1	21.7	49.0
50C45	(0,0,0)	0.375	0.608	0.334	0.330	0.327	0.193	13.6	85.7	73.3
50C46	(0,1,-1)	0.331	0.561	0.2934	0.256	0.507	0.325	29.4	10.6	9.7
50C48	(0,1,1)	0.314	0.463	0.237	0.393	0.858	0.433	20.0	46.0	45.3
50C50	(0,0,0)	0.401	0.589	0.334	0.336	0.697	0.302	19.5	15.4	10.9
50C42	(1,1,0)	0.447	0.341	0.245	0.640	1.011	1.004	30.2	66.3	75.6
50C43	(1,0,1)	0.587	0.387	0.312	0.787	0.666	1.164	25.4	41.8	73.2
50C44	(1,-1,0)	1.030	0.742	0.799	0.760	0.428	0.425	35.5	73.3	88.1
50C47	(1,0,-1)	0.599	0.540	0.439	0.613	0.664	0.531	2.2	18.7	17.2
							Average error %	32.2	42.0	50.2
							[a]Average error at reaction temperatures 200°C	6.7	36.0	39.1
							220°C	17.0	31.5	32.0
							240°C	23.3	50.0	63.5

[a] Average error reported does not include concentrations predicted for experiment #50C38

- This model used the average concentration of lactic acid in the two product streams to predict the concentrations of product.
- The prediction of reaction data comparable to the results of the kinetic analysis reported in section 3.2.

Table C2: Kinetic constants calculated for Kinetic Model B

Reaction	Preexponential factor (k_{io})	Activation energy(J/mol)
Lactic acid $\longrightarrow$ Acetaldehyde + Products	3.76E+01 sec^{-1}	57601.7
Lactic acid + (Cs)Lactate $\longrightarrow$ 2,3-P	5.63 liter $mol^{-1}sec^{-1}$	47872.5
Lactic acid $\longrightarrow$ Acrylic acid	4.90 E-02 sec^{-1}	25396.9
Acrylic acid $\longrightarrow$ Products	1.61 E-02 sec^{-1}	15879.1

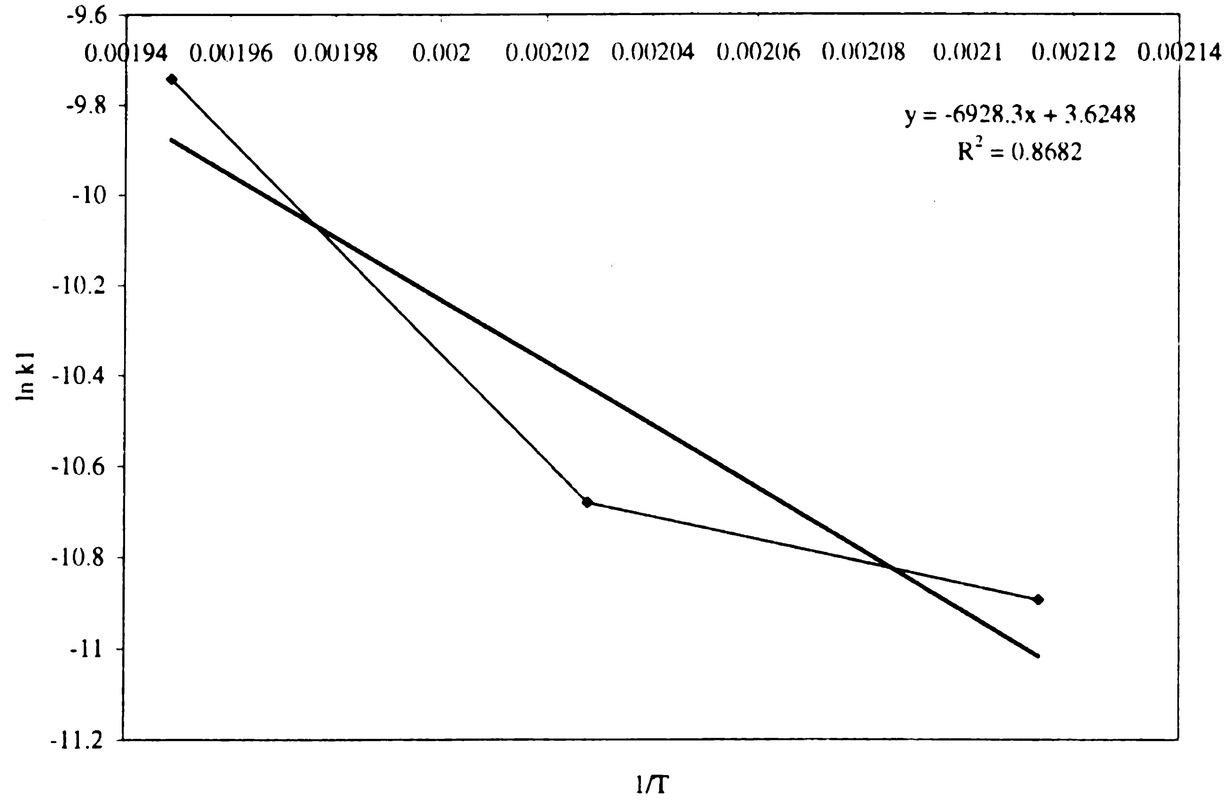


Figure C1: Arrhenius Plot for Reaction 1 (Kinetic Model B)

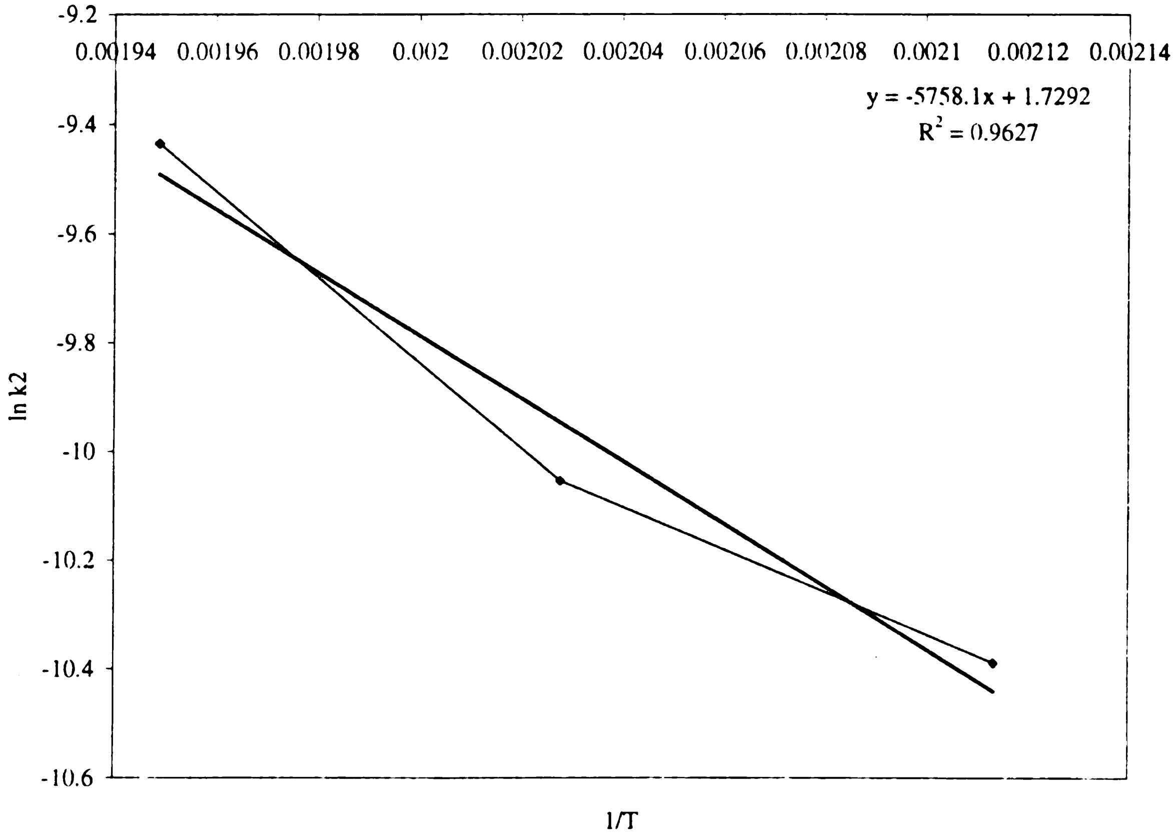


Figure C2: Arrhenius Plot for Reaction 2 (Kinetic Model B)

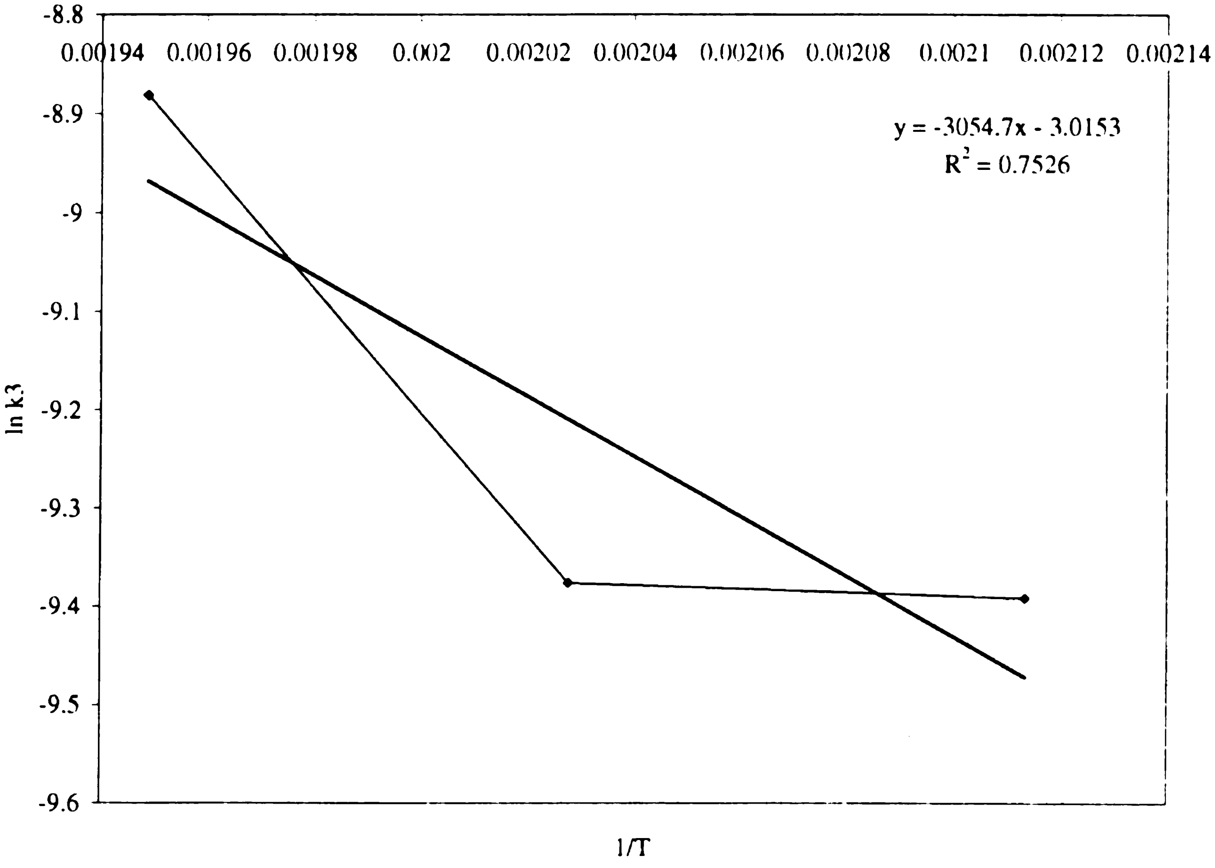


Figure C3: Arrhenius Plot for Reaction 3 (Kinetic Model B)

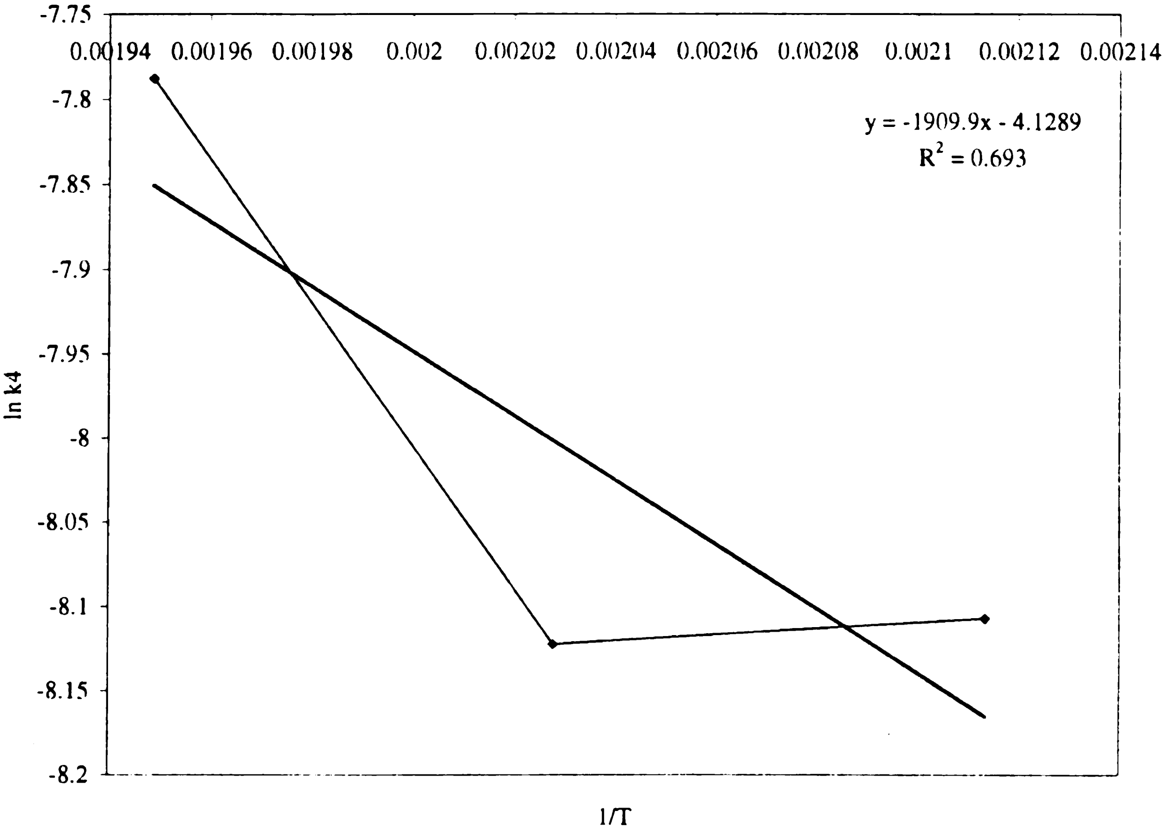


Figure C4: Arrhenius Plot for Reaction 4 (Kinetic Model B)

Appendix D

Table D1: Comparison of Predicted Product Concentration and Experimental Concentration for Kinetic Model C.

		Concentrations predicted (mol/lt)			*Experimental concentrations(mol/lt)*			*Error%*		
Exp #	Coordinate	2,3P	Acrylic	Acetaldehyde	2,3P	Acrylic	Acetaldehyde	2,3P	Acrylic	Acetaldehyde
50C37	(-1,0,1)	0.237	0.530	0.197	0.247	0.561	0.342	4.0	5.6	42.4
50C40	(-1,-1,0)	0.409	0.656	0.322	0.469	0.416	0.231	12.9	57.8	39.0
50C49	(-1,0,-1)	0.233	0.458	0.169	0.244	0.476	0.215	4.7	3.8	21.4
50C51	(-1,1,0)	0.217	0.552	0.197	0.274	1.221	0.505	20.7	54.8	60.8
50C38	(0,-1,-1)	0.653	0.942	0.809	0.222	0.465	0.299	193.9	102.4	170.6
50C39	(0,-1,1)	0.599	0.959	0.782	0.726	0.696	0.473	17.6	37.8	65.6
50C41	(0,0,0)	0.343	0.781	0.475	0.357	0.713	0.635	4.0	9.6	25.1
50C45	(0,0,0)	0.305	0.196	0.113	0.330	0.327	0.193	7.6	40.2	41.4
50C46	(0,1,-1)	0.270	0.444	0.244	0.256	0.507	0.325	5.2	12.5	24.9
50C48	(0,1,1)	0.255	0.391	0.210	0.393	0.858	0.433	35.0	54.4	51.4
50C50	(0,0,0)	0.326	0.541	0.322	0.336	0.697	0.302	2.8	22.4	6.9
50C42	(1,1,0)	0.324	0.583	0.473	0.640	1.010	1.004	49.5	42.3	52.9
50C43	(1,0,1)	0.425	0.585	0.530	0.787	0.666	1.164	45.9	12.2	54.4
50C44	(1,-1,0)	0.746	0.641	0.774	0.760	0.428	0.425	1.9	49.7	82.1
50C47	(1,0,-1)	0.434	0.439	0.402	0.613	0.664	0.531	29.1	33.9	24.2
							Average error %	28.9	36.5	50.8
					[a]Average error at reaction temperatures		200°C	10.6	30.5	40.9
							220°C	12.0	29.5	35.9
							240°C	31.6	34.5	53.4

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[a] Average error reported does not include concentrations predicted for experiment #50C38

- This model used the concentration of lactic acid in the liquid product stream to predict the concentrations of product.
- The Arrhenius plots not as accurate.

Table D2: Kinetic constants calculated for Kinetic Model C

Reaction	Preexponential factor (k_{io})	Activation energy(J/mol)
Lactic acid $\longrightarrow$ Acetaldehyde + Products	8.04E+01 sec^{-1}	64053.65
Lactic acid + (Cs)Lactate $\longrightarrow$ 2,3-P	0.109 liter $mol^{-1}sec^{-1}$	35941.14
Lactic acid $\longrightarrow$ Acrylic acid	4.79 E-03 sec^{-1}	19357.47
Acrylic acid $\longrightarrow$ Products	1.53 E-03 sec^{-1}	6674.889

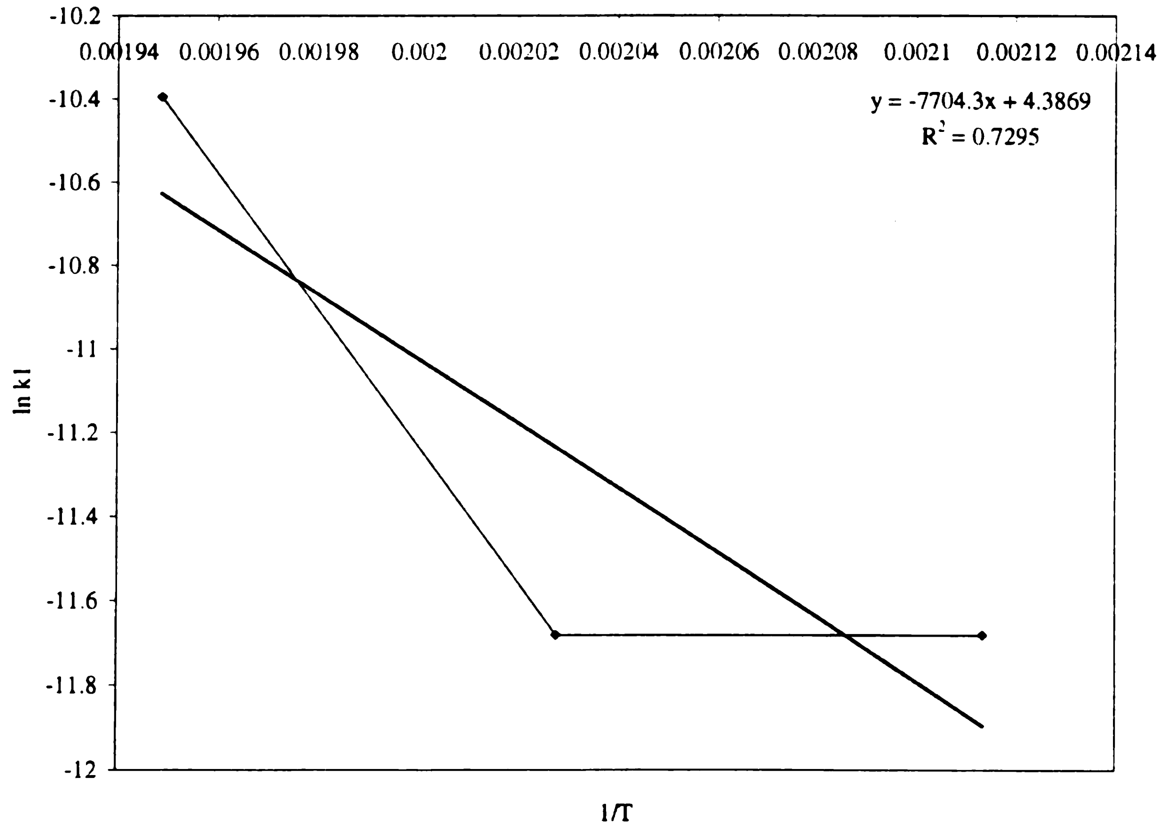

Figure D1: Arrhenius Plot for Reaction 1 (Kinetic Model C)

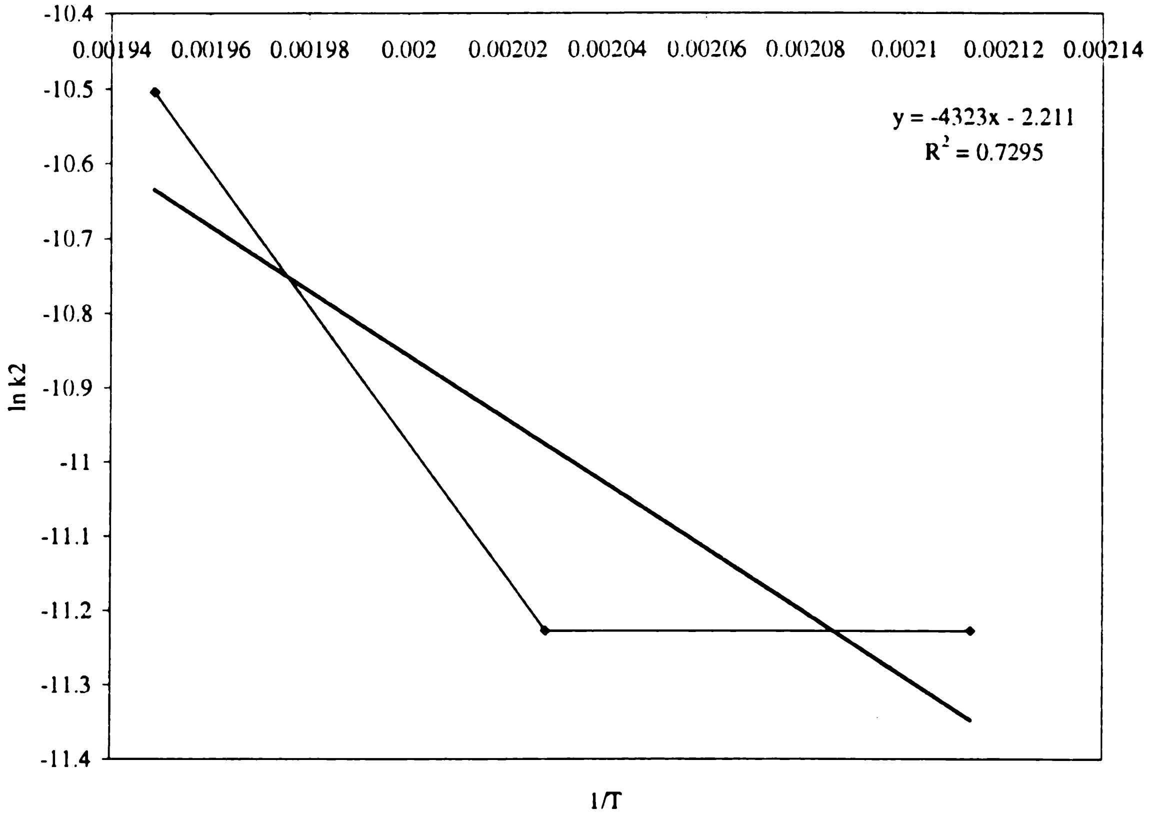

Figure D2: Arrhenius Plot for Reaction 2 (Kinetic Model C)

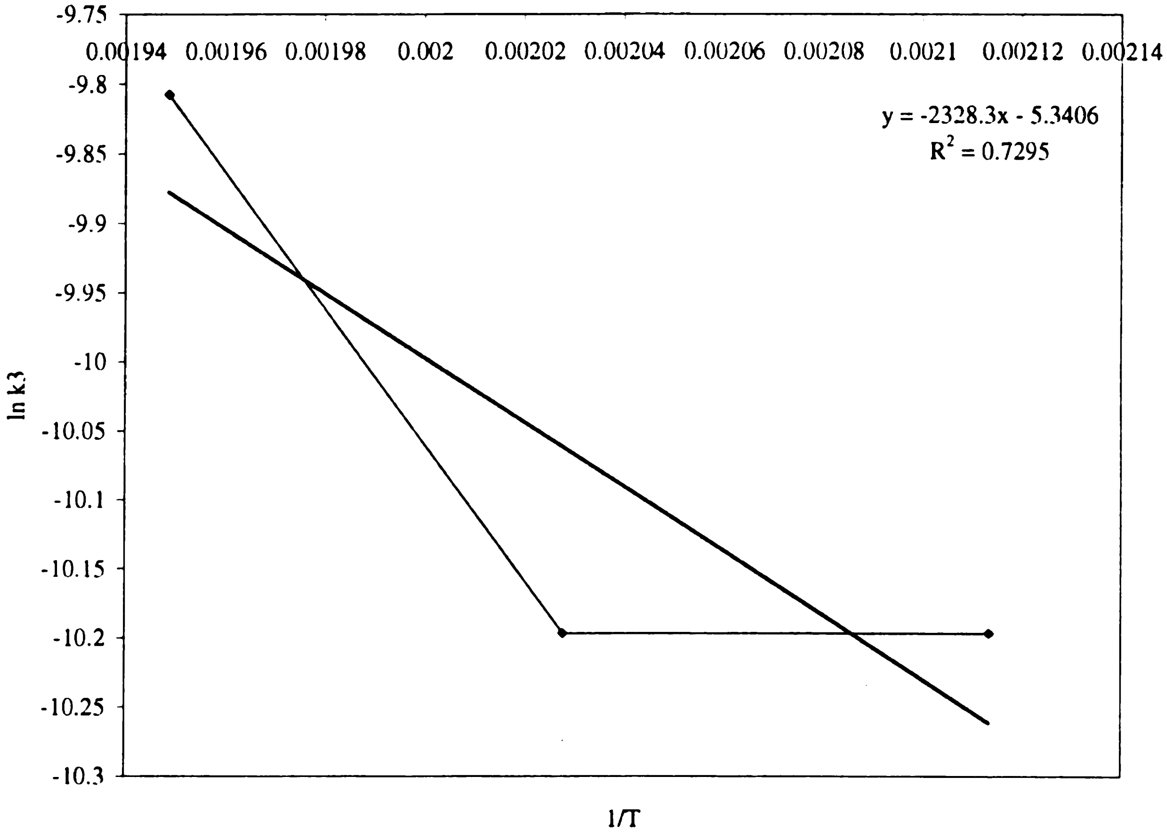

Figure D3: Arrhenius Plot for Reaction 3 (Kinetic Model C)

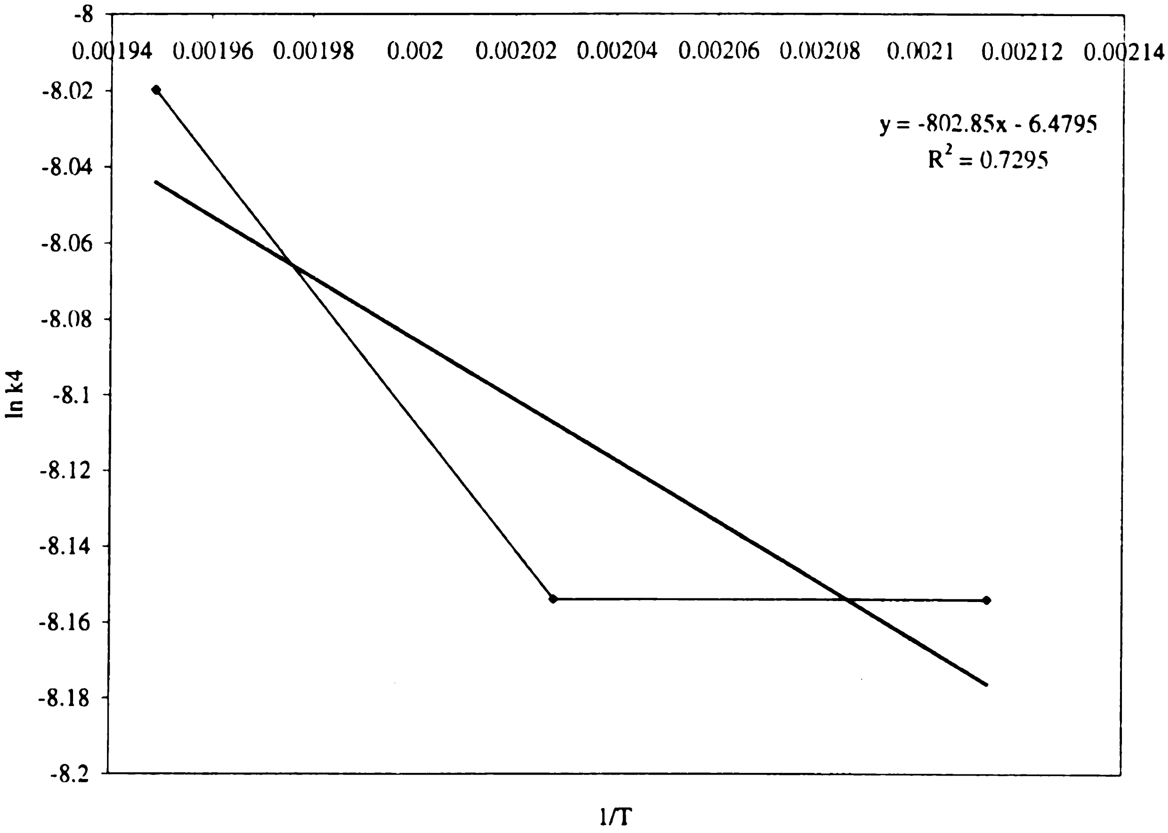

Figure D4: Arrhenius Plot for Reaction 4 (Kinetic Model C)

1.
S

2.
U

3. T
2

4.
1

5. P

6. C

7. H
L

8.
6

9. S

10. D

11. Y

12. L

13. K

14. C
C
S

15. B

16. D

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17. E

18. F

19. F

20. H

21. M

22. C

23. L

24. L

25. B
18

26. Er

27. Ip

28. Gu

29. Mc

30. Fu
CR

31. An

32. Th

33. Ta

34. Ma
63

35. Hs

36. Mc

37. Gu
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