KINETICS OF METHYL LACTATE FORMATION OVER THE ION
EXCHANGE RESIN CATALYSTS

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ABSTRACT

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The recovery of lactic acid from its dilute aqueous solutions is a major problem. The ester of lactic acid, namely, methyl lactate has a wide range of applications. The esterification of an aqueous solution of lactic acid with methanol is a reversible reaction. As excess of amount water is present in the reaction mixture, the conversion is greatly restricted by the chemical reaction equilibrium limitations.

In this study the esterification kinetics of lactic acid with methanol both in the absence and presence of an ion exchange resin as a heterogeneous acid catalyst

was investigated with isothermal batch experiments between 40 - 70 ^{0} C and at atmospheric pressure. Self-polymerization of lactic acid was enlightened by considering the hydrolysis reaction of lactoyllactic acid at the reaction temperatures and at various initial concentrations. Both homogeneous and heterogeneous reaction rate constants were evaluated.

Methyl lactate process development was also investigated. The process was based on the recovery of 10% lactic acid by reaction with methanol in a absorption column using ion-exchange resin Lewatit SPC-112 H$^+$.

The effect of various parameters including lactic acid concentration or reactant molar ratio, lactic acid feed flow rate, methanol and inert carrier rate on reactor performance were studied. The reaction of methyl lactate formation over the ion exchange resin catalyst was observed to be slower than the mass transfer rate whereas mass transfer of methanol in gas phase was the limiting step for methanol transfer to the liquid mixture. Mass transfer of water from liquid phase to the gas phase was controlled by the mass transfer resistance of liquid phase. Thus, it can be concluded that the counter-current gas-liquid reactors with acidic solid catalysts can be used as simultaneous reaction and separation equipment.

ÖZ

İYON DEĞİŞTİRİCİ REÇİNE KATALİZÖR ÜZERİNDE METİL LAKTAT OLUŞUMUNUN KİNETİK İNCELENMESİ

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Laktik asitin seyreltik sulu çözeltilerinden geri kazanımı önemli bir sorundur. Laktik asitin metil laktat adı verilen esterinin çok geniş bir uygulama alanı vardır. Laktik asit içeren sulu çözeltinin metanol ile esterifikasyonu tersinir bir reaksiyondur. Reaksiyon karışımındaki su fazlalığından dolayı dönüşüm denge limitleriyle kısıtlanmaktadır. Bu sebepten dolayı etkin ve ucuz metil laktat üretimi suyun ve metil laktatın reaksiyon ortamından uzaklaştırılmasını gerektirir.

Laktik asitin metanol ile esterifikasyonu, heterojen asit katalist olarak kullanılan iyon değiştiricili reçineli ya da reçinesiz olarak 40 - 70 ^{0}C sıcaklık aralığında ve atmosferik basıç altında izotermal kesikli reaktör deneyleriyle çalışılmıştır. Laktik asitin kendi kendine polimerleşmesi, laktollaktik asit hidroliz reaksiyonunun değişik başlangıç konsantrasyonlarını içeren reaksiyon sıcaklıklarında araştırılmasıyla açıklığa kavuşturulmuştur. Homojen ve heterojen reaksiyon hız sabitleri hesaplanmıştır.

Metil laktat prosesinin gelişimi incelenmiştir. Proses, iyon değiştirici reçine olan Lewatit SPC-112-H$^+$ kullanılarak absorpsiyon kolonunda metanol ile reaksiyona giren %10 luk laktik asitin geri kazanımına dayanır.

Laktik asit konsantrasyonu, laktik asit beslemesi akış hızı, metanol ve inert taşıyıcı hızı gibi çeşitli parametrelerin reaktör performansındaki etkisi incelenmiştir. İyon değiştirici reçine katalistinin üzerinde, metil laktat oluşum reaksiyonunun, kütlesel transfer hızından daha yavaş olduğu; buna karşılık, metanolün sıvı karışıma transferinde kısıtlayıcı adımın metanolün gaz fazındaki kütlesel transferinin olduğu ve suyun sıvı fazından gaz fazına kütlesel transferinin, sıvı fazındaki kütlesel transfer direnci ile kontrol edildiği bulunmuştur. Sonuç olarak asidik katı katalistler içeren ters akış gaz- sıvı reaktörlerin aynı anda reaksiyon ve ayırma ekipmanı olarak kullanılabileceği söylenebilir.

Anahtar Sözcükler: Esterifikasyon; Laktik Asit; Metil Laktat; İyon Değiştirici Reçineler, Absorpsiyon; Kütle Transferi.

To my beloved Family…

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

NOMENCLATURE

C_I : Species concentration, mol/lt

D_A : Liquid phase diffusion coefficient of the solute in the solvent

GC : Gas chromatography

k_g : Gas phase mass transfer resistance, m/s

k_l : Liquid phase mass transfer resistance, m/s

k_1 : Overall forward reaction rate constant of reaction I, l/mol.min

k_2 : Overall backward reaction rate constant of reaction I, l/mol.min

k_3 : Overall forward reaction rate constant of reaction II, l/mol.min

k_4 : Overall backward reaction rate constant of reaction II, l/mol.min

K_{eq} : Equilibrium constant, dimensionless

L_1 : Liquid product flow rate; g/min , gmol/min

L_2 : Liquid feed flow rate; g/min , gmol/min

m : High reactant solubility

MW_i : Molecular Weight species, g/mol

N : Normality of solution , eq/lt

N_A : Mass Transfer Flux, moles/m^2.min

N_I : Species mole

n.b.p : Normal boiling point

R : Ideal gas constant, 1.987 cal / mol.K

R.F : Relative Response Factor

SPC : Strong cationic, macroporous

T : Temperature, Kelvins / ^{0} C

V : Volume, ml/lt

V_1 : Vapor feed flow rate, g/min, gmol/min

V_2 : Vapor product flow rate, g/min, gmol/min

W : Gram species, gr

x : Conversion, dimensionless

y : Species gas phase mole fraction

y_i : Species interface mole fraction

$\Delta H^0 rxn$: Heat of reaction, cal /mole

δ_i : Distance from interface, m

ϕ : Reaction enhancement factor

CHAPTER 1

INTRODUCTION

Organic esters are very important class of chemicals having applications in variety of areas such as perfumery, flavors, pharmaceuticals, plasticizers, solvents and intermediates. Obviously different approaches have been employed on both laboratory and commercial scales to prepare esters, and the traditional homogeneous catalyzed reactions are being less favored owing to the attendant problems of separation and reuse (1).

Lactic Acid is the simplest hydroxycarboxylic acid with an asymmetric carbon atom. It can be produced from biomass, coal, petroleum, or natural gas liquids. Polymers and copolymers of lactic acid are known to be environmentally compatible because of their degradability into harmless products, which makes them desirable as substitutes of petrochemical polymers. Some of the applications of these

polymers include manufacturing prosthetic devices, pesticide formulation, plastic production etc. For their production highly purified monomeric lactic acid is needed (2).

Esterification is a well understood and extensively used reaction, especially in the pharmaceutical, perfumery and flavor industries. The most common method of making ester is to react the corresponding acid with an alcohol.

Esterification of lactic acid with alcohols can be performed in a number of different ways; the choice of experimental conditions depends on the alcohol to be esterified (3). When equal amounts of acid and alcohol are brought into contact complete conversion never takes place in the process of esterification reaction (4). The reaction proceeds until a state of equilibrium is established. Then at constant temperature the maximum conversion is limited by the equilibrium conversion. Several methods are available to drive the reaction towards the desired product. One of them is to use an excess amount of alcohol while the other technique to remove the ester formed or the co-product water continuously (5).

There are several ways of removing the products such as adsorption, extraction, distillation and membrane separation. Pervaporation process is potentially useful when distillation is difficult to apply, such as, in the case of close-boiling components, isomeric mixtures or alcohol solutions and fractionation of azeotropic mixtures. In this respect, the use of membrane reactor for separation of a reaction product, especially for esterification type reversible reactions, seems to be an attractive method to increase the conversion by shifting the equilibrium. In adsorption and extraction processes, a third component is needed for separation, introducing additional complexity to the process.

An alternative purification process for lactic acid aqueous solutions is to obtain some of its esters, much more volatile than lactic acid itself, and, once purified, hydrolyze them back into lactic acid. Such processes may be carried out by catalytic distillation.

Catalytic distillation offers some advantages over conventional processes where reaction and purification are carried out separately. Some of them are the reduction of capital and operating costs, high selectivity, reduced energy uses, and reduction or elimination of solvents (6). Its major disadvantage is that chemical reaction has to exhibit significant conversion at distillation temperature (7).

Boiling of lactic acid with excess alcohol under reflux has been used to produce many esters; the reaction is generally catalyzed by acids, such as anhydrous hydrogen chloride, sulphuric acid and many other catalysts (3).

In the conventional industrial processes involving homogeneous acids, utilization of cation exchange resin catalysts for low temperature reactions and other heterogeneous catalysts as the replacement is gaining importance due to their ecofriendly nature (8). These catalysts are non-corrosive and easy to separate from the reaction mixture. They can also be used repeatedly over a prolonged period without any difficulty in handling and storing them.

Many present day commercial gas absorption processes involve systems in which chemical reactions take place in the liquid phase. These reactions generally enhance the rate of absorption and increase the capacity of the liquid solution to dissolve the solute, when compared with physical absorption systems (51).

The emphasis of the current work was to study in detail the kinetics of esterification of lactic acid with methanol over inexpensive, easily available catalysts such as ion exchange resins. In the first part of the study, the liquid-phase esterification of aqueous lactic acid solution with methanol catalyzed by acidic cation exchange resins were carried out in a batch reactor. Kinetic parameters such as temperature, conversion (x_{eq}), catalyst, molar ratio, side reactions were determined in a series of experiments and the reaction rate constants were analyzed. Moreover, the hydrolysis reaction of the lactoyllactic acid, which is a polymeric ester of lactic acid occurring naturally in aqueous solutions was investigated. In the second part, the aim was to design a counter-current fixed bed reactor and to determine whether the reaction mechanism was mass transfer controlled or reaction kinetics controlled. The effects of methanol and lactic acid feed rate, temperature and concentration of lactic acid were studied.

CHAPTER 2

LITERATURE SURVEY

2.1 LACTIC ACID

Lactic Acid, $C_3H_6O_3$, was first discovered in 1780 by a Swedish chemist Schele. Industrial manufacture of it was first established in 1881 in the U.S.A and in 1895 in Germany (9).

Lactic acid (2-hydroxypropionic acid) is a commercial chemical consumed at an annual rate of three to five million kilograms. Lactic acid and some of its derivatives (salts and esters) are used in many different areas. Common derivatives of lactic acid, particularly the esters of low molecular weight alcohols, are food-grade, biodegrable products that could find wider applications as solvents and plasticizers, particularly as regulations and consumer preferences increase the demand for such "green chemicals". The food industry has become the most

important outlet for lactic acid and lactates. About 25000 t/a is used in almost every segment of the food industry. Lactic acid has a mild acid taste and acts as preservatives. It is used as a food acidulant, as an ingredient in emulsifiers for bakery products, in agriculture for silage manufacture, in animal feeds to promote correct fermentations in the gut, in the textile industry as a solubilizer, in leather tanning, in metal treatment, pH controlling agent- acidulant, as an ingredient in plasticizers, pharmaceuticals, plastics, solvents and as a chemical intermediate. Polylactic acid is used as a biodegradable polymer for medical purposes. Lactic acid is also used as an intermediate and raw material in the chemical industry for the preparation of derivatives such as lactic salts, ester, amides and nitriles. The high cost of lactic acid is in contrast to the low cost of the abundant raw materials from which it can be made. This contrast is due to the difficulties encountered in isolation and purification of the acid from dilute aqueous solutions. Distillation and crystallization of lactic acid are extremely difficult. In addition its extraction from aqueous solution is inefficient (10, 11, 12).

2.1.1 Physical Properties

Pure and anhydrous lactic acid is a white crystalline solid with a low melting point. But this material is rare because of the physical properties and the difficulties in the preparation of the pure and anhydrous acid. Lactic acid appears generally in the form of more and less concentrated aqueous solutions as syrupy liquids. Good quality lactic acid solutions are colorless and odorless (9).

Lactic acid is miscible with water, ethanol, acetone, ether and glycerol. It is insoluble in chloroform, petroleum ether and carbon disulfide. Due to the presence

of two of the functional groups hydroxyl, ester and ether some lactic acid derivatives have a high solvent power (13).

Lactic acid exists as a mixture of free lactic acid, lactoyllactic acid and other intermolecular esters. It is the simplest hydroxy acid having an asymmetric carbon atom (9). It may exist as either of two stereochemical enantiomers or so-called "optical isomers", D-(+)-Lactic acid and L-(-)-Lactic acid. A mixture of 99% "optical purity is either (a) 99% D and 1% L, or (b)1% D and 99 % L. A mixture of molecules of both forms is called a racemic mixture, or DL-lactic acid (14). Commercial quantities of the acid are normally the racemic mixture (11).

Some of the physical and thermodynamic properties of lactic acid are given in Table 2-1 (11).

Table 2-1 Physical and Thermodynamic Properties of Lactic Acid

Formula Weight	90.08 g
Boiling Point, at 15 torr	122 ^{0}C
Color	Colorless
Density at 15 ^{0}C	10.404 kg/m^3
Specific Gravity	1.249

2.1.2 Chemical Properties

Two functional groups of lactic acid permit a wide variety of chemical reactions. The primary classes of these reactions are oxidation, reduction, condensation and substitution at the alcohol group.

Two important properties of lactic acid are its resistance to heat and its self-esterification reaction in aqueous solutions resulting in the formation of lactoyllactic acid and high linear polyesters (9, 3).

Various chromatographic methods have been used for the separation of lactic acid or its esters from a number of other acids or ester. Free lactic acid has a low volatility and shows a tendency toward self-esterification. For this reason, it is not analyzed directly by gas chromatography but only after esterification yielding volatile derivatives which are more amenable to gas chromatographic analysis.

2.1.3 Production and Formation

The methods for the production of lactic acid can be divided into two groups, biochemical and chemical (9). The principal source of lactic acid is the lactic acid fermentation. Lactic acid is formed in a variety of chemical reactions. The chemical reactions leading to lactic acid may be classified as follows:

1. Hydrolysis of derivatives of lactic acid, e.g. esters or nitrile or liberation from salts.

2. Hydrolysis of other 2-substituted propionic acids

3. Decarboxylation of certain derivatives of 2-methylmalonic acid.

4. Reduction

5. Oxidation

6. Rearrangement and disproportionation

A survey of other possible chemical synthesis routes for lactic acid is given in Figure 2-1

8
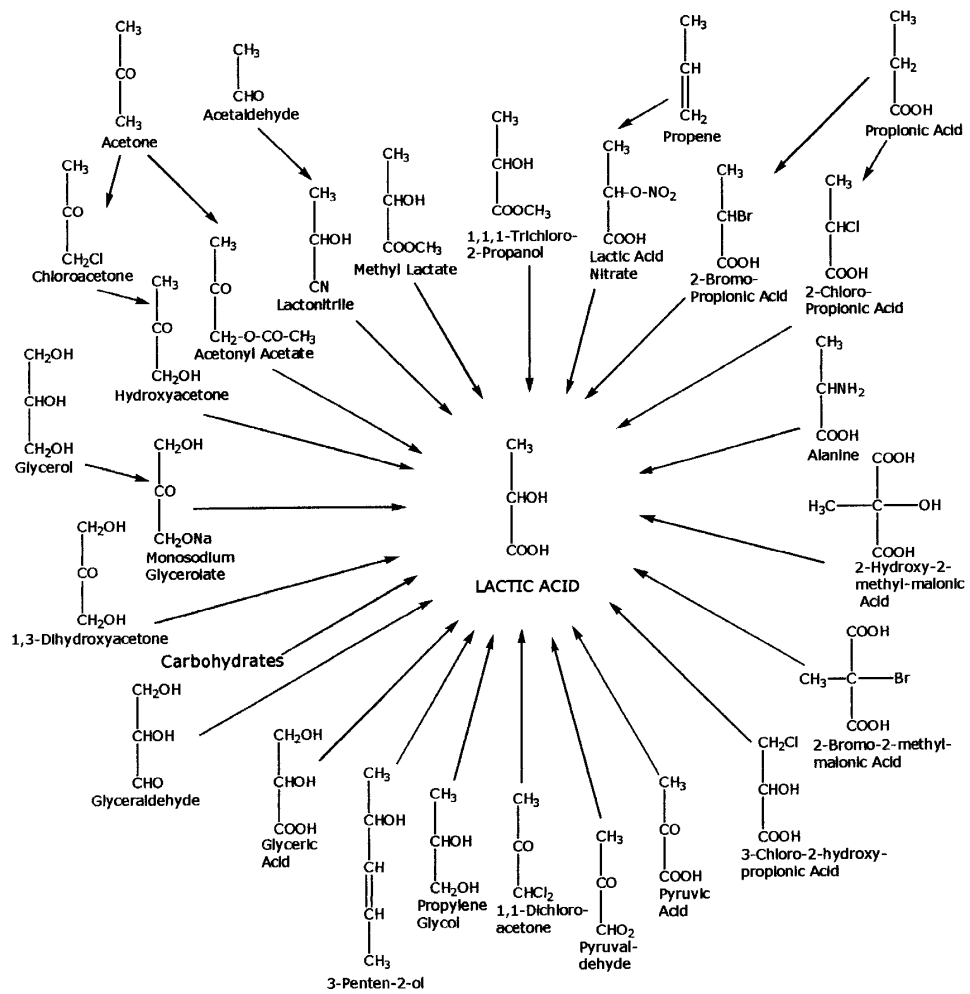
Figure 2-1 Chemical Synthesis Routes for Lactic Acid Production

The purification of fermentation lactic acid is difficult because of its low vapor pressure, tendency to undergo self-esterification, similarity in solubility characteristics to water, and presence of troublesome impurities, such as proteins, inorganic salts, unfermented sugars, and dextrins (11).

2.1.4 Esters of Lactic Acid

A great number of lactate esters are known. Particularly interesting ones are the methyl, ethyl and n-butyl esters. These are used in pharmaceutical and cosmetic industries and as solvents for varnishes, nitrocellulose and polyvinyl compounds (10). Methyl, ethyl and propyl lactates are water-soluble while butyl lactate is only slightly soluble. The lower esters are prepared by direct esterification while the lactic esters of higher alcohols are prepared from methyl or ethyl lactate, by transesterification with the appropriate alcohol (13).

Several methods have been used to prepare esters of lactic acid; these methods can be classified into the following main groups:

A: Direct esterification of lactic acid and alcohol.

B: Transesterification of one ester into another by reaction with alcohol.

C: Conversion of a metal lactate or ammonium lactate into an ester by treatment with alcohol.

D: Reaction of a metal lactate with an alkyl halide.

Methyl Lactate which may also be called lactic acid methyl ester has the following molecular formula $CH_3CH(OH)COOCH_3$. It is a colorless liquid, miscible with water in any ratio. Its boiling point is 145 ^{0}C at 101.3 kPa. It forms an azeotropic mixture with water at 99 – 99.5 ^{0}C (10).

2.1.4.1 Intermolecular Esters

Lactic Acid being both an acid and an alcohol is able to form an ester between two molecules, one acting as acid and one as alcohol. Two bimolecular esters of lactic acid are known, lactoyllactic acid and dilactide which are presented in Figure 2-2

$$CH_3$$
$$|$$
$$CH3 - CHOH - COO - CH - COOH \quad \text{Lactoyllactic acid}$$

$$CH_3$$
$$|$$
$$O - CH - C - O$$
$$|\qquad\qquad|$$
$$O=C - CH - O$$
$$|$$
$$CH3$$
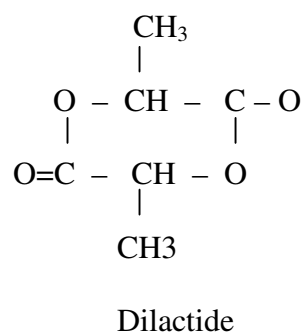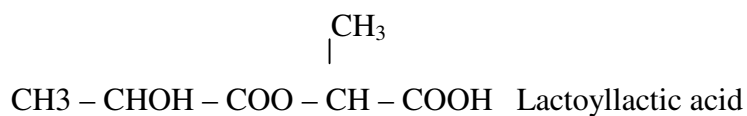
Dilactide

Figure 2-2 Molecular Structure of Lactoyllactic Acid and Dilactide

Lactoyllactic acid is also both an acid and an alcohol, and therefore the intermolecular ester formation can proceed, resulting in molecules containing three or more lactic acid units, and it is possible to prepare polymers of very high molecular weight (9).

The normal components of lactic acid are lactic acid as such, accompanied by lactoyllactic acid and higher-chain polyesters of lactic acid, and water, all in dynamic equilibrium whereas dilactide is normally not present.

An instric difficulty in the study of the equilibria in aqueous lactic acid is the fact that the reaction velocities of the formation and hydrolysis of the esters are very low at room temperature. The hydrolysis reaction of Lactic acid is shown in Figure 2-3.

$$C_6H_8O_4 + H_2O \longrightarrow$$
Dilactide

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
HO - CH - CO - O - CH - COOH & \text{Step 1}
\end{array}
$$
Lactoyllactic Acid

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| & | & | \\
HO - CH - CO - O\,CH - COOH + H_2O \rightleftharpoons & 2\,HO - CH - COOH & \text{Step 2}
\end{array}
$$
Lactoyllactic Acid   Lactic Acid
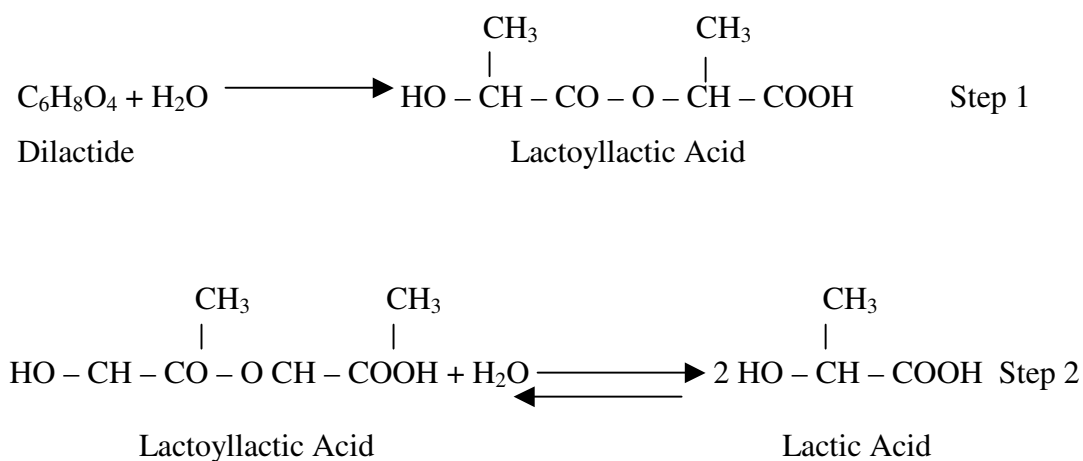
Figure 2-3 Hydrolysis Reaction of Lactic Acid

2.2 ESTERIFICATION

Esters are most commonly prepared by the reaction of carboxylic acid and an alcohol with the elimination of water. The rate at which different alcohols and acids are esterified as well as the extent of the equilibrium reaction are dependent on the structure of the molecule and types of functional substituents of the alcohols and acids. The primary alcohols are esterified most rapidly and completely, i.e, methanol gives the highest yield and the most rapid reaction. Under the same conditions the secondary alcohols react much more slowly and afford lower conversions to ester products.

Esterification of a carboxylic acid with an alcohol is extremely slow at ambient temperatures. However, heating the reaction mixture of carboxylic acid and alcohol to the atmospheric boiling point of the mixture generally does not provide for a suitable practical rate of esterification. The major concern for practical applications is increasing the reaction rate and establishing conditions, which will allow obtaining higher conversions (15).

Since the esterification of an alcohol and an organic acid involves a reversible equilibrium these reactions usually do not go to completion. Conversions approaching 100% can often be achieved by removing one of the products formed, either the ester or the water, provided the esterification reaction is equilibrium limited not rate limited. A variety of distillation methods can be applied to achieve ester and water product removal from the esterification reaction. The concentrations present at equilibrium depend on the characteristics of the alcohols and esters involved (16).

Esterification of the carboxyl group is another important reaction, which is used to recover and purify lactic acid from impure solutions or to produce the ester as the desired end product (11). Esterification of lactic acid with alcohols can be performed in a number of different ways; the choice of the experimental conditions depends on the alcohol to be esterified. A classical method consists of heating a mixture of lactic acid and alcohol in a sealed tube, generally to about 150 ^{0}C. This method has been used to prepare methyl lactate and ethyl lactate however this method cannot be regarded as satisfactory as the yields are generally low (9).

Formation of esters depends, as mentioned above, on the reversible reaction and the yield of ester can therefore be improved when one of the products, ester or

water, is removed from the system while the reaction is going on. Removal of ester has been brought about by distillation or solvent extraction but removal of water is more useful since very high yields can be obtained in this way (16).

Catalytic esterification of alcohols and acid in the vapor phase has received attention because the conversions obtained are generally higher than in the corresponding liquid phase reactions. Therefore the most effective method for the preparation of lactate esters of lower alcohols is passing vapors of the alcohol through the lactic acid previously heated to a temperature above the boiling point of the alcohol. Series of experiments have been made by using this method with methanol and ethanol (17, 18, 19, 20, 21, 22, 23, 24). The esterification has been performed in small and medium scale experiments, as well as in pilot scale. It can be done in batch-wise experiments, as well as in continuous working systems in which lactic acid and alcohol flow countercurrently, the ester is carried out of the apparatus by the excess of alcohol vapors, which then recirculated. Lactic acid can be converted almost quantitatively into the esters, and loss of alcohol is small due to the recirculation. The continuous methods have been recommended for the purification of crude lactic acid; the purified acid is then recovered by hydrolysis of the ester.The equilibrium point of the reaction is not altered by the catalyst; only the rate of esterification is increased.

2.3 CATALYSIS

The properties possessed by ion-exchange resins have resulted in the development of many procedures and processes for use in both research and industry. Many industrially important reactions involving acid or bases as catalysts can also be carried out using cation-exchange or anion-exchange resins since standard ion-exchange resins are insoluble acids or bases.

Catalysis with solid ion-exchange resins has the following advantages over the use of homogeneous catalysts like sulfuric acid (45):

1. The catalyst can be readily removed from the reaction product by decantation or simple filtration.

2. Continuous operations in columns are possible.

3. The purity of the products is higher since side reactions can be completely eliminated or are less significant.

4. It is possible to isolate the reaction intermediates.

5. Ion exchange resins can differentiate between small and large molecules.

6. Environmentally safe operability.

7. No corrosion.

8. A higher local concentration of H^+/OH^- ions.

For liquid phase esterification reactions use of ion-exchange resin as solid catalysts increases with regard to their advantageous properties. In comparison with the conventional homogeneous catalysts, esterification of lactic acid with methanol (33), benzyl alcohol with acetic acid (45), synthesis of butyl lactate (3), synthesis of

isopropyl lactate (5) and esterification of ethanol with acetic acid etc., are carried out and all proved to be active catalysts.

E.Aytürk (49-50) investigated the catalyst characterization of IR-120, S-100 and SPC-112 in 2001. The reaction test with IR-120-H$^+$ indicated that the activity of IR-120-H$^+$ was not more appreciably than the homogeneous reaction, which is catalyzed by lactic acid itself in the absence of ion exchanger catalyst at 343 K, and it was observed that, strongly cationic S-100 and SPC-112 resin catalyzed the lactic acid esterification effectively at various catalyst concentration series. In this study the ion exchange resin Lewatit SPC-112- H$^+$ is used.

Early scientists studied the kinetics of esterification reaction of lactic acid esters by using H_2SO_4 (17, 32, 46). Temperature, concentration of acid catalyst and mole ratio of reactants was the variables that wee studied. Both for 44% lactic acid-methanol and 85% lactic- acid ethanol reactions the order of the esterification reaction did not follow a simple 1st, 2nd or 3rd order kinetics. The resulting rate constant and the equilibrium constant were 42.55 x 10^{-5} lt/mol/min and 3.39 respectively for the 44% lactic acid excess methanol reaction and for the 85% lactic acid with excess ethanol expressed rate constant was found to be 65.24 55 x 10^{-3} lt/mol/min at 80 ^{0}C and equilibrium constant as 1.89. For lactic acid methanol reaction catalyzed by acidic resins, a 2nd order reversible reaction with respect to each reactant was considered. Rate constants were estimated as 3.201 g/mol/min for forward and 0.5176 g/mol/min for backward reaction. Same kinetic model based on inhibition by water and butanol was outlined for the synthesis of butyl lactate. Forward and backward reaction rate constants were reported as 0.077 lt/mol/s/kg and 0.0197 lt/mol/s/kg at 80 ^{0}C (32).

Physical data for the ion-exchange resin which was used in this study is presented in Table 2-2.

Table 2-2 Physical Data for the Ion-exchange resin

Resin	Ionic Form as Shipped	Type	Structure	Density (g/ml)	Capacity Min. (eq/lt)	Diameter (mm)
Lewatit SPC112	H+	Strong Cationic	Macroporous	1.27	1.75	0.6

Ion-exchange resins are also attracting attention as promising catalyst carriers, which show higher activity than the unsupported form of the resin for the synthesis of MTBE, esterification of acetic acid with 1-pentanol, and hydration of 2-methylpropene (47, 48). Resulting activities were attributed by the synergy created from the protons originating both from the ion exchanger and heteropoly acid catalysts.

2.4 REACTIVE (CATALYTIC) DISTILLATION

There is considerable academic and industrial interest in the area of reactive (catalytic) distillation (25). Because of the potential benefits of this technology, the number of publications on the theoretical and experimental performance of special reactive distillation process is rapidly increasing (26, 27).

Catalytic distillation seems to be an energy saving process with lower investment and operating costs in comparison to the traditional processes (28).

Reactive distillation is an emerging technology that has considerable potential as an alternative process for carrying out equilibrium limited liquid phase chemical reactions, exothermic reactions, poor raw materials usage due to selectivity losses, or excessive flow sheet complexity. It is a unit operation that combines simultaneous chemical reaction and multicomponent distillation in the same vessel, which in turn reduces reactor and recycle cost.

Both homogeneous and heterogeneous catalysts can be used in Reactive distillation column. In homogeneously catalyzed processes, generally sulphuric acid is used whereas in heterogeneously catalyzed reactions, acidic polymeric catalysts such as ion-exchange resins in various forms that play a dual role of catalyst as well as tower packing are used. The catalyst particle size used in such operations is usually in the 1-3 mm range. Counter-current operation of gas and liquid phases in fixed beds packed with such particles is difficult because of flooding limitations. To overcome the limitations the catalyst particles have to be enveloped in wire gauze packing. Despite recent advances in this technique, it is still difficult to bring a new reactive distillation process to production because of complexities in design, synthesis, and operability of reactive distillation processes resulting from the interaction of reaction and distillation (25, 26, 27, 29).

As reactive distillation involves the combined effects of reaction and distillation, there are several design and operating variables relevant to multiplicity. The primary operating variables are the reflux ratio and the reboil ratio. The presence of chemical reaction in reactive distillation provides a mean of rapidly

changing product compositions without requiring significant changes in the feed-split or the energy balance. For this reason, it is important to know the operating region (reaction controlled or fractionation controlled) a reactive distillation column is operating and to understand how the column will respond to changes in operating variables (26).

Thus, a study of the effects of chemical kinetics on the multiplicity interval in a reactive distillation column for a given set of operating variables (e.g. reflux ratio, reboil ratio etc.) has significant implications for column design, operation and control (27). A variety of models are available in the literature for screening, analysis, design and optimization of reactive distillation systems (30).

2.5 ABSORPTION WITH CHEMICAL REACTION

Many important technical processes, such as manufacture of nitric and sulphuric acid, soda ash and bleaches, purification of synthesis gases, etc; involve chemical reactions between gases and liquids. In order to improve the overall rate of such heterogeneous processes an intimate interphase contact has to be established and mass transfer has to be improved by increasing turbulence in both phases. The overall rate of the process is governed by both chemical reaction and mass transfer rates (52).

When a gaseous component is absorbed by a liquid under simultaneous reaction with a component of the liquid, the overall rate of reaction proves to be a dimensionless function of four limiting rates:

- The maximum rate of diffusion of the gaseous component through the liquid film

- The maximum rate of diffusion of the liquid-component through the liquid film

- The limiting rate of reaction within the liquid film (during diffusion)

- The maximum rate of reaction within the main body of the liquid

When absorption takes place with simultaneous reaction between the gaseous component A and the liquid component B (within the liquid film) there is a number of possibilities, depending on the magnitude of the chemical reaction velocity (52).

If the liquid-phase reaction is **extremely fast** and irreversible, the rate of absorption may in some cases be completely governed by the gas-phase mass transfer resistance. For practical design purposes one may assume (for example) that this gas-phase mass-transfer limited condition will exist when the ratio y/y_i is less than 0.05 everywhere in the apparatus.

From the basic mass-transfer flux relationship for species A ;

$$N_A = k_G(y - y_i) = k_l(x_i - x)$$

It can be shown that this condition on y/y_i requires that the ratio x/x_i be negligibly small (i.e a fast reaction) and that the ratio $mk_G/k_l = mk_G/k_l^0 \varnothing$ be less than 0.05 everywhere in the apparatus. The ratio $mk_G/k_l^0 \varnothing$ will be small if the equilibrium back pressure of the solute over the liquid solution is small or the reaction enhancement factor $\varnothing = k_l/k_l^0$ is very large or both.

Figure 2-4 illustrates the gas-film and liquid-film concentration profiles one might find in an extremely fast (gas-phase mass transfer limited) second order irreversible reaction system. The solid curve for reagent B represents the case in which there is a large excess of bulk liquid reagent B^0. The dashed curve in the figure represents the case in which the bulk concentration B^0 is not sufficiently large to prevent the depletion of B near the liquid interface.
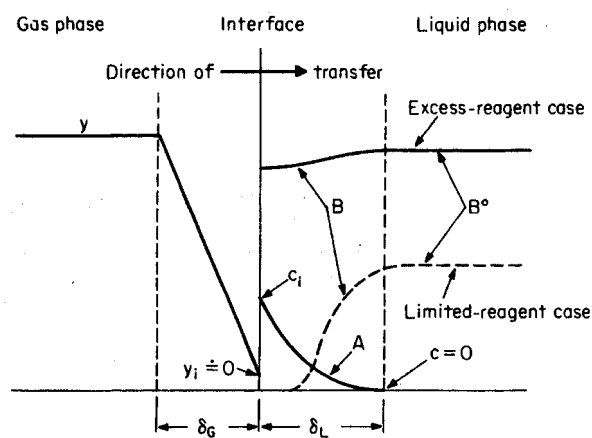
Figure 2-4 Gas-phase and liquid phase solute –concentration profiles for an extremely fast (gas-phase mass-transfer limited) irreversible reaction system A+vB→ products.

The gas phase mass-transfer limited condition is approximately valid, for instance, in the following systems: absorption of NH_3 into water or acidic solutions, vaporization of water into air, absorption of H_2O into concentrated sulfuric acid solutions, absorption of SO_2 into alkali solutions, absorption of H_2S from a dilute-gas stream into a strong alkali solution, absorption of HCl into water or alkaline solutions, or absorption of Cl_2 into strong alkali.

When liquid phase chemical reactions are **extremely slow**, the gas-phase resistance can be neglected and one can assume that the rate of reaction has the predominant effect upon the rate of absorption. The Hatta number N_{Ha} usually is employed as the criterion for determining whether or not a reaction can be considered extremely slow. For extremely slow reactions a reasonable criterion is

$$N_{Ha} = \sqrt{k_1 D_A} / k_0^l \leq 0.3$$

where D_A is the liquid phase diffusion coefficient of the solute in the solvent.

Figure 2-5 illustrates the concentration profiles in the gas and liquid films for the case of an extremely slow (kinetically limited) chemical reaction.
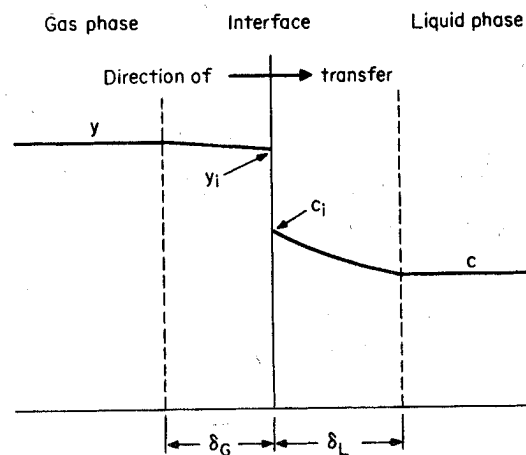
Figure 2-5 Gas-Phase and liquid-phase solute-concentration profiles for an extremely slow (kinetically limited) reaction system for which N_{Ha} is less than 0.3.

2.6 PREVIOUS STUDIES

Dassy Et.al (3) studied the esterification of lactic acid with butanol catalysed by cation-exchange resin was carried out in a batch reactor in dioxane and toluene in 1993. The reaction rate was found to be first order with respect to catalyst and acid concentrations. The inhibiting effect of water and butanol has been evaluated. The rate data were correlated with a kinetic model based on inhibition by water and butanol. Amberlyst-15 was found to be a suitable catalyst for the esterification of n-butanol with the lactic acid aqueous solutions. The effects of the variables such as resin concentration, reactant molar ratio, water concentration and temperature on the reaction rate were evaluated. The importance of external diffusion resistance or pore diffusion was neglected. Equilibrium constants were calculated as 4.14 at 96 ^{0}C and 2.98 at 70^{0}C.

Difficulties involved in the purification of fermentation lactic acid and preparing methyl lactate directly from the crude aqueous lactic acid was studied by Fischer et al (17) in 1946. The method comprises passing methanol vapor through aqueous lactic acid and condensing the effluent vapors. The condensate, a mixture of methanol, methyl lactate and water can be distilled to recover the methyl lactate or hydrolyzed to obtain purified lactic acid. The effect of variables on the volatilization of lactic acid with methanol vapor has been studied. The time required to volatilize a given amount of methanol addition is increased. Increasing the catalyst concentration (concentrated sulfuric acid) accelerates the operation. Approximately 9 moles of methanol are required to volatilize 1 mole of lactic acid from an 82%

solution of the acid, which was kept at 92-100^{0}C over a wide range of methanol addition rates.

Isopropyl Lactate is a very important pharmaceutical intermediate. The homogeneous catalysts are hazardous and disposal of liquid acid effluents poses. The separation of the liquid catalyst and its reuse is another problem. Yadav et .al (5) in 1999 studied the use of a variety of ion-exchange resin catalysts, which are Indion-130, Amberlyst-36, Amberlyst-15, Amberlyst-120, Dowex-50 W, Filtrol-44, in the synthesis of isopropyl lactate from lactic acid and isopropyl alcohol., Amongst these Amberlyst-36 was observed to be the best catalysts. A theoretical kinetic model was developed for evaluation of the slurry reaction. The effects of various parameters on the rate of reaction were evaluated. The reaction was found to be intrinsically kinetically controlled and there were no intraparticle as well as interparticle mass transfer limitations on the rate of reactions.

Troupe et al (32) studied the indication of the kinetic data with 44% technical lactic acid, higher temperatures and higher catalyst concentrations are needed to lower the reaction time to a commercially attractive level. As both factors tend to increase decomposition of the lactic acid and solid impurities are precipitated from the reaction mixture. A flow type reactor with reactants in the liquid phase will probably not be satisfactory.

Catalytic distillation offers some advantages over conventional processes where reaction and purification are carried out separately. Some of them are the reduction of capital and operating costs, high selectivity, reduced energy consumption, and reduction or elimination of solvents. Its major disadvantage is that chemical reaction has to show significant conversion at distillation temperature.

24

Autocatalyzed and heterogeneously catalyzed lactic acid esterification with methanol has been studied by M.T.Sanz et al (2). The effect of catalyst type, stirrer speed, catalyst size, catalyst loading, initial reaction ratio and temperature on reaction kinetics was evaluated. Amberlyst 15 was found to be a good catalyst for this reaction. The reaction rate increased with temperature and catalyst loading. The equilibrium conversion is increased as the methanol/lactic acid ratio increased. The high value of the apparent activation energy supports the assumption that the reaction in the catalyst surface was the rate controlling-step.

The esterification of lactic acid with alcohol can be performed in a number of different ways; the choice of experimental conditions depends on the alcohol to be esterified (14).

The esterification of aqueous lactic acid solution with methanol and its reverse reaction catalyzed by acidic cation exchange resins in a batch system was studied by Choi et al (33). The inhibiting effects of water and methanol on the resins were evaluated. The experimental data were correlated by a kinetic model that the inhibition by methanol and water was included. The reaction rate constants and the adsorption coefficients were determined from the experiments. The internal mass transfer was negligible since the resin size did not affect the reaction rate. The reaction rate by sulfuric acid was larger than that by acidic resin at the initial period but the conversion of the reaction using sulfuric acid was smaller as reaction time increased. The sulfuric acid is less expensive than the resin, but the resins can be recycled several times, and they also offer various advantages over homogeneous catalyst. As the concentration of acidic resins and the reaction temperature were increased the reaction rate increased too. The activation energy of esterification E_{af}

was calculated as 48.975 kJ/mol and the value of its reverse reaction E_{ab} was calculated as 44.605 kJ/mol. The value of adsorption coefficient of methanol obtained from the esterification reaction data is 273.5 g/mol and the reaction rate constant of esterification is calculated as 3.201 g/(mol min).

The esterification of butanol and iso-amyl alcohol with acetic acid has been studied by several investigators. Leyes and Othmer (34) were the first to study this reaction in the presence of sulphuric acid as catalyst. They have reported the kinetic data and also presented some useful information on distillation consideration for this system.

Gomzi and Paje (35) studied the esterification of n-butanol with 98-100% acetic acid in batch mode using wofatite KPS catalyst with 2-16% of divinyl benzene.

Vanko et.al (36) claimed that n-butyl acetate containing little acetic acid can be prepared in a column having bubble -cap plates. In sulphuric acid catalyzed esterification of 1:0.99 mole ratio of acetic acid to n-butanol mixture at reflux temperature of 352.5-353.5 K gave organic phase containing 1.6% H_2O, 8% n-butanol, 89-90% n-butyl acetate and traces of acetic acid.

Combination of reactive distillation with esterification and crude ester refining was studied by Zhang et al. (37) and Huang et al. (38) prepared iso-amyl acetate by continuous esterification in the presence of strong acidic cation exchange resin catalyst, E-921.

Zhicai et.al (39) studied distillation with esterification of butanol and acetic acid experimentally and achieved significant conversion. They have explained the results with mathematical simulation.

Hanika et.al (40) reported a pilot-plant research of butyl acetate synthesis via catalytic distillation. They have performed computer simulation to study the process and to evaluate the experimental data.

Most of the literature deals with the esterification reaction in batch mode of operation using 98-100% carboxylic acid. Neumann and Sasson (41) studied the recovery of acetic acid from 20 to 60% w/w solution through esterification with methanol in a chemo rectification column packed with an acidic organic polymer catalyst and obtained about a substantial acetic acid conversion of 70-80%.

Saha et al (29) studied the recovery of 30% aqueous solution of acetic acid by esterification with n-butanol and iso-amyl alcohol was performed in a reactive distillation column using macroporous Indion 130 cation exchange resin as a catalyst bed. The effect of various parameters, e.g. feed rate, location of feed points, reflux ratio, mole ratio of the reactants etc. were studied and analyzed. At 1:2 mole ratio of acetic acid to n-butanol, ~58% conversion of acetic acid was achieved. At 1:2 mole ratio of acetic acid to iso-amyl alcohol, ~58% conversion of acetic acid was achieved. They have obtained the best result when the column was operated in counter-current mode.

A simulation and modeling methodology for kinetically controlled, stage-wise reactive distillation columns, taking into account equimolar reactions, side-reactions, effects of heat of reaction, non-constant latent heat effects, a distribution of liquid holdups on the reactive stages and hybrid sections in a column were studied by Chen et.al (26). A Damköhler number, which is the ratio of a characteristic liquid residence time to a characteristic reaction time, was introduced in to the model. The

transition behaviour from the nonreactive to the equilibrium reactive limits have been described by changing the damköhler number.

Acid–catalyzed esterification of benzoic acid with ethanol was investigated by Pipus et.al (15) in a continuous tubular flow reactor heated by microwaves. Esterification was catalyzed with sulfuric acid and with ion exchange resins. Rate equations that have been determined under conventional heating were included in the mathematical model to predict the conversion of esterification. They have concluded that the calculated conversions of benzoic acid based on predicted temperature profiles agree with experimental data and found that esterification of benzoic acid is slow reaction and needs several days to reach equilibrium at elevated temperatures (80^0C).

Counter-current operation of a structured catalytically packed-bed reactor was studied by Higler et.al (25). The liquid –phase residence time distribution had been measured in two structured packed column configurations, of 0.1 and 0.24 m diameter, in which the catalyst particles are enclosed within wire gauze envelopes. Computational fluid dynamics (CFD) had been used to model the liquid flow within the packed sandwich structures.

Chen et.al (27) have been developed a model to describe kinetic effects in reactive distillation. TAME and MTBE synthesis by reactive distillation, at least in the configurations were studied, are predicted to have significantly different behaviour. Multiplicities are lost at high values of Da for TAME, while the opposite had been found for MTBE.

2-Methypropylacetate-synthesis process development was studied by Hanika et al (28). The process was based on esterification of acetic acid with 2-

methylpropanol by reactive distillation method. They found that the stripping section efficiency had no effect on acetic acid separation, its concentration in the bottom product depends on the reaction conversion only and it was possible to increase conversion at the value close to 100% by increasing the height of the reaction zone. They concluded that final purification of the crude product was necessary in an industrial 2-methylpropylacetate production via catalytic distillation.

A new catalyst loading method, in which catalyst particles are packed in a reactor with a novel interval by measuring pressure drop, liquid hold up and mass transfer was studied by Han et.al (42) in 2002. They found from experimental results that the internal changes the conventional gas and liquid counter-current flow into a new cross-current flow, so the problems of excessive pressure drop and "flooding" are avoided and concluded that the reactive distillation column with novel interval has the advantages of simple structure, low operating cost, convenience for installation and removal of catalyst, and large catalyst loading fraction.

The esterification kinetics of acetic acid with methanol in the presence of hydrogen iodide as a homogeneous acid catalyst with isothermal batch experiments at 30-60^{0}C was studied by Rönnback et.al (43) in 1997. Rate equations were derived and the kinetic and the equilibrium parameters included in the rate equations were estimated from experimental data with regression analysis.

Mazotti et al (44) studied the kinetics of liquid phase esterification catalyzed by acidic resins and they found that the ability of resin not only to catalyze the esterification reaction but also to shift the corresponding equilibrium conversion, due to its swelling capability.

Aytürk (49) investigated the heterogeneous liquid-phase esterification reaction of lactic acid with ethyl alcohol accompanied with lactoyllactic acid hydrolysis over heteropoly acid supported on ion exchange resin catalysts at 343 K with ethanol to lactic acid molar ratio of 1:1. The catalysts with 5-20% of tungstophosphoric and molybdophosphoric acid type of heteropoly acids over Lewatit S 100 showed higher activities than the resin itself. Reaction rate constants for homogeneous self catalyzed, ion exchange resin catalyzed, and kinetic contribution of heteropoly acid loading were calculated. It was observed that molybdophosphoric acid loaded S-100 catalysts have higher proton efficiency than the tungstophosphoricacid loaded counterpart.

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

$C_3H_6O_3$ (Lactic Acid, 92 wt% Total Acidity): Marketed by Merck, Darmstad-Germany under lot code K26404866 923 was used as an esterification reactant.

CH_3OH (Methyl Alcohol, 99.8%): Marketed by Merck, Darmstad-Germany under lot code K29673109 134 was used as an esterification reactant.

$C_4H_8O_3$ ((-)-Methyl Lactate, 98%): Marketed by Merck, Darmstad-Germany under lot code S28794 036 was used for GC calibration.

KOH (Potassium Hydroxide Pellets, 85 %): Marketed by Merck, Darmstadt-Germany under Art.5032 was used for titration analysis.

HCl (Hydrochloric Acid, 37%): Marketed by Merck, Darmstadt-Germany under lot code K270564414 011 was used for titration analysis.

$C_{20}H_{14}O_4$ (Phenolphthalein): Marketed by Merck, Darmstad-Germany was used as indicator solution for titration analysis.

Lewatit SPC-112 H^+ (Ion-Exchange Resin): Marketed by Bayer AG, Leverkusen-Germany was used as a catalyst in esterification reaction.

3.2 EQUIPMENT

A Clifton model constant temperature water bath, with an inside shaker trolley operating between 0-400 strokes/min and with a PID temperature controller within control capability of $\pm$ 0.1 ^{0}C water temperature fluctuation within 0-100 ^{0}C temperature range was used.

A reaction vessel, which is a pyrex column with a 20 mm diameter and 25 cm height, fitted with a condenser and surrounded by a heating jacket was used for reactive distillation experiments.

Titration set-up consists of a CAT M6/1 magnetic hotplate stirrer with 0–250 ^{0}C heating and 0-1400 rev./min stirring ranges and standard laboratory glassware.

Hewlett-Packard 5890A Gas Chromatograph equipped with a TCD Detector and a 10% packed FFAP/Chromosorb (60/80) Column operating at 120 ^{0}C oven temperature, 170 ^{0}C injection temperature, 180 ^{0}C detector temperature and at a 150 kPa head pressure using Helium as a carrier gas was employed.1 µl Hamilton micro-liter syringe was used for sample injection.

For the drying operation of the catalyst vacuum oven with heating range between 0-200 ^{0}C was used and Micrometrics ASAP-2000 model BET Surface Area Analyzer with nitrogen absorption were used for the catalyst characterization studies.

3.3 EXPERIMENTAL SET UP

The fixed bed reactor experiments were conducted by using the set up that is presented in Figure 3-1.
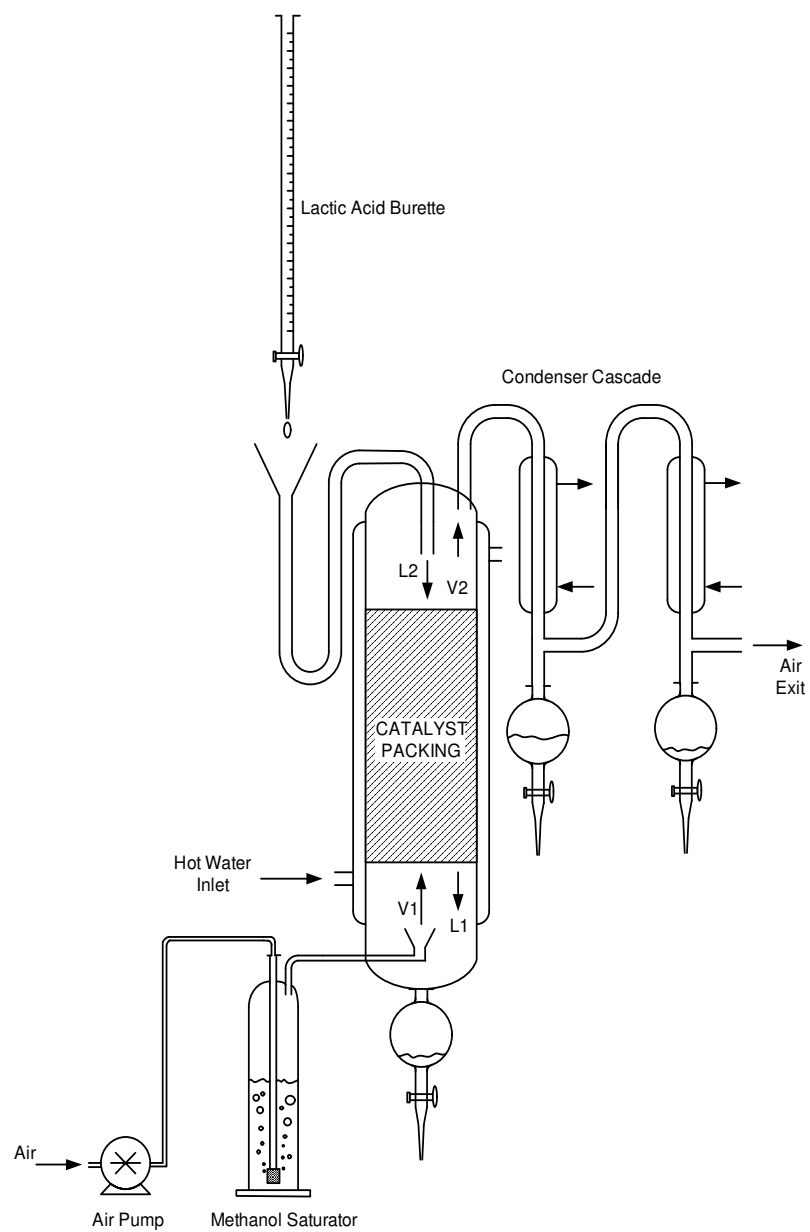
Figure 3-1 Experimental lay out of the counter-current reaction system

3.4 EXPERIMENTAL PROCEDURE

In the first part of the study the reaction experiments or batch reactor reaction experiments are investigated.

The effects of variables such as catalyst concentration, initial reactant molar ratio and temperature on the reaction rate were studied with the catalyst Lewatit SPC-112-H$^+$ (Ion exchange resin). The reaction temperature was selected as 343 K (±1 ^{0}C) in order to avoid inefficient sampling due to methanol vaporization occurring at higher temperatures and to prevent thermal decomposition of lactic acid species. Also the methanol to lactic acid molar ratio was kept at 1:1 in order to observe the effect of catalyst on the reaction rate under the minimized inhibition effect of methyl alcohol. Experiments were carried out in 30 ml sealed vials placed in a constant temperature bath with an inside orbital shaker tray operating at 300 rpm and at atmospheric pressure. Lactic acid (92 wt%, Merck) and methyl alcohol (99.8 wt% Merck) were used as the reagents for all experiments.

The lactic acid and the catalyst were placed in the batch reactor and well mixed. After the attainment of a steady value of the desired reaction temperature, the second reactant methyl alcohol was added and this was taken as time zero for the run. Weighted amounts of liquid samples, approximately 1 ml, were withdrawn at specific time intervals from the reactor for analysis.

In the second part of the study, counter-current fixed bed reactor was investigated.

The effects of methanol and lactic acid feed rate, temperature and concentration of lactic acid were studied. And it was determined that whether the reaction mechanism is mass transfer controlled or reaction controlled.

Lactic acid and methanol vapor-air mixture were passed counter-currently through a Pyrex column which is depicted in Figure 3.1. This comprised a 20 mm diameter and 25 cm long, packed with 0.6 mm ion exchange resin, which was Lewatit SPC-112-H$^+$. The top of the reactor had an inlet tube for introducing the lactic acid solution and an outlet tube for removing vapors. A boiling jacket surrounded the reaction vessel. The temperature of the vessel was maintained between 90-95^{0}C. Methanol/air, contained in a graduated cylinder, which was maintained at a temperature above the boiling point of the alcohol, between 55-60^{0}C, was fed with a constant-rate into the bottom of the reaction vessel. Liquid flows downward, driven by the gravity, mainly through the pores between the catalysts. When the gas and liquid were contacted in a counter current flow pattern in the catalyst bed, mass transfer and catalytic reactions took place.

In a typical experiment, firstly only methanol was fed and the reactor was placed in the thermostatic bath. The aim of this procedure was to preheat the catalyst bed and to remove, as much as possible, the remaining water in the catalyst by methanol percolation. Lactic acid then was added to the feed. Lactic acid solution was introduced from the top and methanol/air was fed from the bottom to achieve maximum conversion. The vapors from the reactor, composed essentially of methanol, water and methyl lactate were withdrawn from the reactor and condensed. After the steady state was attained samples from the top and bottom sections were collected at 10 min interval, weighed and analyzed for their composition. These

36

portions were titrated to determine the lactic acid volatilized principally as methyl lactate. Each experiment was continued for 5 hours. The flow rates of the feed, bottom and overhead were measured and a complete material balance was performed.

3.5 ANALYSIS

During the experimental runs both chemical and instrumental analysis, which are titration and gas chromatograph, were carried out simultaneously.

The concentration of lactic acid in aqueous solutions could be quantitatively determined by an acid-base titration. However, the analysis requires a hydrolysis step in order to determine the total acid content since lactic acid has a tendency to form polymeric lactic esters by self-polymerization. Therefore, examination of the lactic acid and the amount of lactoyllactic acid present in the sample, were done by means of two sequential acid –base titration.

1. Determination of Free Acidity: The free acidity in the sample is determined by titrating a weighted amount of sample product against 0.1 N standardized KOH solution using phenolphthalein as an indicator.

$$F[wt\%] = \frac{N_{KOH}\,(\frac{mol}{lt}).V_{KOH}\,(ml).MW_{LacticAcid}\,(\frac{g}{gmol})}{(\frac{1000ml}{lt}).W_{Sample}\,(g)}.100$$

F: Free Acidity as Lactic Acid, wt %.

N_{KOH}: normality of KOH solution, mol/lt.

V_{KOH}: volume of KOH solution used for the titration, ml.

$MW_{Lactic\ Acid}$:Molecular weight of Lactic Acid, 90.08 g/mol

W_{Sample}: sample weight, in g

2. Determination of Total Acidity: To the titrated solution from (1) an excess of standard alkali, KOH is added and the esters are hydrolysed by boiling; the excess of alkali is then back titrated with standardized HCl solution. The quantity of lactoyllactic acid is calculated from the difference between the consumptions of the two titrations.

$$T[wt\%] = \left[(N_{KOH} + N_{KOH,excess})(\frac{mol}{lt}) * V_{KOH(ml)} - N_{HCl}(\frac{mol}{lt}) * V_{HCl}(ml) \right]$$

$$* \left[\frac{MW_{LacticAcid}(\frac{g}{gmol})}{(\frac{1000ml}{lt}).W_{Sample}(g)} \right] * 100$$

$$LLA[wt\%] = T[wt\%] - F[wt\%]$$

T: Total Acidity as Lactic Acid,-wt%

$N_{KOH,Total}$:total volume of KOH solution including added excess,ml

N_{HCl}:normality of HCl solution, mol/lt

V_{HCl}:volume of HCl solution used for back-titration,ml

The methyl lactate, methanol and water in the reaction mixture were analyzed by a Hewlett-Packard 5890A gas chromatography (GC), which is equipped with a 10% packed FFAP/Chromosorb AW (60/80) column and a TCD detector by using He as the carrier gas. 0.5 µl product samples were injected in the same time intervals of titration samples. GC analyses were carried out by using calibration standards and the relative response factors with respect to the methanol, and the total areas under the chromatograms were corrected with respect to the lactic acid and

lactoyllactic acid contents of the sample-neither acids are volatile species. Gas chromatography data were combined with the titration analysis in order to get the total molar conversion and the product distribution during the reaction. A sample calculation procedure and the details of relative response factor calculations of methyl lactate, methanol and water can be found in Appendix A.

3.6 CATALYST TREATMENT

3.6.1 Resin Regeneration

Ion-exchange resins preferred as suitable supports in the catalyst preparation. In this study Lewatit SPC-112-H$^+$ is used which is a type of strong cationic and used in hydrogen form. A typical regeneration procedure was employed in converting the appropriate ionic forms of strongly acidic ion-exchange resins. Lewatit SPC-112-H$^+$ has a monodisperse particle size (0.6$\pm$0.05 mm).

Catalyst regeneration procedure was divided into four main operations that are batch operation, column operation, washing and drying.

In the first part of the regeneration 200 mL of Ion-exchange resins, which is Lewatit SPC-112-H$^+$ in this study, were placed into an Erlenmeyer flasks and conditioned for 3 days in a 30 %, diluted HCL solution. Then depending on the amount of used resin, a sufficient volume of 30-volume % HCl solution was passed through the regeneration column. After the regeneration, washing and drying of the resins follows the operation. Regenerated resins were rinsed with distilled water to

pH:7, dried and conditioned at 340 K under vacuum for 18 hours. The catalyst samples were kept in a dessicator for further use.

3.7 EXPERIMENTS PERFORMED

3.7.1 Lactoyllactic Acid Hydrolysis Experiments

The hydrolysis reaction of lactoyllactic acid was studied under the reaction time at varying amount of initial lactic acid concentrations and temperature conditions which were 30%, 50%, 90%, about 48 hours and 50 ^{0}C, 60 ^{0}C, 70 ^{0}C respectively, in the presence of catalyst and in the absence of catalyst.

3.7.2 Batch Reaction Experiments

Experiments for the determination of kinetic data of the esterification reaction of lactic acid and methanol were performed at 40 ^{0}C, 50 ^{0}C, 60 ^{0}C, 70 ^{0}C in the presence of catalyst and in the absence of catalyst. The methanol to lactic acid molar ratio was kept at 1:1.

3.7.3 Counter-Current Fixed Bed Experiments

Three set of experiments for performed for the determination of whether the esterification reaction mechanism is mass transfer controlled or reaction rate controlled. In the first set of experiments lactic acid concentrations were 10%, 30%, 50%, 70% and 90% keeping methanol/air flow rate and lactic acid flow rate constant. In the second set of experiments lactic acid concentration was kept

constant as 50% and lactic acid flow rate as 0,0174 gmol/min whereas methanol flow rate was 0.0083 gmol/min, 0.0634 gmol/min, 0.0896 gmol/min, 0.1231 gmol/min and 0.1763 gmol/min. In the third set of experiments lactic acid concentration was kept constant as 50% and methanol flow rate as 0.0897 gmol/min whereas lactic acid flow rate was 0.0096 gmol/min, 0.0174 gmol/min, 0.0395 gmol/min, 0.0764 gmol/min and 0.1216 gmol/min.

All these experiments were performed keeping methanol/air temperature at $60\,^{0}C$ and lactic acid temperature at $95\,^{0}C$.

CHAPTER 4

RESULTS AND DISCUSSIONS

In the present study, application of the ion exchange resins, to the esterification reaction of lactic acid with methyl alcohol as heterogeneous acid catalyst was studied.

$$C_3H_6O_3 \;+\; CH_3OH \;\xrightleftharpoons[k_2]{k_1}\; C_3H_8O_3 \;+\; H_2O \;\ldots\ldots\ldots\; I$$

Lactic Acid   Methanol   Methyl Lactate   Water

$$C_6H_{10}O_5 \;+\; H_2O \;\xrightleftharpoons[k_4]{k_3}\; 2C_3H_6O_3 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; II$$

Lactoyl   Water k_4 Lactic Acid
Lactic Acid
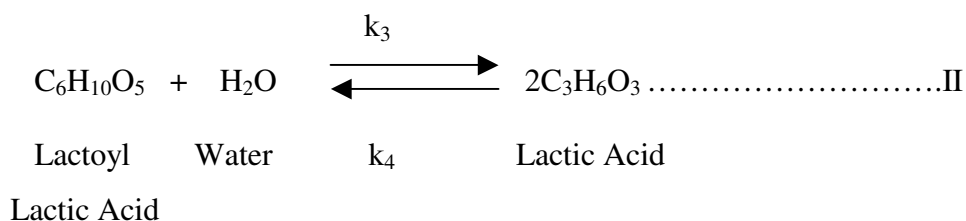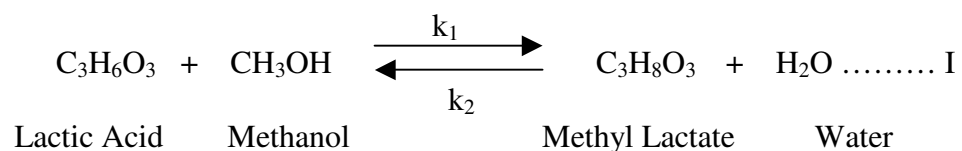
In the first part of the experiments, kinetic analysis were performed on the basis of estimating homogeneous and heterogeneous reaction rate constants by non-linear estimation procedures using the differential form of reaction rate equation.

Kinetic parameters such as temperature, conversion, catalyst, molar ratio and side reactions were determined in a series of experiments and reaction rate constants were analyzed. Moreover, the hydrolysis reaction of lactoyllactic acid was investigated.

In the second part, the effects of methanol and lactic acid feed rate, temperature and concentration of lactic acid solution were determined in order to find out whether the reaction mechanism is mass transfer controlled or reaction controlled.

4.1 REACTION EXPERIMENTS

Lewatit SPC-112-H$^+$ ion exchange resin was used as the test catalyst. Temperature, reactant molar ratio and catalyst, which were the investigated parameters, helped us to understand the behavior of the reaction system.

The results were reported in terms of molar conversions, calculated by the combined procedure of the data obtained both from titration and gas chromatographic analysis. The concentration of Methyl alcohol, water and methyl lactate which were determined by the gas chromatography, were at lactic acid and lactoyllactic acid free basis. A triple calibration routine, based on estimating the relative response factors respectively, was performed in order to couple with the weight percent lactic acid titration data. Corresponding molar conversions were calculated in this way resulting in 99% accuracy in the carbon balance. The details of the calculation procedure are given in Appendix B.

Lactic acid and methyl alcohol consumption produces methyl lactate and water, as the reaction proceeds. Additional lactic acid formation also favors the methyl lactate formation, since water formed from the lactic acid esterification increases the lactoyllactic acid hydrolysis.

4.1.1 Effect of Temperature

Inefficient sampling due to methanol vaporization was observed above 70 ^{0}C, for the tested reaction temperatures between 40 ^{0}C and 85 ^{0}C. Therefore, 70 ^{0}C was chosen as the maximum working temperature for the lactic acid esterification. The effect of temperature on the esterification reaction of lactic acid and methanol is shown in Figure 4-1.
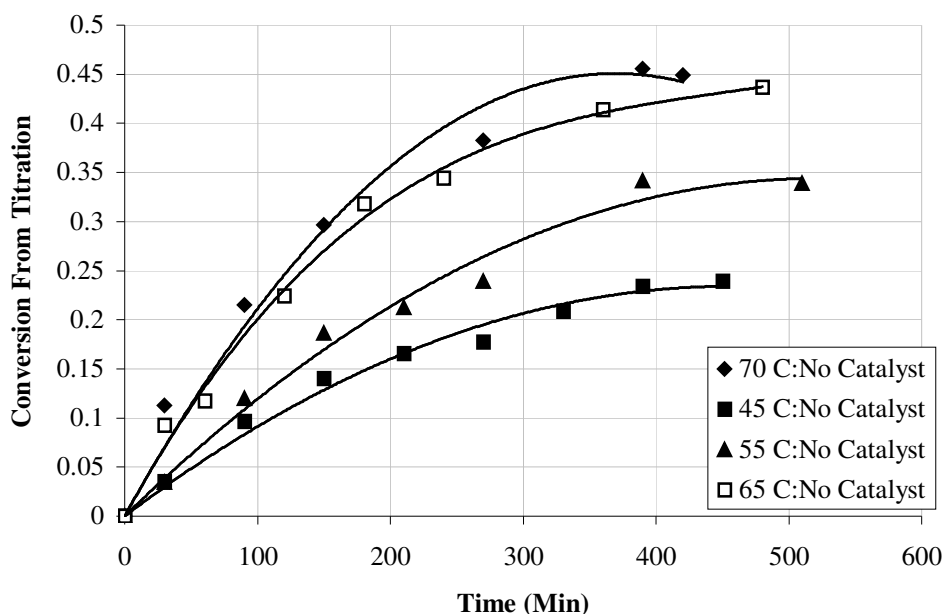
Figure 4-1 Conversion of Lactic Acid 1:1 molar ratio in the absence of catalyst.

As it can be seen from the figures, increasing temperature increases the conversion. At 40 ^{0}C the reaction reaches equilibrium at nearly 0.25 conversion whereas at 70 ^{0}C, the reaction reaches equilibrium at nearly 0.45 conversion.

In addition to the obtained molar conversions, product distribution curves, as molar concentrations, with respect to the reaction time were obtained. The species concentrations at the temperatures 40 ^{0}C, 70 ^{0}C in the absence catalyst runs are shown in Figure 4-2 and Figure 4-3
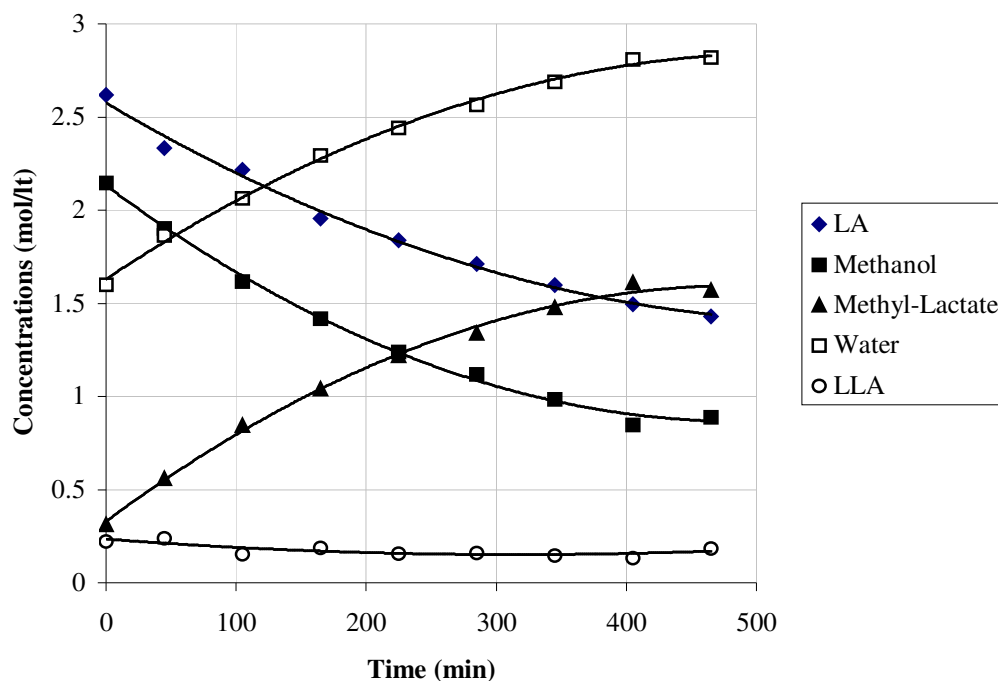
Figure 4-2 Species concentrations vs. time data   at 40 ^{0}C, 1:1 reactant Molar Ratio in the absence of catalyst
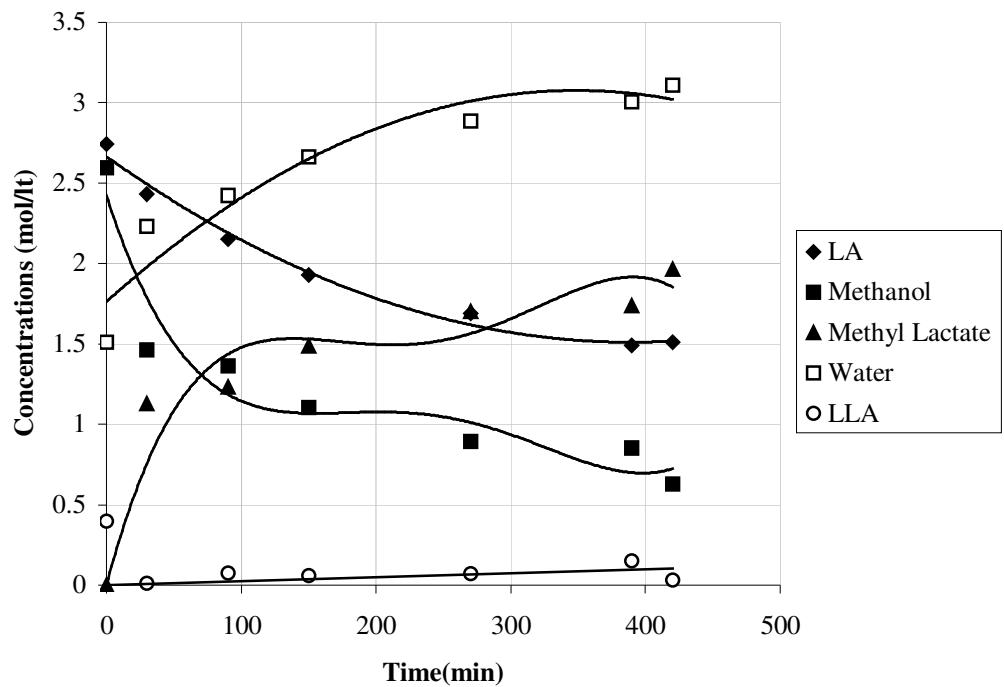
Figure 4-3 Species concentrations vs. time data at 70 ^{0}C, 1:1 reactant Molar Ratio in the absence of catalyst

Increasing H_2O but almost constant Lactoyllactic acid indicate that Reaction I in k_1 direction is favored.

4.1.2 Effect of Catalyst

In order to see the effect of catalyst in the reaction rate methyl alcohol to lactic acid molar ratio was kept at 1:1.

The catalyst had an acceleration effect on the reaction rate and therefore the reaction reaches equilibrium in a shorter time as it can be seen from the runs that are shown in Figure 4-4. In addition, the conversions also shifted up.
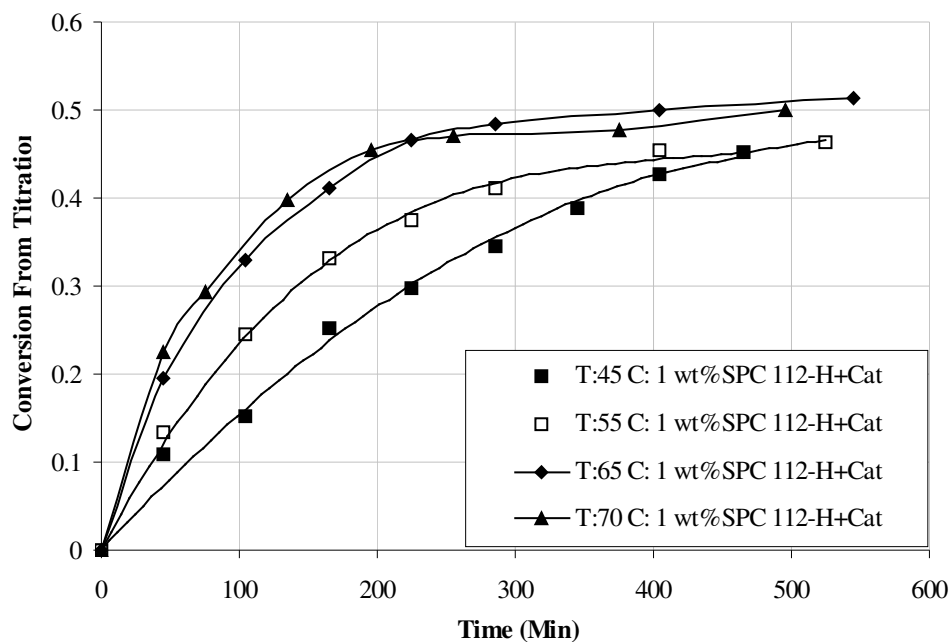
Figure 4-4 Conversion of Lactic Acid 1:1 molar ratio and 1 wt% Lewatit SPC 112 H$^+$ Catalyst Concentration

In addition to the obtained molar conversions, product distribution curves, as molar concentrations, with respect to the reaction time were obtained. Temperature 40 ^{0}C, 70 ^{0}C with catalyst Lewatit SPC 112 runs are shown in Figure 4-5, and Figure 4-6.
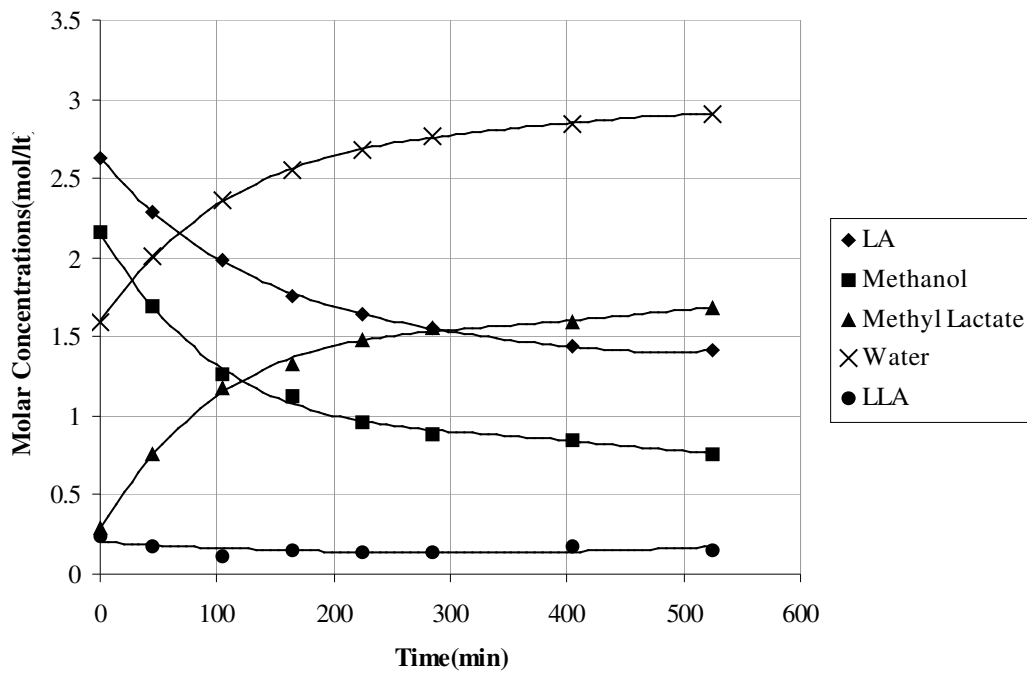
Figure 4-5 Species concentrations vs. time data at 45 ^{0}C, 1:1 reactant Molar Ratio and 1 wt% Lewatit SPC-112-H$^+$ Catalyst Concentration.
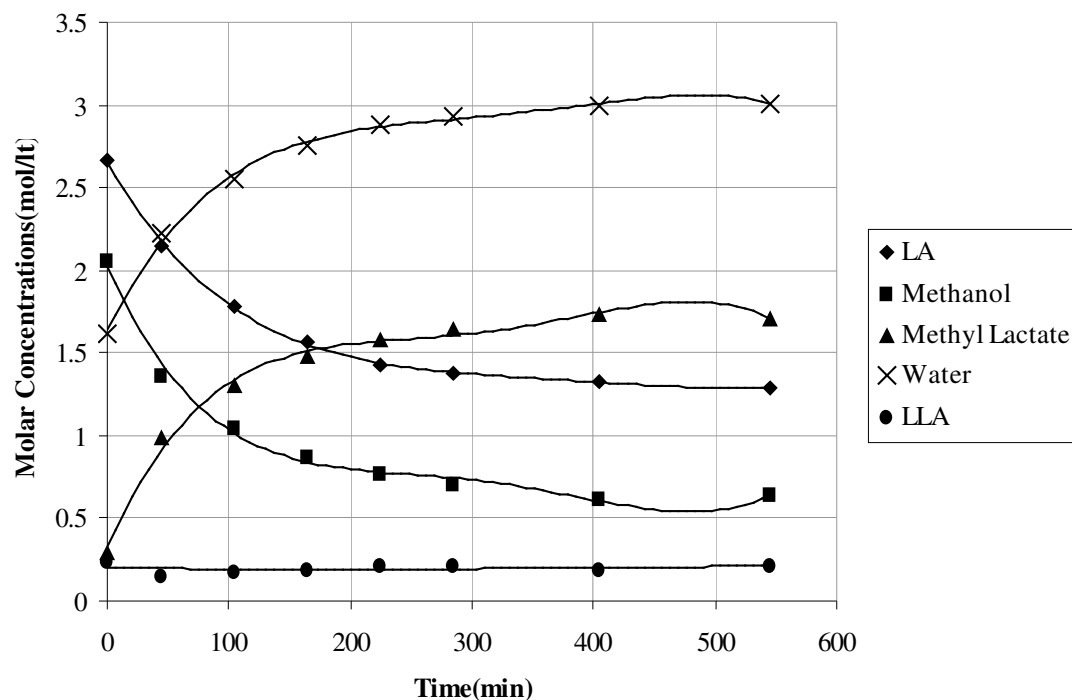
Figure 4-6 Species concentrations vs. time data at 70 ^{0}C, 1:1 reactant Molar Ratio and 1 wt% Lewatit SPC-112-H$^+$ Catalyst Concentration.

The studies which are done at 50^{0}C and 60 ^{0}C in the absence of catalyst and with Lewatit SPC 112-H$^+$ figures can be seen in the Appendix B

4.2 LACTOYLLACTIC ACID HYDROLYSIS

Lactoyllactic acid, which is a normal component of aqueous lactic acid, exists at different amounts, in all forms of lactic acid solutions in a dynamic equilibrium with water. Total acidity of the solution expressed as lactic acid was found to be 92-wt %, with 73-wt % free acidity and 19 wt % polymeric acid under lactoyllactic acid form.

The hydrolysis reaction of lactoyllactic acid was studied under the reaction time and temperature conditions, at varying amount of initial water concentrations about 48 hours and 50 ^{0}C, 60 ^{0}C, 70 ^{0}C respectively, in the presence of catalyst. The catalyst did not affect the dynamic equilibrium of the crude lactic acid, lactoyllactic acid and water solution. It was seen that dilution enables the hydrolysis of lactoyllactic acid to lactic acid and accelerates the equilibration in Figure 4-7, Figure 4-8 and Figure 4-9

Lactoyllactic acid hydrolysis is a slow reaction and the rate-limiting step in the methyl lactate formation under excess alcohol concentration.
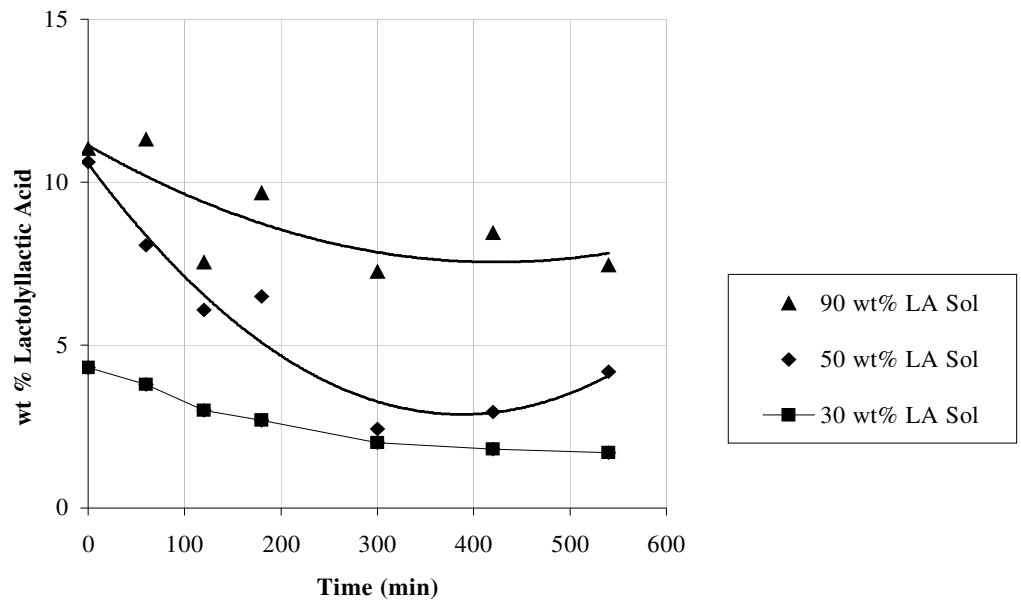
Figure 4-7 Lactoyllactic acid hydrolysis at 50 ^{0}C, for 30%, 50% and 90% Lactic Acid Concentrations
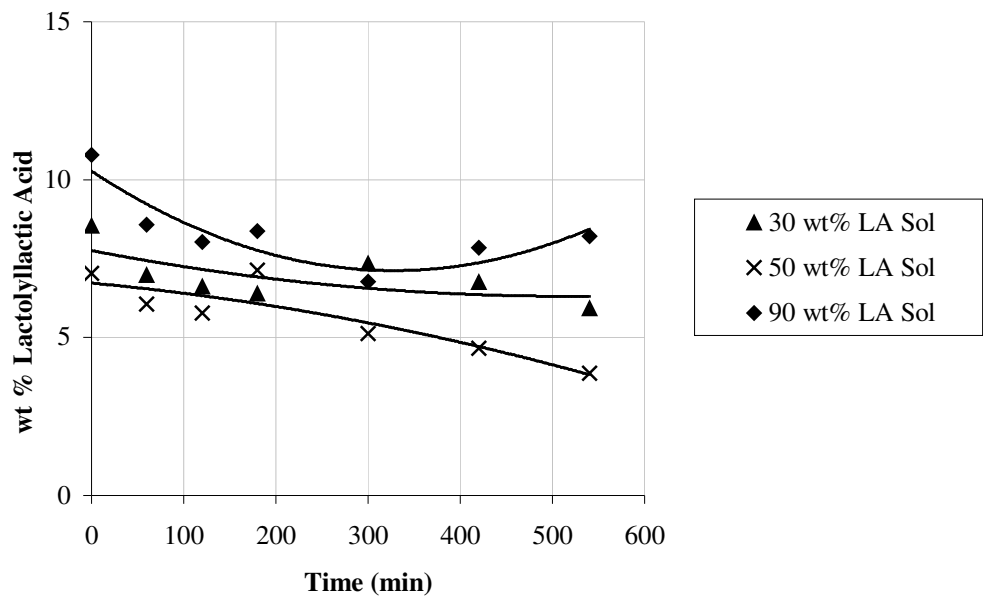
Figure 4-8 Lactoyllactic acid hydrolysis at 60 ^{0}C, for 30%, 50% and 90% Lactic Acid Concentrations
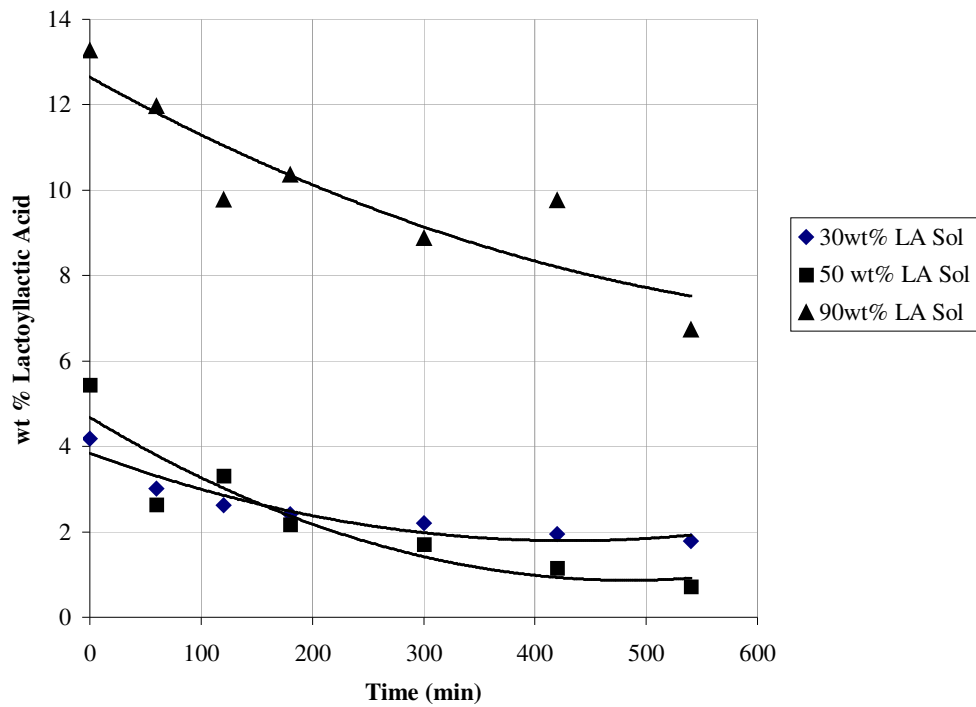
Figure 4-9 Lactoyllactic acid hydrolysis at 70 ^{0}C, for 30%, 50% and 90% Lactic Acid Concentrations

4.3 ESTERIFICATION KINETICS

In the first part of the experiments the esterification reaction of lactic acid with methanol was carried out in a batch reactor, where as in the second part of the experiments the esterification reaction of lactic acid with methanol was carried out in a fixed bed reactor.

4.3.1 Batch Reactor Experiments

The general form of the mole balance is as follows:

$$\frac{dNj}{dt} = \int_V rj dV$$

The variations in the rate of reaction through out the reactor volume were neglected by assuming no density change of reaction medium with conversion and negligible sample withdrawal . Then balance equation becomes;

$$\frac{dNj}{dt} = rj.V$$

Reactor mole balance is expressed as follows with the constant –volume reactor assumption;

$$\frac{1}{V}\frac{dNj}{dt} = \frac{d(Nj/V)}{dt} = \frac{dCj}{dt} = rj$$

For the proposed esterification reactions, which are both reversible, construction of the stoichiometric table written as follows:

Table 4-1 Stoichiometric Table

Species	Initial (mole)	Change (mole)	Final (mole)
LA	N_{LA0}	$- N_{LA0}.X_1 + 2. N_{LLA0}.X_2$	$N_{LA} = N_{LA0} - N_{LA0}.X_1 + 2. N_{LLA0}.X_2$
MetOH	N_{MetOH0}	$- N_{LA0}. X_1$	$N_{MetOH} = N_{MetOH0} - N_{LA0}. X_1$
Methyl Lactate	N_{Ester0}	$+ N_{LA0}. X_1$	$N_{Ester} = N_{Ester0} + N_{LA0}. X_1$
H_2O	N_{H2O0}	$+ N_{LA0}. X_1 - N_{LLA0}.X_2$	$N_{H2O} = N_{H2O0} + N_{LA0}. X_1 - N_{LLA0}.X_2$
LLA	N_{LLA0}	$- N_{LLA0}.X_2$	$N_{LLA} = N_{LLA0} - N_{LLA0}.X_2$

The rate of disappearance of lactic acid can be written as follows:

$$-\frac{dCLA}{dt} = k_1.C_{LA}.C_{MethOH} - k_2.C_{Meth.Lact}.C_{H_2O} - k_3 .C_{LLA}.C_{H_2O} + k_4.C_{LA}^2$$

k_1 and k_2 are forward and backward overall reaction rates of esterification reaction of Lactic acid and Methanol and k_3 and k_4 are forward and backward overall reaction rates of reaction of Lactoyllactic acid hydrolysis.

In the present study, analyzing rate data was performed by means of a computational non-linear regression analysis, with the help of a program package Statistica[TM].

Nonlinear Estimation contains several function minimization methods that can be used to minimize any kind of loss function. Quasi Newton and the Hooke-Jeeves Pattern Moves methods were used mainly, through out the determination of reaction rate constants.

The species concentrations are available as a function of time. Then species concentration versus time data was fitted by the use of a 3 parameter hyperbolic decay function and the rate of disappearance of species was calculated at each time interval.

$$C_i = yo + \frac{a.b}{b + Time(\min)}$$

$$-\frac{dCi}{dt} = \frac{a.b}{(b + Time(\min)^2)}$$

Species concentrations, the rate of lactic acid disappearance as the variables and the overall reaction rate constants are evaluated by entering the rate equation as a user defined regression equation.

By the use of 9 lactoyllactic acid experiments that are performed at different temperatures; 50^0C, 60^0C and 70^0C and at different lactic acid

concentrations; 30%, 50% and 90%, the homogeneous forward and backward reaction rate constants of lactoyllactic acid hydrolysis, k_3 and k_4 respectively, were estimated.

The resulting conversions at the 48th hour of experiment were taken as the equilibrium conversions for these reactions and used in calculating the corresponding equilibrium concentrations.

$$-\frac{dC_{LLA}}{dt} = k_3 . C_{LLA} . C_{H_2O} - k_4 . C_{LA}{}^a$$

By using the outlined procedure, rate equation of lactoyllactic acid hydrolysis was fitted for estimating the rate constants at different temperatures. The results are listed in Table 4-2, Table 4-3 and Table 4-4 respectively.

Table 4-2 Rate Constants and Equilibrium Constants of Hydrolysis Reaction of Lactoyllactic Acid at 50^{0}C

	Lactic Acid Concentrations		
	30%	**50%**	**90%**
k_3 (lt/mol.min)	$37.8*10^{-6}$	$36.9*10^{-6}$	$37.6*10^{-6}$
k_4 (lt/mol.min)	$3.6*10^{-6}$	$3.9*10^{-6}$	$3.6*10^{-6}$
K_{eq}	10.5	9.5	10.4

Table 4-3 Rate Constants and Equilibrium Constants of Hydrolysis Reaction of Lactoyllactic Acid at 60^0C

	Lactic Acid Concentrations		
	30%	50%	90%
k_3 (lt/mol.min)	$38*10^{-6}$	$38.4*10^{-6}$	$38.8*10^{-6}$
k_4 (lt/mol.min)	$4.2*10^{-6}$	$4.16*10^{-6}$	$3.7*10^{-6}$
K_{eq}	9.0	9.2	10.5

Table 4-4 Rate Constants and Equilibrium Constants of Hydrolysis Reaction of Lactoyllactic Acid at 70^0C

	Lactic Acid Concentrations		
	30%	50%	90%
k_3 (lt/mol.min)	$41.7*10^{-6}$	$42.6*10^{-6}$	$43*10^{-6}$
k_4 (lt/mol.min)	$5.4*10^{-6}$	$5.58*10^{-6}$	$5.36*10^{-6}$
K_{eq}	7.7	7.6	8.0

As it was seen from the tables the concentration did not affect lactoyllactic acid hydrolysis and this shows the accuracy of the experiments and the regression.

Finally, the average values of the overall rate constant of lactoyllactic acid hydrolysis experiments are tabulated in Table 4-5.

Table 4-5 Average values of Rate Constants and Equilibrium Constants of
Hydrolysis Reaction of Lactoyllactic Acid at 50^0C, 60^0C and 70^0C

Temperature	Over all rate constants		Equilibrium Constants
	k_3 (lt/mol.min)	k_4(lt/mol.min)	K_{eq}
50^0C	$37.44*10^{-6}$	$3.6*10^{-6}$	10.4
60^0C	$39.06*10^{-6}$	$4.2*10^{-6}$	9.3
70^0C	$42.4*10^{-6}$	$5.4*10^{-6}$	7.9
70^0C (engin)	$43.0*10^{-6}$	$5.38*10^{-6}$	8.0

E. Aytürk studied the esterification reaction of lactic acid with ethanol. As
it can be seen from the results the hydrolysis reaction of Lactoyllactic acid is free
from alcohol type.

The equilibrium constant decreases with increasing temperature that means
the reaction is an exothermic reaction. Activation energy value of this reaction is
calculated as 18679.93 j/mol. Then at temperature 95^0C the rate constants and the
equilibrium constant are calculated as; k_3, $78.0*10^{-6}$ lt/mol.min, k_4, $17.0*10^{-6}$lt/mol.min. and 4.6 respectively.

4.3.1.1 Temperature Effect

For the homogeneous reaction, in the absence of catalyst, forward and
backward homogeneous reaction rate constants, k_1 and k_2 values of the esterification
reaction of lactic acid and methanol were evaluated. The calculated values are
tabulated below.in Table 4-6

Table 4-6 Rate Constants and Equilibrium Constants of Esterification Reaction of Lactic acid and Methanol at 40^0C, 50^0C, 60^0C and 70^0C in the absence of catalyst at 1:1 molar ratio

Temperature	Over all rate constants		Variance of regression	Equilibrium Constant(K_{eq})
	k_1 (lt/mol.min)	k_2(lt/mol.min)		
40^0C	$108.5*10^{-6}$	$23.08*10^{-6}$	97.443	4.7
50^0C	$134.2*10^{-6}$	$43.29*10^{-6}$	86.741	3.1
60^0C	$160.5*10^{-6}$	$64.20*10^{-6}$	84.858	2.5
70^0C	$185.6*10^{-6}$	$93.11*10^{-6}$	92.868	1.9
70^0C (49)	$175.0*10^{-6}$	$104.0*10^{-6}$	-	1.7

As it can be seen from the above table the results at 70^0C for the esterification reaction of lactic acid with methanol and the esterification reaction of lactic acid with ethanol are very close to each other therefore it can be said that ethyl lactate formation reaction is a similar reaction with methyl lactate formation reaction. Increase of temperature increases the reaction rate and decreases the equilibrium constant.

4.3.1.2 Catalyst Effect

For the heterogeneous reaction, in the presence of catalyst, which is the heteropoly acid loaded SPC112-H$^+$, forward and backward heterogeneous reaction rate constants, k_1 and k_2 were evaluated. The calculated values are tabulated below in Table 4-7

Table 4-7 Rate Constants and Equilibrium Constants of Esterification Reaction of Lactic acid and Methanol at 40^0C, 50^0C, 60^0C and 70^0C with the Catalyst 1wt% Lewatit SPC 112–H^+

| Temperature | Over all rate constants | | Variance | Equilibrium Constant |
	k_1 (lt/mol.min)	k_2(lt/mol.min)		(K_{eq})
40^0C	$136.5.*10^{-6}$	$25.27*10^{-6}$	98.137	5.4
50^0C	$169.5*10^{-6}$	$39.42*10^{-6}$	86.464	4.3
60^0C	$188.2*10^{-6}$	$52.28*10^{-6}$	84.713	3.6
70^0C	$223.1*10^{-6}$	$79.67.*10^{-6}$	90.408	2.8
95^0C	$254.1*10^{-6}$	$115.5*10^{-6}$	81.743	2.2

The catalyst enhances the reaction rate, increases the rate constants, decreases the equilibrium constants and therefore the reaction reaches equilibrium in a shorter time

The optimum reaction temperature is 70^0C. Similar to lactoyllactic acid hydrolysis reaction the esterification reaction of Lactic acid is an exothermic reaction; increasing temperature decreases the equilibrium constant.

Equilibrium constants, obtained at two different reaction temperatures, were used to calculate the heat of reaction by using Van't Hoff equation.

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0_{rxn}}{R.T^2}$$

where;

ΔH^0_{rxn}:standard state enthalpy change for the reaction

R: ideal gas constant, 1.987 cal.mol^{-1}.K^{-1}

T: temperature in kelvins, K

With the assumption of heat of reaction is approximately independent of temperature, integrated form of the equation between T_2 and T_1 is as follows.

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta H_{rxn}^0}{R.} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

By using the above equation heat of reaction for lactic acid esterification with methanol is calculated as:

ΔH_{rxn}^0: -3146.6 cal/mol

Calculated value for heat of reaction is in a good agreement indicating an exothermic reaction, where equilibrium constant decreases with the increasing temperature.

4.3.2 Counter-Current Reaction System Experiments

In the second part of the present study, the possible production process of methyl lactate was investigated. As it was presented in introduction section and as it was discussed on the previous section, the esterification of lactic acid with lower alcohols has some difficulties on the separation of water to shift equilibrium conversion to the complete conversion. The separation of water in the presence of low boiling alcohol (e.g. methanol (n.b.p.= 64.5˚C)) seems very difficult because of low vapor pressure of water at the boiling point of alcohol (0.24 bar at 64.5˚C). Thus, in order to remove water with a conventional ways such as distillation from such a mixture requires elevated reaction temperatures, which is not a best choice because of possible decomposition reactions of lactic acid above 90˚C. So it is not

possible to keep reaction mixture for a long time at such a high temperature to achieve complete conversion. A typical lay-out of such a system is given in Figure 4-10.
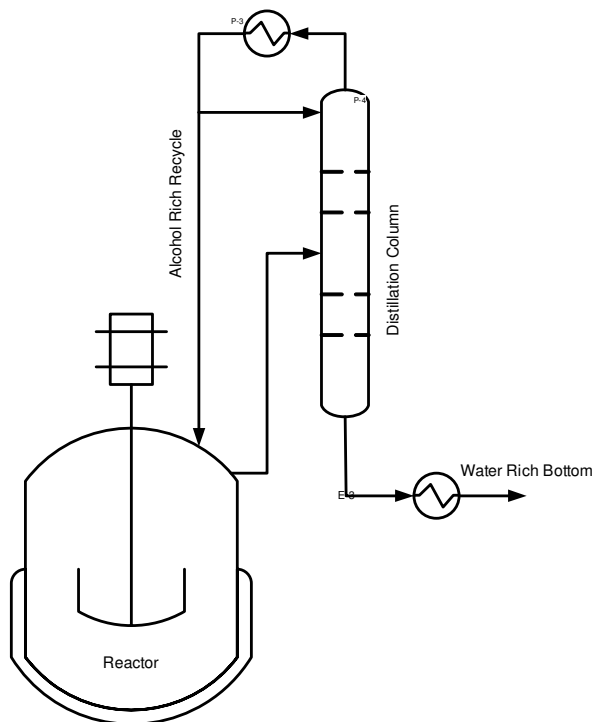
Figure 4-10 Semi-batch reactor with distillation column.

In the conventional esterification processes, where low boiling point alcohols are utilized with higher boiling point carboxylic acids and esters, azeotropic distillation columns are integrated into the semi-batch reactors. In this method, the boiling point of azeotropic mixture of alcohol-water mixture is broken with the addition of aromatic solvents such as toluene or some amine derivatives. This process is not suitable for lactic acid process because of the inevitable trace impurities of aromatics or amines are not tolerable for food grade products and green

chemistry considerations. One successful possibility as membrane separation was also studied İnal (2003).

The other possibility is the reactive distillation process where lighter components are separated and reaction proceeds simultaneously within the same unit. The most obvious advantages of such a process are the possibility of lower residence time on the distillation temperature and in-situ separation of the reaction products which may help to shift equilibrium conversion as well as economics.

On the other hand the lactic acid which has no boiling point cannot be fed into any distillation system. One solution could be the counter-current column which operates in a similar way of absorption column where the lactic acid is fed to the column from top and contact with methanol vapor. The packing for such a column can be selected to improve mass transfer from vapor phase alcohol to the acid rich liquid film where the reaction proceeds homogeneously (non-catalytic) or the solid heterogeneous catalyst may serve as packing as well. As it will be figured out easily, such a system can be named as absorption process where alcohol solute in carrier gas solvent is absorbed by liquid film which is comprised of non-volatile carboxylic acid and the less volatile reaction product ester. The other volatile liquid specie, which is water, is also transferred into the vapor-gas phase. However there are few publications existing in the literature regarding the operation of reaction with absorption and almost all of the previous studies are on the non-catalytic inorganic acid-base reactions over the commercial non-catalytic packings which are developed for gas scrubbing and stack gas cleaning applications. Danckwerts studied the gas-liquid reactions in 1970 (53) and Astarita et al. studied in 1983 (54).

As the second part of this study, the viability of such column was investigated. The process is illustrated in Figure 4-11.
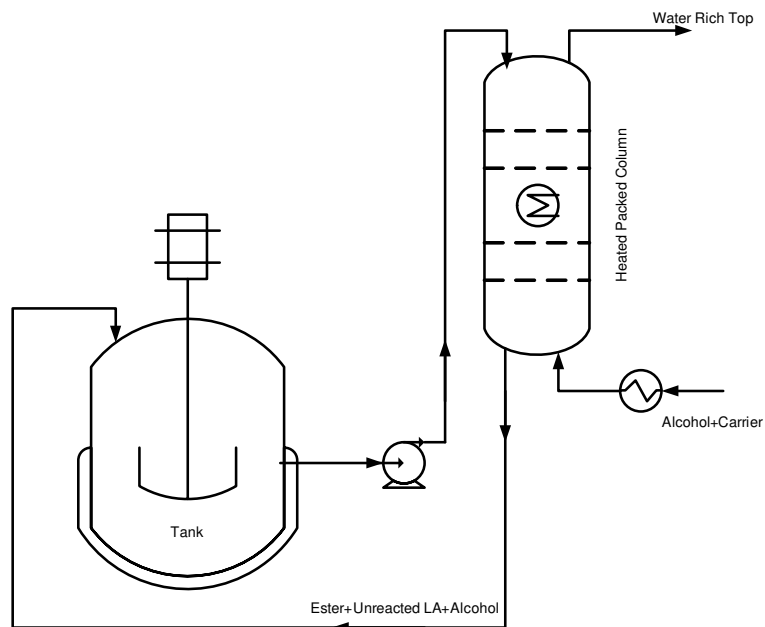
Figure 4-11 Proposed counter current reactor system.

As it is shown in Figure 4-11, the tank which is initially filled with lactic acid is fed to a heated catalyst-packed column and contacted with alcohol vapor stream in a counter-current configuration. The inert carrier such as air or in the present of oxidative decomposition of reaction species, an inert gas such as N_2 can be also fed with alcohol vapor to enhance water removal from the column. The liquid stream from the bottom of the tank is re-cycled back to the tank and circulation of the liquid species in the tank over the column is terminated when the desired conversion is achieved. Any excess alcohol accumulation in the system can be handled resolved by controlled feed ratio of alcohol/carrier gas or at the end, volatile alcohol could be easily removed by vacuum and/or evaporation. Another

foreseen advantage of the proposed system is the operability of the system with dilute lactic acid feeds, which might be coupled easily to a fermentation system so that in-situ water evaporation and reaction operations take place. Another important advantage of such configuration might be higher fractional conversion than the equilibrium conversion because of the counter-current contact of the species with higher and conserved concentration differences along the column.

In order to check the viability of the proposed process, the counter current column which is packed by the catalyst Lewatit SPC 112 H [+]was tested under different conditions. The 25 cm long 2 cm I.D. Pyrex column was packed with ion exchange resin. The flow layout of the system is depicted in Figure 4-12.
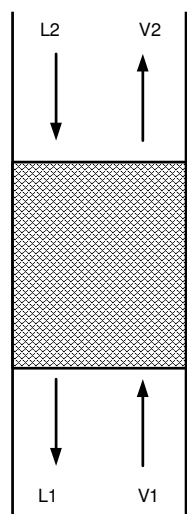
Figure 4-12 Flow pattern of the counter-current reaction system

During these experiments, effect of lactic acid feed (L2) flow rate, lactic acid feed concentration, and methanol vapor feed (V1) flow rate were tested as a parameter under the constant column packing height and diameter. During these experiments temperature was also kept constant with a water jacket at 90°C. Dry air was utilized as an inert carrier and methanol was evaporated by using saturator which was kept at 60°C water bath. On each experiment, the samples collected from liquid outlet stream (L1) were weighted with respect to time to calculate Liquid product flow rate, and the composition of the liquid product (L1) stream were measured by titration and GC analysis of the samples as it is described in the experimental section. Similarly, methanol feed rate was measured with respect to time by weighting saturator bottle, and air flow rate was also measured on each experiment. The experimental setup is shown in Figure 3-1. The vapor exit stream

which is supposed to be comprised of air (inert), water and residual methanol was calculated using the stoichiometry around the overall system. The quality of experimental measurements were tested by carrying out C, O and H balance around the system and as it is shown in Appendix C. The value for the confidence limits of the majority of the experimental results are within the range of 95-100% for C, and O. The worst results were obtained for H which deviates 33% in some cases which is also in acceptable limits because of low molecular weight of hydrogen and the presence of low and high molecular weight species on the same system. From the experimental results the reactor performances were examined by the evaluating the water separation (evaporation) rate, methanol uptake rate to the liquid phase and steady state conversion of lactic acid.

4.3.2.1 Effect of Lactic Acid Concentration

The effect of lactic acid concentration on the reactor performance was tested under the constant flow-rates of lactic acid solution. During these experiments, the methanol concentration and flow rates were also kept constant. The lactic acid flow-rates were kept constant as much as possible within the range of 0.46-0.51 g/min with various lactic acid stock solutions within the wide range of 9 to 90 wt%. In all experiments, the air flow rate as an inert carrier was kept at 354 ml/min and 2.4 g/min of methanol vapor feed was obtained as a result of saturation at 60˚C and fed to the reactor. The detailed experimental parameters, and analysis results are shown in Table 4-8.

Table 4-8 Effect of lactic acid feed concentration on the reactor performance

FEED COMPOSITION (wt %)				PRODUCT COMPOSITION (wt %)						FLOW RATES (g/min)				LACTIC ACID CONVERSION %
Liquid Feed, L2		Vapor Feed V1		LIQUID PRODUCT, L1				VAPOR PRODUCT, V2(*)		INLET		OUTLET		
Lactic Acid	Water	Methanol	Air	Lactic Acid	Methanol	Methyl Lactate	Water	Methanol	Water	L2	V1	L1	V2	
9.0	91.0	15.0	85.0	6.10	15.30	15.70	62.80	88.98	11.02	0.46	2.83	0.21	3.08	69.0
27.0	73.0	15.0	85.0	19.90	10.32	12.38	57.40	95.26	4.74	0.48	2.83	0.42	2.88	35.0
45.0	55.0	15.0	85.0	18.75	22.04	9.71	49.50	100.00	n.d.	0.49	2.83	0.81	2.50	30.9
63.0	37.0	15.0	85.0	33.99	25.96	8.65	31.40	100.00	n.d.	0.51	2.83	0.77	2.56	18.0
90.0	10.0	15.0	85.0	37.61	38.70	5.49	18.20	100.00	n.d.	0.46	2.83	0.97	2.31	11.2

FEED COMPOSITION (mole %)				PRODUCT COMPOSITION (mole %)						FLOW RATES (gmoles/min)				LACTIC ACID CONVERSION %
Liquid Feed, L2		Vapor Feed V1		LIQUID PRODUCT, L1				VAPOR PRODUCT, V2		INLET		OUTLET		
Lactic Acid	Water	Methanol	Air	Lactic Acid	Methanol	Methyl Lactate	Water	Methanol	Water	L2	V1	L1	V2	
1.9	98.1	15.0	85.0	1.62	11.41	3.60	83.37	81.94	15.30	0.0237	0.0897	0.0088	0.1020	69.0
6.9	93.1	15.0	85.0	5.74	8.36	3.09	82.81	87.72	6.58	0.0209	0.0897	0.0163	0.0897	35.0
14.1	85.9	15.0	85.0	5.57	18.40	2.49	73.54	100.00	n.d.	0.0174	0.0897	0.0304	0.0701	30.9
25.4	74.6	15.0	85.0	12.51	26.87	2.76	57.86	100.00	n.d.	0.0141	0.0897	0.0234	0.0745	18.0
64.3	35.7	15.0	85.0	15.53	44.91	1.96	37.60	100.00	n.d.	0.0072	0.0897	0.0263	0.0644	11.2

(*) Air free basis

As it is seen from the Table 4-8 for all lactic acid concentrations, both top and bottom composition of the column represents the excess methanol cases. When liquid exit stream (L1) is considered, the molar ratio of methanol to lactic acid varied between 7.1 and 1.4. It was also observed that when feed lactic acid concentration increased, the molar ratio of methanol to lactic acid in L1 stream is also decreases as a result of lower conversion levels at the higher lactic acid feed concentrations. The steady state fractional conversion of lactic acid versus feed lactic acid concentration is shown in Figure 4-13
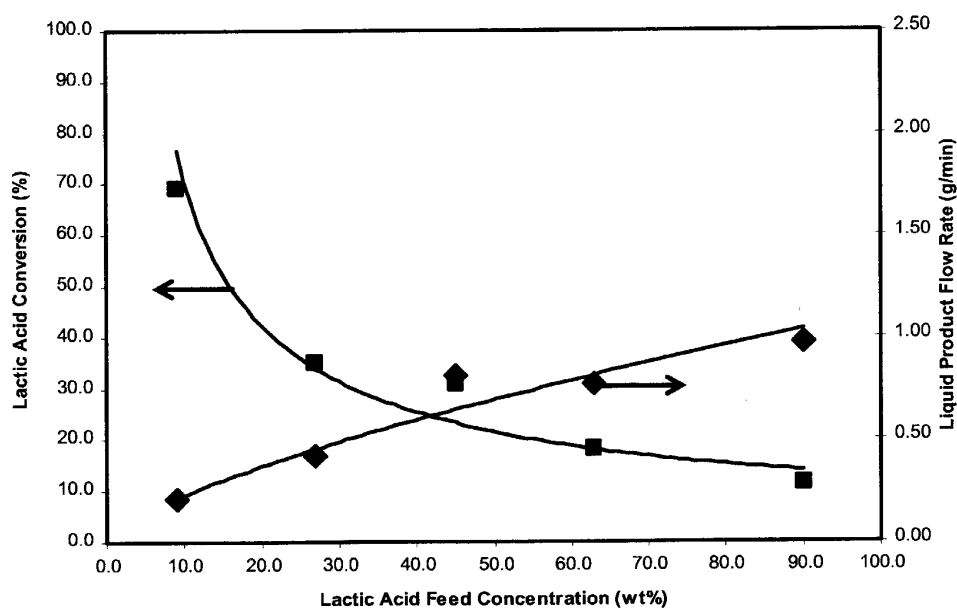
Figure 4-13 Effect of lactic acid fee concentration on steady state conversion and Liquid product (L_1) flow rate

In this set of experiments, maximum steady state conversion was obtained at 9 wt% initial lactic acid concentration as 69%. This value is quite satisfactory for esterification reactions, however the conversion level diminishes drastically with

increasing lactic acid feed concentrations. At 90 wt% feed concentration, 11% conversion was observed. On the other hand, the mass flow rate of the liquid outlet stream L1 increases with increasing feed lactic acid concentration because of the less water (volatile) content of the feed stream. Higher concentrations of lactic acid feeds perform higher liquid outlet flow rates, which results in smaller residence time over the packing, and results with lower conversions. When the effect of feed lactic acid concentration over the methanol uptake from the vapor phase is considered, it is very obvious from the Figure 4-14 that, more methanol is absorbed by the liquid phase with increasing feed concentration of lactic acid, because of higher mole fractions of methanol in the vapor phase because of the less water is evaporated and less conversion is achieved at higher lactic acid concentrations as a result of smaller residence time over the column.
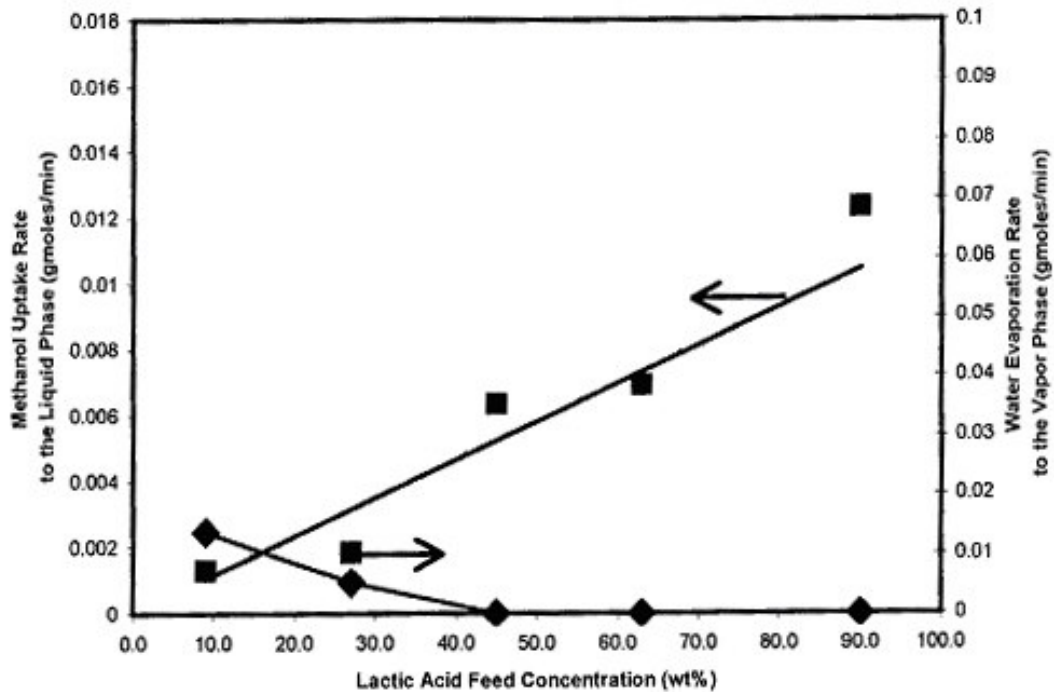
Figure 4-14 Effect of lactic acid feed concentration on methanol uptake rate to the liquid phase and water evaporation rate to the vapor phase

As it is seen from Figure 4-14 the water concentration on the liquid exit stream decreases with increasing feed concentration. Also the increase of lactic acid concentration may cause increase in the viscosity which will yield thicker liquid film around the solid catalyst packing. Another reasonable possibility is the increase of liquid film thickness as a result of higher liquid flow rates and shorter contact times which may also cause higher hold-up of the liquid and gas phase in the column. In literature, very little information is given for column hydraulics for gas-liquid contact over micro-porous and/or macro reticular packings. The liquid film thickness may cause higher mass transfer resistance if the mass transfer of methanol within the lactic acid medium is controlling the overall mechanism. However, the

increased amount of methanol concentration on the liquid phase validates that reaction is much slower step than the mass transfer of methanol from gas phase to the liquid phase and mass transfer resistance in liquid phase is generally much smaller than the mass transfer resistance in vapor phase. However, in spite of less water is added with lactic acid feed with increasing feed concentration, water which is transferred to the vapor+inert carrier stream decreases drastically. This can be explained by the hydrophilic nature of the lactic acid which is the common property of all carboxylic acids. Thus increasing the acid content of the column, the mass transfer of water to the vapor phase is limited. At the present point, the esterification reaction in counter current gas-liquid column performs very different picture than the single phase conventional co-current catalytic tubular reactors where the liquid and/or vapor stream flows along the reactor with pressure gradient. However, the absorption column configuration, vapor/gas phase flows from the bottom of the column to the top with a pressure gradient while the liquid phase flow through the reactor from top to bottom (counter-current) with gravitational forces. However, the single phase tubular reactor will perform much better performance on the conversion per pass with the increase of reactant feed concentrations (assuming reaction rate order is greater than zeroth order) without regarding whether the reaction is limited by equilibrium or not.
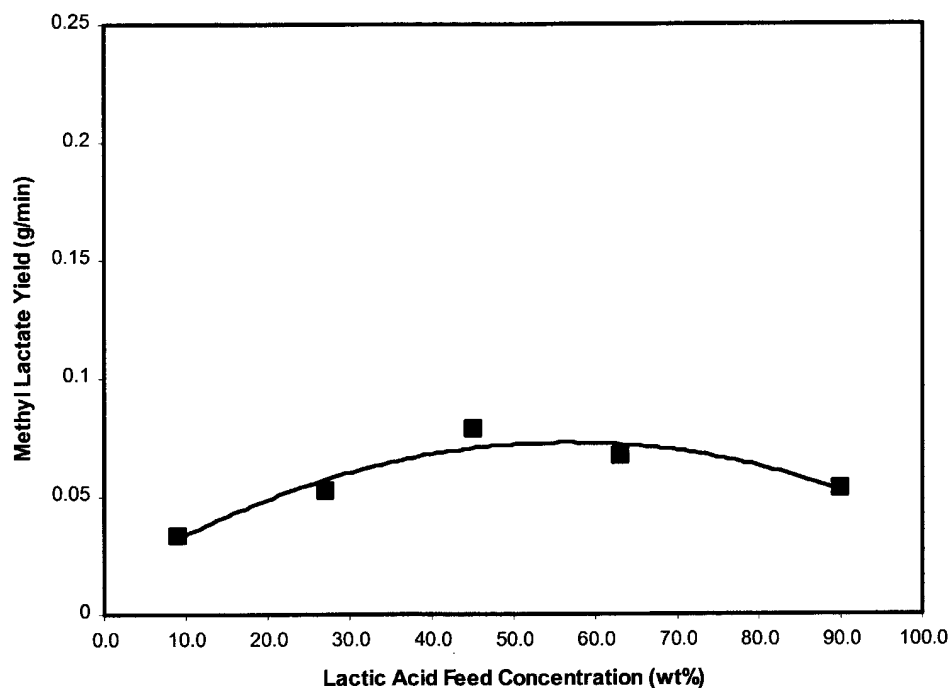
Figure 4-15 Effect of lactic acid feed concentration on methyl lactate yield

In Figure 4-15 the change of methyl lactate yield (g/min) with lactic acid feed concentration is shown. As it is seen from the figure, methyl lactate yield slightly increases first with increasing the feed lactic acid concentration and then slightly decrease. On the first part, where the methyl lactate yield increase with lactic acid feed concentration, liquid exit stream flow rate also increases from 0.21 to 0.81 g/min, which means increasing feed concentration kinetically favors the reaction in spite of the less residence time. The second regime, where methyl lactate yield decreases with lactic acid feed concentration, the mass flow rate of the liquid outlet stream increase slightly from 0.81 to 0.97 g/min which means more material is entrained within the column where viscosity effect causes larger film thickness and reaction is limited with mass transfer.

73

4.3.2.2 Effect of Lactic Acid Feed Flowrate

In order to understand better the kinetic and mass transer limitations of the methyl lactate formation reaction in the counter-current gas-liquid contactor, effect of lactic acid feed flow rate on the reactor performance was also examined. In this set of experiments, lactic acid feed concentration was kept constant at 45wt% and mass flow-rates of lactic acid feed were adjusted between 0.27-3.42 g/min. Air as an inert carrier and methanol mass flow-rates and concentrations in all experiments in this part were kept constant at the same values that are tested in the lactic acid feed concentration experiments as 354 ml/min air and 2.4 g/min of methanol. In these experiments, no flooding was observed within the flow rate range that was tested and steady state conditions were assessed. The experimental conditions and results are summarized in Table 4-9.

Table 4-9 Effect of lactic acid feed rate on the reactor performance

FEED COMPOSITION (wt %)				PRODUCT COMPOSITION (wt %)						FLOW RATES (g/min)				LACTIC ACID CONVERSION %
Liquid Feed, L2		Vapor Feed V1		LIQUID PRODUCT, L1				VAPOR PRODUCT, V2(*)		INLET		OUTLET		
Lactic Acid	Water	Methanol	Air	Lactic Acid	Methanol	Methyl Lactate	Water	Methanol	Water	L2	V1	L1	V2	
45.0	55.0	15.0	85.0	5.41	49.53	7.46	37.60	100.00	n.d.	0.27	2.83	1.02	2.07	54.4
45.0	55.0	15.0	85.0	18.75	22.04	9.71	49.50	100.00	n.d.	0.49	2.83	0.81	2.50	30.9
45.0	55.0	15.0	85.0	30.12	36.50	8.34	25.04	86.43	13.57	1.11	2.83	1.34	2.60	19.3
45.0	55.0	15.0	85.0	47.33	22.10	10.21	20.36	69.50	30.49	2.15	2.83	1.72	3.25	15.7
45.0	55.0	15.0	85.0	61.11	15.00	9.52	14.37	55.60	44.39	3.42	2.83	2.22	4.03	11.8

FEED COMPOSITION (mole %)				PRODUCT COMPOSITION (mole %)						FLOW RATES (gmoles/min)				LACTIC ACID CONVERSION %
Liquid Feed, L2		Vapor Feed V1		LIQUID PRODUCT, L1				VAPOR PRODUCT, V2		INLET		OUTLET		
Lactic Acid	Water	Methanol	Air	Lactic Acid	Methanol	Methyl Lactate	Water	Methanol	Water	L2	V1	L1	V2	
14.1	85.9	15.0	85.0	1.59	41.04	1.90	55.46	100.00	n.d.	0.0096	0.09	0.0386	0.0541	54.4
14.1	85.9	15.0	85.0	5.57	18.40	2.49	73.54	100.00	n.d.	0.0174	0.09	0.0304	0.0701	30.9
14.1	85.9	15.0	85.0	11.35	38.69	2.72	47.24	79.59	18.84	0.0395	0.09	0.0394	0.0885	19.3
14.1	85.9	15.0	85.0	21.50	28.22	4.01	46.27	64.01	42.33	0.0764	0.09	0.0421	0.1309	15.7
14.1	85.9	15.0	85.0	33.31	22.99	4.49	39.20	51.20	61.64	0.1216	0.09	0.0452	0.1854	11.8

(*) Air free basis
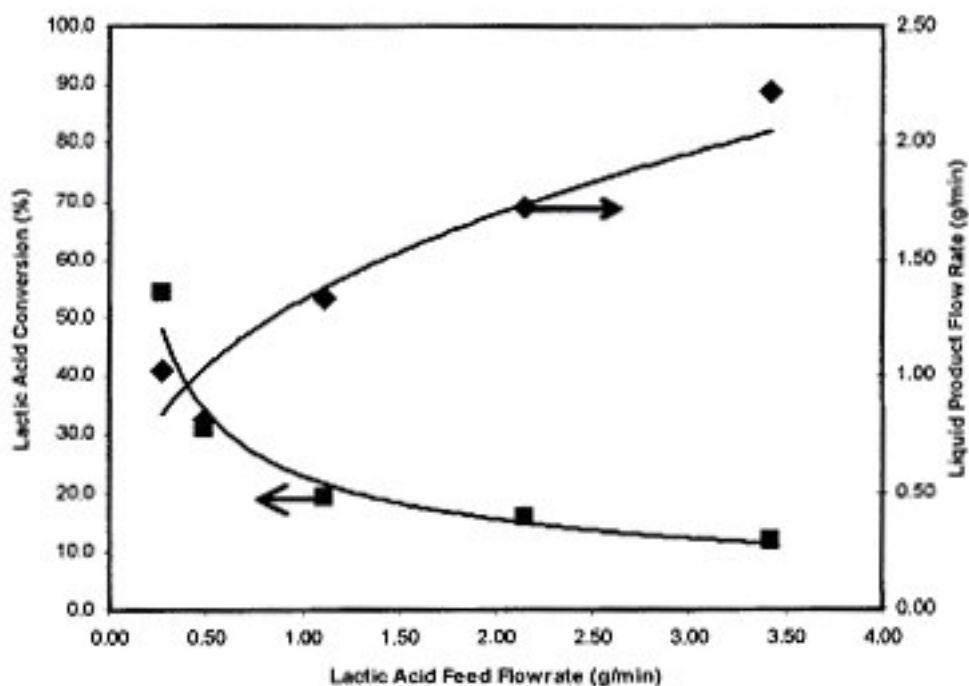
Figure 4-16 Effect of lactic acid feed flowrate on the lactic acid conversion and liquid product (L_1) flow rate

In Figure 4-16 the effect of lactic acid feed flow rate on the lactic acid conversion and resultant liquid product (L1) flow rate are shown. Similar trends to the case of lactic acid concentration change were observed. However less fractional conversion was obtained at 0.27 g/min (45 wt%) lactic acid feed as 54% than 69% conversion at 0.46 g/min (9 wt%) feed in the previous section. This result validates that concentration of lactic acid has more adverse effect on the reactor performance than flow rate which points viscosity effect on mass transfer resistance and/or hydrophilic structure of lactic acid which hinders water evaporation.
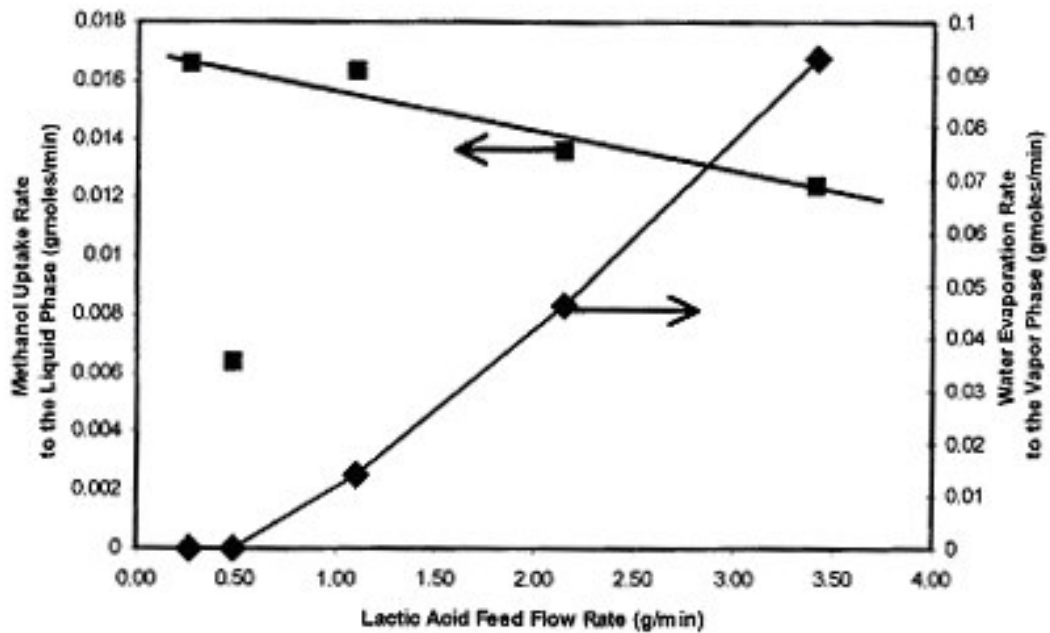
Figure 4-17 Effect of lactic acid feed flow rate on the methanol uptake rate to the liquid phase and water evaporation rate to the vapor phase

In Figure 4-17 the effect of lactic acid feed flow rate on the methanol uptake rate to liquid phase and water evaporation rate to gas phase is given. As it is seen clearly from the Figure 4-17, with the increase of liquid flow rate, methanol uptake rate to the liquid phase is not strongly affected with the increase of lactic acid flow rate which was observed as a strong function of feed lactic acid concentration in the previous section. It can be concluded that methanol uptake rate is controlled only by mass transfer and increasing liquid flow rate restrict the mass transfer of methanol to the liquid phase by decreasing liquid-gas contact area and contact time. On the other hand, the tremendous increase in water evaporation rate with lactic acid feed flow rate within the same conditions. This adverse behavior can only be explained as mass transfer resistance in gas phase controls the methanol absorption and it is not

77

favored by increasing liquid flow rates. The water evaporation rate is controlled by liquid side mass transfer coefficient and improved significantly by liquid flow rate in spite of less contact time is achieved at higher flow rates.
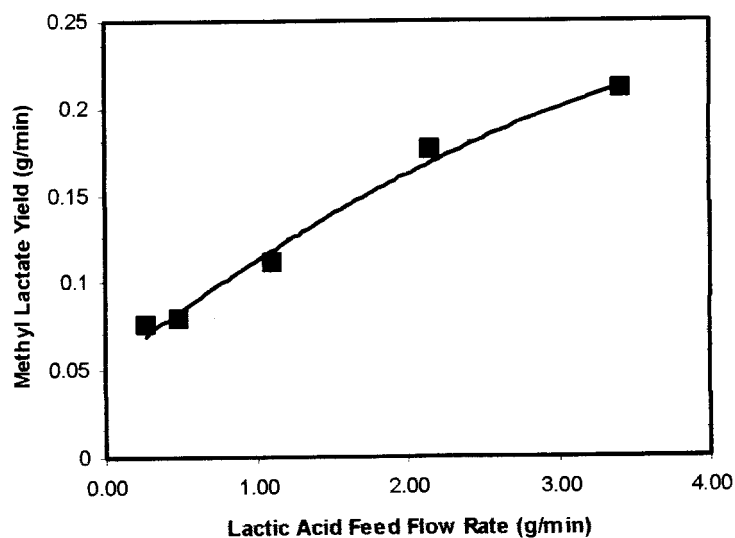
Figure 4-18 Effect of lactic acid flow rate on the methyl lactate yield

The change of methyl lactate yield with lactic acid feed flow rate Figure 4-18 also reveals that reactor performance is favored by improved water removal rate from the liquid phase and no adverse effect of viscosity was observed because of lactic acid feed concentration was kept constant. In this case, much higher methyl lactate yields were obtained compared to the higher feed concentration of lactic acid cases in spite of less space time. It can be concluded that, concentration of lactic acid limits the mass transfer by higher viscosities and mass transfer limitations by its hydrophilic nature and mass transfer of water to the gas phase controls the overall reaction rate.

4.3.2.3 Effect of Methanol and Inert Carrier Rate on reactor Performance

In order to better understand and evaluate the performance of the counter-current gas-liquid reactor effect of vapor feed flow rate was also examined. For this purpose, methanol saturator was operated with different air flow rates. Because of high vapor pressure of methanol (n.b.p. = 64.5°C), in all cases methanol evaporation rates were achieved to the saturation concentration of methanol in air at 60°C. So this group of experiments is classified to test effect of vapor feed (V2) flow rate. For this purpose, reactor performance was tested with different vapor flow rates between 0.0083-0.18 gmoles/min by keeping the lactic acid concentration and flow rate constant (0.49 g/min of 45 wt% lactic acid). The detailed experimental conditions and results are given in Table 4-10.

Table 4-10 Effect of vapor feed rate on the reactor performance

FEED COMPOSITION (wt %)				PRODUCT COMPOSITION (wt %)						FLOW RATES (g/min)				LACTIC ACID CONVERSION %
Liquid Feed, L2		Vapor Feed V1		LIQUID PRODUCT, L1				VAPOR PRODUCT, V2(*)		INLET		OUTLET		
Lactic Acid	Water	Methanol	Air	Lactic Acid	Methanol	Methyl Lactate	Water	Methanol	Water	L2	V1	L1	V2	
45.0	55.0	15.0	85.0	42.29	15.50	4.65	37.56	59.60	40.40	0.49	0.26	0.48	0.28	8.7
45.0	55.0	15.0	85.0	24.73	18.30	7.32	49.65	100.00	n.d.	0.49	2.00	0.71	1.78	20.4
45.0	55.0	15.0	85.0	18.75	22.04	9.71	49.50	100.00	n.d.	0.49	2.83	0.81	2.50	30.9
45.0	55.0	15.0	85.0	19.41	35.60	14.50	30.49	97.53	2.46	0.49	3.88	0.69	3.68	39.3
45.0	55.0	15.0	85.0	7.16	40.70	13.80	38.34	100.00	n.d.	0.49	5.56	1.15	4.90	65.5

FEED COMPOSITION (mole %)				PRODUCT COMPOSITION (mole %)						FLOW RATES (gmoles/min)				LACTIC ACID CONVERSION %
Liquid Feed, L2		Vapor Feed V1		LIQUID PRODUCT, L1				VAPOR PRODUCT, V2		INLET		OUTLET		
Lactic Acid	Water	Methanol	Air	Lactic Acid	Methanol	Methyl Lactate	Water	Methanol	Water	L2	V1	L1	V2	
14.1	85.9	15.0	85.0	15.22	15.68	1.45	67.65	54.88	56.09	0.0174	0.0083	0.0147	0.0121	8.7
14.1	85.9	15.0	85.0	7.47	15.54	1.91	75.07	100.00	n.d.	0.0174	0.0634	0.0261	0.0502	20.4
14.1	85.9	15.0	85.0	5.57	18.40	2.49	73.54	100.00	n.d.	0.0174	0.0896	0.0304	0.0701	30.9
14.1	85.9	15.0	85.0	6.82	35.16	4.41	53.61	89.81	3.42	0.0174	0.1231	0.0218	0.1120	39.3
14.1	85.9	15.0	85.0	2.20	35.17	3.67	58.96	100.00	n.d.	0.0174	0.1763	0.0417	0.1402	65.5

(*) Air free basis
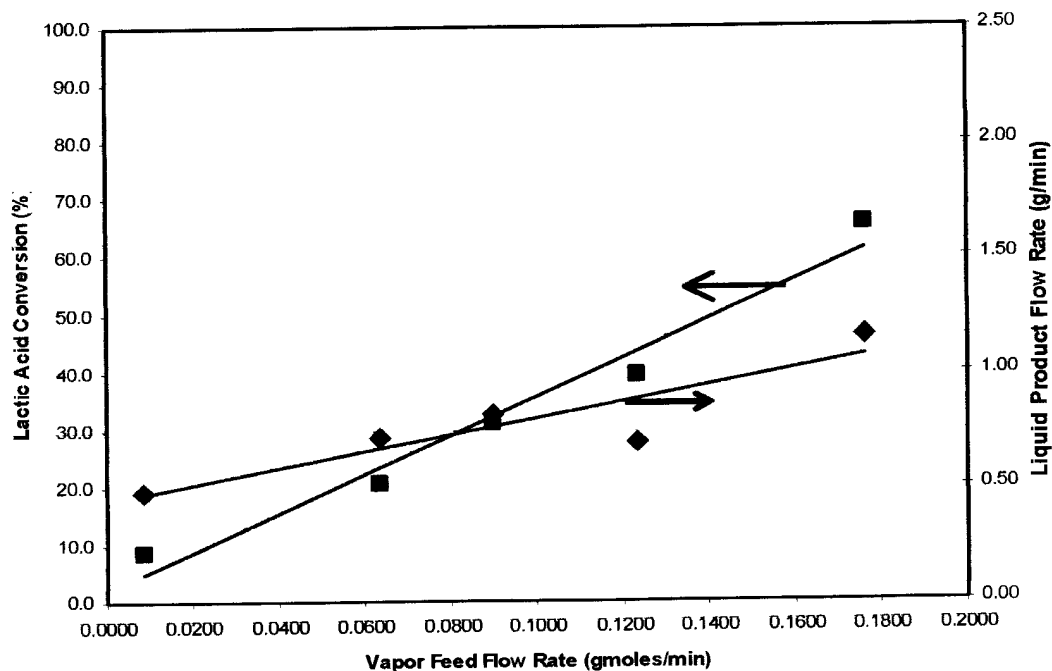
Figure 4-19 Effect of vapor feed (V_1) rate on lactic acid conversion and liquid product (L_1) flow rate

In Figure 4-19 the change of lactic acid conversion and liquid product (L1) flow rate with vapor feed (V1) flow rate are summarized. As it is seen from the figure, the fractional conversion is improved by the higher vapor flow rates and liquid product (L1) flow rates. From these results, it is clear that in spite of excess methanol were observed on the previous higher lactic acid feed concentration and flow rate tests, upward flow of vapor phase enhances both mass transfer rate of methanol to the liquid phase and increases the liquid space time. The liquid product flow rate is also increases with vapor feed flow rate because of more methanol is transferred to the liquid phase.
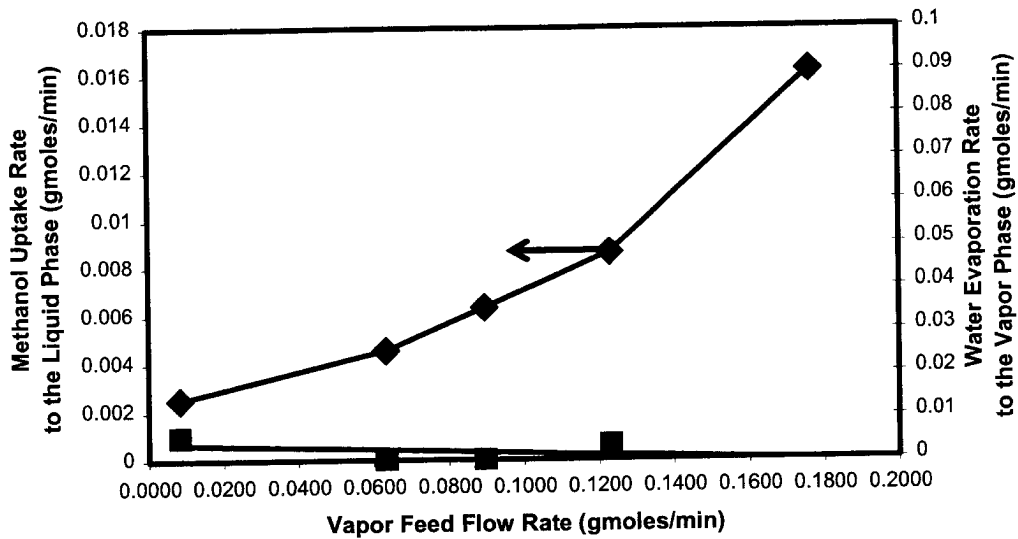
Figure 4-20 Effect of vapor feed (V_1) flow rate on the methanol uptake rate to the liquid phase and water evaporation rate

The methanol uptake rate is also favored with the increase of vapor feed flow rate as it is given in Figure 4-20 compared with the Figure 4-17. These results also validates the mass transfer of methanol is controlled by the vapor phase mass transfer resistance and methanol uptake rate can be easily adjusted by vapor phase flow rate. The water evaporation rate is not effected with vapor feed flow rate as expected because of reaction is slower than mass transfer rate and it is also validated that water mass transfer rate to the vapor phase can only be improved by increasing liquid flow rate. In addition, the lower water removal rate does not limit the reaction, however in order to increase reactor performance, better water removal rates are essential.
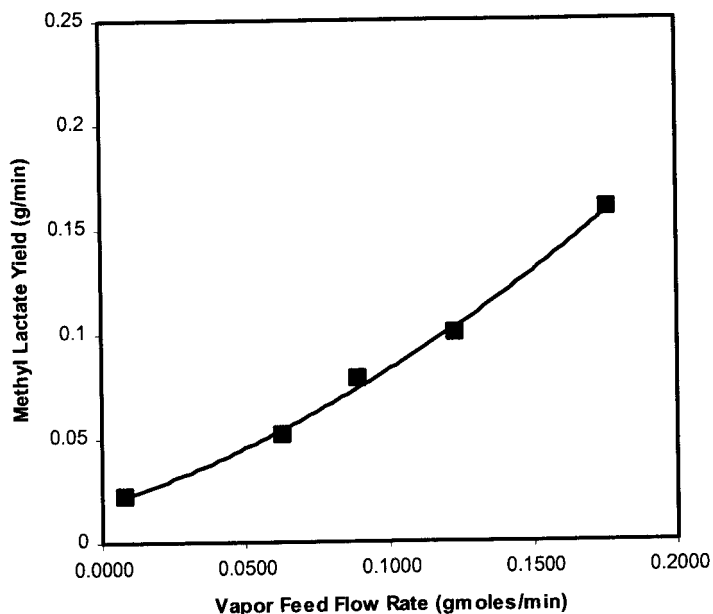
Figure 4-21 Effect of vapor feed (V_1) on the methyl lactate yield

In Figure 4-21, the change of methyl lactate yield with vapor feed flow rate is summarized. As it is seen from the figure, yield is favored by enhanced mass transfer in the vapor phase and quite satisfactory yield can be obtained.

The lack of literature regarding the mass transfer with chemical reaction and the gas-liquid mass transfer over the microporous/macro reticular particles prevents the further evaluation of the data. However, the promising results above indicate the viability of the simultaneous process for separation and reaction of esterification and carboxylic acid purification operations.

CHAPTER 5

CONCLUSIONS

In the first section of this study, the esterification and its reverse reaction of lactic acid with methanol were studied.

On the basis of the experiments done the following conclusions are reached.

- Catalyst enhances conversion and rate.

- Lewatit SPC-112-H$^+$ was found to be a good catalyst for this reaction.

- The reactions are exothermic. In both Lactic Acid hydrolysis reaction and Esterification reaction equilibrium constant decreases with increasing temperature.

- Heat of reaction for lactic acid esterification reaction with methanol is calculated as –3146.6 cal/mol.

- The effect of temperature on conversion was studied in the range of 40-70 ^{0}C. It was seen that the ester conversion increases with temperature.

- Hydrolysis experiments showed that, produced water from lactic acid esterification reaction, catalyzed the lactoyllactic acid hydrolysis and favored methyl lactate formation.

- Overall reaction rate constants were studied separately as homogeneous and heterogeneous and the participation of the catalyst on the forward and backward rates were outlined. Equilibrium constants were estimated.

In the second section of this study the possible production process of methyl lactate was investigated. The results prove that the counter-current gas-liquid reactors can be used for esterification systems with high boiling point or heat sensitive carboxylic acids and esters to solve azeotropic separation problems due to low boiling point alcohols. By selecting carefully the flow conditions, counter-current gas-liquid esterification systems may also serve as a separation unit to separate undesired components within the carboxylic acid (e.g. water from lactic, acetic, fumaric acids as a fermentation broth). However little information exists in the literature about the gas-liquid mass transfer over the microporous and /or macro reticular ion exchange resins as packing. On the other hand, one can conclude that,

- Methyl lactate formation reaction is slower than mass transfer rate.

- Mass transfer of methanol in gas phase is limiting step for methanol transfer to the liquid mixture.

- Mass transfer of water from liquid phase to the gas phase is controlled by the mass transfer resistance of liquid phase.

- Lactic acid has hydrophilic component and higher lactic acid concentrations hinders the water mass transfer to the gas phase.

- The viscosity of the liquid phase increases with lactic acid concentration and this property hinders the water mass transfer to the gas phase.

- Ion exchange resins can be utilized as packing and catalyst for counter-current gas-liquid reactions. However insufficient information exists on the column hydraulics and mass transfer.

- The counter-current gas-liquid reactors with acidic solid catalysts may serve as simultaneous reaction and separation equipment.

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APPENDIX A

GC ANALYSIS

Gas chromatography data were combined with the titration analysis in order to get the product distribution throughout the reaction time.

Table A- 1 Peak areas and area fractions of methyl lactate, water,and methanol

Area of the peak				Area Fractions		
Methanol	Water	Methyl Lactate	Total	Methanol	Water	Methyl Lactate
4817	9182	3214	17213	0.28	0.53	0.19
4613	9247	3148	17008	0.27	0.54	0.19

Injected solution contains lactic and lactoyllactic acid at high concentrations. However, FFAP column that was used for general esterification

applications, detects alcohol, water and lactate ester respectively. For this purpose, a calibration methodology relating the wt% titration data with the resulting chromatograph signals is needed.

The weight fractions are calculated by using the area fractions and response factors obtained from the calibration curves. For this purpose, extensive calibration trials at varying concentrations were performed. Resulting differences between the total areas with respect to prepared solutions were analytically combined together with the estimation of relative response factors of the species at lactic acid and Lactoyllactic acid free basis. Methyl Alcohol, which gave precise and definite peaks at the lowest retention time was used as the reference component in calculations. From the calibration trials, best response factors were estimated representing the actual reaction concentrations.

Resulting areas were corrected by multiplying with the corresponding relative response factor.Procedure is as follows:

$$(R.F)_{species} = \frac{(Area(MetOH)/wt\%(MetOH))}{(Area(species)/wt\%(species))}$$

Table A- 2 Relative Response Factors

Relative Response Factors(R.F):	
Methanol	1.0000
Water	2.94301
Lactate	2.63509
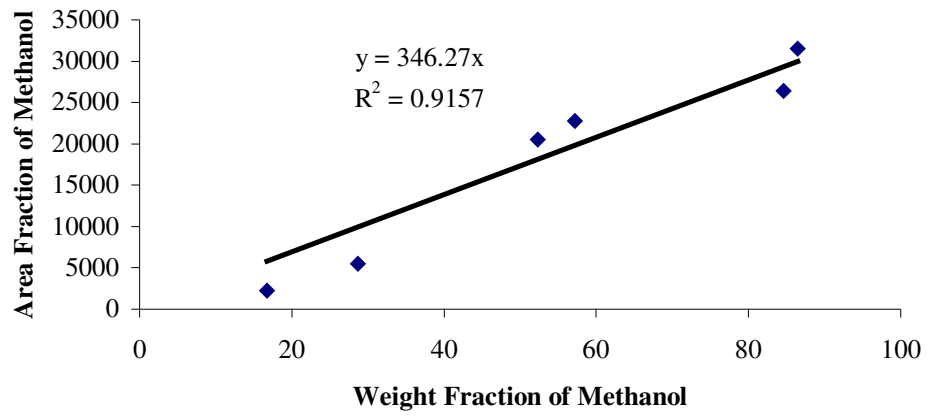
Figure A- 1 GC calibration curve for Methanol
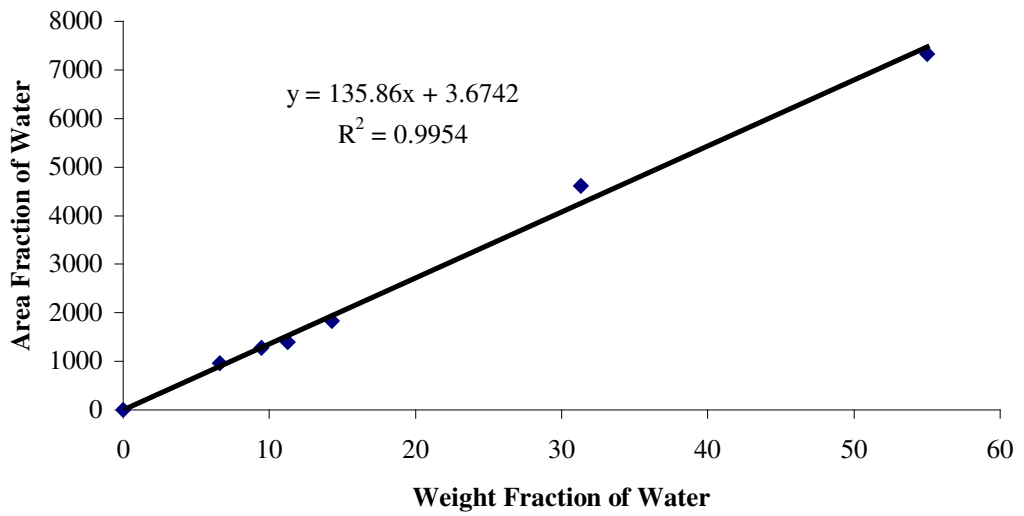
Figure A- 2 GC calibration curve for Water

$$y = 156.48x + 300.29$$
$$R^2 = 0.9606$$
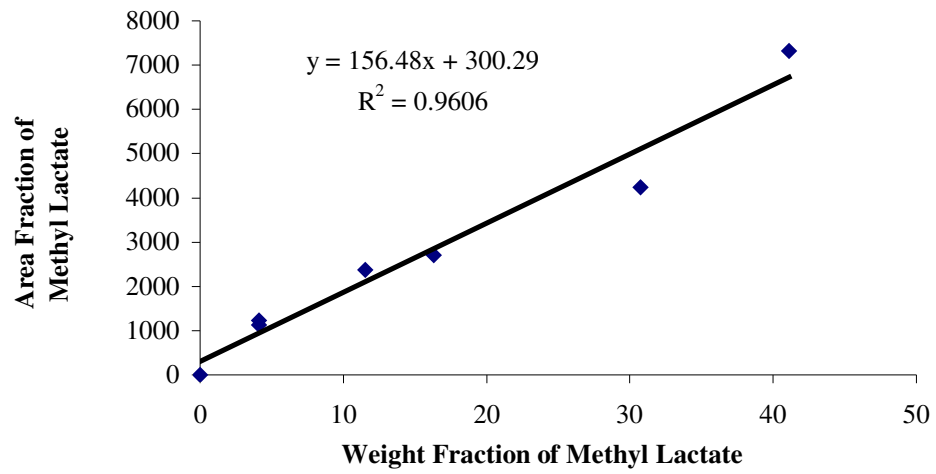
Figure A- 3 GC calibration curve for Methyl Lactate

APPENDIX B

SAMPLE CALCULATIONS I

In order to calculate the lactic acid conversions and the product distributions throughout the "batch reactor experiments" by using the experimental data obtained with the Lewatit SPC112-H$^+$ catalyst the below procedure was followed.

Potassium hydroxide solution, used in titrations, was standardized by using potassium hydrogen phthalate,$KHC_8H_4O_4$.The hydrochloric acid solution was standardized by using the standard potassium hydroxide solution.

$$N_{KOH} = \frac{1000 x W_{KHC8H4O4(gr)}}{MW_{KHC8H4O4(g/gmol)} . V_{KOH(ml)}}.$$

$$N_{HCl} = \frac{N_{KOH} . V_{KOH}}{V_{HCl}}$$

Conditions for the experimental run are as follows:

Table B- 1 Batch reactor experimental conditions

T:	70 ^{0}C
NKOH:	0.0844 mol/lt
NHCl:	0.074 mol/lt
~ 1 wt% cat:	0.38 gr

Lactic Acid Solution:	60.149 g
Methanol Solution:	14.44 g
Reaction Mixture:	27.142 g

Lactic Acid solution having 92 wt% total acidity, contains 73 wt % free acidity as lactic acid and 19wt% as lactoyllactic acid. Methanol solution was 99.5 wt%.

	wt% Species	g.species	Mol Species	Initial concentrations mol/lt
Lactic Acid:	0.588676	15.97785	0.177374	2.608886
Methanol:	0.193207	5.244026	0.163671	2.047118
Water:	0.0649	1.761506	0.097861	1.619496
Methyl Lactate:	0	0	0	0.360222
Lactoyllactic Acid:	0.153217	4.158618	0.02567	0.197461

Initial Molar Ratios	
$\Theta_1 = N_{MetOH}/N_{LA}$	0.922746
$\Theta_2 = N_{H2O}/N_{LA}$	0.551724
$\Theta_3 = N_{LLA}/N_{LA}$	0.144725

At regular intervals, small amounts of samples were withdrawn from the reaction medium for titration and 0.5 μL samples were injected for gas chromatography analysis.

Unconverted lactic acid was found by using the following formulas:

$$F(wt\%) = \frac{N_{KOH}(mol/lt).V_{KOH}(ml).MW_{LacticAcid}(g/gmol)}{(1000ml/lt).W_{Sample}(g)}.100$$

$$T(wt\%) = \left[(N_{KOH} + N_{KOH,excess}).V_{KOH}(ml) - N_{HCl}(mol/lt).V_{HCl}(ml)\right]$$

$$\cdot\left(\frac{MW_{LacticAcid}(g/gmol)}{(1000ml/lt).W_{Sample}(g)}\right).100$$

$$P(wt\%) = T(wt\%) - F(wt\%)$$

where;

F=free acidity as wt% lactic acid

T=total acidity as wt% lactic acid

P=polymeric esters, as wt% lactoyllactic acid

N_{KOH}=potassium hydroxide volume used for titration,ml

$N_{KOH,excess}$=volume of hydrochloric acid used in back titration, ml

Time (min)	Sample weight (gr)	VKOH(ml)	VKOH, excess (ml)	VHCl(ml)	F(wt%)	T(wt%)	P(wt%)
0	0.245	18.1	25	21	56.16727	76.60991	20.44264
45	0.29	16.6	-	-	43.5192	-	-
75	0.205	10.7	-	-	39.68266	-	-
135	0.276	12.3	-	-	33.88183	-	-
195	0.181	7.3	-	-	30.66303	-	-
255	0.345	13.5	-	-	29.7499	-	-
375	0.23	8.9	-	-	29.41934	-	-
495	0.222	8.2	-	-	28.08224	-	-

FFAP column, used for general esterification applications, detects alcohol, water and lactate ester respectively. However, injected solution contains lactic acid and lactoyllactic acid. Therefore, a calibration methodology relating the wt% titration data with the resulting chromatograph signals is needed.

Gas chromatography data were combined with the titration analysis in order to get the product distribution throughout the reaction time. Methanol, which gave precise and definite peaks at the lowest retention time, was used as the reference component in calculations. From the calibration trials, best response factors were estimated representing the actual reaction concentrations. Resulting areas were corrected by multiplying with the relative response factor of each species.

Procedure is as follows;

Actual lactic acid and lactoyllactic acid free basis weight and mole fractions were calculated:

	LA+LLA Free wt%			LA+LLA Free mol Fractions		
Time (min)	MetOH	H_2O	Lactate	MetOH	H_2O	Lactate
0	50.02537	27.39372	22.58092	0.388292	0.543382	0.068236
45	20.18717	27.80073	52.0121	0.181036	0.637133	0.181831
75	15.23255	29.4206	55.34685	0.136012	0.671337	0.192651
135	11.45509	28.89621	59.6487	0.105525	0.680269	0.214206
195	9.120923	30.31635	60.56273	0.082763	0.703008	0.214229
255	8.297514	29.38265	62.31983	0.077057	0.69733	0.225613
375	8.14752	29.63207	62.22041	0.07535	0.700332	0.224319
495	7.590009	28.43254	63.97746	0.072154	0.69075	0.237095

Conversion with respect to lactic acid esterification was calculated from the stoichiometric relations of material balances:

$$LA + MetOH \longleftrightarrow ESTER + H_2O \quad X_1$$

$$LLA + H_2O \longleftrightarrow 2LA \quad X_2$$
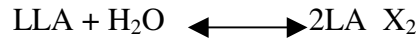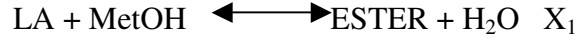
Species	Initial (mole)	Change (mole)	Final (mole)
LA	N_{LA0}	$- N_{LA0} + 2. N_{LLA0}.X_2$	$N_{LA} = N_{LA0} - N_{LA0} + 2. N_{LLA0}.X_2$
MetOH	N_{MetOH0}	$- N_{LA0}. X_1$	$N_{MetOH} = N_{MetOH0} - N_{LA0}. X_1$
Methyl Lactate	N_{Ester0}	$+ N_{LA0}. X_1$	$N_{Ester} = N_{Ester0} + N_{LA0}. X_1$
H_2O	N_{H2O0}	$+ N_{LA0}. X_1 - N_{LLA0}.X_2$	$N_{H2O} = N_{H2O0} + N_{LA0}. X_1 - N_{LLA0}.X_2$
LLA	N_{LLA0}	$- N_{LLA0}.X_2$	$N_{LLA} = N_{LLA0} - N_{LLA0}.X_2$

$$R_1 = \frac{yEster}{yMetOH} = \frac{(N_{LA0}.X_1)/N_T}{(N_{MetOH,0} - N_{LA0}.X_1)/N_T}$$

$$R_2 = \frac{yEster}{yH_2O} = \frac{(N_{LA0}.X_1)/N_T}{(N_{H2O,0} + N_{LA0}.X_1 - N_{LLA,0}.X_2)/N_T}$$

Time (min)	R_1	R_2	X_1
0	0.175965	0.125742	0.138075
45	1.004395	0.28539	0.462385
75	1.416433	0.286967	0.540883
135	2.029917	0.314884	0.618201
195	2.588466	0.304733	0.665604
255	2.927886	0.323538	0.687824
375	2.977031	0.320303	0.690727
495	3.285947	0.343243	0.707451

X1 is known then X_2 conversion relating to the lactoyllactic acid hydrolysis was calculated by expressing the titration data of the free acidity as mol free lactic acid.

Time (min)	Free Acidity as LA(wt%)	Gram Free Lactic Acid	Mole Free Lactic Acid	X_2
0	56.16727	15.24492	0.169238	0477025
45	43.5192	11.81198	0.131128	0.819481
75	39.68266	10.77067	0.119568	0.854696
135	33.88183	9.196206	0.102089	0.765009
195	30.66303	8.32256	0.092391	0.73079
255	29.7499	8.074718	0.089639	0.751392
375	29.41934	7.984999	0.088643	0.741089
495	28.08224	7.622081	0.084615	0.716619

Concentrations and the rate of disappearance of lactic acid from Lactic

Acid (mol/lt) were calculated using material balance for the batch reactor.

Moles: Calculated using material balance;

MOLES, (mol):

Time(min)	N_{LA}	N_{MetOH}	N_{Ester}	N_{h2o}	N_{lla}	TOTAL MOLES
0	0.177374	0.13918	0.024491	0.110107	0.013425	0.464577
45	0.137432	0.081656	0.082015	0.15884	0.004634	0.464577
75	0.125316	0.067733	0.095939	0.17186	0.00373	0.464577
135	0.106997	0.054018	0.109653	0.187876	0.006032	0.464577
195	0.096833	0.04561	0.118061	0.197163	0.006911	0.464577
255	0.093949	0.041669	0.122002	0.200575	0.006382	0.464577
375	0.092905	0.041154	0.122517	0.201354	0.006646	0.464577
495	0.088683	0.038188	0.125483	0.204949	0.007275	0.464577

Initial weight of reaction mixture:27.142 gr

Weights, (gr):

Time(min)	W_{LA}	W_{MetOH}	W_{ESTR}	W_{H2O}	W_{LLA}	TOTAL WEIGHT
0	15.97785	4.459337	2.547154	1.981924	2.174855	27.14102
45	12.37987	2.616263	8.529566	2.859121	0.750708	27.13552
75	11.28849	2.170151	9.977619	3.093474	0.604266	27.134
135	9.638332	1.730749	11.40389	3.38177	0.977239	27.13198
195	8.722684	1.461356	12.27833	3.548926	1.11954	27.13083
255	8.462925	1.335076	12.68823	3.610351	1.033868	27.13045
375	8.368893	1.318578	12.74178	3.62438	1.076714	27.13034
495	7.988527	1.22354	13.05027	3.689079	1.178473	27.12989

Concentrations, (mol/lt):

Time (min)	$(-)dc_{LA}/dt$	C_{LA}	C_{MetO}	C_{ESTER}	C_{H2O}	C_{LLA}
0	0.0119	2.608886	2.047118	0.360222	1.619496	0.197461
45	0.008543	2.021402	1.201031	1.20631	2.336282	0.068159
75	0.006575	1.8432	0.996237	1.411103	2.527779	0.054863
135	0.003287	1.573761	0.794524	1.612817	2.763356	0.088726
195	0.000863	1.424252	0.670855	1.736485	2.899944	0.101646
255	0.000697	1.381839	0.612884	1.794456	2.950136	0.093867
375	0.001225	1.366485	0.605311	1.802029	2.9616	0.097758
495	0.001703	1.304378	0.561682	1.845658	3.014468	0.106997
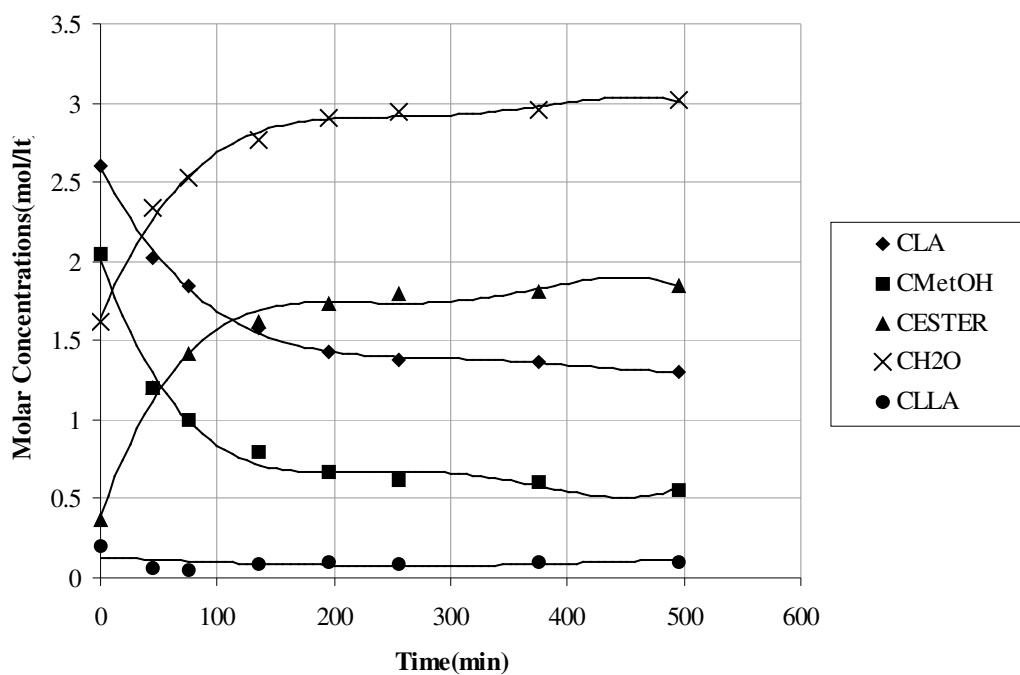
Figure B- 1 Concentration vs.Time Data at 70 ^{0}C for 1 wt% Lewaitit SPC-112-H$^+$
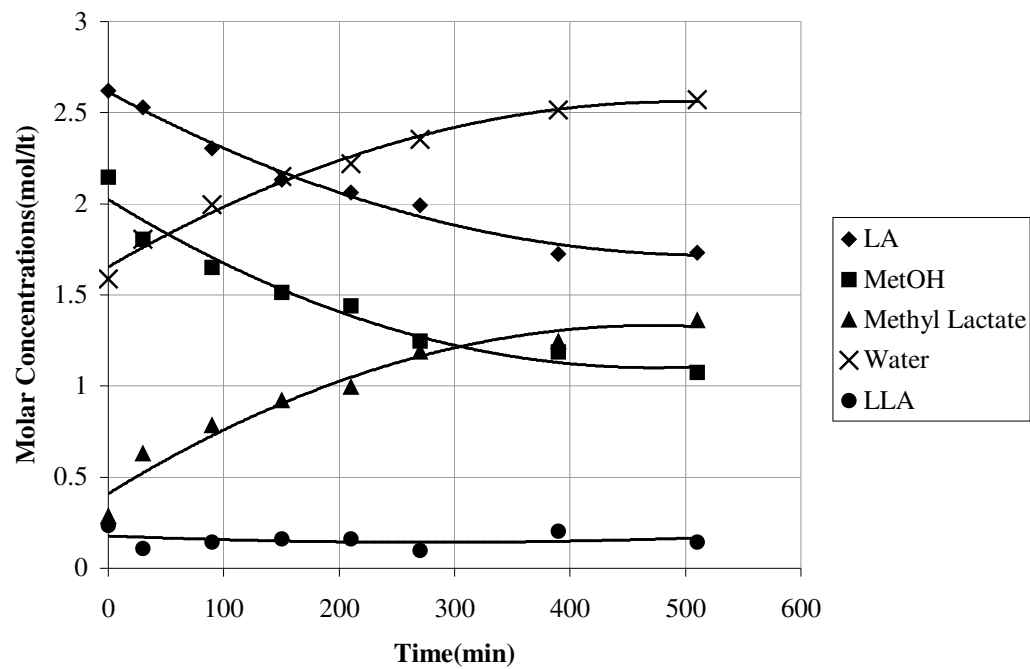
Figure B- 2 wt% concentrations at 50 C, 1:1 Molar Ratio and without catalyst
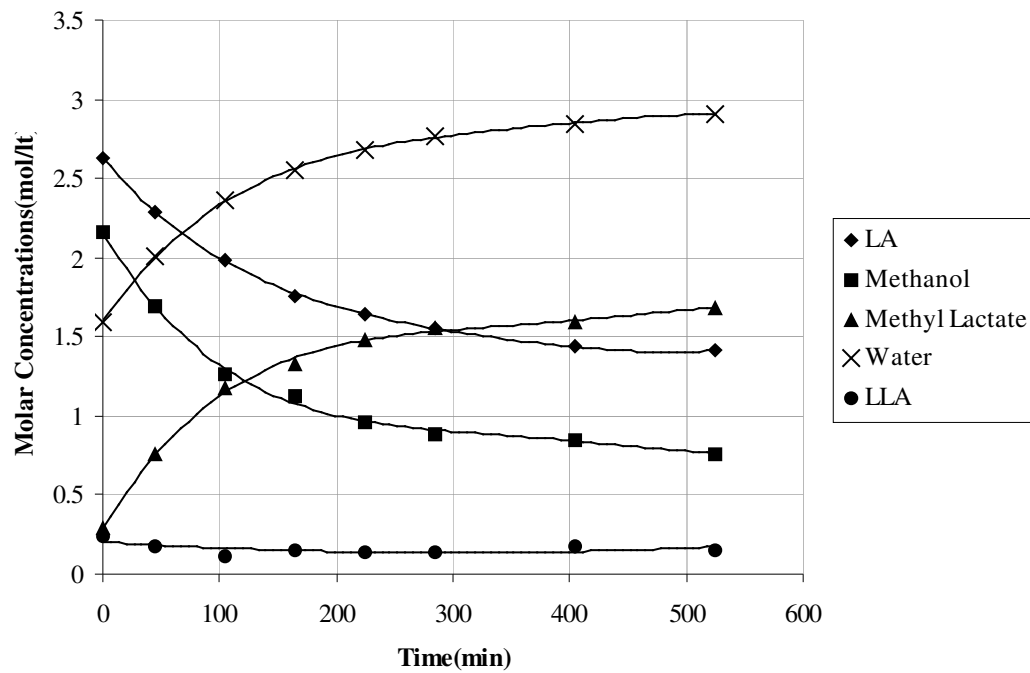
Figure B- 3 wt% Concentrations at 50 ^{0}C, 1:1 Molar Ratio and 1 wt% Catalyst Concentration, Lewatit SPC-112-H$^+$
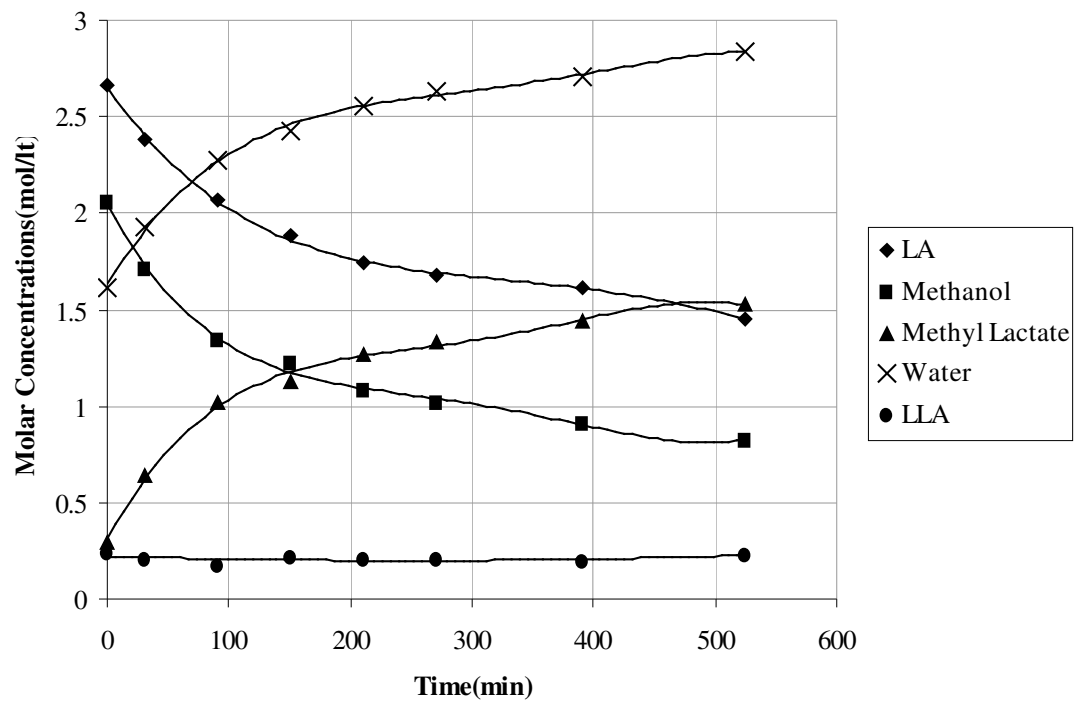
Figure B- 4 wt% Concentrations at 60 ^{0}C, 1:1 Molar Ratio and without Catalyst.
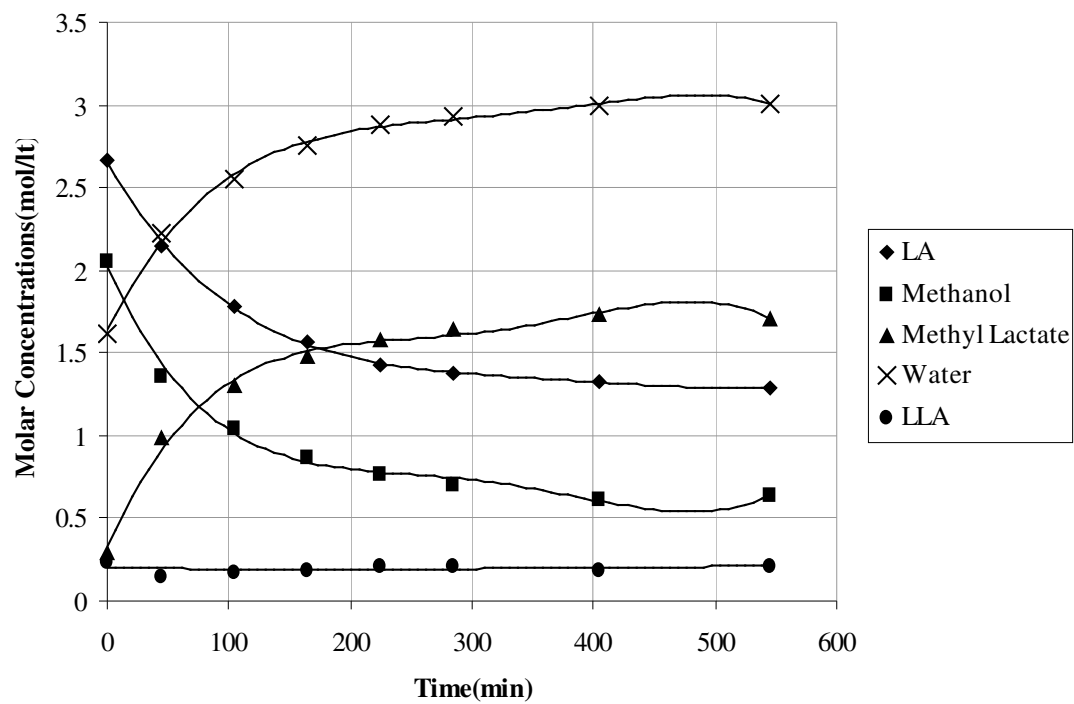
Figure B- 5 wt% Concentrations at 60 ^{0}C , 1:1 Molar Ratio and 1wt% Catalyst Concentration.

APPENDIX C

SAMPLE CALCULATIONS II

In order to calculate the lactic acid conversions and the product distributions throughout the fixed bed reactor experiments by using the experimental data obtained with the Lewatit SPC112-H$^+$ catalyst the below procedure was followed.

Potassium hydroxide solution, used in titrations, was standardized by using potassium hydrogen phthalate,$KHC_8H_4O_4$.The, hydrochloric acid solution was standardized by using the standard potassium hydroxide solution.

$$N_{KOH} = \frac{1000 x W_{KHC8H4O4(gr)}}{MW_{KHC8H4O4(gr/gmol)} . V_{KOH(ml)}}$$

$$N_{HCl} = \frac{N_{KOH} . V_{KOH}}{V_{HCl}}$$

Conditions for the experimental run are as follows:

Table C- 1 Fixed bed reactor experimental conditions

T (Methanol):	60 ^{0}C
T (Lactic Acid):	95 ^{0}C
NKOH:	0.0844 mol/lt
NHCl:	0.10065 mol/lt
Bed Height:	25 cm
Bed Diameter:	2 cm

	Concentration of Feed Species	
	wt %	Mole %
Lactic Acid	9.0	1.9
Water	91.0	98.1
Methanol	15.0	15.0
Air	85.0	85.0
	Flow Rates of Feed Species	
	g/min	gmoles/min
L$_2$	0.46	0.0237
V$_1$	2.83	0.0897

At regular intervals, small amounts of samples were withdrawn from the reaction medium for titration and 0.5 μL samples were injected for gas chromatography analysis.

Time (min)	Sample weight (gr)	VKOH (ml)	VKOH, excess (ml)	VHCl (ml)	F(wt%)	T(wt%)	P(wt%)
0	0.349	3.2	2.8	1.6	0.433881	2.35163003	1.91774903
210	0.406	6.5	-	-	12.121418	-	-
270	0.343	4.4	-	-	16.334419	-	-
330	0.289	9.5	-	-	24.888107	-	-
360	0.291	8.6	-	-	22.375439	-	-

F=free acidity as wt% lactic acid

T=total acidity as wt% lactic acid

P=polymeric esters, as wt% lactoyllactic acid

Gas chromatography data were combined with the titration analysis in order to get the product distribution throughout the reaction time. Resulting areas were corrected by multiplying with the relative response factor of each species.

Time (min)	GC MetOH Area	GC H_2O Area	GC Lactate Area	MetOH Area Corrected	H_2O Area Corrected	Lactate Area Corrected
0	22811	0	0	22811	0	0
210	21782	3482	2650	21782	10247.56082	6982.9885
270	22309	2865	2137	22309	8431.72365	5631.18733
300	2907.88	5806	6531	2907.88	17087.11606	17209.77
330	13435	3469	6317	13435	10209.30169	3470.41353
360	17519	2319	6907.72	17519	6824.84019	1838.554995

By using the above experimental data Lactic Acid (wt%) out, Methyl Lactate (wt %) out, water (wt %) out and methanol (wt %) out are calculated.

The quality of the experimental measurements were tested by carrying out Carbon, Oxygen and Hydrogen mass balance around the system presented in

.

After the reaction has reached equilibrium the weight % ratios are;

PRODUCT COMPOSITON (wt%)

LIQUID PRODUCT, L_1				VAPOR PRDUCT, V_1	
LA	Methanol	Methyl Lactate	Water	Methanol	Water
6.10	15.30	15.70	62.80	88.98	11.02

PRODUCT COMPOSITON (mole%)

1.62	11.41	3.60	83.37	81.94	15.30

Lactic Acid conversion is calculated as 69.0 %.

For each regular interval the above calculation procedure is applied to experimental raw data.

Table C-2 Carbon, Hydrogen and Oxygen balance analysis around the system

Con.of LA wt%	L2 (Lactic Acid Soln.)		V1(Methanol+air flow rate in)		Product Composition, L1 (wt %), (mol %)				L1 (g/min)	V2 (wt %)		V2 (g/min)	X
	g/min	gmol/min	g/min	gmol/min	LA	MetOH	Lactate	H2O		MetOH	H2O		
wt %													X
10	0.46	0.023715147	2.4	0.075	6.1	15.3	15.7	62.8	0.210307	88.9791	11.0209	2.6496935	69.01281
					0.0677180	0.477528	0.1508165	3.489	4.184951	2.77713	0.61227	3.3893977	
					1.618121	11.4106	3.6037822	83.37	0.008801	81.9357	15.3004	0.0898086	

H2O (wt%)	LA (wt%)			
91	9			

H2O (mol%)	LA (mol%)	Tot. (mol%)
5.055555556	0.09991119	5.1554667
98.06203405	1.937965949	

COMPLETE V2 ANALYSIS

	IN	OUT	Conf. %		Air	MetOH	H2O	TOTAL
C	0.0763790	0.0762855	99.88	gr/min	0.4263	2.35767	0.29202	3.07599
O	0.0996340	0.0970468	97.4	mol/min	0.0147	0.07359	0.0137411	0.10203
H	0.348809	0.351687	100.8	wt%	8.70598	48.1488	5.9636859	
				mol%	10.4826	52.4737	9.7987722	

	Air	Methanol
wt%	15	84
mol%	16.4	83.6
Air Flow (ml/min)	354	
Air Flow (mol/min)	0.0147	
TOTAL V1 (mol/min)	0.0897	

APPENDIX D

EXPERIMENTAL DATA

1.Batch Reactor Experiments

Table D- 1 Lactic acid conversions at 40 ^{0}C, 1:1 Molar Ratio in the absence of catalyst

Time (min)	W_{sample} (gr)	V_{KOH} (ml)	X
0	1.7	130.8	0
30	0.493	36.6	0.035115
90	0.259	18	0.096738
150	0.133	8.8	0.140052
210	0.405	26	0.165628
270	0.305	19.3	0.177571
330	0.22	13.4	0.208368
390	0.263	15.5	0.234021
450	0.263	15.4	0.238962

Table D- 2 Lactic acid conversions at 40 ^{0}C, 1:1 Molar Ratio and 1 wt% Catalyst Concentration – Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	1.7	130.8	0
45	0.357	24.5	0.108053
105	0.138	9	0.152373
165	0.127	7.3	0.252932
225	0.398	21.5	0.297904
285	0.443	22.3	0.345752
345	0.353	16.6	0.388812
405	0.507	22.3	0.42834
465	0.404	17	0.453099

Table D- 3   Lactic acid conversions at 50 ^{0}C, 1:1 Molar Ratio in the absence of Catalyst

Time min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	0.37	27	0
30	0.298	21	0.034303
90	0.26	16.7	0.119801
150	0.394	23.4	0.186125
210	0.348	20	0.212431
270	0.227	12.6	0.239354
390	0.233	11.2	0.341281
510	0.535	25.8	0.339148

Table D- 4 Lactic acid conversions at 50 ^{0}C, 1:1 Molar Ratio and 1 wt% Catalyst Concentration – Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	0.37	27	0
45	0.37	23.4	0.133333
105	0.316	17.4	0.245429
165	0.254	12.4	0.331
225	0.23	10.5	0.374396
285	0.396	17	0.41171
405	0.382	15.2	0.454722
525	0.332	13	0.463409

Table D- 5 Lactic acid conversions at 60 ^{0}C, 1:1 Molar Ratio in the absence of catalyst

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	0.268	21	0
30	0.268	18.8	0.104762
90	0.27	16.4	0.224832
150	0.468	25.9	0.293732
210	0.179	9.2	0.344081
270	0.162	8	0.369782
390	0.082	3.9	0.393031
525	0.448	19.1	0.455910

Table D- 6 Lactic acid conversions at 60 ^{0}C, 1:1 Molar Ratio and 1 wt% Catalyst Concentration – Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	0.268	21	0
45	0.309	19.5	0.194637
105	0.16	8.4	0.330
165	0.384	17.7	0.411756
225	0.382	16	0.465470
285	0.188	7.6	0.484093
405	0.202	7.9	0.500896
545	0.41	15.6	0.514425

Table D- 7 Lactic acid conversions at 70 ^{0}C, 1:1 Molar Ratio in the absence of Catalyst

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	0.245	18.1	0
30	0.182	12.2	0.092648
60	0.184	12	0.117223
120	0.075	4.3	0.223941
180	0.254	12.8	0.317875
240	0.223	10.8	0.344449
360	0.224	9.7	0.413847
480	0.221	9.2	0.436514

Table D- 8 Lactic acid conversions at 70 ^{0}C, 1:1 Molar Ratio and 1 wt% Catalyst Concentration – Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X
0	0.245	18.1	0
45	0.29	16.6	0.225186
75	0.205	10.7	0.293491
135	0.276	12.3	0.396769
195	0.181	7.3	0.454076
255	0.345	13.5	0.470334
375	0.23	8.9	0.476219
495	0.222	8.2	0.500025

2.Hydrolysis of Lactoyllactic Acid Experiments

Table D- 9 %30 Lactic acid concentration at 50 ^{0}C 1 wt% Catalyst Concentration - Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.251	6.8	0
60	0.203	5.5	0.1795
120	0.305	8.9	0.0757
180	0.119	5	0.2168
300	0.228	6.3	0.1956
420	0.237	6.7	0.4490
540	0.239	6.5	0.1331

Table D- 10 %50 Lactic acid concentration at 50 ^{0}C 1 wt% Catalyst Concentration - Lewatit SPC-112 H^{+}

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.27	12.7	0
60	0.205	9.7	0.24124
120	0.244	11.2	0.428038
180	0.239	11.4	0.388571
300	0.258	12.1	0.771204
420	0.213	10.4	0.722867
540	0.307	14.8	0.606327

Table D- 11 %90 Lactic acid concentration at 50 ^{0}C 1 wt% Catalyst Concentration – Lewatit SPC-112 H^{+}

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.215	17.9	0
60	0.357	30.5	0.03
120	0.242	21.5	0.1243
180	0.277	25.1	0.3174
300	0.239	20.4	0.2351
420	0.308	26	0.3248
540	0.305	26.8	0.3429

Table D- 12 %30 Lactic acid concentration at 60 ^{0}C 1 wt% Catalyst Concentration - Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.265	7.6	0
60	0.241	7.4	0.1831
120	0.276	8.6	0.2241
180	0.302	9.5	0.2510
300	0.225	6.8	0.1394
420	0.226	7	0.2073
540	0.287	9.2	0.3051

Table D- 13 %50 Lactic acid concentration at 60 ^{0}C 1 wt% Catalyst Concentration - Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.268	12.3	0
60	0.248	11.7	0.14023
120	0.263	12.5	0.17865
180	0.236	10.8	0.16546
300	0.279	13.5	0.27258
420	0.294	14.4	0.33739
540	0.2	10	0.44901

Table D- 14 %90 Lactic acid concentration at 60 ^{0}C 1 wt% Catalyst Concentration Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.467	38.2	0
60	0.235	19.9	0.20577
120	0.267	22.8	0.25663
180	0.325	27.6	0.22306
300	0.308	26.8	0.37227
420	0.285	24.4	0.27239
540	0.222	19.9	0.23820

Table D- 15 %30 Lactic acid concentration at 70 ^{0}C 1 wt% Catalyst Concentration – Lewatit SPC-112 H$^+$

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.206	5.5	0
60	0.117	3.3	0.27764
120	0.209	8.7	0.25183
180	0.207	6	0.42150
300	0.188	5.5	0.47123
420	0.25	7.4	0.53477
540	0.208	6.2	0.57306

Table D- 16 %50 Lactic acid concentration at 70 ^{0}C 1 wt% Catalyst Concentration - Lewatit SPC-112 H^{+}

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.231	10.7	0
60	0.267	12.8	0.51408
120	0.17	8.3	0.3917
180	0.181	8.9	0.60112
300	0.144	7.1	0.68607
420	0.218	11.15	0.78731
540	0.203	10.6	0.86867

Table D- 17 %90 Lactic acid concentration at 70 ^{0}C 1 wt% Catalyst Concentration - Lewatit SPC-112 H^{+}

Time (min)	W$_{sample}$ (gr)	V$_{KOH}$ (ml)	X$_2$
0	0.353	29.8	0
60	0.3	25.6	0.09894
120	0.31	26.5	0.26367
180	0.255	22.3	0.21893
300	0.263	22.5	0.33122
420	0.224	19.9	0.26494
540	0.226	19.6	0.49312