PRODUCTION OF LACTIC ACID ESTERS BY REACTIVE DISTILLATION

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ÖZGEN YALÇIN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

SEPTEMBER 2011

Approval of the thesis:

PRODUCTION OF LACTIC ACID ESTERS BY REACTIVE DISTILLATION

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ABSTRACT

PRODUCTION OF LACTIC ACID ESTERS BY REACTIVE DISTILLATION

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September 2011, 104 pages

The esterification of lactic acid with ethanol over Lewatit S 100, strong cation ion exchange resin catalyst, was studied in counter current vapor-liquid contactor type differential reactor by feeding ethanol and lactic acid solution as vapor and liquid phases, respectively. The ethanol vapor phase was diluted by dry air and the water removal was achieved by the mass transfer of water from liquid to vapor phase. Effect of ethanol to lactic acid feed molar ratio and vapor flow rate on fractional conversion and water removal efficiency were tested at 40-70°C of column temperature range.

It was observed that Lewatit S 100 was adequate catalyst for esterification of lactic acid with ethanol. Increase in ethanol to lactic acid feed molar ratio enhanced both lactic acid conversion and water removal by upper product stream. However, lactic acid conversion was suppressed by the increase of inlet vapor flow rate because of the decrease in ethanol concentration in gas phase which affected both esterification reaction rate and mass transfer rate. The reaction temperature is the other important parameter that affects the mass transfer of ethanol from vapor to liquid phase. Although reaction rate and equilibrium conversion values were promoted by temperature, the lower solubility of ethanol in liquid phase limited the fractional conversion while promoted the water mass transfer from liquid to vapor phase. The optimized vapor phase velocity and temperature can yield higher conversions than the equilibrium conversion at the same temperature and initial composition. Therefore, low pressure organic acids such as lactic acid can be successfully esterified by using counter current V-L contactor type reactors and by using integrated reaction and separation units.

Keywords: Esterification; Lactic Acid; Ethyl Lactate; Reactive Distillation; Ion Exchange Resin

ÖZ

LAKTİK ASİT ESTERLERİNİN TEPKİMELİ DAMITMA KOLONUNDA ÜRETİMİ

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Laktik asitin etanol ile esterleşmesi Lewatit S 100, güçlü katyon iyon değiştirici reçine katalizör, üzerinde, etanol ve laktik asit çözeltisini sırasıyla buhar ve sıvı halde besleyerek, zıt akış buhar-sıvı temas şeklindeki ayırıcı reaktörde çalışılmıştır. Etanol buhar fazı kuru hava ile seyreltilmiş ve suyun, buhar fazdan sıvı faza kütle aktarımı ile ayrılması başarılmıştır. Etanol/laktik asit molar besleme oranının ve hava akış miktarının dönüşüm ve su ayrılma verimine etkisi 40-70°C kolon sıcaklığı aralığında test edilmiştir.

Lewatit S 100'ün laktik asitin etanol ile esterleşmesi için uygun katalizör olduğu gözlenmiştir. Etanol/laktik asit molar besleme oranındaki artış, gerek laktik asit dönüşümünü gerekse suyun üst ürün akıntısıyla ayrılmasını artırmıştır. Buna rağmen, esterleşme tepkime hızı ve kütle aktarımı hızını etkileyen gaz fazdaki etanol derişiminin düşmesi nedeniyle, laktik asit dönüşümü, hava akış miktarının artmasıyla bastırılmıştır. Tepkime sıcaklığı, etanolün buhardan sıvı faza kütle aktarımını etkileyen diğer önemli bir parametredir. Tepkime hızı ve denge dönüşüm değerleri sıcaklıkla artsada, etanolün sıvı fazdaki düşük çözünürlüğü, suyun sıvı fazdan buhar faza kütle aktarımı artarken dönüşümü kısıtlamıştır. En iyi buhar fazı hızı ve sıcaklık, aynı sıcaklık ve başlangıç bileşimindeki denge dönüşümünden daha yüksek dönüşümleri sağlayabilir. Onun için, laktik asit gibi düşük basınç organik asitler zıt akış gaz-sıvı temas şeklindeki reaktörler ve birleştirilmiş tepkime ve ayırma birimleri kullanılarak başarıyla esterleşebilirler.

Anahtar Kelimeler: Esterleşme; Laktik Asit; Etil Laktat; Tepkimeli Damıtma; İyon Değiştirici Reçine

To my beloved family,

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisor, Prof. Dr. Gürkan Karakaş for his scientific guidance, support and advice throughout this research. Without his motivation, I could not come to the end of this thesis. I also would like to thank Prof. Dr. Haluk Hamamcı for his support.

I would like to express my appreciation to Mahmut Engin Aytürk and Serap Akbelen Özen for the guidance of their thesis.

I acknowledge Kerime Güney for her endless encouragement and motivation, for not being me alone during my experiments, and for her technical guidance. I also acknowledge İsa Çağlar for his assistance about my experimental setup and glass objects. I also want to thank Gülten Orakçı for her help with the GC analyses, Turgut Aksakal and all the staff in the machine shop for their technical assistance.

I am grateful to Berker Fıçıcılar, Birsu Aydoğdu, Bade Kavurt, Nisa Ilgaz, A. Eren Vedin, Egemen Agi, Emre Yılmaz, Emre Tatlı, Fulya Akpınar, Ayça Abakay, Deniz Ayan and Deniz Güloğlu for their friendship, suggestions, advices and sharing tough days of my life.

Lastly, I want to express my deepest thanks and respect to my parents; Fahriye and Mustafa Yalçın, my brother Özkan, my sister Özgün and her husband Deniz İyidinç, and my little and lovable niece; Derin İyidinç. I feel always their everlasting love, support, and encouragement, sacrifice and trust in me.

Finally, Scientific and Research Council of Turkey (TUBiTAK) is kindly acknowledged for the National Scholarship during MSc (2210 Yurt İçi Yüksek Lisans Burs Programı).

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NOMENCLATURE

C: Temperature dependence constant

C_i: Species concentration, mol/L

$C_{W,L}$: Water concentration in the reaction medium, mol/L

$C_{W,G}$: Water concentration of the inlet gas stream, mol/L

D: Diameter of the column, m

J: Mass flux

k_H: Henry's law constant for solubility in water at any temperature, mol/kg*bar

k_H^o: Henry's law constant for solubility in water at 298.15 K, mol/kg*bar

k_La: Mass transfer coefficient, m/s

k_1: Overall forward reaction rate constant of Eqn. (4.1), L/(mol.min)

k_2: Overall backward reaction rate constant of Eqn. (4.1), L/(mol.min)

k_3: Homogeneous forward rate constant of Eqn. (4.2), L/(mol.min)

k_4: Homogeneous backward rate constant of Eqn. (4.2), L/(mol.min)

K: Equilibrium constant, dimensionless

L_{LA}: Volumetric flow rate of liquid stream, L/min

MW_i: Molecular weight of species

N_i: Normality of solution, mol/mL

N_{io}: Initial moles of species, g mole

N_{iu}: Moles of upper product species, g mole

N_{ib}: Moles of bottom product species, g mole

N_{Re}: Reynolds number of empty column

$R.F_i$: Relative response factor of species

T^o: Reference temperature, K

T: Temperature, K

W_i: Weight of species, g

wt%: Weight percentage

V_i: Volume, mL

$V_{gas\ stream}$: Volumetric flow rate of gas stream, L/min

V_s: Superficial velocity, m/s

GREEKS:

P_{air}: density of air, kg/m^3

μ_{air}: viscosity of air, kg/m.s

ABBREVIATIONS:

Es: Ethyl lactate

EtOH: Ethanol

Exp. #: Experiment code

FA: Free acid

GC: Gas Chromatography

HCl: Hydrochloric acid

HPLC: High-performance liquid chromatography

KHP: Potassium hydrogen phthalate

KOH: Potassium hydroxide solution

L: Liquid phase

LA: Lactic acid

LLA: Lactoyllactic acid

TCD: Thermal Conductivity Detector

V: Vapor phase

CHAPTER 1

INTRODUCTION

Lactic acid is an important species that can be produced by fermentation by using renewable carbohydrates, biomass, coal, petroleum, or natural gas liquids. It is possible to make polymers, copolymers, plastics, fibers, solvents, and oxygenated chemicals from lactic acid. Polymers of lactic acid are environmentally compatible and can be used instead of petrochemical polymers (Sanz et al., 2002; Datta and Henry, 2006). Solvents derived from lactic acid are accounted as green solvents. They are environmentally friendly, because they are derived from the agricultural crops. Green solvents are environmentally friendly alternative to petrochemical solvents which are the key of most chemical processes (Doble and Kruthiventi, 2007).

Ethyl lactate, which is the main member of lactic acid esters, is one of the alternative organic solvents. It can be produced from carbohydrate feedstock. Low-cost agricultural waste can be a source of carbohydrates. Ethyl lactate is 100% biodegradable. This means that ecotoxicity is very low and biodegradation time is very short. It is non-ozone depleting and noncorrosive. It has favorable toxicological properties. It is non carcinogenic and not teratogenic. It does not show any potential health risk and it can be easily recycled. Besides of low vapor pressure and low surface tension, ethyl lactate has high solvency power and high boiling point. Low toxicity makes it possible to use in food products such as beer, wine and soy products (Vu et al., 2006). It is alternative solvent for replacing toluene, acetone, xylene, methylene chloride, chloroform, etc. It can be used as cleaning solvent for the manufacturing of magnetic and electronic devices and for the polyurethane industry. It can be used as paint stripper, graffiti remover, and remover of greases, oils, adhesives, and solid fuels from metal surfaces (Doble and Kruthiventi, 2007; Aparicio and Alcalde, 2009).

The production of ethyl lactate can be provided by the esterification of lactic acid with ethanol. This is equilibrium limited reaction does not reach completion and leads to low conversion. Esterification reactions occur over acidic or basic catalysts and they can be self-catalyzed by the lactic acid. This is slow process and needs homogeneous or heterogeneous catalyst (Pereira et al., 2008; Aytürk, 2001). As homogeneous catalyst, strong mineral acids such as sulfuric acid, phosphoric acid, and hydrogen chloride can be used (Chahal and Starr, 2006). However, homogeneous catalyst has some drawbacks such as causing equipment corrosion and side reactions (Qu et al., 2009). On the other hand, heterogeneous catalyst has some advantages such as eliminating the corrosive environment, being easily removed from the reaction mixture by decantation or filtration, and eliminating the side reactions thus provides the highly pure products (Altıokka and Çıtak, 2003). As solid heterogeneous catalyst, acid-treated clays, heteropolyacids, iodine, zeolites and ion exchange resins can be used. However, the most commonly used one is ion exchange resins whose effectiveness in liquid phase esterification has been proved (Pereira, 2008; Aytürk, 2001).

Because of the reversible and equilibrium limited nature of the esterification reactions, several methods can be applied to drive the reaction towards the desired product. It can be obtained by using excess amount of alcohol or removing the formed ester or the co-product water continuously (Yadav and Kulkarni, 2000). Removing the products from the system can be possible by applying reaction and separation simultaneously. Reactive separation processes have been used commercially for decades. Also today, academic and industrial communities have interest on the development and applying reactive separations technology (Kulprathipanja, 2002). These separative reactors provide the shift of the reaction product composition beyond the equilibrium by an in-situ removal. These type reactors are the member of multifunctional reactors which is one of the basic components of process intensification. At this view point, reactive distillation, reactive adsorption, membrane reactors, reactive extraction, and reactive absorption can be used to separate products in situ reaction. Reactive distillation is potentially interesting options for esterification, which is also applied commercially by Eastman Chemical to produce methyl acetate (Stankiewicz, 2003).

Reactive distillation can be applied to reversible chemical reactions, in which conversion of the reactants is limited with equilibrium. The combination of reaction and distillation in one unit provides enhancing the conversion by Le Chatelier's principle, suppressing undesired side reactions, obtaining high conversions with stoichiometric feed flow rates, avoiding the hot spot problems by using heat of reaction for separation (Bessling et al., 1998). Carrying out the esterification reaction in a countercurrent reactor under two phase conditions has many benefits. Liquid acid flows down through the column from the top and alcohol vapors flows upward from the bottom. Alcohol vapor can absorb produced water and carries it up. Removing of water by the alcohol derives the reaction to the ester side, thus achieves high conversion. In such a system, using solid catalyst, ion exchange resins, enhance the reaction rate and there is no catalyst removal from the process streams (Doble and Kruthiventi, 2007).

In typical esterification reactions with reactive distillation, ester is the volatile component which can be separated from reaction mixture by distillation. However, esterification of lactic acid is not fit into these categories. Ethanol is the most volatile component with the boiling point of 78 °C. Lactic acid has almost no volatility and decomposes by heating above 90 °C. Ethyl lactate (boiling point is 155 °C) and water (100 °C) are the intermediate components (Asthana et al., 2005). Moreover, lactic acid purity is also important on esterification reactions. The most concentrated lactic acid is available as 90 wt% commercially; because of the formation of lactides and self polymerization occur by the further removal of water. However, 90 wt% lactic acid contains to 46 mole% water which is very high concentration limiting the esterification equilibrium conversion. Limited number of studies has been published in literature about lactic acid esterification and reactive separation systems.

In this study, esterification reaction of concentrated lactic acid solution and ethanol vapor over strong acid cation exchange resin, Lewatit S-100, through continuous reactive separation system was investigated. For this purpose, the counter current packed type vapor-liquid contactor separation/reaction system is proposed. This system aims the reaction between lactic acid solution which is fed from the top of the column with ethanol vapor-dry air gas phase fed counter currently. The effect of ethanol/lactic acid feed rate, air flowrate and temperature on the conversion and water removal efficiency were examined.

CHAPTER 2

LITERATURE SURVEY

2.1 LACTIC ACID

Lactic acid, $CH_3CHOHCOOH$, is an alpha- hydroxyl-acid. Lactic acid occurs in nature and also it can be produced by fermentation or chemical synthesis (Datta, 2004). It was first discovered in 1780 by Swedish chemist Scheel being isolated from sour milk. After being produced by fermentation by the French Scientist, Fremy, its industrial production was started in 1881. (Dutta and Dutta, 2006; Chahal and Starr, 2006; Kirk-Othmer, 1991). The detailed history of lactic acid can be found in the book of Benninga (1990).

Lactic acid is a commodity chemical with some advantages of being made from biomass, coal, petroleum, or natural gas liquids, having both a hydroxyl group and a carboxyl acid group, and being optically active (McKetta, 1988). These properties make lactic acid a mature fine chemical in order to use new applications. Traditionally, lactic acid was used for food preservative and acidulent. Lactic acid has very large-volume uses in widely chemical reactions for because of hydroxyl and carboxyl acid groups (Parimal et al., 2009).

2.1.1 PHYSICAL PROPERTIES

Lactic acid is the simplest hydroxycarboxylic acid. It occurs as a racemate (DL) and in two optically active forms, L (+) lactic acid and D (-) lactic acid because of an asymmetrical carbon atom (Chahal and Starr, 2006). Although L (+) lactic acid occurs naturally in blood, racemic mixture, both L (+) lactic acid and D (-) lactic acid, is produced by chemical reactions and fermentation (Kirk-Othmer, 1991). Figure 2.1 gives the enantiomers of lactic acid.

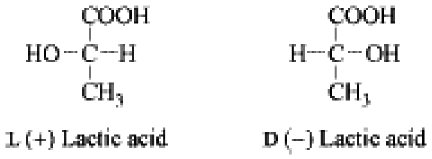


Figure 2.1 Enantiomers of Lactic Acid

Since there is difficulty in anhydrous lactic acid production, a range of melting point can be given as 18-33 ℃ (Ullmann, 1990). However, melting point property is affected by the optical composition; melting point of the crystalline acid is estimated to be 52.7-52.8 ℃ (Kirk-Othmer, 1991). The boiling of anhydrous lactic acid was estimated as approximately 125-140 ℃ at 27kPa (Ull mann, 1990).

Lactic acid is normally obtained as concentrated solution, up to 90 wt%. Since it is which is very hygroscopic, it contains significant amount of lactoyllactic acid and other lactic acid oligomers (Ullmann, 1990).

Synthetically produced lactic acid, racemic mixture, is optically inactive; on the other hand, produced form by fermentation is optically active (Chahal and Starr, 2006). The D(-) enantiomer is laevorotatory and The L(+) enantiomer is dextrorotatory; whereas, the esters and salts of L(+) lactic acid are leovorotatory. According to content of lactoyllactic acid of L(+) lactic acid, an aqueous solution can be laevorotatory, because L(+) lactoyllactic acid is laevorotatory. Lactoyllactic acid content also affects the rotation angle of lactic acid; optical rotation of 20 wt% and 80 wt% aqueous solutions were determined as +2.53° and +5.10°, respectively. The dissociation constant K of lactic acid is 1.38×10^{-4} at 25 ℃ (pK=3.86). 10 wt% solution has the pH as 1.75. It is possible to prepare lactic acid-lactate buffers in the pH range of 2.75-4.75. Some physical data of lactic acid at 25 ℃ are given in Table 2.1 (Ullmann, 1990).

Table 2.1 Physical data of aqueous lactic acid solutions at 25 ℃

Concentration, wt%	Density, g/mL	Viscosity, mPa s	Refractive index	Conductivity, mS/cm
6.29	1.0115	1.042	1.3390	3.670
25.02	1.0570	1.725	1.3586	3.823
54.94	1.1302	4.68	1.3909	1.530
88.60	1.2006	36.9	1.4244	0.0567

2.1.2 CHEMICAL PROPERTIES

Oxidation, reduction, condensation and substitution at the alcohol group are the reactions of lactic acid (Kirk-Othmer, 1991; Datta, 2004)).

2.1.2.1 Oxidation

Under photochemical activation, oxidation by strong oxidizing agents leads to the formation of decomposition products. The type of the oxidant and the reaction mechanism affect the yield and specificity of the products (Kirk-Othmer, 1991; Datta 2004).

2.1.2.2 Reduction

By reduction, the carboxyl group can be converted to an alcohol group by catalytic hydrogenolysis or hydrogenating chemicals. Propylene glycol can be produced from the esters of lactic acid. Optical configuration is affected by using hydrogenating chemicals or applying catalytic hydrogenolysis. (Kirk-Othmer, 1991; Datta, 2004).

2.1.2.3 Condensation

Condensation of lactic acid involves the reaction with the hydroxyl or the carboxyl or both groups of the acid. Dehydration, aminolysis, and the esterification (intramolecular or with another alcohol or acid) in high yields are the types of reactions (Chahal and Starr, 2006). Lactic acid undergoes intramolecular or self-esterification reactions. Lactoyllactic acid, linear polyesters, and higher poly(lactic acid)s,or dilactide are the products of these reactions. By removal of water it is possible to produce linear polyesters, lactoyllactic acid and higher poly(lactic acid)s (Kirk-Othmer, 1991; Datta, 2004).

2.1.2.4 Substitution at the Alcohol Group

Aliphatic, aromatic, and other substituted derivatives are the products of the substitution at the OH group of lactic acid (Kirk-Othmer, 1991; Datta, 2004).

2.1.3 PRODUCTION AND MANUFACTURING TECHNOLOGIES

Lactic acid can be produced by chemical synthesis or by carbohydrate fermentation. In recent years all lactic acid production is based on carbohydrate fermentation (Datta and Henry, 2006).

2.1.3.1 Chemical Synthesis

Commercial process is based on lactonitrile. Equations 2.1-2.4 give the reaction steps. Firstly lactonitrile is produced by the reaction of hydrogen cyanide and acetaldehyde in the presence of base catalyst. By distillation recovered and purified crude lactonitrile is hydrolyzed to lactic acid using either concentrated hydrochloric or sulfuric acid. Ammonium salt is also produced as by-product. It is further esterified with methanol to produce methyl lactate. At the end, lactic acid is produced by hydrolyzing the purified methyl lactate with water (Kirk-Othmer, 1991; Datta, 2004).

$$CH_3CHO + HCN \rightarrow CH_3 - CHOH - CN \tag{2.1}$$

$$CH_3CHOHCN + 2\ H_2O + \tfrac{1}{2}\ H_2SO_4 \rightarrow CH_3CHOHCOOH + \tfrac{1}{2}\ (NH_4)_2SO4 \tag{2.2}$$

$$CH_3CHOHCOOH + CH_3OH \rightarrow CH_3CHOHCOOCH_3 + H_2O \tag{2.3}$$

$$CH_3CHOHCOOCH_3 + H_2O \rightarrow CH_3CHOHCOOH + CH_3OH \tag{2.4}$$

2.1.3.2 Fermentation

As traditional technologies, homolactic organisms such as *Lactobacillus delbrueckii*, *L. bulgaricus*, and *L. leichmanii* are used in the commercial carbohydrate fermentation processes. Acid is neutralized by the excess calcium hydroxide/carbonate, it maintains pH around 5-6, and calcium salt of acid is produced in the broth. 2-4 days are needed to complete the fermentation in a batch or fed-batch mode. Calcium lactate containing broth is filtered to remove cells. It is treated with carbon, evaporated and acidified with sulfuric acid. Thus, the salt is converted into lactic acid and insoluble calcium sulfate which is removed by filtration. Technical-grade lactic acid is produced by purification of the filtrate by carbon columns and ion-exchange and then evaporation. High-purity product can be produced by esterification of technical-grade lactic acid by methanol or ethanol, recovering of the ester by distillation and hydrolyzing with water (Kirk-Othmer, 1991; Datta, 2004). The conventional process for lactic acid manufacture from carbohydrate is given by Figure 2.2 (Datta and Henry, 2006).

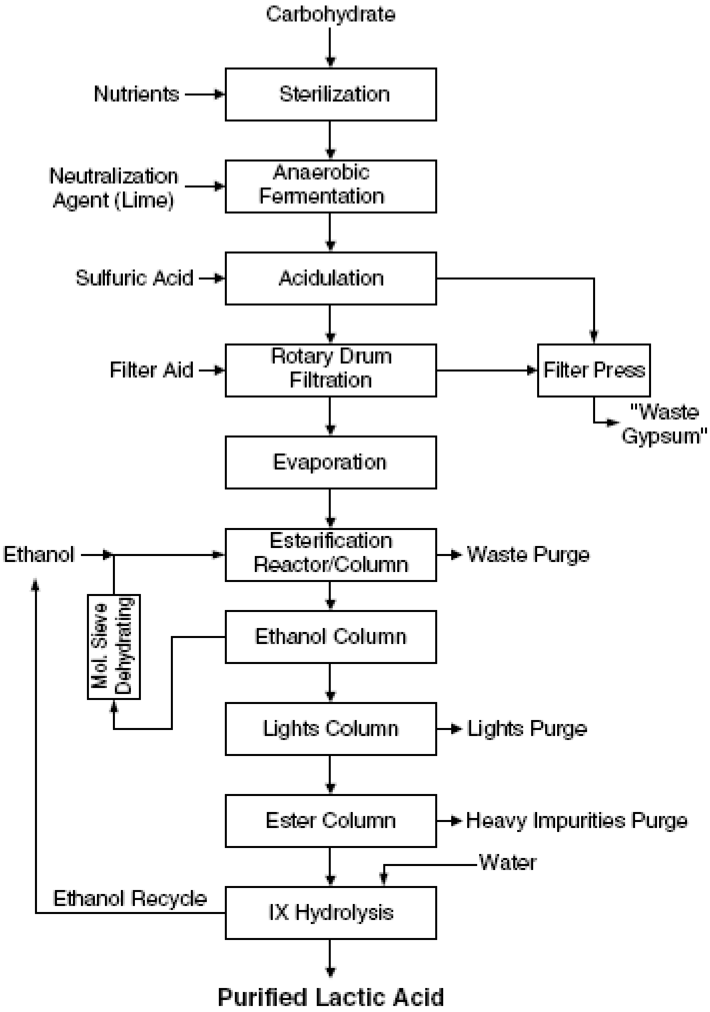


Figure 2.2 Conventional process for lactic acid manufacture from carbohydrate

Membrane-based separation and purification technologies such as microfiltration, ultrafiltration and electrodialysis (ED) are the novel and advanced processes which do not produce a salt waste.

2.1.4 ESTERS OF LACTIC ACID

Since lactic acid has both hydroxyl and carboxyl functional groups, it is possible to obtain lactic acid esters by intramolecular or self-esterification reactions and esterification with alcohols.

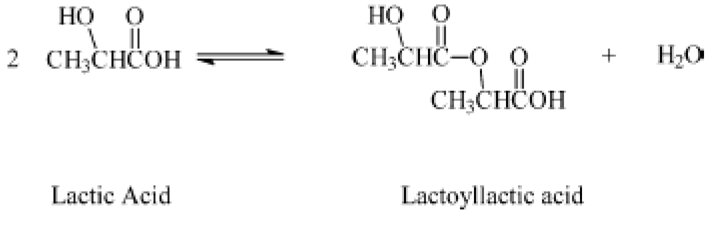
2.1.4.1 Lactic Acid Esters, Formed via Combination of Alcohols

Esterification reactions are used to recover and purify lactic acid from impure solutions or to produce esters..

Direct reaction of lactic acid with low molecular weight alcohols such as ethanol, butanol and methanol is more effective with passing the vapors of alcohol through lactic acid previously heated to a temperature above the boiling point of the alcohol. Transesterification is used to produce higher alcohol esters from methyl or ethyl lactate in the presence of catalyst (sulfuric acid, toluene sulfonic acid or aluminum isopropylate). Ammonium lactate can be converted to ammonia and the esters by alcoholysis. Also there are some processes based on pervaporation based on esterification of ammonium lactate to ethyl lactate. (Kirk-Othmer, 1991; Ullmann, 1990; Datta, 2004).

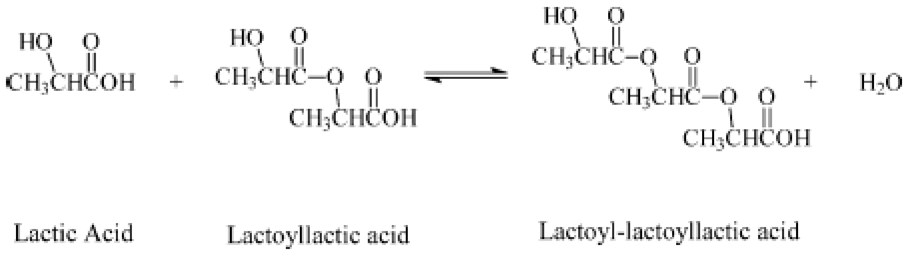
2.1.4.2 Intermolecular Esters

Lactic acid tends to undergo self-esterification and produces an ester. Experimental results has shown that dilute (<20 wt.%) solutions contain only monomer form. It can form lactoyllactic acid, linear polyesters, higher poly(lactic acid)s, or the cyclic dimer, dilactide in concentrated lactic acid solutions. By intermolecular self-esterification, higher oligomers can be formed with increasing degree at high acid and low water concentration, and high temperature. Equation (2.5) gives the lactoyllactic acid formation and the structure of it (Kirk-Othmer, 1991; Vu et al., 2005; Datta, 2004).



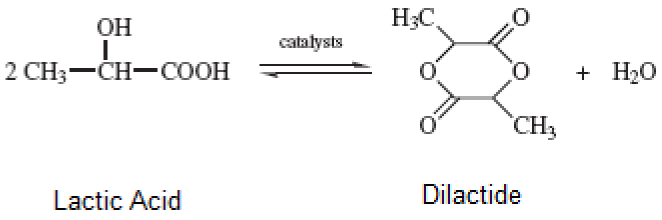
$$2\ \mathrm{CH_3CH(OH)C(=O)OH} \rightleftharpoons \mathrm{CH_3CH(OH)C(=O){-}O{-}CH(CH_3)C(=O)OH} + \mathrm{H_2O} \qquad (2.5)$$

Lactoyllactic acid can also be estrified with lactic acid to form the trimer lactoyllactic acid. It is possible to produce higher chain intermolecular polyesters by this way. Equation (2.6) gives the trimer lactoyllactic acid formation (Vu et al., 2005).



(2.6)

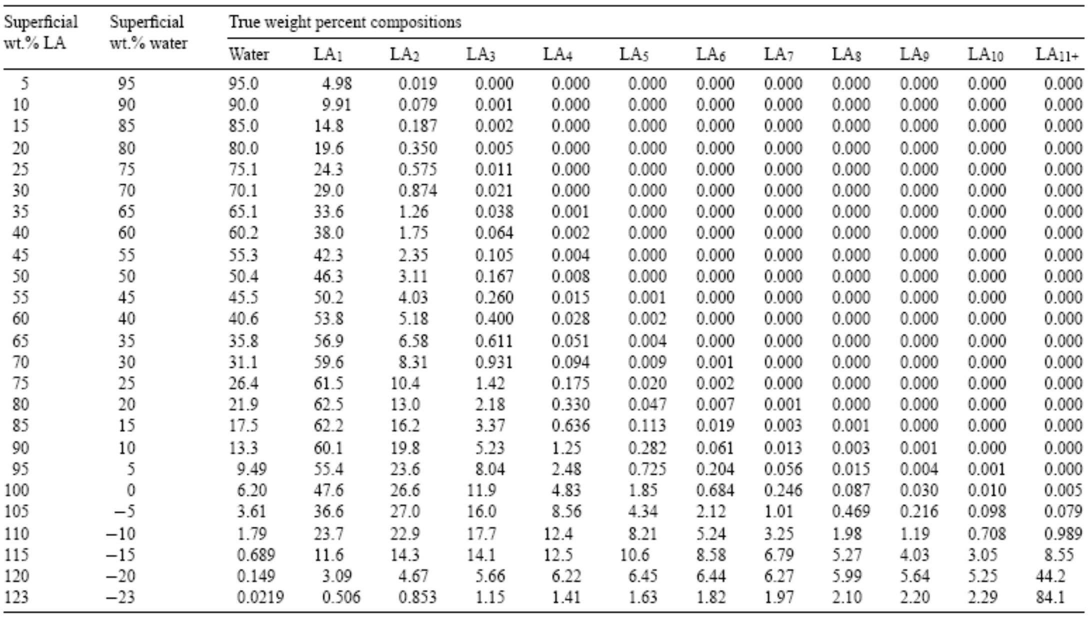
Dilactide, a cyclic ester, is formed from a recemic (DL) mixture of lactic acid. In the presence of primarily weakly basic catalyst, dilactide can be produced as following reaction (Kirk-Othmer, 1991; Datta, 2004).



(2.7)

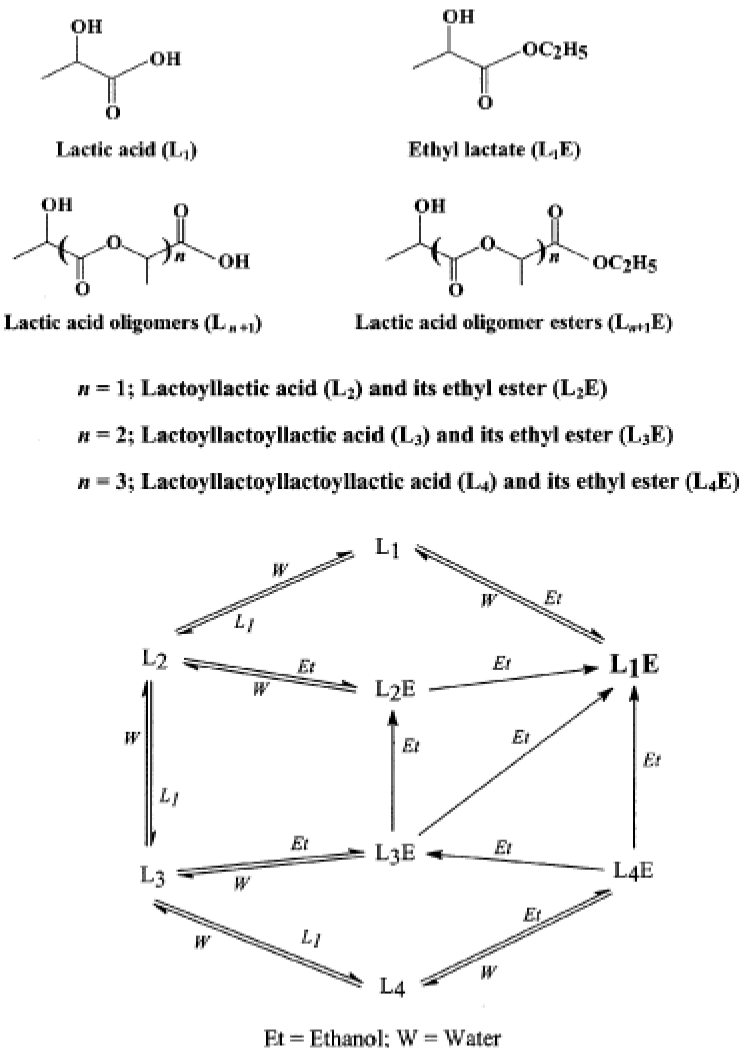
Commercially available aqueous solutions contain varying amounts of lactoyllactic and polylactic esters, depending on the concentration and age of the solution. The concentration of purchased lactic acid solution is expressed in wt.%, which is superficial weight percentage. The superficial weight percent is the weight of total monomer with the corresponding water of hydrolysis divided by total solution weight. True weight percent express actual percentage of free acid and oligomers of lactic acid. It is the division of the mass of a particular sample and the total mass of the individual species. The composition of lactic acid and its oligomers in solution can be found using combination of titration, GC analysis and HPLC analysis. Table 2.2 gives the results of oligomer distribution in lactic acid solutions. (Vu et al., 2005).

Table 2.2 Model calculations of true wt.% of lactic acid oligomers for various superficial compositions



Superficial wt.% LA	Superficial wt.% water	True weight percent compositions											
		Water	LA_1	LA_2	LA_3	LA_4	LA_5	LA_6	LA_7	LA_8	LA_9	LA_{10}	LA_{11+}
5	95	95.0	4.98	0.019	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	90	90.0	9.91	0.079	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
15	85	85.0	14.8	0.187	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	80	80.0	19.6	0.350	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
25	75	75.1	24.3	0.575	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
30	70	70.1	29.0	0.874	0.021	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
35	65	65.1	33.6	1.26	0.038	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
40	60	60.2	38.0	1.75	0.064	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
45	55	55.3	42.3	2.35	0.105	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000
50	50	50.4	46.3	3.11	0.167	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000
55	45	45.5	50.2	4.03	0.260	0.015	0.001	0.000	0.000	0.000	0.000	0.000	0.000
60	40	40.6	53.8	5.18	0.400	0.028	0.002	0.000	0.000	0.000	0.000	0.000	0.000
65	35	35.8	56.9	6.58	0.611	0.051	0.004	0.000	0.000	0.000	0.000	0.000	0.000
70	30	31.1	59.6	8.31	0.931	0.094	0.009	0.001	0.000	0.000	0.000	0.000	0.000
75	25	26.4	61.5	10.4	1.42	0.175	0.020	0.002	0.000	0.000	0.000	0.000	0.000
80	20	21.9	62.5	13.0	2.18	0.330	0.047	0.007	0.001	0.000	0.000	0.000	0.000
85	15	17.5	62.2	16.2	3.37	0.636	0.113	0.019	0.003	0.001	0.000	0.000	0.000
90	10	13.3	60.1	19.8	5.23	1.25	0.282	0.061	0.013	0.003	0.001	0.000	0.000
95	5	9.49	55.4	23.6	8.04	2.48	0.725	0.204	0.056	0.015	0.004	0.001	0.000
100	0	6.20	47.6	26.6	11.9	4.83	1.85	0.684	0.246	0.087	0.030	0.010	0.005
105	−5	3.61	36.6	27.0	16.0	8.56	4.34	2.12	1.01	0.469	0.216	0.098	0.079
110	−10	1.79	23.7	22.9	17.7	12.4	8.21	5.24	3.25	1.98	1.19	0.708	0.989
115	−15	0.689	11.6	14.3	14.1	12.5	10.6	8.58	6.79	5.27	4.03	3.05	8.55
120	−20	0.149	3.09	4.67	5.66	6.22	6.45	6.44	6.27	5.99	5.64	5.25	44.2
123	−23	0.0219	0.506	0.853	1.15	1.41	1.63	1.82	1.97	2.10	2.20	2.29	84.1

Asthana et al. (2005) reported the complexity of the self-esterification and esterification of lactic acid with specifically ethanol in following figure.



n = 1; Lactoyllactic acid (L_2) and its ethyl ester (L_2E)

n = 2; Lactoyllactoyllactic acid (L_3) and its ethyl ester (L_3E)

n = 3; Lactoyllactoyllactoyllactic acid (L_4) and its ethyl ester (L_4E)

Figure 2.3 Lactic acid oligomerization and esterification reactions

2.1.5 PRODUCTS AND USES

Traditionally, lactic acid is used in mostly food and food-related applications. The development and the commercialization of the biopolymers increase the use of lactic acid. In the future, the growth of lactic acid is expected to use as a feedstock for biodegradable polymers, green solvents and oxygenated chemicals (Vu et al., 2005; Datta, 2004).

Lactic acid is nonvolatile, odorless and has a mild acidic taste, a good preservative and pickling agent. In a wide variety of processed foods, lactic acid is used in conjunction with other acidulants as an acidulant, flavoring, pH buffering agent or inhibitor of bacterial spoilage. To increase shelf-life and reduces the growth of anaerobic spoilage organisms, lactic acid solutions and salts are added in the disinfection and packaging of poultry and fish. Esters of lactate salts with longer chain fatty acids are the emulsifying agents used in foods (Vu et al., 2005; Datta, 2004).

Technical-grade lactic acid is used in the leather tanning industry, textile-finishing operations and acid dying of wool. Lactic acid and ethyl lactate is used in pharmaceutical and cosmetic applications and formulations. Ethyl lactate is the active ingredient in many antiacne preparations. Optically active lactic acid or its esters are used for synthesis of drugs, agrochemicals, and herbicide (Vu et al., 2005; Datta, 2004).

L-isomer of lactic acid is preferred as the feedstock for dilactide production and dilactide, itself, is also primary feedstock for polymerization to make high molecular weight polymers of lactic acid, biodegradable thermoplastics. The properties of lactic acid copolymers can approach the properties of petroleum-derived polymers such as polystyrene, flexible poly(vinyl chloride) and vinylidene chloride. The products of polydilactide-based resins are used for plastics/packaging applications and the products of polydilactide-based fibers are used in textiles and fiber applications (Datta and Henry, 2006).

In many processes such as chemical reactions, separation and product purification procedures, product carriers, washing and cleaning, and heat or mass transfer operations, solvents play an important role. Many of the organic solvents commonly used nowadays are volatile compounds and hazardous air pollutants, flammable fluids and toxic for humans or surrounding environment. Alternative compounds with low environmental impact, low toxicity both for humans and animals, readily biodegradable, easily recyclable, stable, with high solvency ability, readily available, and inexpensive. Especially, lactate esters of low molecular weight alcohols such as ethyl, propyl and butyl lactate are the potential growth area for lactic acid derivatives as environmentally friendly, green solvents. Ethyl lactate is very adequate alternative green solvent with environmental, toxicological, technological, and economical advantages for many applications. It is biodegradable, easy recyclable, noncorrosive, and non-ozon-depleting, and has suitable physical and chemical properties without any potential health risk (Aparicio and Alcalde, 2009). Lactate esters can be used in electronics and precision cleaning. Blends with other biologically derived solvents have solvating and cleaning properties. Ethyl lactate and butyl lactate are inert ingredients for use in the formulation of pesticides and other bioactive compounds.

Figure 2.4 (Datta and Henry, 2006) summarizes the potential products and uses of lactic acid.

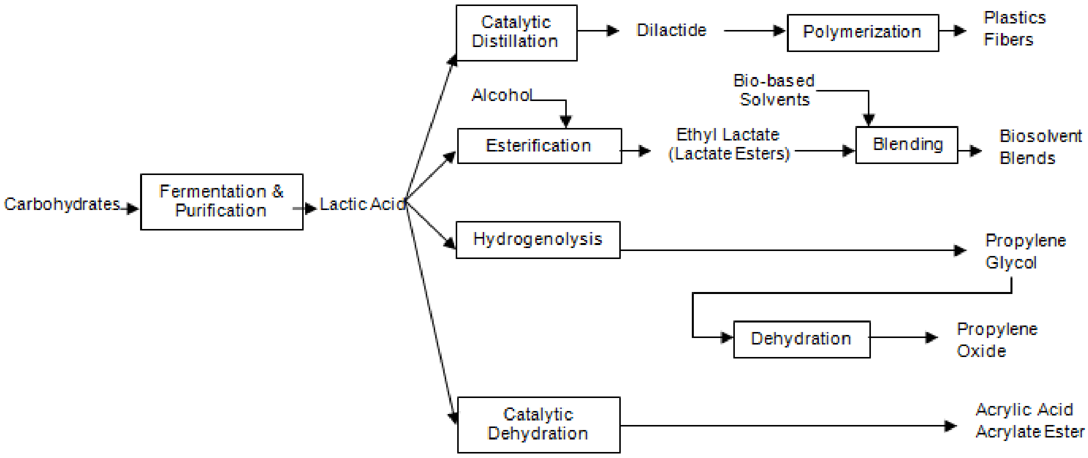


Figure 2.4 Lactic acid-based potential products and uses

2.2 ESTERIFICATION

The simplest and most common method of esterification is the reaction of carboxylic acid and an alcohol with the elimination of water. The structure of alcohols effect the reaction; primary alcohols such as methyl, ethyl, n-propyl, and n-butyl alcohols, give higher yield and the more rapid reaction than the reaction with secondary and tertiary alcohols (Kirk-Othmer, 1991; Aslam et al., 2000).

In esterification reactions, there is an equilibrium between the reactants and products; acid, alcohol, produced ester and water. This equilibrium is expressed with equilibrium constant. In general, when the equilibrium constant is below unity, ester is not prepared by direct interaction of alcohol and acid; the acid anhydrides or acid chlorides are used in these cases (Kirk-Othmer, 1991; Aslam et al., 2000).

Because of the equilibrium, esterification reactions usually do not go to completion. By removing one of the products; either ester or water, it is possible to achive conversion approaching to 100%. Distillation, reactive extraction and reverse osmosis are the used method to remove the esterification products. Moreover, azeotropes can be used to remove water from the system. Binary azeotropes of the alcohol and water can be utilized for the completion of the reaction of higher boiling, nonvolatile esters. Entraining steam or inert gases are other possible methods to shift the reaction (Kirk-Othmer, 1991; Aslam et al., 2000).

Esterification is usually carried out in batch reactor; however, in commercial production, continuous production is preferred. Vapor phase esterification of alcohols and acids gives generally higher conversion than in the corresponding liquid-phase reactions (Kirk-Othmer, 1991; Aslam et al., 2000).

Catalyst is used in these reactions to accelerate the reaction. Otherwise, only strong carboxylic acids react quickly without a catalyst. Strong mineral acids; sulfuric acid, phosphoric acid, hydrogen chloride, ion exchangers; cation exchangers such as sulfonated polystyrene, zeolites, Lewis acids; boron trifluoride, and other compounds; graphite hydrogen sulfate are possible catalysts for esterification reactions (Chahal and Starr, 2006).

2.3 CATALYSTS

Catalysts are commonly divided into two basic types: heterogeneous and homogeneous. Heterogeneous catalysts are in different phase to the reaction medium, reactants being in the gaseous phase. They are widely used in industry as surface catalysts; reaction takes place on the surface of the catalyst which is the external surface or the surface within the internal pores of the solid. On the other hand, homogeneous catalysts are uniformly distributed in the reaction medium which is liquid phase. Table 2.3 compares the advantages and disadvantages of homogeneous and heterogeneous catalysts (Lancaster, 2002).

Table 2.3 Comparison of heterogeneous and homogeneous catalysts

Heterogeneous	Homogeneous
Usually distinct solid phase	Same phase as reaction medium
Readily separated	Often difficult to separate
Readily regenerated and recycled	Expensive/difficult to recycle
Rates not usually as fast as homogeneous	Often very high rates
May be diffusion limited	Not diffusion controlled
Quite sensitive to poisons	Usually robust to poisons
Lower selectivity	High selectivity
Long service life	Short service life
Often high-energy process	Often takes place under mild conditions
Poor mechanistic understanding	Often mechanism well understood

The catalytic reagents reduce the energy of the transition state, thereby reducing the energy input required for a process. The regeneration and reversibility of catalysts are good for green processes (Doble and Kruthiventi, 2007). This re-generation property can be obtained by heterogeneous catalysts.

For direct esterification reactions, typical catalysts such as sulfuric acid alone, sulfuric acid in conjunction with molecular siceves, hydrogen chloride, arylsulfonic acids, acidic ion exchange resins coupled with calcium sulfate, polymer-bound aluminum chloride (both as Lewis acid and a dehydrating agent), intercalated graphite bisulfite, boron trifluoride, and trifluoroacetic anhydride can be used (Yadav and Mehta, 1994). Ion exchange resins can act as insoluble acids and bases for the catalysis of chemical reactions. They can be easily separated from the liquid phase by filtration or other suitable means, used in continuous operation in fixed beds and they are generally more selective (Inglezakis and Poulopoulos, 2006).

2.3.1 ION EXCHANGE RESIN

Ion exchange is a process in which cations or anions (charge in a solution) are exchanged with cations or anions on a solid sorbent (the ion exchanger) reversibly. By interchanging cations with other cations and anions with other anions, electroneutrality is maintained in both liquid and solid phases (Ullmann, 1989; Kirk-Othmer, 1995; Velizarov and Crespo, 2010).

Many naturally occurring inorganic and organic materials have ion exchange properties (Velizarov and Crespo, 2010). It was firstly discovered by absorbing ammonium sulfate and converting to calcium sulfate in a tube filled with soil. Moreover, certain types of coal were sulfonated to give a chemically and mechanically stable cation exchanger. The synthetic polymers for ion exchange were produced by Adams and Holmes. They produced cation and anion exchangers by polycondensation of phenol with formaldehyde and a polyamine, respectively (De Dardel and Arden, 2008). Although water softening by ion exchange was known, the deionization of water, which requires stable materials capable of performing both cation and anion exchange, became possible (Nachod and Schubert, 1956; Ullmann, 1989; Abrams and Millar, 1997).

Softening and deionization of water are the principle application for ion exchange. Moreover, catalysis and purification of chemicals are the applications of it (Kirk-Othmer, 1995; Velizarov and Crespo, 2010).

2.3.1.1 Types of Ion Exchange Resins

There are many naturally occurring and synthetic ion exchangers. Natural inorganic ion exchangers are many natural minerals, such as clays (e.g. bentonite) and zeolites (e.g. clinoptilolite). Crystalline aluminosilicates are the common natural minerals with cation exchange properties. Some common natural organic ion exchangers are polysaccharides, such as cellulose and peat. Synthetic inorganic ion exchangers are synthetic zeolites and titanates and silico-titanates. Synthetic organic ion exchangers are the largest group available today. The resin matrix is flexible network of hydrocarbon chains. The resins are made insoluble by cross-linking of these chains. The degree of cross-linking determines the many of the resin properties, such as resistance to mechanical degradation and porosity. The type ion exchangers have high capacity, wide versatility, and low cost compared to some synthetic inorganic media; however, they have radiation and thermal stability limitations, such as 150 °C is the maximum temperature that cation-exchange resins can withstand, this value is 70°C for anion-exchange resins (Inglezakis and Poulopoulos, 2006).

Synthetic organic ion exchange resins are categorized according to functional groups attached to a polymeric matrix. Matrices for ion exchangers are obtained by polymerization of styrene, acrylate, methacrylate or acrylonitrile. Four primary types of functionalities are strong acid, weak acid, strong base and weak base (Ullmann, 1989; Kirk-Othmer, 1995; De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

2.3.1.1.1 Strong Acid Cation Exchange Resins

Polystyrene beads give cross-linked polystyrene 3-sulfonic acid after treatment with concentrated sulfuric or chlorosulfonic. Therefore, this type resins have sulfonic acid groups, $–SO_3^-H^+$, attached to an insoluble polymeric matrix. Amberlite IR 120, Dowex HRC, Duolite C 20, and Lewatit S 100 are the commercial examples of this type (De Dardel and Arden, 2008; Velizarov and Crespo, 2010).
Functional groups can be in either hydrogen or sodium form. In many industrial applications, resins are used in the hydrogen form. The selectivity of resin for Na^+ is greater than it is for H^+.

$$\mathrm{resin} - \mathrm{SO_3^-H^+} + \mathrm{Na^+} + \mathrm{OH^-} \leftrightarrow \mathrm{resin} - \mathrm{SO_3^-Na^+} + \mathrm{HOH} \qquad (2.8)$$

Exchange reactions are reversible reactions which allow resins to be used many times by regeneration procedure, return resins to the hydrogen form. For regeneration of strong acid ion exchangers, dilute hydrochloric acid, sulfuric acid or other mineral acids are used.

2.3.1.1.2 Weak Acid Cation Exchange Resins

Poly(acrylic acid) matrix presences in this type of resins. They have carboxylic acid groups, -COOH, attached to the polymer matrix. Amberlite IRC 76, Duolite C 433, and Relite CC are the commercial examples of this type. Possible exchange reaction is given with Equation 2.3 (De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

$$\mathrm{resin-COO^{-}H^{+}+Na^{+}+HCO_3^{-}\leftrightarrow resin-COO^{-}Na^{+}+H_2CO_3} \tag{2.9}$$

2.3.1.1.3 Strong Base Anion Exchange Resins

Chloromethylated polystyrene is the polymer matrix of this group. The chlorine in the chloromethylated group can be replaced by an amine or by ammonia. According to the selected reaction, they can be strongly or weakly basic. Resins with quaternary ammonium groups, $-N^{+}R_3OH^{-}$, where R is usually CH_3, are strongly basic. When anions are adsorbed from the liquid phase, hydroxide ions are released by the resin. Thus, acidity in the liquid can be eliminated and the resin is converted to a salt form. Regeneration is occurred with the dilute solution of NaOH (De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

$$\mathrm{resin-N^{+}(CH_3)_3OH^{-}+H^{+}+Cl^{-}\leftrightarrow resin-N^{+}(CH_3)_3Cl^{-}+HOH} \tag{2.10}$$

2.3.1.1.4 Weak Base Anion Exchange Resins

They have primary, secondary and tertiary amines as the functional group. The most common one is tertiary amine, $-N(CH_3)_2$. They are preferred for removal of strong acids because of ease in regeneration. They can adsorb weak organic acids; e.g. formic acid and acetic acid, but cannot remove weak organic acids; e.g. carbonic acid and silicic acid (De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

$$\mathrm{resin-N(CH_3)_2H^{+}OH^{-}+H^{+}+Cl^{-}\leftrightarrow resin-N(CH_3)_2H^{+}Cl^{-}+HOH} \tag{2.11}$$

2.3.1.2 Properties of Ion Exchange Resins

2.3.1.2.1 Degree of Cross-Linking and Porosity

Increase in the degree of cross-linking produces harder and less elastic resins. Higher degrees of cross-linking provide more resistance to oxidizing conditions. Moreover, if the structure is too dense, ionic motion is slow down. It reduces the operating capacity of the resin. Increase in degree of cross-linking is needed when greater differences in ionic affinity are required. Lower levels of cross-linking may be chosen when easier desorption and regeneration efficiency are required, especially in water softening. Ion exchange resins can be either microporous or macroporous structure. Degree of cross-linking is higher in macroporous resins than in micropororus resins. Cross-linking degree and amount of solvent added modify the porosity and the mechanical strength of the resins. Microporous resins are referred as gel or gelular type resin. The porosity is meaningful for this type resins when the particles are swollen with water or other solvent. When the resin is dry, there is no porosity. Exchange is faster in a macroporous resin. Macroporous resins are used when reversible uptake of large molecules is necessary without fouling the resin (Ullmann, 1989; Kirk-Othmer, 1995; De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

2.3.1.2.2 Exchange Capacity

Capacity is a measure of the quantity of ions, acid, or base removed by an ion-exchange material. There are two types of capacity: total capacity and operating capacity. Total capacity represents the number of active sites available. It is a measure of equivalents on a weight or volume basis. Operating capacity is a measure of the quantity of ions, acids or bases adsorbed, or exchanged, under the conditions existing during batch or columnar operation. It depends on concentration and quantity of regenerant, concentration and type of ions to be absorbed, rate of percolation, temperature and depth of resin bed (Ullmann, 1989; Kirk-Othmer, 1995; De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

2.3.1.2.3 Stability and Service Life

It can be divided some parts as chemical stability of the matrix, thermal stability of active groups, mechanical stability, osmotic stability, radiation stability, and resistance to drying (Ullmann, 1989; Kirk-Othmer, 1995; De Dardel and Arden, 2008; Velizarov and Crespo, 2010).

Chemical stability of the matrix: Highly oxidizing conditions such as presence of chlorine or chromic acid can attack the matrix of ion exchange resin and destroy cross-linking. Cross-linking is broken down and sulfonated organic compounds are released, thus the resin swells until it softens. Highly cross-linked resins with a greater resistance to oxidation should be used when oxidizing agents are present.

Thermal stability of active groups: When the temperature limit, which is recommended by the manufacturer, is exceeded, both cation- and anion- exchange resins lose their functional groups. This loss rate increases exponentially as the temperature rises above the upper limit.

Mechanical stability: Polymerization type affects the resin’s mechanical stability. Poly-condensation type resins are fragile and it is suitable to use them in fixed beds. By suspension polymerization, it is possible to produce perfect spheres which can be used in continuous moving bed ion exchange plants without any damage. Gel type anion resins are poor at withstanding compression and they are weaker than cation exchange resins.

Radiation stability: When the radiation exceeds the limits of tolerance, both cation and anion exchange resins lose weight and capacity, their cross-linking is removed and water-soluble components are released.

Resistance to drying: Resins should be kept moist in order to prevent the stresses created by repeated drying and rewetting.

2.3.1.2.4 Particle Shape and Size

Resins are mostly small and round beads with diameter between 0.3 and 1.2 mm. The speed of the exchange reaction can increase with small beads. For high flow rates required systems, coarse type resins minimize the head loss in columnar operations; however, they are subject to a greater rate of breakage.

2.3.1.2.5 Density

Density of an ion exchange resin defines the weight of wet resin per unit volume. Resin density is an important property and characteristic for the resins. It is dependent on the copolymer structure, the degree of cross-linking, functional group's nature and the ionic form of the functional groups. Resin density determines the hydrodynamic behavior in counterflow system. For strong acid cation ion exchange resins, the density range is 1.18-1.38. If there is a change in the density after more usage, it means that there is a chemical degradation (Velizarov and Crespo, 2010).

2.3.1.2.6 Moisture and Water Content

Ion exchange resins contain both fixed and mobile ions. Water molecules located in the beads always surround these ions. Water content is characteristic for resins since it depends on the resin matrix, the structure of the functional groups, and the ionic form of these groups. Therefore, this water retention capacity governs the exchange capacity, mechanical strength and the kinetics of the ion exchange resins (De Dardel and Arden, 2008).

2.3.1.3 Principles of Ion Exchange Kinetics

The diffusion of the mobile ions is the rate determining step rather than the chemical reaction between fixed ions and mobile counter ions in fully ionized systems (Ullmann, 1989; De Dardel and Arden, 2008).

For example, the cation concentration is much greater in the cation exchange resin than that in solution. Diffusion of any cations out of the resins into the dilute solution creates a negative charge in the solid phase and a net positive charge in the solution. This is called as Donnan Potential which provides anions presence in the resin. Therefore, the anion does not participate in the cation ion exchange process (De Dardel and Arden, 2008).

Figure 2.5 (De Dardel and Arden, 2008) illustrates the uptake of Na^+ ions by a bead of H^+ form resin.

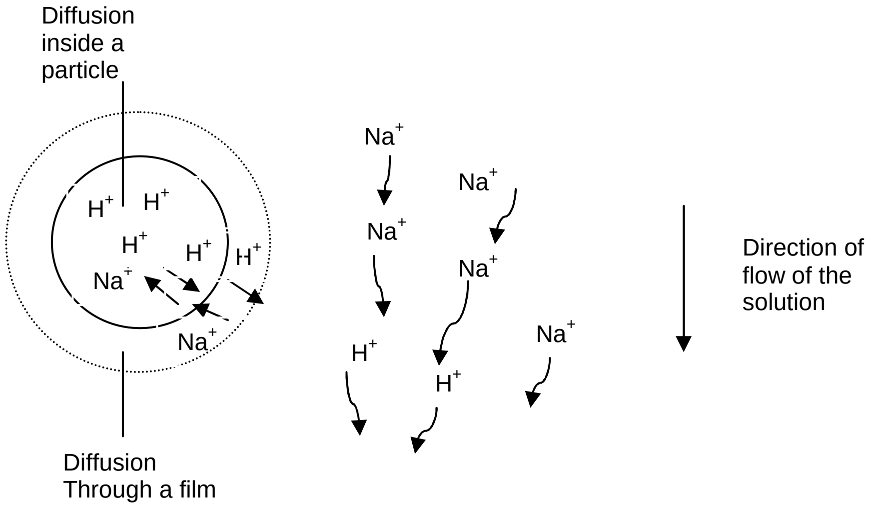


Figure 2.5 Diffusion through a film and inside a particle

There are large excess of available Na^+ ions in the bulk solution. The Nernst film (a static layer of solution, Figure 2.6) surrounds the bead. This film is not affected from convection (flow) around the bead; diffusion only occurs. High flow rate decreases the film thickness. Concentration gradient occurs within Nerst film not outside of it (De Dardel and Arden, 2008).

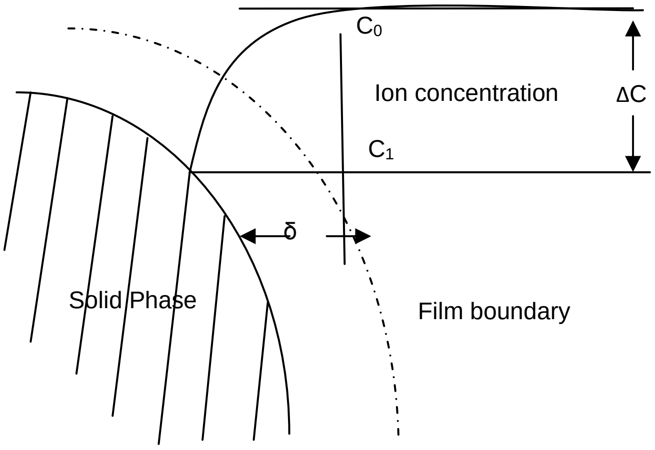


Figure 2.6 Nernst Film

Diffusion of ions within the resin (particle diffusion) and diffusion in the Nernst film (film diffusion) are two steps which may be rate determining because of the different rates. The slower step controls the overall ion exchange rate.

Generally, forward and reverse exchange rates differ. In a conventional strong acid cation exchange resin, H^+ / Na^+ exchange, uptake of Na^+ ions, forward exchange, is faster than regeneration (reverse exchange). The mobility of the H^+ ion is higher. If there is faster ion initially in the resin, exchange will be faster (De Dardel and Arden, 2008).

2.3.1.4 Ion Exchange Catalysis

Standard ion exchange resins can be used in many organic reactions because of the insoluble properties of acid or bases. Especially the strong acid type is an excellent substitute for sulfuric acid and other similar catalytic agents (Ullmann, 1989; Kirk-Othmer, 1995). Heterogeneous catalysis can be carried out in aqueous or nonaqueous solvents solutions and in reactions in the gas phase. Although there are two phases, solid and liquid, it is more adequate to describe the catalysis by ion exchangers as homogeneous catalysis in the pore phase instead of heterogeneous catalysis. The reason is that the ions of the exchangers that are involved in the catalytic reaction are dissolved in the pores of the solid, where they act as in a homogeneous solution (Inglezakis and Poulopoulos, 2006).

There are several advantages to the use of ion exchange resins (Nachod and Schubert, 1956):

1. By a simple filtration step, catalyst-free products can be obtained.
2. The catalyst can be recovered frequently by means of a simple filtration step.
3. Continuous reactions can be obtained by passage of the reactants through beds of ion exchange resin catalyst.
4. Unusual selective effects are possible.
5. Side reactions can be kept at a minimum.
6. Special corrosion resistant equipment is not necessary as in the case of some soluble catalysts.

The use of cation exchange resins as catalysts is increased due to the increased stability and specific control of structure. Although there are certain selectivity effects and special problems such as low porosity, the reactions catalyzed by soluble salts and acids are also catalyzed by cation exchange materials. In general, esterification, ester hydrolysis, alcoholysis, acetal condensation, and sugar inversion are the systems that have been studied. By cation exchange catalysis, reduction in side reactions and occasional specificity is observed.

Continuous process for the esterification of ethyl alcohol with acetic acid using a cation exchange resin as the catalyst was studied by Saletan and White (Nachod and Schubert, 1956). They assumed following mechanism for the reaction:

$$\mathrm{R'COOH + H^+ \leftrightarrow R'C^+(OH)_2} \tag{2.12}$$

$$\mathrm{R'C^+(OH)_2 \leftrightarrow R'C^+ = O + H_2O} \tag{2.13}$$

$$\mathrm{R'C^+ = O + ROH \leftrightarrow R'COOR + H^+} \tag{2.14}$$

Since the reactants must reach the exchange site before any catalytic effect can be expected, the problem of diffusivity of reactants through the liquid and resin phases must be considered. According to their study, they correlated a volumetric efficiency factor, which relates the rate of reaction inside the resin particles with the reaction rate at the surface of the exchanger. They concluded that mass transfer in the liquid stream will be negligible factor in determining overall rates because in the resin phase diffusivities are much lower than in the liquid phase.

2.4 REACTIVE SEPARATION

The concepts of process intensification were pioneered by Colin Ramshaw and his co-workers at ICI in the 1970s (Doble and Kruthiventi, 2007). This concept is defined as ‘technologies and strategies that enable the physical sizes of conventional process engineering unit operations to be significantly reduced’ with improving mass-transfer rates to match that of the reaction, improving heat-transfer rates to match the exothermicity of a reaction, and having an appropriate residence time for the reaction (Lancaster, 2002). By decreasing equipment volume, energy consumption, or waste formation, and leading to cheaper, safer, and sustainable technologies, it presents the development of innovative apparatuses and techniques that offer drastic improvements in chemical manufacturing and processing (Stankiewicz, 2001). Process intensification is applied in chemical process industry to reduce investment and operating costs of chemical plants to increase profitability and mitigate greenhouse gas emissions (Dautzenberg and Mukherjee, 2001). Figure 2.7 gives the basic components of process intensification (Stankiewicz, 2003).

One of the components of process intensification is multifunctional reactors. It can be defined as reaction equipment in which performance is enhanced by combining at least one more additional function (Agar, 1999; Stankiewicz, 2003; Stitt, 2004). The desired improvements in multifunctional reactors are yield and productivity, investment and operating costs, and flexibility and safety.

The most significant type of these reactors is the integration of reaction and separation in one unit. This integration can be divided into two: non-interrelating or interrelating. In non-interrelating integration, neither reaction affects the separation nor does the separation have influence upon the reaction. The aim is smaller inventory, compacter plant layout or better energy management. On the other hand, in interrelating integration, the aim is to benefit from the interaction between reaction and separation. In-situ separation shifts the reaction beyond the equilibrium and chemical reaction enhances the separation efficiency (Stankiewicz, 2003). In those cases, one can speak about reactive separations or separative reactors.

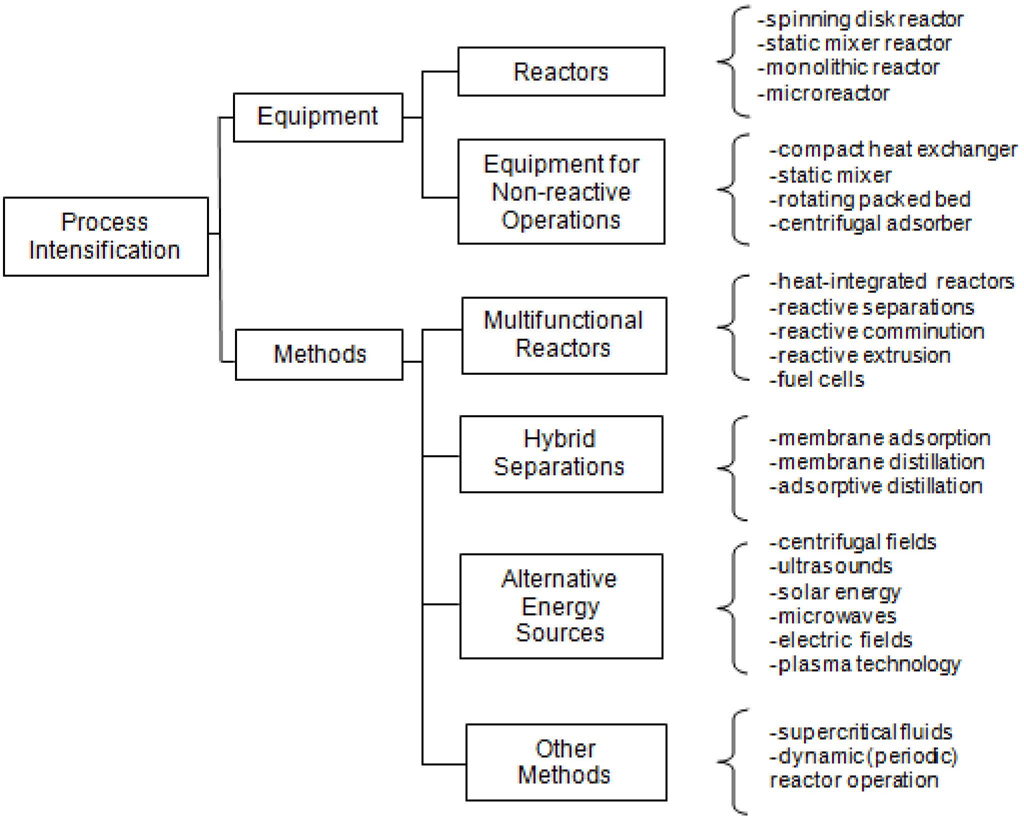


Figure 2.7 Process intensification and its components

The reactor and the separator operations are integrated into a single process operation with simultaneous reaction and separation in the reactive separation process. This process can occur under milder process conditions; e.g. reduction in reaction temperature, solution acidity, reaction pressure. This provides the improvements in reaction selectivity, product quality, catalyst life, run lengths, and capital savings. This enhances reaction rate and conversion. This leads to alternative design options for heat addition and removal. Reduced equipment fouling and coking and designing of inherently safer unit are achieved in this process by suppressing the byproduct formation, polymer or heavies formation. Besides these advantages, regarding as new technology also causes some disadvantages. The advantages and disadvantages associated with developing and operating reaction separation technologies are summarized in Table 2.4 (Kulprathipanja, 2002).

Table 2.4 Advantages and disadvantages of reactive separation process

Advantages	Disadvantages
Enhanced reaction rates Increased reaction conversion Enhanced reaction selectivity Reduced reaction severity Increased catalyst life Simplified separations Improved product quality Heat integration benefits Reduced equipment fouling/coking Inherently safer unit Reduced operating costs Reduced capital investment Novel process configurations Novel equipment designs	Relatively new technology Limited applications window Extensive experimental development Complex modeling requirements Extensive equipment design effort Increased operational complexity Significant development costs Increased scale-up risks

Reactive distillation, extraction with reaction, absorption with reaction, adsorption with reaction, reactive membrane separation and reactive crystallization are the classes of reactive separation. Graça et al. (2011) and Pereira et al. (2009) studied the synthesis of 1,1-Dibutoxyethane and ethyl lactate, respectively, in a fixed-bed adsorptive reactor using Amberlyst 15. Silva et al. (2011) studied the production of ethyl lactate in the simulated moving bed membrane reactor. Lux et al. (2010) studied the combination of esterification with extractive separation of methyl acetate by using n-decane as solvent.

2.4.1 REACTIVE DISTILLATION

Reactive (catalytic) distillation is a good example of process innovation and commercially used in methyl-acetate synthesis by Eastman Chemicals (Stankiewicz, 2003; Dudukovic, 2009).

As a multifunctional reactor, in a reactive distillation, separation and reaction occur in the same vessel. A distillation column is filled with catalytically active packing. The catalyst may be present as a solid-phase packing or in the same phase as the reacting species. The catalyst used for heterogeneous reactive distillation is incorporated into a porous spherical baskets, cylindrical container for catalyst particles, fiber-glass and horizontally disposed wire-mesh supporting structures, gutters or tubes, or structured catalysts, e.g. Sulzer's KATAPAK-S and Koch-Glitsch's KATAMAX, can also be used (Taylor and Krishna, 2000). In the column, reacting species are converted on the catalyst while reaction products are continuously separated by fractionation (Kulprathipanja, 2002; Stankiewicz, 2003). In a conventional chemical plant, there are reaction sections and separation sections, separately, are often linked together by material and energy recycles. On the other hand, in reactive distillation system, there are significant reductions in both energy and equipment (Luyben and Yu, 2008).

There are some advantages and disadvantages of reactive distillation. In equilibrium limited reactions in column reactor, it is possible to remove the product in situ by reactive distillation. Removing one or more products from the reaction phase provides the shifting of equilibrium; therefore, establishing high conversion. Also, when the relative volatilities are favorable, it is possible to maintain the reagents in the column and remove only the products. It leads to reduction in plant cost, capital savings. If the reaction is exothermic, the heat of the reaction can be used to vaporize the species and reduce the reboiler duty. In conventional processes, there should be many distillation columns and entrainers should be used to break the azeotropes formed by species. Instead, according to the reactive distillation conditions, it can allow the azeotropes to be reacted away in a single vessel. Removing one of the products from the reaction mixture can reduce the rates of side reactions, thus, improves the selectivity for the desired products. Against these advantages, there are also disadvantages. If there is a long residence time requirement, a large column size and large tray hold-ups will be needed. If the optimum conditions of temperature and pressure for reaction and distillation are far from each other, if the reagents and products do not have suitable volatility, and if there are very large flow rates, it is not preferable to use reactive distillation (Kulprathipanja, 2002).

According to the types of reactions, the types of reactive distillation column changes (Luyben and Yu, 2008). Let us consider the system in which chemical reaction, liquid phase and reversible, involves the two reactants (A & B) and two products (C & D).

$$\mathrm{A} + \mathrm{B} \underset{\mathrm{catalyst}}{\Longleftrightarrow} \mathrm{C} + \mathrm{D} \tag{2.15}$$

Relative volatilities have important role on the design of the column. Being of the products as lightest and heaviest components with the reactants as the intermediate boiling ones is the ideal case. In this case, lighter reactant is fed into the lower section of the column and the heavier reactant is fed into the upper section of the column (Luyben and Yu, 2008). The section below the fresh feed of lighter reactant, stripping section, separates heavier product from the lighter components, and the section above the fresh feed of heavier reactant, rectifying section, separates the lighter product from the heavier components. Other parameters for reactive distillation are column pressure, temperature in the column, and holdup (or the amount of the catalyst) (Luyben and Yu, 2008).

Luyben and Yu (2008) gave the all possible effects on the design of reactive distillation in their books. When they gave the possible configurations according to the boiling point rankings, they proposed additional column to separate the products for the following situation. In the production of biobased esters and biodiesel, a typical example is the recovery of lactic acid, both two reactants are the heaviest and lightest components of the system where the products as the intermediate boiling components. This situation in an ideal case is not possible, unless the consumption of all of the heaviest reactant before it reaches the bottom of the reactive zone and reaction with all of the lightest reactant before it reaches the top of the reactive distillation are provided (Luyben and Yu, 2008). For this situation, they proposed reacting the reactants in a reactive distillation column and taking the products by a side stream and then feeding into the additional column in order to separate the products.

The operation of reactive distillation is more complex than the conditions in conventional reactors or distillation columns because in situ separation and reaction causes the complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion and chemical kinetics (Taylor and Krishna, 2000).

Figure 2.8 and 2.9 give the transport processes in reactive distillation with homogeneous liquid phase reaction and heterogeneous catalyzed reactions, respectively (Taylor and Krishna, 2000).

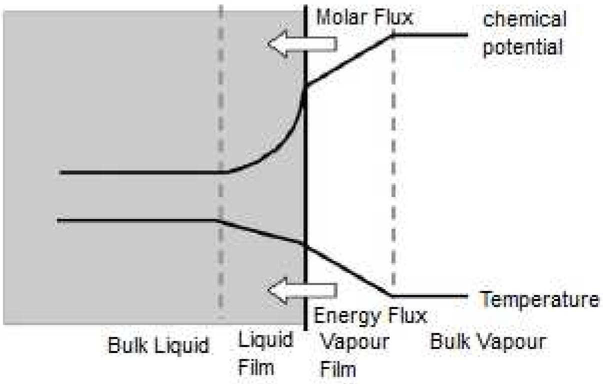


Figure 2.8 Transport process with homogeneous liquid-phase reaction

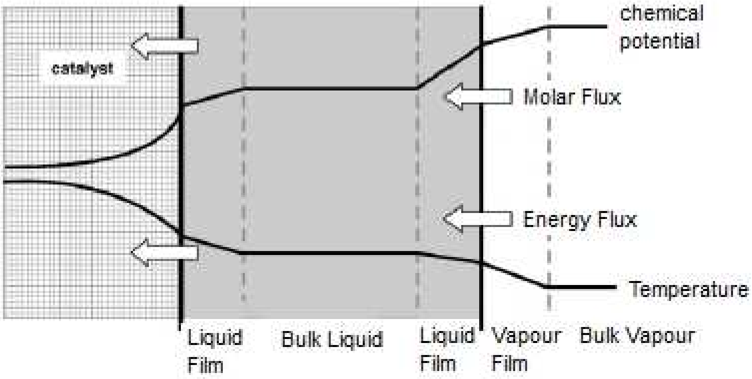


Figure 2.9 Transport process with heterogeneous catalyzed reactions

In the homogeneous reactive distillation, reaction occurs only in the bulk liquid phase. When the reaction is rapid, reaction will also occur in the liquid film. When the reaction is very fast, the reaction occurs only in the film. On the other hand, when the reaction is very slow, it takes place in the film whereas its effect on the mass transfer can be disregarded.

In heterogeneous reactive distillation, transport processed occur at length scales of pore diameter of solid and column dimensions and time scales of diffusion within the solid and column dynamics. The interaction between the time and length scale and the nonlinearities forced by the in situ diffusion and chemical kinetics in counter-current contacting create the multiple steady-states and complex dynamics. Mass transport to the catalyst and diffusion and the reaction if the catalyst is porous, inside the catalyst particle, if the catalyst is not porous, at the surface should be taken into account (Taylor and Krishna, 2000). It can be assumed that there is no reaction in the vapor or liquid films. Mass transfer through the vapor-liquid interface can be given with Maxwell-Stefan equations. Diffusion equations should be used for the diffusion of reactants to the catalyst surface and products away from the solid catalyst surface. If reaction occurs at the surface of the solid catalyst, the boundary conditions at the liquid-solid interface can be found by the reaction kinetics. If reaction occurs inside the porous catalyst, it is necessary to model diffusion and reaction inside the catalyst with transport from bulk liquid to the catalyst surface and bulk liquid from the catalyst surface (Taylor and Krishna, 2000). Design of reactive distillation column can be based on either equilibrium stage models or non-equilibrium stage models (Taylor and Krishna, 2000).

2.5 ESTERIFICATION STUDIES

The production of ethyl lactate has been studied since the study of Troupe and Dimilla (1957). They studied the kinetics of esterification reaction of ethyl alcohol and lactic acid, 85 and 44 wt % analytical garde, using sulfuric acid as catalyst in sealed tubes in constant temperature bath. They corrected the possible side reaction of sulfuric acid with ethyl alcohol and total catalyst amount in the reaction mixture.

According to the previously mentioned comparison of homogeneous and heterogeneous type catalysts, using heterogeneous catalysts in esterification reactions has gained importance. Marchetti and Errazu (2008) studied the esterification of oleic acid and various alcohols, anhydrous and 96% ethanol, 1-propanol, 2-propanol and butanol, with the comparison of different heterogeneous catalysts such as solid ion exchange resin (Dowex Monosphere 550A), zeolites and enzymes. They mainly studied with solid resin in order to compare the effects of alcohols; however, they concluded that enzyme gave the highest activity and conversion but in 3 days. Moreover, Tesser et al. (2010) studied the esterification of fatty acid on acid exchange resins, Amberlyst 15 and Relite CFS. There are many studies where acetic acid is used as a reactant in esterification reaction on solid resin. Esterification of acetic acid with isobutanol, n-amyl alcohol, and methanol in the presence of Amberlite IR-120, Amberlyst-36 and Amberlyst 15 was studied by Altıokka and Çıtak (2003), Akbay and Altıokka (2011) and Pöpken et al. (2000).

Yadav and Kulkarni (2000) studied the kinetics of the esterification of lactic acid with isopropanol over various ion exchange resins, calys, and clay supported heteropoly acids. They checked the effects of catalyst type, speed of agitation, catalyst loading, intraparticle diffusion, and mole ratio on the kinetics of the reaction.

Qu et al. (2009) studied the kinetics of esterification of dilute lactic acid with isobutanol and n-butanol over acid ion-exchange resins. They concluded that reaction rate increased with increase in temperature and catalyst loading, equilibrium conversion increased with the increase in the molar ratio of alcohols to lactic acid. Three models, pseudo-homogeneous, Langmuir-Hinshelwood and Eley-Rideal, could be used to decribe the system; however, pseudo-homogeneous model could be preferred with its simple mathematical form.

Delgado et al. (2007) studied the esterification of lactic acid with ethanol and also the hydrolysis of ethyl lactate over Amberlyst 15. They used dilute solution of lactic acid in order to deal with monomer lactic acid and water. By studying the effects of stirrer speed, catalyst size, catalyst loading, initial molar ratio and temperature, they tried to provide a general kinetic model for the system. Stirrer speed, to study the external mass transfer resistance, showed that there is little effect on the overall reaction rate. Also, no significant differences were found for different catalyst size. Reaction rate increased with the increase in reaction temperature, increase in the catalyst loading, separately and the conversion increased with the increase in the initial reactant molar ratio. They correlated the experimental data with the pseudo-homogeneous (PH) model and the Langmuir-Hinshelwood (LH) model; they obtained better results for LH model, but also results of PH model were in an good agreement because of the high polarity of the reacting medium.

Zhang et al. (2004) studied the esterification of lactic acid with ethanol over different strong acid cation exchange resins. They investigated the effects of catalyst type, catalyst loading and temperature on the reaction kinetics. They used activities instead of concentrations in order to take into account the nonideality of the liquid phase. According to their FTIR experiments, they found that water and ethanol absorbed on the resin much stronger than lactic acid and ethyl lactate did. They concluded that LH model was suitable for esterification of lactic acid with ethanol.

Asthana et al. (2006) studied the kinetics of esterification of lactic acid and its oligomers with ethanol over cation-exchange resin, Amberlyst 15. They investigated the effects of reactant molar ratio, catalyst loading, reaction temperature and lactic acid feed composition, 20%, 50%, and 88 wt % lactic acid solution. They took into account the dimer hydrolysis and esterification with ethanol and take other oligomers as one oligomer and made calculations with this assumption. They described the related esterification reaction with using simple nth- order reversible rate expressions because of the uncertainity in the absorption of the species in the liquid phase environment within the resin. They reported that at higher lactic acid concentrations, there were little or no free water for absorption onto the resin.

Engin et al. (2003) studied heterogeneous liquid-phase esterification of lactic acid with ethanol over heteropoly acid supported ion exchange resins. Those reactions were studied in batch reactor at 343 K with ethanol to lactic acid molar ratio of 1:1. They compared the catalytic activity of tungstophosphoric and molybdophosphoric acids supported Lewatit® S 100 and Amberlite® IR-120 in H^+ form. They also considered lactoyllactic acid hydrolysis. They concluded that the bare resin catalytic activity of Lewatit® S 100 was higher than Amberlite® IR-120. Moreover, the catalytic activity of molybdophosphoric acids supported Lewatit® S 100 was higher than the catalytic activity of tungstophosphoric acids supported Lewatit® S 100.

Özen (2004) investigated the kinetics of methyl lactate formation over ion exchange resin catalyst with isothermal batch experiments between 40-70 °C at atmospheric pressure. Moreover, recovery of 10% lactic acid was investigated in an absorption column using Lewatit SPC-112 H^+, ion exchange resin. After investigation of the effects of lactic acid concentration, lactic acid feed flow rate and methanol and inert carrier rate on reactor performance, it was concluded that reaction rate was slower than the mass transfer rate of methanol from gas phase to liquid phase, mass transfer resistance of liquid phase controlled the transfer of water from liquid phase to gas phase, and the increase in lactic acid concentration increased the viscosity of the liquid phase which hinders the water mass transfer to the gas phase.

Steinigeweg and Ghemling (2003) studied esterification of fatty acid decanoic acid with methanol over Amberlyst 15 counter-currently in the reactive distillation column. Structured packings, Katapak-S or Katapak-SP, were used in order to immobilize the resins inside the column. According to their experimental results, higher acid conversion was observed by separately using excess amount of ethanol and decreasing reflux ratio. At higher reflux ratios, higher amount of water presented in the reactive section. Water was the main product of esterification reactions; therefore high amounts of it affected the acid conversion. Katapak-S provided higher conversion with a smaller reactive section than Katapak-SP. Their column also included non-reactive sections, Sulzer BX, above of acid feed point and below of methanol feed point.

Kumar and Mahajani (2007) investigated the esterification of lactic acid with n-butanol over cation exchange resin, Amberlyst-15. Kinetic study was done in a batch reactor. Moreover, esterification was performed in batch and continuous reactive distillation column. They compared experimental and simulation results from Aspen plus process simulator. They mentioned the tendency of lactic acid to form oligomers and studied with dilute lactic acid solution. They concluded that increasing ratio of ethanol to lactic acid decreased the concentration of n-butyl lactate in the bottom product and nonreactive zones did not much effect on the performance of the column.

Thotla and Mahajani (2009) confirmed their investigation of reactive distillation with side draw with the esterification reaction of lactic acid with methanol over Katapak-S packing filled with cation exchange resin, Amberlyst 15®. Their column consisted of reactive and non-reactive sections. They proposed the removal of the products from both bottom of the column and another point through the column. Therefore, a weir was provided in order to create an accumulation of liquid hold up (methyl lactate, water and methanol) for side withdrawal. They studied the column under total reflux. According to the comparison of the results of conventional reactive distillation (RD) and reactive distillation with side draw (RDS), increasing mole ratio of methanol to lactic acid, increased the lactic acid conversion in RD, on the other hand, lactic acid conversion was not affected from increased ratio after a point because the conversion reached to higher values at the low ratio of methanol to lactic acid in reactive distillation side draw. They also mentioned that because of avoiding possible ester hydrolysis, they also avoided instability in column operation.

Asthana et al. (2005) pointed out the possible negative effects of the dilute lactic acid solution and studied with concentrated solution. Effects of ethanol/lactic acid feed ratio, ethanol feed temperature and reflux ratio on the performance of pilot-scale reactive distillation column, packed with Katapk-S filled with Amberlyst-15 and consisted of reactive and non-reactive stripping and enriching sections, were studied. It was shown that operating the column without reflux was logical because there was no positive effect of reflux on ethyl lactate formation. They aimed to reduce the amounts of water and ethanol in the bottom stream in order to recover ethyl lactate from the stream with a single column. They succeeded that aim by preheating the ethanol feed stream and decreasing ethanol/lactic acid ratio; whereas, ethyl lactate yield and lactic acid conversion were also lowered. Concentrated lactic acid feed provided lower ethanol requirement and less water in the column for removing; however, concentrated lactic acid feed caused the existence of oligomer acids and esters. They proposed a vacuum distillation column for ethyl lactate recovery from the bottom product of a reactive distillation column and a transesterification column in order to convert oligomers, from the bottom product of vacuum distillation column, to ethyl lactate.

Smejkal et al. (2009) proposed an experimental setup which consisted of an equilibrium fixed-bed primary reactor and a reactive distillation column for the esterification of acetic acid with ethanol. They aimed to start the reaction of equimolar mixture of ethanol and acetic acid in the primary reactor, feed the outlet

stream which is at chemical equilibrium to the reactive distillation column, and finish the reaction in this column. Moreover, they used the ternary heterogeneous azeotrope of ethanol-ethyl acetate- water to separate the organic and water phase after condenser by decanter. Therefore, they only re-fluxed the organic phase, ethyl acetate and made the production of high purity ethyl acetate possible.
Kırbaşlar et al. (2001) studied the esterification of acetic acid with ethanol over acidic ion-exchange resins, Amberlyst 15, in both batch reactor and reactive distillation column. They feed acetic acid and ethanol counter-currently to the column whose bottom section was filled with Raschig ceramic rings and catalyst and upper section filled with only Raschig rings. They examined the effects of reflux ratio and feed flow rate on the continuous reactive distillation. They collected ethyl acetate and unreacted ethanol as distillate and water as bottom product; therefore they concluded that ethyl acetate content of distillate increased by increasing reflux ratio and increasing feed flow rate decreased the content of ethyl acetate in the distillate stream. According to their study, thermodynamic equilibrium conditions were surpassed by operating in distillation column.

Beers et al. (2001) studied the liquid phase esterification reaction of hexanoic acid and 1-octanol over a specifically shaped monolith coated with a solid catalyst in-situ removing of water by counter-current stripping operation using inert carrier gas, nitrogen. In this study, liquid phase, hexanoic acid and 1-octanol, and gas phase, nitrogen, were fed to reactor from top and from bottom of column, respectively. They showed the advantage of the removal of the water by comparing the results of a closed system (autoclave) and under removal of water; just after 90 min, acid conversion reached 100% with water removal; on the other hand, in the closed system, reaction did not reach equilibrium after 120 min. They also reported the results of reaction, without any catalyst added, with stripping; reaction, in the presence of an uncoated monolith, with stripping; reaction, in the presence of coated monolith; reaction, in the presence of coated monolith, with counter-current water stripping. Removing water enhanced the acid conversion which was obtained by the reaction with coated monolith.

Nijhuis, et al. (2002) studied the effect of water in esterification reaction of alcohol with a carboxylic acid and the solid-acid catalyst coated monolith’s replacement for conventional homogeneous catalysts. They reported that without water removal by reactive stripping, conversion was lower and effect of water on the catalyst changed for different solid-catalyst types; water had inhibiting effect on the catalysts. Co-current stripping and counter-current stripping were also compared; although there was a flooding problem for counter-current stripping, higher conversion of acid was observed by counter-current stripping of water.

Jeong and Lee (1997) developed a water removal system in order to carry out the lipase-catalyzed esterification of caprylic acid and n-butanol in cyclohexane. They stripped the produced water during the reaction by continuously sparging dried air and then removed by a water trap. They removed water in the inlet air stream with passing through silica blue and analyzed the water content in the solvent medium by Karl-Fischer titrator. They observed the effects on aeration rate on the agglomeration of enzyme and the conversion of acid.

Gubicza et al. (2000) studied the enzymatic esterification of acetic acid with ethanol in organic solvent. They selected n-pentane as organic solvent and tried to remove the produced water continuously by hetero-azeotropic distillation; n-pentane and water created azeotropic mixture. They concluded that hetero-azeotropic distillation was suitable to control the water content in the reactor for large scale productions.

Bessling et al. (1998) reported the formation of methyl acetate in a reactive distillation column by using ion exchange resin supported Raschig rings as a heterogeneous catalyst at ambient pressure with a stoichiometric feed ratio. They used a technique which uses the analysis of reactive distillation line diagrams and is the combination of heuristic rules and numeric information about the feasibility of reactive distillation processes in order to design a column. After investigation of the rules of this technique, they studied in a reactive distillation column with a nonreactive stripping section at the bottom, a reactive section in the middle, and a nonreactive rectifying section at the top by introducing methanol (lower boiling reactant) below and acetic acid (higher boiling reactant) above the reactive section, respectively, in a countercurrent movement. They mainly checked the effect of reflux ratio on the conversion of the reactants and concluded that there was an optimal reflux ratio range and above and below this range conversion was decreased by being methyl acetate/methanol azeotrope and high content of acetic acid in the top product.

The present study suggests a new system for esterification reaction of concentrated lactic acid solution with ethanol. Ethanol will be fed to the system as vapor form. Lactic acid and ethanol vapor are contacted in counter-current V-L contactor type column. Moreover, in order to examine the effect of inert carrier gas in-situ removing produced water from the system; dried air will be used. Air and ethanol gas stream can be fed to the system as vapor phase. Strong cation ion exchange resin can be used as catalyst in such a system. Flowrates of the reactants and the column temperature are the possible factors which affect the response of the system.

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

$C_3H_6O_3$ (L(+)-Lactic Acid, 90% solution in water): Marketed by Acros Organics, New Jersey-USA under lot. No. A0282782 was used as an esterification reactant.

C_2H_5OH (Ethyl Alcohol, 99.5%, Baker HPLC analyzed): Marketed by J.T.Baker, Deventer-The Netherlands under lot. No. 0935209002 was used as an esterification reactant.

$C_5H_{10}O_3$ (Ethyl L(-)-lactate, 97%): Marketed by Acros Organics, New Jersey-USA under lot. No. A0261521 was used for GC calibration.

KOH (Potassium Hydroxide, Pellets, 85+%, A.C.S. reagent): Marketed by Sigma-Aldrich, Steinheim-Germany under lot. No. S47631-138 was used for titration analysis.

$C_8H_5KO_4$ (Potassium hydrogen phthalate, primary standard p.a.): Marketed by Acros Organics, New Jersey-USA under lot. No. A015256901 was used for standartization of potassium hydroxide solution.

HCl (Hydrochloric Acid, 37%): Marketed by Merck, Darmstadt-Germany under lot code K28679114 101 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 MonoPlus S 100 sodium form (Ion-Exchange Resin): Marketed by Fluka Analytical, Switzerland under lot. No. 0001451230 was used as a catalyst in esterification reaction.

3.2 EQUIPMENT

3 necked 250 mL glass reactor fitted with long condenser and placed in constant temperature water bath is used for self esterification reaction of lactic acid magnetically stirred.

As a reaction vessel, a pyrex column with 40 mm inner diameter and 35 cm height, which is surrounded by a heating jacket and is outfitted with condenser is used.

Chemap AG MV MSC 1 Type peristaltic pump for lactic acid solution feeding, aquarium air pump for air feeding, Cole-Parmer and Fischer & Porter Rotameters for measurement of air flow rate.

A titration setup consists of a magnetic hotplate stirrer and standard laboratory glassware.

Karl-Fischer volumetric titrator, KF Titrino 701 (Metrohm AG, Switzerland) was used for measuring water content in the samples. As titrant Hydranal composite 5 and as solvent methanol were used.

Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a TCD Detector and packed column (2.16 mm x 1.83 m SS) containing Porapak-Q as the stationary phase, operating at 135 °C oven temperature, 160 °C injection temperature, and 250 °C detector temperature, using 13.6 mL/min. nitrogen as a carrier gas. The column temperature is programmed initially holding at 135 °C for 2 min, heating to 230 °C at 25 °C/min, and holding at 220 °C for 10 min. For sample injection, 10 μL Hamilton micro-liter syringe was used.

3.3 EXPERIMENTAL SET UP

Continuous reactive separation experiments were conducted by using the set up that is presented in Figure 3.1. Vapor flow rate is adjusted by air line which works as by-pass.

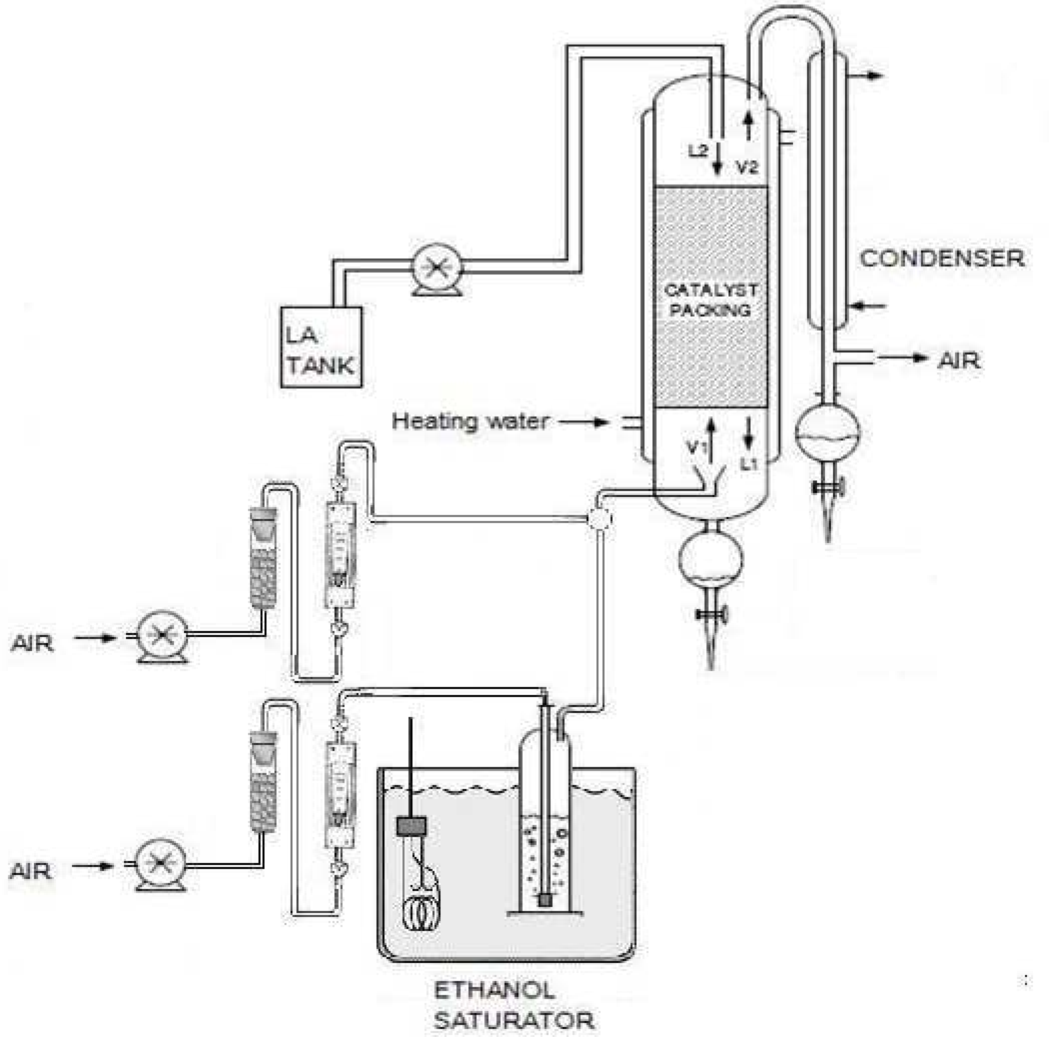


Figure 3.1 Continuous reactive separation system

3.4 EXPERIMENTAL PROCEDURE

In the main part of the study, lactic acid esterification was investigated in counter-current fixed bed reactor.

The effects of the ratio of ethanol to free lactic acid, column temperature, and vapor flow rate were studied.

Figure 3.1 illustrates the experimental setup. It contained a Pyrex column with the dimension of 40 mm diameter and 35 cm height, packed with 0.6 mm ion exchange resin. Lewatit S 100 was used as packing material. Void fraction of the bed is 0.7 when the catalyst bed height is 4 cm; density and the amount of the resins are 1.28 g/mL and 20 g, respectively. The column was surrounded by a jacket which supply heating medium. The circulated water bath temperature was maintained at 4 different values; 40, 50, 60 and 70 °C. This column was outfitted with a condenser. In order to provide temperature of -10 °C, ethylene glycol-water solution was used. Lactic acid and ethanol vapor-air mixture were passed counter-currently through the column. Lactic acid was fed to the system from the top of the column; peristaltic pump was used for lactic acid feeding. Flow of acid through the column, through the pores between resins, was driven by the gravity. Ethanol was poured into the gas washing bottle and heated in the water bath. Constant flow air passed through this bottle after passing through silica gel to obtain dry air. At the end, ethanol-air vapor mixture was fed to the system from the bottom of the column. With one more air feed line, air flow rate was adjusted. Samples from the bottom of the column and the outlet of the condenser were collected in order to be analyzed as reaction products.

In a typical experiment, firstly, column was filled with resins then, waited until temperatures of the jacket and the condenser have reached to set value. After, all temperatures (jacket, condenser, water bath for gas washing bottle) reached the desired value, firstly, only ethanol was fed to the system. The aim of that was to preheat the resin bed and to relocate remaining water in the catalyst by ethanol. Afterwards, peristaltic pump was started to feed lactic acid to the system. When first drop of bottom product was observed at the bottom of the filter, reaction time was started. Samples from the top and the bottom sections were collected, weighed and analyzed for their composition. The flow rates of the feed were calculated by weighing the feed container before and after reaction. After all, a complete material balance was performed around the system.

Temperature effect detection experiments were continued for 4 hours. At an hour interval, samples were collected from both upper and bottom sections. Ethanol to lactic acid ratio effect and vapor flow rate effect detection experiments were continued for 3 hours and at half an hour interval, samples were collected from both upper and bottom section.

3.5 ANALYSIS

Concentrations of components were determined by the combination of chemical and instrumental analyses; titration and both gas chromatography and Karl Fisher titration, respectively.

Total free acidity of the aqueous solutions (concentration of lactic acid) can be measured by acid-base titration. Because of the tendency of lactic acid to form polymeric lactic esters by self-polymerization, determination of total monomer lactic acid concentration requires hydrolysis step. Therefore, determination the amounts of lactic acid and lactoyllactic acid present in the sample, were done by means of two sequential acid-base titrations (Aytürk, 2001):

1. Free Acidity: Free acidity of the samples as weight percentage was measured by titration with 0.1 N standardized KOH solution using phenolphthalein indicator.

$$\mathrm{F[wt\%]} = \frac{\mathrm{N_{KOH}}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right).\mathrm{V_{KOH}(mL)}.\mathrm{MW_{LA}}\left(\frac{\mathrm{g}}{\mathrm{gmol}}\right)}{\left(\frac{\mathrm{1000mL}}{\mathrm{L}}\right).\mathrm{W_{sample}(g)}}.100 \qquad \mathbf{(3.1)}$$

Where F: Free acidity as lactic acid, wt %

N_{KOH}: normality of KOH solution, mol/L

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

MW_{LA}: molecular weight of lactic acid, g/mol
W_{sample}: sample weight, g

2. Polymeric lactic acid: Monomer lactic acid found in the sample as lactoyllactic acid form was determined by dilution, addition of excess KOH solution into the titrated solution sample. By boiling for a certain time, sample was allowed to hydrolyze all esters to lactic acid. After cooling, solution sample was back titrated with 0.1 N standardized HCl solution.

$$\mathrm{P[wt\%]} = \frac{[\mathrm{N_{KOH}}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right).\mathrm{V_{KOH,ex}(mL)} - \mathrm{N_{HCl}}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right).\mathrm{V_{HCl}(mL)}].\mathrm{MW_{LA}}(\frac{\mathrm{g}}{\mathrm{gmol}})}{\left(\frac{1000\mathrm{mL}}{\mathrm{L}}\right).\mathrm{W_{sample}(g)}}.100 \quad (\mathbf{3.2})$$

Where P: Lactic acid in polymeric form, wt %
N_{KOH}: normality of KOH solution, mol/L
$V_{KOH,ex}$: excess volume of KOH solution added before heating, mL
N_{HCl}: normality of HCl solution, mol/L
V_{HCl}: excess volume of HCl solution added before heating, mL
MW_{LA}: molecular weight of lactic acid, g/mol
W_{sample}: sample weight, g

Total monomer lactic acid quantity was calculated from the summation of both titration results.

$$\mathrm{T[wt\%]} = \mathrm{F[wt\%]} + \mathrm{P[wt\%]} \quad (\mathbf{3.3})$$

Detection of water amounts of all collected samples was done by Karl Fisher volumetric titrator. The known amount samples were titrated with a specific Karl Fischer component (iodine in methanol solution), and results were taken in weight percentage.

Besides these anaysis, detection of ethanol, ester and also water was done by gas chromatography equipped with a TCD detector. To get the correct data, calibration was done by using prepared reference solutions of ethyl lactate, water and ethanol. GC calibration details are given in Appendix A. Then corresponding peak areas were standardized by estimating the relative response factors of ethyl lactate, water and ethanol. Both bottom and upper products were analyzed by GC. In bottom products, there were high amount of unreacted lactic acid. Under the working conditions of GC, there were some wrong results because of continuation of esterification reaction in GC column. This claim was studied with comparison of the GC results of synthetically prepared samples with known amounts of components and results of experiment in weight fractions. According to the data from Table 3.1, the weight fraction of prepared ethanol is higher than the others. This difference forces the reaction to shift to ethyl lactate formation direction. Since, only ethanol, water and ethyl lactate peaks can be observed in GC results, the lactic acid and lactoyllactic acid free weight fractions were compared. As a result, when prepared sample weight fractions and GC results are compared, it is clearly seen that there is an increase in ethyl lactate and water, but decrease in ethanol fraction. This can be explained with reaction continuation at GC working conditions. This situation is also true for one more trial, can be seen in Table 3.2. In this case, lactic acid weight fraction is relatively high, and trend of the GC results are similar with previous one. Therefore, GC analysis results were only applied for calculation of upper product. Bottom product water component was determined by Karl Fischer titration, and other's amounts were determined with mass balance.

Table 3.1 Trial 1 for GC result correction analysis

Trial 1	**Lactic Acid**	**Lactoyllactic Acid**	**Ethyl Lactate**	**Ethanol**	**Water**
Experiment result, wt%	16.21	7.576	21.77	51.11	4.361
Prepared sample, g	1.621	0.7576	2.177	5.111	0.4361
Prepared sample, wt%	16.74	3.87	22.56	52.92	3.91
Prepared sample, LA & LLA free wt%			28.41	66.66	4.93
GC results of prepared sample, LA & LLA free wt%			41.85	51.95	6.21

Table 3.2 Trial 2 for GC result correction analysis

Trial 2	**Lactic Acid**	**Lactoyllactic Acid**	**Ethyl Lactate**	**Ethanol**	**Water**
Experiment result, wt %	47.69	14.71	21.02	6.451	10.12
Prepared sample, g	4.769	1.471	2.102	0.6451	1.012
Prepared sample, wt %	49.45	11.42	21.77	6.84	10.52
Prepared sample, LA & LLA free wt %			55.63	17.48	26.89
GC results of prepared sample, LA & LLA free wt %			73.84	9.52	16.64

All data from titration and equipment analysis were combined and product distribution throughout the reaction was completed. All calculation details can be found in Appendix B.

3.6 RESIN REGENERATION

Since ion exchange resins create a distinct solid phase and acidic medium, they can be used as solid catalyst in the column operation. In this study, Lewatit® MonoPlus S 100 was used. It is strongly acidic, cation exchange resin which is shipped in Na^+ form. Typical regeneration procedure should be applied in converting H^+ form. One can find some properties of the resin in Appendix C.

200 mL of resins were placed into erlenmeyer flask and conditioned for 3 days in 10 vol. % HCl solution. After regeneration, resins were treated with ultra pure water in the column until pH of the outlet stream of the column corresponded with the pH of the ultra pure water, 7. Then, dried in the oven at 70 °C until the wieght of the resin remains constant.

CHAPTER 4

RESULTS AND DISCUSSION

In the present study, esterification reaction of lactic acid with ethanol over ion exchange resin as heterogeneous acid catalysts was investigated in a continuous absorption/desorption process. Then, the effects of ethanol to lactic acid feed ratio, inlet vapor flow rate, and the column temperature were determined in order to examine the reaction and separation responses of the column.

Purchased lactic acid (90 wt%) was analyzed as described in experimental section. The actual analysis of 90 wt% lactic acid was found as 70.7 wt % of free lactic acid, 16.3 wt% of lactoyllactic acid, and 13.6 wt% of water assuming oligomeric lactic acid species as dimer form. Therefore, the esterification reaction system can be described as the esterification of free lactic acid with ethanol (4.1) and self esterification of lactic acid (4.2).

$$\underbrace{C_3H_6O_3}_{\text{Lactic acid}} + \underbrace{C_2H_5OH}_{\text{Ethanol}} \leftrightarrow \underbrace{C_5H_{10}O_3}_{\text{Ethyl lactate}} + \underbrace{H_2O}_{\text{Water}} \tag{4.1}$$

$$2\,\underbrace{C_3H_6O_3}_{\text{Lactic acid}} \leftrightarrow \underbrace{C_6H_{10}O_5}_{\text{Lactoyllactic acid}} + \underbrace{H_2O}_{\text{Water}} \tag{4.2}$$

4.1 LACTIC ACID ESTERIFICATION KINETICS

The kinetics of esterification reaction system of lactic acid and ethanol was studied in detail by Aytürk in his M.Sc. thesis in 2001 (Aytürk, 2001). Equation 4.3 and 4.4 give the rate expressions of the reactions (4.1) and (4.2).

$$-\frac{dC_{LA}}{dt} = k_1.C_{LA}.C_{EtOH} - k_2.C_{Es}.C_{H2O} + k_3.C_{LA}^2 - k_4.C_{LLA}.C_{H2O} \tag{4.3}$$

$$-\frac{dC_{LLA}}{dt} = k_3.C_{LLA}.C_{H2O} - k_4.C_{LA}^2 \tag{4.4}$$

Where;

k_1: Overall forward reaction rate constant of Eqn. (4.1), L/(mol.min)
k_2: Overall backward reaction rate constant of Eqn. (4.1), L/(mol.min)
k_3: Homogeneous forward rate constant of Eqn. (4.2), L/(mol.min)
k_4: Homogeneous backward rate constant of Eqn. (4.2), L/(mol.min)

He concluded that Lewatit S 100 worked better for esterification reaction at 70 °C and reaction rate constants and equilibrium constant were found as following:

k_1: 0.000217 L/(mol.min)
k_2: 0.000115 L/(mol.min)
k_3: 0.00000538 L/(mol.min)
k_4: 0.000043 L/(mol.min)
K: Equilibrium constant, 1.771

The reaction rate constants show that the self esterification reaction is slow process. According to the study of Aytürk (2001), the lactoyllactic acid and lactic acid concentrations were not affected from the temperature and catalyst concentration. Moreover, he concluded that dilution of the solution enabled the hydrolysis of the lactoyllactic acid which was a slow reaction and the rate limiting step in the ethyl lactate formation. This can be important for the batch reaction system; however, it can be ignored in the continuous system where the residence time is small.

In addition, the self esterification of lactic acid was studied at 70 ℃ in the absence of catalyst. One can follow from Figure 4.1 that there is a dynamic equilibrium between lactic acid, water, and lactoyllactic acid and this equilibrium and the concentrations of lactic acid and lactoyllactic acid do not change. The average value of total acidity was found as 86 wt %, with 70 wt % free lactic acid and 16 wt % lactoyllactic acid.

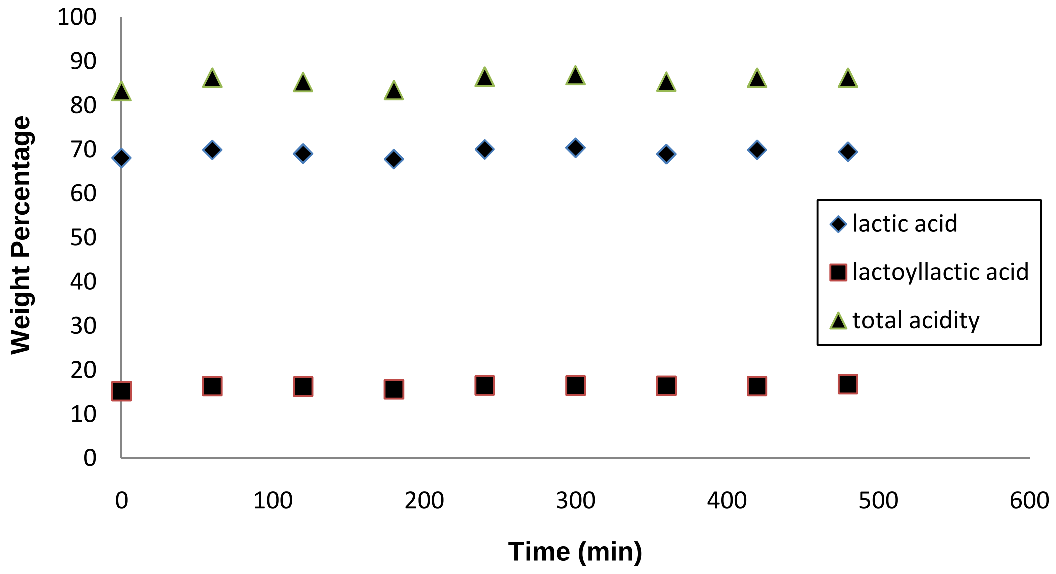


Figure 4.1 Dynamic equilibrium of lactic acid, lactoyllactic acid and water in the absence of catalyst at 70 ℃

4.2 COUNTER-CURRENT COLUMN REACTION EXPERIMENTS

Counter-current absorption system setup was established as described in experimental part. By this separation system, it is possible to remove light product (H2O) by using continuous inert gas phase. On the other hand, the most volatile reactant (ethanol) can be introduced to the reaction medium (continuous liquid phase) by absorption as depicted in Figure 4.2. Continuous gas phase should be an inert gas such as dry air or nitrogen. The counter-current operation of such system enhances the mass transfer rate by increasing driving force and decreasing film thickness, enhances the conversion by increasing the contact between the reactants.

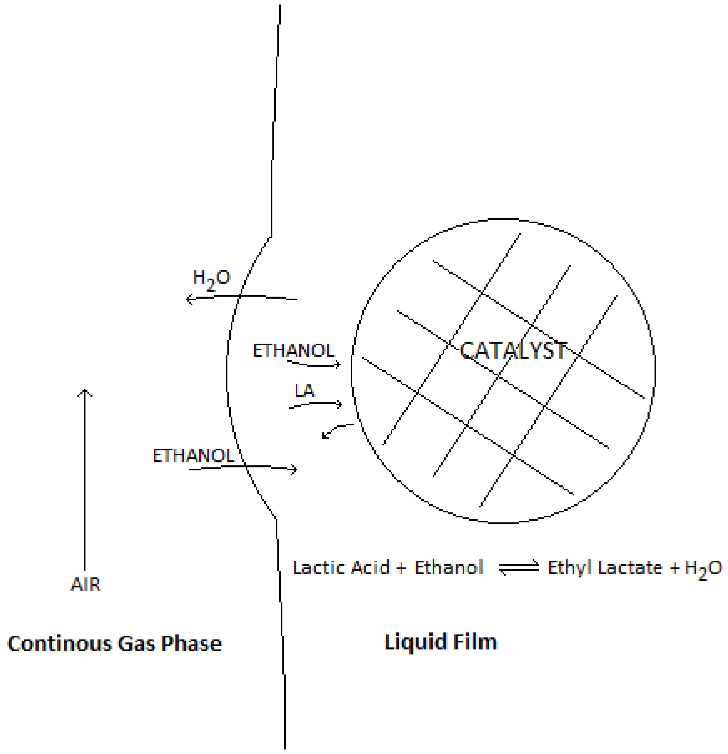


Figure 4.2 Transport and reaction processes in the presence of solid catalyst

Counter current (L:V) systems are prone to flooding problems at higher gas flow rates, small packing size, etc. Under these limitations, the experimental parameters were determined as following:

1. 20 g Lewatit S 100 was placed in the 40 mm inner diameter and 35 cm height of Pyrex column forming 4 cm of total height of catalyst bed.
2. The lactic acid was fed to the column from the top with 0.30-1.53 g/min of flow rates.
3. Ethanol was fed to the column with 0.04-4.78x10^{-3} gmole EtOH/L gas of concentration in air and the total inlet flow rate of continuous gas stream was applied as 400 mL/min-3400mL/min.

Although column height was suitable for more stages, all experiments were done with one differential stage comprising of 4 cm catalyst bed. Except for temperature experiments, all experiments had continued for 3 hours. The status of system was checked by periodical analyzing samples and steady state was achieved within one and half hour of the experiments. Therefore, the results were obtained by taking samples in every 30 minutes and the average values of last three samples were used in data analysis. The analysis of samples were carried out as described in Experimental section by using GC and titration methods and the fractional conversion and the complete stream analysis were checked by material balances around the overall system. The consistency of hydrogen and oxygen balances was found as 90-93%. The total mass balance around the system was found as 85-90% consistent because of the inevitable loss of ethanol vapor from condenser. Especially, higher air flow rates reduce the condenser efficiency considerably. The details of the sample analysis and calculations can be found in Appendix B.

4.2.1 EFFECT OF ETHANOL TO LACTIC ACID FEED MOLAR RATIO

The effect of ethanol to lactic acid feed molar ratio was tested by keeping the ethanol feed flow rate constant and adjusting the flow rate of lactic acid. Concentrated lactic acid feed solution (90 wt%) was used in all experiments. In all experiments, dry air flow rate was also kept constant as 400±10 mL/min. Ethanol saturator was placed into the water bath at 70 °C. The ethanol concentration was determined by measuring the weight difference of ethanol bottle for certain period of time. The detailed experimental parameters and results of analysis at steady state values are given in Table 4.1. In this set of experiments, the overall mass balance around the system was achieved with 97% of consistence. Ethanol to lactic acid feed molar ratio was calculated with Eqn. (4.5) and was adjusted as 1.42, 1.86, 3.23, and 5.08 for the experiments which were given under the code as E1, E2, E3, and E4, respectively.

$$\mathrm{Ratio} = \frac{\mathrm{C_{EtOH}.V_{gas\ stream}}}{\mathrm{C_{LA}.L_{LA}}} \qquad (4.5)$$

Where;

C_{EtOH}: Concentration of ethanol in the gas feed stream, gmole/L gas stream

C_{LA}: Concentration of lactic acid in the liquid feed stream, gmole/L liquid stream

$V_{gas\ stream}$: Volumetric flow rate of gas stream, L/min

L_{LA}: Volumetric flow rate of liquid stream, L/min

Table 4.1 Effect of ethanol to lactic acid feed molar ratio in dry air free basis

Exp. #	**FLOW RATES (g/min)**				**FEED COMPOSITION (wt%)**			**PRODUCT COMPOSITION (wt%)**								**Conversion**
	INLET		**OUTLET**		**Liquid Feed**			**Bottom Product**					**Upper Product**			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E1	1.44	0.74	0.45	1.75	70.70	16.32	13.57	47.17	13.41	12.89	13.99	12.53	92.02	1.25	6.73	18.80
E2	0.94	0.63	0.46	1.13	70.70	16.32	13.57	43.29	13.66	10.66	20.32	12.06	91.51	1.28	7.21	26.85
E3	0.47	0.55	0.47	0.58	70.70	16.32	13.57	36.62	13.84	6.24	30.42	12.88	92.43	1.57	5.99	38.89
E4	0.37	0.69	0.58	0.47	70.70	16.32	13.57	29.20	12.42	18.14	30.38	9.86	92.33	1.88	5.78	45.73

Exp. #	**FLOW RATES (g moles/min)**				**FEED COMPOSITION (g mole %)**			**PRODUCT COMPOSITION (g mole %)**								**Water Percentage As Upper Product %**
	INLET		**OUTLET**		**Liquid Feed**			**Bottom Product**					**Upper Product**			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E1	0.024	0.016	0.011	0.03	47.89	6.15	45.96	30.80	4.87	16.45	6.97	40.90	83.88	0.44	15.68	13.02
E2	0.015	0.013	0.011	0.02	47.89	6.15	45.96	29.35	5.15	14.13	10.51	40.86	82.86	0.45	16.69	16.63
E3	0.008	0.012	0.011	0.009	47.89	6.15	45.96	25.41	5.34	8.46	16.10	44.69	85.29	0.57	14.14	28.83
E4	0.006	0.015	0.014	0.008	47.89	6.15	45.96	20.28	4.79	24.63	16.09	34.22	85.61	0.68	13.71	40.94

As it can be seen from Table 4.1, flow rates of bottom products are higher than the inlet lactic acid solution flow rates. This proves that ethanol transported from gas phase to liquid phase. This absorption of ethanol by liquid phase shows that the necessary condition for the esterification reaction was provided. The average of the inlet concentration of ethanol was 0.035 g mole/ L inlet gas. According to product composition of bottom and upper product, it can be concluded that water amount in upper product remains constant. This can be explained with the constant value of dry air flow rate. The dew point of the gas stream is calculated as 63 °C; thus, the stream is superheated at 70 °C which makes the system be saturated. Therefore, upper product already carries maximum water amount. The amount of water in the system is changed by the change of the feed lactic acid flow rate. The produced amount of water by the reaction decreases with the increase of the lactic acid flow rate due to lower space time. The separation efficiency of the system can be defined as

$$\text{Water Removal }\% = \frac{\text{g moles of water in upper stream}}{\text{g moles of water introduced into the system by LA feed} + \text{g moles of water produced by reaction}} \tag{4.6}$$

Figure 4.3 shows change the water removal by upper product stream with ethanol to lactic acid feed molar ratio.

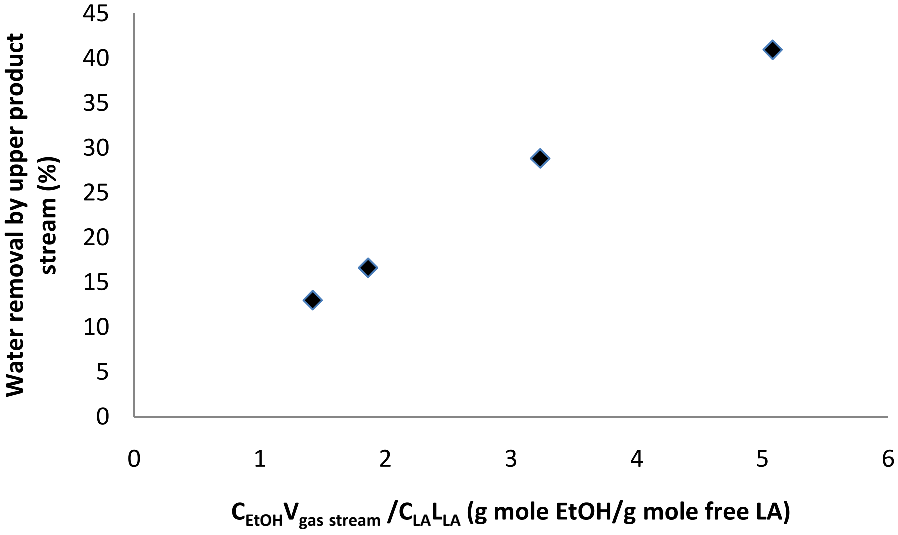


Figure 4.3 Effect of ethanol to lactic acid feed molar ratio on water removal by upper product stream

As it can be seen from Figure 4.3, water removal by upper product stream increases with the increase in ethanol to lactic acid feed molar ratio. In this system, reaction occurs on the surface of the catalyst and liquid phase. As explained previously with Figure 2.9, there are vapor and liquid films which create mass transfer resistance and thus limit the reaction. Lactic acid feed flow rate also gives some explanations for separation efficiency of the system. When the flow rate increases, this means that there is more carboxylic acid which tends to keep water with its hydrophilic nature. This situation limits the transfer of water from liquid phase to vapor phase.

Ethyl lactate is the main component of the bottom product stream; however, because of purging with gas stream some ethyl lactate was taken as gas form at the upper product stream. When ethyl lactate amount in the upper product stream is considered, it can be said that increase in the ethanol to lactic acid ratio, increases the lactic acid conversion and also increases total amount of ethyl lactate which causes the higher weight percentages in the upper product stream. Figure 4.4 shows this situation.

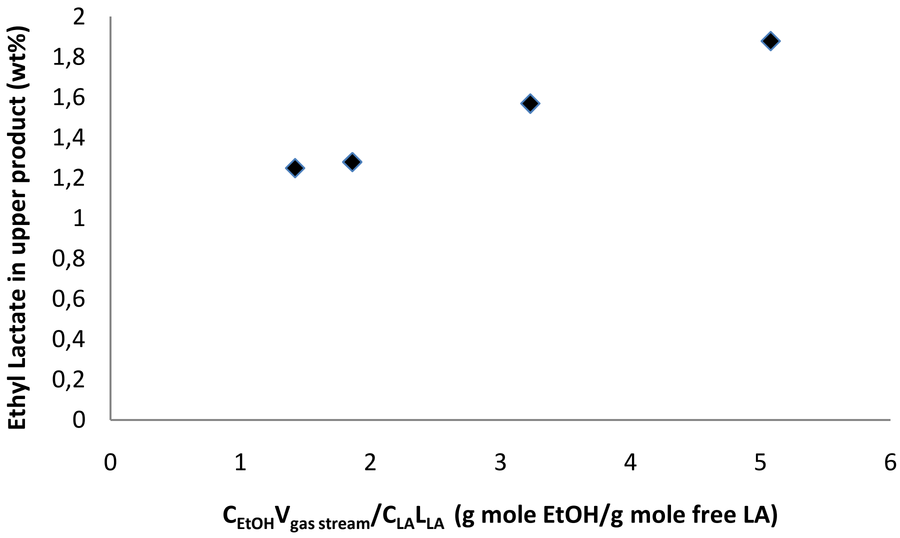


Figure 4.4 Effect of ethanol to lactic acid feed molar ratio on ethyl lactate percentage in upper product

Figure 4.5 shows the change of lactic acid conversion with respect to feed molar ratio of ethanol to lactic acid.

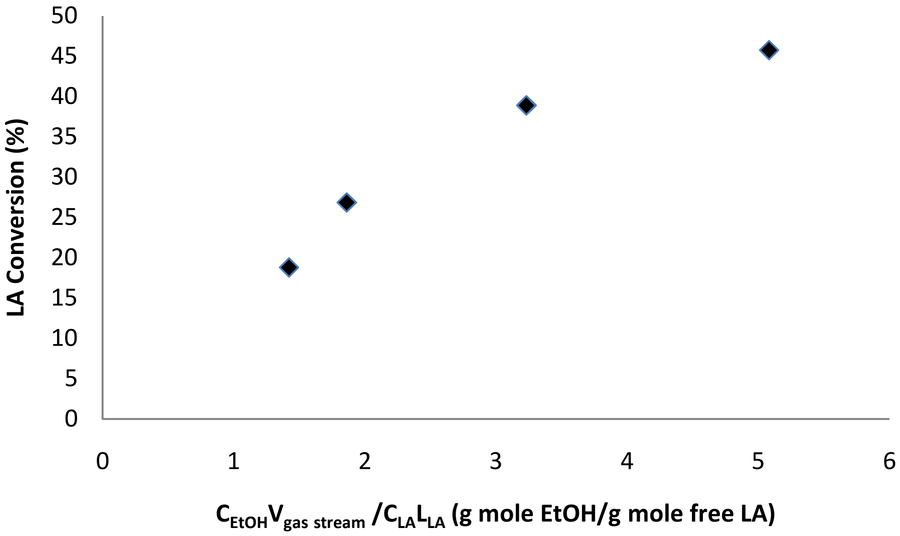


Figure 4.5 Effect of ethanol to lactic acid feed molar ratio on lactic acid conversion

As it can be seen from the figure, lactic acid conversion increases with the increase of ethanol to lactic acid feed molar ratio. The equilibrium conversion is shifted by the excess amount of reactant. These results are in good agreement with previous results which were obtained in batch reaction experiments. On the other hand, the space time which is also associated with the liquid hold-up in catalyst packed section also increases with decreasing liquid flow rate. Measurement of the space time is the detailed study in such complex system which is the out of the scope of this study. However, by assuming no vapor flow to have an idea about the space time, space time can be given for the range of LA feed 1.53-0.30 g/min as 27.4-139.7 min.

4.2.2 EFFECT OF VAPOR FLOW RATE

The effect of inert carrier gas flow rate on the separation efficiency was studied by changing the flow rate of dry air by keeping ethanol to lactic acid ratio constant. However, the effect of vapor flow rate was examined in previously studied ethanol to lactic acid ratio range. In these series of reactions, concentrated lactic acid solution (90 wt%) was used as feed solution. The comparison of the effect of different vapor flow rates was done with 4 different vapor flow rates: 400 mL/min, 1200 mL/min, 2400 mL/min, and 3400 mL/min. Experimental results for vapor flow rate of 400 mL/min was already introduced with Table 4.1. Table 4.2, Table 4.3, and Table 4.4 give the experimental results for air flow rate of 1200 mL/min, 2400 mL/min, and 3400 mL/min, respectively. In these experiments, the reaction temperature (70 °C) and catalyst bed size were kept constant. Ethanol concentration were calculated as 0.014, 6.34E-3, and 4.78E-3 gmole/L inlet gas for vapor flow rate of 1200 mL/min, 2400 mL/min, and 3400 mL/min, respectively.

Table 4.2 Experimental results with air flow rate of 1200 mL/min in dry air free basis

Exp. #	FLOW RATES (g/min)				FEED COMPOSITION (wt%)			PRODUCT COMPOSITION (wt%)								Conversion
	INLET		OUTLET		Liquid Feed			Bottom Product					Upper Product			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E5	1.49	0.87	0.65	1.55	70.70	16.32	13.57	46.80	14.04	12.79	15.51	10.86	80.40	7.58	12.02	23.04
E6	0.81	0.78	0.70	0.88	70.70	16.32	13.57	46.26	14.33	12.03	16.26	11.11	84.94	5.88	9.17	25.46
E7	0.37	0.70	0.69	0.37	70.70	16.32	13.57	45.68	15.40	12.54	16.55	9.82	87.77	6.23	5.99	31.53
Exp. #	**FLOW RATES (g moles/min)**				**FEED COMPOSITION (g mole %)**			**PRODUCT COMPOSITION (g mole %)**								**Water Percentage As Upper Product %**
	INLET		**OUTLET**		**Liquid Feed**			**Bottom Product**					**Upper Product**			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E5	0.024	0.019	0.016	0.028	47.89	6.15	45.96	32.11	5.36	17.15	8.12	37.26	70.48	2.59	26.93	29.45
E6	0.013	0.017	0.017	0.015	47.89	6.15	45.96	31.75	5.47	16.15	8.512	38.13	76.74	2.07	21.19	38.47
E7	0.006	0.015	0.016	0.006	47.89	6.15	45.96	32.52	6.09	17.46	8.98	34.94	83.17	2.30	14.52	51.96

Table 4.3 Experimental results with air flow rate of 2400 mL/min in dry air free basis

Exp. #	FLOW RATES (g/min)				FEED COMPOSITION (wt%)			PRODUCT COMPOSITION (wt%)								Conversion
	INLET		OUTLET		Liquid Feed			Bottom Product					Upper Product			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E8	1.42	0.64	0.50	1.43	70.70	16.32	13.57	54.94	14.53	11.87	7.87	10.79	78.47	8.39	13.14	12.69
E9	0.73	0.75	0.63	0.74	70.70	16.32	13.57	47.69	13.48	22.36	7.41	9.06	81.24	9.44	9.32	18.33
E10	0.54	0.73	0.62	0.54	70.70	16.32	13.57	45.79	13.10	25.35	7.24	8.52	83.86	7.77	8.37	19.29
E11	0.37	0.68	0.57	0.55	70.70	16.32	13.57	34.86	11.15	36.14	11.65	6.19	83.28	7.54	9.18	27.80

Exp. #	FLOW RATES (g moles/min)				FEED COMPOSITION (g mole %)			PRODUCT COMPOSITION (g mole %)								Water Percentage As Upper Product %
	INLET		OUTLET		Liquid Feed			Bottom Product					Upper Product			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E8	0.023	0.014	0.012	0.026	47.89	6.15	45.96	37.58	5.24	15.87	4.11	36.92	68.04	2.84	29.12	27.40
E9	0.012	0.016	0.015	0.015	47.89	6.15	45.96	31.82	4.99	29.17	3.77	30.24	74.70	3.38	21.91	41.93
E10	0.009	0.016	0.015	0.011	47.89	6.15	45.96	30.38	4.83	32.88	3.66	28.25	77.43	2.79	19.77	47.34
E11	0.006	0.015	0.013	0.009	47.89	6.15	45.96	22.99	4.09	46.62	5.86	20.44	75.92	2.68	21.40	59.02

Table 4.4 Experimental results with air flow rate of 3400 mL/min in dry air free basis

Exp. #	**FLOW RATES (g/min)**				**FEED COMPOSITION (wt%)**			**PRODUCT COMPOSITION (wt%)**								**Conversion**
	INLET		**OUTLET**		**Liquid Feed**			**Bottom Product**					Upper Product			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E12	1.5254	0.8237	0.7865	1.5327	70.70	16.32	13.57	59.41	14.81	10.42	1.89	13.46	78.98	9.39	11.62	7.37
E13	0.6268	0.6916	0.5214	0.6161	70.70	16.32	13.57	55.61	14.09	12.79	5.26	12.24	80.74	8.88	10.37	14.33
E14	0.3032	0.7290	0.6233	0.2898	70.70	16.32	13.57	35.26	10.82	42.57	3.28	8.07	81.38	8.78	9.84	24.79

Exp. #	**FLOW RATES (g moles/min)**				**FEED COMPOSITION (g mole %)**			**PRODUCT COMPOSITION (g mole %)**								**Water Percentage As Upper Product %**
	INLET		**OUTLET**		**Liquid Feed**			**Bottom Product**					**Upper Product**			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E12	0.0250	0.0179	0.0188	0.0293	47.89	6.15	45.96	37.89	5.25	13.00	0.92	42.93	70.29	3.26	26.44	28.32
E13	0.0103	0.0150	0.0125	0.0155	47.89	6.15	45.96	28.87	4.06	33.21	2.08	31.77	72.92	3.13	23.94	37.81
E14	0.0049	0.0158	0.0148	0.0085	47.89	6.15	45.96	21.07	3.59	49.74	1.49	24.10	74.01	3.11	22.88	62.44

Effect of vapor flow rate on the lactic acid conversion can be seen in Figure 4.6.

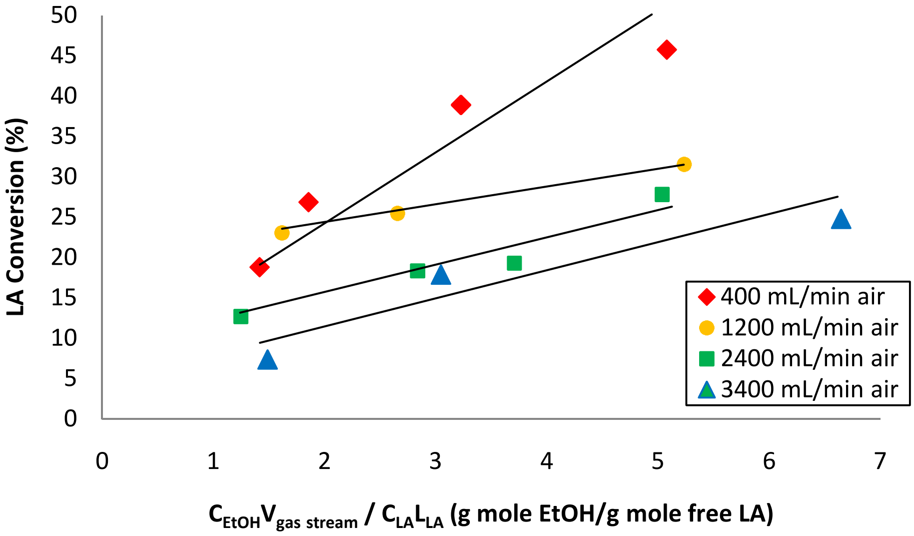


Figure 4.6 Effect of inlet vapor flow rate on lactic acid conversion

Increase in the air flow rate with constant ethanol to lactic acid ratio causes the decrease in the concentration of ethanol in gas phase. Increase in air flow rate will obviously enhance the overall mass transfer coefficient. However, the decrease in ethanol concentration in gas phase will lead a drop in driving force. As it is shown in Figure 4.6 the decrease in lactic acid conversion under higher air flow rate conditions can be explained by the mass transfer limitation.

To compare the efficiency of the column reaction with the results from batch reactor, the equilibrium constant from the thesis study of Aytürk (2001) was used. He found the equilibrium constant as 1.771 for the 48 hours reaction experiments performed at 70 °C. Table 4.5 gives the calculated lactic acid conversion values for 6 different initial molar ratios of ethanol to lactic acid by using the equilibrium constant from the study of Aytürk (2001).

Table 4.5 Equilibrium conversion values

Ethanol / Lactic Acid Molar Ratio	Lactic Acid Conversion
1	57.10
2	74.78
3	82.39
4	86.52
5	89.09
6	90.85

Figure 4.7 shows the equilibrium conversion values from batch reactor and the conversions obtained from the column reaction experiments. It is seen that results of column experiments are lower than the equilibrium value. This can be explained by the complexity of the column experiment with 3 phases; liquid lactic acid, vapor ethanol and solid catalyst. Reaction occurs in the liquid phase and some experimental conditions decreases the transfer of ethanol from vapor phase to liquid phase. Moreover, residence time in the column experiments was very low which decreases the contact time of ethanol and lactic acid. These explanations could be the reason of less lactic acid conversion in column experiments than the value of batch reactor experiment.

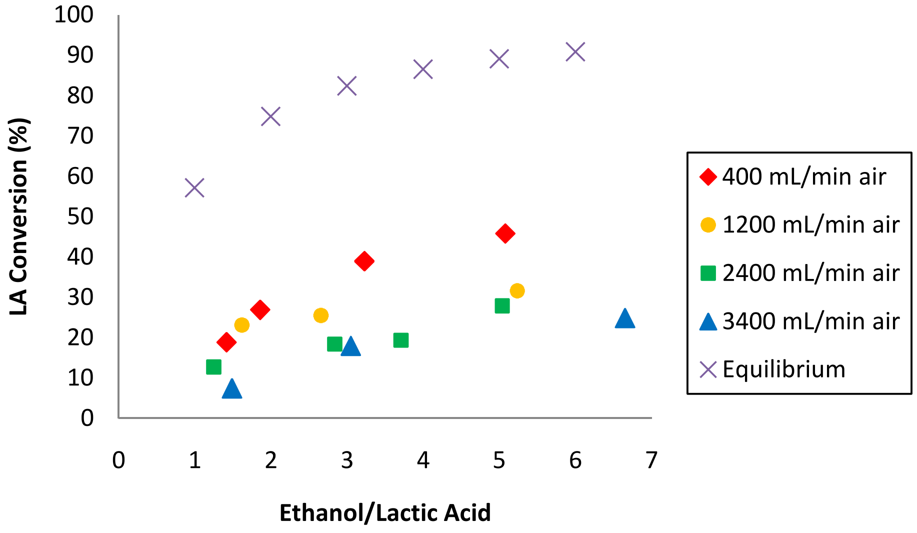


Figure 4.7 Comparisons of experimental conversions with equilibrium conversions

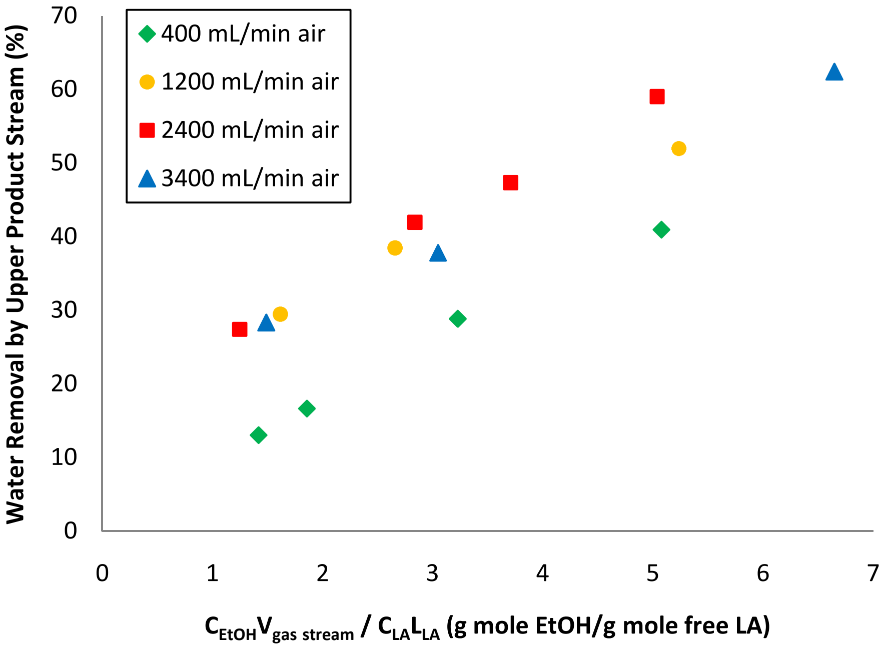


Figure 4.8 Effect of vapor flow rate on water removal by upper product stream

Effect of vapor inlet flow rate on water removal by upper product stream is given in Figure 4.8. It is obvious that, increase the vapor flow rate increases the water removal by upper product stream. Water removal rate can be controlled by gas flow rate. This can be explained by following equation (Jeong and Lee, 1997):

$$J = k_L a(C_{W,L} - C_{W,G}) \tag{4.7}$$

Where, $k_L a$: Mass transfer coefficient, m/s

$C_{W,L}$: Water concentration in the reaction medium, mol/L

$C_{W,G}$: Water concentration of the inlet gas stream, mol/L

Dry air was fed to the system; therefore water concentration of the inlet gas stream can be taken as zero. The water removal rate can be increased by the increase of carrier gas flow rate, since the value of the mass transfer coefficient is larger at higher gas flow rates. However, this removal increase can be provided up to a point. As it can be seen from the figure, increasing inlet vapor flow rate does not increase the water removal value so much with higher vapor flow rate. Moreover, it can be said that higher vapor flow rates than 400 mL/min provides nearly similar water removal value.

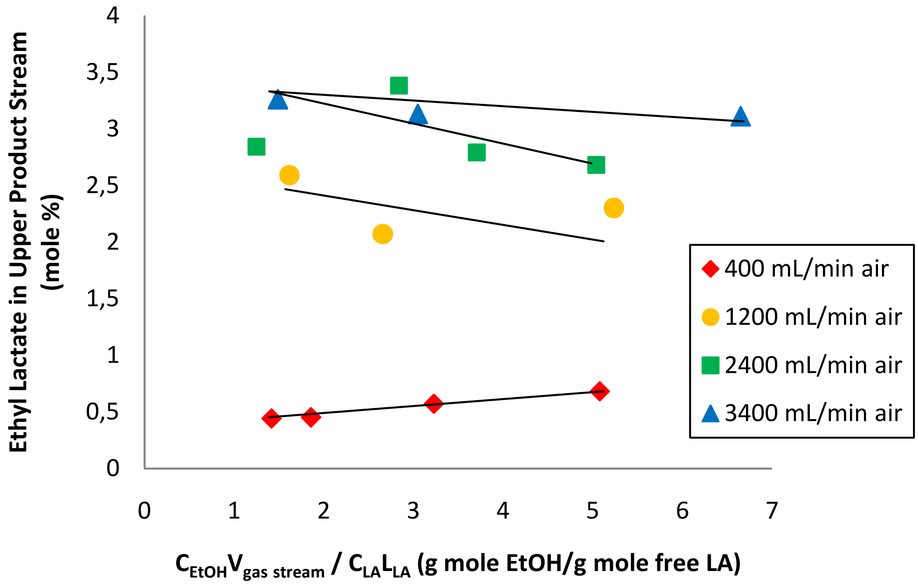


Figure 4.9 Effect of vapor flow rate on ethyl lactate amount in upper product

As it can be seen in Figure 4.9, although lactic acid conversion decreases with increase in the air flow rate, the purging of ethyl lactate with air through upper product increases. Ethyl lactate is the main product of the bottom stream; therefore although the increase is not so much, this is an unwanted result.

The responses of the system as reaction and separation to air flow rate factor show that separation property of the column reactor is enhanced by increasing the inlet air flow rate up to a point; however, reaction property diminished by the increase in the inlet air flow rate. It can be said that there should be an optimum operation parameter which give both high conversion and water removal.

This system can also be checked according to the superficial velocity of gas stream. The superficial velocities of different vapor flow rates in the 0.04 m column diameter are given in Table 4.6. Figure 4.10, 4.11, and 4.12 give the change of LA conversion and water removal by upper product for 3 different initial molar ratio of ethanol to lactic acid.

Table 4.6 Superficial velocities of 4 different gas stream flow rate

Air Flow Rate (mL/min)	400	1200	2400	3400
Superficial Velocity (cm/min)	30.83	95.49	190.98	270.56

These 3 figures are in agreement about the decrease in lactic acid conversion and increase in water removal by upper product stream by increase in superficial velocity of gas stream.

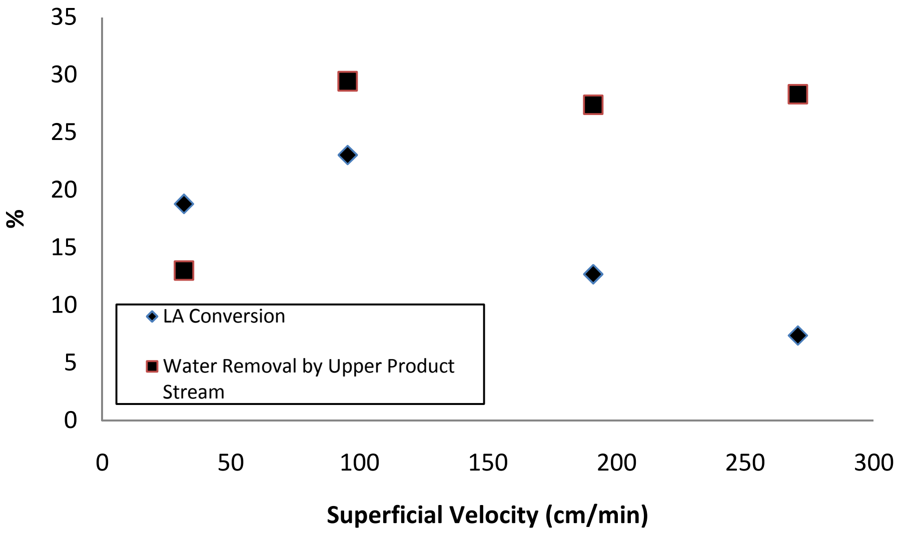


Figure 4.10 Effect of superficial velocity for ethanol to lactic acid feed molar ratio of 1.45

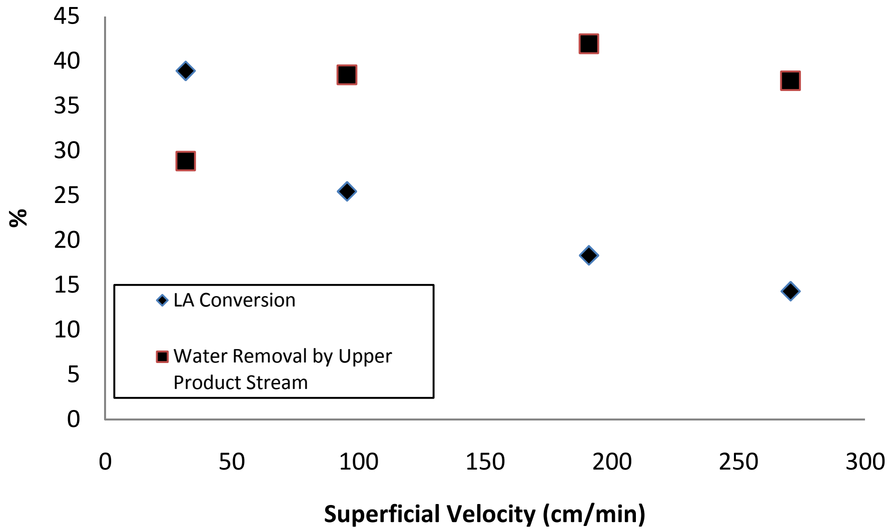


Figure 4.11 Effect of superficial velocity for ethanol to lactic acid feed molar ratio of 2.95

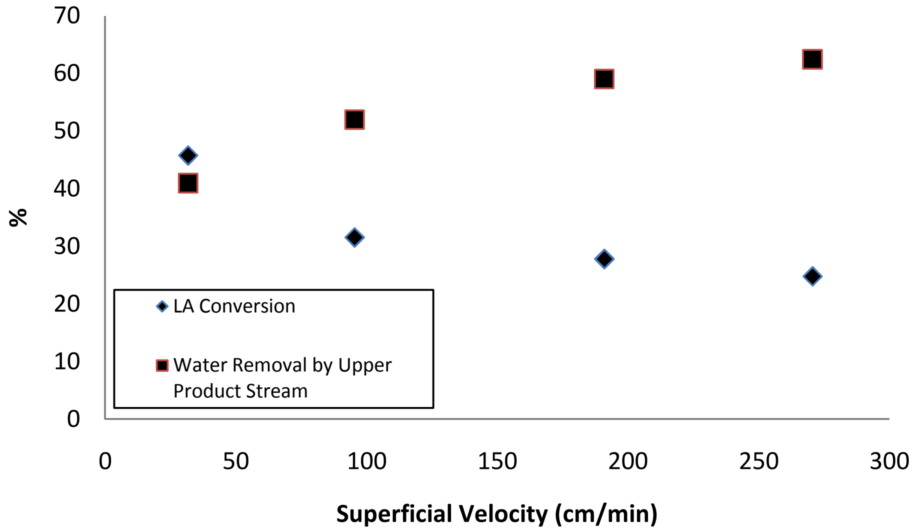


Figure 4.12 Effect of superficial velocity for ethanol to lactic acid feed molar ratio of 5.53

Moreover, flow type through the column can be defined as laminar or turbulent. Ethanol concentration of gas stream is very low; therefore data for Reynolds number were taken according to the air at 70 °C. Table 4.7 gives the Reynolds numbers of each air flow rate. According to the results, there are laminar flows in empty column because the values are less than the limit values for laminar flows of 2100 in empty column (Geankoplis, 1993). Calculations are given in Appendix B.

Table 4.7 Reynolds number on the superficial velocity bases

Gas Flow Rate (mL/min)	Reynolds Number of Empty Column
400	11
1200	32
2400	64
3400	91

4.2.3 EFFECT OF TEMPERATURE

The effect of column temperature was also tested. Ethanol was fed to the system at 33 °C. Four different column temperatures (40, 50, 60, and 70 °C) were studied. Ethanol to lactic acid feed molar ratio was tried to be kept as 1.5:1; however, because of the some oscillations in air pump there were some deviations. Vapor flow rate was 450 mL/min. Table 4.8 gives the experimental results for these experiment series. E15, E16, E17, and E18 denote the reactions at 40, 50, 60, and 70 °C, and ethanol to lactic acid ratio were 1.4, 1.7, 1.5, and 1.8, respectively.

Table 4.8 Effect of column temperature

Exp. #	FLOW RATES (g/min)				FEED COMPOSITION (wt%)			PRODUCT COMPOSITION (wt%)								Conversion
	INLET		OUTLET		Liquid Feed			Bottom Product					Upper Product			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E15	0.22	0.11	0.07	0.23	70.70	16.32	13.57	43.97	12.85	12.28	13.93	16.98	79.10	5.59	15.30	21.03
E16	0.18	0.11	0.09	0.19	70.70	16.32	13.57	48.48	13.75	14.26	12.81	10.70	79.68	4.33	15.98	18.62
E17	0.21	0.11	0.09	0.21	70.70	16.32	13.57	52.30	14.43	14.18	10.03	9.05	73.92	17.36	8.72	16.36
E18	0.16	0.11	0.08	0.16	70.70	16.32	13.57	49.26	13.12	24.75	4.36	8.54	64.44	13.55	22.01	13.29

Exp. #	FLOW RATES (g moles/min)				FEED COMPOSITION (g mole %)			PRODUCT COMPOSITION (g mole %)								Water Percentage As Upper Product %
	INLET		OUTLET		Liquid Feed			Bottom Product					Upper Product			
	LA Soln.	Ethanol	Upper Product	Bottom Product	Free LA	LLA	Water	Free LA	LLA	Ethanol	Ethyl Lactate	Water	Ethanol	Ethyl Lactate	Water	
E15	0.004	0.002	0.018	0.005	47.89	6.15	45.96	25.77	4.19	14.07	6.22	49.75	65.69	1.81	32.49	18.69
E16	0.003	0.002	0.002	0.003	47.89	6.15	45.96	32.92	5.19	18.94	6.63	36.31	65.18	1.38	33.43	37.54
E17	0.003	0.002	0.002	0.004	47.89	6.15	45.96	37.11	5.69	19.67	5.43	32.10	60.74	2.79	36.47	42.66
E18	0.003	0.002	0.002	0.003	47.89	6.15	45.96	32.64	4.83	32.06	2.19	28.28	51.14	4.20	44.66	51.44

Figure 4.13 shows the effect of column temperature on the lactic acid conversion. Lactic acid conversion decreases with increase in the column temperature. Although lactic acid conversion is low at high temperature, water removal by upper product is high, Figure 4.14.

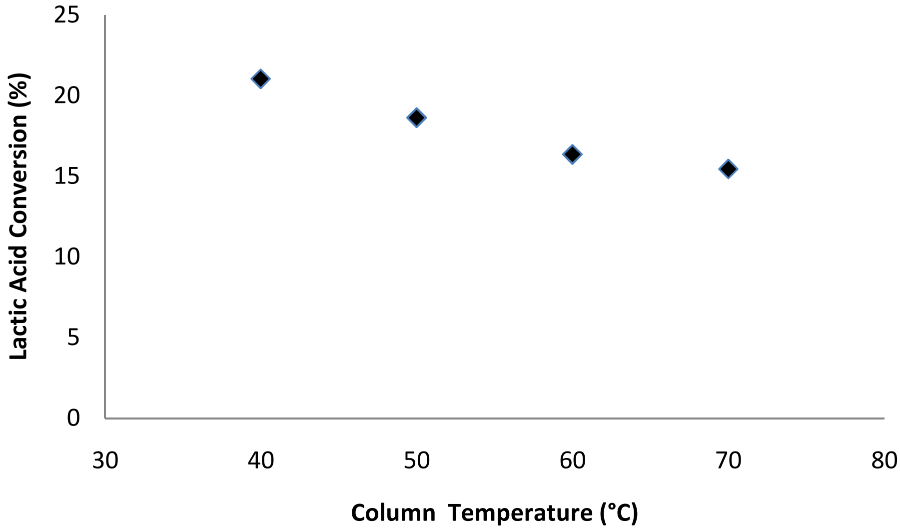


Figure 4.13 Effect of column temperature on conversion

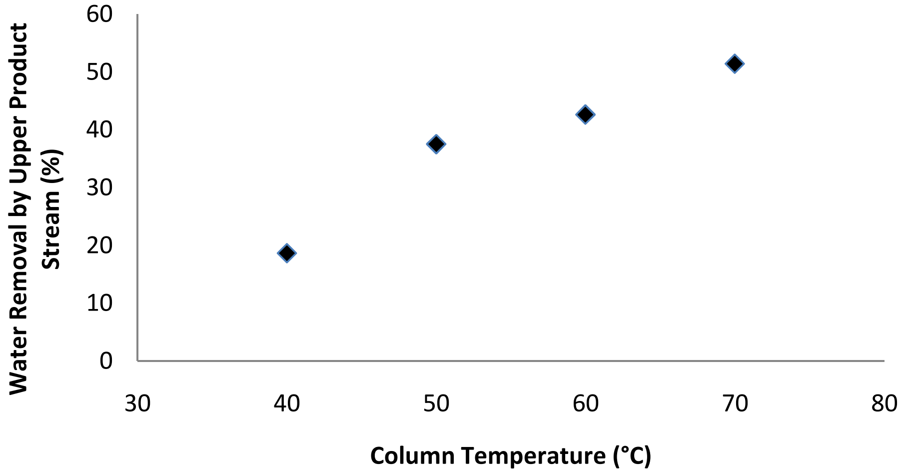


Figure 4.14 Effect of column temperature on water removal by upper product

The main reason of the decrease in the lactic acid conversion is the decreasing the solubility of ethanol in the liquid phase at high temperatures. The solubility decrease of ethanol in water according to the temperature can be given with Henry's law constant, Eqn. 4.8 (NIST). Table 4.9 gives the Henry's Law constant of ethanol at 40, 50, 60, and 70 °C.

$$\mathrm{k_H} = \mathrm{k_H^o} \exp\left[\mathrm{C}\left(\frac{1}{\mathrm{T}} - \frac{1}{\mathrm{T^o}}\right)\right] \qquad (4.8)$$

Where;

k_H: Henry's law constant for solubility in water at any temperature, mol/kg*bar

k_H^o: Henry's law constant for solubility in water at 298.15 K, mol/kg*bar

C: Temperature dependence constant, 6600

T^o: Reference temperature, 298.15 K

Table 4.9 Henry's Law constant of ethanol at different temperatures

Temperature (°C)	40	50	60	70
Henry's Law Constant (mol/kg*bar)	66.47	34.60	18.73	10.51

Since reaction occurs in the liquid phase, lactic acid conversion is limited by the increase in column temperature. According to the batch experiment results (Aytürk, 2001), increase the reactor temperature enhanced the lactic acid conversion. However, in the column experiments, although there is a lower reaction rate constant at low temperatures, the effect of ethanol concentration in the liquid phase is more dominant. Therefore, high ethanol transfer from gas phase to liquid phase at low temperature enhances the lactic acid conversion.

Although the water production decreases with increase in temperature because of the decrease of lactic acid conversion, the water removal by upper product increases. This can be explained with the increase of the vaporization of presence water at higher temperatures.

CHAPTER 5

CONCLUSIONS

In the present study, esterification reaction of lactic acid with ethanol in the strong cation ion exchange resin filled reactive distillation column was investigated. In order to understand the reaction or separation responses of the column, effect of ethanol to lactic acid feed molar ratio, vapor flow rate and the column temperature were studied. Following conclusions can be drawn:

- Counter current feeding of lactic acid in liquid phase and ethanol in gas phase to the reactive distillation column provided the ethyl lactate production.
- Reactive distillation column serves as simultaneous reaction and separation equipment for the esterification of lactic acid.
- Ethanol to lactic acid feed molar ratio had positive effect both on lactic acid conversion and water removal by upper product.
- Increase in lactic acid feed flow rate hindered the water mass transfer to the gas phase because of the hydrophilic property of lactic acid.
- Lactic acid conversion in column experiments was lower than the equilibrium conversion value of 48 hour batch reactor experiment because of the less residence time of reactants in the column used in this study.
- Air can be used as inert carrier gas in order to remove produced water from the system.

- Increase in inlet air flow rate increased the water removal by upper product, since mass transfer coefficient increases with the increase in gas flow rate. However, lactic acid conversion decreased with the increasing of inlet air flow rate because of the decrease in concentration of ethanol in the gas phase so decrease in the driving force, therefore decrease of the conversion.

- Temperature of the column had negative effect on lactic acid conversion; on the other hand enhanced the water removal by upper product. Lactic acid conversion decreased with the increasing of column temperature because of the decrease in the solubility of ethanol in liquid phase; however, water removal by upper product increased because of the more vaporization of water.

CHAPTER 6

RECOMMENDATIONS

- More detailed distribution of the bottom product may be studied by HPLC. Lower working temperature of HPLC will not cause any reaction continuation of the bottom product stream.

- Narrow column with smaller inner diameter may be used in order to equal wet the catalyst at low flow rates of lactic acid solution (drop by drop feed).

- Synthesized catalyst may be used in bead form in order to compare the efficiency of the resin catalyst.

- Longer column may be used to reach the equilibrium conversion value of lactic acid taken from the batch reaction experiment.

- Lower column temperature gave the higher conversion values than the higher temperatures; therefore studied parameters may be investigated again at lower column temperature.

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APPENDIX A

CALIBRATION OF GAS CHROMATOGRAPGH

Reaction mixture contains lactic acid, ethyl lactate, ethanol, water, and lactoyllactic acid. However, Porapak Q column could not detect lactic acid and its oligomers. Water, ethanol, and ethyl lactate can only be detected by the column. Therefore, calibration was applied for GC analysis. For calibration, known amounts of ternary mixtures from water, ethanol and ethyl lactate were prepared and analyzed through GC. In order to calculate relative response factors from Equation A.1, ethanol was selected as base component and thus its correction factor was taken as 1.

$$\mathbf{(R.F)_{species}} = \frac{\mathbf{Area_{base}/wt\%_{base}}}{\mathbf{Area_{species}/wt\%_{species}}} \tag{A.1}$$

Calibration curves were drawn with the GC analysis results of prepared varying concentration solutions. Figure A.1, Figure A.2, and Figure A.3 shows the calibration curves of ethanol, ethyl lactate, and water, respectively. Slope of these curves were used in Equation A.1 and relative response factors are summarized in Table A.1.

Table A.1 Relative response factors

Relative Response Factors	
Ethanol	1.0
Ethyl Lactate	4.6580
Water	0.6012

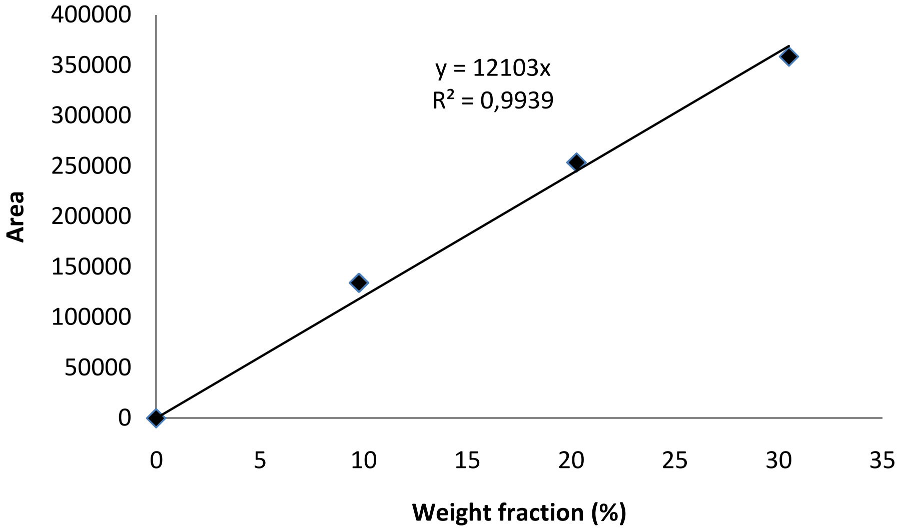

Figure A.1 Calibration curve for ethanol

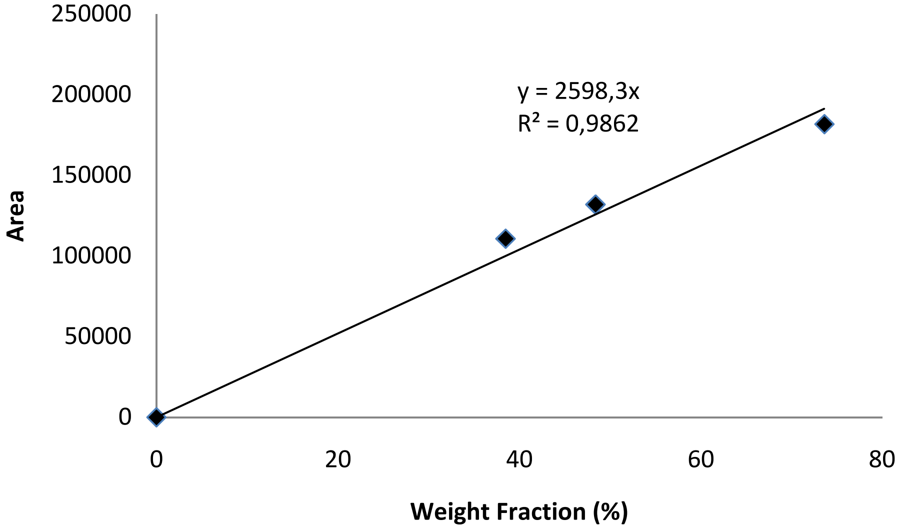

Figure A.2 Calibration curve for ethyl lactate

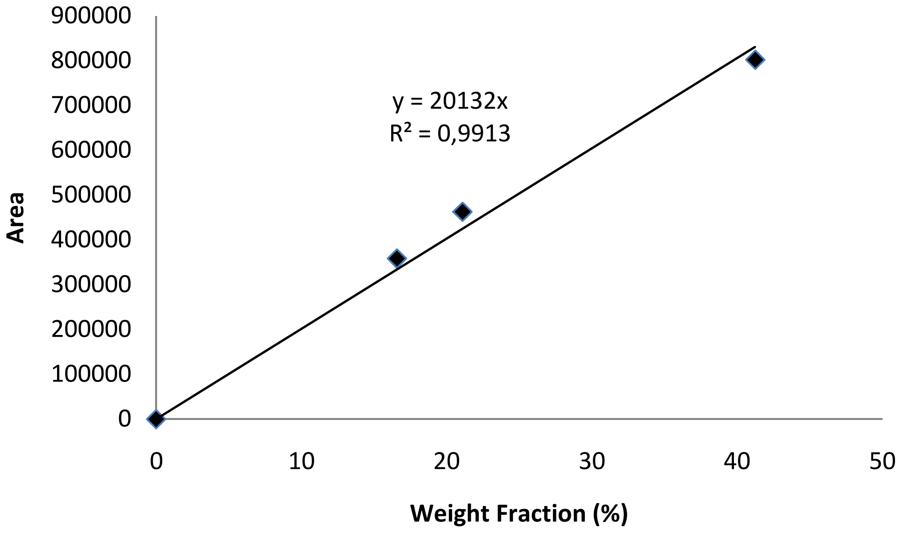

Figure A.3 Calibration curve for water

APPENDIX B

SAMPLE CALCULATIONS

Sample calculation procedure of product distributions and lactic acid conversion is given by using the experimental data given below.

Table B.1 Experimental conditions

Column Jacket Temperature, ℃	70
Ethanol Feed Temperature, ℃	70
Ethanol/Lactic acid feed ratio	2.84
Catalyst amount in the column, g	20.02
Air flow rate, mL/min	2400

Feed flow rates of ethanol and lactic acid solution were measured by the change of the weights of the feed tanks with respect to time. Flow rates of bottom and upper products were calculated by weighing the tubes of samples collected at each time intervals, half an hour. Table B.2 gives the flow rates in gram per minute unit.

Table B.2 Flow rates of feed species and products

Time (min)	**Flow Rates, g/min**			
	Lactic Acid Solution Feed	**Ethanol Feed**	**Bottom Product**	**Upper Product**
30	0.72691	0.74722	0.74924	0.6909
60	0.72691	0.74722	0.7534	0.63702
90	0.72691	0.74722	0.74216	0.62711
120	0.72691	0.74722	0.73592	0.62317
150	0.72691	0.74722	0.73223	0.61177
180	0.72691	0.74722	0.74551	0.61065

The amounts of free lactic acid and lactoyllactic acid in lactic acid feed solutions and amounts of lactic acid in the bottom product was determined by titration with potassium hydroxide solution. Standardization of potassium hydroxide solution was done by using potassium hydrogen phthalate, $KHC_8H_4O_4$. Equation B.1 gives the relation between prepared KOH solution normality and required amount of KOH solution for titration of certain amount of KHP.

$$\mathrm{N_{KOH}} = \frac{\mathrm{w_{KHP}}}{\mathrm{MW_{KHP}} * \mathrm{V_{KOH}}} \qquad (\mathrm{B.1})$$

Where, N_{KOH}: Potassium hydroxide solution normality, g-mole/L
w_{KHP}: Weight of potassium hydrogen phthalate, g
MW_{KHP}: Molecular weight of potassium hydrogen phthalate, g/g-mole
V_{KOH}: Volume of potassium hydroxide solution for titration, L

Amounts of lactoyllactic acid were determined by back titration of the sample with hydrochloric acid solution. Standardization of HCl solution was done by prepared KOH solution. N_{KOH} and N_{HCl} were 0.086104 and 0.10062, respectively.

Water amounts in the feed lactic acid solution and bottom product were determined by Karl Fisher Titration. Titrator gives the weight percentage of water in the certain amount of sample directly; therefore there was no calculation for water amounts.

Weight percentages of free lactic acid, lactoyllactic acid and water in the feed stream (when time equals to zero) and bottom product were tabulated in Table B.3. Free lactic acid weight percentage (FA) and lactoyllactic acid weight percentage (LLA) were calculated by using Equation 3.1 and Equation 3.2 which were given in Chapter 3 under the topic of Analysis.

Table B.3 Composition of lactic acid feed stream and bottom product

Time (min)	**Sample Weight (g)**	**V_{KOH} (mL)**	**$V_{KOH,ex}$ (mL)**	**V_{HCl} (mL)**	**FA (wt%)**	**LLA (wt%)**	**Water (wt%)**
0 (Feed sample)	0.3314	31.1	15	6.5	70.703	16.324	13.57
30	0.5092	35.7	-	-	54.379	-	9.99
60	0.5283	38	-	-	55.790	-	10.67
90	0.5344	40.8	-	-	56.494	-	10.90
120	0.4950	37.8	-	-	56.322	-	10.91
150	0.4562	35.3	-	-	56.885	-	10.67
180	0.5800	44.3	-	-	57.496	-	10.71

Composition of upper product was determined with the results taken from GC analysis. Table B.4 and Table B.5 give the GC analysis results and weight percentages of ethanol, ethyl lactate, and water in upper product, respectively.

Table B.4 Gas chromatography data of upper product

Time (min)	**GC Ethanol Area**	**GC Ethyl Lactate Area**	**GC Water Area**	**Corrected Ethanol Area**	**Corrected Ethyl Lactate Area**	**Corrected Water Area**	**Corrected Total Area**
30	820265	16152	131705	820265	75235	79178	974678
60	817926	17426	137756	817926	81172	82816	981914
90	808698	18882	141775	808698	87955	85233	981886
120	820107	20001	152118	820107	93167	91450	1004724
150	813131	19736	161124	813131	91932	96865	1001928
180	839417	23394	172444	839417	108969	103669	1052055

Table B.5 Composition of upper product

Time (min)	Ethanol (wt%)	Ethyl Lactate (wt%)	Water (wt%)
30	84.158	7.719	8.124
60	83.299	8.267	8.434
90	82.362	8.958	8.681
120	81.625	9.273	9.102
150	81.157	9.176	9.668
180	79.788	10.358	9.854

By using flow rates in g/min and weight percentages of the streams, distribution of the components throughout the reaction time was obtained in mole/min unit. Lactoyllactic acid amount was kept constant during the reaction and initial amount of it was used in the calculation of the bottom product distribution.

Molecular weights of components:

Lactic acid: 90.08
Ethanol: 46.07
Ethyl Lactate: 118.13
Lactoyllactic Acid: 162.066
Water: 18.02

Table B.6 gives the all amounts of the components and C, H and O balances around the system. According to the last 1.5 hours experimental data, it can be said that system reaches to the steady state. Therefore, the average of these last three data was used to calculate lactic acid conversion and C, O, and H balances. Ethanol amount in the bottom product could not be found directly unless gas chromatography analysis data was used. Therefore, ethanol amount was calculated by using carbon balance around the system. Thus carbon balance was calculated as 100 % exactly. Moreover, although the consistency of inlet total weight and outlet total weight was less than 100%, for H and O balances consistency was got more than 100%. The reason was that although there was some weight loss with air in the upper product, we calculated the amount of ethanol as there were no any losses.

Table B.6 Carbon, hydrogen and oxygen balances around the system

	Feed LA Solution (g mole/min)			Feed Ethanol g mole/min	Upper Product (g mole/min)			Bottom Product (g mole/min)				
Time (min)	**N_{LAo}**	**N_{LLAo}**	**N_{H2Oo}**	**N_{Eto}**	**N_{Etu}**	**N_{Esu}**	**N_{H2Ou}**	**N_{LAb}**	**N_{LLAb}**	**N_{Esb}**	**N_{H2Ob}**	**N_{Etb}**
30	0.005705	0.000732	0.005474	0.016219	0.012621	0.000451	0.003115	0.004523	0.000732	0.000731	0.004154	0.002416
60	0.005705	0.000732	0.005474	0.016219	0.011518	0.000446	0.002982	0.004666	0.000732	0.000594	0.004461	0.003662
90	0.005705	0.000732	0.005474	0.016219	0.011211	0.000476	0.003021	0.004654	0.000732	0.000575	0.004489	0.003957
120	0.005705	0.000732	0.005474	0.016219	0.011041	0.000489	0.003148	0.004601	0.000732	0.000615	0.004456	0.004074
150	0.005705	0.000732	0.005474	0.016219	0.010777	0.000475	0.003282	0.004624	0.000732	0.000606	0.004336	0.004361
180	0.005705	0.000732	0.005474	0.016219	0.010576	0.000535	0.003339	0.004758	0.000732	0.000412	0.004431	0.004696
Average	**0.005705**	**0.000732**	**0.005474**	**0.016219**	**0.010901**	**0.000494**	**0.003197**	**0.00466**	**0.000732**	**0.000552**	**0.004428**	**0.004272**

N_{Eto}/N_{LAo}	**...BALANCE**	**INLET**	**OUTLET**	**Consistency (%)**				
2.84	**CARBON**	0.053948	0.053948	100	**Water Removal by Upper Product**			
CONVERSION (%)	**HYDROGEN**	0.149818	0.152029	101.475	**N_{H2Ou}**	**N_{H2Ob}**	**Total**	**%**
18.33168	**OXYGEN**	0.042470	0.043576	102.603	0.003197	0.004428	0.007625	41.93

Reynolds number of empty column (N_{Re}) can be calculated from equation B.2 (Geankoplis, 1993). Sample calculation was done for the gas flow rate of 2400 mL/min.

Air properties at 70 °C (Geankoplis, 1993);

ρ_{air}: density of air, 1.0305 kg/m^3

μ_{air}: viscosity of air, 2.049x10^{-5} kg/m.s

$$\mathrm{N_{Re}} = \frac{\mathrm{Dv\rho_{air}}}{\mathrm{\mu_{air}}} \tag{B.2}$$

Where;

N_{Re}: Reynolds number of empty column

D: Diameter of the column, 0.04 m

V_s: Superficial velocity of the gas phase (volumetric flowrate/cross sectional area of the column), m/s

$$V_s = \frac{2400\left(\frac{mL}{min}\right).\left(\frac{1\,m^3}{10^6 mL}\right).\left(\frac{1\,min}{60\,s}\right)}{\left(\frac{\pi}{4}\right).(0.04)^2(m^2)} = 0.03183\,\frac{m}{s} \tag{B.3}$$

Then;

$$\mathrm{N_{Re}} = \frac{(0.04\ \mathrm{m})\left(0.03183\,\frac{\mathrm{m}}{\mathrm{s}}\right)(1.0305\,\frac{\mathrm{kg}}{\mathrm{m^3}})}{2.049 * 10^{-5}\,\frac{\mathrm{kg}}{\mathrm{m}}.\mathrm{s}} = 64.03 \tag{B.4}$$

APPENDIX C

SPECIFICATION FOR LEWATIT S 100

Table C.1 General description of Lewatit S 100

Ionic form as shipped	Na^+
Functional group	Sulfonic acid
Matrix	Styrene-divinylbenzene
Structure	Gel type beads
Appearance	Brown, translucent

Table C.2 Physical and chemical properties of Lewatit S 100

Mean bead size, mm	0.6 (+/- 0.05)
Bulk density, g/L	830
Density, approx. g/mL	1.28
Water retention, wt%	42-48
Total capacity, min.eq/L	2.0
Volume change ($Na^+ \rightarrow H^+$), max. vol. %	8
Stability, pH range	0-14
Storability, max. years	2
Storability, °C	-20 - 40
Limit temperature, max. °C	120

APPENDIX D

EXPERIMENTAL DATA

Table D.1 Dynamic equilibrium of lactic acid, lactoyllactic acid and water in the absence of catalyst at 70 °C

Time (min)	Free lactic acid (wt%)	Lactoyllactic acid (wt%)	Total Acidity (wt%)
0	68.085	15.222	83.307
60	69.913	16.409	86.322
120	69.068	16.297	85.365
180	67.840	15.686	83.526
240	70.032	16.521	86.553
300	70.397	16.498	86.895
360	68.964	16.457	85.421
420	69.921	16.378	86.299
480	69.486	16.839	86.325

Table D.2 GC analysis of upper product of E1 at 70 °C, 400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	862841.2	1854	100125.4	862841.2	8636.1	60193.6
60	872603.6	1934	100357.6	872603.6	9008.7	60333.2
90	949480	2347	102631	949480	10932.4	61699.9
120	845868.6	2220	105300	845868.6	10340.9	63304.5
150	859420.3	2877.3	110310.6	859420.3	13402.6	66316.8
180	857359	2796.8	107761.3	857359	13027.6	64784.2

Table D.3 E1 at 70 °C, 400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	1.4362	0.738	0.5089	1.7626	47.97	11.82	92.80	0.87	3.98
60	1.4362	0.738	0.4993	1.7340	47.85	12.46	92.64	0.96	6.40
90	1.4362	0.738	0.4501	1.6708	47.47	12.46	92.89	1.07	6.04
120	1.4362	0.738	0.4238	1.7826	48.29	12.75	91.99	1.12	6.88
150	1.4362	0.738	0.4304	1.7004	48.21	12.79	91.51	1.43	7.06
180	1.4362	0.738	0.5002	1.7351	47.52	12.86	91.68	1.39	6.93

Table D.4 GC analysis of upper product of E2 at 70 °C, 400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	887284	1140	110375.7	887284	5310.2	66355.9
60	878357.2	2096	111284	878357.2	9763.3	66901.9
90	859205	1935	110468.6	859205	9013.3	66411.7
120	851575.6	1940	110794	851575.6	9036.6	66607.4
150	848808	2693.3	112635.8	848808	12545.5	67714.6
180	844713.7	3642.4	112231	844713.7	16966.5	67471.3

Table D.5 E2 at 70 °C, 400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.94051	0.63099	0.49155	1.1656	43.425	11.47	92.53	0.55	6.92
60	0.94051	0.63099	0.47129	1.1408	43.358	11.71	91.97	1.02	7.01
90	0.94051	0.63099	0.4626	1.1198	42.939	12	91.93	0.96	7.11
120	0.94051	0.63099	0.45737	1.0876	43.076	11.77	91.84	0.98	7.18
150	0.94051	0.63099	0.43445	1.1400	43.655	12.07	91.36	1.35	7.29
180	0.94051	0.63099	0.48121	1.1714	42.553	12.11	90.91	1.83	7.26

Table D.6 GC analysis of upper product of E3 at 70 °C, 400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	850631	2496	91584.1	850631	11626.48	55058.71
60	851213.6	2656	90357.6	851213.6	12371.77	54321.36
90	848468	2845.2	92631	848468	13253.07	55688.09
120	839641.6	2906.1	95300	839641.6	13536.75	57292.64
150	867779	2922	93531	867779	13610.81	56229.15
180	851583	3111.1	91847.1	851583	14491.65	55216.82

Table D.7 E3 at 70 °C, 400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.46678	0.54571	0.41061	0.60836	39.658	13.66	92.730	1.267	6.002
60	0.46678	0.54571	0.45505	0.59875	34.831	11.78	92.734	1.348	5.918
90	0.46678	0.54571	0.43966	0.60957	34.997	12.27	92.485	1.445	6.070
120	0.46678	0.54571	0.42696	0.58324	34.769	12.18	92.221	1.487	6.293
150	0.46678	0.54571	0.4786	0.58048	33.408	12.15	92.551	1.452	5.997
180	0.46678	0.54571	0.47937	0.56399	34.851	11.95	92.434	1.573	5.993

Table D.8 GC analysis of upper product of E4 at 70 °C, 400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	904411	2984	90448	904411	13899.61	54375.71
60	878791	3006	92037	878791	14002.09	55330.99
90	894810	3527	93923	894810	16428.93	56464.82
120	875863.6	3465	94785	875863.6	16140.13	56983.04
150	864960.3	3699	92254.6	864960.3	17230.11	55461.8
180	863162.4	3789.4	89917.6	863162.4	17651.2	54056.84

Table D.9 E4 at 70 °C, 400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.37323	0.6865	0.55867	0.48065	36.257	9.36	92.981	1.429	5.590
60	0.37323	0.6865	0.56216	0.47705	31.839	10.7	92.687	1.476	5.836
90	0.37323	0.6865	0.58312	0.47125	30.683	10.54	92.467	1.698	5.835
120	0.37323	0.6865	0.57959	0.47172	30.324	10.18	92.295	1.701	6.005
150	0.37323	0.6865	0.57264	0.46892	30.563	10.1	92.247	1.838	5.915
180	0.37323	0.6865	0.57961	0.46517	30.508	10.39	92.330	1.888	5.782

Table D.10 GC analysis of upper product of E5 at 70 °C, 1200 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	885234.3	8052.4	194124	885234.3	37508.45	116703.9
60	897444.3	10080.2	213373.2	897444.3	46954.04	128276.1
90	891151.7	15673.9	217124.7	891151.7	73009.75	130531.5
120	898371.9	19475	222431.6	898371.9	90715.45	133721.9
150	860727.4	18131.7	213215.9	860727.4	84458.29	128181.6
180	865740.6	18108.6	221353.2	865740.6	84350.69	133073.6

Table D.11 E5 at 70 °C, 1200 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	1.4891	0.87067	0.69428	1.52233	47.982	10.96	85.164	3.609	11.228
60	1.4891	0.87067	0.67711	1.55466	52.131	11.9	83.664	4.377	11.959
90	1.4891	0.87067	0.68225	1.49364	49.438	11.74	81.407	6.669	11.924
120	1.4891	0.87067	0.60831	1.5859	53.533	12.35	80.011	8.079	11.910
150	1.4891	0.87067	0.67169	1.59234	53.187	12.04	80.189	7.869	11.942
180	1.4891	0.87067	0.65098	1.53128	52.682	12.36	79.927	7.787	12.286

Table D.12 GC analysis of upper product of E6 at 70 °C, 1200 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	892816.9	11416.8	167308.1	892816.9	53179.98	100582.6
60	936073.3	12998.3	161203.6	936073.3	60546.68	96912.7
90	873268.3	12062.2	154102.7	873268.3	56186.28	92643.77
120	869264.2	13239.7	158013	869264.2	61671.13	94994.57
150	889792.6	13702	162551.1	889792.6	63824.55	97722.8
180	884484.1	13386.4	157257.4	884484.1	62354.47	94540.32

Table D.13 E6 at 70 °C, 1200 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.81309	0.78235	0.74158	0.84281	48.659	12.74	85.308	5.081	9.611
60	0.81309	0.78235	0.74652	0.83968	48.465	11.45	85.601	5.537	8.862
90	0.81309	0.78235	0.74704	0.83233	48.138	11.67	85.438	5.497	9.064
120	0.81309	0.78235	0.71977	0.84548	48.222	11.43	84.729	6.011	9.259
150	0.81309	0.78235	0.68373	0.86836	49.584	11.6	84.634	6.071	9.295
180	0.81309	0.78235	0.65613	0.95413	49.794	12.29	84.934	5.988	9.078

Table D.14 GC analysis of upper product of E7 at 70 °C, 1200 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	811129.8	12753.6	109106.3	811129.8	59406.86	65592.74
60	835502.2	13500.8	99830.2	835502.2	62887.35	60016.12
90	857477.2	13753.3	97236.8	857477.2	64063.5	58457.01
120	836350.8	12766.7	92376.2	836350.8	59467.88	55534.91
150	857999.8	12826	97649.6	857999.8	59744.1	58705.18
180	838185	12337.6	97901.8	838185	57469.11	58856.8

Table D.15 E7 at 70 °C, 1200 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.36888	0.69868	0.63193	0.4002	47.982	10.57	86.647	6.346	7.007
60	0.36888	0.69868	0.61502	0.39795	52.131	10.64	87.176	6.562	6.262
90	0.36888	0.69868	0.6939	0.39144	51.286	10.25	87.497	6.537	5.965
120	0.36888	0.69868	0.68105	0.36487	48.551	10.27	87.912	6.251	5.837
150	0.36888	0.69868	0.70826	0.35048	46.858	10.49	87.869	6.119	6.012
180	0.36888	0.69868	0.68572	0.36765	46.822	10.65	87.813	6.021	6.166

Table D.16 GC analysis of upper product of E8 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	839117.4	11805	156057.4	839117.4	54988.23	93818.9
60	812608.2	14234.2	190449.5	812608.2	66303.56	114494.8
90	811354.1	17276.7	208321.6	811354.1	80475.66	125239.2
120	786980.3	18085.8	220007.4	786980.3	84244.49	132264.5
150	777909.8	17886.3	214408.5	777909.8	83315.21	128898.5
180	793186.8	19612.6	241129.1	793186.8	91356.39	144962.5

Table D.17 E8 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	1.41856	0.64223	0.47293	1.36896	63.494	11.74	84.937	5.566	9.497
60	1.41856	0.64223	0.4725	1.431623	62.203	12.29	81.800	6.674	11.526
90	1.41856	0.64223	0.48927	1.43539	61.029	12.23	79.774	7.913	12.314
120	1.41856	0.64223	0.5299	1.44364	61.572	11.97	78.424	8.395	13.181
150	1.41856	0.64223	0.49295	1.40403	61.809	11.95	78.567	8.415	13.018
180	1.41856	0.64223	0.46556	1.42447	61.071	12.09	77.045	8.874	14.081

Table D.18 GC analysis of upper product of E9 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	820265.4	16151.7	131704.7	820265.4	75235.36	79178.49
60	817925.6	17426.2	137755.3	817925.6	81172.04	82816.01
90	808698.3	18882.3	141775.4	808698.3	87954.62	85232.82
120	820106.6	20001.3	152117.6	820106.6	93166.98	91450.36
150	813131.3	19736.2	161123.8	813131.3	91932.13	96864.73
180	839416.7	23393.7	172443.5	839416.7	108968.9	103669.9

Table D.19 E9 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.72691	0.74722	0.6909	0.74924	54.379	9.99	84.158	7.719	8.124
60	0.72691	0.74722	0.63702	0.7534	55.79	10.67	83.299	8.267	8.434
90	0.72691	0.74722	0.62711	0.74216	56.494	10.9	82.362	8.958	8.680
120	0.72691	0.74722	0.62317	0.73592	56.322	10.91	81.625	9.273	9.102
150	0.72691	0.74722	0.61177	0.73223	56.885	10.67	81.157	9.176	9.668
180	0.72691	0.74722	0.61065	0.74551	57.496	10.71	79.788	10.358	9.854

Table D.20 GC analysis of upper product of E10 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	849078.2	14031	97472.5	849078.2	65357.04	58598.71
60	817510.7	14417.5	113410.4	817510.7	67157.38	68180.29
90	822200.6	15917.5	127373.7	822200.6	74144.45	76574.78
120	856622.6	15880.2	139434.2	856622.6	73970.7	83825.33
150	828169.9	16000	140568.9	828169.9	74528.74	84507.49
180	818428.8	18378.9	144711.5	818428.8	85609.76	86997.95

Table D.21 E10 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	**FLOW RATES (g/min)**				**Titration of Bottom Product**		**GC Result of Upper Product**		
	LA Soln.	**Ethanol Vapor**	**Upper Product**	**Bottom Product**	**% FA**	**% H_2O**	**%EtOH**	**% Es**	**% H_2O**
30	0.54472	0.73078	0.679462	0.39585	58.041	10.95	87.261	6.717	6.022
60	0.54472	0.73078	0.609482	0.41117	56.782	10.83	85.797	7.048	7.155
90	0.54472	0.73078	0.609942	0.54138	57.369	10.75	84.509	7.621	7.871
120	0.54472	0.73078	0.618772	0.55123	57.382	10.94	84.445	7.292	8.263
150	0.54472	0.73078	0.638742	0.52182	58.144	10.96	83.890	7.550	8.560
180	0.54472	0.73078	0.616852	0.54538	57.394	10.2	82.583	8.628	8.779

Table D.22 GC analysis of upper product of E11 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	**EtOH Area**	**Ethyl Lactate Area**	**H_2O Area**	**Corrected EtOH Area**	**Corrected Ethyl Lactate Area**	**Corrected H_2O Area**
30	854126	8496.2	150814.7	854126	39575.69	90667.08
60	867881	9126.3	151247	867881	42510.73	90926.97
90	849856	10854.8	153698	849856	50562.16	92400.47
120	858795	13698.7	156324	858795	63809.17	93979.17
150	853280	14853.2	155986	853280	69186.89	93775.98
180	864270	15422.7	158531	864270	71839.65	95305.98

Table D.23 E11 at 70 °C, 2400 mL/min vapor flow rate

Time (min)	**FLOW RATES (g/min)**				**Titration of Bottom Product**		**GC Result of Upper Product**		
	LA Soln.	**Ethanol Vapor**	**Upper Product**	**Bottom Product**	**% FA**	**% H_2O**	**%EtOH**	**% Es**	**% H_2O**
30	0.37422	0.68221	0.57679	0.36709	58.18	10.56	86.769	4.020	9.211
60	0.37422	0.68221	0.55436	0.35557	57.467	10	86.674	4.245	9.081
90	0.37422	0.68221	0.59113	0.36186	54.276	9.94	85.600	5.093	9.307
120	0.37422	0.68221	0.62379	0.34722	53.249	9.64	84.479	6.277	9.245
150	0.37422	0.68221	0.52939	0.34408	53.848	9.32	83.964	6.808	9.228
180	0.37422	0.68221	0.52301	0.36538	54.055	9.4	83.795	6.965	9.240

Table D.24 GC analysis of upper product of E12 at 70 °C, 3400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	828383.3	9530.95	180052.8	828383.3	44395.6	108244.5
60	854773.4	15988.2	139934.6	854773.4	74473.77	84126.16
90	847528.4	18512.6	167956.1	847528.4	86232.54	100972.2
120	858344.7	19941.3	180505.8	858344.7	92887.49	108516.8
150	813964.7	23651.1	238710.5	813964.7	110167.9	143508.5
180	834186.1	23793.1	237746.4	834186.1	110829.4	142928.9

Table D.25 E12 at 70 °C, 3400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	1.5254	0.82368	1.0154	1.5267	61.194	13.73	84.441	4.525	11.034
60	1.5254	0.82368	0.95573	1.49435	62.631	14.39	84.349	7.349	8.302
90	1.5254	0.82368	0.7702	1.53016	64.135	15.35	81.908	8.334	9.758
120	1.5254	0.82368	0.78804	1.5348	64.291	14.11	80.995	8.765	10.240
150	1.5254	0.82368	0.73293	1.5727	66.201	14.82	76.240	10.319	13.442
180	1.5254	0.82368	0.7865	1.493	66.107	14.8	76.675	10.187	13.138

Table D.26 GC analysis of upper product of E13 at 70 °C, 3400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	809399.1	10944.7	159550.3	809399.1	50980.92	95918.77
60	830870.7	17397	147418	830870.7	81036.03	88625.05
90	834031.4	17868	154932.2	834031.4	83229.97	93142.45
120	816229.4	20317.6	162159.1	816229.4	94640.32	97487.13
150	821979.1	19226.5	188335.5	821979.1	89557.92	113223.9
180	822942.3	20520.3	204195.3	822942.3	95584.5	122758.5

Table D.27 E13 at 70 °C, 3400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.6268	0.69163	0.53054	0.63394	56.642	14.85	84.639	5.331	10.030
60	0.6268	0.69163	0.49308	0.63219	65.114	14.28	83.043	8.099	8.858
90	0.6268	0.69163	0.54791	0.58217	65.212	14.64	82.544	8.237	9.218
120	0.6268	0.69163	0.56543	0.62293	64.99	14.67	80.946	9.385	9.668
150	0.6268	0.69163	0.4787	0.63597	65.872	14.28	80.212	8.739	11.049
180	0.6268	0.69163	0.4937	0.62335	66.116	14.16	79.031	9.179	11.789

Table D.28 GC analysis of upper product of E14 at 70 °C, 3400 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
30	795653.8	9891.3	137323.6	795653.8	46074.13	82556.48
60	834314.8	17180.3	140884.2	834314.8	80026.63	84697.05
90	840482.8	19911.8	154285.4	840482.8	92750.08	92753.61
120	801605.6	18413.6	155730.4	801605.6	85771.4	93622.31
150	836473.4	19127.3	174285.3	836473.4	89095.84	104777.2
180	838597.5	19405.2	182173.1	838597.5	90390.31	109519.2

Table D.29 E14 at 70 °C, 3400 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
30	0.30319	0.72904	0.58351	0.23104	46.492	13.33	86.083	4.985	8.932
60	0.30319	0.72904	0.53763	0.23859	52.93	12.34	83.512	8.010	8.478
90	0.30319	0.72904	0.58557	0.25369	54.457	12.19	81.919	9.040	9.040
120	0.30319	0.72904	0.62545	0.30953	55.018	12.31	81.713	8.743	9.544
150	0.30319	0.72904	0.66585	0.30992	56.849	12.9	81.183	8.647	10.169
180	0.30319	0.72904	0.61613	0.28592	56.053	13.49	80.750	8.704	10.546

Table D.30 GC analysis of upper product of E15 at 40 °C, 450 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
60	790788.4	6678.5	411459.1	790788.4	31108.76	247361.8
120	807128.6	14715.5	322915.6	807128.6	68545.48	194131
180	810683.3	10214.7	272469.2	810683.3	47580.54	163803.6
240	820224.6	14560.3	252208.8	820224.6	67822.55	151623.4

Table D.31 E15 at 40 °C, 450 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
60	0.2151	0.10503	0.06061	0.23757	59.296	20.72	73.957	2.909	23.134
120	0.2151	0.10503	0.06676	0.22298	53.61	21.02	75.446	6.407	18.146
180	0.2151	0.10503	0.06956	0.23374	52.334	20.49	79.318	4.655	16.027
240	0.2151	0.10503	0.06985	0.22222	53.046	20.19	78.893	6.523	14.584

Table D.32 GC analysis of upper product of E16 at 50 °C, 450 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
60	857784.2	7109.4	329930.1	857784.2	33115.91	198348
120	863043.1	9073.3	317230.9	863043.1	42263.85	190713.5
180	869432.3	9484.6	286740.8	869432.3	44179.7	172383.4
240	858625.1	10666.5	289948.7	858625.1	49685.05	174311.9

Table D.33 E16 at 50 °C, 450 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
60	0.18197	0.11227	0.06621	0.16157	59.514	12.35	78.750	3.040	18.210
120	0.18197	0.11227	0.0797	0.17656	56.235	12.05	78.743	3.856	17.401
180	0.18197	0.11227	0.08712	0.18818	54.517	12.06	80.059	4.068	15.873
240	0.18197	0.11227	0.0866	0.19379	55.107	12.13	79.310	4.589	16.101

Table D.34 GC analysis of upper product of E17 at 60 °C, 450 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
60	832869.3	11343.4	390675.3	832869.3	52838.08	234867
120	828622.9	18339.4	340952.1	828622.9	85425.77	204974.3
180	831912.6	18966.7	332493.1	831912.6	88347.76	199888.9
240	824838.7	22821.3	315317.5	824838.7	106302.7	189563.2

Table D.35 E17 at 60 °C, 450 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
60	0.20664	0.11232	0.06514	0.21378	61.23	12.21	74.325	4.715	20.960
120	0.20664	0.11232	0.0752	0.20656	60.235	11.23	74.049	7.634	18.317
180	0.20664	0.11232	0.08682	0.20818	59.517	10.49	74.268	7.887	17.845
240	0.20664	0.11232	0.09438	0.20387	59.107	10.03	73.600	9.485	16.915

Table D.36 GC analysis of upper product of E18 at 70 °C, 450 mL/min vapor flow rate

Time (min)	EtOH Area	Ethyl Lactate Area	H_2O Area	Corrected EtOH Area	Corrected Ethyl Lactate Area	Corrected H_2O Area
60	620769.4	14195.3	608104.9	620769.4	66122.36	365581.7
120	690119.9	25839	477675	690119.9	120359.3	287169.6
180	714252.6	30342.8	422685.3	714252.6	141338.2	254110.8
240	720906.3	34481.9	392522.4	720906.3	160618.3	235977.4

Table D.37 E18 at 70 °C, 450 mL/min vapor flow rate

Time (min)	FLOW RATES (g/min)				Titration of Bottom Product		GC Result of Upper Product		
	LA Soln.	Ethanol Vapor	Upper Product	Bottom Product	% FA	% H_2O	%EtOH	% Es	% H_2O
60	0.1597	0.10948	0.0775	0.16766	60.995	10.52	58.982	6.283	34.735
120	0.1597	0.10948	0.078	0.16486	60.206	10.39	62.873	10.965	26.162
180	0.1597	0.10948	0.0818	0.16235	60.628	10.43	64.364	12.737	22.899
240	0.1597	0.10948	0.0815	0.16378	59.456	10.38	64.511	14.373	21.117