Esterification of Bioplatform molecules

Babita Saikia¹ Dolly Gandhi²

¹Masters of chemical engineering, Vishwakarma Government Engineering College, Chandkheda, Ahmedabad, Gujarat, India-382424.

ABSTRACT

The current chemical industry consumes non renewable resources, due to limited stock of non renewable resources and severe environmental impact chemical industry shift towards to develop industry based on renewable resources. The biorefinery used the renewable resources and produce a wide range of low environmental impact products from biomass in an economically effective and environmentally benign. Succinic acid among the potential platform chemicals of the future biorefineries has been reported as a promising candidate. It is used as surfactant, detergents, pharmaceuticals and food additives as well as ingredient in animal feeds. Succinic esters have a broad spectrum of application among succinic acid derivatives. Succinic esters are of a high interest for the chemical, pharmaceutical, food and cosmetic industries. Succinic esters are produced by the esterification of succinic acid with alcohol, because of reaction is reversible and very slow reaction it require catalyst to increase reaction rate. In this report the esterification reactions of succinic acid with Ethanol as alcohol and Zeolite beta as catalyst are studied. The effect of reaction parameters on esterification reactions such as, Acid to Alcohol ratio, Reaction time and Amount of catalyst are determined. Comparison with the previous experimental results with another catalyst.

Chapter 1

INTRODUCTION

The world in which we live relies heavily on the use of fossil energies (petroleum, coal, natural gas) as main energy resources, and as a feedstock for the products we use in new chemical industry. The current chemical industry consumes these non renewable resources over one billion barrels of oil per year and over 30 billion barrels per year of liquid fuels such as crude oil and natural gas.

Due to the limited stock of fossil fuels and increasingly severe environmental impact due to the use of these non renewable resources and rapidly increasing costs of petroleum and petrochemicals there is an accelerating shift towards to develop a chemical industry based on

renewable resources. A biological material, biomass is a renewable energy source, derived from plants and animals or living organisms [1].

Biorefineries used the biomass as starting material. The dual structure of Biorefineries is shown in Figure 1.1. There are two steps, in a first step; the production of renewable platform chemicals is carried out by fermentation of biomass. The fermentation of biomass could replace the C1 to C6 petroleum-derived building-block chemicals. In a second step, Bio-derived platform chemicals are transformed into valuable chemicals. Building block chemicals are molecules with multiple functional groups that possess the potential to be transformed into new families of useful molecules. The twelve sugar-based building blocks are presented in Table 1.1 Glucaric acid is also called aldaric acids, which are produced from sugar by mild oxidation.

Thus it is obtained from D-glucose by oxidation with dilute nitric acid. Levulinic acid is produced when starch is boiled in dilute sulfuric acid. 2,5 Furan dicarboxylic acid is produced by oxidative dehydration of C6 sugars, e.g., glucose. 3-Hydroxybutyrolactone is obtained by oxidative degradation of starch. Sugar alcohols, sorbitol and the corresponding C5 alcohols, xylitol and arabinitol is produced by chemical hydrogenation of glucose, xylose, and arabinose respectively. 1,4 Diacids (succinic, fumaric and malic), 3 Hydroxy propionic acid and the two amino acids glutamic acid and aspartic acid are metabolites from metabolic pathways, and they are easily produced by fermentation of sugar than by chemical routes. Itaconic acid is produced either by distillation of citric acid, has attracted a lot of attention in the last decade and that could be used for the production of a large range of derivatives. [1]



Fig.1.1Bio- Based chemical industries

Table1.1 Top bio-derived building blocks

1.1 Bioderived Plateforms

Future green and sustainable chemistry will rely on the creation of new product supply chains based on platform molecules derived from biomass. Although there is a large body of reported work on the production of these platform molecules, especially by fermentation technology, now extending to new industrial scale processes, it is very important that we develop effective processes for adding value to these compounds through clean and efficient downstream chemistry. Fig 1.2 shows conversion of the Bioplatform molecules from biomass. [1]



Fig 1.2 conversion of the Bioplatform molecules from biomass

Bioplatform molecules are largely polar, oxygenated and multi-functional and much of the downstream chemistry research effort to date has, not surprisingly, focused on reducing functionality.

However, the multi-functionality of a molecule, such as itaconic acid (one of the more important platform molecules available from the fermentation of carbohydrates), presents opportunities for further fictionalization to produce some very interesting molecular structures that may be very

difficult and expensive to access when starting from traditional, low-functional petro-platform molecules.

Polyketones, for example, can be useful as chelators, an application area in which greener chemicals is desirable. It is important that any additional chemistry carried out on bioplatform molecules is based on the principles of clean synthesis with a minimum number of steps and (benign) auxiliaries. In this way we can move towards genuinely green and sustainable chemical products [11].

Herein, we report our preliminary results from studies on the base-catalyzed functionalization of unsaturated bioplatform molecules, using itaconic and fumaric acids as examples. We found that KF/alumina, one of the first well-studied solid bases for clean synthesis, can be an effective catalyst for such reactions.

1.2 Succinic acid

Succinic acid among the other bio platform chemicals of the future biorefineries has been reported as a promising candidate [4]. This dicarboxylic acid (succinic acid) is an intermediate of the tricarboxylic acid cycle that could replace the maleic anhydride which is produced from oil as a C4 building-block chemical [6]. As succinic acid is an intermediate, the catalytic reactions for the production of the derivatives directly in the fermentation broth are profitable. The bio succinic acid market was 51,000 tons in 2013 and is expected to increase to 593,400 tons by 2020. It would avoid the expensive purification of succinic acid from the fermentation broth. The resulting derivatives from the succinic acid should have different physico-chemical properties that will ease their final purification. This constitutes the primary motivation to select succinic acid among the other bio-based organic acid.

1.3 Objectives

To determine the conversion of succinic ester by esterification of succinic acid with Ethanol using Beta zeolite as a catalyst and to determine the effect of reaction parameters on esterification reaction such as:

- Acid to Alcohol ratio
- Reaction time
- Amount of catalyst
- Reaction temperature

Chapter 2

SUCCINIC ACID

2.1 Background

Succinic acid is a 1,4-diacid, also called butanedioic acid or, in the IUPAC system, ethane- 1,2dicarboxylic acid, is a dicarboxylic acid with four carbon atoms, that has become a chemical of significance in recent years. It was first extracted from amber (succinumin Latin) by Georgius Agricola in 1546. It is a common metabolite in plants, animals and microorganisms, and in a report released by the US Department of Energy the succinic acid identified as one of the top twelve value-added chemicals to be produced from biomass Succinic acid is used as surfactant, detergents, pharmaceuticals and food additives as well as it can also be used as an ingredient in animal feeds and used to stimulate growth in plants [4]. It can also be used as an intermediate chemical in the creation of 1,4-butanediol, a chemical that was expected to have a demand of 4,79,000 tons per year by 2008 and 1.5 million tons per year by 2011 Succinate salts were being consumed at a rate of 92,000 tons per year as of 2003. The chemical derivatives of succinic acid are shown in Table 2.1.

Physical properties of succinic acid	
CAS Number	110-15-6
Molecular Formula	(CH ₂ COOH) ₂
Molecular weight	118.09g/mol
Melting point	188 ⁰ C
Boiling Point	Decomposes at 235 [°] C
Specific gravity	1.56
Solubility	100g/100ml at 100 ⁰ C

Table 2.1 Physical Properties of succinic acid

Succinic acid can be produced anaerobically through fermentation and is an intermediate of the reductive TCA cycle [8, 13]. When succinic acid produced by biochemical, Succinic acid exists in its dissociated form since the pH of fermentation is greater than its pKA values of 4.20 and 5.61. When succinic acid from bioproduction it is considered naturally produced as it is sourced from biomass whereas succinic acid is labeled as chemically produced when it synthesized from petrochemical. The way of production of succinic acid, chemical versus natural can change the area in which succinic acid can be used as well as affect the selling price. To avoid potential health hazards from production residues, industries such as foods and pharmaceuticals will prefer to use succinic acid produced from renewable resources. Because of production of succinic acid

by fermentation is a more cost-efficient and the number of chemicals synthesized from succinic acid increases, demand of succinic acid will rise.

2.2 Application

Succinic acid is a precursor to some specialized polyesters. It is also a component of some alkyd resins. Succinic acid is used in the food and beverage industry, primarily as an acidity regulator. Global production is estimated at 16,000 to 30,000 tones a year, with an annual growth rate of 10It is also sold as a food additive and dietary supplement, and is generally recognized as safe for those uses by the U.S. Food and Drug Administration. [10] As an excipient in pharmaceutical products it is used to control acidity and, more rarely, in effervescent tablets.

2.3 Current Production of Succinic Acid from Oil

The industrially used succinic acid produced from the petroleum derived maleic anhydride. [10] The maleic anhydride can by hydrogenated into succinic anhydride then it is hydrated into succinic acid. Maleic acid is hydrogenated into succinic acid when maleic anhydride is hydrated to maleic acid, as shown in Figure



Fig. 2.1 Synthesis of succinic acid from maleic anhydride through succinic anhydride or maleic acid.

Chapter 3

ESTERIFICATION

3.1 Background

• Esterification reaction is developed by Emil Fischer (1852-1919). Esterification reaction is the reaction to formester. Following are the fundamental routes to formester

- Esterification reaction between carboxylic acid and an alcohol in the presence of an acid
- Catalyst Alcoholysis of anhydrides and acid chlorides
- Reaction between salt and an alkyl halide or sulfate
- Trans esterification reaction

The most widely used method is the reaction of carboxylic acid with an alcohol in the presence of acid catalyst. In this reaction a carboxylic acid is heated with an alcohol while removing water that is formed. [2, 3]



3.2 Mechanism

In the esterification reaction, first the attack of nucleophilic alcohol on the protonated carbonyl group of the carboxylic acid to form a tetrahedral intermediate. Then tetrahedral intermediate collapse and regenerated the carbonyl group and produce the ester and water. [12].

Overall mechanism is shown in the Figure Esterification reactions are reversible and very slow reactions. In the absence of catalyst it requires several days to reach equilibrium. So, catalysts are required to increase the reaction rates



CATALYSIS

4.1 Introduction to catalysts for esterification

Catalysis is a phenomenon by which the rate of chemical reactions is accelerated by small quantities of foreign substances, called catalysts. Catalysts are substances that are capable of directing and accelerating thermodynamically feasible reactions, they cannot change the thermodynamic equilibrium of reactions. The word catalysis comes from the Greek kata-, means "down," and lyein, means "loosen".

The phenomenon of catalysis was first employed by the great Swedish chemist Jöns Jacob Berzelius in 1835 [7]. The substances promoting various reactions, like the conversion of starch to sugar by Gottlieb Sigismund Constantin Kirchhoff; the combustion of gases by Sir Humphry Davy, were defined catalysts, and the action of an unknown catalytic force postulated by Berzelius. In 1991 the catalyst world market a turnover of about 6 billion increased to 8-9 billion in 1996, and in 2008 it reached 13 billion, and according to Fredonia Group the global catalyst demand is rise 6% per year to 17.2 billion in 2014. The catalyst sold to the chemical industry is approximately 24-28% of produced catalysts14 and 38-42% of produced catalysts to petrochemical industries including refineries.

3-5% of solid catalysts were used in the production of pharmaceuticals and 28-32% used in environmental protection. A great part of the pharmaceuticals, fertilizers, energetic vector and of the materials used by human beings are produced via catalytic processes, so catalysis and catalysts play a primary role in today technology. For chemicals and materials production, for fuel and other energy conversion systems, for combustion devices, for fuel cells, and for pollution control systems chemical catalysis is an essential tool.

For increase the profit and the greening of industry catalysis is a key technology. Because of the improvement in catalyst performances, reduction of both wasteful byproducts and energy consumption, moving in the direction of a sustainable chemistry. Catalysts may be gaseous, liquids, or solids. Liquids and solids are most industrial catalysts. In the chemical industry is shown by the fact that 75% of all chemicals are produced with the aid of catalyst and in newly developed processes its 90%. Various organic intermediate products, required for the production of plastics, dyes, synthetic fibers, crop protection agents, resins, pharmaceuticals and pigments can only be produced by catalytic processes

4.2 Properties and Characteristics of Catalysts

Fundamental properties of catalysts are activity, selectivity and stability. Industrial applications require that a catalyst be regenerable, thermally and mechanically stable, economical and possess suitable morphological characteristics.

• Activity The catalytic activity is a way of indicating the effect the catalyst has on the rate of reaction and can be expressed in terms of the rate of the catalytic reaction, the relative rate of a chemical reaction (i.e. in comparison to the rate of the uncatalysed reaction) or via another parameter, such as the temperature required 15to achieve a certain conversion after a particular time period under specified condition.

• Selectivity is the ability of catalyst to give one particular reaction product. High selectivity of catalyst produces high yields of a desired product while suppressing undesirable competitive consecutive reactions. In some cases, catalysts may be used primarily to give high reaction selectivity rather than high activity.

• Stability: The thermal, chemical and mechanical stability of a catalyst determines its lifetime in industrial reactors. Catalyst stability is affected by numerous factors, including coking, decomposition and poisoning.

• Morphology:

The external morphological characteristics of a catalyst must be suited to the corresponding process such as its formed grain size.

• Mechanical Strength:

The mechanical strength of a catalyst is described by its resistance to crushing. It is also described by the resistance of the grains to attrition through rubbing, which can cause an increase in the pressure drop in a catalytic bed.

• Thermal Characteristics

High thermal conductivity of the catalysts leads to reduced temperature gradients within the grain, as well as in the catalytic bed, for exothermic or endothermic reactions, by improving heat transfer. A high specific heat of catalysts permits a catalytic cracking to carry a large thermal load from the combustion of coke back to the endothermic cracking reaction, where it is usefully consumed. So for certain catalysts thermal conductivity and specific heat require consideration.

• Regenerability:

The regenerability of a catalyst is a measure of how well it responds to treatments to bring back its activity and selectivity after deactivation. Many solid catalysts are regenerated by burning off carbonaceous deposits.

4.3 Zeolite as catalysts

Zeolites are crystalline, hydrated aluminosilicates. Their structure is a framework based on an infinitely extending three dimensional network of SiO4 and AlO4 tetrahedra linked to each other by sharing oxygen atoms. The framework contains channels or interconnected voids, which are in micropore range. These channels and voids are occupied by water molecules, and the cations; mainly alkali or alkaline earth metal ions, so as to balance the negative charge of the framework (Breck, 1974). [16]

The general crystallographic unit cell formula of a zeolite is given as:

Mx/m [(AlO2) x (SiO2) y]. z H2O

where, M represents the non-framework metal cation, m is its charge, z is the number of water molecules and x and y are integers such that $y/x \ge 1$. The expression enclosed in the square brackets shows the anionic framework composition.

Zeolite was first discovered as a new type of mineral in 1756 by the Swedish mineralogist Cronstedt. The word "zeolite" derived from two Greek words "zeo" and "lithos". They mean "to boil" and a "stone" because when gently heated, the mineral loses water rapidly and thus seems to boil. Zeolites can be grouped as; natural and synthetic zeolites. Today, about 50 species of zeolite minerals and numerous types of synthetic zeolites are known.

Until the 1950's, when the synthetic zeolites became available as a new type of commercial adsorbents, zeolites did not have much significance. Since then, the utilization of zeolites as catalysts, adsorbents, and ion exchangers has been developed in the most fields of the chemical industry. Zeolites took place of the non-zeolite adsorbents, catalysts and ion exchangers as a

result of the improved performance. Therefore, the consumption of zeolites in these fields has grown continuously.

Zeolites are formed in nature by the chemical reaction occurred between volcanic glass and saline water. This natural reaction is favored in temperatures between 27 °C to 55 °C, and the typical pH value is changing from 9 to 10. To complete this reaction nature requires 50 to 50000 years. Natural zeolites are rarely phase-pure and they are contaminated to varying degrees by other minerals such as; quartz, other zeolites, amorphous glass etc. Thus, naturally occurring zeolites are not used in many important commercial applications where uniformity and purity are essential. [16]

On the other hand, synthetic zeolites, which are often crystallized by nucleation from inhomogeneous supersaturated mother liquors are uniform and.

Chapter 5

BACKGROUND OF BETA ZEOLITE

One of the synthetic zeolites is Zeolite Beta. It is a high silica, large pore, and crystalline aluminosilicate. It was first synthesized hydrothermally from a reaction mixture containing silicon, aluminum and sodium oxides and tetraethylammonium hydroxide at a temperature of about 75 °C – 200 °C by Wadlinger et al. in 1967.

Zeolite beta is an intergrowth hybrid of two distinct structures and has a stacking disorder. These complexities hampered the structural characterization of zeolite beta until 1988. Newsam et al. (1988) determined the crystal structure of this zeolite by using high resolution electron microscopy, electron diffraction, computer assisted modeling and powder X-ray diffraction. It was reported that in zeolite beta structure, the ordered and disordered framework coexist and there are three mutually intersecting channels. [15]



Figure 5.1 Framework Structure of Zeolite Beta [14]

The framework structure has two types of 12 membered ring pores. The channel system of zeolite beta has pore diameters of 5.6 x 5.6 Å and 7.7 x 6.6 Å (Bárcia et al., 2005). The framework structure and the channel system of zeolite beta are schematically shown in Fig. 5.1 & 5.2 respectively.



Figure 5.2 Channel system of Zeolite Beta [15]

Because of its high Si/Al ratio and higher acidic strength zeolite beta is usually preferred rather than faujasite type zeolites in various hydrocarbon conversion reactions such as hydrodewaxing and pour point lowering of petroleum (Eapen et al., 1994). In addition, high Si/Al ratio makes zeolite beta hydrophobic and thermally stable even at high temperatures, therefore it can be utilized in separation and catalytic applications.

Chapter 6

EXPERIMENTAL SETUP

6.1Apparatus

The esterification reaction of succinic acid with different alcohols are carried out

in a round bottom flask in a constant temperature oil bath. Round bottom flask attached to Dean-Stark apparatus to remove the water formed during the reaction and condenser to remove heat. It is also attached to thermometer to measure the temperature of reaction mixture. Round bottom flask with oil bath is placed on heating mental. The reaction mixture is agitated using magnetic stirrer which is placed into the round bottom flask. Stop watch to note the time for the reaction. Titration set to determine acid content into the reaction mixture. Measuring cylinder require to measure the chemicals.



6.2 Procedure

Add succinic acid and ethanol in round bottom flask (Different acid to alcohol ratio

for different experiment). Heat the reaction mixture at desired temperature ($65-75^{\circ}C$). After the desired temperature is achieved add the acid catalyst (Different amount of catalyst for different experiment). Allow the reaction mixture to react for different time interval.

For different time interval determine the acid content remain into the reaction mixture by collecting 2gm of reaction mixture and titrating it with 1N NaOH solution use phenolphthalein as indicator. Calculate the conversion of succinic acid wt% at different amount catalyst loading, time and temperature.

ARIE

Figure 6.1: Experimental setup



Figure 6.2: Schematic Diagram





6.3 CALCULATIONS

To calculate the conversions of succinic acid throughout the batch reactor experiments, the 1Nsodiumhydroxide solution used in titration was standardized by using the standard 1 N hydrochloric acid solution and the normality of sodium hydroxide (NaOH) was calculated from the following Equation:

 $N_{NaOH} = \frac{V_{HCl} * N_{HCl}}{V_{NaOH}}$

 N_{NaOH} : normality of NaOH solution, mol/L N_{HCl} : normality of HCl solution, mol/L V_{NaOH} : volume of NaOH solution used for the titration,mL V_{HCl} : volume of HCl solution used for the titration, mL

At regular time intervals, about 2g from each reaction sample was withdrawn, for titration against 1 N standardized sodiumhydroxide solution using phenolphthalein as an indicator. To assess the reliability of the titration method, unconverted succinic acid was calculated by the following Equation:

$$F(wt\%) = \frac{N_{NAOH}(mol/L) * V_{NAOH}(mol/L) * MW_{succinicacid}(g/mol) * 100\%}{W_{Sample}(g) * 100(mL/L)}$$

F: Free Acidity as Succinic Acid, wt% N_{NaOH}: Normality of NaOH solution,mol/L V_{NaOH}: volume of NaOH solution used for the titration,mL M_wFormic Acid: Molecular weight of Succinic Acid, 118.09 g/mol WSample: Sample weight, in g

Conversion (X %) at different time with respect to the succinic acid is calculated by the following Equation:

X % = 100 - F%

6.4 Results and Discussion

MolecularWeight of Succinic acid	118.09 g/mol
MolecularWeight of Butanol	46.06844 g/mol
Type of Catalyst	Beta Zeolite
Si/Al ratio	35-36
N of NaOH	1 N
Indicator	Phenolpthelain

Table 6.1 Properties of the chemicals used

The esterification of succinic acid with ethanol was carried out for the different acid to alcohol mole ratio and different amount of catalyst loading beta Zeolite. The temperature of the reaction medium was 65^{0} C.

Succinic acid (gm)	Ethanol (gm)	Acid to Alcohol ratio	Catalyst (gm)	Time (hr)	B.R	Unconverted S.A wt%	conversion of S.A wt%
10	10	1:1	0.6	3	4.1	24.20845	75.79155
10	20	1:2	0.6	3	4	23.618	76.382
10	30	1:3	0.6	3	3.3	19.484	80.515
10	10	1:1	1	3	4.3	25.38935	74.61065
10	20	1:2	1	3	3.7	20.66375	79.3425
10	30	1:3		3	3.3	20.66575	79.3425
10	20	1:2	0.6	6	3.6	21.07	77.925
10	30	1:3	0.6	6	3.2	20.66575	81.1056
10	30	1:3	1	6	3	18.8	81.2
10	20	1:2	1	9	3.4	20.075	78.93
10	30	1:3	1	9	3.1	18.303	81.69605

Effect of Reactant Molar Ratio

The effect of Succinic acid: Ethanol molar feed ratio was studied over the range of 1:1 to 1:3. An increase in overall acid conversion was observed with increasing molar ratios (Fig. 6.3, 6.4) up to 1:3. Little enhancement in acid conversion was seen when the feed molar ratio was increased from 1:1 to 1:3. [5]



Figure 6.3: conversion of S.A VS acid to alcohol ratio, for reaction time 3 hours and 0.6 gm Catalyst.



Figure 6.4: conversion of S.A VS acid to alcohol ratio, for reaction time 6 hours and 0.6 gm Catalyst.



Figure 6.5: conversion of S.A VS Reaction Time, for acid to mole ratio of 1:2 and 0.6 gm Catalyst.

Effect of Reaction Time:

It was observed that the conversion of the acid is increasing with the increase in Reaction time, however there is not much yield difference observed between the duration 6 to 9 hours.



Figure 6.6: conversion of S.A VS Reaction Time, for acid to mole ratio of 1:2 and 0.6 gm Catalyst.



Figure 6.7: conversion of S.A VS Reaction Time, for acid to mole ratio of 1:2 and 1 gm Catalyst.

Effect of Catalyst Loading. The effect of resin catalyst loading on esterification rate over the range of 0 to 5 wt% of total solution mass was studied. The absolute initial rate of acid conversion was found to increase linearly with catalyst loading



Figure 6.8: conversion of S.A VS Amount of catalyst used, Reaction Time of 6 Hours, for acid to mole ratio of 1:3.



Figure 6.9: Comparison of yield received with ZSM-5 and Beta Zeolite at different mole ratio and for 3 hours.



Figure 6.10: Comparison of yield received with ZSM-5 and Beta Zeolite at different mole ratio and for 6 hours.

Chapter 7

CONCLUSIONS

- Esterification of Succinic acid with ethanol using heterogeneous solid acid catalyst Zeolite beta at constant temperature 65^oC at 3,6 and 9 hr time it shows that the higher conversion of succinic acid was attain
- At the 1:3 mole ratio of acid to alcohol 80.515, 79.629 and 81.1056, 82.2865 for the amount of catalyst 0.3 and 0.6 gm respectively.
- The conversion of S.A was higher for 1:3 mole ratio of acid to alcohol for 1gm catalyst loading at 6 hr time period. So, we can conclude that the conversion of succinic acid increase with the amount of catalyst and time period.
- Comparing the yield of the experiments carried with ZSM-5 and Zeolite Beta, it was found that the conversion if higher with Zeolite beta and hence there could be vast results found at different temperatures.



Nomenclature

gm/mol= Gram per mole ml = milliliter TCA = Tri-Chloroacetic Acid ⁸A = Angstrom is a unit of length equal to 10^{-10} m N= Normality V = Volume F(w%) = Unconverted succinic acid X(wt%) = converted succinic acid W = Weight of the sample after experiment Vs = Versus S.A = Succinic acid ZSM-5 = Zeolite Socony Mobil–5

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