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# Kinetics of mixed succinic acid/acetic acid esterification with Amberlyst 70 ion exchange resin as catalyst

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ABSTRACT

Liquid phase esterification of succinic acid, acetic acid and succinic/acetic acid mixtures with ethanol was studied using Amberlyst 70 strong cation exchange resin as catalyst. Batch isothermal reactions were performed at different ethanol:acid molar ratios (1:1–27:1), temperatures (343–393 K) and catalyst loadings (1.0–9.3 wt% of solution). Esterification kinetics is described using both pseudo-homogeneous mole fraction and NRTL-based activity based models that take ethanol dehydration to diethyl ether into account. The models accurately predict the esterification of individual acids, and a simple additive combination of independent kinetic models provides a good description of mixed acid esterification. The kinetic models can be used in simulation of reactive distillation processes for mixed acid esterification.



## 1. Introduction

Among several carboxylic acids obtained by fermentation, succinic acid (1,4-butanedioic acid, herein succinic acid (SA)) has been recognized as a renewable platform molecule for many chemical derivatives of industrial interest [1–6]. Its potential use as feedstock for 1,4-butanediol, tetrahydrofuran and γ-butyrolactone production opens the opportunity for a growing and sustainable market of renewable polymers [7,8]. Because SA is a common metabolite in many anaerobic and facultative microorganisms, a number of promising fermentation processes have been developed using bacteria isolated from gastrointestinal systems in animals, including *Anaerobiospirillum succiniciproducens* (~50 kg/m$^3$), *Actinobacillus succinogenes* (94-106 kg/m$^3$), *Mannheimia succiniciproducens* (~52 kg/m$^3$), and *Escherichia coli* (~99 kg/m$^3$) [9–12].

Two major challenges in SA fermentation are achieving high SA titer (g/l) and avoiding loss of selectivity via byproduct formation. In addition to cell growth and incomplete conversion, sugar substrate is lost via formation of significant quantities of acetic, formic, pyruvic, and lactic acids depending on the organism. Typical acid concentrations found in SA fermentation broths are listed in Table 1.

According to recent studies, recovery of succinic acid from these mixtures can be accomplished by esterification with ethanol (EtOH). Succinate and other carboxylic acid salts can react directly with EtOH using sulfuric acid as an acidulant and catalyst. A mixture of free acid and esters in EtOH is produced, while sulfate salts are removed by precipitation. The ethanolic solution is fed into a reactive distillation column for complete esterification and selective separation of esters [13].

Esterification of SA proceeds sequentially through two reactions in series in the presence of an acid catalyst, with monoethyl succinate (MES) as intermediate and diethyl succinate (DES) as final product (Fig. 1). Because of chemical equilibrium limitations in esterification and the low solubility of SA in ethanol (~10% by weight at 298 K), excess EtOH is required in reaction. Further, achieving high rates and overcoming chemical equilibrium limitations requires continuous water ($H_2O$) removal, thus making esterification an attractive reaction system for reactive distillation (RD). For esterification of carboxylic acids, a single continuous RD column can selectively separate either product water or ester from the acid reactant as it is formed. In this way, even dilute acid solutions produced via fermentation [14–16] can be directly esterified to obtain esters as high purity products.

In SA esterification, it is not known whether the presence of byproduct acids (Table 1) accelerates or inhibits SA conversion, or whether formation and recovery of byproduct acid esters overcomplicates the recovery process. As part of our efforts to develop RD strategies for succinic acid esterification, we have carried out this study of esterifying mixtures of SA and acetic acid (AcAc), the byproduct in greatest concentration in SA fermentation (Table 1), with ethanol (EtOH) for the purpose of understanding

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**Nomenclature**

| | |
|---|---|
| AcAc | acetic acid |
| $a_{ij}$ | binary energy parameter in NRTL equation for pair *ij* |
| $b_{ij}$ | binary parameter for NRTL equation for pair *ij* (K) |
| $C_i$ | concentration of component *i* in the bulk phase (kmol/m$^3$) |
| $C_T$ | total molar concentration in liquid phase (kmol/m$^3$) |
| $C_{SA}$ | concentration of SA in the bulk phase (kmol/m$^3$) |
| DEE | diethyl ether |
| $D_{eff}$ | effective diffusivity of SA inside the catalyst pores (m$^2$/s) |
| $D_{SA}$ | molecular diffusivity of SA in liquid phase (m$^2$/s) |
| DES | diethyl succinate |
| $d_P$ | catalytic particle diameter (m) |
| $E_{a,m}$ | energy of activation of forward reaction *m* (kJ/kmol) |
| EtOH | ethanol |
| EtAc | ethyl acetate |
| $f_{ABS}$ | sum of absolute differences (objective function in regression) |
| $G_{ij}$ | binary parameter for NRTL equation for pair *ij* |
| $K_{a,m}$ | equilibrium constant for reaction *m*, activity basis |
| $K_{x,m}$ | equilibrium constant for reaction *m*, mole fraction basis |
| $K_{\gamma,m}$ | activity coefficient ratio for reaction *m* |
| $k_{0,m}$ | pre-exponential factor of forward reaction *m* (kmol/kg$_{CAT}$ s) |
| MES | monoethyl succinate |
| MW | molecular weight of component *i* (kg/kmol) |
| $N_i$ | number of moles of component *i* (kmol) |
| $N_T$ | total number of moles (kmol) |
| $n$ | number of experimental samples |
| $r_m$ | rate of reaction per volume of liquid in reaction *m* (kmol/m$^3$ s) |
| $r_m^\dagger$ | rate of reaction per mass of catalyst in reaction *m* (kmol/kg$_{CAT}$ s) |
| $R$ | ideal gas constant (kJ/mol K) |
| SA | succinic acid |
| $t$ | time (s) |
| $T$ | temperature (K) |
| $V$ | reaction volume (m$^3$) |
| $V_P$ | catalytic particle volume (m$^3$) |
| $w_{CAT}$ | catalyst loading (kg$_{CAT}$/kg solution) |
| $x_i$ | mole fraction of component *i* |

*Greek letters*

| | |
|---|---|
| $\alpha_{ij}$ | non-randomness parameter of NRTL equation |
| $\varepsilon$ | porosity of solid catalyst |
| $\phi$ | Thiele modulus |
| $\gamma_i$ | activity coefficient of component *i* |
| $\mu_{liquid}$ | viscosity of liquid phase (cP) |
| $\eta$ | effectiveness factor |
| $\rho_{CAT}$ | density of the catalyst (kg/m$^3$) |
| $\rho_{sol}$ | density of the liquid solution (kg/m$^3$) |
| $\tau$ | tortuosity of solid catalyst |
| $\tau_{ij}$ | binary parameter of NRTL equation |
| $\theta_{i,m}$ | ratio of stoichiometric coefficients of component *i* to the reference component in reaction *m* |
| $\Phi_w$ | Weisz–Prater modulus |
| $\nu_i$ | stoichiometric coefficient of component *i* |

*Subscripts and superscripts*

| | |
|---|---|
| ABS | absolute |
| Avg | average |
| EQ | equilibrium |
| dry | dry state of the catalyst |
| Calc | calculated data |
| Exp | experimental data |
| *i* | component identification |
| Obs | observed |
| *m* | reaction identification |
| $N_C$ | number of components |
| Sol | solution |
| swollen | swollen state of the catalyst |

**Table 1**
Typical product concentrations in SA fermentation [12].

| Component | Concentration (kg/m$^3$) |
|---|---|
| Succinic acid | 40–110 |
| Acetic acid | 5–40 |
| Pyruvic acid | 0–20 |
| Lactic acid | 0–14 |
| Formic acid | 0–5 |

how AcAc affects SA esterification under process-relevant conditions.

In recent papers [17–19] it has been demonstrated that the strong cation exchange resin Amberlyst 70®, a low cross linked sulfonated and chlorinated styrene-divinylbenzene resin, showed superior performance (e.g. higher turnover frequency) as an acid catalyst relative to the more commonly used macroreticular ion exchange resins (e.g. Amberlyst 15) that are only sulfonated. The high temperature stability of Amberlyst 70 (up to 443 K in most environments) [19,20] also makes it more attractive for use in reactive distillation, where high reaction rates and thus elevated temperatures are required for efficient column operation [21,22].

While there are reports of SA [21,22] and AcAc [23–29] esterification with EtOH using ion exchange resins, none have used Amberlyst 70 as catalyst. We thus have measured and report here the kinetics of AcAc and SA esterification, both individually and in mixtures, over Amberlyst 70 resin. In addition to ester formation, dehydration of EtOH to diethyl ether (DEE) occurs at elevated temperatures, so we include it as an integral part of the kinetic model. The kinetics of mixed acid esterification, along with associated physical property and phase equilibrium data, are useful in designing reactive distillation systems for fermentation-derived SA esterification.

## 2. Material and methods

### 2.1. Materials

Succinic acid (>99.5%, Sigma–Aldrich), acetic acid (99.9%, Aristar), diethyl succinate (99.92%, Sigma–Aldrich), monoethyl succinate (89.3%, Sigma–Aldrich), ethyl acetate (HPLC grade, J.T. Baker), ethanol (200 proof, Decon Labs), water (HPLC grade, J.T. Baker), diethyl ether (99.9%, EMD chemicals) *n*-butanol (99.9%, Mallinckrodt), and acetonitrile (HPLC grade, EMD) were used without further purification for experiments and calibrations. Species purity was confirmed by gas chromatography; no impurities, other than small amounts of water, were detected in appreciable concentrations. Hydranal-coulomat E solution (Riedel-de Haën) was used in Karl–Fisher analysis for water measurement. Amberlyst 70® resin was purchased from Dow Chemical Company; its physical and chemical properties are listed in Table 2.