Optimal Reaction Conditions for the 3-Stage Esterification of Citric Acid with Ethanol

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INTRODUCTION

Citric acid ($C_6H_8O_7$) is an organic acid found in a variety of fruits and vegetables, most notably in citrus fruits. It was first discovered in the 8th century. Since then, it has steadily gained importance, with the first industrial-scale production by extraction performed in the mid-1800s, and the first chemical synthesis in 1880 [1]. Today, citric acid is produced through fermentation, yielding around 2.8 million tons globally in 2022 [2].

Most of the citric acid produced is used directly in consumer food and beverages as an acidulant. However, citric acid can also be further processed/reacted to produce other products. One of the most discussed in literature is the esterification of citric acid with alcohols such as ethanol. The produced esters/polyesters are non-toxic and biodegradable, thus they are used as plasticizers in the preparation of medical-grade plastics, as food packaging, as food additives, and as a cosmetic ingredient [1].

Of particular interest in this project is the three-stage esterification of citric acid (CA) with ethanol (EtOH) to produce triethyl citrate (TEC) as the desired product (Figure 1). Monoethyl citrate (MEC) and diethyl citrate (DEC) are produced in the intermediate steps and water (H2O) is formed in all three stages.

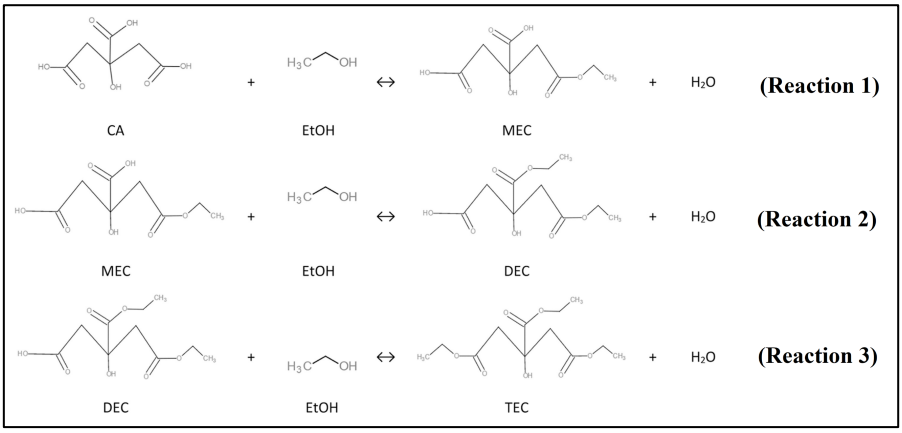

Figure 1. Three-stage esterification of citric acid (CA) with ethanol (EtOH) to form monoethyl citrate (MEC), diethyl citrate (TEC), and triethyl citrate (TEC) [3].

In this project, the equilibrium of the CA-EtOH-MEC-H2O-DEC-TEC reactive system was modeled in Python to investigate its equilibrium composition for various reaction conditions (initial molar ratios of EtOH and temperatures). The results were used to propose the best reaction conditions to obtain maximum TEC concentration at equilibrium.

METHODOLOGY

To determine the equilibrium composition from a set of initial conditions ($n_{0,i}$ initial moles of component i and reaction temperature T), the reaction extent approach was used. For each reaction j, an extent of reaction ξ_j was assigned, signifying the number of moles that each reaction will proceed until equilibrium. Thus, the molar composition of each component at equilibrium, x_i, are as follows:

$$n_i = n_{0,i} + \sum_j v_{i,j}\xi_j \qquad [Eq.1]$$

$$x_i = \frac{n_i}{\sum_k n_k} \qquad [Eq.2]$$

Considering the presence of ethanol and water, which are highly polar in comparison to the other components, the system will exhibit strong nonideal behavior [4]. As such, the UNIQUAC model was used to determine the activity coefficients γ_i of the components in the liquid phase. UNIQUAC binary interaction parameters were taken from the results of Bohorquez et al. [3], while the formulation for the UNIQUAC model was taken from Perry's Chemical Engineers' Handbook [6].

The kinetics and equilibrium of the CA-EtOH-MEC-H2O-DEC-TEC reactive system was first investigated by Kolah et al. in 2007 [4] and then further studied by Bohorquez et al. in 2020 [3]. Their results show that the equilibrium constants for the three-stage reaction are: $K_{R1} = 6.35$, $K_{R2} = 2.72$, and $K_{R3} = 3.78$. Kolah et al. assumed these to be independent of temperature within the temperature range of the experimental data (78 – 120 ºC) [4].

An expression for the equilibrium constant from the definition $K \equiv \exp(-\Delta G^o/RT)$ can be written as

$$K = \prod_i \left(\hat{f}_i/f_i^o\right)^{v_i} = \prod_i \left(\frac{x_i \gamma_i f_i}{f_i^o}\right)^{v_i} = \prod_i (x_i\gamma_i)^{v_i}\left(\frac{f_i}{f_i^o}\right)^{v_i}$$

where $\hat{f}_i$ is the fugacity of component i in the mixture, f_i^o is the fugacity of pure component i at its standard state, v_i is the stoichiometric number of component i in the reaction, x_i is the mole fraction of component i, $\gamma_i \equiv \hat{f}_i/(x_i f_i)$ is the activity coefficient of component i, and f_i is the fugacity of pure component i. For liquid-phase reactions such as the reactions in consideration here, the ratio f_i/f_i^o is usually taken as unity because fugacities of liquids are weak functions of pressure [5]. Hence, the expression for K is reduced to the following, where $a_i = x_i\gamma_i$ is the activity of component i.

$$K = \prod_i (x_i\gamma_i)^{v_i} = \prod_i a_i^{v_i} \qquad [Eq.3]$$

This model, as described above, was then programmed in Python. Initially, an EtOH: CA was set, as well as a reaction temperature. Then, with the help of the algebraic solver "fsolve" from the Scipy module, the equilibrium composition was solved through iteration. Using an initial guess for the extent of reaction ξ_j, the equilibrium amounts and mole fractions were computed using $Eq.1$ and $Eq.2$. Then, using the equilibrium mole fractions, temperature, UNIQUAC binary interaction parameters, and the UNIQUAC formulation from [5], the activity coefficients γ_i were computed. Lastly, using the equilibrium constants from literature and the activity coefficients, the solver checks if $Eq.3$ is satisfied within tolerance. If not, a new extent of reaction is used. If $Eq.3$ is satisfied, the model is considered solved and the final mole fractions of the components at equilibrium are outputted and saved.

RESULTS AND DISCUSSION

The Python model generally provided a moderately good fit to the experimental data (Table 1) [4], signifying that proper/correct modeling of the system was performed. Nonetheless, significant errors were observed at lower temperatures (~78ºC) and on the mole fraction of CA, which may be due to insufficient reaction time in the experimental data and errors when reading from literature graphs.

Table 1. Error between experimental and model for mole fraction of components.

Mole Ratio (EtOH:CA)	Temperature (ºC)	Component	Experimental x_i [4]	Model x_i	Error (%)
15:1	78	DEC	0.040	0.0213	46.75
		TEC	0.018	0.0382	112.22
		MEC	0.010	0.0029	71.00
		CA	0.000	0.0001	-
	100	DEC	0.022	0.0201	8.64
		TEC	0.038	0.0398	4.74
		MEC	0.003	0.0026	13.33
		CA	0.000	0.0001	-
	120	DEC	0.022	0.0189	14.09
		TEC	0.045	0.0412	8.44
		MEC	0.003	0.0023	23.33
		CA	0.000	0.0001	-
5:1	120	DEC	0.068	0.0700	2.94
		TEC	0.085	0.0702	17.41
		MEC	0.020	0.0242	21.00
		CA	0.001	0.0023	130.00

The mole fractions of TEC at equilibrium for various initial EtOH: CA molar ratios and temperatures are shown below. A maximum is observed at ~3.5 EtOH: CA mole ratio, corresponding to a TEC mole fraction of ~0.075 for all temperatures. Thus, it is recommended to perform esterification at this initial molar ratio to maximize TEC production and decrease the cost for further separation. Additionally, the maximum mole fraction is not very sensitive to temperature. As such, the esterification should be performed at the lowest temperature possible to reduce heating requirements. This is at around 80°C, the lowest temperature experimentally studied. Further kinetic studies at lower temperatures can be performed to determine any significant drop-offs in equilibrium TEC mole fraction.

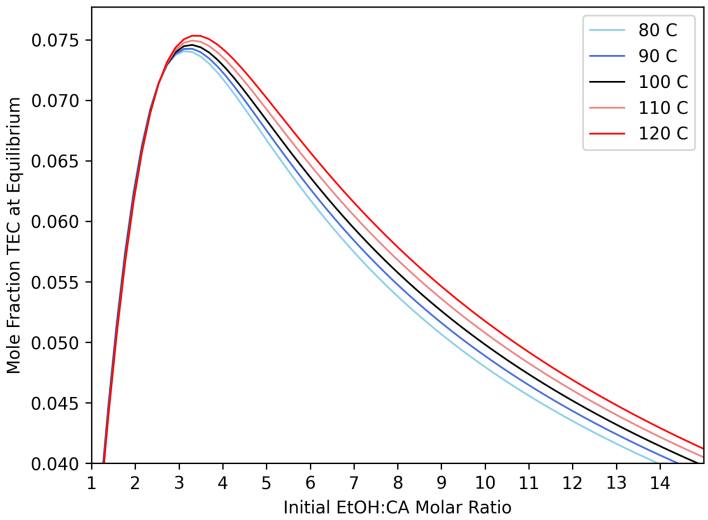

Figure 2. Mole fraction of TEC at equilibrium for various reaction conditions.

CONCLUSIONS

Citric acid ($C_6H_8O_7$) is an organic acid found in a variety of fruits and vegetables, most notably in citrus fruits. Besides its use as an acidulant, citric acid can also be esterified with alcohols such as ethanol and n-butanol. The produced esters/polyesters are non-toxic and biodegradable, thus they are used as plasticizers in the preparation of medical-grade plastics, as food packaging, as food additives, and as a cosmetic ingredient [1]. Of particular interest in this project is the three-stage esterification of citric acid (CA) with ethanol (EtOH) to produce triethyl citrate (TEC) as the desired product. The reactive system was modeled in Python using the extents of reaction approach and the UNIQUAC activity coefficient model. The model was then used to determine the reaction conditions for optimal TEC concentration at equilibrium. Results show that maximum TEC mole fraction at equilibrium (~0.077 mole fraction) is achieved at ~3.5 EtOH: CA initial reactant mole ratio. Additionally, the maximum TEC mole fraction is not very sensitive to temperature. As such, the esterification should be performed at the lowest temperature possible, currently at around 80°C.

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