Importance of Dimer Quantification for Accurate Catalytic Evaluation of Lactic Acid Dehydration to Acrylic Acid

Yu Noda,[†] Hongbo Zhang,[†] Rajesh Dasari,[‡] Ramnik Singh,[‡] Cenan Ozmeral,[‡] Yuriy Román-Leshkov,[§] and Robert M. Rioux*,[†,∥]

[†]Department of Chemical Engineering and [∥]Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, United States

[‡]Myriant Corporation, 66 Cummings Park, Woburn, Massachusetts 01801, United States

[§]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

S Supporting Information

ABSTRACT: Catalytic dehydration of lactic acid in the presence of water is a potentially green, synthetic approach for the production of acrylic acid, and development of a highly selective catalyst is a primary challenge, leading to a resurgence in catalyst exploration and discovery. However, because the complexity in the analytical assessment of the efficiency of catalysts stemming from the possible presence of dimers in lactic acid feedstocks has often been neglected in the literature, we demonstrate, without consideration of the dimer during catalyst evaluation, that they can have a substantial influence on the determination of conversion of lactic acid and selectivity to acrylic acid in aqueous solution. In one example of a modified zeolite catalyst, a true acrylic acid of selectivity of 64% was overestimated to be 80% if the dimers in the feed solution were neglected in the analytical analysis. A survey of the literature demonstrated very few researchers account for the possible presence of lactic acid dimers in the lactic acid solution; therefore, the reported catalyst performance should be carefully considered in light of the potentially significant impact of lactic acid dimers. We further demonstrate that the heat treatment of a lactic acid feed solution prior to the reaction can hydrolyze dimers back to monomers, avoiding analytical misinterpretation and providing an accurate measure of the catalytic performance.
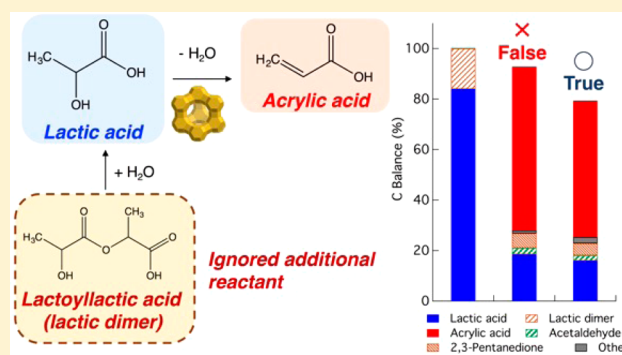
INTRODUCTION

Chemical conversion of a biomass feedstock to fuels and chemicals is a grand challenge that has drawn significant attention from chemists and chemical engineers.[1−3] The catalytic production of acrylic acid (AA) via dehydration of lactic acid (LA) is a perfect example because (i) LA is produced in industry at $(0.3−0.4) \times 10^6$ tons/year via the fermentation of carbohydrates[1,4,5] and (ii) AA is an important chemical for the production of polymers with numerous applications in absorbents, adhesives, coatings, paints, paper, and textiles.[6] Because AA is currently produced by the partial oxidation of propylene, a petroleum derivative,[7] and its market (5×10^6 tons/year) is expected to grow 4−5% per year,[8] dehydration of biomass-derived LA is a greener, more sustainable synthetic approach.

The first report of LA conversion to AA, performed over pelleted phosphate and/or sulfate catalysts, dates back to 1958,[9] and with the current interest in biomass-to-chemical conversion via heterogeneous catalysis, an increasing amount of research on this reaction has been published recently. A series of papers by Miller and co-workers in the 1990s with phosphates[10,11] and sodium salt catalysts[12,13] advanced our understanding of promising catalyst compositions, competing reactions (e.g., decarbonylation and condensation), and the sensitivity of the catalytic performance to the reaction parameters. More recent research focused on the development of highly selective novel catalysts in water-rich environments, for instance, surface-modified zeolites,[14−17] phosphates,[18−20] hydroxyapatite,[21−24] and sulfates.[25,26] For each of these types of catalysts, >70 mol % AA selectivity has been claimed, with the best AA yield of 78% reported for calcium-deficient hydroxyapatite.[23] Another approach starts with lactate ester to produce acrylate, aiming for better total selectivity to acrylic species (acid and/or esters).[27−29]

At the reaction conditions for LA dehydration, there are a number of competing reactions occurring that remain challenging to control (Scheme 1); decarbonylation (acetaldehyde and carbon monoxide) and condensation (2,3-pentanedione, carbon dioxide, and water) are often the major side reactions that limit the selectivity toward AA.
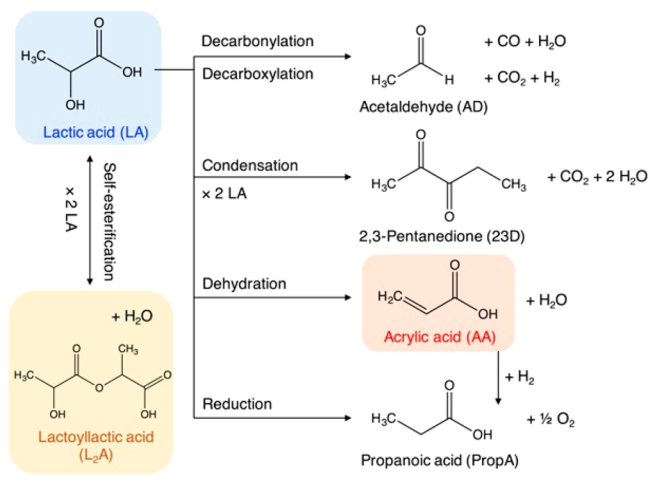
Scheme 1. Reaction Pathways for LA to Chemicals

Accurate quantification of the reactants and products is indispensable for proper catalyst evaluation. This is especially important when key reactants speciate in solution and are analytically distinct from each other (e.g., differing chromatography elution times). This needs to be emphasized particularly in the case of LA determination during LA-to-AA conversion because oligomers of LA can be present in aqueous solutions of LA. In most of the recent work on the catalytic dehydration of LA to AA found in the literature,[14−26] aqueous solutions of LA with different concentrations (20−50%) represent typical feed conditions. Because of the equilibrium between the self-esterification of LA and rehydrolysis back to LA, analytical rigor is essential for accurate calculation of the LA conversion and product selectivity. This leads to incorrect determination of the LA conversion and AA selectivity, and therefore any reports of the turnover frequency/site time yield would be incorrect. Nevertheless, this issue is overlooked in the majority of the existing work.

In this study, we demonstrate LA oligomers impart a substantial influence on the reported catalytic conversion and AA selectivity, in particular the linear dimer lactoyllactic acid (L$_2$A), if LA and AA analytics are not appropriately considered. A cyclic dimer of LA, dilactide (or simply lactide), is another lactic derivative, but it is unstable in water[30] and hydrolyzes upon dissolution, and thus in this study we only considered L$_2$A. Additionally, because the fraction of larger oligomers (>2 lactic) should be negligible (<0.1 mol % lactic) in diluted systems (e.g., <20 wt %),[30] we only considered the dimer L$_2$A for our study using 20 wt % LA solutions. We chose a catalyst system based on NaY zeolite because it is one of the most well-studied catalysts for the dehydration of LA.[15,16,31−33] Modification of NaY with alkali phosphates has one of the highest reported AA selectivity (>75%) values in the literature.[16,17] As an effective means of avoiding misrepresentation of the reaction results, the use of high-performance liquid chromatography (HPLC), rather than gas chromatography (GC), for accurate LA and L$_2$A determination and a feed pretreatment approach to hydrolyze L$_2$A bask to LA are discussed.

■ EXPERIMENTAL SECTION

Chemicals. Concentrated lactic acid (LA) aqueous solution (88.4−88.7 wt %, ADM USP 175830) was obtained from Archer Daniels Midland (ADM). Deionized (DI) water was prepared using a Millipore Milli-Q filtration system and purified to 18.1

MΩ resistivity. LA feed solutions were freshly prepared by diluting the stock concentrated LA solution with DI water. The LA concentration in aqueous solutions was calculated on a nominal LA weight basis. NaY zeolites (SiO$_2$/Al$_2$O$_3$ ratio ∼ 6.3) were provided by TriCAT. Analytical-grade sodium dihydrogen phosphate dehydrate (NaH$_2$PO$_4$·2H$_2$O), dipotassium phosphate (K$_2$HPO$_4$), dilactide (3,6-dimethyl-1,4-dioxane-2,5-dione), L-LA, 2,3-pentanedione (23P), hydroxyacetone (HyAce), propionic acid (PropA), and acrylic acid (AA) were acquired from Sigma-Aldrich and used without further purification.

Catalyst Preparation. 14.8 wt % (1.0 mmol/g$_{zeolite}$) K$_2$HPO$_4$ was loaded on NaY zeolite by a wet impregnation method. A required amount of the K$_2$HPO$_4$ precursor salt was dissolved in DI water, and the solution was slowly added to the zeolite drop by drop in a mortar with ample mixing. The sample was dried at room temperature for 2 h, followed by 393 K for 10 h, and then calcined at 723 K for 3 h under a flow (50 mL/min) of air.

Catalyst Characterization. The surface acidity of the catalysts was quantified with NH$_3$ temperature-programmed desorption using a Micromeritics Autochem 2910 instrument. Powder X-ray diffractograms were collected using a PANalytical Empyrean X-ray diffractometer (Cu Kα radiation). Nitrogen adsorption−desorption measurement was performed using a Micromeritics Gemini V at 77 K after the sample was degassed at 200 °C for 8 h under vacuum (∼10^{-2} Torr), and Brunauer−Emmett−Teller surface areas[34] a relative pressure (P/P$_0$) range of 0.05−0.25. Additional details of the methods and all catalyst characterization data are provided in the Supporting Information. Representative catalyst characterization data are provided in Figures S1 and S2. Additional details on the catalyst characterization and the relationship between the catalyst structure and reactivity/AA selectivity will be published in a future manuscript.

Catalytic Testing. LA dehydration reactions were conducted in a trickle-bed titanium tubular reactor ($^1/_2$ in. diameter) feeding the nominal 20 wt % LA aqueous solution over a catalyst (1.0−1.1 g) at a constant rate of 0.1 mL/min (0.22 mmol of LA/min) with a syringe pump in a carrier flow (55 mL/min) of helium at a reaction temperature of 603 K. We performed product analysis with both GC and HPLC. Gaseous products (i.e., CO and CO$_2$) were separated with a Supelco 60/80 Carboxen-1000 packed column and analyzed online with an Agilent 7890A gas chromatograph. Condensable products were collected after each hour of the reaction with an inline condenser held at 277 K located at the bottom of the reactor and analyzed offline using the same GC system on an Agilent HP-FFAP column with a flame ionization detector (more details are given in the Supporting Information). For accurate determination of LA and L$_2$A, a Shimadzu 10A high-performance liquid chromatograph with a SPD-10A UV−vis detector at 210 nm was employed with a Phenomenex Synergi 4 Hydro-RP column. Successful separations of monomer and dimer with linear calibrations were demonstrated with standard solutions (Figures S3 and S4).

■ RESULTS AND DISCUSSION

Definition of the Conversion and Selectivity. Before a presentation and discussion on the impact of L$_2$A on the conversion of LA and selectivity to AA, definitions used in this manuscript will be defined. For analysis of the LA dehydration reaction, we calculated the conversion of LA and selectivity to products by two different approaches: method A only considers the monomer LA, and method B includes L$_2$A in addition to LA.

Table 1. Impact of Neglecting L₂A on the Conversion of LA and the Molar Selectivity to Products during Dehydration of LA in a Nominal 20 wt % Aqueous LA Feed Stream over a 1 mmol/g K₂HPO₄/NaY Catalyst[a]

	time (h)	solution weight recovery (%)	conversion of LA (%)	AD	selectivity (%)			
					23P	HyAce	PropA	AA
entry 1	1	95.1	94.5	2.6	7.7	0.9	2.0	55.7
exp #1	2	95.1	85.9	3.0	6.9	1.1	2.4	78.9
method A	3	95.4	77.9	3.4	6.5	1.4	2.4	92.1
only LA	4	100.9	67.7	3.6	7.2	1.6	2.9	99.1
	overall	96.6	81.5	3.1	7.1	1.2	2.4	79.5
entry 2	1	95.1	94.4	2.1	6.3	0.7	1.6	45.1
exp #1	2	95.1	87.3	2.4	5.5	0.9	1.9	62.7
method B	3	95.4	81.2	2.7	5.0	1.1	1.8	71.5
LA + L₂A	4	100.9	73.1	2.7	5.4	1.2	2.2	74.2
	overall	96.6	84.0	2.5	5.7	1.0	1.9	64.3
entry 3	1	95.8	89.4	2.2	4.8	0.5	1.2	71.6
exp #2	2	94.7	84.3	2.8	4.7	0.7	1.3	70.3
method A	3	95.8	80.1	3.4	5.1	0.8	1.5	67.7
only LA	4	101.0	78.1	3.8	5.4	0.9	1.8	68.8
	overall	96.8	83.0	3.0	5.0	0.7	1.5	69.7
entry 4	1	95.8	88.5	2.2	4.8	0.5	1.2	71.2
exp #2	2	94.7	82.2	2.8	4.8	0.7	1.3	71.0
method B	3	95.8	78.6	3.5	5.1	0.8	1.6	67.9
LA + L₂A	4	101.0	76.4	3.8	5.4	0.9	1.9	69.3
	overall	96.8	81.4	3.0	5.0	0.7	1.5	69.9

[a]Exp#1 (feed with no pretreatment): LA, 17.3%; L₂A, 3.3%. Exp #2 (feed heat treated prior to the reaction): LA, 21.0%; L₂A, 0.3%. AD = acetaldehyde; 23P = 2,3-pentanedione; HyAce = hydroxyacetone; PropA = propionic acid; AA = acrylic acid; catalyst (1 mmol/g K₂HPO₄/NaY) = 1.1 g; temperature = 603 K. Solution weight recovery = ratio of the measured weight of the solution collected to the expected weight.

Both analyses are on a molar basis. It should be noted that the stoichiometric coefficient differs for the different parallel reactions (e.g., 1 mol of LA converts to 1 mol of AA, while 2 mol of LA reacts to form 1 mol of 23P).

Method A:

$$\text{LA conversion (\%)}$$
$$= 1 - [\text{moles of LA in the product solution (unreacted)}]$$
$$/[\text{moles of LA in the feed solution (initial)}] \quad (1)$$

$$\text{molar selectivity (\%)} = \frac{a \times \text{moles of a product}}{\text{moles of LA reacted}} \quad (2)$$

where a is the stoichiometric coefficient with respect to LA in each possible reaction ($a = 2$ for 23P and L₂A; $a = 1$ for others)

Method B:

$$\text{LA conversion (\%)}$$
$$= 1 - [(\text{moles of LA} + 2 \times \text{moles of L}_2\text{A})$$
$$\text{in the product solution (unreacted)}]$$
$$/[(\text{moles of LA} + 2 \times \text{moles of L}_2\text{A})$$
$$\text{in the feed solution (initial)}] \quad (3)$$

$$\text{molar selectivity (\%)}$$
$$= \frac{a \times \text{moles of a product}}{\text{moles of LA} + 2 \times \text{moles of L}_2\text{A reacted}} \quad (4)$$

Dehydration of LA (Impact of a Lactic Dimer in the Feed). The LA reaction results over a 1.0 mmol/g K₂HPO₄/NaY catalyst were compared by utilizing the two described definitions for conversion and selectivity (Table 1). Solution weight

recovery is defined as the ratio of the measured weight of the solution collected from each sampling from the condenser to the expected weight based on the flow rate and time-on-stream. Any discrepancy from perfect recovery (100%) should reflect gaseous product formation, holdup of liquid in the reactor system, and/or any loss during the sampling. The catalyst exhibited a good AA selectivity with acetaldehyde (AD) and 23P as the two major side products. As a general trend, during the first hour, we observed the highest conversion of LA and the lowest selectivity to AA, which we ascribe to holdup in the reactor. This is supported by the lower total mass recovery. All of our discussion regarding the LA conversion and AA selectivity is based on the 4 h overall result. In entry 1 of Table 1, where only LA is accounted in the feed, the 4 h averaged molar selectivity (eq 2) to AA reached 79.5%. The individual samplings at 3 and 4 h led to a calculated AA selectivity of >90%. Furthermore, the sum of the product selectivity (selectivity for AD + 23P + HyAce + PropA + AA) for these entries exceeded 100%, which disobeys the law of mass action. HPLC analysis confirmed the presence of L₂A in the feed (3.3 wt %), which was not accounted for in the original carbon mass balance. Hydrolysis of the dimer in the reactor can serve as an unknown source for additional LA. In such a case, method A leads to an artificially lower conversion of LA, which leads to a higher selectivity value than the actual value when LA and L₂A are both included in the selectivity calculation. Repeat (five times) experiments for the standard reaction conditions demonstrated that the standard error for the conversion and selectivity was <5%.

The higher selectivity value determined from method A can be corrected if a more appropriate definition of the selectivity (method B) is implemented. If L₂A is included in the carbon balance, the calculated value of the conversion and selectivity change for the same experiment (entry 2). The conversion is higher (84.0%), and the selectivity to each product is consistently

lower than that calculated by method A. From method B, the true 4 h average AA selectivity is 64.1%, which is nearly 20% lower than the AA selectivity calculated by method A (79.5%).

These data clearly illustrate the importance of inclusion of L_2A in the analytical evaluation. However, the impact of L_2A is ignored in LA dehydration studies because very few have analyzed for the absence or presence of L_2A in feed solutions. We carefully surveyed the recent literature[14−26,35,36] and found that only Blanco and co-workers[18] mentioned a small quantity of L_2A detected by GC−mass spectrometry (MS) in the product stream, but they too failed to discuss the presence of L_2A in the feed solution. On the other hand, instead of accounting for L_2A, Näfe et al. pretreated the LA solution at 363 K under reflux for a minimum of 7 days to convert L_2A to LA.[35,36] As we demonstrate in a future section of the Discussion, heat treatment is an effective approach to minimizing the analytical issues caused by the presence of oligomeric species.

An additional analytical challenge arises for this particular system. Accurate determination of LA is complicated because its limited volatility and thermal stability hamper straightforward analysis by GC without actual derivatization of LA.[37−39] Therefore, we implement HPLC for the quantification of LA because it is often more useful and reproducible with HPLC. Yet only a few studies appear to pay attention to this and use multiple analytical techniques (e.g., HPLC[22,23,40] and/or ion chromatography[24]) to ensure analytical accuracy. Yan and co-workers[24] have stated that analysis solely based on GC will fail to provide accurate quantification when LA concentrations are below 15 wt %.

LA−L_2A Concentrations in Diluted Aqueous Solutions. A series of nominal 20 wt % LA solutions were prepared by diluting the original concentrated ∼88 wt % LA solution at 298 K and analyzed with HPLC within 12 h of solution preparation. As shown in Figure 1, all solutions contained L_2A with
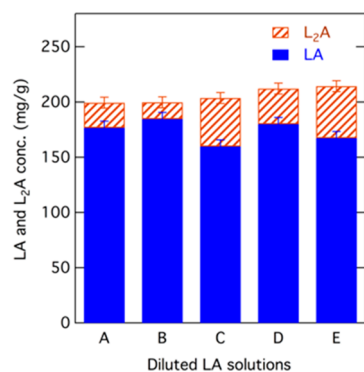
Figure 1. Speciation of carbon between LA and L_2A for nominally diluted 20 wt % LA solutions. The nominal mixtures were produced by diluting out a ∼88 wt % LA aqueous solution with DI water. The solution equilibrated at room temperature for 12 h before LA and L_2A quantification.

concentrations (1.5−4.4 wt %) differing between batches, yet the total lactic (LA + L_2A) quantity was reasonably constant at 20−21 wt %. Vu et al. reported that only a negligible amount of dimer is found in a diluted LA solution (<20 wt %).[30] The apparent discrepancy between our observation and Vu et al. is presumably due to the fact we prepared our solution from a >88% concentrated LA solution, and at the time of HPLC analysis, LA−L_2A equilibrium might not have been reached in the diluted aqueous system. This could also explain why

fluctuations in the concentration of LA were observed in the individual batches in Figure 2. It should also be noted in the
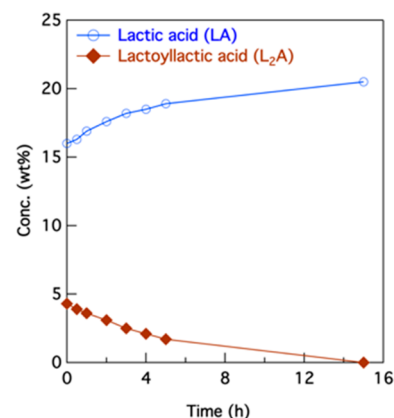
Figure 2. Time course for hydrolysis of dimer L_2A to LA at 353 K.

literature that LA dehydration reactions in aqueous solutions have been mostly studied with concentrations of 20% or higher, up to 50%.[21] A more concentrated LA solution contains more oligomers, and thus the impact of the dimers on the analytical evaluation of the LA conversion, AA selectivity, and overall carbon balance is even greater.

With the proven impact of L_2A in the feed solution LA dehydration analytics, we examined the kinetics for hydrolysis of L_2A to LA (Scheme 2) at 353 K. A slightly higher temperature

Scheme 2. Hydrolysis of L_2A to LA
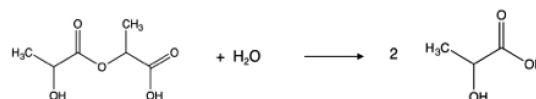
than room temperature was utilized because we previously observed (Figure 1) that the hydrolysis reaction was slow at room temperature. The as-prepared nominal 20 wt % LA solution was heated at 353 K under reflux conditions, and the concentrations of LA and L_2A were monitored with HPLC (Figure 2). LA consistently increased with the reaction time at the expense of L_2A, and after 15 h, most of L_2A (>96%) was converted to LA. Figure 3 demonstrates that a maximum of 16 h
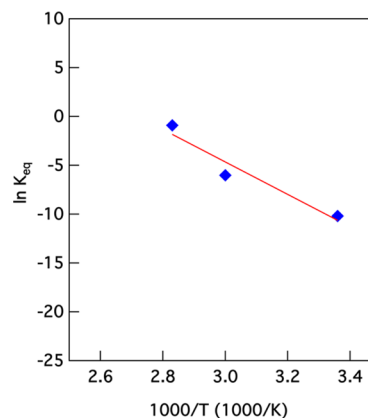
Figure 3. van't Hoff plot for hydrolysis of L_2A to LA from 298 to 353 K. Over the temperature range studied, no dehydration product or other side products were detected in the aqueous solution.

at 353 K is required to hydrolyze L_2A back to LA. On the basis of the experimental measurement of the $L_2A \rightarrow 2$ LA + H_2O equilibrium constant (see below), there will be some L_2A still present in the LA solution, but this amount proves to be negligible enough to only have a minor influence on the overall carbon balance.

We further investigated the influence of heat treatment of a L_2A solution on the LA−L_2A ratio at different temperatures. Because the isolated L_2A solid is not commercially available, the L_2A solution was prepared by dissolving dilactide (Sigma-Aldrich) in water with the assumption of complete hydrolysis of dilactide to L_2A upon dissolution. At room temperature, solutions with a nominal L_2A concentration greater than 3 wt % could not be prepared because of the limited solubility of dilactide in a period of 24 h of mixing. This is an interesting observation because we measured L_2A concentrations as high as 4.4 wt % in LA−L_2A solutions prepared from the stock ∼88 wt % LA obtained from ADM. It is possible that higher oligomers of LA are present in highly concentrated LA solutions, leading to complex multiequilibrium relationships among LA oligomers.[30]

The 3 wt % (0.19 M) L_2A aqueous solution was heat treated at three different temperatures (298, 333, and 353 K) for 15 h, and the LA and L_2A concentrations were determined with HPLC (Table 2). The equilibrium constant (eq 5) was calculated with

Table 2. LA−L_2A Concentrations at Different Temperatures and the Calculated van't Hoff equilibrium Constant

	temp (K)		
	298	333	353
LA [mol/L] (wt %)	0.02 (0.17)	0.13 (1.16)	0.40 (3.60)
L_2A [mol/L] (wt %)	0.18 (2.86)	0.13 (2.07)	0.01 (0.12)
apparent K_{eq}	3.75×10^{-5}	2.42×10^{-3}	4.04×10^{-1}

the assumption that the molar concentration of water is constant (55.56 M) and the solutions reach equilibrium after 15 h. At 298 K, >90% lactic exists in dimer (L_2A) form, which contradicts our previous observation of the LA−L_2A ratio in a typical 20 wt % LA solution (Figure 1) and the report by Vu et al.[30] of negligible dimer concentration in <20 wt % aqueous solutions. This contrast is clear evidence that, even after 15 h, the system is not at equilibrium and the hydrolysis has a substantial activation barrier. The estimated K_{eq} value at this temperature is most likely a lower limit. The LA−L_2A ratio reverses at 353 K and >96% is monomer LA, demonstrating the sensitive character of the kinetics of this reversible process. A van't Hoff plot of the apparent K_{eq} (Figure 3) demonstrates the endothermic nature of low-temperature hydrolysis to LA. The heat of reaction is calculated to be 138 kJ/mol, which is significantly endothermic and generally too large for a hydrolysis reaction. Esterification and its reverse (hydrolysis) have a small change in enthalpy; for example, the esterification of LA with methanol is only slightly exothermic (−16 kJ/mol).[41] The difficulty to reach equilibrium at room temperature in this LA−L_2A mixture even at low concentration (3 wt %) corroborates the importance of heat treatment to accelerate hydrolysis in order to minimize L_2A in the solution used for catalytic study. On the basis of this result of L_2A hydrolysis to LA monomer, we applied the heating of L_2A-containing feed solutions at 353 K for 15 h as the pretreatment protocol for our study of catalytic LA dehydration.

$$K_{eq} = \frac{[LA]^2}{[L_2A][H_2O]} \tag{5}$$

Dehydration of LA (Pretreating an LA Feed Solution). Using the 14.8 wt % (1.0 mmol/$g_{zeolite}$) K_2HPO_4/NaY catalyst, the impact of preheating the feed prior to the LA dehydration reaction was examined. After preheating, the feed composition was determined as 21.0 wt % LA and 0.3 wt % L_2A, demonstrating that more than 90% of the initially present L_2A was converted to LA. The conversion and selectivity results (exp #2 in Table 1) successfully demonstrate the negligible difference in the LA conversion (81−83%) and AA selectivity (69−70%) between methods A and B. The other minor products were also consistent (3% AD, 5% 23P, 0.7% HyAce, and 1.5% PropA). The nearly identical conversion and AA selectivity results demonstrate the effectiveness of preheating the aqueous LA solution. This is also illustrated in a comparison of the overall carbon balance (Figure 4). Here, we calculated the product yield (LA
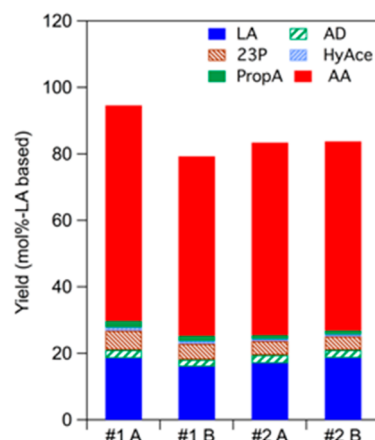

Figure 4. Influence of the feed pretreatment on the product yield and analytics (A and B). Exp #1: reaction with the feed untreated. Exp #2: reaction with the feed heat-treated. LA dehydration reaction at 603 K for 4 h.

conversion × molar selectivity). As mentioned above, work that appropriately addressed this issue or clearly mentioned preheating of the feed in the methodology is very limited.[35,36] This protocol should be applied when studying any catalysis in LA aqueous systems.

Interestingly, in addition to the benefit on the analytical reliability, the preheating appears to have enhanced the AA selectivity, reaching up to nearly 70% (exp #2, method B) compared to 64% (exp #1, method B). Although it is difficult to monitor the actual monomer−dimer (oligomer) relationship in the reactor and/or on the catalyst surface under the reaction conditions (high water content and elevated temperature), this result suggests differences in reactivity between the two lactic species.

Reactivity of LA and L_2A. To further investigate any possible differences in the reactivity, we conducted a catalytic study of LA and L_2A solutions. Diluted aqueous solutions of LA and L_2A were prepared from Sigma reagents with concentrations of 3 wt % (LA basis), and the reaction experiments over a 1.0 mmol/g K_2HPO_4/NaY catalyst were performed with freshly prepared solutions. Because of the low initial concentration, accurate determination of unreacted LA or L_2A was not possible; we therefore assumed complete conversion, and the molar product yield (a × moles of a product/initial moles of LA; a = stoichiometric coefficient) was reported instead of the selectivity (Table 3).

Table 3. Yield of Identified Product Dehydration of Diluted (3 wt %) LA and L$_2$A^a

| | time (h) | solution weight recovery (%) | AD | carbon-based yield (%) | | | |
				23P	HyAce	PropA	AA
LA	1	93.3	2.2	2.4	1.3		20.3
	2	93.5	2.2	2.4	0.4	1.5	35.3
	3	93.8	2.5	2.8	0.2	1.5	43.3
	4	99.8	2.2	2.4	0.1	1.7	52.4
	overall	95.1	2.3	2.5	0.5	1.2	38.7
L$_2$A	1	92.8	8.6	1.4	0.8	0.7	32.0
	2	92.0	10.3	2.0	0.3	0.8	37.2
	3	91.3	9.7	2.2	0.2	0.8	37.9
	4	99.4	7.5	2.5	0.2	1.0	45.8
	overall	93.9	9.0	2.0	0.3	0.8	38.2

^{a}AD = acetaldehyde; 23P = 2,3-pentanedione; HyAce = hydroxyacetone; PropA = propionic acid; AA = acrylic acid; catalyst (1 mmol/g K$_2$HPO$_4$/NaY) = 1.1 g; temperature = 603 K. Solution weight recovery = ratio of the measured weight of the solution collected to the expected weight.

We observed a minor difference of the reactivity of LA and L$_2$A. The AA yield for individual sampling peaked at 52% at 4 h from the reaction of LA and 46% at 4 h from L$_2$A. The 4 h overall AA yield was comparable at 38−39%. A slightly higher AA formation from LA than L$_2$A corroborates the observation in the reaction of the preheated 20 wt % LA. For L$_2$A to form AA, it must be hydrolyzed first back to LA, which may require different optimized reaction conditions. The difference in acidity and geometry of the two reactants may also play a role in determining reactivity. Meanwhile, L$_2$A yielded more AD, with the difference between the other minor products being relatively small between LA and L$_2$A. The abundance of water in the system complicates the elucidation of any possible differences of the reaction mechanisms.

■ CONCLUSION

We synthesized potassium phosphate-modified NaY zeolite catalysts and investigated the catalytic performance, with a focus on the influence of L$_2$A, a linear dimer of LA, on the analytical determination of the LA conversion and AA selectivity. Because the oligomers are hydrolyzed back to LA under reaction conditions, when not accurately quantified or incorporated in the analytics, they may serve as a hidden source of additional LA, and this can consequently lead to artificially lower LA conversion and higher selectivity of the products. In one example, without accounting for the dimers, a very high AA selectivity (80%) was falsely calculated, in comparison to the true value of 64%. In most published work on LA dehydration, the potential impact of dimers on the analytics has been overlooked, and the catalytic performance may be incorrectly reported. To avoid false calculation of the conversion and selectivity, we stress the need for analytical rigor to account for total lactic, both monomer and dimer. In addition, reaction experiments of a diluted solution of lactic monomers and dimers revealed a minor difference in the reactivity in water-rich conditions, which might possibly affect the true AA selectivity. Preheating the feed for hours (>10 h) is shown to be an effective treatment to minimize such oligomers in the feed and allows more reliable, reproducible analytics of the LA conversion and AA selectivity calculations.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b00864.

Figures S1−S4 and additional details of the analytical methods (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: rioux@engr.psu.edu. Phone: (814)867-2503.

ORCID ⓘ
Yuriy Román-Leshkov: 0000-0002-0025-4233
Robert M. Rioux: 0000-0002-6019-0032

Notes
The authors declare no competing financial interest.

Biographies

Yu Noda obtained his Ph.D. in Energy and Mineral Engineering with a minor in Chemical Engineering in 2012 from Pennsylvania State University under the supervision of Professor Chunshan Song. During his Ph.D. studies, he worked on hydrolytic depolymerization of lignocellulosic biomass materials. He was a postdoctoral scholar at Penn State in the Department of Chemical Engineering, working in Robert M. Rioux's research group on the surface functionalization of micro- and mesoporous materials for catalytic applications (2012−2015). Since 2016, he has been a postdoctoral researcher at Charles University and the Institute of Organic Chemistry and Biochemistry, both in Prague, Czech Republic. His current research interests include catalytic transformation of biomass to chemicals and materials and the surface science of two-dimensional organic frameworks.

Hongbo Zhang is currently a postdoctoral associate in the Department of Chemical and Biomolecular Engineering at the University of Illinois

at Urbana—Champaign. He received his Ph.D. from the Dalian Institute of Chemical Physics in 2012, working with Prof. Xinhe Bao and Prof. Xiulian Pan on the confinement effect of double-walled carbon nanotubes in catalysis. After graduation, he joined Argonne National Laboratory, working with Dr. Chris Marshall for 2 years on biomass conversion and in situ/operando catalyst characterization with X-ray absorption spectroscopy over atomic-layer-deposition-modified catalysts. Following his postdoc position at Argonne, he moved to Penn State, working with Prof. Robert M. Rioux on the catalytic dehydration of lactic acid. His research interests are biomass conversion, atomic layer deposition, kinetics, and in situ/operando characterization.
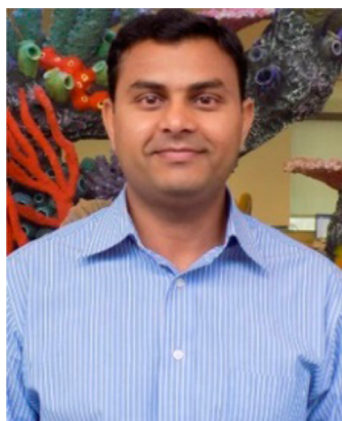
Rajesh (Raj) Dasari is currently working in a Principal Engineer role with Wave Life Sciences, a Cambridge-based preclinical genetic medicine company focused on advancing best-in-class stereopure nucleic acid therapies for patients impacted by rare diseases utilizing an innovative and proprietary synthetic chemistry platform. He is leading the Engineering team to build Wave Life Sciences' first clinical manufacturing facility. Prior to Wave Life Sciences, he worked in various roles at Myriant Corporation and played a key role in downstream purification process development and their "first to the market" product commercialization for polymer-grade biosuccinic acid. He received his Ph.D. in Chemical Engineering from the University of Louisville, Louisville, KY, in 2008.


Ramnik Singh is the former technical manager for the acrylic acid project at Myriant Corporation. Ramnik held the position of Senior Director of Process Development at Myriant, leading R&D efforts on downstream process development. He joined Myriant (previously called BioEnergy International) in April 2008 and continued there until March 2016. Prior to Myriant, he worked at a biofuel company in Colorado and has many years of biomass-related research experience at the University of California, Berkeley. He received his Ph.D. in Wood Science & Technology from the University of California, Berkeley, in 1998. Ramnik is currently seeking his next suitable opportunity.
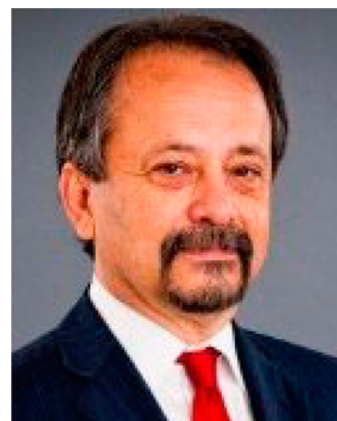
Cenan Ozmeral retired from Myriant Corporation in 2015 after serving as President and CEO (2013−2015), Chief Operating Officer (2010−2013), and Executive Vice President (2008−2010). Prior to joining Myriant, he worked for 29 years at BASF Corporation in multiple roles. From 1996 to 2008, he served as senior vice president in numerous businesses, including industrial solvents, petrochemicals, and acrylic polymers. He received a B.S. degree from American University (Istanbul, Turkey), a M.S. degree from Pennsylvania State University, and a Ph.D. degree from the University of New Orleans, all in chemistry. He also holds a Masters of Business Administration from Louisiana State University.

Prof. Yuriy Román-Leshkov was born in Mexico City, Mexico. He obtained his B.S. degree in Chemical Engineering at the University of Pennsylvania (2002) and his Ph.D. in Chemical Engineering at the University of Wisconsin—Madison (2008) under the guidance of Prof. James Dumesic. At the University of Wisconsin—Madison, he worked on developing catalytic strategies to convert biomass-derived carbohydrates into platform chemicals. He completed a 2-year postdoc at California Institute of Technology, working with Prof. Mark E. Davis on the synthesis of zeolites and mesoporous materials. Yuriy joined the Department of Chemical Engineering at Massachusetts Institute of Technology in 2010 and was promoted to Associate Professor in 2014. His research lies at the interface of heterogeneous catalysis and materials design, where a wide range of synthetic, spectroscopic, and reaction engineering tools are applied to study the chemical transformation of molecules on catalytic surfaces. A strong emphasis is placed on the application of catalytic materials to tackle relevant problems associated with sustainable energy, small-molecule activation, and renewable chemicals.
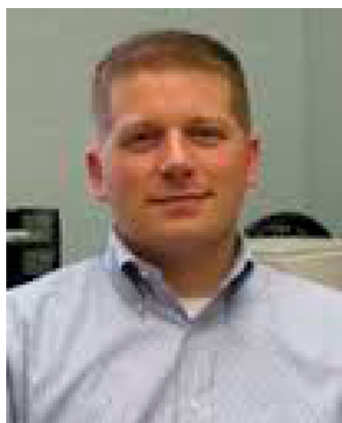
Robert (Rob) M. Rioux is the Friedrich G. Helfferich Associate Professor of Chemical Engineering at the Pennsylvania State University. He joined Pennsylvania State University in 2008. In 2014, he became an Associate Professor of Chemistry. Prior to Penn State, he was an NIH Postdoctoral Fellow at Harvard University in the Department of Chemistry and Chemical Biology. He received his Ph.D. in Physical Chemistry from the University of California, Berkeley, in 2006, working for Professor Gabor Somorjai. His group's current research focuses on the development of spatially and temporally resolved spectroscopic techniques for imaging catalytic chemistry, elucidating reaction mechanisms in nanoscale systems, and the development of solution calorimetric techniques to understand catalytic processes at the solid–liquid interface.

■ REFERENCES

(1) Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502.

(2) Wettstein, S. G.; Alonso, D. M.; Gurbuz, E. I.; Dumesic, J. A. A roadmap for conversion of lignocellulosic biomass to chemicals and fuels. *Curr. Opin. Chem. Eng.* **2012**, *1*, 218−224.

(3) Besson, M.; Gallezot, P.; Pinel, C. Conversion of Biomass into Chemicals over Metal Catalysts. *Chem. Rev.* **2014**, *114*, 1827−1870.

(4) Datta, R.; Henry, M. Lactic acid: recent advances in products, processes and technologies - a review. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1119−1129.

(5) Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Makshina, E.; Sels, B. F. Lactic acid as a platform chemical in the biobased economy: the role of chemocatalysis. *Energy Environ. Sci.* **2013**, *6*, 1415−1442.

(6) Ohara, T.; Sato, T.; Shimizu, N.; Prescher, G.; Schwind, H.; Weiberg, O.; Marten, K.; Greim, H., Acrylic Acid and Derivatives. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

(7) Lin, M. M. Selective oxidation of propane to acrylic acid with molecular oxygen. *Appl. Catal., A* **2001**, *207*, 1−16.

(8) Biddy, M. J.; Scarlata, C.; Kinchin, C. Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential. *National Renewable Energy Laboratory (NREL) Technical Report NREL/TP-510065509*; 2016;10.2172/1244312

(9) Holmen, R. E. Production of acrylates by catalytic dehydration of lactic acid and alkyl lactates. U.S. Patent 2,859,240, 1958.

(10) Gunter, G. C.; Miller, D. J.; Jackson, J. E. Formation of 2,3-Pentanedione from Lactic-Acid over Supported Phosphate Catalysts. *J. Catal.* **1994**, *148*, 252−260.

(11) Gunter, G. C.; Craciun, R.; Tam, M. S.; Jackson, J. E.; Miller, D. J. FTIR and P-31-NMR spectroscopic analyses of surface species in phosphate-catalyzed lactic acid conversion. *J. Catal.* **1996**, *164*, 207−219.

(12) Gunter, G. C.; Langford, R. H.; Jackson, J. E.; Miller, D. J. Catalysts and Supports for Conversion of Lactic-Acid to Acrylic-Acid and 2,3-Pentanedione. *Ind. Eng. Chem. Res.* **1995**, *34*, 974−980.

(13) Tam, M. S.; Gunter, G. C.; Craciun, R.; Miller, D. J.; Jackson, J. E. Reaction and spectroscopic studies of sodium salt catalysts for lactic acid conversion. *Ind. Eng. Chem. Res.* **1997**, *36*, 3505−3512.

(14) Wang, H. J.; Yu, D. H.; Sun, P.; Yan, J.; Wang, Y.; Huang, H. Rare earth metal modified NaY: Structure and catalytic performance for lactic acid dehydration to acrylic acid. *Catal. Commun.* **2008**, *9*, 1799−1803.

(15) Sun, P.; Yu, D. H.; Tang, Z. C.; Li, H.; Huang, H. NaY Zeolites Catalyze Dehydration of Lactic Acid to Acrylic Acid: Studies on the Effects of Anions in Potassium Salts. *Ind. Eng. Chem. Res.* **2010**, *49*, 9082−9087.

(16) Zhang, J. F.; Zhao, Y. L.; Feng, X. Z.; Pan, M.; Zhao, J.; Ji, W. J.; Au, C. T. Na2HPO4-modified NaY nanocrystallites: efficient catalyst for acrylic acid production through lactic acid dehydration. *Catal. Sci. Technol.* **2014**, *4*, 1376−1385.

(17) Zhang, X. H.; Lin, L.; Zhang, T.; Liu, H. O.; Zhang, X. F. Catalytic dehydration of lactic acid to acrylic acid over modified ZSM-5 catalysts. *Chem. Eng. J.* **2016**, *284*, 934−941.

(18) Blanco, E.; Delichere, P.; Millet, J. M. M.; Loridant, S. Gas phase dehydration of lactic acid to acrylic acid over alkaline-earth phosphates catalysts. *Catal. Today* **2014**, *226*, 185−191.

(19) Tang, C. M.; Peng, J. S.; Fan, G.; Li, X. L.; Pu, X. L.; Bai, W. Catalytic dehydration of lactic acid to acrylic acid over dibarium pyrophosphate. *Catal. Commun.* **2014**, *43*, 231−234.

(20) Tang, C. M.; Peng, J. S.; Li, X. L.; Zhai, Z. J.; Jiang, N.; Bai, W.; Gao, H. J.; Liao, Y. W. Strontium pyrophosphate modified by phosphoric acid for the dehydration of lactic acid to acrylic acid. *RSC Adv.* **2014**, *4*, 28875−28882.

(21) Ghantani, V. C.; Lomate, S. T.; Dongare, M. K.; Umbarkar, S. B. Catalytic dehydration of lactic acid to acrylic acid using calcium hydroxyapatite catalysts. *Green Chem.* **2013**, *15*, 1211−1217.

(22) Matsuura, Y.; Onda, A.; Ogo, S.; Yanagisawa, K. Acrylic acid synthesis from lactic acid over hydroxyapatite catalysts with various cations and anions. *Catal. Today* **2014**, *226*, 192−197.

(23) Matsuura, Y.; Onda, A.; Yanagisawa, K. Selective conversion of lactic acid into acrylic acid over hydroxyapatite catalysts. *Catal. Commun.* **2014**, *48*, 5−10.

(24) Yan, B.; Tao, L. Z.; Liang, Y.; Xu, B. Q. Sustainable Production of Acrylic Acid: Catalytic Performance of Hydroxyapatites for Gas-Phase Dehydration of Lactic Acid. *ACS Catal.* **2014**, *4*, 1931−1943.

(25) Zhang, J. F.; Lin, J. P.; Cen, P. L. Catalytic Dehydration of Lactic Acid to Acrylic Acid over Sulfate Catalysts. *Can. J. Chem. Eng.* **2008**, *86*, 1047−1053.

(26) Peng, J. S.; Li, X. L.; Tang, C. M.; Bai, W. Barium sulphate catalyzed dehydration of lactic acid to acrylic acid. *Green Chem.* **2014**, *16*, 108−111.

(27) Li, C.; Wang, B.; Zhu, Q. Q.; Tan, T. W. Efficient catalytic dehydration of methyl lactate to acrylic acid using sulphate and phosphate modified MCM-41 catalysts. *Appl. Catal., A* **2014**, *487*, 219−225.

(28) Murphy, B. M.; Letterio, M. P.; Xu, B. J. Selectivity Control in the Catalytic Dehydration of Methyl Lactate: The Effect of Pyridine. *ACS Catal.* **2016**, *6*, 5117−5131.

(29) Murphy, B. M.; Letterio, M. P.; Xu, B. J. Catalytic dehydration of methyl lactate: Reaction mechanism and selectivity control. *J. Catal.* **2016**, *339*, 21−30.

(30) Vu, D. T.; Kolah, A. K.; Asthana, N. S.; Peereboom, L.; Lira, C. T.; Miller, D. J. Oligomer distribution in concentrated lactic acid solutions. *Fluid Phase Equilib.* **2005**, *236*, 125−135.

(31) Yan, J.; Yu, D. H.; Li, H.; Sun, P.; Huang, H. NaY zeolites modified by La3+ and Ba2+: the effect of synthesis details on surface structure and catalytic performance for lactic acid to acrylic acid. *J. Rare Earths* **2010**, *28*, 803−806.

(32) Yu, D. H.; Sun, P.; Tang, Z. C.; Li, Z. X.; Huang, H. Modification of Nay by La3_ for the Dehydration of Lactic Acid: The Effect of

Preparation Protocol on Catalyst Microstructure and Catalytic Performance. *Can. J. Chem. Eng.* **2011**, *89*, 484−490.

(33) Zhang, J. F.; Zhao, Y. L.; Pan, M.; Feng, X. Z.; Ji, W. J.; Au, C. T. Efficient Acrylic Acid Production through Bio Lactic Acid Dehydration over NaY Zeolite Modified by Alkali Phosphates. *ACS Catal.* **2011**, *1*, 32−41.

(34) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309−319.

(35) Nafe, G.; Lopez-Martinez, M. A.; Dyballa, M.; Hunger, M.; Traa, Y.; Hirth, T.; Klemm, E. Deactivation behavior of alkali-metal zeolites in the dehydration of lactic acid to acrylic acid. *J. Catal.* **2015**, *329*, 413−424.

(36) Nafe, G.; Traa, Y.; Hirth, T.; Klemm, E. True Catalytic Behavior of Lactic Acid Dehydration on Zeolite Na-Y in the Gas Phase Measured by Means of a Novel Apparatus Design. *Catal. Lett.* **2014**, *144*, 1144−1150.

(37) Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Jacobs, P. A.; Sels, B. F. Shape-selective zeolite catalysis for bioplastics production. *Science* **2015**, *349*, 78−80.

(38) Nassos, P. S.; Schade, J. E.; King, A. D.; Stafford, A. E. Comparison of HPLC and GC Methods for Measuring Lactic Acid in Ground Beef. *J. Food Sci.* **1984**, *49*, 671−674.

(39) Cocchi, M.; Lambertini, P.; Manzini, D.; Marchetti, A.; Ulrici, A. Determination of Carboxylic Acids in Vinegars and in Aceto Balsamico Tradizionale di Modena by HPLC and GC Methods. *J. Agric. Food Chem.* **2002**, *50*, 5255−5261.

(40) Aida, T. M.; Ikarashi, A.; Saito, Y.; Watanabe, M.; Smith, R. L.; Arai, K. Dehydration of lactic acid to acrylic acid in high temperature water at high pressures. *J. Supercrit. Fluids* **2009**, *50*, 257−264.

(41) Sanz, M. T.; Murga, R.; Beltran, S.; Cabezas, J. L.; Coca, J. Kinetic study for the reactive system of lactic acid esterification with methanol: Methyl lactate hydrolysis reaction. *Ind. Eng. Chem. Res.* **2004**, *43*, 2049−2053.