Raman spectroscopic monitoring of multiproduct chemical reaction kinetics; the case of ester hydrolysis

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Supplementary Information

1 Simulated admixtures preparation

Simulated admixtures were made by mixing the reaction components according to the ratios shown in Table S1.

Table S1: Ratios of the propyl acetate hydrolysis reaction components for simulated admixtures

Admixture No.	**Propyl acetate (mL)**	**Water (mL)**	**1-Propanol (mL)**	**Acetic Acid (mL)**
0	1	10	0	0
1	0.9	9.9	0.1	0.1
2	0.8	9.8	0.2	0.2
3	0.7	9.7	0.3	0.3
4	0.6	9.6	0.4	0.4
5	0.5	9.5	0.5	0.5
6	0.4	9.4	0.6	0.6
7	0.3	9.3	0.7	0.7
8	0.2	9.2	0.8	0.8
9	0.1	9.1	0.9	0.9
10	0	9	1	1

2 Problem Based Nonlinear least squares (NLS) Fitting

This section illustrates the results for problem based nonlinear least squares fitting analysis.

2.1 Simulated Admixtures

Simulated admixtures data was fitted with the nonlinear least squares fitting protocol. The results of the fitting analysis are shown below in Figure S1 to Figure S11 for 11 different admixtures, made by varying the concentrations of reactants and products starting from 0% product to the 100% product concentration in the mixtures.

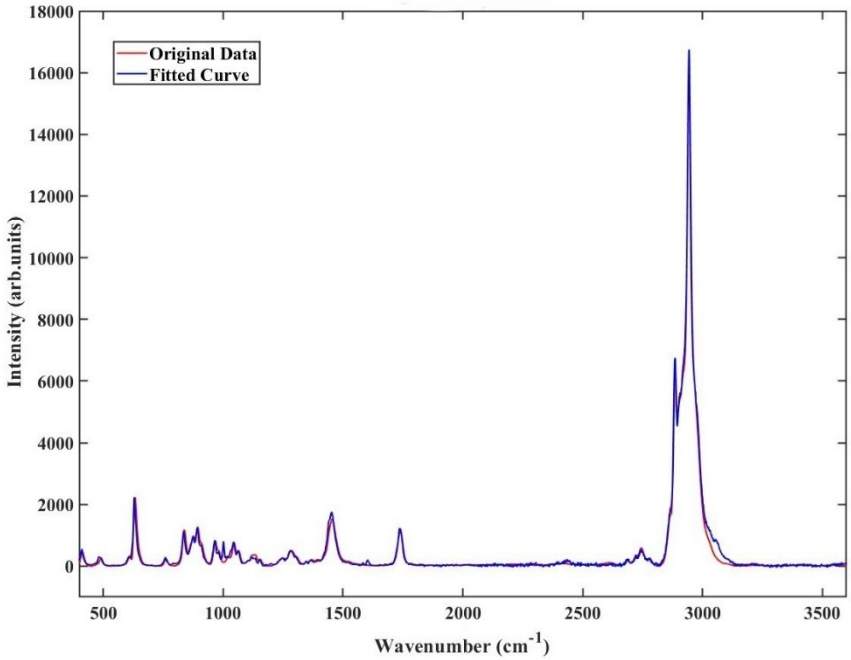

Figure S1: Nonlinear least squares fitting of pure reactant (0% product)

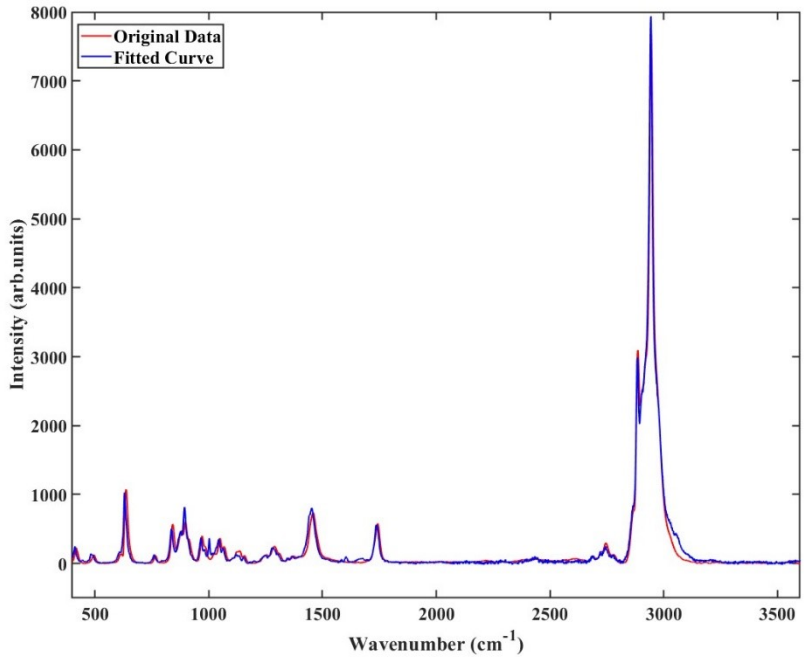

Figure S2: Nonlinear least squares fitting of simulated admixture containing 10% product

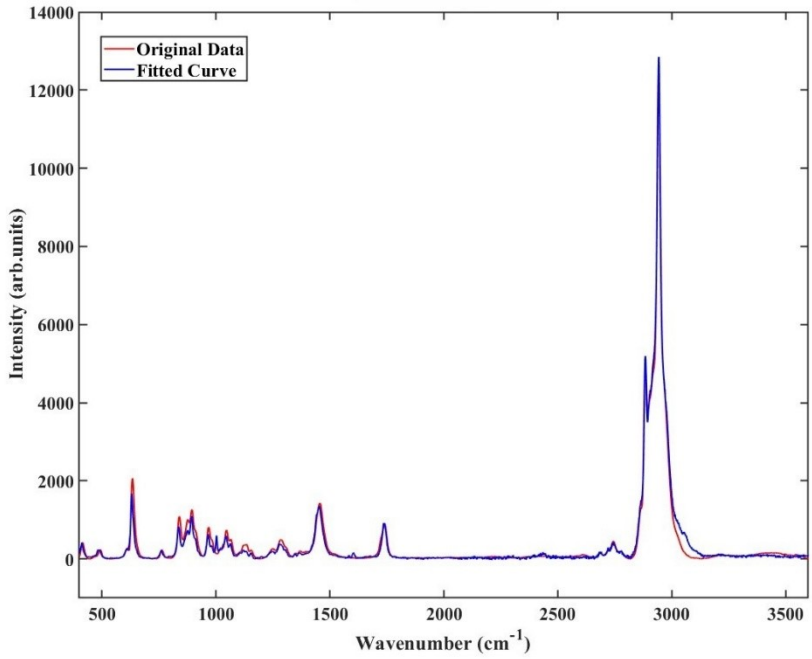

Figure S3: Nonlinear least squares fitting of simulated admixture containing 20% product.

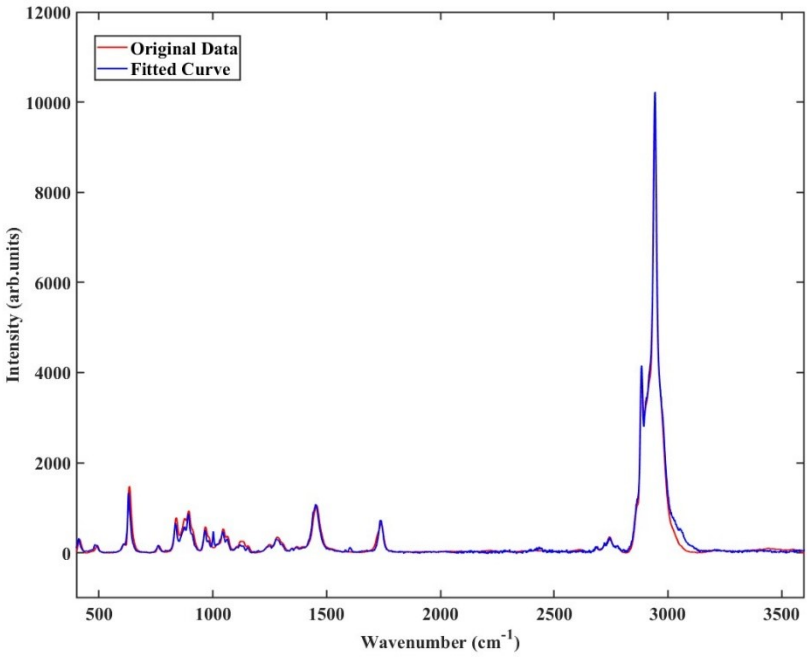

Figure S4: Nonlinear least squares fitting of simulated admixture containing 30% product concentration

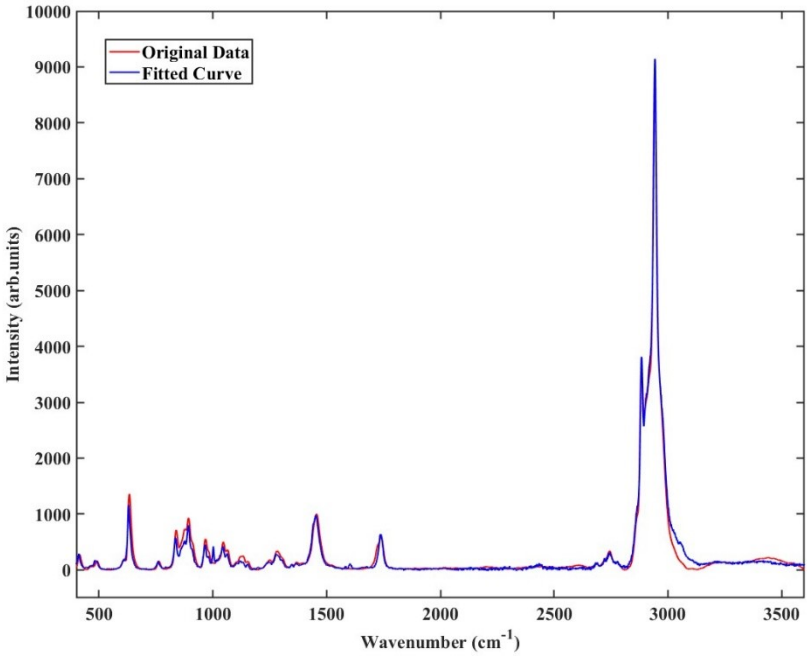

Figure S5: Nonlinear least squares fitting of simulated admixture containing 40% product admixture.

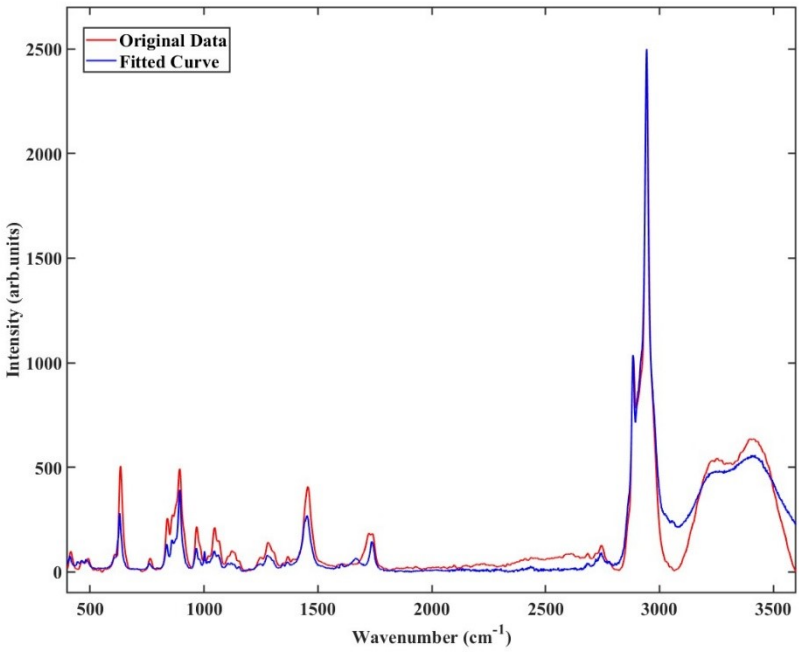

Figure S6: Nonlinear least squares fitting of simulated admixture containing 50% product concentration

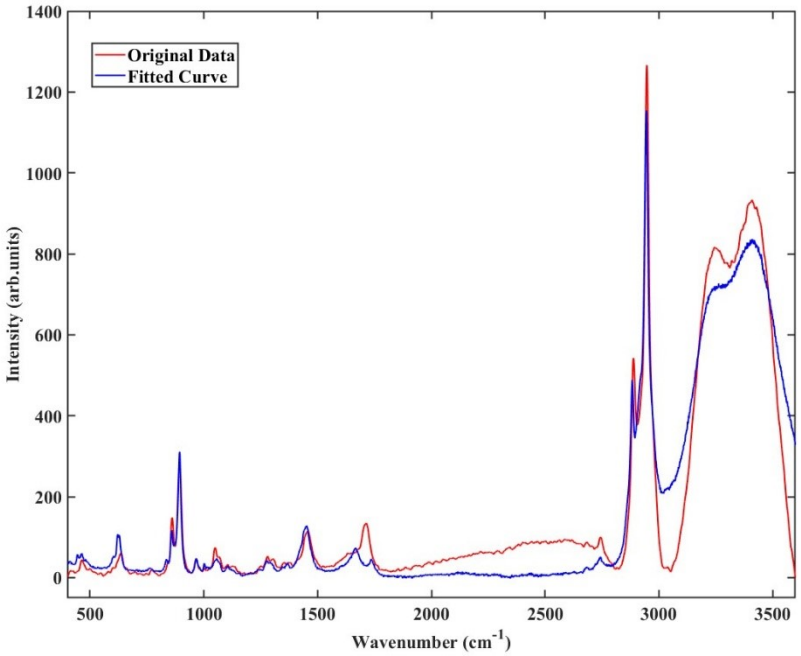

Figure S7: Nonlinear least squares fitting of simulated admixture containing 60% product

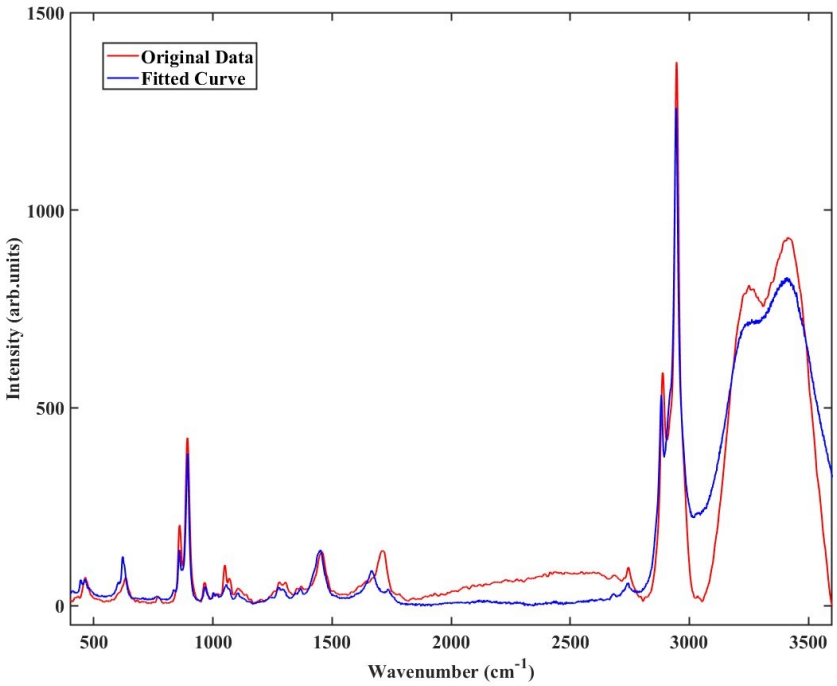

Figure S8: Nonlinear least squares fitting of simulated admixture containing 70% product concentration

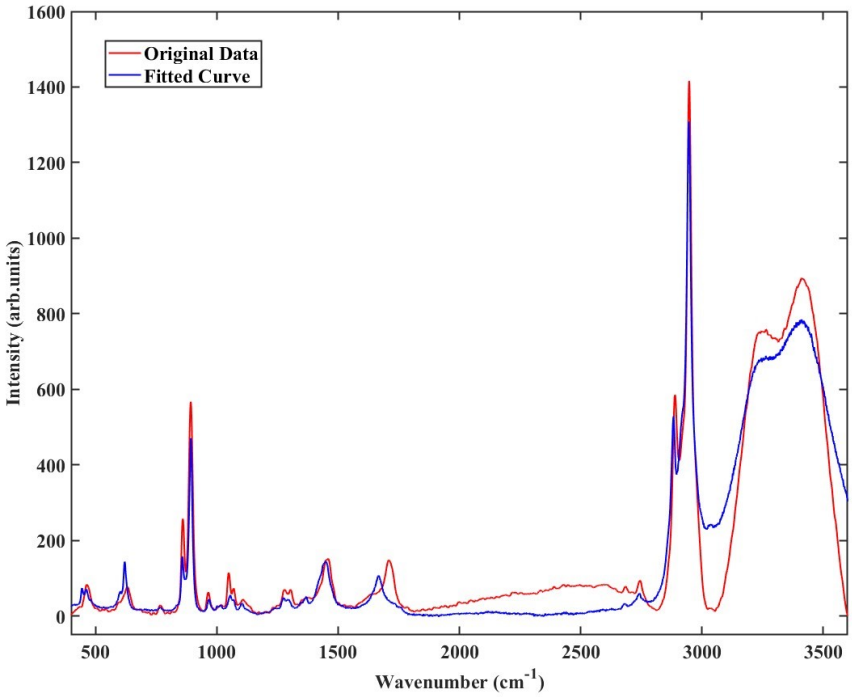

Figure S9: Nonlinear least squares fitting of simulated admixture containing 80% product admixture

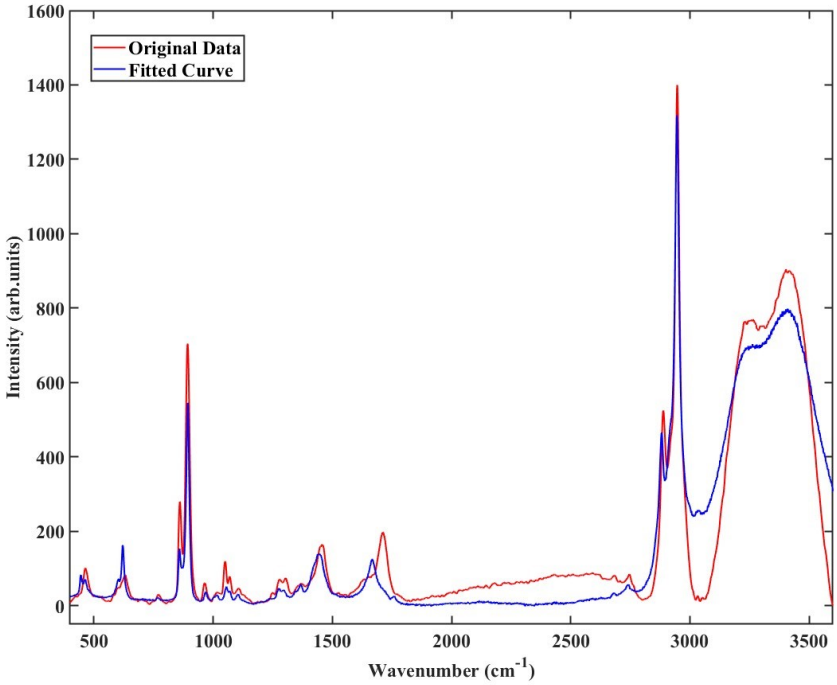

Figure S10: Nonlinear least squares fitting of simulated admixture containing 90% product concentration

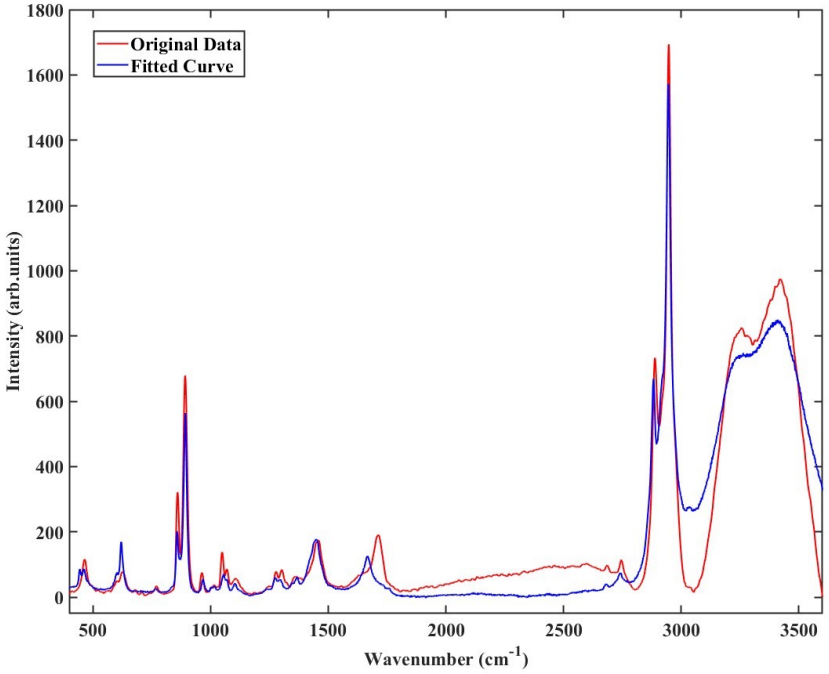

Figure S11: Nonlinear least squares fitting of simulated admixture containing pure products (100%)

2.2 Propyl acetate hydrolysis reaction

Data recorded from the actual propyl acetate reaction was fitted using problem based nonlinear least squares fitting at 30 different time points, from 0-250 minutes of reaction progress. The figure S12 to figure S41 show the fitting responses for the reaction data.

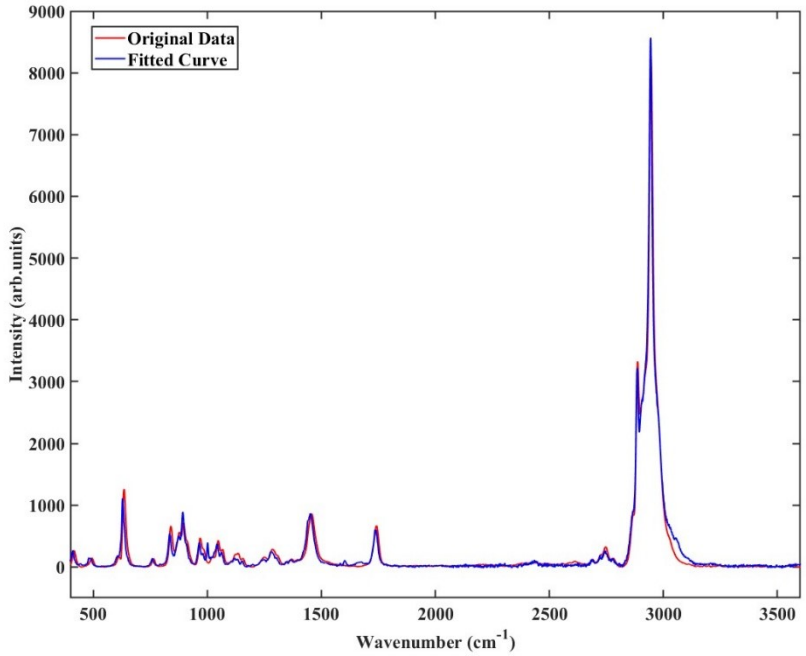

Figure S12: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 0 minutes

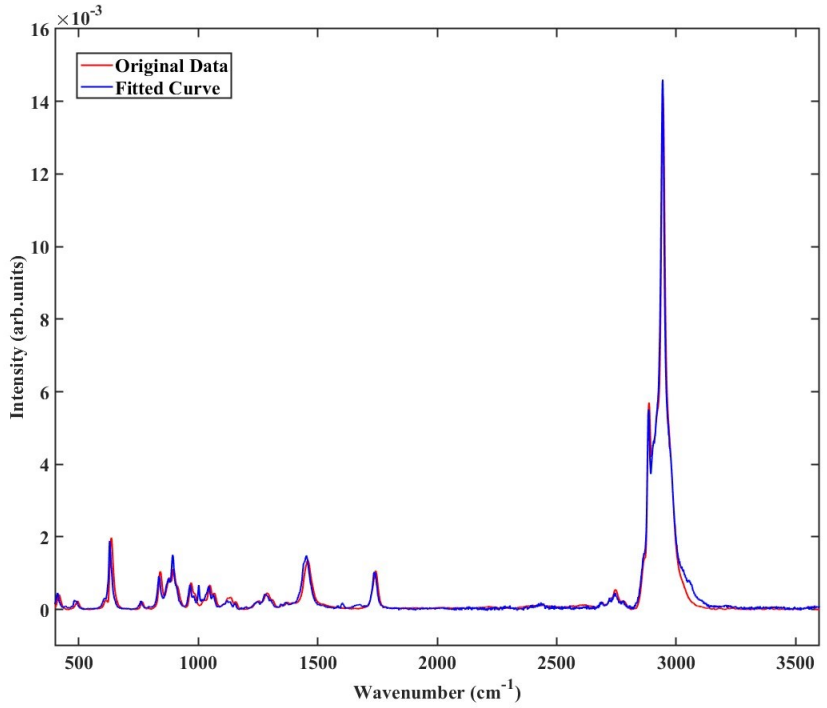

Figure S13: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 5 minutes.

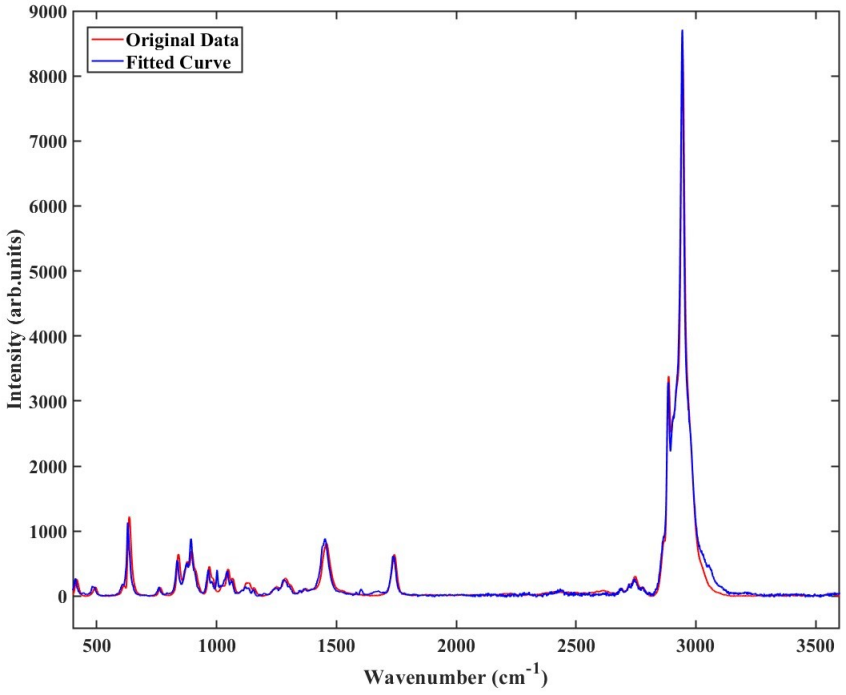

Figure S14: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 10 minutes.

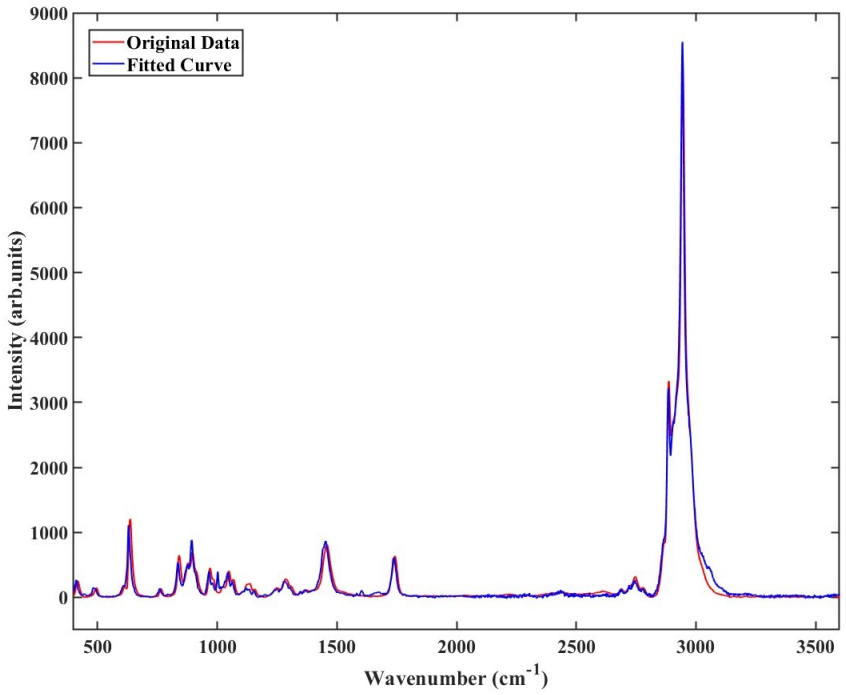

Figure S15: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 15 minutes

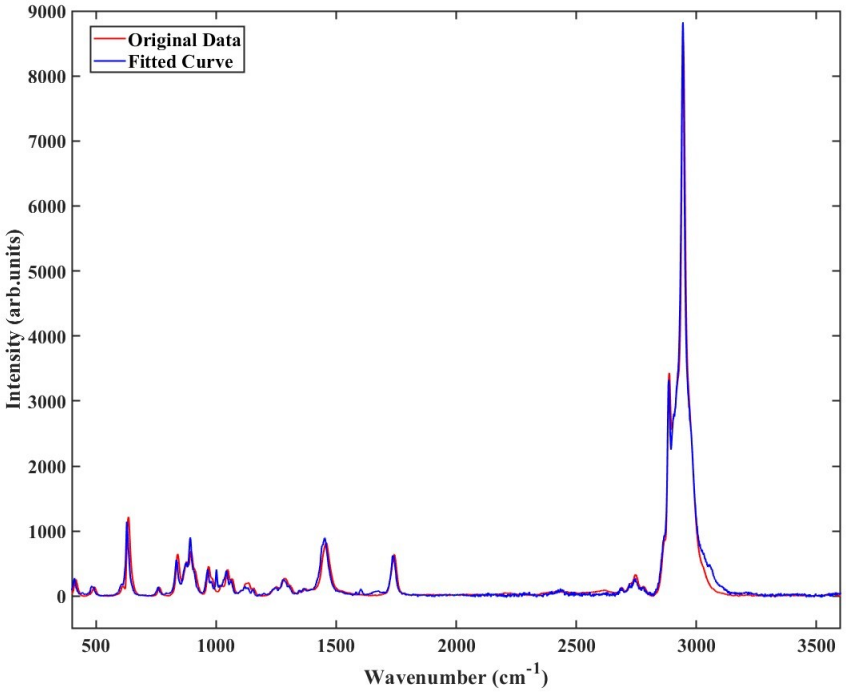

Figure S16: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 20 minutes

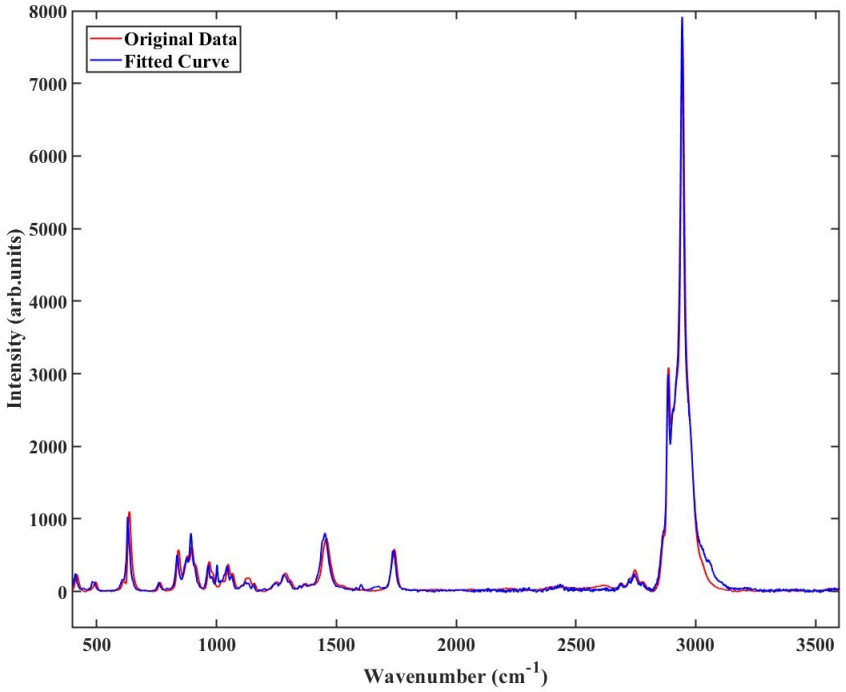

Figure S17: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 25 minutes.

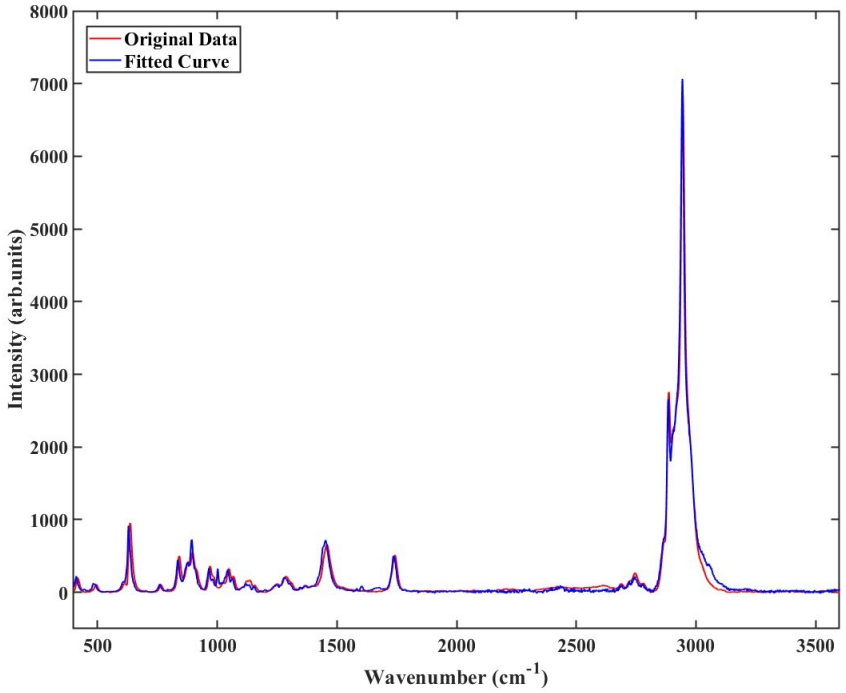

Figure S18: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 30 minutes

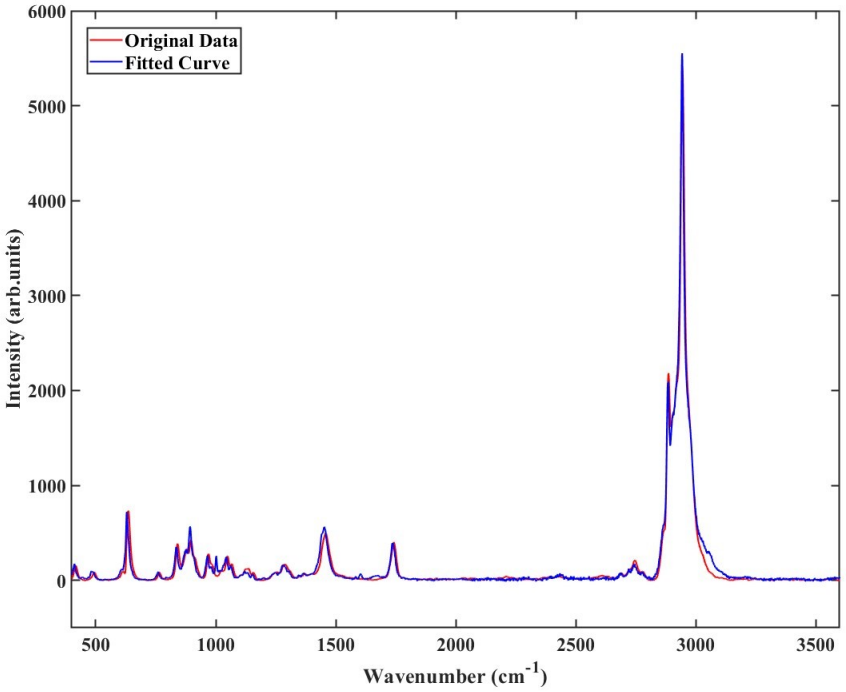

Figure S19: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 35 minutes

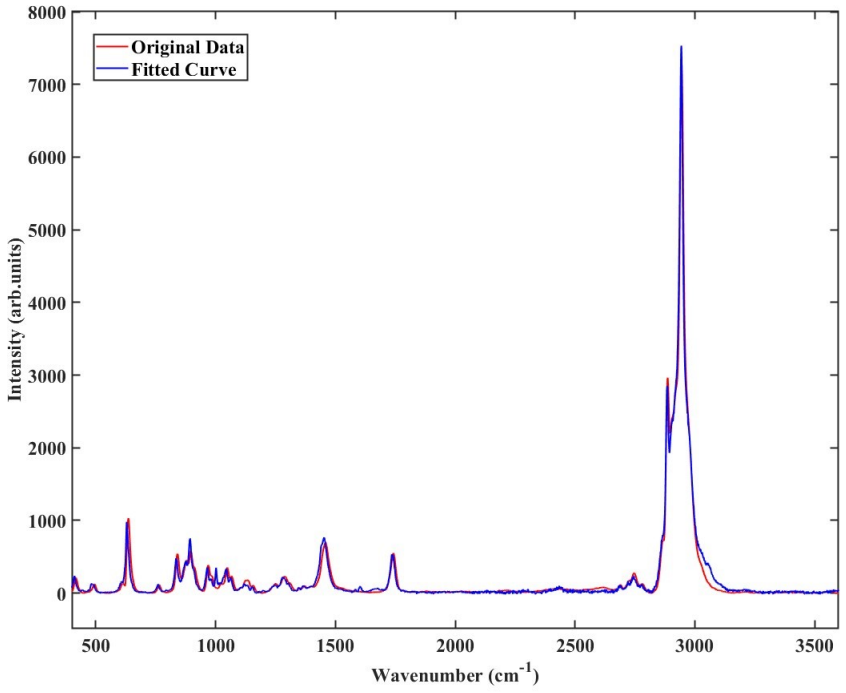

Figure S20: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 40 minutes

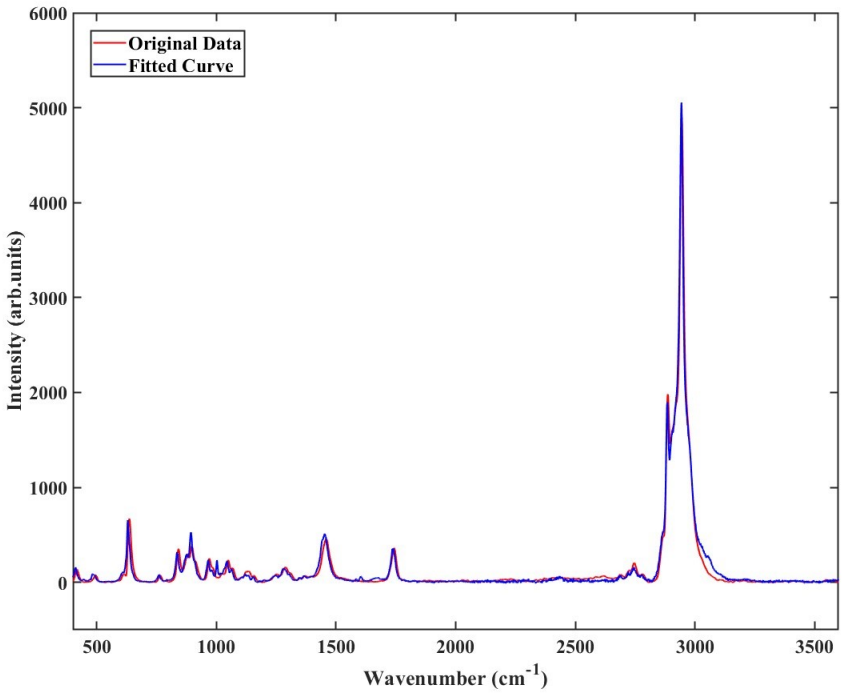

Figure S21: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 50 minutes

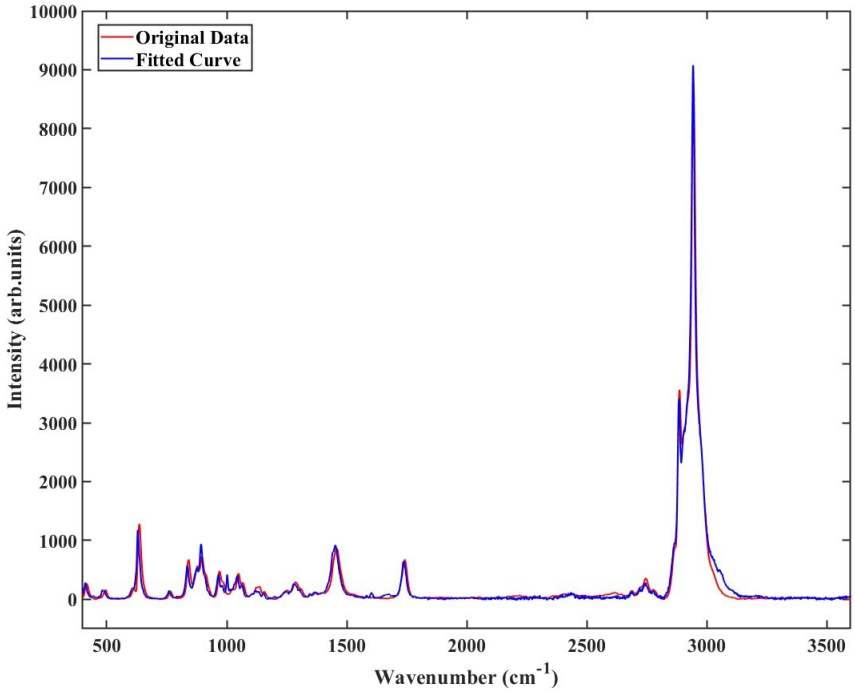

Figure S22: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 60 minutes

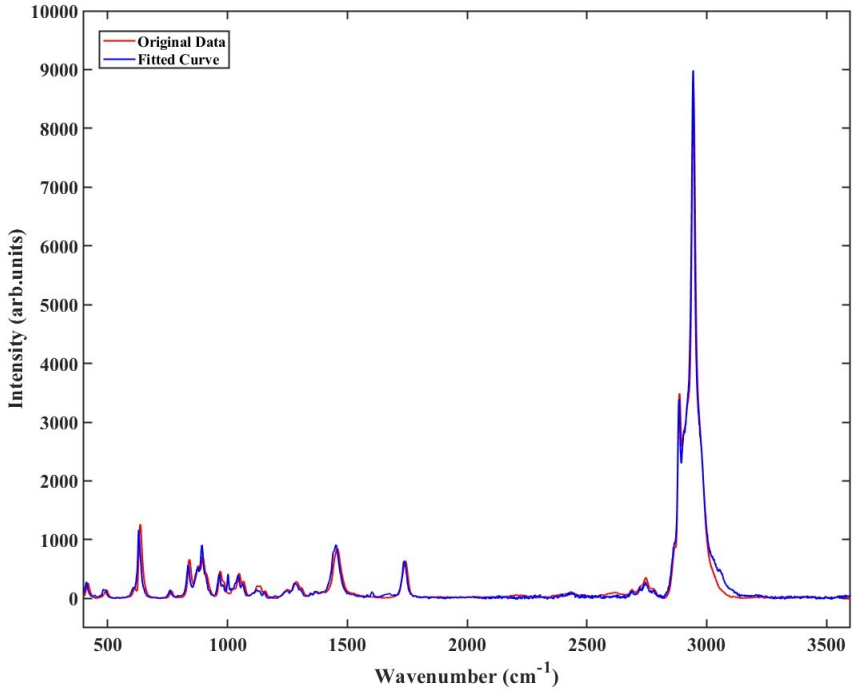

Figure S23: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 70 minutes

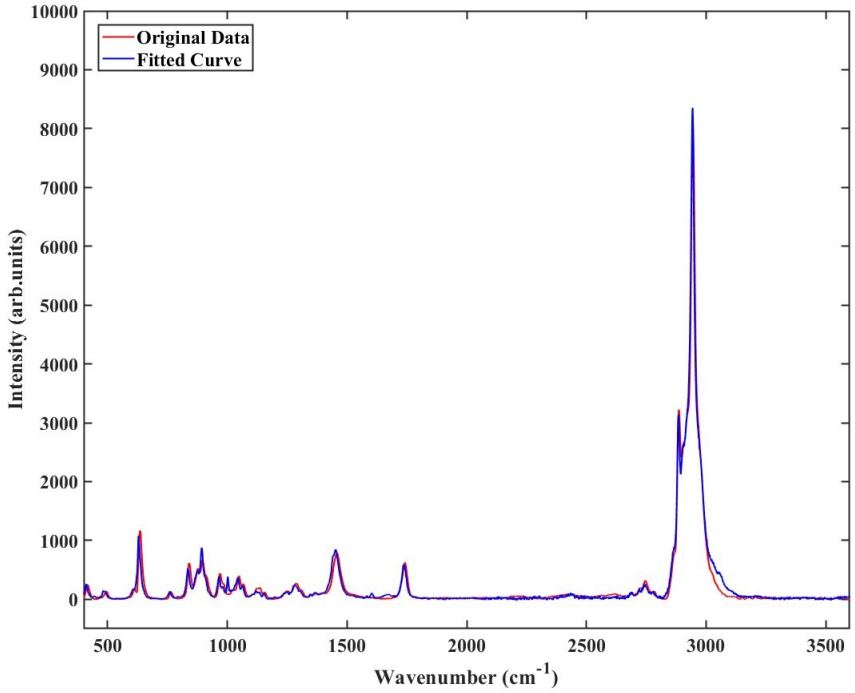

Figure S24: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 80 minutes

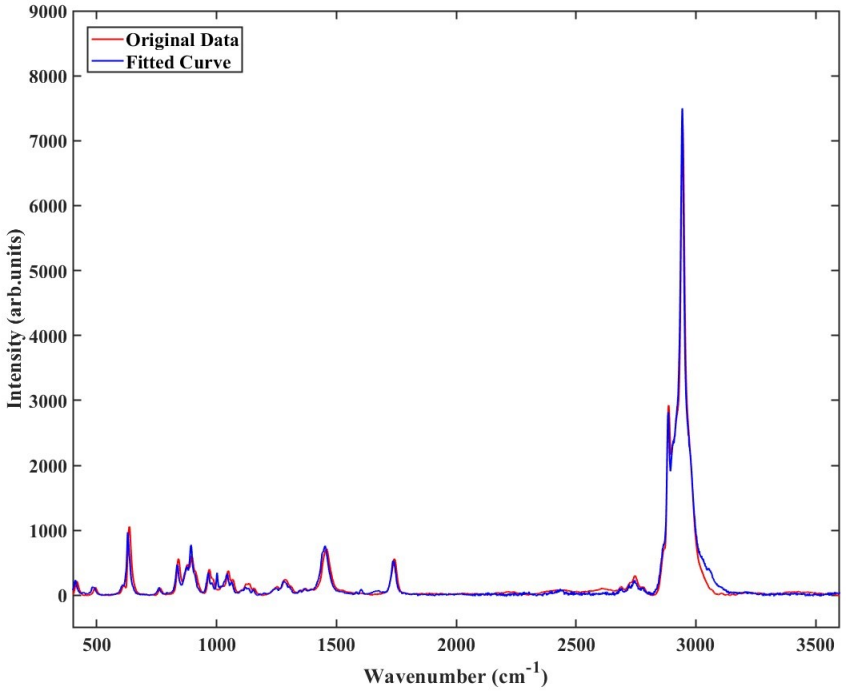

Figure S25: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 90 minutes

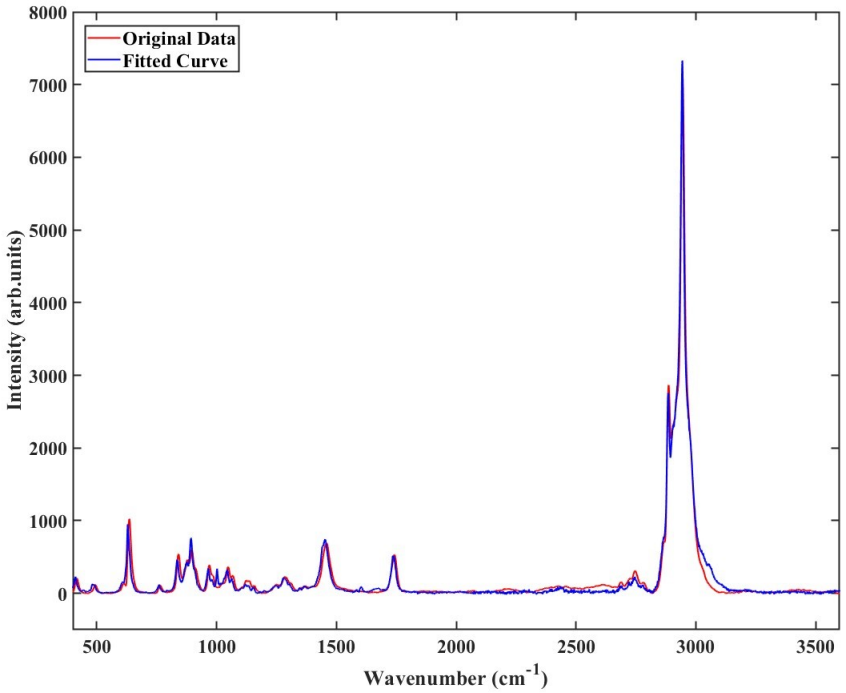

Figure S26: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 100 minutes

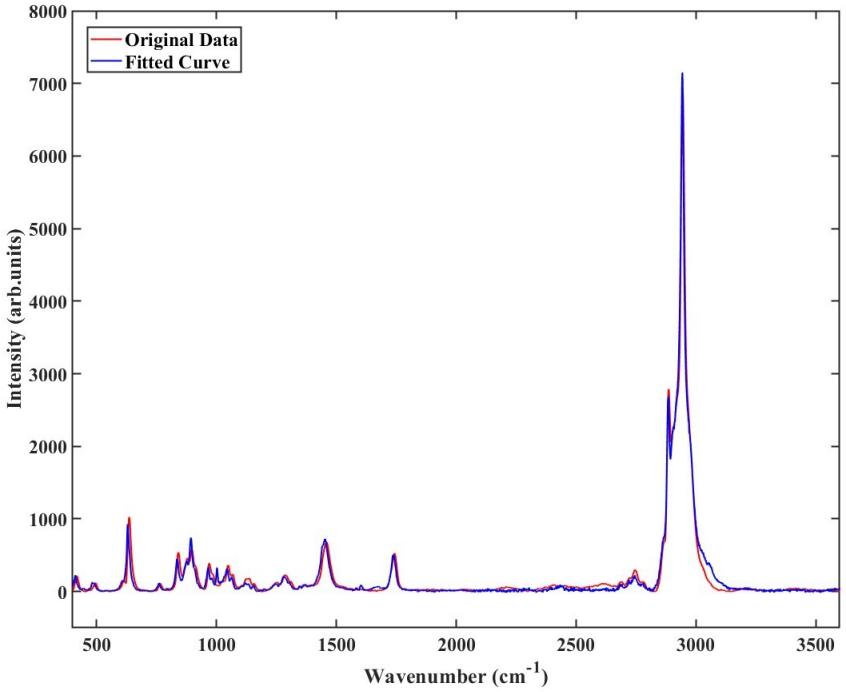

Figure S27: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 110 minutes

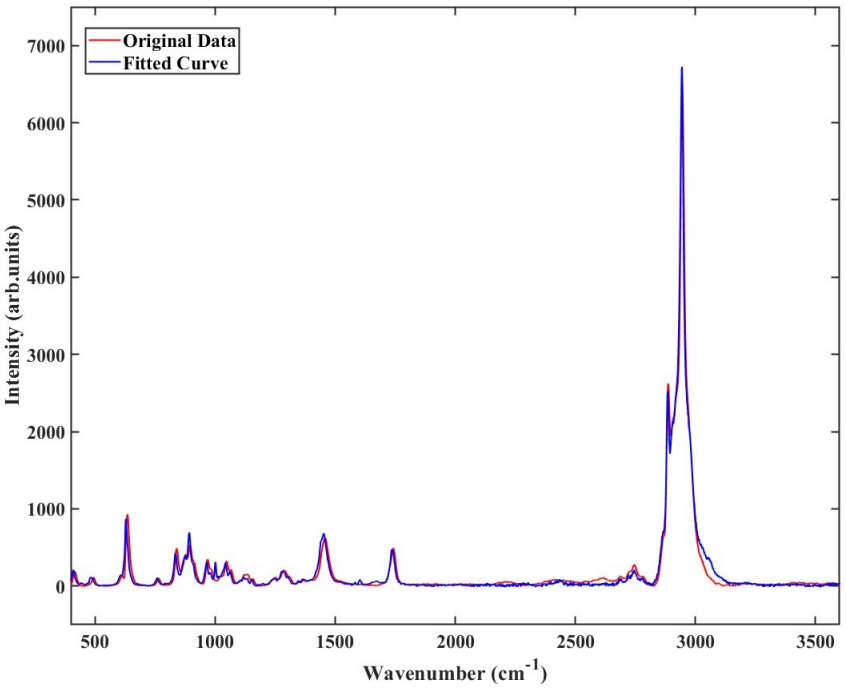

Figure S28: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 120 minutes

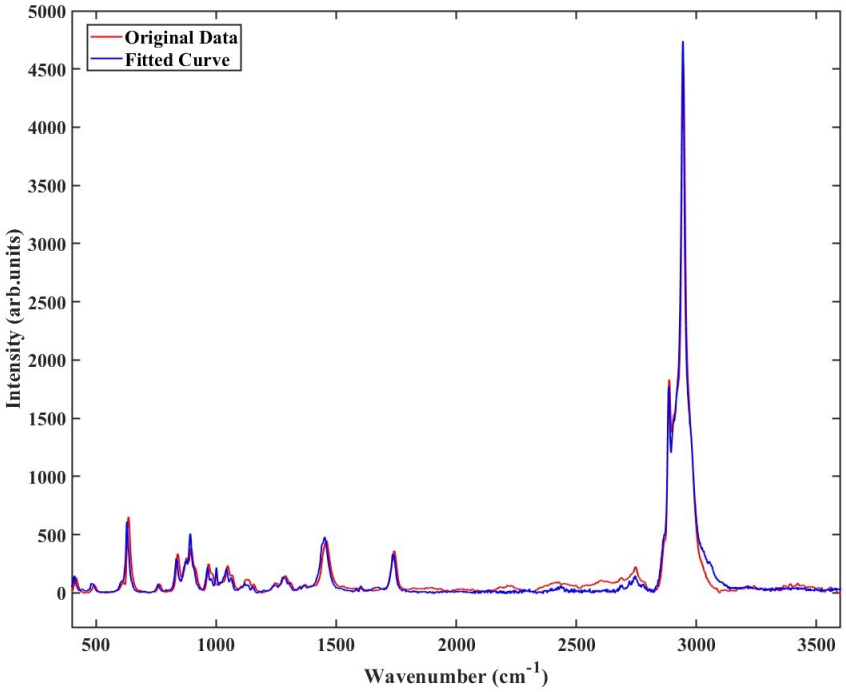

Figure S29: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 130 minutes

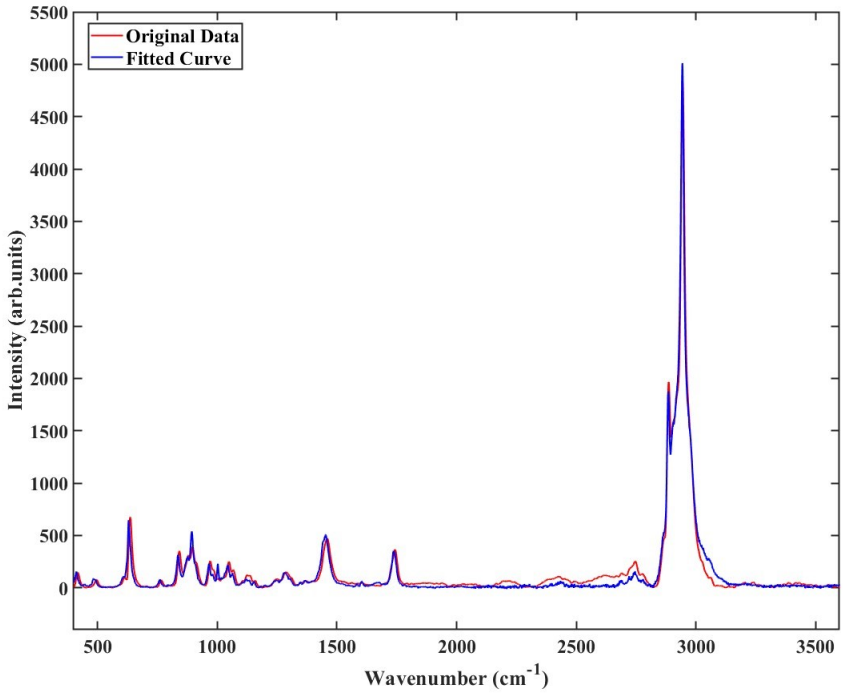

Figure S30: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 140 minutes

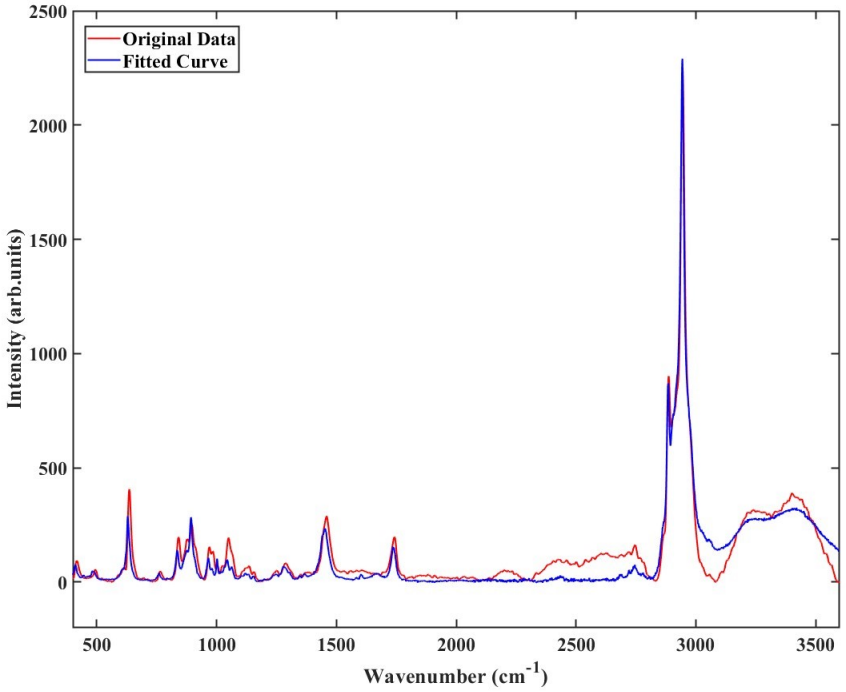

Figure S31: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 150 minutes

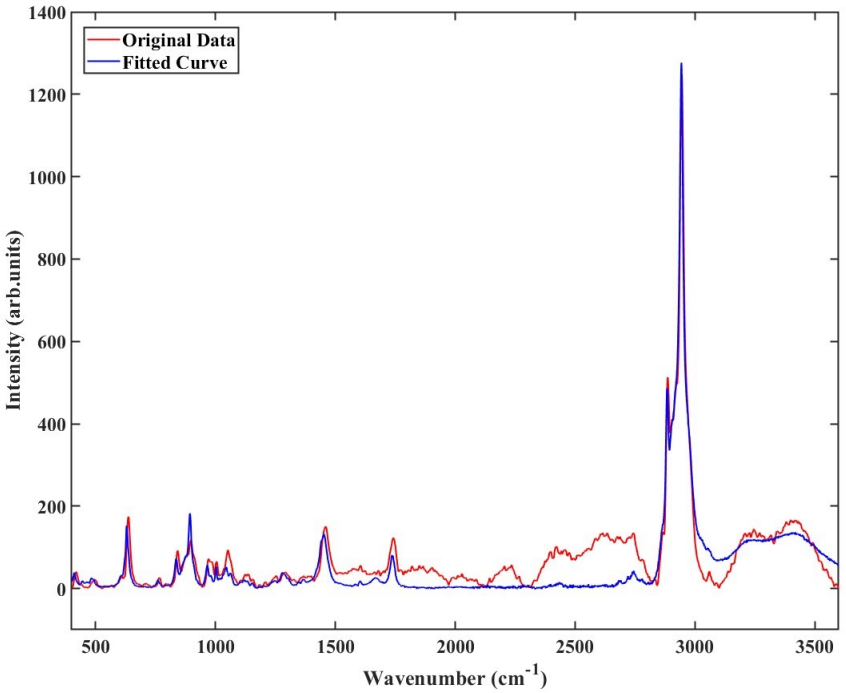

Figure S32: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 160 minutes

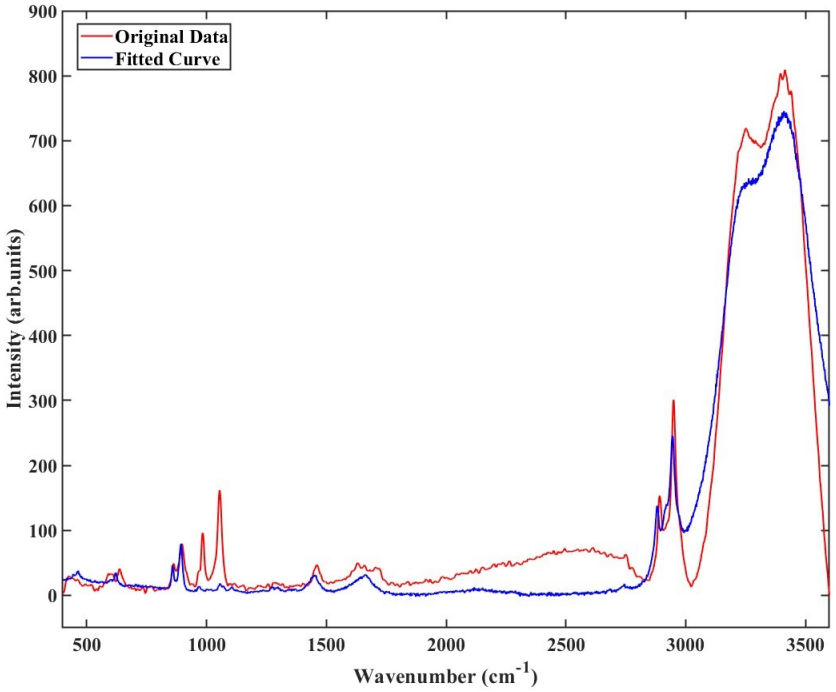

Figure S33: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 170 minutes

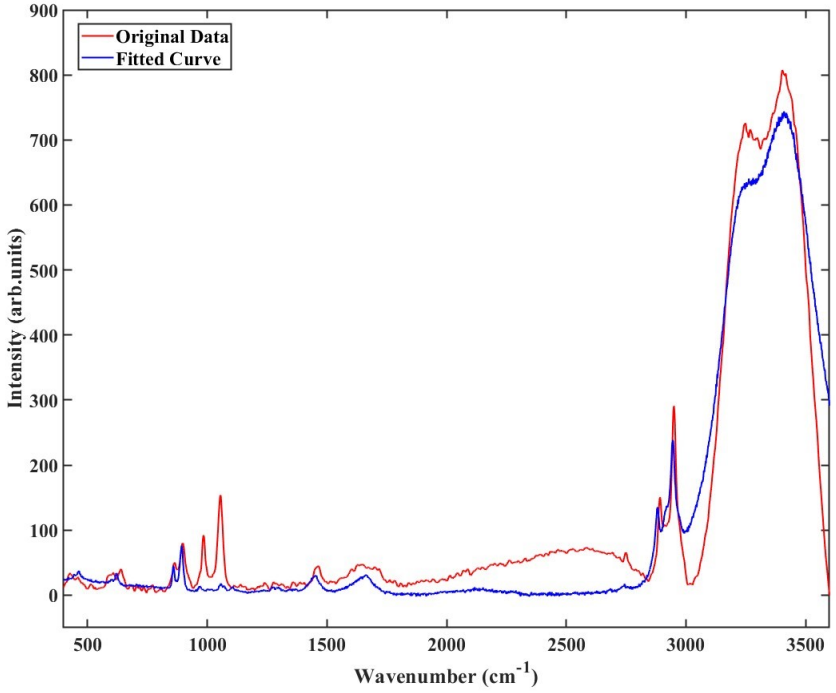

Figure S34: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 180 minutes

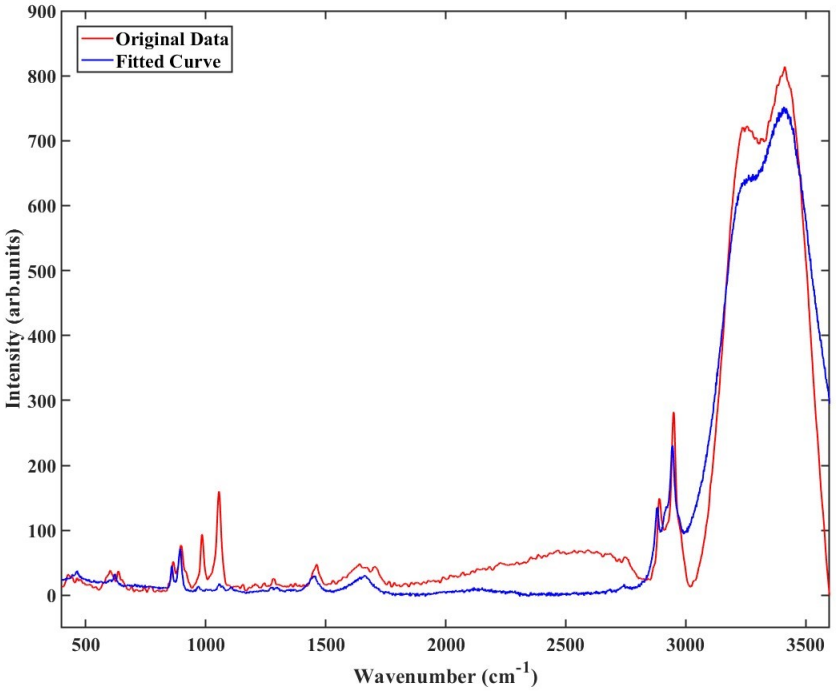

Figure S35: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 190 minutes

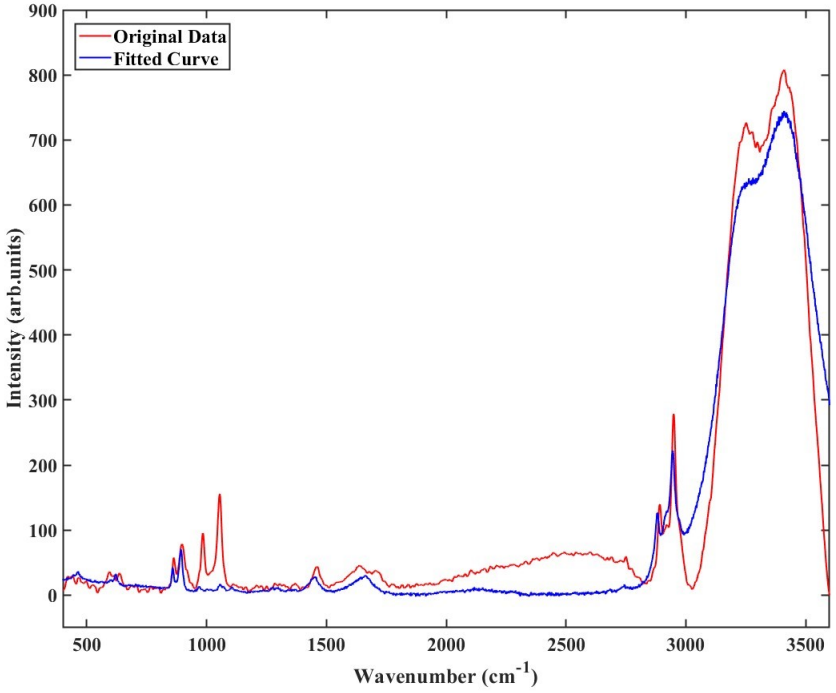

Figure S36: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 200 minutes

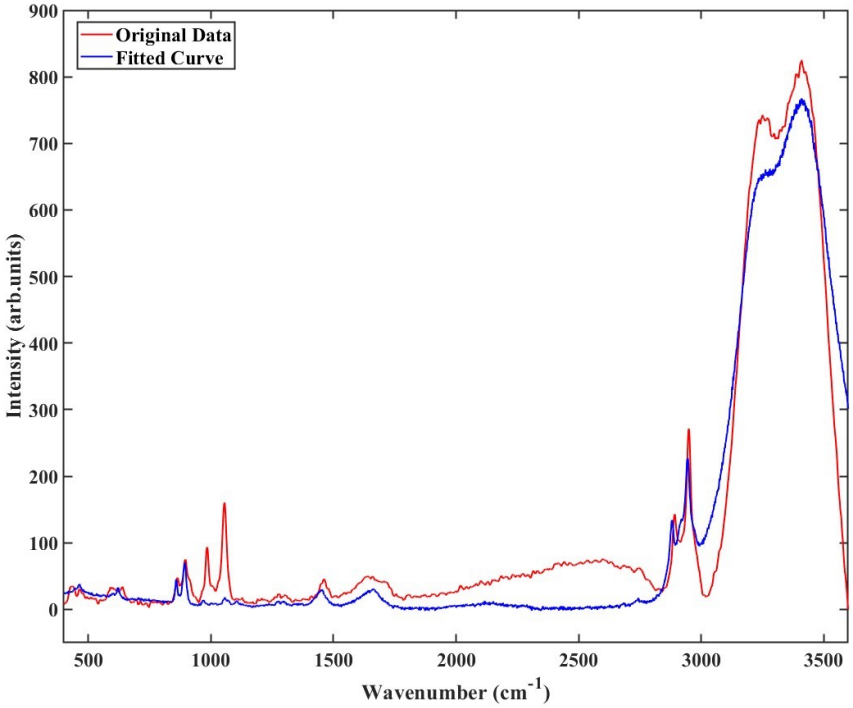

Figure S37: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 210 minutes

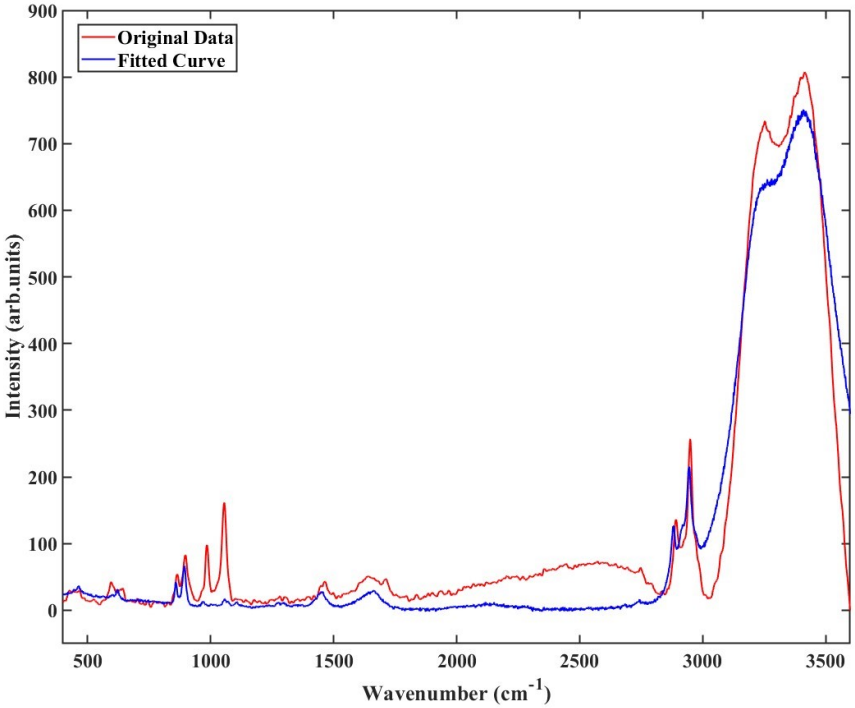

Figure S38: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 220 minutes

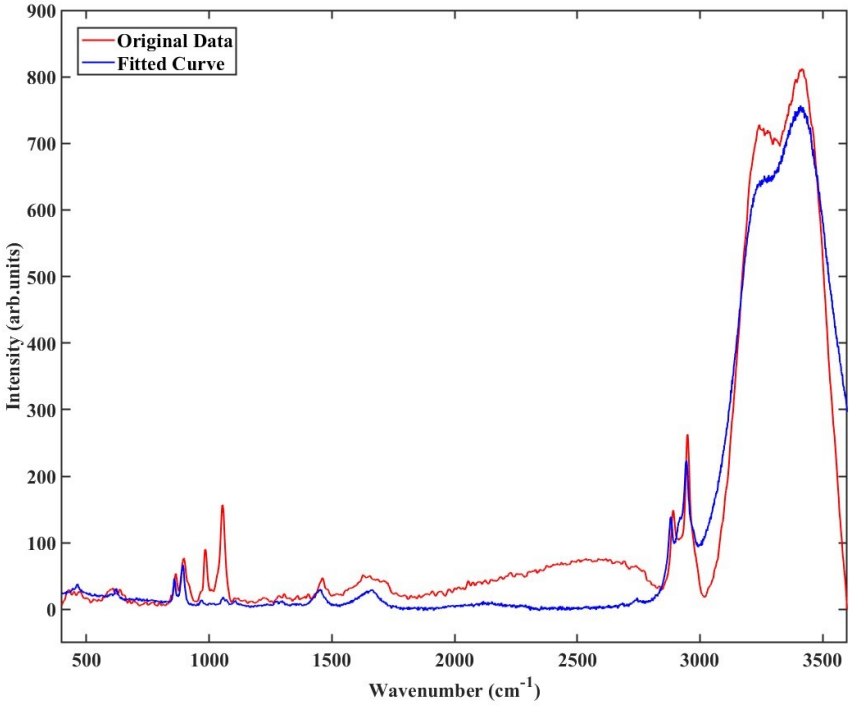

Figure S39: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 230 minutes.

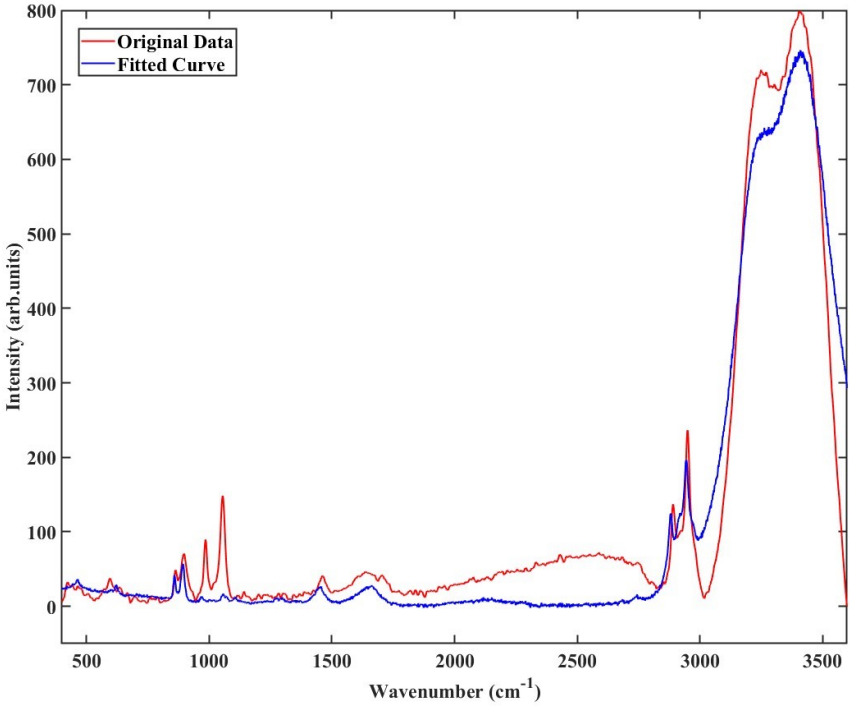

Figure S40: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 240 minutes

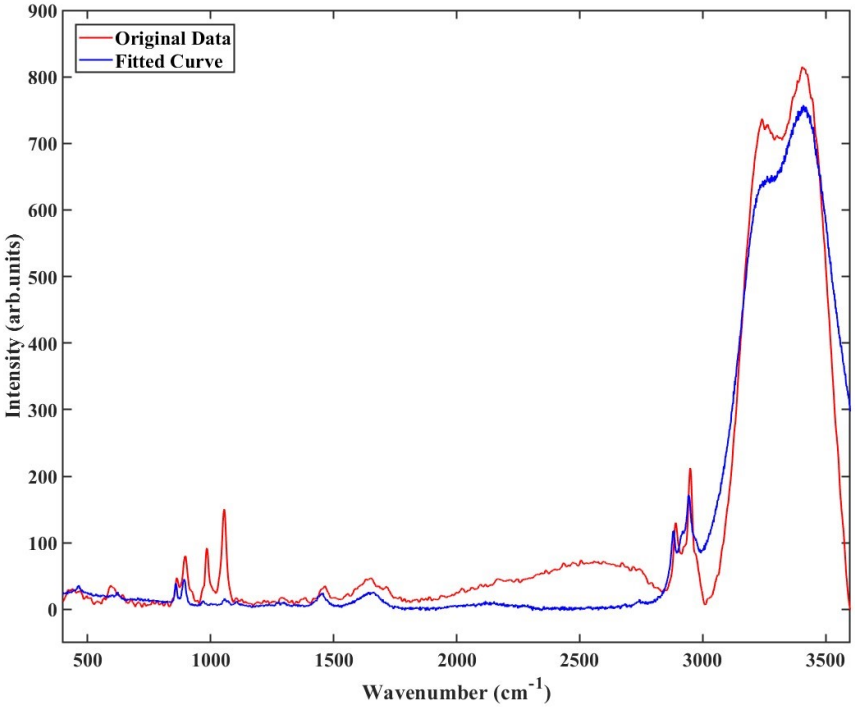

Figure S41: Nonlinear least squares fitting for propyl acetate hydrolysis reaction at 250 minutes

3 Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) Analysis

MCR-ALS for both the reaction data and simulated admixtures data is detailed in the following sections, for unsupervised and supervised analysis.

3.1 Unsupervised MCR-ALS Analysis

This section shows the spectral data for the selection of components by unsupervised MCR-ALS, selecting 4 components in the singular value decomposition (SVD) window for both the actual propyl acetate reaction data and the simulated admixtures data. The components are apparently quite different than the actual components participating in the reaction. The incorrect selection of the components results in the misprediction of the concentration evolution profile on the later stage.

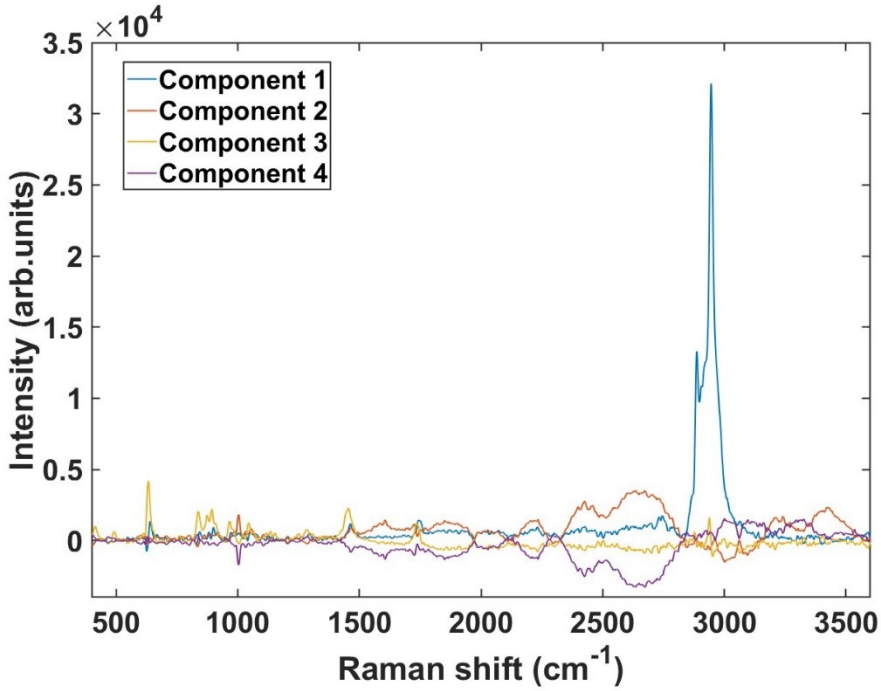

Figure S42: Component selection for the propyl acetate hydrolysis reaction data selecting 4 components in SVD, by unsupervised MCR-ALS

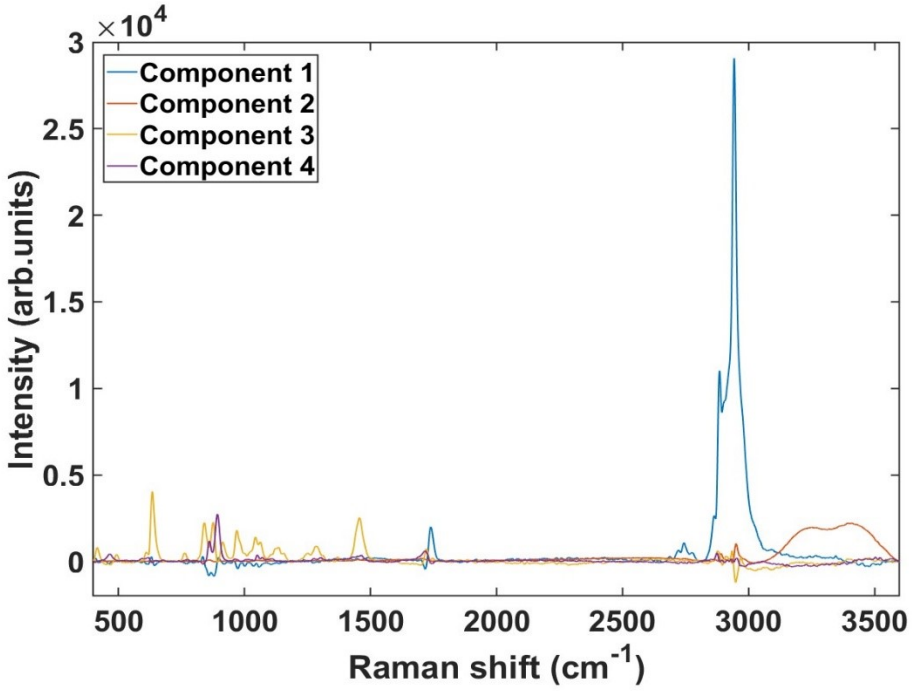

Figure S43: Component selection for the simulated admixtures data selecting 4 components in SVD, by unsupervised MCR-ALS

3.2 Supervised MCR-ALS Analysis

This section illustrates the concentration evolution profile for the supervised MCR-ALS along with the component selection for the propyl acetate hydrolysis reaction data and simulated admixture solutions. Again, the selected component spectra do not match to those of the

originally participating component spectra both for the reaction and admixtures, which results in an inaccurate concentration evolution profile.

3.2.1 Propyl acetate hydrolysis reaction

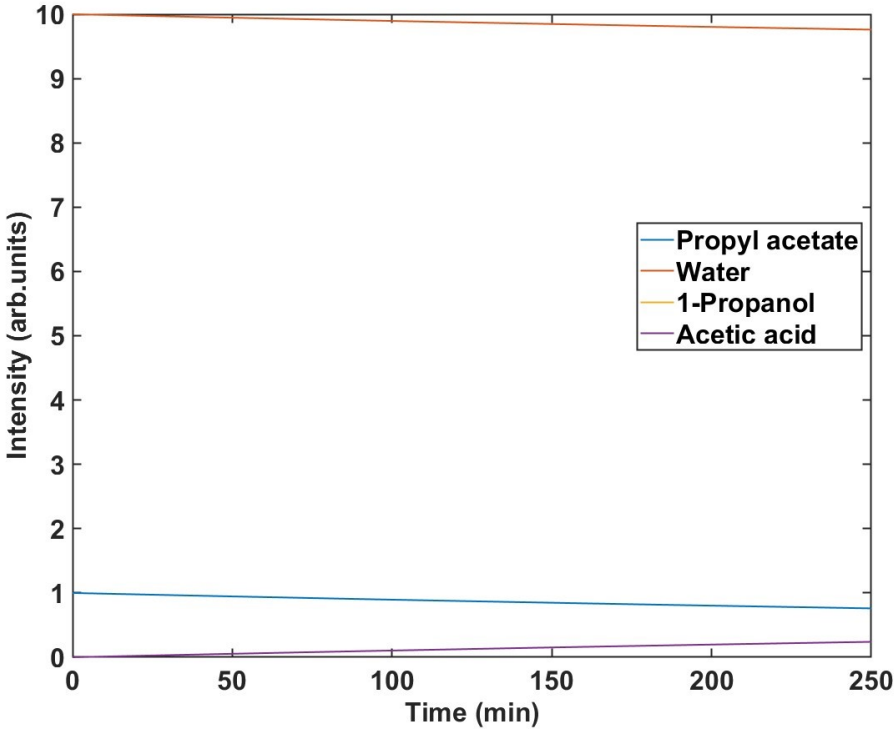

Figure S44: Time evolution of components in reaction data using Supervised MCR-ALS for the model A+B⟶C+D if A=1 and B=10 for the propyl acetate hydrolysis reaction data.

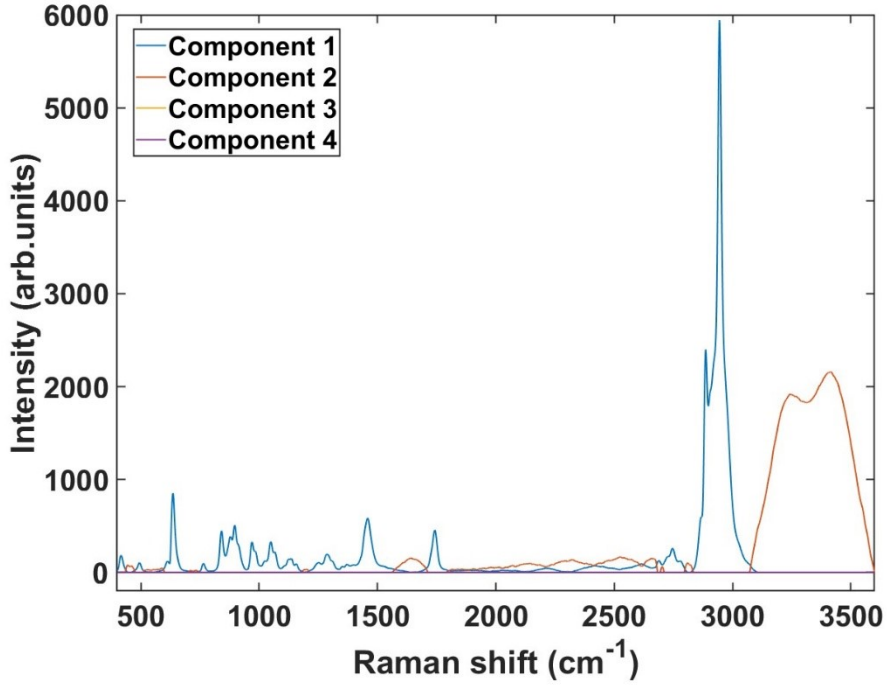

Figure S45: Component selection for the propyl acetate hydrolysis reaction data by supervised MCR-ALS for the mode A⟶B+C+D

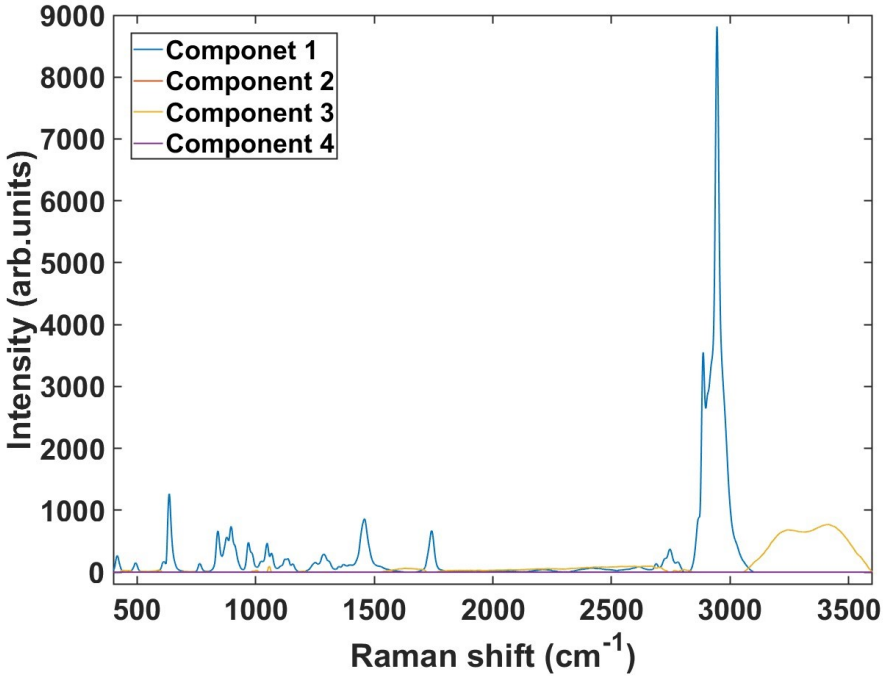

Figure S46: Component selection for the propyl acetate hydrolysis reaction data by supervised MCR-ALS for the model A+B⟶C+D when A=B

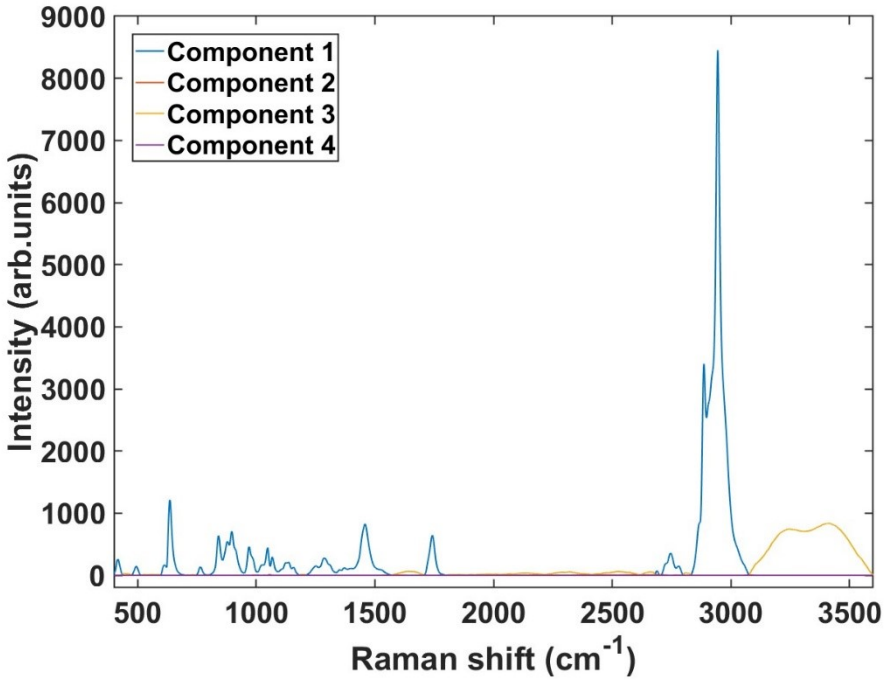

Figure S47: Component selection for the propyl acetate hydrolysis reaction data by supervised MCR-ALS for the model A+B⟶C+D when A=1, B=10

3.2.2 Simulated Admixtures

This section demonstrates the concentration evolution profile for simulated admixture solutions generated by MCR-ALS and the selected components by the algorithm for 4 components

models. The selected components either do not match the original components or look like only two components resulting in incorrect concentration profile or kinetics.

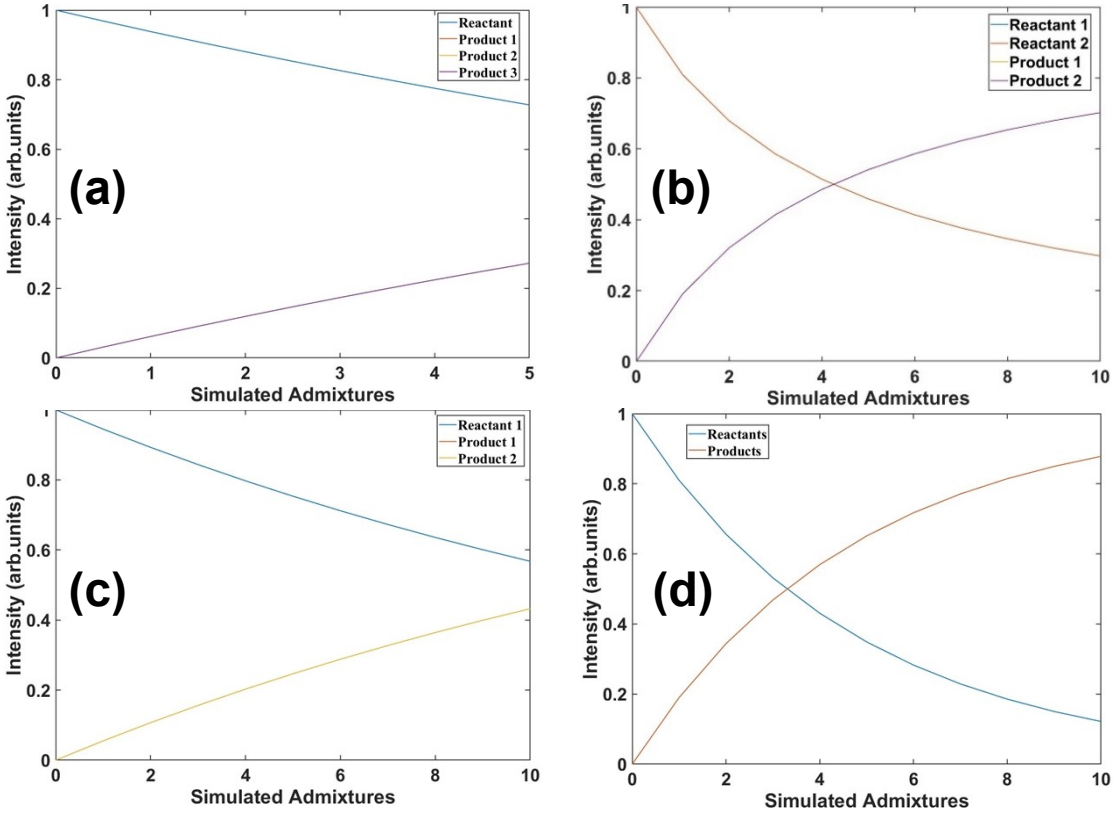

Figure S48: Time evolution of components in simulated admixtures data using Supervised MCR-ALS (a) 4 components A→B+C+D (b) 4 components A+B→C+D (c) 3 components A→B+C (d) 2 components A→B

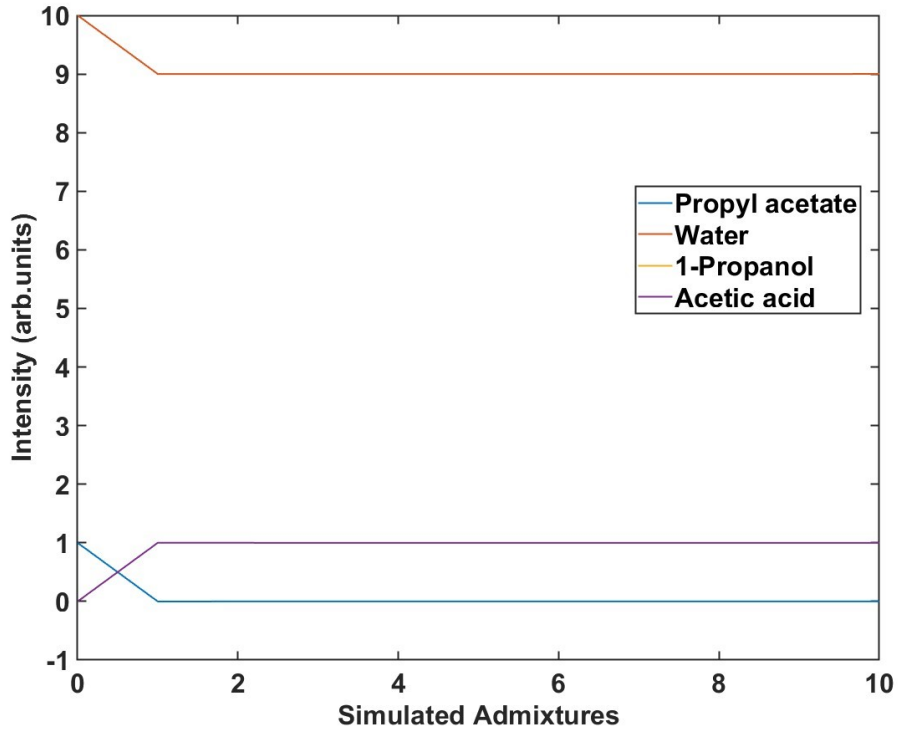

Figure S49: Time evolution of components in reaction data using Supervised MCR-ALS for the model A+B⟶C+D if A=1 and B=10 for the simulated admixtures data.

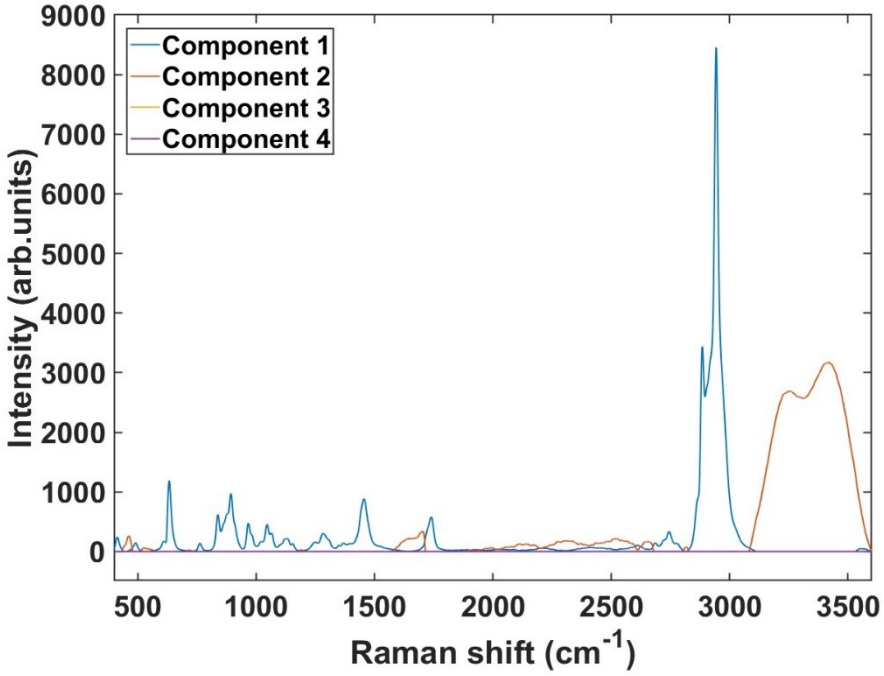

Figure S50: Component selection for the simulated admixtures data by supervised MCR-ALS for the model A⟶B+C+D

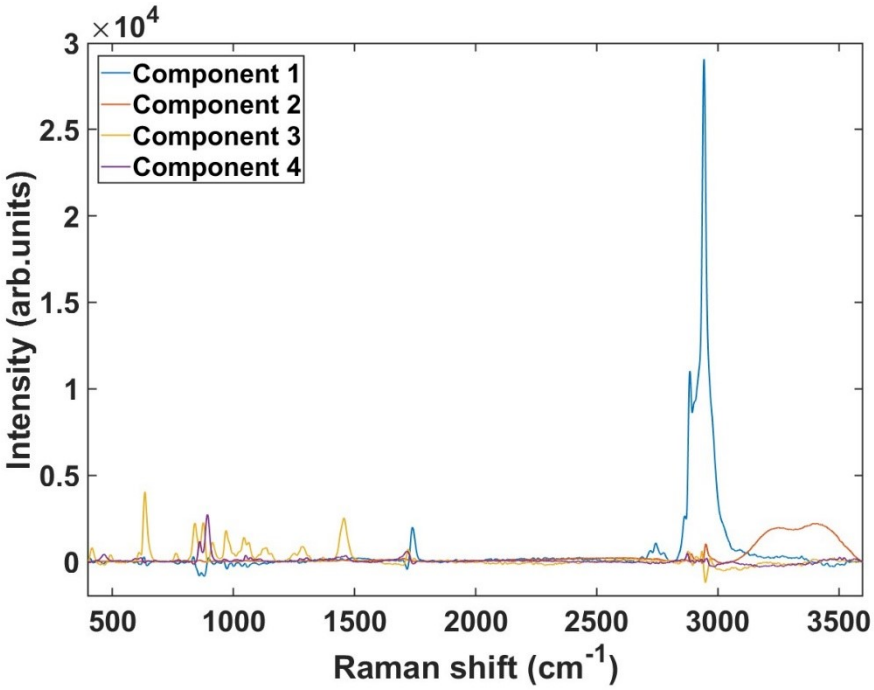

Figure S51: Component selection for the simulated admixtures data by supervised MCR-ALS for the model A+B⟶C+D when A=B

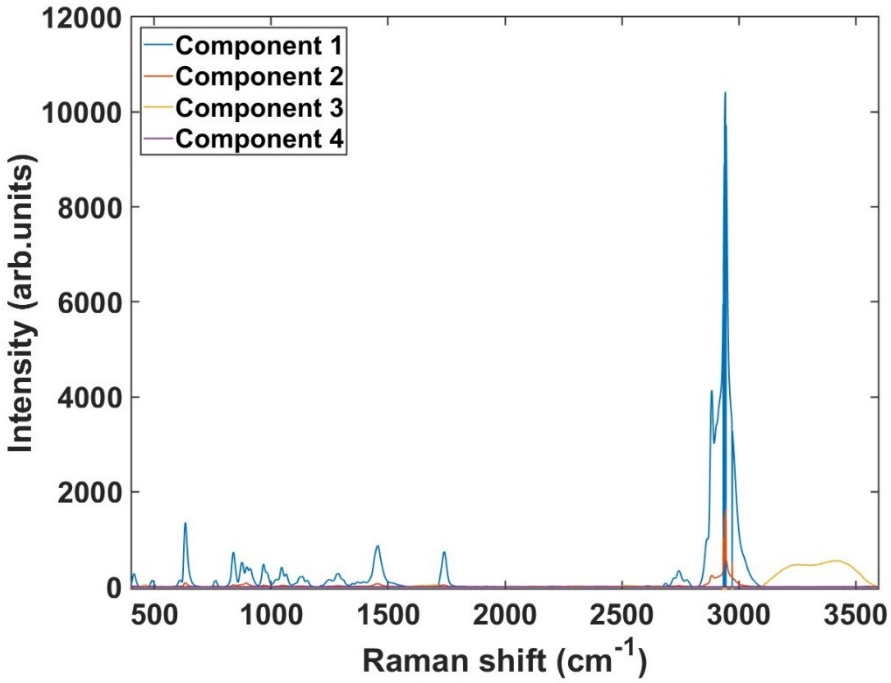

Figure S52: Component selection for the simulated admixtures data by supervised MCR-ALS for the model A+B⟶C+D when A=1, B=10

3.3 Optimization of seeding

This section describes the seeding optimization process for the propyl acetate hydrolysis reaction, illustrating that how the SUMR values are affected by increasing the seed weight.

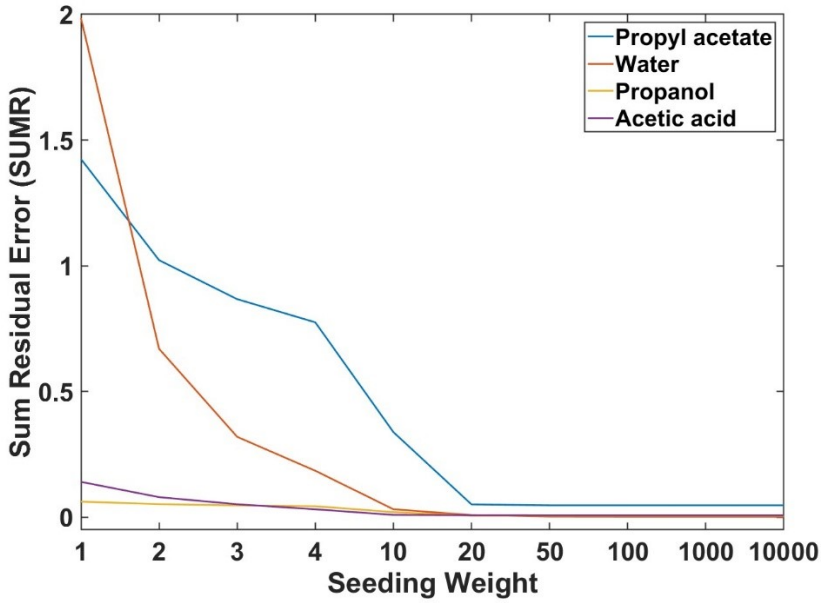

Figure S53: Seeding optimization for hydrolysis reaction, seeding weight vs SUMR.

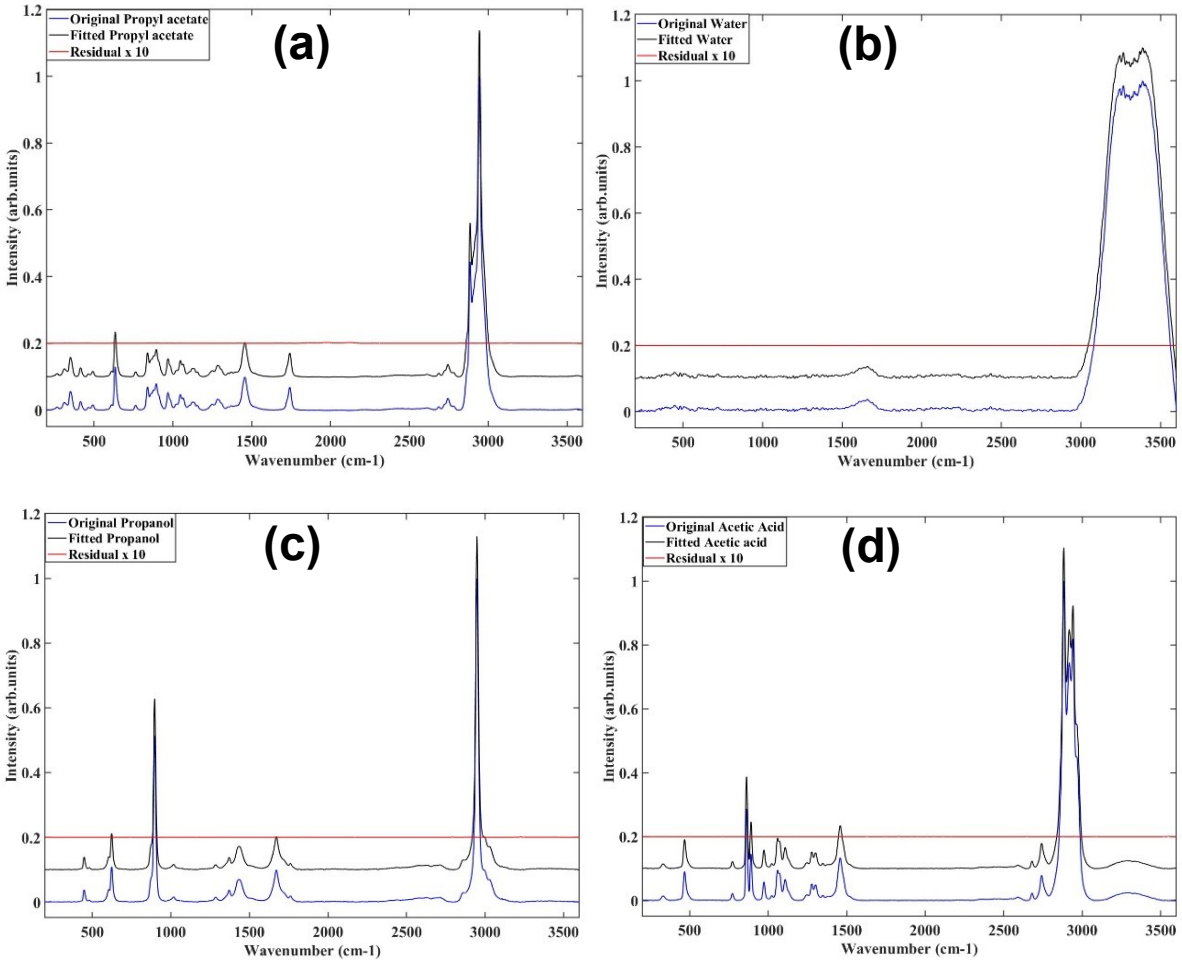

Figure S54: Original components spectra vs identified components spectra by seeded MCR-ALS along with 10x residual response spectra for hydrolysis reaction, offset for clarity (a)

component A: propyl acetate (b) component B: water (c) component C: 1-propanol (d) component D: acetic acid.