

SUPPORTING INFORMATION

Kinetic modelling of maleic acid isomerization to fumaric acid catalyzed by thiourea determined by attenuated total reflectance Fourier-transform infrared (ATR/FT-IR) spectroscopy

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S1. Assessment of Product Purity

Figures S1 and S2 display the chromatograms of the initial and final samples collected during a typical isomerization reaction. Figure S1 shows one peak with retention time of 7 min, indicating only the presence of maleic acid; however, a very small peak is observed at a reaction time of 12 min. The second peak appeared in the fumaric acid retention time, which is normal because the maleic acid usually contains traces of fumaric acid. The HPLC analysis was performed using an UV-Vis detector set at 210 nm. Fumaric acid has a high absorption of light at this wavelength, so even traces of this substance can generate small peaks such as the observed in Figure S1. Likewise, Figure S2 and S3 shows two peaks with retention time of 7 and 12 min corresponding to maleic and fumaric acid respectively. The reason for the two peaks, and not only the maleic acid's peak, is because the sample analyzed in Figure S2 was collected in 30 min, and the one analyzed in Figure S2 was collected in 150 min, which indicates that this time was not enough to achieve 100 % conversion. However, it should be noticed that the presences of byproducts (other peaks) was not detected.

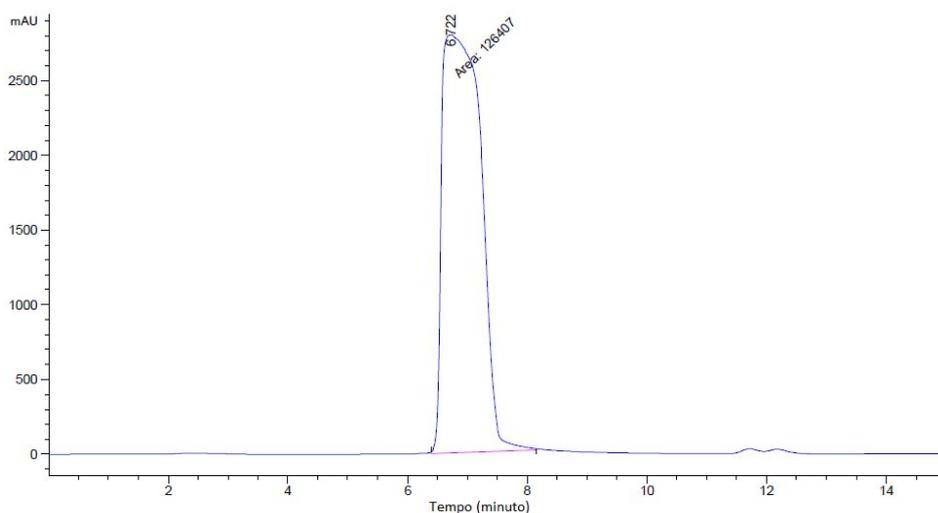


Figure S1. Chromatogram of the sample at time zero of the reaction at 40 °C and 4% of Thiourea. Maleic acid peak shown at 7 min.

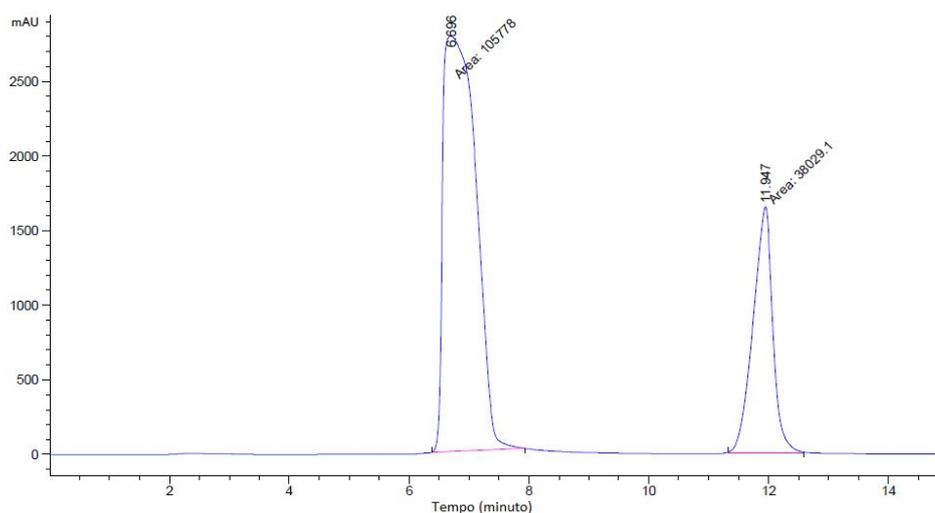


Figure S2. Chromatogram of the sample at time 30 minutes of the reaction at 40 °C and 4% of Thiourea. Maleic acid peak at 7 min and fumaric acid peak at 12 min.

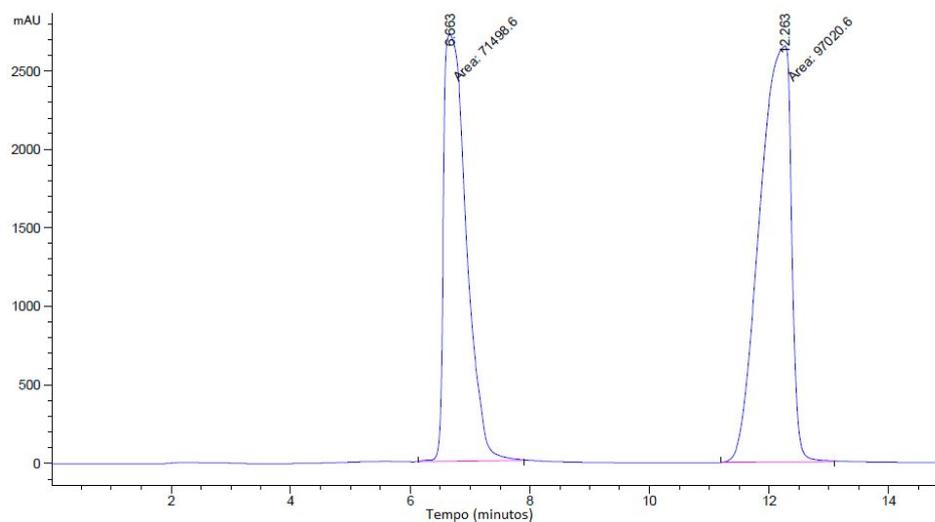


Figure S3. Chromatogram of the sample at time 150 minutes of the reaction at 40°C and 4% of thiourea. Maleic acid peak shown at 7 min and fumaric acid peak shown at 12 min.

The absence of byproducts can also be evaluated by the precipitation and analysis of the fumaric acid formed at the end of the reaction. Figure S4 shows the comparison between the infrared spectra of the standard fumaric acid and the one produced in the

reaction. The two spectra are very similar, and no new band is observed in the sample produced by the reaction, which would be related to any byproduct.

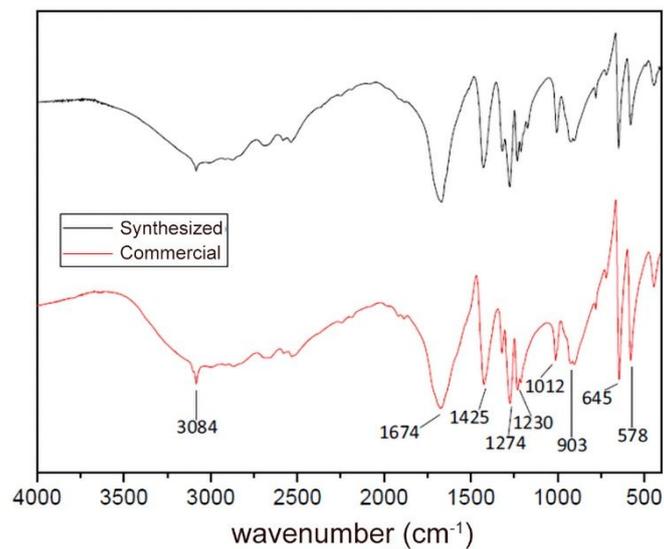


Figure S4. Infrared spectra of fumaric acid. Red line: commercial and black line: synthesized in this work.

S2. Maleic and Fumaric Acid Quantification by HPLC

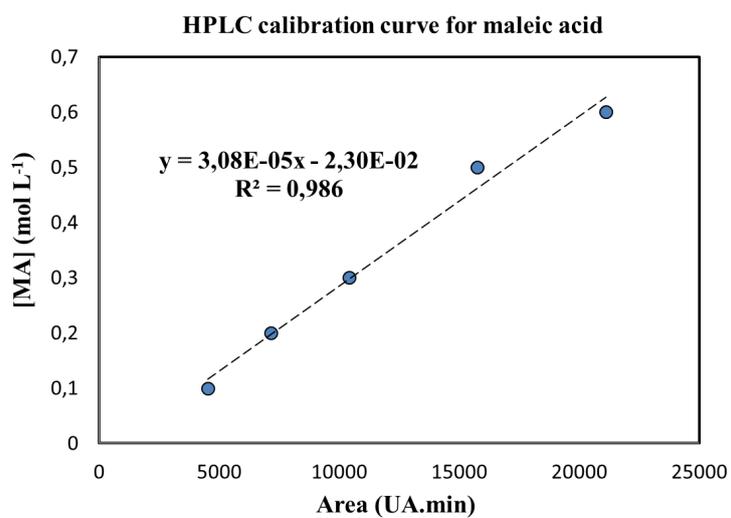


Figure S5. Calibration curve of maleic acid concentration determined by HPLC.

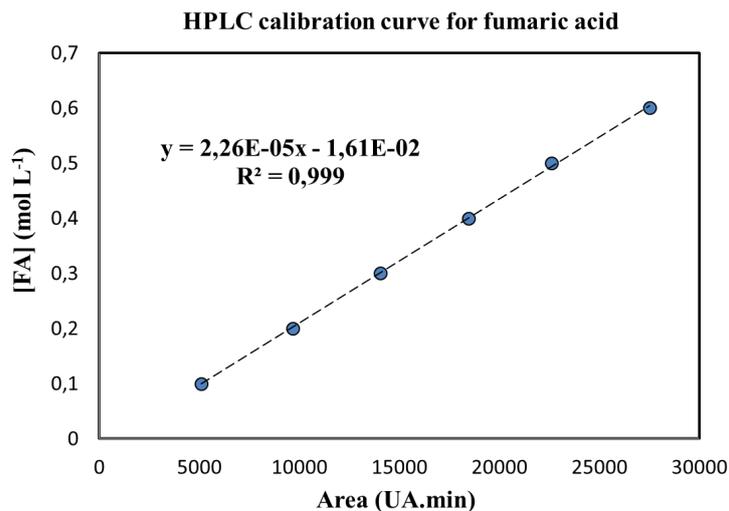


Figure S6. Calibration curve of fumaric acid concentration determined by HPLC.

S3. ATR/FT-IR Differentiation Method

To estimate the profile of maleic acid concentration over the experimental time, measured by ATR/FT-IR, a dummy exponential function was used. We have chosen this function not due to any previous kinetic information, but because it simulated very accurately the profile of the concentration for all experiments, in order that the differentiation could be performed satisfactorily. This is important because differentiating noisy data leads to greater noise and would not let the estimation of the reaction rate be possible. This was a two-term exponential function of the type:

$$y = y_0 + A_1 * \exp\left(-\frac{(x-x_0)}{t_1}\right) + A_2 * \exp\left(-\frac{(x-x_0)}{t_2}\right)$$

Where y_0 , A_1 , A_2 , x_0 , t_1 and t_2 are coefficients estimated by non-linear regression; y is the MA concentration and x is the time, in minutes.

An example of this dummy function being used to acquire the concentration profile is shown in Figure S7, for experiments at 20°C (less curvilinear profile) and at 60°C (more curvilinear profile). The dummy function was able to estimate the profile for both the experiments.

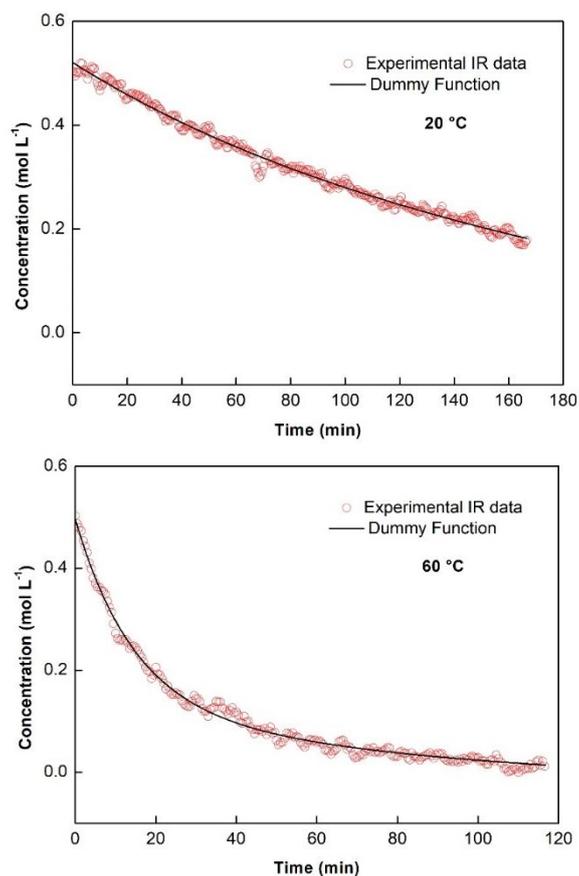


Figure S7. Using the exponential dummy function to estimate the concentration profile of maleic acid for experiments at 20°C (less curvilinear profile) and at 60°C (more curvilinear profile).

After this function was estimated, it was then analytically differentiated, as to estimate the reaction rate. The reaction rates estimated for the reactions with different catalyst concentrations are presented in Figure S8.

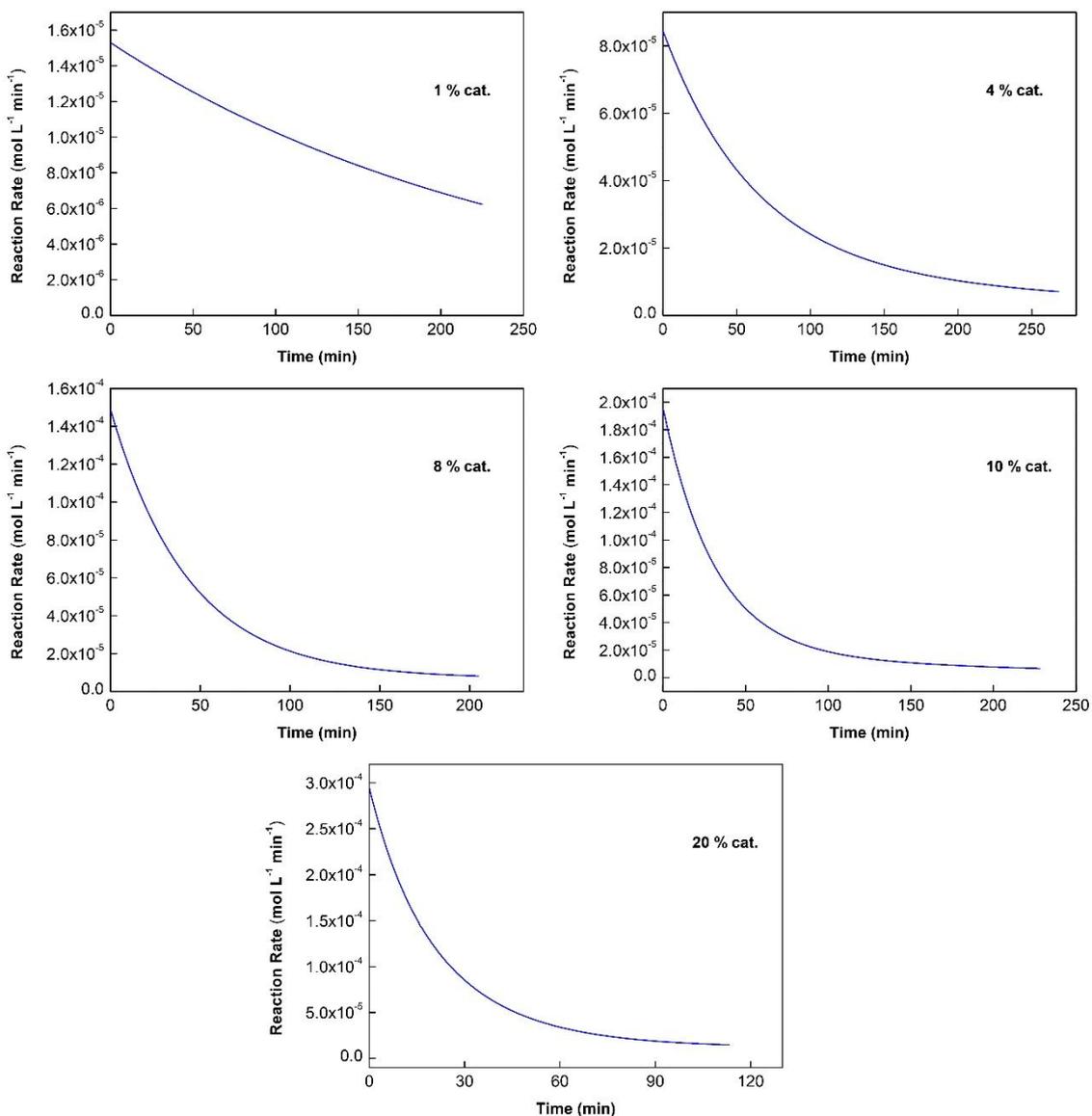


Figure S8. Example of estimated reaction rates for the experiments at different catalyst concentration.

S4. Validation of the Kinetic Model by HPLC Quantification

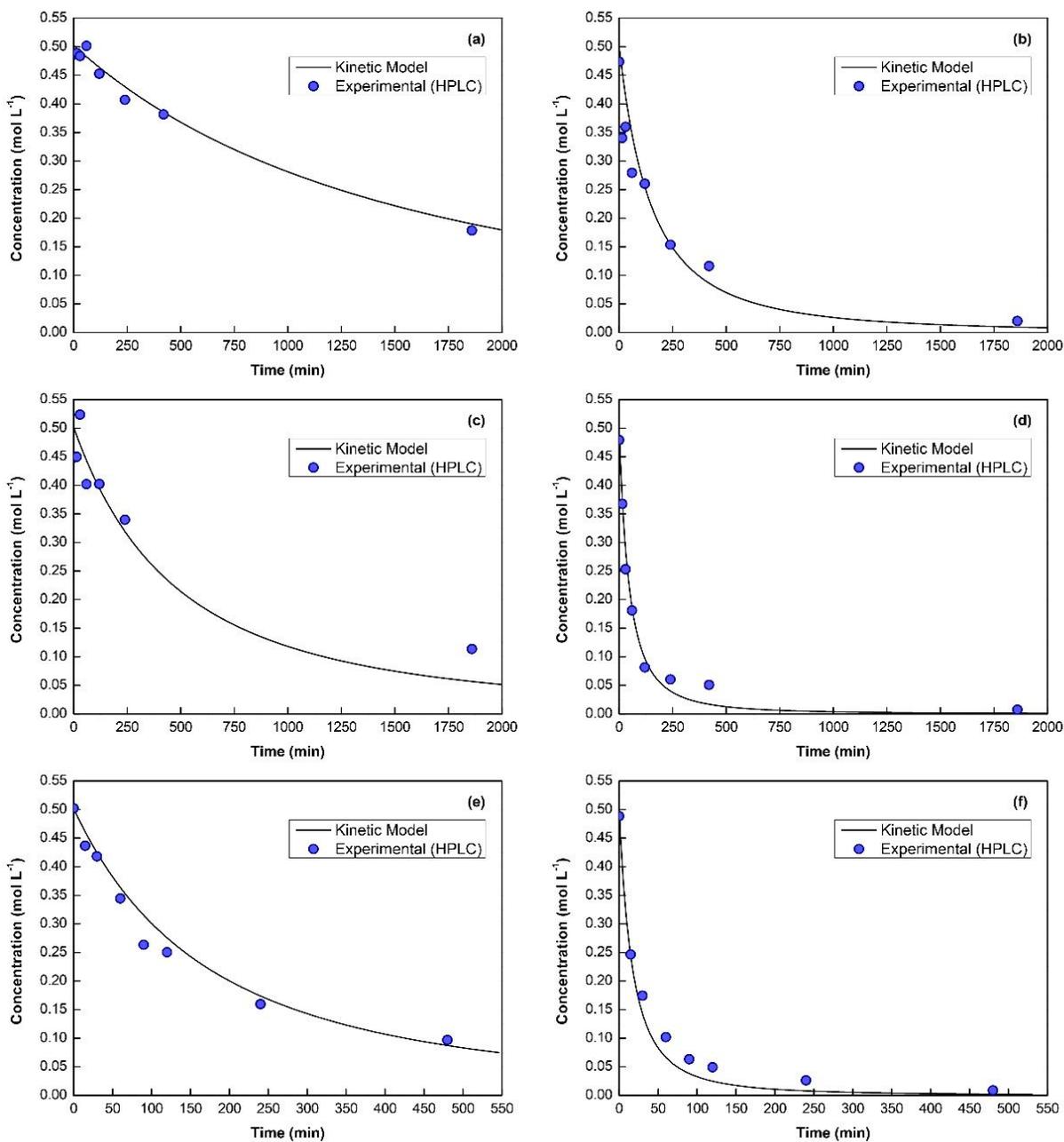


Figure S9. Kinetics of consumption of maleic acid during the isomerization reaction at different temperatures and concentrations of thiourea (% mol): (a) 20 °C and 1 %, (b) 40°C and 1%, (c) 20 °C and 10 %, (d) 40°C and 10%, (e) 60 °C and 1 %, (f) 60 °C and 10 %.