

Experimental:

The feasibility of the decomposition of the calcium salt of levulinic acid was assessed using thermogravimetric analysis (TGA). Calcium levulinate, purchased from Sigma Aldrich (CAS 5743-49-7), was compared to anhydrous calcium acetate, also purchased from Sigma (CAS 114460-21-8). Experiments were conducted using a TA Instruments Q500 TGA. Approximately 5 mg samples were loaded onto platinum pans as very thin layers to minimize mass transfer limitations caused by the melting calcium levulinate salt, which forms a “a pasty, porous and spongy mass”¹ that can trap product vapors. The TGA was performed as a 20 °C/min ramp from 25 °C to 1000 °C using nitrogen (liquid N₂ boil-off) as a sweep gas.

Kinetic parameters were determined using TGA coupled with the distributed activation energy model (DAEM). DAEM assumes many parallel, irreversible, first-order reactions, and has been applied to both coal and biomass pyrolysis.²⁻⁸ Using TGA, the mass loss is considered to be the fractional conversion, which allows the determination of the activation energy assuming a constant frequency factor.

Equation 1 is adapted from biomass pyrolysis,²⁻³ where V^* represents the total volatile fraction of biomass and V represents the amount of biomass volatilized at time t . When applied to TDO, V/V^* effectively represents the fractional conversion, x , at time t . $f(E)$ represents the normalized probability density function of pseudo-first-order reactions with activation energy E and frequency factor k_0 .

$$1 - V/V^* = \int_0^\infty \exp(-k_0 \int_0^t e^{-E/RT} dt) f(E) dE \quad (1)$$

Following the procedure outlined in Beis et al.,⁹ it is possible to determine the fractional conversion using the regression capabilities of the commercially available software Mathcad. Equation 2 is used to calculate fractional conversion as a function of temperature rather than time.

$$x = 1 - \int_0^\infty \exp(-\frac{k_0}{\beta} \cdot \int_{T_0}^T e^{-E/RT} dT) \cdot f(E) dE \quad (2)$$

In equation 2, T_0 is the initial temperature, T is the temperature at time t , and β represents the heating rate. It is possible to estimate k_0 for each reaction in the distribution by using an Arrhenius-like analysis of the temperature at a given conversion for different heating rates. However, the uncertainties for k_0 determined by such analyses typically span three or four orders of magnitude. Since the value of E is not very sensitive to the value of k_0 and realizing the choice of pseudo first order kinetics is arbitrary, k_0 was assumed as 10^{13}

s⁻¹ which is a typical value ($\approx \frac{k_B T}{h}$) for first order reactions. Equation 2 was solved via

numerical integration in Mathcad, taking the energy integral as a Riemann Sum with a step size of 1 kJ/mol and a maximum activation energy of 450 kJ/mol. Integration in this manner expedites calculation, as only five fitting parameters were required – the two mean activation energies and their standard deviations as well as a weighting parameter between the two. The parameters were determined by a fit to the TGA data with a ramp

rate of 10 °C/min. The results of the model are shown along with the experiment data in Figure 1.

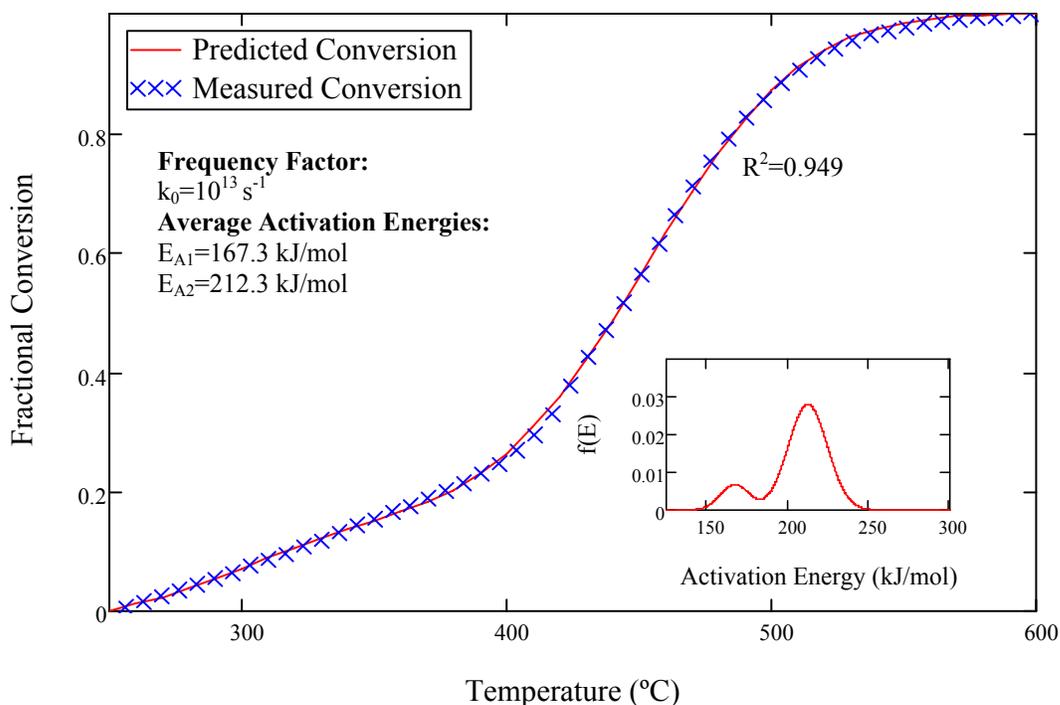


Fig. 1 Comparison of measured and predicted fractional conversion with a TGA ramp of 10°C/min. The bimodal Gaussian $f(E)$ distribution is also shown.

The TDO of levulinic acid was performed using a Parr 300 mL stirred tank reactor. Calcium levulinate was prepared by neutralizing levulinic acid (Acros Organics, CAS 123-76-2) with calcium oxide (Sigma, CAS 1305-78-8) slaked in water at 50 °C for 10 minutes. The resulting salt was dried in an oven at 105 °C, crushed, and screened through a number 150 USA Standard Sieve. The Parr reactor was configured to allow the flow-through of nitrogen sweep gas (industrial grade) with a liquid nitrogen condenser on the outlet. Glass beads were used to enhance heat transfer. Two different temperature regimes were characterized by ramping the reactor temperature to both 350 °C and 450 °C.

The products of TDO were characterized using calorimetry for heating value, nuclear magnetic resonance (NMR) spectroscopy, and gas chromatography/mass spectrometry (GC/MS). Higher heating value was measured using a Parr Model 1241 oxygen bomb calorimeter. Chemical functional group analysis was carried out using a Varian Unity Plus 400 NMR. Samples were diluted in 1:1 volume ratio with dimethyl sulfoxide as a solvent and using tetramethylsilane as an internal standard. Functional groups were determined using a library of proton and ^{13}C measurements made on more

than 50 compounds common in pyrolysis oils.⁹ The chemical shift regions representative of different functional groups were integrated to determine the percent of carbon which exists as each functional group.

Total carbon analysis was performed by the University of Maine Analytical Laboratory and Maine Soil Testing Service. The analysis is a combination of total organic and total inorganic carbon. Samples are combusted in an oxygen atmosphere between 1050-1350 °C. Helium is used as a carrier gas to transfer the released gasses through an infrared detector to determine carbon dioxide concentration. Steel wool is used to remove excess oxygen.

The structures of prominent compounds in the products were elucidated using a Shimadzu GCMS-QP2010S equipped with a Shimadzu SHRX1-5MS column. Samples were diluted in dichloromethane and dried over sodium sulfate. This analysis was qualitative as no internal standard was used. Chemical structures were determined by comparison with several NIST libraries provided in Shimadzu's GCMSsolution software. The temperature program for the GC column oven ramped from 40 °C to 120 °C at 1.5 °C/min and then held at 120 °C for 10 minutes. The oven was then ramped from 120 °C to 220 °C at 5 °C/min and held at 220 °C for 10 minutes. Finally, the column was ramped from 220 °C to 250 °C at 25 °C/min and held at 250 °C for 10 minutes. The mass spectra for the compounds which were identified in the chromatograms of Figure 2 are presented along with the library spectra for comparison in Figures 3 through 15.

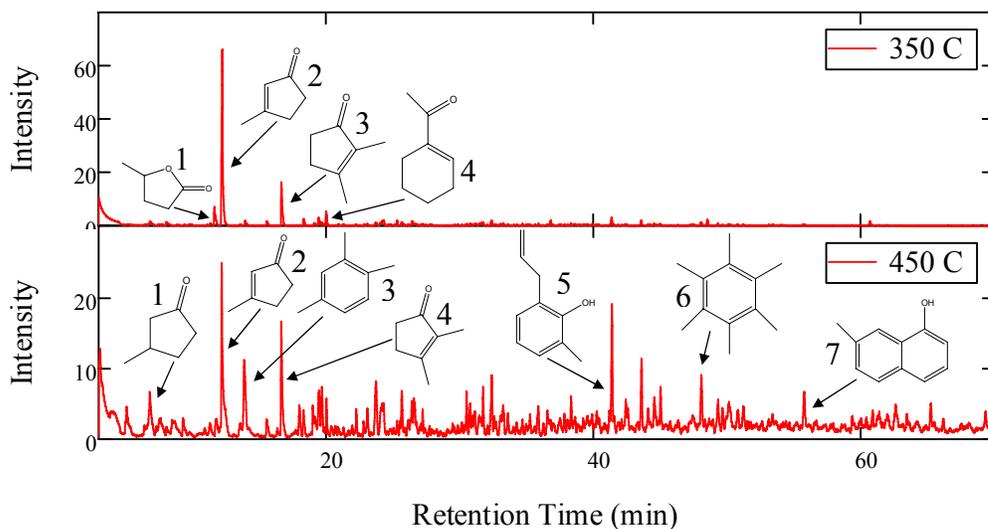


Fig. 2 Comparison of GC/MS chromatograms of the hydrocarbon products of TDO. At 350 °C the product molecules tend toward lower molecular weight, substituted cyclic compounds. At 450 °C aromatic compounds are formed in addition to the cyclopentenones formed at 350 °C.

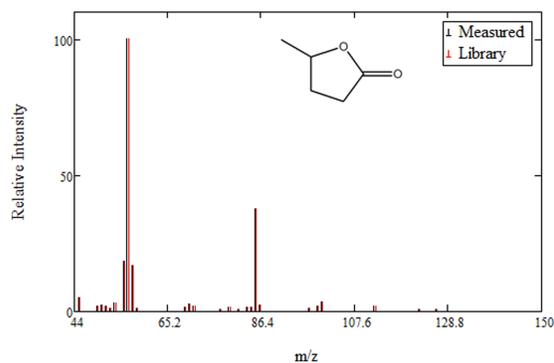


Fig. 3 Mass Spectra for Compound 1 formed at 350 °C.

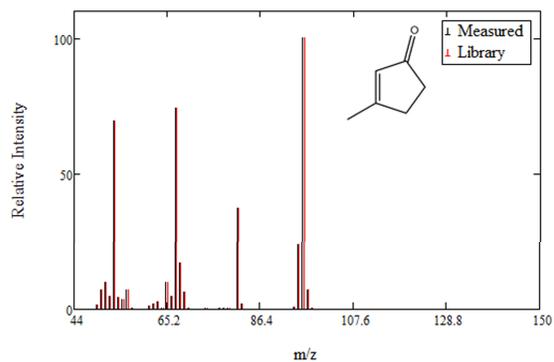


Fig. 4 Mass Spectra for Compound 2 formed at 350 °C.

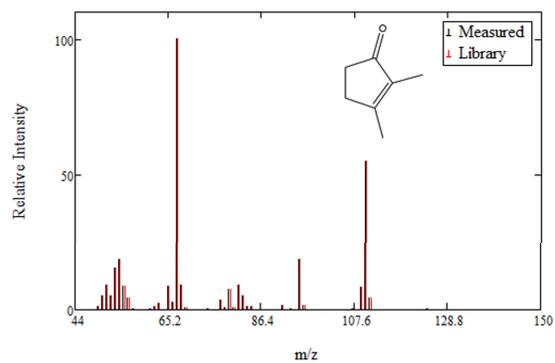


Fig. 5 Mass Spectra for Compound 3 formed at 350 °C.

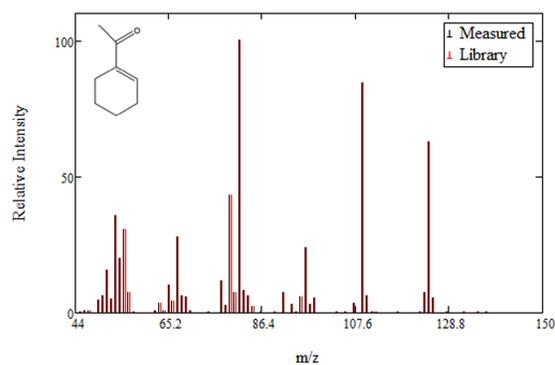


Fig. 6 Mass Spectra for Compound 4 formed at 350 °C.

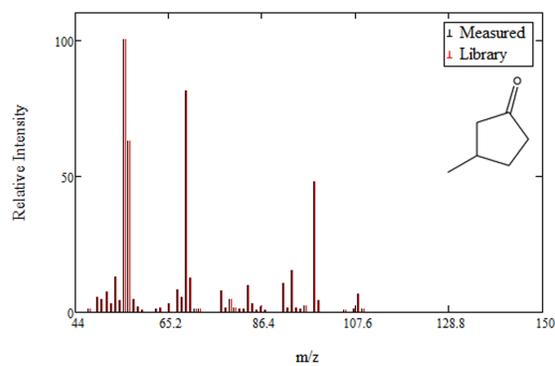


Fig. 7 Mass Spectra for Compound 1 formed at 450 °C.

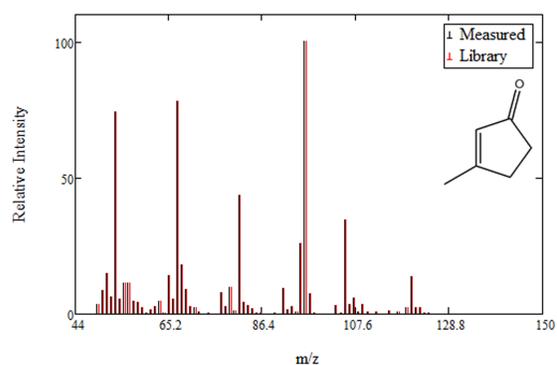


Fig. 8 Mass Spectra for Compound 2 formed at 450 °C.

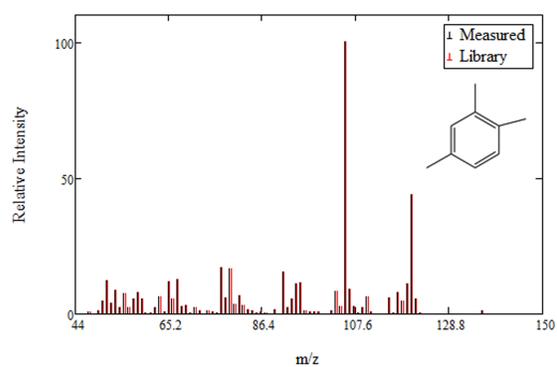


Fig. 9 Mass Spectra for Compound 3 formed at 450 °C.

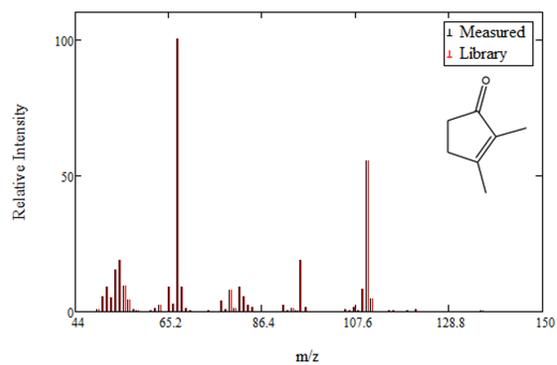


Fig. 10 Mass Spectra for Compound 4 formed at 450 °C.

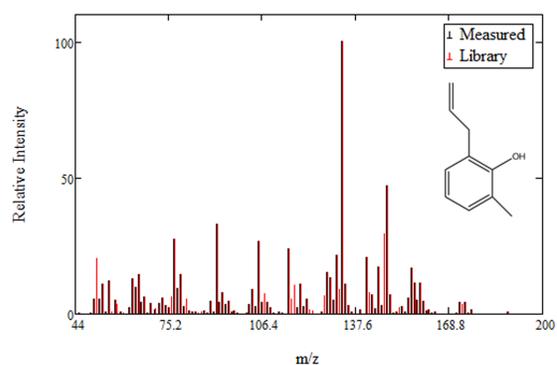


Fig. 11 Mass Spectra for Compound 5 formed at 450 °C.

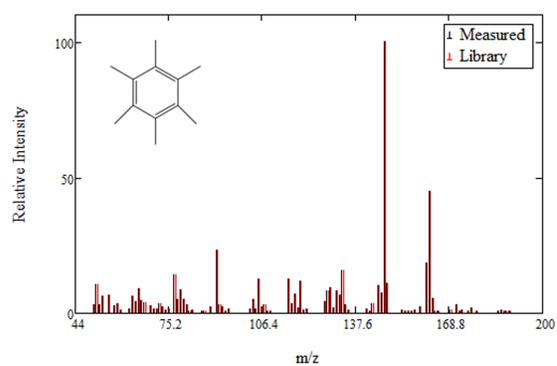


Fig. 12 Mass Spectra for Compound 6 formed at 450 °C.

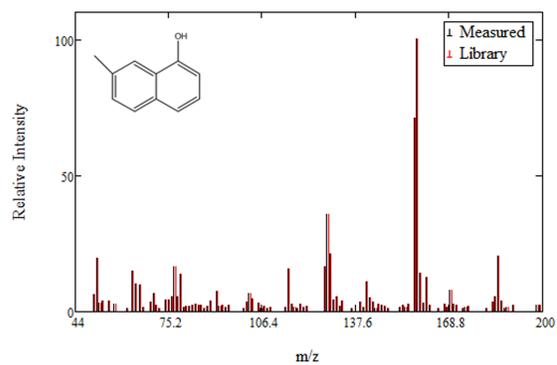


Fig. 13 Mass Spectra for Compound 7 formed at 450 °C.

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