Chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy has proven to be a well-suited technique for the rapid study and spectral identification of molecular species due to its ultra-broadband capability and excellent specificity to molecular structure from high-resolution rotational transitions. This talk will describe initial results from combining CP-FTMW detection with a hyperthermal nozzle source. This source has the advantage of producing traditionally high thermal product densities in a pulsed supersonic expansion with a short contact time compared to conventional pyrolysis. Used in tandem, CP-FTMW spectroscopy and the hyperthermal nozzle in a supersonic expansion is a powerful method that can produce and detect changes in conformation and isomer populations, and characterize important intermediates on the reaction surface of a precursor. In particular, we show its utility to provide insight into the unimolecular decomposition pathways of model lignin compounds and alternative biofuels. Preliminary results will be discussed including spectroscopic evidence for formation of cyclopentadienone in the pyrolysis of a lignin derivative guaiacol (o-methoxyphenol).