

# LEVULINIC ACID OXIDATION AS A STRATEGY FOR THE PRODUCTION OF MALEIC ANHYDRIDE

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Levulinic acid (LA) has long been an interesting biochemical for its relatively straightforward synthesis from various lignocellulosic sugars. As a bifunctional oxygenate, it offers considerable synthetic flexibility and numerous downstream upgrading options that suggest it could play an important role in the production of bio-based commodities. Unfortunately, levulinic acid has thus far failed to gain traction in commercial markets. As a potential application, we describe here the aerobic, oxidative cleavage of levulinic acid, which produces maleic anhydride (MA) in good yield. The strategy is interesting in that it connects lignocellulose, via levulinic acid, with the existing maleic anhydride market, which is robust and relatively high-value.

Oxidative cleavage of LA occurs over supported vanadates, and we have demonstrated single-pass MA yields as high as 71% of the theoretical maximum at 573K.<sup>1</sup> Further, at a fundamental level, the chemistry underlying levulinic acid oxidation is intriguing: the general expectation of oxidative cleavage is that it will preferentially cleave C-C bonds that are internally positioned relative to the ketone group. However, formation of maleic anhydride (C<sub>4</sub>) from levulinic acid (C<sub>5</sub>) requires selective cleavage of the terminal carbon. We demonstrate that monofunctional ketones, such as 2-pentanone, will preferentially cleave at internal positions; thus, this unanticipated selectivity is unique to bifunctional LA. To probe the source of selectivity for methyl cleavage in this system, we additionally consider the oxidative cleavage of several LA and 2-pentanone analogs.

1. Chatzidimitriou, A. and Bond, J.Q., "Oxidation of levulinic acid for the production of maleic anhydride: breathing new life into biochemicals." *Green Chemistry*, 17, 8, 4367-4376, 2015.