Biorenewable Processes to Acrylic Acid

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Introduction

Biomass derived sugars provide opportunities for new, potentially low cost routes to chemical intermediates. One example is the transformation of glucose to acrylic acid. In recent times the cost of propylene has been marked by volatility and is still rising. Biobased sugars provide a price stable feedstock alternative. In addition to being cost competitive with conventional propylene derived material, bio-derived acrylic acid must provide the same level of purity and reactivity for producing esters and polymeric derivatives.

A combination of fermentation and chemical catalysis provide multiple routes to acrylic acid. The literature shows three plausible fermentation intermediates (**Figure 1**). Only one of the intermediates, lactic acid, is commercially available today. Polylactic acid provided the initial market impetus for commercial large scale lactic acid production and more capacity could be readily added if warranted. Cargill is currently working on a fermentation route to 3-hydroxypropionic acid and in the future it may also become economically attractive and thus provide a competitive route to lactic acid.

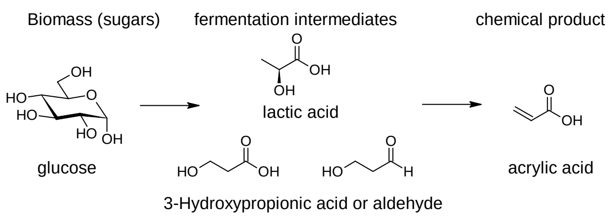

Figure 1. Renewable routes to acrylic acid

This presentation will cover the requirements for realizing a process that converts biomass to acrylates. Of the three fermentation intermediates lactic acid is the only one produced in large amounts and hence it may be considered the nearest term option. Although there is a ready supply of purified lactic acid and its methyl ester, to date an effective and attractive process for conversion of lactic acid to acrylates has not been realized commercially. The difficulty with lactic is the recalcitrant nature of the dehydration step. This is somewhat rectified by use of catalysts [1]. Other approaches, such as acetoxylation, seek to improve the leaving group capability of the α-hydroxy group [2]. A problem with this approach is expense associated with using reagents such as acetic anhydride which have been claimed in the literature.

This paper will focus on the barriers to renewable acrylate production and efforts at Pacific Northwest National Laboratory (PNNL) to overcome these barriers. Particular attention will be paid to lactic acid and novel methods for activating the α-hydroxyl group to dehydration.

Materials and Methods

Lactic acid, acetic acid, sulfuric acid, solid acids and succinic acid were purchased from Aldrich or other commercial vendors. All work was carried out under a nitrogen atmosphere using standard laboratory experimental procedures.

Results and Discussion

Two novel methods have been utilized to enhance the difficult dehydration of lactic acid via acetoxylation—esterification of the α-hydroxy group. In one approach acetic acid is used as an azeotropic solvent. Using this technique at mild conditions (70 °C and 150 mmHg) acetoxylation can be achieved in greater than 90% yield. In this way inexpensive acetic acid serves as a replacement for expensive acetic anhydride [3]. A second approach considers easily formed anhydrides, such as fermentation derived succinic anhydride (SA), as an activating agent. The esterification of lactic at the α-hydroxy group with SA has been accomplished in 98% yield at 70 °C [4].

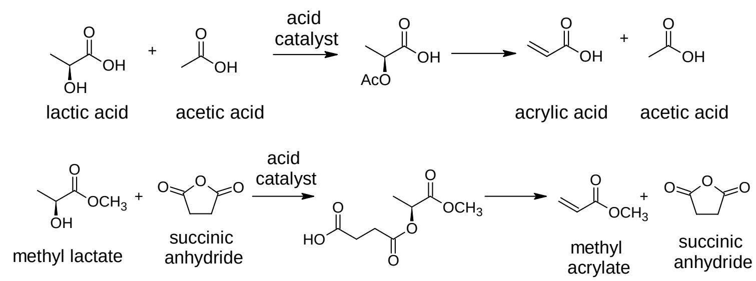

Figure 2. Novel approaches for "acetoxylation"

Relevant pyrolysis data on methyl lactate will also be presented, including successful catalyst compositions for pyrolysis of non-activated systems [1]. Finally a process flow diagram that offers a potentially attractive commercial route will be presented.

Significance

Industrial relevant options for conversion of biomass to acrylic acid and acrylates will be important to efficient utilization of renewable resources and to reduction of our dependence on ever more expensive petroleum. A discussion of challenges that need to be overcome to make acrylates from renewables a reality and work at PNNL to address those barriers is included.

References

1. Walkup, P.C., Rohrmann, C.A., Hallen, R.T. and Eakin, D.E. *US Patent* 5,252,473 (1993).
2. Ratchford, W.P. and Fisher C.H. *Industrial and Engineering Chemistry* 37, 382 (1945).
3. Lilga, M.A., Werpy, T.A. and Holladay, J.E. US Patent Application 0110974 (2004).
4. Werpy, T.A., Lilga, M. A. US Patent 6,545,175 (2004).