Recovery of polymerization-grade aconitic acid from acidified cane molasses using ethyl acetate

Akanksha Kanitkar, Giovanna Aita* and Lee Madsen

Audubon Sugar Institute, LSU AgCenter, St. Gabriel, LA 70776

Abstract

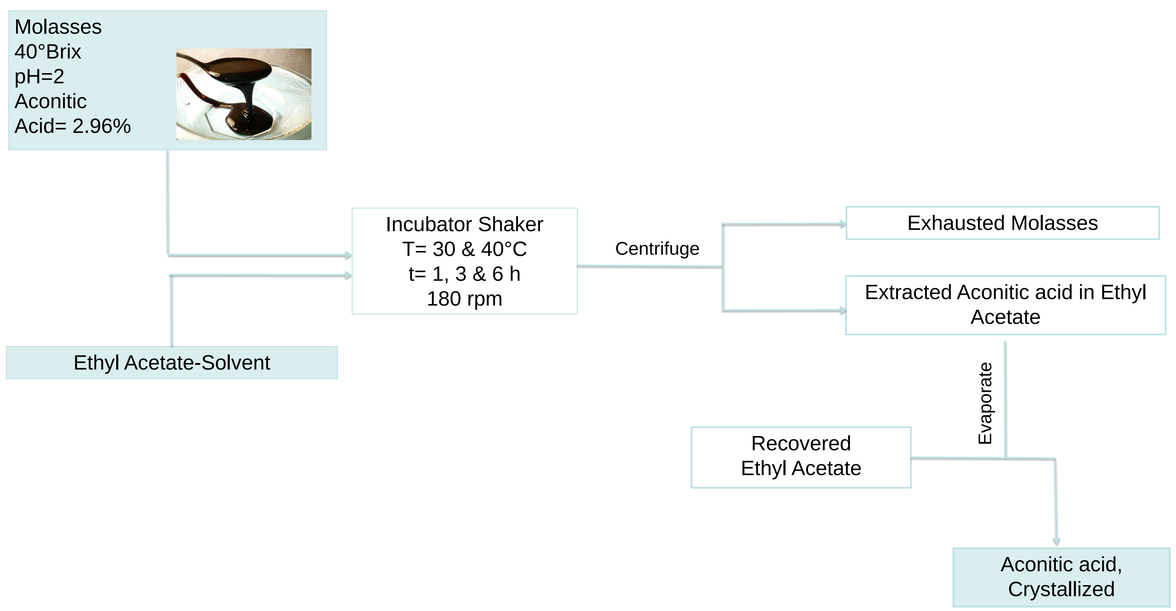
Aconitic acid (*trans*-propene-1, 2, 3- tricarboxylic acid) is the most prevalent organic acid found in sweet sorghum and sugar cane. Aconitic acid content in cane may reach 0.1-0.2% resulting in as much as 3-7% in molasses. It is used in the food processing industry as an acidulant and can be used as a precursor in the organic synthesis of plasticizers. Many routes, including precipitation, adsorption with ion-exchange resins and liquid-liquid extraction have been examined. In this study, recovery of aconitic acid was carried out via liquid-liquid extraction of acidified sugarcane molasses with ethyl acetate (EtOAc). Diluted sugarcane molasses (~40 g/100g refractive dry solids) was acidified to pH 2 (H_2SO_4) and extracted (molasses: solvent ratio = 1:3) under six combinations of time and temperature. The conditions ranged from 1-6 h at either 30 or 40 °C. In order to conserve solvent, the EtOAc was recovered by distillation and reused for subsequent extraction steps. Under the most efficient set of conditions, 40-60 % (HPLC) of the aconitic acid was recovered as the free acid. The purity of the product is sufficient for the preparation of biodegradable polyesters, which will be polymerized with glycerol (biodiesel process waste) and functionalized with cinnamic acid (pretreatment effluent from the production of cellulosic ethanol). Because molasses and bagasse are both byproducts of the sugarcane industry, the production of polyesters has the potential to further 'close the cycle' while adding value to the industry.

Introduction

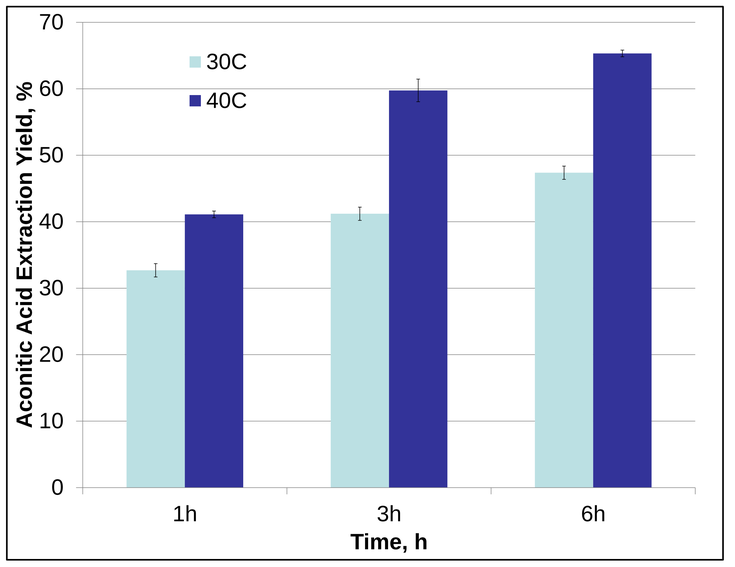
Aconitic acid (1, 2, 3- propene tri-carboxylic acid) is an unsaturated, tribasic organic acid that exists in two geometric forms, the trans-isomer (TAA) and cis-isomer, of which TAA is the favored form. The processing of raw sugar from sugar cane generates residual syrup, molasses, that contain high concentrations of certain organic acids in addition to sucrose and reducing sugars. Aconitic acid is the dominant organic acid present in the molasses in addition to malic, oxalic and citric acids[1]. The amount of aconitic acid, present either in free form or in combined form as calcium or magnesium salts varies widely depending on the variety of cane and the final molasses can contain 3-7% aconitic acid[2]. Biodegradable polyesters will be generated using recovered aconitic acid from this study, glycerol and cinnamic acid.

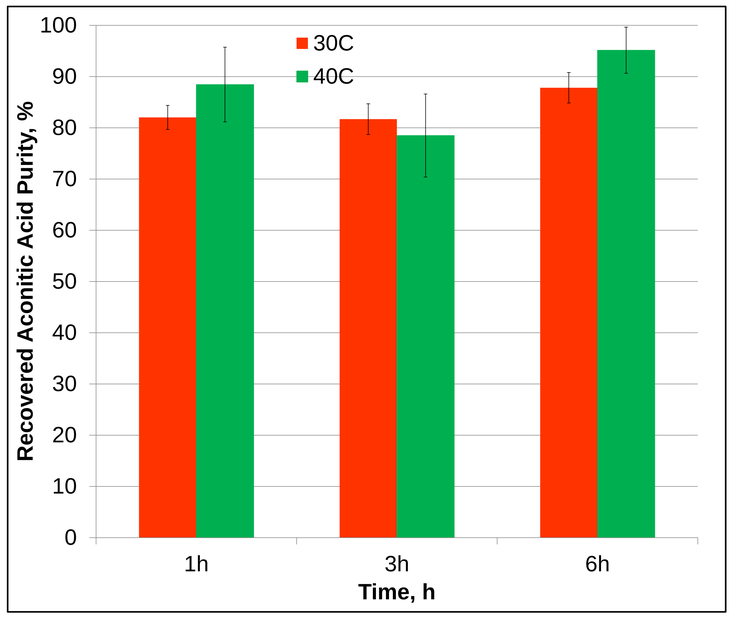
Materials and Methods

Molasses of 80°Brix were diluted to 40°Brix and acidified to pH= 2 using 98% sulfuric acid. Extractions were carried out with ethyl acetate at a solvent to molasses ratio of 3:1. Extractions were carried out at 30 and 40°C for 1, 3 and 6 h using a incubator- shaker (Amerex Instruments Inc. Lafayette, CA). After the extraction was complete, the material was centrifuged at 1800 rpm (*g*-force= 313 *g*) for 10 min to separate the solvent from molasses. Ethyl acetate was then evaporated using a rotary evaporator and the concentrated mixture was dissolved in acetic acid and allowed to crystallize. The recovered ethyl acetate was used for subsequent extractions. The crystallized aconitic acid was decolorized using activated carbon and crystallized again. The concentration of aconitic acid was analyzed by HPLC with a BioRad Aminex HPX-87H ion exclusion column using a diode-array ultraviolet-visible detector.



Results





- The aconitic acid yields increased with increase in extraction time and temperature.
- 30-65% of the aconitic acid originally present in the molasses was extracted under the given set of conditions.
- Temperature of 40°C extracted around 40% more TAA from molasses as compared to 30°C.
- Extraction time of 6 h at 40°C gave the highest yield of 65% under the tested conditions.
- The purity (concentration) of aconitic acid in the crystallized product ranged between 78-95%. The extraction at 40°C- 6 h gave the highest purity product of 95%.
- Studies have shown that ethyl acetate is a selective solvent for extracting TAA though suffers from the disadvantage of low yields[3].
- The next step would be to synthesize polymers using lab-grade aconitic acid and to ensure that the purity of ~95% is sufficient for the preparation of biodegradable polyesters.
- More studies need to be performed to determine the optimal set of conditions for aconitic acid extraction from molasses using ethyl acetate.

References

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*Contact Information

Dr. Giovanna Aita, gaita@agcenter.lsu.edu

Conclusions

Extraction of aconitic acid from molasses using ethyl acetate as a solvent was investigated in this study. Yields of 30-65% of aconitic acid were obtained under the given set of conditions. The purity of product (~95%) should be sufficient enough to synthesize biodegradable polymers using TAA, glycerol and cinnamic acid. The solvent was recycled and reused for subsequent extractions thus minimizing its consumption.

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