Rhenium Catalyzed Production of Bio-Based Acrylates From Glyceric Acid

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Bio-based glyceric acid, an oxidation product of glycerol, was converted into acrylic acid and its esters, crucial polymer precursors, using a new catalytic approach in a sustainable manner. Avoiding gaseous H_2 or dangerous chemicals, the crucial step is Re-catalyzed deoxydehydration (DODH) in an alcoholic medium. In addition to being a solvent and hydrogen donor, alcohol also forms protective ester groups with acrylic and glyceric acids. This study examined several catalysts, alcohols, the presence of H_2, and temperatures. Acrylic acid and methyl acrylate were produced in 72 hours with a 65% combined yield using a Re/C catalyst and methanol at 150 °C under N_2. This versatile process can also be transferred to other alcohols enabling the production of various alkyl acrylates and monomers.

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1 Introduction

Acrylic acid (AA) and acrylate esters are essential building blocks in the polymer industry. To reduce a dependency on fossil fuels, bio-based production of acrylic acid and its ester from glycerol has been explored. Various routes have been explored in review articles (Avasthi et al., 2020; Beerthuis et al., 2015; Sun et al., 2017) and detailed studies (Katryniok et al., 2011a; Wang et al., 2022a). Mainly conversion from glycerol to acrylic happen through catalytic dehydration to acreloin (Abdullah et al., 2022; Katryniok et al., 2010 or ally alcohol (Dethlefsen & Fristrup, 2015; Jentoft, 2022), which are then further oxidized to acrylic acid (Li & Zhang, 2016; Yang et al., 2016).

Another conversion route involves glycerol oxidation to lactic acid (Razali & Abdullah, 2017b) or glyceric acid (GA) (Fan et al., 2021b), followed by dehydration to acrylic acid or acrylates (Huang et al., 2023a, 2023b). Our study presents the first heterogeneously catalyzed conversion of GA into AA or esters, avoiding toxic reagents like indoline (Boucher-Jacobs & Nicholas, n.d.) and relying on solid Re catalysts.

From our previous study for DODH of mucic acid (Brigita Hočevar et al., n.d.; Harth et al., 2024) the commercial Re/C showed the most promising results and that is why it was chosen for that reaction as well. In this study different temperatures in either hydrogen or an inert atmosphere were observed over time.

2 Material and Methods

2.1 Chemicals used

Glyceric acid (GA; 20–22 wt% aqueous solution, LD-2,3-dihydroxypropanoic acid) was sourced from TCI Chemicals. Methanol (MeOH; >99.8%) was obtained from J.T. Baker, while alternative alcohols such as ethanol (99.9%, J.T. Baker), iso-propanol (>99.8%, Merck), n-propanol (>99.5%, Sigma-Aldrich), n-butanol (>99.9%, Honeywell), and n-pentanol (>99%, Sigma-Aldrich) were also tested. Homogeneous catalysts, including Re_2O_7, $(NH_4)ReO_4$, and KReO4 (≥99%, Sigma Aldrich), were used without pretreatment. Supported rhenium catalysts (5 wt% Re) such as Re/C, Re/TiO_2, Re/SiO_2, Re/Al_2O_3, and Re/H-ZSM-5 were procured from

Riogen Inc. and underwent pre-treatment via reductive heating at 400 °C under H_2 flow. N_2 (5.0) and H_2 gases were provided by Messer.

2.2 Reaction set up

Catalytic experiments were conducted in stainless steel high-pressure batch reactors (Parr 5000 Multi Reactor System, 75 mL capacity) (Figure 1) with magnetic stirring and independent heating. A typical experiment involved adding 500 mg of GA solution and 45.0 mL of alcohol (*e.g.,* methanol) to achieve a ~20 mM GA solution. Rhenium catalysts were added at a fixed GA-to-Re molar ratio of 25:1, corresponding to 0.04 mmol of Re. The reactor was sealed, purged three times with N_2, pressurized to 5 bar_g with N_2 or H_2, and stirred at 600 rpm. Heating was set to a ramp of 4 $K\ min^{-1}$ to the desired temperature (typically 150 °C, with additional tests at 120, 165, and 180 °C) and held isothermal for 72 hours. After the reaction, the reactor was cooled to room temperature, depressurized, purged with N2, and opened to collect the product mixture for analysis. Samples were taken during reaction as well.

Figure 1: Parr reactor system

2.3 Analyical methods

Gas chromatography-mass spectrometry (GC-MS) analysis was performed using a Shimadzu GCMS-QP 2010 Ultra system (Kyoto, Japan) equipped with a Zebron ZB-5MSi nonpolar capillary column (length: 60 m, diameter: 0.25 mm, film thickness: 0.25 μm). Compound identification was conducted via mass spectrometry, scanning fragment ions in the range of 35–500 m/z, and matching against the NIST 17 (National Institute of Standards and Technology) library. Quantification was achieved using a flame ionization detector (FID). The analysis employed a temperature-programmed method: the column oven was initially held at 333 K for 5.5 minutes, then ramped to 563 K at a rate of 20 K min^{-1} and held constant for 8 minutes. The injector and detector were maintained at 563 K, with an injection volume of 0.5 μL and a split ratio of 5:1. Product quantification was based on FID peak areas and external calibration curves derived from commercially available reference compounds. Although GA could not be detected, probably due to its decomposition or low volatility, several products were successfully identified, including glycerate esters, acrylic acid, propanoic acid and its methyl esters — methyl acrylate and methyl propanoate.

3 Results and discussion

3.1 GCMS analysis

All results of the reaction products were analyzed by GC-MS. Figure 2 represents a typical chromatogram of product spectra.

3.2 Screening of different temperatures and gas phases

The results of the screening of different temperatures and different gas phases are represented in the Figure 2. The temperature variation shows that expectedly all reactions involved are enhanced with increasing temperature, i.e. DODH, hydrogenation and esterification, which results in other products. However, considering the market value of the unsaturated products acrylic acid and methyl acrylate, the most optimal temperature for N_2 atmosphere is 150 °C, and yields near 60 % were obtained after 72 h.

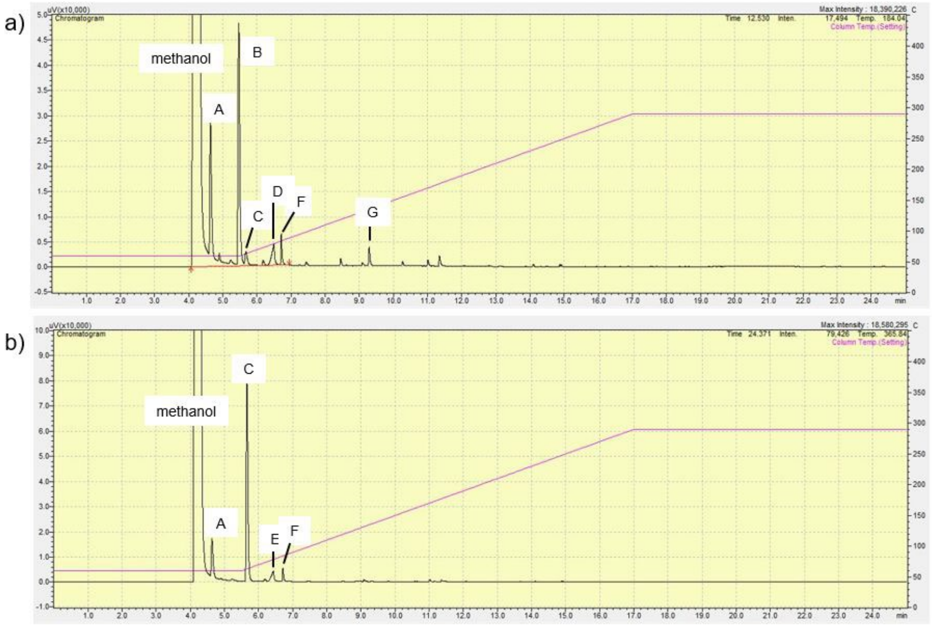

Figure 2: Representative gas chromatograms of product mixtures. Pink line represents a GC oven temperature. The main product are: A – methylal, oxidation product of methanol; B – methyl acrylate (5); C – methyl propanoate (7); D – acrylic acid (4); E – propanoic acid.

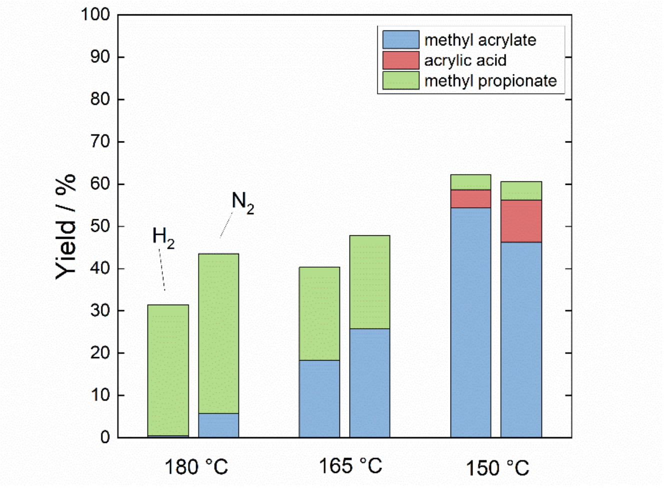

Figure 2: Yields of DODH products after 10 and 72 h of glyceric acid over Re/C in methanol at different reaction temperatures and under either inert N_2 gas or reducing H_2 gas atmosphere of 5 bar_g

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3.3 Reaction over time

All samples were measured with GCMS. By stopping the reaction at shorter intervals, it becomes possible to obtain other products as well. The results are represnted in the Figure 3. To gain a deeper understanding of the reaction mechanism and kinetics, microkinetic models will be employed in future studies.

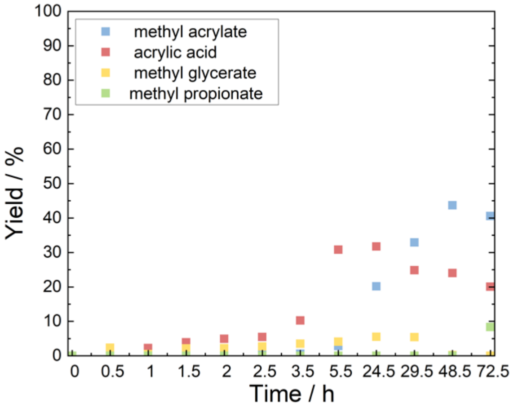

Figure 3: Example of one reaction with yields over time of deoxydehydration products over Re/C (Riogen) catalysts in methanol at T = 150°C, 5 bar_g, N_2 atmosphere. Reaction conditions: 100 mg of glyceric acid, 45.0 mL methanol, 140 mg catalyst, 150 °C, 5 bar N2, 72 h.

4 Conclusion

This study demonstrates that the Re-catalyzed deoxydehydration (DODH) of glyceric acid is a promising and sustainable method for converting glycerol-derived glyceric acid into acrylates. The reaction was successfully carried out using Re/C, surpassing typical homogeneous catalysts. The process, conducted in alcohols that also act as reducing agents, eliminates the need for hazardous reagents like H_2. Acrylic acid readily form alkyl acrylates with alcohols, and different alcohols enable the production of a variety of alkyl acrylates. The highest yield of methyl acrylate (>45 %) was achieved over Re/C at 150 °C in methanol after 72 hours.

This approach not only improves acrylate production efficiency but also opens new research directions. Future work should focus on enhancing catalyst activity, selectivity, stability, and reusability, as well as applying microkinetic models to better understand and optimize acrylate formation.

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