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POSTER COMMUNICATION

Continuous recycled packed bed reactor technology: effect of liquid flowrate on arabinose oxidation

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Abstract
The catalytic oxidation of arabinose to arabinonic acid was investigated in a recycled packed bed reactor to address pH control issues in continuous processes. Packed bed reactors are pivotal in the valorization of biomass, making the shift from batch to continuous systems critical for industrial applications. The setup used 2.1% Au/γ-alumina catalyst extrudates and incorporated a tandem reactor system with a liquid recycling loop to maintain a controlled pH of 8, ensuring optimal reaction conditions. Experiments were conducted at a reactor temperature of 70 °C, with liquid flow rates of 40 and 70 mL/min. The results demonstrated that the liquid flow rate significantly influences arabinonic acid production, particularly during the initial stages, where the overall reaction rate is flow rate dependent. The higher flow rate (70 mL/min) resulted in faster arabinonic acid formation, attributed to increased reactant-catalyst contact and improved mass transfer, which also mitigated potential catalyst deactivation. These findings highlight the importance of flow rate optimization for enhanced sugar acid yields in continuous reactor systems and underscore the need for further research to optimize the reactor design and operation.

Keywords
arabinose, flow rate, extrudates, gold, oxidation

1. INTRODUCTION

Packed beds are among the most used reactors in many sectors of chemical industries, including valorization of biomass. In this context, catalytic oxidation of the monomeric sugars extracted from hemicellulose biomass to sugar acids is an attractive way to valorize biomass in areas with a high forest coverage such as Northern European countries. Extensive research on this reaction (Correia et al., 2019; Kusema et al., 2011; Simakova et al., 2011; Smolentseva et al., 2011; van der Klis et al., 2018) has been published based on batch mode experiments. However, to approach the industrial reality, intensive research on continuous systems and catalyst extrudates is necessary.

The shift from batch to continuous operation leads to an uncontrolled pH in the system, thereby reducing the sugar acid selectivity. To maintain the pH control in a continuous system, this study incorporated a tank reactor for pH regulation into the reactor setup, along with a pump for recycling the liquid phase. In this work, the aim was to reveal the effect of liquid flowrate on the conversion of arabinose using the tandem reactor system.

2. METHODS

Powdered 2.1%Au/γ-alumina catalyst was synthesized by the homogeneous deposition–precipitation method described previously (Demidova et al., 2013; Simakova et al., 2023). The oxidation of arabinose was conducted in semi-batch mode with a constant flow of molecular oxygen, regulated by a gas flow controller (Brooks 5850S). The setup included a laboratory-scale glass column with a heating jacket connected with a mechanically stirred tank reactor. The reactor temperature was maintained at 70 °C with isothermal operation ensured by two thermocouples allowing a temperature variation of about 0.02 °C. The pH was controlled at 8 using a Metrohm Titrando 907 and 1 M NaOH solution. The liquid volume was 150 mL with an L-arabinose concentration of 0.133 M (Sigma-Aldrich, $\geq$ 99%). Samples were periodically withdrawn and analyzed using HPLC to determine reactant and product concentrations. Two flowrates were tested (40 and 70 ml/min). Fresh catalysts were used in the experiments.

3. RESULTS

The obtained results reveal a pronounced effect of flowrate on the efficiency and dynamics of arabinonic acid formation. At a higher flow rate of 70 mL/min, a rapid increase in the arabinonic acid concentration was obtained, approaching a maximum value of approximately 0.06 M within the first 100 minutes. The subsequent plateau indicates that the reaction rate decreases significantly as the system approaches a steady-state concentration. This behavior suggests that, under these conditions, the reaction becomes limited either by the substrate availability at the catalyst surface or by the intrinsic reaction kinetics of the catalyst extrudates. The early onset of saturation indicates that the catalytic sites

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become saturated or that the product formation reaches an equilibrium state relatively quickly.

In contrast, at the lower flow rate of 40 mL/min, the concentration of arabinonic acid increases steadily and does not exhibit a plateau over the 250-minute duration. This more gradual and linear increase suggests that the reaction is primarily kinetically limited, with mass transfer effects influencing the overall reaction environment but not dictating the reaction rate. The lower flow rate likely reduces the effectiveness of reactant transport to the catalytic surface, resulting in a slower and more prolonged accumulation of arabinonic acid.

The observed differences between the two flow rates underscore the significance and interaction of mass transfer and flow dynamics in the catalytic sugar oxidation using extrudate catalysts. At 70 mL/min, the enhanced flow likely improves the mass transfer, thereby facilitating a higher initial rate of the reactant delivery to the active sites of the catalyst. This leads to a rapid reaction and accumulation of arabinonic acid, but the approach towards the equilibrium or substrate limitations eventually slows down the further product formation. This kind of behaviour is characteristic for systems where the catalytic efficiency is high, but the reaction rate eventually becomes constrained by product inhibition or depletion of reactants at the catalyst interface.

At the lower flow rate of 40 mL/min, the more limited transport of reactants to the catalyst surface results in sustained but slower arabinonic acid production. The reaction kinetics under these conditions appear to be influenced predominantly by mass transfer limitations, emphasizing the critical role of flow rate in maintaining effective reactant-catalyst interactions. This observation indicates that optimizing the flow conditions is crucial for maximizing the catalytic efficiency, especially when using extrudate-based catalysts, where external and internal mass transfer resistances can play a significant role.

4. CONCLUSIONS

The results showed that the flowrate has also an impact on the production of arabinonic acid in a recycled tandem reactor system. This is because of the contact time between the reactants and the catalyst which is related to the flow rate, which plays a crucial role. Increasing the flow rate reduces the contact time but improves mass transfer efficiency, enhancing acid production and preventing catalyst deactivation by maintaining a dynamic reaction environment.

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Continuous recycled packed bed reactor technology: effect of liquid flowrate on sugar oxidation

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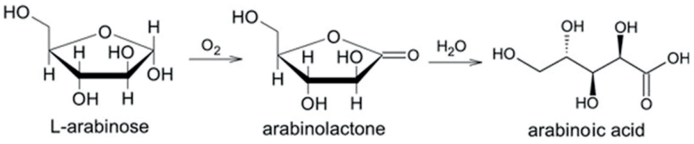
MOTIVATION

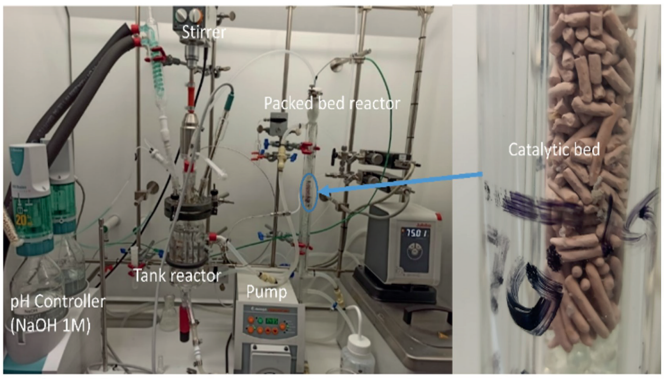
Continuous catalytic oxidation of monomeric sugars extracted from hemicelluloses appearing in biomass is regarded as an attractive way to valorise biomass. The shift from batch to continuous operation leads to an uncontrolled pH and flowrate in the system. The proposed system solves this issue by adding a tank reactor and pump to recycle the liquid flowrate. In the current work, the aim was to study the effect of liquid flowrate on the conversion of arabinose using this tandem reactor system.

REACTION STOCHIOMETRY AND CONDITIONS



- T= 70 °C
- P= 1 atm
- pH= 8
- Stirring speed = 700 rpm

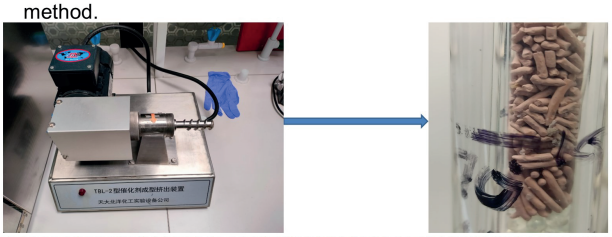
REACTOR SETUP



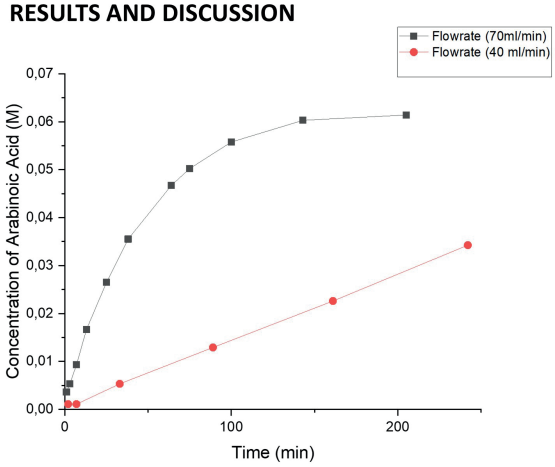
Photograph of the experimental setup for sugar oxidation in the recycled packed bed reactor

CATALYST

- Gold on alumina (2.1%) catalyst extrudates were used.
- Catalysts were prepared by extrusion using 2.1 wt% Au/alumina in the powder synthesized by homogeneous deposition–precipitation method.



RESULTS AND DISCUSSION



Concentration of arabinoic acid at various liquid flow rates

The results showed that the flowrate has also an impact on the production of arabinoic acid in a recycled tandem reactor system. This is because of the contact time between the reactants and the catalyst is proportional to the liquid phase flowrate which enhanced the acid production and even prevented eventual catalyst deactivation.

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