Kinetic study, process design and techno-economic assessment of a liquid phase furfuryl alcohol production

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Highlights
- Process: furfural extraction, reaction (chromite free catalyst) & purification
- Competitive furfuryl alcohol MSP: 1300 $/t in eco-friendly process
- A Langmuir-Hinshelwood kinetic model with 2 active sites (metal–acid) is developed
- Low H_2O concentrations compete for sites with furfural but without side-reactions

1. Introduction

The conventional industrial process for FOL production involves the hydrogenation of furfural, a step essential in its synthesis. However, existing processes involve energy-intensive purification steps and the usage of chromite based catalyst. Our study focuses on refining the FOL production process to enhance competitiveness and environmental sustainability. We aim to optimize the process by minimizing energy-intensive purification steps, reducing chemical usage, and replacing hazardous catalysts. Our proposed integrated process operates in the liquid phase and starts from non-purified aqueous furfural obtained through conventional steam-stripping hydrolysis reactors. This innovative approach involves liquid-liquid extraction, reaction, and purification steps, with 2-methyltetrahydrofuran (MTHF) chosen as the extracting and reaction solvent due to its stability, high partition coefficient for FUR, and ability to promote desired hydrogenation reactions. Additionally, we explore chromite-free copper-based catalysts, CuZnAl, renowned for its high activity and stability at an industrial scale. A kinetic study will analyze the effect of the presence of water in the reaction medium, and through the calculated kinetic rates and process optimization, we seek to develop a technically viable and environmentally friendly alternative for FOL production. Finally, our economic analysis evaluates the process's competitiveness and identifies key factors influencing the minimum selling price of FOL.

2. Methods

2.1. Kinetic study

The study conducted the liquid-phase FUR reaction using a commercial copper-based catalyst (HiFUEL® W220) (52 wt% CuO, 30 wt% ZnO, 17 wt% Al_2O_3, and 1 wt% activated carbon). Prior to testing, the catalyst underwent grinding, sieving, and pretreatment under a reductive hydrogen atmosphere. Activity tests were conducted in 50 mL autoclave reactors containing a 10 ml solution of 10-15 wt% FUR in MTHF. Some experiments included water (1-5 wt%). The FUR-to-catalyst weight ratio varied between 10 and 20, depending on the reaction temperature (105-135 °C). Reactors were pressurized to maintain a constant hydrogen partial pressure of 30 bar. After the set reaction time, stirring ceased, and products were analyzed by a GC-FID, using 1-pentanol as an internal standard.

2.2. Process modeling

Aspen Plus and Aspen Custom Modeler V12 software were utilized for process modelling. UNIQUAC-HOC was the property method selected. The purchased equipment costs were obtained from the Aspen Process Economic Analyzer V12, which uses a 1st quarter 2021 pricing. The OpEx was estimated by the addition of the cost of the raw materials, the utilities, the catalyst and the added costs.

3. Results and discussion

In the kinetics study a LHHW-based model has been proposed in this research and the reaction was studied at three different temperatures (105 °C, 120 °C, and 135 °C). The initial reaction concentrations

were stablished as the outlet concentrations obtained after the LL extraction of FUR+H_2O stream by MTHF (79.7 wt% MTHF, 15.0 wt% FUR, and 5.3 wt% H_2O). The effect of the presence of water was studied. The results showed a high selectivity even at near complete conversions and follow a dual site LHHW model behavior. The presence of water reduces the reaction rate (see Fig 1) by competing for active sites with FUR and FOL but it does not promote the formation of other by-products.
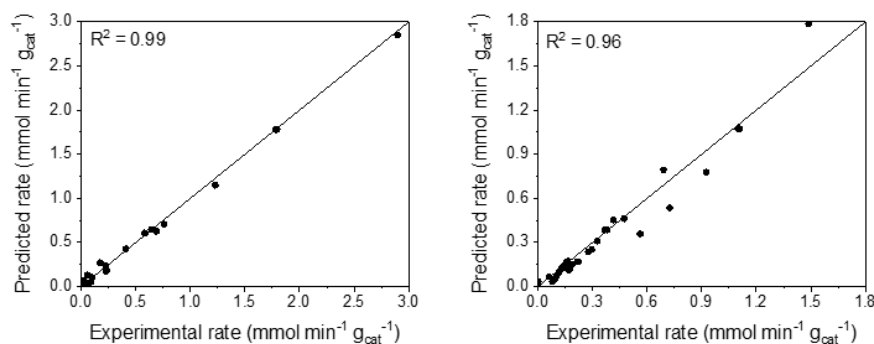

Figure 1. Comparison of experimental and predicted rates at various temperatures without water (left) and with water in concentrations ranging 1-5 wt% (right).

Various process configurations were assessed. The presence of water in the reacting solution lowers reaction rates, necessitating additional reactors with longer residence times to achieve 97% FOL yield. Water removal by pervaporation (PV) prior to reaction section reduces both, the reactor count and residence times, but PV module costs offset reaction section savings. MF separation from MTHF solvent is costly, making hydrogenation of MF to MTHF the most economical. Consequently, the proposed process achieves net solvent production. When water has been removed, the produced MTHF purity is higher than 99 wt%.
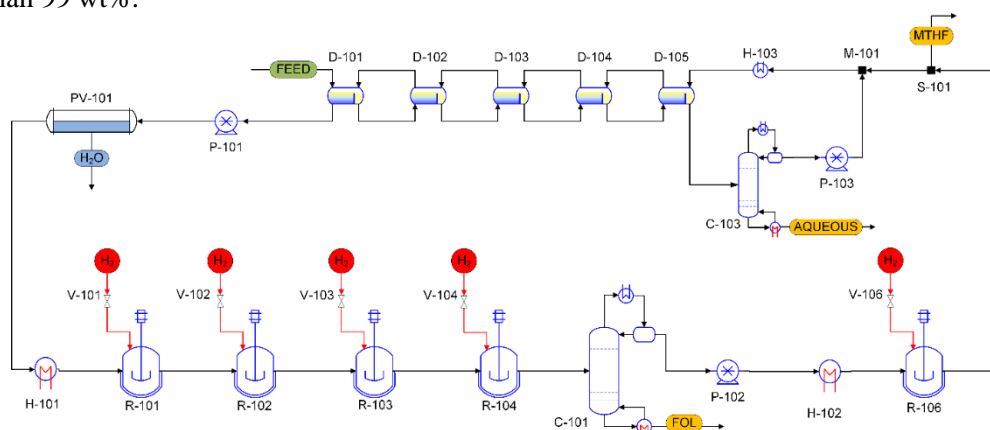

Figure 2. Flowsheet diagram of CASE III (conversion of MF into MTHF), incorporating the PV module.

4. Conclusions

Activity tests with commercial CuZnAl catalyst demonstrate high selectivity to the target product, with MF as the only detected by-product in minimal quantities. The kinetic study validates a double-site Langmuir-Hinshelwood model, considering the impact of low water content, which competes with FUR and FOL for active sites, although it does not promote the formation of additional by-products. Reactor optimization achieves a 97% FOL yield. For final purification, transforming MF into MTHF proves the optimal method for solvent recirculation, preventing MF accumulation and yielding a net production of the green solvent. Economic analysis indicates a promising FOL MSP of $1,326/t, just 30% higher than the considered FUR price. Moreover, the process addresses key environmental concerns by minimizing energy consumption in purification, reducing toxic waste with a chromite-free catalyst, and co-producing a green solvent, thus enhancing overall sustainability in furfural-based processes.

Keywords
Kinetic study; Process intensification; Furfuryl alcohol; Biorefinery