Sustainable synthesis of ketals from ethyl levulinate and glycerol

Francesco TADDEO[*,1], Rosa VITIELLO[1], Rosa TURCO[1], Riccardo TESSER[1], Vincenzo RUSSO[1], Martino DI SERIO[1]
[1]*University of Naples Federico II, Chemical Sciences Department, Via Cintia, Napoli, Italy.*
** francesco.taddeo@unina.it*

Significance and Relevance

The use of renewable sources offers significant environmental and health benefits by replacing fossil-derived products with sustainable chemicals from biomass. Among these, ketals derived from levulinic acid and its derivatives have emerged as promising compounds with several applications, including fuel additives, plasticizers, solvents, and precursors for biopolyol and polyurethane synthesis. This study explores the catalytic synthesis of ketals, comparing the performance of various catalysts to identify those with the best characteristics. A kinetic investigation was conducted in both batch and continuous reactors, providing the data for a possible future scale-up of the process.

Preferred and 2nd choice for the topic: 1. Green Chemistry and biomass transformation, renewable resources conversion; 2. Circular economy.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral only

Introduction and Motivations

The development of sustainable chemical processes through biomass valorization is a key strategy to replace fossil derived chemicals with renewable alternatives. In this context, levulinic acid and its derivatives play an important role.[1] Among these, ethyl levulinate can be considered a particularly attractive compound, derived from biomass based raw material and ethanol, combining low production costs with the use of renewable resources. This makes it a valuable precursor for further chemical transformations. Glycerol, a by-product of biodiesel production, contributes to the sustainability of the process by enabling industrial waste valorization. The advantages in using the esters, such as ethyl levulinate, can be found in avoiding the occurrence of the competitive esterification reaction. The ketalization of ethyl levulinate with glycerol produces ketals, versatile compounds with numerous industrial applications, due to their valuable properties. It involves the formation of a five-membered ketal as the main product, in addition to a six-membered ketal and water.[2] Catalysis plays a fundamental role in this process, and both homogeneous catalysts (e.g., mineral acids) and different heterogeneous catalysts are commonly employed. While homogeneous catalysts often ensure high conversions, heterogeneous catalysts offer significant environmental and operational advantages, including reusability, resistance to high temperatures, and simplified recovery processes.[3] This study focuses on the kinetic investigation of ethyl levulinate ketalization with glycerol in the presence of heterogeneous catalysts. A catalytic screening was made in order to identify those with the most promising properties, followed by kinetic studies. Experiments were conducted in both batch and continuous reactors to explore the effect of operating conditions on reaction rates to provide data useful for the possible scale-up of the process.

Materials and Methods

The kinetic batch experiments were performed in a 0.3 L Hastelloy reactor under varying conditions of temperature, stirring rate, ethyl levulinate/glycerol molar ratio and catalyst loading. For continuous experiments, a milli-reactor 8 cm long with an internal diameter of 0.3 cm, packed with the heterogeneous catalyst, was employed. In the continuous setup experiments were made at different temperatures and volumetric flowrates. Samples were analyzed through ^{1}H-NMR in order to evaluate the reached conversion.

Results and Discussion

The ketalization of ethyl levulinate with glycerol was investigated through a comprehensive screening of various catalytic systems in order to identify the most promising ones. Kinetic investigations were performed in a batch reactor, varying the operative conditions to assess their influence on the reaction rate. Among the tested catalysts, Strata-XL-C showed outstanding performance. Experiments were performed by varying stirring rate to evaluate the possible presence of the fluid-solid mass transfer resistance, while temperature variation allowed the determination of activation energy and reaction enthalpy, obtaining higher conversions at higher temperatures, confirming the endothermicity of the reaction. The ethyl levulinate/glycerol molar ratio was varied to investigate its influence on the reaction rate and on the thermodynamic plateau, and catalyst loading to assess the contribution of autocatalysis and the effect of the catalyst on the initial reaction rate. With increased catalyst loading, equilibrium was achieved in a short time, less than 10 minutes, highlighting the catalyst efficiency. Continuous experiments were conducted in a milli-reactor under varying temperatures and flow rates to verify the process feasibility in continuous operation, collecting data useful for model validation.

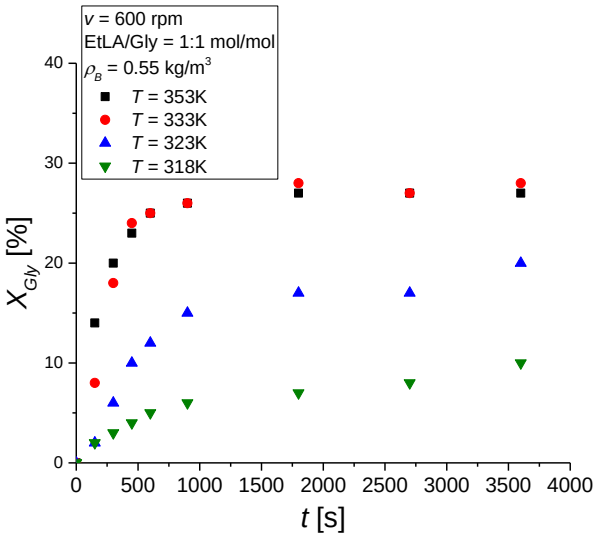

Figure 1 Temperature effect for experiments promoted by Strata-XL-C fixing, v = 600 rpm, ρ_B = 0.55 kg/m^3, EtLA/Gly = 1:1 mol/mol.

References

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