Kinetic Investigation of Oleic Acid Esterification with Trimethylolpropane to Optimize Bio-Based Lubricant Synthesis from Used Cooking Oils (UCO)

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Highlights

- Oleic acid esterification with TMP display a strong autocatalytic behaviour.
- The kinetic model accurately simulates system's behavior, predicting reaction product profiles.
- Significant catalytic effect at high temperatures were observed with >1 wt% catalyst.

1. Introduction

There is a new interest in the use of lubricants obtained from waste vegetable oils due to growing concern over the environmental impact of petroleum-derived products. This renewed focus aligns with the principles of the circular economy, promoting the repurposing of waste materials for sustainable applications. These bio-based lubricants, primarily composed of fatty acid alkyl esters, are characterized by low toxicity and high biodegradability [1].

The esterification of oleic acid (OA) with trimethylolpropane (TMP) is crucial for synthesizing trimethylolpropane trioleate, a commercially significant bio-based lubricant. Oleic acid is most frequently used to produce bio-based lubricants due to its huge abundance in the vegetable oils [2]. On the other side, branched polyols, such as trimethylolpropane (TMP), have been widely used to produce polyol esters with enhanced tribological properties as well as thermal and oxidation stability [3]. A comprehensive knowledge of the kinetic aspects involved in this reaction holds paramount significance in the optimization of the synthesis process for bio-based lubricants derived from more complex blends, i.e. used cooking oils (UCO).In fact, oleic acid, selected for its prevalence in vegetable oils, acts as a representative of these oils. Despite its importance, the kinetics of this reaction is underexplored, especially when promoted by heterogeneous catalysts.

This research work deals with the kinetics of OA esterification with TMP in a batch reactor. The study compares results from the uncatalyzed reaction with those obtained using a heterogeneous catalyst (such as tungsten oxide supported on silica, etc.). Specifically, the effects of temperature, catalyst bulk density, and reactants' molar ratios on esterification kinetics were explored. Furthermore, a kinetic model was developed to describe the system's behavior under the studied conditions. The experimental data underwent nonlinear regression analysis to derive kinetics and thermodynamic parameters.

2. Methods

The kinetics experiments were conducted using a jacketed batch reactor. The reactor contained TMP and the prepared catalyst, and agitation was sustained through a mechanical stirrer. Upon reaching the target temperature, pre-heated oleic acid was injected into the reactor using a pressurized syringe, enabling the collection of a time zero sample at specified temperature. To prevent the partitioning of water between the gas and liquid phases, the reactor pressure was held constant at 20 bars. Blank tests, performed without the catalyst, were carried out in the same manner to provide a comparative baseline for the experimental results. The conversion of oleic acid was calculated from the acidity number which was evaluated by acid-base titration of the collected sample with an ethanolic solution of KOH. ^{1}H-

NMR technique was adopted to determine the amount of mono-, di- and tri-esters in order to get the products' distribution.

3. Results and discussion

The temperature's influence on reaction kinetics was explored from 80°C to 180°C. Higher temperatures resulted in increased oleic acid conversion (Figure 1A). A strong autocatalytic effect of the reaction due to the acidic nature of OA which can catalyze its own esterification was observed and the influence of catalyst bulk density revealed a significant catalytic effect with catalyst amounts exceeding 1 wt%.

The effect of the molar ratio between reactants was investigated for both uncatalyzed and catalyzed reactions. Higher alcohol hydroxyl group excess led to faster kinetics and increased oleic acid conversion but decreased triesters selectivity. It's worth noting that a substantial concentration of triesters is achievable only when the reaction is conducted under stoichiometric conditions between the acid and the functional groups of the polyol (Figure 1B).

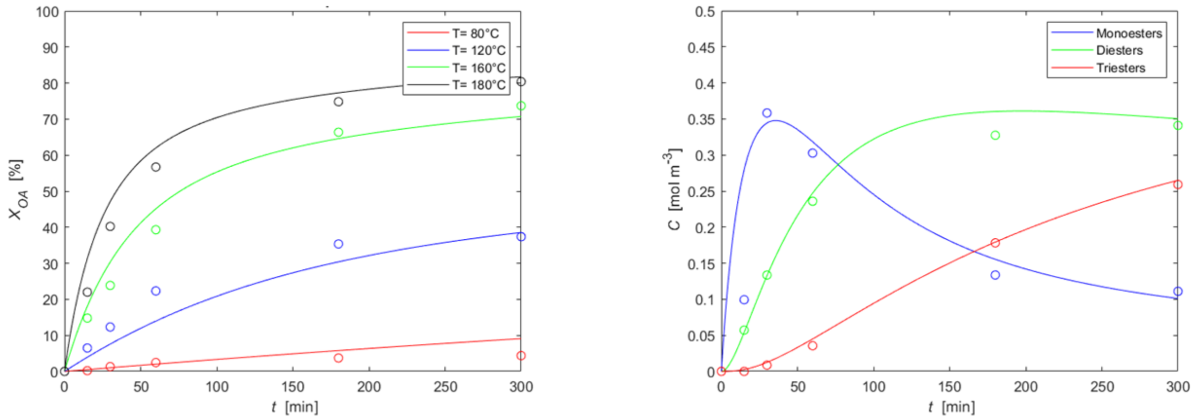

Figure 1- A) Oleic acid conversion profiles at different temperatures. **B)** Mono-, di- and tri-esters concentration profiles obtained at T=180°C and with OA/TMP molar ratio equals to 3/1. In both figures, symbols represent experimental data and lines are the results of the model's fit.

4. Conclusions

The kinetics of oleic acid esterification in a batch reactor with and without a heterogeneous catalyst were investigated in this work. The developed kinetic model accurately described experimental observations, allowing for estimating kinetics and equilibrium constants essential for scaling up the process. These findings provide a good foundation for future studies, such as switching to a continuous system and expanding the study to include used cooking oils (UCO).

References

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Keywords Fatty acid esterification, Heterogeneous catalysis, synthesis of polyol esters; bio-based lubricants.