Kinetic Modeling Comparison on the Epoxidation of Vegetable Oils and their corresponding Fatty Acid Methyl Ester

Yudong Meng[1,2], Nasreddine Kebir[2], Sebastien Leveneur[1]*

1 INSA Rouen Normandie, UNIROUEN, Normandie Univ, LSPC, UR4704, F-76000 Rouen, France ;

2 Univ Rouen Normandie, INSA Rouen Normandie, CNRS, PBS UMR 6270, F-76000 Rouen

*Corresponding author: sebastien.leveneur@insa-rouen.fr

Highlights

- The reaction rate of epoxidation by propionic acid for CSO was faster than CSO-FAME.
- The reaction rate of the ring-opening reaction of epoxide group for CSO-FAME was faster than CSO.
- Epoxidation rate constant ratio of CSO over CSO-FAME decreases over temperature.

1. Introduction

Vegetable oils (VO) and their functional derivatives can be considered good alternatives to replace petroleum-derived products due to their low toxicity, renewability, and biodegradable properties [1]. One of the best approaches to functionalize vegetable oils is the epoxidation of the unsaturated groups [2]. The Prileschajew approach is the most common method to generate epoxidized vegetable oil using in situ-produced percarboxylic acids [3]. To overcome the negative effects of performic and peracetic acids, the epoxidation reaction of vegetable oil by perpropionic acid over a solid acid catalyst was investigated and a reliable cottonseed oil epoxidation model was found [4]. The transesterification of vegetable oils into fatty acid methyl esters (FAME) could decrease steric hindrance during epoxidation[5]. However, few studies compare the kinetics of epoxidation of vegetable oils and their corresponding FAME and none of them have proposed such a comparison on kinetic modeling of epoxidation by propionic acid over solid catalysts. Hence, a deeper investigation was carried out for the comparison of kinetic modeling on the epoxidation of cottonseed oil (CSO) and its corresponding fatty acid methyl esters (CSO-FAME) to understand the relationship and the reactivity difference between VO and FAME. A systematic kinetic modeling comparison between CSO and CSO-FAME was explored in this study to help predict the epoxidation of VO with propionic acids by only knowing the fatty acids composition.

2. Methods

The esterification reactions were operated as follows: 50 mL of methanol with 2.1g NaOH was added to 200 g preheated vegetable oils in the reactor for 1.5h. The FAME was collected after being washed three times with distilled water.

The epoxidations of CSO and CSO-FAME by propionic acid were operated as follows: A mixture of organic phase, hydrogen peroxide, distilled water, and amberlite IR-120 was added to the reactor for 6 h. The epoxidized VO and FAME samples were collected over time.

The concentration of double bond and oxirane ring (epoxide group) in the organic phase and the concentration of acids and hydrogen peroxide in the aqueous phase were measured by an automatic titrator. Athena Visual Studio was used for the modeling.

3. Results and discussion

As displayed in Figure 1, the reaction rates of epoxidation for CSO and CSO-FAME increase with the temperature from 50 to 70 °C. The ring-opening reaction can be observed from the concentration of DB and EP at the end of the epoxidation kinetic profiles. The production rate of the epoxidized group is faster for CSO than for CSO-FAME, and the final production of the epoxidized group is higher for CSO than for CSO-FAME. This observation is a priori surprising because one could expect that the double bond from CSO-FAME is more accessible than the one from CSO, and thus rates of double bond epoxide

production should be faster. This kinetic observation could be explained by the fact that the ring-opening reactions and consecutive oligomerization reactions produce different oligomer structures between ECSO and ECSO-FAME.
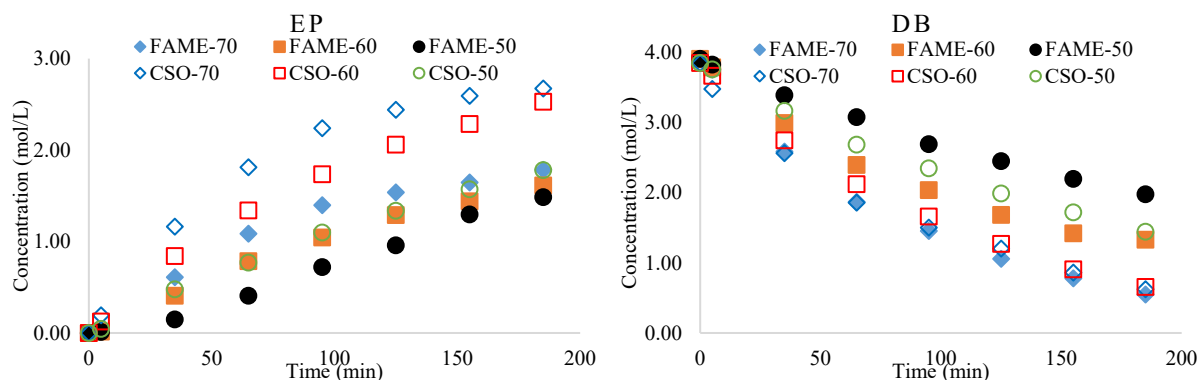

Figure 1. Effects of reaction temperature on the epoxidation of CSO and CSO-FAME by perpropionic acid.

The reaction rate constant (k) ratios for the kinetic model of epoxidation between CSO over CSO-FAME are displayed in Figure 2. Generally, the reaction rate constant increases over the temperature, but the epoxidation ratio between CSO over CSO-FAME decreases which means the *kep* increased faster in CSO-FAME than CSO. Lower densities and viscosities in CSO-FAME could provide lower steric hindrance during the epoxidation. Meanwhile, the benefits of the epoxidation could be also applied to the ring-opening reactions, so similar situations could be also found in *kro*.
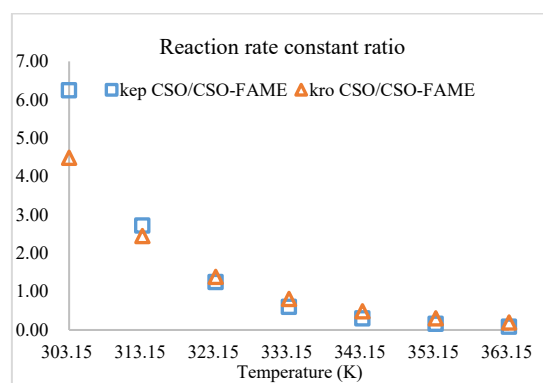

Figure 2. Reaction rate constant ratio of epoxidation and ring-opening for CSO over CSO-FAME

4. Conclusions

The reaction rate of epoxidation by propionic acid for CSO was faster than CSO-FAME. The reaction rate of ring-opening reaction of epoxide groups for CSO-FAME was faster than CSO. Two reliable kinetic models for the epoxidation of CSO and CSO-FAME were found. Epoxidation rate constant ratio of CSO over CSO-FAME decreases over temperature.

References

[1]   G. Lligadas, J. C. Ronda, M. Galià, and V. Cádiz, Mater. Today, 16 (2013) 337–343.
[2]   W. Y. Pérez-Sena, X. Cai, N. Kebir, L. Vernières-Hassimi, C. Serra, T. Salmi, S. Leveneur, Chem. Eng. J., 346 (2018) 271–280
[3]   J. Wisniak, E. Navarrete, Ind. Eng. Chem. Prod. Res. Dev., 9 (1970) 33–41
[4]   Y. Meng, N. Kebir, X. Cai, S. Leveneur, Catalysts, 13 (2023) 274
[5]   T. S. Omonov, E. Kharraz, and J. M. Curtis, RSC Adv., 6 (2016) 92874

Keywords

"epoxidation", "kinetic model", "vegetable oils", "fatty acid methyl ester"