Revealing Kinetics Parameters for Delignification of Oil Palm Empty Fruit Bunch through Ozonolysis Pre-treatment via Sparse Nonlinear Optimizer

Zhahidah Husna Hassan[1], Amnani Shamjuddin[1], Wan Nor Nadyaini Wan Omar[1], Pavitra Thevi Arnandan [1], Mohd. Asmadi Mohammed Yussuf [1], Nor Aishah Saidina Amin [1*], Sharul Nizam Hasan[2], Himiyage Chaminda [3], Hemaka Badulsena[3]

1 Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia; 2 Reservoir Management Group (RMG), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia; 3 Department of Chemical Engineering, Loughborough University, LE11 3TU, UK.

**Corresponding author: noraishah@cheme.utm.my*

Highlights

- Limited study on kinetics parameters estimation of ozonolysis pre-treatment, which are crucial to understand the reaction involved throughout the process.
- A reaction model was developed using COMSOL Multiphysics® software, simulating a lab-scale well-mixed OzBiONY® reactor.
- Parameter Estimation tools were employed to evaluate kinetics parameters for ozonolysis pre-treatment and solved through the Sparse Nonlinear OPTimizer (SNOPT) solver.
- The reaction model developed provided insights on plausible pathway for the delignification reaction during ozonolysis pre-treatment.

1. Introduction

Ozonolysis pre-treatment emerges as a promising eco-friendly alternative due to its robust oxidative features, facilitating simultaneous delignification and oxidation [1]. This process has demonstrated significant improvements in lignin degradation [2] and glucose yield [3]. However, a comprehensive understanding of the underlying reaction mechanisms during pre-treatment remains limited. The proposed model for the ozonation of wheat and rye straw exhibited conflicting results compared to experimental data [4], prompting the introduction of the cuticle layer theory to enhance the model [5]. The kinetics of ozone consumption revealed a two-phase behavior, starting with a falling rate and transitioning to a constant rate [6]. While previous investigations, utilizing COMSOL Multiphysics software, studied the combined model of [4] and [5] on Empty Fruit Bunch (EFB) biomass, focusing on the impact of pressure drop and ozone velocity on the ozonolysis reaction, these studies were confined to the kinetic analysis within a packed-bed reactor system. Additionally, none of the studies provided a framework for estimating kinetic parameters. Therefore, this study aims to assess the performance of ozonolysis on EFB biomass within a semi-batch well-mixed reactor using COMSOL Multiphysics® software. This exploration is anticipated to contribute valuable insights into sugar recovery production from biomass technology.

2. Methods

100g of Empty Fruit Bunch (EFB) with a moisture content of 40% underwent treatment using the innovative OzBiONY® system under optimal operating conditions. The concentrations of ozone outlet, insoluble lignin (iLg), and soluble lignin (sLg) were systematically monitored at various time intervals to generate kinetics data. A mathematical model for the simplified ozonolysis reaction was developed using the Chemical Reaction Engineering Module within the COMSOL Multiphysics® software. The chemical reactions inherent to ozonolysis pre-treatment were incorporated into the numerical model to visualize the variations in ozone, iLg, and sLg concentrations throughout the process. The unknown parameters were determined using the Parameter Estimation tools and the Optimization SNOPT solver.

3. Results and discussion

From the experimental findings, it was evident that the concentrations of ozone, insoluble lignin (iLg), and soluble lignin (sLg) decreased over time. This observation confirmed the taking place of delignification during the pre-treatment of EFB biomass. The reaction model for ozonolysis pre-treatment provided the values of the unknown parameters, namely k_1, k_2, α_2, α_3, and α_5, as outlined in Table 1. A graphical representation of ozone, iLg, and sLg concentrations over time was generated based on the kinetics data, aligning with the trend observed in the experimental work, as depicted in Figure 1.

Table 1. Concentration profile of ozone, sLg and iLg against time.

Parameters	k_1 (m^3/s.mol)	k_2 (m_3/s.mol)	α_2	α_3	α_5
Estimated value	4.817	100.000	10.000	10.000	2.4922

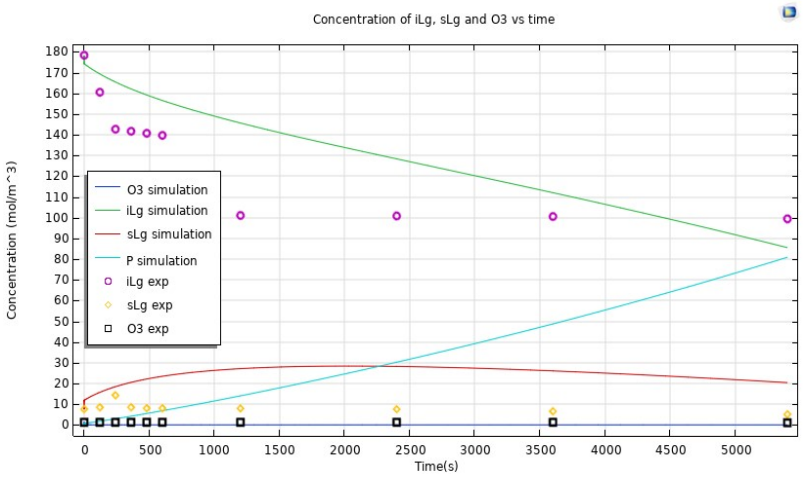

Figure 1. Concentration profile of ozone, sLg and iLg against time.

4. Conclusions

In summary, the examination of the OzBiONY® system under optimal conditions affirmed its effectiveness in degrading lignin. The development of a successful reaction model for the ozonolysis of EFB biomass was achieved. The kinetic model demonstrated a good fit with the experimental data, enabling the assessment of kinetic parameters and the prediction of the ozonolysis reaction within a semi-batch well-mixed reactor.

References

[1] Ab Rasid, N.S., Zainol, M.M., & Amin, N.A.S., 2020. Pre-treatment of agroindustry waste by ozonolysis for synthesis of biorefinery products. Refining Biomass Residues for Sustainable Energy and Bioproducts: Technology, Advances, Life Cycle Assessment, and Economics, pp. 303-336.

[2] Omar, W. N. N. W. & Amin, N. A. S., 2016. Multi response optimization of oil palm frond pre-treatment by ozonolysis. Industrial Crops and Products,85, 389-402.

[3] Shamjuddin, A., Ab Rasid, N., Michele Raissa, M., Abu Zarin, M., Wan Omar, W.N.N., Syahrom, A., Mohd Szali Januddi, M., & Saidina Amin N.A., 2021. Kinetic and dynamic analysis of ozonolysis pre-treatment of empty fruit bunch in a well-mixed reactor for sugar production. Energy Conversion and Management, 244.

[4] García-Cubero, M.T., Palacín, L.G., Gonzalez-Benito, G., Bolado, S., Lucas, S., Coca, & M., 2012. An analysis of lignin removal in a fixed bed reactor by reaction of cereal straws with ozone. Bioresource Technology, 107, pg 229– 34.

[5] Bhattarai, S., Bottenus, D., Ivory, C.F., Gao, A.H., Bule, M., & Garcia-Perez, M., 2015. Simulation of the ozone pre-treatment of wheat straw. Bioresource Technology, 196, 78–87.

[6] Li, X., Sun, C., Zhou, B., & He, Y., 2015. Determination of hemicellulose, cellulose and lignin in moso bamboo by near infrared spectroscopy. Scientific Reports, 5 (1), p. 17210.

Keywords

Ozonolysis; Kinetic Study; SNOPT; Parameter Estimation