Modelling of ozone multiphase flow behaviour in an ozonolysis pretreatment reactor

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Abstract. Ozonolysis pretreatment of lignocellulosic biomass (LB) is envisaged as a green and effective method to selectively remove lignin for subsequent bio-based processing. Herein, this study investigates the ozone multiphase flow behaviour of an ozonolysis pretreatment reactor for lignin degradation of oil palm empty fruit bunch (EFB). A coupled transport-reaction model is simulated using Computational Fluid Dynamic (CFD) via COMSOL Multiphysics® software to visualize the ozone multiphase flow behaviour in non-porous and porous bed regions. Numerical findings indicate the pressure drop across porous bed linearly increases with superficial ozone velocity. Simulation results also reveal that the relative pressure across the biomass bed reduces by reducing the biomass bed length. The present work provides preliminary insights for ozonolysis reactor design and optimum operations of biomass pretreatment for up-scaling and commercialization purposes.

1. Introduction

Lignocellulose is the most abundant biopolymer available on earth as waste biomass. Lignocellulosic biomass (LB) from oil palm plantation, forestry, and agriculture sectors have huge potential to be utilized. Alternative and sustainable bio-based energy and chemicals derived from oil palm waste (OPW) or generally LB in a biorefinery could be a potential key to overcome the issue on waste management and create an opportunity to generate income in biomass industry [1]. The rigid and complex structure of LB hinder its conversion into higher value-added bio-based products. Therefore, pretreatment process is required to modify the lignocellulosic components by altering the structural arrangement and removing the lignin component to expose the internal structure of cellulose and hemicellulose for further reactions into sugars. Hence, the total yield of liberated sugars is enhanced in acid hydrolysis step [2]. In ozonolysis pretreatment, ozone is used as an oxidizing agent to selectively delignify the LB with minimal degradation of cellulose and hemicelluloses due to higher reaction rate of ozone with lignin [3]. The ozonation process also does not produce toxic compounds and can be performed at room temperature and atmospheric pressure, which reduces the capital and energy costs [4].

LB bed inside the ozone reactor comprised of a group of LB particles containing void spaces or pores (spaces between solid particles) where a liquid or a gas can pass through them. A porous bed is most often characterized by its porosity. The bed porosity commonly attributes from i) particle to column
diameter ratio [5], ii) particle size [6] and shape [7], iii) mechanical properties of the particles [8], iv) loading method [8], and v) the external agitation of the column or fluidization [9]. Pressure drop across the porous bed is one of the most important parameters in the design, scale-up, operation of packed bed reactors, and prediction of solid-liquid mass transfer. The effects of pressure drop on the reaction system should be properly accounted for since it is the key factor to indicate the success or failure of the reactor operation [10]. Hence, an elucidation of pressure drop across the porous bed inside the reactor can enable us to understand the ozone flow behaviours.

Although many studies have been conducted on ozonolysis, mathematical models, which explicitly predict delignification phenomena are rare and limited. Computational Fluid Dynamics (CFD) analysis with porous media formulation has been exploited in the simulation study of diffusive-reactive transport of ozone gas in rice grains [11], distribution and behaviour of ozone gas flow during pretreatment of wheat straw [12], effect of pretreatments in bubbling fluidized bed reactor [13], and solid phase flow structure in circulating fluidized bed combustion process [14]. Other studies include airflow simulation in rice storage system with different grain mass configurations and porosity [15] and the phosphine flow during wheat grain fumigation in leaky cylindrical silos [16].

Therefore, the purpose of this study is to develop a numerical model to simulate the ozone multiphase flow inside the fixed-bed reactor during ozonolysis pretreatment of oil palm empty fruit bunch (EFB). The mathematical model is developed to elucidate the effects of ozone inlet velocity and biomass bed length on the pressure drop across the porous bed. The CFD simulation is carried-out using finite element method (FEM) COMSOL Multiphysics® v5.3a software. The performance of ozonolysis reactor can be measured by predicting the pressure drop across the porous bed. Ozone inlet velocity and bed length are varied to study the influence of ozone flow rate and biomass loading, respectively in developing pressure drop during ozonolysis process. The simulation results could provide insights to improve the selection, design, optimization, and scaling-up of the ozonolysis pretreatment system for preparation of downstream process.

2. Methodology

2.1. Measurement of bulk density, \( \rho_s \), of empty fruit bunch (EFB)
The bulk density of EFB was determined according to the ASAE standard S269.4 DEC 91 [17]. EFB sample was filled into a 50 ml cylindrical container and further compacted to 10 cm in height. The weight of the EFB with the container was recorded. The net weight of the sample, \( W_s \), was calculated by subtracting the weight of empty container from the weight of EFB compacted container. The experiment was repeated for the moisture contents of 40\%, 30\%, and 20\%. The bulk density, \( \rho_s \), of the bed of EFB was calculated by dividing the weight of the sample, \( W_s \), by the volume of the container, \( V_s \), as equation (1):

\[
\rho_s = \frac{W_s}{V_s} \tag{1}
\]

2.2. Measurement of void fraction, \( \varepsilon \), of empty fruit bunch (EFB)
The void fraction, \( \varepsilon \), of the packed EFB was determined using two equal-volumes cylindrical containers in the laboratory via a volume displacement method. The first container was filled with water and the second container was filled with the EFB sample. Then, the water from the first container was continuously poured into the second container until the EFB became saturated. The volume of remaining water in the first container was recorded. The volume of voids, \( V_v \), was equal to the volume of water poured into the second container. The volume of water poured in the second container was the difference between the initial volume of water and the final volume of water. Meanwhile, the volume of solid, \( V_s \), was equal to the initial volume of container. The void fraction is calculated as equation (2):

\[
\varepsilon = \frac{V_v}{V_s} \tag{2}
\]
\[
\varepsilon = \frac{V_o}{V_s}
\]

2.3. Ozonolysis pretreatment of empty fruit bunch (EFB)
Ozonolysis pretreatment of EFB was conducted using a novel OzBiONY® technology system (Figure 1) consists of (1) oxygen cylinder tank, (2) ozone generator (model LAB 2A, Triogen, Scotland), (3) mass flow rate controller (Aalborg), (4) conventional semi-batch horizontal acrylic ozone reactor, (5) ozone monitor (Eco Sensors, UV-106M), and (6) ozone destructor. The system was set-up under a ventilation system. Prior to the experiments, 20 g of EFB sample was moistened with distilled water at 40 wt.% moisture content using gravimetric method (oven dried method). Then, the EFB was kept in the chiller for 24 hrs before conducting the ozonolysis pretreatment. The moistened EFB was placed in the ozone reactor which was connected to ozone generator and ozone destructor. The inlet and outlet ozone concentrations were measured by ozone monitors, while ozone feed flow rate was controlled by mass flowrate controller to ensure a steady flow into the reactor. At the end of the reaction, the ozone generator was switched off and the reactor was flushed with oxygen for 5 min. The ozone-treated EFB was oven dried for 24 hrs at 105°C to reduce the moisture content until zero.

![Ozonolysis pretreatment system](image)

**Figure 1.** Ozonolysis pretreatment system consists of (1) oxygen tank, (2) ozone generator, (3) mass flow meter, (4) ozone reactor, (5) ozone monitor, and (6) ozone destructor.

2.4. Modelling of ozonolysis pretreatment of empty fruit bunch (EFB)
The experimental set-up of an ozonolysis pretreatment system was designated in this numerical study to simulate the ozone flow behaviour in a fixed-bed reactor during the ozonolysis pretreatment of EFB. Figure 2(a) illustrates the expanded schematic views of a biomass bed inside a fixed-bed reactor. The morphology of EFB sample was performed using scanning electron microscope, SEM-5410LV with 500X magnification. Figure 2(b) imposes the surface of untreated EFB is very irregular, rough, and porous. The pore distribution of EFB is a multi-pore structure; majoring the mesopores and some micropores. In addition, the untreated EFB surface is seen rigid as the lignin layer hinders the cellulose and hemicellulose contents. The schematic design of an ozonolysis reactor consists of a packed-bed of biomass particles loosely packed and assumed to be homogenous in size and shape (Figure 2(c)). In this simulation study, the fixed-bed ozonolysis reactor model is constructed as in Figure 2(d) with an injection tube at the main axis of a tubular structure for ozone supply. The delignification reaction occurs in a fixed porous-bed region (purple coloured in Figure 2(d)).
Figure 2. (a) Expanded schematic views of a biomass bed inside the ozonolysis reactor, (b) Surface of empty fruit bunch characterized by SEM before ozonolysis. (c) Schematic diagram of the fixed-bed ozonolysis reactor and (d) Two-dimensional (2D) ozonolysis reactor model with user-controlled mesh for finite element analysis.

Figure 3 illustrates the modelling strategy for ozone flow behaviour in the reactor during ozonolysis pretreatment. Momentum and mass balances that governed the delignification process via ozonolysis pretreatment are coupled in a single numerical simulation model. The following assumptions are used for developing the current numerical model:

1. EFB particles are isotropic, loosely packed in a shallow bed, and homogenous in size and shape.
2. EFB particles are assumed to be not temperature-dependent.
3. The stationery bed of EFB particles is rapidly and uniformly exposed to the mobile ozone phase, and the mass transfer from the gas phase to the solid phase is rapid.
4. The ozone flow is streamed in one direction (x-axis) and laminar (Reynolds number < 2000) everywhere in the reactor vessel.
5. The reactor is operated at steady state assuming isothermal condition. The mass flow rate at any point of reactor is equal to the entering mass flow rate.
6. Ozone molecules are dilute; its concentration is small compared to a solvent fluid (in this case is air).
7. Ozone only reacts with lignin component to delignify the EFB.
8. Ozone decomposition in air is negligible.

![Figure 3. Flowchart of modelling strategy for ozonolysis.](image)

2.5. Governing equations

2.5.1. Momentum Balance. The model coupled the Navier-Stokes equation and Brinkman’s extension of Darcy’s law using the free and porous media flow physics in the CFD module of COMSOL software. The stationary Navier-Stokes equation describes the fluid flow in the free-flow regions while, the integration of the laminar flow physics with the Brinkman equation (also accredited to Ergun) defines the fluid flow in the porous media as (equation (3)):

$$\rho_f \frac{\partial \mathbf{u}}{\partial t} = \nabla \cdot \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \nabla P$$

where $\mathbf{u}$ is the velocity in the free-porous region outside the packed bed of reactor (m/s), $\mu$ denotes the dynamic viscosity (Pa·s), $\rho_f$ is the fluid density (kg/m³), $P$ is the pressure (Pa) and $t$ is time (s). Using COMSOL software, the Navier-Stokes equation is solved to determine the components of velocity ($u, v, w$) and the relative pressure, $P$ (Pa) that describe the fluid flow.

The fluid flow in the porous packed bed region of the reactor is described with the Brinkman equation as (equation (4)): 
\[
\rho_f \frac{\partial \mathbf{u}}{\partial t} = \nabla \cdot \left[ -P \mathbf{I} + \frac{\mu}{\varepsilon} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2\mu}{3\varepsilon} (\nabla \cdot \mathbf{u}) \mathbf{I} \right] - \left( \frac{\mu}{k} + \beta_F |\mathbf{u}| + \frac{\rho_F \nabla \cdot (\mathbf{u})}{\varepsilon^2} \right) \mathbf{u} + \mathbf{F}
\]

(4)

where \( \mathbf{u} \) is the superficial velocity in the packed bed (m/s), \( k \) is the permeability of the bed (m²), \( \varepsilon \) is the porosity or void fraction of the bed (-) and \( \beta_F \) is the Forchheimer drag coefficient (kg/m³).

To solve the equations (3)-(4), the following initial and boundary conditions are adopted: no-slip on the walls; zero pressure at the outlet; and first-order contour condition at the inlet, with a mass flow rate of 2 L/min [12]. There is no viscous stress acted on the outlet flow.

2.5.2. Mass Balance. The evolution of ozone molecules transported by diffusion and convection mechanisms is specified by the convection-diffusion equation. A Fickian approach for the diffusion term in mass transport is utilized by assuming that the modeled species are present in low concentrations compared to the carrier gas. The ozone molecules moved primarily within a fluid flow that filled (saturated) or partially filled (unsaturated) the voids in a solid porous medium. The inclusion of adsorption and reaction effects in the solid phase is accounted in the current model. The diffusion-convection-reaction model [18] calculates the concentration field of ozone molecules in the porous bed region as (equation (5(a)-(d))):

\[
P_{1,\text{O}_3} \frac{\partial c_{\text{O}_3}}{\partial t} + P_{2,\text{O}_3} - D_{\text{O}_3} \nabla c_{\text{O}_3} + \mathbf{u} \cdot \nabla c_{\text{O}_3} = \alpha_1 R_1 + S_{\text{O}_3}
\]

(5a)

\[
P_{1,\text{O}_3} = (\varepsilon + \rho_f k_{p,\text{O}_3})
\]

(5b)

\[
P_{2,\text{O}_3} = (c_{\text{O}_3} - \rho_p c_{p,\text{O}_3}) \frac{\partial \varepsilon}{\partial t}
\]

(5c)

\[
k_{p,\text{O}_3} = \frac{\partial c_{p,\text{O}_3}}{\partial c_{\text{O}_3}}
\]

(5d)

In these equations, \( \mathbf{u} \) is the superficial velocity in the porous phase (m/s), \( c_{\text{O}_3} \) denotes the molar concentration of ozone (mol/m³), \( c_{p,\text{O}_3} \) is the amount of ozone adsorbed on the solid particles (mols per unit dry weight of the solid), \( \rho_p \) is the solid density (kg/m³), \( D_{\text{O}_3} \) is the diffusivity of ozone (m²/s), \( k_{p,\text{O}_3} \) is the adsorption isotherm of ozone (m³/kg), \( R_1 \) is elementary bimolecular reaction rate for ozone in the solid phase reacting with lignin (mol/(m³·s)), and \( S_{\text{O}_3} \) is an arbitrary source term of ozone. The equation for the time evolution of lignin is given by García-Cubero et al. [19] as (equation (6)):

\[
\frac{\partial c_{\text{L}_g}}{\partial t} = -\alpha_2 R_1
\]

(6)

where \( c_{\text{L}_g} \) is lignin concentration (mol/m³). In the packed bed of biomass, the ozone consumption is described by irreversible, second-order reaction and its kinetic expression such that:

\[
\alpha_1 \text{O}_3 + \alpha_2 \text{L}_g \rightarrow P \quad \text{yields} \quad R_1 = -k(c_{\text{O}_3})(c_{\text{L}_g})
\]

(7)

where \( \alpha_1 \) (dimensionless) and \( \alpha_2 \) (\( k \text{g}_{\text{L}_g}/\text{kg}_{\text{O}_3} \)) are stoichiometric ratios, \( P \) represents product formed during ozonolysis, and \( k \) is kinetic rate constant (m³/mol·s). The reaction term is zero in the free-flow regions as the reaction only occurs inside the porous bed.
To solve the equations (5) - (7), the initial lignin concentration, \( c_{Lg, in} \) inside the porous bed at initial time is calculated based on 25% lignin in 20 g EFB sample [20]. At the reactor outlet, convection is assumed to dominate the mass transport and reflect the absence of diffusional flux.

2.6. Numerical simulation

The properties of ozone and EFB to be incorporated in the numerical simulation are summarized in Table 1. All required input values of operating parameters to numerically solve the equations (3) – (7) are as listed in Table 2. The numerical model is simulated within 340 s with time step of 1 s.

| No. | Properties | Values | References |
|-----|------------|--------|------------|
| 1.  | Ozone dynamic viscosity, \( \mu \) (Pa s) | 1.908 \( \times 10^{-5} \) | [21] |
| 2.  | Ozone density, \( \rho_f \) (kg/m\(^3\)) | 2.154 | [22] |
| 3.  | Diffusion coefficient of ozone, \( D_{O_3} \) (m\(^2\)/s) | 1.0 \( \times 10^{-6} \) | [11] |
| 4.  | Porosity or void fraction of the bed, \( \varepsilon \) (-) | 0.73 | [8] |
| 5.  | Density of solid, \( \rho_P \) (kg/m\(^3\)) | 191.65 | [23] |
| 6.  | Permeability of the bed, \( \kappa \) (m\(^2\)) | 1.26\( \times 10^{-11} \) | [12] |

| No. | Parameters | Values | References |
|-----|------------|--------|------------|
| 1.  | Reference temperature, \( T_{ref} \) (K) | 293.15 | [20] |
| 2.  | Reference pressure, \( P_{ref} \) (Pa) | 1.01325\( \times 10^5 \) | [20] |
| 3.  | Forchheimer drag coefficient, \( \beta_F \) (kg/m\(^4\)) | 2.48\( \times 10^6 \) | [12] |
| 4.  | Inlet ozone concentration, \( c_{O_3, in} \) (mol/m\(^3\)) | 45 | [12] |
| 5.  | Initial lignin concentration, \( c_{Lg, in} \) (mol/m\(^3\)) | 256 | [20] |
| 6.  | Inlet ozone velocity, \( u_{in} \) (m/s) | 0.01 | [12] |

CFD-FEM numerical approach via COMSOL software is exploited to visualize the motion and flow pattern of ozone in the reactor and to elucidate if the EFB bed is uniformly contacted with ozone during ozonolysis. The flow of ozone inside the reactor is simulated using COMSOL reacting flow in porous media physics interface. Apart from porous media region, the flow model is considered as the regions with free flow. The composition of ozone moving through the bed is simulated using COMSOL transport of diluted species in porous media physics interface. Brinkman equations in the reacting flow physics interface are combined with the transport of diluted species in porous media physics interface including the reaction term. In this study, the ozone diffusion is modelled by assuming the diffusion coefficients of biomass and ozone are constant and independent of temperature and pressure. The physics interfaces
are solved in stationary and time-dependent analyses. The porous medium has a continuum description thus, a detailed knowledge of the pore microstructure does not need to be specified. The geometrical configuration of ozonolysis reactor is modelled in two-dimensional (2D) plane and the user-controlled mesh is chosen for finite element analysis. Appropriate pressure drop trend across the biomass bed provides the analyst with an accurate tool to assess the impact of the most pronounced design parameters on the ozone reactor. The present numerical simulations are performed to investigate the effect of ozone inlet velocity and biomass bed length on the ozone multiphase flow behaviour inside the reactor. All results have been analysed in 2D for simplicity.

3. Results and discussion

3.1. Effect of EFB moisture content on the void fraction and bulk density
Physical properties of EFB such as void fraction and bulk density were investigated at various moisture contents (40%, 30%, and 20%) with particle size of 0.5 mm. Figure 4(a) shows that the void fraction of EFB is reduced with the increment of moisture content. Meanwhile, the bulk density of EFB is enlarged with the increasing of moisture content (Figure 4(b)). The presence of water particles among EFB particles has changed the physical characteristics of EFB.

![Figure 4. The effects of moisture content on (a) void fraction and (b) bulk density of EFB.](image)

3.2. Kinetic study and parameter estimation
The experimentally determined lignin content data were fitted to the kinetic reaction model to determine the three unknown parameter values (Figure 5(a)). Both prediction and experimental data establish that delignification reaches to 70% after 1000 s. The presence of residual lignin after long exposure to ozone could be attributed to the formation of a mass transfer barrier or “cuticle” region where ozone mass transport is reduced in proportion to the mass of unreacted insoluble lignin in the cuticle [12]. The dependent stoichiometric parameter, \( \alpha_1 \) is taken as 1 [12]. The best-fit parameter values along with their initial guesses are shown in Table 3.
Figure 5. (a) Evolution of lignin concentration over reaction time during ozonolysis pretreatment, (b) Relative pressure across the biomass bed, (c) Changes in predicted pressure drop with superficial velocity, and (d) Profile of relative pressure against the biomass bed length for three biomass bed lengths: 40mm, 70mm, and 100mm.

The loss of moisture during ozonolysis of biomass could also retard the delignification reaction as the low moisture content could have been insufficient to degrade the lignin [20]. The biomass delignification via ozonolysis pretreatment is governed by complex multi-physics phenomena and
mechanisms including transport properties of ozone and biomass [24], ozone-lignin kinetics reaction [11], multiphase ozone flow behaviours [21] and operating parameters [20].

| No. | Parameters                                      | Initial guess | Best-fit estimate |
|-----|-----------------------------------------------|---------------|-------------------|
| 1.  | Stoichiometric parameter 2, $\alpha_2$       | 0.001         | 0.17072           |
| 2.  | Kinetic rate constant, $k$ (m$^3$/mol·s)     | 0.001         | 0.01              |
| 3.  | Final value of objective function, $Z$       | -             | 0.001414638249    |

3.3. Pressure drop in ozone flow across the reactor bed
Figure 5(b) depicts distribution of relative pressure across the reactor bed at 0.01 m/s incoming uniform velocity. The relative pressure is constant and maximum at 68.99 Pa inside the free-flow region before reaching the biomass bed region, when the relative pressure declines to 0.9 Pa.

3.3.1. Influence of ozone inlet velocity on pressure drop. Figure 5(c) plots the calculated pressure drop for various flow rates of ozone in the range of 0.5–3.5 L/min by studying three incoming uniform velocities: 0.001 m/s, 0.005 m/s and 0.01 m/s. The findings infer that the pressure drop across the biomass bed increases from 102 Pa/m to 1020 Pa/m with the increment of superficial velocity from 0.001 m/s to 0.010 m/s. In laminar flow, pressure losses are linearly proportional to fluid velocity corresponding to Darcy flow as Re number increases when the axial inlet velocity increases [25]. The pressure drop in the ozone stream passing the biomass porous bed can be attributed from the effect of fluid viscosity at the gas-solid interfaces [21], energy dissipation [26] and surface friction [25]. The flow channels for ozone are so small due to the presence of porous bed region consisting of biomass particles. Therefore, a very sudden change to the ozone flow path contributes to the significant pressure loss. Energy dissipation occurs in the fluid flow passing through a restriction due to large velocity gradients in the flow. The surface friction generated between ozone and biomass particles can be increased due to the surface roughness of the biomass particles.

3.3.2. Influence of biomass bed length on the relative pressure. The effect of biomass bed length on the relative pressure inside the reactor is examined by comparing three biomass bed lengths: 40 mm, 70 mm, and 100 mm. The biomass bed length quantifies the amount of biomass volume placed in the reactor. Figure 5(d) outlines relative pressure profile across the biomass bed for three biomass bed lengths. The findings expose that the relative pressure values at the initial position of biomass bed are at 45 Pa, 79 Pa, and 112 Pa with the biomass bed lengths of 40 mm, 70 mm, and 100 mm, respectively. Hence, the relative pressure across the biomass bed reduces by reducing the biomass bed length. This is possibly due to ozone molecules are easier to flow and diffuse at shorter biomass bed length since it took shorter time to reach stabilization and homogeneity between ozone molecules and biomass particles. Thus, the shorter biomass bed length is recommended to enhance surface contact of ozone molecules with biomass particles and to reduce the mass transfer resistance hence, increasing the reaction rate for lignin degradation. This simulation study supports evidence from previous observations by Garcia-Cubero et al. [19] that the ozone distribution in thicker bed length is not good. The reduction profile of relative pressure across the biomass bed could also be attributed to the decreasing ozone concentration across the bed [10].
4. Conclusion
The model for transport-reaction in ozonolysis of biomass has been established. The simulated results reveal pressure drop across the porous biomass bed increases with the increment of superficial velocity and biomass bed length. The modelling for delignification fit-well with the experimental results inferring the model could also predict ozonolysis behaviour using various types of LB to elucidate the ozonolysis reactor performance.

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