Mathematical Modelling and Simulation of Hydrotropic Delignification

Indah Hartati[1,2]*, Wahyudi Budi Sediawan[1]*, Hary Sulistyo[1], Muhammad Mufti Azis[1], and Moh Fahrurrozi[1]

[1]Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada
Jl Grafika No. 2 Kampus UGM, 55281Yogyakarta
[2]Department of Chemical Engineering, Faculty of Engineering, Universitas Wahid Hasyim
Jl. Menorah Tengah X No 22, 50236 Semarang
*Alamat korespondensi: hartatiprasetyo@gmail.com (IH); wbsediawan@ugm.ac.id (WBS)

A B S T R A C T

Delignification is a fundamental step in bio-refinery for lignocellulose feedstock processing. Hydrotropic delignification is considered as a promising alternative compared to other conventional delignification processes due to the use of mild chemicals. In this paper, a quantitative description of hydrotropic delignification for a cylindrical biomass particle is presented by using fundamental concepts of chemical kinetics and transport processes. The development of hydrotropic delignification model was based on following assumptions: i) lignin in the biomass is immobile, ii) delignification is considered as a simultaneous process which involves intra-particle diffusion of hydrotropic agent followed by second order reaction for lignin and hydrotropic chemical, as well as intra-particle product diffusion. Finite difference approximation was applied to solve the resulting partial and ordinary differential equations. The simulation results of the proposed model may describe the concentration profiles of lignin, hydrotropic agent and soluble product distributions in a cylindrical solid particle as a function of radial position and time. In addition, the model could also predict the concentration of hydrotropic agent and soluble product in the liquid phase as well as the yield and conversion as a function of time. A local sensitivity analysis method using one factor at a time (OFAT), has been applied to investigate the influence of particle size and hydrotropic agent concentration to the yield and conversion of the hydrotropic delignification model. Validation of the proposed model was conducted by comparing the numerical results with an analytical solution for a simple case diffusion in cylinder with constant surface concentration and in the absence of chemical reaction. The validation result showed that the hydrotropic delignification model was in good agreement with the analytical solution.

Keywords: cylindrical particle; delignification; hydrotropic; modelling; simulation

A B S T R A K

   Delignifikasi merupakan tahap penting dalam proses biorefineri biomassa berlignoselulosa. Delignifikasi hidrotropi adalah salah satu alternative proses yang memiliki beberapa kelebihan dibandingkan proses-proses delignifikasi konvensional karena tidak menggunakan bahan kimia berbahaya. Dalam artikel ini disajikan deskripsi kuantitatif proses delignifikasi hidrotropi untuk partikel berbentuk silinder dengan menggunakan konsep fundamental kinetika reaksi dan proses-proses perpindahan. Penyusunan model proses delignifikasi hidrotropi dilakukan berdasarkan asumsi-asumsi bahwa i) lignin pada biomassa bersifat *immobile*, ii) proses delignifikasi dipandang sebagai

suatu rangkaian proses simultan yang terdiri atas proses difusi intrapartikel senyawa hidrotrop, reaksi order dua terhadap lignin dan senyawa hidrotrop, serta difusi intrapartikel produk delignifikasi. *Finite difference approximation* (FDA) digunakan untuk menyelesaikan persamaan simultan berbentuk persamaan diferensial ordiner dan persamaan diferensial parsial dalam tahap pemodelan. Hasil simulasi memberikan gambaran profil distribusi konsentrasi lignin, konsentrasi senyawa hidrotrop dan produk delignifikasi di dalam partikel padatan yang berbentuk silinder sebagai fungsi posisi dan waktu. Model yang dikembangkan juga dapat memprediksi konsentrasi senyawa hidrotropik dan produk di fasa cairan, serta yield dan konversi sebagai fungsi waktu. Metode analisis sensitivitas lokal, yakni metode *one factor at a time (OFAT)*, digunakan untuk mengkaji pengaruh ukuran partikel dan konsentrasi senyawa hidrotropik terhadap yield dan konversi proses delignifikasi. Validasi model yang diajukan dilakukan dengan membandingkan hasil analisa numerik dengan hasil penyelesaian analitis untuk kasus difusi pada silinder dengan konsentrasi permukaan yang konstan serta tidak melibatkan reaksi kimia. Hasil validasi model menunjukkan bahwa model delignifikasi hidrotropi yang diajukan memiliki kesesuaian yang tinggi dengan hasil penyelesaian analitis.

Kata kunci: delignifikasi; hidrotropi; pemodelan; silinder; simulasi

1. Introduction

Bio-refinery is defined as an integrated and sustainable processing of biomass feedstock to produce a range of both energetic and non-energetic marketable value-added products (Özdenkçi et al., 2017). Based on the feedstock types, bio-refinery is classified into 1st generation, which utilizes dedicated edible crops, and 2nd generation, which utilizes non-edible feedstocks or side streams as the raw material (Cherubini et al., 2009; Özdenkçi et al., 2017). Lignocellulose is a composite material mainly composed of polymeric carbohydrates consists of cellulose and hemicellulose which are encapsulated in lignin matrix. As a result, it gives a complex macro-molecular assembly. Lignocellulose is one of the most abundant type of biomass resources for 2nd generation bio-refinery with world-wide production rate of approximately up to 200 billion ton per year (De Bhowmick et al., 2017; Zhao et al., 2018). Elimination and reduction of lignin is an important step to obtain high quality cellulose. The presence of lignin, an amorphous and complex aromatic polymer, has become one of the most significant challenges in bio-refinery processing (De Bhowmick et al., 2017; Li et al., 2016).

Pretreatment technology is one of the most common applied strategy in the lignin reduction process rather than the other ones i.e. perturbing lignin biosynthesis, enzyme engineering and modification technology (Li et al., 2016).

Basically, lignocellulose pretreatment can be conducted via physical method (comminution, hydrothermolysis and steam explosion), chemical method (Kraft, soda, organosolv, hydrotropic, and ionic liquid), and biological method (De Bhowmick et al., 2017; Hassan et al., 2018). Among the three delignification methods available, due to its effectiveness, chemical method is the most common method for lignin removal. However, the implementation of Kraft, Soda, Organosolv and ionic liquid processes for delignification remains challenging due to the low possibility of chemicals and lignin recovery (Ansari and Gaikar, 2014).

Compared to other conventional delignification processes, hydrotropic delignification is considered as a promising alternative since hydrotropic solution can be recovered and reused. Besides, the lignin from delignification effluent could be separated by adding a certain amount of water to bring the solution below the Minimum Hydrotrope Concentration (MHC) level (Ansari and Gaikar, 2014; Devendra and Pandey, 2016). The hydrotrope term was introduced by Carl A. Neuberg in 1916 for a diverse class of small molecular weight of amphiphilic molecules that, at high concentrations, could considerably enhance the solubility of poorly soluble organic substances in aqueous solutions, often by several order of magnitude, by mediating the interaction between hydrophilic and hydrophobic molecules (Devendra and Pandey, 2016; Dhapte and Mehta,

2016; Hodgdon and Kaler, 2007; Kunz et al., 2016; Mou et al., 2016). The application of several hydrotropes, benzene-derived hydrotropic salts, in pretreatment of various lignocellulose biomass was initiated and patented by McKee in 1943, which later hydrotropism is gaining higher attentions due to its outstanding advantages (Mou et al., 2016).

The study of mathematical modelling of hydrotropic delignification process, to our knowledge, is scarcely reported in the present literature e.g. in that of Ansari and Gaikar (2014). Here, the model of sugarcane bagasse hydrotropic delignification was developed by assuming that the sugarcane bagasse was of flat shape particle and the quantitative description was applied to take into account the lignin diffusion (Ansari and Gaikar, 2014). In addition, the use of delignification agents to remove lignin is gaining higher attention and their kinetics can be found in several publications (Dang and Nguyen, 2006; Grenmann et al., 2010; Pande and Roy, 1996).

SEM micrographs of raw sugarcane bagasse showed that the milled sugarcane particle was in cylindrical shape (Chimenez et al., 2013). By using cylindrical biomass particle, a model is proposed in this paper by assuming that diffusion and chemical reaction were the two consecutive phenomena occurring in the hydrotropic delignification process. The diffusing materials in this case was the hydrotrope and product of the lignin degradation.

The utilization of hydrotropes as the delignification agent also opened an opportunity to produce several by-products, e.g. lignin, formic acid, acetic acid, dissolved hemicelluloses, sugar monomers, and furfural (Gabov et al., 2013; Gabov, 2018). The advantages of hydrotropic delignification have been reported for a number of biomass (Ansari and Gaikar, 2014; Chen et al., 2017; Devendra and Pandey, 2016; Gabov et al., 2013; Gabov, 2018). However, among the researches related to hydrotropic delignification processes, there is still limited paper which reported the quantitative description in the form of mathematical model for hydrotropic delignification. Hence, the

objective of present work was to develop a hydrotrope delignification model to improve scientific understanding related to the hydrotropic delignification for any type of biomass that is assumed to have a cylindrical shape, and each type of biomass has its own effective diffusivity. The resulting model was expected to support a basic design for commercial unit.

2. Research Methodology

2.1 Model development

The hydrotropic delignification model was developed by applying basic assumption that there are two kinds of consecutive phenomena occurring in the delignification process namely diffusion and chemical reaction. The initial mechanism of delignification involved mass transfer of the hydrotrope solution (A) from the bulk solution to the outer surface of biomass which was followed by mass transfer of A by internal diffusion through the capillary pores of biomass structure. Subsequently, chemical reaction of lignin (B) with hydrotrope solution (A) occurred simultaneously with internal diffusion step (Gabov, 2018). The chemical reaction proposed here was to represent the hydrotropic delignification step where lignin was altered and fragmented due to the cleavage of lignin-lignin and lignin-carbohydrate linkages (Gabov, 2018; Kunz et al., 2016). It is proposed that the rate of lignin degradation follows 2nd order chemical reaction with 1st order to lignin and hydrotrope, respectively. It is also assumed that the raw lignin is immobile in the solid particle, while the soluble product (C) diffuses from the interior part to the outer surface of biomass which was followed by mass transfer to the bulk of the liquid. The model takes into account the rate of internal diffusion of hydrotrope in the biomass, chemical reaction between hydrotrope and lignin and eventually the diffusion of the product from the interior part of biomass. The mass transfer of the hydrotrope from the bulk of the liquid to the solid surface and the mass transfer of the soluble product from the solid surface to the bulk of the liquid are

relatively fast because of the effective agitation and hence their effects were neglected.

Diffusion of the hydrotrope (A) and of the soluble product (C) in the biomass particle follows Fick's equation, as shown in Equation (1) and (2).

$$N_A = -D_{eA}.\frac{\partial C_A}{\partial x} \tag{1}$$

and

$$N_C = -D_{eC}.\frac{\partial C_C}{\partial x} \tag{2}$$

Further, it was reported that the kinetic model of delignification step was set to be proportional to the delignification agent concentration and the immobile lignin (Pande and Roy, 1996). Hence, the rate of chemical reaction here is approximated by a simple kinetic as Equation (3).

$$-r_A = -r_B = r_C = k_r.C_A.C_B \tag{3}$$

where C_B is in moles of equivalent monomer per unit volume.

Furthermore, the biomass particle is assumed to have a cylindrical shape, and the volume element in one dimensional simultaneous radial diffusion and chemical reaction was simplified as in Figure 1.
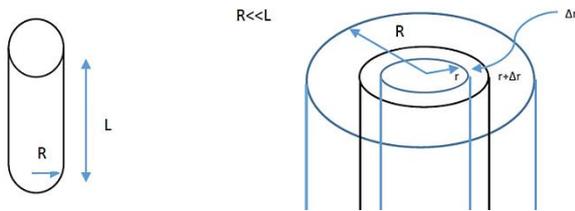
Figure 1. Schematic diagram of delignification in cylindrical biomass particle

The mathematical model of delignification was developed based on mass balance equations. Mole balance of the hydrotrope (A) in the solid volume element of $\Delta V = 2\pi r \Delta r L$ can be written as Equation (4).

$$-\left(-DeA\frac{\partial C_A}{\partial r}\Big|_{r+\Delta r}\right)2\pi(r+\Delta r)L - \left(DeA\frac{\partial C_A}{\partial r}\Big|_r\right)2\pi r L - 2\pi r L\Delta r k_r C_A C_B = 2\pi r L\Delta r \varepsilon \frac{\partial C_A}{\partial t} \tag{4}$$

By taking the limit that Δr approaches to zero, the following differential equation was formed (Equation (5)).

$$\frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_A}{\partial r} - \frac{k_r C_A C_B}{D_{eA}} = \frac{\varepsilon}{D_{eA}}\frac{\partial C_A}{\partial t} \tag{5}$$

The mole balance of lignin (B) in the volume element was developed by assuming that the immobile lignin reacts with the hydrotrope (A) and produced a soluble product (C), and the result is:

$$\frac{\partial C_B}{\partial t} = -\frac{k_r C_A C_B}{\varepsilon} \tag{6}$$

Based on the assumption that the product of the reaction diffuses to the solid surface of the biomass, the material balance of C can be formulated, and the result is presented as in Equation (7).

$$\frac{\partial^2 C_C}{\partial r^2} + \frac{1}{r}\frac{\partial C_C}{\partial r} + \frac{k_r C_A C_B}{D_{eC}} = \frac{\varepsilon}{D_{eC}}\frac{\partial C_C}{\partial t} \tag{7}$$

The initial conditions for Equation (5)-(7) are as shown in Equation (8).

$$t = 0; C_A = 0; C_B = C_{B0}; C_C = 0 \tag{8}$$

Meanwhile the boundary conditions comprised of both conditions at the solid surface and at the center of the solid cylinder for Equation (5)-(7) are:

$$r = 0; \frac{\partial C_A}{\partial r} = 0; \frac{\partial C_B}{\partial r} = 0; \frac{\partial C_c}{\partial r} = 0 \tag{9}$$

$$r = R; C_A = C_{Af}; \frac{\partial C_B}{\partial r} = 0; C_C = C_{Cf} \tag{10}$$

Equation (9) is a mathematical representation of the assumptions that the concentration of A in the center of the solid particle is minimum, while the concentration of B is maximum, and the concentration of C is radially symmetric. Meanwhile Equation (10) is formulated based on the assumptions that the mass transfers of A, B and C from the solid surface to the bulk of the liquid through the liquid film are relatively fast due to sufficient agitation in the liquid solution.

The mass balance of A in the liquid phase could be described as Equation (11).

$$0 - D_{eA} 2\pi r L N b \frac{\partial C_A}{\partial r}\Big|_R = V_L \frac{dC_{Af}}{dt} \tag{11}$$

After rearrangement, Equation (11) becomes Equation (12).

$$\frac{dC_{Af}}{dt} = -\frac{D_{eA}}{V_L} 2\pi r L N b \frac{\partial C_A}{\partial r}\bigg|_R \qquad (12)$$

Similarly, the mass balance of component C in the bulk liquid is reported in Equation (13).

$$\frac{dC_{Cf}}{dt} = -\frac{D_{eC}}{V_L} 2\pi r L N b \frac{\partial C_C}{\partial r}\bigg|_R \qquad (13)$$

Equation (12)-(13) were solved based on the following initial conditions:

$$t = 0; C_A = C_{A0}; C_C = 0$$

2.2 Simulation method

Finite difference approximation (FDA) method was applied to solve a set of resulting partial differential equations. Equation (5)-(10) were solved from r=0 to R due to symmetrical system of the cylindrical particle. Central finite difference approach has been used to discretize the first and second order differential equation in radial direction for FDA computation. Ordinary differential equation (ODE) solver in MATLAB and FORTRAN have been applied to solve Equation (5)-(10) for all grids in the cylinder. Analytical solution for simple case was applied to test the validity of the mathematical modelling and the solutions.

In order to get a quantitative view on the hydrotropic delignification system, our simulation results were presented as a function of time and radial position as displayed in a colormap of figure 2. Conversion was calculated as the total amount of lignin reacted divided by the initial amount of lignin. The conversion of lignin as a function of time was also presented.

Simulations were also conducted to investigate the influence of particle diameter thickness and hydrotrope concentration to the yield of C in the liquid phase. One Factor at a Time (OFAT) method, in which simulations were performed by changing only one factor or variable at a time while keeping others fixed (Ranjbar and Gaemi, 2013), was used in the evaluation of the influence of each parameter of hydrotropic delignification.

2.3 Validation

Model validation could be performed by at least one of the following methods, i.e. correspondence test, consistency test, and pragmatic test. In this paper, the model proposed for the hydrotropic delignification was validated by applying consistency test, in which the numerical analysis of the model proposed was validated and compared to the analytical solution of a simple case for diffusion in cylinder with constant surface concentration. In the case of a long circular cylinder where diffusion occurred in radial direction, the concentration is a function of radius r and time t only, and the diffusion equation becomes (Crank, 1975):

$$\frac{\partial C_A}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C_A}{\partial r}\right) \qquad (14)$$

Moreover, for constant surface concentration, the boundary conditions are as follows:

$$C = C_{Af0}, \ r = R, \ t \geq 0 \qquad (15)$$

$$\frac{\partial C}{\partial r} = 0, \ r = 0, \ t \geq 0 \qquad (16)$$

$$C = f(r), \ 0 < r < R, \ t = 0 \qquad (17)$$

If the initial concentration is zero throughout the cylinder, then the solution is as follows (Charzyzka et al., 2012).

$$C = C_{Af0}\left(1 - \frac{2}{a}\sum_{n=1}^{\infty}\frac{\exp(-D_{eA}\alpha_n^2 t/\varepsilon)J_0(\alpha_n r)}{\alpha_n J_1(\alpha_n R)}\right) \qquad (18)$$

where α_n is the positive roots of $J_0(\alpha_n R)=0$; $J_0(x)$ is the Bessel function of the first kind of order zero and $J_1(x)$ is the Bessel function of the first order. This phenomenon is a special case of our generalized model, in which the initial hydrotrope concentration in solid is zero, while the volume of the hydrotropic solution is very large compared to the volume of the solid particle, so that the concentration of hydrotrope in the bulk of liquid is almost constant, C_{Af}. Moreover, the reaction rate of hydrotrope and lignin is very small.

3. Results and Discussion

The set of equations representing the hydrotropic delignification was then numerically solved by FDA. For the base case, following parameters have been used: the effective diffusivity of hydrotrope (D_{eA}) of 3.10^{-5} cm^2/min, the effective diffusivity of delignification product D_{eC} of 1.10^{-5} cm^2/min, reaction rate constant of delignification reaction (k$_r$) of 2.10^{-1} cm^3/(mol.min). Moreover, the simulations were run at the volume of the liquid (V$_L$) of 5.10^2 cm^3, the number of the biomass particle (N$_B$) of 4.10^2, the biomass particle porosity (ε) of 4.10^{-1}, the initial lignin concentration in the biomass (C$_{B0}$) of 3.10^{-3} mol/cm^3, the initial concentration of hydrotrope solution (C$_{A0}$) of 5.10^{-3} mol/cm^3, and the radius (R) and length (L) of the cylindrical biomass particle of 2.5 cm and 1 cm, respectively. The effective diffusivity of delignification product (C) and hydrotrope (A) applied in this simulation were reasonable as their values were smaller than those of molecular diffusivities in liquid. The effective diffusivity is equal to liquid diffusivity multiplied by the porosity and divided by tortuosity factor. It was mentioned that molecular diffusivities in liquid is normally around 6.10^{-4} cm^2/min (Zhao et al., 2018). Fig.2a-c showed the simulation results which comprised of the concentration profile of hydrotrope (A), lignin (B) and the soluble product (C) in the solid particle as functions of position and time.

As seen on Fig.2a, along with the increase of reactive extraction time, the concentration of the hydrotrope (C$_A$) at the surface of the cylinder is decreasing. This phenomenon is logical since the hydrotrope diffused to the inner part of the cylinder and the concentration in the liquid phase decreased. Figure 2a also shows that the concentration of the hydrotrope in the inner part of the cylinder is lower than the concentration at the surface at the same time. This phenomenon is also conceivable since the movement of the diffusion is from the outer part to the inner part. In Fig. 2a, it was also observed that the hydrotrope concentration at the centre of the cylinder is increasing by the increase of the

reaction time. This phenomenon is also conceivable since the sources of the hydrotrope is from the liquid outside the cylinder and the diffusion to the inner part of the cylinder was relatively slow. It also appeared that above 500 min, the concentration of A is nearly the same as the liquid and thus decreasing the mass transfer rate of A to the inner part of cylinder.

(a)

(b)

(c)
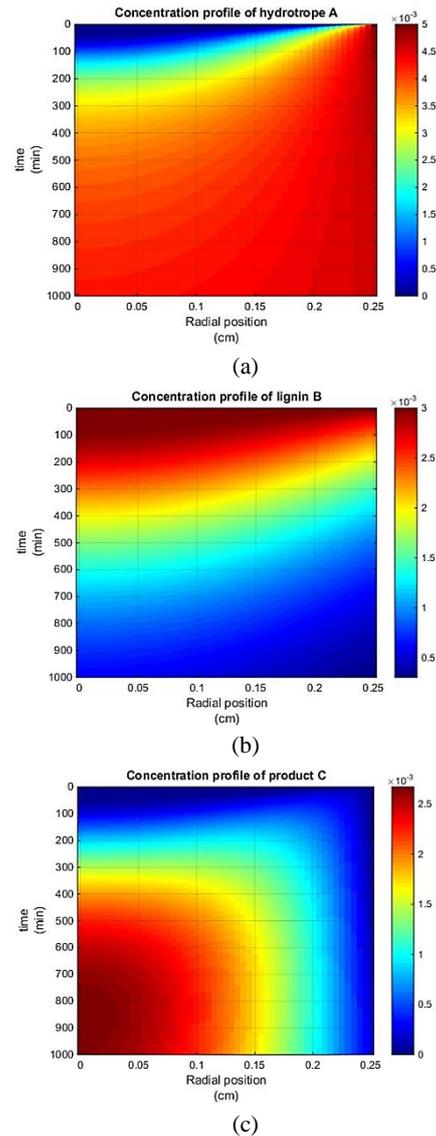
Figure 2. **Concentration distribution profile of: (a) hydrotrope (A), (b) lignin, and (c) soluble product in the cylindrical biomass particle**

Figure 2b shows the concentration profile of the immobile lignin at the cylinder (C$_B$). From inspection on radial direction, it appeared that the concentration of the immobile lignin decreased by the increase of the extraction time. This phenomenon is conceivable since the immobile

lignin reacts with the hydrotrope. Since the flux of the hydrotrope is mostly from the surface of the cylinder, the concentration of the hydrotrope in the inner part will be lower resulted in the slower reaction rate. As a result, the degradation of immobile lignin in the inner part of the cylinder tends to be slower.

Figure 2c illustrates the profile of the product of the hydrotropic delignification at the cylinder (C). By increasing the extraction time, the concentration of delignification product at every position increases due to the progress of the reaction. Along with the increase of extraction time, the concentration of product in the centre of cylinder gradually increases and reaches the maxima at ca. 900 min. Due to the high internal diffusion resistance or lower diffusivities for product C, the model shows that most of the product remains in the biomass which is accompanied by gradual release of product C. This is noteworthy on how diffusivity really affects the yield of hydrotropic delignification and illustrates how modelling helps to understand the mechanism and determine the rate controlling step.

The model could also predict the simulated concentration of hydrotrope and product concentration in the liquid phase as illustrated in Fig. 3. In addition, the predicted conversion and yield of the hydrotropic delignification as a function of time were displayed in Fig 4. As seen on Fig. 3, as time progresses, the hydrotrope concentration is decreasing because it diffuses to the biomass which is followed by the increase of product concentration. These phenomena are caused by the diffusion of the active compound to the inner part of the cylinder and the transfer of the product to the liquid. Further, from Fig. 4, it can be seen that both conversion and yield increased with the hydrotropic delignification time. Conversion of immobile lignin as high as 84% as well as 60% yield are achieved after 1000 min of hydrotropic delignification process.
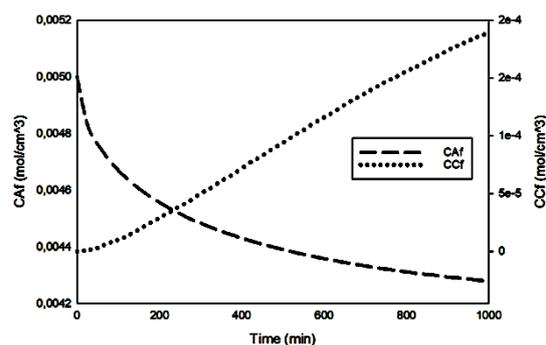
Figure 3. Concentration of the Liquid Phase of Hydrotrope (C_{af}) and Product (C_{cf})
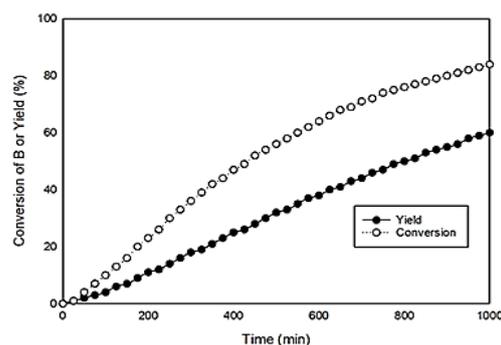
Figure 4. Conversion and Yield of the Hydrotropic Delignification
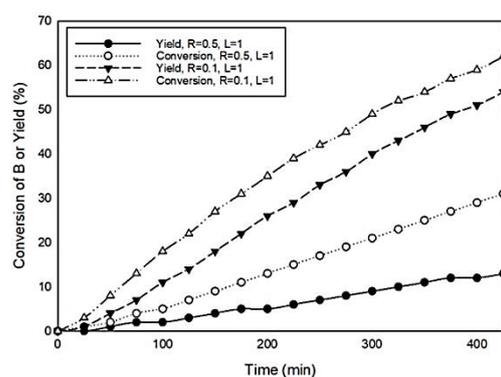
(a)
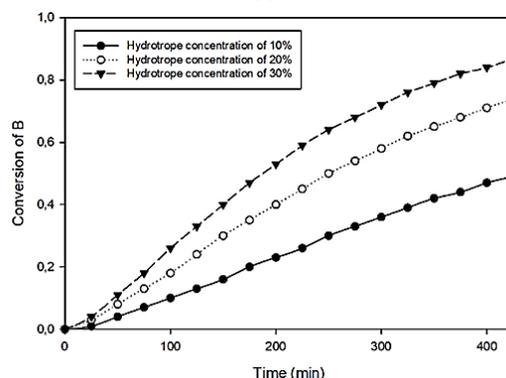
(b)

Figure 5. The influence of radius of the cylinder and hydrotrope concentration to the yield and conversion of the hydrotropic delignification

Furthermore, we have also conducted sensitivity analyses to the model. Sensitivity analysis is an important aspect of mathematical modelling which investigates the relation between parameters of a mathematical model and the responses of the observable outcome, hence the influence of the model parameters toward the performances of the process can be predicted (Charzyzka et al., 2012; Ranjbar and Gaemi, 2013). Sensitivity analysis could be evaluated in either one of three kind of methods which are local, global and screening method (Ranjbar and Gaemi, 2013). One Factor at a Time (OFAT), which examined one parameter while keeping the other parameters fixed, is one of the examples of local sensitivity analysis. OFAT was applied in the sensitivity analysis of hydrotropic delignification due to its simple concept and low cost of simulation. OFAT method was performed to investigate the influence of particle size (radius of the cylinder) and the influence of hydrotrope concentration (C_{A0}) towards the yield and conversion of the hydrotropic delignification process.

Figure 5a shows the influence of radius of the cylinder towards the yield and conversion of the hydrotropic delignification. Meanwhile the influence of hydrotrope concentration towards the yield and conversion of the hydrotropic delignification process is illustrated in Fig. 5b. It can be seen in Fig.5a that reducing the radius of the cylinder would increase of both yield and conversion. Besides, the difference between conversion and yield decreases as the radius of the cylinder is reduced. Moreover, Fig. 5b shows that higher hydrotrope concentration in the hydrotropic delignification is beneficial as it leads to higher conversion. It is reasonable as shown on Equation (3), that the rate of product formation is proportional to the hydrotrope and lignin concentrations. Figure 5b also shows that the conversion of the delignification process for hydrotrope concentration of 30% is approximately 1.7 higher than the one with the hydrotrope concentration of 10%.

In general, this proposed simulator can be applied to predict the optimum condition of the process depending on the objective function set up. For example, for hydrotrope concentration of 30%, the increase of the conversion is relatively small after the time of 300 minutes. Hence, it can be said that the wise time applied is around 300 minutes.
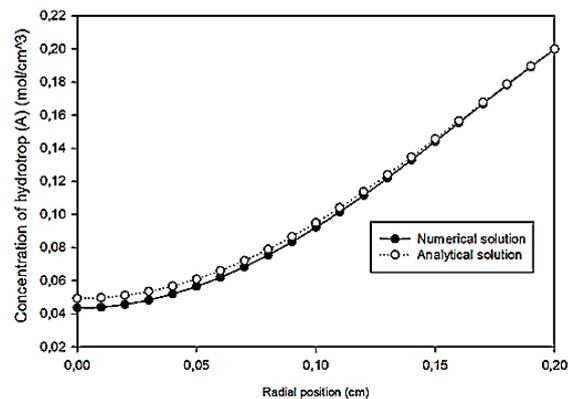
Figure 6. The comparison of the results of the model proposed and the analytical solution of a simple case of diffusion in cylinder with constant surface concentration

Validation of the accuracy of the proposed mathematical model was also performed. The hydrotropic delignification model was validated by comparing the numerical solution with the analytical solution of a simple case which was the diffusion in cylinder with constant surface concentration and no reaction. This simple case is a special form of the model proposed in which the volume of the liquid is very large so the concentration of the hydrotrope in the liquid is almost constant and the reaction rate constant is close to zero. Hence for validation, a simulation was run at the values of the parameters as follow: the effective diffusivity of hydrotrope (D_{eA}) was 1.10^{-5} cm^2/min, the effective diffusivity of delignification product (D_{eC}) was 1.10^{-5} cm^2/min, constant rate of delignification reaction (k_r) was reduced to 1.10^{-10} cm^3/mol/min (relatively small), the volume of the liquid (V_L) was 2.10^3 cm^3 (relatively large), the number of the biomass particle (N_B) was 1.10^1, the biomass particle porosity is (ε) was 4.10^{-1}, the initial lignin concentration of the biomass ($C_{B\,0}$) was 1.10^{-1} mol/cm^3, the initial concentration of hydrotrope solution ($C_{A\,0}$) was 2.10^{-1} mol/cm^3, and the radius (R) and length (L) of the cylindrical biomass particle were 0.2 cm and 1 cm, respectively.

Figure 6 displays the comparison of the numerical simulation using the hydrotropic delignification model and the analytical solutions of a simple case of diffusion in cylinder with constant surface concentration. Figure 6 confirms that the model results are very close to the analytical solutions. This result validates that the model of the hydrotropic delignification proposed for this special case is consistent.

4. Conclusion

A mathematical model for hydrotropic delignification in a cylindrical biomass particle has been constructed, simulated, and validated. Two consecutive phenomena, diffusion and chemical reaction, were assumed to occur in the delignification process. FDA method was applied in solving the simultaneous equations. Yield and conversion as a function of hydrotropic delignification time, and the concentration profile of hydrotrope, immobile lignin and delignification product at various radial position and time were successfully simulated. OFAT, a local sensitivity analysis method, has been chosen to investigate the influence of the model parameters toward the yield and conversion of the hydrotropic delignification model. An analytical solution of a simple case of diffusion in cylinder with constant surface concentration has been applied in validating the numerical analysis of the model proposed, and the results showed that the model gave good agreement with the analytical solution.

Notation

C_A = concentration of hydrotrope agent in the liquid in the pore of the solid, mol/cm^3

C_{Af} = concentration of hydrotrope agent in the bulk of the liquid, mol/cm^3

C_B = concentration of lignin in the liquid in the pore of the solid, mol/cm^3

C_C = concentration of hydrotropic delignification product in the liquid in the pore of the solid, mol/cm^3

C_{Cf} = concentration of hydrotropic delignification product in the bulk of the liquid, mol/cm^3

D_{eA}, D_{eC} = effective diffusivity of A and C, respectively, cm^2/min

ε = cylinder porosity, -

k_r = reaction rate constant, cm^3/(mol.min)

L = cylinder length, cm

N_b = the number of cylinders, -

r = radius of the cylinder, cm

V_L = volume of liquid, cm^3

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