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Nonlinear partial differential equations model related to ethanol production

Ahmad Izul Fakhruddin Azimi,[1] and Norazaliza Mohd Jamil[1]

[1] Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia

E-mail: ahmadizul.azimi@gmail.com

Abstract. Despite improvements in fermentation method, recent studies still discover numerous weaknesses throughout the entire fermentation process. Accordingly, this calls for a new improvised study. This study presents a mathematical model of an ethanol production system via fermentation; 1) shaker fermentation, and 2) shaker-free fermentation. This model was extended from an established model to examine mass transfer and the inhibition effects on microbial such as yeasts or bacteria, sugar as its substrate and ethanol for the product. For critical view on the description of mass transfer, the study of the coupled diffusion-reaction and coupled diffusion-reaction-advection models from a previous mathematical model was also carried out. The understanding of the models enabled accurate prediction on the behaviour of mass transfer effect on fermentation scenarios. The effect of the diffusion coefficient and the advection coefficient were investigated to simulate the dynamical behaviour of the system. Since the model is nonlinear partial differential equations (PDEs), Gear's algorithm, a numerical method was employed to solve the system while the Nelder–Mead method was utilised to estimate the value of the parameters. The result shows that the diffusion was insignificant on the whole ethanol production system but is on the contrary to advection. In order to affect the ethanol production system, only tiny advection value is needed, however, a big diffusion value is necessary to achieve the same effect.

1. Introduction

In the global economy, energy industry plays a crucial role. Rising prices of fossil fuel, energy security problems and environmental issues have pushed and pressured energy development into advancing alternative and renewable energy sources. Bioethanol is often seen as a prominent substitute to the dominant fossil fuel in the world market and the manufacturing has grown significantly [1]. Fermentation and synthetic method are the most well-known productions of ethanol. Synthetic ethanol's original resources are from petroleum by-products while natural fermentation ethanol resources are by the substrate.

One of the factors which has brought the attention to ethanol production by fermentation, also known as bioethanol, is the enormous number of its natural resources. To name a few, oil palm trunk (OPT) juice is one of the abundant resources in the palm oil-producing countries such as Malaysia. Saccharomyces cerevisiae Kyokai no.7 in fermented without shaker using OPT juice as the substrate in the experiment [2] shows that this microbial produces the highest ethanol yield compared to others, which is also recommended for use in large-scale productions. The manufacturing of ethanol by fermentation is however very complicated to comprehend and costly to operate.

A research of the kinetic model is designed to enhance ethanol production through learning of the microbial and substrate behaviour consumed in fermentation [3]. A number of experiments to enhance ethanol production by fermentation too have been performed. For instance, the evaporation technique was incorporated into studies conducted in [4] to remove ethanol during fermentation processes. This is due to the fact that ethanol itself may inhibit fermentation hence the process is believed to have improved production, increased the use of the equipment and reduced its waste of water. In addition, evaluation on ethanol ultrasound treatment allegedly used during fermentation to enhance the mass transfer of substrates, production and yeast cells was done by [5]. Unlike previous studies, the result in [5] shows that the levels of substrates uptake and manufacture of ethanol were significantly lower than non-ultrasound and even reduced yeast cell density and viability. In spite of the improvement of the fermentation method, numerous weaknesses are still hard to resolve throughout the entire operation of the ethanol fermentation process.

The use of the mathematical model is one of the effective ways to experiment with ethanol production. A lot of attention has to be paid to all the parameters and important variables in the models in order to have a comprehensive knowledge of microbial nature and consequently optimize the manufacturing yield. The knowledge of the fermentation process model is believed to increase the output of production. The study of the mathematical model [6] on the anthocyanin dissolved between the grape skin and the solution found that there were two types of mass transfer involved in wine-making which have the same concept with ethanol fermentation ie diffusion, random movement of substances in a fluid, and advection, the transport of substances affected by fluid velocity. Two kinds of laboratory fermentation can be performed by scientists, to the best of researcher's understanding, are shaker fermentation and shaker-free fermentation. Such fermentations can be represented by couple reaction-diffusion and couple reaction-diffusion-advection mass transfer in a mathematical model.

A study by [7] concluded that Saccharomyces cerevisiae, as a common microbial in ethanol production, can experience inhibition in extremes such as high temperatures, high concentrations of ethanol, and high sugar levels. Accordingly, a comprehensive mass transfer research as shown in [8] should be performed to prevent such circumstances. The research in [8] evaluates the existence of the system model and its uniqueness and regularity.

Although it did employ the same concept as for ethanol production, the goal of this study is to optimise the substrate consumed by the yeast to obtain a wine of high quality. Many studies have been considered in order to highlight the situation in the fermentation and translate it into the system of mathematical model. A mathematical model which includes the inhibition effect was introduced in [9]. The integration of inhibitory parameters is seen as significant as it is essential for optimal manufacturing of ethanol. This model does not only consider the effect of the substrate and the product inhibition on microbial growth, but also on the formation of the product.

2. Mathematical models
This section describes the mathematical model in [9] and [8] with the explanation behind the modifications of the model.

Various mathematical models have described the rate of the fermentation reaction of ethanol. As stated in the previous section, [9] had taken account inhibitory parameters. Because this research also highlights the same issue, the same reaction model was used. In the equations below, M is microbial concentration, P is ethanol concentration and S is substrate concentration.

$$\frac{\partial M}{\partial t} = \mu_{\max} SM \left(K_{SM} + S + \frac{S^2}{K_{IM}} \right)^{-1} \left(1 - \frac{P}{P_M} \right) - K_d M \tag{1}$$

$$\frac{\partial P}{\partial t} = v_{\max} SM \left(K_{SP} + S + \frac{S^2}{K_{IP}} \right)^{-1} \left(1 - \frac{P}{P_P} \right) \tag{2}$$

$$\frac{\partial S}{\partial t} = -\frac{1}{Y_{MS}}\left[\mu_{max}SM\left(K_{SM} + S + \frac{S^2}{K_{IM}}\right)^{-1}\left(1 - \frac{P}{P_M}\right) + K_dM\right]$$
$$-\frac{1}{Y_{PS}}\left[v_{max}SM\left(K_{SP} + S + \frac{S^2}{K_{IP}}\right)^{-1}\left(1 - \frac{P}{P_P}\right)\right] - mM \tag{3}$$

Table 1 depicts the parameters used in this mathematical model. In the meantime [8] integrated a diffusion factor in the improved version of reaction model by [10], a model which only considers the saturation coefficient in the system as follows:

$$\frac{\partial M}{\partial t} = Q\frac{\partial^2 M}{\partial x^2} + \mu_{max}MT\left(\frac{S}{K_{SM} + S}\right)\left(\frac{N}{K_N + N}\right)\left(\frac{O}{K_O + O}\right) - K_dM \tag{4}$$

$$\frac{\partial P}{\partial t} = Q\frac{\partial^2 P}{\partial x^2} + v_{max}MT\left(\frac{S}{K_{SP} + S}\right)\left(\frac{K_{IP}}{K_{IP} + P}\right) \tag{5}$$

$$\frac{\partial S}{\partial t} = Q\frac{\partial^2 S}{\partial x^2} - \alpha MT\left(\frac{S}{K_{SM} + S}\right)\left(\frac{N}{K_N + N}\right)\left(\frac{O}{K_O + O}\right)$$
$$-\beta MT\left(\frac{S}{K_{SP} + S}\right)\left(\frac{K_{IP}}{K_{IP} + P}\right) \tag{6}$$

Table 2 lists the parameters and variable used in [8]. [8] incorporated product inhibition, P_P into the rates of product formation, but not in microbial growth rate, P_M. In addition, the model still fails to consider the presence of the substrate inhibition in microbial growth rates, K_{IM} as well as the product formation rate, K_{IP}.

Table 1. Parameters used in the mathematical model.

Symbol	Description	Value	Unit
μ_{max}	Maximum specific rate for microbial growth	0.7790	h^{-1}
v_{max}	Maximum specific rate for ethanol production	50.1145	h^{-1}
K_{SM}	Substrate half-saturation coefficient for microbial growth	257.9958	gL^{-1}
K_{SP}	Substrate half-saturation coefficient for ethanol production	26.3216	gL^{-1}
K_{IM}	Inhibition substrate coefficient in microbial growth	182.3467	gL^{-1}
K_{IP}	Inhibition substrate coefficient in ethanol production	0.1221	gL^{-1}
P_M	Inhibition product coefficient in microbial growth	31.2110	gL^{-1}
P_P	Inhibition product coefficient in ethanol production	25.7261	gL^{-1}
K_d	Microbial death rate	0.0225	h^{-1}
m	Maintenance coefficient of microbial	0.0017	h^{-1}
Y_{MS}	Yield coefficient for the substrate used on microbial growth	2.7793	*dimensionless*
Y_{PS}	Yield coefficient for the substrate used on ethanol production	1.2606	*dimensionless*

Table 2. Parameters and variable used in [8].

Symbol	Description
Q	Diffusivity coefficient
T	Temperature
N	Concentration of nitrogen
O	Concentration of oxygen
K_N	Nitrogen half-saturation coefficient
K_O	Oxygen half-saturation coefficient
α & β	Yield coefficient

The next section combines the work of [9] and [8] which addressed reactions and diffusion to gain an extensive knowledge of mathematical model inhibitory and mass transfer effects in a shaker-free fermentation. This model was later modified to extend the understanding of the shaker fermentation problem.

3. Reaction-diffusion model
The main objective of this model was to describe the system of microbial growth, ethanol production, and substrate consumption associated with batch fermentation as represented by the following equations.

$$\frac{\partial M}{\partial t} = Q\frac{\partial^2 M}{\partial x^2} + \mu_{\max} SM\left(K_{SM} + S + \frac{S^2}{K_{IM}}\right)^{-1}\left(1 - \frac{P}{P_M}\right) - K_d M \tag{7}$$

$$\frac{\partial P}{\partial t} = Q\frac{\partial^2 P}{\partial x^2} + v_{\max} SM\left(K_{SP} + S + \frac{S^2}{K_{IP}}\right)^{-1}\left(1 - \frac{P}{P_P}\right) \tag{8}$$

$$\frac{\partial S}{\partial t} = Q\frac{\partial^2 S}{\partial x^2} - \frac{1}{Y_{MS}}\left[\mu_{\max} SM\left(K_{SM} + S + \frac{S^2}{K_{IM}}\right)^{-1}\left(1 - \frac{P}{P_M}\right) + K_d M\right]$$
$$- \frac{1}{Y_{PS}}\left[v_{\max} SM\left(K_{SP} + S + \frac{S^2}{K_{IP}}\right)^{-1}\left(1 - \frac{P}{P_P}\right)\right] - mM \tag{9}$$

The model presented is a PDE that reflects the spatial coordinate, x and time observation, t as two independent variables where $0 \le x \le 100$ meter and $0 \le t \le 100$ hours. Parameter estimation `fminsearch`, a Matlab toolbox that adopts Nelder–Mead method was used to estimate the parameters value based on the experimental data in [2].

The set of initial conditions obtained from the experimental data in [2] was defined by the following equations

$$M(x,0) = 3.8757\ gL^{-1}, \qquad P(x,0) = 0.0111\ gL^{-1}, \qquad S(x,0) = 87\ gL^{-1} \tag{10}$$

and the boundary conditions were implemented as proposed by [8] as followed:

$$\begin{cases} \dfrac{\partial M(0,t)}{\partial x} = 0; & \dfrac{\partial P(0,t)}{\partial x} = 0; & \dfrac{\partial S(0,t)}{\partial x} = 0 \\[2ex] \dfrac{\partial M(100,t)}{\partial x} = 0; & \dfrac{\partial P(100,t)}{\partial x} = 0; & \dfrac{\partial S(100,t)}{\partial x} = 0 \end{cases} \tag{11}$$

The model with the given initial and boundary condition in equation (4) and equation (5) were solved using `pdepe`, a Matlab toolbox that run Gear's algorithm to solve the parabolic PDE problem. The study of the diffusion effect on the ethanol production system is then discussed in the following section conclusively.

4. Diffusion effect on the ethanol production system

This section discusses the analysis of microbial diffusivity, diffusivity of ethanol, and diffusivity of substrates towards the model. The assessment began with a tiny diffusivity value for all three variables, i.e. microbial, ethanol and substrate, but as in [8], there was no important transition to the model. In addition, the change in the model became apparent when the diffusivity values were 1×10^{12} $m^2 h^{-1}$. Therefore the research was conducted with the initial diffusivity coefficient at 1×10^{11} $m^2 h^{-1}$ and the parameter D in the following equation describes the diffusivity values.

$$Q = 1 \times 10^{D} \ m^2 h^{-1}, \quad D = 11, 12, \ldots, 21 \tag{12}$$

4.1. Diffusivity in microbial growth

Figure 1(a) illustrates the investigation of parameter D towards microbial growth rate. There were four clear different lines indicating parameter D values in the graph which were 17, 18, 19 and 20. While the lines for $D = 11$, 12, 13, 14, 15, 16 and 21 overlapped, such distinguished lines of D value shows a big difference in microbial growth when it is $t = 20h$ as well as when the microbial concentration at the end of the process. At the end of the process, the greatest concentration of microbial among all was $D = 19$, while the smallest was $D = 18$. The following research of the D values towards microbial development are presented in Figure 1(b). The figure demonstrates the different last concentration of microbial for $D = 14$, 15, 16 and 20 along with their growth rate 1 hour before the end of the process. Whereas Figure 1(c) explains the remaining viable microbial by controlling the parameter D with a value of 11, 12, 13, 14 and 21.
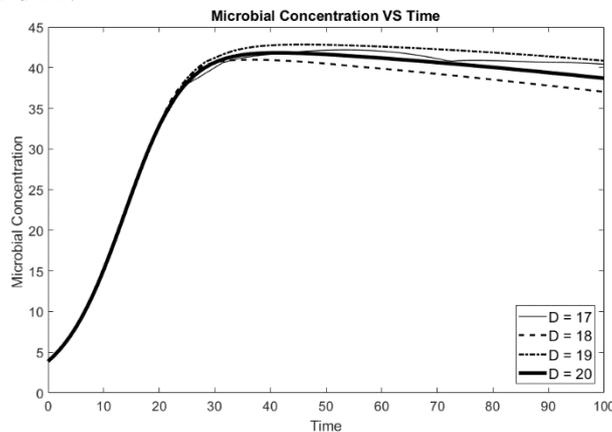
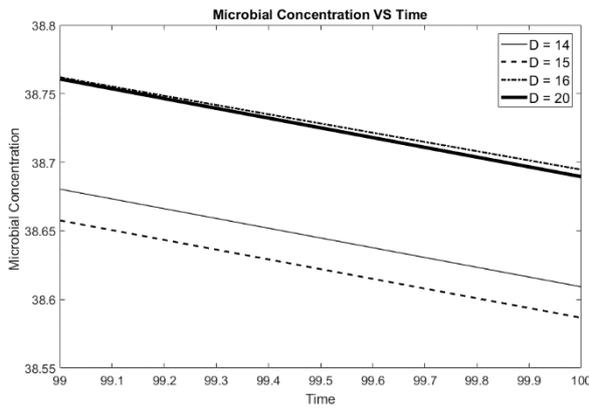

Figure 1(a). Microbial growth for $D = 17$, 18, 19 and 20.

Figure 1(b). Microbial growth an hour before the process ends for $D = 14$, 15, 16 and 20.
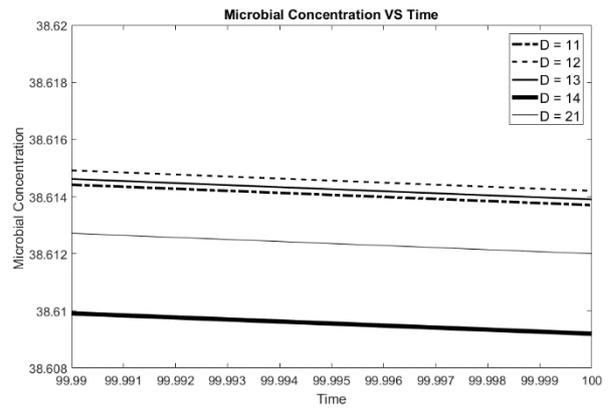

Figure 1(c). Microbial growth 0.05 hour before the production stops for $D = 11$, 12, 13, 14 and 21.

4.2. Diffusivity in substrate consumption

Analysis of diffusivity in substrate consumption is shown in Figure 2(a). This analysis used the same diffusivity values as in the previous experiment. However, there were only four lines with distinct D values which were 17, 18, 19 and 20. The figure also exhibits the entire process of substrate utilised by microbial in ethanol production. It is noticed that after 20 hours of the process, the adjustment in parameter D started to affect the consumption rate. The highest substrate concentration remained at the end of the process was when $D = 17$ and the lowest was $D = 18$, respectively at 50.4006 and 47.1872. The concentrations of substrate left in the fermenter for other parameter D were between the two values.

The diffusivity was further investigated by setting the parameter D at lower value but only four lines displayed in Figure 2(b). The lines represented the last hour of substrate concentration behaviour for $D = 14$, 15, 16 and 20 and the final amount of substrate for $D = 16$ offered the most significant difference compared to others. Then, Figure 2(c) explains the study of diffusivity on substrate consumption by examining the value of parameter D with 11, 12, 13, 14 and 21. The evaluation time was set at 0.05h before the production stopped to clearly distinguish the D values.
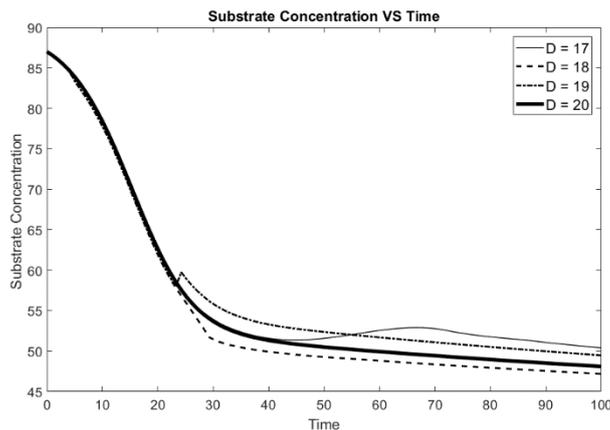

Figure 2(a). Substrate consumption for $D = 17$, 18, 19 and 20.
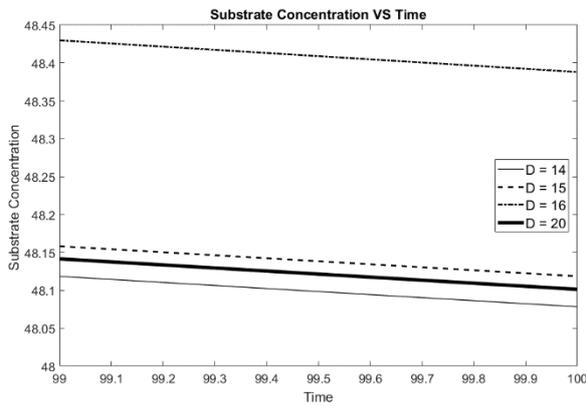
Figure 2(b). Substrate consumption an hour before the process ends for $D=14$, 15, 16 and 20.
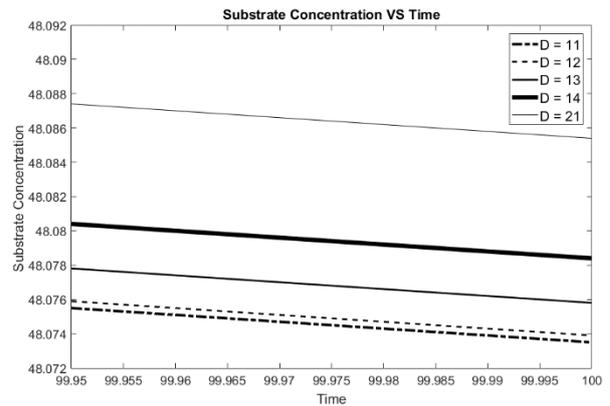
Figure 2(c). Substrate consumption 0.05 hour before the production stops for $D=11$, 12, 13, 14 and 21.

4.3. Diffusivity in ethanol production

Diffusivity inspection over the production of ethanol showed very limited outcomes as portrayed in Figure 3. Only three production rates appeared in Figure 3(a) and other five sets of ethanol concentration produced in a fermentation tank depicted in Figure 3(b) and Figure 3(c) even though the study was conducted with 13 variety of parameter D. A remarkable change in production flow was notable after 20 hours of the manufacturing when $D=17$, 18 and 20 but not for $D=19$ similar with what happened in microbial growth and substrate consumption. Once the parameter $D=18$ was allocated, the largest amount of ethanol generated, but the results showed otherwise for $D=17$. Lines in Figure 3(c) disclose three sets of ethanol production with an assorted value of D that bounded under the $D=20$ line in Figure 3(b) yet these dissimilarities were very small (approximately 0.0003 different between the values).
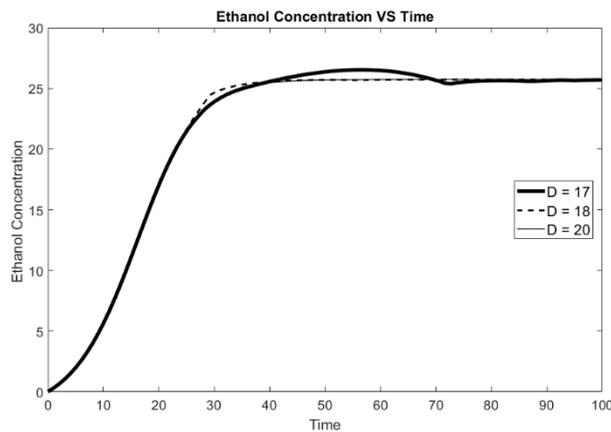

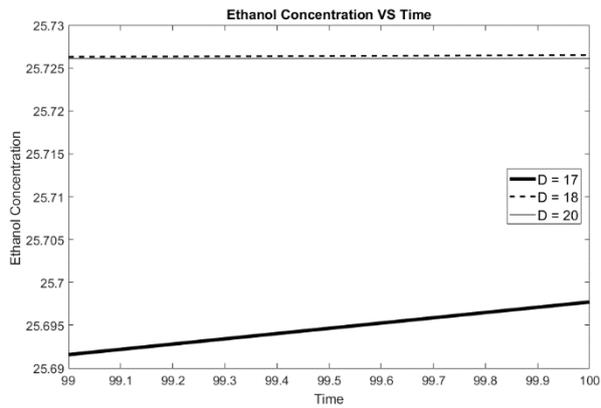**Figure 3(a).** Ethanol production for $D=17$, 18 and 20.

Figure 3(b). Ethanol production an hour before the process ends for $D = 17, 18$ and 20.
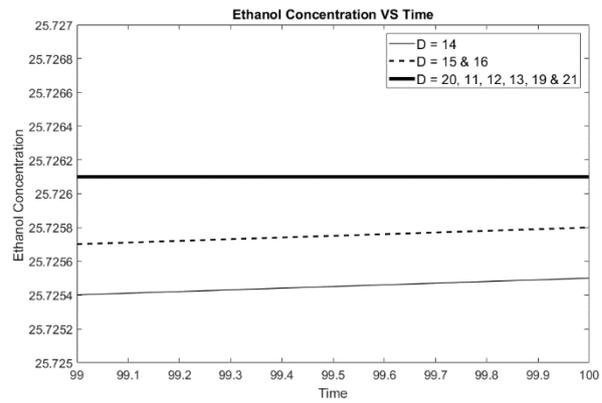

Figure 3(c). Ethanol production an hour before the production stops for $D = 11, 12, 13, 14, 15, 16, 19, 20$ and 21.

5. Reaction-diffusion-advection model

This section demonstrates the extension of the earlier mathematical model in section 4 with the advection element as shown in the following equations where U is velocity coefficient.

$$\frac{\partial M}{\partial t} = Q\frac{\partial^2 M}{\partial x^2} + \mu_{max}SM\left(K_{SM} + S + \frac{S^2}{K_{IM}}\right)^{-1}\left(1 - \frac{P}{P_M}\right) - K_d M - U\frac{\partial M}{\partial x} \tag{13}$$

$$\frac{\partial P}{\partial t} = Q\frac{\partial^2 P}{\partial x^2} + v_{max}SM\left(K_{SP} + S + \frac{S^2}{K_{IP}}\right)^{-1}\left(1 - \frac{P}{P_P}\right) - U\frac{\partial P}{\partial x} \tag{14}$$

$$\frac{\partial S}{\partial t} = Q\frac{\partial^2 S}{\partial x^2} - \frac{1}{Y_{MS}}\left[\mu_{max}SM\left(K_{SM} + S + \frac{S^2}{K_{IM}}\right)^{-1}\left(1 - \frac{P}{P_M}\right) + K_d M\right]$$
$$- \frac{1}{Y_{PS}}\left[v_{max}SM\left(K_{SP} + S + \frac{S^2}{K_{IP}}\right)^{-1}\left(1 - \frac{P}{P_P}\right)\right] - mM - U\frac{\partial S}{\partial x} \tag{15}$$

The model is inspired by the agitation in fermentation, considering the advection factor in the model. This research adopted settings, parameter values and methods of the previous experiments, but with alteration of diffusion coefficient Q which was set to 10 $m^2 h^{-1}$. The following section examines in depth the advection effect on the ethanol production system.

6. Advection effect on the ethanol production system

Advection research was conducted in the study of the velocity coefficients for microbial growth, ethanol production and use of the substrate. As in the previous study in section 4, the value of the velocity coefficient was channelled to a small value, but no changes were shown. Since the changes were visible at $U = 1 \times 10^6 \ mh^{-1}$, this study discussed only the findings of the study starting with $U = 1 \times 10^5 \ mh^{-1}$. The velocity coefficient in the next equation was described in the parameter V to facilitate interpretation of the finding.

$$U = 1 \times 10^V \ mh^{-1}, \quad V = 5, 6, 7, \ldots, 12 \tag{16}$$

6.1. Velocity impact on microbial growth

Figure 4 summarizes the microbial growth rate analysis of parameter V. As shown in Figure 4(a), $V = 8, 10, 11$ and 12 contributed to major variations in microbial growth. While $V = 10$ and $V = 11$ generated the same line patterns, the $V = 8$ and $V = 12$ values had a significant impact on microbial growth. Moreover, in examining the growth rate at different agitation rate, the findings from [11] demonstrate the same pattern as in Figure 4(a). In fact, in Figure 4(b), $V = 8$ and $V = 12$ yielded for the highest and smallest concentration of microbial, which were 71.6532 and 35.0464, respectively. The results of the study on $V = 9$ is not explained since this value does not well represent the real growth rate of the microbial. Figure 4(c) shows the various last microbial concentrations of $V = 5$, 6, 7, and 10 together with the rate of growth of an hour before the process completion.
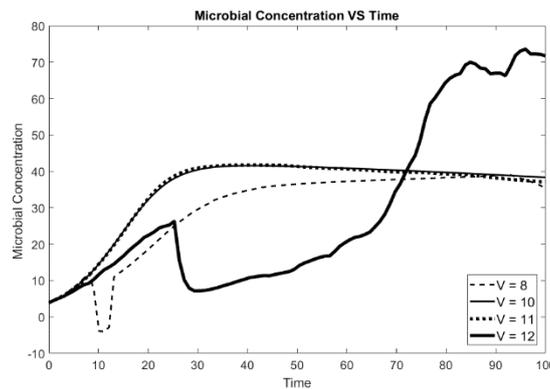

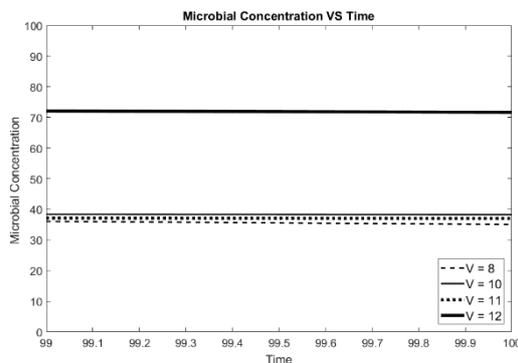**Figure 4(a).** Microbial growth for $V = 8$, 10, 11 and 12.

Figure 4(b). Microbial growth an hour before the process ends for $V = 8$, 10, 11 and 12.
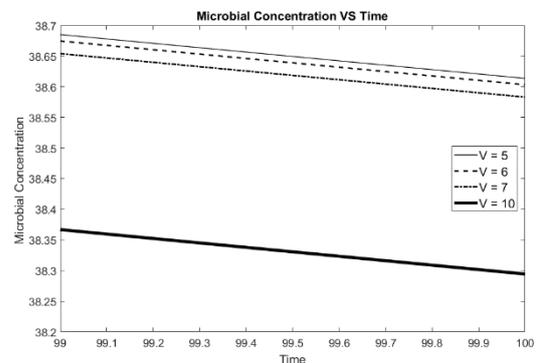

Figure 4(c). Microbial growth an hour before the production stops for $V = 5$, 6, 7 and 10.

6.2. Velocity impact on substrate consumption

Effect of advection velocity on substrate consumption rate was studied by comparing the parameter V from 5 to 12 is presented in Figure 5. The velocity V=9 generated unrealistic consumption rate of substrates, as in the microbial growth. This is the same reason it is not reviewed. Figure 5(a) indicates $V = 8$, 10, 11 and 12 consumption rates. In the fermentation, the maximum substrate left was 54.0915 g/L at $V = 12$ whereas the minimum was 21.9482 g/L at $V = 8$ and the difference was 32.1433 g/L, illustrated in Figure 5(b). The velocity was also tested by setting the low value of parameter V, as shown in Figure 5 (c). The lines represent the last hour of the $V = 5$, 6, 7, and 10 substrate concentration behaviour, and $V = 10$ had the smallest last substrate concentration.
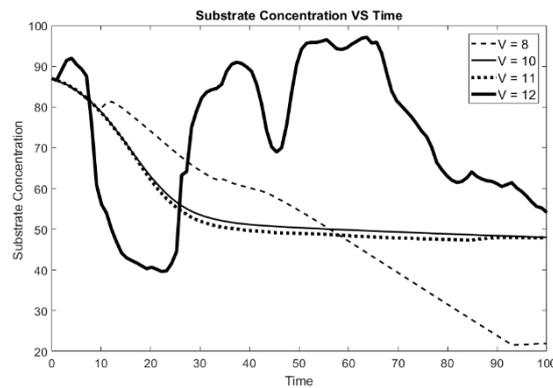
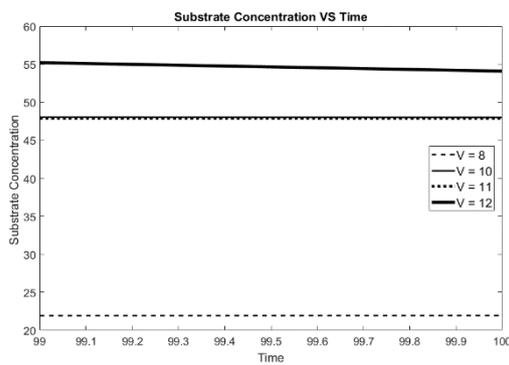**Figure 5(a).** Substrate consumption for $V = 8, 10, 11$ and 12.

Figure 5(b). Substrate consumption an hour before the process end for $V = 8, 10, 11$ and 12.
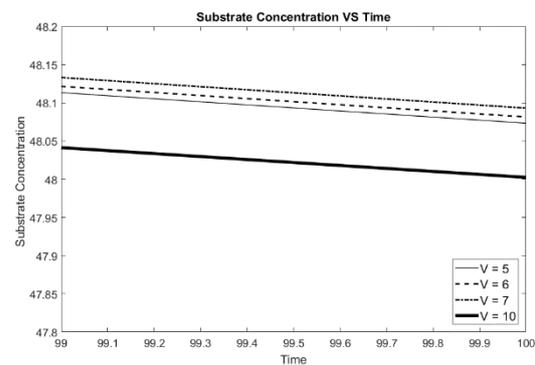

Figure 5(c). Substrate consumption an hour before the production stops for $V = 5, 6, 7$ and 10.

6.3. Velocity impact on ethanol production

The agitation effect on the production of fermentation ethanol studied in [10] proves that the speed of advection has an effect on production yield and that conclusion is also interpreted in Figure 6. The velocity study by parameter $V = 8, 10, 11$ and 12 in Figure 6(a) demonstrates a similar pattern to the experiment in [10]. Although after 20 hours of production the ethanol rate was unstable, the speed at $V = 12$ at the end of the process was 27.4652 g/L at the highest ethanol concentration. On the other hand, $V = 8$ was 25.6950g/L at the smallest concentration. Next, the velocity studies were performed in Figure 6(c) by specifying parameters V with 5, 7, 8 and 9. The lines for V = 5 and 7 overlapped due to the equal production rate and the same amount of ethanol output. Even the figure indicates the different amount of ethanol generated, the differences between the lines were extremely low.
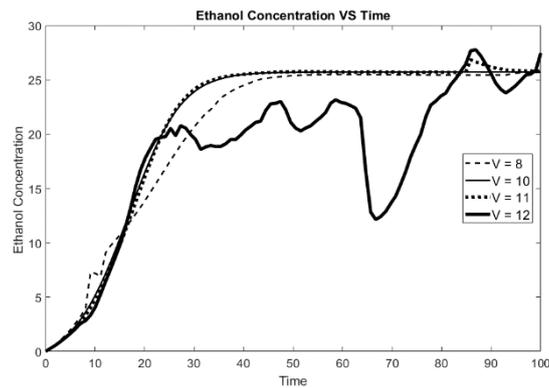
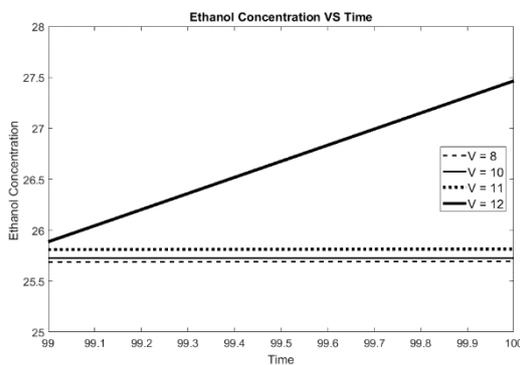**Figure 6(a).** Ethanol production for $V = 8, 10, 11$ and 12.

Figure 6(b). Ethanol production an hour before the process ends for $V = 8, 10, 11$ and 12.
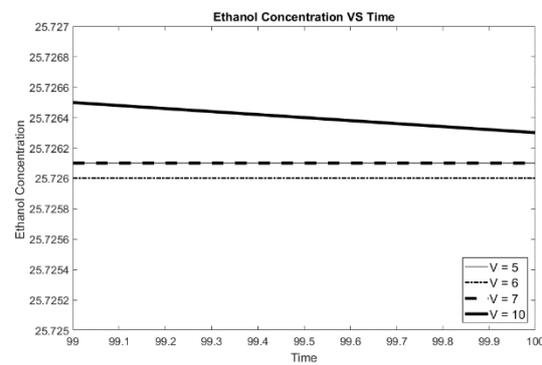
Figure 6(c). Ethanol production an hour before the production stops for $V = 5, 6, 7$ and 10.

7. Conclusion

At first, this research was to formulate a non-linear PDE model for ethanol production via fermentation by coupling diffusion-reaction into the model. Extensive knowledge of the process and inclusion of all significant parameters of the model can properly evaluate ethanol production. Therefore, the diffusivity impact in the model was analysed and the result demonstrates that diffusivity has a minor effect on microbial growth, consumption of the substrate and also in ethanol production. Motivated by the agitation employed in fermentation, the model is extended by proposing the advection unit. Contrary to its diffusivity outcome, even though the advection coefficient was comparatively low, the model demonstrates an apparent change. This expansion model also shows the important advection effect on both microbial growths and substrate used.

8. Acknowledgement

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