

Investigating the Process of Bioethanol Production from Sugarcane Wastes (Molasses)

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Abstract

The development of a mathematical model for a process is reaching assumptions regarding the way the process can be accomplished. Fermentation is an exothermic reaction that causes an increase in the temperature of fermentation environment. Therefore, the present study tries offering an appropriate model for temperature changes of the sugarcane molasses fermentation environment. To thermally model the fermentation process, Fourier heat conduction equations have been utilized. A cylindrical reactor was used to perform the fermentation process; so, Fourier's heat conduction equation was investigated and evaluated in 2D to model heat conduction and investigate the heat distribution trends in fermentation environment following which the 2D model was solved based on finite element method. To do so, heat conduction was once investigated in *xy*-direction and once in *yz*-direction using the same equation. To model the heat conduction along *xy*-direction, the problem domain considered herein was circular and also the circle quarter was employed for modeling due to the axial symmetry of the circle and parallel to reducing the number of calculations. The domain (quadrant) was divided into 6-nod triangular elements following which the model's geometrical shape was drawn in the form of a quadrant with 466 elements and 1062 nodes. The modeling of the temperature changes during the fermentation process and investigation of the temperature distribution in reactor shows that the fermentation environment temperature increases by 10°C to 15°C as a result of microorganisms and this has also been confirmed by the other researchers.

Keywords: Bioethanol, Molasses, Thermal Simulation, Sugarcane Wastes

Introduction

Since the ancient times, plants have been used globally as a valuable and safe natural source of medicine and as agents of therapeutic, industrial and environmental utilities (Kumari et al., 2015). The present study has focused on molasses in order to produce alcohol. In producing alcohol, molasses is different from the other raw materials like corn, millet and potatoes because these plants store carbohydrate in the form of starch. Therefore,

these raw materials should be subjected to such pretreatments as cooking and enzyme injection so that starch could be hydrolyzed to fermentable sugars. Conversely, these materials, carbohydrates, have been previously in the form of fermentable sugars in molasses hence needless of pretreatment. There are numerous models offered in food and conversion industries as well as in agriculture and agricultural products processing grounds. Some mechanical and fluid equations like heat conduction, mass and moisture transfer, stress and strain analysis and so forth can be used for the analysis of the phenomena and processes related to food and agriculture industries. There are carried out extensive researches in this regard by various researchers. For example, Ahmad Ganaie et al. (2017) used silico screening models to show that safranal and crocin have significant potential to influence the metabolic activity of CYP2C9 enzyme. Fanaei et al. (2009) offered a heat conduction model for the fermentation of wheat bran and solved it numerically based on Runge-Kutta differential equation.

Jiang et al. (1987) dealt with a finite element method for the modeling of heat distribution in broccoli stems upon being subjected to cold air streams. Hunt and Gu dealt (2006) used heat conduction differential equation in two dimensions to investigate the effect of thermal conductivity on wood as well as the effect of macroscopic characteristics and moisture content of wood on heat conduction inside soft wood. Following introducing proper differential equations for the case model (heat conduction differential equation) and in order to obtain differential equation responses, they solved the intended equation under preliminary and special boundary conditions based on finite element method (Baini and Langrish, 2007).

In parallel, Hartmann et al. (2006) offered a partial differential equation that investigated the differential of the mechanical stress created in the cell structures as a result of being subjected to high hydrostatic pressure for which purpose *Saccharomyces Cerevisiae* yeast cells were utilized and subjected to various hydrostatic pressures and the amounts of pressure and stress imposed on them were measured following which it was nonlinearly modeled. They, as well, used finite element method to solve the stress equation of the yeast cells and the responses were displayed graphically.

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In the finite element method, the physical problems are mostly solved assisted by differential equations governing the system or via minimizing the potential energy in such a manner that the overall geometrical model is divided into smaller parts. Input values (loading and boundary conditions) and output values (results) are assigned to each nod.

Connely et al. (2004) modelled paste deformations during mixing and the obtained model was solved using finite element method. Lin et al. (1995) modeled the heat conduction and distribution in microwave oven during the baking of foodstuff and the obtained model was solved based on finite element method. Oliviera et al. (2000) and Ratanadecho et al. (2001) implemented a 3D finite element method to describe heat conduction in microwave oven during cooking potatoes that had been given the shapes of cylinders or plates.

In regard of bread baking, Ma et al. (2009) modeled heat transfer and bread paste moisture variations during baking. The differential equations presented by them investigated and evaluated heat conduction and moisture transfer with the change in the paste volume. They, as well, solved these equations numerically and simply based on finite element method and finally compared the obtained responses with the laboratory data. Bakalis et al. (2009) used finite element method for modeling the moisture transfer process in rice grains when boiling in water. To describe the process, they used Fickian absorption model followed by its solving based on finite element method.

Hernandez and Belles (2007) offered a 3D finite element model to investigate the hardness of sunflower seed shells. To come up with an appropriate model, they made use of partial differential equation to investigate stress and strain of the biological materials. Singh et al. (2004) dealt with the effect of the initial temperature and moisture of barley seeds and soybeans on their drying rates and eventually modeled it using differential equations that were solved based on finite element method. Muthakumarappan et al. (1994) modeled the mass transfer and heat conduction processes during moisture absorption by the corn seeds and solved the model using finite element method.

Study Objectives:

The present study tries offering models for the optimization of fermentation process regarding the temperature distribution in the fermentation environment using partial differential equations that will be solved based on finite element method. The present study's objectives are as listed below:

- 1) Investigation of the temperature distribution inside the reactor during fermentation process
- 2) Modeling the progress of fermentation process using finite element method.

Materials and Methods

The present study was conducted in Recycling Laboratory of Agriculture Faculty of Islamic Azad University, Shoushtar Branch, in 2016.

As Sudha et. al, (2012) declared, method development involves a series of simple steps. The following experiments were carried out in several stages and the obtained data were noted for the thermal simulation.

The Specifications of the Sugarcane Molasses Used in the Experiments:

Preparation of sugarcane molasses sap syrup

Preparation of alcohol from sugarcane molasses sap

Also, the variables used for the investigation of fermentation process and the progress rates of the process were measured, including the followings:

- 1) Brix Measurement
- 2) Alcohol Measurement
- 3) Temperature Measurement
- 4) Measurement of CO₂ or the gases produced during the process

Generally, the formulation of the physical and natural and other phenomena and processes leads to the creation of mathematical equations that are mostly of the differential equations type in such a way that the values and amounts intended for the perception or designing of a process depend thereon. The development of the mathematical model of a process is recounted as reaching assumptions regarding the way they can be done. In a numerical simulation, a numerical and computer-based method is employed to evaluate the mathematical model and estimate the process characteristics (Arroyo- Lopez et al., 2009).

Finite Element Method:

Mathematical equations are proposed in two forms of simple mathematical equations and differential equations. In either of the cases, the relationships between a dependent variable and one or several independent variables are investigated and demonstrated. Models posited in differential equation form can be either simple differential equations or partial differential equations. In the former, the dependent variable of choice is only associated with one independent variable but, in the latter, the dependent variable of interest is correlated with several independent variables. Heat conduction equation presented below is a simple differential equation in one respect and it can be easily solved and an exact answer can be found for it.

$$\frac{d}{dx} \left(k \frac{dT}{dx} \right) = 0 \quad (1)$$

Equation (1) only shows heat conduction along an axis. The general heat conduction equation is a partial differential equation as displayed below. In solving the partial differential equations, the boundary and the initial conditions should be taken into consideration.

$$\frac{d}{dx} \left(k_x \frac{dT}{dx} \right) + \frac{d}{dy} \left(k_y \frac{dT}{dy} \right) + \frac{d}{dz} \left(k_z \frac{dT}{dz} \right) + q = \rho C_\mu \frac{dT}{dt} \tag{2}$$

A great many of the natural phenomena can be defined in the form of differential equations. For example, heat conduction, wave, Poisson, Laplace, telegraph, moisture transfer and other differential equations can be defined.

In general, there are three methods for solving mathematical equations:

- Exact Solution Method
- Numerical Solution Method
- Experimental Solution Method

Amongst the aforesaid methods, the numerical solution method one subset of which is finite element is most widely applied in solving the engineering problems.

The advantages of the numerical solution method, especially those of the finite element method, as compared to the other methods, are as summarized below:

The substantial weakness of the laboratory method is its costliness and time-consuming nature while these are missing from numerical solution method.

The majority of the equations offered for the growth curves include such mathematical parameters as a, b, c etc. it is via expressing these equations in the form of ordinary mathematical parameters that their investigation for the biological process becomes a little difficult thus the mathematical parameters should be turned into biological ones so as to ease their understanding. However, most of the mathematical equations of growth are reparametrized and rewritten based on biological parameters and such mathematical parameters as a, b and c are replaced by such biological parameters as v, μ_m , λ and A.

Growth Function Re-Parametrization:

To obtain the curve's turning point from the growth function, it is subjected to two times of differentiation in respect to t and the first derivative and second derivative become as shown in equations (3) and (4), respectively.

$$\frac{dy}{dt} = ac \cdot \exp[-\exp(b-ct)] \cdot \exp(b-ct) \tag{3}$$

$$\text{Exp} [-\exp(b-ct)] \cdot \exp(b-ct) \cdot [\exp(b-ct)-1] \frac{d^2 y}{dt^2} = ac^2 \tag{4}$$

In $t=t_i$ in the point of curve, the second derivative value equals zero. So, we have (equation 5):

$$\frac{d^2 y}{dt^2} = 0 \rightarrow t_i = b / c \tag{5}$$

Now, inserting t_i in the first order derivative of the growth function in the growth speed equation, the maximum growth speed of the function can be obtained in the point of curve as shown below:

$$\mu_m = \left(\frac{dy}{dt} \right)_{t_i} = \frac{ac}{e} \tag{6}$$

By obtaining c from equation (6), substituting it in the growth equation and describing the line gradient in the point of curve, we will have (equation 7):

$$y = \mu_m t + \frac{a}{e} - \mu_m t_i \tag{7}$$

The interception point of t-axis with the line gradient obtained in equation (7) gives the delay time (λ) as shown below:

$$u = \mu_m \lambda + \frac{a}{e} - \mu_m t_i \tag{8}$$

Combining equations (6), (7) and (8) gives delay time equal to (9):

$$\lambda = \frac{(b-l)}{c} \tag{9}$$

Parameter b in Gompertz equation can be substituted by the following term:

$$b = \frac{\mu_m e}{a} \lambda + 1 \tag{10}$$

And, the asymptotic value of function when t is tending towards infinity is calculated as shown in equation (11):

$$t \rightarrow \alpha : y \rightarrow a \Rightarrow A = a \tag{11}$$

Therefore, Gompertz equation is corrected as shown in equation (12) with the insertion of a, b and c values:

$$y = A \exp \left\{ -\exp \left[\frac{\mu_m e}{A} (\lambda - t) + 1 \right] \right\} \tag{12}$$

Another tri-parametrical growth equation is logistic model that is parametrized in the same way and its general and modified equations are as shown in (13) and (14) equations:

$$y = \frac{a}{[1 + \exp(b-ct)]} \tag{13}$$

$$y = \frac{A}{\{1 + \exp[\frac{\mu_m}{A}(\lambda - t) + 2]\}} \quad (18)$$

Another parameter named shape parameter is added to the equation in the tetra-parametrical equations like Richards' model. Therefore, three various models were offered based on the obtained diagrams to model the amounts of products (ethanol and CO₂) produced. These models are Gompertz model, logistic model and bi-parametrical exponential model. The first two was perfectly explained previously and the third model is introduced in the form of equation (15) due to the exponential nature of the production curve.

$$y = -a \cdot \exp(bt) + a \quad (15)$$

Model parameters were obtained using Matlab VER 7.2.

Temperature Modeling Using Finite Element Method:

Fermentation is an exothermic reaction meaning that heat is generated during the process and it causes the fermentation environment temperature to go up. Therefore, the present study has attempted to offer an appropriate model for temperature variations of the fermentation environment. To thermally model the fermentation process, Fourier heat conduction equations have been utilized. Fourier heat conduction equation is as shown in equation (16).

$$pc \frac{dt}{dt} - \frac{\partial}{\partial x} (k_x \frac{\partial T}{\partial x}) - \frac{\partial}{\partial y} (k_y \frac{\partial T}{\partial y}) - \frac{\partial}{\partial z} (k_z \frac{\partial T}{\partial z}) = q_b \quad (16)$$

In such a manner that T=T(x, y, z) denotes temperature in various directions, P is density, C is specific heat capacity and k is the object's heat conduction that is associated with x, y and z coordinates. It is assumed herein that heat conduction is identical in all directions and q_b is the production rate of metabolic heat by the microorganisms. Fourier heat conduction equation is solved based on finite element method. To do so, equation (16) is considered to be 2D in which case heat production in z-direction is dismissed and the equation takes the form shown in equation (17):

$$pc \frac{dT}{dt} - \frac{\partial}{\partial x} (k_x \frac{\partial T}{\partial x}) - \frac{\partial}{\partial y} (k_y \frac{\partial T}{\partial y}) = q_b \quad (17)$$

Solving the partial 2D differential equation of heat conduction based on finite element method and assuming a fixed value for k in various directions, we will have (equation 18):

$$\int_{\pi} wpc \frac{\partial T}{\partial t} dx dy + k \int_{\pi} [\frac{\partial w}{\partial x} \frac{\partial t}{\partial x} + \frac{\partial w}{\partial y} \frac{\partial t}{\partial y}] dx dy - \int_{r'} kw [\eta_x \frac{\partial T}{\partial x} + \eta_y \frac{\partial T}{\partial y}] ds - \int_{\pi} f w dx dy = 0$$

Implementing the finite element method and essential and natural boundary conditions, we will have equation (19):

$$\sum_j^n = \mathbb{I}[-\lambda c^e + k^e] T_i = f_i^e + q_i^e \quad (19)$$

Where, K is the hardness matrix and C is the mass matrix and f is the force vector or source vector. They are calculated in the form of equations (19).

Modeling the fermentation process

Modeling the amount of reactants (sugars)

The sugar in the fermentation environments is the main reactant of the fermentation process, which, as the graphs are shown in the previous section, it changes as a descending chart and it starts at a maximum value and descends with a relatively high speed and high slope to reach the lowest possible extent. And finally the chart is fixed; in other words, the amount of sugar intake is fixed or slowed down. Two models were used to model this process. 1) Exponential model 2) Modified logistic model.

After obtaining the parameters of the proposed models, the parameters were put in the model and, based on this, equations 20 and 21 show the final equations for examining and predicting the process of sugar consumption (glucose) over time. In each of the equations, (Y) is the amount of sugar consumed in terms of brix at time (T), and (t) is the time per day.

$$Y = \exp [2.58 + -1.355 / 1 + \exp (-0.6775(t - 0.12))] \quad (20)$$

$$Y = 10.5 \times \exp (0 - 0.621t) + 8.65 \quad (21)$$

To compare the presented models with each other and to find the best model for reviewing and modeling, the two comparison criteria of the coefficient of determination (R²) and the second root mean square error (RMSE) were used. Their values are shown in Table 1. This table shows that both models can well justify our experimental data and have a good agreement (With R² of more than 0.98). However, the modified logistic model with a higher R² and less RMSE could better justify the data, and therefore it is a better model for determining the concentration of sugar in the fermentation environment over time during the fermentation process of sugarcane molasses.

Table 1- Comparison of two models presented for determining the concentration of sugar in the fermentation environment

| Model | R ² | RMSE |
|-------------------|----------------|--------|
| Modified logistic | 0/9896 | 0/2154 |
| exponential | 0/9871 | 0/2365 |

The graphs show the ability of modified logistic and exponential models to justify and describe the laboratory data, and according to the graphs shown, the models presented for modeling the amount of sugar during the fermentation process of sugar

molasses can be well understood. The graphs show that the first model (modified logistic model) has passed better from inside laboratory data and is more consistent with the experimental data.

Modeling the amount of products (ethanol, carbon dioxide)

The chemical equation of the fermentation process shows that during the process of fermentation, two different materials, which are the products produced during the reaction, are produced, which are: 1) ethanol, 2) carbon dioxide gas. Therefore, to model this process, we present models for both products, which we examine each below.

Modeling the process of ethanol change

By looking at the obtained graphs for the products, it can be seen that the overall shape of the graphs was similar to that of circular curves for yeast growth. Therefore, to model the production of each of the products (ethanol production, carbon dioxide gas), it was attempted to use the proposed models for circular curves for the growth of microorganisms. For this purpose, two models of three-parameter models (1) gompertz, 2) logistic were introduced and parameterized for the biological process, and each of the parameters was defined for the process; additionally, due to the similarity of the obtained graphs with exponential function graphs, an exponential two-parameter model was also used. Finally, the proposed models were compared by comparing R² coefficient of determination and the root mean square error (RMSE) with the experimental data for suitability of each model. In each step, the best model was used to justify the fermentation process.

In Table 2, the values of A, μ_m, λ, t_∞ parameters for the gompertz and logistic models are shown which obtained by passing the models from the data sets to justify the amount of alcohol produced during the fermentation process of sugarcane molasses; by placing each of the parameters, its specific equation is obtained. In which (A) is the maximum amount of alcohol production μ_m, is the maximum speed of alcohol production, λ is the latency; in other words, the time it takes to begin the process, and finally t_∞ is the burnout stages, which is the maximum time it takes for ethanol to reach its maximum value, and then its amount is almost constant and, in other words, it shows the stopping time of the process.

Table 2- The values of estimated parameters for determining the amount of alcohol produced during the fermentation process of sugarcane molasses

| model | A | m (day ⁻¹)μ | (day) λ | (day) t _∞ |
|----------|---|-------------------------|---------|----------------------|
| gompertz | 8 | 2/69 | 0/56 | 8 |
| logistic | 8 | 2/56 | 0/67 | 6 |

Due to the similarity of the resulting curve with the exponential function, the exponential two-dimensional model was used. After obtaining its parameters with Matlab software and putting in the model, its specific equation was obtained as Equation 22. In the equation (Y) is the average volume of alcohol generated at time

(t) which is based on (mm / mm) and (t) is the time per day.

$$Y = -6.855 \times \exp(-0.4226t) + 7.954 \tag{22}$$

As shown in Table 3, the presented models well justify the laboratory data (with R² more than 0.98). Therefore, it can be argued that all three models are suitable for justifying the process and are well suited to justify and estimate the amount of alcohol produced over time with little error; however, from these three models presented to determine the amount of alcohol produced in the process, gompertz fermentation model was recognized as the best model. This model, other than high R² of the exponential mode due to clarity of its parameters, it can be easily understood by taking into account the parameters of the process. On the other hand, the model can be used to compare the alcohol production from different products during the fermentation process, and thus it can be used as a model that has the best product in terms of maximum production and maximum production speed, and therefore the selection of a product that has the shortest time to produce the maximum amount of alcohol. Therefore, gompertz model was chosen as the most suitable model in comparison to two other models.

Table 3- Comparison of R² and RMSE values for different models presented to justify the amount of alcohol produced

| model | R ² | RMSE |
|-------------|----------------|--------|
| gompertz | 0/9826 | 0/2015 |
| logistic | 0/9751 | 0/2362 |
| exponential | 0/9651 | 0/2515 |

Modeling the changes of p carbon dioxide gas process

Another product obtained during the chemical reaction of fermentation, which is measurable, is carbon dioxide gas. And as shown in the diagram in the previous section, it is similar to the cyclic curves of microorganisms' growth. Therefore, for modeling and determining the amount of carbon dioxide gas over time, the same three models presented for modeling the production of alcohol were used and after obtaining parameters of the model with the help of Matlab software, the parameters of each of the presented models were put into the model and for each, the values of R² and RMSE were obtained so that the capabilities of each of the models could be presented to justify the obtained experimental data. Table 4 shows the values of the estimated parameters for both gompertz and logistic models, and finally, from Table 4, we can extract the values of R² and RMSE to compare the models with one another. According to Table 4, it can be concluded that gompertz model can be useful in determining the amount of Carbon Dioxide gas production during the process. Therefore, the Gompertz model can easily and accurately explain the production of both products produced during the fermentation process.

Table 4- Estimated parameter values for determining the amount of produced carbon dioxide

| model | A | m (day ⁻¹)μ | (day) λ | (day) t _∞ |
|-------|---|-------------------------|---------|----------------------|
|-------|---|-------------------------|---------|----------------------|

| | | | | |
|----------|-----|--------|------|----|
| gompertz | 320 | 104/96 | 0/67 | 14 |
| logistic | 320 | 108/56 | 0/93 | 11 |

Due to the similarity of the obtained curve with the exponential function, the exponential two-dimensional model was used, and after obtaining its parameters with the help of Matlab software and putting in the model, the specific equation was obtained as follows. In the equation 23, (Y) is the average volume of alcohol produced at 10:01 am (t), in terms of (mm / mm), and (t) is used per day.

$$Y = -365.2 \times \exp(-0.256t) + 365.2 \quad (23)$$

Conclusion:

It can be stated based on the investigations and modeling activities performed herein that the process terminates after almost five days and the proposed models have been sufficiently successful in justifying the laboratory data. As it was mentioned, one objective of modeling is the use of the model in designing bioreactors and optimization of fermentation process so that the highest ethanol production could be achieved within the shortest time and with the lowest spending of costs following process optimization. The followings are general summary results of the present study:

- 1) The investigation of sugar variation trend indicated that the process undergoes decline during the early days in a high speed in such a manner that brix of the fermentation environment is decreased from 20 to 9 and it reaches to 8.5 during the next 15 days, i.e. on the 20th day, and this is indicative of the idea that the sugar reduction rate after the fifth day is decreased proportionately with the pass of time and it becomes fixed after a while.
- 2) The investigation of ethanol production variation trend demonstrated that the ethanol production is increased with the pass of time very rapidly (from zero to eight volumetric percentage) and the ethanol production ascending trend is associated with sugar consumption; in other words, the increase in the speed of sugar consumption causes an increase in ethanol production and, resultantly, the other product, to wit carbon dioxide gas, ethanol production is reduced when the yeast cells' activity slows down and the ethanol production is nearly ceased when the microorganisms' activity stops.

It was figured out from the temperature variations during the fermentation process and investigation of temperature distribution in reactor that the fermentation environment temperature is increased by about 10 to 15 degrees as a result of microorganisms' activities and this latter finding has also been affirmed by the other researchers. Moreover, the temperature distribution in reactor indicated that the temperature increase is higher in the reactor center than the other spots so this point has to be carefully taken into account when designing large-scale industrial reactors. Thus, it has to be taken into consideration when designing bioreactors that the initial temperature of the fermentation environment should be set so as to prevent the

temperature increase from destroying the yeast cells and, also, it has to be made clear whether the temperature increase in the reactor center is harmful or not and whether it causes reduction in microorganisms' activities or not.

There is a need for certain equipment to be installed in the fermentation environment in the reactor for cooling down the bioreactor and exhausting the heat produced therein. Amongst the methods that are currently being used for cooling reactor are the use of water circulation around the reactor and the use of cold air circulation as well as a combination of the two thereby to make heat migrate from reactor center to the reactor walls and exhausted through them.

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