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Ethanol production from acid-pretreated and detoxified tea processing waste and its modeling

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ABSTRACT

Lignocellulosic materials are good feedstocks for ethanol production. Mathematical models give information about kinetic-metabolic nature of fermentation. The objectives of this study were to determine the chemical composition of non-detoxified tea processing waste hydrolysate (ND-TPWH) and detoxified tea processing waste hydrolysate (D-TPWH), to generate the ethanol from the D-TPWH, and to model the ethanol fermentation in D-TPWH using models including modified Gompertz, re-modified Gompertz, modified logistic, re-modified logistic, modified Richards, re-modified Richards, Stannard, Baranyi, Weibull, and Morgan-Mercer-Flodin. Results indicated that 11.91% of D-glucuronic acid, 7.28% of acetic acid, 98.12% of hydroxymethylfurfural, and 76.88% of phenolics were adsorbed by detoxification process. Ethanol yields by *Saccharomyces cerevisiae* and *Scheffersomyces stipitis* (ATCC 58784 and ATCC 58785) were 35.9, 38.98, and 33.87%, respectively. Regarding modeling, depending on the model comparison results including root-mean-square-error, mean-absolute-error, and regression coefficient, the experimental data of ethanol production and sugar consumption were successfully forecasted using Baranyi and Weibull models for *S. cerevisiae*; using Morgan-Mercer-Flodin model for *S. stipitis* (ATCC 58784); and using Stannard model for *S. stipitis* (ATCC 58785), respectively. Consequently, this was the first report on the ethanol production from D-TPWH and its modeling. TPW can be a good feedstock for ethanol production by the xylose-fermenting yeasts. Suitable flexible models could be applied for more progress of ethanol production process in D-TPWH.

1. Introduction

The present substantial expansion of the agricultural production and followed by various agro-industrial applications associated with continuous increasing of the world's population are increased the requirement for energy resources every passing day [1]. Furthermore, interests have been gained attention for production of alternative fuels to petroleum from renewable resources due to depletion of petroleum reserves, instability in petroleum price, and increasing global warming and environmental pollution [2]. Ethanol, an eco-friendly biofuel, is one of the most significant biofuels produced from renewable resources. Also it is the broadest volume biofuel utilized in the transport sector. Therefore, its production is increased day by day, especially in the United States of America from corn plant (starch-based) and in Brazil from sugarcane plant (sucrose-based) [1]. In this respect, while total world production of ethanol was 13.096 million gallons in 2007, it was 25.682 million gallons in 2015, ~2-fold [3].

Ethanol is utilized as a raw material, solvent, and fuel for a great variety of implementation containing beverages, pharmaceuticals, cosmetics, biofuel, chemicals, dye, etc. [1]. Globally, a great majority of ethanol (90–95%) is produced through microbial fermentation technology. Its rest (5–10%) is also generated by chemical technology [1,3]. Renewable resources used to produce the ethanol by biotechnological processes are the most abundant available and affordable materials in the nature. Tea processing waste (TPW) is also one of the bioresources released as a post-harvest waste of tea factory in tea growing countries such as China, Iran, Turkey, etc. In Turkey, TPW is annually generated ~30–50 thousand tons. TPW consists of cellulose (13.6%), hemicellulose (32.16%), lignin (33.38%), and extractives (20.86%) [4]. Therefore, it can be evaluated for production of value added products as a potential substrate source due to its carbohydrate content (~46% of dry basis). For this purpose, the steps of pretreatment, fermentation, and distillation are applied for the production of TPW-based bioethanol. Among these, an important stage in the production of bioethanol from TPW is pretreatment [5,6]. Several pretreatment strategies such as physical, chemical, physico-chemical, biological, and combinations thereof are applied for pretreatment of TPW in order to liberate the fermentable sugars such as glucose and xylose. Dilute acid

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Nomenclature

A_m	Upper asymptote for product formation and sugar consumption curves, g/L
A_o	Lower asymptote for product formation and sugar consumption curves, g/L
A_t	The predicted ethanol and sugar concentration at time "*t*", g/L
BR	Baranyi, –
e	Euler number, 2.718, –
h_o	Dimensionless parameter calculating the initial physiology state of the cells, –
k	A parameter governing the rate at which the response variable approaches its potential maximum, –
MAE	Mean-absolute-error, g/L
MG	Modified gompertz, –
ML	Modified logistic, –
MMF	Morgan-mercer-flodin, –
MR	Modified richards, –
n	Number of observations, –
P	Ethanol concentration or production, g/L
Q	Maximum production, consumption, and growth rate, g/L/h
Q_P	Maximum ethanol production rate, g/L/h
Q_S	Maximum sugar consumption rate, g/L/h
Q_X	Maximum cell growth rate, g/L/h
R^2	Regression coefficient, –
R-MG	Re-modified gompertz, –
R-ML	Re-modified logistic, –
R-MR	Re-modified Richards, –
RMSE	Root-mean-square-error, g/L
RSC	Residual sugar concentration, g/L
ST	Stannard, –
SUY	Sugar utilization yield, %
t	Sampling time, h
v	Dimensionless shape parameter, –
W	Weibull, –
X	Biomass concentration, g/L
x_t	Experimental value at time "*t*", g/L
$Y_{P/S}$	Ethanol yield, %
y_t	Predicted value at time "*t*", g/L
$Y_{X/S}$	Biomass yield, g/g
β	Growth displacement, –
δ	Allometric constant, –
λ	Lag time, h

pretreatment is one of the common used pretreatment strategies using some inorganic acids such as HCI, H_2SO_4, and HNO_3 and organic acids such as oxalic acid and peracetic acid [5,6]. On the other hand, dilute H_2SO_4 hydrolysis of biomass is the most popular pretreatment strategy in industrial applications where the conditions used are either higher temperature for a short time (i.e., 180 °C and a couple of minutes) or at lower temperature for a long time (i.e., 120 °C and 30–90 min) [5,7]. Additionally, some inhibitor compounds such as hydroxymethylfurfural (HMF), 2-furaldehyde (2-F), phenolics (PH), acetic acid, formic acid, uronic acid, and levulinic acid are released during dilute acid pretreatment, which are known to inhibit the ethanol fermentation of renewable hydrolysates. In order to effectually convert the fermentable sugars to ethanol during fermentation, the detoxification of renewable hydrolysates is required to be carried out prior to ethanol fermentation [5,8]. Physical (vacuum evaporation), chemical (activated charcoal, diatomaceous earth, ion-exchange resins, pH adjusting with a combination of acids (H_2SO_4, and H_3PO_4) and bases (NaOH, $Ca(OH)_2$, CaO, and NH_4OH)), biological methods (laccase and peroxidase), and thereof combination are utilized to remove toxic components (HMF, 2-F, PH, organic acids) in the pretreated-raw material hydrolysate during detoxification process. The productivity of the detoxification method based on the microorganism and hydrolysis method due to different degree of tolerance of microorganisms to inhibitors and different degree of toxicity of hydrolysate. Besides, the feedstock and its hydrolysate are also significant factors in choosing of the method to be used in detoxification of hydrolysate [8,9].

Yeasts have been employed for ethanol production from synthetic carbon sources (glucose, sucrose, xylose, etc.), industrial plants (sugar cane, sugar beet, etc.) or by-products of food industry (whey, molasses, TPW, etc.) for many years [10]. *S. cerevisiae* is the most widely utilized yeast in industrial applications from past to present. It is known that this yeast is effective in the fermentation of sugary liquids including hexoses and some disaccharides, which has the ability to quickly and effectively convert sugar into bioethanol and carbon dioxide. *S. cerevisiae* has a very high metabolic rate, rapid growth rate, and the ability to bring rapid chemical changes [10,11]. On the other hand, there is a need for microorganisms capable of effectively fermenting sugars such as glucose, xylose, arabinose, mannose, galactose, rhamnosus and cellobiose which are released as a result of the hydrolysis of renewable resources. In this concept, naturally occurring yeasts *Scheffersomyces stipitis*, *Candida shehatae*, and *Pachysolen tannophilus* in nature can be applied to more efficiently convert the sugar mixture into ethanol [12–16]. Among these, *S. stipitis* is one of the most promising yeasts for industrial ethanol production with high yield due to its ability to ferment the sugar mixture found in the lignocellulosic biomass hydrolysate [17]. Besides, it is a Crabtree negative, homothallic yeast, fundamentally found in haploid form, and has respiratory capacity. Due to being its Crabtree negative, pentose sugars can be converted into ethanol with high yield (35–44%) close to theoretical yield at low oxygen transfer rate [18]. Additionally, *S. stipitis* can be ferment xylose to ethanol under anaerobic conditions since it has both NADH and NADPH specific xylose reductase cofactor [12]. Therefore, *S. stipitis* is a gene source for no pentose-fermenting microorganisms in genetic engineering and has also been considered for the production of ethanol from lignocellulosic biomass [18]. Accordingly, the yeasts *S. cerevisiae* and *S. stipitis* were employed for ethanol production from TPW in this study.

In recent times, researchers have been modeling substrate consumption, product formation, and microbial growth of the studies performed with different types of bioreactors, different fermentation strategies and modes, and different carbon sources. Because, the importance of modeling is increasing every passing day. Mathematical models can decrease the number of fermentation studies. Therefore, they reduce process time and cost. Additionally, mathematical models provide process optimization, predictive capability, and process automation and facilities [19]. In addition, mathematical models are approved tools to define the behavior of microorganisms, ethanol production, and sugar consumption during fermentation [20]. In the literature, there are numerous studied with related to modeling of ethanol fermentation. However, mathematical modeling of ethanol fermentation with TPW hydrolysate was not performed yet. In current study, modeling of ethanol production conditions in shake flask fermentation with D-TPWH was performed. For this, modified Gompertz (MG), re-modified Gompertz (R-MG), modified logistic (ML), re-modified logistic (R-ML), modified Richards (MR), re-modified Richards (R-MR), Stannard (ST), Baranyi (BR), Weibull (W), and Morgan-Mercer-Flodin (MMF) models are used to fit well the experimental data [19–27]. Therefore, in this study, ten flexible models were employed to predict the experimental data of ethanol production and sugar consumption using model parameters obtained from this study. Overall, the