Kinetic Models and Effects of Mn(II) Ion on Ethanol Production from Cornstalks

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This paper presents a kinetic study of ethanol production by simultaneous saccharification and fermentation (SSF) from Mn(II)-catalyzed cornstalks. The optimal conditions of ethanol production were as follows: 1:2 inoculation proportion (ratio of *Pachysolen tannophilus* to *Saccharomyces cerevisiae*), 30 °C fermentation temperature, 15% inoculation quantity, 4 mg/g addition amount of Mn^{2+}, and 10 U/g cellulase dosage. An optimal ethanol yield of 0.359 g/g was obtained from cornstalks under optimum conditions. A 38.5% increase in the yield was observed compared with the control group without the addition of Mn^{2+}. The relationship between ethanol yield and fermentation time followed a Langmuir isotherm model. The relationship between the rate constant and fermentation time in the conversion of cornstalks to ethanol was fractal like. The findings elucidate the complex characteristics of ethanol production from cornstalks with Mn^{2+} catalysis and will be useful in improving production yield.

Keywords: Cornstalks; Manganese catalysis; Fractal-like; Kinetic; SSF; Fuel; Ethanol

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INTRODUCTION

Lignocellulosic biomass is a high potential feedstock for bio-ethanol production; as such, it has the potential to reduce the pollution caused by the use of fossil fuels (Iqbal *et al.* 2012; Arevalo-Gallegos *et al.* 2017; Bilal *et al.* 2017a). Ethanol produced from lignocellulosic biomass could become the dominant global renewable fuel, and therefore there is a need for advanced development of ethanol fuel technology, such as determining the optimal factors of production (Asgher *et al.* 2014a). The optimal production of bioethanol requires efficient conversion in the three major steps of pretreatment, enzymatic hydrolysis, and fermentation (Gaur *et al.* 2016).

In previous work, the effects of several parameters on straw stalk used for ethanol fuel production were investigated, and the results showed that the optimal conditions were a fermentation temperature of 38 °C, a fermentation time of 72 h, a yeast inoculation quantity of 15%, a yeast inoculation proportion of 2:1, and a cellulose enzyme dosage of 20 U/g (Chen *et al.* 2013). Catalysts serve vital roles in lignocellulosic ethanol conversion. Acids and enzymes facilitate the hydrolysis of cellulose, and metal ions and biological catalysts can also improve the conversion rate (Hayes 2009; Asgher *et al.* 2014b; Bilal *et al.* 2017b).

Mn^{2+} catalytic ethanol production is a promising chemical approach (Ahmed and Lewis 2007; Liu *et al.* 2017). Liu *et al.* (2017) observed that Mn^{2+}can improve the efficiency of conversion of lignocellulosic biomass to fermentable sugars for the production of bioethanol. Manganese (Mn^{2+}) catalysts, which influence ethanol production, have been applied in the catalytic liquefaction of various biomasses (Chen *et al.* 2012; Lakkana *et al.* 2012). However, the addition of Mn^{2+} has no significant effect on sugar yield, and the saccharification yields for the samples with Mn^{2+} are the same or similar to those of the saccharification samples without added metal ions (Ramachandran *et al.* 2015). Ethanol production does not change considerably at higher concentrations of Mn^{2+} (Saxena and Tanner 2011). However, trace manganese enhances butyric acid production (Liu *et al.* 2015). Moreover, supplementation with Mn^{2+} and nitrogen coupled with a small amount of aeration improves ethanol production efficiency (Saxena and Tanner 2011; Deesuth *et al.* 2015). However, high concentration of Mn^{2+} may be toxic because it affects the permeability of membranes, causing a decrease in both yeast growth and fermentation activity (Stehlik-Tomas *et al.* 2004). Manganese ions can enhance cell growth (Xue *et al.* 2008; Pereira *et al.* 2010) and increase the activity of cellulase (Guerfali *et al.* 2011; El-Gindy *et al*. 2015). Cellulase enzyme production is relatively costly, which requires the enzyme to be used as fully as possible (Zhang *et al.* 2012). Therefore, further research on manganese supplementation is needed to optimize the process of manganese catalyzed ethanol production.

The study of fermentation kinetic parameters is important for understanding the impacts of process parameters on ethanol production (Wang and Feng 2010; Zhang *et al.* 2012). Moreover, a mathematical model is both an important tool for understanding the mechanism of a complex reaction and the base for largescale process model development (Wang and Feng 2010). The Langmuir equation has been utilized to describe the complex, fractal-like process of converting lignocellulosic materials to ethanol (Chen *et al.* 2014). Moreover, kinetic parameters can be used with mathematical models to predict the dynamics of the ethanol production rate (Yao *et al.* 2011; Zhang *et al.* 2012). The current understanding of the kinetic model of ethanol production is underdeveloped. Fractal kinetic analysis provides another point of view of heterogeneous chemical reactions to identify the optimal conditions of ethanol production from cornstalks (Chen *et al.* 2014; Nguyen *et al.* 2015).

The effects of enzyme loading, fermentation time, substrate concentration, fermentation temperature, and size distribution on cellulose hydrolysis have been examined in previously proposed kinetic models (Yao *et al.* 2011; Zhang *et al.* 2012; Chen *et al.* 2013; Chen *et al.* 2014), but few papers considered the effect of manganese catalyst on ethanol yield. Consequently, the kinetic models of ethanol production, the optimization of ethanol production from cornstalks, and productivity should be examined systemically. Kinetic models of ethanol production from Mn^{2+}-catalyzed cornstalks will be helpful for scaling-up ethanol production plants.

In this study, the effects of $MnSO_4$ (Mn^{2+}) on the production of ethanol from cornstalks liquefaction pretreated *via* SSF were investigated. The aim was to identify the optimal conditions for the production of ethanol from cornstalks. Kinetic models were proposed to describe the effects of Mn^{2+} on the kinetic parameters of ethanol production, which should provide a better understanding of the effects of Mn^{2+} on the ethanol yield from cornstalks *via* SSF. Kinetic analysis of ethanol preparation from cornstalks catalyzed with the addition of different amounts of Mn^{2+} was considered and characterized. This information will be helpful for improving the energy utilization of cornstalks and the theoretical development of ethanol production.

EXPERIMENTAL

Materials

The cornstalks used in this study were collected from a household in Bishan of Chongqing. Cellulase (filter paper activity, 15000 U/g) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), and yeast (*Pachysolen tannophilus* 1770 and *Saccharomyces cerevisiae* 1001) were purchased from the China Center of Industrial Culture Collection (Beijing, China). Potassium dichromate, ethanol, sulfuric acid, glycol, $MnSO_4$ (Mn^{2+}), glucose, agar, wort, and peptone were purchased from Baimadang Chemical Storage (Chongqing, China). The oven (101-1), grinding mill (XQM-2L), portable steam sterilizer (YX280B), spectrophotometer (722), microscope (XSP-2CA) and hemocytometer (7108) were purchased from Shanghai CSOIF Company Limited (Shanghai, China).

Methods

Material pretreatment

The cornstalk material was placed in an oven at 40 °C for 25 h. It was sheared and milled until the entire sample passed through an 80-mesh sieve. The material was then dried to constant weight at 105 °C for 24 h. A total of 20 g of dried cornstalks powder and 120.0 g of glycol were put into a three-mouth flask with a magnetic rotor. The middle mouth of the three-mouth flask was connected to a condenser tube. The flask was placed in a water bath with magnetic stirring (90 °C, 100 rpm). The side mouth of the flask had a perforated rubber stopper, through which a thermometer was inserted into the reaction mixture. The other side of the mouth was a feed inlet (a loaded rubber plug without a hole). After 10 min of preheating, the rubber plug of the feed inlet was removed, and 25 m·mol of concentrated sulfuric acid was added to the flask. A rubber plug was inserted, and the reaction solution was stirred for 75 min at 90 °C.

After completion of the reaction, the flask and condenser pipe were separated, and the stirrer was removed. The reaction mixture in the flask was diluted with hot water. The reaction was poured into the funnel of the vacuum suction filter and filtered. The reaction mixture was filtered twice more, with 20 mL of methanol added to the filtrate each time. This process was repeated twice with 20 mL of hot water. The final product containing the fermentation substrate was obtained by drying the filter cake for 1 h at 105 °C.

Preparation of the slant, seed, fermentation medium

The media were prepared as described by Li *et al.* (2013). Medium I was used for slant medium, and it was composed of 10% wort with 2% agar and 2% peptone. Medium II was used for seed culture, and it was composed of 10% wort with 2% peptone. Medium III was used for fermentation and was composed of fermentation substrate (10 g), 1.0% dilute sulfuric acid, 30% NH_4HCO_3, and had a solid-liquid ratio of 1:15 (m:m). All media were adjusted to pH 6 and sterilized for 30 min at 121 °C. The seed culture of the strains (*P. tannophilus* and *S. cerevisiae*) was grown aerobically in a 250 mL Erlenmeyer flask containing 30 mL of the seed medium and shaken at 160 rpm for 24 h at 30 °C.

Activation and dilution of yeast strains

P. tannophilus and *S. cerevisiae* were collected from the test tube slant and activated in liquid medium, respectively (30 °C, 24 h). The mixture was stirred (160 rpm, 2 h); samples were counted by hemocytometer and diluted to 10^8 cell/mL with sterile water.

Design of ethanol optimization experiment and kinetic experiment

Pretreated cornstalks were used as raw material. The solid-to-liquid mass ratio was 1:15, and the fermentation time was 72 h. The orthogonal optimization experiment was designed with specific values of fermentation temperature, amounts of added Mn^{2+}, inoculation quantity, inoculation proportions (ratio of *P. tannophilus* to *S. cerevisiae*), and cellulase dosage as factors. The results of the orthogonal experiment are listed in Table 1. Additionally, the control groups without the addition of Mn^{2+} are shown in Table 2.

Based on previous research results, using the optimized values (inoculation quantity, inoculation proportion, cellulase dosage, and fermentation temperature) obtained from the orthogonal experiment, the kinetics and effects of different concentrations of Mn^{2+} (4 mg/g, 6 mg/g, 8 mg/g, and 10 mg/g) on ethanol production *via* SSF of cornstalks were investigated.

Determination method

The contents of cellulose, hemicellulose, and lignin in the cornstalks were determined as previously described (Sluiter *et al.* 2012). Ethanol concentrations were determined as described in He *et al.* (2013). All experiments were performed in duplicate under the same conditions. Potassium dichromate spectrophotometry was used to determine the ethanol concentration at every 12 h. The standard curve is shown in Eq. 1,

$$Y = 0.3854X + 0.0065 \qquad R^2 = 0.9985 \tag{1}$$

where Y is the absorbance (g/L) and X is the ethanol concentration (g/L). The ethanol production rate was calculated according to the following equation,

$$\boldsymbol{Y = CV/M} \tag{2}$$

where $\boldsymbol{C}$ is alcohol concentration that was obtained from contrasting with a standard curve (g/L), $\boldsymbol{V}$ is the total volume of liquid in the container (fermentation liquid volume + inoculation quantity) (L), $\boldsymbol{M}$ is the pretreated cornstalks (g), and $\boldsymbol{Y}$ is the ethanol yield (g/g).

RESULTS AND DISCUSSION

Process Optimization of Ethanol Production from Cornstalks

The range analysis summarized in Table 1 showed that the order of importance of the five major influencing factors in ethanol preparation from cornstalks was inoculation quantity > inoculation proportion > addition amount of Mn^{2+} > cellulase dosage > fermentation temperature. Through orthogonal experiments and analysis, the optimum conditions were identified as follows: 1:2 inoculation proportion, 30 °C fermentation temperature, 15% inoculation quantity, 4 mg/g added Mn^{2+}, and 10 U/g cellulase dosage. An analysis of variance showed that at $F_{0.05}$, the effect of the five factors on ethanol production from cornstalks reached a significant level. The verification test was carried out under these optimized conditions. The ethanol yield was 0.359 g/g.

Table 1. Results of SSF Orthogonal Experiments in Addition of Mn^{2+} to Fermentation Broth

		Inoculation Proportion (P.:S.)	Temperature (°C)	Inoculation Quantity (%)	Mn^{2+} Addition (mg/g)	Cellulase Dosage (U/g)	Yield (g/g)
Serial number	1	1:1	28	5	4	10	0.162±0.0053
	2	1:1	32	10	6	20	0.141±0.0043
	3	1:1	36	15	8	30	0.183±0.0022
	4	1:1	40	20	10	40	0.146±0.0036
	5	1:2	28	10	8	40	0.167±0.0028
	6	1:2	32	5	10	30	0.135±0.0037
	7	1:2	36	20	4	20	0.286±0.0029
	8	1:2	40	15	6	10	0.325±0.0029
	9	1:3	28	15	10	20	0.249±0.0057
	10	1:3	32	20	8	10	0.349±0.0051
	11	1:3	36	5	6	40	0.088±0.0024
	12	1:3	40	10	4	30	0.187±0.0043
	13	2:1	28	20	6	30	0.240±0.0054
	14	2:1	32	15	4	40	0.335±0.0033
	15	2:1	36	10	10	10	0.162±0.0014
	16	2:1	40	5	8	20	0.155±0.0016
Index the sum	K1	0.158	0.204	0.135	0.242	0.250	
	K2	0.228	0.240	0.164	0.198	0.208	
	K3	0.218	0.180	0.273	0.214	0.186	
	K4	0.223	0.203	0.255	0.173	0.184	
R (Range)		0.070	0.061	0.138	0.069	0.066	

The experiments were performed in duplicate and the test results were expressed as mean ± SD. The value of K_1, K_2, K_3, K_4, and R were calculated from the mean.

The range analysis summarized in Table 2 illustrates that the order of importance of the four major influencing factors in the preparation of ethanol from cornstalks were fermentation temperature > inoculation quantity > cellulase dosage > inoculation proportion. By orthogonal experiment and analysis, the optimal conditions of the control groups were obtained as follows: the inoculation proportion was 2:1, the fermentation temperature was 32 °C, the inoculation quantity was 20%, and the cellulase dosage was 20 U/g. The verification experiment was carried out under the optimal conditions. The results showed that the ethanol yield was higher than that of the control orthogonal experiments group. The ethanol yield was 0.267 g/g. Accordingly, the optimal conditions of the control group were as follows: 2:1 inoculation proportion, 32 °C fermentation temperature, 20% inoculation quantity, and 20 U/g cellulase dosage. Under these conditions, the ethanol yield was 0.267 g/g.

Compared with the control group, ethanol yield in the group with added Mn^{2+} increased by 38.5% under optimal conditions. Furthermore, the addition of Mn^{2+} both initiated the anaerobic fermentation reaction at a lower temperature and decreased the cellulase dosage from 20 U/g to 10 U/g. Due to the reduced cellulose dosage and the reduced energy consumption allowed by the initiation of the anaerobic fermentation reaction at lower temperature (Yanase *et al.* 2010; Lupoi and Smith 2011), ethanol production costs in the group with the addition of Mn^{2+} were reduced. Table 3 shows that the hemicellulose content of cornstalks increased from 32.7% to 54.9%.

Lignin content was decreased from 16.8% to 11.2% by liquefaction pretreatment, increasing the binding sites between cellulase and substrate. Mn^{2+} is an essential trace element for microbial growth that improves the activity of cellulase and yeast (Saxena and Tanner 2011; Lakkana *et al.* 2012). The increase in activity and cellulose content is favorable for fermentation (Li *et al.* 2013; Deesuth *et al.* 2015). The results showed that the ethanol yield from cornstalks was improved by adding appropriate amounts of Mn^{2+}, which was economically feasible.

Table 2. Results of SSF of Control Orthogonal Experiments

		Inoculation Proportion (P.:S.)	Temperature (°C)	Inoculation Quantity (%)	Cellulase Dosage (U·g^{-1})	Yield (g·g^{-1})
Serial number	1	1:1	28	5	10	0.120±0.0036
	2	1:1	32	10	20	0.210±0.0037
	3	1:1	36	15	30	0.197±0.0041
	4	1:1	40	20	40	0.123±0.0033
	5	1:2	28	10	40	0.063±0.0022
	6	1:2	32	5	30	0.158±0.0024
	7	1:2	36	20	20	0.245±0.0043
	8	1:2	40	15	10	0.164±0.0029
	9	1:3	28	15	20	0.084±0.0024
	10	1:3	32	20	10	0.238±0.0022
	11	1:3	36	5	40	0.187±0.0033
	12	1:3	40	10	30	0.107±0.0050
	13	2:1	28	20	30	0.176±0.0050
	14	2:1	32	15	40	0.233±0.0045
	15	2:1	36	10	10	0.137±0.0036
	16	2:1	40	5	20	0.181±0.0049
Index the sum	K1	0.162	0.111	0.162	0.165	
	K2	0.158	0.210	0.129	0.180	
	K3	0.154	0.192	0.170	0.160	
	K4	0.182	0.144	0.196	0.151	
R (Range)		0.028	0.099	0.066	0.029	

The experiments were performed in duplicate and the test results were expressed as mean ± SD. The value of K_1, K_2, K_3, K_4, and R were calculated from the mean.

Table 3. Composition of Corn Stalks (Percentage of Total Dry Weight)

	Cellulose	Hemicellulose	Lignin	Ash	Moisture
Before treatment	32.73%	31.52%	16.83%	10.20%	9.72%
After treatment	54.89%	20.61%	11.24%	12.18%	1.08%

Effects of Mn^{2+} Addition on Ethanol Yield

Based on the results of the optimization process, the effect of different Mn^{2+} concentrations (4 mg/g, 6 mg/g, 8 mg/g, and 10 mg/g) on ethanol fermentation was investigated. A comparison of the ethanol yield in the liquefaction of cornstalks with different quantities of Mn^{2+} added is given in Fig. 1. Ethanol yield, which reached 0.357 g/g, was the highest with a Mn^{2+} addition of 8 mg/g after 72 h of fermentation.

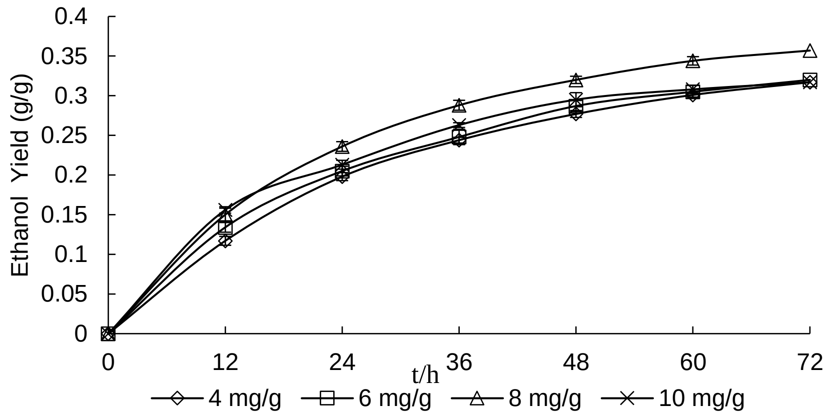

Fig. 1. Effect of the level of addition of $MnSO_4$ on ethanol yield. The experiments were performed in duplicate and the test results were expressed as mean ± SD.

In a certain range of concentrations, there was a positive correlation between biological activity and the amount of Mn^{2+} added (Guerfali *et al.* 2011). However, a high content of Mn^{2+} can lead to loss of activity in yeast and cellulose (Chen *et al.* 2008). If the amount of manganese ion is too high, it may lead to excessive activity in yeast and destroy the dynamic synergy between *P. tannophilus* and *S. cerevisia*e, causing a decrease in ethanol yield due to the assimilation of ethanol by Mn^{2+}. In this study, low concentrations of Mn^{2+} (at 4 mg/g, 6 mg/g, 8 mg/g) improved ethanol yield from cornstalks. However, higher concentration additions of Mn^{2+} (at 10 mg/g) decreased ethanol yield from cornstalks. Therefore, the addition of Mn^{2+} increased the ethanol yield to a certain extent, as shown in Fig. 1. The results showed that the microorganism partially inhibits the biochemical reaction by adding Mn^{2+} under anaerobic conditions. The ethanol yield increased with the increase of the amount of Mn^{2+} (at the amount of Mn^{2+} ≤8 mg/g), and the ethanol yield declined at 10 mg/g.

Kinetic Analysis Based on Addition of Mn^{2+}

Two-constant kinetics model

Kinetic modeling is important in designing and controlling bioprocess efficiency, and kinetics analysis improves product yield (Xu *et al.* 2008; Chen *et al.* 2014). As shown in Fig. 1, the ethanol yield (*Y*) gradually increased with increasing *t* values under different amounts of Mn^{2+} addition. The rate of ethanol preparation was faster at the starting stage, and the curve was similar to that of the Langmuir adsorption isotherm. Accordingly, Eq. 3 could be used to describe the relationship between *Y* and *t*,

$$Y = abt/(1 + bt) \quad (3)$$

where *Y* is the ethanol yield (g/g), *a* is the capacity for ethanol production by fermentation (*g/g*), *b* is the rate constant (h^{-1}), and t is fermentation time (h). Equation 3 can also be expressed as Eq. 4.

$$t/Y = 1/(ab) + t/a \quad (4)$$

The experimental data from Fig. 1 were fitted into Eq. 4 by one-dimensional nonlinear regression for each amount of Mn^{2+} addition. The values of *a* and *b* determined from the fit are shown in Table 4. The regression analysis results are also listed in Table 4.

Table 4. Calculation Results from the Two-Constant Experiential Model

Additon of Mn^{2+} (mg/g)	Modeling Equation	*a*(*g/g*)	*b*(h^{-1})	R^2
4	t/Y = 39.599 + 2.7574 t	0.3627	0.0696	0.9120
6	t/Y = 33.623 + 2.8025 t	0.3568	0.0834	0.9372
8	t/Y = 28.996 + 2.5011 t	0.3998	0.0863	0.9412
10	t/Y = 26.602 + 2.8762 t	0.3477	0.1081	0.9607

The values were calculated from the mean.

Table 4 shows that the catalytic kinetics of Mn^{2+} in the process of preparing ethanol was well-described by a two-constant experiential model. Table 4 shows that parameter *a* decreased with an increasing initial addition of Mn^{2+} (except the addition of 8 mg/g of Mn^{2+}). Moreover, ethanol peaked with the addition of 8 mg/g of Mn^{2+}. Parameter *b* increased with the increasing addition of Mn^{2+}. Parameter *b*, representing rate constant, reached the fastest level with the addition of 10 mg/g of Mn^{2+}. The peak rate of ethanol fermentation was achieved with the addition of 10 mg/g of Mn^{2+}. Taking into account the maximum yield, the addition of 8 mg/g of Mn^{2+} was selected as the optimal process factor. Thus, the two-constant Langmuir isotherm model adequately described the kinetics of Mn^{2+} in ethanol production from cornstalks. The reliability of the relative coefficient with different amounts of Mn^{2+} addition exceeded 95.5%.

Fractal-like kinetics model

The rate constant of a reaction is independent of time in classical chemical kinetics. However, recent studies have shown that the rate of reaction is not proportional to the integral power of reaction time (*t*). The kinetics of most heterogeneous reactions do not follow the classical kinetics law, and the rate constant (*k*) was correlated with reaction time (Yao *et al.* 2011; Chen *et al.* 2014). The relationship can be expressed as Eq. 5,

$$k = k_1 t^{-h} \tag{5}$$

where k is the time-dependent rate coefficient, h is the constant that measures the degree of local heterogeneity, and k_1 is a constant that is not related to time.

Considering the first-order kinetic integral equation, the rate coefficient k at t (t_1, t_2, t_3, *etc.* were different fermentation moments) can be calculated by using the change of ethanol yield from t_1 to t_2, and the k at t_3 can be obtained by using the change of ethanol yield from t_2 to t_3 in the dynamic state. The others were deduced by analogy. The k values at t could be calculated using Eq. 6 (Liu *et al.* 2002); Table 5 lists the remaining k values.

$$ln\frac{Y_2}{Y_1} = k(t_2 - t_1) \tag{6}$$

As shown in Table 5, k decreased as fermentation time increased with different amounts of Mn^{2+}. The kinetics of reaction of the fermentation process is fractal-like, and these k values appear to vary irregularly with different amounts of Mn^{2+} addition. The rate coefficient in this paper, which was time-dependent in the fractal kinetics, was different from the rate constant in classical kinetics. The time-dependent rate coefficient is related to the fractal exponent. The ethanol yield steadily decreased with increased addition of Mn^{2+} at the fermentation time of 72 h. Thus, these k values might increase or decrease as the addition of Mn^{2+} increases.

Table 5. Reaction Rate Coefficient *k* at Different Addition of Mn^{2+} in Reaction Time

t/h	10^3 k/h $^{-1}$			
	4 g/g	6 g/g	8 g/g	10 g/g
24	43.959	35.406	37.918	25.740
36	17.508	15.540	16.523	17.825
48	10.516	12.196	8.824	9.362
60	7.097	5.295	6.081	3.764
72	4.209	3.971	3.092	2.423

The values were calculated from the mean.

To explore the quantitative relationship between the rate coefficient and time, Eq. 5 can also be expressed as follows:

$$\log k = -\text{h}\log t + \log k_1 \quad (7)$$

The experimental data were regressed using Eq. 5, and the relationship between $\log k$ and $\log t$ was described with Eq. 7. The results are listed in Table 6. The reliability of the relative coefficient with various amounts of Mn^{2+} addition exceeded 96.9%. Thus, Eq. 5 and Eq. 7 were adapted to describe the quantitative relationship between the fermentation rate coefficient of cornstalks and time. Namely, the fermentation kinetics of cornstalks with different additions of Mn^{2+} are fractal-like. Although values of k_1 and h appear to vary irregularly with the increase of the amount of Mn^{2+} added, k is concerned with h and t. Therefore, parameter h is relative to the fractal dimension. The fractal dimension and the order of reaction could not be obtained. However, as h was larger than 1, it is certain that the process of fermentation from cornstalks with different amounts of Mn^{2+} addition is fractal-like.

Table 6. Modeling Results for log*k* and log*t*

Addition of Mn^{2+}	Modeling Equation	h	k_1	R^2
4 g/g	**log*k*** = -2.1018 **log*t*** + 1.5503	2.1018	35.5059	0.9942
6 g/g	**log*k*** = -2.0264 **log*t*** + 1.3788	2.0264	23.9221	0.9702
8 g/g	**log*k*** = -2.2392 **log*t*** + 1.7039	2.2392	50.5708	0.9899
10 g/g	**log*k*** = -2.2839 **log*t*** + 1.6931	2.2839	49.3287	0.9397

The values were calculated from the mean.

CONCLUSIONS

1. Compared with the group without the addition of Mn^{2+} under the optimal conditions, ethanol yield increased by 38.5% in the group with added Mn^{2+}. The addition of Mn^{2+} both initiated the anaerobic fermentation reaction at a lower temperature and decreased the cellulase dosage.
2. The time course of the conversion of cornstalks to ethanol under different conditions of added Mn^{2+} was matched with the fractal-like kinetic model. The relationship between the ethanol yield and fermentation time could be described using the Langmuir isotherm model and inverse power function.
3. The good fit of the experimental data confirmed the applicability of the kinetic model

to describe the complex characteristics of ethanol production from cornstalks with Mn^{2+} catalysis. This kinetic model provides a new way to analyze the complex kinetics of ethanol production from cornstalks with Mn^{2+} catalysis.

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