Chapter 6
Kinetic Models for Hydrogen Production

List of Symbols

HPB	Hydrogen-producing bacteria
H	Cumulative value
$H_{\max}$	Maximum cumulative value
R	Rate
$R_{\max}$	Maximum rate
λ	Lag time
t	Cultivation time
X	Biomass
$X_{\max}$	Maximum biomass
X_0	Initial biomass
S	Substrate concentration
S_0	Initial substrate concentration
S_{Crit}	Critical substrate concentration
P	Product
C	Inhibitor concentration
C_{Crit}	Critical inhibitor concentration
$Y_{X/S}$	Biomass yield coefficient
$Y_{P/S}$	Product yield coefficient
$Y_{P/X}$	Growth-associated product yield coefficient
β	Nongrowth-associated product yield coefficient
k_c	Apparent specific growth rate
K_S	Half-saturation constant
K_I	Inhibition constant
K_C	Constant
k_d	Biomass decay constant
K_a	Constant
K_b	Constant
m	Constant
n	Constant
A	Constant
B	Constant

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I_{pH}	pH inhibition constant
pH_{UL}	Higher pH limit
pH_{LL}	Lower pH limit
$pH_{\min}$	Minimum pH
$pH_{\max}$	Maximum pH
T	Temperature
$T_{\min}$	Minimum temperature
T_{opt}	Optimal temperature
$T_{\max}$	Maximum temperature
E_a	Activation energy
R_g	Ideal gas constant
$[H^+]$	H^+ concentration
D	Dilution rate

6.1 Introduction

During fermentative hydrogen production, when substrate is degraded, the growth of hydrogen-producing bacteria (HPB) occurs simultaneously with the production of hydrogen, as well as some soluble metabolites. Some kinetic models such as the modified Gompertz model have been proposed to describe the progress of substrate degradation, HPB growth, hydrogen production and some soluble metabolite formation in a batch fermentative hydrogen production process. Such kinetic models can be used to predict the substrate degradation, HPB growth, hydrogen production, and some soluble metabolite formation at a given time in a batch fermentative hydrogen production process, which can help to elucidate such process (Wang et al. 2008; Wang and Wei 2008).

In addition, many factors such as substrate concentrations, inhibitors, temperatures, pH, and dilution rate can influence the fermentative hydrogen production (Wang and Wan 2009a, b; Hsia and Chou 2014). Some kinetic models have also been proposed to describe the effects of these factors on the rates of substrate degradation, HPB growth, hydrogen production, and some soluble metabolite production, as well as the concentrations of substrate, biomass, hydrogen, and some soluble metabolites. Such kinetic models could be used to explain the effects of these factors on the fermentative hydrogen production quantitatively. In addition, the kinetic constants obtained from these models can provide useful information for the analysis, design, and operation of a fermentative hydrogen production process (van Niel et al. 2003; Mu et al. 2006; Wang and Wei 2009; Boboescu et al. 2014).

Moreover, there usually exist some relationships among the substrate degradation rate, the HPB growth rate, and the product formation rate. Some kinetic models have also been proposed to describe these relationships.

This chapter attempts to summarize the kinetic models, which have been proposed to describe the progress of batch fermentative hydrogen production process, the effects of various factors on fermentative hydrogen production process, and the relationships among the substrate degradation rate, the HPB growth rate, and the product formation rate.

6.2 The Progress of Hydrogen Production Process

During fermentative hydrogen production, substrate concentrations, HPB growth, hydrogen, and some soluble metabolites change regularly. Some kinetic models have been proposed to describe such changes. Among them the modified Gompertz model (Eq. 6.1) developed by Zwietering et al. (1990) was widely used to describe the progress of substrate degradation, HPB growth, hydrogen production, and some soluble metabolite production in a batch fermentative hydrogen production process (Lay et al. 1999; Wu et al. 2004; Fang et al. 2005; Cheong and Hansen 2007; Lin et al. 2008a, b).

$$H = H_{\max} \cdot \exp\left\{-\exp\left[\frac{\mathrm{R}_{\max} \cdot e}{H_{\max}} \cdot (\lambda - t) + 1\right]\right\} \tag{6.1}$$

$$H = \frac{H_{\max}}{1 + \exp[4R_{\max} \cdot (\lambda - t)/H_{\max} + 2]} \tag{6.2}$$

When Eq. (6.1) was used to describe the progress of substrate degradation in batch tests, H and $H_{\max}$ denote the cumulative degraded substrate value and the maximum degraded substrate value, respectively. When Eq. (6.1) and (6.2) were used to describe the progress of HPB growth in batch tests, H and $H_{\max}$ denote the cumulative HPB growth value and the maximum HPB growth value, respectively.

As shown in Fig. 6.1, in a batch test, H increases very slowly with increasing cultivation time from 0 to λ, and then increases rapidly almost at the rate of $R_{\max}$ and finally reaches an asymptotic value $H_{\max}$ with further increasing the cultivation time.

Table 6.1 summarizes several studies using the modified Gompertz model to describe the progress of a batch fermentative hydrogen production process.

Recently, the modified Logistic model (Eq. 6.2), whose curve is very similar to that of the modified Gompertz model, was used by Wang and Wan to describe the progress of hydrogen production in the batch tests using glucose as substrate. In addition, it was also used by Mu et al. (2007) to describe the progress of HPB growth in batch tests.

Furthermore, Mu et al. compared the ability of the modified Gompertz model, modified Logistic model, and modified Richards to describe the progress of HPB growth in batch tests and concluded that the modified Gompertz model was the most suitable one (Mu et al. 2007).

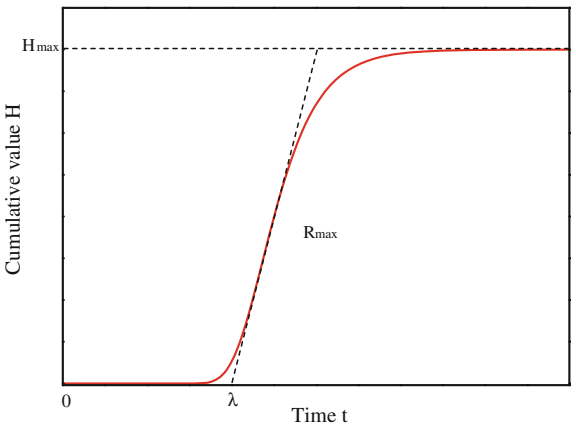

Fig. 6.1 A curve for modified Gompertz model

In addition, a Logistic model (Eq. 6.3) was also used by Mu et al. (2006) to describe the progress of HPB growth in the batch tests.

$$X = \frac{X_0 \cdot \exp(k_c \cdot t)}{1 - (X_0/X_{\max}) \cdot (1 - \exp(k_c \cdot t))} \tag{6.3}$$

Compared with the Logistic model (Eq. 6.3), the modified Logistic model (Eq. 6.2) can obtain the lag time of HPB growth directly by fitting the experimental data, thus using it to describe the progress of HPB growth in the batch tests is recommended.

$$X = X_0 + Y_{X/S} \cdot (S_0 - S) \tag{6.4}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{-1}{Y_{X/S}} \cdot \frac{R_{\max} \cdot S}{K_S + S} \cdot X \tag{6.5}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{-1}{Y_{X/S}} \cdot \frac{R_{\max} \cdot S}{K_S + S - S^2/K_I} \cdot X \tag{6.6}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{-1}{Y_{X/S}} \cdot \frac{R_{\max} \cdot S}{K_S + S + S^2/K_I} \cdot X \tag{6.7}$$

where $R_{\max}$ is the specific HPB growth rate.

Kumar et al. (2000)compared the ability of two groups of models developed from a classical Monod model (Eqs. 6.4 and 6.5) and a modified Andrew model (Eqs. 6.4 and 6.6) to describe the progress of glucose degradation and *Enterobacter cloacae* IIT-BT 08 growth in batch tests and concluded that the latter was the most suitable one. In addition, Nath et al. (2008) also compared the ability of two groups of models developed from a classical Monod model (Eqs. 6.4 and 6.5) and an Andrew model (Eqs. 6.4 and 6.7) to describe the progress of glucose degradation

Table 6.1 Several studies using modified Gompertz model

Seed	Substrates	Described objectives	Correlation coefficient	References
Digester sludge	Glucose	Hydrogen	0.968	Yin and Wang (2016)
Digested sludge and soy bean-meal silo	Organic municipal solid waste	Hydrogen	Over 0.90	Lay et al. (1999)
Wasted activated sludge	Molasses	Hydrogen	0.993–1.0	Wu et al. (2004)
Municipal sewage sludge	Glucose	Hydrogen	0.977–1.0	Chen et al. (2002)
Anaerobic digester sludge	Rice slurry	Hydrogen	Over 0.98	Fang et al. (2005)
Cattle manure sludge	Glucose	Hydrogen	0.990–1.0	Cheong and Hansen (2006)
Clostridium pasteurianum CH4	Hydrolyzed starch	Hydrogen	–	Chen et al. (2007)
Clostridium butyricum CGS2	Hydrolyzed starch	Hydrogen	–	Chen et al. (2007)
Anaerobic sludge	Starch	Hydrogen	Over 0.95	Zhang et al. (2003)
Wasted activated sludge	Xylose	Hydrogen	0.987–0.999	Lin et al. (2008)
Anaerobic sludge	Sucrose	Hydrogen	0.990–1.0	Lee et al. (2001)
Wasted activated sludge	Sucrose	Hydrogen	0.996–1.0	Lin and Lay (2004)
Cracked cereals	Starch	Hydrogen	0.964–0.999	Liu and Shen (2004)
Sewage sludge	Xylose	Hydrogen	0.994–0.999	Lin et al. (2006)
Cow dung compost	Cornstalk wastes	Hydrogen	0.989	Zhang et al. (2007)
Sewage sludge	Sewage sludge	Hydrogen	0.991–1.0	Cai et al. (2004)
Cattle manure sludge	Synthetic wastewater	Hydrogen	0.995–1.0	Cheong and Hansen (2007)
Municipal sewage sludge	Starch	Hydrogen	0.976–1.0	Wang et al. (2007)
Municipal sewage sludge	Pineapple waste	Hydrogen	0.982–0.996	Wang et al. (2006)
Sewage sludge	Starch	Hydrogen	0.997–0.999	Lin et al. (2008)
Wasted activated sludge	Sucrose	Hydrogen	0.955–1.0	Lin and Shei (2008)
Clostridium saccharoper-butylacetonicum	Cheese whey	Hydrogen	0.989–0.996	Ferchichi et al. (2005)
Granular sludge	Sucrose	Hydrogen	Over 0.95	Li and Fang (2007)
Digester sludge	Microcrystalline cellulose	Hydrogen	Over 0.90	Lay (2001)
Anaerobic sludge	Sucrose	Hydrogen	0.999	Mu et al. (2006)
Anaerobic sludge	Sucrose	Hydrogen	0.999	Mu et al. (2007)
Mixed microbial consortium	Beer-brewing wastewater	Hydrogen	–	Boboescu et al. (2014)
Clostridium sp. FS3	Corn stalk	Hydrogen	–	Song et al. (2014)
Digested sludge	Waste activated sludge	Hydrogen	Over 0.937	Yin and Wang (2015)
Enterobacter aerogenes and *Clostridium butyricum*	Biodiesel waste	Hydrogen and substrate degradation	0.95	Pachapur et al. (2016)
Anaerobic sludge	Sucrose	Substrate degradation	0.994	Mu et al. (2007)
Anaerobic sludge	Glucose	HPB growth	0.937–0.994	Mu et al. (2006)

(continued)

Table 6.1 (continued)

Seed	Substrates	Described objectives	Correlation coefficient	References
Anaerobic sludge	Sucrose	HPB growth	0.998	Mu et al. (2007)
Anaerobic sludge	Sucrose	Acetate	0.999	Mu et al. (2006)
Anaerobic sludge	Sucrose	Acetate	0.992	Mu et al. (2007)
Anaerobic sludge	Sucrose	Butyrate	0.997	Mu et al. (2006)
Anaerobic sludge	Sucrose	Butyrate	0.997	Mu et al. (2007)
Digester sludge	Microcrystalline cellulose	VFA[a]	–	Lay (2001)
Digester sludge	Microcrystalline cellulose	Alcohol[b]	–	Lay (2001)

[a]VFA is the total of acetate, propionate and butyrate
[b]Alcohol is the total ethanol, propanol and butanol

and *Enterobacter cloacae* DM11 growth in batch tests and concluded that the latter was the most suitable one. The possible reason for this was that the models developed from a modified Andrew model and Andrew model took into consideration the effects of substrate inhibition, while the models developed from a classical Monod model did not take into consideration the effects of substrate inhibition.

$$I_{pH} = \exp\left[-3 \cdot \left(\frac{pH - pH_{UL}}{pH_{UL} - pH_{LL}}\right)^2\right] \tag{6.8}$$

$$\frac{dS}{dt} = \frac{-1}{Y_{X/S}} \cdot \frac{R_{\max} \cdot S}{K_S + S} \cdot X \cdot I_{pH} \tag{6.9}$$

$$\frac{dX}{dt} = \frac{R_{\max} \cdot S}{K_S + S} \cdot X \cdot I_{pH} - k_d \cdot X \tag{6.10}$$

where $R_{\max}$ is the specific HPB growth rate.

Two models developed by Ntaikou et al. from a modified Monod model incorporating low pH inhibition and the biomass decay (Eqs. 6.8, 6.9 and 6.10) were used to describe the progress of glucose degradation and *Ruminococcus albus* growth in batch tests (Ntaikou et al. 2008).

In addition, the anaerobic digestion model No. 1 (ADM1) developed by the International Water Association (IWA) task group was modified by Lin et al. (2007) to describe the progress of glucose degradation, *Clostridium* growth, and the productions of hydrogen, butyrate, acetate, and ethanol in batch tests.

In general, the modified Gompertz model can be easily used to describe the progress of substrate degradation, HPB growth, hydrogen production and some soluble metabolite production in a batch fermentative hydrogen production process, which makes it nearly an omnipotent model. Moreover, using it some constants that

have biological meanings, which may be of great importance to a better understanding of a process, can be obtained.

Even though the modified Logistic model has a similar property as the modified Gompertz model and using it can also obtain some constants that have biological meanings, it has been not used widely as the modified Gompertz model. Thus, using it to describe the progress of a batch fermentative hydrogen production process is recommended.

Even though the models developed by Kumar et al. (2000), Nath et al. (2008) and Ntaikou et al. (2008) took into consideration the effects of some inhibitions or biomass decay, they were only used to describe the progress of substrate degradation and HPB growth in batch tests, and thus using them to describe the progress of hydrogen production and some soluble metabolite production to examine their suitability for such applications is recommended.

Even though the modified ADM1 developed by Lin et al. could also be used to describe the progress of substrate degradation, HPB growth, hydrogen production, and some soluble metabolite production in a batch fermentative hydrogen production process, the development and the application of the model are very complex, which may limit its application.

In addition, the studies on the comparison of the ability of different models to describe the progress of a batch fermentative hydrogen production process are limited, thus more researches to compare them are recommended.

6.3 The Effect of Substrate Concentration on Hydrogen Production

Substrate is usually carbohydrates that can provide carbon and energy sources for HPB, thus is it of great importance to HPB growth and thus for fermentative hydrogen production. Some kinetic models have been proposed to describe the effects of substrate concentrations on the rates of substrate degradation, HPB growth and hydrogen production. Among them the classical Monod model (or Michaelis–Menten model) (Eq. 6.11) was widely used.

$$R = \frac{R_{\max} \cdot S}{K_S + S} \tag{6.11}$$

As shown in Fig. 6.2, R increases with increasing S and finally reaches an asymptotic value $R_{\max}$. It also suggests that at lower substrate concentration (relative to the half-saturation constant), R is approximately proportional to substrate concentration (first order in substrate concentration), while at higher substrate concentration, R is independent of substrate concentration (zero order in substrate concentration). Table 6.2 summarizes several studies using the Monod model (or Michaelis–Menten model) to describe the effects of substrate concentrations on the rates of substrate degradation, HPB growth, and hydrogen production.

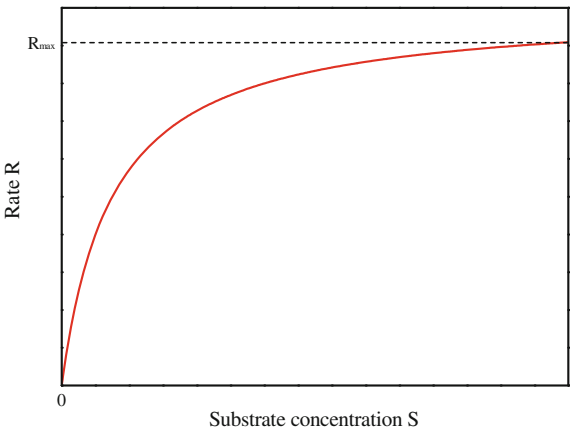

Fig. 6.2 A curve for the Monod model

When a substrate inhibits a fermentative hydrogen production process at much higher concentrations, the classical Monod model becomes unsatisfactory. In this case, modified Monod models with the item of substrate inhibition can be used to describe the effects of substrate concentrations on the hydrogen production rate and specific HPB growth rate. Among these models, the Andrew model (Eq. 6.12) was most widely used (Table 6.3).

$$R = \frac{R_{\max} \cdot S}{K_S + S + S^2/K_I} \tag{6.12}$$

$$R = \frac{R_{\max} \cdot S}{K_S + S - S^2/K_I} \tag{6.13}$$

In addition, Kumar et al. (2000) used a modified Andrew model (Eq. 6.13) to describe the effects of substrate concentrations on specific *Enterobacter cloacae* IIT-BT 08 growth rate in batch tests.

Moreover, Wang and Wan (2008) used the Han–Levenspiel model (Eq. 6.14), an extended Monod model, to describe the effects of glucose concentrations on hydrogen production rate in batch tests. In addition, Wang and Wan also compared the ability of the Andrew model and the Han–Levenspiel model to describe the effects of glucose concentrations on hydrogen production rate in batch tests and concluded that the Han–Levenspiel model was the most suitable one.

$$R = \frac{R_{\max} \cdot S \cdot \left(1 - \frac{S}{S_{Crit}}\right)^m}{S + K_S \cdot (1 - S/S_{Crit})^n} \tag{6.14}$$

$$R = \frac{R_{\max} \cdot S \cdot \left(1 - \frac{S}{S_{Crit}}\right)^m}{S + K_S} \tag{6.15}$$

Table 6.2 Several studies using the Monod model

Reactor type	Seed	Substrates	Described objectives	Correlation coefficient	References
Batch	*Enterobacter cloacae* IIT-BT 08	Glucose	Specific HPB growth rate	–	Kumar et al. (2000)
Batch	*Enterobacter cloacae* DM11	Glucose	Specific HPB growth rate	–	Nath et al. (2008)
Batch	*Clostridium butyricum* CGS5	Xylose	Specific HPB growth rate	0.881	Lo et al. (2008)
Batch	*Clostridium pasteurianum* CH4	Sucrose	Specific HPB growth rate	0.970	Lo et al. (2008)
Batch	*Enterobacter cloacae* IIT-BT 08	Glucose	Specific HPB growth rate	–	Kumar and Das (2000)
Batch	*Escherichia coli* BL-21	Glucose	Specific HPB growth rate	–	Chittibabu et al. (2006)
Batch	*Thermoanaerobacterium thermosaccharolyticum* PSU-2	Sucrose	Specific HPB growth rate	–	O-Thong et al. (2008)
Batch	Anaerobic digested sludge	Sucrose	Hydrogen production rate	0.858	Chen et al. (2006)
Batch	Anaerobic digested sludge	Nonfat dry milk	Hydrogen production rate	0.980	Chen et al. (2006)
Batch	Anaerobic digested sludge	Food waste	Hydrogen production rate	0.976	Chen et al. (2006)
Batch	*Clostridium butyricum* CGS5	Xylose	Specific hydrogen production rate	0.952	Lo et al. (2008)
Batch	*Clostridium pasteurianum* CH4	Sucrose	Specific hydrogen production rate	0.935	Lo et al. (2008)
Continuous	Municipal sewage sludge	Sucrose	Specific hydrogen production rate	0.94	Lin et al. (2006)
Batch	Municipal sewage sludge	Starch	Volumetric hydrogen production rate	0.973	Lee et al. (2008)
Continuous	Municipal sewage sludge	Sucrose	Volumetric hydrogen production rate	0.90	Lin et al. (2006)
Batch	Anaerobic sludge	Sucrose	Specific substrate degradation rate	0.963	Mu et al. (2006)
Continuous	Anaerobic sludge	Gelatin	Specific substrate degradation rate	–	Fang and Yu (2002)
Batch	Anaerobic sludge	Dairy wastewater	Specific HPB growth rate	0.997	Gadhe et al., (2014)

Table 6.3 Several studies using the Andrew model

Reactor type	Seed	Substrates	Described objectives	Correlation coefficient	References
Batch	Anaerobic digested sludge	Glucose	Hydrogen production rate	0.902	Wang and Wei (2008)
Batch	Anaerobic sludge	Glucose	Hydrogen production rate	–	Hang et al. (2008)
Batch	*Enterobacter cloacae* DM11	Glucose	Specific HPB growth rate	–	Nath et al. (2008)
Batch	Anaerobic sludge	Glucose	Specific HPB growth rate	–	Majizat et al. (1997)
Batch	Anaerobic sludge	Dairy wastewater	Specific HPB growth rate	0.980	Gadhe et al. (2014)

$$R = \frac{R_{\max} \cdot S}{K_S + S} \cdot X \cdot I_{pH} \tag{6.16}$$

In addition, van Niel et al. (2003) used a modified Han-Levenspiel model (Eq. 6.15) to describe the effects of sucrose concentrations on hydrogen production rate in batch tests.

Sometimes low pH will inhibit HPB growth and will inhibit their ability to degrade substrate accordingly, thus a modified Monod model incorporating low pH inhibition may describe the effects of substrate concentrations on the substrate degradation rate and HPB growth rate better. In addition, biomass decay may also affect the activity of HPB, and a modified Monod model incorporating biomass decay may be a better choice in such cases.

Ntaikou et al. (2008) used a modified Monod model incorporating low pH inhibition and biomass decay (Eq. 6.10) to describe the effects of glucose concentrations on the *Ruminococcus albus* growth rate. In addition, Ntaikou et al. (2008) and Lin et al. (2007) used a modified Monod model (Eq. 6.16) incorporating low pH inhibition to describe the effects of glucose concentrations on glucose degradation rate.

In general, the classical Monod model can be used easily to describe the effects of substrate concentrations on the rates of substrate degradation, HPB growth, and hydrogen production. In addition, some terms such as various inhibitions or biomass decay can be added to this model when necessary, which can make it describe the effects of substrate concentrations on the rates of substrate degradation and HPB growth better. Furthermore, different modified Monod models may have different property, thus, comparison of them to obtain the most suitable model for a given fermentative hydrogen production process is recommended.

So far, however, to the best of our knowledge, the classical Monod model and its modified forms have not been used to describe the effects of substrate concentrations on some soluble metabolite production rate during fermentative hydrogen production, thus more researches in this aspect are recommended.

6.4 The Effect of Inhibitor Concentration on Hydrogen Production

It has been demonstrated that some salts or hydrogen may change the intracellular pH of HPB, increase the maintenance energy requirement of HPB or inhibit some specific enzymes related to fermentative hydrogen production and thus they can inhibit HPB growth and then inhibit the fermentative hydrogen production.

So far, some kinetic models have been proposed to describe the inhibitory effects of some salt concentrations or hydrogen on the fermentative hydrogen production. Among them, the modified Han–Levenspiel model (Eq. 6.17) was widely used. As shown in Fig. 6.3, R value decreases from $R_{\max}$ to zero with increasing inhibitor concentrations from 0 to C_{Crit}.

$$R = R_{\max} \cdot \left(1 - \frac{C}{C_{Crit}}\right)^{m} \tag{6.17}$$

$$R = \frac{R_{\max}}{1 + (C/K_C)^{m}} \tag{6.18}$$

$$R = \frac{R_{\max} \cdot K_C}{K_C + C} \tag{6.19}$$

$$R = R_{\max} \cdot \frac{S}{K_S + S} \cdot \left(1 - \frac{S}{S_{Crit}}\right)^{m} \cdot \left(1 - \frac{C}{C_{Crit}}\right)^{n} \tag{6.20}$$

Table 6.4 summarizes several studies using the modified Han–Levenspiel model to describe the inhibitory effects of some salts or hydrogen on the hydrogen production rate and specific HPB growth rate.

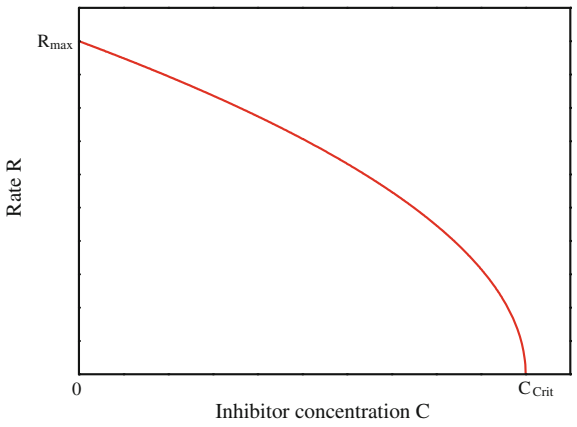

Fig. 6.3 A curve for modified Han–Levenspiel model

In addition, Wang et al. (2008) used Eq. (6.18) to describe the inhibitory effects of sodium acetate concentrations on the specific rates of sucrose degradation and hydrogen production in batch tests. Moreover, Liu et al. (2006) used Eq. (6.19) to describe the inhibitory effects of butyrate concentrations on specific growth rates of wild *Clostridium tyrobutyricum ack* and deleted mutant of *Clostridium tyrobutyricum* in fed-batch tests.

Furthermore, van Niel et al. (2003) used Eq. (6.20) to describe the combined inhibitory effects of sucrose and sodium acetate concentrations on specific growth rate of *Caldicellulosiruptor saccharolyticus* in batch tests. In addition, van Niel et al. (2003) also developed a model (not shown) incorporating cell lysis to describe the inhibitory effects of sodium acetate concentrations on specific growth rate of *Caldicellulosiruptor saccharolyticus* in batch tests.

So far, the description of the inhibitory effects of some salt concentrations or hydrogen on the rates of hydrogen production, substrate degradation, and HPB growth using these models were mostly made for batch tests; thus, the description of the inhibitory effects for continuous tests using these models is recommended.

The modified Han–Levenspiel model was only used to describe the inhibitory effects of some salt concentrations or hydrogen on hydrogen production rate. The description of the inhibitory effects of some salt concentrations or hydrogen on the rates of substrate degradation, HPB growth, and some soluble metabolite production using this model is recommended.

In addition, to the best of our knowledge, up to now, there have been no studies using models to describe the inhibitory effects of ethanol or propionate on fermentative hydrogen production. However, in some cases, ethanol can be dominant in the soluble metabolites (Wang et al. 2007), and in other cases, propionate can be dominant in the soluble metabolites (Khanal et al. 2004). At a high concentration, ethanol and propionate may also inhibit HPB growth and then inhibit the fermentative hydrogen production accordingly, thus the description of the inhibitory effects of ethanol or propionate concentrations on fermentative hydrogen production using certain models is recommended.

Moreover, the studies on the comparison of the ability of different models to describe the inhibitory effects of various inhibitors on fermentative hydrogen production are limited, thus more researches in this aspect are recommended.

6.5 The Effect of Temperature on Hydrogen Production

Temperature is one of the most important factors influencing fermentative hydrogen production, because temperature can affect the activity of HPB considerably by influencing the activity of some essential enzymes such as hydrogenases.

So far, Arrhenius model (Eq. 6.21) has been used a lot to describe the effects of temperatures on fermentative hydrogen production.

Table 6.4 Several studies using modified Han–Levenspiel model

Reactor type	Seed	Substrates	Inhibitor	Described objectives	Correlation coefficient	References
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Sodium acetate	Hydrogen production rate	0.99–1.0	van Niel et al. (2003)
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Sodium chloride	Hydrogen production rate	0.98–1.0	van Niel et al. (2003)
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Sodium lactate	Hydrogen production rate	0.90	van Niel et al. (2003)
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Potassium acetate	Hydrogen production rate	0.81	van Niel et al. (2003)
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Potassium chloride	Hydrogen production rate	0.98	van Niel et al. (2003)
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Hydrogen	Hydrogen production rate	0.79–0.98	van Niel et al. (2003)
Batch	Anaerobic sludge	Glucose	Sodium butyrate	Specific hydrogen production rate	0.989	Zheng and Yu (2005)

$$R = A \cdot \exp\left(-\frac{E_a}{R_g \cdot T}\right) \tag{6.21}$$

where T is the absolute temperature.

Table 6.5 summarizes several studies using the Arrhenius model to describe the effects of temperature on fermentative hydrogen production.

In addition, the Arrhenius model was only used to describe the effects of temperatures on hydrogen production rate and HPB growth rate, using it to describe the effects of temperatures on the substrate degradation rate and some soluble metabolite production rate is recommended.

Table 6.5 Several studies using the Arrhenius model

Reactor type	Seed	Substrates	Described objectives	Correlation coefficient	References
Batch	Anaerobic sludge	Glucose	Hydrogen production rate	0.945	Mu et al. (2006)
Batch	*Enterobacter cloacae* IIT-BT 08	Glucose	Hydrogen production rate	–	Kumar and Das (2000)
Continuous	Municipal sewage sludge	Xylose	Hydrogen production rate	0.98	Lin et al. (2008)
Batch	*Enterobacter aerogenes*	Starch hydrolysate	Maximum hydrogen production rate	0.97–0.99	Fabiano and Perego (2002)
Batch	Anaerobic sludge	Glucose	HPB growth rate	0.984	Mu et al. (2006)

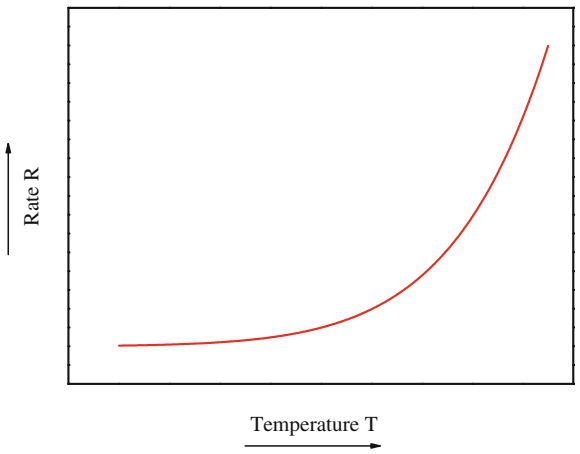

Fig. 6.4 A curve for the Arrhenius model

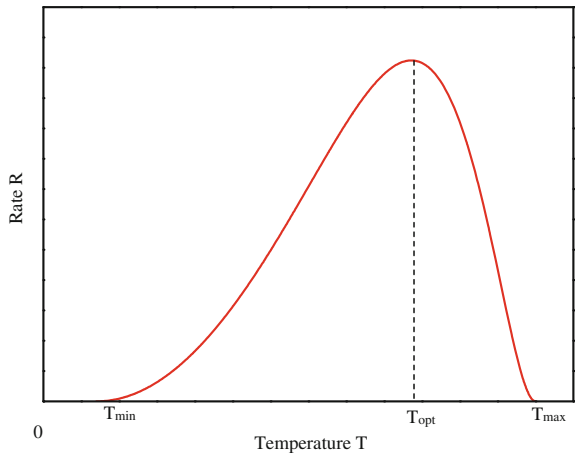

Fig. 6.5 A curve for the Ratkowsky model

One drawback of the Arrhenius model is that it cannot account for the decrease in the R with increasing temperatures above the optimal temperatures, because as shown in Fig. 6.4, R increases with increasing temperatures all the time. Thus, using models that can describe the effects of temperature on fermentative hydrogen production throughout the entire biokinetic temperature range is recommended. For such purposes, the Ratkowsky model (Eq. 6.22) may be a better choice. For R increases with increasing temperatures from $T_{\min}$ to T_{opt} and then decreases with further increasing temperatures from T_{opt} to $T_{\max}$, as shown in Fig. 6.5.

$$R = [A \cdot (T - T_{\min})]^2 \cdot \{1 - \exp[B \cdot (T - T_{\max})]\}^2 \tag{6.22}$$

6.6 The Effects of pH on Hydrogen Production

pH is another important factor influencing fermentative hydrogen production, because it can affect the activity of HPB considerably by influencing the ionization states of the active components of the cells and substrates (Mu et al. 2007).

The Andrew model (Eq. 6.23) was adopted to describe the effects of H^+ concentration on the specific hydrogen production rate (Wang and Wei 2009). In addition, using it to describe the effects of H^+ concentration on the rates of substrate degradation, HPB growth, and some soluble metabolite production is recommended.

$$R = \frac{R_{\max} \cdot [\mathrm{H}^+]}{K_a + [\mathrm{H}^+] + [\mathrm{H}^+]^2 / K_b} \tag{6.23}$$

As shown in Fig. 6.6, R value increases first and then decreases with increasing H^+ concentration.

In practice, it may be convenient to use pH rather than H^+ concentration in the model. In addition, the Ratkowsky model (Eq. 6.24) may also be a good candidate to describe the effects of pH on R.

$$R = [A \cdot (pH - pH_{\min})]^2 \cdot \{1 - \exp[B \cdot (pH - pH_{\max})]\}^2 \tag{6.24}$$

6.7 The Effect of Dilution Rate on Hydrogen Production

Dilution rate is a very important factor influencing fermentative hydrogen production in a continuous test, because it can affect the ability of HPB to degrade substrate and thus can influence the fermentative hydrogen production process.

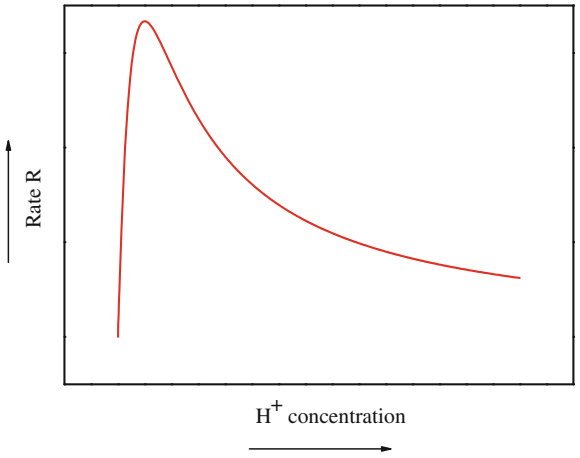

Fig. 6.6 A curve for the Andrew model

Some models have been proposed to describe the effects of dilution rates on hydrogen production rate, hydrogen production, and concentrations of substrate, biomass, and some soluble metabolites in a continuous fermentative hydrogen production process (Chen et al. 2001; Whang et al. 2006).

$$S = \frac{D \cdot K_S}{R_{\max} - D} \tag{6.25}$$

$$S = \frac{(D + k_d) \cdot K_S}{R_{\max} - D - k_d} \tag{6.26}$$

$$X = Y_{X/S} \cdot (S_0 - S) \tag{6.27}$$

$$P = Y_{P/X} \cdot X \tag{6.28}$$

where $R_{\max}$ is the specific HPB growth rate.

As shown in Fig. 6.7, S value increases with increasing dilution rate from 0 to $R_{\max}$ and is a constant with further increasing the dilution rate.

Chen et al. (2001) used the single-substrate models without biomass decay (based on Eqs. 6.25, 6.27 and 6.28) to describe the effects of dilution rates on hydrogen production and concentrations of sucrose, biomass, acetate, propionate, butyrate, and ethanol in a continuous stirred tank reactor for hydrogen production.

Moreover, Whang et al. (2006) compared the ability of three different models (based on Eqs. 6.25, 6.26, 6.27 and 6.28), namely the single-substrate model without biomass decay, the single-substrate model with biomass decay, and the dual-substrate model with biomass decay, to describe the effects of dilution rates on the hydrogen production rate and the concentrations of glucose, peptone, biomass, ammonium nitrogen, formate, acetate, and butyrate in a continuous stirred tank

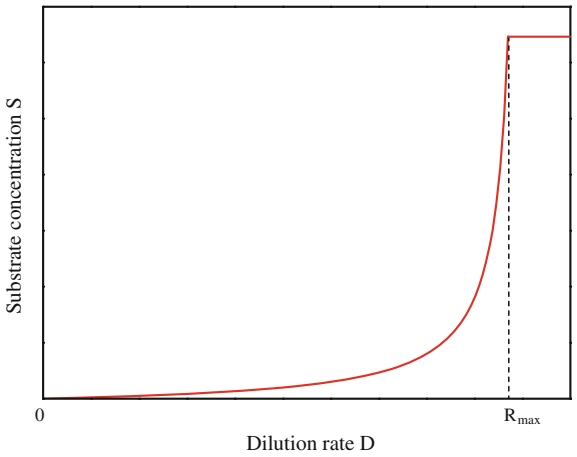

Fig. 6.7 Effect of dilution rates on substrate concentration in a continuous test

reactor for hydrogen production, and concluded that the dual-substrate model with biomass decay was the most suitable one.

In addition, other continuous hydrogen production reactors such as the packed-bed reactors, trickling biofilter, fluidized-bed reactors, and membrane bioreactors may have different property from a continuous stirred tank reactor, thus using these models to describe the effects of dilution rates on such continuous hydrogen production reactors is recommended (Wang and Wan 2009a, b).

In addition, Chang and Lin (2004) used Eq. (6.29) to describe the effects of dilution rates on the specific sucrose degradation rate in an up-flow anaerobic sludge blanket reactor for hydrogen production.

$$R = \frac{D + k_d}{Y_{X/S}} \tag{6.29}$$

6.8 The Relationship Among Substrate Degradation Rate, HPB Growth and Product Formation

The Leudeking–Piret model (Eq. 6.30) and its modified form (Eq. (6.31)) were widely used to describe the relationship between HPB growth rate and product formation rate.

$$\frac{dP}{dt} = Y_{P/X} \cdot \frac{dX}{dt} + \beta \cdot X \tag{6.30}$$

$$\frac{dP}{dt} = Y_{P/X} \cdot \frac{dX}{dt} \tag{6.31}$$

$$\frac{dP}{dt} = -Y_{P/S} \cdot \frac{dS}{dt} \tag{6.32}$$

$$\frac{dX}{dt} = -Y_{X/S} \cdot \frac{dS}{dt} \tag{6.33}$$

Table 6.6 summarizes several studies using the Leudeking–Piret model and its modified form to describe the effects of temperature on fermentative hydrogen production.

Mu et al. (2006) used Eq. (6.32) to describe the relationship between the rate of substrate degradation and the rates of hydrogen production, acetate production and butyrate production, while van Niel et al. (2002) used Eq. (6.33) to describe the relationship between substrate degradation rate and the growth rates of *Caldicellulosiruptor saccharolyticus* and *Thermotoga elfii*.

In addition, since sometimes propionate, ethanol, or formate are formed as soluble metabolites during fermentative hydrogen production, using Eq. (6.32) to

Table 6.6 Several studies using the Leudeking–Piret model and its modified form

Reactor type	Seed	Substrate	Described objective	Correlation coefficient	Reference
Batch	Anaerobic sludge	Sucrose	Hydrogen production rate	0.834	Mu et al. (2006)
Batch	*Clostridium butyricum* CGS5	Sucrose	Hydrogen production rate	Over 0.910	Lo et al. (2008)
Batch	*Clostridium pasteurianum* CH4	Xylose	Hydrogen production rate	Over 0.910	Lo et al. (2008)
Continuous	Municipal sewage sludge	Sucrose	Hydrogen production rate	0.799	Chen et al. (2001)
Batch	*Enterobacter cloacae* IIT-BT 08	Glucose	Specific hydrogen production rate	–	Kumar et al. (2000)
Continuous	Anaerobic sludge	Glucose and peptone	Formate production rate	–	Whang et al. (2006)
Continuous	Anaerobic sludge	Glucose	Formate production rate	–	Whang et al. (2006)
Batch	Anaerobic sludge	Sucrose	Acetate production rate	0.890	(Mu et al. 2006)
Continuous	Municipal sewage sludge	Sucrose	Acetate production rate	0.960	Chen et al. (2001)
Continuous	Anaerobic sludge	Glucose	Acetate production rate	–	Whang et al. (2006)
Continuous	Anaerobic sludge	Glucose and peptone	Acetate production rate	–	Whang et al. (2006)
Batch	*Thermotoga elfii*	Glucose	Acetate production rate	–	Niel et al. (2002)
Batch	*Caldicellulosiruptor saccharolyticus*	Sucrose	Acetate production rate	–	Niel et al. (2002)
Continuous	Municipal sewage sludge	Sucrose	Propionate production rate	0.824	Chen et al. (2001)
Batch	Anaerobic sludge	Sucrose	Butyrate production rate	0.964	Mu et al. (2006)
Continuous	Municipal sewage sludge	Sucrose	Butyrate production rate	0.957	Chen et al. (2001)
Continuous	Anaerobic sludge	Glucose	Butyrate production rate	–	Whang et al. (2006)
Continuous	Anaerobic sludge	Glucose and peptone	Butyrate production rate	–	Whang et al. (2006)
Continuous	Municipal sewage sludge	Sucrose	Ethanol production rate	0.941	Chen et al. (2001)
Batch	Anaerobic sludge	Dairy wastewater	Acidogenic products	0.980	Gadhe et al. (2014)

describe the relationship between the rate of substrate degradation and the production rates of propionate, ethanol or formate is recommended.

Moreover, mixed cultures may have different property from pure cultures, thus using Eq. (6.32) to describe the relationship between substrate degradation rate and some product formation rates by pure cultures and using Eq. (6.33) to describe the relationship between substrate degradation rate and the growth rate of some mixed cultures are recommended.

6.9 Conclusions

Some kinetic models, which were proposed to describe the progress of a batch fermentative hydrogen production process, the effects of substrate concentrations, inhibitor concentrations, temperatures, pH, and dilution rates on a fermentative hydrogen production process, and the relationships among the substrate degradation rate, the hydrogen-producing bacteria growth rate, and the product formation rate have been reviewed. The following conclusions can be drawn from this review.

The modified Gompertz model was widely used to describe the progress of a batch fermentative hydrogen production process, while the Monod model was widely used to describe the effects of substrate concentrations on the rates of substrate degradation, hydrogen-producing bacteria growth and hydrogen production. Arrhenius model was used a lot to describe the effects of temperatures on fermentative hydrogen production, while modified Han–Levenspiel model was used a lot to describe the effects of inhibitor concentrations on fermentative hydrogen production. The Andrew model was used a lot to describe the effects of H^+ concentration on the specific hydrogen production rate, while the Leudeking–Piret model and its modified form were widely used to describe the relationship between hydrogen-producing bacteria growth rate and product formation rate. And more researches on these kinetic models have been recommended.

In addition, a further survey of the literature showed the lack of models that incorporate important parameters affecting hydrogen production like hydrogen partial pressure and regulation mechanisms, such as $NADH/NAD^+$. Thus more researches in this respect should be carried out in the future.

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