

# Chapter 19

## Biomass Steam Gasification for Hydrogen Production: A Systematic Review

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**Abstract** The production of hydrogen as a clean and sustainable fuel is becoming attractive due to the energy crisis and increasing environmental issues associated with fossil fuel usage. Biomass steam gasification with in situ carbon dioxide capture has good prospects for the production of hydrogen-rich gas. Furthermore, hydrogen yield can be enhanced using catalyst steam gasification. This chapter comprises the literature review on both the approaches, i.e., experimental and modeling used to study the hydrogen production from biomass gasification specifically using pure steam as gasification agent. There were several modeling approaches for

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gasification process based on the kinetics, equilibrium, and the fluid dynamics behaviors. A detailed discussion has been carried out in this chapter on modeling and simulation for hydrogen production from biomass based on kinetics modeling. Experimental studies have been published on steam gasification and steam gasification with CO<sub>2</sub> capture and catalytic steam gasification has been discussed. Gasification for hydrogen production from oil palm empty fruit bunch has also been discussed.

**Keywords** Biomass • Steam gasification • CO<sub>2</sub> capture • Hydrogen • Kinetics modeling

## 19.1 Introduction

Hydrogen is one of the potential alternative energy sources that could be used to replace the existing fossil fuels. Besides the zero carbon footprints, hydrogen is expected to become a prominent energy carrier for stationary and mobile power generation applications such as in transport, industrial, commercial, and residential applications (Clark Ii and Rifkin 2006; Solomon and Banerjee 2006). The utilization of renewable sources including the biomass of forestry, agricultural, and municipal waste has become a new source of energy due to the abundance of these wastes. Consequently, producing hydrogen from biomass not only offers a zero net carbon emission and burning to get electricity and heat which is clean, it can also be stored and transported and be used in existing technology and infrastructure (Jacobson 2009). Biomass gasification is considered as one of the potential alternatives for the production of hydrogen, but the quality of hydrogen and product gas varies with the different gasification agents used (Holladay et al. 2009; Kalinci et al. 2009; Kumar et al. 2009). Biomass gasification can be performed using different gasification agents such as air, air–steam and oxygen–steam mixtures, or pure steam. It is reported that the use of pure steam is more economical and in favor of producing more hydrogen yield compared to the other conventional gasification agents (Gil et al. 1999; Balat 2008; Corella et al. 2008a, b; Balat et al. 2009). This chapter comprises the literature review on both the approaches, i.e., experimental and modeling used to study the hydrogen production from biomass steam gasification. Studies have been published on steam gasification (Ptasinski 2008) and steam gasification with CO<sub>2</sub> capture (Florin and Harris 2008) and catalytic steam gasification has been discussed (Guo et al. 2010; Tanksale et al. 2010; Serrano-Ruiz and Dumesic 2011). Furthermore, the availability of palm oil empty fruit bunch (EFB) is abundant in Malaysia (Sumathi et al. 2008; Mohammed et al. 2011a, b), so the work reported on EFB gasification for hydrogen production has also been discussed. There were several modeling approaches for gasification process based on the kinetics, equilibrium, and the fluid dynamics behaviors (Nemtsov and Zabaniotou 2008; Wang and Yan 2008; Gómez-Barea and Leckner 2010; Puig-Arnavat et al. 2010; Ahmed et al. 2012; Guo et al. 2012). A detailed discussion has been carried

out in this chapter on modeling and simulation for hydrogen production from biomass based on kinetics modeling. Finally, chapter comprises a short summary to identify the gap of study in the specific fields.

## 19.2 Steam Gasification for Hydrogen Production

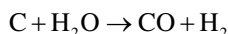
Several scientific studies have been carried out using steam gasification for higher yield of hydrogen from different biomasses. Gil et al. (1999) have analyzed the effect of gasification agents on the product gas obtained from biomass gasification in fluidized bed using small chips of pine as biomass. Air, Steam-O<sub>2</sub> mixture, and pure steam have been studied for hydrogen production. They conclude their results for hydrogen purity as follows in this order:

Pure steam (53–55 vol.%) > Steam-O<sub>2</sub> (25–30 vol.%) > Air (8–10 vol.%)

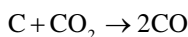
Their results show that for hydrogen production the steam gasification is the best option. But on the other hand the steam gasification produced maximum tar yield compared to other gasification agents.

Franco et al. (2003) have studied the biomass steam gasification in fluidized bed reactor at atmospheric pressure. They operated gasifier with three different types of biomass, i.e., soft wood, hard wood, and globules. Temperature and steam/biomass were studied on the product gas composition, energy conversion, and higher heating value. They reported that both temperature and steam are in favor of more hydrogen yield. They predict that water gas shift is dominant in the biomass gasification with pure steam in the main five reactions of biomass gasification as follows.

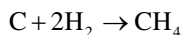
Char gasification



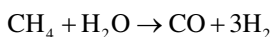
Boudouard



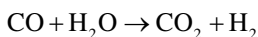
Methanation



Steam reforming



Water gas shift



They reported that the rise in temperature forecast increase in hydrogen and decreases in carbon monoxide. Furthermore, they also proved that hydrogen amount

through biomass steam gasification is higher compared to pyrolysis. The maximum of hydrogen purity was obtained at 1,073 K and steam/biomass ratio of 0.5, i.e., 45 mol%.

Ahmed and Gupta (2009) studied experimentally both pyrolysis and steam gasification using paper as biomass within the temperature range of 873–1,273 K. They investigated the syngas flow rate, hydrogen flow rate, yield, and thermal efficiency of the product gas. They reported that hydrogen yield is much higher in gasification compared to pyrolysis. They obtained around 60 vol.% of hydrogen at 1,173 K. They reported that gasification process has advantage due to mainly char gasification reaction.

Weerachanchai et al. (2009) investigated the effect of steam gasification on the product gas composition using larch wood as biomass in fluidized bed reactor. Along with the temperature they also investigated the different types of bed materials. The maximum hydrogen was obtained at 1,023 K with 55.68 vol.%, 96 % of carbon conversion efficiency, 75.88 % cold gas efficiency, and 14.76 of lower heating value of product gas.

Umeki et al. (2010) have studied high temperature steam gasification process for hydrogen-rich product gas from wood as biomass. Both temperature and steam/carbon ratio have been investigated on the product gas composition, carbon conversion efficiency, H<sub>2</sub>/CO ratio, cold gas efficiency, higher heating value, and total gas yield. In the experiment results they reported that the most dominant reaction is water gas shift reaction in steam gasification. The highest cold gas efficiency was predicted 60.4 % with the hydrogen of 55 vol.% at the outlet of the updraft fixed bed gasifier.

### 19.3 Steam Gasification with In Situ CO<sub>2</sub> Capture for Hydrogen Production

Several studies have been published on steam gasification using CaO as sorbent. Acharya et al. (2009) worked on the hydrogen production from sawdust using steam gasification and CaO as CO<sub>2</sub> sorbent in bubbling fluidized bed reactor. Furthermore, they proposed the regenerator along the gasifier for the regeneration of calcium carbonate in the system. They predict through experimental setup around 71 vol.% of H<sub>2</sub> with 0 vol.% of CO<sub>2</sub> at 853 K, steam/biomass ratio of 1.0, and Ca/C ratio of 1. They also proved that using CaO as sorbent the purity of hydrogen increased more than 30 vol.% compared to the process without CaO. Moreover, CaO not only captures CO<sub>2</sub> from the system, but also increases the efficiency of the system due to the exothermic nature of carbonation reaction as follows.

Carbonation reaction



They also reported that in steam gasification with in situ CO<sub>2</sub> capture, the water gas shift reaction moves in the forward direction due to the low partial pressure of CO<sub>2</sub> in the system, as CaO absorbs the CO<sub>2</sub>.

Pfeifer et al. (2009) used dual fluidized bed gasifier to study the effect of CaO on the product gas composition from biomass steam gasification. The hydrogen content in the product gas achieved 40 vol.% without CaO, but with the CaO the hydrogen content increased to 75 vol.%. They named this concept as “absorption enhanced reforming—AER concept.”

Furthermore, they presented a simplified flow sheet for power generation using AER process for 100 kW at Vienna University of Technology, Austria.

Guoxin and Hao (2009) studied hydrogen production using pine tree sawdust as wet biomass in quartz reactor. They investigated the effect of temperature, Ca/C ratio, and the moisture content of the biomass on hydrogen production. They predicted that the CaO not only acts as sorbent but also acts as catalyst. Furthermore, CaO has strong impact on watergas shift reaction rather than steam reforming of methane. Moreover, the high temperature is not in favor of carbonation reaction. They reported that the optimum temperature for biomass steam gasification with CaO as sorbent is 923–973 K. Their results showed more than 55 vol.% of hydrogen in the product gas at 923 K with Ca/C ratio of 0.5.

Acharya et al. (2010) have reported biomass steam gasification using sawdust as biomass and CaO as sorbent. They investigated the effect of variables (temperature, steam/biomass ratio, and CaO/biomass ratio) on the hydrogen purity and hydrogen yield. They predicted 54.43 vol.% of hydrogen at 943 K, steam/biomass ratio of 0.83, and CaO/biomass ratio of 2. Furthermore, they have reported that hydrogen yield increased by increasing temperature.

Han et al. (2011) studied on biomass steam gasification in the presence of CaO. They investigated the effect of temperature (762–1,013 K), steam/C ratio (1.2–2.18), and CaO/C ratio (0–2) on the hydrogen purity and yield. Taking sawdust as biomass they performed experiments in the fluidized bed gasifier.

They reported that all three factors, i.e., temperature, steam/C ratio, and CaO/C ratio, are in favor of hydrogen production. The addition of steam along with CaO is in favor of more hydrogen as it shifts the thermodynamic equilibrium of char gasification and water gas shift reaction to product side. They have predicted the maximum hydrogen concentration 62 vol.% with yield of 72 g/kg of biomass at 1,013 K, steam/C ratio of 2.18, and CaO/C ratio of 1. In addition, they observed that carbonation reaction temperature range is 753–1,043 K best for the gasification process in order to get more pure hydrogen by absorbing CO<sub>2</sub> from the system. They reported that within these temperature ranges not only the carbonation reaction moves in forward direction but also water gas shift reaction moves to product side due to the lower partial pressure of CO<sub>2</sub> in the system. In addition the results showed that by increasing temperature H<sub>2</sub> and CO<sub>2</sub> increase while CO and CH<sub>4</sub> decrease.

A detailed comparison of the literature based on the operating conditions, optimized parameters, and results based on optimum conditions is given in Table 19.1.

**Table 19.1** Comparison of literature for the steam gasification with in situ CO<sub>2</sub> capture for hydrogen production

References	Feed	Flow rate	Particle size	Operating parameters range				Optimum conditions at optimized product gas				Optimized gas compositions (max H <sub>2</sub> and Min CO <sub>2</sub> ) mol% or vol.%				Scale/reactor
				Temp (°C)	P (atm)	St/b	Sb/b	Temp	Sr/b	Sb/b	H <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub> yield (NTP)/g of b)	
Guoxin and Hao (2009)	Pine tree saw dust	-	<150	650-700-750	1	0.9	0-0.1-0.3-0.5-0.7-1 (Ca/C)	650	0.9	0.5 (Ca/C)	55	5	25	18	400 (mL)	Lab/Fixed Bed
Acharya et al. (2010)	White fir	-	425-500	600-670-710	1	0.58-0.83-10.8-1.58	0-1.0-1.5-2.0	670	0.83	2	54	2	23	22	375 (ml/g)	Lab/Cylinder Tube
Hanaoka et al. (2005)	Japanese oak	-	106-250	600-650-700	3-6-13-20-64-84	-	1-2-4 (Ca/C)	700	-	2 (Ca/C)	-	-	-	-	840 (ml)	Lab/Autoclave
Mahishi and Goswami (2007)	Pine bark	5 g	-	500-600-700	1	1	-	700	1	-	65	26	4	3	780 (ml/g)	Lab/Fixed Bed
Wei et al. (2008)	Pine sawdust	1 g	600-900	650-700-750-800	1	0.35-0.38-0.42-0.46-0.56-0.59	8-19-20-21-26-39	800	0.56	26	68	22	5	4.8	-	Lab/Fixed Bed
Acharya et al. (2009)	Sawdust	0.5 kg/h	-	500-580	1	1.5	1 (Ca/C)	580	1.5	1 (Ca/C)	72	1	7	20	-	Bench/Fluid Bed
Koppatz, Pfeifer et al. (2009)	Wood chips	-	-	650-660-670-680-700	1	0.83-1.24-1.62	-	700	1.62	-	60	11	18	11	-	Bench/Dual Fluid Bed
Weerachanchai et al. (2009)	Larch wood	0.21 g/min	250-600	650-750	1	-	-	750	-	-	40	25	5	5	-	Lab/Fluid Bed
Pfeifer et al. (2009)	Wood pellets	25 kg/h	-	645-841	1	0.63-0.79	-	645	0.81	-	73	6	6	11	3.264 kg/h	Pilot/Dual Fluid Bed
Xu et al. (2005)	Coffee grounds	475 g/h	-	722-795	1	1.26 (St/C)	-	722	1.26 (St/C)	-	25	8	4	6	-	Bench/Fluid Bed
Marquard-Möllenstedt et al. (2004)	Wood	15 kg/h	100	630-650-680	1	-	-	640	-	-	67	10	3	13	-	Bench/FICFB

## 19.4 Catalytic Steam Gasification for Hydrogen Production

Different kind of catalyst used in biomass gasification using different kind of reactors has been published in the literature. Corella et al. (2008a, b) used small pine wood chips as biomass in fluidized bed gasifier along with steam reformer reactor and two shift reactors for hydrogen production. They have reported 73 vol.% of hydrogen with 140 g/kg of biomass yield using Ni-based commercial catalyst. Furthermore, they stated that 90 % CO conversion to H<sub>2</sub> via water gas shift reaction due to using of catalyst in the shift reactors. Along with the high production rate they have stated that not only the system is very complex with fluidized bed, steam reformer, and two shift reactors but also the hydrogen production cost is very high. Along with this they stated that the overall process is technically feasible, meaning that there are no technical major problems.

Li et al. (2009) studied the palm oil waste (mixture of EFB + fiber + shell) for hydrogen production. They used fixed bed reactor with pure steam as gasification agent and tri-metallic catalyst, i.e., Ni<sub>1</sub>L<sub>a</sub>F/γ-Al<sub>2</sub>O<sub>3</sub>. They have investigated the effect of steam/biomass ratio, temperature, and particle size on the hydrogen production. They reported 59 vol.% hydrogen with yield of 133.25 g/kg of biomass at 1,173 K and steam/biomass ratio of 1.33. Their results showed that hydrogen is increased by increasing temperature. For steam/biomass ratio, initially hydrogen increased by increasing steam/biomass ratio, but at high steam/biomass ratio hydrogen decreased. This is due to the decrease of temperature at high steam/biomass ratio in fixed bed reactor. Furthermore, the smaller biomass particles produced more hydrogen compared to the bigger particle size. They have reported that the catalyst has a strong impact on the hydrogen yield in steam gasification of biomass. Hydrogen yield without catalyst was reported 39.75 g/kg of biomass and by using catalyst hydrogen yield increased till 101.78 g/kg of biomass under the same conditions. Furthermore, the type of catalyst also plays important role for hydrogen production in biomass steam gasification.

He et al. (2009) studied the catalytic steam gasification of municipal solid waste in bench scale fixed bed gasifier using calcined dolomite as catalyst. They reported that the catalyst not only increased the hydrogen yield but also completed decomposed tar in the system in the presence of steam at high temperature. The highest hydrogen concentration was obtained 53.29 mol% with the yield of 84 g/kg of biomass. Furthermore, they reported that the system has potation to produce 140 g/kg of biomass hydrogen yield at high temperature. The use of catalyst has proved that there is remarkable increase in the hydrogen yield and concentration and decrease of CO and CH<sub>4</sub> due to the water gas shift reaction and steam reforming of the hydrocarbons. They did not detect any tar during the catalytic steam gasification.

Xiao et al. (2010) utilized large amount of animal waste (livestock manure compost) as biomass. They investigated the effect of temperature, steam, and catalyst using fluidized bed gasifier and Ni–Al<sub>2</sub>O<sub>3</sub> as catalyst. They reported that the both temperature and steam are in favor of hydrogen concentration and yield in catalytic steam gasification, as the methane reforming and water gas shift reaction moves to the product side. Furthermore, catalyst simultaneously promotes tar cracking and steam reforming reactions.

## 19.5 EFB Gasification for Hydrogen Production

The work on biomass gasification using EFB as biomass is limited in the literature. Ogi et al. (2013) investigated EFB gasification in entrained flow gasifier using steam and steam-O<sub>2</sub> as gasification agent. They reported that pure steam gasification is in favor of more hydrogen production compared to steam-O<sub>2</sub> for EFB gasification. Because of using steam-O<sub>2</sub> the amount of CO<sub>2</sub> increased while H<sub>2</sub> and CO decreased in the system. Furthermore, TG analysis shows that EFB decomposed easily to the gases in the presence of steam and there is very low amount of tar in steam gasification of EFB. Furthermore, they observed that the EFB well gasified in the presence of steam compared to the cedar wood under same operating conditions and predicts high gasification rate as well.

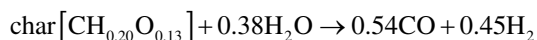
Lahijani and Zainal (2011) investigated EFB air gasification in pilot scale fluidized bed gasifier. They studied the effect of temperature and equivalence ratio on the product gas composition. They predicted maximum of 20 vol.% hydrogen at 1,323 K. The maximum carbon conversion and cold gas efficiency was predicted 93 % and 72 %, respectively.

Mohammed et al. (2011a, 2011b) studied for hydrogen-rich gas from EFB as biomass in fluidized bed gasifier using air as gasification agent. They investigated the effect of temperature, particle size, and equivalence ratio on the hydrogen production using bench scale system. They predicted maximum 38.02 vol.% of hydrogen at 1,273 K. They reported that lower particle size of EFB is in favor of more hydrogen.

Ismail et al. (2011) investigated the effect of CaO on EFB gasification in the presence of O<sub>2</sub> and H<sub>2</sub>. They reported that CaO played a very good catalyst for the gasification of EFB. The H<sub>2</sub>/CO ratio was increased by increasing temperature in the presence of CaO. Furthermore, nanosize of CaO increased 56 % more hydrogen compared to the bulk CaO. Their results showed that the high production of hydrogen can be obtained at 973 K using EFB in dry conditions via O<sub>2</sub>-H<sub>2</sub> gasification.

## 19.6 Kinetics Modeling for Hydrogen Production via Biomass Gasification

There are several studies being carried out on kinetics modeling for biomass gasification using air-steam gasification, but limited studies on pure steam gasification. Corella and Sanz (2005) developed a reaction kinetics model based on pyrolysis and gasification in circulating fluidized bed gasifier. Several reactions have been considered in the modeling including fast pyrolysis reaction, oxidations reactions, steam reforming of methane, tar reforming, char reforming, and water gas shift reaction. The char gasification reaction is presented as follows:





The kinetics for all reactions has been considered first order based on the easiest or simplest kinetics available in the literature. For example the kinetics for the char gasification reaction was selected from the literature (Gonzalez-Saiz 1988) as follows:

$$r_{10} = k_{10} C_{\text{char}2} C_{\text{H}_2\text{O}} \quad k_{10} = 2.0 \times 10^5 \exp(-6,000 / T)$$

Furthermore, the all rate equations for all reactions were solved using Chemical Reaction Engineering rules. For example the overall volumetric rate equation for hydrogen was presented as follows:

$$R_{\text{H}_2} = \text{eq.1} + d_8.r_8 + d_9.r_9 + d_{10}.r_{10} - r_4$$

Nikoo and Mahinpey (2008) have presented a comprehensive model for biomass air–steam gasification in fluidized bed using pine saw dust as biomass. Both kinetics and hydrodynamics parameters have been considered with few assumptions.

For the reactions kinetic model, the reaction equations for combustion (CO) and steam gasification (SG) given by Lee et al. (1998) were chosen as follows:

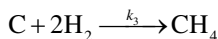
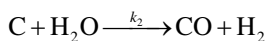
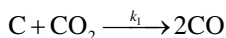
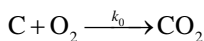
$$\frac{dX_{\text{CO}}}{dt} = k_{\text{CO}} \exp\left(\frac{-E_{\text{CO}}}{RT}\right) P_{\text{O}_2}^n (1 - X_{\text{CO}})^{2/3}$$

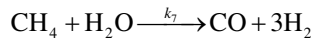
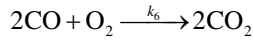
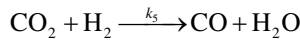
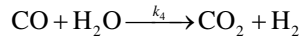
$$\frac{dX_{\text{SG}}}{dt} = k_{\text{SG}} \exp\left(\frac{-E_{\text{SG}}}{RT}\right) P_{\text{H}_2\text{O}}^n (1 - X_{\text{SG}})^{2/3}$$

$$r_c = \left(\frac{dX_{\text{CO}}}{dt} + \frac{dX_{\text{SG}}}{dt}\right) \times \frac{\rho_c \varepsilon_s Y_c}{M_c}$$

Furthermore, the model was validated with the experimental data taken from the literature and the mean error calculated between the experimental value and the predictions. The parametric studies have been done with temperature, steam/biomass ratio, equivalence ratio, and particle size on the product gas composition and carbon conversion efficiency.

Lü et al. (2008) considered fluidized bed reactor for kinetics model of biomass air–steam gasification using assumptions of isothermal and steady state conditions. Furthermore, pyrolysis has been considered as instantaneous process. The wood powder has been taken as biomass and the following eight reactions (adopted from Lü et al. (2008)) have been solved in MATLAB.





The all kinetics constants ( $k_0$ – $k_7$ ) have been chosen from the literature. Furthermore, the model has been validated with experimental data of pine sawdust taken from the literature.

Ji et al. (2009) presented a kinetics model for steam gasification of biomass for enriched hydrogen gas production from biomass. A simplified flow sheet has been also presented to get pure hydrogen based on fluidized bed gasifier, steam reformer, and  $\text{H}_2$  membrane water gas shift reactor. Several reactions have been considered in all reactors. The rate of reactions for all reactions has been solved using the kinetics data from the literature. Furthermore, the model has been validated with the experimental data taken from the literature. The effect of temperature and steam/biomass ratio has been studied on the hydrogen purity and yield. The temperature and steam/biomass range was taken 960–1,120 K and 0.5–3.0, respectively. The hydrogen purity was predicted more than 60 mol% at 1,023 K and steam/biomass ratio of 3.0. Furthermore, they reported that the lower heating value of the product gas decreased by increasing both temperature and steam/biomass ratio due to the increase of hydrogen in the product gas.

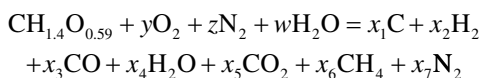
### 19.6.1 Kinetics Modeling Along with Kinetics Parameters Determination

There are very limited literature on kinetics modeling for biomass gasification supported by kinetics parameters determined using experimental data. Sheth and Babu (2009) estimated kinetics parameters for biomass pyrolysis process using kinetics modeling approach. The kinetics constant of two reactions involved in the pyrolysis was calculated by minimization of least square error between the model results and the experimental data. The experimental data were chosen from the literature. The values of activation energy and pre-exponential factor of Arrhenius constants for both reactions were calculated by the minimization of the objective function as follows:

$$k_i = A_i \exp\left(\frac{-E_i}{RT}\right)$$

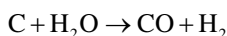
$$F(A_1, E_1, A_2, E_2) = \sum_{j=1}^n (W_{\text{exp},j} - W_{\text{cal},j})^2$$

Wang and Kinoshita (1993) developed a reaction kinetics model for biomass O<sub>2</sub>-steam gasification. The wood was taken as biomass and the generalized equation was presented as follows:

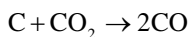


Furthermore, four main reactions were considered including char gasification, boudouard, methanation, and methane reforming reaction as follows:

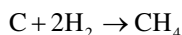
Char Gasification



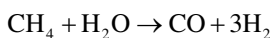
Boudouard



Methanation



Steam Reforming



The rate constant of all these reactions was calculated by the minimization of the difference between the experimental data and calculated data. The equation used was as follows:

$$\text{Min f}(k_{a1}, k_{a2}, k_{a3}, k_{a4}) = \text{Min} \sum_{j=1}^m \sum_{i=1}^6 (x_{ij} - x_{\text{exp},ij})^2$$

The experimental data were taken from their previous work on O<sub>2</sub>-steam gasification using sawdust as biomass (Wang and Kinoshita 1992). Moreover, the modeling results were validated with the experimental work. In addition, residence time, temperature, pressure, equivalence ratio, and moisture have been investigated on the product gas composition.

Resende and Savage (2010) described the kinetics model for the supercritical steam gasification for hydrogen production. The model consists of 11 reactions. The rate equations of each reaction were taken as first order for each species. The final concentration was calculated using mole balance equations; for example, the concentration of CO<sub>2</sub> was calculated using the equation as follows:

$$\frac{dC_{\text{CO}_2}}{dt} = xk_4 C_1 C_w + k_6 C_1 + k_{10} C_{\text{CO}} C_w + k_{10r} C_{\text{CO}_2} C_{\text{H}_2}$$

where  $k_{10}$  is for forward water gas shift reaction and  $k_{10r}$  is for reversible water gas shift reaction. The equilibrium constant for the water gas shift reaction was calculated as follows:

$$K_{10} = \frac{C_{H_2} \cdot C_{CO_2}}{C_{CO} \cdot C_{H_2O}}$$

The kinetics parameters were calculated by the minimization of the objective function which is the sum squared difference between the model results and experimental values. The experimental data were taken from their previous work based on the supercritical steam gasification of lignin and cellulose (Resende and Savage 2009). Furthermore, the model was validated with the experimental data and the results showed good agreement.

Salaices (2010) developed a reaction kinetics model for catalytic steam gasification of biomass surrogates using as model compounds. The kinetics model was based on the coherent reaction engineering approach. The reaction rates were based on the dominant reactions. The reactions like methanation and boudouard reactions were neglected. So the rate of each species was calculated as follows;

$$r_i = \sum r_{ij} = r_{WRG} + r_{SR} + r_{DRM}$$

There are only dominant reactions, i.e., water gas shift, steam reforming, and dry methane reforming considered. For example, the rate of formation of hydrogen was calculated as follows:

$$\begin{aligned} \frac{dp_{H_2}}{dt} = & \frac{k_{WGS} K_{CO_2}^A P_{CO} P_{H_2O}}{1 + K_{CH_4}^A P_{CH_4} + K_{CO_2}^A P_{CO_2}} \left[ 1 - \frac{P_{CO_2} P_{H_2}}{K_{WGS} P_{CO} P_{H_2O}} \right] + \\ & + \frac{k_{SR} K_{CH_4}^A P_{CH_4}}{1 + K_{CH_4}^A P_{CH_4}} \left[ 1 - \frac{P_{CO} P_{H_2}^3}{K_{SR} P_{CH_4} P_{H_2O}} \right] + \\ & - \frac{k_{DRM} K_{CO_2}^A K_{CH_4}^A P_{CO_2} P_{CH_4}}{1 + K_{CH_4}^A P_{CH_4} + K_{CO_2}^A P_{CO_2}} \left[ 1 - \frac{P_{CO}^2 P_{H_2}^2}{K_{DRM} P_{CO_2} P_{CH_4}} \right] \end{aligned}$$

Furthermore, the kinetics constants have been calculated using experimental data with best parameter estimations and minimizing the least squares objective function via optimization toolbox of MATLAB.

## 19.7 Conclusion

The literature review on the experimental work of biomass steam gasification showed that the pure steam is best gasification agent for hydrogen production. Steam gasification with CaO as sorbent improved the concentration of hydrogen in

the system and also acts as catalyst. Catalytic steam gasification showed higher yield of hydrogen. So, there is need to integrate steam, CaO, and catalyst together for high purity and higher yield. Furthermore, EFB has potential for hydrogen production, so there is also need to study the biomass steam gasification using EFB as biomass for hydrogen production. The literature review on the modeling and simulation of biomass gasification showed that there are several works published on kinetics modeling for conventional gasification but limited work on biomass steam gasification specifically for hydrogen production. So there is a need to develop reaction kinetics model including the carbonation reaction along with the main steam gasification reactions. As kinetics model provides important data regarding the conversion of biomass to hydrogen which is essential to improve the process. The predictions from the kinetics model are more accurate compared to the thermodynamic equilibrium models, so the process can be simulated better with the experimental data. In addition, there is also need to work on the determination of the Arrhenius kinetic constant for all reactions involved in steam gasification with CaO for hydrogen production from biomass.

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