

SIMULATION OF CORN STOVER AND DISTILLERS GRAINS GASIFICATION WITH ASPEN PLUS

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ABSTRACT. A model was developed to simulate the performance of a lab-scale gasifier and predict the flowrate and composition of product from given biomass composition and gasifier operating conditions using Aspen Plus software. Mass balance, energy balance, and minimization of Gibbs free energy during the gasification were applied to determine the product gas composition. Carbon conversion efficiency and tar content were provided to the model as inputs as these could not be predicted by the model based on minimization of Gibbs free energy. Experiments for validation of the model were performed on a lab-scale fluidized bed gasifier using corn stover and distillers grains as the feed materials. Steam to biomass ratio, equivalence ratio, and furnace temperature were varied during the gasification. The results show that temperature of the gasifier bed was most influential on the product gas composition. However, higher freeboard temperature may have increased formation of CO and decreased CO₂ in the final gas composition.

Keywords. Aspen Plus model, Bioenergy, Biomass, Corn stover, Distillers grains, Gasification, Simulation, Thermochemical conversion.

Thermochemical conversion of biomass to gaseous and liquid fuels is an attractive alternative route to meet energy demands on a sustainable basis. Gasification and pyrolysis are the two main thermochemical conversion techniques for biomass. Pyrolysis produces mostly liquid fuel, pyrolytic oil or bio-oil, in the absence of an oxidizing agent, while gasification produces mainly gaseous fuel in the presence of an oxidizing agent (Huber et al., 2006; Wang et al., 2008).

The goal of gasification is to break down the biomass polymers to gases, namely CO, CO₂, H₂, and CH₄, with the help of high temperature, oxidizing agents, and catalysts. Biomass mainly consists of three types of carbohydrate polymers, i.e., lignin, cellulose, and hemicellulose (McKendry, 2002). Their polymers chain lengths and the interlinking between the polymers are not consistent within the same biomass and among different types of biomass such as agricultural residues, forestry residues, perennial crops, and other organic wastes. Inconsistency in structure and composition of biomass polymers, and their unknown reaction pathways during the thermal degradation process,

lead to complexities in predicting the composition and flowrates of the final product gas from gasification.

Factors influencing gasification process can be broadly divided into two categories: characteristics of the biomass, and design and operating conditions of the gasification system. Biomass characteristics include proximate and ultimate analyses, bulk density, particle size distribution, and energy content. The operating conditions of the gasification system include biomass flowrate, steam to biomass ratio, equivalence ratio, temperatures of air and steam, temperature profile of the gasifier reactor, and heat energy input to the gasifier. Other gasification conditions that affect the process include amount and type of catalyst employed inside the gasifier. In this article, characteristics of the biomass and operating conditions of the gasification system are both taken into account while developing a model to predict composition and properties of the product gases. Catalysts, other than sand as a fluidizing medium, were not used during this study.

Since Aspen Plus contains a large property database for conventional compounds and convergence algorithms for solving minimization problems, we decided to develop a gasification model in Aspen Plus (Aspen, 2007). Many researchers have used Aspen Plus to develop gasification and downstream models for coal and biomass. Feasibilities of using co-products of the dry grind ethanol process and corn stover to generate combined heat and power (CHP) were analyzed using Aspen Plus (De Kam et al., 2007). Mansaray et al. (2000a, 2000b, 2000c) developed and analyzed a model for fluidized bed gasification of rice husks. Ersoz et al. (2006) simulated an integration of a fuel cell to generate electricity with coal or biomass gasification. In this research, corn stover and dried distillers grains with solubles (DDGS) were used as the biomass feedstocks. DDGS are the unfermentable portion of corn when converted to ethanol. DDGS has the potential to displace electricity and natural gas used through gasi-

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fication and combustion at corn-to-ethanol conversion facilities (Tiffany et al., 2007).

Aspen Plus contains built-in models for common (conventional) downstream equipment and processes such as cyclone separators, heaters, and gas turbines, but it lacks a gasification model. Since the downstream processing of syngas is heavily dependent on the composition of the syngas, which is a result of the gasification conditions, it is crucial that the predictions of the gasification model are close to the experimental results. Previous models of gasification developed by numerous authors (Nikoo and Mahinpey, 2008; Sharma, 2008; Shen et al., 2008; De Kam et al., 2007) involved an Ryield reactor, available in Aspen Plus, which decomposed the biomass into individual components with given mass yields before feeding them into the gasification reactor (RGibbs) for the subsequent reactions to take place. According to the authors, decomposition of the biomass was necessary because the Aspen Plus database lacks the properties of the biomass but does contain the properties of the decomposed elements. However, it should be realized that the elemental decomposition results in products (C, H₂, O₂, N₂, S, and ash) that can only be possible with extremely severe reaction conditions, far greater than the severity of gasification. These products may change the reaction pathways of the gasification process because of their different chemical stability and degree of involvement in reversible and irreversible reactions.

The novelty of the proposed model is the change in the major assumption regarding biomass decomposition. We assumed that the biomass does not decompose into individual elemental compositions; rather, the biomass decomposes into only the main possible products of gasification found in the literature and in our experimental results. This also allowed us to incorporate the prediction of char and tar yields during biomass decomposition. The products from this decomposition were then sent to gasification reactors (RGibbs) for heterogeneous reactions to occur at varying reactor conditions and in the presence of steam and air as oxidizing agents. Hence, the objectives of this study were to develop a new improved Aspen Plus-based gasification model that incorporates char and tar yields, and to validate the predicted results with the experimental results.

MATERIAL AND METHODS

BIOMASS SAMPLE

Corn stover samples were obtained from the Rogers Memorial Farm of the University of Nebraska-Lincoln (Lincoln, Neb.). DDGS samples were obtained from the Nebraska Energy, LLC, ethanol plant in Aurora, Nebraska. The moisture contents of the corn stover and DDGS were 6.2% and 12.16% wet basis, respectively. The proximate and ultimate analyses of the corn stover and DDGS were reported by Kumar et al. (2008) and Wang et al. (2009), respectively. The energy contents (HHV) of the corn stover and DDGS were 18.45 and 27.2 MJ kg⁻¹ on a dry basis, respectively. The corn stover samples were ground with a hammer mill to pass through a screen size of 6.35 mm (1/4 in.). Optimum screen size of the hammer mill for proper feeding into the gasifier was determined by preliminary gasification experiments with various sizes of ground corn stover.

Table 1. Operating conditions of corn stover gasification with measured carbon conversion efficiency and tar content.

Experiment	Furnace Setpoint Temp. (°C)	ER	S/B	C _{eff} ^[a] (%)	Tar (g per kg biomass)
1	750	0.2	0	82.11	23.10
2	750	0.1	0	64.64	33.88
3	750	0.2	1.8	96.11	20.82
4	750	0.2	1	91.51	30.65
5	850	0.2	1	99.95	16.70
6	750	0.3	0	85.20	46.61

[a] C_{eff} = carbon conversion efficiency

GASIFICATION SETUP AND EXPERIMENT

Experiments were performed on a lab-scale, fluidized bed gasification system. The throughput of the system was 0.68 and 0.81 kg h⁻¹ for corn stover and DDGS, respectively. The gasification system consisted of a feeder, a steam boiler, air supply to the feeder and gasifier bed, a tube furnace, a cylindrical fluidized bed gasifier, a cyclone separator, a heat exchanger, a condensate collecting flask, an air filter, a desiccator column, a gas chromatography system, and a data acquisition system. Steam and air were used as fluidizing and oxidizing agents. Gas samples were collected and analyzed using gas chromatography (GC). The GC apparatus contained two columns and a thermal conductivity detector. Helium, with 8.5% hydrogen, was used as the carrier gas. The percentage compositions of CO₂, CO, CH₄, N₂, O₂, and H₂ in the sample gas were obtained. The schematic of the gasification system, detailed descriptions of the unit operations, and the procedures for the experimental runs are described elsewhere (Kumar et al., 2009). Based on experience from the previous experiments, the gasifier was modified to increase the conversion efficiency. The gasifier bed temperature was increased to 500°C by installing electrical heaters around the gasifier bed. An air-preheater was installed to increase the temperature of the air supplied to the gasifier bed to 350°C. Temperature controllers were installed with the heaters to monitor and control the temperatures of the air-preheater and the gasifier bed. Carbon conversion efficiency was calculated as the percentage of biomass carbon that was converted into the carbon available in the product gas. The mathematical formula for the calculation is described by Kumar et al. (2009). Experimental conditions of the six experimental runs, with replications, are shown in table 1. Temperatures were varied by changing the setpoint temperature of the furnace surrounding the gasifier. Equivalence ratio (ER) and steam to biomass ratio (S/B) were varied by changing the flowrates of air and steam, respectively.

ASPEN PLUS MODEL DEVELOPMENT

A model for the gasification system was developed in Aspen Plus (version 2007, Aspen Technology, Inc., Burlington, Mass.). The thermochemical properties of the corn stover and DDGS were supplied to the model. The air contained N₂ and O₂ with molar fractions of 0.79 and 0.21, respectively. The temperatures of the air before and after the preheater were 25°C and 350°C, respectively. The temperature and pressure of the steam were 175°C and 1 atm, respectively. The components in the Aspen Plus model were corn stover, DDGS, air, water, O₂, N₂, CO, CO₂, CH₄, C, H₂, S, SO₂, SO₃, NH₃, and ash.

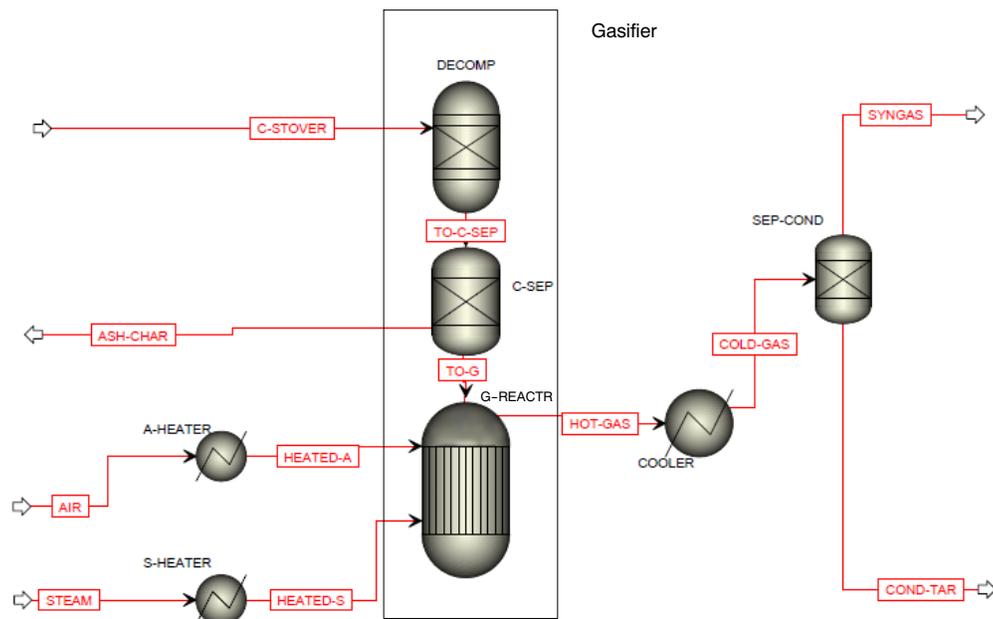
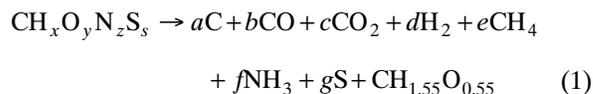


Figure 1. Aspen Plus gasification model.

The model included all unit operations for simulating our experimental setup. The Aspen Plus model for the gasification system is shown in figure 1. In this model, the gasifier and cyclone separator were represented by a combination of DECOMP, C-SEP, and G-REACTR, shown in the boxed area in figure 1. C-SEP separated ash and char from the products of DECOMP before G-REACTOR. DECOMP and G-REACTOR were Ryield and RGibbs types of reactors, respectively. DECOMP (Ryield) in this model was used to decompose the biomass into C, CH₄, CO, CO₂, H₂, H₂O, ash, NH₃, S, moisture, and ash. Based on equation 1, given below, yields of each decomposed product were supplied to the DECOMP reactor. The RGibbs reactor is advantageous where multiple reactions are unknown, and only the possible products are known for the overall reaction (Aspen, 2007). During gasification, since multiple reactions take place simultaneously, and kinetics for all reactions were not known for each biomass, RGibbs seemed to be the best option to represent the gasification reactor, G-REACTR (Mansaray et al., 2000a, 2000b, 2000c; Mathieu and Dubuisson, 2002). G-REACTR calculated the concentration of each possible product based on minimizing the total Gibbs free energy of the product from the gasifier. Other unit operations (blocks) in the model were preheaters (A-HEATER and S-HEATER for preheating of air and steam, respectively). Similar to the experimental setup, air and steam were preheated to 350°C and 175°C, respectively, using A-HEATER and S-HEATER. The product from the separator (TO-G), heated air, and steam were fed to the Gibbs reactor (G-REACTR). Flowrates of the air and steam were supplied to the Gibbs reactor at the experimental conditions. The temperature and pressure of the Gibbs reactor were 300°C to 850°C and 1 atm, respectively. As the char and ash were removed before the Gibbs reactor, products of the Gibbs reactor contained only gas with unreacted steam and tar. The product of the Gibbs reactor (HOT-GAS) was cooled to about 16°C using a COOLER. The condensate and tar were separated from the gas using a separator (SEP-COND).

The chemical formula of the biomass was determined from the ultimate analysis of the dry and ash-free (daf) biomass. The chemical formula for the corn stover and the DDGS were calculated to be CH_{1.268}O_{0.603}N_{0.0139}S_{0.00245} and CH_{1.745}O_{0.626}N_{0.080}S_{0.008} on a dry and ash-free (daf) basis, respectively. Five equations were obtained by balancing the mass of each element (C, H, N, O, and S) for equation 1. Coefficient *a* was determined from the fixed carbon fraction of biomass (from the proximate analysis). It was assumed that the fixed carbon would remain in solid form at these gasification temperatures and in the absence of an oxidizing agent. One more equation was needed to determine the seven coefficients (*a* through *g*). Hence, a ratio of CO/CO₂, *r*, was considered to be one of the model parameters. It was observed that this ratio did not impact the final gas composition from the Gibbs reactor since the gas composition was rebalanced inside the Gibbs reactor based on the final energy of the product at the specified temperature.



The main assumptions involved in this model were:

1. The biomass instantaneously decomposed into C, CO, CO₂, H₂, CH₄, N₂, S, tar, and ash (as given in eq. 1).
2. Carbon conversion efficiency (or char yield) and tar yield were known. The amount of char was determined from the carbon conversion efficiency and tar yield.
3. The chemical formula of tar was CH_{1.55}O_{0.55} based on the ultimate analysis of tar (Fagbemi et al., 2001).
4. The reactions during gasification reached equilibrium. Therefore, the gas composition during gasification was determined by minimization of the Gibbs energy of the products and reactants (Jarunghammachote and Dutta, 2008; Nikoo and Mahinpey, 2008; Li et al., 2001; Melgar et al., 2007).

5. Since the fluidization characteristics were not considered in this model, it was assumed that heat was sufficiently available for all biomass particles to increase its temperature and volatilize.

The temperature along the gasifier was not constant but increased from the bed to the center and then decreased from there to the top of the gasifier. Therefore, we varied the temperature of the Gibbs reactors in the model to find an equivalent temperature. The temperature of the Gibbs reactor for which the product composition was closest to experimental product composition was considered as the equivalent reactor temperature. Varying the temperature of the Gibbs reactor also allowed us to tune the model for our experimental conditions because a temperature profile could not be considered in the Gibbs reactor.

EXPERIMENTAL DESIGN

The predictions from the model were validated with two sets of experimental data. The first set of data was obtained for corn stover. The experimental conditions for corn stover are presented in table 1. Another set of data was available from our previous experimental study of DDGS (Kumar et al., 2009). In addition to the difference in type of biomass, there was one major difference between the gasification conditions for these two experimental setups. The corn stover

gasification was carried out on the improved gasifier for which the gasification bed temperature was increased by installing heaters around the bed and adding a preheater for the inlet air. For the second data set of the DDGS gasification, the yields of tar were not available. The tar yield for DDGS gasification was assumed to be 28.63 mg per g of DDGS, which was the average for the corn stover gasification. Carbon conversion efficiency for DDGS gasification was assumed to be 85%.

RESULTS AND DISCUSSION

CORN STOVER GASIFICATION

When no steam was added, the equivalent temperature of the Gibbs reactor was found to be 450°C with a furnace temperature of 750°C. Looking at the recorded temperature, we observed that 450°C was the temperature of the bed for that condition. The total gas predicted by the model was in good agreement with the experimental results. It must, however, be realized that the yields of tar and char were given to the model. Therefore, agreement between the model prediction and the experimental results of total gas flow suggest that model correctly predicted the fraction of steam that reacted during gasification, given that the mass of all reactants must exit in the form of final product.

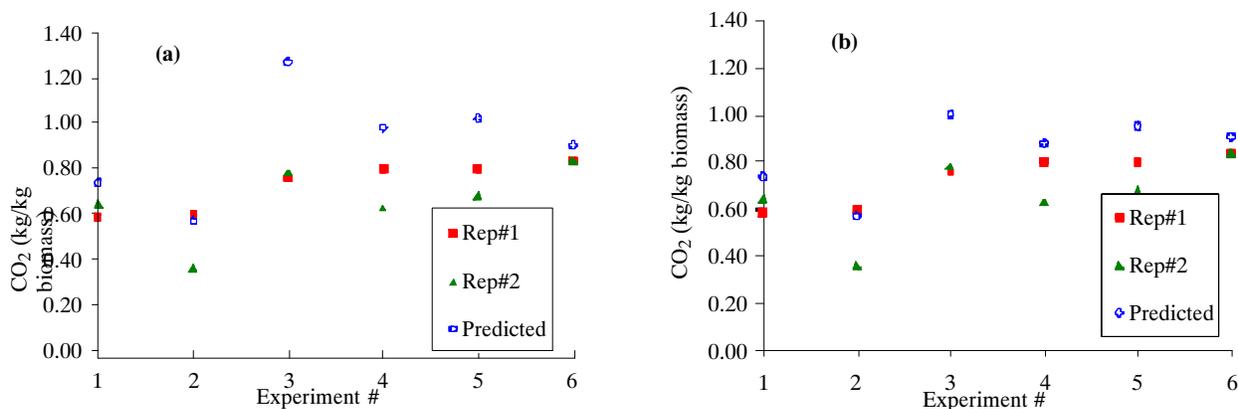


Figure 2. Predicted and experimental CO₂ yield for gasification conditions given in table 1 (with replications): (a) before and (b) after temperature adjustment.

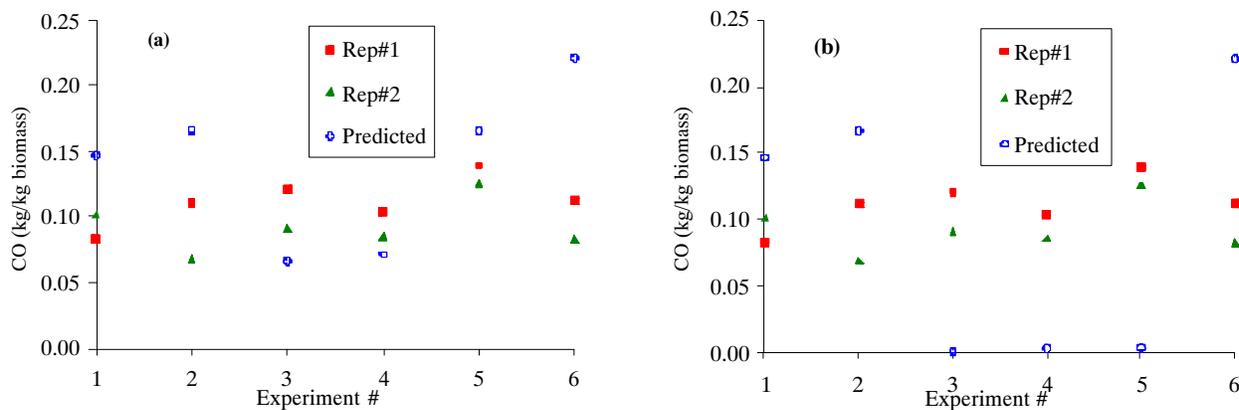


Figure 3. Predicted and experimental CO yield for gasification conditions given in table 1 (with replications): (a) before and (b) after temperature adjustment.

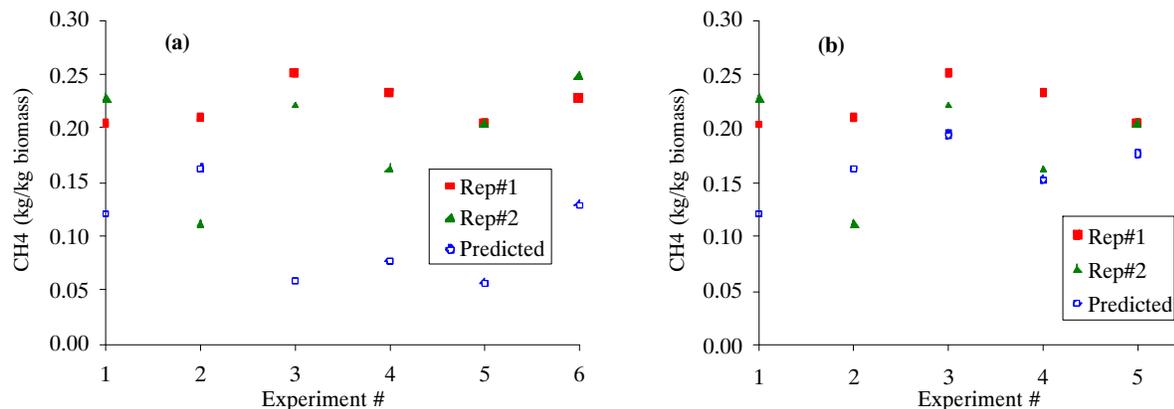


Figure 4. Predicted and experimental CH₄ yield for gasification conditions given in table 1 (with replications): (a) before and (b) after temperature adjustment.

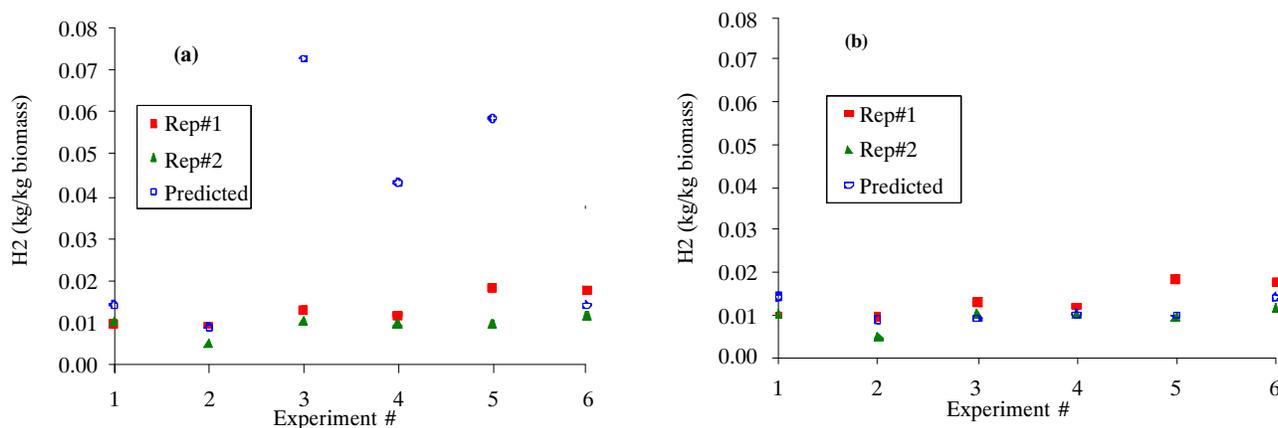


Figure 5. Predicted and experimental H₂ yield for gasification conditions given in table 1 (with replications): (a) before and (b) after temperature adjustment.

Predictions for CO₂ yields were higher than the experimental values when steam was supplied to the gasifier (fig. 2a, experiments 3, 4, and 5). However, for other conditions, the model predictions were in agreement with the experimental values. The predicted CO was higher when steam was not supplied but similar when steam was introduced (fig. 3a, experiments 1, 2, and 6). The predicted CH₄ was less than the experimental results at almost all conditions (fig. 4a, experiments 1 through 6). The predicted H₂ content was in agreement with the experimental results when no steam was added (fig. 5a, experiments 1, 2, and 6). However, after adding steam, the predicted H₂ was much higher as compared to the experimental results.

Since the results of steam gasification deviated from the experimental results, we looked at the recorded bed temperature and found that although the temperature setpoints were fixed for the gasifier bed around 500°C, after introducing steam (which was at 175°C), the temperature of the gasifier bed decreased to 350°C and 300°C at S/B values of 1.0 and 1.8, respectively. Adjusting the temperature of the Gibbs reactor in the model for cases when steam was added achieved different results: total gas flow was similar, CO₂ and CH₄ flows increased, and CO and H₂ flows decreased. The new predicted H₂ and CH₄ improved significantly after adjusting the temperature of the Gibbs reactor (figs. 5b and 4b). But CO₂ and CO further deviated (CO₂ increased and CO decreased) after adjusting the temperature during steam

gasification (figs. 2b and 3b). These trends imply that temperature of the gasifier bed had significant influence on product composition, which reliably predicted yields of H₂. However, temperature of the gasifier freeboard region also affected part of the gas yields, mainly CO and CO₂. This trend is clearer in figure 6, which shows that increasing the temperature of the Gibbs reactor (in the model) above approximately 550°C resulted in a decrease in CO₂ yield and an increase in CO yield. Previous authors reported that the

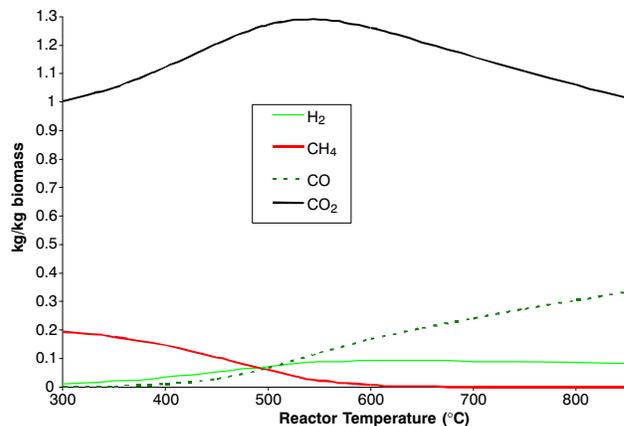


Figure 6. Effects of Gibbs reactor temperature on gas composition predicted by the model.

Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) predominates at higher temperatures (Gupta and Cichonski, 2007; Lucas et al., 2004). Higher temperatures in the middle section of the gasifier may have resulted in lower CO_2 and higher CO , as observed.

DDGS GASIFICATION

The experiments for DDGS were performed on a gasifier with a lower gasifier bed temperature as compared to those for corn stover. This resulted in a different temperature profile in the gasification reactor. In the model, the temperature of the Gibbs reactor was adjusted accordingly to reflect the experimental conditions.

The trends were more apparent for this data set because a large number of data points was available for this experimental setup. By adjusting the temperature of the Gibbs reactor in the model, the results from the model predictions and experimental results were compared using coefficient of regression (r^2) for the linear regression. The predicted yields of total gas and H_2 were in good agreement, with r^2 of 0.91 and 0.71, respectively, when the gasifier bed temperature was supplied as the temperature of the Gibbs reactor (fig. 7). However, the predicted yield of CO_2 was higher and CO and CH_4 were lower than the experimental values corresponding to the bed temperature. The gasifier bed temperature, and therefore the equivalent temperature of the Gibbs reactor, decreased after introducing steam into the gasifier. Increasing the temperature of the Gibbs reactor significantly improved the predictions for CO and CO_2 . These trends were similar to the observations for corn stover gasification. Hence, it can be concluded that the yields of the individual gases were affected primarily by the bed temperature, but temperature in the freeboard region also contributed to the shift in gas composition. Since the Gibbs reactor was not able to incorporate the effects of temperature profile for the gasification reactor, it can be inferred from these observations that its predictions will be far more accurate for a gasifier with constant temperature.

Depending on the desired gas composition of the product, the model can estimate the required operating conditions of gasification. This will enable us to modify the gasification operating conditions for specific applications of product gas, such as its conversion to fuels and chemicals, and generation

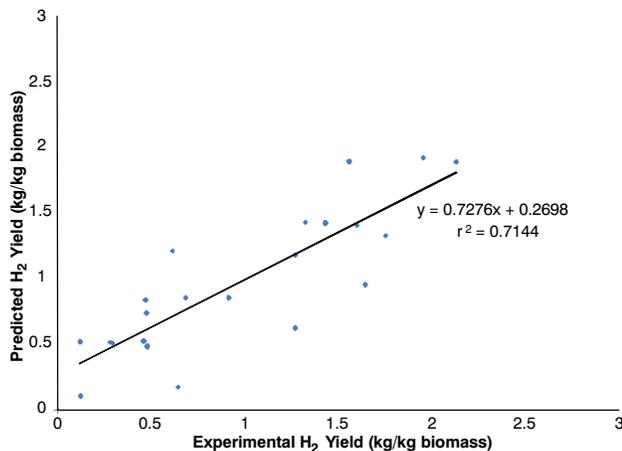


Figure 7. Comparison between experimental and predicted H_2 yield of DDGS gasification.

of combined heat and power. Higher temperatures of the gasifier bed and steam as oxidizing agent may be required for high H_2 content. For high CO and low CO_2 content in the product gas, higher temperature is required for the gasification reaction (fig. 4).

CONCLUSIONS

An Aspen Plus model was developed to simulate biomass gasification with corn stover and DDGS as the feedstocks. Because of lack of biomass properties in the Aspen Plus database, corn stover and DDGS were decomposed into possible products of gasification. The model results show that temperature of the gasifier bed was able to reliably predict yields of total gas flow and H_2 . However, yields of CO and CO_2 were influenced by the temperature of the gasifier freeboard rather than that of the gasifier bed. Hence, temperatures of both the bed and the freeboard of the gasifier affected the final gas composition. The model enables us to adjust the desired product gas composition by estimating the corresponding gasification operating conditions.

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