# Simulation of Methanol Production from Biomass Gasification in Interconnected Fluidized Beds

**Yanan Zhang, Jun Xiao,\* and Laihong Shen**

*Thermoenergy Engineering Research Institute, Southeast University, Nanjing, 210096, Jiangsu Province, China*

Simulation of methanol synthesis via $H_2$-rich biomass-derived syngas from biomass gasification in interconnected fluidized beds is carried out, using Aspen Plus software to establish this model. In the case of $CaCO_3$ catalysis, the effects of operating parameters, including gasification temperature and pressure, steam /biomass ratio ($S/B$), and liquefaction temperature and pressure, on the methanol yield are analyzed. The results are as follows: In the case of $CaCO_3$ catalysis, biomass steam gasification can obtain 82.13% hydrogen-rich gas and when the Cu-based catalyst in China which is composed of 58.1% $CuO$ + 30.06% $Al_2O_3$ + 31.7% $ZnO$ + 4.0% $H_2O$ is adopted as the methanol synthesis catalyst; the gasification temperature is suggested to be controlled at about 750 °C in the interconnected fluidized beds biomass gasification system with the purpose of methanol production. Furthermore, the gasification pressure is proposed to approach to the ambient pressure and the $S/B$ ratio of 0.4−0.5 operates better. On the optimal operating condition, the maximum of 12.19 mol/(kg biomass (daf)) of methanol yield may be obtained. The research provides useful results for the further study of biomass gasification and methanol synthesis from biomass syngas.

## 1. Introduction

As one kind of renewable clean energy, biomass can achieve the goal of $CO_2$ zero-emissions and reduce the greenhouse effect during the industrial utilization. Nowadays, the development and employment of biomass has obtained attention all over the world.[1] Methanol synthesis through biomass gasification has several advantages such as high efficiency, low cost, and large-scale production. So, it becomes one of the most promising methods of producing liquid fuel from biomass.[2−6] Biomass instead of fossil fuel such as coal, natural gas, and heavy oil can be used to make syngas. Then, the syngas can be synthesized to produce methanol, gasoline, and diesel oil, which can be used as transportation fuels. The usage of biomass not only meets daily increasing human demand for liquid fuel but also alleviates the environmental pollution engendered by the large usage of fossil fuel.

There is a vast amount of literature dealing with methanol synthesis from biomass-derived syngas. Yin and Leung[7] studied the characteristics of the synthesis of methanol using biomass-derived syngas. Lee[8] focused on investigating the liquid phase methanol synthesis (LPMeOH) process and developed a novel liquid phase process for coproduction of dimethylether (DME) and methanol. Bae[9] investigated the coproduction of methanol (MeOH) and dimethylether (DME) from biomass-derived synthesis gas on coprecipitated $Cu−ZnO−Al_2O_3/\gamma\text{-}Al_2O_3$ hybrid catalysts to overcome the equilibrium conversion of CO on the MeOH only synthetic reaction in $H_2$-deficient conditions. Kumabe[10] designed the BTL-MeOH (biomass to liquid process) system. Also, the environmental and economic analysis of the process was performed from the viewpoint of $CO_2$ emissions, capital, and operating costs. The Center for Solar Energy and Hydrogen Research (ZSW) of Germany focused on the synthesis of methanol from biomass/$CO_2$ resources and proposed an acceptable method for partial compensation of the carbon excess by adding electrolytic hydrogen (using the oxygen for the

gasifying process), saving about half of the carbon from the biomass and avoiding extremely high investment and electricity costs.[11]

In fact, many countries such as the United States (USA) and Japan began to develop projects for methanol synthesis via biomass gasification twenty years ago. The Hynol Process Project in the USA focused on converting biomass and hydrogen into syngas used to produce liquid methanol at high temperatures and high pressures. This process has three characters which are self-balance of heat, a suitable $H_2/CO$ ratio, and an integrated cycle process for the system.[12] In the NREL (National Renewable Energy Laboratory) biomass program of the USA, one kind of one-step catalyst for methanol synthesis had been devised. This catalyst can eliminate the tar and hydrocarbon as well as adjust the $H_2/CO$ ratio in order to meet the requirement of methanol synthesis.[13] The BAL-Fuels (Biomass-Derived Alcohols Fuels) project in Sweden introduced the self-heated reformer ATR (autothermal reforming), converting the methane and steam into $H_2$ and CO and compelling them to go back to the methanol synthesis reactor. This new reformer may lead to the result of more methanol production.[14] In the BoiMeet Project in Sweden, the processes of steam reforming and $H_2/CO$ regulation are left out. Moreover, the raw materials are sent into the liquid-phase methanol synthesis reactor. Although the methanol yield was somewhat lower, the unreacted gas may be used in other places such as the integrated gasification combined cycle (IGCC), resulting in the improvement of system efficiency.[10] The BLGMF project in Sweden adopted a jet flow gasifier to gasify the black liquor from paper production. This project deserves much attention. On one hand, the pollution from black liquor can be controlled; on the other hand, the products from black liquor gasification can be used to synthesize liquid fuels for cars.[15]

In this paper, a new method of methanol synthesis via biomass gasification in interconnected fluidized beds is proposed. The process simulations are carried out by the Aspen Plus program. On the basis of $CaCO_3$ catalysis, the effects of operating parameters, including gasification temperature ($T_g$), gasification pressure ($P_g$), steam/biomass ratio ($S/B$), liquefaction temper-

* To whom correspondence should be addressed. Tel.: +86-25-83793452. Fax: +86-25-83793452. E-mail address: jxiao@seu.edu.cn.
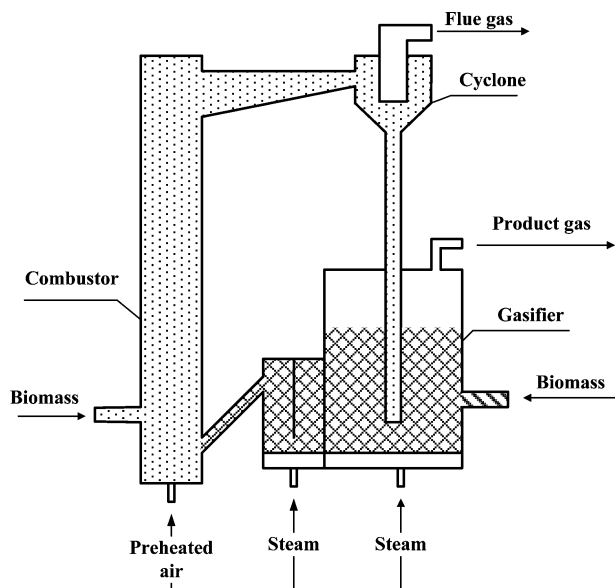
**Figure 1.** Biomass gasification in interconnected fluidized beds.

ature ($T_m$), and liquefaction pressure ($P_m$), on the methanol yield are analyzed. The research provides reference data for the further study on biomass gasification and methanol synthesis from biomass syngas.

## 2. Technology of Biomass Gasification in Interconnected Beds

The scheme of biomass gasification in interconnected beds is illustrated in Figure 1. It is in a loop with end-to-end configuration composed of a circulating fluidized bed as a combustor, a cyclone, and a bubbling fluidized bed as a gasifier. The circulating fluidized bed is designed for combustion fed with air and the bubbling fluidized bed for biomass gasification fed with steam. Interconnected fluidized beds technology is used to separate gasification and combustion processes; the gasification-required heat is achieved by means of the circulation of bed particles (catalyst particles, sand, ash, etc.) which serve as the heat carrier and circulate in the system.[16]

The whole biomass material fed to interconnected beds can be divided into two parts. One part of the biomass is fed into the bubbling fluidized bed. As soon as biomass is fed into the bottom of the bubbling fluidized bed, an exquisite mixture of biomass, steam, and hot bed particles occurs, followed by the intense exchange of heat and mass. Then the volatile compounds in biomass evaporate, followed by the pyrolysis of the biomass. The reactions between gaseous product after pyrolysis combined with solid residual and steam occur, where gases such as CO and $H_2$ are generated. The other part of biomass is burnt in the circulating fluidized bed where the bed particles mass a great deal of heat. On one hand, semigasified biomass particles and bed particles that have released heat in the gasifier are back-passed into the circulating fluidized bed to combust. On the other hand, flue gas caring hot bed particles from the combustor passes through the cyclone. The hot particles are separated from the flue gas and back-passed into the gasifier, offering the gasification-required heat. The unseparated particles are expelled from the system in the form of blowing ash with the flue gas.

Adding catalysts to bed particles may achieve the function of biomass catalytic gasification. The circulating fluidized bed is designed for combustion fed with air and the reaction temperature was maintained at the range of 900−980 °C. The

catalyst particles were circulating between the gasifier and the combustor. Along with the combustion of the cumulated carbon on the surface of catalyst particles, rebirth of the catalyst was achieved. In this paper, $CaCO_3$ was added into the inert bed particles. As an additive for bed particles, $CaCO_3$ could be used to effectively eliminate tar in the biomass gasifier under the effect of the gasification agent. Besides, a quantity of $CaCO_3$ was sent into the combustor and turned into CaO after being calcined. The CaO could help to absorb $CO_2$ and improve biomass pyrolysis, affecting gasification equilibrium and adjusting the proportions of $H_2$ and CO in the gas product. The produced $CaCO_3$ particles from the reactions between CaO and $CO_2$ may decompose and release $CO_2$ again when heated, resulting in the rebirth of CaO and lengthening the utilization longevity of catalyst. Furthermore, $CaCO_3$ could fix the sulfur in product gas and attain the effect of desulfurization.

Biomass gasification in interconnected fluidized beds is a novel process and has several advantages. Because the combustor is connected to the gasifier through the cyclone, it reduces the diluting effect of nitrogen from air and eliminates the need for an oxygen plant when oxygen is used as the gasification medium. Besides, catalyst deactivation is eliminated because the carbon on the catalyst surface can be burnt out in the circulating fluidized bed. Generally, performing a typical IGCC coupled with a methanol plant to produce methanol requires the adoption of pure oxygen as the gasification agent. There would be a complex process for converting the air to pure oxygen which may be expensive as fas as capital and energy are concerned. However, steam is used as the gasification agent in the process of biomass gasification in interconnected fluidized beds. Steam gasification may produce a gaseous fuel with a relatively higher $H_2$ content. This will be beneficial for methanol synthesis via biomass-derived syngas since syngas from biomass gasification usually contains insufficient hydrogen. Moreover, steam gasification is capable of maximizing the gas product with higher heating rates involved and the efficient tar and char reduction brought about by steam reforming.

## 3. System Configuration and Models

**3.1. System Flow.** The technology of biomass gasification in interconnected beds is adopted in order to produce the biomass-derived syngas which is suitable for methanol synthesis. In most cases, biosyngas is a $CO_2$-rich and $H_2$-deficient feed gas, which can be tailored in the downstream process by the water−gas shift reaction, methane reforming, $CO_2$ removal, or supplying $H_2$ to readjust its composition before entering into the synthesis loop.[7] However, the syngas from biomass gasification in interconnected fluidized beds is of rich $H_2$ content. So one-step synthesis of methanol was employed in this paper. Product gas from biomass gasification in interconnected bed is turned into biomass syngas after purge and separation processes. Then, it is compressed with the circle gas at a high pressure and sent into the synthesizer. At the catalyst layer of the synthesizer, the reactions of methanol synthesis occur. The outlet gas, including methanol, steam, and some unreacted gases such as $H_2$, CO, $CO_2$, and inert gases ($N_2$ and $CH_4$) are refrigerated by the water cooler where methanol and water are condensed. Then the gas and liquid are separated in the separator. The separated crude methanol sends off the dissolved gas to the flasher. After that, it is fed into the further rectification section. The gas from the top of the separator goes through the splitter with partial emission. This process of partial emission may achieve the purpose of eliminating some inert gases brought by the material gas and maintaining the pressure of the whole

system. The rest of the gas is compressed with the fresh biomass syngas and sent to the reactor for methanol synthesis. The system process of methanol synthesis via biomass gasification in interconnected fluidized beds is illustrated in Figure 2.

**3.2. Unit Models.** On the basis of Aspen Plus, the whole system can be regarded as the combination of two subsystems, i.e. the gasification subsystem, where the biomass is converted into syngas, and the liquefaction system, where the syngas is converted into liquid methanol.

In order to simulate the chemical steps occurring in the process of biomass gasification in interconnected fluidized beds, the Aspen Plus software is adopted. Aspen Plus is a kind of universal software for simulation, design, and optimization of a complicated chemical process. It is applied to establishing the models of biomass gasification process on the basis of principles of mass, chemical, and energy balance and the methanol synthesis process on the basis of the chemical kinetics.[17]

**3.2.1. Gasification Model.** The main reactions of biomass gasification considered in the gasifier are as follows:

$$\text{Water gas}$$
$$C + H_2O \rightarrow CO + H_2 + 131.5 \text{ kJ/mol} \tag{1}$$

$$\text{Boudouard}$$
$$C + CO_2 \rightarrow 2CO + 172 \text{ kJ/mol} \tag{2}$$

$$\text{Water-gas shift}$$
$$CO + H_2O \rightarrow CO_2 + H_2 - 41 \text{ kJ/mol} \tag{3}$$

$$\text{Methanation}$$
$$C + 2H_2 \rightarrow CH_4 - 74.8 \text{ kJ/mol} \tag{4}$$

$$\text{Steam reforming}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 - 206 \text{ kJ/mol} \tag{5}$$

In this paper, the $CaCO_3$ was added to the gasifier so the reactions related to $CaCO_3$ also considered in the gasifier are as follows:

$$\text{Solidification}$$
$$CaO + CO_2 \rightarrow CaCO_3 - 178 \text{ kJ/mol} \tag{6}$$

$$\text{Sulfuration}$$
$$CaO + H_2S \rightarrow CaS + H_2O - 63.2 \text{ kJ/mol} \tag{7}$$



**Figure 2.** System process of methanol synthesis via biomass gasification in interconnected fluidized beds.



**Figure 3.** Process simulation of methanol production from biomass gasification in interconnected fluidized beds.

The following assumptions are made on the basis of the application of Aspen Plus software:[18]

• The combustor and the gasifier were operated under a steady state, and the reactions reached chemical equilibrium.

• Ash in biomass as well as in bed particles (sand) was inert and did not participate in any chemical reactions.

• The product gases of biomass gasification were $H_2$, CO, $CO_2$, $CH_4$, $H_2O$, $N_2$, $H_2S$, $NH_3$, COS, and $SO_2$; tar was not considered in the simulation.

• The pressure loss in the combustor and the gasifier was not taken into account in the simulation.

• The temperatures of biomass particles were uniform and there is no temperature gradient.

Process simulation of biomass catalytic gasification in interconnected beds is shown in Figure 3. The whole model consisted of seven blocks, four heat streams (demonstrated in broken lines), and several material streams. The seven blocks are the pyrolyzer block, combustor block, gasifier block, pyrolysis product separator block, combustion product separator block, gasification product separator block, and product gas separator block.

The pyrolyzer block is merely a decomposer, which corresponds to the Ryield block of Aspen Plus; its function is to decompose biomass into simple components. Biomass decomposition temperature is needed to specify this module. However, the specific numerical value of the temperature has no influence on the simulated results for the whole flow according to the characteristics of the Ryield block. Due to the usage of the Ryield block, product yield should be specified or calculated by a FORTRAN subroutine. Yield percentage is adopted in the specification in order to maintain the whole material balance. In the simulation system, a defined FORTRAN subroutine with the specified yield distribution is used to calculate the yield. This specified yield distribution serves as the initial value for iterative calculation in procedure circulation. Besides, the components attribution should be specified for unconventional components as well.
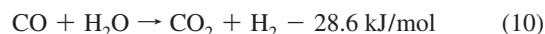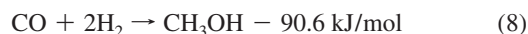
The whole model of gasifier block and combustor block are both on the basis of the principle of minimization of Gibbs' free energy, which originated from the Rgibbs block of Aspen Plus. In the system of biomass gasification, elements of C, H, O, N, and S are considered as existing elements. The components of the outlet gas consist of CO, $H_2$, $CO_2$, $CH_4$, $H_2O$, $N_2$, $H_2S$, $NH_3$, COS, $SO_2$, C (solid), and S. The Gibbs free energy is minimal when the chemical equilibrium for the process is achieved.

Separator A divides the pyrolysis product from pyrolyzer block into two material streams. One steam is sent to the combustor for combustion and the other is sent to the gasifier for gasification. Biomass syngas (consist of $N_2$, CO, $H_2$, $CO_2$, and $CH_4$) is separated from the product gas through separator D.

In industrial production, biomass syngas should undergo a series of purge processes in order to remove the impurity gases such as $H_2S$, $H_2N$, COS, and $SO_2$. However, the simple Sep block is used to simulate separation processes for the reason that this paper focuses on studying methanol synthesis from biomass syngas in interconnected beds.

**3.2.2. Liquefaction Model.** Methanol synthesis is a complex process, and methanol synthesis catalyst should be used to promote the reactions related to methanol synthesis. In the liquefaction model, five components of the biomass syngas are taken into account. Those components are CO, $H_2$, $CO_2$, $CH_4$, and $N_2$, among which $N_2$ and $CH_4$ are inert. Three possible reactions exist in the methanol synthesis system, and two of them are undependable. In this paper, reactions 8 and 9 below are adopted as the undependable reactions and the main reactions considered in liquefaction process are as follows:

$$CO + 2H_2 \rightarrow CH_3OH - 90.6 \text{ kJ/mol} \qquad (8)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O - 49.5 \text{ kJ/mol} \qquad (9)$$

$$CO + H_2O \rightarrow CO_2 + H_2 - 28.6 \text{ kJ/mol} \qquad (10)$$

The following assumptions for the liquefaction model are made on the basis of the application of Aspen Plus software:[19]

• Pressure loss in the methanol synthesizer was not taken into account.

• Material gas is preheated sufficiently, and the temperatures in the methanol synthesizer were assumed to be uniform.

• The gas phase in the methanol synthesizer is supposed to be a flat steam, and no backmixing exists.

Typical gas-phase Lurgi methanol synthesis is applied to the process of converting biomass syngas to liquid methanol in this paper. Usually, a methanol synthesizer is a multitubular catalytic reactor. So, a pipe catalytic reactor with heat transfer is adopted in this paper, which originated from the Rplug block of Aspen Plus. The Rplug block is a rigorous model of a plug flow reactor. It is assumed that the flow is mixed in the radial direction rather than the axial direction. Besides, no backmixing is in the tubes. The reactor model of Rplug may be adopted for single-, two-, and three-phase chemical equilibrium and has four groups of built-in model parameters which are model specification, reactor configuration, chemical reaction, and pressure. In this paper, the model specification of appointing reactor temperature is adopted. Specified reactor temperature is constant and chosen given the geometry. The parameters including tube numbers, length, and diameter are input to the configuration of reactor with effective state specification. The reactions for methanol synthesis are input to the reaction set. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) global kinetic models were proposed in the form of the reactant fugacity of the hydrogenation of carbon monoxide and carbon dioxide. Stoichiometric and LHHW coefficients for the components in each reaction are input to the reaction input forms. The parameters were on the basis of the Cu-based catalyst of 58.1% CuO + 30.06% $Al_2O_3$ + 31.7% ZnO + 4.0% $H_2O$ in China,[20,21] and the Langmuir–Hinshelwood–Hougen–Watson (LHHW) global kinetic models are as follows:

$$\gamma_{CO} = -\frac{dN_{CO}}{dW} = \frac{k_1 f_{CO} f_{H_2}^2 (1 - \beta_1)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^3} \qquad (11)$$

$$\gamma_{CO_2} = -\frac{dN_{CO_2}}{dW} = \frac{k_2 f_{CO_2} f_{H_2}^3 (1 - \beta_2)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^4} \qquad (12)$$

$$\beta_1 = \frac{f_M}{K_{f_1} f_{CO} f_{H_2}^2} \qquad (13)$$

$$\beta_2 = \frac{f_M f_{H_2O}}{K_{f_2} f_{CO_2} f_{H_2}^3} \qquad (14)$$

Where the rate of CO hydrogenation to $CH_3OH$ and the rate of $CO_2$ hydrogenation to $CH_3OH$ were defined as $\gamma_{CO}$ and $\gamma_{CO_2}$. $N_{CO}$ and $N_{CO_2}$ represented the molar flow of CO and $CO_2$. The terms $f_{CO}$, $f_{CO_2}$, $f_{H_2}$, and $f_M$ were the fugacities of CO, $CO_2$, $H_2$,

**Table 1. Approximate and Elemental Analysis of Biomass**

| proximate analysis (wt %, ad) | | | ultimate analysis (wt %, ad) | | | | | | heating value (MJ/kg) |
|---|---|---|---|---|---|---|---|---|---|
| moisture | fixed carbon | volatile matter | ash | car | H | O | N | S | |
| 9.1 | 16.75 | 63.69 | 10.46 | 35.37 | 4.82 | 39.15 | 0.96 | 0.14 | 14.4 |

**Table 2. Input Data for System Simulation**

| parameter | value |
|---|---|
| combustor temperature | 980 °C |
| gasifier temperature | 650−850 °C |
| biomass flow rate | 1.0 kg/s |
| air flow rate | 2.2 kg/s |
| air inlet temperature | 20 °C |
| feed water inlet temperature | 20 °C |
| outlet cold fuel gas temperature | 135 °C |
| carbon conversion of biomass | 99% |
| heat loss | 3% of input heat |
| specific heat volume of bed particles (sand) | 1.2 kJ/(kg K) |
| CaCO₃/biomass ratio | 1.5 |
| liquefaction temperature | 200−300 °C |
| liquefaction pressure | 3−10 MPa |
| proportion of the circle gas | 0.97 |

and $CH_3OH$. Also, $k_1$ and $k_2$ were the reaction rate constants of reactions 8 and 9. $K_{CO}$, $K_{CO_2}$, and $K_{H_2}$ were the adsorption equilibrium constants of CO, $CO_2$, and $H_2$. $K_{f_1}$ and $K_{f_2}$ were equilibrium constants of reactions 8 and 9 represented by fugacities, and $W$ was the catalyst mass.

The Flash2 block in Aspen Plus can be used to simulate a flash drum, evaporator, liquid separate pot, and other single-stage separators. The inlet materials sent into the Flash2 block are divided into two steams of outlet materials, and the Flash2 block may accomplish the balance calculation of gas−liquid and gas−liquid−liquid. Given that, the Flash2 block of Aspen Plus is adopted, serving as the separator and flash tank. It performs the function of simulating the process of two-phase gas−liquid separation.

## 4. Operating Conditions and Primary Parameters

The biomass material studied here is the straw from Jiangsu Province, China. The proximate analysis and the ultimate analysis of biomass are given in Table 1. The general process calculation basis and conditions are reported in Table 2.

## 5. Results and Discussion

To provide some process fundamentals biomass gasification in interconnected fluidized beds, the adaptation of sand as the bed particle, which plays the role of the heat carrier particle between the combustor and the gasifier, was discussed in this study.

**5.1. Model Validation. 5.1.1. Comparison between Simulated and Experimental Results of Gas Composition.** The 10 kW interconnected beds of Southeast University are adopted as the experimental equipment. The bubbling fluidized bed is a rectangular bed, with a cross section of (230 × 40) mm² and a height of 1500 mm. The inner seal inside the bubbling fluidized bed is also a rectangular section of (23 × 40) mm². A 60° conical distributor connected with a tube with 20 mm i.d. is mounted at the bottom of the bubbling fluidized bed. The high velocity fluidized bed is a circular column of 50 mm i.d. and 2000 mm height, having a perforated plate as an air distributor.[22]

The biomass gasification model was validated by the experimental results of the circulating fluidized bed serving as biomass gasifier. Operating conditions and primary parameters in the simulation were as follows: room temperature 20 °C, biomass flow rate 3.0 kg/h, steam flow rate 2.4 kg/h, air flow rate 7

m³/h, combustor temperature 920 °C, gasifier temperature 770−920 °C, steam temperature 600 °C, system pressure 0.1 MPa, carbon conversion of biomass 99%, and loss heat is calculated as 3% of the input heat. The biomass used in the study was straw from Jiangsu Province, China.

Figure 4 shows the simulated and experimental results of gas composition at the gasification temperatures of 770−920 °C. We can see from the comparison between the simulated and experimental results that the simulated results of CO and $CO_2$ agree with the experimental ones. However, the simulated data of $CH_4$ is lower. Some errors exist in this designed system. In the experiment, the reforming reaction of $CH_4$ and steam is limited by the reaction time so it cannot reach the complete equilibrium state. Due to the reasons given above, the simulated data of $CH_4$ is somewhat higher. Although there is error between the numerical value of simulation and that of the experiment, the changing trend of the gas composition is consistent. So the simulated results can reflect the changing trend of the product gas in the gasification process so as to attain the expected purpose of predicting the gas composition of biomass gasification in interconnected fluidized beds.

**5.1.2. Comparison between Simulated and Experimental Results of Methanol Yield.** In order to validate the liquefaction model, experimental data from methanol synthesis in a laboratory-scale methanol synthesizer was used; details of the experimental device and results can be found elsewhere.[23] The Cu-based catalyst composed of 58.1% CuO + 30.06% $Al_2O_3$ + 31.7% ZnO + 4.0% $H_2O$ was used in the experiments, and the inlet molar flow of the syngas (converted to standard state) is 0.10−1.5 mol/h. Under the conditions of liquefaction temperature of 230−260 °C and liquefaction pressure of 5 MPa, experimental data of methanol synthesis was measured. Small error between simulated results and experimental results exists in the liquefaction model, as indicated in the comparison between simulated and experimental results (Table 3).

Validations for the biomass gasification and methanol synthesis models indicate that the system model in this paper has the function of forecasting the influence factors of the methanol production via biomass gasification in interconnected beds.

**5.2. Simulation Results and Discussion. 5.2.1. Effect of Gasification Temperature and Pressure.** Under the basic conditions of a CaCO₃/biomss ratio of 1.5, S/B ratio of 0.4,
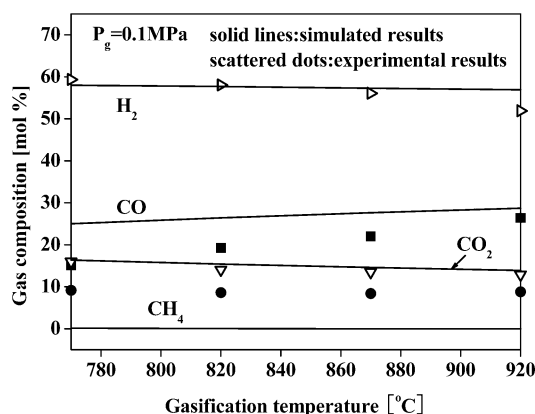


**Figure 4.** Comparison between simulated and experimental results of gas composition.

**Table 3. Different Experimental Conditions**

| condition | temperature (K) | inlet flow (mol/h) | inlet gas composition (%) | | | | | methanol yield (kg/mol) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | CO | $CO_2$ | $N_2$ | $C_NH_M$ | $H_2$ | experimental results | simulated results |
| 1 | 503.15 | 0.72 | 11.83 | 10.76 | 45.13 | 1.04 | 31.24 | 1.291 | 1.064 |
| 2 | 503.15 | 0.98 | 11.83 | 10.76 | 45.13 | 1.04 | 31.24 | 1.320 | 1.085 |
| 3 | 513.15 | 0.89 | 10.8 | 8.87 | 42.81 | 0.88 | 36.64 | 0.998 | 0.975 |
| 4 | 523.15 | 0.84 | 11.27 | 8.32 | 44.29 | 0.95 | 35.17 | 0.979 | 0.930 |
| 5 | 533.15 | 0.13 | 10.49 | 7.95 | 34.63 | 0.89 | 46.04 | 1.379 | 1.245 |

liquefaction temperature of 230 °C, liquefaction pressure of 5 MPa, and gasification pressure of 0.1 MPa, we study the effect of gasification temperature at the range of 650−900 °C on the product gas and methanol yield.

**5.2.1.1. Effect of Gasification Temperature and Pressure on the Product Gas from Gasification.** In the case where the gasification temperature was varied from 650−900 °C and the combustor temperature was 980 °C, results referring only to a steam/biomass ratio of 0.4 are presented to demonstrate the effect of the gasifier temperature. The dry gas composition is shown as a function of the gasifier temperature, as indicated in Figure 5a. In order to see the effect of the WGS reaction, the water composition is added into Figure 5b.

Along with the increasing of the reaction temperature, $H_2$ content increased slightly at the beginning then decreased remarkably. $H_2$ content reached a maximum of 82.13% at the gasifier temperature of around 700 °C and kept almost constant when the temperature reached 800 °C. This is because the produced CaO in combustor plays the role of catalysis rather than $CaCO_3$. When the temperature is below 750 °C, CaO reacted with $CO_2$ produced in gasifier and formed the $CaCO_3$. The reduction of $CO_2$ promoted the equilibrium of water gas reaction 1 toward the direction where $H_2$ production was favored. As a

result, the $H_2$ content in the product gas increased. The produced $CaCO_3$ in the gasifier decomposed gradually along with the rise of gasifier temperature and reached the complete decomposition sate at the gasifier temperature of 800 °C under the reductive atmosphere. Therefore, due to the gradual decline trend of absorption function of CaO, the change of gas composition is mainly presented as the dramatic reduction of $H_2$ content and the gradual increase of CO and $CO_2$ contents. In Figure 5b, the water composition is added in order to the see the effect of the WGS reaction.

The effect of gasification pressure on gas composition is indicated in the Figure 6. The CO content and $CO_2$ content decreased at different degrees, $H_2$ content increased continuously from 59.42% to 78.55%, and an evident increase in $CH_4$ content existed. Because the increase of pressure would promote the gasification reactions toward the direction that leads to volume constriction, pressure increase favored the methanation reaction 4, leading to the generation of more $CH_4$. As a result, $CH_4$ content rose from 0.20% to 5.93%.

$H_2$ and CO are the main components in methanol synthesis and play crucial roles in methanol yield. The rate and heat of CO hydrogenation to $CH_3OH$ is higher than that of $CO_2$ hydrogenation to $CH_3OH$. The role of carbon dioxide on the methanol synthesis reaction is also very important and was studied by carrying out different sets of experiments.[8,24] A suitable $CO_2$ concentration may make the temperature of the catalyst bed stable and prolong the catalyst longevity. In this paper, the ratio of hydrogen to carbon was defined as $M$ ($M = H_2/(CO + 1.5CO_2)$(molar ratio)). $M$ and $CO_2/CO$ (molar ratio) were investigated in this study. If $M$ is too small, side reactions may increase resulting in the rise of impurities in the raw methanol and even the reduction of catalyst longevity. Contrarily, a too high ratio of hydrogen to carbon may lead to redundant $H_2$ accumulation in the system and result in the rise of energy consumption. The effect of gasification temperature on them is shown in Figure 7. From this figure, it was illustrated that, on one hand, $M$ increased first, decreased sharply over the temperature range of 700−750 °C, and stayed almost constant over 800−900 °C. $M$ reached a maximum of 4.64 at a temperature
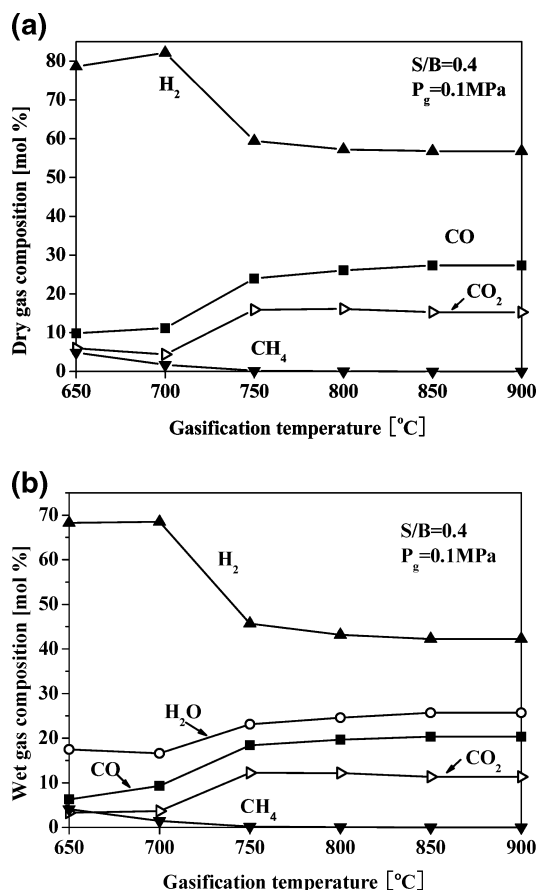


**Figure 5.** Effect of gasification temperature on gas composition.
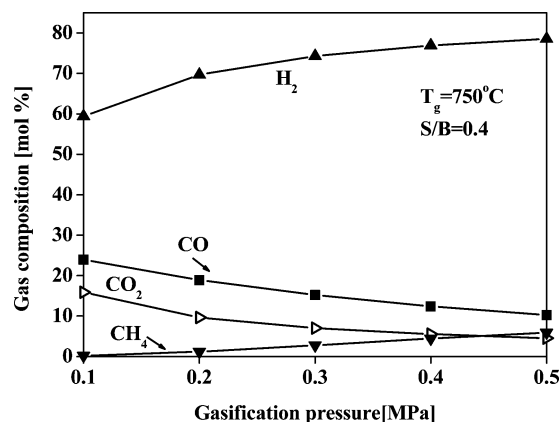


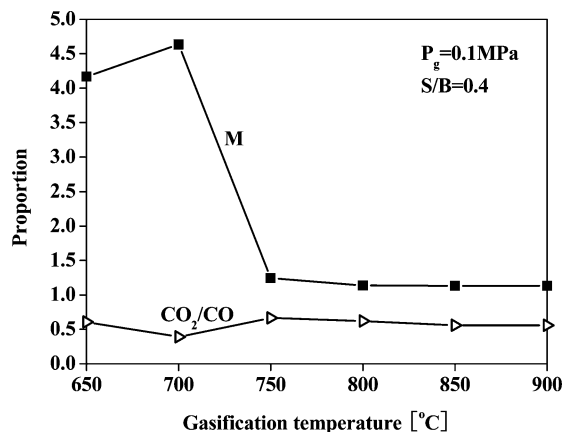**Figure 6.** Effect of gasification pressure on gas composition.

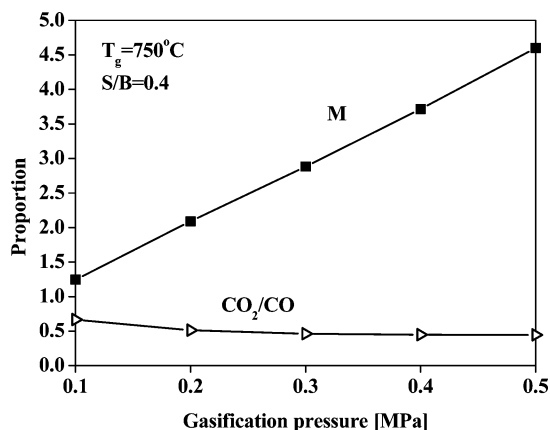**Figure 7.** Effect of gasification temperature on the ratio of hydrogen to carbon $M$ and the $CO_2/CO$ ratio.



**Figure 8.** Effect of gasification pressure on the ratio of hydrogen to carbon $M$ and the $CO_2/CO$ ratio.
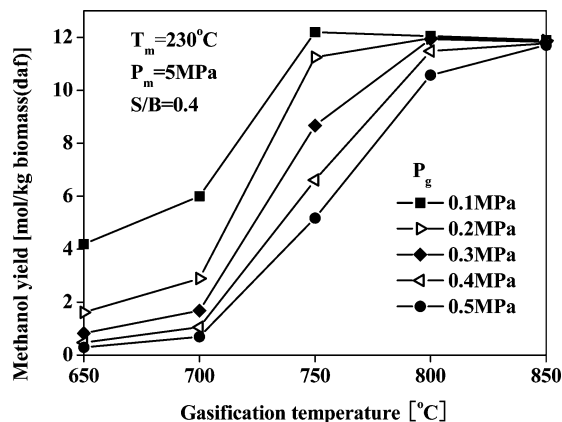


**Figure 9.** Effect of gasification temperature on methanol yield at different gasification pressures.

of 700 °C and was around 1.13 between 800 and 900 °C. On the other hand, $CO_2/CO$ increased slightly and decreased slightly, reaching the maximum of 0.66 at a temperature of 750 °C. The effect of gasification pressure on the ratio of hydrogen to carbon $M$ and $CO_2/CO$ is indicated in Figure 8. $M$ increased at a sharp speed from 1.24 to 4.60 with the rise of gasifier pressure. However, $CO_2/CO$ decreased smoothly with the increase of gasifier pressure from 0.66 to 0.44.

**5.2.1.2. Effect of Gasification Temperature and Pressure on Methanol Yield.** As indicated in Figure 9, methanol yield increased remarkably with the rise of the gasifier temperature and then stayed nearly constant. In the case where the
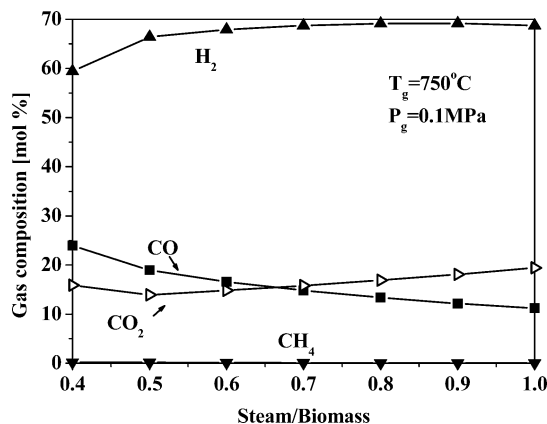


**Figure 10.** Effect of $S/B$ on gas composition.

gasifier temperature was 750 °C and the gasifier pressure was 0.1 MPa, the methanol yield reached the maximum of 12.19 mol/(kg biomass (daf)). When the gasifier temperature was below 800 °C, the methanol yield increased dramatically along with the rise of gasifier temperature. For example, when the gasifier pressure was 0.1 MPa and the gasifier temperature was varied from 650 to 750 °C, the methanol yield increased from 4.19 to 12.19 mol/(kg biomass(daf)), increasing by 8.0 mol/(kg biomass (daf)) in total. $CaCO_3$ catalytic gasification may increase $H_2$ content and reduce CO and $CO_2$ content. So the ratio of hydrogen to carbon $M$ may increase. As shown in Figure 7, $M$ increased from 1.24 to 4.64 when the temperature decreased from 750 to 700 °C, accordingly. Due to the existence of an optimal range for the ratio of hydrogen to carbon, a value too large or too small disadvantages the methanol synthesis. When the temperature is below 750 °C, $M$ is too large. As a result, the methanol yield decreased evidently below 750 °C with the effect of $CaCO_3$. It was illustrated in Figure 9 that the ambient pressure favors the methanol synthesis when other conditions are the same. This is because, when the gasification pressures reach to the ambient pressure, the ratio of hydrogen to carbon $M$ and $CO_2/CO$ of the syngas are more suitable for methanol synthesis as indicated in Figure 8.

**5.2.2. Effect of Steam/Biomass Ratio ($S/B$).** Under the base conditions of a $CaCO_3$/biomass ratio of 1.5, gasification temperature of 750 °C, gasification pressure of 0.1 MPa, liquefaction pressure of 5 MPa, and liquefaction temperature of 230 °C, we study the effect of the $S/B$ ratio on the product gas from gasification and methanol yield. The steam/biomass ratio was varied by changing the steam flow while keeping the biomass flow constant.

**5.2.2.1. Effect of the Steam/Biomass Ratio on the Product Gas from Gasification.** As shown in Figure 10, the $CO_2$ content increased gradually along with an increase of $S/B$. $H_2$ content increased at first and decreased slightly, reaching the maximum of 69.16% at an $S/B$ ratio of 0.9. Due to the effect of CaO, $CO_2$ and CO contents were somewhat small and $H_2$ content was quite large. The CO content decreased evidently, and $CH_4$ decreased slightly. In the respect that the $CH_4$ content is minute, the changing trend is inconspicuous. In the way of chemical equilibrium, the increase of steam implied the increase of reactant content, which promoted the water gas reaction, water−gas shift reaction, and steam-reforming toward the positive direction. In other words, the reaction extent was broadened and more CO and $CH_4$ were consumed to produce $H_2$ and $CO_2$. From this point of view, augmenting the amount of steam benefited the production of $H_2$-rich product gas from gasification whereas it increased $CO_2$ content and decreased CO
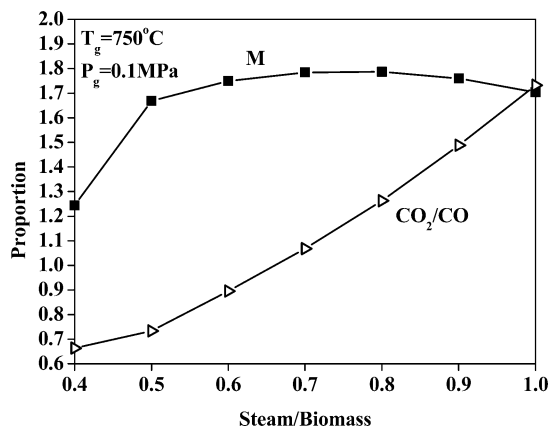
**Figure 11.** Effects of *S/B* on the ratio of hydrogen to carbon *M* and the $CO_2/CO$ ratio.
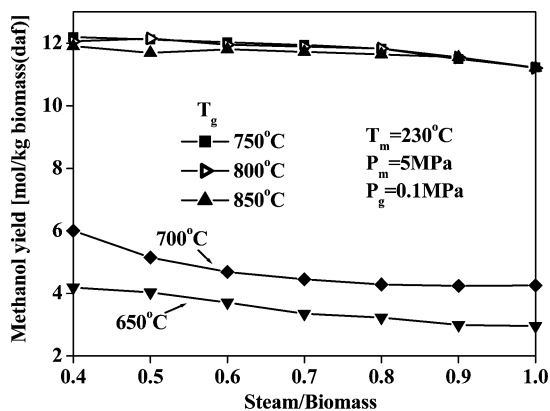


**Figure 12.** Effect of *S/B* on methanol yield at different gasification temperatures.

content which disadvantaged the methanol production.

Under the basic operating conditions, the effects of the *S/B* on ratio of hydrogen to carbon *M* and $CO_2/CO$ ratio are shown in Figure 11. When the *S/B* ratio was at 0.4–0.5, the ratio of hydrogen to carbon *M* increased rapidly from 1.24 to 1.67; when the *S/B* was varied from 0.5 to 1.0, the change range of the ratio of hydrogen to carbon *M* was quite small and the ratio of hydrogen to carbon changed by inches, varying from 1.67 to 1.79. The $CO_2/CO$ ratio was varied from 0.66 to 1.73, increasing rapidly with the rise of the *S/B* ratio.

**5.2.2.2. Effect of Steam/Biomass (*S/B*) on Methanol Yield.** As illustrated in Figure 12, the methanol yield decreased at different gasification temperatures. In the low temperature section of 650–700 °C, the methanol yield was quite low, but between temperatures of 750 and 850 °C, it was comparatively a great deal higher especially at 750 °C. When the gasifier temperature was 750 °C and *S/B* was 0.4, the methanol yield reached the maximum. As indicated in Figure 11, the $CO_2/CO$ ratio of the product gas increased from 0.66 to 1.73 with the rise of the *S/B* ratio. According to the corresponding research results, methanol synthesis takes place primarily by $CO_2$ hydrogenation and the presence of $CO_2$ is also important to avert catalyst deactivation, whereas CO must be present in the feed to enable the forward water–gas shift reaction to take place.[8,24] The presence of some $CO_2$ assisted methanol production whereas too much $CO_2$ undermined the $H_2$ and CO adsorption function of the catalyst due to $CO_2$'s competition for adsorption. So due to the increase of $CO_2/CO$, the whole reaction velocity was reduced resulting in low methanol yield. As indicated in Figure 5, when the temperature is above 800 °C, gasification
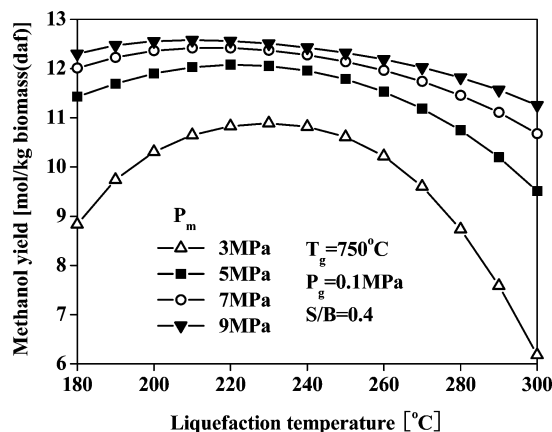


**Figure 13.** Effect of liquefaction on methanol yield at different liquefaction pressures.

products returned to normal levels and the content of $H_2$, CO, and $CO_2$ of the product gas was almost unchanged. So, methanol yield is nearly same in methanol synthesis. The two lines presenting methanol yields at the gasifier temperatures of 800 and 850 °C were nearly superimposed on each other, as illustrated in Figure 12.

**5.2.3. Effect of Liquefaction Temperature and Pressure.** Under the basic conditions of a $CaCO_3$/biomass ratio of 1.5, *S/B* ratio of 0.4, gasification temperature of 750 °C, and gasification pressure of 0.1 MPa, we study the effect of liquefaction temperature in the range of 200–300 °C on the methanol yield at different liquefaction pressures from 3 to 9 MPa.

As indicated in Figure 13, the methanol yield increased first, reached the maximum, and decreased at last along with the rise of liquefaction temperature. The methanol yield changed in a parabola pattern with the increase of temperature and reached a comparatively higher level at the liquefaction temperature of 220–240 °C. So, the methanol production from straw catalytic gasification has an optimal temperature. As we all know, reactions 8–10 in the methanol production process are all intensive exothermic reactions. With the consideration of thermodynamics, an increase of the liquefaction temperature reduces the equilibrium conversion, which baffles the reaction process. However, the rise of liquefaction temperature favors methanol production from the viewpoint of kinetics. Experiments proved that[25] optimal catalytic activity occurs between 230 and 240 °C. The catalytic activity of the catalyst would be undermined at low temperatures, and the reverse of reaction 8 and methane production would dominate. Besides, $CO_2$ occupies the adsorption sites for catalytic activity preferentially and the desorption rate is slow. In conclusion, the maximum methanol production is in existence, which agrees with the theory that the reversible exothermic reaction has the optimal reaction temperature.

Reactions 8 and 9 in methanol production process are reversible reactions that reduce the gas volume. As a result, the rise of liquefaction pressure favors the process of methanol production; the methanol yield increases along with the rise of liquefaction pressure at different liquefaction temperatures. When it is below 5 MPa, the liquefaction pressure plays a crucial role on methanol production, but at the pressure of 6–9 MPa, the role was weaken. When we synthesize the methanol from straw syngas with the usage of Cu-based catalyst 58.1% CuO + 30.06% $Al_2O_3$ + 31.7% ZnO + 4.0% $H_2O$, a pressure as low as 5 MPa is proposed to be the most desirable. We can predict that maximum methanol yield may be obtained when 5

MPa liquefaction pressure is adopted and the rest of the technical conditions are optimal.

## 6. Conclusions

Simulation of methanol production from biomass gasification in interconnected fluidized beds is carried out, using Aspen Plus software to establish the model of process of synthesizing methanol from biomass syngas in interconnected fluidized beds. Some useful results were achieved as follows:

• When $CaCO_3$ was added to the biomass gasification process, the $H_2$ content of the product gas reached a maximum of 82.14% at a temperature around 700 °C. The effect of $CaCO_3$ declined gradually at the gasifier temperature of 700−800 °C, and reduction of $H_2$ content occurred. When the temperature reached above 800 °C, the catalytic effect was not evident. The increase of $S/B$ favored the production of $H_2$-rich product gas from biomass gasification whereas the $CO_2/CO$ ratio was lifted, which baffled the methanol production.

• When the biomass was gasified in interconnected fluidized beds with catalyst, the gasification performance was improved observably. However, the effect of the catalyst was weakened along with the increase of $S/B$ and the rise of gasifier temperature; $CO_2$ content and CO content decreased and $H_2$ content increased, which increased the ratio of hydrogen to carbon $M$ as a whole and the methanol yield was also comparatively increased.

• A temperature of 750 °C favored methanol production from the syngas while ambient pressure for gasification was suggested. The $S/B$ ratio has a weak effect on the methanol yield, and a ratio of 0.4−0.5 was suitable. Under the optimal operating conditions, a maximum methanol yield of 12.19 mol/(kg biomass (daf)) of methanol yield may be obtained.

• On the basis of the Cu-based catalyst 58.1% CuO + 30.06% $Al_2O_3$ + 31.7% ZnO + 4.0% $H_2O$, the optimal liquefaction pressure was 5 MPa for methanol production from the biomass syngas in interconnected fluidized beds. The methanol yield was varied evidently corresponding to the pressure change when the basic pressure was 5 MPa, and this liquefaction pressure was well situated so as to decrease the investment on facilities. At the pressure of 5 MPa, the optimal liquefaction temperature was in the range of 220−240 °C when the methanol was produced from biomass syngas with the usage of the Cu-based catalyst.

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