Korean J. Chem. Eng., **24**(1), 181-185 (2007)

An integrated biomass-derived syngas/dimethyl ether process

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(*Received 25 August 2006 • accepted 15 September 2006*)

Abstract−A Cu-Zn-Al methanol catalyst combined with HZSM-5 was used for dimethyl ether (DME) synthesis from a biomass-derived syngas containing nitrogen. The syngas was produced by air-steam gasification of pine sawdust in a bubbling fluidized bed biomass gasifier with a dry reforming reaction over ultra-stable NiO-MgO catalyst packed in a downstream reactor for stoichiometric factor (H_2, CO, CO_2) adjustment. It constantly gave syngas with H_2/CO ratio of 1.5 and containing trace CH_4 and CO_2 during a period of 150 h. The obtained N_2-containing biomass-derived syngas was used directly for DME synthesis. About 75% CO per-pass conversion and 66.7% DME selectivity could be achieved under the condition of 533 K, 4 MPa and 1,000-4,000 h^{-1}. The maximized DME yield, 244 g DME/$Kg_{biomass}$ (dry basis), was achieved under a gasification temperature of 1,073 K, ER (Equivalence Ratio) of 0.24, S/B (Steam to Biomass Ratio) of 0.72 and reforming temperature of 1,023 K with the addition of 0.54 Nm^3 biogas/$Kg_{biomass}$ (dry basis).

Key words: Biomass, Syngas, Dimethyl Ether

INTRODUCTION

Renewable energy (e.g. solar, wind and biomass) could play a major role in reducing greenhouse gas emissions. Only biomass offers the possibility to produce liquid, carbon neutral, transportation fuels on foreseeable terms [Williams et al., 1994; Faaij et al., 2001; Rodjeen et al., 2006]. DME is an important chemical for the production of gasoline, ethylene, aromatics and other chemicals. It is ultraclean, emitting none of the air pollutants SO_x, NO_x, COS or dust and could provide a major alternative for the transport sector world-wide in a green house gas constrained world. DME can be synthesized from CO/H_2 in a single step, which is much more thermodynamically and economically favorable. The gasification of biomass at 1,073-1,273 K is known to produce syngas (H_2+CO), which can potentially be used as a feed-stock for the synthesis of DME [Ng et al., 1999; Ge et al., 1998; Park et al., 2003].

The utilization of biomass for DME production via gasification faces the problem of low H_2/CO ratio and a large excess of carbon in form of carbon dioxide in the produced syngas. The stoichiometric adjustment can be accomplished by adding hydrogen or by removing excess carbon dioxide; however, it makes the production cost very high [Specht et al., 1998]. Reforming is a logical subsequent step in a downstream reactor to maximize CO and H_2 production. Several groups have investigated a system of raw gas cleaning that involves a dolomite or alkali catalyst for the removal of tar followed by the adjustment of the gas composition (reforming of CH_4 and the other hydrocarbons) by using nickel steam reforming catalysts. Using these catalysts, there is generally an increase in the hydrogen and carbon monoxide content of the effluent gas, with elimination or reduction of the hydrocarbons and methane content [Aznar et al., 1993; Baker et al., 1987; Gebhard et al., 1994]. Sutton et al. investigated the dry reforming of CH_4 and other hydrocarbons in a model gas stream similar in composition to that from biomass steam gasification. At 800 °C, the CO_2 content in the gas stream was completely consumed via the dry reforming reaction [Sutton et al., 2002]. In order to avoid removing carbon dioxide from syngas for desired stoichiometric factor (H_2, CO, CO_2), an acceptable way is reforming the excess carbon dioxide by adding biogas to syngas stream for stoichiometric adjustment due to the low content of methane (4-8 mol%) inherent in the biomass raw syngas.

In this work, we tried to initiate a route for biomass-derived syngas production by pine sawdust air-steam gasification combined reforming raw syngas with addition of biogas. The obtained N_2-containing biomass-derived syngas was used directly for DME synthesis. It would have promised to produce low-cost biomass-derived DME.

EXPERIMENTAL

1. Feed Materials

Pine sawdust obtained from a timber mill in Guangzhou City, China, was used as the feedstock for experimental runs. The parti-

Table 1. Proximate and ultimate analysis of pine sawdust

Moisture content (wt% wet basis)	13
Higher heating value (KJ/Kg)	19576
Proximate analysis (wt% dry basis)	
Volatile matter	82.7
Fixed carbon	16.2
Ash	1.1
Ultimate analysis (wt% dry basis)	
C	46.28
H	8.58
O	44.59
N	0.28
S	0.27

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‡This paper was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006

cle size of this pine sawdust was between 0.3 and 0.45 mm. Its proximate and ultimate analysis is reported in Table 1.

2. Catalyst Preparation

Calcined dolomite and NiO-MgO catalyst were used in experiments. The dolomite was crushed and sieved to a particle size 0.3-0.45 mm, and calcined in air at 1,173 K for 4 h. It contains 58 wt% CaO, 41 wt% MgO and trace minerals SiO_2, Fe_2O_3 and Al_2O_3.

NiO-MgO catalyst was prepared by the co-precipitation from aqueous solution of $Ni(CH_3COO)_2{\cdot}4H_2O$ (>98.0%, Haotian Chemical Co. Ltd., China) and $Mg(NO_3)_2{\cdot}6H_2O$ (>99.2%, Haotian Chemical Co. Ltd., China) using K_2CO_3 (99.5%, Haotian Chemical Co. Ltd., China) as the precipitant. After being filtered and washed with hot water, the precipitate was dried at 393 K for 12 h, and then calcined in air at 1,223 K for 10 h. The catalyst was pressed into disk, then crushed and sieved to a particle size 0.3-0.45 mm.

The DME synthesis catalyst precursors were prepared by co-precipitation method. An aqueous solution of $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ (Cu/Zn/Al molar ratio=6/3/1) and an aqueous solution of Na_2CO_3 were dropped simultaneously into a vessel at pH of 8 and 343 K. The coprecipitate sample obtained was further calcined in air at 623 K for 6 h.

3. Apparatus

The tests were performed in an atmospheric pressure, indirectly heated, fluidized-bed gasification system, which is shown schematically in Fig. 1. It is composed of a fluidized-bed gasifier, a biomass feeder, a steam generator, an air compressor, a cyclone and a catalytic reforming reactor. The biomass was fed into the gasifier through a screw feeder driven by a variable-speed metering motor. The air (as the gasification agent) from the air compressor was preheated to 338 K before entering the gasifier for better performance. Steam of 427 K from a stream generator was fed into the gasifier. The raw gas from gasifier passed through a cyclone for particles removing, mixed with biogas (68 mol% CH_4, 32 mol%CO_2), into the reforming reactor. 120 g of calcined dolomite mixed with 30 g of silica sand (0.2-0.3 mm) was put in the gasifier before the test. Additional calcined dolomite was mixed with the pine sawdust carefully and continuously fed into the gasifier to attain a steady state.

NiO-MgO catalyst in the reforming reactor was reduced under the condition of 750 °C, atmospheric, 30 min by the raw syngas from the gasifier. The obtained N_2-containing syngas was dehydrated, deoxygenated and pressurized by compressor to the gas container. Periodically, gas samples were taken from points A and B and analyzed on a gas chromatograph (model GC-2010, Shimadzu, Japan), which was fitted with a GS-carbon plot column (30 m×0.530 mm× 3.00 μm), FID and TCD detectors, helium as carrier gas.

The obtained N_2-containing biomass syngas was used as feed gases for DME synthesis. The conditions were 260 °C, 4 Mpa and 1,000-4,000 h^{-1} of GHSV. The catalyst was pre-reduced by mixed gas (H_2 5 mol%, N_2 95 mol%) at 260 °C for 10 h. The products were analyzed by on-line chromatography with TCD detector, helium as a carrier gas, 1 m TDX-01 column for N_2, CO, CH_4, CO_2 separation and with the FID detector, N_2 as the carrier gas, 2 m GDX-401 column for CH_4, CH_3OH, DME and light hydrocarbons separation. The conversion of CO and selectivity of products were calculated based on the balance of carbon and constant value of the carbon-to-nitrogen ratio before and after DME synthesis.

RESULTS AND DISCUSSIONS

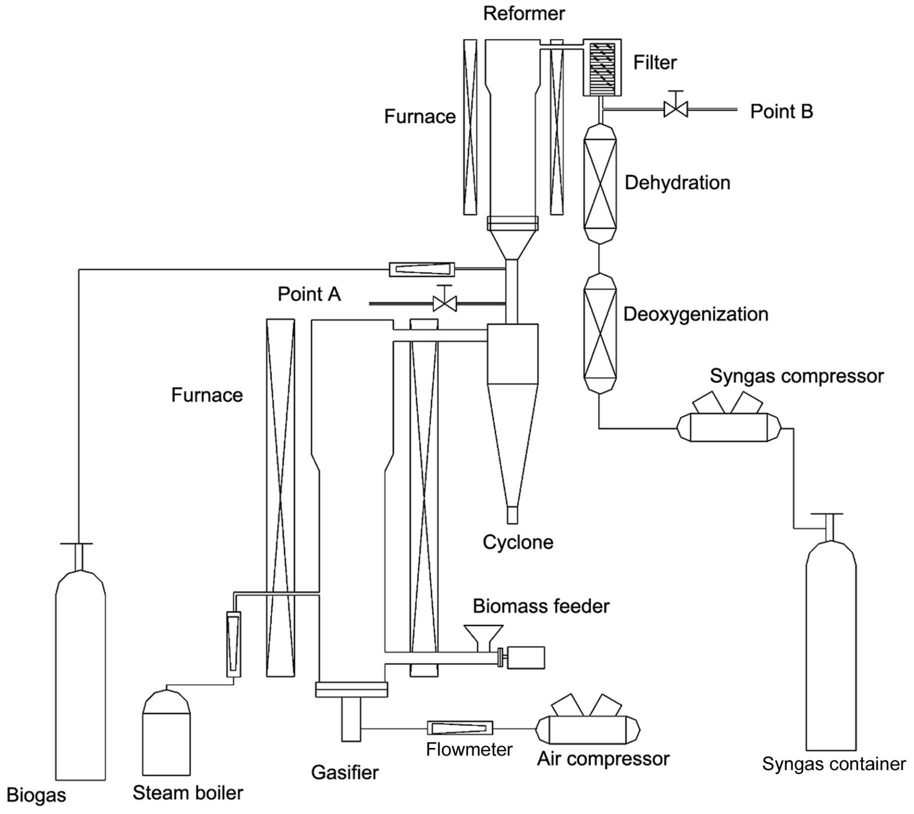

Fig. 1. Schematic diagram of biomass-derived syngas production.

Table 2. Operating conditions and gas composition

	Runs no.				
	1	2	3	4	5
Gasifier bed temperature (°C)	800	800	800	800	800
Equivalence ratio	0.23	0.24	0.24	0.24	0.24
Steam-to-biomass ratio	0	0.23	0.72	0.72	0.72
Raw syngas composition (dry, mol%)					
H_2	10.3	12.8	18.8	18.8	18.8
CO	16.6	19.4	17.9	17.9	17.9
CO_2	15.7	21.6	18.6	18.6	18.6
CH_4	3.6	3.6	4.3	4.3	4.3
C_2	1.7	3.2	2.7	2.7	2.7
N_2	52.1	39.5	37.7	37.7	37.7
H_2/CO	0.62	0.66	1.05	1.05	1.05
Raw syngas yield (Nm^3/Kg of biomass, dry basis)	2.06	2.08	2.24	2.24	2.24
Biogas/Kg of biomass (Nm^3/Kg)	0	0	0	0.54	0.80
Biomass-derived syngas composition (dry, mol%)					
H_2	17.3	25.3	25.2	37.8	38.3
CO	23.6	22.1	14.7	25.1	26.9
CO_2	8.8	14.8	21.5	4.8	3.0
CH_4	0.3	0.8	0.5	3.3	5.9
C_2	0.4	0.4	0.4	0.4	0.6
N_2	49.2	37.1	35.4	26.0	25.0
H_2/CO	0.73	1.15	1.72	1.51	1.42
Syngas yield (Nm^3/Kg of biomass, dry basis)	2.18	2.22	2.38	3.40	3.67

1. Biomass-derived Syngas Production

The composition of raw syngas produced by biomass air gasification does not profit for DME synthesis due to the low H_2/CO ratio and excess CO_2 content. Increasing the H_2 content for desired H_2/CO ratio and maximized useful synthesis gas (H_2+CO) is necessary [Turn et al., 1998]. It is known that steam plays an important role in hydrogen production via biomass gasification. As shown in Table 2, the H_2-rich raw syngas was produced by biomass air-steam gasification. The H_2/CO ratio increased from 0.62 to 1.05. However, the content of CO was not increased greatly. It indicated that a water shift gas (WSG) reaction took place to shift the energy value of the CO and H_2O to H_2.

The H_2-rich raw syngas yield of per kg of biomass increased from 2.06 to 2.24. The H_2/CO ratio increased from 0.62 to 1.05. Higher gasification temperature (1,173 K) led to higher H_2 content and yield of raw syngas, but not for H_2/CO ratio. However, the large amounts of CO_2 in the H_2-rich raw syngas stream are excess for the synthesis section which should be removed for desired stoichiometric ratio of H_2, CO and CO_2. It would lead to only 40% carbon content of biomass to be converted to syngas and high DME production cost.

Reforming is a logical subsequent step in a downstream reactor to maximize CO and H_2 production. Sutton et al. investigated the dry reforming of CH_4 and other hydrocarbons in a model gas stream similar in composition to that from biomass steam gasification. At 1,073 K, the CO_2 content in the gas stream was completely consumed via a dry reforming reaction [Sutton et al., 2002]. In order to avoid removing carbon dioxide from H_2-rich raw gas for desired stoichiometric factor (H_2, CO, CO_2), an acceptable way is reforming the excess carbon dioxide by adding biogas to syngas stream for stoichiometric adjustment due to the low content of methane (4-8 mol%) inherent in the raw syngas.

Some typical operating conditions and test results are also listed in Table 2. They indicate that the stoichiometric factor (H_2, CO and CO_2) was adjusted by the reforming reaction. The content of CO_2 and CH_4 was below 5 mol% and 3 mol%, respectively, in the effluent stream. The content of CO was increased greatly from 17.9 mol% to 25.1 mol%. The H_2 content was increased slightly from 18.8 mol% to 37.8 mol%. The C_2 content was below 0.4 mol%. It can be concluded that a CH_4-CO_2 dry reforming reaction (Eq. (1)) and reverse water gas shift (RWGS) reaction (Eq. (2)) occurred in the reforming reactor simultaneously. Under the reforming reaction conditions, the steam was also reformed with CH_4 to produce syngas (Eq. (3)). Elimination of the CO_2 was also achieved by the dry reforming of the hydrocarbons present according to Eq. (4).

$$CH_4+CO_2 \rightarrow 2CO+2H_2 \tag{1}$$

$$CO_2+H_2 \rightarrow CO+H_2O \tag{2}$$

$$H_2O+CH_4 \rightarrow CO+3H_2 \tag{3}$$

$$C_nH_m+nCO_2 \rightarrow 2CO+(m/2)\,H_2 \tag{4}$$

The typical composition of biomass-derived syngas was 37.8 mol% H_2, 25.1 mol% CO, 3.3 mol% CH_4, 4.8 mol% CO_2, 0.4 mol% C_2 and 26 mol% N_2. The H_2/CO ratio was about 1.5. With the biogas addition of 0.54 Nm^3 per Kg of biomass, the yield of syngas was 3.40 Nm^3 per Kg of biomass. The products obtained under abovementioned conditions remained stable during a 150 h life test.

2. DME Synthesis from Biomass-derived Syngas Containing N_2

The direct synthesis of DME from syngas involves three reactions:

$$CO+2H_2=CH_3OH,\ \Delta H=-90.7\ KJ/mol \tag{5}$$

$$CO+H_2O=CO_2+H_2,\ \Delta H=-40.9\ KJ/mol \tag{6}$$

$$2\ CH_3OH=CH_3OCH_3+H_2O,\ \Delta H=-23.4\ KJ/mol \tag{7}$$

The overall reaction is as below:

$$3CO+3H_2=CH_3OCH_3+CO_2,\ \Delta H=-245.7\ KJ/mol \tag{8}$$

The biomass-derived syngas contained 26 mol% N_2. The effective ($CO+H_2$) partial pressure was lowered due to the presence of N_2. The Cu-Zn-Al/HZSM-5 was used as the catalyst, which would allow the DME synthesis from syngas containing N_2 to be operated at as low a pressure as possible. Conventional syngas (62 mol% H_2, 31 mol% CO, 5 mol% CO_2 and 2 mol% N_2) was also used as feed gas for comparison.

The impact of pressure and GHSV on the yield of DME and conversion of CO was investigated over the Cu-Zn-Al/HZSM-5 catalyst at 553 K, space velocity of 1,000-4,000 h^{-1}. The results depicted in Fig. 2 show that the yield of DME increased gradually as the space velocity increased. The reverse tendency was observed for conversion of CO. The yield of DME and CO conversion of biomass-derived syngas was lower than that of conventional syngas under the same reaction conditions. The difference of DME yield between two kinds of syngas increased from 0.045 to 0.16 $g/g_{cat}\cdot h$ with increasing GHSV from 1,000 to 4,000 h^{-1} at the pressure of 3 MPa. Higher pressure reduced the difference slightly. The 75% CO conversion of biomass-derived syngas could be achieved at a GHSV of 1,800 h^{-1} and pressure of 4 MPa. These results at least show that DME synthesis from biomass-derived syngas containing N_2 could occur over Cu-Zn-Al/HZSM-5 catalyst at the pressure of conventional methanol synthesis but relatively low space velocity.

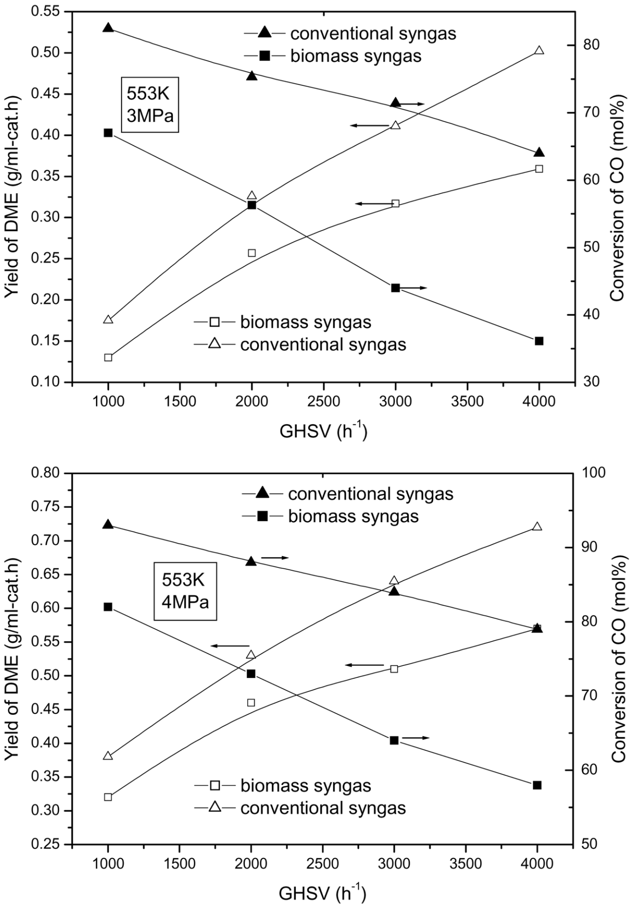

Fig. 2. The yield of DME and conversion of CO as function of GHSV.

The stability test exhibited that the CO conversion and DME selectivity were kept at about 75% and 66.7%, respectively, during the period of 150 h. There was no need to recycle the unconverted gas due to the high per-pass conversion. The composition of the tail gases after DME separation was as follows: 21.6 mol% H_2, 31.3 mol% N_2, 10.9 mol% CO, 9.2 mol% CH_4, 27.0 mol% CO_2. For increasing the energy efficiency of the process, the tail gases with high pressure (4.0 Mpa) are suggested to be utilized by following steps: (1) Through an expanded turbine to recover part of the compressed energy, stored in large amount of nitrogen and to drive the syngas compressor; and (2) Plenty of heat available to drive steam turbine could be further recovered by combusting the remaining 41.7 mol% gases ($H_2+CO+CH_4$) in the tail gases.

The 150 h continuous experiment indicated that the maximized DME yield, 244 g DME/$Kg_{biomass}$ (dry basis), was achieved under a gasification temperature of 1,073 K, ER of 0.24, S/B of 0.72 and reforming temperature of 1,023 K with the addition of 0.54 Nm^3 biogas/$Kg_{biomass}$ (dry basis).

CONCLUSIONS

The addition of biogas into the raw syngas produced by biomass air-steam gasification could adjust the stoichiometric factor (ratio of components H_2, CO and CO_2) of biomass-derived syngas. The composition of obtained syngas (37.8 mol% H_2, 25.1 mol% CO, 3.3 mol% CH_4, 4.8 mol% CO_2, 0.4 mol% C_2 and 26 mol% N_2) was desired for the DME synthesis. The H_2/CO ratio of syngas is about 1.5.

With the biogas addition of 0.54 Nm^3 per Kg of biomass, the yield of syngas was 3.40 Nm^3 per Kg of biomass. The CO conversion and DME selectivity were kept 75% and 66.7%, respectively, during the period of 150 h. The maximized DME yield, 244 g DME/$Kg_{biomass}$ (dry basis), could be achieved with the addition of 0.54 Nm^3 biogas/$Kg_{biomass}$ (dry basis).

ACKNOWLEDGMENT

The financial support received from the National Natural Science Foundation of China (Project No. 50506030) is gratefully appreciated.

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