Process conditions for preparing methanol from cornstalk gas

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Abstract

The low-heat-value cornstalk gas produced in the down-flow fixed bed gasifier was tentatively used for methanol synthesis. The cornstalk gas was purified and the technical procedures such as deoxygenation, desulfurization, catalytic cracking of tar, purification and hydrogenation were studied. The catalytic experiments of methanol synthesis with cornstalk syngas were carried out in a tubular-flow integral and isothermal reactor. The effect of reaction temperature, pressure, catalyst types, catalyst particle size, syngas flow at entering end and composition of syngas was investigated. The optimum process conditions and yield of methanol from cornstalk syngas were obtained. The experimental results indicated that the proper catalyst for the synthetic reaction was C301 and the optimum catalyst size was 0.833 mm × 0.351 mm. The optimum operating temperature and pressure were found to be 235°C and 5 MPa, respectively. The suitable syngas flow 0.9–1.10 mol/h at entering end was selected and the best composition of syngas were CO 10.49%, CO_2 8.8%, N_2 37.32%, C_nH_m 0.95% and H_2 40.49%. The best methanol yield was 0.418 g/g cornstalk. This study provided the technical support for the industrial test of methanol production from biomass (cornstalk) gas.

Key words: cornstalk syngas; fuel gas; purification; catalyst; methanol; synthesis

Introduction

Biomass is a kind of renewable energy resource and its utilization has caused so much attention all over the world. China is one of the largest agricultural countries with extremely rich biomass resources and a great amount of agricultural residues are produced every year, in which the cornstalk amounts to about 100 million tons (Gao *et al.*, 2003). However, most of the cornstalks are discarded or burnt easily and only a small portion is utilized. It leads to serious environmental pollution and wastes a large amount of resources. Therefore, the utilization of biomass becomes an urgent need and biomass gasifying is selected till now. The commercial equipments of biomass gasifying are classified as the up-flow and down-flow fixed bed gasifier to produce low-heat-value fuel gas (4–6 MJ/nm³), which was mainly used for cooking and heating in the countryside or the outskirts of town. Most of the biomass gasifier runs only 3–4 h every day because of the low utilization ratio of biomass fuel gas. In addition, the fuel gas leads to pollution of the underground water due to its high content of tar and block of the fuel gas installation which involves higher cost of maintenance. It is necessary to further study the exploitation of the biomass resources for high-grade products and to utilize the renewable resources more reasonably and effectively.

The technology of methanol catalytic synthesis from biomass is an effective approach for the utilization of agricultural residues. Meanwhile, methanol is mainly made from fossil fuel such as natural gas, oil and coal, and the technology for methanol synthesis from biomass has not been developed till now. In fact, methanol can be produced from the original biomass. Some countries such as America and Japan began to study the technology more than twenty years ago (Baker *et al.*, 1983; Beenackers and van Swaajj, 1984; Baker and Brow, 1984; Borgwardt, 1998; Demirbas, 2000; Tsutomu, 2000; Goudeau *et al.*, 1983; Helena and Ralph, 2001; Hirano *et al.*, 1998; Palmer, 1984) and many methanol factories are running now. However, expensive equipments are always employed in the methanol factory, which hinders the development of methanol synthesis in China. The equipments for biomass gasifying are relatively cheap enough to be used in most part of China but the resulted fuel gas is always directly used without any treatment. In this research, the low-heat-value fuel gas was made from cornstalk in a cheap down-flow fixed bed gasifier and is firstly utilized to produce methanol after purification through the fuel gas, which usually contains high content of nitrogen. This work was creatively designed to produce methanol from low-heat-value cornstalk gas and such an approach would be preferable for the biomass transformation into methanol.

1 Experiments and methods

1.1 Preparation of biomass feedstock gas and syngas

1.1.1 Preparation of biomass feedstock gas

The feedstock of cornstalks was gathered from the farms of Xinzheng, Henan Province, China. The average diameter of the cornstalks is about 3 cm and the cornstalks were processed in XFF-1000 Biomass Gasifier producing the biomass gas of low heat value (LHV). The analysis data of feedstock gas from cornstalks are given as follows: CO 15.80%, CO_2 12.50%, H_2 12.60%, CH_4 1.40%, O_2 2.07%, C_2H_4 0.50%, C_2H_6 0.10%, C_2H_2 0.03%, N_2 55.00%, LHV 5873 kJ/m, tar 24.6 mg/m^3, and sulfides 3.48 mg/L.

1.1.2 Preparation of biomass syngas

There are still a small amount of oxygen, sulfide, and tar in feedstock and they can destroy the catalytic activity of catalyst. There is a great need to remove them from the feedstock gas before use. In addition, the content of H_2 is too low to satisfy the theoretic ratio required by carbon and hydrogen in synthetic process. Therefore, the feedstock gas was pretreated for desulfurization, deoxy, catalytic cracking of tar, purification and hydrogenation.

TR catalyst made by authors themselves was used for tar cracking. Active carbon and thin copper wire acted as deoxidizer and ZnO power was used for desulphurization. The following experiments were conducted between 600–800°C in a 623–1.3 Type tubular electric stove using ZK-1 silicon voltage regulator. It was proved that the content of sulfide was about 1.2×10^{-3} mg/L and oxygen and tar were not determined in the pretreated feedstock gas. The biomass syngas was prepared by adding a definite amount of high pure hydrogen in the pretreated feedstock gas. Then the biomass syngas was compressed into a high pressure steel bottle through compressor and reserved for two months before use. The components of biomass syngas treated from feedstock gas are presented in Table 1.

Table 1 Components of biomass syngas treated from feedstock gas

H_2 (%)	CO (%)	CO_2 (%)	C_nH_m* (%)	N_2 (%)
30.4–75.77	5.85–13.16	3.23–10.55	0.37–1.35	17.7–45.38

* C_nH_m=CH_4, C_2H_2, C_2H_4, C_2H_6.

1.2 Experimental equipments and processes

1.2.1 Main experimental equipments and catalyst reduction

The following experimental devices in methanol synthesis were used: JA-Five troughs direct-flow isothermal integral reactor (the size of reaction pipe is 14 mm × 2 mm and 110 mm long; homothermic region is about 5 cm; the difference in temperature is in the range from +0.5 to –0.5°C); TCS-A intellectual temperature controller; ZK-50 silicon voltage regulator; YF-2 pressure control valve; GC-900C gas chromatograph; HW-2000 chromatographic working station; precision pressure gauge, rotor flowmeter. Homemade Cu-supported catalysts (C301, C302, NC306)

were used in these experiments. The cylindrical catalyst was ground into particles with the size of 0.991 mm × 0.833 mm, 0.833 mm × 0.351 mm, 0.351 mm × 0.246 mm, 0.246 mm × 0.175 mm, dried over heat and cooled to the room temperature. The same size quartz sand was mixed evenly after weighed. A proper thin layer of quartz sand (particle size is 0.833 mm × 0.351 mm) was fitted in catalytic reaction pipe, then experimental catalyst with different size was added slowly. Finally, the quartz sand with particle size of 0.833 mm × 0.351 mm, china ring of 0.991 mm × 0.833 mm and thin copper wire were put into orderly and pressed solid. The catalytic reduction condition was the same as that of industrial catalyst (Fang et al., 1990). The synthetic experiment could not be done unless the catalyst activity was stable by test after reduced for 86 h.

1.2.2 Experimental processes

Fig.1 presents the experimental circuit. It shows that the biomass syngas entered the reaction vessel after it came out from steel bottle, then flowed through control valve which control the pressure to be the same as the main reaction. Methanol and water were separated when the gas flowed through condenser at the end of reaction. The remaining gas was reduced to atmospheric pressure by pressure reducer valve. One part of the gas measured by flowmeter was tapped. The other part flowed into gas chromatograph where automatic collection and data processing were finished by chromatographic working station (Zhu et al., 2003).

The biomass syngas contained eight chemical components (CO, CO_2, H_2, N_2, CH_4, C_2H_2, C_2H_6, C_2H_4) among which three reactions occurred over the Cu-supported catalyst:

$$CO + 2H_2 \Longrightarrow CH_3OH \tag{1}$$

$$CO_2 + 3H_2 \Longrightarrow CH_3OH + H_2O \tag{2}$$

$$CO_2 + H_2 \Longrightarrow CO + H_2O \tag{3}$$

The Reactions (1) and (2) are exothermic, so the molecular number becomes less after reaction. Reaction (3) absorbs heat and the molecular number is unchanged before and after reaction. The theory of chemical reactions
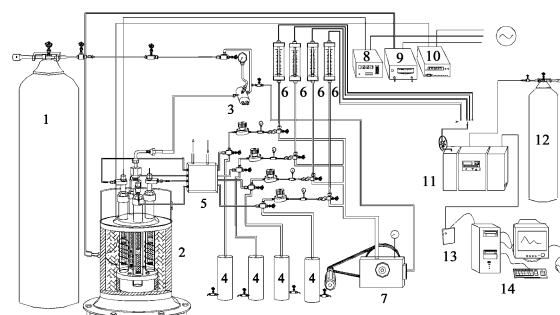

Fig. 1 Schematic layout of the test facilities. (1) biomass syngas; (2) methanol synthesis reactor; (3) pressure control valve; (4) product collector; (5) condenser; (6) rotor flow meter; (7) compressor; (8) temperature controller; (9) power and control board; (10) temperature programmer; (11) gas chromatograph; (12) carrier gas; (13) data counter; (14) computer.

shows that the increase of pressure and the decrease of temperature are beneficial to the two synthesis reactions (1) and (2). By changing one of the six technological parameters–temperature, pressure, catalyst, catalyst size, composition of syngas, and syngas flow at entrance (the other five parameters remained constant), the seeking of the optimum experimental parameters were accomplished (every experiment was repeated three times), and better technological conditions of methanol synthesis were accordingly obtained.

2 Results and discussion

2.1 Reaction temperature and pressure

The conditional experiments for reaction temperature were carried out with C301 catalyst by changing temperature between 220°C and 261°C to find out the effect of temperature on time-space yield of CH_3OH under the pressure 5 MPa when the other conditions of the reaction remained constant values. The experimental results presented in Fig.2 indicate that reaction temperature exerts a tremendous influence on the chemical equilibrium and reaction rate of reactants. The time-space yield of methanol changed in parabola pattern with the increased temperature. The optimum temperature under the given condition was at 235°C with CH_3OH yield of 25%.

The effect of reaction pressure of cornstalk syngas were investigated by changing reaction pressure between 4 and 8 MPa when the other conditions remained constant. The experimental results are presented in Fig.3 and it is observed that the time-space yield of methanol increased gradually with the increasing reaction pressure. The changing ratio of time-space yield to pressure (slope of the curve) is low at the pressure of 4 and 8 MPa, and comparatively higher at 5, 6 and 7 MPa. Subsequent experiments were conducted under other identical conditions and the reaction pressure
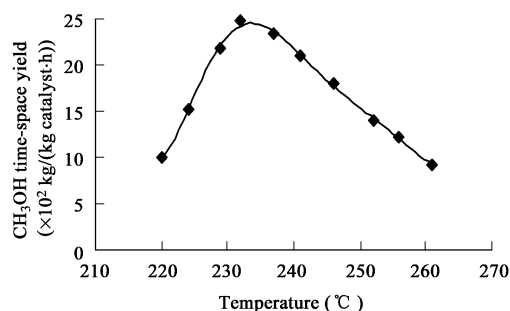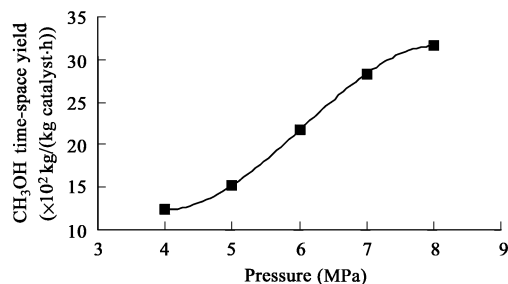

Fig. 3 Influence of reaction pressure time-space yield of CH_3OH. Temperature: 235°C; catalyst C301 with size: 0.991 mm × 0.833 mm; composition of entrance syngas (%): CO 12.95, CO_2 10.55, N_2 43.82, C_nH_m 1.35, H_2 31.48.

varied from 5–7 MPa. It was proved that the ratio of time-space yield of methanol to pressure is the highest at 5 MPa. So 5 MPa was chosen in the following experiments.

2.2 Catalyst and size of the particle

Selection of low pressure catalyst for methanol synthesis is regarded as a key solution to reduce the production cost of methanol. Cu-supported catalyst is commercially available and characterized as high activity and selectivity. It is industrially used in methanol production from coal by many factories in China. Three kinds of low pressure Cu-supported catalyst: C301, C302, NC306 were employed in the experiments. The experiments were carried out at 235°C and 5 MPa pressure for each kind of catalyst by changing the entrance syngas-flow. The results presented in Fig.4 illustrates that the time-space yield of methanol is the highest using catalyst C301, while the lowest with catalyst NC306 under the other identical conditions. Although the experimental results indicate that all these three kinds of catalyst can be used to synthesize methanol with cornstalk syngas, it is obvious that C301 is the best one for methanol synthesis. The composition of C301 Cu-supported catalyst are CuO (58.1%), ZnO (31.7%), Al_2O_3 (30.06%) and H_2O (4.0%).

The optimum catalyst particle size was also investigated. Catalyst C301 was employed and the related experiments were conducted with different particle sizes of catalyst under above-mentioned conditions and the results are presented in Table 2.

Table 2 indicates that both the conversion of carbon monoxide and time-space yield of methanol increased with the decrease of particle size of catalyst. However, the conversion of carbon dioxide changed in the same trend as that of carbon monoxide and methanol except when the catalyst particle size of 0.833 mm×0.351 mm was selected. It is also observed that the yield of methanol varied in a small range. In addition, the power consumption will increase rapidly due to the sharp pressure drawdown using

Fig. 2 Influence of reaction temperature on time-space yield of CH_3OH. Pressure 5 MPa; catalyst C301 with size: 0.833 mm × 0.351 mm; catalyst weight: 5.1532 g; composition of entrance syngas (%): CO 11.41, CO_2 8.96, N_2 37.63, C_nH_m 1.03, H_2 42.9.

Table 2 Effect of catalyst particle sizes on the conversion of CO, CO_2 and time-space yield of CH_3OH

Particle size of catalyst (mm)	0.991 × 0.833	0.833 × 0.351	0.351 × 0.246	0.246 × 0.175
Conversion of CO (%)	12.37	16.98	18.79	20.23
Conversion of CO_2 (%)	0.30	0.27	0.87	2.01
Time-space yield of CH_3OH (10^2 kg/(kg cat·h))	10.02	13.36	14.39	16.10

Pressure: 5 MPa; temperature: 235°C; catalyst: C301; composition of entrance syngas (%): CO 13.16, CO_2 9.84, N_2 45.38, C_nH_m 1.16, H_2 30.4.
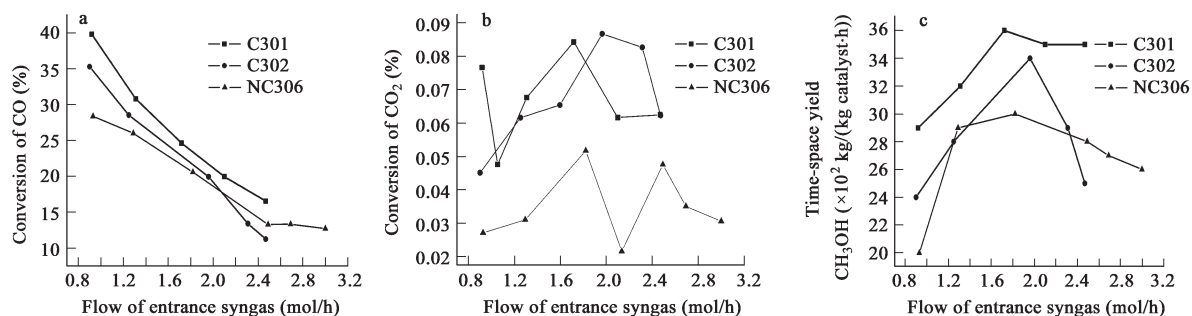
Fig. 4 Effect of different catalyst on CO conversion (a), CO_2 conversion (b) and CH_3OH time-space yield (c), respectively. Pressure: 5 MPa; temperature: 235°C; catalyst: C301, C302 and NC306 with size: 0.991 mm × 0.833 mm, composition of entrance syngas (%): CO 11.2, CO_2 5.98, N_2 32.73, C_nH_m 0.76, H_2 46.61.

the small size of catalyst particle. Therefore, the optimum particle size of catalyst is 0.833 mm×0.351 mm.

2.3 Cornstalk syngas ratio

The composition of the cornstalk syngas is also an important parameter to be investigated during methanol production. Five kinds of cornstalk syngas with different proportion of components were prepared according to the designed reaction condition. The effect of the content of each component in syngas on the yield of CH_3OH under the other identical conditions was determined experimentally by keeping the other parameters constant. The results are presented in Table 3.

The experimental results show that the conversions of CO and CO_2 are the highest when hydrogen-carbon ratio (mol) value is 7.08, but the concentration of them was lower in reaction system. The time-space yield of CH_3OH gained by test was not the highest yet, because the inverse alternation reaction of CO_2 strongly restrained the conversion from CO_2 to methanol in high concentration of H_2. The time-space yield of CH_3OH is the highest when M value is 1.71 and thereafter the proper composition of cornstalk syngas under the experimental condition are CO 10.49%, CO_2 8.8%, N_2 37.32%, C_nH_m 0.95%, and H_2

40.49%.

2.4 Flow of entrance syngas

The flow velocity of entrance syngas is also regarded as a key parameter which would influence the yield of methanol greatly. The experiment was conducted by changing the flow velocity of entrance syngas under other identical conditions.

Fig.5 illustrates the effect of flow of the entrance syngas. It was observed in Fig.5a that the conversion of CO decreased gradually with the continuous increase of entrance syngas flow. Fig.5b demonstrates that the conversions of CO_2 increased at first, then came to a drop, and subsequently came to a rise and a drop again. When the flow velocity of entrance syngas is 1.1 mol/h, the conversion of CO_2 reached the maximum value 6.85%. Fig.5c indicates that time-space yield of CH_3OH also increase at first, then drop. The changing slope of time-space yield of CH_3OH is relatively small and the entrance syngas flow velocity is in the range of 0.49–1.62 mol/h. When the syngas flow velocity is 1.10 mol/h, the time-space yield of CH_3OH reached the maximum. Based on all the above results, the entrance syngas flow velocity in the range of 0.9–1.10 mol/h was selected.
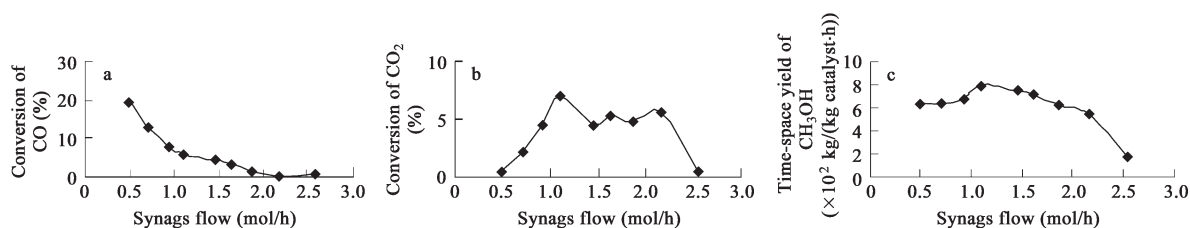

Fig. 5 Influence of syngas flow (entrance) on CO conversion (a), CO_2 conversion (b) and time-space yield of CH_3OH. Pressure: 5 MPa; temperature: 235°C; catalyst C301 with size: 0.246 mm ×0.175 mm; composition of entrance syngas (%): CO 9.36, CO_2 6.85, N_2 32.92, C_nH_m 0.81, H_2 50.81.

Table 3 Effect of syngas composition on time-space yield of CH_3OH

Syngas composition (%)					Ratio of $H_2/(CO+1.5CO_2)$	Conversion of CO (%)	Conversion of CO_2 (%)	Time-space yield of CH_3OH (10^2 kg/(kg cat·h))
CO	CO_2	N_2	C_nH_m	H_2				
13.09	9.8	42.63	1.12	31.46	1.13	9.82	0.38	7.98
10.49	8.8	37.32	0.95	40.49	1.71	22.49	5.88	20.81
9.22	6.85	31.99	0.76	51.1	2.62	15.88	9.23	14.75
8.64	5.03	27.69	0.65	61.85	3.82	19.46	5.39	12.37
5.85	3.23	17.7	0.37	75.77	7.08	22.62	26.40	16.43

Pressure: 5 MPa; temperature: 235°C; catalyst: C301 with size: 0.246 mm × 0.175 mm.

Under the optimum experimental conditions examined above, 0.418 g methanol could be obtained from 1 g of cornstalk. Some reports suggest that 0.283–0.487 g of methanol are yielded from 1 g of woody biomass (including wood chips, pine bark, straw and bagasse pellets, etc.) by optimizing the gasification and synthesis conditions (Beenackers and van Swaajj, 1984; Baker and Brow, 1984; Borgwardt, 1998; Demirbas, 2000; Tsutomu, 2000; Goudeau *et al.*, 1983; Helena and Ralph, 2001; Hirano *et al.*, 1998; Palmer, 1984). It is also reported that 0.64 g of methanol is yielded theoretically from 1 g of microalgal biomass (Hirano *et al.*, 1998). The methanol yield from cornstalks in experiments was in accord with the above cases of woody biomass and was lower than the theoretical value from microalgal biomass. The microalgal biomass did not need purification due to small and uniform particles and thus the complete gasification and the optimum process conditions are explored to get higher methanol yield.

3 Conclusions

Methanol was creatively designed to produce from the low-heat-value cornstalk gas in a comparatively cheap down-flow fixed bed gasifier. The optimum experimental conditions for methanol synthesis with cornstalk syngas were examined in order to lower the production cost. It was proved that the yield of CH_3OH reached 0.418 g/g cornstalk under the optimum experimental condition examined. The optimum experimental condition in this research is selected as the follows. The temperature and pressure of synthetic system are controlled at 235°C and 5 MPa; C301 catalyst with particle size of 0.833 mm × 0.351 mm is employed in the synthetic reaction; the suitable syngas flow at entering end is 0.9–1.10 mol/h; the best composition of syngas is CO 10.49%, CO_2 8.8%, N_2 37.32%, C_nH_m 0.95% and H_2 40.49%.

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