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SESSION 3: INNOVATIVE BIOENERGY TECHNOLOGIES

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Synthesis of DME via Catalytic Conversion of Biomass

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Abstract

The utilization of biomass for Dimethyl ether production via gasification faces the problem of a large excess carbon in form of carbon dioxide in the produced synthesis gas. The stoichiometric adjustment can be accomplished either by adding hydrogen or by removing carbon in form of carbon dioxide. But hydrogen admixture to the syngas requires supplementary investments for an electrolysis unit. The removal of carbon dioxide, due to the extremely low carbon conversion efficiency of about 20% of the biomass carbon content, makes the DME production cost very high.

The novel stoichiometric adjustment concept was investigated by dry reforming carbon dioxide with methane. The addition of methane for reforming allows a nearly complete utilization of the carbon contained in the biomass. At 750°C, the CO_2 content of the gas stream was completely consumed via dry reforming reaction. This concept is an acceptable way for avoiding about 60% the carbon removing from the biomass and avoiding extreme high investment for electrolytic hydrogen.

1. 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 term [1,2]. This is particularly relevant since transport is responsible for a large part of global CO_2 emissions.

Dimethyl ether (DME) is an important chemical for the production of gasoline, ethylene, aromatics and other chemicals. Its applications as a fuel or a fuel additive for vehicles and family cooking have been studied. It is reported that DME can be synthesized from H_2/CO in a single step. It is much more thermodynamically and economically favourable [3-5].

In contrast to gasification process for electricity production, the requirement for the syngas composition for the DME generation process is a high hydrogen content, because a main part of the biomass carbon is converted to CO_2 in the gasification step. In the produced gas of biomass air-steam gasification, there exists a lot of CO, CH_4 and other hydrocarbons that can be converted to hydrogen through steam reforming reaction (converts CH_4 with steam to CO and H_2) and water gas shift reaction (adjusts the H_2/CO ratio by converting CO with steam to H_2 and CO_2) [6]. Interestingly, optimum DME synthesis over Cu-ZnO/γ-Al_2O_3 catalysts requires about 5% CO_2 in the inlet gas. If the CO_2 content is lower or higher, the DME formation rate drops. Furthermore, the DME formation apparently does not occur if the synthesis gas is free of CO_2 and H_2O [6].

The present paper investigates DME generation concepts via synthesis gas production of biomass. As the biomass gasification processes generally lead to a synthesis gas with a carbon excess in form of carbon dioxide, The stoichiometric adjustment of raw synthesis gas was investigated by dry reforming carbon dioxide with methane. Different pathways for meeting the required stoichiometry for the DME synthesis are compared and analysed.

2.Experimental

2.1 Catalyst Preparation

The $Ni_{0.03}Mg_{0.97}O$ solid solution reforming catalyst was prepared by co-precipitating nickel acetate and magnesium nitrate aqueous solutions with potassium carbonate aqueous solution. After being filtered and washed with hot water, the precipitate was dried overnight at 393K and then calcined in air at 1223K for 10h in order to form a solid solution [7].
The DME synthesis catalyst was prepared by the conventional wet impregnation method with $Cu(NO_3)_2$, Mn $(NO_3)_2$, mixed aqueous solution taken in appropriate ratio (Cu/Mn). The support was γ-Al_2O_3, 20-40 mesh. Catalyst was dried at 120°C followed by calcinations in air steam for a certain time.

2.2 Catalytic reforming

Conversion of biomass to an H_2 and CO containing feed gas that is suited for DME synthesis takes place in pilot air-steam gasification units. The raw syngas from the gasifier was passed through the fluidized catalyst bed ($Ni_{0.03}Mg_{0.97}O$, 100ml) under a total pressure of 1MPa at a temperature of 750°C. The products were analyzed by gas chromatograph (Shimadzu GC-20B) with a thermal detector.

2.3 DME synthesis

DME synthesis reaction was carried out by using a high pressure reactor (i.d.=12mm) after introducing pre-treatment gas (H_2/N_2=5:95) at 300°C for 3h. The reactant gas was passed through the catalyst bed (2ml, 20-40 mesh) under a total pressure of 3.0-5.0 MPa and a spaced velocity of $1800h^{-1}$, at a temperature of 230-290°C. The products were analyzed by gas chromatograph (Shimadzu GC-2010) with a thermal detector, in which columns Porapak-Q was used to separate reaction products.

3.Results and Discussion

3.1 Concept of DME synthesis via catalytic biomass conversion

The biomass gasification processes generally lead to a synthesis gas with a carbon excess in form of carbon dioxide. The raw syngas needs to be cleaned and processed to make it suitable for DME synthesis. In the present paper, dry reforming was applied to manipulate the syngas composition prior to the DME synthesis reactor. The basic schematic view is shown in Fig.1.

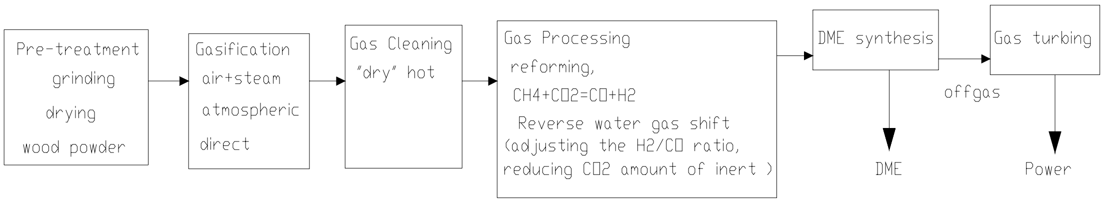

Fig.1. A basic schematic view of the key components for the conversion of biomass to DME combined with gas turbine (combined cycle) power generation.

The syngas produced by the gasification process contains condensable tars and particulates. A dry hot gas cleaning process was adopted because dry reforming reaction was carried out with high temperature (>700°C). A tar cracking reactor was designed to destroy condensable tars and filtrate particulates. The temperature of the cracking reactor was above 950°C with log combustion. Almost all the tars were destroyed and 80% of the particulates were filtrated. The dry reforming for gas composition adjustment was carried out in a fluidised bed reactor over $Ni_{0.03}Mg_{0.97}O$ catalyst at 750°C which avoided the reactor to be jammed by remaining particulates. The off gas from reforming reactor with stoichiometric composition was cleaned by wet cold cleaning processes to DME synthesis. Due to the high single-step CO conversion (>70%) of DME synthesis, the off gas from the DME synthesis reactor need not be recycled and could be used in a gas turbine for power generation.

3.2 Stoichiometric adjustment of synthesis gas

As shown in table 1, the raw syngas composition by biomass air-steam gasification (V1) is carbon dioxide rich gas which leads to low DME production. After dry reforming with methane by adding methane for CH_4/CO_2 ratio of 1, the stoichiometric synthesis gas composition was gained with H_2/CO ratio of 1.5 and content of CO_2 and CH_4 below 4 mol% because carbonic oxide rich synthesis gas is suitable for DME synthesis. Several authors [8] choose 10MW gasifier to meet the goal of decentralized fuel production from biomass with a capacity of <50 tons of methanol per day. Different ways of oxygen production for gasification and stoichiometric adjustment of the synthesis gas (V2, V3, V4) are shown in table 1.

Table 1. Different pathways for stoichiometric adjustment of synthesis gas

Name	V1	V2	V3	V4
Gasifier process type	Direct Air-steam Atmospheric	Direct Electrolysis-O_2 Atmospheric	Direct Electrolysis-O_2 Atmospheric	Direct PAS-O_2 Atmospheric
Composition of raw syngas (mol% dry)				
H_2	31.5	37.3	37.3	37.3
CO	14.8	15.8	15.8	15.8
CO_2	18.6	34.7	34.7	34.7
CH_4	5.4	11.4	11.4	11.4
N_2	21.3	0.3	0.3	0.3
Others	4.4	2.5	2.5	2.5
Adjusting process type	Dry reforming by adding methane, 750°C	Adding electrolysis-H_2	Adding electrolysis-H_2	
Removing percentage of total CO_2 (%)	0	61	0	95
Composition of synthesis gas (mol% dry)				
H_2	41.6	63.5	68.7	55.6
CO	27.8	13.6	7.8	23.6
CO_2	3.4	11.7	17.3	2.6
CH_4	2.7	9.8	5.6	17.0
N_2	19.1	0.2	0.15	0.5
Others	5.4	1.2	0.45	0.7
H_2/CO ratio	1.5	4.6	8.8	2.3

The H_2/CO ratio in the process of V2, V3 and V4 is 4.6, 8.8 and 2.3, respectively, which is preferable for the methanol synthesis requirements. But process V1 may be a best way of stoichiometric adjustment for DME synthesis requirement although the content of N_2 in the gas is relatively high which leads to higher synthesis pressure.

3.2 DME synthesis

DME synthesis reaction was carried out by using a high pressure reactor with model gas stream according to biomass gasification and dry reforming experiment results. As shown in table 2, the CO conversion and selectivity to DME in all products was increased by 39% and 49%, respectively, by stoichiometric adjustment through dry reforming. Compared to ideal gas composition, the 5MP synthesis pressure is needed for the high DME production due to the high content of N_2 in the biomass air-steam gasification syngas.

Table 2 DME synthesis of Different gas composition

	Composition						CO conversion	Selectivity to DME	
	H_2	CO	CO_2	N_2	CH_4	others		All products	Organic products
A 3MP	55.3	28.7	4.6	6.3	0	5.1	78.2	71.3	98.7
B 5MP	31.5	14.8	18.6	21.3	5.4	4.4	54.1	46.7	96.5
C 5MP	41.6	27.8	3.4	19.1	2.7	5.4	75.3	69.6	98.4

A-- ideal gas composition, B—biomass raw syngas, C—synthesis gas after dry reforming
DME synthesis condition: 260°C; 3-5MP

4.Conclusion

The utilization of biomass for Dimethyl ether production via gasification faces the problem of a large excess carbon in form of carbon dioxide in the produced synthesis gas. The stoichiometric adjustment can be accomplished by reforming with methane. The preferable ratio of CH_4/CO_2 is 1. At 750°C, the CO_2 content of the gas stream was completely consumed via dry reforming reaction. The CO conversion and selectivity to DME in all products has increased by 39% and 49%, respectively, by stoichiometric adjustment through dry reforming. This concept is an acceptable way for avoiding about 60% of the carbon removing from the biomass and avoiding extreme high investment for electrolytic hydrogen.

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