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Synthesis of dimethyl ether from syngas obtained by coal gasification

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Abstract−The characteristics of a tubular fixed-bed reactor for the direct synthesis of dimethyl ether (DME) from syngas obtained by coal gasification have been developed. DME synthesis test was conducted with a hybrid DME synthesis catalyst ($CuO/ZnO/Al_2O_3$ for methanol forming, γ-alumina for methanol dehydration) to understand the performance under the conditions of 6.0 MPa, 260 °C and GHSV=3,000 *l*/kg-cat·h. The H_2 conversion and CO conversion were 85-92%, 37-45%, respectively. About 68-80% of DME selectivity was observed. DME synthesis reactor also operated at the productivity of 4.6-4.9 mol/kg-cat·h, which is slightly higher than that in the Peng's prediction results in case of H_2 : CO=0.5.

Key words: Coal Gasification, Syngas, Dimethyl Ether, Tubular Fixed-bed Reactor

INTRODUCTION

Dimethyl Ether (DME) is the simplest ether which is expressed by the chemical formula CH_3OCH_3. DME is a clean and alternative fuel which can be produced from various resources as coal, natural gas, biomass or other organic resources through the synthesis gas. It has been increasingly used in recent years as a propellant in aerosol formulations of household products to replace chlorofluorocarbons, which are found to destroy the ozone layer of the atmosphere.

It is a colorless gas which boils at −25 °C at ambient pressure and is easily liquefied under pressure. It is a chemically stable compound with properties similar to those of propane and butane. Its toxicity is very low, less than that of methanol and comparable to that of LPG. Its calorific value is lower than that of propane but higher than methanol (lower level: 29,000 kJ/kg). Over 50% of the demand for DME worldwide (currently between 100,000 and 150,000 t/y) is for this application.

The current production of DME is by using a conventional two step indirect process comprising methanol synthesis and dehydration of the methanol to DME. These processes are licensed by licensors such as Lurgi, Haldor-Topsoe, Mitsubishi Gas Chemical (MGC) and Toyo Engineering (TEC).

But DME can also be made in a single step by combining mainly three reactions in a single reactor [1]:

$CO+2\,H_2 \rightarrow CH_3OH$ (methanol synthesis)

$2\,CH_3OH \rightarrow CH_3OCH_3+H_2O$ (methanol dehydration)

$CO+H_2O \leftrightarrow CO_2+H_2$ (water gas shift)

Single step DME synthesis processes have been proposed by such companies as Haldor-Topsoe, JFE [2] and Air Products [3], but none of them have been commercialized yet. The single step syngas to DME, i.e., converting methanol and then future converting methanol to DME in the same reactor, frees the overall syngas conversion from the equilibrium constraint imposed by the thermodynamics of methanol synthesis alone [4]. Also, the single-step syngas-to-DME reaction system allows greater productivity in the single-reactor system because of synergy among the three reactions as above mentioned. However, its downstream separation is more complex and costly as compared to the two step process. This trade-off makes it necessary to optimize the productivity of the reactor to produce DME at a lower cost.

The objective of the present study is to develop and evaluate a demonstration of the single step process of DME as mixed co-product with the methanol from syngas obtained by coal gasification.

EXPERIMENTAL

The block flow diagram of coal gasification and DME synthesis system in this study is shown in Fig. 1. Coal is pulverized and dried in the pulverizing system and then moved into the coal feeding system. Coal, oxygen and steam (if used) enter the gasifier through the tangential injection burners located in the common horizontal plane. The gasifier produces the product gas (or syngas) composed primarily of carbon monoxide and hydrogen. Product gas leaves the top of the gasifier and is immediately cooled in the indirect con-

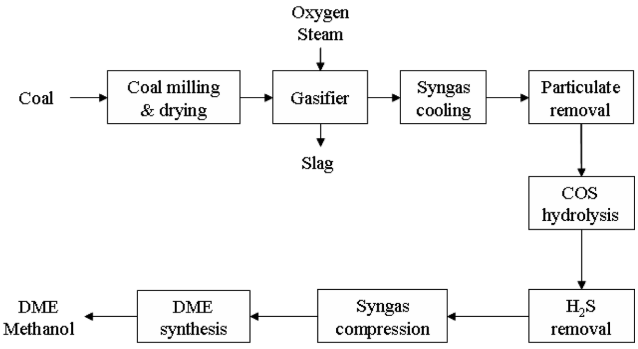

Fig. 1. Schematic diagram of coal gasification and DME synthesis system.

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Table 1. Design conditions of the syngas compression system

Item	Design condition	Remark
Syngas flow rate	100 Nm^3/h	
Inlet pressure	0-8 kg/cm^2	Gauge pressure
Inlet temperature	40 °C	
Outlet pressure	90 kg/cm^2	Gauge pressure
Outlet temperature	40 °C	
Type of compressor	Reciprocating type	4 stages, piston

tact heat exchanger. The cooled product gas then enters the particulate removal system using metal filters, which remove most of the solidified fly slag and the un-reacted coal char from the product gas stream. The particulate removal efficiency was above 99.8%. The COS hydrolysis unit is employed before the H_2S removal system. In the fixed-bed catalytic COS hydrolysis system, COS is reacted with the steam to form H_2S and CO_2. The level of COS in the feed gas is generally in the 50 to 1,000 ppm range and is reduced in the COS hydrolysis system to a value of 10-25 ppm.

The desulfurization of the product gas takes place through the adsorption of H_2S and the partial oxidation to elementary sulfur. The product gas flow is sprayed with a solution of iron chelate. The trivalent iron of the chelate oxidizes H_2S and is reduced to bivalent iron. The complex formation of iron as chelate prevents the deposition of iron hydroxide or iron sulphide. The concentration of H_2S has been reduced to below 0.5 ppm at the exit of a desulfurization facility. The clean syngas then enters the syngas compression system and DME synthesis system.

The design conditions of the syngas compression system are shown in Table 1. The inlet design temperature and pressure of the syngas compressor are 40 °C and 0-8 kg/cm^2 (gauge pressure) to compress the 100 Nm^3/hr of syngas. The syngas compression system consists of 4-stage compressors, three heat exchangers to cool the compressed syngas for the next stage compressing, and four surge vessels to remove condensing water. The outlet design temperature and pressure for syngas compressing system are 40 °C and 90 kg/cm^2. A picture of the syngas compressing system is shown in Fig. 2.

The design conditions of the DME synthesis system are shown in Table 2. The operating temperature and pressure of the DME synthesis reactor are 260 °C and 60 kg/cm^2. The DME synthetic system consists of two heat exchangers, one tubular fixed bed reactor, two vessels to control the reactor temperature by boiler feed water,

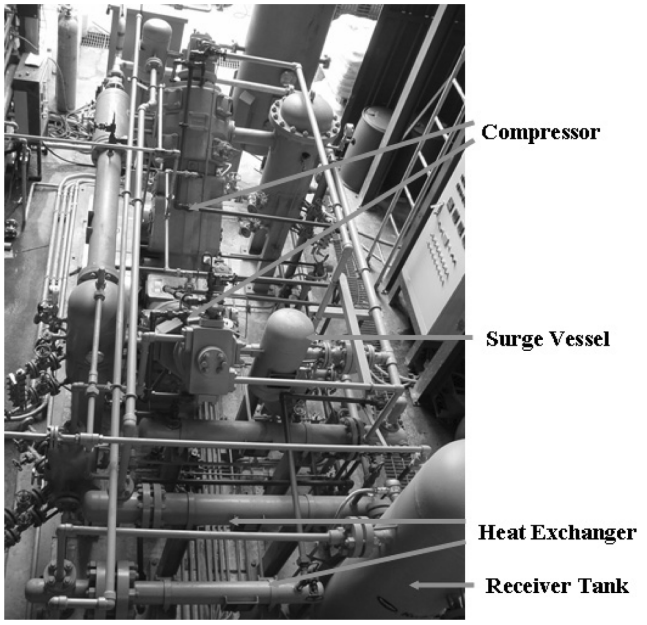

Fig. 2. The syngas compressing system.

and one steam condenser. Fig. 3 shows the pictures of the DME synthetic system installed in the pilot-scale gasification system. The syngas from the compressing system at 90 kg/cm^2 is preheated to 230 °C in the two heat exchangers, and then flows into the DME synthesis reactor.

The DME synthesis process uses a shell-and-tube reactor in which a highly selective catalyst based on copper is packed in vertical tubes contained within a reactor shell filled with boiling water. The DME synthesis section can be held on a hot standby by feeding saturated water into the reactor cooling jacket. The heat of reaction is removed by the generation of steam, thereby controlling the temperature of the reactor. The pressure of DME synthesis reactor was controlled to 60 kg/cm^2 by a pressure control valve located at the DME synthesis reactor exit.

The $Cu/ZnO/Al_2O_3$ catalyst was used for methanol synthesis while gamma alumina was used as a methanol dehydration catalyst. Catalyst used was prepared by mechanically mixing the two types of catalysts at a desired ratio (catalyst mixing ratio is about 1 : 1 by weight). Jinnli [5] showed that CO conversion was affected by the catalyst mixing ratio, but product selectivity was not sensitive to

Table 2. Design conditions of the DME synthesis system

Item	Design condition	Remark
Syngas flow rate	Max. 100 Nm^3/h	
Operating pressure	Max. 90 kg/cm^2	
Operating temperature	Max. 350 °C	
Reactor type	Tubular fixed bed	Shell side: Cooling agent (Saturated water/steam) Tube side: Catalyst
Temperature control	Saturated water/steam in shell side	
Catalyst loading amount	Max. 55 kg	
Catalyst	Methanol synthesis: $Cu/ZnO/Al_2O_3$ Dehydration: γ-alumina	Catalyst mixing ratio=1 : 1

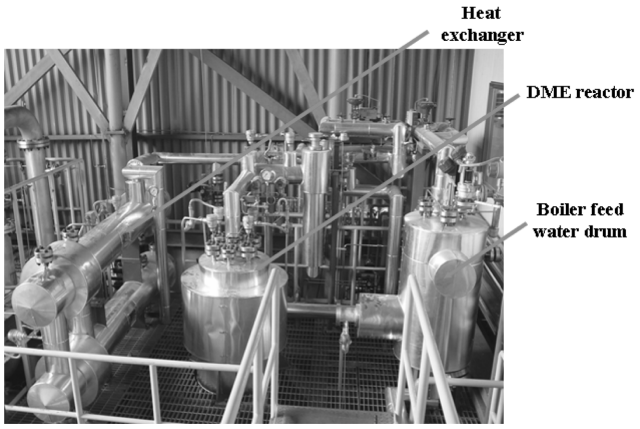

Fig. 3. The DME synthesis system.

Fig. 4. The DME synthesis catalyst.

the change of catalyst ratio, and the optimal catalyst mixing ratio appeared to be about 1 : 1 by weight. The designed maximum loading amount of catalysts was 55 kg to convert syngas to DME. Fig. 4 shows the picture of DME synthesis catalysts manufactured by the company in Korea.

DME and the unconverted syngas from the DME synthesis reactor are cooled by exchanging heat with the syngas from the compressor in two heat exchangers. After cooling, DME and the unconverted syngas without any separation and/or purification flow to the flare stack, where DME and unconverted syngas are burned after mixed with ambient air.

Table 3. Analysis data feed coal used at the coal gasification and DME synthesis plant

Coal		Composition
Proximate analysis (as-fed, wt%)	Moisture	3.26
	Volatile matter	43.13
	Fixed carbon	46.59
	Ash	7.02
Ultimate analysis (moisture-free, wt%)	C	65.67
	H	4.03
	O	21.74
	N	1.00
	S	0.30
	Ash	7.26
Ash chemical composition (wt%)	Al_2O_3	18.0
	SiO_2	51.3
	Fe_2O_3	11.0
	TiO_2	0.92
	MnO	0.15
	CaO	9.77
	MgO	3.9
	K_2O	2.41
	Na_2O	1.1
	P_2O_5	-
Higher heating value (kcal/kg)		6154

The DME and methanol concentrations at the exit of DME synthesis reactor were analyzed by on-line gas chromatography (MAXUM EDITION II Process Gas Chromatography) equipped with TCD detectors. GC column used was 80/120 CARBOBLACK B 3 m manufactured by Siemens AG. A temperature program of 5 °C to 225 °C was chosen for the analysis.

RESULTS AND DISCUSSIONS

The chemical characteristics of Indonesia Rotto coal gasified for

Table 4. DME production results from syngas

Item		Run 1		Run 2		Run 3	
		Reactor inlet	Reactor outlet	Reactor inlet	Reactor outlet	Reactor inlet	Reactor outlet
Gas composition (%, dry basis)	CO	37.8	31.3	37.4	31.4	37.7	30.5
	H_2	14.2	2.9	14.3	2.8	14.2	1.5
	CO_2	8.0	14.6	8.0	15.1	9.3	15.8
	N_2	40.1	46.6	40.3	46.1	38.9	47.2
	DME	-	4.4	-	4.4	-	4.8
	Methanol	-	0.2	-	0.1	-	0.2
H_2 conversion (%)		85		86		92	
CO conversion (%)		37		40		45	
DME selectivity (%)		70		68		80	
DME productivity (mol/kg-cat·h)		4.9		4.6		4.8	

Table 5. Performance comparison of syngas conversion to DME in different reactor configurations

Reactor configuration		Air product slurry reactor	PNNL micro channel reactor	This study tubular fixed bed
Reaction conditions	T (°C)	250	280	260
	P (kg/cm^2)	52	38	60
	GHSV	4,500	10,238	3,000
	H_2/CO	0.7	2.0	0.38
Performance	CO conversion (%)	37	86	37-45 (H_2 conversion: 85-93)
	CO_2 selectivity (%)	32	22	18-31

this study, including proximate and ultimate analyses and ash composition, are shown in Table 3. Coal feed was the identical size with that of conventional power plants using pulverized coal, as 80-90% passing 200 mesh size. Pulverized coal was pneumatically conveyed with nitrogen gas at dense-phase into the feeding nozzle system, where 99%-purity oxygen and steam were mixed with the coal powder. Steam was not used for the gasification of Rotto coal.

Table 4 exhibits the coal gas compositions of DME reactor inlet and outlet. The syngas composition of reactor inlet syngas is comprised mainly of CO and hydrogen at about 38% and 14% in dry basis (H_2 : CO=0.38). Higher N_2 concentration in the syngas compared to that of commercial coal gasifiers is due to the increased transportation nitrogen for coal injection into the gasifier.

A DME synthesis test was conducted with the hybrid DME synthesis catalyst to understand the performance under the conditions of 6.0 MPa, 260 °C and GHSV=3,000 *l*/kg-cat·h. As shown in Table 4, the H_2conversion and CO conversion is 85-92%, 37-45%, respectively. Also a DME selectivity of about 68-80% was observed.

Peng and co-work [4] have proposed that the very strong dependence of the DME productivity on the H_2 : CO ratio was observed and maximum productivity (10.9 mol/kg·h) occurred at a H_2 : CO ratio of 1.0; also, the productivity dropped by about 65% (3.8 mol/kg·h) and 44% (6.1 mol/kg·h) when the ratio changed to 0.5 and 1.5, respectively. As shown in Table 4, the reactor operates at a productivity of 4.6-4.9 mol/kg·h. This is slightly higher than that in the Peng's prediction results in case of H_2 : CO=0.5.

Currently, no commercial production data are available for the direct DME synthesis. As a reference for this study [2,3], Air Products commercial demonstration results (slurry reactor) and PNNL microchannel reactor (fixed bed reactor) were compared with our hybrid catalyst/tubular fixed bed reactor system. The performance results are listed in Table 5. It is very difficult to find exactly the same reaction conditions for different types of reactors. What we need to address here is that the comparison results are preliminary and intended to show the difference in the overall productivity, but by no means to compare the advantages of different reactor configurations.

CONCLUSIONS

The properties of DME are suitable for the production of power generation fuel, transportation fuel and chemicals. Single-step synthesis technology of DME has been developed by IAE (Institute for Advanced Engineering). For the development of this technology, three tons/day (maximum coal feed rate) coal gasification and DME synthesis system operation have been carried out with Korean government support.

A DME synthesis test was conducted with the hybrid catalyst (methanol forming+methanol dehydration) to understand the performance under the conditions of 6.0 MPa, 260 °C and GHSV= 3,000 *l*/kg-cat·h. H_2 conversion and CO conversion are 85-92%, 37-45%, respectively. DME selectivity of about 68-80% was observed. A DME synthesis reactor also operates at a productivity of 4.6-4.9 mol/kg-cat·h.

Additional investigation is necessary to extend the current work to evaluate the various catalysts characteristics and operation conditions.

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