CSCanada
Energy Science and Technology
Vol. 2, No. 2, 2011, pp. 79-84
DOI:10.3968/j.est.1923847920110202.103

ISSN 1923-8460[PRINT]
ISSN 1923-8479[ONLINE]
www.cscanada.net
www.cscanada.org

Replacing an Existing Product's Production Within a Similar Product Production by Using a Replacement Technique

Anita Kovač Kralj[1,*]; Dejan Bencik[2]

[1]Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, Maribor, Slovenia
[2]Nafta-Petrochem d.o.o., Lendava, Slovenia
[*]Corresponding author.
Email: anita.kovac@uni-mb.si

Received 13 September 2011; accepted 17 October 2011

Abstracts

Existing processes for specific products cannot sustain operational profitably over a long period. The product's price is not much higher than the raw material costs and it is necessary to make certain modifications by using savings or replacements during product production. In our case, the production of methanol having a low market value would be replaced by the production of dimethyl ether (DME). This would create greater demand, especially from the environmental perspective, and can be achieved by using replacement technique. We want to keep and transfer as many of the existing units from the previous production to the new production. Dimethyl ether is an organic compound with the formula CH_3OCH_3. It is a colourless gas that is a useful precursor to other organic compounds, and an aerosol propellant. DME can act as a clean fuel when burned in engines properly optimized for DME. The direct production of DME would be cheaper than indirect when applied for new buildings. The same applies for retrofits, or the replacing of existing methanol - specific production – a similar DME product plant would be more rational for the direct production of DME, because of greater efficiency, productivity of DME production, profit, and for 20 % more electricity generation.

Key words: Dimetyl ether; Replacement; Methanol process; Indirect method; Direct method; Retrofit

Kralj, A.K., & Bencik, D. (2011). Replacing an Existing Product's Production Within a Similar Product Production, by Using a Replacement Technique. *Energy Science and Technology, 2*(2), 79-84. Available from: URL: http://www.cscanada.net/index.php/est/article/view/j.est.1923847920110202.103 DOI: http://dx.doi.org/10.3968/j.est.1923847920110202.103

INTRODUCTION

Recently, much research has been conducted regarding alternative fuels. This is due to an increasing demand for lower fuel consumption and lower exhaust emissions. The potentials of dimethyl ether (DME) mass production and its use as a fuel are promising[1]. DME is attracting great attention as an energy source for the 21st century because of its multiple sources and excellent physical, chemical, and storage properties. In Asia, the demand for fuel is rapidly increasing for both household and transportation purposes, making DME very promising as an alternative fuel[2, 3].

The toxicity of DME is low, and its ozone generation via photochemical reactions is equal to that of LPG (liquefied petroleum gas). Therefore, certain amounts of DME are being commercially-produced as a propellant for spray cans because of its non-toxicity, and suitable solubility and vapour pressure at room temperature[2]. At first glance, DME seems to be an excellent, efficient alternative fuel for use in diesel engines with almost smoke-free combustion, not only because of its low auto-ignition temperature and its almost instantaneous vaporization, but also because of the absence of a direct C–C bond in the molecular structure, and the presence of oxygen (around 35% by mass) in the fuel[4]. Moreover, with a properly designed fuel supply system, NOx emissions have been found to be lower with DME than with diesel[5, 6, 7].

There are two methods for DME preparation, the indirect (two step) approach and the direct (single-

Copyright © Canadian Research & Development Center of Sciences and Cultures

step) one. In the indirect method, DME is produced by methanol dehydration using acidic catalysts within an adiabatic fixed bed reactor. DME can also be prepared directly from synthesis gas utilizing bi-functional catalysts that have two kinds of active sites: one for methanol formation and the other for methanol dehydration[8]. The direct method is more economical than the indirect one when applied for new buildings because:

- The methanol concentration in the reaction medium becomes lower (due to consumed methanol) which decreases the thermodynamic equilibrium limitation of methanol synthesis.
- The methanol purification unit can be eliminated because only one reactor is required for DME synthesis[9].

Thereupon the production costs for the single-step process are 20% lower than for the two-step, and the initial investment is also smaller[10, 11].

There are several articles discussing the modelling and simulation of direct and indirect syntheses regarding DME. Nasehi et al.[12] modelled and simulated the indirect synthesis of DME within an industrial adiabatic fixed-bed reactor, and investigated the effects of changes in inlet conditions on the reactor's operation. Song et al.[13] studied a direct process for DME production from synthesis gas within a pilot-scale fixed-bed reactor. They applied a one-dimensional heterogeneous model and found good agreement between their model-based simulation and the experimental results. A mathematical model of the pipe-shell fixed-bed reactor was built, based on the global kinetics of the direct synthesis of DME from synthesis gas on a bi-functional catalyst by Hu et al.[14].

This paper presents the replacement of existing methanol product production by similar DME product production, using a replacement technique.

1. REPLACEMENT TECHNIQUE

Retrofitting refers to the addition of new technology or features to older systems within chemical plant, thus improving plant efficiency, increasing product production, and reducing emissions. Retrofit projects replace or add equipment to existing plants, thus improving their energy efficiencies and extending their lifespan. The benefits of the retrofit are the optimization of an existing plant, and the adaptation of the plant for new or changed products. Principally, retrofitting describes those measures taken within the chemical industry that allow new or updated parts to be fitted to old or outdated assemblies.

The replacement of an existing product's production within a similar product production by using a replacement technique, consists of three stages (Fig. 1):

1. analysis of the old product's production
2. analysis of the new product's production
3. replacing the old within the new one.

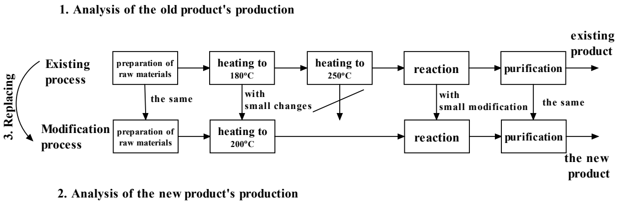

Figure 1
Presentation of a Replacement Technique

The first step includes an analysis of existing product production and the operations of all processing units (Fig. 1). The operations of individual units must be understandable. The existing processing units are simulated by using computer software (Aspen Plus, GAMS). If the simulation is well suited to the actual parameters, we know that we have satisfactory models.

The second step involves learning about the new product's production. All of the new product production alternatives and their advantages and disadvantages have to be recognized, and the existing simulation models needing to be replace by a new similar simulated product production. On this basis, it is easier to adapt the old to the new production, which is the third step. The main goal of the replacement is to keep as many processing units, or make small changes in order to modify them. Process replacement is more easily enforced in the case of appropriate simulation models.

2. CASE STUDY

This replacement technique was tested on an existing methanol process, which was replaced by DME production.

2.1 Analysis of the Old Product Production

The existing Lurgi methanol production is no longer profitable, so it needs to be replace with another. The methanol process is composed of three subsystems[15]:

- production of synthesis gas
- production of crude methanol and
- purification of methanol (F301, D301-D304).

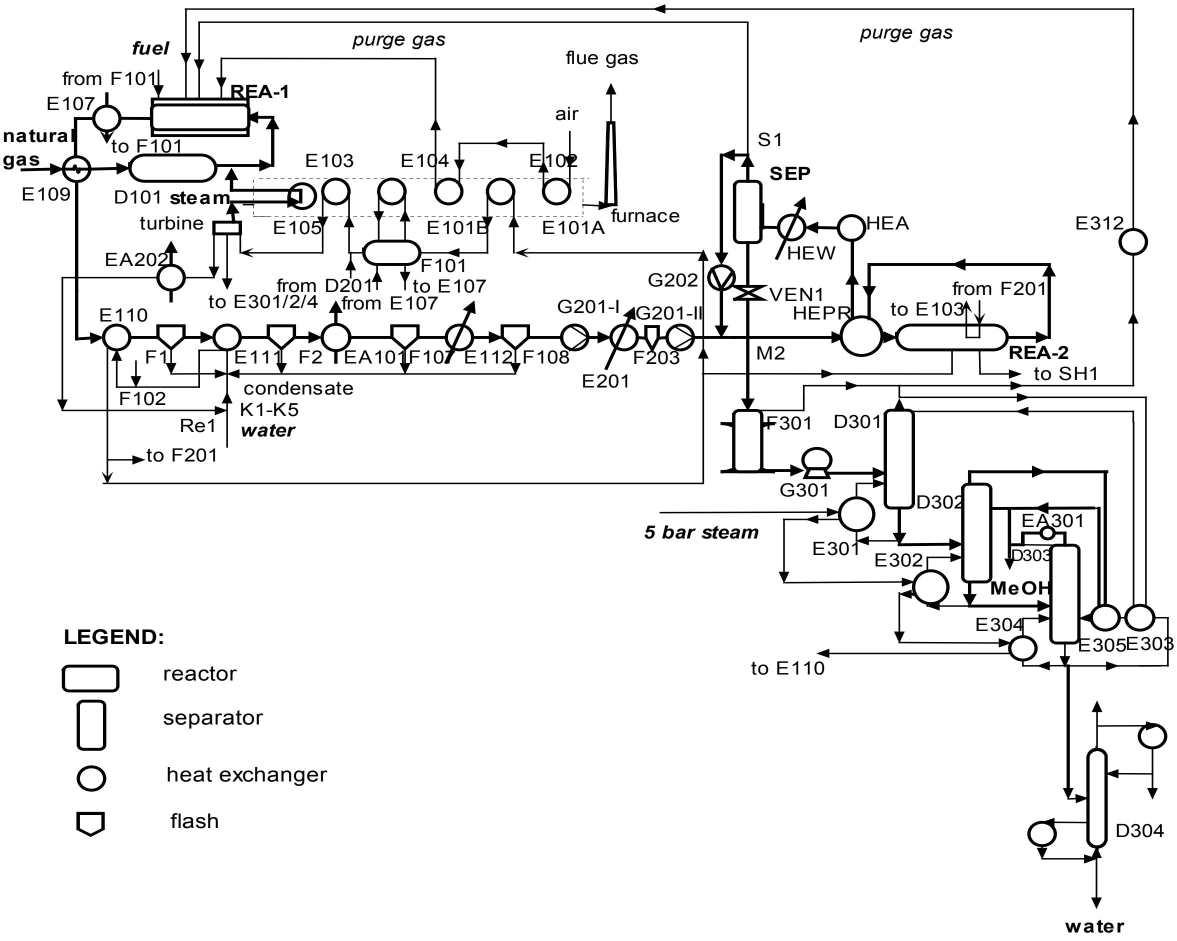

Figure 2
Process Flow-Diagram of a Low-Pressure Lurgi Methanol Plant

The raw material (natural gas) is first desulphurized (D101) and then heated-up within a steam reformer (REA-1), where synthesis gas is produced from the raw material (natural gas) and steam, at 825 °C 15 bar:

$3C_2H_6 + 6.5H_2O \rightarrow 2CO + 12H_2 + 1.75CH_4 + 2.25CO_2$
$\Delta_r H^{298} = 196.17$ kJ/mol (R1)

$3C_3H_8 + 10H_2O \rightarrow 3.5CO_2 + 17H_2 + 3CO + 2.5CH_4$
$\Delta_r H^{298} = 277.88$ kJ/mol (R2)

$3C_4H_{10} + 13.5H_20 \rightarrow 4.75CO_2 + 22H_2 + 4CO + 3.25CH_4$
$\Delta_r H^{298} = 361.48$ kJ/mol (R3)

$CH_4 + H_2O \leftrightarrows CO + 3H_2$ $\Delta_r H^{298} = 206.08$ kJ/mol (R4)

$CO + H_2O \leftrightarrows CO_2 + H_2$ $\Delta_r H^{298} = 41.17$ kJ/mol (R5)

The hot-stream of synthesis gas is cooled in an E107 boiler, within E109, E110, E111 heat-exchangers in an EA101 air-cooler, and in an E112 water-cooler. The condensate is expanded in flashes: F1, F2, F107, and F108. All the condensates are collected (K1—K5) during the process. The synthesis gas is compressed in G201I and G201II two-stage compressors.

In the second subsystem, methanol is produced by the catalytic hydrogenation of carbon monoxide and/or carbon dioxide within a REA-2 reactor, using three main reactions:

$CO + 2H_2 \leftrightarrows CH_3OH$ $\Delta_r H^{298} = 90{,}77$ kJ/mol
$X_{CO} = 56$ % (R6)

$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $\Delta_r H^{298} = 49{,}58$ kJ/mol
$X_{CO2} = 30{,}5$ % (R7)

$CO_2 + H_2 \leftrightarrows CO + H_2O$ $\Delta_r H^{298} = 41{,}19$ kJ/mol
$X_{CO2} = 0{,}2$ % (R8)

The REA-2 high-pressure reactor is operated within the existing parameters, and the non-converted gas recycled. The inlet-stream of the reactor is heated by a process stream (HEPR). Furthermore, the stream is cooled using air (HEA) and water (HEW) coolers before entering the flash (SEP). The liquid-stream during the separation is the product and the recycled gas-stream is compressed

Copyright © Canadian Research & Development Center of Sciences and Cultures

to 51 bar in a new, two-stage compressor (COMP1, 2) with intermediate water-cooling (HEW1). The purge gas is separated from the crude methanol in the F301 flash. Purification includes the distillation columns (D301-D304). All process units of the methanol production are simulated using Aspen Plus (Fig. 3) and correspond very well with the real values, the deviations being only

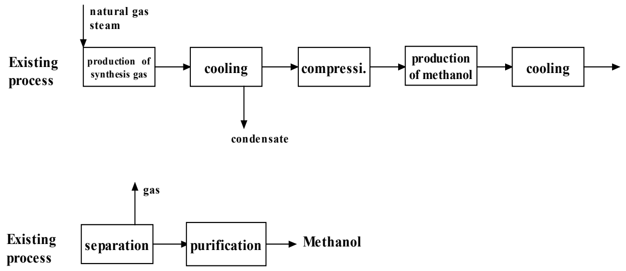

Figure 3
Process Units Presentation of Simulated Methanol Plant

2.2 Analysis of the New Product Production

DME can be produced from a variety of feed-stock such as natural gas, crude oil, residual oil, coal, waste products, and bio-mass. DME is an innovative clean fuel which can be used within various sectors: household, transportation, power generation, etc. There are two methods for DME preparation, the indirect (two step) approach and the direct (single-step). Approximately 200,000 tons/year are produced worldwide by the dehydration reaction of methanol. As methanol itself is produced from synthesis gas (hydrogen and carbon monoxide), it would be more efficient to produce DME directly from synthesis gas.

2.2.1 Direct DME Production

DME synthesis reaction and equilibrium conversion to DME synthesis reaction (R9) from synthesis gas (H_2, CO) is composed of three reactions: methanol synthesis reaction (R10), methanol dehydration reaction (R11), and water gas shift reaction (R12). The overall reaction is exothermic and the reaction heat during the methanol synthesis step is dominant[8, 9]:

$$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2 \quad \Delta_r H^{298} = -246 \text{ kJ/mol} \quad (R09)$$

$$2CO + 4H_2 \rightleftharpoons 2CH_3OH \quad \Delta_r H^{298} = -181.6 \text{ kJ/mol} \quad (R10)$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad \Delta_r H^{298} = -23.4 \text{ kJ/mol} \quad (R11)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta_r H^{298} = -41 \text{ kJ/mol} \quad (R12)$$

The equilibrium conversion of synthesis gas (CO conversion plus H_2 conversion) for DME synthesis reaction (R9) is much higher than that for methanol synthesis reaction (R10) and has its maximum peak where the H_2/CO ratio corresponds to the stoichiometric value, that is, with a H_2/CO ratio of 1. A slurry-phase reactor for DME synthesis and catalyst system. As the reaction of DME synthesis is highly exothermic, it is more important to control the reaction temperature than in the case of methanol synthesis, because the higher equilibrium conversion of DME synthesis gives much more reactive heat, and a hot spot within the reactor could damage the catalyst. In the slurry which is composed of an inert solvent containing fine catalyst particles, the reactant gas forms bubbles and diffuses into the solvent, and a chemical reaction takes place on the catalyst. The reactive heat is quickly absorbed by the solvent, which has a large heat capacity, and thanks to highly-effective heat conductivity, the temperature distribution in the slurry could be homogeneous. In the slurry-phase reactor, as catalyst particles are surrounded by the solvent, the mass-transfer mechanism for the reactants and products is different from that in the fixed bed reactor. In this connection, a catalyst system adequate for the slurry-phase reactor was developed. In order to enable a large scale test, a catalyst mass production technology had also been developed.

2.2.2 Indirect DME Production

The production of DME is via the catalytic dehydration of methanol over an amorphous alumina catalyst treated with 10.2 % silica. A methanol conversion of about 80 % is achieved within the reactor[12]. DME is produced by the following reaction:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad \Delta_r H^{298} = -23.4 \text{ kJ/mol} \quad (R13)$$

The catalytic dehydration of pure, gaseous methanol is carried out in a fixed-bed reactor. The product is cooled over two stages and subsequently distilled to yield pure DME. Small amounts of DME are recovered from the off-gas in a scrubber, and re-cycled to the reactor. The non-reactive methanol is separated from the water in a second column, and also recycled.

2.3 Replacement of the Old Within the New

After a detailed investigation, the direct and indirect DME productions could be transferred to the existing production of methanol with a simulated model, by using an Aspen Plus simulator[16].

2.3.1 Replacement of Methanol Production within Direct DME Production

Direct DME production is coordinated with the methanol process until the methanol synthesis reactor, which is replaced by the DME synthesis reactor (at 250 °C and 49 bar, Fig. 4). This is followed by cooling until reaching a temperature of -40 °C under 49 bar. Cooling with refrigerant in the cooling system increases operating and investment costs. At least two cooling systems and a separator should be purchased, which at these low parameters could be separate gases (CO_2, CO) from the liquefied DME. Then, residual gas (CO_2, CO) could be separated in the first existing modified column (10 bar). In the second existing modified column (7 bar) pure DME could be separated (8 050 kg/h of DME by 10 500 kg/h of an existing amount flow rate of natural gas as methanol production). In the third existing modified column (1 bar) pure methanol and water (1 400 kg/h and 2 970 kg/h) could be separated.

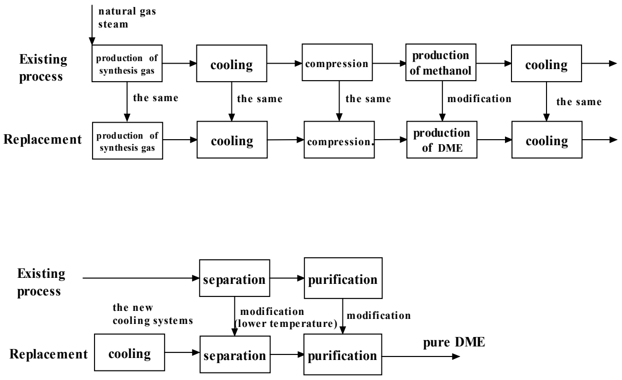

Figure 4
Coordination of the Methanol Process with the Direct DME Plant

2.3.2 Replacing the Methanol Production Within Indirect DME Production

Indirect DME production is coordinated with the methanol process until liquefied methanol separation, followed by heating the crude methanol to 215 °C, synthesizing in a new DME synthesis reactor (at 227 °C) , cooling to 90 oC (Fig. 5). In the first existing modified column (7 bar) pure DME could be separated (7 620 kg/h of DME by 10 500 kg/h of existing amount flow rate of natural gas as methanol production). In the second existing modified column (1 bar) pure methanol and water (1 560 kg/h and 4 790kg/h) could be separated.

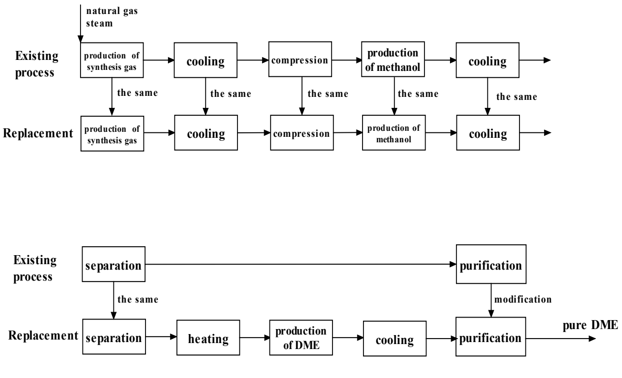

Figure 5
Coordination of the Methanol Process with the Indirect DME Plant

Both processes were compared regarding economical reasons (Table 1). This comparison included modification of the existing process units and the purchase of new equipment. In this regard the direct method exceeded 2.6 times. The direct method included modification of the existing methanol reactor for DME reproduction (60 kEUR/a), cooling with cooling systems by using refrigerant (300 kEUR/a), and the modifications of three columns (60 kEUR/a). The indirect method included the purchase of a new DME reactor (100 kEUR/a), modification of existing the heat exchanger (20 kEUR/a), and the modifications of two columns (40 kEUR/a).

The production of DME was higher (pure 8.05 t/h) by 5. 6 % under the direct method, because of higher conversion. The production of DME was 7.62 t/h under the indirect method at a price 200 EUR/t. 1.4 t/h of pure methanol would be sold under direct DME production, and 1.56 t/h under the indirect at a price of 160 EUR/t. Both processes were operated at 8000 h/a. The total income was 14 670 kEUR/a and 14 190 kEUR/a under direct and indirect processes, respectively (Table 1). The assumption is that the total operating costs for both processes are identical (10 920 kEUR/a). The total cost including the total operating costs (10 920 kEUR/a), and the additional retrofit modification was 11 340 kEUR/a and 11 080 kEUR/a. Total profit was 3 330 kEUR/a and 3 100 kEUR/a under the direct and indirect processes, respectively (Table 1).

The reconstructive changes would be minor within an indirect plant but the direct could be more profitable. The direct plant could bring higher additional profits of 645 kEUR/a (at a price of 430 EUR/kWa) because 1500 kW of higher electricity generation within the existing gas turbine would be managed.

CONCLUSIONS

A methanol production plant could be replaced by a DME production plant, from the environmental and profitability perspectives. Dimethyl ether is a multi-source and multi-purpose clean fuel that can be made from natural gas, coal, or biomass. Recently, it has been increasingly used as an aerosol propellant to replace chloro-fluoro-carbons, which were found to destroy the ozone layer of the atmosphere.

The replacement of existing product production within similar product production by using replacement technique consists of three stages or analyses, first of the old and then of the new productions, thus allowing replacement the old within the new. The main goal of the replacement is to keep many of the processing units, or make small changes in order to modify them. Replacement is easier to implement using simulators and a good knowledge of the old and new processes.

Retrofit, or replacement of the existing specific methanol product within a similar DME product plant would be more rational for the direct production of DME, because of its greater profitability and productivity, and for 20 % more electricity generation. Reconstructive changes would be minor within an indirect plant but the direct could be more profitable. The decision depends on the choice of co-financier.

Table 1
Comparison Between Direct and Indirect Plants

	Direct	Indirect
Income of DME; kEUR/a	12 880	12 190
Income of methanol; kEUR/a	1 790	1 990
Total income; kEUR/a	14 670	14 180
Equipment cost; kEUR/a	- modification of methanol reactor: 60 - new cooling systems: 300 - columns modification: 60	- new DME reactor: 100 - modification of heat exchanger: 20 - columns modification: 40
Operating cost; kEUR/a	10 920	10 920
Total cost; kEUR/a	11 340	11 080
Total profit; kEUR/a	3 330	3 100

REFERENCES

[1] Maroteaux, F., Descombes, G., & Sauton, F. (2001). Performance and Exhaust Emissions of a Diesel Engine Running with DME. *Proceedings of the 2001 ICE Spring Technical Conference, 1*, 73–81.

[2] Japan DME Forum. (2007). *DME Handbook*.

[3] Weidou N., Lijian, T., & Dewei F. (2006). Rational Cognition of DME Market in China. *Proceedings of 3rd Asian DME Conference*, 21–38.

[4] Arcoumanis C., Bae, C., Crookes, R., & Kinoshita, E. (2008). The Potential of Di-Methyl Ether (DME) as an Alternative Fuel for Compression-Ignition Engines: A Review. *Fuel, 87*, 1014–1030.

[5] Longbao Z., Hewu, W., Deming, H., & Zuohua, H. (1999). Study of Performance and Combustion Characteristics of a DME-Fueled Light-Duty Direct-Injection Diesel Engine. *SAE Paper 1999-01-3669*.

[6] Kapus P., & Ofner, H. (1995). Development of Fuel Injection Equipment and Combustion System for DI Diesels Operated on Dimethyl Ether. *SAE Paper 950062*.

[7] Wu J., Huang, Z., Qiao, X., Lu J., Zhang, L., & Zhang, J. (2006). Combustion and Emission Characteristics of a Turbocharged Diesel Engine Fuelled with Dimethyl Ether. *International Journal of Automotive Technology, 7*(6), 645–652.

[8] Ge Q., Huang, Y., Qiu, F., & Li, S. (1998). Bifunctional Catalysts for Conversion of Synthesis Gas to DME. *Appl. Catal., 167*, 23–30.

[9] Nie Zh., Liu H., Liu D., Ying W. & Fang, D. (2005). Intrinsic Kinetics of Dimethyl Ether Synthesis from Syngas. *J. Nat. Gas Chem., 14*(1), 22–28.

[10] Fukunaga T., Ryumon, N., & Shimazu S. (2008). The Influence of Metals and Acidic Oxide Species on the Steam Reforming of Dimethyl Ether (DME). *Appl. Catal. A, 348*, 193–200.

[11] Tan Y., Xie, H., Cui, H., Han, Y., & Zhong (2005). Modification of Cu-Based Methanol Synthesis Catalyst for Dimethyl Ether Synthesis from Syngas in Slurry Phase. *Catal. Today, 104*, 25–29.

[12] Nasehi S.M., Eslamlueyan, R., & Jahanmiri A. (2006). *Simulation of DME Reactor from Methanol*. Proceedings of the 11th Chemical Engineering Conference Iran, Kish Island.

[13] Song D., Cho, W., Lee, G., Park, D.K., & Yoon, E.S. (2008). Numerical Analysis of a Pilot-Scale Fixed-Bed Reactor for Dimethyl Ether (DME) Synthesis. *Ind. Eng. Chem. Res., 47*(13), 4553–4559.

[14] Hu Y., Nie, Z., & Fang, D. (2008). Simulation and Model Design of Pipe-Shell Reactor for the Direct Synthesis of Dimethyl Ether from Syngas. *J. Nat. Gas Chem., 17*(2), 195–200.

[15] McKetta, J.J., & Cunningham, W.A. (1985). *Encyclopedia of Chemical Processing and Design, 29*, 418-474.

[16] Aspen Technology (2002). *ASPEN PLUS User Manual Release 11.1*. Cambridge, USA: Aspen Technology Inc.