CHEMICAL ENGINEERING TRANSACTIONS

VOL. 27, 2012

Guest Editors: Enrico Bardone, Alberto Brucato, Tajalli Keshavarz
Copyright © 2012, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-18-1; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1227005

Replacing the Existing Methanol Production Within DME Production by Using Biogas

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New methodologies are always being sought for the production of useful products from different raw materials. Methanol and further dimethyl ether can be produced from biogas. 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 indirect dimethyl ether by using biogas.

1. Introduction

DME (dimethyl ether) is attracting great interest as an energy source for the 21st century because of its multiple sources and excellent physical, chemical, and storage properties (Vakili et al., 2011). In Asia, the demand for fuel is rapidly increasing for both household and transportation purposes, making DME very promising as an alternative fuel. 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. 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 vapourization, but also because of the absence of a direct C–C bond within the molecular structure, and the presence of oxygen (around 35 % by mass) in the fuel. Moreover, with a properly designed fuel supply system, NO_x emissions have proved to be lower with DME than with diesel (Youn et al., 2011).

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 t/y 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.

The development of biogas technology began at the beginning of the 19-th century. However, owing to the energy crises of the 1970s, anaerobic digestion technology underwent significant development (Lasse, et al., 2011). Increasingly other green alternatives could be replaced fossil energy (Duić et al., 2011; Kelly and Gibson 2011; Redha et al., 2011; Li et al., 2011; García et al., 2011; Tan et al., 2011; Martín and Grossmann, 2011; Touš et al., 2011; Gerber et al., 2011).

Please cite this article as: Kovac Kralj A. and Hosnar J., 2012, Replacing an existing methanol production within dme production, by using biogas, Chemical Engineering Transactions, 27, 25-30 DOI: 10.3303/CET1227005

2. Replacement plant

Retrofitting refers to the addition of new technology or features to older systems within chemical plants, 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 retrofit are the optimization of an existing plant, and the adaptation of that 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 basic goal, by replacing the existing plant within the new one, is the ability to keep the existing process units (Figure 1). A replacement plant would not need great modification, and the crude methanol production would be the same. The DME production would be added, including a heat exchanger and the DME's reactor. DME is cleaned by using the existing processing units with minimal modifications.

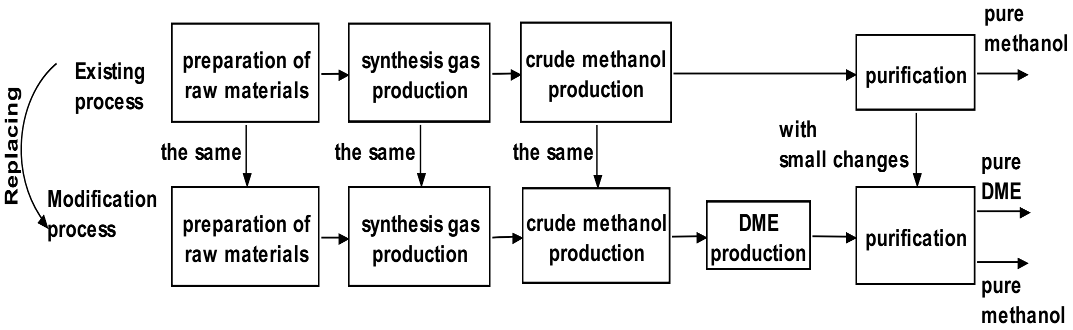

Figure 1: Replacing the existing process within new one

2.1 Existing methanol production

The methanol process is composed of three sub-systems: the production of synthesis gas, the production of crude methanol and the purification of methanol (F301, D301–D304; Figure 2). 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:

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

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

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

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

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

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

$$CO + 2H_2 \leftrightarrows CH_3OH \qquad \Delta_r H^{298} = -90.77 \text{ kJ/mol} \qquad X_{CO} = 56\ \% \qquad \text{(R6)}$$

$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \quad \Delta_rH^{298} = -\ 49.58\ \mathrm{kJ/mol} \quad X_{CO2} = 30.5\ \%$ (R7)

$CO_2 + H_2 \leftrightarrows CO + H_2O \quad \Delta_rH^{298} = \ 41.19\ \mathrm{kJ/mol} \quad X_{CO2} = 0.2\ \%$ (R8)

The REA-2 high-pressure reactor is operated within the existing parameters, and the non-converted gas recycled (Figure 2). 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).

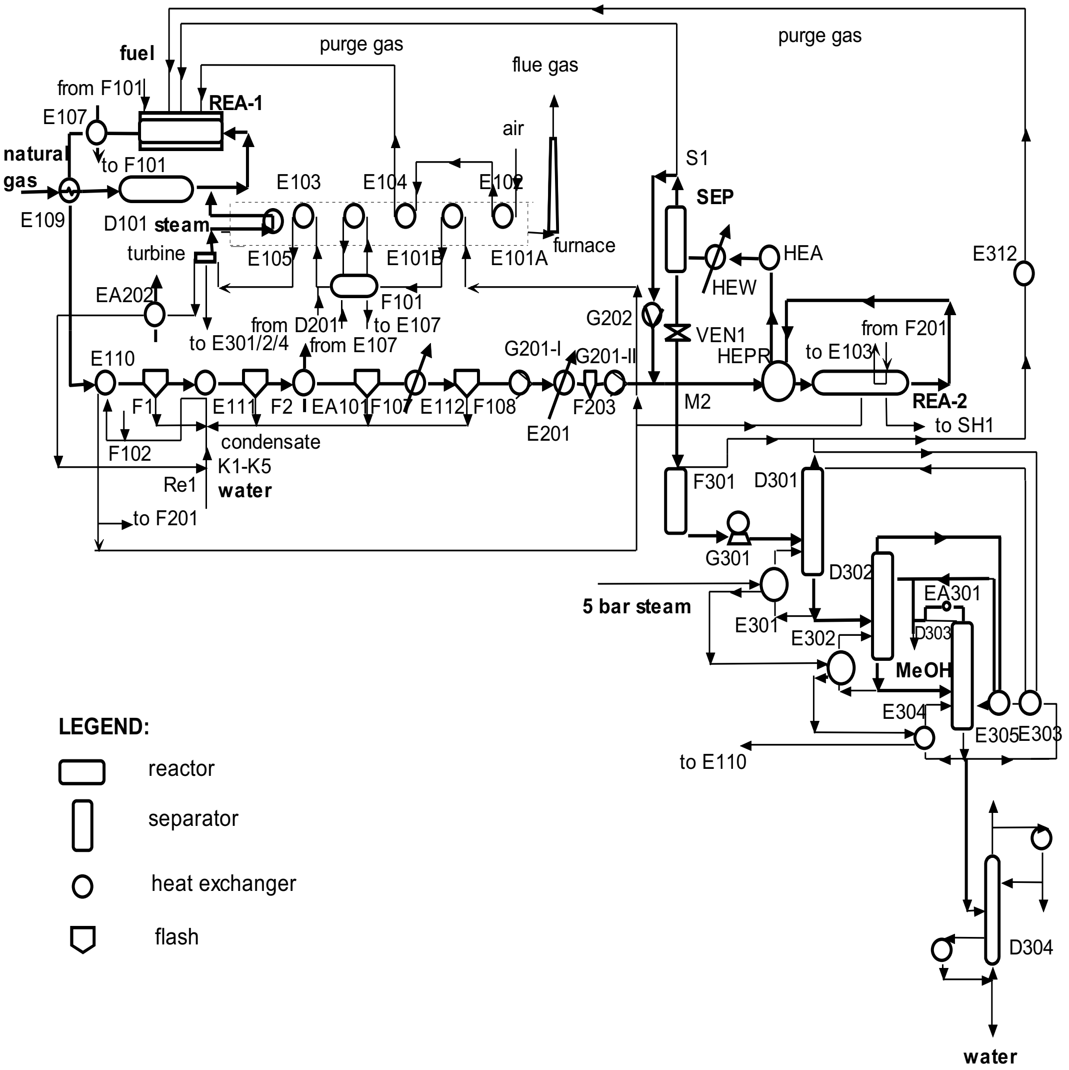

Figure 2: Process flow-diagram of a low-pressure methanol plant

The liquid-stream during the separation is the product and the recycled gas-stream is compressed to 51 bar within 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 (Figure 2) and correspond very well with the real values, the deviations only being between 3 to 5 %.

2.2 Replacing the methanol production within indirect DME production

This paper presents the replacing of pure methanol within DME production, and natural gas with biogas. The existing methanol production is no longer profitable, so it needs to be replaced with another. Natural gas is still an irreplaceable raw material, it gives the best composition for the synthesis gas. However, we are looking for alternatives to replace natural gas with biogas. Synthesis gas could be produced from biogas, which contains 75 % methane (7895 kg/h), 23 % carbon dioxide (2,420 kg/h), and 2 % of hydrogen (210 kg/h). A further 20 % of DME and 80 % of methanol would be produced from the crude methanol as used now.

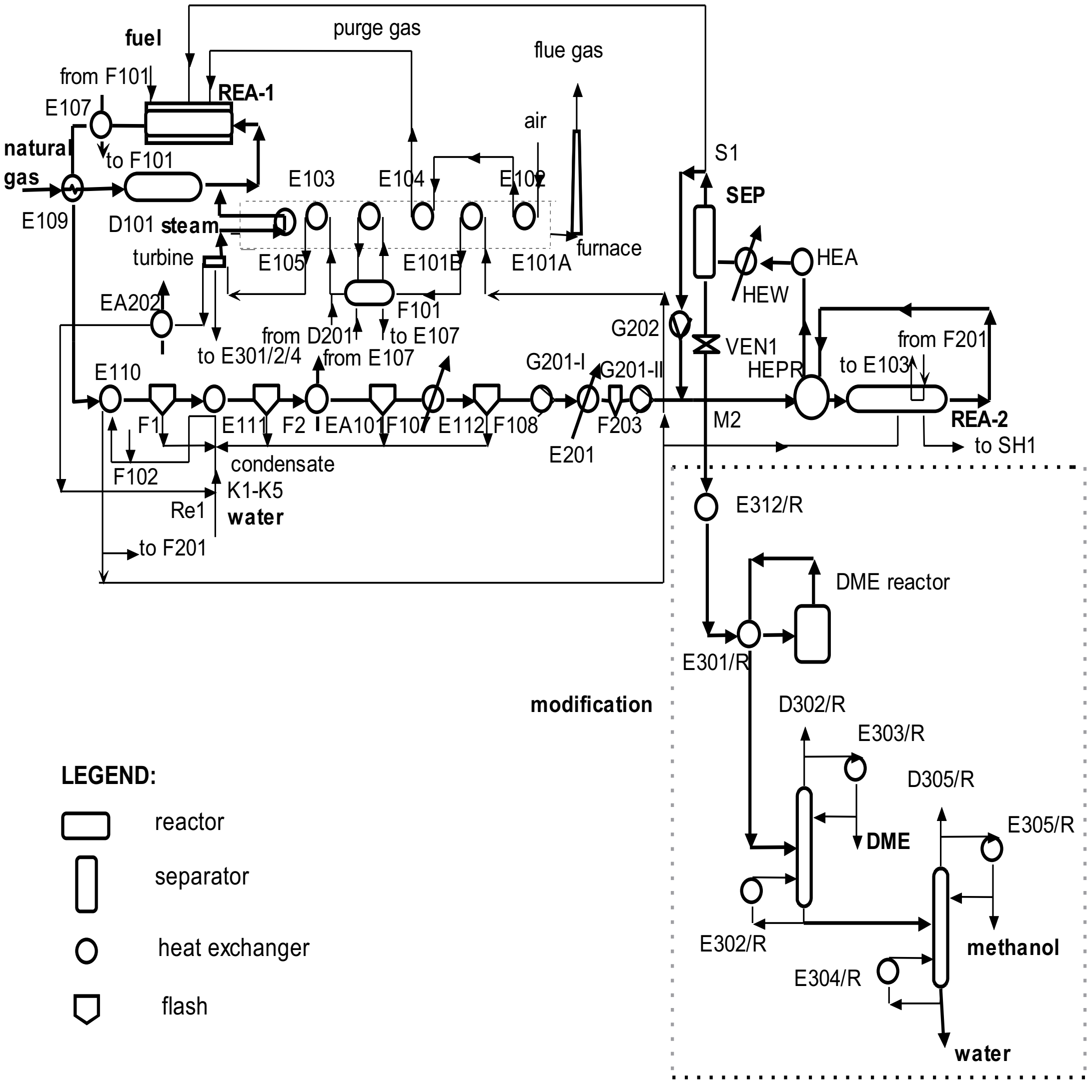

Figure 3: Modified process flow-diagram of a DME and methanol plant

The replacement takes place by using an simulator Aspen Plus, without even testing using a pilot device. Modified syntheses gas conversion can take place during this operation, by applying optimal and upper-limit parametric data within a reformer unit using biogas under a higher temperature (about Δ=30) and lower pressure (about Δ=5). Conversion of methane is higher under these parameters.
The indirect 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. DME is produced by the following reaction:

$2CH_3OH \leftrightarrows CH_3OCH_3 + H_2O \qquad \Delta_r H^{298} = -23.4$ kJ/mol (R9)

The catalytic dehydration of pure, gaseous methanol is carried out within a fixed-bed reactor. The product is cooled over two stages and subsequently distilled to yield pure DME. The non-reactive methanol is separated from the water in a second column, and also recycled or by producing another product (Figure 3).
Indirect DME production is coordinated with the methanol process until liquefied methanol separation, followed by heating the crude methanol to 125 °C, synthesizing in a new DME synthesis reactor (at 170 °C), cooling to 110 °C(Figure 3). In the first existing modified column (5 bar) pure DME could be separated (9,430 kg/h of DME by 10,500 kg/h of amount flow rate of biogas). In the second existing modified column (1 bar) pure methanol and water (1,350 kg/h and 7,180 kg/h) could be separated.

2.3 Economical analysis for replacing methanol production within indirect DME production

This economical analysis included modification of the existing process units and the purchase of a new DME reactor (500,000 EUR/y), modification of six existing the heat exchangers during the purification section (6 · 20,000 = 120,000 EUR/y), and the modifications of two columns (2 · 40,000 = 80,000 EUR/y). The heating in the reformer was higher for Δ = 30 K (30 K · 3,000 EUR/(K·y) = 90,000 EUR/y). The purchase of biogas was 5,000,000 EUR/y at a cost of biogas 60 EUR/t (10.5 t/h · 60 EUR/t · 8,000 h/y). The operating cost was 8,000,000 EUR/y. The total cost was 13,800,000 EUR/y.

The production of DME was 9.4 t/h at a price of 200 EUR/t. The process was operated at 8,000 h/y, therefore income was 15,000,000 EUR/y. The product 1.35 t/h of pure methanol would be sold at a price of 160 EUR/t and income was 1,600,000 EUR/y. Total income was 16,600,000 EUR/y. Total profit was 2,800,000 EUR/y.

3. Conclusions

A methanol production plant could be replaced by a dimethyl ether (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, biogas, coal, or biomass. It has been increasingly used recently as an aerosol propellant to replace chloro-fluoro-carbons, which were found to destroy the ozone layer of the atmosphere. The existing methanol production would be replaced within DME production by making small modifications. The main goal of the replacement is to keep many of the processing units, or make small changes in order to modify them. DME production from biogas could also be effective if the reformer would be operated under a higher temperature. The modification process would produce 88 % of DME and 12 % of methanol from biogas. The modified process would be operated with 2,800,000 EUR/y of total profit.

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