Production of a Green Multi-Purpose Fuel by Reactive Distillation

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Dimethyl ether (DME) is receiving growing attention as a promising alternative and multipurpose green fuel. World production today is primarily by means of methanol dehydration using solid acid catalysts in a fixed bed reactor followed by ordinary distillation columns. In this study, the continuous production via a single reactive distillation (RD) column is studied experimentally in a pilot-scale plant. Kinetics of liquid dehydration of methanol over the sulphonic resin Amberlyst 35 is also studied, using both a batch reactor and a tubular fixed-bed reactor in a temperature range of 100-140°C and a pressure up to 50 bar. The experimental kinetic data are described well by the Eley-Rideal mechanism, and the kinetic parameters are incorporated into a rate-based RD model implemented in the simulation environment Aspen Custom Modeler® (ACM®). The pilot-scale RD experimental results support the feasibility and benefits of the DME synthesis by RD process and are used to validate the predictive RD model. The validated model can be used for future sensitivity analyses and process optimization studies as well as benchmarking compared to the state of the art technology.

1. Introduction

In recent years, DME, which is currently used as raw material for making chemicals and aerosol propellants to replace ozone-destroying chlorofluorocarbons (CFC), is gaining attention as a promising alternative clean fuel to more expensive and polluting conventional fuels. DME is a colourless oxygenate with physical properties similar to LPG (propane/butane). The combined properties of DME, including low auto-ignition temperature, high cetane number, high oxygen content and no impurities of sulphur and metals, make it an excellent fuel for gas turbines, diesel engines and fuel cells. DME combines a high well-to-wheel efficiency with excellent emission. Moreover, it is non-toxic, readily biodegradable and its production, starting from methanol, represents one of the routes for technological innovation in natural gas valorization (Figure 1).

In general, DME is synthesized via methanol dehydration over solid-acid catalysts in a fixed bed reactor followed by several ordinary distillation columns. Several catalysts having activity and selectivity for the catalytic conversion of methanol into DME are well known (Spivey, 1991).The main reaction is:

$$2CH3OH \leftrightarrow CH3OCH3 + H2O \tag{1}$$

The advanced design developed in the last decades in the field of reactive distillation (RD) suggests a promising use of an integrated multifunctional reactor for this process. In a RD column, the two key-steps common to conversion processes, reaction and separation, take place. Since this is an equilibrium-limited reaction system, RD allows the continuous self-separation of reaction products using intrinsic physical/chemical properties, thus increasing the conversion of the limiting reactant. Moreover, in the range of temperature used (120-150°C), no side reactions are expected. In addition, the elimination of one process step implies potential capital savings.

The objective of this study was the experimental investigation in a continuous pilot-scale RD column of the synthesis of DME by catalytic distillation (Sect. 4). There are some studies in the literature on this process, but, to the best of our knowledge, they rely only on mathematical modelling. As a few studies about DME production via catalytic methanol dehydration in the liquid phase with the selected catalyst (sulphonic resin Amberlyst 35) are present in literature, an experimental program was also undertaken to investigate the

reaction kinetics under conditions expected in the RD column (Sect. 2). The experimentally determined reaction kinetic data were used to develop a detailed predictive rate-based model (Sect. 3) and the pilot-scale RD experiments were used to validate the model (Sect. 4). The validated model can be used for future sensitivity analyses and process optimization studies as well as benchmarking compared to the state of the art technology.
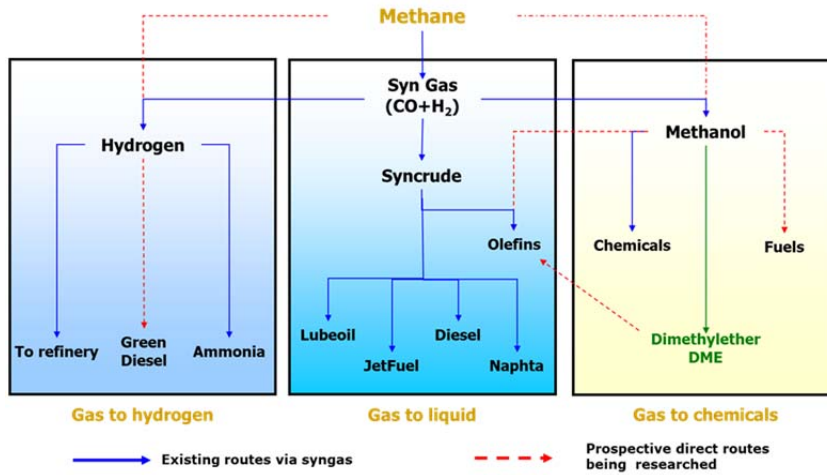

Figure 1: Natural gas valorization routes

2. Evaluation of chemical kinetics

Few and discordant data are present in literature about the kinetic of catalytic dehydration of methanol to DME in the liquid phase over a sulphonic resin of the Amberlyst type (Kiviranta-Paakkonen et al. 1998, An et al. 2004, Hosseininejad et al. 2012). In the present work, the catalytic dehydration has been studied over the sulphonic resin Amberlyst 35 (by Rohm and Haas) both in a batch reactor and in tubular fixed bed reactor filled with catalyst (Figure 2). For both the configurations, the reaction catalyzed by ion exchange takes place in the liquid phase in a temperature range of 100-140°C and pressure up to 50 bar. For the batch experimental investigation, the process variables considered were the reaction temperature, the effect of an initial water concentration and the effect of an inert dilution. The reaction was carried out in a stainless steel autoclave (volume of 450 cm^3 with a catalyst basket volume of 8 cm^3, stirrer speed of 1200 rpm). A thermocouple was mounted inside the autoclave in order to control the reaction temperature. With the tubular reactor experiments, the process variables considered were the reaction temperature and the flow rate of methanol (WHSV, Weight Hourly Spatial Velocity, in the range 0.49 and 7.9 h^{-1}). The reaction was carried out in a stainless steel plug flow reactor (150 mm total length, 90 mm catalyst bed height, 12 mm i.d.) equipped with a thermocouple inside. A HPLC pump (Altech 325) was used for moving the flow along the reactor. The reproducibility of all the experimental data was checked by repeating the experiment three times at the same operating conditions. For both the configurations, the analyses were carried out by gas chromatography using a Hewlett-Packard HP 5890 gas chromatograph (equipped with a Poropak Q column and a thermal conductivity detector). In the range of the selected temperatures no side reactions were observed. According to the experimental evidences and literature works, the reaction pathway can be described by a single site mechanism (Eley-Rideal type). In this approach, the kinetic model is based on the surface reaction as the determining step, and incorporates the effect of competitive chemisorption of water and methanol. The final expression for the formation of DME is given by:

$$r_{DME} = \frac{k_s}{a_{MeOH} + \frac{K_b}{K_a} a_W} \left[a_{MeOH}^2 - \frac{a_W a_{DME}}{K_E} \right] \qquad (1)$$

where, and a_i represents the activity of the i-th component, k_s is the surface reaction constant:

$$k_s = k_{s0}\, exp\left(-\frac{E_a}{RT} \right) \qquad (2)$$

Where R is the gas constant, 8.314 kJ/kmol/K, and T the reaction temperature in Kelvin. K_b/K_a is the ratio of adsorption equilibrium constants of water and methanol:

$$\frac{K_b}{K_a} = exp\left(A + \frac{B}{T}\right) \tag{3}$$

K_E is the equilibrium constant of the global reaction:

$$K_E = exp\left(-2.4348 + \frac{2712.9}{T}\right) \tag{4}$$

The parameters k_{s0}, E_a, A and B (95% confidence limit, standard error of 0.028) have been estimated by means of a combined approach between regression and validation models (Table 1). For this purpose a batch reactor model and a tubular fixed bed reactor model have been developed in ACM[®]13. The thermodynamic model used is the PSRK (Predictive Soave-Redlich-Kwong) group contribution equation of state, where the mixture parameters have been calculated by means of the UNIFAC method. For both the experimental configurations, the model agrees satisfactorily with the experimental results (goodness of the fit, R^2, of 0.991 for the batch experimental data and 0.987 for the tubular fixed bed reactor one). Moreover, the estimated value for the activation energy is comparable with the one (98 vs. 102 kJ/mol) obtained by Kiviranta-Paakkonen et al. Nevertheless, the estimated global rate is lower compared to both the works of Kiviranta-Paakkonen et al. and An et al. According to our opinion, this is due to the fact that An et al. studied the reaction only at the initial condition, while Kiviranta-Paakkonen et al. did not consider the effect of water.

Table 1: Value of DME formation rate parameters with 95% confidence limit.

k_{s0} [kmol/h/kg cat]	E_a [kJ/mol]	A	B [K]
$e^{23.7}$	98	4.67	8.98

3. Simulation model

The pilot scale RD column was modelled based on the rate-based approach (see Taylor and Krishna, 1993, for the mathematical details). The main aspects of the model are briefly summarized in the following. The model implies a stage (segment) description of the column in which the multi-component mass and energy transfer, packing properties and the reaction kinetics are incorporated. In each segment, the gas/vapour-liquid interface was described using the well-known two film model. The steady state mass balance equations were written for each phase with the assumptions that the reaction takes place only in the liquid phase and the reaction term is function of the true catalyst density. The heat balance equations were calculated using mixtures enthalpies. The interfacial transfer equations were written assuming plug flow behaviour for the vapour phase and plug flow with axial dispersion for the liquid phase. All model equations have been implemented in ACM[®]. The thermodynamic (e.g. enthalpy and heat capacity) and transport parameters (e.g. viscosity, thermal conductivity and diffusivity) were calculated using the software package Aspen Properties. The fluid dynamic related parameters (e.g. liquid hold up, pressure drop and mass transfer correlations) and the kinetic parameters (e.g. reaction rate parameters) are packing and process dependent. As for the packing-specific correlations, in particular, the Sulzer BX[®] structured packing was described by using the fluid dynamic and mass transfer correlations from Rocha et al. (1993, 1996). For the Sulzer Katapak[®]-SP structured catalytic packing, the hydraulics and the liquid holdup correlations have been taken from Viva et al. (2011a, 2011b) and Viva and Brunazzi (2009), the mass transfer coefficients from Brunazzi (2015) and the pressure drop from Brunazzi and Viva (2006). As for the kinetics, the founded kinetic model and parameters (see Sect. 2) were incorporated in the reaction term of the equations and implemented into the ACM[®] RD model.

4. Pilot plant experiments and model validation

4.1 Pilot plant

A pilot plant as sketched in Figure 2 was built up to investigate experimentally the rate of integration between the separation and the reaction in a continuous process behaviour. For this reason, the pilot plant was designed to work in two different configurations. In the first one, the reaction takes place inside the pre-reactor while the column works as an ordinary distillation column. In the second configuration, the reactor is by-passed while the column works as a RD column. Both the pre-reactor and the column are made of stainless steel. The pre-reactor is a fixed bed (50 mm internal diameter, 2 m height, filled for 1.73 m with Amberlyst 35 as catalyst and hence with a catalyst load of about 2 kg). The column (50 mm internal diameter), is equipped with an internal reboiler and has an effective packing height of 4 m comprising four sections of 1 m each. The rectifying zone at the top and the stripping zone at the bottom are filled with Sulzer BX[®] packing, while two

middle sections are equipped with either Sulzer BX® packing or Katapak-SP® catalytic packing, according to the working configuration. Amberlyst 35 was incorporated in the catalyst bags of the reactive packing (total catalyst load of about 0.6 kg). All the flow rates are controlled via mass flowmeters. Liquid samples can be taken from all the streams as well as along the column heights and then analysed by means of gas chromatography (HP-6890 for on line acquisitions and HP-5890 for off line acquisitions). Thermocouples are installed along the streams, the reactor and the column height. The vessel is equipped with a heated jacket. All data are recorded by means of a process control system. Several experiments were carried out in the pilot plant with both configurations and the main operative condition are reported in Figure 2c.
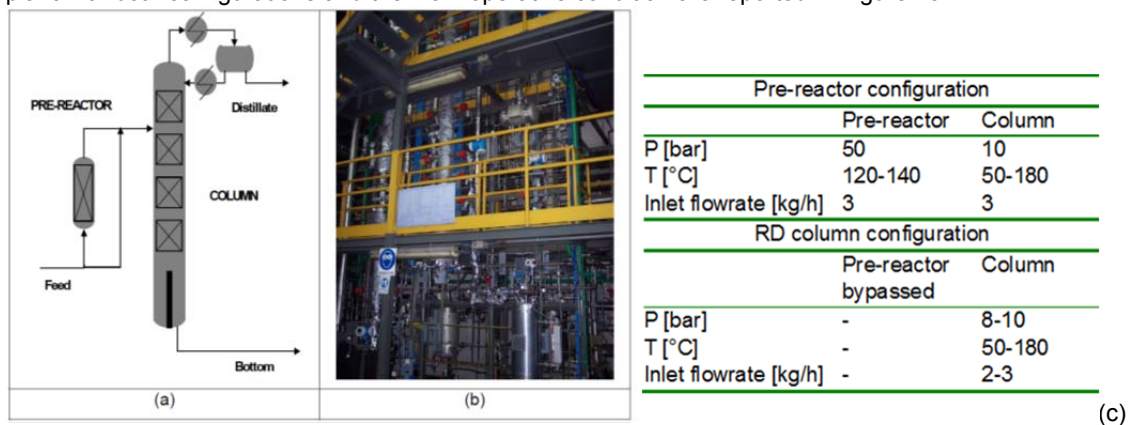

Pre-reactor configuration		
	Pre-reactor	Column
P [bar]	50	10
T [°C]	120-140	50-180
Inlet flowrate [kg/h]	3	3
RD column configuration		
	Pre-reactor bypassed	Column
P [bar]	-	8-10
T [°C]	-	50-180
Inlet flowrate [kg/h]	-	2-3

(c)

Figure 2: Pilot plant: (a) schematic representation, (b) picture and (c) main operating conditions.

4.2 RD column configuration results

The feed stream was pure methanol. The operating variables, reflux ratio (RR) and pressure (P) were changed for the different experiments, while a fixed reboiler duty of 3 kW was used. As an example, the results obtained for a run carried out with a column P of 8 bar, feed flowrate of 3 kg/h and a RR of 15.1, are reported in Figure 3, where the temperature and composition profiles along the column height are shown. The distillate and bottom flow rates were 0.84 kg/h and 2.16 kg/h, respectively, and the conversion obtained was 26.3%. As expected, the concentration of DME, which is the more volatile component with respect to both water and methanol, increases towards the top of the column while water, the least volatile component, increases towards the bottom. Methanol, the intermediate component in terms of boiling point, tends to be retained inside the column and converted to DME and water. A comparison between model predictions and experimental data is also shown in Figure 3. The simulation results, which have been obtained with the RD model (Sect.3), are displayed with continuous lines. A good agreement between experimental and predicted data for both the liquid composition and the temperature profiles can be observed.
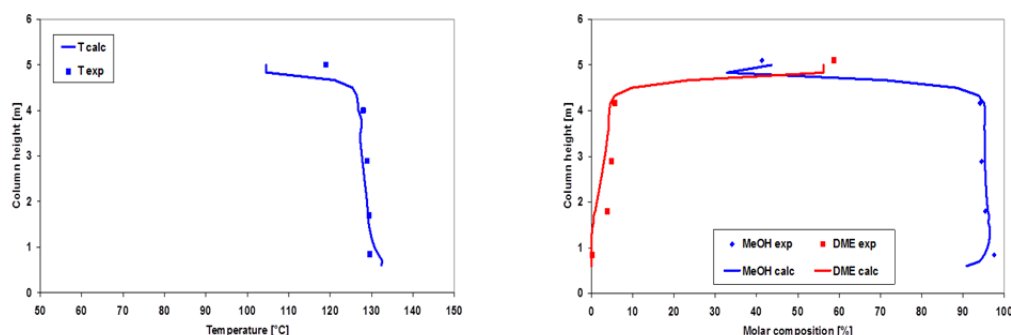

Figure 3: Calculated and experimental profiles with temperature (left) and molar concentrations of DME and methanol (right) along the column.

Figure 4a shows the effect of RR on the distillate composition and a comparison with the model predictions (P=8 bar). The DME concentration in the distillate stream increases proportionally to the RR as expected. Similarly, the temperature of the column head (not shown) decreases with increasing the RR. On the other hand, both the temperature profile in the reactive zone and the conversion rate remain almost constant because of the fixed reboiler duty (3 kW). Figure 4b shows the effect of operating pressure on the temperature

profile in the column. Regardless of the RR, which was varied in the range 8-16 (for P=10 bar), the temperature in the reactive zone of the column was constant, and increased from about 130°C to 140°C with increasing the operating P from 8 to 10 bar. Similarly, a conversion of 48% was obtained with a feed flowrate of 3 kg/h. By decreasing in the feed flowrate from 3 to 2 kg/h (P=10 bar, RR= 15.7), a conversion of 71% was obtained experimentally with a distillate flowrate of 1.1 kg/h and DME molar fraction of 0.9.
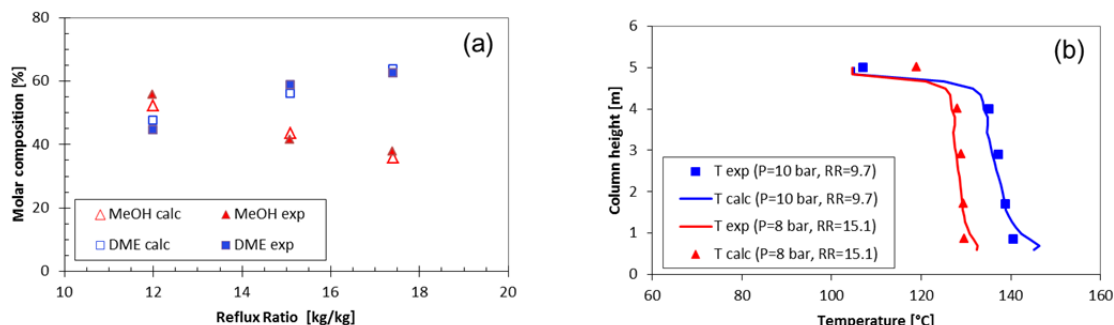

Figure 4: (a) Calculated and experimental distillate composition for varying RR (P=8 bar), (b) Calculated and experimental temperature profiles along the column for varying column working pressure.

4.3 Pre-reactor configuration results

The feed stream to the reactor was pure methanol. The operating conditions, distillate and bottom flowrates for the pre-reactor configuration are summarized in Table 2. The obtained DME conversions were 59.6% (Run I) and 62.9% (Run II). The stream exiting the reactor was fed to the column which was operated as an ordinary distillation column (equipped with Sulzer BX® packing, four sections, height 1 m each). The feed location was not changed with respect to the RD configuration. The product DME left the top of the column together with some of the unreacted methanol. The rest of the methanol left the bottom together with the produced water. Higher DME conversions with respect to the RD configuration were obtained.

Table 2: Pre-reactor configuration operative conditions and obtained conversion, distillate and bottom streams.

Run	Inlet feed flowrate [kg/h]	Feed temperature [°C]	Reactor max temperature [°C]	Reactor pressure [bar]	Column Pressure [bar]	RR	Distillate [kg/h]	Bottom [kg/]
I	3	130	133	50	10	7.8	1.67	1.33
II	3	132	138	50	10	7.1	1.79	1.21

4.4 Comparison between the two configurations

The specific DME production for the two configurations analyzed in this work is compared in Figure 5. It is worth to remind that the catalyst load was about 2 kg in the pre-reactor and just about 0.6 kg in the RD column. Even if higher conversions were obtained with the pre-reactor configurations, the RD configuration allowed to obtain higher specific DME production. The enhanced DME production obtained in the RD configuration is mainly due to the combined effect of reaction and separation.
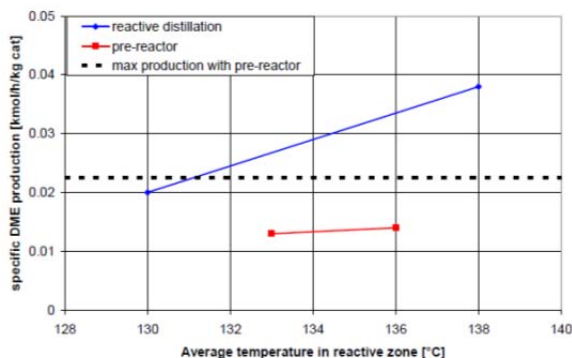

Figure 5. Comparison between the performance of the RD and the pre-reactor configurations.

It is important to highlight that, even if a 100% of methanol conversion is assumed in the reactor (0.0225 kmolDME/kgcat/h), a better specific DME production in the RD configuration is achieved increasing the

average temperature in the reactive zone. Low stability of the chosen catalyst at temperatures above 140°C were observed experimentally. Hence, with the current setup and the chosen catalyst it was not possible to couple high methanol conversion and high DME flow rate in the RD column. Higher methanol conversion and DME flow rate in the distillate could be obtained by combining the pre-reactor with the RD column.

5. Conclusions

The kinetics of liquid dehydration of methanol to DME over Amberlyst 35 as a catalyst was determined experimentally in a temperature range of 100-140°C, using both a batch and tubular fixed bed reactor. The experimentally determined reaction kinetic data were described well by the Eley-Rideal mechanism, in which the surface reaction is the rate-determining step, and were used to develop a detailed RD predictive rate-based model. New RD pilot-scale experimental data were obtained which showed some limitations of the experimental setup and the chosen catalyst, and the following comments can be derived: (a) The low conversion obtained in all the tests was due to the low temperature established in the reactive zone. This low temperature was mainly due to the fact that the maximum working temperature of the chosen catalyst was lower than expected; (b) By increasing the RR, the methanol conversion increased but its concentration was limited by the reaction rate in the reactive zone; the only way to obtain quite pure DME at the top of the column would have been to reduce the distillate flow rate; (c) The pre-reactor configuration showed a high methanol conversion, due to the high catalyst load in the reactor; (d) The RD configuration showed a higher specific DME production, due to the combined effect of reaction and separation; (e) With the chosen catalyst (low stability at temperatures above 140°C) it was not possible to obtain a high methanol conversion together with a high DME flow rate in the RD column.

Overall, the results support the feasibility and potential benefits of the DME synthesis by RD process. The pilot-scale experiments were used to validate a predictive rate-based RD model. The validated model is a useful tool for future sensitivity analyses and process optimization studies as well as benchmarking compared to the state of the art technology.

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