

Energy Integration and Reactive Distillation for Dimethyl Ether Synthesis via Catalytic Dehydration of Methanol

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Distillation is the most widely used separation technique in the process industry. Its main disadvantage is the high consumption of thermal energy: the heat requirements of the distillation columns often represent most part of the total energy cost of the plant, appropriate integration of the distillation columns with the overall process often results in a significant reduction of the energy consumption in many cases.

In this work the concept of the integration has been applied by two integrated design approaches:

- Heat-integrated design; where the distillation system of the process will be heat-integrated with the background process (i.e. integration between the distillation columns and the heat exchangers).
- Reactive distillation design; where the reaction and distillation will be accomplished in the same unit.

The process of dimethyl ether (DME) synthesis by the catalytic dehydration of methanol has been considered as a case study. Heat-integrated design of DME process showed a significant total annual cost saving of 41 % compared to the conventional process, and the reactive DME distillation column design showed highest saving in total annual cost (TAC) by 81 %. In addition to the cost saving of the two proposed designs, also the flue gas emissions have been reduced using process integration methodology, where 51 % of the total emissions has been reduced by the heat-integrated design and 86 % by the reactive distillation column design.

1. Introduction

The dehydration of methanol to produce dimethyl ether, DME falls in a typical class of reaction system. DME is a key intermediate in methanol to gasoline and to olefin processes (Weizhu et. al., 2004), DME has several properties that make it attractive as a fuel or fuel additive for automobile engines (Troy et. al., 2006). The physical properties of DME are similar to those of LPG. The gaseous volume-based heating value is higher than that of methane. The cetane number is between 55 and 60, and is higher than those of diesel fuel. Moreover, DME is non-toxic and reacts quickly in the atmosphere to form CO₂ and water. DME is an ultra-clean alternative fuel that contains no sulfur or nitrogen. The combustion properties of DME are similar to the conventional fuels; hence it is being used as a promising green energy source (Gor et. al., 2020). Presently, DME is also used as feed for the synthesis of chemicals including acetic acid and its esters and other chemicals, as a hydrogen source for fuel cells, as a refrigerant, and as an aerosol propellant in the cosmetic industry.

The potential use of DME as fuel for local power generation, transportation and household gas requires the production of DME on a large scale. Presently, the major process to produce DME on an industrial scale comprises dehydration of methanol using an acidic dehydration catalyst in a fixed bed reactor in the temperature range 250 to 400 °C, followed by rectification of the product stream to recover high purity DME. Recently, there is an increasing need for advanced distillation technologies (e.g. reactive distillation, dividing-wall columns, thermal coupling, heat pump assisted and heat integrated distillation columns) that can significantly reduce the energy usage and the carbon footprint of modern chemical plants (Kiss and Smith, 2020). Reactive distillation (RD) is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that are offered by RD (Zoha et. al., 2014). The suitability of RD for a particular reaction depends on various factors such as

volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible. Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes (Kiss et. al., 2013).

The purpose of this work is to design and simulate the process of synthesizing DME by the methanol dehydration in a conventional DME process, energy-integrated process and RD process. Minimum TAC (capital and operating expenditures) is considered as the objective function for comparison between investigated schemes.

2. Process description

The production of DME is via the catalytic dehydration of vaporized methanol in a fixed-bed catalytic reactor. The equilibrium limited dehydration reaction is shown as:



The outlet of the reactor (stream 6) consists of DME, water and unreacted methanol is cooled and then forwarded to column (T-1) to produce high purity DME, the unreacted methanol is separated from water in column (T-2) and recycled back to the reactor. In the temperature range of normal operation, there are no significant side reactions (Bondiera and Naccache, 1991).

A preliminary process flow diagram for DME manufacture is shown in Figure 1, in which 50,000 t/y plant of 99.6 wt % purity DME product is produced using a single packed bed of catalyst which operates adiabatically (Turton et. al., 1998). Fresh methanol (stream 1) is combined with recycled reactant (stream 13) and vaporized prior to being sent to a fixed-bed reactor operating between 250 and 368 °C. The single-pass conversion of methanol in the reactor is 80 %. The reactor effluent (stream 7) is then cooled prior to being sent to the first of the two distillation columns, T-1 and T-2. DME product is taken overhead from the first column. The second column separates the water from the unused methanol. The methanol is recycled back to the front end of the process, while the water is sent to wastewater treatment to remove trace amounts of organic compounds.

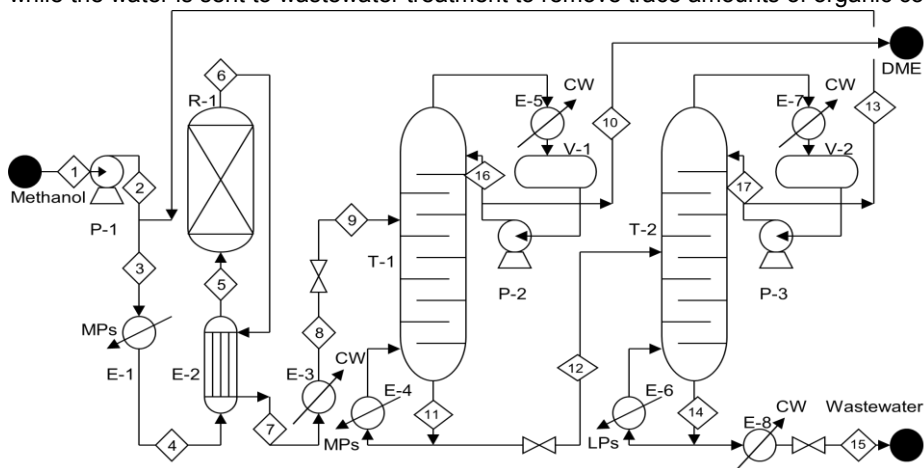


Figure 1: Flow process diagram for DME manufacture from catalytic dehydration of methanol

3. Process simulation approach

The steady state simulation approach is used for design and simulation in Aspen HYSYS environment for conventional DME manufacture process, energy-integrated DME process and RD for DME process. The kinetic model is performed using a heterogeneous unit (Amberlyst 15W) at various temperatures (Song et. al 1998). Process optimization is conducted for all the simulation cases by considering minimum TAC as the objective function and conventional DME manufacture process as the base case. In this work the process feed was assumed to be pure methanol with minimum concentration of 99 % and the rest is only water. This assumption makes the design and simulation of the separation section is easier.

3.1 Thermodynamic model

The thermodynamic fluid package that has been chosen for the vapor liquid phase equilibria is SRK equation of state and UNIQUAC activity model, because it was recommended as an effective fluid package for predicting the equilibrium constant (K) values for this chemical system at low to moderate pressures (Arnab, 2004). This system consists of components have different behavior especially in the liquid phase, where methanol and water are much more polar components than the DME.

3.2 Reaction model and kinetics

The reaction taking place is mildly exothermic with a standard heat of reaction, $\Delta H_{\text{reaction}} (25\text{ }^{\circ}\text{C}) = -11,770$ kJ/kgmol. The equilibrium constant for this reaction at three different temperatures is given as below in Table 1 (Bondiera and Naccache, 1991).

Table 1: Equilibrium constant at different temperatures

Temperature ($^{\circ}\text{C}$)	Equilibrium constant
200	92.6
300	52.0
400	34.7

Significant catalyst deactivation occurs at temperatures above $400\text{ }^{\circ}\text{C}$, and the reactor should be designed so that this temperature is not exceeded anywhere in the reactor. The reaction takes place on an amorphous alumina catalyst treated with 10.2 % silica. There are no significant side reactions below $400\text{ }^{\circ}\text{C}$. Above $250\text{ }^{\circ}\text{C}$, the rate equation is given as: (Bondiera and Naccache, 1991).

$$r_M = k_0 \exp\left(-\frac{E_a}{RT}\right) P_M \quad (2)$$

Where; $k_0 = 1.21 \times 10^6$ kgmol/(m³ catalyst), activation energy $E_a = 80.48$ kJ/gmol, P_M = partial pressure of methanol (kPa), R = universal gas constant (J/mol K) and T = temperature in kelvin.

In order to increase the conversion, dynamic process intensification technology is applied to the reactive distillation of methanol dehydration to DME (Jiyan et. al., 2020) and It indicates that the dynamic process intensification using the nonlinear characteristics of RD can improve the conversion of the system and reduce the energy consumption of RD column.

4. Process simulation cases

The investigated process simulation cases are optimized based on minimum TAC as the objective function which is defined as:

$$\text{TAC } (\$/y) = \text{annualized fixed cost} + \text{operating cost} \quad (3)$$

$$\text{Annualized fixed cost} = \text{fixed cost}/\text{project life} \quad (4)$$

The project life is assumed 10 y and operating cost will include only steam and cooling water costs and operated 350 d/y. The fixed costs calculations are based on the cost correlations extracted from (Douglas, 1988) and updated from mid-1969 to mid-2019 by Marshal and Swift index.

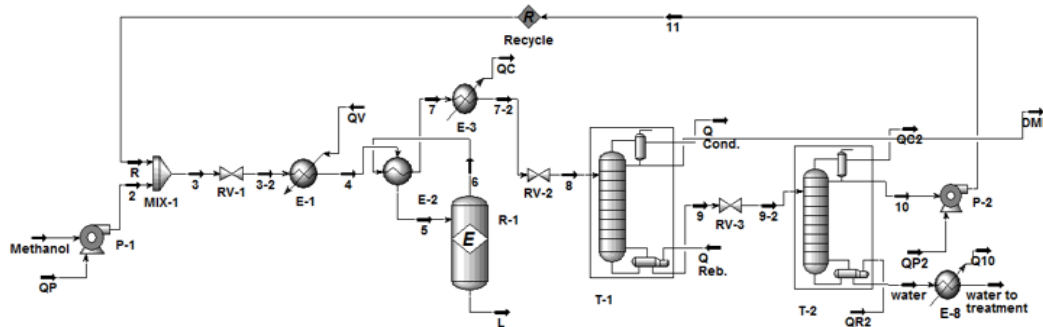


Figure 2: Aspen HYSYS process flow diagram of conventional DME process

4.1 Conventional DME process

The conventional process for producing DME via catalytic dehydration of methanol (Figure 2) consists of reactor zone and distillation train zone, the reactor is simulated based on reaction kinetics and conversion as equilibrium reactor model, the reactor volume is calculated based on 83 % conversion obtained. The reactor outlet temperature from the simulation results was $361\text{ }^{\circ}\text{C}$, and this stream should be cooled prior to being sent to the distillation train. The distillation task is performed first using the short-cut distillation model, where the theoretical number of plates and reflux ratio are determined, then implementing these values into the rigorous distillation column model with target molar composition of 99.5 % DME, 96 % methanol and 99.5 % water.

4.2 Energy-integrated DME process

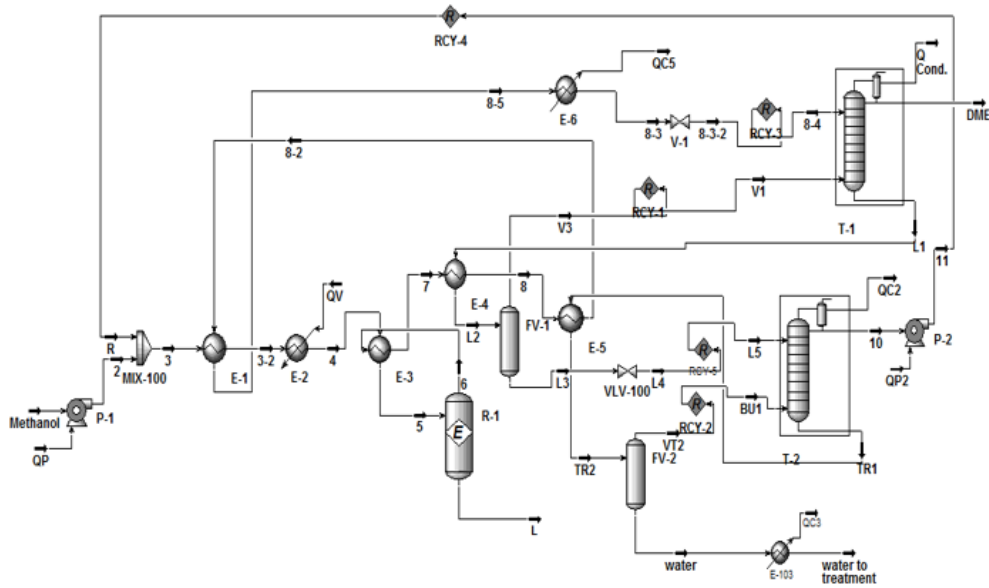


Figure 3: Aspen HYSYS process flow diagram of energy-integrated DME process

The simulation of energy-integrated scheme is similar to the conventional process except for the separation section, where the energy integration of DME process has been performed by utilizing the outlet reactor (stream 6) which is at 361 °C to heat up the reactor feed to the desired reaction temperature (250 °C), this integration already exists in the base case. Providing the DME column (T-1) with the required heat for boiling up, instead of using medium pressure steam. This has been performed in the heat exchanger (E-5). The conducted energy integration will lead to tremendous savings in low pressure steam and cooling water utilities (Figure 3).

4.3 Reactive distillation DME process

RD processes combine both the reaction and separation mechanisms of a process into a single unit known as RD column. Reactants are converted to products with the simultaneous separation of products and recycle of the unused reactants. The main advantages are: reduction of plant items of equipment, increased yield due to overcoming chemical and thermodynamic equilibrium limitations by the continuous removal of products and the recycle of reactants leading to reduction in capital and operating cost.

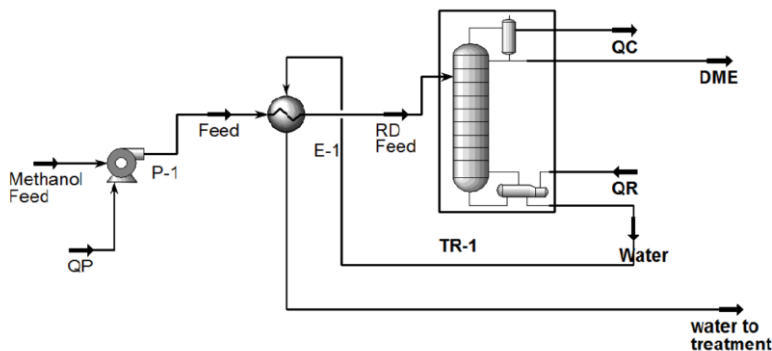


Figure 4: Aspen HYSYS process flow diagram of DME production via reactive distillation

The optimization of the RD column has been performed based on four main parameters: feed temperature, number of theoretical plates, number of reactive plates and location of reactive plates (Figure 4).

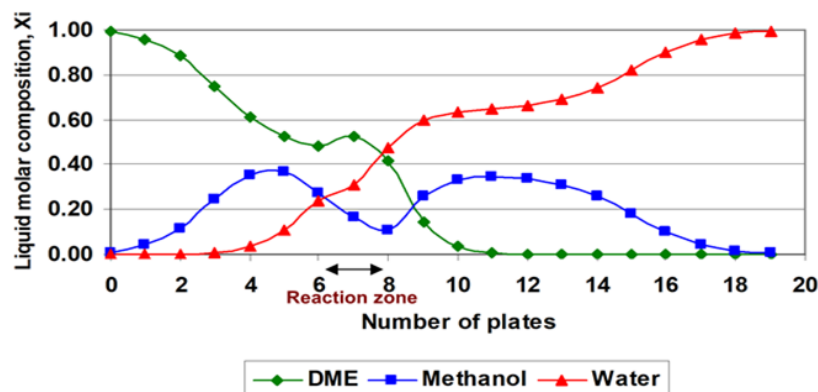


Figure 5: Composition profile in reactive distillation column, molar composition in mol/mol

The composition profile of the RD column is shown in Figure 5, where the DME is concentrated in the rectifying section and reaches its maximum at the top. In the stripping section and especially below the reaction zone, a sharp declining is appeared in the methanol composition curve; this is due to its consumption during the reaction. Water is one of the reaction products and it is the higher boiling point so, it will be separated and concentrated below the reaction zone as shown in the water composition curve. Also, in stripping section the methanol will be concentrated up to a certain limit (36 %), this because of the sharp decrease in the DME concentration in this section. Then while the concentration of water increases the methanol will decrease till reaching its final concentration in the bottom. The same behavior is appeared above the feed and reaction zone, where the methanol will be increased up to (38 %), this because of the decrease in the water composition, and then while the DME is increased the methanol will decrease until reaching its final concentration at the top product.

5. Results and discussion

The economic results are summarized in Figure 6. Based on fixed, operating costs and TAC, it is clear that for the DME process design and manufacture the RD column is the best option with the highest savings in TAC (81 %) compared with the conventional DME process. Energy-integrated process is very good candidate with 41 % saving in TAC especially for revamping of existing DME plants.

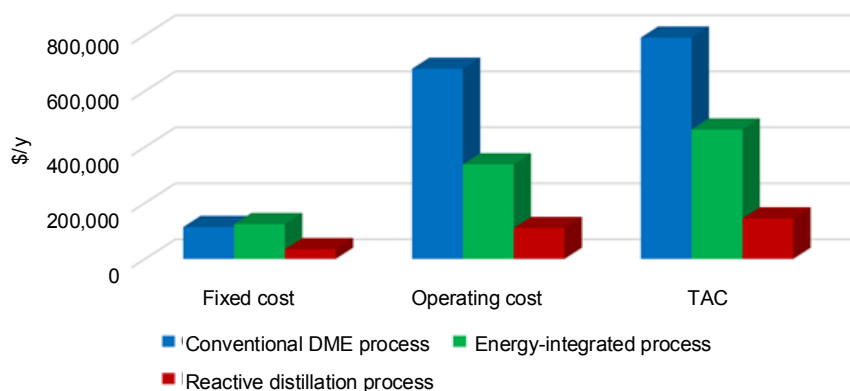


Figure 6: Economic comparison of different DME process scheme

Table 2: Flue gas emissions of different process scheme

	Heating rate (MW)	CO ₂ emissions (kg/h)	SO _x emissions (kg/h)	NO _x emissions (kg/h)	Emissions saving (%)
Conventional DME process	5.32	1072	0.79	0.25	0.0
Energy-integrated process	2.56	522	0.38	0.13	51.3
Reactive distillation process	0.73	148	0.11	0.04	86.2

The flue gas emissions (CO_2 , SO_x , and NO_x) that are generated from the furnaces by the combustion processes of the utility systems are estimated according to the emission factors of steam boilers per unit of heat delivered to the process for natural gas fuel had been obtained by (Smith and Delaby, 1991) using mathematical models based on the stoichiometric of the combustion reaction. The results of emissions saving are shown in Table 2 and they indicate that energy integration and process intensification play important role not just in reducing the total cost of the chemical processes industries but also in reducing or minimizing the utility waste associated with the chemical process industries.

6. Conclusions

DME synthesis by the catalytic dehydration of methanol has been studied in this work using steady state simulation approach, the major conclusions are summarized below:

- The reactive DME distillation column showed highest savings in the capital cost of 69 % and operating cost of 84 % as well as the saving in TAC was 82 % compared with the conventional base case.
- Energy-integrated design of DME process showed a significant energy and operating cost savings of 50 % and TAC saving of 41 % compared to the base case.
- In addition to the cost savings of the two alternative designs, also the flue gas emissions have been reduced in tremendous values following the trend of energy savings with 86 % saving for reactive distillation process and 51 % for energy-integrated process.

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