A novel design of reactive distillation configuration for 2-methoxy-2-methylheptane process

Arif Hussain[1], *Muhammad Abdul* Qyyum[1], *Le Quang* Minh[1], *Hong* Jimin[1], and *Moonyong* Lee[1,*]

[1]Process System Design & Control Laboratory, School of Chemical Engineering, Yeungnam University, Dae-Dong 214-1, Gyeongsan, 712-749, South Korea

Abstract. The study aims to reveal the possibility of reactive distillation (RD) in the 2-methoxy-2-methylheptane (MMH) production process. MMH is getting more industrial and academic interests as a gasoline additive to replace methyl tert-butyl ether. Traditionally, MMH is obtained by carrying out the reaction in the reactor followed by three distillation columns. The high yield of MMH could be achieved by keeping the large reactor size or by using the large excess of 2-methyl-1-heptene (MH). Both former and latter strategies are associated with the high capital and operating costs. To solve these problems, this study proposed an innovative RD configuration to take synergistic benefits of reaction and separation involved. This innovative RD configuration allows the production of MMH with significantly lower capital, operating and total annual costs. For desired MMH yield, the result demonstrates that the proposed RD configuration can reduce energy, capital, and total annual costs up to 7.7, 31.3, and 17.1%, respectively, compared to a conventional process. Furthermore, the influence of some important design parameters on the RD column performance was also explored to overcome the temperature limitation of acid resin catalyst inside the reactive zone of the RD column.

1 Introduction

The invention of the lead-containing compounds to be added to gasoline for reducing the knocking tendency has gained tremendous importance [1]. Methyl tert-butyl ether (MTBE) was considered as an important "oxygenate" to raise the oxygen content of gasoline. However, the restrictive energy and environmental policies have banned the use of MTBE as a fuel additive in gasoline due to its solubility in water and its widespread detection in groundwater [2]. This led to raising interests in higher molecular weight ethers that will exhibit significantly decreased solubility. One possible alternative is the chemical MMH produced through etherification reaction between MH and MeOH. However, the main barrier of this approach is the high investment and operating costs associated with the conventional process of making MMH that uses the reactor followed by three sequenced distillation columns. The high yield of the desired product could be achieved by keeping the large reactor size or by using the large excess of MH. Both former and latter strategies are associated with the high capital and operating costs. For the specified yield of MMH, Luyben [3] studied the optimum

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[*] Corresponding author: mynlee@ynu.ac.kr

values of reactor vessel sizes and the recycle flow rates to minimize the total annual cost. Furthermore, Griffin et al. [4] studied the effect of high and low values of an equilibrium constant on the optimum operating conditions for MMH plant. All these researchers used the conventional MMH process in their studies. The reaction mechanism of MMH process that includes both the equilibrium limited and irreversible reaction is a possible candidate for a more complicated multifunctional reactor technology like RD that offers significant advantages over the conventional reactor-column sequence. However, the RD column design for the MMH process is challenging due to the maximum allowable temperature (by 400 K) of its acid resin catalyst. By designing the innovative equipment and implementing more energy-efficient production processes, the possible solutions to overcome the constraints imposed on various raw materials and products can be found. Process intensification is the novel design strategy aiming to improve existing processes by reducing the equipment sizes, energy consumption, and overall plant footprint. RD falls into the category of process intensification because of its potential to integrate a conventional reactor column sequence into a single shell to improve the performance of reactive processes. Presently, more than 150 RD columns with annual capacities of 100-3000 ktonnes are being operated worldwide [5]. A huge scholarly data deals with the modeling, simulation, and industrial applications on RD can be found elsewhere [6–9]. The industrial RD columns for etherification reactions especially for MTBE process has grown tremendously and globally over the last decades with improved capital and operating savings. The MTBE process is, in fact, the largest application of RD in terms of a number of columns and production capacity [10], but the future is uncertain due to the legislation that prohibits its use. The growing interest in the chemical MMH to replace MTBE needs to increase capacity in a cost-effective way to meet the accelerated growing market demand. This study proposed an innovative RD configuration that allows the production of MMH with significantly lower capital and operating costs. The temperature limitation while designing RD configuration was overcome by selecting an appropriate reactive zone, feed locations, reflux ratio, catalyst holdup, and suitable column pressure. This study emphasized the potential benefits of the proposed RD column configuration to replace the conventional energy-intensive MMH production process.

2 Process studied

The proposed study is based on the conventional flowsheet (Fig. 1) for making MMH, taken from the work of Luyben [3] and Griffin et al. [4] to verify the feasibility of RD configuration. The reaction mechanism involves the desired reversible reaction (Eq. 1) between methanol (MeOH, CH_3OH) and 2-methyl-1-heptene (MH, C_8H_{16}) to form 2-methoxy-2-methylheptane (MMH, $C_9H_{20}O$). The same reactants producing dimethyl ether (DME, C_2H_6O) and 2-methyl-2-heptanol (MHOH, $C_8H_{18}O$) as by-products in an undesirable irreversible reaction (Eq. 2).

$$CH_3OH + C_8H_{16} \leftrightarrow C_9H_{20}O \tag{1}$$

$$2CH_3OH + C_8H_{16} \rightarrow C_2H_6O + C_8H_{18}O \tag{2}$$

The corresponding rate equations in terms of the mole fraction for the desired and undesired reactions are represented by (Eq. 3) and (Eq. 4), respectively:

$$R_D = k_{Df}X_{MeOH}X_{MH} - k_{Dr}X_{MMH} \tag{3}$$

$$R_U = K_U(X_{MeOH})^2 \tag{4}$$

where k_{Df} and k_{Dr} are the forward and backward rate constants for the desired reaction. K_U is the rate constant for the undesired reaction. Table 1 lists the values of reaction rate constants and the activation energies for both reactions [4].

Table 1. Kinetic parameters [4].

		kmol s^{-1}kgcat^{-1}			kJ/kmol
k_{Df}	=	6.7×10^7	E_{Df}	=	90000
k_{Dr}	=	2.1×10^{-6}	E_{Dr}	=	900
k_U	=	1.3×10^9	E_U	=	105900
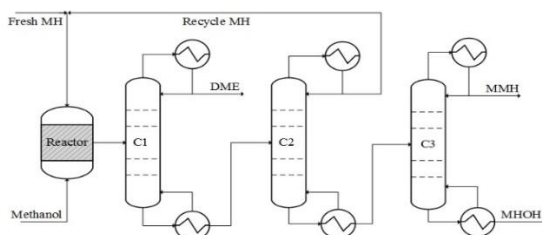
Fig. 1. Conventional flowsheet of making MMH [3–4].

3 Phase equilibrium

All the unit operations were simulated using Aspen Plus® built in "UNIQUAC" physical property method. The components MMH and MHOH were generated using the molecular structure (Fig. 2) because they were not available in the Aspen databank. The result of the base case was retrieved to confirm the phase equilibrium diagrams for both reaction and separation. Figs. 3a and 3b show the T-xy diagrams for separating DME/MeOH and MMH/MHOH used in this simulation, respectively.
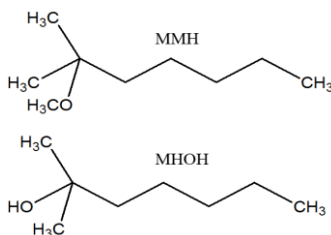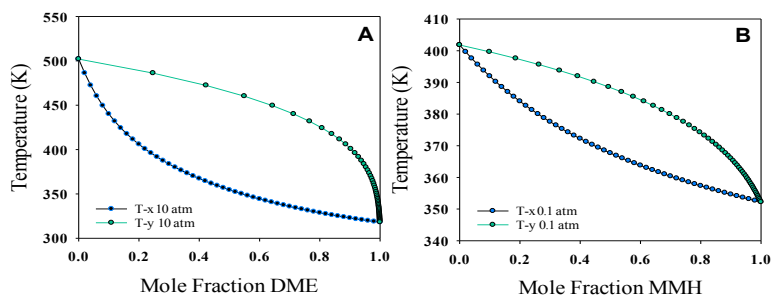

Fig. 2. Molecular structure for MMH and MHOH.

Fig. 3. VLE diagram (A) DME/MeOH at 10 atm, and (B) MMH/MHOH at 0.1 atm.

4 Proposed configuration

4.1 RD–Column

The newly proposed configuration based on RD column is shown in Fig. 4. The RD column has total 35 stages. There is no rectifying section, the reactive zone is between stage 2–12 and the stripping section at the bottom. The stages are numbered according to Aspen Plus stage notation with stage 1 and 35 being the condenser and reboiler, respectively. The fresh MeOH stream as a low boiling point reactant is fed on stage 13, while the fresh MH stream as a heavier reactant combined with a recycle stream that gives the total of 128.98 kmol/h is introduced on stage 1. The column is operated at 1 atm. The high MH/MeOH ratio makes this process be a suitable candidate for the RD implementation. A total estimated load of 291.6 kg of acid resin catalyst per stage was used within the reactive zone.

4.2 Column–C2

The column C2 serves the purpose of delivering high purity DME to be utilized as a green energy source as a distillate product, while the unreacted MeOH and MH to be recycled from the bottom. The distillate from the RD column is fed to stage 5 of a 12-stage distillation column. The normal boiling point of DME is 248.2 K. The operating pressure of C2 column is set at 10 atm, that permits the use of cooling water in the condenser. The small distillate stream of 0.513 kmol/h with 99.9 mole % DME gives the condenser duty of 0.0044 MW. The bottom stream contains the unreacted MeOH and MH, which is recycled to RD column. The reboiler duty was 0.86 MW with the base temperature of 501.9 K that uses high–pressure steam. The column diameter from Aspen tray sizing was 0.9 m.
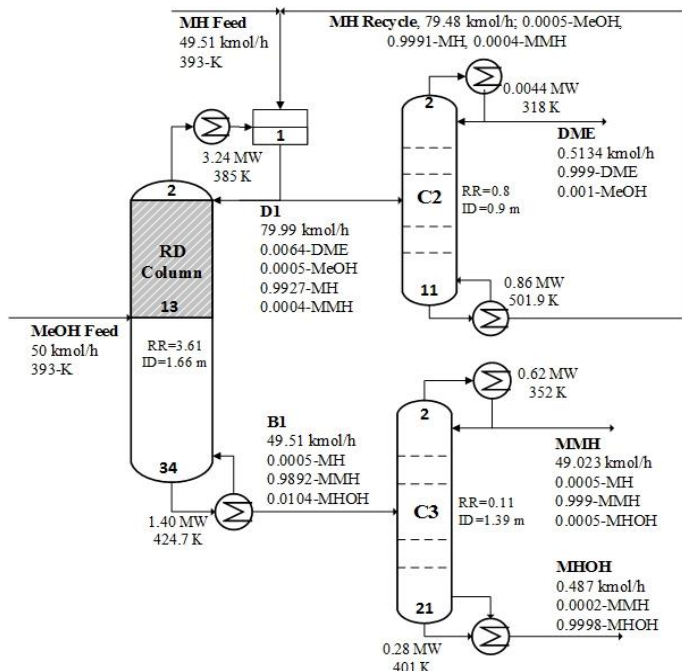
Fig. 4. Proposed RD configuration for MMH process.

4.3 Column–C3

The column C3 receives a feed stream from the bottom of RD column. This column has total 22 stages with stage 12 being the feed location. The distillate product was 49.02 kmol/h with 99.9 mole % MMH. The bottom was 0.487 kmol/h with 99.9 % of undesired MHOH. This column operates at 0.1 atm and gives 0.62 and 0.28 MW condenser and reboiler duties, respectively. The reflux drum temperature was 352 K, and the bottom temperature was 401 K that uses the medium pressure steam. The column diameter was estimated at 1.39 m.

5 Design economics

For an economic evaluation, the capital costs (column shell, heat exchangers, catalyst) and the energy costs (steam in the reboilers) were taken into consideration. The economic assessment of the proposed configuration for the desired yield of MMH was carried out in terms of total annual cost (TAC), expressed by Eq. 5:

$$\text{TAC} = \frac{\text{Capital cost}}{\text{Payback period}} + \text{Energy Cost} \tag{5}$$

The basis for economics and equipment sizing are summarized in Table 2 taken from Douglas [11] and Turton et al. [12]. The payback period of three years and energy costs for LP, MP, and HP steams were taken similarly as in the base case for a fair comparison.

Table 2. Basis for economic and equipment sizing.

Column Shell Cost	$17640 * (D)^{1.066} * (L)^{0.65}$
Column Diameter (m)	Aspen Tray Sizing
Column Length (m)	NT trays with 0.61m spacing plus 20% extra length.
Heat Exchanger Capital costs	
Condenser	
Capital Cost ($)	$7296 * (A_{con})^{0.65}, A_{con} = \dfrac{Q_{con}}{U_{con} + \Delta T_{con}}$
Heat Transfer Coefficient	$U_{con} = 0.852 \text{ kW}/(\text{K}.\text{m}^2)$
Differential Temperature (K)	$\Delta T_{con} = \text{Reflux Drum Temp} - 318 \text{ K}$
Reboiler	
Capital Cost ($)	$7296 * (A_{reb})^{0.65}, A_{reb} = \dfrac{Q_{reb}}{U_{reb} + \Delta T_{reb}}$
Heat Transfer Coefficient	$U_{reb} = 0.568 \text{ kW}/(\text{K}.\text{m}^2)$
Differential Temperature (K)	$\Delta T_{reb} = 34.8 \text{ K}$
Energy Cost ($/year)	LP steam = $7.78/GJ MP steam = $8.22/GJ HP steam = $9.88/GJ
Catalyst Cost ($)	$10/kg

6 Results and discussion

6.1 RD column

The bottom product at stage 35 produces the desired MMH and small quantity of undesired MHOH product. The distillate product is a small quantity of DME which is produced as a by–product together with unreacted MeOH and excess MH to be recycled. MeOH and MH conversions are 99% and 38.5%, respectively. The last stage temperature of the reactive stage was 399 K, which satisfied the temperature constraint in the reactive zone. The reboiler duty was 1.40 MW with the bottom temperature of 424.7 K, which uses the medium pressure steam. The column diameter from Aspen tray sizing was 1.66 m. Figs. 5a and 5b show the temperature and composition profile of RD column.
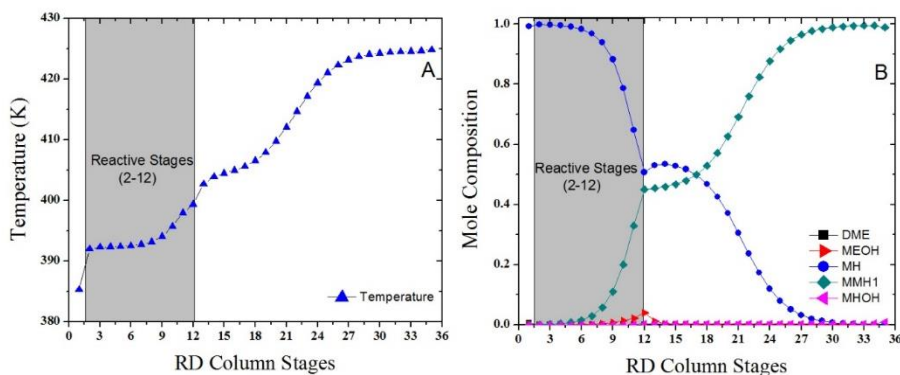
Fig. 5. (A) Column temperature profile and (B) Mole composition profile.

6.2 Column C2

The distillate contains the small flow rate of 0.5149 kmol/h with 99.9% DME purity. The condenser duty was 0.0044 MW with reflux drum temperature of 318 K. The bottom stream is mostly excess MH with the small amount of unreacted MeOH that is recycled back to the RD column. The reboiler duty was 0.859 MW with the base temperature of 501 K. The column diameter from Aspen tray sizing was 0.9 m. Figs. 6a and 6b show the temperature and composition profiles of C2 column, respectively.
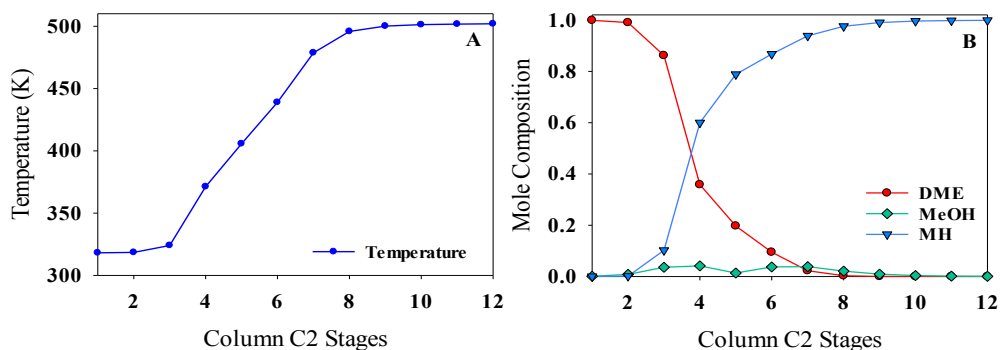

Fig. 6. Column C2 (A) Temperature profile, and (B) Mole composition profile.

6.3 Column C3

The column separated the bottom stream from the RD column into MMH and MHOH. The distillate is 49.02 kmol/h with 99.9% MMH. The condenser duty was 0.62 MW with reflux drum temperature of 352 K. The bottom stream is 0.4870 kmol/h with 99.99 % MHOH. The reboiler duty was 0.28 MW with the base temperature of 401 K that uses the medium pressure steam. The column diameter was 1.39 m. The temperature and composition profiles of C3 column are shown in Figs. 7a and 7b, respectively.
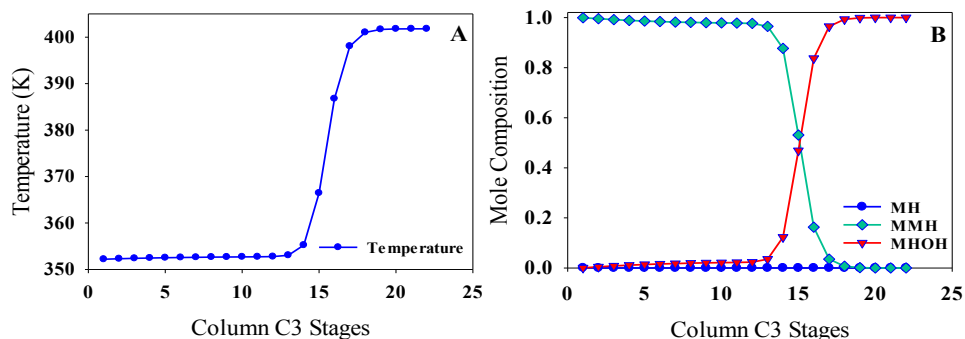
Fig. 7. Column C3 (A) Temperature Profile, and (B) Mole composition profile.

7 Economic analysis

The economic analysis was carried out for the proposed RD configuration in terms of TAC. For the desired yield of MMH, the proposed RD configuration can reduce energy, capital, and TAC up to 7.7, 31.3, and 17.1%, respectively. Table 3 summarized the economic analysis of the proposed RD configuration.

Table 3. Economic comparison of RD configuration with the base case.

Economic Analysis	Base Case	Proposed Case
Reactor Cost		
Reactor Capital (106$)	0.1091	-
Catalyst (106$)	0.12	-
C1/ RD Column		
H(m)	8.05	24.15
ID (m)	1.084	1.66
Catalyst Cost (106$)	0	0.035
Column Vessel Cost (106$)	0.095	0.389
Exchanger Costs (106$)	0.128	0.201
Energy Costs (106$/year)	0.4424	0.398
C1 Column		
H(m)	30.01	7.32
ID (m)	2.044	0.9
Column Vessel Cost (106$)	0.5668	0.077
Exchanger Costs (106$)	0.213	0.09
Energy Costs (106$/year)	0.2244	0.267
C2 Column		
H(m)	15.37	14.64
ID (m)	1.589	1.39
Column Vessel Cost (106$)	0.249	0.215
Exchanger Costs (106$)	0.1284	0.087
Energy Costs (106$/year)	0.141	0.079
Total Capital Cost (106$)	1.6082	1.105
Total Energy Cost (106$/year)	0.808	0.745
TAC (106$/year)	1.344	1.114

8 Conclusions

An energy efficient configuration based on RD column was proposed for MMH production. A desired yield of MMH in the conventional process is usually obtained by keeping the large reactor size or by using the large excess of MH. Both strategies are expensive in terms of capital and operating costs. The proposed configuration uses the RD technology to obtain the desired MMH yield at significantly lower capital, and operating costs. The result demonstrates that the RD configuration can significantly reduce energy, capital, and total annual cost by 7.7, 31.3, and 17.1%, respectively compared to the conventional process.

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