

# Feasibility Study of Reactive Distillation Configuration for 2-Methoxy-2-methylheptane

Arif Hussain, Moonyong Lee\*

School of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea.  
mynlee@yu.ac.kr

Owing to the strict environmental policies which has banned the use of methyl-tert-butyl-ether (MTBE), a novel gasoline additive 2-methoxy-2-methylheptane (MMH) that possess higher molecular weight and low solubility in water was proposed. Based on process intensification (PI) principles, the conventional process of MMH was examined for reactive distillation (RD) configuration. The optimal design of reactive distillation configuration for 99 % MMH yield was proposed and compared with the conventional reactor-separation-recycle configuration. For desired MMH yield, process intensification using RD brings significant savings in energy, and total annual costs by up to 14.85, and 8.71 %, respectively, in comparison with the conventional energy intensive scheme.

## 1. Introduction

To advance the cleaner consumption of gas and thus diminishing the unsafe discharges from vehicles, the ether 2-methoxy-2-methylpropane (MTBE) have had a major role during the last two decades (Srivastava and Hancsok, 2014). However, it has been banned in California by the end of year 2003 because of its widespread detection in groundwater (Anderson and Elzinga, 2014). The strict environmental policies imposed on MTBE has forced the existing refineries in the world to find some viable alternatives that possess low solubility in water and are able to produce high octane gasoline. In this context, a higher molecular weight ether 2-methoxy-2-methylheptane (MMH) is proposed that exhibit low solubility in water (Griffin et al., 2009). The component 2-methoxy-2-methylheptane (MMH) is produced by reversible etherification reaction between 2-methyl-1-heptene (MH) and methanol (MeOH). The reactants (MH) and (MeOH) also produces dimethyl-ether (DME) and 2-methyl-2-heptanol (MHOH) in an undesired irreversible reaction. The yield of the desired product (MMH) in the conventional process can be enhanced by either keeping the large reactor volume or by maintaining the large recycle flow rate of 2-methyl-1-heptene (MH). Both strategies lead to high investment and operating costs. Process intensification can bring enormous benefits to the existing processes by effectively utilizing the energy thereby reducing the plant capital investment (Hussain et al., 2017). Reactive distillation is proven to be an excellent process intensified configuration because it has ability to integrate the conventional reactor-column sequence thereby reducing the plant capital and operating investments (Harmsen, 2007). Recently, (Lu et al., 2017) studied reactive distillation process for methyl acetate synthesis by optimizing various design variables to minimize the total annual cost (TAC). In addition, (Chang and Lee, 2017) explored potential benefits of reactive distillation using feed-splitting arrangement for diphenyl carbonate process. The application of industrial RD columns for the ether 2-methoxy-2-methylpropane (MTBE) have shown tremendous growth but the future is uncertain due to its high solubility (Luyben, 2008). For a specified yield of 99 % MMH, (Luyben, 2010) studied the optimal design that minimizes the TAC based on conventional reactor-column configuration. The conventional energy intensive process of MMH necessitates an increase in the capacity in a cost-effective way through the principles of process intensification. This study proposed an innovative RD configuration that has shown significant savings in energy and total annual costs when compared to the existing conventional process of MMH. Furthermore, the influence of various design parameters are carefully examined to overcome the temperature limitation of acid resin catalyst.

## 2. Conventional Process

The traditional process of MMH production features a fixed bed reactor where the liquid phase reaction occurs. The reactor effluent is fed to the three distillation column connected in a direct sequence. Higher yield of MMH in the conventional reactor-column sequence is obtained either by keeping the large reactor volume (high capital investment) or large recycle flow rate of 2-methyl-1-heptene (high operating cost). Both strategies are major cost factors in the conventional process. Another constrained of MMH process is the temperature limitation of its acid resin catalyst which is limited to 423 K to sustain catalyst activation. The conventional process reported by (Luyben, 2010) based on optimum reactor size and recycle flow rate in terms of minimum TAC is shown in Figure 1. The feasibility of reactive distillation is based on the reactants flow rates and MMH production rate from (Luyben, 2010) work to correlate the key economic indicators.

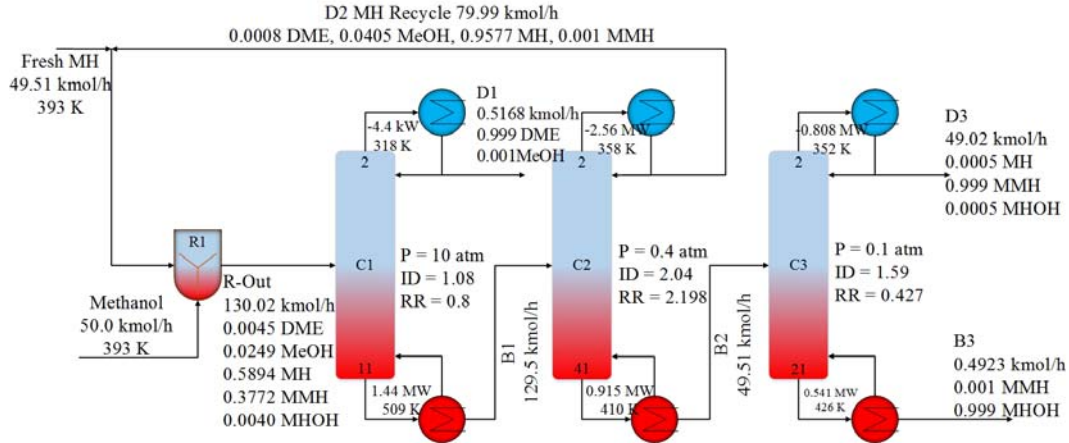


Figure 1: Conventional MMH production process (Luyben, 2010).

## 3. Reaction Mechanism

The production of 2-methoxy-2-methylheptane (MMH) from 2-methyl-1-heptene (MH) and methanol (MeOH) is a non-equimolar, reversible reaction, and can be expressed as follows:



The main reaction is also associated with an irreversible reaction, producing dimethyl-ether (DME), and 2-methyl-2-heptanol (MHOH) as a by-product and can be expressed as:



The corresponding rate equations for above reactions are:

$$R_D = k_{Df} x_{MeOH} x_{MH} - k_{Dr} x_{MMH} \quad (3)$$

$$R_U = k_2 x_{MeOH}^2 \quad (4)$$

The kinetic parameters are generated by fitting pseudo-homogeneous model based on mole fraction shown above to kinetic data reported by (Karinen and Krause, 1999).

$$k_{Df} = 6.7 \times 10^7 \exp\left(\frac{-90000}{RT}\right) \quad (5)$$

$$k_{Dr} = 2.1 \times 10^{-6} \exp\left(\frac{-900}{RT}\right) \quad (6)$$

$$k_2 = 1.3 \times 10^9 \exp\left(\frac{-105900}{RT}\right) \quad (7)$$

The reaction chemistry and the kinetic parameters of the MMH process are possible candidate for a reactive distillation column as confirmed in an article by (Griffin et al., 2009).

## 4. Proposed Configuration

The steady state optimal design of the proposed RD configuration is shown in Figure 2. All the unit operation are simulated using Aspen plus UNIQUAC thermodynamic model as suggested in the base case by (Luyben,

2010). The fresh MeOH and fresh MH together with recycle from column C1 was introduced into 35 stage RD column. The reactive zone is between stage 2 to 12. The distillate product of the RD column contains unreacted MeOH and excess MH that is fed to 12 stage column C1. Column C1 separated the DME in the distillate and excess MH is obtained from the bottom to be recycled back to RD column. The bottom of the RD column produces the main product MMH together with small amount of MHOH which is by-product. The bottom of the RD column is fed into 15 stage column C2. The column C2 separates the MMH and MHOH as a distillate and bottom products, respectively.

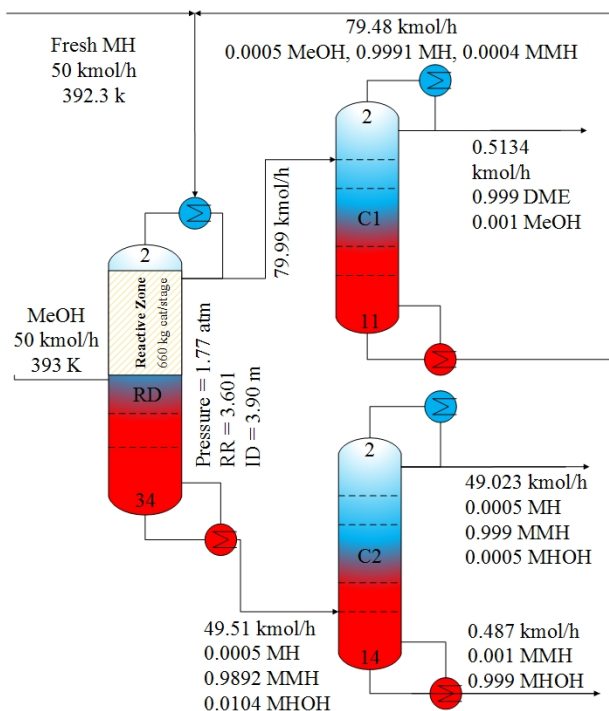


Figure 2: Optimal flowsheet of the proposed RD configuration.

#### 4.1 Selection of operating pressure

At different operating pressures, the catalyst amount on the reactive stages are manipulated for obtaining the desired MMH yield of 99 % keeping in view the upper limit of catalyst deactivation temperature. The kinetic parameters of MMH reaction reveals that high temperature favour conversion. This means that higher operating pressure actually enhance conversion due to high temperature on the reactive trays as illustrated in Figure 3a. However, the selectivity towards the desired product decreases because of the inverse relationship between the conversion and selectivity as shown in Figure 3b. The reboiler duty decreases as the pressure increases as shown in Figure 3c because the reaction mostly occur towards the bottom of the reactive zone which is favourable in terms of internal heat integration between the reaction and the separation (Wang et. al., 2010). Figure 3d illustrate that higher RD operating pressure requires less catalyst to achieve 99 % MMH yield. It is noteworthy to mentioned that operating pressure of 1-atm require 3300 kg catalyst per stage to achieve 99 % yield. The corresponding diameter of the RD column that satisfied the hydraulic limitation to accommodate this catalyst is estimated at 8.76 m. This is a very large distillation column and it require large capital investment. The temperature profile at different operating pressure is shown in Figure 3e. It can be seen that up to the operating pressure of 1.77 atm, the temperature of the reactive zone is within the permissible range where catalyst deactivation can be avoided. At 2.0 atm, the temperature of the reactive zone being exceeded. Therefore, the optimum pressure was selected at 1.77 atm where the reboiler duty is minimum. The required catalyst to achieve 99 % MMH yield at 1.77 atm is estimated at 660 kg catalyst per stage. The corresponding column diameter to accommodate this catalyst is estimated at 3.90 m.

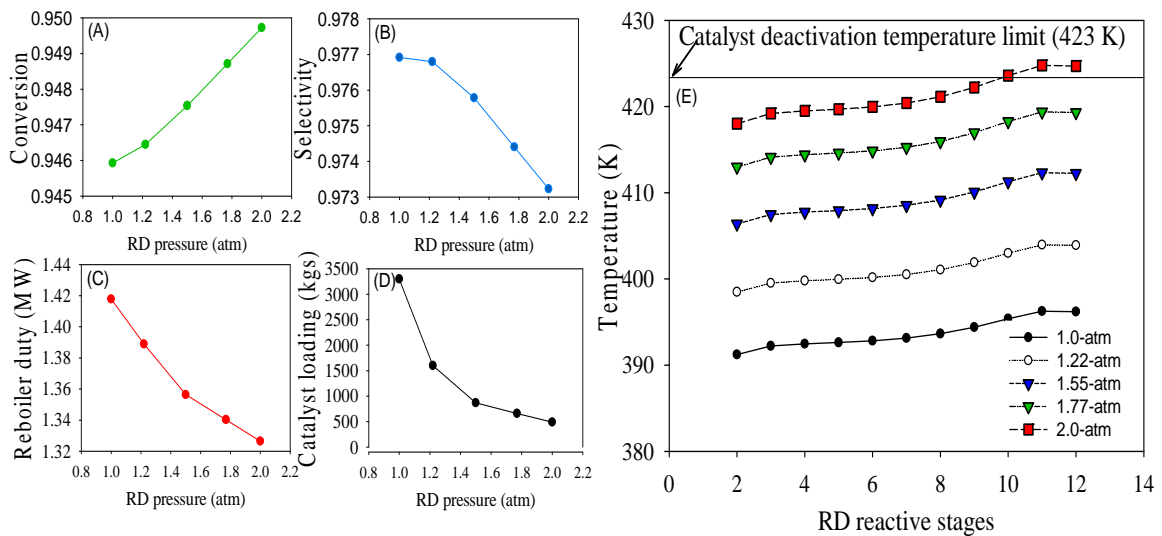


Figure 3: Effect of RD pressure on (A) conversion, (B) selectivity, (C) reboiler duty, (D) catalyst loading, (E) reactive zone temperature.

Table 1 summarized the optimal design parameters for the simulation.

Table 1: Specification for the simulation of the MMH reactive distillation configuration

Block	Number of stages	Feed location	Reflux ratio	Diameter (m)	Reboiler Duty (MW)	Condenser Duty (MW)
RD	35	1/13	3.61	3.90	1.403	2.33
C1	12	5	0.8	0.80	0.72	$4.51 \times 10^{-3}$
C2	15	8	0.154	1.40	0.185	0.647

## 5. Result and discussion

### 5.1 RD column

The RD column has total 35 stages including the condenser and the reboiler. The distillate contain the unreacted (MeOH) together with excess (MH) and small quantity of (DME) produced as a by-product. The condenser duty was 2.33 MW and the corresponding temperature was 402 K that permits the use of cooling water to condense the top vapors. The bottom of the RD column produces the desired MMH product with small amount of MHOH produced as a by-product. The reboiler duty was estimated at 1.403 MW. The bottom temperature was 448 K that uses the high-pressure steam. The reflux ratio required to maintain 99 % MMH yield was 3.61. The reactive holdup cannot be more than the system liquid holdup, otherwise the catalyst will fill in the stags and cause column hydraulic problems. Keeping in view the hydraulic limitation with standard liquid depth of 0.152 m, the diameter of the RD column calculated with the aid of Eq(8) was found at 3.90 m.

$$D = \sqrt{\frac{(holdup)(4)}{(\pi)(0.152)}} \quad (8)$$

Figure 4a and b show the composition and temperature profile of the RD column.

### 5.2 Column C1

The distillate of the RD column is fed to stage 5 of 12-stage column C1. The column operates at 10-atm. The distillate is very small flow rate of 0.5164 kmol/h DME at 99.9 mol %. The condenser duty is  $4.51 \times 10^{-3}$  MW and the temperature of the condenser is 318 K that allow cooling water to condense vapors. The bottom contains the unreacted reactants and excess MH which is recycled back to RD column. The reboiler duty was 0.72 MW and the corresponding temperature was 501 K that require high-pressure steam to provide vapor boil-up. The diameter of the column using Aspen tray sizing was estimated at 0.8 m. Figure 5a and b show the composition and temperature profile of the C1 column.

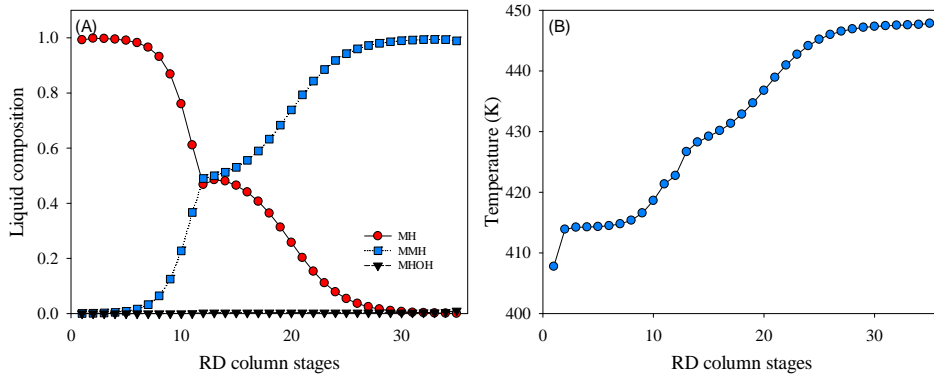


Figure 4: Composition (A) and temperature (B) profiles of the proposed RD column.

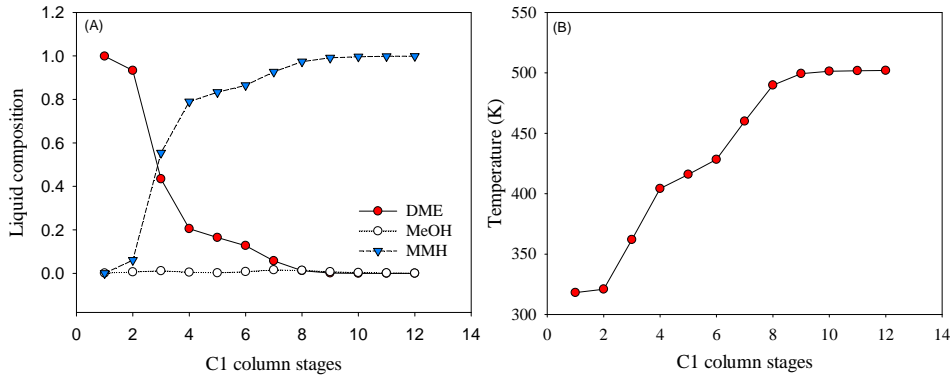


Figure 5: Composition (A) and temperature (B) profiles of the C1 column.

### 5.3 Column C2

The column C2 serves the purpose of separating the main product MMH from the by-product MHOH. There are total 15 stages with stage 8 being the feed location. The distillate is 49.02 kmol/h at 99.9 mol % MMH. The bottom is 0.49 kmol/h at 99.9 mol % MHOH. The diameter of the column using Aspen tray sizing was estimated at 1.40 m. Figure 6a and b show the composition and temperature profile of the C2 column.

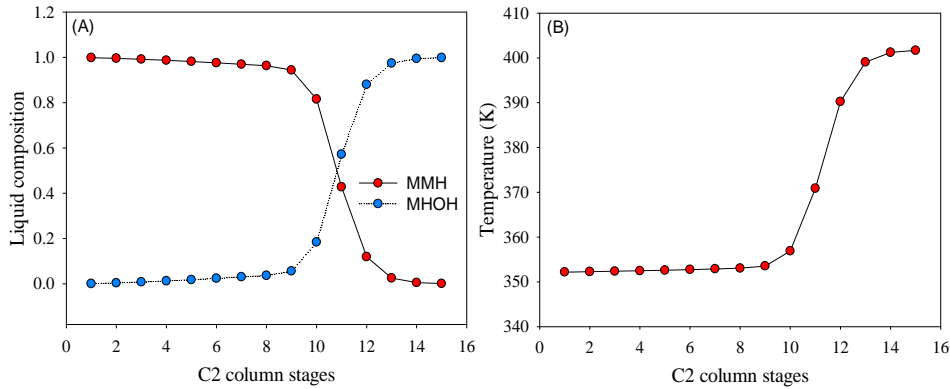


Figure 6: Composition (A) and temperature (B) profiles of the C2 column.

## 6. Economic analysis

The economic analysis of the proposed RD configuration was carried out in terms of total annual cost for comparison with the base case. TAC is calculated with the aid of Eq(9).

$$TAC = \left( \frac{\text{Capital cost}}{\text{Payback period}} \right) + \text{Energy cost} \quad (9)$$

The basis of equipment sizing and economics are taken from the textbooks of (Douglas, 1998) and (Turton et al., 2003) Table 2 summarized the results of the economic analysis. The proposed configuration based on RD brings significant savings in energy and total annual cost by up to 14.85, and 8.71 %, respectively when

compared with the conventional energy intensive configuration. However due to large diameter required for RD column to accommodate solid catalyst, the capital cost was found to be same as for the base case.

*Table 2: Economic evaluation of the proposed RD configuration with the base case.*

Economic Parameters	Base Case	Proposed Configuration			Savings in comparison with the base case
		RD column	C1 column	C2 column	
ID (m)	-	3.90	0.8	1.40	-
Total capital cost (10 <sup>6</sup> \$)	1.608	1.231	0.146	0.240	(-0.52 %)
Total energy cost (10 <sup>6</sup> \$/y)	0.807	0.417	0.225	0.045	(+14.85 %)
Total annual cost (10 <sup>6</sup> \$/y)	1.343	0.827	0.274	0.125	(+8.71 %)

## 7. Conclusions

The feasibility of reactive distillation has been studied for the component 2-methoxy-2-methylheptane which has the potential to replace MTBE as a future gasoline additive. Various design parameters in the design of RD column were studied to overcome the temperature limitation of catalyst involved. The economic steady state design was presented that minimizes the total annual cost (TAC) as an objective function. The results illustrate that application of RD technology for the MMH process can bring significant improvements in terms of energy, and TAC by up to 14.85, and 8.71 %, respectively, when compared with the conventional energy intensive reactor-column sequence. The design is useful for many existing plants to replace RD column for MTBE production with MMH.

## Acknowledgments

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2018R1A2B6001566), Priority Research Centres through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2014R1A6A1031189), and the R&D Center for Reduction of Non-CO<sub>2</sub> Greenhouse Gases (201700240008) funded by the Ministry of Environment as a "Global Top Environment R&D Program".

## References

- Anderson S. P., Elzinga A., 2014, A ban on one is a boon for other: Strict gasoline content rules and implicit ethanol blending mandates, *Journal of Environmental Economics and Management*, 67, 258-273.
- Chang H-N., Lee H. Y., 2017, Innovative design of diphenyl carbonate process via one reactive distillation with a feed-splitting arrangement, *Chemical Engineering Transactions*, 61, 445-450.
- Douglas J. M., 1998, *Conceptual design of chemical processes*, McGraw-Hill, New York.
- Griffin D. W., Mellichamp D. A., Doherty M. F., 2009, Effect of competing reversible reaction on optimal operating policies for plants with recycle, *Industrial & Engineering Chemistry Research*, 48, 8037-8047.
- Harmsen G. J., 2007, Reactive distillation: The front-runner of industrial process intensification: A full review of commercial applications, research, scale-up, design, and operation, *Chemical Engineering and Processing: Process Intensification*, 46, 774-780.
- Hussain A., Minh L. Q., Lee M., 2017, Intensification of the ethylbenzene production process using a column configured with a side reactor, *Chemical Engineering and Processing: Process Intensification*, 122, 204-212.
- Karinen R. S., Krause A. O. I., 1999, Reactivity of some C8-alkenes in etherification with methanol, *Applied catalysis A: General*, 188, 247-256.
- Lu J., Tang J., Chen X., Cui M., Fei Z., Zhang Z., Qiao X., 2017, Global optimization of reactive distillation processes using bat algorithm, *Chemical Engineering Transactions*, 61, 1279-1284.
- Luyben W. L., 2010, Design and control of Methoxy-methylheptane process, *Industrial & Engineering Chemistry Research*, 49, 6164-6175.
- Luyben W. L., 2008, *Reactive distillation design and control*, Wiley, New Jersey.
- Srivastava S. P., Hancok J., 2014, *Fuels and fuels additives*, Wiley, New Jersey.
- Turton R., Bailie R. C., Whiting W. B., Shaelwitz J. A., 2009, *Analysis, synthesis, and design of chemical processes*, Prentice Hall: Upper Saddle River, New Jersey.
- Wang S., Huang K., Lin Q., Wang S. J., 2010, Understanding the impact of operating pressure on process intensification in reactive distillation columns, *Industrial & Engineering Chemistry Research*, 49, 4269-4284.