Methoxy-methylheptane as a cleaner fuel additive: An energy- and cost-efficient enhancement for separation and purification units

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Abstract
Environmental protection agencies have begun imposing stringent regulations on the existing refineries to control the levels of gasoline additives. In this context, a novel compound, 2-methoxy-2-methylheptane (MMH), had drawn attention as fuel additive for cleaner combustion. The conventional process of MMH production features three distillation columns in a direct sequence. These columns are used to maintain the required product purities and to utilize the unreacted reactants through recycling streams. The distillation system of the existing MMH plant can afford significant energy savings, leading to a reduction in the total annual costs (TAC). The aim of this investigation is to demonstrate that the reported conventional process can be significantly enhanced by modifying the design and operational parameters and by replacing two distillation columns with an intensified dividing wall column (DWC) configuration. The DWC design is further optimized using several algorithms such as the modified coordinate method (MCD), robust particle swarm paradigm (PSP), and firefly (FF) with nonlinear constraints. Compared to conventional process, the optimized DWC resulted in 24% and 11.5% savings in the plant operating and total annual costs, respectively.

KEYWORDS
dividing wall column, firefly optimization, methoxy-methylheptane process, particle swarm paradigm, total annual cost
INTRODUCTION

Over the past few decades, refineries around the globe have been looking for new alternative fuel additives because of strict environmental constraints. In this context, methyl-tert-butyl-ether (MTBE) as a fuel additive plays a key role in reducing automobile discharges. However, MTBE is thought to be carcinogenic and is highly soluble in water. In recent years, MTBE has been singled out because the leakage of gasoline-containing MTBE can easily get into groundwater and contaminate wells. To overcome this limitation, a high-molecular-weight ether, 2-methoxy-2-methylheptane (MMH), has been recently proposed. Low solubility of MMH in water makes it an excellent candidate to replace MTBE in the existing plants. MMH can replace MTBE in the existing plants as the former exhibits only a low solubility in water. It is produced by the etherification of 2-methyl-1-heptene (MH) with methanol (MeOH) using a reversible nonequilibrium reaction mechanism. 2-methyl-2-heptanol (MHOH) and dimethyl ether (DME) are also produced as by-products. The manufacturing process of MMH has attracted much attention, and various design configurations have been investigated to optimize the MMH process. Griffin, Mellichamp based their study on moderate to high values of reaction equilibrium constants for exploring the optimal operating parameters. Luyben investigated the conventional reactor-column configuration of the MMH process in terms of the minimum total annual cost (TAC) by optimizing the reactor volume and total recycle flow rate from downstream columns. Hussain, Minh demonstrated process intensification through reactive distillation (RD) for the MMH process. More recently, Hussain and Lee and Hussain, Riaz proposed an optimal design with a side-reactor configuration (SRC) for the MMH process that can effectively overcome the design limitations of the RD column. In a conventional MMH flowsheet, the reaction occurs in a fixed bed reactor followed by reaction in three distillation columns. The MMH process requires an expensive heat source for the separation and purification of reaction products. The demand for high-purity MMH and recycling the excess reactants for maintaining high yields has thus forced academic and industrial researchers to develop energy-efficient schemes to produce this novel gasoline additive.

Separation sequences using typical columns suffer from an inherent inefficiency owing to their thermodynamic irreversibility. This inefficiency is intrinsic to any ternary mixture and can be generalized for multicomponent mixtures. Many alternative design configurations are available that can intensify the existing distillation columns; especially, the energy efficiency of the conventional MMH process can be improved. Because it is thermodynamically equivalent with a Petlyuk column, a dividing wall column (DWC) is considered a promising and practical technology; its usage can lead up to 30% reduction in facility expenditure and operation costs over the conventional configuration. Currently, there are more than 150 DWCs in operation across the world. The energy prerequisite of the DWC design is less intensive than that of its conventional counterparts, because its operating parameters can limit the entropy of mixing formation. There also exist several additional benefits, such as the column requires only one condenser and one reboiler unlike the conventional two-column sequence with two reboilers and two condensers. The use of DWC has been expanded to a number of areas, including extractive distillation, azotropic distillation, reactive distillation, and hybrid distillation. For example, it has been used in the production of dimethyl ether (DME) using a reactive DWC (RDWC) design to produce high-purity DME in a compacted column with low CO₂ emissions and costs. The application of DWC was extended to biofuel processes, such as the production of biobutanol, biodiesel, and bioethanol. Recently, several excellent reviews have been published on the DWC system.

Numerous studies of dynamic control and optimization were presented for evaluation of the economic feasibility of the model via a techno-economic analysis. Choi et al presented the energy optimization methodology of the gas splitting commercial process followed by conducting economic analysis for the modified processes. In their study, the objective function is the sum of the condenser and reboiler duties to replace capital and operating costs. The net present value was compared for the modified configurations and with the base case such that those modified configurations showed a significant improvement. Kwon et al carried out the energy optimization and satisfy the target product purity by using the developed machine learning-based prediction model into the n-butane separation process. The estimated reduction of the steam flow rate was then obtained by using the predicted model. Liang et al reported an excellent literature review to summarize the optimization methods of the pressure-swing distillation system. The optimization can be defined by a single-objective optimization, such as the TAC. Otherwise, there will have a multiobjective optimization that is related to performance, cost, energy, safety, controllability, etc, while there is a trade-off between them. Zhu et al developed a function between the relative volatility and the TAC for screening the solvent selection in the extractive two-column distillation system. To control the disturbance in both feed flow rate and composition, Shi et al presented a robust temperature control structure with selectors for the complicated heat integrated pressure-swing extractive distillation process. Zhu et al currently presented different control structures and compared all of them for finding the best configuration in a pressure-swing distillation recovery process of the benzene and isopropanol. Li et al discussed about the comparison of the optimization results between two pressure-swing batch distillation processes by using the minimum TAC objective.
function. Jia et al.\textsuperscript{32} studied the effect of thermodynamic parameters on the phase behavior and finding the minimum TAC in the extractive distillation process. A guideline developed for the extractive distillation system design was also presented. To solve the MINLP problem for the four product DWC, Ge et al.\textsuperscript{33} applied the sequential iteration optimization approach in which the total number of stages was found based on the TAC calculation. For the given total number of trays, the minimum reboiler duty was selected as the objective function which can be found in the commercial SQP solver for the suboptimization problem. Qian et al.\textsuperscript{34} applied the random optimization which explores different particle swarm optimization approaches to study the optimal design of the four product Kaibel DWC based on the minimum TAC. By considering two conflict objectives such as net revenue and organic Rankine cycle thermal efficiency, Yang et al.\textsuperscript{35} presented the multiobjective optimization for the diethyl carbonate using the heat pump reactive DWC under different dry working fluid. The TAC performance of two of them was then evaluated which showed a significant saving compared to the existing heat pump reactive DWC process.

As discussed, the MMH process requires an expensive heat source for the separation and purification of reaction products. In the current work, the application of DWC followed by robust structural and operational optimization of design variables is presented to improve the energetic efficiency of MMH process. To our knowledge, this is the first study showing the more efficient process intensification technique to reduce the energy requirement in the purification section of MMH process. The results of the optimized DWC design are then compared with the conventional MMH process to demonstrate the savings achieved. The application of DWC, refined by structural and operational optimization of the design variables, resulted in 24% savings in the plant operating costs.

2 | OVERVIEW OF PAPER

In the first section of this study, we examined the full potential of the energy-saving opportunities of the conventional MMH process, which was reported by Luyben.\textsuperscript{5} Some possible modifications in the design and operational parameters are suggested, and discussion on results was made. In the next section, the application of DWC on modified conventional configuration is proposed for improving the energy efficiency of an existing MMH plant. The application of DWC was examined by integrating two sequential conventional columns of the modified flowsheet process to minimize energy requirements. In the next section, the structure of DWC was further optimized through several robust optimization routines, such as the modified coordinate descent (MCD), particle swarm paradigm (PSP), and Firefly (FF) algorithms.

In the final section, the economic evaluation was carried out and results are concluded.

3 | MODIFIED CONVENTIONAL PROCESS: SIMULATION AND DESIGN OPTIMIZATION

Simulation work in the present study is based on an earlier reported work of Luyben.\textsuperscript{5} The components 2-methoxy-2-methylheptane (MMH) and 2-methyl-2-heptanol (MHOH) are not available in Aspen plus data bank. Figure 1 shows the molecular structure used to generate these missing components. The component physical properties are provided in Table 1.

Two competing liquid phase parallel reactions involved in the MMH chemistry are as follows:

\begin{align*}
\text{CH}_3\text{OH} + \text{C}_8\text{H}_{16} & \leftrightarrow \text{C}_9\text{H}_{20}\text{O}^# \quad (1) \\
2\text{CH}_3\text{OH} + \text{C}_8\text{H}_{16} & \rightarrow \text{C}_2\text{H}_6\text{O} + \text{C}_8\text{H}_{18}\text{O}^# \quad (2)
\end{align*}

The reaction is carried out in a continuous stirred tank reactor (CSTR), while being catalyzed over an Amberlyst 35 wet catalyst. The per-pass conversions of MeOH and MH are 93.9% and 39.2%, respectively. The MMH yield was estimated at 99%. The reactor is followed by three distillation columns connected in a direct sequence. The separation and purification sections of the conventional MMH flowsheet reported by Luyben\textsuperscript{5} were modified to achieve maximum energy savings. Two important design aspects were considered.

![Molecular structure of MMH and MHOH](image)

**TABLE 1** Physical properties of MMH and MHOH

| Component                  | Boiling point (K) | Molecular weight (g/mol) |
|---------------------------|-------------------|--------------------------|
| 2-Methoxy-2-methylheptane | 424.4             | 144.25                   |
| 2-Methyl-2-heptanol       | 471.4             | 130.23                   |
to yield the optimal design to minimize the total annual cost. The first is the operating pressure of the three columns (P₁, P₂, and P₃), and the second is the total number of stages in the three columns (N₁, N₂, and N₃) and their corresponding feed locations (NF₁, NF₂, and NF₃).

The separations involved in the five components are easy because there is a significant difference in their boiling point: DME = 248.2 K, MeOH = 337.5 K, MH = 392.2 K, MMH = 424.4 K, and MHOH = 471.4 K. All unit operations were simulated using an Aspen Plus®. For a fair comparison, the proposed study is built on the “UNIQUAC” thermodynamic model, as suggested in the conventional flowsheet of MMH plant. The components 2-methoxy-2-methylheptane (MMH) and 2-methyl-2-heptanol (MHOH) are not available in Aspen Plus data bank, and no vapor-liquid equilibrium studies have been done for this system. The UNIQUAC thermodynamic model considered all components as ideal except DME and MeOH. The binary T-x diagram for DME/MeOH is shown in Figure 2. This study presents preliminary results of a reasonable conceptual design based on a dividing wall column. However, there is a fair amount of uncertainty associated with the chosen thermodynamic model.

The kinetic parameters were sourced from the report by Griffin et al. The sequential sensitivity-based design procedure is shown in Figure 3.

3.1 Optimization of the column pressure

Column C₁ in the conventional MMH process, which purifies DME, is operated at a high pressure (~10 atm) to avoid the use of expensive refrigerants to condense the top vapors. This high-pressure column resulted in a reboiler temperature of 509 K that requires high-pressure steam. Small quantity of DME, flowrate of 0.5168 kmol/h, was produced in column C₁ with a condenser duty of 4.4 kW. As the distillate rate and condenser duty are very small, it means that operating the DME column at low pressures might be economical. Although this results in the need for expensive refrigeration to condense the top vapors, it does reduce the reboiler temperature and thereby reduces the amount of steam needed in the reboiler. These alternative designs for low pressures in column C₁ were briefly explored. Table 2 illustrates the optimization of operating pressures in columns C₁, C₂, and C₃.

As shown in Table 2, a lower operating pressure of column C₁ resulted in a low base temperature and the corresponding reboiler duty decreased, which leads to the requirement of less expensive steam in the reboiler. An operating pressure of 2 atm resulted in a condenser temperature of 265.5 K that would require a 233.5 K refrigerant at $13.11/GJ. The cost of refrigeration is estimated at $4717/y. The reboiler temperature drops from 509 K to 426 K, which now uses medium-pressure steam. The total savings in steam cost was $370 871/y. Owing to the uncertain cost of refrigerant at an operating pressure of 1 atm, column C₁ was optimized to run at 2 atm. Consequently, pressures for subsequent columns C₂ and C₃ were also optimized to be at 0.3 and 0.1 at, respectively.

3.2 Optimization of the number of trays

Usually, adding more column trays reduces the energy requirement in the reboiler and capital investment in the heat exchangers. However, adding more trays directly impacts the capital investment of the distillation column. For optimization, a practical limit of at least ten separation trays is assumed. To minimize TAC, optimal number of trays in columns C₁, C₂, and C₃ were investigated. Table 3 illustrates that the resultant values for C₁, C₂, and C₃ are 10, 35, and 12, respectively.

4 RESULTS AND DISCUSSION

4.1 Modified MMH process

Flowsheet of the modified process is shown in Figure 4. Column C₁ receives the feed from reactor effluent at stage 5. Column C₁ purifies DME up to 99.9% at a distillate flow rate of 0.5168 kmol/h. The operating pressure of column C₁ is set at 2 atm. The condenser temperature is 265.5 K, and the corresponding condenser duty is 11.77 kW. The reboiler temperature is 426 K and uses medium-pressure steam to provide 0.311 MW of heat energy. The bottom of column C₁ is fed to column C₂. The optimum pressure and total number of trays are estimated to be 0.3 atm and 35, respectively. This column serves the purpose of recycling the excess MH and sending the unreacted reactant back to the reactor. The temperature at the condenser using cooling water is 350 K. The
base temperature is 384 K, and low-pressure steam is used to provide 1.194 MW of heat energy. Column C3 receives feed from the bottom of column C2. This column separates MMH from MHOH. The condenser temperature is 352 K at a column pressure of 0.1 atm. The reboiler temperature is 401 K, and it requires low-pressure steam. The diameters of columns C1, C2, and C3 estimated using the Aspen tray sizing option are 0.56, 1.82, and 1.41 m, respectively.

The first column C1 plays an important role in separating high-purity DME from the reactor effluent. Stagewise composition and temperature profiles of this column are presented in Figures 5 and 6, respectively. The composition of the DME is represented by the green line, which indicates that the DME is obtained from the top of the column. On the other hand, the MH and MMH are heavier components and migrate to the bottom section.
The components from the bottom of column C1 are then separated in C2 and C3, which are connected in series. Figure 7 presents the temperature profiles and liquid molar fraction distributions associated with columns C2 and C3. A key advantage is that the two columns exhibit similar temperature ranges even though they operate at 0.1 atm (C2) and 0.3 atm (C3). Therefore, a promising alternative of DWC can potentially provide a working pressure that maintains an approximately similar temperature on both sides of the shell. Simultaneously, highly pure MMH (99.9%) and MHOH are obtained, while high-purity MH is recycled to the reactor.

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5 | SYSTEMATIC APPROACH TO A RIGOROUS OPTIMAL DESIGN OF DWC

The results of the modified configuration reveal that there is a further possibility of reducing the energy requirements of the overall MMH process. The small difference in the pressures of C2 (0.3 atm) and C3 (0.1 atm) suggested that the application of DWC seems appealing. Aiming to further reduce the energy requirements, columns C2 and C3 of the modified configuration were integrated into a DWC.

5.1 | Dividing wall column

Figure 8 illustrates a DWC (Figure 8A) and a Petlyuk column (Figure 8B). A prefractionator (PF) and main section are merged in a single shell with a vertical wall. Liquid splitting is carried out at the top of the dividing wall (DW), while the splitting of vapors occurs at the bottom wall. These splitting processes equally occur in the two parts of the Petlyuk column. Compared to a binary distillation column, the equipment design is more challenging because of the three additional degrees of freedom: one for the side stream, one for the liquid splitting ratio above the DW, and one for the vapor splitting ratio below the DW. Even though most of

| Table 3 | Optimization of the total number of trays and feed location |
|-----------------|-----------------|-----------------|
| **Tot. no. of trays (NT)** | **Column C1** | **Column C2** | **Column C3** |
| 15 | 12 | 10 | 40 | 35 | 30 | 15 | 12 | 10 |
| **Optimum feed location (NF)** | 9 | 6 | 5 | 20 | 18 | 15 | 7 | 5 | 4 |
| **ID (m)** | 0.564 | 0.564 | 0.565 | 1.803 | 1.823 | 1.878 | 1.389 | 1.405 | 1.506 |
| **Reboiler duty, Q_R (MW)** | 0.311 | 0.311 | 0.312 | 1.157 | 1.195 | 1.304 | 0.476 | 0.490 | 0.580 |
| **Condenser duty, Q_C (MW)** | 0.011 | 0.048 | 0.012 | 1.842 | 1.879 | 1.988 | 0.613 | 0.627 | 0.717 |
| **Reactor + catalyst (10^6 $)** | 0.229 | 0.229 | 0.229 | 0.229 | 0.229 | 0.229 | 0.229 | 0.229 | 0.229 |
| **Tot. capital cost (10^6 $)** | 0.335 | 0.324 | 0.317 | 0.677 | 0.634 | 0.603 | 0.256 | 0.231 | 0.229 |
| **Tot. operating cost (10^6 $/y)** | 0.085 | 0.085 | 0.086 | 0.304 | 0.313 | 0.341 | 0.123 | 0.127 | 0.150 |
| **TAC (10^6 $/y)** | 0.197 | 0.193 | 0.191 | 0.529 | 0.525 | 0.542 | 0.209 | 0.204 | 0.226 |

Bold-italic values are to emphasize the results.
the studies performed on the DWC sequence were conducted using shortcut models, such as the Fenske-Underwood-Gilliland method,38 a more rigorous simulation is necessary to optimize the initial design obtained from previous steps. However, estimating the number of stages in both sections is very difficult during simulation. Because the number of stages is an integer variable, while other parameters, such as side stream flow rate, reflux ratio, and liquid and vapor splitting ratio are continuous variables, column optimization becomes a mixed integer nonlinear programming problem (MINLP). Commercially available process simulators face certain limitations in handling such optimization problems. To address this issue, several researchers investigated the optimal design of the DWC using external programs.

5.2 Shortcut design

The initial structure of the DWC was estimated using a shortcut design procedure.38,39 In this method, the first column represents the PF section, whereas the top and bottom sections in the DWC are serviced by the rectification section of the second distillation column and the stripping section of the third distillation column, respectively. The number of stages on both sides of the wall is assumed to be equivalent.40 The column can be divided into four separation sections, namely

**FIGURE 5** Composition profile of the component in column C1

**FIGURE 6** Temperature profile in column C1

**FIGURE 7** Temperature and composition profiles along the C2 and C3 columns
the PF that receives the feed, the right side of the dividing wall that discharges a side product, the top section including a condenser, and the bottom section accompanied by a reboiler above and below the DW, respectively. The initial approximations of the DWC structural design can be easily executed by applying a conventional shortcut design method based on this structural similarity.

6 | OPTIMIZATION OF DWC

6.1 | Problem statement

As mentioned previously, the overall energy requirement of the proposed DWC is dominated by key design parameters, such as feed location, number of stages in each section, and internal flow rate. Therefore, a process model linked to an external optimal program is necessary to handle the non-linear flexibility between output interest and design parameters. Bravo-Bravo et al. studied the design and synthesis of an extractive DWC based on a constrained stochastic multiobjective optimization method. A genetic algorithm (GA)-based multiobjective optimization, developed by Gomez-Castro et al., was used to design DWCs. Long and Lee applied a response surface methodology using the Box-Behnken design for the structural optimization of a DWC. Wang et al. studied an iterative optimization procedure for the optimal design of reactive DWC, azeotropic DWC, and double DWC. On the basis of a combination of a radial basis function neural network (RBFNN) and genetic algorithms, Ge et al. explored a systematic and efficient method for minimizing the total cost of DWC. Qian et al. optimized decision variables using a particle swarm algorithm for the design and synthesis of a reactive DWC. Recently, to find the feasible design parameters in a highly nonlinear and multivariable problem, Jia et al. studied the optimal design of a DWC using a support vector machine (SVM) and particle swarm optimization.

In this study, the optimal structure of the DWC was initially obtained using a shortcut method and consequently optimized by several practical methods such as the MCD, PSP, and FF algorithms. The energy requirements of the proposed DWC are minimized as an output interest that satisfies to a 99.9% purity of MMH and MHOH.

The optimization problem can be formulated as

\[ \text{Min}_{Z} \left( Q_{\text{reboiler}} \right) \]  \hspace{1cm} (3)

and it is subject to

\[ \text{Purity of MMH} (Z) \geq 0.999; \text{MHOH} \geq 0.9999 \]  \hspace{1cm} (4)

where \( Z \) is the vector of the decision variables; \( Z = (N1, N2, N3, N4, N5, FL, FV, RR) \).

Table 4 lists the decision parameters associated with their lower and upper bounds. The key design variables are optimized; they include the feed stage of the PF (N1), number of trays in the PF (N2), number of trays in the top section (N3), side stream location (N4), and reflux ratio (RR).

![Diagram](image)

**TABLE 4** Key decision variables with lower and upper bounds

| Decision variables                        | Lower bound | Upper bound |
|------------------------------------------|-------------|-------------|
| Feed stage of prefractionator (N1)      | 9.0         | 16.0        |
| Number of stages in PREF (N2)           | 27.0        | 32.0        |
| Number of stages in top section (N3)    | 7.0         | 14.0        |
| Side stream location (N4)               | 24.0        | 34.0        |
| Total number of stages (N5)             | 44.0        | 54.0        |
| Internal flow rate of liquid, FL (kg/h) | 2500.0      | 7700.0      |
| Internal flow rate of vapor, FV (kg/h)  | 7000.0      | 12 500.0    |
| Reflux ratio (RR)                       | 1.0         | 1.7         |

**FIGURE 8** Schematic diagram of (A) dividing wall column and (B) Petlyuk column
total number of stages (N5), and internal flow rates of the liquid (FL), and vapor (FV) to the PF (as shown in Figure 8A).

The optimization problem of the proposed DWC has no equality constraint but has inequality constraints, that is, molar purity of MMH ≥ 0.999 and MHOH ≥ 0.999, which were incorporated into the reboiler duty (objective function) through an exterior penalty function.47-49 Finally, a reformulation of the objective function yields an equivalent unconstrained objective function as:

$$\text{MinP}(Z) = \text{Min}(Q_{\text{reboiler}} + r(\max[0, (0.999 - \text{Purity}_{\text{MMH}}(Z)]) + r(\max[0, (0.999 - \text{Purity}_{\text{MHOH}}(Z)])$$

(5)

Table 5 lists the CPU specifications and simulation times to run the optimization.

6.2 | Optimized structure of the DWC using the proposed algorithms

Starting from the preliminary DWC structure and initial operating conditions, rigorous optimization is a challenging task due to the existence of several variables involving both structure and operating variables with highly nonlinear interactions. In the present work, several optimization algorithms regarding the nonlinear constraints are examined in order to improve the energy efficiency of the DWC application.

6.2.1 | Modified coordinate descent (MCD)

The main idea of MCD optimization is that each iterate is obtained by fixing the values of most of the components of the variable vector Z from the current iteration and approximately minimizing the objective with respect to the remaining components.50,51 Because Aspen HYSYS and Visual Basic in Excel interface and exchange values with each other through the component objective model (COM) functionality, Excel can be used to obtain results from HYSYS and then activate the search procedure, which was programmed in Visual Basic. The iterations are individually accomplished through each coordinate by minimizing the objective function with respect to individual coordinate directions. The search to find the second coordinate after obtaining the new optimum result from the first coordinate is continuous. Consequently, the coordinate descent search is executed over a narrow range or the so-called box space with a given step size around the Zmin (a vector of optimized decision variables) to determine more promising solutions in the intermediate vicinity of Zmin. The search is terminated using the termination criterion, which is a user-defined value. More details on the MCD can be found elsewhere.52,53

6.2.2 | Particle swarm paradigm (PSP)

PSP54 is a well-proven algorithm regarding optimization of nonlinear systems such as complex natural gas liquefaction55 and advanced distillation processes.56 Recently, Long et al56 demonstrated the efficacy of PSP for design optimization of the conventional and DWC separation sequences for both zeotropic and azeotropic mixtures. The present study explores PSP for the design optimization of advanced...
separation techniques (DWC) for MMH. The algorithm was coded in MATLAB and linked to Aspen HYSYS® V10 using the ActiveX functionality. Figure 9 shows a working flow diagram of the PSP algorithm. The parameters of PSP used in this study are given in Table 6.

6.2.3 | Firefly algorithm

The FF algorithm\textsuperscript{57,58} was first proposed by Dr Xin-She Yang at Cambridge University in 2007. This algorithm (also based on swarm intelligence) is inspired by the mating or flashing and social interactions of fireflies.

These swarm intelligence-based systems are made up of a population of simple agents. The insects/agents cooperate with each other and their environment. This collective behavior of social interaction leads to an intelligent global behavior. However, several characteristics of the FF are similar to those of other swarm-based algorithms, such as the PSP, artificial bee colony optimization, and ant colony optimization. The difference between these algorithms lies in their degree of conceptual simplicity and easy implementation, especially for nonlinear optimization. Further, Xin-She Yang\textsuperscript{57} reported that the FF is superior to the PSP, mainly due to its overall global behavior. A firefly is capable of generating a natural flash/light to captivate a mate or prey. The concept of FF is based on the intensity/brightness ($I$) of a flash decreasing as the distance ($r$) increases; hence, they are capable of communicating only up to several hundred meters. During FF implementation, the flashing light is associated with the objective function to be optimized. The concept of FF is mainly based on the following elements:

- A firefly is always captivated by other fireflies, irrespective of its gender.
- This attractiveness is directly related to the brightness of the generated flash and decreases with an increase in the separating distance.
- The objective function in FF is based on the brightness of a firefly.

As mentioned previously, the optimization of these parameters becomes a MINLP. There are five discrete variables and three continuous variables that need to be handled by a complicated procedure to reduce the reboiler duty required for the DWC. The working pattern of FA is shown in Figure 10.

7 | RESULTS AND DISCUSSION
(REPLACING C2 AND C3 WITH A DWC)

7.1 | Using modified coordinate descent

The reboiler duty of DWC is set at 1.532 MW, which is 9.08% of the two-column sequence. For rigorous simulation, the internal vapor and liquid splitting ratios (RV and RL) were optimized at 0.517 and 0.637, respectively, to obtain

![Working flow diagram of the firefly optimization algorithm](image)
the minimum reboiler duty, while maintaining product purity. Note that the RV and RL are ratios of the internal flows of the vapor and liquid of the PF to that of the main column, respectively. The dividing wall is installed from the 17th stage to the 43rd stage of the column. Meanwhile, the MMH main product (99.9% mole purity) was collected at the side stream. The total number of stages is 50, including the condenser and reboiler. Table 7 lists the optimized design variables obtained through MCD, PSP, and FA algorithms.

### 7.2 Using the particle swarm paradigm

The optimization results were obtained after 500 iterations; the optimum design variables of DWC are shown in Table 7. The required energy of the DWC is 1.43 MW, which is 15.13% of the energy required for the two-column configuration. It is noted that there occurs no heat transfer through the wall. The RV and RL values were optimized at 0.658 and 0.503, respectively, to obtain the minimum reboiler duty, while satisfying the product purity constraints. The dividing wall is installed from the 9th stage to the 39th stage of the column. Meanwhile, the MMH main product (99.9% mole purity) was collected from the side stream at stage 26.

### 7.3 Using Firefly algorithm

Figure 11 shows the proposed configuration, which replaces columns C2 and C3 by a single DWC. Based on the decision variables listed in Table 4, the reboiler duty as an objective function was minimized using the state-of-the-art firefly optimization algorithm.

The feed stream from the bottom section of column C1 is introduced into stage 11 of a 28-stage PF (PF). The main column (MC) has a total of 47 stages including the condenser and the reboiler. The distillate of the MC serves the purpose of recycling the excess MH together with the unreacted methanol back to the reactor. The side product withdrawn at stage 32 from the MC produces the desired MMH product (99.9% molar purity) at a feed rate of 49.10 kmol/h. The bottom stage produces the by-product MHOH of 99.9% molar purity. The diameter of the DWC estimated using the Aspen tray sizing option is 2.37 m. The maximum flooding is about 80% for smooth operation of the column. The operating pressure of the PF and main column was set at 0.3 atm, which is similar to that of C2 in the base case. Using the Firefly algorithm, by varying the decision variables of the DWC, the reboiler duty was optimized at 1.137 MW. The optimal liquid and vapor splitting ratios (RL and RV) were estimated to be 0.332 and 0.583, respectively. High-pressure steam was used in the reboiler to achieve the base temperature of 430 K. The condenser duty was 1.803 MW, and cooling water was used to condense the top vapors at 350 K. Table 8 lists the optimum values of the decision variables and the hydraulic conditions of the DWC.

The profiles (Figures 12 and 13) in the DWC are very similar to columns C2 and C3, as described previously. In particular, as shown in Figure 12, the temperature profile of the main column from stages 1 to 39 exhibits a temperature range similar to that of the C2 column, while the temperature trend of column C3 is similar to that of the main column from stage 40 to the end of column. Furthermore, it can be observed in Figure 12 that the temperature difference between two sides of the wall is very small (less than 15 K), which indicates that a practical application can be achieved with only a little heat transfer and a negligible effect on the column performance. In other words, as shown in Figure 13, there are sharp modifications in the composition profiles around the feed location—between stages 10 to 20. The 45-stage shell includes the wall which is located from stages 14 to 40. High-purity MH (95.77% mole purity) is delivered as the top distillate for recycling, while extremely high-purity MHOH is collected as the bottom product. The main product, MMH, is obtained at stage 32 as the side product with 99.9% mole purity. On the side product section, the MMH content is highly pure on a large array of trays, from stages 25 to 35, which indicates that the product purity is maintained even when the side stream location is varied. At the same time, the MHOH content is found to be highly pure in the stripping section and is collected in the bottom stream.

### 8 Economic Analysis

Economic analysis was carried out in terms of minimum TAC using Equation (1.6) after assuming a payback period of 3 years. The basis for design and equipment costing was
sourced from Turton and Douglas. The details of equipment capital estimation and steam costs are shown in Table 9.

\[
TAC = \left( \frac{\text{Capital cost}}{\text{Payback period}} \right) + \text{Operating cost} \quad (6)
\]

Total capital cost (TCC), operating cost (TOC), and TAC were estimated for economic analysis of the proposed DWC configuration. Table 10 summarizes the key economic indicators between the conventional and proposed DWC configurations. The application of DWC by replacing two conventional columns (C2 and C3) resulted in 24% savings in terms of the plant operating costs. The TCC of the proposed DWC configuration was $1,243,000. This capital investment is around 5.2% higher when compared to that of the conventional process; this is mainly due to the costs associated with the additional trays. The application of DWC is more attractive for reducing the overall reboiler heat energy, which is 27.4% less than that of the conventional process.

### TABLE 8 Optimal design parameters of the DWC using the Firefly algorithm

| Design parameters                  | Value     |
|------------------------------------|-----------|
| Flow rate of feed stream (kg/h)    | 15,850    |
| Temperature of feed stream (K)     | 426.4     |
| Pressure of feed stream (atm)      | 2         |
| Number of stages\(^a\)             | 47        |
| Diameter of column (m)             | 2.37      |
| Feed stage                         | 18        |
| Wall position\(^b\)                | 14/40     |
| Reflux ratio                       | 1.25      |
| Operating pressure (atm)           | 0.3       |
| MMH mole purity                    | 0.999     |
| MMH flow rate (kmol/h)             | 49.1      |
| MHOH mole purity                   | 0.999     |
| MHOH flow rate (kmol/h)            | 0.47      |
| Reboiler duty (MW)                 | 1.137     |
| Condenser duty (MW)                | 1.803     |

\(^a\)Including condenser and reboiler; \(^b\)From/to stage.

MMH exhibits great potential as replacement of MTBE in near future due to its low solubility in water. The separation section of the conventional MMH process has three distillation columns, which require significant energy loads to deliver the required product purities and recycling the excess reactant. To improve the energy efficiency and economic performance, DWC was employed instead of
conventional two separation columns; this was followed by structural optimization using several optimization algorithms. Among these, the Firefly algorithm-based optimization results were found to yield the best performance. As per authors knowledge, this is the first study which address the application of process intensification through DWC technique to reduce the energy requirement in the purification section of MMH process. The results reveal that DWC can be applied to reduce energy consumption by 24% in comparison to the conventional reactor-column MMH process.

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Nomenclature

DWC Dividing wall column
TAC Total annual cost
MMH 2-methoxy-2-methylheptane
MCD Modified coordinate method
PSP Particle swarm paradigm
FF Firefly
MTBE Methyl-tert-butyl-ether
MH 2-methyl-1-heptene
MeOH Methanol
SRC Side-reactor configuration
DME Dimethyl ether
CSTR Continuous stirred tank reactor
DW Dividing wall
MINLP Mixed integer nonlinear programming problem
GA Genetic algorithm
RBFNN Radial basis function neural network
SVM Support vector machine

**TABLE 10** Economic analysis of the conventional, re-optimized conventional, and DWC configurations

| Key economic indicators/distillation arrangement | Conventional process | Dividing wall column (DWC) (proposed) | Savings (%) in comparison to the conventional process |
|-------------------------------------------------|----------------------|--------------------------------------|--------------------------------------------------|
| Number of trays \( (N_T) \)                     | 10                   | 10                                   | -                                                |
| Column C1                                        |                      |                                      |                                                  |
| Column C2                                        | 35                   | -                                    | -                                                |
| Column C3                                        | 12                   | -                                    | -                                                |
| Dividing wall column (DWC)                       |                      | 47                                   |                                                  |
| Total heat duty (MW)                             | 1.997                | 1.449                                | (+27.4%)                                         |
| Economic data                                    |                      |                                      |                                                  |
| Reactor + catalyst cost \((10^6 \dollar)\)       | 0.229                | 0.229                                |                                                  |
| Tot. capital cost \((10^6 \dollar)\)            | 1.182                | 1.243                                | (−5.2%)                                          |
| Tot. operating cost \((10^6 \dollar/y)\)        | 0.526                | 0.399                                | (+24.0%)                                         |
| Tot. annual cost \((10^6 \dollar/y)\)          | 0.920                | 0.814                                | (+11.5%)                                         |

FIGURE 13 Composition profile of the DWC (PF and main column)

TABLE 9 Basis of equipment design and economics

| Equipment   | Design equations for economics                                                                 |
|-------------|-----------------------------------------------------------------------------------------------|
| Reactor capital | \( 17 \cdot 640(D)^{1.066}L^{0.802} \) Length and diameter in meters                          |
| Catalyst cost         | $10/kg                                                                                     |
| Column capital         | \( 17 \cdot 640(D)^{1.066}L^{0.802} \) Length and diameter in meters Diameter: from Aspen tray sizing Length: NT trays with 2 ft. spacing + 20% extra length |
| Heat exchanger cost   | Condenser \( 7296(area)^{0.65} \) \( \Delta T = \text{reflux drum temperature} − 310 \text{K} \) \( U = 852 \text{W m}^{-2} \text{K}^{-1} \) |
|                       | Reboiler \( 7296(area)^{0.65} \) \( \Delta T = 34.8 \text{K} \) \( U = 568 \text{W m}^{-2} \text{K}^{-1} \) |
| Utility costs          | LP steam = $7.78/GJ (6 bar, 160°C) MP steam = $8.22/GJ (11 bar, 184°C) HP steam = $9.88/GJ (42 bar, 254°C) Cooling water = $0.354/GJ Refrigerant at 5°C = $4.43/GJ Refrigerant at −20°C = $7.89/GJ Refrigerant at −50°C = $13.11/GJ |
| Payback period         | 3 y                                                                                         |
CONFLICT OF INTEREST
The authors declare no conflict of interest.

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