Heat transfer studies for the design and optimisation of a distillation column to separate an automotive fuel

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Abstract. Methylal, an automotive fuel has been noticed as a diesel alteration additive with relatively high hydrogen-to-carbon ratio. Methylal is more volatile than diesel fuel but it is used as a diesel fuel component because of its 100% miscibility with diesel fuel. An attractive feature of methylal is the reduction of particulate emissions of toxic pollutants without affecting the energy density. Unfortunately, methylal is found to form a minimum boiling azeotrope with methanol whose separation by conventional distillation is impossible. Here, we have introduced an enhanced technique of pressure swing distillation which separates methylal and methanol by exploiting its pressure sensitivity. This work has addressed the design and optimisation of a pressure swing distillation column to separate the azeotropic mixture of methylal-methanol. A novel technique of pressure swing distillation has resulted in the production of pure methylal and pure methanol. The pressure in high pressure column of pressure swing distillation process has been optimised in such a way that there is minimization of overall cost of the process with maximization of product purities. Later on, a process intensification technique of heat integration has been developed which has resulted in 55.2% savings in energy by reducing the overall load of reboiler.

1. Introduction
Methylal is the formaldehyde with a wide range of applications. In the recent past, methylal has grown steadily owing to its use as a diesel fuel component. Methylal contains 42% oxygen by weight, and has a relatively high hydrogen-to-carbon ratio which makes it 100% miscible with diesel fuel. One of the key features of methylal is that it reduces the particulate emissions of toxic gas pollutants. Although, methylal is found to be more volatile than diesel fuel, but its use as a diesel fuel component is highly appreciating [1,2]. The research indicates that methylal can be an effective blend stock for diesel fuel provided design changes are made to vehicle fuel handling systems [3]. Methylal being a derivative product of coal chemicals and natural gas could be a sustainable solution for the depleting petroleum resources. The pharmaceutical, paint and coating industries consume bulk of methylal because of its desirable attributes of low toxicity, high solvent power and low viscosity etc. The potential of methylal as an automotive fuel and its property as a diesel modification additive has been explored and extensive research regarding its design parameters for the separation purposes has been undertaken in this case study.

There is a tremendous increase in the global demand of methylal because of its use as an intermediate for the production of household goods, reduction in volatile organic compounds (VOC) emissions and fuel components. Moreover, methylal possesses 55% of the energy density of the fuel [4–6]. The production of methylal occurs by a catalytic, reversible reaction between methanol and formaldehyde or paraformaldehyde. This reaction results in the formation of a minimum boiling
azeotrope between methanol and methylal with 94.06% methylal at atmospheric pressure [7]. Due to the formation of complex azeotrope between methylal and methanol, it is essential to explore a separation technique which could effectively separate the azeotropic mixture of methylal and methanol. A survey of separation techniques has been carried out to find a suitable method for the separation of methylal-methanol azeotropic mixture. A detailed literature survey reveals that there are numerous enhanced separation techniques available in literature for the separation of azeotropic mixtures but only few techniques could turn out to be effective. In a broader classification of separation techniques, we can either go for membrane separations or distillation techniques. But due to the technical disadvantage of membrane separation processes like high maintenance costs, poor membrane permeability, and wear and tear issues related to membranes, we have switched to distillation methods. Regarding distillation methods, again we have two alternatives available with us, either to go with those distillation methods which make use of third component (entrainer) to break the azeotrope between two components of a binary mixture or to explore a technique which can separate different components of an azeotropic mixture without the use of any external agent (entrainer) to break the azeotropes. Those techniques which use entrainer to separate the azeotropic mixtures are known as Extractive distillation (ED) and Azeotropic distillation (AD) and the other type of separation which doesn’t make use of entrainer to break the azeotropes is known as Pressure swing distillation (PSD). If we have a survey of literature about these two separation alternatives, we will come to know that the technique of PSD is economically as well as environmentally more viable than AD and ED techniques [8–15]. The reason behind this lies in the fact that use of third component mainly causes environmental concerns, adds to cost and the recovery of this entrainer is very much complex and cost sensitive process. Because of the said reasons, we have explored the technique of PSD in this study. The PSD process works on the principal of exploiting the pressure sensitivity of azeotropes. Therefore, a pre-requisite for the PSD is that the azeotrope should be pressure sensitive. Fortunately, methylal-methanol is found to be pressure sensitive azeotrope. For a PSD technique, a change in pressure shifts the azeotropic composition of azeotropic mixture which results in the separation in an easier way in comparison to any other separation technique. Since, the process of PSD utilises two distillation columns operating at two different pressures; therefore, there is a possibility of heat integration between the two columns which reduces the energy consumption of the entire process. The heat integration is done by transferring the heat of condenser of high pressure column (HPC) to the reboiler of low pressure column (LPC) in order to reduce the load of reboiler. As the price of fuels is touching sky, researchers have to pay attention towards the energy saving techniques. The technology of heat integration in distillation columns is gaining very popularity in chemical industries because it is turning towards energy savings. In addition to energy savings, this technique is environmental friendly as there is no addition of third component to the system which can lead to environmental pollution [16]. Therefore, extensive research has been carried out on PSD along with its heat variant [17–22].

This work is based on the steady state simulation of a pressure swing distillation column for the separation of an automotive fuel (methylal) which is forming a minimum boiling azeotrope with methanol. The technique of pressure swing distillation has been adopted in this work which includes pressure optimisation for high pressure column to minimize the overall cost of the process. This work has been carried out using simulation software of Aspen Plus V8.8. To separate our valuable component (methylal) from methanol, we have done steady state analysis by synthesising a flow sheet which consists of two distillation columns operating at two different pressures to separate the mixture of methylal-methanol azeotropic mixture.

2. Design of pressure swing distillation column

Since, methylal is used as a diesel fuel blend; hence it is necessary to remove all the compounds associated with methylal which are altering its purity. But we have come to know that the methylal is forming a minimum boiling azeotrope with methanol, therefore, its separation process has become a crucial process to be sought out. To separate methylal from methanol, we have deduced a technique of pressure swing distillation (PSD) to obtain highly pure methylal. The technique of PSD is based on the principal of shifting the azeotropic composition by changing the pressure of azeotropic mixture. Pressure swing distillation process consists of two distillation columns operating at two different
pressures. The column which operates at low pressure is known as Low pressure column (LPC) and the column which operates at high pressure is known as high pressure column (HPC). Usually LPC is operated at atmospheric pressure but the selection of pressure in HPC is a critical step in the whole process because it affects the economy of the process. The basic objective here is to separate methylal form methanol. For that, we have designed a process flow sheet schematic of PSD process which is shown in figure 1. From figure 1, we can observe that the configuration consists of two distillation columns operating at two different pressures (1 atm and 3 atm). To separate methylal from methanol, we have considered an equimolar feed of methylal and methanol which is fed to the low pressure column (LPC) at stage no 11 operated at 1 atm. The LPC has 20 number of stages in total. The design spec/ vary tool of Aspen Plus is used to obtain pure methanol (METH) from the bottom of LPC and the distillate of LPC is sent forward to high pressure column (HPC). The HPC is operated at a higher pressure than the LPC (which is operated at 1 atm) so as to have the significant drift in the azeotropic composition of methylal and methanol. The pressure of HPC has to be chosen in such a way that the azeotrope between methylal and methanol breaks easily and the load on reboiler should be optimised. Therefore, there is a trade-off between pressure and total annual cost of HPC. Hence, the expertise lies in the fact that an optimum pressure should be selected for HPC which will minimise total annual cost (TAC) and will maximise the purity of both products (methylal and methanol). The details of pressure selection and optimisation have been discussed in next section. For HPC, we have considered total 20 number of stages with the feed stage location at stage no 9. From the bottom of HPC, pure methylal (METHY) is obtained which is our main product and the distillate from HPC is recycled back to LPC at stage no 7. The purpose of recycle is to enhance the purity of both products (methylal and methanol). By this design schematic, we have met our objective of obtaining both products with 99.9% purity.

Figure 1. Steady state design flow sheet for pressure swing distillation process
### 2.1 Pressure optimisation

The selection of pressure in a high pressure column (HPC) is an important design variable in a pressure swing distillation process. In our case study, the HPC pressure is operated at 3 atm because of following reasons:

i) There is a significant drift in azeotropic composition from 1 atm to 3 atm which was sufficient to break the azeotrope between methylal and methanol.

ii) As the pressure is increased from 1 atm to 3 atm, there is an increase in the vapor-liquid distribution ratio (K-values) across the trays which help in getting high purity desired product.

iii) Increase in the pressure from 1 atm to 3 atm has resulted in improving the separation process between methylal and methanol as there is an increase in the relative volatility of two products.

But a key point to be noticed here is that the pressure shouldn’t be increased beyond a certain limit as it results in an increase in the recycle flow rates which increases load on the reboiler and thereby adds to the cost of the entire process. The pressure of 3 atm is found to be optimum for HPC as it doesn’t lead to high total annual costs (TAC). From figure 2, it can be observed that the TAC is minimised at a pressure of 3 atm, hence, HPC is operated at 3 atm pressure. The cost correlations are adopted from Douglas [23]. The payback period has been taken as 3 years. The cost calculations for both pressure swing distillation (PSD) technique as well as Heat integrated pressure swing distillation (HIPSD) technique has been evaluated using correlations given in Table 1.

![Figure 2. Effect of pressure on total annual cost](image)

#### Table 1- Cost calculations

| Basis of Economics |
|-------------------|
| **Column vessel cost:** |
| $C_1 = \left(\frac{M & S}{280}\right) \times 937.636 \times ID^{1.066} \times H^{0.802} \times (2.18 + F_c)$ |
| $Length, H = 0.6 \times \left(\frac{N_t}{0.75}\right) - 3 + 6, (m)$ |

Diameter: ID is calculated by “Tray sizing” function in Aspen Plus, (m)

$N_T$ is the number of Trays, 6 refers to installation height

$F_c = F_m \times F_p,$

$F_m = 3.67,$

$F_p$ can be obtained by the following
| Pressure (atm) | ≤3.4 | 6.8 | 13.6 |
|---------------|------|-----|------|
| $F_p$         | 1.00 | 1.05| 1.15 |

**Plate cost:**

$$C_2 = \left( \frac{M \times S}{280} \right) \times 97.243 \times I_D^{1.55} \times H \times F_c$$

$$F_c = F_s + F_i + F_m,$$

$$F_s = 1,$$

$$F_i = 0,$$

$$F_m = 1.7$$

$F_c = 0$ (Sieve plate column)

0.6 is the typical distance between the trays (m)

**Heat Exchanger cost**

$$C_3 = \left( \frac{M \times S}{280} \right) \times 474.668 \times A^{0.65} \times (2.29 + F_c)$$

Area of Heat exchanger: $A = \frac{Q}{\Delta t \times k}$

$Q$ is the duty of Heat exchanger, (Kw)

$\Delta t$ is the temperature difference, (K or °C)

$k$ is the Heat transfer coefficients, 0.852 (kW/(K.m²)) for condensers and 0.568 (kW/(K.m²)) for reboilers.

$$F_c = (F_d + F_p) \times F_m$$

$F_m = 3.75$

$F_d = 1.35$ (Kettle reboiler)

$F_d = 0.8$ (for the fixed tube sheet heat exchangers),

$F_p$ as shown in the following table

| Pressure (atm) | ≤10.2 | 20.4 | 27.2 | 54.2 |
|---------------|-------|------|------|------|
| $F_p$         | 0     | 0.10 | 0.25 | 0.52 |

$F_s, F_d, F_p, F_m$ are correction factors

**Annual steam cost**

$$C_4 = C_s \times Q_R$$

$Q_R$ is reboiler duty (GJ)

$C_s$ is steam price ($/GJ)$

**Annual cooling water cost**

$$C_5 = C_w \times Q_c$$

$Q_c$ is condenser duty (GJ)

$C_w$ is price of cooling water which is 0.354 ($/GJ)$.

For the refrigerated water, the price is 4.43 ($/GJ)$.

**Energy cost**

LP steam (433K) = 7.72 ($/GJ)$

MP steam (457K) = 8.22 ($/GJ)$

HP steam (537K) = 9.88 ($/GJ)$
Here, M&S are Marshall and Swift Index, M&S = 1431.7 (data from CEPCI).
Capital cost = Column vessel cost (C1) + Plate cost (C2) + Heat exchangers cost (C3)
Operating cost = Annual steam cost (C4) + Annual cooling water cost (C5)

\[ \text{TAC} = \frac{\text{Capital cost}}{\text{Payback period}} + \text{Operating cost} \]

3. Design of heat integrated pressure swing distillation column

The objective of obtaining pure methylal and methanol is fulfilled by the design of pressure swing distillation technique but if we have a look on reboiler duties of both columns, to our surprise, we observe that the total heat load is 9.6MW which is too high for a process to be economical. This has urged us to search for a process intensification technique which can reduce the total heat load of the process. A technique of heat integration has been found to be the most competent technique which can reduce the energy consumption of a process in a safe and better way. The heat integration in distillation columns is obtained by transferring the heat of condenser of HPC to the reboiler of LPC which reduces the overall load of the process. To achieve heat integration in a process, the heat duty of condenser of HPC and the heat duty of reboiler of LPC should be equalised so that an equal amount of heat from condenser should be transferred to reboiler.

The heat transfer is governed by the equation given below [24].

\[ Q_{\text{reb}}^{\text{LPC}} = -Q_{\text{cond}}^{\text{HPC}} = UA(T_{\text{cond}}^{\text{HPC}} - T_{\text{reb}}^{\text{LPC}}) \quad \ldots \quad (1) \]

Where, \( Q_{\text{reb}} \) represents the amount of heat of reboiler of LPC; \( Q_{\text{cond}} \) represents the amount of heat of condenser of HPC; \( U \) is the heat transfer co-efficient; \( A \) is the heat transfer area and \( T \) represents the temperature of stage.

The above equation can be satisfied by using Design spec tool of Aspen Plus where the duties of condenser and reboiler are equalised by varying the heat duty of reboiler of HPC. The process flow sheet schematic for heat integrated pressure swing distillation process is shown in figure 2. From figure 2, we can observe that the load on the reboiler of LPC is taken by the condenser of HPC as all the heat is supplied by the condenser of HPC to boil the liquid of LPC, resulting in the reduction of net energy consumption in the process. The overall heat duty in a heat integrated process design has been reduced to 4.3 MW only resulting in about 55.2% savings in operating cost of the process.
4. Results and discussion

The technique of pressure swing distillation used for obtaining pure methylal (automotive fuel) has been designed using two distillation column schematic. The key factor of the entire flow sheet is to optimise the pressure of high pressure column (HPC) with the objective of minimising the cost of entire process. The analysis shows that a pressure of 3 atm is optimum for obtaining pure methylal from HPC and also this pressure has rendered the entire process economical. The saving of 55.2% operating cost has been calculated from the cost analysis done for both Pressure swing distillation (PSD) and Heat integrated pressure swing distillation (HIPSD) processes. Refer to figure 1, the base case design flow sheet of pressure swing distillation process shows that the reboiler duty (QR1) of low pressure column (LPC) is 5.29 MW and that of high pressure column, HPC (QR2) is 4.3 MW respectively. The total reboiler duty (which is the summation of QR1+QR2) equals to 9.59MW. Coming to the steady state design flow sheet of heat integrated pressure swing distillation column (HIPSD) (refer to figure 3) , we can observe that the reboiler duty (QR1) of LPC is eliminated as the entire heat is supplied from the condenser of HPC. Therefore, the total duty of HIPSD constitutes of only the reboiler duty of HPC which equals to 4.3MW only. The percentage savings in the total duty of PSD and that of HIPSD is calculated as

\[
\text{Percentage savings in energy} = \left( \frac{9.59 - 4.3}{9.59} \right) \times 100 = 55.2\%
\]

The desired products, pure methanol is obtained from the bottom of low pressure column (LPC) while as the pure methylal is obtained from the bottom of High pressure column (HPC). The temperature, flow and composition profiles of two distillation columns (LPC and HPC) are shown in figure 4. In figure 4, we have plotted temperature profiles of both columns side by side, liquid and vapor compositions of both columns side by side and then the liquid and vapor flow rates of both columns side by side.
5. Conclusion

This work has successfully addressed the technique of pressure swing distillation (PSD) which is used to separate an automotive fuel of methylal (which is used as a diesel fuel additive) from its associated components. The technique of PSD has been found to be a competent, economical, reliable and environment friendly. Methylal which is forming a minimum boiling azeotrope with methanol has been obtained with 99.9% purity. The heat transfer studies in a heat integrated pressure swing distillation column have been highlighted to reduce the net energy consumption in the process. The selection of pressure in high pressure column has been optimised by minimizing the total annual cost. Heat integration in pressure swing distillation process has resulted in significant energy savings of about 55.2%.

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