Simulation of Methoxy methyl heptane (MMH) production using unisim design R460.1

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Abstract. Various fuel additives are employed till now like ethanol, ethyl tertiary butyl ether (ETBE), MTBE, Di Isopropyl alcohol (DIPA) etc. after the phase-out of lead-based compounds to enhance the octane number of fuel. MMH is suggested as an alternative to methyl tertiary butyl ether (MTBE) and similar ethers since they causes groundwater contamination. The liquid phase reversible reaction of methanol (MHOH) with 2-methyl-1-heptene (MH) produces MMH. But there is an undesirable reaction also to form Dimethyl ether (DME) and 2-methyl -2-heptanol (MHOH). The process of MMH production is simulated using Unisim Design software R460.1. Conventionally, MMH is produced through a reactor and three distillation column sequences for yielding high purity MMH. This reactor - column sequence requires either high MH recycle or large-sized reactor to have the desired yield. Both results in large capital and operating costs. A reactive distillation concept can tackle these constraints with reactor and distillation in a single column known as reactive distillation column (RDC). The feasibility of RDC and analysis of the process can be observed using Unisim Design software since pilot plants are costly for this type of RD process. The simulation of the process using different test bed Unisim R460.1 is not explored yet.

1. Introduction

Addition of fuel additives increases the octane no. of gasoline, thereby reducing the carbon monoxide and other soot emissions effectively. Various fuel additives are employed till now like ethanol, ethyl tertiary butyl ether (ETBE), most commonly used MTBE, Di Isopropyl alcohol (DIPA) etc. after the phase-out of lead-based compounds. The primary purpose of fuel additive is to decrease the emissions of carbon monoxide and ozone from automobiles. The details and conclusions relating the risk of MTBE to California’s groundwater supplies are well studied in the literature [11]. Presence of small amount of MTBE causes foul smell and bad taste for water. It is also a carcinogen to living beings. Tertiary amyl methyl ether (TAME), Tertiary amyl ethyl ether (TAEE) etc. are the newly proposed fuel additives. They also cannot be concluded as the perfect solution to overcome the groundwater contamination problem. Whereas, 2-methoxy-2-methyl heptane (MMH) is considered as the best candidate to replace these fuel additives.

Groundwater contamination is assessed mainly by the temperature dependency of the solubility of ether when they release to the ground. High molecular weight and branched fuel additives exhibit less pollutant character due to their decreased solubility in water. However, the 2-methoxy-2-methyl heptane (MMH), a higher molecular weight ether is considered as an excellent alternative. There is an excellent potential for MMH to become essential and most produced chemical globally as a fuel additive. Large scale production MMH is very much needed because of its spectrum of application.
The production and optimization of MMH synthesis process using conventional reactor-distillation column sequence are well studied in the literature. Luyben studied the design and control of the Methoxy-Methyl-Heptane Process using Aspen plus software [2]. Hussain et al. have proposed a novel reactive distillation column configuration for the preparation of MMH [3] using Aspen plus software. The major objective of the present work is to model and simulate the MMH synthesis process replacing the conventional reactor-distillation configuration with a reactive distillation sequence using Unisim Design R460.1. Production of Methoxy methyl heptane (MMH) and further case study analysis using Unisim are not explored yet. Activity model like Wilson, UNIQUAC and NRTL are varied to study the effect on Methoxy methyl heptane (MMH) concentration. Besides, activity model, effect of other operation variables like reboiler duty and reflux ratio are also analysed by performing sensitivity analysis. The study gives evidence about a successful simulation with UNISIM because the results are close with the experimental data [3] at the same operating conditions. Simulations gives insights of the actual performance of process under changes. And these are time efficient, cheaper and safer method of analysis.

2. MMH Process

The major reactions involved in the production of 2-methoxy-2-methyl heptane (MMH) is shown below.

$$\text{CH}_3\text{OH} + \text{C}_8\text{H}_{16} \rightleftharpoons \text{C}_9\text{H}_{20}\text{O} \tag{1}$$

There is also an undesirable reaction to form dimethyl ether (DME) and 2-methyl-2-heptanol (MHOH).

$$2\text{CH}_3\text{OH} + \text{C}_8\text{H}_{16} \rightarrow \text{C}_2\text{H}_6\text{O} + \text{C}_8\text{H}_{18}\text{O} \tag{2}$$

The overall reaction rates have units of kmol s\(^{-1}\) kgcat\(^{-1}\). Concentrations are in terms of mole fractions.

$$\text{RD} = k_{DF}X_{\text{MeOH}}X_{\text{MH}} - k_{DR}X_{\text{MMH}} \tag{3}$$

$$\text{RU} = k_U(X_{\text{MeOH}})^2 \tag{4}$$

\(k_{DF}\) and \(k_{DR}\) represent the forward and backward rate constants (Eq. 1), respectively. \(k_U\) indicates the undesired reaction rate constant. The activation energy of the forward MMH reaction is more significant than that of the reverse reaction, which means that high reactor temperatures should favor conversion. The upper-temperature limit of the resin catalyst is about 400K. Methoxy Methyl Heptane (MMH) production involves bounded etherification chemistry with the reversible desired reaction. The kinetic parameters for MMH synthesis are given below in Table 1.

| Activity | kmol s\(^{-1}\) kgcat\(^{-1}\) | J kmol\(^{-1}\) |
|----------|--------------------------|----------|
| \(k_{DF}\) | 6.7 x 10\(^7\) | E\(_{DF}\) | 90000 |
| \(k_{DR}\) | 2.1 x 10\(^{-6}\) | E\(_{DR}\) | 900 |
| \(k_U\) | 1.3 x 109 | E\(_U\) | 105900 |

The catalyst used in the synthesis is the industrial-grade Amberlyst 35 Wet (Rohm & Haas). It is macro reticular, strongly acidic, cationic and polymeric [3]. The maximum operating temperature and the density were reported as 150°C and 800 gL\(^{-1}\), respectively [3]. The flow sheet for the production of MMH conventionally is illustrated in Fig 1. Fixed bed catalytic reactor was utilised to carry out the reaction between MeOH and MH.
Luyben, W. L [2] simulated the process using Aspen, but this paper utilized a different test bed, which is Unisim Design environment.

3. Process simulation

3.1 Steady state simulation of conventional MMH production
The simulation started with the development of steady state model. Thermodynamic properties of the vapours and liquids estimated by UNIQUAC were used in all units of the process. Since MMH and 2-methoxy-2-heptanol (MHOH) were not in the Unisim databank, hypothetical components were generated by using create a hypo component tool under simulation basis manager in Unisim. The data used for building hypothetical components was as listed in Table 2 for MMH and MHOH. Other unknown properties of the components were estimated by using these inputs.

| Component Name     | MMH  | MHOH |
|--------------------|------|------|
| Chemical Formula   | C₆H₁₄O | C₆H₁₈O |
| Molecular Weight   | 144.3 | 130.2 |
| Normal Boiling Point (°C) | 151.2 | 198.2 |
| Ideal Liquid Density (kgm⁻³) | 793 | 820.0 |

The process flow sheet developed for the steady state simulation of the process is shown in Figure 2.
The reactor is a 12 m$^3$ continuous stirred tank reactor (CSTR) operating at 400 K and 12 atm. A fresh methanol stream (MeOH) is fed at 50 kmol h$^{-1}$. Fresh 2-methyl-1-heptene (MH) is supplied to the reactor at 49.51 kmol h$^{-1}$ and combined with a recycle stream from a downstream distillation column to give a total of 129.5 kmol h$^{-1}$ of MH fed to the reactor. In column C1, the reactor effluent is fed on stage 8 of a 12-stage distillation column. The column operates at 10 atm, which gives a reflux-drum temperature of 318 K and thus allows cooling water in the condenser. The bottom from C1 is fed to column C2 that separates the product MMH from the recycle MH. The column has 42 stages and is supplied on stage 23. It operates under vacuum conditions (0.4 atm) with a reflux-drum temperature of 358 K. A reflux ratio of 2.198 is required to achieve the specified separation.

The base temperature is 410 K so that medium-pressure steam can be used in the reboiler (11 bar, 457 K). The diameter of the column C2 is 2.04 m. The third column C3 has 22 stages and is fed on stage 14. The distillate is the MH product (49.02 kmol h$^{-1}$). Column C3 operates under vacuum (0.1 atm). The reflux drum temperature is 352 K, and the base temperature is 426 K using medium-pressure steam. The reflux ratio is 1.59. The column diameter is 1.59 m. The MMH process provides an interesting example of the classical trade-off between reactor sizes and recycles. The high reactor temperature is favoured due to raised activation energies. But it is limited by catalyst activity to 400 K. By either increasing reactor size or keeping the concentration of methanol less by using a substantial excess of Methyl heptene (MH), MMH production can be increased.

The reactor effluent is 132.1 kmol h$^{-1}$. Thus the per-pass conversion of methanol is 80.94%, and the per-pass conversion of MH is 42.61%.

**Table 3.** Result of the simulation.

| Product stream (Overhead product of column C3) | Flow rate (Kmol/hr) | MMH present (%) |
|---------------------------------------------|---------------------|-----------------|
| MMH                                         | 49.00               | 97.8            |
Table 4. Per-pass conversion of MeOH and MH

| Per-Pass Conversion of MeOH | Per-Pass Conversion of MH |
|---------------------------|---------------------------|
| 80.94%                    | 42.61%                    |

In case study 1, the graph for actual % conversion with MH recycle flow rate is plotted. The actual percentage conversion of reactant into the product is increasing gradually for the feed MH to the reactor. Excess of MH as the result of MH recycle stream enhance the forward reaction as per kinetics. And thereby increase the conversion to MMH. In case study 2, the actual percentage conversion with MeOH flow rate is plotted. An increase in the flow rate of the MeOH results in the less conversion of reactant into the MMH product. As per the kinetics, the increase in MeOH flow rate results in the unwanted side reactions and this will be adversely affecting the product yield. MMH production also favours an increased reactor temperature and volume. But the activation energies of the two competing reactions support high reactor temperature. At the same time the yield of catalyst activity is limited to 400 K. The desired product yield is achieved by either increasing reactor size or excess of MH. In case study 3, the relation between MMH productions with reactor temperature is investigated. Case study 4 depicted the relation between actual percentage conversions with reactor volume.

Figure 3. RXN% conversion relation with MH –recycle (a), RXN% conversion relation with MeOH (b), MMH production relation with reactor temperature (c), RXN% conversion relation with a reactor volume (d).
Large recycle of MH increases separation costs and increasing the reactor size results in high capital cost. An RD configuration could substantially reduce the cost of energy, and total annual costs (TACs) compared to those for a conventional case.

### 3.2. Feasibility of reactive distillation for 2-methoxy-2-methyl heptane (MMH) process

The reaction for the production of Methoxy methyl heptane is very much suitable for a reactive distillation configuration [1]. The MMH synthesis shows the problem of chemical equilibrium limited conversion for the desired reaction. Also, there is an irreversible undesired side reaction. Reactive distillation can overcome the limitations of equilibrium and increase selectivity. Another standard for the economic feasibility of reactive distillation is the temperature difference between reaction (TR-main) and distillation operation (TD). This should not be over 50°C. Usually, this reaction chooses to occur around 400 K due to the limitation of the activity of the catalyst. Besides, distillation temperature is maintained around 426 K. Since the difference in temperature between the separation and reaction is lesser than 50°C, reaction and separation in a single unit can provide substantial economic and technical benefits.

The chemical equilibrium constant (Keq) has substantial effects on the reactive distillation design. The value of Keq should be greater than 1 for the choice of the RD column. The constant of equilibrium for the preferred reaction can be found by $k_\text{Df}/k_\text{Dr}$. Based on Table 2.1, Keq at 423 K provides a value of 316, which shows that the MMH system has the most favourable reaction kinetics for the implementation of RD column design. Since the desired reaction is the exothermic operating temperature of the RD column (TRD) should be maintained lesser than that of undesired side reactions (TS) occurred. Here, the temperature of the undesired side reaction is relatively larger than the TRD of RD. Besides, RD is financially viable for production rate in the range of 0.5-1.0 ktyear$^{-1}$. Since the rate of production of MMH is 62 ktyear$^{-1}$, RD process is economically feasible.

### 3.3. Steady state modelling of Reactive Distillation

Reactive distillation (RD) is unique in the sense it cooperates both reaction and separation in a single column. This type of process intensification brings significant improvements in manufacturing and processing of chemicals. However, RD substantially reduces the equipment size, recycling rate, energy consumption and production of waste. Process intensification such as RD is perfect for limited equilibrium reactions like MMH production. The RD column which operates around 1.77 atm consists of 35 stages. There is only one rectifying section; the reactive zone is between stages 2 and 12, followed by the stripping section at the bottom. The stages are numbered according to the UNISIM Design stage notation with stage 35 being the reboiler. The fresh MeOH stream as a low-boiling point reactant is supplied at the 13th stage while the fresh MH stream mixed with MH recycle from column C2 accounts a total of 128.98 kmol h$^{-1}$. It is fed to 1st stage of RD column. The ratio of M.H./MeOH seems to be higher. Around 660 kg catalyst was used for each stage of the reactive section chosen [3]. The feed, distillate from RD column is supplied to 5th stage of 12 stages C2 column. It provides DME as the distillate while the bottom is returned back at the bottom to RD column. Column C2 operating pressure was set at 10 atm. DME is produced around 0.518 kmol h$^{-1}$ with 99.99% purity [3]. Column C3 is supplied with a feed stream from the bottom of the RD column. Column constitutes 15 stages, and 8th stage was considered as the feed stage. The distillate product was 49.02 kmol h$^{-1}$ with 99.9 mol % MMH. The bottom was 0.49 kmol h$^{-1}$ with 99.99% of undesired MHOH. This column operated under 0.1 atm pressure. The reflux drum temperature was assumed around 352 K, and the temperature at the bottom was maintained 401 K, associated by low-pressure steam. The column diameter was 1.42m[3].
Figure 4. Steady-state model of reactive distillation sequence.

Figure 5. Temperature (a) Composition profile (b) of reactive distillation column.

Conventional reactor column sequence requires reactor, column C1, C2 & C3 to achieve the desired MMH product purity. Whereas the RD configuration meets the desired product by a single reactive distillation unit and thereby reduce the capital cost significantly.

Table 5. The product purity of Conventional & RD configuration.

|                     | Conventional case            | Reactive distillation |
|---------------------|------------------------------|-----------------------|
| Product purity (%)  | 37.061(reactor-C1)           | 94.78 RD              |
|                     | 97.82(reactor-C1-C2-C3)      | 99.47(RD-C2-C3)       |

The effect on Methoxy methyl heptane (MMH) concentration for various thermodynamic models like Wilson, UNIQUAC and NRTL were studied to obtain the best suitable model. Mole fraction of MMH along the reactive column stage location was analysed. UNIQUAC was chosen as the better model which gives relatively large amount of MMH along the column. Also, the results obtained through simulation was closer with the published data [3] for the UNIQUAC thermodynamic model. Other three activity model has shown the similar result. Although the end stage composition was almost similar.

![MMH composition profile](a) (b) (c)

**Figure 6.** MMH composition profile for various activity models (a), various reboiler pressure, (b) and various reflux ratio (c).

In addition to the search for best thermodynamic models, the effect of other operation variables like reboiler duty and reflux ratio was also studied by performing sensitivity analysis. Relatively large MMH mole fraction was provided by chosen reboiler pressure of 190.5 kPa than 202 kPa. There were convergence issues relating wide change in operation variables. MMH concentration gradually increased with reflux ratio. But increase in reflux also cause increase in diameter and there by increased total capital cost. Present steady state model of RD was developed based on operating parameters like reboiler pressure 190.5 kPa, reflux ratio 3.61 and UNIQUAC activity model.
3.4 Validity of RD steady state model

The model validity could be determined by the comparison with the experimental result or even with different theoretical results that use different simulation method.

Temperature and composition profile of the present model and Arif Hussain work [3] were compared and shown relatively good agreement with each other. But some sort of difference in the path (or error) might be due to using different thermodynamic models and energy correlations. The main difference was because of Arif Hussain, Moonyong Lee [3] experimental work and our present model developed in UNISIM Design software. For the same feed specifications, mole fractions of (2-methyl1-heptene, 2-methoxy2-methyl heptane, dimethyl ether) of distillate in this model were 0.822, 0.00344, and 0.010 respectively. Besides, Arif Hussain, Moonyong Lee works illustrated the profile in the order 0.9927(MH), 0.004(MMH) and 0.0064(DME). Mole fractions of bottom stream (2-methoxy2-methylheptane, 2-methyl1-heptene, 2-methyl2-heptanol) from present model were 0.948, 0.051, 0.0005 respectively. Corresponding referred work [3] values were 0.989, 0.0005, and 0.0104 accordingly. Relatively there was a good agreement of mole fractions in the bottom and distillate in comparison with the referred work [3].

4. Conclusion

Production of Methoxy methyl heptane, a recently proposed gasoline additive was simulated using Unisim Design R460.1. Steady state simulation of both conventional and process intensified approach such as reactive distillation were studied. These steady-state simulations could be used extensively for the design, analysis and optimization of MMH production processes. Simulated model was validated against the published works. The effect of flow rate of MH and MeOH on MMH production was analysed through case study of conventional scheme. However there was an increase in the conversion of reactant into product for increase in MH flow or reactor size. Both strategy were costly. Hence, results obtained from the simulations have revealed that the reactive distillation configuration was better than the conventional process method in producing high purity of fuel additive MMH with lower capital and equipment cost.

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