Design of Extraction Column Methanol Recovery System for the TAME Reactive Distillation Process

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Abstract

This paper studies the synthesis and the design of methanol recovery system for TAME reactive distillation process using extraction column with water as a solvent. The design of the extraction column system has not been studied in the literature. The effect of operating conditions such as solvent flowrate, extraction column temperature, and number of equilibrium trays are studied. It is found that methanol could be recovered completely from the hydrocarbon when 5 equilibrium trays in the extraction column are used. The column is operated isothermally at an optimum temperature of $40^{o}C$ and the optimum solvent to process ratio is found to be close to one. The recovery system consists of a methanol distillation column which was optimized to recover methanol and recycle water to the extraction column. Other auxiliary units are designed to complement the overall process flowsheet.

Keywords: TAME, liquid extraction, methanol recovery

1. Introduction

A process of producing TAME via reactive distillation has been presented by Subawalla and Fair (1999). In their work, the process consists of a fixed bed pre-reactor to carry out the bulk of the reaction between C_5 and methanol to produce TAME and a reactive distillation. Methanol forms a minimum boiling azeotrope with the different C_5 components present in the system. The overhead of the reactive distillation is drawn near the azeotrope. Subawalla and Fair work did not handle the recovery of methanol from the overhead. Al-Arfaj and Luyben (2003) used Subawalla and Fair design and supplemented it with a methanol recovery system to complete the production process flowsheet. They have found that methanol plays an important role in the design of the overall flowsheet as it is consumed by the reaction and required by the azeotrope mixture in the overhead of the reactive distillation. They used pressure swing distillation to separate the methanol and the C_5 components. Their recovery system consists of two conventional distillation columns operated at different pressures to work around the azeotrope. Al-Arfaj and Luyben (in press) have developed a plantwide control scheme to control the entire process.

This work is the first of two series. The first part which is detailed in this paper is aimed at developing an alternative methanol recovery system to separate methanol from the

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C_5. This new recovery system utilizes a liquid-liquid extraction process and a conventional distillation column. Aspen Plus and Distil were used in this part. In the second part under progress, the preliminary design developed here will be used to study the plantwide control of the entire TAME production process including the reactive column and this new recovery system.

Stichlmair and Fair (1998) presented a schematic diagram for a process to produce TAME using reactive distillation and liquid extraction to recover methanol. The design of the liquid extraction recovery system for the TAME process and the impact of various operating parameters on the performance of the recovery system have not been published in the open literature.

The objective of this work is to develop a preliminary design for this recovery system. This work is useful as benchmark problem for researchers and for engineers who are using TAME reactive distillation technology or for investment evaluation.

2. Design Procedure

In order to design this recovery system, the overall flowsheet should be synthesized first. This recovery system takes its feed from the overhead of the reactive distillation which is obtained from Al-Arfaj and Luyben (2003) - see Table 1. In order to minimize the degrees of freedom to synthesize this system, the feed flowrate and composition were assumed constant. The recovery system consists of: extraction column, decanter, heat exchangers, distillation column and a pump. UNIFAC was used as the basis for the VLE and LLE calculations in this work. Mole basis are used throughout this work.

2.1 Extraction Column

The liquid-liquid extraction column without agitation is the heart of this recovery system. It is selected over other extractor types due to its simplicity and practicality. The objective of this column is to extract the methanol (solute) from the C_5 (carrier). The first thing to select is the solvent that will be used to achieve this extraction. Stichlmair and Fair (1998) indicated that water could be used as a solvent. C_5 components are immiscible in water and it has high affinity for methanol. Designing a liquid extraction column for this multicomponent system cannot follow the graphical design procedures as they are mostly limited to ternary systems. Therefore, the procedure that is followed here is to highlight the important design parameters and then conduct a through sensitivity analysis to find the optimum design. For a completely specified feed, there are seven major design parameters to describe the liquid extraction column:

1- Column pressure: pressure has little effect on the LLE and thus is not an important design parameter. However, the pressure must be selected to be greater than the bubble point pressure of the two liquid phases at all trays at the operating temperature (Seader and Henley, 1998). Most extractors operate around ambient temperature; therefore, a column pressure is set to 2 bars which will ensure that all the components are in the liquid phase around the ambient temperature (20-60°C).

2- Process feed location: most liquid extraction columns have the process feed at the bottom before the first tray. In order to minimize the design analysis, the process feed is set to enter the extractor before the first tray in the bottom.

3- Solvent feed location: similar to the process feed, the solvent feed is set to enter the column above the last tray in the top of the column according to typical columns.

4- Solute impurity in the solvent: this plays important rule in determining the degree of solute impurity in the extractor overhead. However, this is set by the distillation column as this feed is the bottoms of the distillation column. The effect of this parameter is discussed in Section 3.

5- Number of equilibrium trays: this is an important design parameter that will be discussed in Section 3.

6- Solvent feed flowrate: this plays an important role as shown in Section 3.

7- Column temperature: if the solvent feed enters the column at the same temperature as the process feed, the column is operated isothermally since the heat of mixing is relatively small. Therefore, the extraction column is designed to operate isothermally. The effect of operating temperature is discussed in Section 3.

2.2 Distillation Column

The objective of this column is to separate methanol from water. Therefore, to design this column, a standard binary distillation design procedure is followed. For completely specified feed conditions and products specifications, there are two degrees of freedom: operating pressure and the Reflux Ratio (RR). The column pressure is set to enable the use of cooling water in the condenser. The overhead is mainly methanol; therefore, setting the column pressure to one bar will enable the use of cooling water as the overhead will be around $60^{o}C$. This leaves us with the RR as the major design parameter; however, the feed composition will vary according to the solvent flowrate to the extraction column. Therefore, two extreme cases will be investigated: Case 1- 50% mole water in the feed which corresponds to a solvent flowrate around 275 kmol/hr and Case 2- 90% mole water which corresponds to a solvent flowrate around 2500 kmol/hr.

The solvent flowrate could be varied during operation as this is a recycle flow from the distillation bottoms to the extractor. Therefore, in the design stage, we will design the distillation column based on the worse case scenario to be in the conservative side.

2.3 Auxiliaries

The auxiliaries in this system consists of heat exchanger to cool the solvent feed to the extractor, a pump to increase the pressure of the solvent to 2 bars and a decanter to recover some of the water carried in the extractor overhead (raffinate) and return to the distillation column. The decanter temperature determines the amount of water recovered from the raffinate. Lower temperature will require special cooling medium and might be expensive. The temperature is set to $20^{o}C$. A cooler is used to pre-cool the decanter feed to $20^{o}C$. The heat exchanger is designed to cool the distillation bottoms to the required extractor temperature by heating the extractor bottoms (extract). The heat released due to the cooling is used to heat the extract which is fed to the distillation column. The process flowsheet diagram is shown in Figure 1.

3. Results and Discussion

3.1 Extraction Column

The feed to the extractor, given in Table 1, is around 1078 kmol/hr with around 25% methanol. We need to find out the required equilibrium trays, solvent feed flowrate and the extractor operating temperature. The most important specifications are the methanol in the raffinate and the total C_5 in the extract. In order to find the optimum design, the

following ranges were investigated: number of trays (2-10), solvent flowrate (500-2000kmol/hr) and extractor's temperature (20-60°C).

It was found that the higher the methanol impurity in the solvent feed the higher the methanol impurity in the raffinate at a fixed number of trays. That methanol impurity decreases when extractor's temperature decreases. This shows that the distillation specifications for bottoms impurity should be strict to minimize the methanol impurity in the raffinate.

To find the required number of trays, the extractor's temperature is fixed and the methanol flowrate in the raffinate is checked for various number of trays and solvent flowrate. Figure 2 shows that after five equilibrium trays methanol in the overhead could not be improved by additional trays but it could be improved by increasing the solvent flowrate. This sets the number of equilibrium trays to 5. The actual number of trays could be four times or more than the equilibrium number due to the low tray efficiency in the liquid-liquid extraction columns without agitation.

At fixed number of equilibrium trays, the solvent flowrate is varied for a fixed extractor's temperature and the extract total C_5 flowrate is observed. The C_5 flowrate decreases as the solvent rate is increased till 1000 kmol/hr then they started to increase again. Although the methanol in the raffinate deceases as the solvent flowrate increases, the rate of this decrease reduces as the solvent rate increases (see Figure 2). In addition, higher solvent flowrate means higher recycling which requires more energy and thus will be more expensive to operate. For a fixed solvent flowrate, increasing the extractor temperature from 20°C decreases the total C_5 in the extract till 40°C is reached where the C_5s in the extract starts to increase again. Figure 3 shows the impact of solvent flowrate on the total C_5 in the extract at various extractor temperature. It is clear from this result that the optimum extractor temperature is 40°C and the solvent flowrate is around 1000 kmol/hr (solvent to feed ratio around 1).

3.2 Distillation Column

As discussed in Section 2, the column is design according to standard procedure. The column product specifications is set high in order to minimize the methanol impurity in the bottoms and consequently in the extractor raffinate. The bottoms and overhead impurity specifications (water in overhead and methanol in bottoms) were set to be 0.01% mol. As discussed in Section 2.2, two extreme cases were studied: Case 1 and Case 2. Although the optimum solvent rate is found to be 1000 kmol/hr, during operation higher recycle could be encountered and thus the column should be designed according the worst scenario (Case 2).

For a specified feed conditions and product specifications, setting a RR sets the number of trays and the feed location according to McCabe Thiele method. Figure 4 shows the required number of trays for various reflux ratios for both extreme cases. For Case 1, a column could be designed with 17 trays and a RR around 3. Fewer trays will require higher reflux and will not be optimum due to the high energy consumption. However, if the column was designed this way and the recycle flowrate is increased, i.e. water composition in the feed to the distillation increased (Case 2); the RR would have to be increased to 2 or 3 times to meet the specifications. The difference between the required reflux ratios in the two extreme cases to meet the specification for a fixed number of trays is shows in Figure 4 as well. The difference in RR is constant at higher number of trays but increases rapidly at lower number of trays. From this we can find that the

optimum number of theoretical trays of is 23 (excluding reboiler and condenser) with a RR set by the worst case to be 3 and a feed location of 16 (numbering top bottom).

4. Conclusion

The liquid extraction recovery system for the TAME process has been developed. The system consists of a liquid extraction column, a distillation column plus some other auxiliaries. The extraction column has 5 equilibrium trays and is running isothermally at 40°C at 2 bars. The solvent flowrate is around 1000 kmol/hr. the methanol distillation column has 23 theoretical trays with a total condenser and a partial reboiler and the feed at the 16th tray from top bottom. The RR is 3 and the operating pressure is 1 bar. The decanter cooler is operated at 20°C with a duty of -0.7864 Mw. The decanter is operated at 20°C and 2 bars. The heat exchanger is operated to cool the distillation bottoms to 40°C with a heat duty of -1.2241 Mw which is used to heat the extract to 80.6°C. The pump is operated at a discharge pressure of 2 bars. This design will be used as a basis to conduct a plantwide control study on the TAME process adopting this recovery system. It is a preliminary design which could be refined further to detailed design.

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Table 1: Process mole balance and stream conditions

	PROCESS	SOLVENT	C5S	EXTRACT	METHANOL	B	MAKEUP
Temp. C	40	40	20	40	56	99.6	40
Press. bar	2	2	2	2	1	1	2
Mole Flow - kmol/hr	1078.56	995.10	808.39	1260.39	276.30	988.98	6.12
Mol Frac							
MEOH	0.2531	0.0000	0.0000	0.2166	0.9881	0.0000	0.0000
2M1B	0.0030	0.0000	0.0040	0.0000	0.0001	0.0000	0.0000
2M2B	0.0143	0.0000	0.0190	0.0001	0.0003	0.0000	0.0000
NC5	0.0818	0.0000	0.1089	0.0002	0.0008	0.0000	0.0000
IC5	0.4645	0.0000	0.6182	0.0010	0.0045	0.0000	0.0000
1C5=	0.0352	0.0000	0.0464	0.0003	0.0015	0.0000	0.0000
2C5=	0.1480	0.0000	0.1959	0.0010	0.0047	0.0000	0.0000
WATER	0.0000	1.0000	0.0076	0.7808	0.0000	1.0000	1.0000
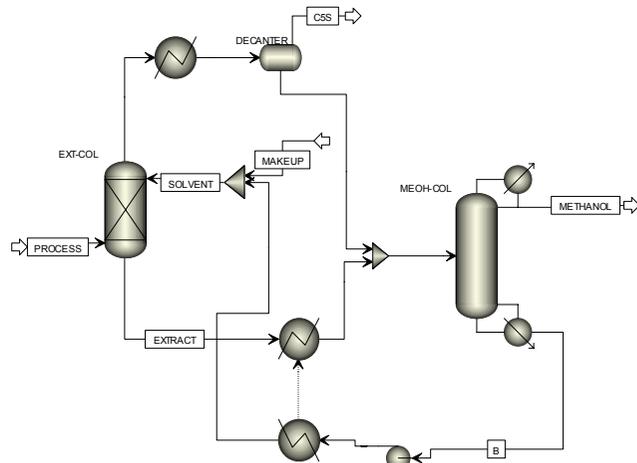
Figure 1: Overall recovery flowsheet

Figure 2: Impact of extractor number of trays and solvent rate on methanol in extractor overhead (raffinate)

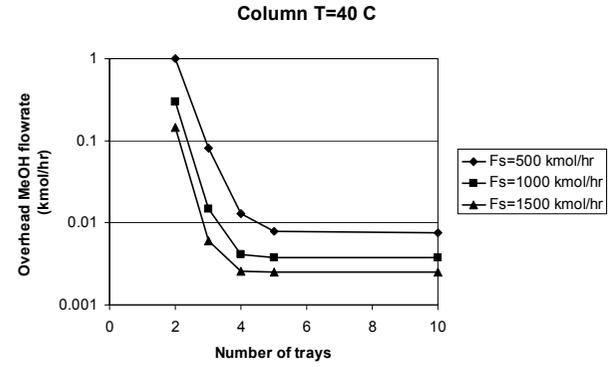
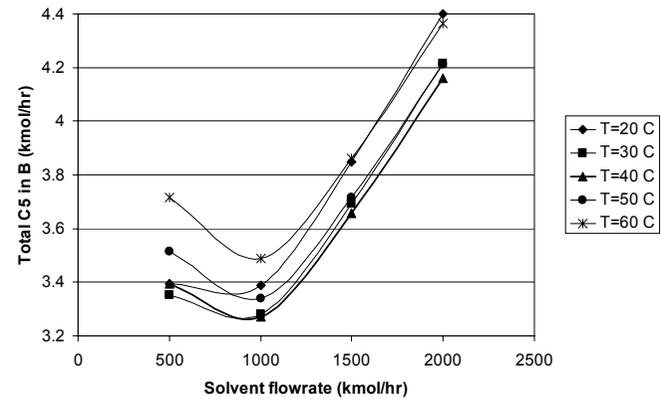Figure 4: Required reflux ratio for methanol distillation column

Figure 3: Impact of solvent rate and extractor temperature on C_5 in the extractor bottoms (extract)