

The effect of solvent selection on energy-integrated extractive distillation for aromatics recovery from pyrolysis gasoline: simulation and optimization

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In this work two approaches have been proposed in order to reduce energy consumption of an industrial extractive distillation process. These approaches subscribe to either heat integrating conventional distillation arrangements, or to the design of thermally-coupled configurations. The optimization of studied configurations is made over the very critical parameters, which are the selection of solvent type and solvent/feed ratio. The recovery of aromatics (benzene, toluene, and mix xylene) from pyrolysis gasoline feedstock has been simulated rigorously as industrial case study. The economic analysis proved that heat-integrated configuration is the best candidates compared to Petlyuk column and divided-wall column. Solvent feed ratio of 2 vol % found to be the optimum ratio from energy and material consumption point of view. NMP solvent provides the lowest total annual cost (TAC) and perfect separation of non-aromatics and aromatics for conventional configuration. DMF solvent gives the highest saving percentage for heat-integrated configuration with 40 %, with 98 % recovery of the solvent and the least recycled solvent temperature of 153.6°C compared to other solvents.

1. Introduction

Extractive distillation process is commonly applied in petrochemical industry for separating hydrocarbons with close boiling points, such as C4, C5, C6 mixtures. In this process an additional solvent (entrainer) is fed to a tray above the main feed stream to alter the relative volatility of the components to be separated.

The aromatic components come from the catalytic reformer or steam cracker pyrolysis gasoline is found with other close-boiling hydrocarbons, some of which form azeotropes with the aromatics. This makes it impossible to separate pure aromatics by classical distillation; the use of a solvent in distillation to enhance the separation efficiency is widely used to separate close-boiling mixtures. The aromatics can be purified using selective solvents that have a differential attraction to the aromatic ringed compounds. There has been an ever-increasing demand for a higher purity of aromatics as a feedstock for chemical synthesis, many solvents such as Sulfolane (Lee and Kim, 1998), N-methylpyrrolidone [NMP] (Muller, 1973), and N-formylmorpholine [NFM] (Cinelli et.al., 1972 and Kolbe and Wenzel, 2004) are used to extract aromatics such as

benzene, toluene and xylene from hydrocarbon mixtures. The initial equipment cost and the operating cost for the whole plant can be reduced by the decision of the optimum solvent/feed ratio, and also by applying energy integrated techniques.

Kolbe and Wenzel (2004) have investigated extractive distillation process for separating aromatics from pyrolysis gasoline and they have developed a simulation tools to find the optimum design of divided wall column based on total annual cost. The column meets all expectations regarding energy consumption, product yield and purity.

Luyben (2008) have studied extractive distillation process and a pressure-swing distillation process, the extractive system showed lower costs and equivalent dynamic behaviour compared to the pressure swing process, using heat integration reduces energy costs, although capital costs in the extractive system are the same with and without heat integration.

In this work, energy-integrated extractive distillation including heat-integrated extractive distillation and Petlyuk column configurations are designed, simulated and optimized rigorously using different solvents such as Sulfolane, N-methylpyrrolidone [NMP], Tri-ethylene glycol [TEG] and N,N-di methylene formamide [DMF]. All configurations are compared with the conventional extractive distillation (base case) by considering minimum total annual cost (TAC) as the economic objective function.

2. Simulation of Extractive Distillation Process

2.1. The case study

The feed is a pyrolysis gasoline mixture made up of three cuts C5 cut (142 kgmol/hr), C6-C8 cut (366 kgmol/hr) and C9 cut (21.02 kgmol/hr). The feed condition is a liquid at bubble point. The feed mixture contains 30 components, C5 cut is mostly cyclopentene and cyclopentane, C6-8 cut is mostly benzene, toluene and mixed xylenes, and C9 cut is mostly n-nonane. HYSYS commercial process simulators is utilized to predict qualitatively the influence of the operating variables on the column performance, provided that the interaction binary parameters for the studied mixture are available in their own data-bank. The accuracy of the simulated results is strongly dependent on the quality of the binary parameters for the liquid-phase activity coefficient models. The UNIQUAC thermodynamic package is selected in this study. The extractive distillation configurations are designed and simulated rigorously at steady-state with different selected solvents. Overall evaluation of the best extractive distillation configuration is made based on maximum aromatic recovery, recycled solvent purity and economic assessment.

2.2. Selected Solvents

Since the solvent is the core of extractive distillation process, more attention should be paid on the selection of potential solvents. Of all possible entrainers that can be used for the separation of non aromatics and aromatics from azeotropic multi-component hydrocarbon mixture. Four pure solvents have been chosen which are recommended as a potential entrainers in separation of hydrocarbons: N-methyl pyrrolidone [NMP], Di methylene formamide [DMF], Sulfolane and Tetra ethylene glycol [TEG]. In order to verify the effect of the above mentioned solvents, the solvent recovery percentage in stripper column as vital parameter could effect all the process, the recycled solvent out let stream has to be cooled down and enter the extractive distillation column at suitable temperature never exceed 60 °C.

2.3. Studied Extractive Distillation Configurations

In the conventional extractive distillation configuration (Figure 1), the hydrocarbon mixture is introduced to the first column (extractive distillation column) where the low-boiling fraction is recovered as the top product and the high-boiling fraction (entrainer) remains as the bottom product. Another arrangement is thermally coupled column known as Petlyuk column (Figure 2), the medium-boiling fraction accumulates in the main column and is taken as a side draw. Compared to the previously mentioned option, the Petlyuk column requires only one heating and condensing device for both columns. In addition, the thermodynamic advantages of this arrangement over conventional extractive distillation, which result in lower energy requirements, have long been known. A further development of the above stages is to incorporate the prefractionator column in the main column, thus resulting in considerably lower investment costs. This arrangement is referred to as the divided-wall column (DWC).

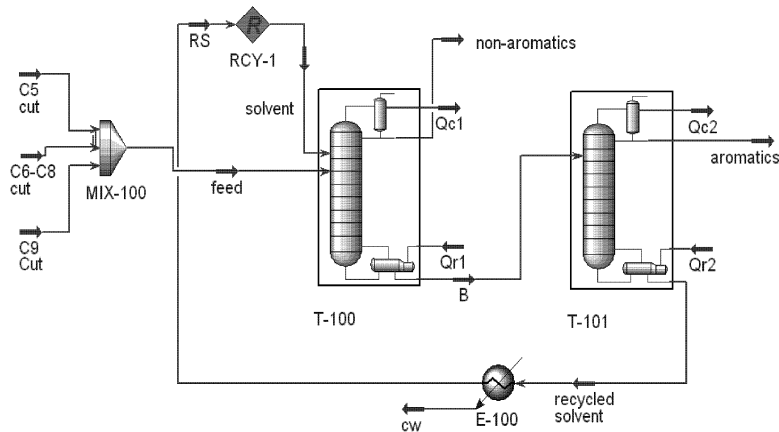


Figure 1. Conventional extractive distillation

boiling fraction is distilled off as the top product and the high-boiling fraction (entrainer) remains as the bottom product. Another arrangement is thermally coupled column known as Petlyuk column (Figure 2), the medium-boiling fraction accumulates in the main column and is taken as a side draw. Compared to the previously mentioned option, the Petlyuk column requires only one heating and condensing device for both columns. In addition, the thermodynamic advantages of this arrangement over conventional extractive distillation, which result in lower energy requirements, have long been known. A further development of the above stages is to incorporate the prefractionator column in the main column, thus resulting in considerably lower investment costs. This arrangement is referred to as the divided-wall column (DWC).

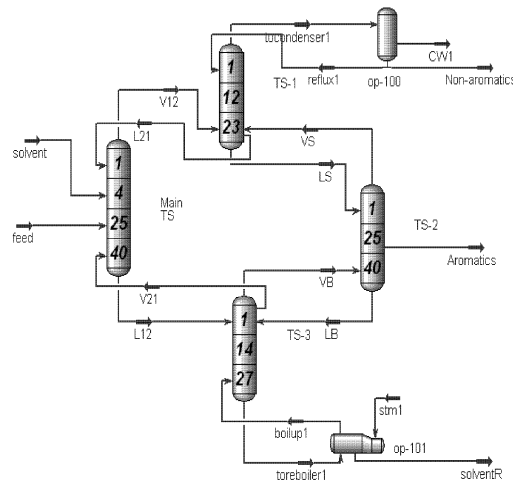


Figure 2. Petlyuk column (DWC)

The third studied configuration is conventional ED with backward heat integration (Figure 3), it is based on the idea of utilizing the overhead vapors of the stripper column to provide heat source for boiling up the extractive distillation column and in this case the stripper column is operated at higher pressure compared to extraction column. The conventional heat-integrated configuration applied the same techniques and assumptions for those in conventional ED distillation scheme with the following modifications:

- Raise operating pressure in the stripper column to keep EMAT at 8 °C.
- Keep the lower pressure column at atmospheric pressure.
- Add the needed heat utilities.
- Remove reboiler of extractive distillation column and condenser of stripper column

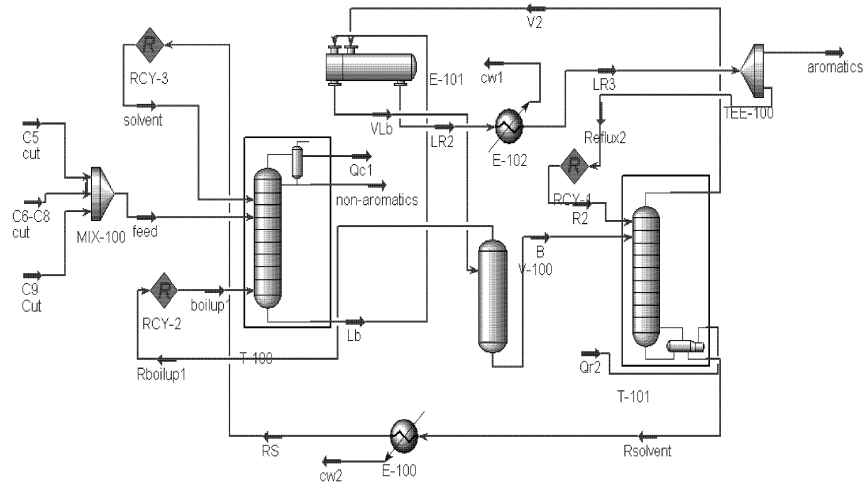


Figure.3 Conventional ED with backward heat integration

3. Optimization Procedure

In order to reach the global optimum economic solution for the studied configurations, a local optimum has to be found by specifying some variables (e.g. feed locations, aromatics recovery and recycled solvent purity) and using the total heat load as a reference variable. Design variables are selected based on market demands or physical conditions. In our study we specified the temperature, pressure, flowrate and composition of feed mixture. We also specified distillate purity and recovery of non-aromatics in the extractive distillation column, distillate purity of aromatics and bottom purity of solvent in the stripper column. For each extractive distillation configuration, the number of trays, feed location, solvent feed location, solvent/feed ratio and solvent type are considered as optimization variables. The constraints are represented by, the amount of benzene in non-aromatic stream should never exceed 0.1 mol % due to environmental regulations (Kolbe and Wenzel, 2004) and recycled solvent purity has to be greater than 98%. Solvent-to-feed ratio which found to be a very critical and having a significant effect on the reflux ratio in both columns, and therefore on the total reboiler heat duty. So, the local optimization is made over this variable. In each configuration, the solvent-to-feed ratio is then adjusted to minimize the total reboiler heat duty. Finally the global optimum is achieved by running simulated extractive distillation configurations rigorously and then the capital and operating costs are

conducted and evaluated based on minimum TAC as objective function, cost correlations are extracted from (Emtir et.al., 2001).

4. Simulation and Optimization Results

Based on conventional extractive distillation, simulation results of different solvents are shown in Table 1, it is observed that NMP and TEG show the maximum recovery compared with other solvents which give less recovery by about 1.18% for sulfolane and 1.19% for DMF. Also there is an obvious effect of changing solvent type on recycled solvent temperature which has a direct effect on cooling demand and heat source of the stripper column and consequently the TAC. DMF shows the least recycled solvent temperature, NMP also shows an accepted temperature for recycling stream which is still in HP-steam temperature level. TEG and Sulfolane give recycled stream temperatures higher than HP-steam temperature level, which could lead to higher

Table 1. Effect of solvent type on solvent recovery and recycled solvent temperature

Solvent type	NMP	TEG	Sulfolane	DMF
Solvent recovery percent	0.9999	0.9998	0.988	0.98
Recycled Solvent temperature C°	202.3	278.3	287	153.6

operating cost compared to other selected solvents. NMP has been chosen in order to investigate the energy and TAC potential of the studied configurations at different solvent feed ratio (S/F). It is obvious that S/F ratio has a direct effect on operating cost and TAC of the extractive distillation configurations as shown in Table 2, minimum TAC is achieved at S/F = 2 for both conventional ED and Petlyuk column.

Table 2. Optimization results of ED configurations at different solvent feed ratios

S/F	Conventional ED			Petlyuk column		
	3.0	2.5	2.0	3.0	2.5	2.0
Annual capital	5.08	4.75	4.54	3.94	3.41	3.34
cost (\$/year)*10 ⁵						
Annual operating cost (\$/year)*10 ⁶	3.48	3.25	3.04	2.36	2.39	1.85
	3.99	3.73	3.49	2.75	2.73	2.19
TAC (\$/year)*10 ⁶						

Considering S/F = 2.5 as the optimum during operation, different entrainers has been investigated for conventional ED by considering TAC as the indicator (Table 3). For each case of conventional ED, heat integration is applied between the extraction column and stripper column to measure the maximum TAC savings of selected entrainer as shown in Table 4, DMF is showing the maximum saving value of 40 % compared to other entrainers.

Table 3. Effect of solvent type on TAC for conventional ED (base case)

Solvent type	NMP	TEG	Sulfolane	DMF
Annual capital cost (\$/year)*10 ⁵	4.75	6.79	7.04	4.24
Annual operating cost (\$/year)*10 ⁶	3.25	5.80	5.87	3.53
TAC (\$/year)*10 ⁶	3.73	6.48	6.57	3.95

Table 4. Saving percentage for extractive distillation with backward heat integration

Solvent type	NMP	TEG	Sulfolane	DMF
TAC (\$/year)*10 ⁶	2.61	5.82	5.00	2.36
TAC saving % compared to base case	30	10	24	40

5. Conclusions

Energy-integrated extractive distillation configurations (Petlyuk column or DWC and heat-integrated ED) proved to be an attractive alternative configurations to conventional extractive distillation by showing a higher savings of energy and capital cost ranging from 10 to 40 % in TAC savings. Solvent/Feed ratio plays an important role in minimizing operating and capital cost, for this industrial case study the optimum solvent to feed ratio is found S/F=2. The energy and TAC savings of the studied extractive distillation configurations are strongly affected by the selection of the solvent type, the ranking of solvents in terms of TAC savings achievement are DMF, NMP, Sulfolane and TEG respectively. Solvents with higher boiling points are indicating less TAC saving which is due to the cost of high pressure steam used. DMF entrainer prove to be the best choice regarding TAC savings of 40 % which is attributed to low recycled entrainer temperature that allows for the usages of LP-steam and less cooling rates.

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