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A Novel Synergistic 4-column Methanol Distillation Process

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This work is enlightened by recent progresses in heat pump concepts, proposed to upcycle waste heat to compensate energy supply, A novel synergistic 4-column methanol distillation scheme is developed by using heat pump upon double-effect distillation through an intermediate heater to shunt reboiler heat load. Compared with the original scheme, the synergistic one can considerably reduce utility depletion as well as operating costs. The success of adding heat pump to double-effect encourages extending applications to process industrial communities other than methanol purification.

1. Introduction

As one of the most important and widespread thermal separation methods in process industry (Smith et al., 2013), distillation is a big user of the approximate 43 % of thermal energy used for industrial applications resenting a large part of the global energy usage (Bor et al., 2015). In particular, distillation alone is responsible for approximately 40 % of the thermal energy consumption in the chemical process industry, which is the impetus of various energy saving programs launched for improving its performance (Cui et al., 2016). One major drawback of distillation is low thermodynamic efficiency by consuming high quality energy in reboiler(s) and rejecting similar amount of waste heat from condenser(s) at a lower temperature (Jana, 2010). To make improvement, several heat pump candidates were proposed to upcycle waste heat discharged from condenser to reduce valuable utilities consumption (Kiss et al., 2012). Under certain conditions, the margin of energy savings by heat pump assisted distillation (HPAD) can predictably be around 20 - 50 % (Bor et al., 2015).

In methanol industry, crude methanol must be refined through distillation before further utilization (Sun et al., 2012a). To date, a 4-column double-effect methanol distillation scheme has been most readily and widely adopted in China (Cui et al., 2017a). Although the 4-column scheme (designated as the prototype scheme) has resulted in a significantly greater decrease in energy consumption than that expected through heat integration, it still consumes approximately 80 % of the total hot utility in the PC reboiler and over 75 % of all cold utility in the AC condenser The literature surveys (Cui et al., 2017a) demonstrated that previous works are mainly focused on using sole double-effect configuration to achieve higher energy efficiency, ignoring the application of HPAD. As a continuation of our previous efforts (Cui et al., 2017a), we propose a novel synergistic 4-column methanol distillation process, combining double-effect distillation (DED) and heat pump (HP). The synergistic scheme attempts to make full use of the HP to cool part of the AC top vapor in parallel with the condenser, and it can upcycle the waste heat available for certain heat sinks at higher temperatures. Because the AC reboiler is driven by the PC top vapor in the prototype scheme, in the synergistic scheme, a side-reboiler is designed at the AC stripping section, which acts as a new heat receiver at suitable temperatures for the donator by shunting part of the reboiler duty.

2. Heat integrated distillation operations

In the distillation technology, heat is used as a separating agent. Therefore, a distillation column can be considered as a heat engine that produces separation instead of work. A conventional distillation column (CDiC) has very low thermodynamic efficiency (typically around 5 %) (Cui et al., 2017b).

To improve the thermal efficiency of a CDiC, various techniques, such as intermediate cooler or heater, DED columns (Sun et al., 2012b), HPs (Sun et al., 2014), and secondary reflux and vaporization, have been

explored. Basically, the idea is to reduce the external energy inputs by effectively utilizing the heat energy from the distillation columns and to distribute the heat more uniformly along the length of the columns. Three main heat integration arrangements for a CDiC are proposed below to facilitate energy-saving purpose for methanol distillation scheme:

- (i) For HPAD columns, the overhead vapor is compressed and used to drive the bottom reboiler.
- (ii) For DED columns, the hot distillate vapor steam can be thermally coupled with the LPC bottom liquid in the reboiler.
- (iii) For heat integrated distillation columns, the rectifying and stripping sections are internally coupled through heat exchangers. A compressor and an expansion valve are installed between the two sections for maintaining the driving force.

Because type (iii) columns have not been used in industry due to their controllability problems (Jana, 2014), this study only considers the first two types. It should be noted that each type of distillation operation has suitable range. For example, HPAD is more suitable for separating close-boiling components, while double-effect distillation might be better in wide-boiling mixtures (Cui et al., 2017c). Significant energy reduction can be obtained with the combination of these two types.

2.1 Double-effect distillation column

As shown in Figure 1, DED implements two columns instead of one in CDiC. It uses the overhead vapor from high-pressure column (HPC) to drive the subsequent reboiler of the low-pressure column (LPC), combining the condenser of the former with the reboiler of the latter, eliminating a heat exchanger as well as the corresponding utilities. Instead of treating the entire crude feed in one column, the feed is split into two approximately same streams and entered into HPC and LPC, respectively. The pressure difference of adjacent columns provides temperature difference between HPC overhead and LPC bottom, driving heat transfer from the pressured stream to the heat-receiving column. Compared to CDiC, DED column could upgrade half of low-grade heat and reuse it as hot utility, saving considerable energy.



Figure 1: Conventional distillation column (CDiC) and double-effect distillation (DED) column.

2.2 Heat pump assisted distillation column

HPAD facilitates the upgraded waste heat by compressing overhead vapor instead of enhancing pressure of entire column to achieve heat upgrade and transfer, safely avoiding elaborate automatic control scheme that DED required.

HPAD is classified into different patterns aiming at escalating and utilizing heat capacity of stream from the column top to drive its bottom. Vapor compression (VC) and mechanical vapor recompression (MVR) are usually available for commercial purposes. The schemes of VC and MVR heat pump are shown in Figure 2.

938



Figure 2: Vapor compression (VC) and mechanical vapor recompression (MVR).

In VC, working fluid evaporated by top vapor of column discharges heat to the reboiler through a compressor to provide required work input and an expansion valve to close the cycle. As a remarkable feature, all units involved are external to the distillation process. Consequently, the column does not require major modifications except for possible adjustments in heat exchangers for changing utilities. On the other hand, MVR compresses overhead vapor of column to heat the reboiler, preventing the intermediate medium from cooling below the boiling point of the top products, thus saving one more heat exchanger and enjoying lower investments than VC. For this reason, this study chooses the MVR as a representative of HPAD.

The coefficient of performance (COP) is usually used to evaluate the performance of heat pump. It is defined, as discharging heat in condenser over electrical power required for upgrade the energy. The higher the COP of a heat pump is, the better its performance is.

3. The prototype scheme

3.1 Process description

The prototype scheme is an industrialized 4-column double-effect methanol distillation scheme optimized in our previous work by focusing on the energy saving, which is presented in Figure 3 (Cui et al., 2017a). In this particular process, a two-stage condenser system is designed for the light ends column (LEC) overhead vapor to be partially condensed stepwise, first at 70 °C and then at 40 °C, with both condensates being collected in the reflux drum. Fresh water (10 % wt., with respect to the crude feed) is pumped into the reflux drum as an extraction agent to help remove light impurities soluble in methanol. Compared with the one-stage condenser, this configuration saves cooling water (CW) by preventing a considerable part of the liquid from deeper cooling. After removing the light ends from the top of the LEC, the crude methanol feed is pumped into the PC from the LEC bottom. The PC bottom stream enters the AC for further separation.

On the other hand, the PC overhead vapor drives the AC bottom, resulting in DED by combining the PC condenser with the AC reboiler, saving a condenser or reboiler along with heating or cooling utilities. To ensure a sufficient temperature difference between the PC top and AC bottom, the pressure difference between these two columns is maintained over 650 kPa. Refined methanol products are obtained from both PC and AC tops, with the majority of purified wastewater leaving from the AC bottom. Additionally, a side stream is drawn from a point slightly lower than the AC feed stage to control organic impurities, such as ethanol, in the top product. The side stream containing fusel oil is pumped into the water column (WC) to recover more methanol from the purified wastewater remaining at the bottom.



Figure 3: Schematic diagram of the 4-column double-effect methanol distillation (the prototype scheme)

3.2 Simulation results

In this study, NRTL (Non-random two liquid) equation is selected for phase equilibrium, with binary interaction data fitted for systems of alcohols, water, and other polar compounds. The theoretical stages of the LEC, PC, AC, and WC are 31, 51, 54, and 46, in accordance with the industrial setup (Cui et al., 2017a). The corresponding top pressures of the LEC, PC, AC, and WC are 150 kPa, 850 kPa, 110 kPa, and 110 kPa with sub-cooled condensers and thermosiphon reboilers without baffles for the PC, AC, and WC. The hot and cold utilities are a 600 kPa saturated steam (~159 °C) and CW working between 25 - 40 °C. The quality of the refined methanol meets the requirements of US federal specification O-M-232 M Grade "AA": methanol purity not lower than 99.85 % (wt.) and ethanol not more than 10 ppm (wt.). In addition, the methanol content in wastewater is specified as no more than 10 ppm (wt.) for water treatment requirements. Because the refined for reference, following the on-site date. These are approximately 46 % for the PC and 52.5 % for the AC of pure methanol in feedstock, with the remaining amount of approximately 1 % from the WC. The results are in agreement with the on-site data and show a mass yield distribution of 46.2 %, 52.7 %, and 1.1 %, from the PC, AC, and WC. The quality of refined methanol is better than the "AA" standard, with methanol approaching 99.98 %, the expected methanol content in waste water, and a reasonable fusel oil rate.

3.3 Heat integration analysis

In this study, the minimum temperature difference is specified as 15 °C. To show the potential Heat Integration of process streams, the Grand Composite Curve (GCC) (Kemp, 2007) is shown in Figure 4.



Figure 4: The GCC of the prototype scheme

The GCC indicates a hot stream pinch temperature of 81.8 °C and a cold counterpart of 66.8 °C, along with energy targets of 139.89 MW and 138.47 MW for heating and cooling. The circled areas are the pockets, which represent the potential energy integration within the heat cascade. The potential energy integration can be achieved by using four heat exchangers marked in Figure 3.

4. The synergistic scheme

The synergistic scheme is shown in Figure 5. It is interesting to note that if only MVR is selected without considering DED Heat Integration, the compression ratio of compressor will be much higher, because methanol-water being separated has widely different boiling points. DED plus HP configuration can bring a synergistic effect – DED creates lower temperature heat sinks for HP and HP recovers waste heat for DED.



Figure 5: Schematic diagram of the synergistic methanol distillation

The purified methanol yield is 99.63 %, which is nearly identical to the prototype (99.62 %), while energy targets for heating and cooling are decreased to 81.36 MW and 90.67 MW, as presented in Figure 6. Notably, one more pocket appears by using the MVR. Using the Grid Diagram (Kemp, 2007), these energy targets can be achieved by HEN (heat exchanger network) shown in Figure 7. Compared with the prototype, these values show a decrease of 41.8 % and 34.5 % for heating and cooling. However, the electricity consumption increases by 12.30 MW.



Figure 6: GCC of the synergistic scheme



Figure 7: HEN of the synergistic scheme

5. Conclusions

In this study, a novel synergistic 4-column methanol distillation scheme is proposed, featuring DED plus HP technology. An intermediate heater, driven by the upcycled energy, is introduced to the AC to shunt the heat load in the reboiler. The results show significant improvements are achieved. Energy consumption for heating and cooling are reduced by 41.8 % and 34.5 %. The synergistic scheme is worth introducing to the methanol community. Moreover, the authors encourage the use of the DED plus HP technology and the schematic optimization procedure in other industrial plants.

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