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Short communication

Self-heat recuperative dividing wall column for enhancing the energy efficiency of the reactive distillation process in the formic acid production process

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ABSTRACT

This paper proposes a novel self-heat recuperative dividing wall column configuration to enhance energy efficiency of a reactive distillation process in the formic acid production process. A patented formic acid production process as a base case was optimized for further evaluation. Both external heat integration and thermal coupling were examined by placing a side-reboiler onto the reactive distillation column and by configuring the reactive distillation column to a top dividing wall column. A novel self-heat recuperative dividing wall column configuration was finally proposed to take synergistic advantage of the thermally-coupled and heat-integrated structures. The proposed configuration requires no compressor and provides preferable conditions for the self-heat recuperation by avoiding the remixing effect and reducing the energy requirements. The proposed self-heat recuperative dividing wall column configuration can also be applied to other similar distillation processes to improve the energy efficiency.

1. Introduction

Formic acid (FA), which is the simplest carboxylic acid, is a popular chemical used in many industries, such as leather, agriculture, textiles, rubber cohesion processing, chemicals, and pharmaceuticals [1]. Several processes have been reported for the commercial production of FA based on different main reactions, including the acidolysis of formate salts, oxidation of hydrocarbons, hydrolysis of formamide, mineral acid catalysis, and the hydrolysis of lower alkyl formates [2–4]. Recently, a FA production process based on methyl formate (MF) hydrolysis was proposed to overcome the main limitations of existing processes, such as a slow reaction time, undesirable byproducts, high investment costs, and environmental issues [5]. Huang et al. [6] proposed a novel process by integrating a reactor and a conventional distillation column in the MF hydrolysis-based process into a single reactive distillation (RD) column. The RD by combining the reaction and separation operations in a single vessel can have many advantages [7]: (1) the yield and selectivity are improved, (2) energy requirements decrease, and (3) hot spots are avoided. The application of a RD has enabled the production of FA of the desired purity with significantly reduced operating and capital costs.

Distillation is one of representative separation units with large energy requirements. 60% of energy used in chemical industry is from distillation processes [8]. Most of the energy required in the FA production process is also due to its distillation process. Thermally coupled distillation column (TCDC) and dividing wall column (DWC) as its fully intensified form have attracted considerable attention to reduce energy consumption and capital cost in distillation processes [9]. Recently, a heat pump technology has been investigated as a prominent mean for heat integration in combination with the RD [10], DWC [11], and reactive DWC [12] to improve energy efficiency in DWC and RD processes. However, practical restrictions and worries associated with the introduction of compressor into the column retard the expansion of the heat pump assisted heat integration in conservative process industries.

In this study, a novel heat pump free self-heat recuperative DWC was proposed to improve the energy efficiency of the distillation process in the MF hydrolysis-based FA production process. The conventional FA process was first optimized. Heat-integration and thermal coupling between the RD and conventional columns were explored. Based on this analysis, a novel DWC configuration was proposed to take synergistic advantage of thermally coupled and heat integrated structures. The potential of the DWC structure for taking advantage of self-heat integration was also discussed.

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2. Process description

In this study, the process configuration patented by Huang et al. [6] was chosen and used as a base process after process optimization. The process consists mainly of a reactor for the carbonyl reaction and three distillation columns, including one reactive distillation column for MF hydrolysis and separation. Fig. 1 shows the overall process flow sheet under the optimized conditions.

In this process, the carbonyl reaction in Eq. (1) occurs in a high pressure adiabatic continuous stirred tank reactor (CSTR) by the reaction of methanol and carbon monoxide with a sodium methoxide (CH_3ONa) heterogeneous catalyst or ion-exchange resin catalyst.

$$CH_3OH + CO \leftrightarrow HCOOCH_3 \tag{1}$$

MF formed in the CSTR is then separated as a distillate in the methanol recovery column (C1), and fed into the RD column. A small amount of carbon monoxide remaining is purged through a partial condenser in the column against its accumulation. The unreacted methanol is separated from the C1 bottom and recycled to the CSTR with the accompanied catalyst.

In the RD column, FA and methanol are formed by the hydrolysis of MF with external water according to the following reaction:

$$HCOOCH_3 + H_2O \leftrightarrow HCOOH + CH_3OH \tag{2}$$

The separation between reactants (MF and water) and products (FA and methanol) also occurs in the RD column simultaneously, which improves both the reaction and separation efficiency significantly compared to the system of a separate reaction and separation. The RD column consists of a reactive tray section (1st–19th tray), where each tray is filled with a heterogeneous ion exchange resin catalyst, and a stripping section below the reactive section.

FA and water are separated from methanol and MF at the bottom of the FA separation column (C2), and 85 wt.% FA is obtained as the final main product. Methanol in the distillate is recycled to the CSTR to maximize product conversion.

3. Process simulation

A simulation study was performed using an Aspen Plus V7.3 simulator. The UNIQUAC-HOC model was used as a thermodynamic method of simulation to cope with the solvation of polar compounds and dimerization of the vapor phase in the mixtures containing carboxylic acids by using the Hayden-O'Connell equation [13]. The pairing of MF hydrolysis used in this study has six sets of thermodynamic parameters. The UNIQUAC model parameters for methanol–MF, MF–water, MF–FA, and water–FA pairings were obtained through thermodynamic model regression using the vapor–liquid equilibrium data from Polak and Lu [14], Reichl et al. [15], Zeng et al. [16], and Ito and Yoshida [17], respectively. Methanol–water pairing employs the UNIQUAC model parameters taken by Pöpken et al. [18]. The UNIQUAC Functional-group Activity Coefficient (UNIFAC) method was applied to estimate the missing parameters of methanol-FA pairing. Table 1 shows the parameter values used for the MF–water–methanol–FA system.

The reaction kinetics of the carbonyl reaction for the CSTR was chosen from [19] under the experimental conditions at $T = 60$–$110\,^\circ C$, $P = 2$–4 MPa:

$$\begin{aligned} r = {} & (1.414 \times 10^9)\exp\left(\frac{-70748}{8.314451T}\right)[\text{cat}]_L[\text{MeOH}]_L[\text{CO}]_L \\ & -(2.507 \times 10^{12})\exp\left(\frac{-92059}{RT}\right)[\text{cat}]_L[\text{MF}]_L \end{aligned} \tag{3}$$

where r is the reaction kinetic rate (mol/L min), R is the universal gas constant (J/(mol/K)), the subscript L denotes the concentration of the liquid phase, $[CO]_L = [CO]_G = 0.154\ P_{CO}/RT$, and [] denotes the component concentration (mol/L).

The reaction kinetics of the hydrolysis reaction for the RD simulation was taken from reference [20]:

$$r = k_0 \exp\left(-\frac{63100\text{kJmol}^{-1}}{8.31451T}\right)\left(\frac{[H_2O][MF] - [MeOH][FA]}{0.4492\exp(-251/T)}\right) \tag{4}$$

where r is the reaction rate (mol/L min), $k_0 = \frac{6.530 \times 10^6}{1 + 0.869[H_2O]^2}$, and [] denotes the component concentration (mol/L).

An equilibrium stage model was used for the simulation of all distillation and RD columns. Tray efficiency was simply assumed as 100%. The liquid holdup for the rate-controlled reaction was specified as 0.15 m^3 at every stage in the RD section.

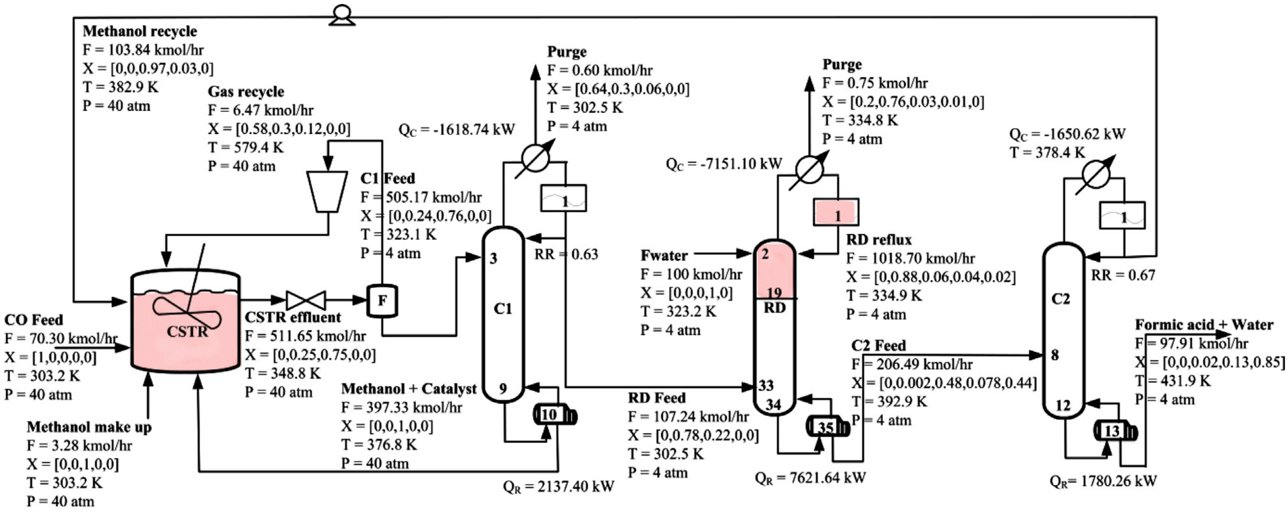

Fig. 1. Process flow sheet of Huang's patented process under the optimized conditions, X denotes $[X_{CO}, X_{MF}, X_{MeOH}, X_{H2O}, X_{FA}]$ in mass fraction (in Figs. 1, 8 and 11).