

# Novel reactive distillation process with two side streams for dimethyl adipate production



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## ABSTRACT

Reactive distillation presents a distinct advantage for the combination of reaction and separation. However, when reactants are the lightest and the heaviest components and products are the intermediate ones, the configuration should be well designed to maintain the merits of the reactive distillation. In this work, two new processes, whose reactive distillation column with one side stream (RDC-S1) and with two side streams (RDC-S2) are proposed for dimethyl adipate production by the esterification of adipic acid with methanol. The two new processes are simulated using Aspen Plus and analyzed with minimum total annual cost (TAC) as the objective function. Then the carbon dioxide emissions of the proposed processes are calculated. The RDC-S1 and RDC-S2 processes are compared with the conventional reactive distillation process and the reactive distillation column with a top-bottom external recycle process. The results show that RDC-S2 process requires the lowest energy and has the smallest carbon dioxide emissions when compared with other processes. Thus considering the remarkable economic and environmental benefits, RDC-S2 is an attractive configuration for the production of dimethyl adipate.

## 1. Introduction

Dimethyl adipate (DMA) is an important chemical product and also a kind of organic raw material, which can replace toxic organic solvents in many chemical industrial processes [1]. Nowadays the demands for DMA is increasing faster and faster, while the current method for DMA production still has some problems, such as the complexity in the follow-up treatment, the low reaction conversion and the high energy requirement. Since the energy is mainly from the burning of fuels, large amount of carbon dioxide (CO<sub>2</sub>) would be discharged to the environment leading to the greenhouse effect.

Reactive distillation (RD) combines reaction and distillation process in a column, which has a remarkable advantage in energy saving and capital investment [2–8]. RD is especially suitable for the reversible reaction since it can facilitate positive reaction and improve the conversion by separating products and reactants in time [9–11]. The esterification of fatty acids was studied by Gómez-Castro et al., and the results showed the RD process has a better economic benefits than the conventional one [12]. Kiatkittipong et al. [13] investigated the kinetic model parameters and proposed a RD configuration for the glycerol etherification with *tert*-butyl alcohol, and the suitable parameters of the RD process were obtained by the simulation and experiments.

In a quaternary reacting system, when two reactants are the lightest and the heaviest components and two products are the light and heavy key components, it is difficult to have a large amount of these two reactants in the liquid phase simultaneously, and thus it is unfavorable for the positive reaction. Tung and Yu [14] proposed several RD configurations according to the difference in relative volatilities between reactants and products. In order to increase reactants concentration in the reaction zone, they suggested that the reactive zone can be set at the top of the column (light component enrichment area) or the bottom of the column (heavy component enrichment area).

Fig. 1 shows the flowsheet of the reactive distillation with reactive zone at the top and bottom sections of the column. As shown in Fig. 1, the heavy component is fed into the top of the column, at the same time, the light component is fed into the bottom of the column, and thus the two reactants can fully contact and react. In this RD column, the products can be obtained in the side stream and further separated in another column. For the system of adipic acid (AA) esterification with methanol (MeOH), reactants AA and MeOH are respectively the heaviest and lightest components while the final products are intermediates. Hung et al. [15] investigated this system based on the mentioned RD configuration, and the results proved that the reactive distillation can be well used for the production of DMA.

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**Nomenclature**

A	Exchanger area
AA	Adipic acid
CC	Capital cost
$C_i$	Concentration of components $i$
CO <sub>2</sub>	Carbon dioxide
CRD	Conventional reactive distillation
D	Column diameter
DMA	Dimethyl adipate
DR	Distillate rate
$F_c$	Correction factor
H	Column length
H <sub>2</sub> O	Water
$k$	Rate constant
$K_{eq}$	Equilibrium constant
LP steam	Low pressure steam
MeOH	Methanol
MP steam	Medium pressure steam
MMA	Monomethyl adipate

M&S	Marshall & swift index
$N_T$	the number of stages
$N_{T31,AA}$	Location of the feed stream AA in RDC-S1 process
$N_{T31,S}$	Location of the side stream in RDC-S1 process
$N_{T31,RE}$	The number of reactive stages in RDC-S1 process
$N_{T32}$	The number of stripper stages in RDC-S1 process
$N_{T41,AA}$	Location of the feed stream AA in RDC-S2 process
$N_{T41,S1}$	Location of the side stream S1 in RDC-S2 process
$N_{T41,S2}$	Location of the side stream S2 in RDC-S2 process
$N_{T41,RE}$	The number of reactive stages in RDC-S2 process
$N_{T42}$	The number of stripper stages in RDC-S2 process
$N_{RE}$	The reactive stage numbers of RD column
OC	Operating cost
$Q_r$	Reboiler duty
RD	Reactive distillation
RDC-S1	Reactive distillation column with a side stream
RDC-S2	Reactive distillation column with two side streams
RDC-TBER	Reactive distillation column with a top-bottom external recycle
TAC	Total annual cost

For the difficult separation system as mentioned above, Chen et al. [16] proposed a RD column with a top-bottom external recycle (RDC-TBER) process, which is classified to exothermic reaction and endothermic reaction as shown in Fig. 2. Unreacted reactants are recycled to the reactive zone through the external recycle stream and the products are withdrawn from a side stream, through which the quality and energy integration in this reactive distillation process can be enhanced. In addition, the separation capacity of this new configuration can also be increased. Yao et al. applied [17] RDC-TBER sequence (shown in Fig. 2a) to produce DMA, and the results showed that this innovative configuration presented more energy saving potentials than the process proposed by Hung et al.

Although Hung et al. and Yao et al. have investigated the RD processes for DMA production, these sequences are characteristic with complex subsequent separation processes. In the present work, two new configurations for DMA production are proposed based on the work of Hung et al. and Yao et al. Firstly, steady-state simulation for the processes mentioned above are performed by the simulation software Aspen Plus. And then the parameters of each process are determined with minimum total annual cost (TAC) as the objective function. Finally the energy requirement, economic benefits and CO<sub>2</sub> emissions of the proposed configurations are compared.

## 2. Reaction kinetics and thermodynamic analysis

### 2.1. Reaction kinetics

We adopted the kinetics data [18] reported by Chan et al. The

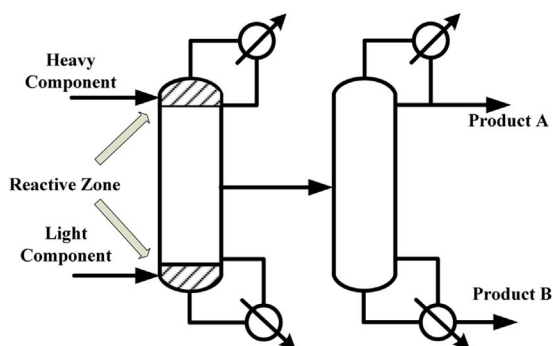


Fig. 1. Flowsheet of RD column with reactive zone at the top and bottom.

esterification of AA with MeOH to produce DMA and water (H<sub>2</sub>O) with monomethyl adipate (MMA) as an intermediate product are shown in Eqs. (1) and (2):



Chan et al. conducted the experiment of the esterification of AA with MeOH over acidic ion exchange resin Amberlyst 35, and they proposed the reaction rate as follows [18]:

$$r_{AA} = -k_1 C_{AA} C_{MeOH} + k_2 C_{MMA} C_{H_2O} \quad (3)$$

$$r_{MeOH} = -k_1 C_{AA} C_{MeOH} + k_2 C_{MMA} C_{H_2O} - k_3 C_{MMA} C_{MeOH} + k_4 C_{DMA} C_{H_2O} \quad (4)$$

$$r_{MMA} = k_1 C_{AA} C_{MeOH} - k_2 C_{MMA} C_{H_2O} - k_3 C_{MMA} C_{MeOH} + k_4 C_{DMA} C_{H_2O} \quad (5)$$

$$r_{H_2O} = k_1 C_{AA} C_{MeOH} - k_2 C_{MMA} C_{H_2O} + k_3 C_{MMA} C_{MeOH} - k_4 C_{DMA} C_{H_2O} \quad (6)$$

$$r_{DMA} = k_3 C_{MMA} C_{MeOH} - k_4 C_{DMA} C_{H_2O} \quad (7)$$

where  $C_i$  is the molar concentrations of the component  $i$  (mol/cm<sup>3</sup>). Eqs. (8) and (9) present the forward reaction rate constants (cm<sup>6</sup>/(g·min·mol)):

$$k_1 = 5.587 \times 10^6 \exp(-4097.8/T) \quad (8)$$

$$k_3 = 2.204 \times 10^6 \exp(-4201.1/T) \quad (9)$$

Because thermal heats effect of the esterification can be ignored, the equilibrium constants are independent of temperature [15]. The relationship between the rate constants of the forward and the backward reaction are expressed as follows:

$$K_{1eq} = K_1/K_2 = 0.997 \quad (10)$$

$$K_{2eq} = K_3/K_4 = 2.56 \quad (11)$$

### 2.2. Thermodynamic model

Simulation software Aspen Plus is used to simulate all the proposed processes. In this work, for the activity coefficient, Aspen Plus built-in parameters have no parameters except H<sub>2</sub>O-MeOH pair. Therefore

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