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# Design and Control of Thermally Coupled Reactive Distillation for the Production of Methyl Valerate

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***Abstract*—Methyl valerate (VAME), also known as methyl pentanoate, is the methyl ester of the pentanoic acid (valeric acid). VAME is usually used as fragrance in the production of beauty care, soap and laundry detergents. High purity of VAME can also be used as plasticizer. This study presents the design details of the process for the manufacture of VAME. Reactive distillation column (RDC) is used in the production process to overcome equilibrium limitation of the esterification reaction. Two products of the reaction can be separated by two strippers and a decanter. A thermally coupled design is then developed to reduce the remixing effect in the rectifying section of the RDC. The simulation results show that 30% energy saving can be achieved by using the proposed thermally coupled reactive distillation process. Two control structures are proposed with the capability of maintaining high purity product under throughput and composition disturbances.**

## I. INTRODUCTION

Process intensification is an important trend in process technology and draws a lot of attention in both industry and research communities. Since the crude oil price keeps increasing, conservation of energy becomes one of the researches of interests. Replacing some single function units with an integrated multifunctional unit is one effective way. Reactive distillation (RD) is one of the important applications. RD is the combination of a reactor and a separation system which has potential for capital productivity improvements, selectivity improvements and energy reduction. In recent years, more and more papers studying RD are published. Malone and Doherty[1] give a good review paper. Luyben and Yu[2] show 1,105 related publications and 814 U.S. patents between 1971 and 2007 in their book. Luyben and Yu[2] also highlighted 236 reaction systems which can be designed with RD configuration. Also, Sundamacher and Kienle[3] summarized more than 100 industrially important reactions for applications. The above references show the importance of the RD in industry.

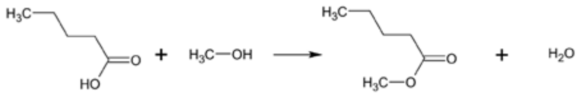
Reactive distillation (RD) with thermally coupled design combines two promising technologies of process intensification, which can bring substantial economic benefits. The first open literature that combines RD with DWC is proposed by Mueller et al[4]. Reactive divided wall column (RDWC) is used for the simultaneous esterification of methanol and butanol with acetic acid to yield methyl acetate, butyl acetate and byproduct water. Wang et al.[5] follow the work of Tung and Yu[6] and investigated thermally coupled reactive distillation for ideal quaternary reaction systems with different ranking of relative volatility. This provides a framework to study thermally coupled reactive distillation. Lee et al.[7] study the production of isopropyl acetate using thermally coupled reactive distillation. The result shows 23.14% of energy saving than the design without thermally coupling.

In this paper, we compare the design with RD only and the design with thermally coupled reactive distillation. Steady state design, process optimization and control strategy will also be studied. Commercial simulators, Aspen Plus and Aspen Plus Dynamics, are used for simulation.

## II. PHASE EQUILIBRIUM AND REACTION KINETICS

### A. Kinetics Data

In the VAME production process, Valeric acid (VA, $C_4H_{10}O_2$) reacts with methanol (MeOH, $CH_4O$) to produce water ($H_2O$) and methyl valerate (VAME, $C_5H_{12}O_2$). The solid catalysts used are the acidic ion-exchange resins Amberlyst 35. The reactions are reversible and the stoichiometric balance equation is shown as the following:



$C_4H_{10}O_2$ (A) + $CH_4O$ (B) → $C_5H_{12}O_2$ (C)+ $H_2O$ (D)

$$-r_A = \frac{1.1246\times10^{12}\exp(\frac{-5374.07}{T})\left[a_A\, a_B - 6.44\times10^{-5}\times\exp(\frac{2093.60}{T})a_C a_D\right]\times m_{cat}}{\left[1+10.2930a_A+79.1875a_B+3.8427a_C+274.48a_D\right]^2}$$

(1)

A rate expression is shown in Eq. 1 which is developed by Lee[8]. The kinetic equation is expressed in LHHW ( Langmuir- Hinshelwood) model form where "a" and "$m_{cat}$" represent activity coefficient and catalyst weight in the unit of kg. The reaction rate has the unit mol/min. T is absolute temperature in Kelvin.

The catalyst weight is calculated by assuming that solid catalyst occupies 50% of the tray holdup and downcomer area occupies 10% tray area. The catalyst's density of 800kg/$m^3$ is used to convert the volume to catalyst weight. In Aspen Plus, LHHW model cannot be used in reactive distillation column.

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TABLE 1 BOILING POINT RANKINGS

| Component | Temperature(℃) | Composition (mole basis) |
|---|---|---|
| MeOH | 64.53 | 1 |
| VAME/Water | 86.77 | (0.2729,0.7271) |
| Water | 100 | 1 |
| VAME | 128 | 1 |
| VA | 185.84 | 1 |

Therefore, a FORTRAN subroutine is written in Aspen Plus to calculate the reaction rate of each tray.

### *B. Phase Equilibrium*

The VAME process has one azeotrope and noideal phase behavior. Therefore, the selection of a thermodynamic model that can accurately represent the phase equilibriums of the process becomes very important. NRTL model is chosen to account for vapor-liquid equilibrium (VLE) and vapor-liquid-liquid (VLLE) equilibrium for the quaternary system. However, in Aspen Plus database, there is no data of VAME. Hence, NRTL parameters have to be regressed in Aspen Plus with the boiling point and specific gravity. MeOH-water binary parameters are taken from Aspen built-in database. For other five sets of parameters, without Aspen built-in parameters or experimental data, UNIFAC contribution method is used to estimate NRTL parameters.

The boiling point rankings for pure components and azeotropic information of all azeotropes in VAME process are shown in Table 1. Figure 1 shows the residue curve map of water, MeOH and VAME. There is a liquid-liquid separation between two products, VAME and water, in the process. This indicates that using a decanter can break the azeotrope and avoid getting products with azeotropic composition.

## III. PROCESS DESIGN

The VAME process is classified as the type $\mathrm{I}_{R}$ system in Tang et al.[6]. In this type of system, reactants are the heaviest and lightest components, which will make the design of reactive distillation column more difficult because of poor distribution of reactants in the reaction zone.

### *A. Conventional Design without Thermal Coupling*

Figure 2 shows the optimal design for the proposed conventional VAME process without thermal coupling. The goal of this design is to get 99% conversion of valeric acid in the reaction section and 99 mol% VAME and 99 mol% water in the separation section. Based on boiling point rankings, the heaviest component is reactant valeric acid so that there is no bottom outlet stream of the reactive distillation column (RDC). Both VA and MeOH are fed to the RDC from the bottom. The 14 stage RDC is operated at 0.7 bar because the temperature of reactive stages cannot be more than 150 ℃ which is the maximum temperature the catalyst can be operated at. Since the bottom has no need for separation, there is no stripping section in the RDC. There are 7 reactive stages and 5 rectifying stages. Reflux rate is adjusted to reach the specification of the conversion of VA. The top composition leaving the column lies well inside liquid-liquid separation envelope. It is also seen that the tie lines are toward the pure water so pure water can be recovered from the aqueous phase of a decanter located at the top of the RDC. The tie lines can also travel across the distillation boundary so that a stripper can be used to obtain high purity VAME. Two reboiler duty are used to reach the specification of product purity. Total annual cost (TAC) analysis is used to find the optimal design. The formula is given in Eq. 2 where the payback period, n is 3 years and AOC, TIC stand for annual operating cost and total installed cost, respectively.

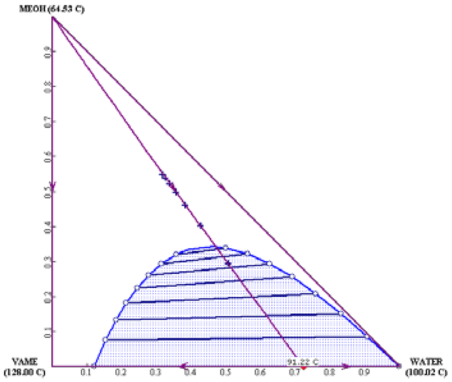

Figure 1. Residue curve map of Water, MeOH and VAME.

$$TAC = AOC + \frac{TIC}{n} \qquad (2)$$

Figure 3 shows the composition profile of the RDC. VAME composition in the upper section of the RDC goes through a maximum value and then decrease. This is the so-called remixing effect. This indicates that there is potential for energy-savings by using thermally coupled design.

### *B. Thermally Coupled Design*

The RD with thermally coupled design is proposed in the Figure 4. To complete the design, the vapor stream from the top of the RDC should go to the same sidedraw location at C1. C1 feed location is used to minimize TAC. The flow rate of the sidedraw is adjusted to reach conversion specification in the RDC. The reboiler duty of the RDC is 2.88 Gcal/hr which is almost the same as that in the conventional RD system in Figure 2. However, the reboiler duty of C1 is only 0.15 Gcal/hr, which is significantly lower than that in the conventional design. The comparison is shown in Table 2. The total energy consumed of the design with thermally coupling is 30% lower than the conventional design. Figure 5 gives the composition profile of RDC in the thermally coupled design. The reason for resulting energy savings is related to the eliminated remixing effect.

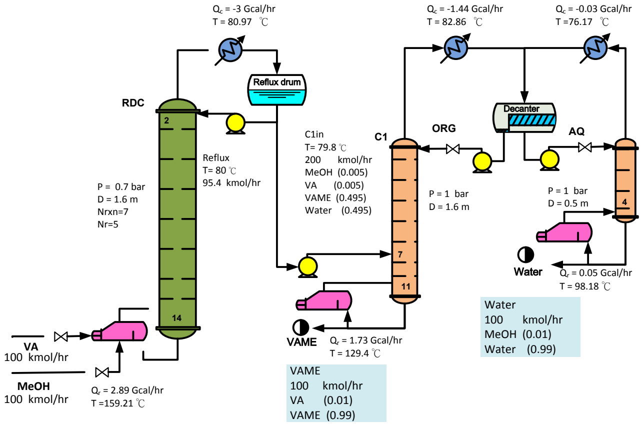

Figure 2. Optimal Design of Conventional Configuration.

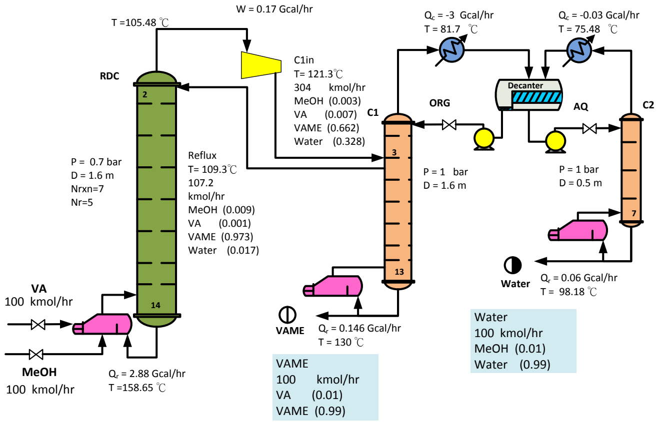

Figure 4. Optimal Design of Thermal Coupled Configuration

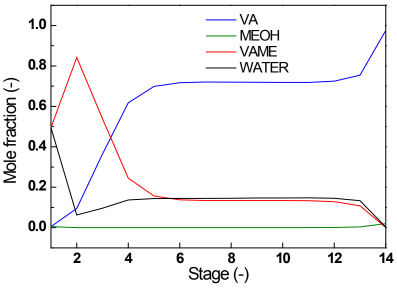

Figure 3. Composition Profile in the RDC of Conventional Configuration.

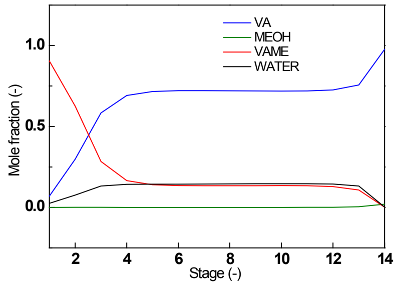

Figure 5. Composition Profile in the RDC of Thermal Coupled Configuration.

TABLE 2 COMPARISON OF TWO CONFIGURATIONS.

| | Reboiler Energy & Compressor Electricity (Gcal/hr) | TAC ($10^6$ $) |
|---|---|---|
| Neat Design | 4.66 | 2.25 |
| Neat thermo-coupling Design | 3.25 | 1.63 |
| Saving Percentage (%) | **30.3** | **17.6** |

## IV. OVERALL CONTROL STRATEGY

### A. *Control Structure*

The purpose of the control strategies is to keep the conversion of VA at 99 % and the mole fraction of VAME and water from the bottom of two strippers at 99%. Figures 8 and 9 show the control structures for the conventional configuration and the thermal coupled configuration, respectively. The conventional Proportional-Integral (PI) controllers are used for flow, temperature and pressure control loops. Simple Proportional (P) controller is used for level control. In both designs, temperature controller is used to replace composition controller, since the latter is very expensive and may cause time delay of measurements. In the RDC, feed ratio serve as the manipulating variable for the temperature control because when there are feed composition disturbances, feed ratio should be adjusted to reject the them. In C1 and C2, two reboiler duty are manipulating variables. Open loop sensitivity test is conducted to find controlled variables for temperature control. Controlled variables should have the largest sensitivity gain of manipulating variables. The result is shown in Figure 6 and 7. Temperature of 4th stage in the RDC, 8th stage in C1 and 1st stage in C2 have the largest gain. In conventional configuration, temperature of the 4th tray of the RDC is controlled by manipulating the feed ratio and the reflux rate is set to be proportional to the total feed flow rate, which applies the concept of feedforward control. Reboiler duties of C1 and C2 are used to control the temperature of 8th tray in C1 and 1st tray in C2, respectively. In the thermal coupled configuration, temperature of 5th tray is controlled by manipulating the feed ratio. Temperatures of 5th tray in C1 and 1st tray in C2 are controlled by two reboiler duty. The flow rate of side draw of C1 is set proportional to the total feed flow rate in RDC. Temperature controllers are tuned using the auto tune variation (ATV) method (Åström and Hägglund, 1984) [17]. ATV starts from relay-feedback method which can help us get ultimate gain and ultimate period. Then controller parameters are set using the Tyreus-Luyben turning relations. The sequential iterative tuning procedure is used to find the final settings. Moreover, two first order time lags are added in temperature control loop for improving the realism of the simulation.

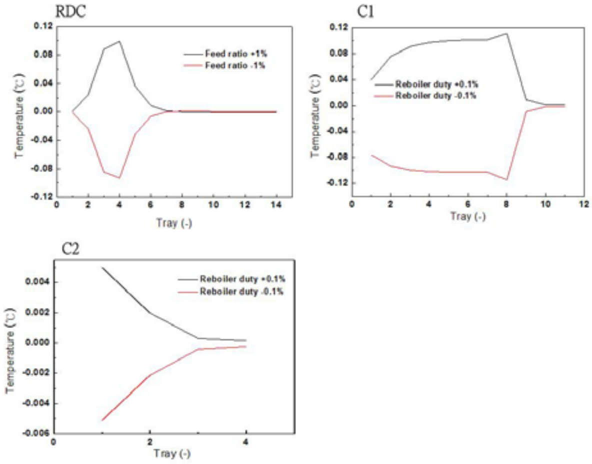

Figure 6. Open Loop Sensitivity Test of Conventional Design

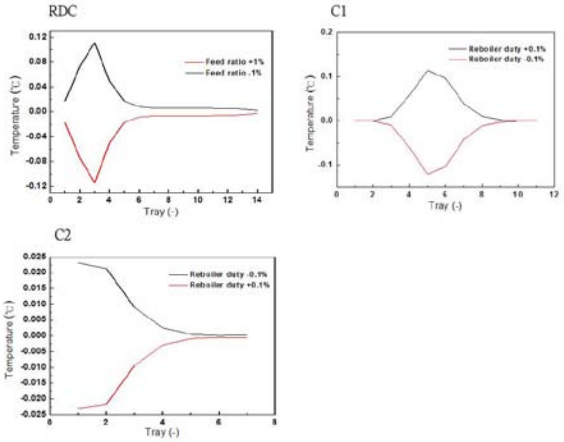

Figure 7. Open Loop Sensitivity Test of Thermally Coupled Design

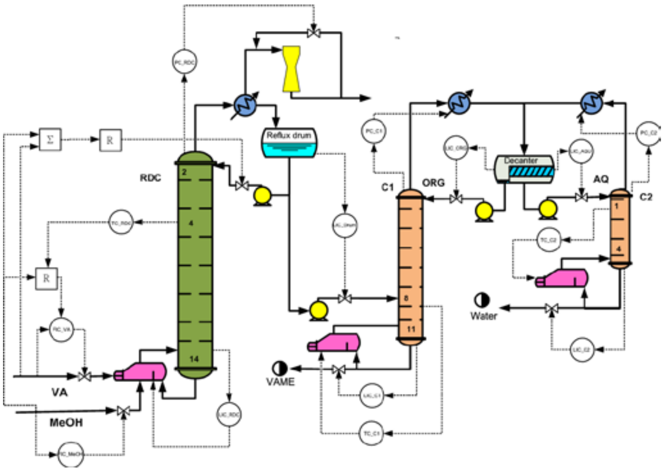

Figure 8. Control Structure of Conventional Configuration.

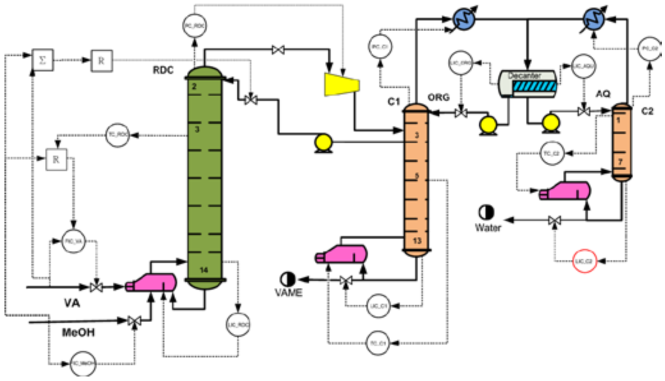

Figure 9. Control Structure of Thermal Coupled Configuration.

### *Dynamic Performances*

After the control structures are designed, both throughput disturbances (feed flow rate ±20%) and composition disturbances (methanol flow contains 3%, 5% water) are given to the process in order to see the performance of disturbances rejection. Aspen Plus Dynamics is used to simulate the dynamic responses. Figures 10 and 11 show the dynamic responses. It can be seen that both control structures can reject disturbances very well.

## V. CONCLUSION

Process intensification is an important issue in the industry and research community. Reactive distillation and thermal coupling are two applications. In this article, methyl valerate process is designed with conventional reactive distillation column and thermally coupled reactive distillation column. The simulation result shows that the thermally coupled configuration can save 30% energy consumption in the whole system. However, due to an extra compressor required in thermally coupled design, only 17.6% of total annual cost savings is reached.

Overall control strategy is also proposed for both configurations with only one temperature control loop in each column. Variations in feed composition and throughput changes are investigated. All product compositions can be maintained at high purity.

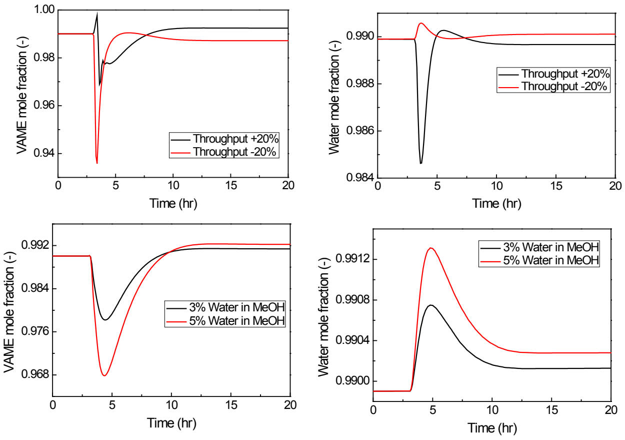

Figure 10. Dynamic Responses of Conventional Configuration.

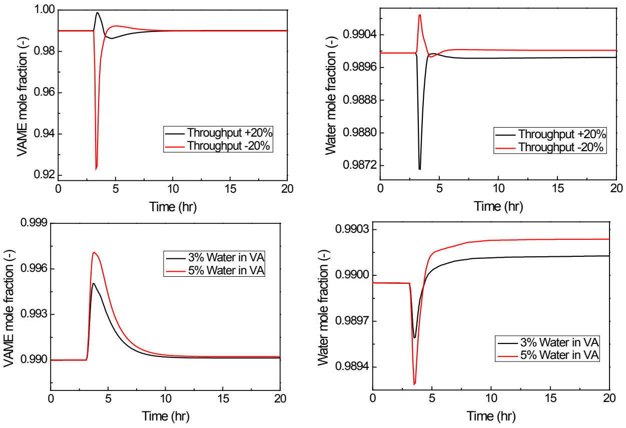

Figure 11. Dynamic Responses of Thermal Coupled Configuration

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