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Improving the Maximum Productivity for Ethyl Acetate Synthesis using gPROMS

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In this work, productivity of the desired distillate product in batch reactive distillation for production of ethyl acetate is maximised for different case studies with varying amount of reactants in the feed (including the cases with no water in the feed). For this a dynamic optimisation problem is formulated incorporating rigorous process model equations. The dynamic optimization problem is converted into a nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved by using efficient SQP method within gPROMS. Piecewise constant reflux ratio profile (with multiple time intervals) and batch times are optimised subject to product purity. The optimization results show that, increasing the amount of water in the feed leads to a reduction in the productivity of the distillate product. The results also show that the productivity of the desired product improves significantly when the column operates with multi-reflux policy.

1. Introduction

Due to the flexibility and lower equipment investment batch distillation processes are used in the chemical industry for production of small amount of product with high added values. In many chemical process industries, reaction and separation take place separately in a batch reactor followed by a batch distillation column (Charalambides, *et al*, 1994; Krishna, 2002). The integration of both processes in one unit operation results in batch reactive distillation. It allows a significant of capital and operational cost savings, especially in the case of equilibrium limited reactions, such as esterification and etherification reactions. Due to the continuous removal of products from the reaction zone, both conversion and selectivity are increased.Little attention has been given to modelling, simulation and optimisation of batch reactive distillation compared to those given to continuous reactive distillation. Various published papers can be found on design studies and steady-state simulation of continuous reactive distillation processes. A comprehensive overview is given by Taylor and Krishna (2000). Only few authors have discussed the design, control and optimal operational aspects of batch reactive distillation processes.

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Egly *et al*. (1979) were the first to consider the optimal operation of batch reactive distillation. They used a detailed dynamic column model to study the reversible reaction scheme. The reflux ratio and feed rate of one of the reactants were used as control variables. A conjugate gradient technique was used to obtain the optimal results. By controlling these variables they were able to reduce the batch cycle time by 40 % compared to constant reflux ratio. They also considered the separation of isomers (feed composition is 2 % low-boiling, 38 % medium-boilingt and 60 % high-boiling product) using batch distillation. The total batch cycle time was reduced by 51 % using the optimal reflux ratio profile compared to constant reflux operation. The simulation of batch reactive distillation was considered by Cuille and Reklaitis (1986) with reaction occurring on the plates, in the condenser and in the reboiler. They posed the system as a set of differential and algebraic equations (DAEs) and used a stiff solution method for the integration. Mujtaba and Macchietto (1997) presented computationally efficient framework for dynamic optimisation of batch reactive distillation. They considered a maximum conversion problem, subject to given product purity constraints. These polynomials were used to formulate a maximum profit problem. Mujtaba and Greaves (2006) replaced rigorous dynamic model by neural network (NN) based dynamic model and developed an NN based optimization framework for batch reactive distillation involving esterification of acetic acid with ethanol to produce ethyl acetate. Wajge and Reklaities (1999) developed an optimization framework (RBDOPT) for batch reactive distillation processes. The ethanol esterification process was modelled based on the rigorous model. They considered and solved the maximum conversion problem subject to ethyl acetate purity as a constraint. Reflux ratio was optimised. They showed the optimal results for ethanol esterification system are relatively insensitive to the operation policy. The small conversion obtained despite the use of a reactive distillation column was due to the use of non-catalyzed reaction kinetics.Edreder *et al*. (2008) studied optimal operation of batch reactive distillation operation involving an esterification reaction of ethanol and acetic acid to produce ethyl acetate (main product) and water. Different cases with varying feed composition (including cases with no water in the feed) were considered. Maximum conversion problem was considered and solved with varying batch time. The results indicated that the increasing amount of water in the feed leads to reduction in both conversion and distillate product. In this work, optimisation in terms of maximum productivity for ethanol esterification process is carried out for a range of feed compositions. Piecewise constant reflux ratio profile (with single and multiple time intervals) is considered as a control variable. The dynamic optimization problem includes a detailed process model (Edreder et al., 2008) and is converted to nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved by using efficient SQP method within gPROMS (general PROcess Modelling System) - PSE, 2004.

2. Process Model

Figure 1 shows a detailed dynamic model (Mujtaba and Macchietto, 1997, Edreder et al., 2008) including mass and energy balance equations, column holdup, rigorous phase equilibria, and chemical reaction taking on the plates, in the reboiler and in the condenser.

Internal Plates, j = 2, N-1

Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j$$

Component Mass Balance:

$$H_j \frac{dx_{ji}}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - L_j x_{ji} - V_j y_{ji} + r_{ji} H_j$$

Energy Balance:

$$0 = L_{j-1} h^L{}_{j-1} + V_{j+1} h^V{}_{j+1} - L_j h^L{}_j - V_j h^V{}_j$$

Equilibrium:

$$y_{ji} = K_{ji} x_{ji} \,,$$

Restrictions:

$$\sum y_{ji} = 1$$

Relations defining physical properties:

$$K_{ji} = K_{ji}(y_j, x_j, T_j, P)$$

$$h^L{}_j = h^L{}_j(x_j, T_j, P)\,,\ h^V{}_j = h^V{}_j(y_j, T_j, P)$$

$$r_{ji} = r_{ji}(k_{ji}, x_{ji})\,,\ \Delta n_j = \sum r_{ji}$$

Reboiler: j = N

Total Mass Balance:

$$\frac{dH_N}{dt} = L_{N-1} - V_N + \Delta n_N H_N$$

Component Mass Balance:

$$H_N \frac{dx_{Ni}}{dt} = L_{N-1}(x_{N-1,i} - x_{Ni}) - V_N (y_{Ni} - x_{Ni}) + r_{Ni} H_N - \Delta n_N H_N x_{Ni}$$

Energy Balance:

$$0 = L_{N-1}(h^L{}_{N-1} - h^L{}_N) - V_N(h^V{}_N - h^L{}_N) + Q_R$$

Condenser and Distillate Accumulator: j=1

Accumulator Total Mass Balance:

$$\frac{dH_a}{dt} = L_D$$

Component Mass Balance:

a) Accumulator:

$$H_a \frac{dx_a}{dt} = L_D(x_{D,i} - x_{a,i})$$

b) Condenser Holdup Tank

$$H_c \frac{dx_{Di}}{dt} = V_2 y_{2,i} + r_{1,i} H_c - (V_2 + \Delta n_1 H_c) x_{Di}$$

EnergyBalance:

$$0 = V_2 h^V{}_2 - (V_2 + \Delta n_1 H_c) h^L{}_1 - Q_c$$

Other Equation

$$L_1 = R(V_2 + \Delta n_1 H_c)\,,\ L_D = (V_2 + \Delta n_1 H_c)(1 - R)$$

$$T_1 = T_1(x_{D,i}, P)\,,\ h^L{}_1 = h^L{}_1(x_{D,i}, T_1, P)$$

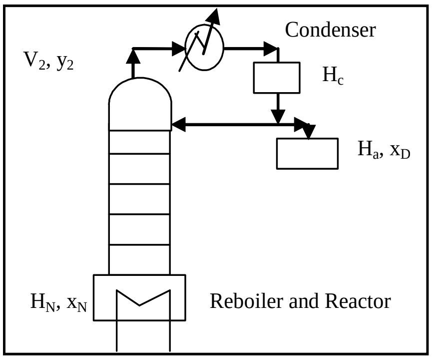

Figure 1: Model Equations

3. Optimization Problem Formulation

Here the dynamic optimization problem (Eq. 1) is formulated to maximizing the Productivity, (Prod. = amount of distillate /t_f). In words, find the optimal operation in terms of reflux ratio R and batch time which maximizes the productivity, subject to model equations (equality constraints), control variable bounds and product purity (inequality constraints) . Mathematically the problem can be stated as:

$$\mathit{OP1} \qquad \max_{R(t)} \ \mathit{Prod} \qquad (1)$$

subject to :

$$x_{EtAc} = x^*_{EtAc} \pm \varepsilon \qquad \text{(Inequality constraint)}$$

$and \quad f(t, x', x, u, \upsilon) = 0$ (Model Equation, equality constraint)

$with \quad f(t_0, x'_0, x_0, u_0, \upsilon) = 0$ (Initial condition, equality constraint)

$Linear\ bound\ on\ R$ (Inequality constraint)

4. Case Study

4.1 Specifications

In this work, five case studies are investigated with varying amount of water in the feed while keeping the amount of ethanol and acetic acid the same to study the effect of amount of water in the feed on the productivity of ethyl acetate. The column consists of 10 plates (including condenser and reboiler) and run with condenser vapour load of 2.5 kmol/h. The total column holdup is 4 % of the initial feed and the maximum reboiler capacity is 5 kmol. Stage compositions, product accumulator compositions, reboiler compositions are initialized to those of the feed compositions. The specification of feed is presented in Table 1. The given product purity of main product is 0.7 mole fraction of ethyl acetate for different cases.

Table 1 Amount of feed (kmol) for different case studies

	Case 1	Case 2	Case 3	Case 4	Case 5
Acetic acid	2.0	2.0	2.0	2.5	2.25
Ethanol	2.0	2.0	2.0	2.5	2.25
Ethyl acetate	0.0	0.0	0.0	0.0	0.0
Water	0.0	0.2	0.4	0.0	0.5
Total	4.0	4.2	4.4	5.0	5.0

4.2 Vapour-Liquid Equilibrium and reaction rate models

The vapour-liquid equilibrium is calculated using the temperature only dependent correlation proposed by Suzuki et al. (1970) based on experimental data (Eq. 2). Also the catalyzed reaction rate expression (Eq. 3) was taken from Bogacki et al. (1989). The liquid and vapour enthalpies and other physical properties such as densities were calculated using Ideal Physical Properties Foreign Objective (IPPFO) which is linked with gPROMS modelling software

Vapour –liquid Equilibrium: $\mathrm{AcOH} + \mathrm{EtOH} \Leftrightarrow \mathrm{AcOEt} + \mathrm{H_2O}$

$$K_{AA} = 2.25 \times 10^{-2} T - 7.812 \qquad T > 347.6\ K$$

$$\mathrm{K_{AA}} = 0.001 \qquad \mathrm{T} \le 347.6\,\mathrm{K}$$

$$\ell\mathrm{ogK_{EtOH}} = \frac{-2.3 \times 10^3}{\mathrm{T}} + 6.588$$

$$\ell\mathrm{ogK_{EtAc}} = \frac{-2.3 \times 10^3}{\mathrm{T}} + 6.742$$

$$\ell\mathrm{ogK_{H_2O}} = \frac{-2.3 \times 10^3}{\mathrm{T}} + 6.484 \qquad (2)$$

Kinetic Data: Rate of reaction, $r_i = k_f\, C_{AcOH} C_{EtOH} - k_r C_{AcOEt} C_{H_2O}$ (3)

Where rate constants are $k_f = 4.76 \times 10^{-4}$ and $k_r = 1.63 \times 10^{-4}$ (L/gmol-min) and C_i is the component concentration in gmol/L and r_i in gmol/(L-min); .

4.3 Results and Discussion

SingleReflux Ratio Operation (Scenario 1): Table 2 presents the optimisation results for all the case studies using single reflux ratio. As can be seen that, the operation time is reduced by about 8% and productivity improved by 13 % and the column operated at lower reflux ratio in Case 1 (no water in the feed) compared to Case 3 (with water in the feed). A comparison of the results between Case 4 and Case 5 (the column operating at maximum capacity of the reboiler i.e. 5 kmol) shows that the productivity improved by 25 % with no water in the feed (Case 4). The column can be also operated at lower reflux ratio and shorter operation time (saving time 6 %) compared to Case 5 (with water in the feed).

Table 2 Summary of the results (Scenario 1)

Case	t_f, h	R	D, kmol	Prod.1
1	9.12	0.932	1.55	0.17
2	9.51	0.936	1.52	0.16
3	9.90	0.94	1.49	0.15
4	9.60	0.92	1.92	0.20
5	10.21	0.935	1.63	0.16

Multi Reflux Ratio Operation (Scenario 2): The optimisation results for all the case studies using multi reflux ratio are also shown in Table 3. It can be seen that in the first time interval, an initial total reflux operation was required for all cases. Increasing water in the feed (Cases 2, 3, 5) leads to higher reflux ratio for the second time interval. Moreover the productivity has been decreased with increasing water in the feed.

Table 3 Summary of the results (Scenario 2)

Case	t_f, h	t_1,R_1	R_2	D, kmol	Prod. 2
1	6.78	1.99,1.0	0.884	1.39	0.21
2	7.06	1.99,1.0	0.895	1.36	0.19
3	7.28	2.06,1.0	0.899	1.32	0.18
4	7.35	1.92,1.0	0.873	1.72	0.24
5	7.86	2.02,1.0	0.896	1.47	0.19

Table 4 gives the percent improvement (IP) in productivity for Scenario 2 compared to Scenario 1. It can be seen that the benefit of using multi reflux policy (scenario 2) is very clear and more effective operation.

Table 4 Percent improvements in the productivity

Case	1	2	3	4	5
IP %	23.3	18.8	20.0	20.0	18.8

Note: IP = 100.0 * (Prod.2- Prod.1) /Prod.1

5. Conclusion

In this work a detailed dynamic model in terms of mass and energy balances and thermodynamic properties within gPROMS modelling software was used. Optimization problem was formulated to maximize the productivity of ethyl acetate while optimizing the reflux ratio (single and multi interval time) subject to satisfaction of ethyl acetate purity of 0.7 mole fraction in the distillate product. Piecewise constant reflux ratio profile was considered for the process. It can be seen from the results that the increasing of water amount in the feed leads to reduction the productivity and the column needed to operate at higher reflux ratio and longer operation time compared to the case with no water in the feed. Finally, a comparison of operating scenarios shows that the productivity has been improved by 20 % and batch time saving by 24 % when the column operates with multi-reflux policy.

References

Bogacki M.B., Alejski K. and Szymanowski J.,1989,. The fast method of the solution of a reacting distillation problem, Comp. and Chem. Eng.13 (9), 1081-1085.

Charalambides M.S., Shah N. and Pantelides C.C., 1994, optimal batch process synthesis, In Proceedings IChemE Research Event, London, 2, 908-910.

Cuille P.E., and. Reklaitis G.V, 1986, Dynamic simulation of multicomponent batch rectification with chemical reaction ,Comp. and Chem Eng. 10 (4), 389-398.

Edreder E.A, Emtir M. and Mujtaba I.M., 2008. Improving the maximum conversion of ethanol esterification,, Chemical Product and Process Modelling, 3 (1), article 36.

Egly H., Ruby V. and Seid B., 1979, Optimum design and operation of batch rectification accompanied by chemical reaction, Comp. and Chem. Eng. 3, 169-174.

Process System Enterprise Ltd (PSE), 2004, gPROMS, London, UK

Krishna R. and Sie S. T., 1994, Strategies for multiphase reactor selection Chem. Eng. Sci. 49, 4029-4065.

Mujtaba I.M and Macchietto S., 1997, Efficient optimization of batch distillation with chemical reaction using polynomial curve fitting techniques, Ind. Eng. Chem. Res. 36 , 2287-2295.

Mujtaba, I. M., 2004, Batch distillation: Design and operation. Imperial College Press, London, UK

Mujtaba I. M and Greaves M. A., 2006, Neural network based modeling and optimization in batch reactive distillation, IChemE Symposium 152, 868-876.

Suzuki, I.,Yagi H., Komatsu H. and Hirata M., 1970, Formulation and Prediction of Quaternary Vapour-liquid Equilibrium Accompanied by Esterification, J. Chemical. Engineering Japan 3, 152-157.

Taylor R.. and Krishna R., 2000, Modelling of reactive distillation-Review, Chemical Engineering Science 55, 5183-5229..

Wajge R.M. and. Reklaities G.V., 1999, A general-purpose object oriented module for distributed campaign optimization of reactive batch distillation, Chem. Eng. J. 75 (1), 57