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BatchColumn Application Example

Production of high purity methyl acetate by reactive distillation

Example purpose
This example allows you to understand the simulation with BatchColumn of a reactive distillation: the esterification of acetic acid. This example also proposes setting up multiple stop events for the same operation step.

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Corresponding BatchColumn files	*BATCHCOL_EX_EN-Reactive-distillation.pbpc*

Energy

Fives ProSim
Siège social : Immeuble Stratège A - 51 rue Ampère - 31670 Labège - FRANCE
Tél. : +33 (0)5 62 88 24 30
S.A.S. au capital de 147 800 € - 350 476 487 R.C.S. Toulouse - Siret 350 476 487 00037 - APE 5829C - N° TVA FR 10 350 476 487
www.fivesgroup.com / www.fives-prosim.com

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1. INTRODUCTION

Reactive distillation is the combination of a reactor and a distillation column into a single piece of equipment. This unit operation can be carried out with two processes taking place simultaneously, namely reaction and separation. The reactive zone can be the boiler and/or the column itself. Reactive distillation has advantages over conventional distillation: increased conversion, improved process efficiency and product selectivity, reduced investment costs, reduced energy costs due to reduced boiler heat duty in the case of exothermic reactions, and avoidance of azeotropic mixtures [AKK15].

Reactive distillation is suitable for equilibrium reactions, such as esterification reactions, like methyl acetate synthesis:

$$C_2H_4O_2 + CH_4O \leftrightarrow C_3H_6O_2 + H_2O$$

Methyl acetate is used as a solvent in adhesives and nail polish removers, in polyester production, in coating resins and inks [AKK15], [EDR15]. Acetic acid reacts with methanol to produce methyl acetate and water. As the reaction is reversible, its conversion is limited by the concentration of the products. To move the reaction in the direct direction, the removal of methyl acetate and water from the system is important. The separation process plays an important role in this. Reactive distillation can be used in this case.

BatchColumn, Fives ProSim's batch distillation column simulation software, makes it possible to simulate reactive distillation processes. Among other things, it makes it possible to study the influence of the feed position of the reactants, to adapt the scenario in order to maximize the production and purity of the product of interest, to reduce operating time, energy consumption, etc.

In this example, the boiler is previously loaded with methanol and acetic acid is fed. Methanol will be reactant in excess. As the catalyst is only present in the boiler, the chemical reactions will only take place in this part of the installation. The table below presents, in ascending order of bubble temperatures, the 4 pure compounds and the two homogeneous azeotropes that methyl acetate forms with methanol and water. It should be noted that the water-methyl acetate binary has a liquid phase splitting.

Compound		T_{buble} or $T_{azeotrop}$ (°C)	Mass fraction of compound 1	System type
1	2			
Methanol	Methyl acetate	53.9	0.1710	Homogeneous
Methyl acetate		57.1		
Methyl acetate	Water	57.7	0.9172	Homogeneous
Methanol		64.5		
Water		100.0		
Acetic acid		118.0		

It is proposed to divide the scenario into 4 parts in order to recover and produce enough methyl acetate at the desired purity:

1) Column filling

This step heats the initial load of the column from its storage temperature (20°C) to its boiling temperature and then fills the liquid hold-ups of the internals and the condenser.

2) Starting of the reaction

The acetic acid feed is open. The synthesis of methyl acetate begins.

3) Maintain of the reaction

In order to maintain the reaction, the methanol supply is opened. The distillate recipe tank is changed when the required purity of methyl acetate is reached. When the acetic acid amount is deemed sufficient, its supply is stopped and replaced by methanol to maintain the excess methanol.

4) Finalization

Both feeds are closed. The reaction continues until the acetic acid is exhausted. The scenario is stopped when the excess methanol arrives at the distillate.

Water being the heaviest compound, it will remain in the boiler at the end of the operations.

2. COMPOUNDS

The compounds considered in the simulation are the following ones:

Name	Formula	CAS number[1]
Acetic acid	$C_2H_4O_2$	64-19-7
Methanol	CH_4O	67-56-1
Methyl acetate	$C_3H_6O_2$	79-20-9
Water	H_2O	7732-18-5

The compounds are extracted from the standard database of Simulis Thermodynamics, the calculation server of physico-chemical properties and phase equilibria used in BatchColumn. The physico-chemical properties stored in this database are taken from the DIPPR database [ROW25].

3. THERMODYNAMIC MODEL

Due to the pressure level in this process (1 atm) and the polar nature of the compounds, the thermodynamic profile “UNIFAC original Hayden-O'Connell” [FRE75] was chosen. This model is based on a heterogeneous approach. It is a predictive model and therefore does not require binary interaction parameters. The Hayden-O'Connell equation of state [HAY75] allows us to take into account the dimerization of acetic acid in the gas phase. Liquid phase splitting is taken into account to correctly represent the liquid-liquid-vapor equilibrium of the water-methyl acetate binary.

4. CHEMICAL REACTIONS

The acetic acid – methanol esterification reaction can be described by two reactions, one being the reverse of the other, for which the kinetics are known:

$$C_2H_4O_2 + CH_4O \rightarrow C_3H_6O_2 + H_2O \quad (r_1)$$

$$C_3H_6O_2 + H_2O \rightarrow C_2H_4O_2 + CH_4O \quad (r_2)$$

The kinetic models follow Arrhenius' laws expressed in molar concentration. Their parameters are presented in the table below. The reactions take place in the liquid phase.

Reaction	$\boldsymbol{k_0}\ \left(\boldsymbol{h^{-1}/(mol/l)}\right)$	$\boldsymbol{Ea}\ (\boldsymbol{cal/mol})$	$\boldsymbol{\Delta H_R}\ (\boldsymbol{cal/mol})$
(r_1)	$7.2\text{x}10^7$	10 200	-4 773.901
(r_2)	$1.385\text{x}10^7$	10 200	4 773.901

[1] *CAS Registry Numbers® are the intellectual property of the American Chemical Society and are used by Fives ProSim SAS with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate.*

5. SIMULATION

5.1. Process description

5.1.1. Column

The column is made up of 15 theoretical stages, including the boiler and the condenser.

Two collection tanks will be used during the distillation step.

Two feeds will be used: one in the boiler and one on stage 6.

The initial load is detailed below:

✓	Temperature	20°C	
✓	Total mass	500 kg	
✓	Mas composition	Acetic acid	5%
		Methanol	95%
		Methyl acetate	0%
		Water	0%

The liquid hold-ups are supposed to be constant all along the distillation:

- ✓ Condenser 20 l
- ✓ Column 3 l for each theoretical stage

The pressure profile is also supposed to be constant all along the distillation process:

- ✓ Condenser 1 atm
- ✓ Pressure drop 0 atm (no pressure drop)

The stages efficiency is assumed to be equal to 1 (each stage is assumed to be a theoretical stage).

5.1.2. Condenser

The condenser is assumed to be ideal total all along the distillation process.

5.1.3. Boiler

In this example, the geometry of the boiler heating system, and the corresponding utility, are not defined. The heating system is defined directly in the operating steps by the amount of heat involved.

5.2. Operating mode

The operating mode consists of six steps. The operating parameters of these steps are detailed in the tables below. The following settings are the same for all steps:

- ✓ Operating mode: Constant heat duty
- ✓ Reactive stage: 15 (the reactions take place only on the boiler)
- ✓ Condenser: Ideal total

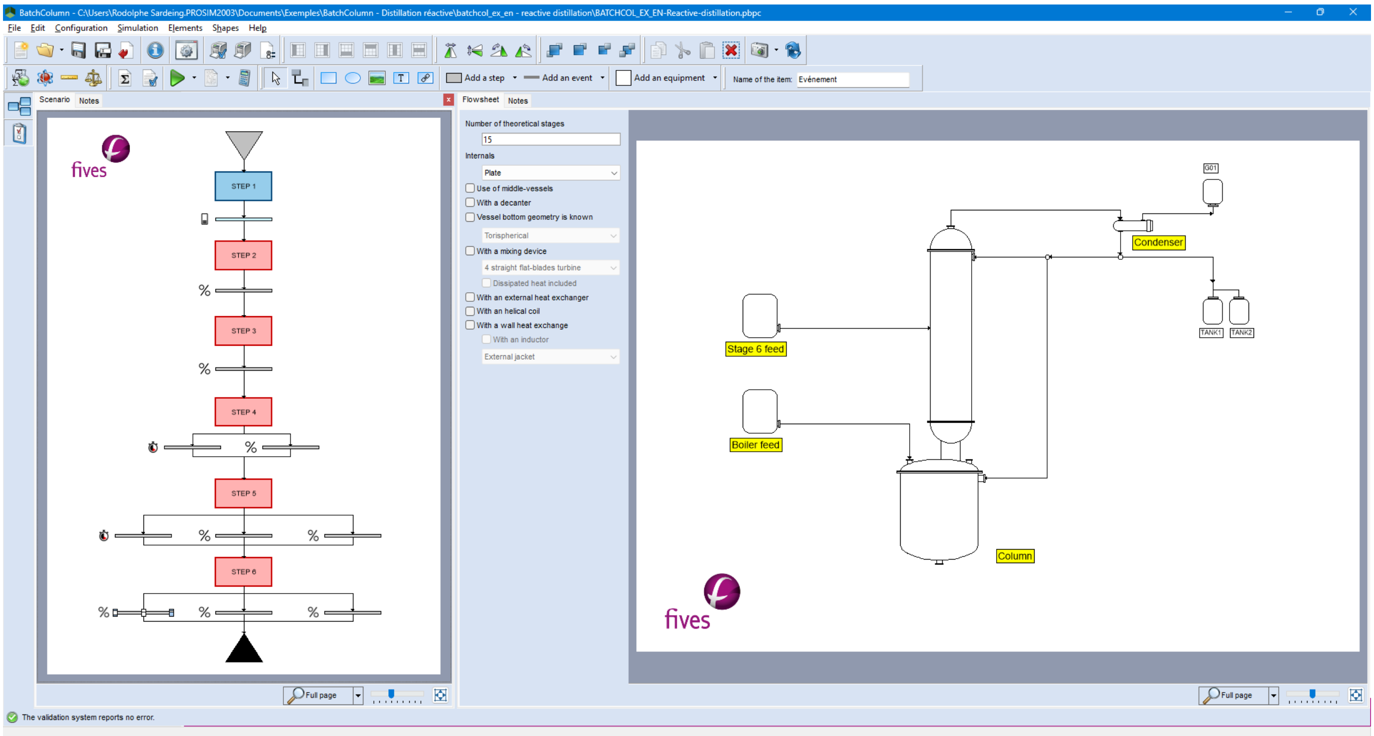
<table>
<tr><th>Parameter</th><th>Step 1</th><th>Step 2</th><th>Step 3</th></tr>
<tr><td>Type</td><td>Filling</td><td colspan="2">Distillation</td></tr>
<tr><td>Active feed</td><td>None</td><td>Boiler</td><td>Stage 6
Boiler</td></tr>
<tr><td>Reflux ratio</td><td>-</td><td colspan="2">3</td></tr>
<tr><td>Boiler heat duty (kcal/h)</td><td colspan="2">200 000</td><td>100 000</td></tr>
<tr><td>Collection tank</td><td>-</td><td colspan="2">Tank 1</td></tr>
<tr><td>Stop event</td><td>Column is filled</td><td>Fraction inside the distillate in methyl acetate = 73% wt.</td><td>Fraction inside the distillate in methyl acetate > 80% wt.</td></tr>
</table>

<table>
<tr><th>Parameter</th><th>Step 4</th><th>Step 5</th><th>Step 6</th></tr>
<tr><td>Type</td><td colspan="3">Distillation</td></tr>
<tr><td>Active feed</td><td>Stage 6
Boiler</td><td>Boiler</td><td>None</td></tr>
<tr><td>Reflux ratio</td><td>4</td><td>10</td><td>5</td></tr>
<tr><td>Boiler heat duty (kcal/h)</td><td colspan="3">100 000</td></tr>
<tr><td>Collection tank</td><td colspan="3">Tank 2</td></tr>
<tr><td>Stop event</td><td>Step duration = 5 h
or
Fraction inside the distillate in acetic acid > 0.01% wt.</td><td>Step duration = 6 h
or
Fraction inside the boiler in acetic acid < 0.01% wt.
or
Fraction inside the boiler in methanol < 0.01% wt.</td><td>Fraction inside the tank 2 in methyl acetate < 80% wt.
or
Fraction inside the boiler in acetic acid < 0.01% wt.
or
Fraction inside the boiler in methanol < 0.01% wt.</td></tr>
</table>

The following table shows the characteristics of the two feeds.

	Stage 6 feed	Boiler feed	
Step	3 & 4	2 to 4	5
Temperature (°C)	50		
Pressure (atm)	1		
Flow rate (kg/h)	100	200	50
Mass composition			
Acetic acid	0	1	0
Methanol	1	0	1
Methyl acetate	0		
Water	0		

The scenario is presented on the left of the following screenshot and the flowsheet on the right part.

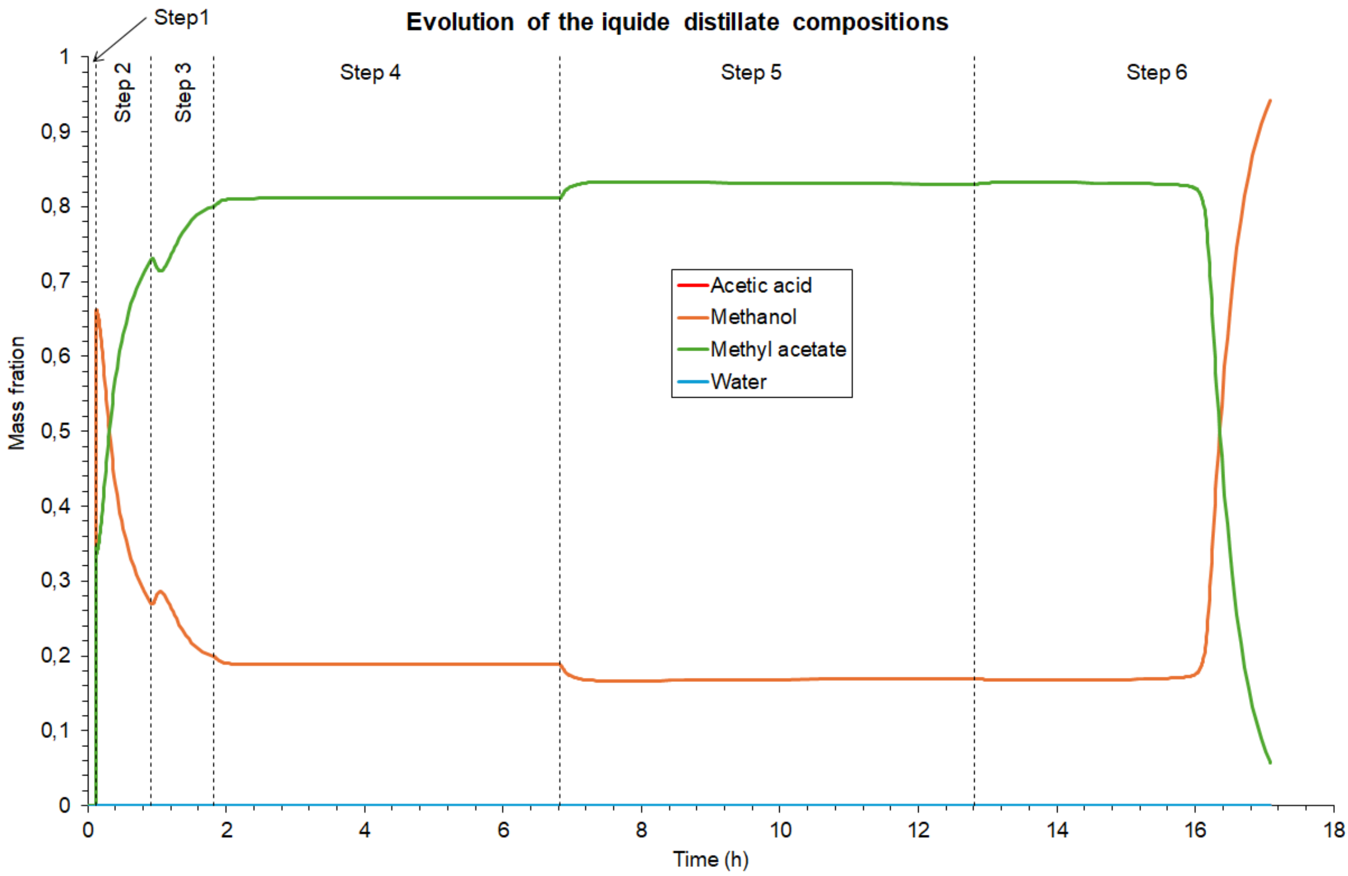


6. Results

6.1. Profiles

Several profiles are available at the end of the simulation (temperatures, liquid distillate and boiler compositions, tank compositions, etc.), including the figure below. This figure shows the evolution of the mass fractions in the liquid distillate. This shows the evolution of the mass fractions in the liquid distillate. These profiles make it possible to visualize, among other things:

- ✓ The steady increase in methyl acetate content and the decrease in methanol content.
- ✓ Methyl acetate production has a relatively constant composition



6.2. Tabulated results

The Word report generated at the end of the simulation contains summary tables, including the table below. This table shows the contents of the collection tanks, the boiler and the liquid hold-ups (condenser and internals) at the end of the operation. This table shows that tank 2 collects the methyl acetate produced. At the end of the operation, the boiler contains an aqueous mixture of methanol and the liquid hold-ups (condenser + stages), mostly methanol. One objective could be to reduce the loss of methyl acetate in tank 1.

	Tank 1	Tank 2	Boiler	Liquid hold-ups
Weight (kg)	423	1745	515	45
Composition (% wt.)				
Acetic acid	0	0	0.01	0
Methanol	33.15	19.85	21.08	92.56
Methyl acetate	66.85	80.15	0.01	2.10
Water	0	0	78.90	5.34

7. REFERENCE

[AKK15] AKKARAVATHASINP S., NARATARUKSA P., PRAPAINAINAR C., "The Effect of Feed Location of a Semi-Batch Reactive Distillation via Esterification Reaction of Acetic Acid and Methanol: Simulation Study", Energy Procedia, 79, 778-783 (2015)

[EDR15] EDREDER E., MUJTABA I.M., EMTIR M., "Optimal Operation of Batch Reactive Distillation Process Involving Esterification Reaction System", Chem. Eng. Trans., 43, 1387-1392 (2015)

[FRE75] FREDENSLUND A., JONES R.L., PRAUSNITZ J.M., "Group Contribution Estimation of Activity Coefficients in Non-Ideal Liquid Mixtures", AIChE J., 21, 1086-1099 (1975)

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[ROW25] ROWLEY R.L., WILDING W.V., OSCARSON J.L., GILES N.F., "DIPPR® Data Compilation of Pure Chemical Properties", Design Institute for Physical Properties, AIChE (2025).

