An industrial design/control study for the vinyl acetate monomer process

Michael L. Luyben* and Björn D. Tyréus

DuPont Central Research & Development, Experimental Station - Bldg 357, P.O. Box 80357, Wilmington, DE 19880-0357, USA

Abstract

This work presents design details of an industrial process for the manufacture of vinyl acetate monomer. Our purpose is to offer a realistic example that is uniquely suited for academic researchers pursuing simulation, design, and control studies. The vinyl acetate process has common, real chemical components. It contains many standard unit operations in a realistic flowsheet. And it illustrates the types of systems of industrial research interest in the areas of process design, optimization, simulation, and control. Vapor-phase reactions convert ethylene, oxygen, and acetic acid into vinyl acetate with water and carbon dioxide as byproducts. The process contains a packed tubular reactor, a feed-effluent heat exchanger, an absorber, a vaporizer, an azeotropic distillation column with decanter, and both gas and liquid recycle streams. All physical property, kinetic, and flowsheet data have been compiled from sources in the open literature. We detail the flowsheet information required to construct rigorous steady state and dynamic mathematical models of the process and present the process control requirements and objectives. Finally, we briefly describe the rigorous nonlinear dynamic simulation we have constructed for this process using TMODS, DuPont's in-house dynamic simulator. Models of this process have also been developed by Aspen Technology and Hyprotech in their commercial simulators and are available directly from the vendors. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: industrial design/control study; vinyl acetate monomer process

1. Introduction

Downs and Vogel (1993) published an industrial plantwide control test problem that has proved to be a beneficial service to the academic process control community. A number of researchers have utilized this example to test their ideas and technical developments. Many publications have appeared about the Eastman process, which was provided as a dynamic simulation in Fortran code. The problem has usefully served as a realistic check on the industrial and practical relevance of the ever-increasing amount of process control publications in chemical engineering.

We have heard of continued interest among academic researchers within the process design and control areas to have additional industrial examples of realistic processes that can be used in assessing new technology. We also recognize the need in the literature for plantwide design, optimization, and control studies that grapple with: (1) a realistically large process flowsheet containing standard chemical unit operations; (2) a process with the typical industrial characteristics of recycle streams and energy integration; and (3) real nonideal chemical components.

This paper presents design details of an industrial process for the production of vinyl acetate monomer and thus goes a step beyond the Eastman process control challenge problem. The reaction loop section of the vinyl acetate process contains a flowsheet and unit operations that are typical of many chemical plants. It has both gas and liquid recycle streams with real components.

We have chosen to convey this study as if we had been assigned the task of designing the control system for a proposed new vinyl acetate process that is to be built. We have been given a particular preliminary design that has *not* been optimized. The design could potentially be improved with modifications to the flowsheet or design parameters.

The data we provide in this paper are what would typically be available or easily obtainable: (1) kinetic reaction parameters and physical property data, (2) a flowsheet structure with stream and equipment information, and (3) the location of control valves

*Corresponding author. E-mail: luybenml@esvax.dnet.dupont.com.

included in the preliminary design. However, we would not be given a linear transfer function model. We certainly would not have a rigorous nonlinear dynamic simulation. Steady state and dynamic models would have to be constructed by using a commercial software simulation package or by writing the code in some chosen programming language. As a result, unlike Downs and Vogel (1993), we do not make available any code that simulates the vinyl acetate process. Based upon the information provided in this paper, models have been developed by Aspen Technology and Hyprotech in their commercial simulators.
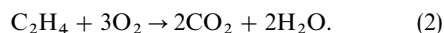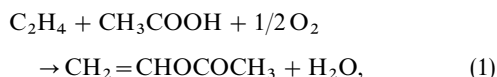
We have ourselves built a rigorous nonlinear dynamic model of the process described in this paper using TMODS, DuPont's in-house dynamic simulator. This model has been used to verify the feasibility of the simulation and to test the plantwide control strategy proposed in Luyben et al. (1997). We believe that this process should serve as a useful example for researchers who are interested in working on industrially relevant problems in simulation, design, and control.

The industrial process for the vapor-phase manufacture of vinyl acetate monomer is quite common (Daniels, 1989) and utilizes widely available raw materials. Vinyl acetate is used chiefly as a monomer to make polyvinyl acetate and other copolymers. Hoechst-Celanese, Union Carbide, and Quantum Chemical are reported US manufacturers. DuPont also currently operates a vinyl acetate process at its plant in LaPorte, Texas. To protect any proprietary DuPont information, all of the physical property and kinetic data, process flowsheet information, and modeling formulation in this work come from sources in the open literature. We cite each source of data and our process flowsheet is based upon the description in Report 15B by SRI International (1994). No relation, either implied or intended, exists between this published study and the DuPont process.

2. Vinyl acetate process

Figure 1 shows the eleven basic unit operations proposed for the reaction section of the vinyl acetate process, which is the focus of this study and the plant we wish to design and operate. Three raw materials, ethylene (C_2H_4), oxygen (O_2), and acetic acid (HAc), are converted into the vinyl acetate (VAc) product. Water (H_2O) and carbon dioxide (CO_2) are byproducts. We assume that an inert component, ethane (C_2H_6), enters with the fresh ethylene feed stream. We consider the following two reactions:

$$C_2H_4 + CH_3COOH + 1/2\,O_2$$
$$\rightarrow CH_2{=}CHOCOCH_3 + H_2O, \qquad (1)$$
$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O. \qquad (2)$$

The exothermic reactions occur in a reactor containing tubes packed with a precious metal catalyst on a silica support. Heat is removed from the reactor by generating steam on the shell side of the tubes. Water flows to the reactor from a steam drum, to which make-up water (BFW) is supplied. The steam leaves the drum as saturated vapor. The reactions are irreversible and the reaction rates have an Arrhenius-type dependence on temperature.

Fig. 1. Vinyl acetate monomer process flowsheet.
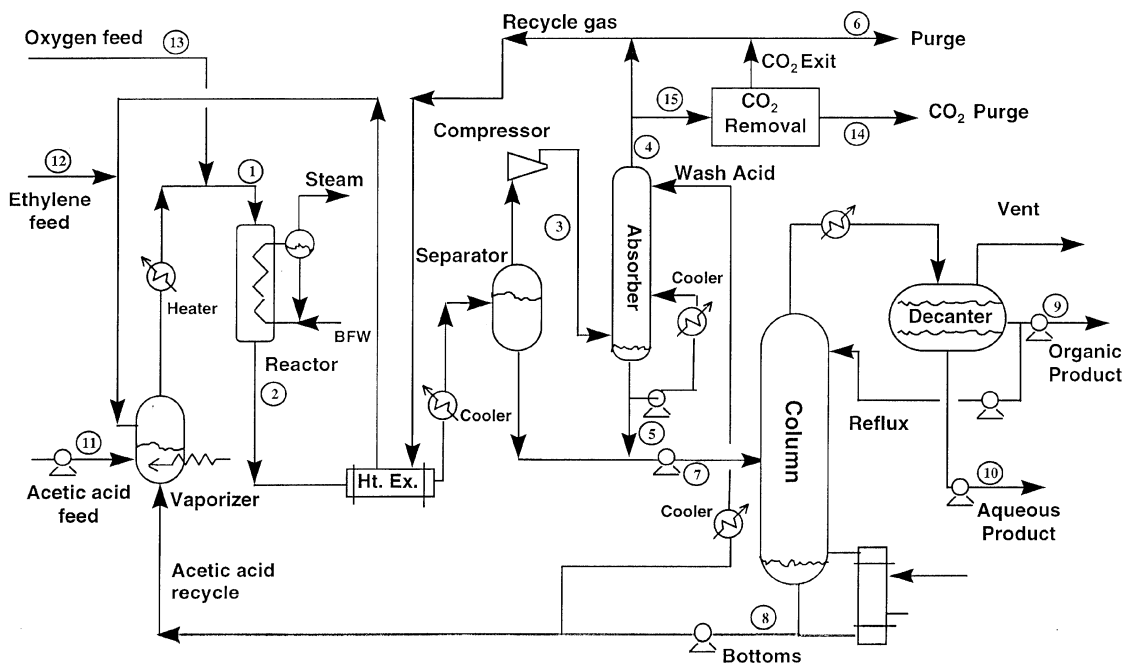
We located plots of experimental kinetic data in Samanos *et al.* (1971) for a particular vinyl acetate catalyst. As summarized by Neurock *et al.* (1996), various mechanisms have been proposed for the formation of vinyl acetate (i.e. Samanos *et al.*, 1971; and Nakamura and Yasui, 1970, develop completely different expressions). However, we derived the following rate expressions that provide the best fit to the experimental data.

$$r_1 = 0.1036 \exp(-3674/T)$$

$$\times \frac{p_O p_E p_A (1 + 1.7 p_W)}{(1 + 0.583 p_O (1 + 1.7 p_W))\,(1 + 6.8 p_A)}, \quad (3)$$

$$r_2 = 1.9365 \times 10^5 \exp(-10,116/T)$$

$$\times \frac{p_O (1 + 0.68 p_W)}{1 + 0.76 p_O (1 + 0.68 p_W)}, \quad (4)$$

where r_1 has units of moles of vinyl acetate produced/min/(g catalyst) and r_2 has units of moles of ethylene consumed/min/(g catalyst). T is the absolute temperature in Kelvin and p_i is the partial pressure of component i (O is oxygen, E is ethylene, A is acetic acid, and W is water) in psia.

The standard state heat of reaction is -42.1 kcal/mol of vinyl acetate for r_1 and -316 kcal/mol of ethylene for r_2. These values are calculated using heats of formation from the DIPPR database. Thus the reactions are quite exothermic, particularly the combustion reaction to carbon dioxide, which also is more sensitive to temperature because of the higher activation energy.

The reactor effluent flows through a process-to-process heat exchanger, where the cold stream is the gas recycle. The reactor effluent is then cooled with cooling water and the vapor (oxygen, ethylene, carbon dioxide, ethane) and liquid (vinyl acetate, water, acetic acid) are separated. The vapor stream from the separator goes to the compressor and the liquid stream from the separator becomes a part of the feed to the azeotropic distillation column. The gas from the compressor enters the bottom of an absorber, where the remaining vinyl acetate is recovered. A liquid stream from the base is recirculated through a cooler and fed to the middle of the absorber. Liquid acetic acid that has been cooled is fed into the top of the absorber to provide the final scrubbing. The liquid bottoms product from the absorber combines with the liquid from the separator as the feed stream to the distillation column.

Part of the overhead gas exiting the absorber enters the carbon dioxide removal system. This could be one of the several standard industrial CO_2 removal processes. Here we simplify this system by treating it as a component separator with a certain efficiency that is a function of rate and composition. The gas stream minus carbon dioxide is split, with part going to the purge for removal of the inert ethane from the process.

The rest combines with the large recycle gas stream and goes to the feed-effluent heat exchanger. The fresh ethylene feed stream is added. The gas recycle stream, the fresh acetic acid feed, and the recycle liquid acetic acid stream enter the vaporizer, where steam is used to vaporize the liquid. The gas stream from the vaporizer is further heated to the desired reactor inlet temperature in a trim heater using steam. Fresh oxygen is added to the gas stream from the vaporizer just prior to the reactor to keep the oxygen composition in the gas recycle loop outside the explosivity region.

The azeotropic distillation column separates the vinyl acetate and water from the unconverted acetic acid. The overhead product is condensed with cooling water and the liquid goes to a decanter, where the vinyl acetate and water phases separate. The organic and aqueous products are sent for further refining to another distillation section. Here we ignore the additional separation steps required to produce vinyl acetate of sufficient purity because there is no recycle from the refining train back to the reaction loop. The bottom product from the distillation column contains acetic acid, which recycles back to the vaporizer along with fresh make-up acetic acid. Part of this bottoms stream is the wash acid used in the absorber after being cooled.

3. Physical property data

The vapor–liquid equilibrium (VLE) data for the three nonideal component pairs are given in Table 1. These data come from the vapor-liquid equilibrium data collection in the Chemistry data series published by DECHEMA. VLE calculations are performed assuming an ideal vapor phase and a standard Wilson liquid activity coefficient model. This takes the form

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp(-a_{ij}/RT), \quad (5)$$

where T is the absolute temperature in K, R is the gas constant (1.987 cal/mol K), and V_i is the molar volume of component i given in DECHEMA and listed in Table 1.

The Wilson parameters we use for the VAc–H_2O pair are assumed to be the same as the parameters for ethyl acetate and water. The reason for this assumption is that no VLE data are presented in DECHEMA for vinyl acetate and water, but ethyl acetate and vinyl acetate are quite similar species and should behave essentially identically. The liquid-liquid equilibrium solubility data for the VAc–H_2O pair in the column decanter come from Smith (1942) extrapolated to the decanter temperature of $40\,^\circ$C.

Acetic acid dimerizes in the vapor phase. The Wilson parameters listed in DECHEMA for the H_2O–HAc pair assume the effect of dimerization is modeled. Without considering the vapor-phase association, the DECHEMA parameters predict the existence of an azeotrope close to pure water. Such an

Table 1. Wilson parameters a_{ij} and molar volumes V_i

a_{ij}	VAc	H_2O	HAc	V_i (ml/mol)
VAc	0	1384.6	−136.1	93.1
H_2O	2266.4	0	670.7	18.07
HAc	726.7	230.6	0	57.54

From DECHEMA vapor–liquid equilibrium data collection Vol. 1.
VAc–H_2O: Part 1b, p. 236.
VAc–HAc: Part 5, p. 90.
H_2O–HAc: Part 1, p. 127.

Table 3. Component vapor pressure antoine coefficients $-\ln P^s = A + B/(t + C)$, where P^s in psia and t in °C

Component	A	B	C
O_2	9.2	0	273
CO_2	7.937	0	273
C_2H_4	9.497	−313	273
C_2H_6	9.497	−313	273
VAc	12.6564	−2984.45	226.66
H_2O	14.6394	−3984.92	233.426
HAc	14.5236	−4457.83	258.45

temperature dependence for the bubble point calculations to function properly.

4. Process data and constraints

4.1. Design requirements

azeotrope does not exist for this system. The VLE behavior close to pure acetic acid is acceptable without a model of dimerization. Since we operate in the process where the VLE behavior is acceptable, we have used the parameters in Table 1 without special provisions for vapor-phase association.

Table 2 shows the pure component physical property data, which we obtained from the DIPPR database. These data include the molecular weight MW, the liquid specific gravity (based on the density of water at 0°C), the latent heat of vaporization ΔH_v at 0°C (in cal/mol), and the liquid c_p^l and vapor c_p^v heat capacity parameters. The heat capacity expressions we use have the following temperature dependence:

$$c_p = a + bt, \tag{6}$$

where c_p is in cal/(g°C) and t is the temperature in°C.

Component vapor pressures P^s in psia (Table 3) are calculated using the Antoine equation, with the Antoine coefficients listed in the DECHEMA volumes.

$$\ln P^s = A + B/(t + C), \tag{7}$$

where t is the temperature in °C. For the four gas components, the A parameters of the Antoine equation were estimated based upon the vapor pressure at the operating conditions in the absorber. We removed the temperature dependence to facilitate the dynamic simulation. However, in the case of ethylene and ethane, we found that we needed to include a small

The process design that we use is based upon the flowsheet shown in SRI Report 15B. We assume that the production basis of our process with new catalyst is 785 mol/min VAc and at the given conditions 85 mol/min CO_2 is also produced. For a plant with 90% operating utility, this corresponds to an annual production rate of 32×10^6 kg/yr, if the VAc rate is sustained over the life of the catalyst. We assume that the catalyst lifetime is one year.

The ethylene and oxygen feed streams come from supply headers. Acetic acid comes from a storage tank. The carbon dioxide is released to the atmosphere. The gas purge stream is sent to a thermal converter. The vinyl acetate and water products from the decanter are fed to other distillation columns in a refining train. Available on the plant are the following utilities: cooling tower water at a supply temperature of 30°C, steam at supply pressures of 50 and 200 psia, refrigeration at −25°C, and electricity and process water. Economic data for raw material and energy costs are listed in Table 4. Any capital equipment and vessel cost data can be found in Guthrie (1969). The costs should be updated to current prices. Also, the appropriate material of construction factors should be used. Cost correlations for some equipment are given in Douglas (1988).

Table 2. Pure component physical properties (c_p in cal/(g °C))

Component	Molecular weight	Specific gravity	Latent heat (cal/mol)	Liquid ht capacity a–b	Vapor ht capacity a–b
O_2	32	0.5	2300	0.3–0	0.218–0.0001
CO_2	44.01	1.18	2429	0.6–0	0.23–0
C_2H_4	28.05	0.57	1260	0.6–0	0.37–0.0007
C_2H_6	30.05	0.57	1260	0.6–0	0.37–0.0007
VAc	86.09	0.85	8600	0.44–0.0011	0.29–0.0006
H_2O	18.02	1	10684	0.99–0.0002	0.56– −0.0016
HAc	60.05	0.98	5486	0.46–0.0012	0.52–0.0007

Table 4. Economic data for vinyl acetate process

Item	Cost/price
Acetic acid	$0.596/kg
Oxygen	$0.044/kg
Ethylene	$0.442/kg
Vinyl acetate	$0.971/kg
200 psia steam	$11/1000 kg
50 psia steam	$8.8/1000 kg
Cooling tower water	$0.02/1000 l
Process water	$0.15/1000 l
− 25°C refrigeration	$0.12/h, ton
Electricity	$0.065/kwh

Tables 5–7 contain the flow, temperature, pressure, and composition data for selected streams in the process. The corresponding stream numbers are shown in Fig. 1. In our simulation, all gas is removed in a component separator prior to the distillation column. This involves the liquid from the separator and the absorb-

er. The gas is sent back and combines with the vapor product from the separator to form the vapor feed to the absorber. Tables 8–10 contain certain vessel data that are required to size the equipment and construct the simulation. These data come from our TMODS dynamic simulation and not from a commercial steady-state simulation package.

The reactor contains 622 tubes packed with catalyst. The tube diameter is 3.7 cm and length 10 m. Steam is generated on the shell side of the reactor to remove the heat of reaction. We have modeled the reactor in 10 sections in the axial direction. The reactor temperature profile is shown in Fig. 2. The flowsheet design conditions are for a new catalyst with an activity of 1. However, the catalyst does deactivate over the course of operation. This deactivation via sintering is a nonlinear function of operating time (t_{yr}) and temperature, since higher temperatures within the tubes (t_{tube}) promote deactivation. We assume that the activity (a) decays exponentially with time from 1.0 to 0.8 after 1 yr according to

$$a = f(t_{tube}) \exp(- t_{yr}/0.621). \qquad (8)$$

Table 5. Process stream data Table I

	Reactor in	Reactor out	Absorber vapor in	Absorber vapor out	Absorber liquid out	Purge flow
Stream Number	1	2	3	4	5	6
Flow (mol/min)	19250	18850	16240	15790	1210	3
Temperature (°C)	148.5	158.9	80	40.4	47.7	40.4
Pressure (psia)	128	90[b]	128	128	128	128
O_2 (mol frac)	0.075	0.049	0.057	0.058	0.001	0.059
CO_2	0.007	0.011	0.013	0.014	0.001	68[a]
C_2H_4	0.583	0.551	0.642	0.658	0.025	0.667
C_2H_6	0.216	0.221	0.256	0.263	0.010	0.266
VAc	0	0.043	0.021	0.002	0.255	0.002
H_2O	0.009	0.055	0.007	0.001	0.129	0.001
HAc	0.110	0.070	0.004	0.004	0.579	0.005

[a]moles/million.
[b]Pressure drop in gas loop assumed to be in reactor.

Table 6. Process stream data Table II

	Column feed	Column bottoms	Organic product	Aqueous product	Fresh HAc feed
Stream number	7	8	9	10	11
Flow (mol/min)	3820	2160	826	831	785
Temperature (°C)	42.5	137.2	40	40	30
Pressure (psia)	84	30	18	18	150
VAc (mol frac)	0.206	11[a]	0.950	0.002	0
H_2O	0.281	0.093	0.050	0.998	0
HAc	0.513	0.907	370[a]	370[a]	1

[a]moles/million.

Table 7. Process stream data Table III

	Fresh C_2H_4 feed	Fresh O_2 feed	CO_2 purge	CO_2 Removal in flow
Stream number	12	13	14	15
Flow (mol/min)	831	521	85	6411
Temperature (°C)	30	30	40.4	40.4
Pressure (psia)	150	150	128	128
O_2 (mol frac)	0	1	0	Same
CO_2	0	0	1	as
C_2H_4	0.999	0	0	stream
C_2H_6	0.001	0	0	4

Table 8. Reactor and vaporizer equipment data

Catalyst weight	2590 kg
Catalyst porosity	0.8
Catalyst bulk density	0.385 kg/l
Catalyst heat capacity	0.23 cal/g °C
Overall heat transfer coefficient	150 kcal/h °C m²
Number of tubes	622
Tube length	10 m
Tube diameter	3.7 cm
Circumferential heat transfer area	725 m²
Shell side temperature	133°C
Reactor heat duty	2.8×10^6 kcal/h
Steam drum volume	2 m³
BFW to steam drum	79.5 kg/min
Reactor feed heater duty	5.3×10^5 kcal/h
Vaporizer duty	1.3×10^6 kcal/h
Vaporizer total volume	17 m³
Vaporizer working level volume	4 m³
Vaporizer temperature	119°C

Table 9. FEHE, separator, and absorber equipment data

FEHE duty	4.4×10^5 kcal/h
FEHE hot outlet temperature	134°C
FEHE UA	6800 kcal/h °C
Separator cooler duty	2.7×10^6 kcal/h
Separator volume	15 m³
Separator working level volume	8 m³
Gas loop volume	170 m³
Approximate compressor size	350 kW
Absorber base volume	8 m³
Absorber bottom section	2 theoretical stages
Absorber top section	6 theoretical stages
Absorber stage efficiency	50%
Absorber tray holdup	14 kmol
Absorber liquid recirculation	15 kmol/min
Absorber cooler duty	6.5×10^5 kcal/h
Absorber wash acid feed	756 mol/min
Absorber wash acid cooler duty	1.3×10^5 kcal/h

If the tube temperature has not exceeded 180°C, then $f(t_{tube}) = 1$. Above this temperature, then $f(t_{tube}) = \exp[-(t_{tube} - 180)/50]$, where t_{tube} is in °C.

Two parameters define the performance of the catalyst: selectivity (SEL) and space-time yield (STY). Catalyst selectivity determines the fraction of the ethylene consumed that makes the desired vinyl acetate product.

$$SEL = 100 \frac{\text{mol/min VAc}}{\text{mol/min VAc} + 0.5\,\text{mol/min } CO_2}. \quad (9)$$

For conditions at the design basis with fresh catalyst, the selectivity is 94.8%. At a catalyst activity of 0.8, higher reactor temperatures are required to achieve about the same VAc production rate, increasing the production rate of CO_2 to 126 mol/min and reducing the selectivity to 92.4%. The space–time yield quantifies the activity of the catalyst by volume.

$$STY = \text{g VAc/h/liter catalyst.} \quad (10)$$

Table 10. Column and decanter equipment data

Theoretical stages	20
Feed stage	15 from bottom
Stage efficiency	50%
Tray holdup	2.3 kmol
Reboiler duty	4.0×10^6 kcal/h
Condenser duty	3.9×10^6 kcal/h
Base working level volume	6 m³
Decanter working level volume	5 m³

For conditions at the design basis, the STY is 603 since the total volume of catalyst (tube volume) is 6724 l.

The CO_2 removal system is assumed to be a component separator that removes just carbon dioxide at a certain efficiency, which is the fraction in the feed leaving in the CO_2 purge. This efficiency (Eff) is a function of the feed rate (F_{CO_2} in mol/min) and composition (x_{CO_2} in mole fraction). At the design conditions, the efficiency is 0.995 for a feed rate of 6410 mol/min at 0.014 mol fraction CO_2. The
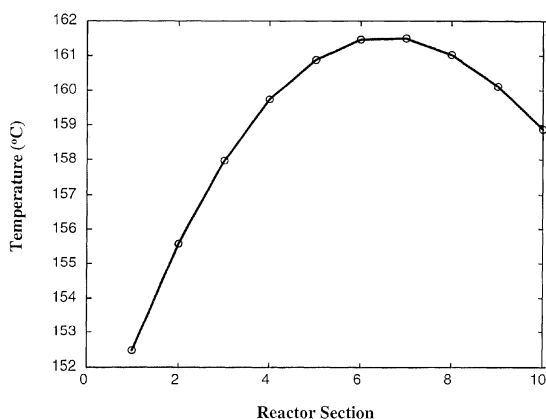
Fig. 2. Reactor temperature profile.

maximum allowable feed rate to the CO_2 removal system is 8000 mol/min set by its capacity. The following correlation determines the system efficiency

$$\text{Eff} = 0.995 - 3.14 \times 10^{-6}(F_{CO_2} - 6410)$$
$$- 32.5(x_{CO_2} - 0.014), \tag{11}$$

where the efficiency must lie between 0 and 1.

Two key safety constraints exist in the process. First, the oxygen composition *must not exceed* 8 mol % anywhere in the gas recycle loop to remain outside the explosivity envelope of ethylene (Coward and Jones, 1952). Continuous and reliable O_2 analyzers will be installed in the process at the inlet of the reactor to monitor oxygen composition. Second, the pressure in the gas recycle loop and distillation column *cannot exceed* 140 psia because of the mechanical construction limit of the process vessels. Pressure measurements are readily available and will be installed at appropriate locations. Exceeding either the oxygen concentration or pressure limits will shut down the process via interlocks.

Several other operational constraints must also be satisfied during process operation. The peak reactor temperature along the length of the tube must remain below 200°C, otherwise mechanical damage occurs to the catalyst requiring shutdown. Liquid levels in the vaporizer, separator, absorber base, distillation column base, and decanter must operate within the limits of 10–90%. The vessel volumes listed have been proposed for the working liquid inventories between the level taps.

Reactor inlet temperature must exceed 130°C to prevent condensation of liquid in the reactor. The hot side exit temperature from the feed-effluent heat exchanger (FEHE) must remain above 130°C to avoid condensation in the exchanger, which has been designed to handle only vapor-phase flow. In the azeotropic distillation column, the acetic acid in the decanter organic phase must not exceed 600 mol/million to prevent product contamination. A decanter composition analysis for acetic acid is available from the laboratory every 4 h. Also, the vinyl acetate composition in the bottoms stream must remain below 100 mol/million to minimize polymerization and fouling in the column reboiler and vaporizer. The column temperature profile is plotted in Fig. 3.

4.2. Control requirements

Figure 4 shows the location of the 26 control valves that have been proposed in the preliminary design. Flow, temperature, pressure, and level measurements are readily available and can be installed in any location needed for control. The O_2 analyzers at the reactor inlet are specialized instruments that are fast and reliable. However, if additional composition measurements are used, they must be conventional chromatographic analyzer types that are characterized by sampling frequency and reliability problems. It must be assumed that any chromatographic analyzer used in this process has a 10 min sampling frequency and 10 min deadtime. Also, this analyzer has a 90% utility. The remainder of the time the instrument is off-line for maintenance or calibration. Hence, when an analyzer is not on line, the plant must be able to continue producing vinyl acetate. Further, it must be demonstrated how the control system functions when an analyzer is down and one of the disturbances listed below occurs.

The control system which we are asked to design for this process must be able to operate in the face of several known disturbances and changes we anticipate *a priori*.

1. The process will operate at a catalyst activity of 0.8 (or lower based upon reactor temperature) at the end of 1 yr. The control system must still function for the changed conditions.
2. Process operation must be regulated automatically to reflect changes in raw material and operating costs so that the process always runs close to the ecomomic optimum.
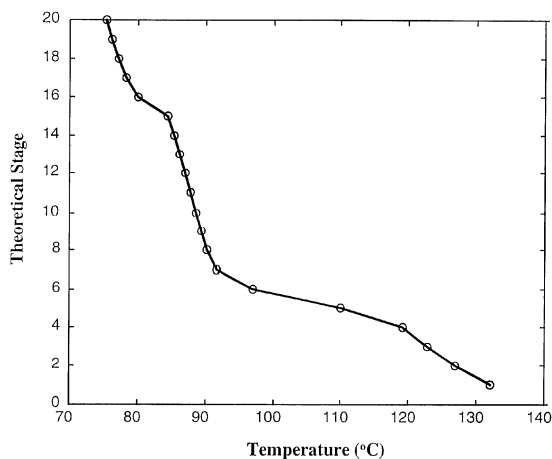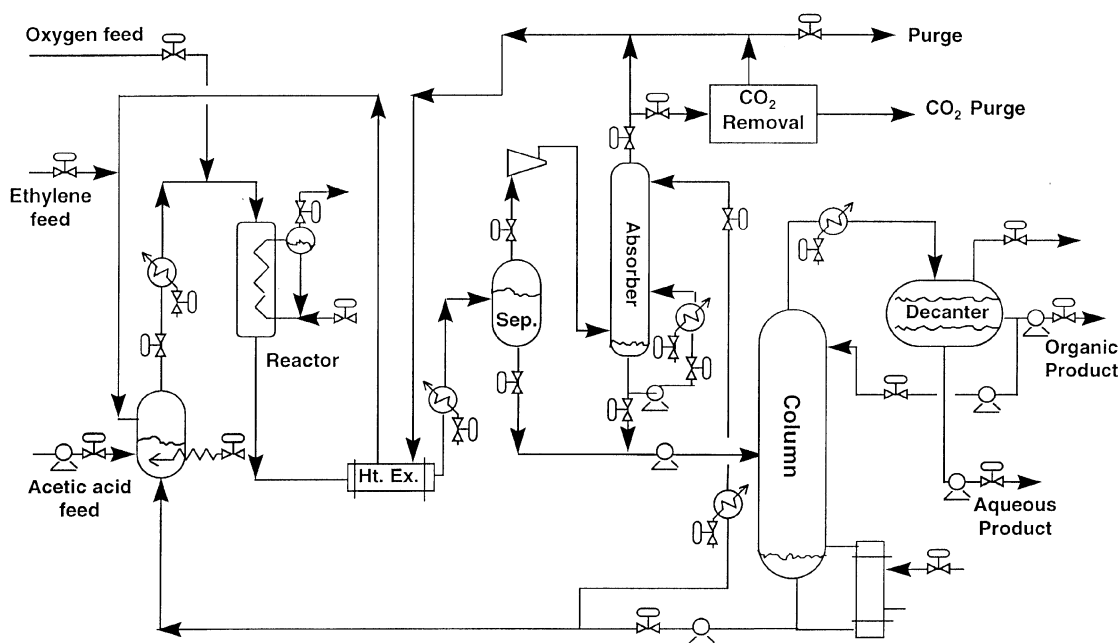

Fig. 3. Azeotropic distillation column profile.

Fig. 4. Location of control valves.

3. The control system must be able to change production rate (as measured by steady organic flow from the decanter) by at least 20% (both up and down) over the course of 6 h. This is due to limits on tank storage.
4. The plant needs to run at half the VAc production design rate but at maximum selectivity. This is the result of an occasionally precipitous drop in the price of vinyl acetate to a third its normal value.
5. In-line (but not operating) spare pumps will be installed for the fresh acetic acid supply line and for the distillation column feed stream. However, it must be demonstrated what the control system does during the course of a 5 min loss of either fresh acetic acid or column feed pump.
6. The control system must handle a step change in the composition of ethane in the fresh ethylene feed stream from 0.001 to 0.003 mol fraction.
7. The control system must not shut down the process due to the loss of fresh oxygen feed flow. Instead, this should result in the process going into "hot recycle" mode.

5. Nonlinear dynamic model

5.1. Background

In this section we provide a brief description of the nonlinear dynamic modules used in TMODS. These modules have been constructed following the practical philosophy toward dynamic simulation outlined in Luyben (1990). Our purpose is to provide a "feel" for the level of detail we use in our dynamic

simulations without divulging exactly how our simulator is implemented.

We would like to point out that the kind of dynamic models we use strike a balance between simulation efficiency and rigor of representation. We have found that simulation speed is of vital importance and we always strive to keep our user interactive simulations running between 10 and 60 times real time. There are basically two ways to meet this goal. We can either limit the scope of the simulation to a few process units that are rigorously simulated or limit the complexity of most units within a plantwide scope. Since we have found the plantwide perspective to be most important for control simulations, we generally opt for the second alternative.

This nonlinear dynamic model has been utilized to confirm the feasibility of the simulation. It is the basis for the data presented in the stream and equipment tables. We also have used the simulation to test the control strategy described in Luyben *et al.* (1997), which was derived following the plantwide control design procedure.

5.2. Physical property calculations

TMODS is implemented in an object-oriented framework (Tyreus, 1992). It consists of a number of generic classes that can be instantiated into objects in the simulation. The objects are given appropriate parameters to reflect the actual piece of equipment they represent. The objects are also connected together by the end user of the simulation to create a flowsheet. The most important aspect of the object-oriented representation is the use of fluid objects. The

fluid objects are instances of the fluid system pertaining to the simulation. The fluid system contains all the physical property constants described earlier including the kinetic parameters. Each fluid object is then able to perform a number of services based upon these parameters. For *homogeneous* (single phase) fluids these services amount to calculating thermodynamic state variables from the knowledge of two intensive state variables and the composition of the fluid. In TMODS these services are implemented to be *explicit* functions of the known state variables. Examples are

$$U = U(P, T, n_1, n_2, \ldots),$$

$$h = h(P, T, x_1, x_2, \ldots),$$

$$T = T(P, u, x_1, x_2, \ldots),$$

$$v = v(P, T, x_1, x_2, \ldots),$$

where P is the total pressure; T is the temperature; n_i is the number of moles of component i; x_i is the mole fraction of component i ($x_i = n_i/\sum n_i$); U is the total internal energy; v is the specific volume, u is the specific internal energy; and h is the specific enthalpy.

In many cases the fluid object represents a *heterogeneous equilibrium* system. Examples are the fluid objects in vaporizers, partial condensers, decanters, and on the trays of a distillation column. Here the thermodynamic state is completely specified by two extensive state variables and the number of moles of each component. The only difference to a homogeneous system is that the unknown intensive state variables are no longer explicit functions of the known entities. For example, to determine the pressure and temperature of a fluid in vapor–liquid equilibrium, we have to solve the following three nonlinear implicit algebraic equations:

$$\sum_{i=1}^{N} \frac{(K_i - 1)(n_i/n)}{1 + \beta(K_i - 1)} = 0, \tag{12}$$

$$V/n - (1 - \beta)v^L - \beta v^V = 0, \tag{13}$$

$$U/n - (1 - \beta)u^L - \beta u^V = 0, \tag{14}$$

where N is the number of components in the system, n is the total number of moles in the fluid object ($\sum n_i$), K_i is the K-value for component i ($K_i = y_i/x_i$), x_i is the mole fraction i in the liquid phase, y_i is the mole fraction i in the vapor phase, β is the fraction of n in the vapor phase; v is the specific volume; and u is the specific internal energy.

The known state variables are total internal energy and total volume that follow from the dynamic energy balance and the equipment size. The total moles of each component follow from the dynamic material balances. The K-values are calculated from the equilibrium requirement that the chemical potential of each component is equal in both phases

$$\mu_i^V = \mu_i^L,$$

or equivalently that the partial fugacities of each component are equal across the phases

$$f_i^V = f_i^L.$$

In TMODS we assume that the vapor phase is ideal such that

$$f_i^V = y_i P.$$

The liquid-phase partial fugacity is calculated with an activity model according to

$$f_i^L = x_i \gamma_i P_i^s$$

where γ_i is the liquid-phase activity coefficient of component i and P_i^s is the vapor pressure of component i.

To reduce the computational burden of iteratively solving the three nonlinear equations, we frequently make simplifying assumptions around two-phase systems. For example, in vapor–liquid equilibria we often assume that the vapor holdup is negligible ($\beta = 0$). This eliminates one of the three equations. The remaining variables can be solved for by making either of the following assumptions. We can solve for T and P explicitly based on the fact that the n_i's and the total U pertain to a single phase (the liquid). Or we can assume that the pressure is known along with the n_i's of the liquid, and we can solve for temperature and vapor compositions via a bubble point calculation.

The role of the unit operations is greatly simplified by the use of fluid objects. The unit operations contain one fluid object for each fluid holdup in the equipment. For example, a vaporizer contains one fluid object and a distillation tray section has a fluid object on each tray. The unit operation is responsible for managing the accumulation of mass and energy into the fluid objects. With the knowledge of the total internal energy, the total volume, and the number of moles of each component, the thermodynamic state is fixed. The fluid objects are then responsible for calculating all other relevant state variables pertaining to the current state.

The equipment equations for accumulation of mass and energy depend upon whether the system is *lumped* or *distributed*.

5.3. Lumped equipment models

Material balances:

$$\frac{dn_i}{dt} = F^{in} x_i^{in} - F^{out} x_i^{out} + R_i. \tag{15}$$

Energy balance:

$$\frac{dU}{dt} = F^{in} h^{in} - F^{out} h^{out} + Q + HR. \tag{16}$$

Auxiliary relations:

$$F^{out} = f(n_i, P, T, \text{equipment configuration}), \tag{17}$$

where F^{in} is the molar flow of all streams entering the vessel, x_i^{in} is the mole fraction i in entering streams, F^{out} is the molar flow of exit streams, x_i^{out} is the mole

fraction i in exit streams, R_i is the net production of i from all chemical reactions; h^{in} is the specific enthalpy of entering streams, h^{out} is the specific enthalpy of exit streams, Q is the heat input to the vessel, and HR is the total heat from reactions.

5.4. Distributed equipment models

Material balances:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial z} - \frac{\partial (c_i v)}{\partial z} + \sum_j v_{ij,} r_j - N_i. \quad (18)$$

Energy balance:

$$\frac{\partial (\rho u_m)}{\partial t} = -\frac{\partial J_q}{\partial z} - \frac{\partial (\rho h_m v)}{\partial z} - \sum_j \Delta H_j r_j$$

$$- \sum_i N_i h_i - q. \quad (19)$$

Momentum balance:

$$\frac{\partial (\rho v)}{\partial t} = -\frac{\partial P}{\partial z} - \frac{\partial (\rho v v)}{\partial z} + \sum_i \rho_i F_i^e. \quad (20)$$

Auxiliary relations:

$$N_i = k_g a(p_i - p_i^*), \quad (21)$$

$$q = h_w a(T - T_w),$$

$$J_i = -D_i \frac{\partial c_i}{\partial z},$$

$$J_q = -k_T \frac{\partial T}{\partial z},$$

where c_i is the molar concentration of i; J_i is the diffusion flux of component i; v is the bulk velocity of fluid; v_{ij} is the stoichiometric coefficient for component i in reaction j; r_j is the specific rate of reaction; N_i is the molar flux of component i; ρ is the fluid density; u_m is the specific internal energy (mass based); J_q is the heat flux due to conduction; h_m is the specific enthalpy (mass based); ΔH_j is the heat of reaction for reaction j; q is the external heat flux per unit volume; F_i^e is the external force acting on component i; k_g is the overall mass transfer coefficient; a is the surface to volume ratio for heat and mass transfer; p_i is the partial pressure for component i; p_i^* is the interface partial pressure for component i; T_w is the interface temperature; D_i is the molar diffusivity coefficient of component i; and k_T is the conductivity coefficient.

5.5. Specific implementations

Catalytic plug flow reactor: The catalytic plug flow reactor is modeled according to equations (18)–(21) on the tube side and equations (15)–(17) on the shell side. Simplifying assumptions are $J_i = 0$, $J_q = 0$, and $\partial (\rho v)/\partial t = 0$. The time-independent momentum equation (20) sets the pressure profile in the reactor. We assume that the entire gas loop pressure drop is repre-

sented by the reactor pressure drop. A simple backward discretization scheme is used for the spatial derivatives.

Gas Separator: This generic flash calculation can be implemented in a number of different ways. In TMODS this unit is implemented with two fluid objects on the process side and a single-phase liquid object on the shell side. In our implementation the process side fluid objects are not in equilibrium with each other. The vapor object determines the system pressure. The shell side fluid determines the static flash temperature. This allows us to use equation (12) to solve for the partition of incoming feeds into the vapor and liquid objects. The vapor object in the gas separator defines the *pressure level* of the gas recycle loop. As mentioned above, the reactor determines the *pressure drop* in the loop.

Absorber: The gas absorber is implemented as two countercurrent versions of equations (18), (19), and (21). Each node, or stage, contains a liquid phase and a vapor phase that are not in equilibrium with each other. Instead, the single-phase state is determined by the integration of equations (18) and (19). The auxiliary equations (21) then use the partial pressure and temperature differences between the two phases to determine the mass and heat transfer rates.

Vaporizer: The vaporizer is implemented as a lumped system with a single fluid object. The vapor holdup is assumed negligible compared to the liquid inventory.

Distillation Column: Each tray is a lumped system and contains a fluid object. The holdup in the vapor phase is ignored. The pressure on each tray is assumed known, which reduces the flash calculation to a bubble point calculation. The energy balance derivative (16) is approximated numerically, which allows us to solve for the vapor rate from stage to stage. This is done to reduce system stiffness.

Decanter: The TMODS decanter contains two fluid objects: one for the light phase and one for the heavy phase. The partition coefficients (K-values) are assumed constant and independent of temperature. This allows us to use equation (12) to determine the distribution of the two liquid phases. Again, this is done to save simulation time.

Heat Exchangers: Heat exchangers are calculated statically with the effectiveness method. This allows for an explicit calculation of the exit temperatures based upon the exchanger effectiveness and the inlet temperatures and heat capacities. The exchanger effectiveness depends on the effective UA, the ratio of stream heat capacities, and the exchanger configuration. The exit temperatures are time-lagged to introduce some realistic dynamics (usually very fast compared to the overall recycle loop dynamics).

6. Conclusions

In this work we have presented design details of an industrial process for the manufacture of vinyl acetate

monomer. The design is preliminary and has not been optimized. We have conveyed the study as if we had been assigned the task of devising a control strategy for this plant that is to be built. We have summarized the design requirements for process operation and the control objectives that must be achieved for various disturbances. A brief description was also provided on the nonlinear dynamic modules in our simulation. The purpose of this paper is to offer a realistic system that can be used by academic researchers who are interested in working on an industrially relevant study in the areas of design, simulation, and control.

Complete models for this vinyl acetate process have been made available by Aspen Technology and Hyprotech. These models can be obtained electronically from the following web sites:

(1) The application file for the vinyl acetate process can be obtained from Aspen Technology's example library Web site:
`http://www.aspentec.com/tspsd/example/example.htm`
Search for "Vinyl Acetate" to find and download the application file.
(2) The case is made available at Hyprotech www.hyprotech.com on the FTP site
(`Papers/VinylAcetateProcess/VA_files.zip`). To download the file directly, users may type the following into their Web browser:
`ftp://ftp.hyprotech.com/pub/Papers/VinylAcetateProcess/VA_files.zip`

References

Coward, H.F. and Jones, G.W. (1952) Limits of flammability of gases and vapors. Bulletin **503**, Bureau of Mines.

Daniels, W.E. (1989) Vinyl ester polymers. In: *Encyclopedia of polymer science and engineering*, 2nd ed. New York: Wiley. Vol. 17, (pp. 393–425).

Downs, J.J. and Vogel, E.F. (1993) A plant-wide industrial process control problem. *Computers in Chemical Engineering* **17**, 245–255.

Douglas, J.M. (1988) *Conceptual design of chemical processes*. New York: McGraw-Hill.

Guthrie, K.M. (1969) Capital cost estimating. *Chemical Engineering* **76**, 114–142. Mar. 24.

Luyben, M.L., Tyreus, B.D., and Luyben, W.L. (1997) Plantwide control design procedure *AIChE J.* **43**, 3161–3174.

Luyben, W.L. (1990) *Process modeling, simulation and control for chemical engineers*, 2nd ed. New York: McGraw-Hill.

Nakamura, S. and Yasui, T. (1970) The mechanism of the palladium-catalyzed synthesis of vinyl acetate from ethylene in a heterogeneous gas reaction. *Journal of Catalysis* **17**, 366–374.

Neurock, M., Provine, W.D., Dixon, D.A., Coulston, G.W., Lerou, J.J. and van Santen, R.A. (1996). First principle analysis of the catalytic reaction pathways in the synthesis of vinyl acetate. *Chemical Engineering Science* **51**, 1691–1699.

Samanos, B., Boutry, P. and Montarnal, R. (1971) The mechanism of vinyl acetate formation by gas-phase catalytic ethylene acetoxidation. *Journal of Catalysis* **23**, 19–30.

Smith, J.C. (1942) The solubility diagrams for the systems ethylidene diacetate–acetic acid–water and vinyl acetate–acetone–water. *Journal of Physical Chemistry* **46**, 229–232.

Tyreus, B.D. (1992) Object-oriented simulation. In: W.L. Luyben, (Ed.), *Practical distillation control*. chap. 5. New York: Van Nostrand Reinhold.