

PRODUCTION OF PROPYL ACETATE BY REACTIVE DISTILLATION: FROM EXPERIMENTS TO SIMULATION

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First steps of the development of a catalysed reactive distillation process for the production of *n*-propyl acetate based on experiments and simulations are proposed. The reaction kinetics catalysed heterogeneously by Amberlyst-15 was investigated and the constants for a pseudo-homogeneous model are presented. Pilot plant experiments were performed using a strong acid catalyst homogeneous acid in a packed column. A top-column decanter is used to withdraw the aqueous phase and to reflux the organic phase. Simulation results are in good agreement with experiment data. Thermodynamics nonidealities are taken into account using VLE and LLE NRTL interaction parameters. Alcohol conversion and *n*-propyl acetate purity higher than 97% can be expected just by adding a stripping section to the pilot plant column. The startup is studied in order to determine the best strategy to achieve steady-state conditions. The strong influence of the composition of the initial charging can be seen and an initial charging of the two-phase top product leads to the fastest startup.

KEYWORDS: reactive distillation, kinetics, start up, experimental data, *n*-propyl acetate

INTRODUCTION

The combination of reaction and distillation in one reactive distillation (RD) unit can lead to significant reduction of investment and operational cost. Many authors use methyl acetate as illustration of their work in reactive distillation but our investigations focus on VLL reactive systems. Experimental investigations have already been published for the production of butyl acetate¹⁶ or amyl acetate² but, to the best of our knowledge, none for *n*-propyl acetate reactive distillation; thus, information about *n*-propyl acetate synthesis can hardly be found in literature.

Investigations on reactive membrane separation have led Huang and al.⁶ to publish data on chemical equilibrium. Bart and al.¹ have published a kinetic modelling of the *n*-propyl acetate synthesis catalysed by an exchange ion resin (Dowex) as well as Steinigeweg¹⁶ with the Amberlyst-15. Unfortunately, none of these works are in agreement on the kinetic rate and the equilibrium constant values. Moreover, no data about reactive distillation pilot-plant experiments is included.

This article presents the two first parts of an approach to the development of RD process for the production of *n*-propyl acetate: the catalysed reaction kinetics is firstly investigated in order to employ a simulation environment based on equilibrium stage model; pilot plant experiments are then carried out in order to validate this theoretical study. On the basis of this results, an optimal start-up strategy is proposed.

EXPERIMENTAL SECTION

CHEMICALS

The chemicals used for the reaction kinetics experiments were of analytical grade (rectapur). Water was bidistilled. The macroreticular ion-exchange resin Amberlyst 15 (Lancaster) was selected as the catalyst. The ion-exchange capacity of the resin was determined by Pöpken and al.¹⁰: a value of 4.77 ± 0.01 meq of $\text{H}^+ \cdot \text{g}^{-1}$ of dry catalyst was obtained, which compares well with the value of 4.75 meq $\cdot \text{g}^{-1}$ given by the manufacturer. For the reactive distillation experiments, the chemicals were of reaction grade (99.5%) and were used without further purification; concentrated sulfuric acid was selected as the catalyst.

ANALYTICS

All samples for reactive distillation experiments were analyzed by gas chromatography (Varian 3800) using cross-linked polyethylene glycol CP-WAX 52 CB 30 m \times 0.32 mm column with FID detector; additional titrations were performed with a METTLER DL 35 Karl-Fischer-Titrator in order to measure the quantity of water formed during the reaction. An accuracy of molar fractions of 3% can be expected.

KINETIC EXPERIMENTS

The experiments were conducted in a thermostated three-neck glass reactor with a volume of 500 cm^3 . One neck was connected to a thermometer and another was devoted to the GC sampling; a cold trap, in addition to a reflux condenser, was installed in the third neck to avoid any loss of volatile components. The temperature of the heating jacket was kept constant within ± 0.1 K. Before each kinetic experiment was started, both reactants were

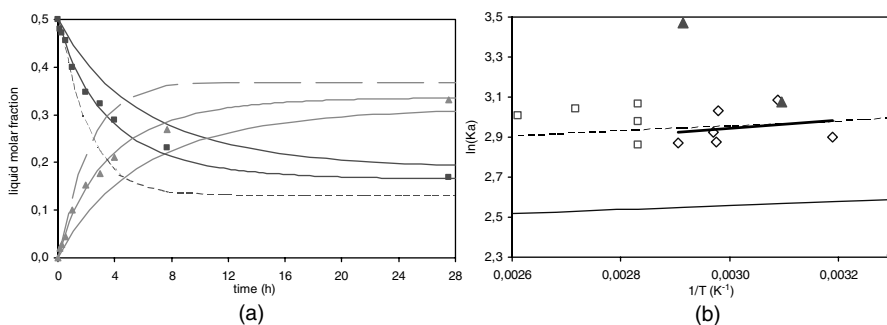


Figure 1. (a) Typical composition of PrOH (■) and PrOAc (▲) against time for a kinetic run – (b) Chemical equilibrium constants K_a (◇) and fit (solid line) of our experimental data compared with Huang et al. (□), Bart et al. (▲), Steinigeweg (short dashes) and an estimation based on thermodynamic data³ (long dashes)

brought to reaction temperature separately; when the desired temperature was reached, reactants and catalyst were added to the reactor and time measurement was started. Liquid samples of about 1 cm³ volume without any catalyst were taken using a syringe and cooled to 253 K to avoid any further reaction. The contents were stirred by a magnetic stirrer. The stirrer speed is fixed in such a manner that it has no influence on the reaction rate¹⁶. Thus, the external mass transfer resistance seems not to be significant, like the internal mass transfer resistance^{9,18}. Most of the experiments were continued until chemical equilibrium was reached.

KINETIC MODELLING

A pseudo-homogeneous model is used to describe the reaction catalysed with Amberlyst 15. This choice is theoretically supported by the fact that the catalyst swells in contact with polar solvents making the sulfonic groups of the catalyst readily accessible to reactants; in such a model, the ion-exchange resin is thought to act as solvated protons; in addition, a comparison of homogeneously (sulfuric acid) and heterogeneously (Amberlyst 15) catalysed esterification of methyl acetate has been previously done and gives an obvious agreement between experiments (from Song et al.¹⁴) and modelling (from, respectively, Rouzineau¹² and Pöpkén et al.¹⁰) for equivalent amounts of H⁺ ions: consequently, rate constants can be expressed as a function of proton amount; its temperature dependency is expressed by Arrhenius' law (2) what means that four adjustable parameters ($k_{f,0}$, $k_{a,0}$, E_f , E_a) have to be fitted (Table 1). The Arrhenius diagram (Figure 2(a)) shows the results from the best fit of all data at a given temperature; the comparison of our results with other published data is performed Figure 2.

$$r = \frac{1}{v_i} \frac{dn_i}{dt} = n_{H^+} K_f \left(a_{HOAc} a_{PrOH} - \frac{a_{PrAc} a_{H_2O}}{K_a} \right) \quad (1)$$

$$K_i = K_{i,0} \cdot \exp\left(-\frac{E_i}{R \cdot T}\right) \quad (2)$$

REACTIVE DISTILLATION SETUP

Each reactant are fed separately in the column. Experiments were performed in a 4-meter glass column with an inner diameter of 80 mm (Figure 2): the reactive section is packed with 8*8 mm glass Raschig rings and the rectifying section contained Sulzer-CY packing.

Table 1. Parameters of the kinetic model fitted

$K_{f,0}$ (mol · s ⁻¹ · mol _{H⁺} ⁻¹)	E_f (J/mol)
$2,576 \cdot 10^6$	52 009
$K_{a,0}$	E_a (J/mol)
13,10	-1 396

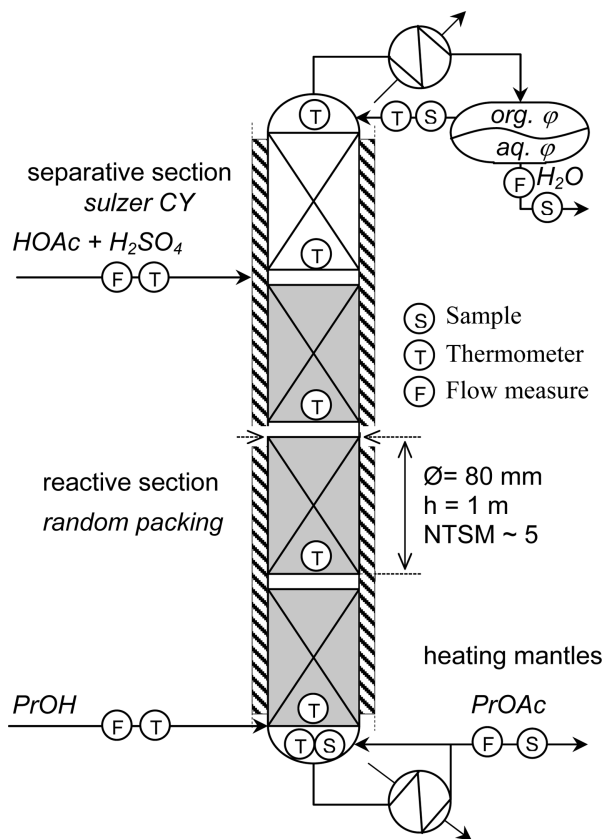


Figure 2. Setup of the reactive pilot plant

Reaction was catalysed by homogeneous sulphuric acid fed at the top of reactive section with a weight amount of 1.3% in the acetic acid flow. Acids and alcohol feeds both were preheated. The reboiler, with a liquid hold-up of approximately 10 dm³, was heated by an oil-boiler and insulated by mineral wool whereas the column was equipped with two couples of heating mantles; the maximal heating power measured was of 3 kW. Distillate was collected in a decanter operated at ambient temperature and all organic phase was refluxed at the top of the column. Feed and product flows were measured by balances. Temperatures were measured by Pt-100 thermometers installed at bottom of each section, in the feed stream, in the reboiler and in the condenser. Liquid samples were withdrawn from outputs, from the vapour phase of reboiler (to avoid homogeneous catalyst presence) and from the organic phase of the decanter.

START-UP

The strategy which has been chosen was to start with the reboiler and the decanter empty; the preheated feeds and a gradual heat duty at the reboiler led the mixture to boiling point. When a sufficient amount of distillate was collected to the decanter, the reflux pump was turned-on and the set-point adjusted in order to reflux all the organic phase.

RD PILOT PLANT EXPERIMENTAL RESULTS

The aim of this run was to obtain experimental data useful to validate our simulations. The material balance of a typical reactive distillation run (Table 2) shows the reliability of the steady-state point obtained. An acetic acid conversion of 79% with a molar purity of *n*-propyl acetate of 64% was achieved. Notice that this pilot plant has not been built especially for this mixture so his design is far from an optimal one but dynamic and steady-state simulation can thus be performed on the base of these experimental results.

SIMULATION**STEADY STATE**

Steady-state simulations based on EQ models were carried out using the commercial software ProSim Plus; the activity coefficients are derived from NRTL model (Table 3) and used for phase equilibriums (LLV and LL) as well as for kinetic models. Vapour phase association due to the presence of acetic acid in the system has been accounted for with the chemical theory⁷. Singular points of the mixtures are shown in Table 4. Specifications of the reactive distillation column simulated (Table 5) were conformed to the experimental setup described Figure 2. A good agreement is observed between the experimental and calculates values of outputs (flow rates, concentrations and temperature). An acetic acid

Table 2. Mass and mol balance of a typical reactive distillation run

	HOAc feed	PrOH feed	Organic phase	Aqueous phase	Boiler	Inputs	Outputs	Deviation (%)
F (kg,h ⁻¹)	2,80	2,46	8,10	0,75	4,51	5,26	5,26	0
F (mol,h ⁻¹)	46,63	41,00	94,80	38,57	53,50	87,63	92,1	5
	Molar composition					Molar flow rates		Cons./prod.
HOAc	1	0	0,021	0,018	0,173	46,63	9,92	36,71
PrOH	0	1	0,079	0,008	0,131	41,00	7,29	33,71
PrOAc	0	0	0,752	0,004	0,638	0	34,29	34,29
H ₂ O	0	0	0,148	0,970	0,058	0	40,57	40,57

Table 3. Thermodynamic datas for the propyl acetate system – NRTL model (cal·mol⁻¹)

	(a) LV equilibria ⁷			(b) LL equilibria ¹²		
	a_{ij}	b_{ij}	α	a_{ij}	b_{ij}	α
HOAc–PrOH	–327,517	256,900	0,3044	0	0	0
HOAc–PrOAc	–484,890	1126,479	0,3000	0	0	0
HOAc–H ₂ O	–219,724	842,608	0,2997	0	0	0
PrOH–PrOAc	369,062	79,428	0,3006	–86,72	470,24	0,2
PrOH–H ₂ O	–80,440	1850,200	0,3000	–1109,28	2968,20	0,2
PrOAc–H ₂ O	667,444	3280,604	0,2564	606,70	3043,40	0,2

conversion of 80% with a molar purity of *n*-propyl acetate of 69% was achieved by the simulation, 79% and 63.8% respectively for experiment. Simulations underline the fact that this setup does not lead to the best result: indeed, dramatic increase of reactant conversion and *n*-propyl acetate purity can be achieved in adding a separative section in the column; a simulation with such a stripping section (5 stages) and with higher reboiler duty (3 kW) led to a conversion of reactant (for equimolar feeds) of 97.5% and a minimum

Table 5. Specifications of the simulation

Number of theoretical plates ^a	22
Plate of HOAc feed	6
Plate of PrOH feed	21
Heat reboiler (kW)	2.0
Heat loss column (W/K/m)	0
Diameter (mm)	80
Total packed height [m]	4
Packed height per section (m)	1
NTSM Raschig (1/m)	5
a_{Raschig} (m ² /m ³)	623
$\epsilon_{\text{Raschig}}$ (m ³ /m ³)	0.73
Thermodynamics' data	Table 2
Kinetics data	Table 1
Holdup (m ³ /m)	4.10 ⁻⁴
$V_{\text{H}_2\text{SO}_4}$ in the boiler (ml) ^b	40.2

^atwo plates for the condenser and the reboiler

^banalysed by plasma torch (Jobin Yvon – ULTIMA 2R). With this equipment the quantity of sulphur in the sample is measured, and with balances, the quantity of H₂SO₄ is calculated

molar purity of PrOAc of 98%; it can be noted that if output flows remain quite unchanged, the molar reflux raises to 4.

START-UP

The start-up of a reactive distillation column is a very complex, time and energy consuming process. The dynamic process behavior becomes even more complex in case of a miscibility gap at the column top which is influenced by the reaction. Special attention has to be paid to the behavior of the decanter during startup in order to rapidly reach conditions leading to the phase split. Reepmeyer et al.¹¹ have analyzed the start-up of homogeneously catalyzed reactive distillation in tray columns and have shown that initial charging of product to the column trays can lead to significant reduction of start-up time. Tran¹⁷ has studied non-reactive three phase distillation in a tray column with a decanter. He

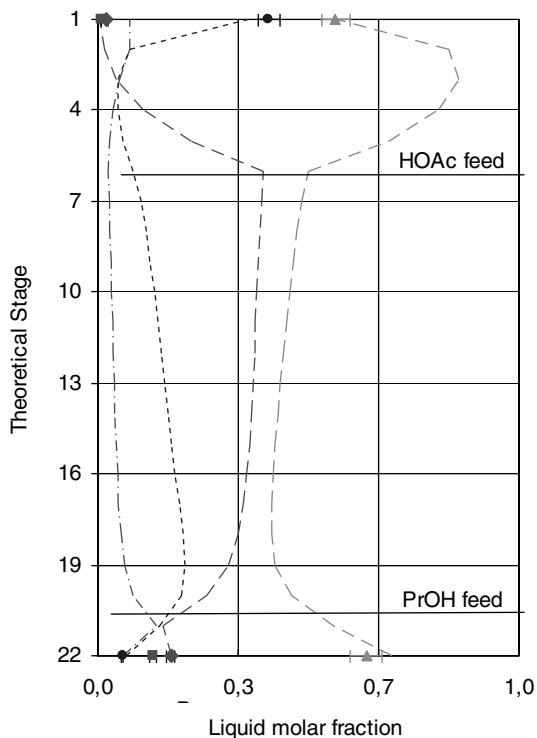


Figure 4. Profile of liquid phase composition – exp. data: HOAc (◆), PrOH (■), PrOAc (▲), H₂O (●)– simulation: HOAc (—), PrOH (---), PrOAc (— · —), H₂O (····)

has shown both by experiment and simulation that the start-up time depends strongly on the composition of the initial holdup in the decanter. Surprisingly for the system ethanol/water/cyclohexene, initial charging of ethanol (bottom product) led to a reduction of about 60% of start-up time. On the other hand charging a two phase mixture close to steady state composition extended the start-up time.

The start-up process which is considered in this contribution begins when feed is entering the initially cold and empty column. The dry packing is wetted and the column bottom is filled up until the reboiler is switched on. Vapour starts rising in the column and partly condenses at the cold internals. When it reaches the top, reflux from the condenser enters the column and finally all variables reach the steady-state values. During this process the hydraulic and thermodynamic variables underlie large changes. The hold-up in the column and the flow rates change from zero to their steady state values. The temperatures rise from ambient temperature to the boiling temperature corresponding to the operating pressure and the compositions.

Due to these transitions different sets of equations are needed for the different distinguishable phases of the start-up which requires a switching between these model equations at certain points. This modelling procedure has been explained in detail by Reepmeyer et al.¹⁵. The final model that is used for conditions close to the operating point is an equilibrium stage model consisting of the MESH equations, reaction kinetics and hydraulic correlations (correlations for pressure drop and liquid holdup from Engel et al.⁴). The two outflows from the decanter are related to the corresponding level via a Torricelli type correlation.

Following the results presented by Tran¹⁷ for non-reactive three phase distillation, the start-up process is analyzed with different initial charging of the decanter. During all the simulation runs the reboiler is initially empty and filled by the feed entering the column. When the level is high enough the reboiler duty is directly set to its steady-state value. Since the decanter is already filled at the start, the reflux is turned on as soon as the first vapour condenses. As in the experiments the organic phase is completely returned to the column as the reflux, the aqueous phase is withdrawn from the system. Specifications are taken from the experimental setup.

Figure 5 shows the comparison of the trends of the *n*-propyl acetate fraction in the organic phase in the decanter for the different start up strategies. The strong influence of the composition of the initial charging can be seen. As expected, initial charging of the two-phase top product leads to the fastest start-up (1). The composition of the organic phase deviates only very little and only for a short period of time from the steady state values. The prolonging of start-up time due to charging of the two phase product to the decanter as described by Tran¹⁷ could therefore not be observed for this process.

CONCLUSION

The first part of this article is devoted to experimental results obtained on two kinds of device: stirred reactor and RD pilot plant. A kinetic model has been derived and compare with previous publications. The second part of this article concerns the simu-

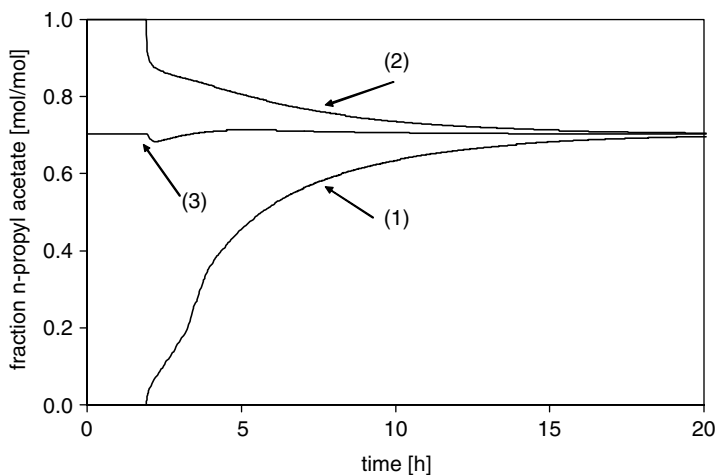


Figure 5. Comparison of the *n*-propyl acetate fraction in the organic phase in the decanter during start-up for different simulation runs. (1): initial charging of *n*-propanol, (2): initial charging of *n*-propyl acetate, (3): initial charging with two phase mixture (steady state composition).

lation of the pilot plant. Both steady state and start up have been investigated. Our steady state model has been validated by the experiments and from the start up simulation a new strategy has been recommended.

In the near future, an optimal design of RD column will be achieved based on our model and using MINLP approach. And in a second time, the performances of this new design will be experimentally checked in an heterogeneous catalysed column located in TU Berlin.

NOMENCLATURE

LATIN LETTERS

HOAc	Acetic Acid
PrOH	<i>n</i> -Propanol
PrOAc	<i>n</i> -Propyl Acetate
H ₂ O	Water
H ₂ SO ₄	Sulfuric Acid
x_i	molar composition
a_i	activity
K_i	kinetic of equilibrium constant
K_o	pre-exponential factor

E_i	activation energy ($\text{J}\cdot\text{mol}^{-1}$)
n_{H^+}	H^+ mol amount (mol)
R	ideal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
F	flow rate ($\text{kg}\cdot\text{h}^{-1}$; $\text{mol}\cdot\text{h}^{-1}$)
a	specific area ($\text{m}^2\cdot\text{m}^{-3}$)

GREEK LETTERS

ν	stoichiometric coefficient
ε	vaccum ratio

SUBSCRIPTS

i	component
f	esterification reaction
a	chemical equilibrium in activity

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