Part III: Continuous Esterification of Butanol in a Rotating Disc Extractor

The esterification of n-butyl alcohol with acetic acid has been carried out continuously in a Rotating Disc Extractor (RDC) in a two phase water-n-heptane system. Peculiar phase inversion characteristics have been observed under some experimental conditions during simultaneous transfer of the acid and alcohol, and this has been explained in terms of the changes in the concentration gradients of these two species along the length of the column.

A mathematical model has been developed of the continuous process incorporating the equilibria correlations presented in Part I of this study and the kinetic data presented in Part II to predict the performance of the RDC. The predicted results have been compared with the experimental results and good agreement was obtained.

SCOPE

The feasibility of esterifying n-butanol in a continuous extractive-reaction process has been studied under ambient conditions in order to understand and evaluate the important parameters controlling simultaneous extraction-reaction processes. The equilibrium correlations developed in Part I of this investigation, and the kinetic and two phase batch-reaction studies described in Part II have been combined to analyze and interpret the performance of a Rotating Disc Extraction Column performing this extractive-reaction.

The mass transfer characteristics of acetic acid and n-butanol in water-n-heptane solvents has been studied individually and simultaneously in the RDC and the mass transfer coefficients estimated under different experimental conditions. Discrete drops could be seen, photographed and counted to estimate the interfacial area when acetic acid was being transferred but not during the mass transfer of n-butanol.

When acetic acid and butyl alcohol transfer occurred simultaneously in opposite directions, phase inversion was observed in the RDC and this has been explained in terms of the direction of transfer, to or from the dispersed phase, and the concentration gradients along the column.

The correlations obtained in Parts I and II of this study have been combined into a mathematical description of the continuous extractive-reaction process in the RDC and an appropriate computer program has been compiled to predict the performance of the RDC as an extractive-reactor. These results have been compared with the results obtained from the butanol esterification experiments in the RDC and good agreement has been obtained.

CONCLUSIONS AND SIGNIFICANCE

The continuous esterification of n-butanol and acetic acid in the presence of a sulphuric acid catalyst in a water-n-heptane two phase system has been studied experimentally and theoretically and it has been shown that the ester can be produced under near ambient conditions in a simultaneous extraction-reaction process. However, under certain flow conditions and concentration ranges, phase inversion occurs in the column and it was possible to continue to operate the process under these conditions.

The mass transfer coefficients of acetic acid during transfer from the hydrocarbon phase to the aqueous phase was found to increase with the feed concentration. This confirms previous studies.

A mathematical model was developed of the continuous extractive-reaction process in the RDC which incorporated the equilibrium correlations, derived in Part I, and the kinetic data, obtained from Part II of this study, in the form of subroutines in an overall computer program of the extractive-reaction process. The results predicted by the model for the experimental conditions employed compared favorably with the results obtained from the column.

INTRODUCTION

The continuous esterification of n-butanol and acetic acid in the presence of a sulphuric acid catalyst has been studied in a Rotating Disc Extraction Column (RDC) using n-heptane as solvent in order to assess the suitability of the RDC as a continuous Extractive-Reactor. The R.D.C. was chosen because of its versatility and, in addition, because numerous studies had confirmed its hydrodynamic performance and mass transfer characteristics. Thus, Mumford and Al-Hemeri (1974), Komasowa and Ingham (1978) and Kung and Beckmann (1961) have discussed the correlations of dispersed phase hold-up, while the effects of drop size and size distribution on mass transfer rates have been studied by Chartres and Korchinsky (1978), and the different correlations have been compared by Laddha (1978). However, the use of an RDC as an extractive-reactor has not hitherto been considered, although it appears to be a very suitable extractor for the study of the continuous esterification of n-butanol with acetic acid.

EXPERIMENTAL

A flow diagram of the equipment used for this part of the study is shown in Figure 1. The extraction column consisted of a 0.101 m diameter 0.92 m long glass section divided into 18 compartments each

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0.05 m high. The diameter of the rotating discs was 0.05 m and the stator openings were 0.076 m in diameter. Five sampling points were provided at 0.15 m intervals along the column length. Each point consisted of a 10 mm diameter hole fitted with a quick-acting toggle valve. Additional sampling points were provided at the respective phase inlets and outlets. The column internals were fabricated from 18/8 stainless steel and the stators were fitted closely at the column walls and supported by three equispaced lengths of 1 mm stainless steel wire. The thickness of the discs and stators was 2 mm. The rotor shaft, was fabricated from a 9.6 mm stainless steel rod and supported by bearings at three points throughout the column length. There was no support bearing within the effective column length.

The heavy phase was introduced into the column through a stainless steel distributor plate at a point just above the top compartment and was removed via a pipe at the bottom of the column. The heavy phase inlet could, if desired, pass through a stainless steel distributor and hence constitute the dispersed phase. The lighter phase was similarly introduced via a distributor plate. Each distributor consisted of forty six holes each of 2 mm diameter arranged on a 6 mm triangular pitch inside a 0.10 m diameter circle. There was a small upward projection around the periphery of each hole to ensure the formation of discrete drops.

The column end plates were made from 8 mm thick 18/8 stainless steel plate. The bottom plate supported the distributor and a P.T.F.E. end step bearing. The top end plate housed a P.T.F.E. bearing and the necessary inlet and outlet pipes were integral with the end plates.

The agitator shaft was driven by a 0.25 h.p. A.C. motor, controlled by a variable voltage mains transformer. The drive shaft of the motor was coupled to the column shaft via a flexible rubber joint. The other end was attached to a high precision electronic tachometer of range 0-300 rpm. Process fluids were stored in any of four 50 L spherical glass vessels mounted on special supports. Two of these served as reservoir and receiver for the light phase. The pipe work was mainly 16 mm i.d. borosilicate glass, but P.T.F.E. tubing was used in certain sections. Flowrates were measured by rotameters with stainless steel floats. Provision for the circulation of the liquids in the reservoirs, or between two vessels containing the same liquid was also included.

The fluids were transferred by means of two stainless steel centrifugal pumps, capable of handling 1.25/0.45 L/s against a hydrostatic head of 2.0/10.0 m. The speed of each pump could be varied by means of a variable voltage unit.

The organic phase was always n-heptane with or without the appropriate solute and the aqueous phase consisted of water with acetic and sulphuric acids for the extractive-reaction experiments. Phase inversion phenomena was observed and therefore studied for the water/heptane system without any mass transfer occurring. An unusual type of phase inversion phenomena was observed when mass transfer occurred simultaneously from the organic to the aqueous and vice versa. Physical mass transfer studies were undertaken for both acetic acid and butanol transfer from the organic (dispersed) to the aqueous phase. Finally, the extractive-reaction experiments were performed with the organic phase consisting of butanol/heptane (dispersed) and the aqueous phase of water, acetic acid and sulphuric acid.

COLUMN OPERATION

Phase Inversion with No Mass Transfer

The following procedure was adopted for all experiments: At a set rotor speed and continuous phase flow rate, the dispersed phase flow was increased incrementally until inversion occurred. After each increase, sufficient time was allowed for the system to reach steady state conditions. This procedure, when adopted for water in heptane dispersions led to the phase inversion starting from the bottom of the column immediately above the lower distributor. No flooding occurred prior to phase inversion, i.e., the dispersed phase droplets were not rejected. Instead an oil in water dispersion was directly formed. This consisted of very well packed droplets, accompanied by intense mixing, which gradually moved up the column until the whole section between the upper and lower distributors was full of regular polygonal shaped drops similar in appearance to that of a gas-liquid foam. The droplets were of the same size as those ensuing from the distributor; i.e., there seemed to be no coalescence or break-up. When the flows were continued at the same rate, the droplets at the bottom started coalescing so that a "normal" *O/W* dispersion was formed starting from the bottom and gradually moving up until the whole column was a "normal" *O/W* dispersion instead of the well packed dispersion formed initially as a result of phase inversion. The process was generally very slow and took from 30-45 minutes for the column to invert from a *W/O* dispersion to "normal" *O/W* dispersion.

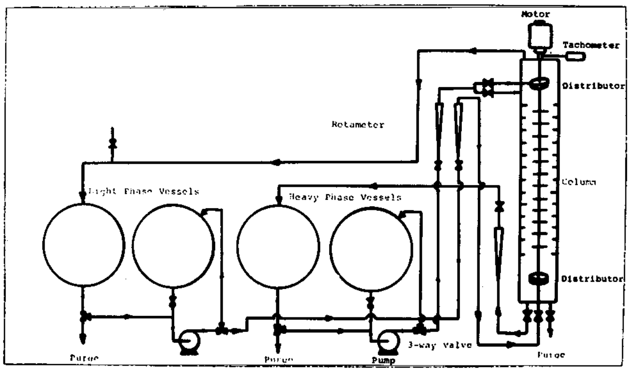
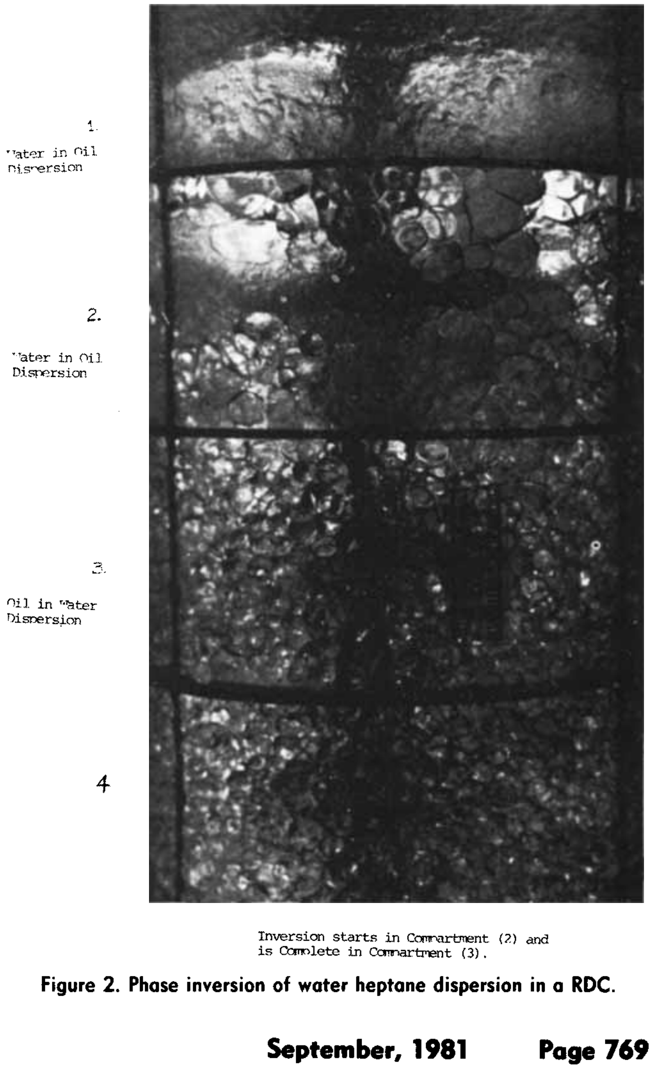


Figure 1. Flow diagram of experimental equipment.

It was observed that the rotor speed had no noticeable effect on phase inversion characteristics and surprisingly it was possible to obtain phase inversion with the same droplet sizes with the rotor stationary.

Phase inversion also occurred when initiating from heptane in water dispersions. Phase inversion in this case started from the top and moved down until the whole column was filled with a close packed *W/O* dispersion which partially coalesced very slowly reverting to a "normal" *W/O* dispersion as described above, but starting from the top and moving downwards.

A characteristic feature observed with all the phase inversion runs was the very wide hysteresis gap; i.e., once inversion occurred, very high changes in phase flows were required to reinvert the dispersion. Figure 2 shows *W/O* dispersion inversion occurring.



Inversion starts in Compartment (2) and is Complete in Compartment (3).

Figure 2. Phase inversion of water heptane dispersion in a RDC.

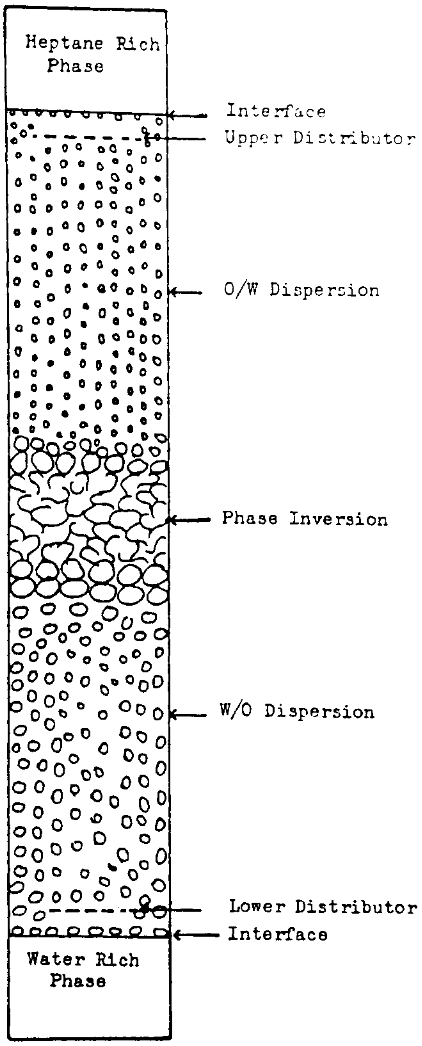


Figure 3. Phase inversion phenomenon in an RDC column due to "two way" mass transfer.

Phase Inversion with Two Way Mass Transfer

The column was filled with the aqueous phase and the flow rate adjusted to the required value. The agitator was also set to the required speed and the light phase introduced through the distributor. As the *O/W* dispersion filled the column, it was noticed that phase inversion commenced at the bottom of the column and gradually moved up until it reached about half way where it stabilised and the column continued operating with an *O/W* dispersion in the upper part of the column while in the lower part a *W/O* dispersion existed; and about 20 cm in the middle an inversion band. This is illustrated in Figure 3.

Mass Transfer

Mass transfer experiments were performed for acetic acid and butanol. In both cases the investigations were limited to mass transfer from n-heptane dispersed phase to the water continuous phase.

The following procedure was followed for these experiments. First the raffinate solution was prepared to the required concentration. The column was filled with the continuous phase and the agitator speed adjusted to that desired for the experiments. The dispersed phase was introduced into the column and its flow rate adjusted to a set value. Then the continuous phase flow was adjusted to the required value. After steady state conditions had been reached, normally after about 10 minutes, samples were taken from the raffinate and extract. For the case of acetic acid mass transfer, it was also possible to get samples of the continuous phase from sampling points along the length of the column. However, in the case of butanol mass transfer a dispersion was obtained from these sampling ports. Photographs were taken for drop size measurements and finally the samples were analysed by titration with 0.1 N NaOH in the case of acetic acid and by gas liquid chromatography in the case of butanol.

In general mass transfer resulted in violent interfacial agitation as the dispersed phase was discharged from the distributor and coalescence occurred as the dispersed phase moved up the column. In the case of butanol mass transfer, the dispersed phase droplets were of very irregular shape; and at high rpm's it appeared that a double dispersion was formed. Under these circumstances no meaningful drop size count could be obtained for the butanol-heptane/water dispersions.

Mass Transfer with Chemical Reaction

Initial investigations were undertaken to determine the approximate time taken for the column to reach steady state conditions. This was done by taking samples of the light phase extract at three minute intervals until identical values of the ester concentration were obtained. Subsequently measurements were taken only after approximately twice this minimum time had elapsed.

The concentration range of acetic acid studied was 60-80% while that of the sulphuric acid catalyst was 4-10%. The concentration of butanol was restricted to 20-25% since this was found to increase conversion due to salting effects.

Although the concentration of the reactants was extremely high, separation was found to be complete with practically no entrainment of the outflowing phases.

DISCUSSION

Phase Inversion with No Mass Transfer

The phase inversion phenomenon observed in this study for the heptane-water system displayed some "peculiar" characteristics:

(1) No "proper" flooding preceded phase inversion. Instead droplets of the hitherto continuous phase started building up from the distributor onwards until the whole column was filled with well packed polygonal droplets. Coalescence of these droplets was slow taking from 15-30 minutes before the column reverted to normal operation. One explanation for this phenomenon may be that instead of flooding "proper" whereby one or both phases is rejected, the hitherto continuous phase is "rejected" but the high agitation caused by the onset of flooding jostles the droplets, preventing coalescence, and in this case it seems flooding is characterised by formation of a dense droplet layer rather than a dense monophase of coalesced droplets which is a characteristic feature of "flooding proper."

Similar shaped drops have been reported by Robinson and Hartland (1971) in a study of the effect of adjacent drops on the drop shape approaching a liquid-liquid interface, when the coalescence rate of droplets was slow so that an array of droplets was built up on the interface.

The hold-up when all the column was full of the well packed drops was considered as the inversion hold-up. This varied from 60-80%. However, as mentioned earlier, the well packed droplets cleared gradually until the hold-up was back to the "normal" values of 3-10% range.

(2) Once inversion set in by way of the well packed drops, it was not possible to reverse the process and very large changes in phase ratios were needed to reinvert. Sarkar (1976) and Al-Hemiri (1973) have reported that a 2-3% change in phase flow rate was sufficient to disturb the inversion and revert to the original dispersion.

Phase Inversion with Two Way Mass Transfer

The interesting phase inversion phenomena observed when mass transfer was occurring in both directions simultaneously, i.e., when there were two solutes one being transferred from the organic into the aqueous phase while the other is being transferred in the opposite direction can be explained as follows:

It is generally agreed that transfer of a third component from the continuous phase to the dispersed phase stabilizes the droplets, whereas diffusion out of the drops accelerates coalescence (Lawson and Jeffreys, 1965). This has been attributed to the formation of interfacial gradients, a phenomenon described by Davies and Jeffreys (1971). The phase inversion phenomenon encountered when two-way mass transfer was taking place agrees with Davies and Jeffreys' postulation.

Considering the top of the column, mass transfer is predominantly from the aqueous to the organic phase since the driving force for the transfer of acetic acid is high, whereas the organic phase is lean in the second solute (butanol) and the driving force is much less. Hence, the flux of molecules is much greater in the direction aqueous-organic. This stabilizes the *O/W* dispersion. However, as the aqueous phase descends down the column, acetic acid molar flux from the aqueous to the organic phase decreases while the butanol flux increases in the reverse direction. Eventually the latter flux predominates; a process which leads to enhanced coalescence of the organic phase droplets and eventual phase inversion. The aqueous phase droplets thus formed continue to receive an increasing flux of butanol molecules while the reverse flux is decreased further. Thus from the inversion point downwards, conditions are more and more conducive to formation of a stable *W/O* dispersion.

Mass Transfer

Values of the area based experimental mass transfer coefficient K_Ga were evaluated from the mass balance and log mean driving force for both acetic acid transfer and butanol transfer from the organic to aqueous phase. For acetic acid mass transfer the interfacial area per unit volume of column "a" was evaluated from the drop size measurements and K_G estimated. It was not possible to evaluate the interfacial area for butanol transfer due to the very irregular nature of the heptane/butanol drops.

The K_Ga values for acetic acid were found to range between $(1.23\text{-}1.78) \times 10^{-2}$ cm/s; while the values for butanol were $(2.16\text{-}2.68) \times 10^{-3}$ cm/s. From the values obtained for acetic acid, it was observed that K_G was not constant but tends to increase with solute feed concentration, i.e., the driving force. This is in accordance with observations of Edwards and Himmelblau (1961) and of Lewis (1958).

Analysis of Continuous Countercurrent Extraction-Reaction Processes

Consider an extraction-reaction column which operates continuously under steady state conditions as shown in Figure 4, where $L_0 \cdot$ kg/min of butanol/n heptane solution is fed into the base of the column to ascend as the dispersed phase. The ascending organic phase will be termed the extractive phase. This is contacted with a countercurrent aqueous stream consisting of water, acetic and sulphuric acids; which is the reactive phase, entering the top of the column where the flow is $V_H \cdot$ kg/min. Butanol is transferred from the extractive phase to the reactive phase where it reacts with acetic acid to form the ester which is transferred back into the extractive phase. The following assumptions were made in the analysis presented below:

(1) No reaction takes place in the extractive phase.

(2) The solubility of water in the extractive phase and heptane in the reactive phase are negligible throughout the column.

(3) All components attain equilibrium between the two phases instantaneously.

(4) There are no volume changes on mixing, or during the course of the reaction.

(5) Dispersed phase hold-up is constant and independent of position in the column.

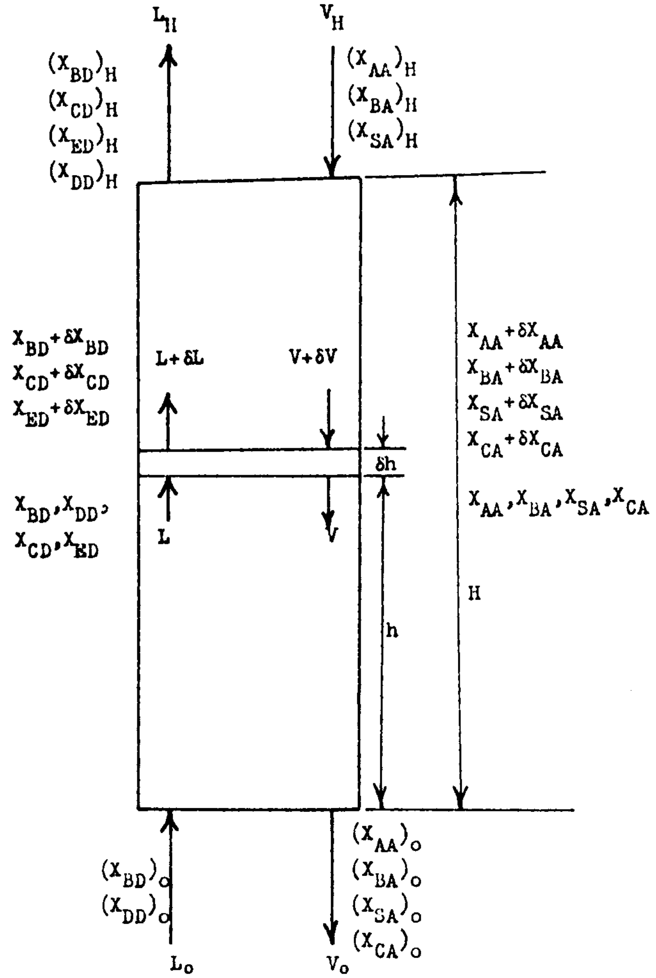


Figure 4. Continuously operating extraction-reaction column under steady-state conditions.

Taking an element of the column of height δh as shown in Figure 4, the rate of ester formation is:

$$\frac{dE}{dh} = k_2 S \rho_c \phi_c X_{BA} X_{CA} \frac{\delta h}{U_c} - k_2' S \rho_c X_{AA} X_{EA} \frac{\delta h}{U_c} \qquad (1)$$

where S is the cross sectional area of the column. ϕ_c is the fractional hold-up volume of the continuous phase. X_{EA} is the mole fraction of the ester assumed to be momentarily present in the aqueous phase causing the reverse reaction to occur. In a short column where conversion is not high, the quantity of the ester in the system is small and since most of this will be extracted into the extractive phase, the concentration of the ester remaining in the reactive phase will be very small. Thus, the last term of Eq. 1 can be ignored and the equation is reduced to:

$$\frac{dE}{dh} = k_2 S \rho_c \phi_c X_{BA} X_{CA} \frac{\delta h}{U} \qquad (2)$$

An ester balance over the element is:

$$\begin{aligned} &(L)\,(X_{ED}) + (L)\,(X_{CD})/\nu \\ &\quad + (V + \delta V)\left(X_{CA} + \frac{dX_{CA}}{dh}\right)\delta h/\nu \\ &\quad = \left(X_{ED} + \frac{dX_{ED}}{dh}\,\delta h\right)(L + \delta L) \\ &\quad\quad + \left(X_{CD} + \frac{dX_{CD}}{dh}\right)(L + \delta L)/\nu \qquad (3) \end{aligned}$$

An equivalent ester balance between the element and the

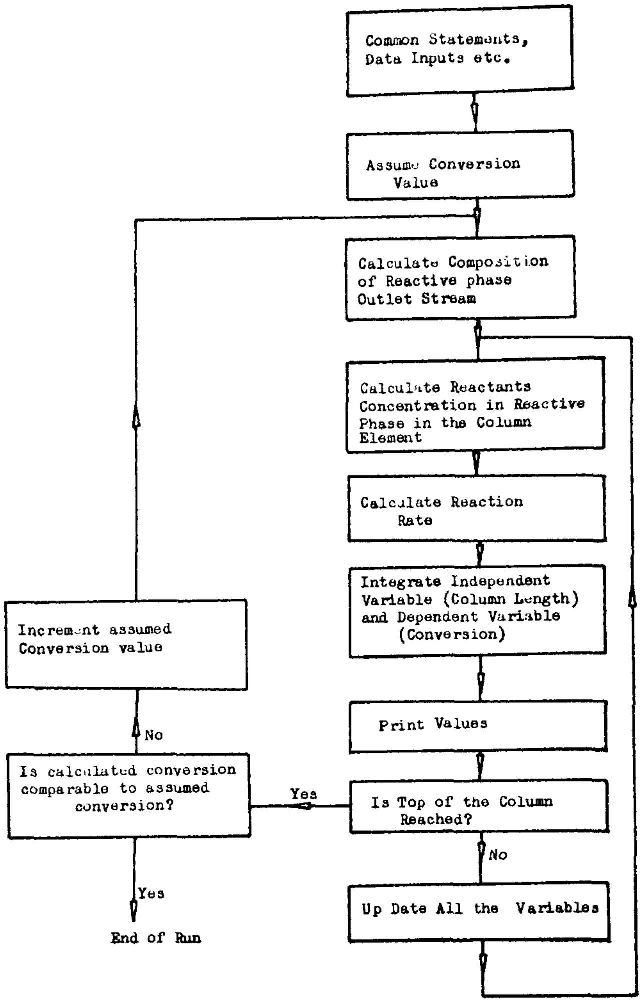


Figure 5. General arrangement of computer program for calculating conversion in the RDC.

base of the column is:

$$(L_o)\,(X_{BD})_o/\nu + V(X_{EA})/\nu = (L)\,(X_{ED}) + L(X_{CD})/\nu \qquad (4)$$

The relationship between water, acetic acid, butanol, n-heptane and ester entering and leaving the element is governed by the distribution equations developed in Part I of this study and then Eqs. 2 to 4 are sufficient for numerical integration starting from the bottom of the column; provided the concentration of B and C, i.e., $(X_{BA})_o$ and $(X_{CA})_o$ are known for the initiation of the integration. To do this a certain conversion from the bottom to the top of the column was assumed and values for $(X_{BA})_o$ and $(X_{CA})_o$ computed. Then the numerical integration was started and the ester produced was calculated from Eq. 2. Equilibrium was assumed inside each integration element, i.e., local extractive/reactive phases equilibrium. Hence application of the distribution correlation determined new values of X_{BA} and X_{CA}. Conversion was calculated, after each integration step through the column, until the total height was reached. Finally the conversion value attained at the top was compared with the value assumed for starting the iteration procedure, and if the convergence criteria was not attained, the conversion value was incremented and the computation recycled.

Table 1. Experimental vs. Computed Conversions in the RDC

Heavy Phase Composition wt. % Basis				Light Phase Composition wt. % Basis			
						Conversion %	
Run No.	Water	Acetic Acid	Catalyst	Butanol	Heptane	Exp.	Calc.
1	10.0	80.1	9.9	25.0	75.0	22.9	21.8
2	10.9	81.0	8.1	25.1	74.9	19.8	18.4
3	11.5	32.6	5.9	24.9	75.1	17.4	17.0
4	10.2	36.0	3.8	25.3	74.7	12.2	13.2
5	23.0	67.0	10.0	22.0	78.0	19.9	21.5
6	22.0	70.1	7.9	24.8	75.2	16.3	19.6
7	24.1	69.8	6.1	25.0	75.0	13.7	17.6
8	26.1	69.9	4.0	24.9	75.1	9.7	12.5
9	39.9	50.1	10.0	25.2	74.8	5.7	6.7
10	9.9	80.1	10.0	20.2	79.8	38.6	33.0
11	9.8	82.2	8.0	21.3	28.7	28.7	24.5
12	10.0	83.9	6.1	20.0	23.6	23.6	20.2

Flows: light phase = 0.700 kg/min; heavy phase = 0.680 kg/min.

The hold-up of continuous phase ϕ_c appears in Eq. 3 and was evaluated as follows. Thus, the hold-up varies throughout the column due to three phenomena:

(a) Purely hydrodynamic variations due to the characteristics of extraction column construction.

(b) Mass transfer effects.

(c) Creation and destruction of species by chemical reaction.

The last two effects are significant in the extractive-reaction processes and were accounted for by recalculating the dispersed phase volume after each integration step. However the changes in hold-up due to hydrodynamical effects alone were assumed to be negligible and seem to be justified in a short column from previous research (Ladda, 1978).

The logic flow diagram of the computer program, used to calculate conversion in the continuous countercurrent extraction-reaction column is shown in Figure 5. It consisted of a main program and four subroutines. The subroutines were similar to the corresponding subroutines developed for the batch extraction.

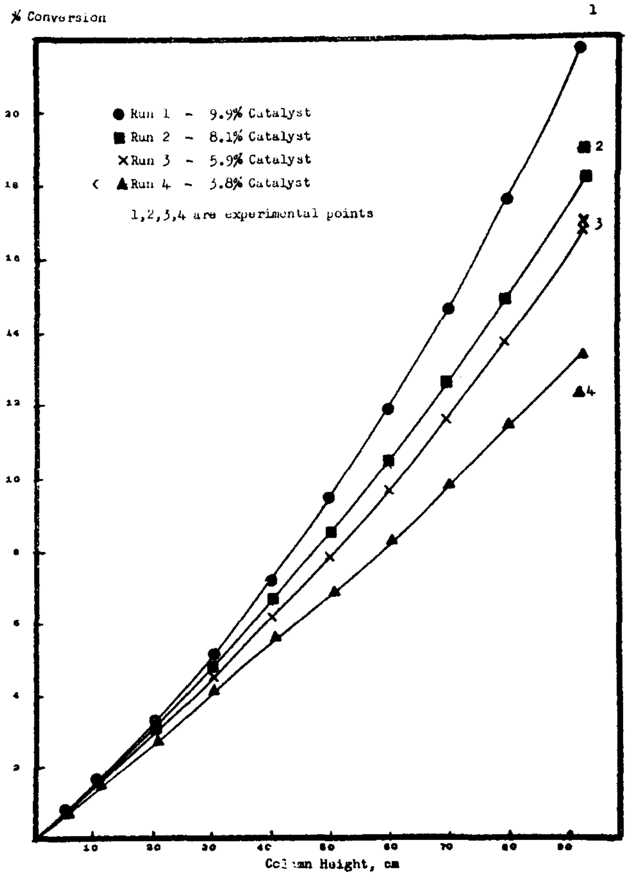


Figure 6. Esterification reaction in the RDC computed conversion vs. column height.

Experimental and computer conversion values are tabulated in Table 1 and Figure 6 presents typical calculations of conversion up the column for the first four experiments with 10% water and 3.8-9.9% catalyst. The figure shows how conversion is increased with increasing catalyst concentration and column height. Due to sampling difficulties it was not possible to measure the conversion along the column, except at the top, i.e., after phase separation was complete. The experimental conversion values at the top of the column are given in Figure 6 and good agreement was achieved between experimental and calculated conversion values.

NOTATION

A = water
a = interfacial area per unit volume
B = acetic acid
C = n-Butyl alcohol
D = n-Heptane
E = n-Butyl acetate
H = total height of column
h = height from bottom of column
K_G = overall mass transfer coefficient
k_2 = second order forward reaction rate constant
k_2' = second order reverse reaction rate constant
L = light phase flow
O/W = oil in water
S = cross-sectional area of column
S' = sulphuric acid
U = fluid velocity
V = heavy phase flow
W/O = water in oil
X = mole fraction

Greek Letters

δ = density
ϕ = volumetric hold-up
ν = stoichiometric coefficient

Subscripts

A,B,C = components, $A,B,C, \ldots$, respectively
X_{AB} = mole fraction of A in B rich phase
c = continuous phase
H = top of column
o = bottom of column

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An Analytical Carnahan-Starling-van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids

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Data have been taken by a new flow technique for the solubility of nonpolar hydrocarbons in nonpolar supercritical fluids. These results for molecularly simple molecules provide a basis for the analytical representation of such systems by relatively simple equations of state.

SCOPE

Supercritical fluid extraction (SFE) is a new separation process which can offer substantial advantages in certain situations. Although many applications of SFE have appeared in the patent literature, there is no fundamental understanding of the phase behavior. For rational process design it would be highly desirable to have appropriate mathematical models of the thermodynamic behavior of supercritical solutions. The first purpose of this work was to establish a data base of molecularly simple supercritical solubility data. In order to gain the advan-

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