MODELING AND SIMULATION OF KÜHNI COLUMN FOR WATER-ACETONE-TOLUENE SYSTEM

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
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By

GOPALA KRISHNA SURISETTY

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the dissertation entitled **"MODELING AND SIMULATION OF KÜHNI COLUMN FOR WATER-ACETONE-TOLUENE SYSTEM"** in partial fulfillment of the requirement for the award of the degree **Master of Technology in Chemical Engineering** with Specialization in **Computer Aided Process Plant Design (CAPPD)**, and submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology Roorkee**, under the kind guidance of **Dr. (Mrs.) Shashi**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute / University.

Place: Roorkee

Date: 25th June, 2005

S.Gopalakrishna

(GOPALA KRISHNA SURISETTY)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Shashi 25/6/05

(Dr.(Mrs.) Shashi)

Assistant Professor,

Department of Chemical Engineering

Indian Institute of Technology, Roorkee

Roorkee - 247667

ABSTRACT

There is hardly any chemical process, which does not involve separation of liquid mixtures or recovery of valuable components from the reaction products. Liquid-liquid extraction processes have been increasingly used with advantage in these operations. The development of sound methods of equipment design has present trend. In recent times the approach to data interpretation has undergone a shift towards better modeling of transport processes yielding new methods of scaleup and design.

Liquid extraction modeling demonstrates the performance of extraction equipment which includes concentration profile hold up of dispersed phase along the column height, fluid dynamics etc. In the present study the modeling of extraction column has been carried out which describes the concentration profile of solute in the dispersed phase and continuous phase.

In this thesis, a one-dimensional dynamic and steady state mathematical models have been developed for the simulation of a Kühni extraction column. The effect of different parameters on the performance of the column has been discussed. To solve the model equations, input data physical properties of the system chosen and correlation are taken from the literature. The model equations are solved for step response dynamic, steady state conditions by using MATLAB 6.5 software. The model gives the results of Kühni column for water acetone toluene system. The obtained results from the model equation have been validated with experimental data available in the literature.

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NOMENCLATURE

a	specific interfacial area, m^{-1}
A	amplitude, m
C_0	discharge coefficient
d_0	plate perforation diameter, m
d_s	sauter mean drop diameter, m
D	axial dispersion coefficient, $m^2 \cdot s^{-1}$
D_m	molecular diffusivity coefficient, $m^2 \cdot s^{-1}$
f	frequency, s^{-1}
g	acceleration due to gravity, $m^2 \cdot s^{-1}$
h	level, m
h_0	plate spacing, m
k_1, k_2	constants
k	film mass transfer coefficient, $m \cdot s^{-1}$
K	overall mass transfer coefficient, $m \cdot s^{-1}$
L	column height, m
m	distribution coefficient
$\dot{m}$	mass flow rate, $kg \cdot s^{-1}$
M	molecular weight
Q	volumetric flow rate, $m^3 \cdot s^{-1}$
S	cross sectional area, m^2
t	time, s
U	superficial velocity, $m \cdot s^{-1}$
V	velocity, $m \cdot s^{-1}$
V_s	slip velocity, $m \cdot s^{-1}$
x	weight fraction of solute in continuous phase

X	solute concentration in the dispersed phase, $\mathrm{kmol \cdot m^{-3}}$
X^*	solute concentration in equilibrium with Y
y	weight fraction of solute in dispersed phase
Y	solute concentration in the continuous phase, $\mathrm{kmol \cdot m^{-3}}$
Y^*	solute concentration in equilibrium with X

Greek Letters

ε	holdup of dispersed phase (volume fraction)
μ	viscosity, $\mathrm{kg \cdot m^{-1} \cdot s^{-1}}$
ρ	density, $\mathrm{kg \cdot m^{-3}}$
$\bar{\rho}$	mean density, $\mathrm{kg \cdot m^{-3}}$
$\Delta\rho$	density difference, $\mathrm{kg \cdot m^{-3}}$
σ	interfacial tension, $\mathrm{N \cdot m^{-1}}$
α	fractional open area of plate
Ψ	power dissipation per unit volume of dispersion, $\mathrm{w \cdot m^{-3}}$
Ψ_1	mechanical power dissipation per unit volume, $\mathrm{w \cdot m^{-3}}$

Subscripts

c	Continuous phase
d	Dispersed phase

CHAPTER–1

INTRODUCTION

1.1 INTRODUCTION

There is hardly any chemical process, which does not involve separation of liquid mixtures or recovery of valuable components from reaction products. Separation process as a branch of mass transfer operation plays a major role in chemical engineering. Liquid extraction as a separation process is well found in many chemical processes. Extraction is a process that separates components based upon chemical differences rather than differences in physical properties. The basic principle behind extraction involves the contacting of a solution with another solvent that is immiscible with the original. The solvent is also soluble with a specific solute contained in the solution. Two phases are formed after the addition of the solvent, due to the differences in densities. The solvent is chosen so that the solute in the solution has more affinity toward the added solvent. Therefore mass transfer of the solute from the solution to the solvent occurs. Further separation of the extracted solute and the solvent will be necessary. Extraction is a physical method of separation and as such is related to separation by distillation, adsorption, crystallization etc. The addition of a solvent in this process corresponds to the addition of heat in the case of separation by distillation. A characteristic feature of the physical methods is that they do not involve a chemical change in the materials treated. In this respect, they are in contrast with the chemical separation methods, which do cause a chemical change of at least one of the components in the feed stock. Physical methods of separation have some important advantages over chemical methods for instance **(Laddha and Degaleesan)**

- The absence of chemical conversion and of by product formation. In chemical process some of the components are lost by these conversions. Frequently the by products thus formed are difficult to remove. The properties of the final products obtained by physical separation are therefore often superior.
- Physical separation processes are usually cheaper, since the operating costs are almost exclusively related to the heat requirements.
- Among the physical separation methods, distillation is the most commonly employed and usually the cheapest process. The components to be separated, however, must have both a suitable absolute volatility and a sufficient difference in volatility. If either of these conditions is not fulfilled, extraction will be a better choice, provided that the components of the mixture should show a suitable absolute solubility and sufficient difference in solubility in an external and immiscible liquid. . However, these separation costs may be desirable in contrast to distillation and other separation processes for situations where extraction is applicable.

The factors determining both volatility and solubility characteristics of a compound are its molecular size and its potentiality of molecular interactions related to its chemical nature (e.g. its polarity or polarizability). In the case of volatility, the molecular size is the predominant influence and the chemical nature in general of less importance. In the case of solubility characteristics the situation is approximately the reverse. The differences in solubility are mainly determined by the physical properties which depend on a chemical structure of the molecule; thus in general hydrocarbons and alcohols can easily be separated by extraction. Water could for instance be used as the external and immiscible solvent in this case.

Many separation processes in chemical industry, which do not involve a chemical change, are usually the separation by liquid extraction. It is abundantly found in petroleum industry, coal tar industry, metallurgical industry, and in many organic and inorganic industries. It is increasingly used in processes containing oils and fats and different pharmaceutical products.

A general extraction column has two input stream and two output streams. The input streams consist of a solution feed at the top containing the solute to be extracted and a solvent feed at the bottom which extracts the solute from the solution. The solvent containing the extracted solute leaves the top of the column and is referred to as the extract stream. The solution exits the bottom of the column containing only small amounts of solute and is known as the raffinate. Further separation of the output streams may be required through other separation processes.

1.2 PROCESS OPERATION

For the design of new extractors it is essential that pilot-plant experiments be performed under conditions as nearly like those expected in the large-scale equipment as possible. The rate of extraction that we observe in an extractor is known to depend upon the characteristics of both the chemical system involved and the process conditions, as well as those of the equipment. The principal difficulty in obtaining an understanding of extractor performance lies with the very large number of variables which influence the performance. The factors that influence the extraction rate include the following.

There are certain design variables that must be assigned in an extraction process. **(Treybal)**

- Operating Temperature
- Operating Pressure
- Feed Flow Rate
- Composition
- Temperature of entering stream
- Pressure of entering stream
- The liquid system

1. Chemical identity and corresponding physical properties. In this category may be included the presence or absence of surface-active agents, finely divided solids, and the like.

2. Concentration of solute, since this influences physical properties..

3. Direction of extraction, whether from aqueous to organic, from continuous to dispersed phase.

4. Total flow rate of the liquids.

5. Ratio of liquid flows.

The equipment:

1. Design, which includes not only the gross and obvious design such as whether the extractor is a packed or a sieve-tray tower, but also the details such as size and shape of packing and size and number of perforations in a plate.
2. Nature and extent of mechanical agitation, whether rotary or pulsating, whether fast or slow.
3. Materials of construction, which influence the relative wetting by the liquids.

4. Height of extractor and the end effects.
5. Diameter of extractor and the extent of axial mixing.

As in many separation processes, the pressure and temperature conditions play a large role in the effectiveness of the separation. In order for a good split of the feed the pressure and temperature must be such so as to ensure that all components remain in the liquid phase. The process will be adversely affected if one or more of the components are allowed to become a vapour, or the extraction may not occur at all if a large enough portion of a component is allowed to vaporize. In addition, the temperature should be high enough that the components are all soluble with one another. If extremes in temperature are present, finding a suitable solvent for extraction can be problematic. This is however generally not the case since one of the biggest benefits in the extraction process is that it can be done at ambient pressures and temperatures.

In many applications, a separation process is desired where an extreme temperature will destroy the desired product such as the pharmaceutical industry. For these applications, extraction is ideally suited, since the only temperature requirement is that dictated by the solubility. At this point the biggest challenge would be finding a suitable solvent for the extraction.

We can also use the pharmaceutical industry in another example for the benefits of extraction and this has to do with the volumes involved for effective extraction. The extraction process can become very expensive if the solvent needed to be used is costly these expenses can be contained if a batch process is being used and this is often the case in medicines. In a non-batch process the solvent would need to be constantly supplied and this would involve either a huge amount of solvent or another separation process in order to recycle the solvent.

1.3 APPLICATIONS OF LIQUID-LIQUID EXTRACTION SYSTEM

Applications of liquid-liquid extraction fall into several categories, those where extraction is in direct competition with other separation methods and those where it seems uniquely qualified. In the first category relative costs are important. Distillation and evaporation are direct separation methods, the products of which are composed of essentially pure substances. Liquid extraction on the other hand, produces new solutions which must in turn be separated, often by distillation or evaporation. Thus for example, acetic acid can be separated from dilute solution with water, with difficulty by distillation or with relative ease by extraction into a suitable solvent followed by distillation of the extract. For more dilute solutions particularly, where water must be vaporized in distillation, extraction is more economical especially since the heat the vaporization of most organic solvents is substantially less than that of water. Extraction may also be attractive as an alternative to distillation under high vacuum at very low temperatures to avoid thermal decomposition. For example, long chain fatty acids can be separated from vegetable oils by high vacuum distillation but more economically by extraction with liquid propane. Tantalum and Niobium can be separated by very tedious fractional crystallization of the double fluorides with potassium but with relative ease by liquid extraction of the hydrofluoric acid solutions with methyl isobutyl ketone.

Chemical methods consume reagents and frequently lead to expensive disposal problems for chemical by-products. Liquid extraction, which incurs no chemical consumption or by-product production, can be less costly. Metal separations such as uranium-vanadium, hafnium-zirconium, and tungsten-molybdenum and the fission products of atomic energy processes are more economical by liquid extraction.

Even lower cost metals such as copper and inorganic chemicals such as phosphoric acid, boric acid, and the like are economically purified by liquid extraction, despite the fact that the cost of solvent recovery must be included in the final reckoning.

Aromatic and paraffin hydrocarbons of nearly the same molecular weight are impossible to separate by distillation because their vapour pressures are nearly the same, but they can readily be separated by extraction with any of a number of solvents, e.g., liquid sulphur dioxide, diethylene glycol, or sulfonane. Many pharmaceutical products, e.g., penicillin, are produced in mixtures so complex that only liquid extraction is a feasible separation device.

The case for the use of liquid-liquid extraction will depend upon its either accomplishing a separation that can not be achieved by other operations such as distillation, evaporation and crystallization, or effecting the separation more economically. Liquid-liquid extraction is now being adopted as a more economic alternative to other separation processes and has found immense applications in the separation of **(Laddha and Degaleesan)**.

1) Solutions of components having low relative volatility, especially when vacuum distillation is expensive.
2) Solutions of close boiling and azeotrope forming components.
3) Dissolved solute when evaporation may be impractical.
4) Solutions of heat sensitive components such as antibiotics.
5) Components of differing chemical type whose boiling points may overlap as in the case of petroleum hydrocarbons.

1.4 LIMITATIONS

We must consider the under what extremes extraction can be used as separation process.

1. Suitable Solvent **(separation principles)**

- Solvent partially soluble with the carrier.
- Feed components immiscible with the solvent.
- Solute is soluble in the carrier and at the same time completely or partially soluble in the solvent.
- Different densities than the feed components for a phase separation to facilitate and maintain the capacity of the extractor high.
- Extremely high selectivity for the solute for the solvent to dissolve the maximum amount of solute and the minimum amount of the carrier.
- Large distribution coefficient to reduce the theoretical number of stages contributing to a greater efficiency
- Low viscosity increases the capacity of the extraction column and does not allow for the settling rate of dispersion to be slow.
- Chemically stable and inert toward other components of the system
- Low cost, non-toxic, and non-flammable

2. Equipment

- Interfacial tension and Viscosity
- High interfacial tension and viscosity leads to more power being supplied maintain rapid mass transfer throughout the extraction process.
- Low interfacial tension and viscosity leads to the formation of an emulsion.

3. Temperature preferred to be higher since solubility increases, but temperature not higher than the critical solution temperature.

4. Pressure for condensed system must be maintained below the vapour pressure of solutions such that a vapour phase will not appear and interrupt liquid equilibrium.

5. Separation may only occur for compositions in the region between the feed composition and that apex of the carrier.

1.5 CLASSIFICATION OF EQUIPMENT

In a liquid-liquid extraction process, intimate contact of feed mixture with the solvent and the separation of the resultant mixture into two layers are essential, and equipment used for extraction should be capable of meeting these requirements. The liquid-liquid extraction equipment may be classified, according to the construction and the operational characteristics into two broad groups, stage wise contactors and differential contactors. In the former type of contactors there are discrete number of stages in which two phases are equilibrated and then separated before being passed counter current to each other, whereas in differential contactors the composition of phases changes continuously. In the case of stage wise contactors, since the number of contacting stages could be known accurately and the stage efficiencies are usually high, the design and scale up of the contactors are comparatively simple. As the phases have to be separated after attaining equilibrium in each stage, the settling compartments have to be large and there by the overall units may become bulky, especially if the systems are slow to separate. Differential contactors are more compact for a given throughput and usually require little ground area as they are normally in the form of vertical columns. But the design and scale up of such units are in general, complicated as the two phases are never in equilibrium in differential contactors. The stage wise and the differential contactors are further divided according to the methods adopted for interdispersing the phases, and according to the mode of effecting the separation and producing the counter current flow pattern. Liquid-liquid extraction equipment could be classified also into vertical column type and horizontal extractors. The former are further divided, according to the mode of agitation provided for the interdispersion of liquids, as unagitated, rotor-agitated and pulse-agitated columns.

1.5.1 Mixer-settlers

To provide efficient mass transfer, a mechanical mixer is often used to provide intimate contact between the two phases. Mixer-settlers are used when there will only be one equilibrium stage in the process. For such a system, the two liquid phases are added and mixed. One phase is usually dispersed into the other in the form of small droplets. Sufficient time of contact should be provided for the extraction to take place. Small droplets produce large interfacial areas and faster extraction.

Due to their density differences, one phase will settle out and the mixture will be separated. The downfall to this type of extractor is that it requires a large-volume vessel and a high liquid demand. In Fig 1.1 a typical mixer-settler is shown, where the mixer or agitator is entirely separate from settler .The feed of aqueous phase and organic phase are mixed in the mixer, and then the mixed phases are separated in the settler .in the Fig 1.2 a combined mixer-settler is shown, which is sometimes used in the extraction of uranium salts or copper salts from aqueous solutions. Both types of mixer-settlers can be used in series for countercurrent or multiple-stage extraction. Typical stage-efficiencies for a mixer-settler are 75-100%.

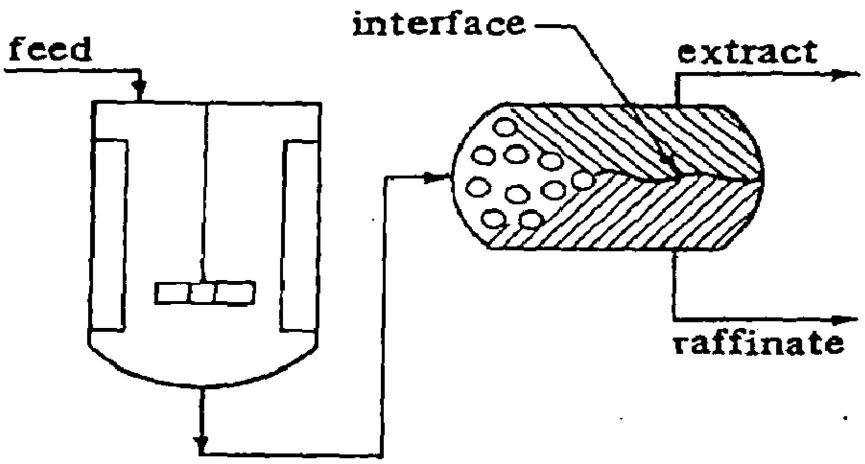

Fig 1.1 Separate mixer-settlers

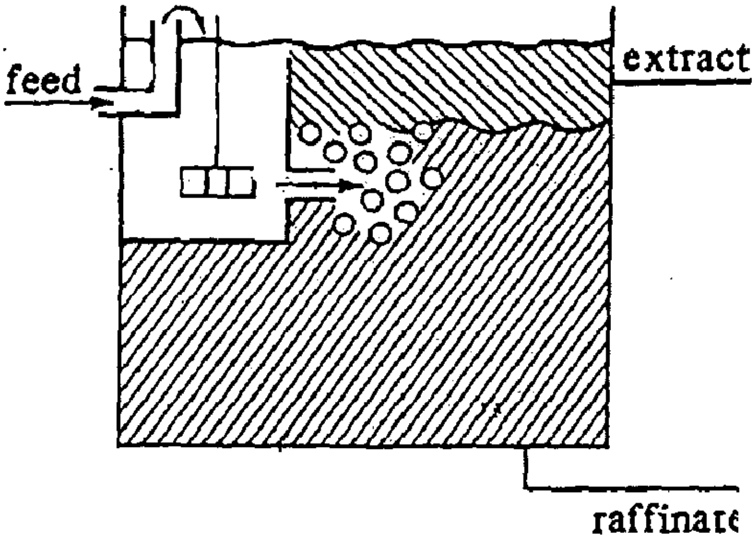

Fig 1.2 Combined mixer-setters

1.5.2 Spray Extraction Towers

Packed and spray-tower extractors give differential contact, where mixing and settling proceed continuously and simultaneously. In the plate–type towers or mixer–settler contactors, the extraction and settling proceeds in discrete stages. In Fig 1.3 the heavy liquid enters at the top of the spray towers, fills the tower as the continuous phase, and flows out through the bottom. The light liquid enters through a nozzle distributor at the bottom, which disperses or sprays the droplets upward. The light liquid coalesces at the top and flows out. In some cases the heavy liquid is sprayed downward into a rising light-continuous phase. The spray tower has very large axial dispersion in the continuous phase. Hence, only one or two stages are usually present in such a tower. Despite its very low cost, this type of tower is rarely used. It can be used when a rapid, irreversible chemical reaction occurs, as in neutralization of waste acids.

1.5.3 Packed Extraction Towers

A more effective type of tower is made by packing the column with random packing such as rasching rings, Berl saddles, Pall rings and so on, which cause the droplets to coalesce and redisperse at frequent intervals throughout the tower. The axial mixing is reduced considerably. A packed tower is more efficient than a spray tower, but back-mixing still occurs and the HETS (height equivalent to a theoretical stage) is generally greater than for the pulsed and mechanically agitated towers.

Packed-towers are used where only a few stages are needed and generally the low interfacial tension systems of about 10 dyn/cm or so. When using random packing, it is preferable to choose a material that is preferentially wetted by the continuous phase. For example, stoneware Raschig rings or Berl saddles are used for water as the continuous phase and carbon rings or saddles for toluene as the continuous phase. Packed towers more often use random packing and less often structured packing.

In packed absorption towers, flooding occurs when the gas velocity is increased until the liquid cannot flow downward and is carried up by the gas out of the tower. In packed liquid extraction towers, flooding occurs when increasing the dispersed or continuous flow rates causes both phases to leave at the outlet of the continuous phase.

1.5.4 Pulsed Packed and Sieve-Tray Towers

There are many types of towers that are mechanically agitated to increase the mass-transfer efficiency and or the throughput. An ordinary packed tower or one with special sieve plates can be pulsed by applying a rapid reciprocating motion of relatively short amplitude to the liquid contents. A reciprocating plunger pump, bellows pump, or high-pressure air pulse is externally connected to the space containing the continuous and dispersed phases enter and exit the tower.

1. **Pulsed packed towers:** Pulsing packed towers reduces the HETS considerably, by about a factor of 2 or so. Pulsing is also useful in handling liquids with high interfacial tensions, up to 30-40 dyn/cm. typical values for HETS in the order of 0.15 – 0.3 m. Since pulsing is uniform across the cross section, scale-up of tower size can be accomplished by using the same value of sum of the velocities of dispersed phase and continuous phase.
2. **Pulsed Sieve-Tray towers.** Typical amplitudes used are from 0.6 to 2.5 cm and frequencies from 100 to 250 cycles/min. Typical hole size is 0.32 cm diameter, with 20-25% free space on the tray and 5.1 cm (2 in) tray spacing.

3. The trays occupy the entire cross section of the tower and there are no downspouts. During upward pulsing, the light liquid is forced through the holes and droplets rise to the tray above During downward pulsing, the heavy liquid behaves in a similar manner.

1.5.5 Mechanically Agitated Extraction Towers

There are many types of mechanically agitated towers, three of the most important of which are the scheibel tower shown in Fig 1.4 the Karr tower shown in Fig 1.5 and kühni column in Fig 1.6

1. Scheibel Tower:

In the scheibel tower, a series of rotating turbine agitators form dispersions which coalesce in passing through the knitted mesh. The mixture then passes through the outer settling zone. The tower thus operates as a series of mixer-settler extraction units.

2, Karr reciprocating-plate tower.

As shown in Fig 1.5 for the Karr column, the perforated trays are moved up and down to increase agitation and to pulse the liquids. This results in a more uniform drop-size distribution because the shear forces are more uniform over the tower cross section as shown in Fig 1.4

3. Kühni column

In this column impellers attached to central shaft as shown in Fig. 1.6 .the agitation created in the column is due to centrifugal action .The droplet size can be controlled by the speed and diameter of the impeller, while the circulation rate can be controlled by the design of the width of the impeller. A perforated plate between each stage can control the droplet hold-up by the percentage of open area in the plate

1.5.6 Centrifugal contactors

Centrifugal contactors are ideal for systems in which the density difference is less than 4%. In addition, this type of system should be utilized if process requires many equilibrium stages. In these systems, mechanical devices are used to agitate the mixture to increase the interfacial area and decrease mass transfer resistance. Many different types of centrifugal contactors exist, and each has its own guidelines for operation and selection i.e. given the following table

Table 1.1 Comparison between extraction equipments

Unit of operation	**Advantages**	**Disadvantages**
Mixer-Settler	• Efficient • Low head room • Induces good contacting Can handle any number of stages	• Large floor • High set-up costs • High operation costs
Columns (with out agitation)	• Small investment costs • Low operating costs	• High head room • Difficult to scale from lab • Less efficient than mixer-settler
Columns (with agitation)	• Good dispersion • Low investment costs • Can handle any number of stages	• Difficult to separate • small density • differences • Does not tolerate high • flow ratios
Centrifugal Extractors	• Can separate small density differences • Short holding time • Small liquid	• High set-up cost • High operating and • maintenance costs • Cannot handle

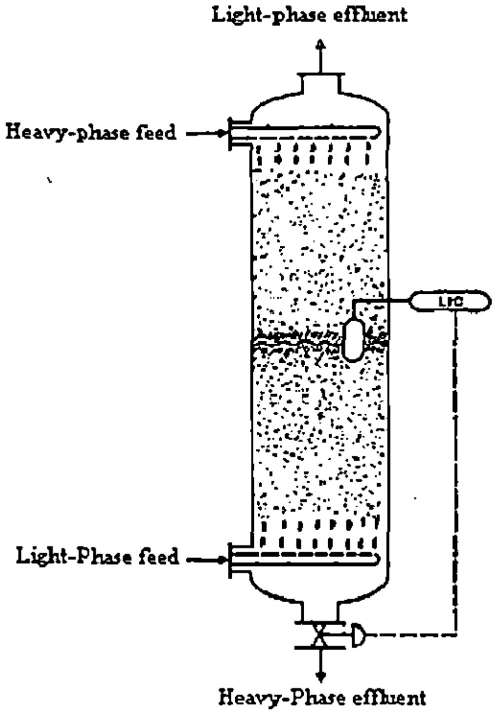

Fig 1.3 Spray –type extraction column

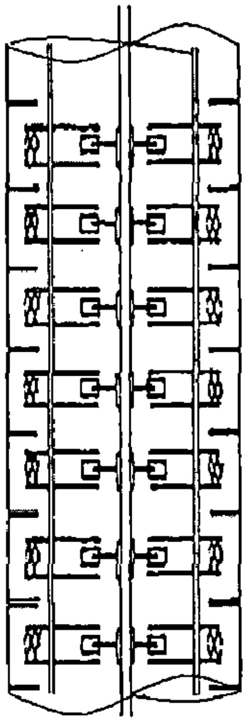

Fig 1. 4 Scheibel rotating – agitator tower

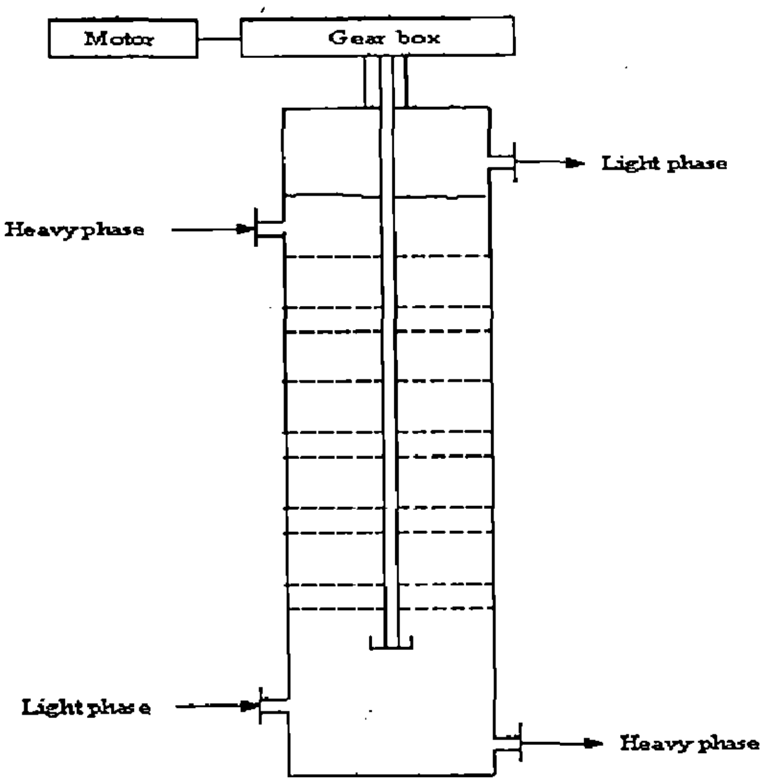

Fig 1.5 Karr reciprocating –plate tower

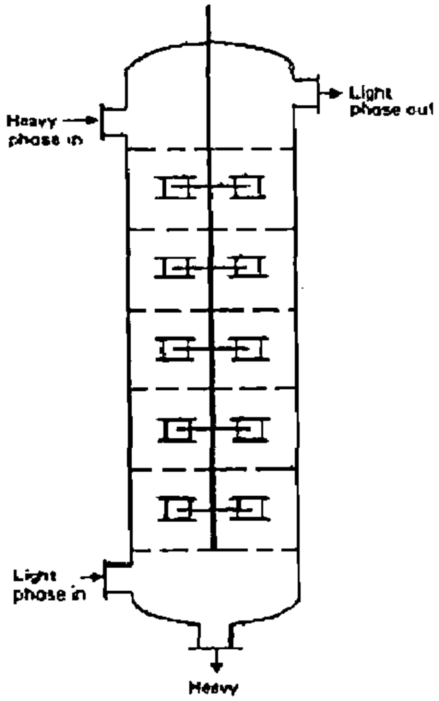

Fig 1.6 kühni column

CHAPTER-2

LITERATURE REVIEW

2.1 GENERAL

There is hardly any chemical process, which does not involve separation of liquid mixtures or recovery of valuable components from the reaction products. Liquid-liquid extraction processes have been increasingly used with advantage in these operations. The development of sound methods of equipment design has been the present trend.

In this chapter we will discuss briefly different literature available on liquid-liquid extraction process. Many papers have been published on the development of liquid-liquid extraction column and its process by different authors. In this chapter a brief description of their work is presented. These papers give information about the process description and extraction phenomena available in the literature. This chapter also presents the models developed by different research workers for the analysis of the performance of the extraction equipment. The works performed by different authors are compared and presented in a tabular form.

This chapter is divided into three sections. The first section gives the process description of different extraction equipment investigated by research workers. The second section describes the liquid extraction phenomena which takes place in laboratory and pilot plants. The third section gives mathematical models developed by research workers.

2.2 PROCESS DESCRIPTION

There are a number of research workers who have worked on liquid-liquid extraction process. They studied about various parameters and their effect on the process. The different processes available on liquid extraction are briefly explained below.

Wilke and Chang (1955) have described about diffusional process occurring in liquid systems during mass transfer. They found that the diffusional process depends upon temperature, pressure and nature of the components. They have also given many correlations for predicting diffusion coefficient of component. They have given correlations of diffusion coefficient assuming spherical molecules of diffusing component.

Baird and Lane (1973) have determined drop size and holdup in a reciprocating plate extraction column. For this purpose they have used four systems with the phases pumped to the column by a positive displacement metering pun with the heavy aqueous dispersed phase going to the top and the organic continuo phase to the bottom. Surge tanks were provided to prevent pulses from the pump fro being transmitted to the column. The column used for this purpose had cross sectiona area 19cm^2, 55% free area at the plates and 28.6 mm plate spacing. They have conducted experiments on kerosene-water, kerosene-mineral oil-water, kerosene-aqueous NaCl solution, and methyl isobutyl ketone-water.

Reissinger *et al.* (1978) have described the selection criteria for liquid-liquid extractors on the basis of available operating experience. The advantages and disadvantages of many extractors have been discussed. They have analyzed equipment selection on the basis of different parameters, efficiency, system, properties, cost consideration etc. The establishment of selection criteria must be preceded by an evaluation and classification of the different extractor types. An attempt has been made to establish a selection procedure where the most important parameters have been taken into consideration.

Graham and Tregurtha (1982) have presented the mechanism of the breakup of uncoalesced liquid-liquid dispersions in a sieve plate column. They have shown that the main mechanism of drop breakup for kerosene water system at low flow rate is the formation of thin jets caused by more than one drop being forced through the restrictions at the same time. The jets do not coalesce with one another and finally breakup into small droplets at distinct nodes. This results in a large number of very small drops after only a few plates resulting in high areas for mass transfer but low flooding capacities and a tendency for excessive entrainment.

Karr *et al.* **(1987)** have conducted experiments on reciprocating plate extraction column for measuring axial mixing coefficients. Axial mixing measurements were taken in single phase (water) in an open-type reciprocating plate column and two phase axial mixing was measured in a smaller column. Under single phase conditions, the axial dispersion coefficients were found to go through a minimum as the agitation level was increased. The results of the work were used in modeling the scale up of reciprocating columns. The existing empirical scale up equation is consistent with an assumption that the continuous phase mixing increased with column diameter but dispersed phase mixing remains unchanged

Rner *et al* **(1987)** have given a comprehensive design procedure for multi component solvent extraction. Their study describes the region of permissible solvent flow rates, for which the specified separation may be achieved using a finite number of theoretical stages, is first determined using an adaptation of the two-solute approach of Prochazka and Jiricny. The number of stages required to achieve the design separation at a set of solvent flow rates selected from the permissible region is then determined. This is done by systematically solving a series of specified operating problems until a configuration is found which satisfies the design separation.

Table 2.1 Mass transfer correlations

Phase	Relationship	Authors
Dispersed	$k_d = \frac{2D_d}{3r_d}$	Newman
Dispersed	$k_d = \frac{8.95D_d}{r_d}$	Kronig,Brink
Dispersed	$k_d = 3.75x10^{-3} pe_d \frac{D_d}{2r_d}$ $pe_d = \frac{r_d u_w}{D_d}$ (pe_d :peclect number of droplets)	Handlos, Baron
continuous	$k_c = \frac{2D_c}{\pi\tau}$ D_d ,D_c: molecular diffusion coefficients of the acid in dispersed phase and continuous phase ,respectively ; τ : contact time of the droplets	Higbie

Warner *et al* (1987) have given a comprehensive design procedure for multi component solven solute approach of Prochazka and Jiricny. The number of stages required to achieve the design separation at a set of solvent flow rates selected from the permissible region is then determined. This is done by systematically solving a series of specified operating problems until a configuration is found which satisfies the design separation.

Schugerl *et al* (1988) have given a brief description on reactive extraction and its classification into subtypes, after which the paper concentrates on the extraction of organic compounds only. The reactive extraction of salicylic acid with a secondary amine and NaOH is taken as an example. The equilibrium constants, overall mass transfer coefficients (evaluated in stirred cells and on fixed, freely suspended, and pulsed droplets), and the partial mass transfer coefficients for the separate phases are investigated. The effects of droplet volume, solute concentration, pH value, and the hydrodynamic state of the droplet on the overall and partial mass transfer coefficients are discussed and compared with mass transfer models from the literature(as shown in the table).

Veglio *et al* **(1996)** have studied of the design of a liquid-liquid extraction column for the possible test system Zn/D2EHPA has been carded out. The results show the behaviour of different reaction kinetic models and the effect of the mass transfer coefficients on the column design. A contamination factor has also been used to determine the effect of changing mass transfer coefficients on the liquid-liquid extraction performance. A sensitivity analysis has been carded out to determine which factors significantly influence the column design for a particular range of conditions. They conclude the following points

1. The chemical kinetic mode is proposed in the literature permit evaluation of the he column contactor height in limited regions of concentrations. Differences have been found when the models were used for ranges of concentrations not investigated experimentally but of interest in industrial application or for testing purposes.

2. The effect of the mass transfer coefficients on the column height has been investigated: the most important factor that influences the column height for extraction is the Zn 2+ mass transfer coefficient in the aqueous phase. Several reasons are presented to explain this behaviour.

3. Significant differences in the contactor height for diffusion and chemical kinetic models were found when extrapolation of the models is made (for high degrees of Zn 2+ extraction).

4. Contamination can seriously influence design. However, the largest Contribution to the column height is still due to the chemical reaction. This is Confirmed by the value of the Da number along the column height.

Waldley *et al.* (2000) have described drop formation in a Hi-Gee packed rotary contactor used for liquid-liquid systems. They have used narrow slot nozzles for injecting dispersed phase into a high voidage packing immersed in the continuous phase. The packing helps to maintain a small drop size, provide a large area for counter current flow and ensure that the phases flow in a radial direction. They have taken measurements of drop size for three systems: 1. TBP, kerosene, distilled water, KNO_3, water. For improving the effectiveness of contacting between liquid phases they have used a redesigned version constructed with narrow slot nozzle in place of peripheral circular nozzle injectors.

Baudot *et al.* (2001) have tested the extraction of aroma compounds from model aqueous feeds to sunflower oil in a hollow-fibre contactor. They have used a membrane based contactor that is fitted with a baffle in the middle to promote turbulence in the shell side. The geometry ensures cross flow of oil and aqueous feed flowing in the shell side and lumen side respectively, thus enhancing the mass transfer outside the fibres. They have shown that the stripping of the aroma compounds is more efficient when flowing the aqueous feed phase in the shell side than inside the fibres. They have concluded that the boundary layer in the aqueous feed is the limiting step for the mass transfer of lipophilic compounds.

Brodkorb. *et al* (2001)show the relation between mass transfer coefficients for ternary and quaternary liquid-liquid systems that can be experimentally obtained from relatively simple single drop experiments and the extraction performance of a pilot plant rotating disc contactor extraction column (RDC). For the ternary toluene-acetone- water system and relatively low holds up. Mass transfer coefficients were the same in the (RDC) as for single drops. However, a different picture was obtained for experiments where phenol was present either in the ternary or the quaternary system: it was not possible to simulate the pilot-plant mass balance operating lines with the mass transfer coefficients derived from the single drop experiments with the same solution. This finding is valid for acetone as well as phenol mass transfer. The reason for this is thought to be agitation-dependent interfacial tension effects on mass transfer coefficients, and perhaps also a change in the hydrodynamic condition inside the column when phenol is present since the hydrodynamic simulation-software used does not predict the effects 01 inhomogeneous hold-up conditions. A similar picture can be drawn for the experiments with additional contamination with SDS. Multi-component interactions between mass transfer coefficients for phenol and acetone seemed unimportant for the solute concentrations used (ca. I wt %).They repeated counter-current experiments (with solutions made up at different times) and showed a repeatability of concentration measurements of better than 95%, and number of plug flow transfer units was very similar, so experimental errors do not invalidate the findings.

Mauri *et al.* (2001) have described the process of solvent extraction of chromium and cadmium from contaminated soils by the use of water solute solvents. One of the most promising methods of separating metal ions is to complex them to a molecule (a ligand or chelator) that exhibits specific binding affinity for a toxic metal.

For the extraction of chromium from volcanic soil Diphenyl carbazide is used as both chelating agent and photometric indicator. For this purpose two types of solvents are used.

1. 50% water-50% ethanol solution
2. 99% water-1%ehanol solution

For cadmium extraction from contaminated soil, they have used 1,5-Diphenylthio carbazone as the chelating agent. Solvents used are

1. 99% distilled water-1% ethanol
2. 50% ethanol- 50% acetone

They finally concluded that soils contaminated with chromium and cadmium can effectively be remediate first by wetting them with water and then washing them with a 99% water-1% ethanol solution, which contains an appropriate chelator, namely diphenyl carbazide for chromium and 1,5-diphenylthio carbazone for cadmium with a 5 to 1 molar ratio between chelant and metal.

Desnoyer *et al* (2002) have carried out the experiment and analyze the drop size distributions of liquid–liquid dispersion in a stirred vessel at high phase ratio. Two liquid–liquid systems have been investigated: one at low and one at high coalescence rate. A sampling technique has been developed in order to measure the drop size distributions in the mixer with the help of a laser granulometer. A statistical approach has been attempted to derive the most probable drop size distribution in the mixer and the results have been compared with the experimental primary distributions. The comparison suggests that the energy dissipation cannot be considered as uniformly distributed in the mixer. The mean diameter of the distribution has been correlated to the global mechanical input power and to the volume phase fraction (phase ratio) for both systems in the frame of the classical

Hinze–Kolmogorov theory. The results show that for each volume fraction studied, the mean diameter of the dispersion is a decreasing power law of the Weber number with an exponent equal to .0:6 at low phase ratio. However, it appears that for both systems studied this exponent is a decreasing function of the phase ratio. This result reveals the existence of a more complex break-up mechanism with high phase ratio than that assumed in the theory which has to be discriminated from dampening effect of the dispersed phase upon the turbulent energy of the bulk phase. The study of the secondary distributions mean diameter seems to be in good agreement with the numerical predictions of Stone. The ratio between the mean diameters of the primary distribution to the satellite drop mean diameter is a growing function of the viscosity ratio.

Lisa *et al.* (2003) have analyzed the mass transfer operation in liquid-liquid extraction in both directions using the ternary systems: water-acetone-chloroform and water-acetone-toluene. The analysis was performed in an improved Lewis cell operating in continuous mode, made out of two baffled compartments equipped with separate driven agitators. The specific resistances on mass transfer were determined in the stirred or non-stirred phases, with the influence of the partition coefficient. The study reveals that the highest mass transfer resistances are located in the phase with the smaller equilibrium solute concentration, regardless of the mass transfer direction and the stirring intensity and the individual resistances are greater whether the mass transfer occurs from the phase having a higher equilibrium concentration than that with a smaller equilibrium, regardless of the phase stirring. The phase resistances are very different if the partition coefficients differ in a great extent from the unit.

2.3 LIQUID EXTRACTION PHENOMENA

Many papers have been published on model development and many correlations are given by research workers, which take into account the basic phenomena occurring during mass transfer in extraction column. These models and correlations include the basic mechanisms such as drop break-up, coalescence, contamination effects, drop size etc. In this section model equations and correlations are given which take into account the above mechanisms.

Baird and Lane (1973) have determined the drop sizes and hold-up in liquid-liquid systems in a 2-inch diameter reciprocating extraction column in the absence of mass transfer. They found that the sauter mean diameter depends on the product of plate amplitude and frequency and on the system properties. The developed model is proposed for the hold up, assuming the droplet diameter to depend on turbulent energy dissipation. The model is consistent with the experimental data if it is assumed that droplets in kerosene undergo hindered circulation while droplets in methyl isobutyl ketone circulate freely.

Slip velocity

$$\frac{U_d}{\phi} + \frac{U_c}{1-\phi} = V_s$$

Hold up

$$\frac{d(1-\phi)^3 g(\rho_d - \rho_c)}{\rho_c U_s^2} = \frac{150\phi}{Re} + 1.75$$

Mechanical power dissipation per unit volume

$$\Psi_1 = 10.8\rho_C (Af)^3$$

Gravitational power dissipation per unit volume

$$\Psi_2 = V_s g\phi\Delta\rho = g\Delta\rho\left(U_d + \frac{\phi}{1-\phi}U_c\right)$$

Drop diameter

$$d_{32} = 0.357\frac{\sigma^{0.6}}{\rho_c^{0.2}(\Psi_1 + \Psi_2)^{0.4}}$$

Baird and Shen (1984) have measured the dispersed phase holdup and flooding conditions in a 5cm diameter reciprocating plate extraction column. A simplified predictive model for holdup and flooding is developed assuming uniform hydrodynamics conditions throughout the column. The model is limited in application by the following factors:

- Mass transfer from dispersed to continuous phase (coalescence effect).
- Wet ability of plates by dispersed phase.
- Axial non-uniformity of hold up (particularly in high interfacial tension System).
- The use of exceptionally high frequencies or low amplitudes of agitation.

Interfacial Area

$$a = \frac{6\phi}{d_{32}}$$

Characteristic velocity

$$V_k(1-\phi) = U_c\left(\frac{1}{1-\phi} + \frac{L}{\phi}\right)$$

Where, $L = U_d / U_c$

Flooding condition occurs at

$$\left(\frac{dU_c}{d\phi}\right)_F = 0$$, which leads to the following equations.

$$\phi_F = \frac{\left(L^2 + 8L\right)^{1/2} - 3L}{4(1 - L)}$$

$$U_{cF} = V_k\left(1 - \phi_F\right)^2\left(1 - 2\phi_F\right)$$

$$U_{dF} = 2V_k\phi_F{}^2\left(1 - \phi_F\right)$$

Kumar and Hartland (1989) presented correlations of slip velocity and dispersed phase hold up for pulsed perforated plate column, Karr reciprocating plate column, rotating disc contactor and spray extraction column.

Pulsed perforated plate columns: They have proposed slip velocity in terms of physical properties, operating conditions and column dimensions on the following basis.

1. The slip velocity is a function of continuous and dispersed phase flow rates but not explicitly dependent on hold up.

2. The effect of continuous phase flow rate can be accounted for by the sum of continuous and dispersed phase superficial velocities $U_c + U_d$.

3. The pulsation velocity is correlating parameter for the amplitude and frequency effects.

4. ρ_c and μ_c do not vary much.

Hold up

$$\phi = 2.10 \times 10^6 \exp\left[44.53\left|Af - (Af)_{min}\right|\right] U_d{}^{0.86} \times \left(U_c + U_d\right)^{0.28}$$

$$\times \left(\Delta\rho\right)^{-0.30} \rho_d{}^{-0.93} \mu_d{}^{0.77} \varepsilon^{-0.56} l^{-0.56}$$

Slip velocity

$$V_s = k_1 \exp\left[k_2 \left|Af - (Af)_{min}\right|\right] \times \Delta\rho^{0.29} \rho_d^{0.67} \mu_d^{-0.66} \varepsilon^{0.44} l^{0.43}$$

Where,

$$k_1 = 6.84 \times 10^{-6} \text{ and } k_2 = -36.80$$

Karr reciprocating plate columns:

Hold up

$$\phi = \left[3.87 \times 10^3 + 3.71 \times 10^7 (Af)^3\right] U_d^{0.81} \times (U_c + U_d)^{0.32} \Delta\rho^{-0.98}$$

Slip velocity

It is assumed that V_s is only a function of $Af, \Delta\rho, \sigma, U_d$ and $U_c + U_d$.

$$V_s = \left[k_3 + k_4 \exp(-8.39Af)\right] \times \Delta\rho^{0.7} \sigma^{0.18} U_d^{0.25}$$

Where,

$$k_3 = -9.18 \times 10^{-3} \text{ and } k_4 = 2.42 \times 10^{-2}$$

Rotating disc contactors:

Hold up

$$\phi = \left[570.53 + 747.78\left(N^2 d_{disc}/g\right)^{1.28}\right] \times \left[d_s^2 l^2 \rho_c g/\left(d_{co}^2 \sigma\right)\right]^{-0.45} (\Delta\rho/\rho_c)^{-0.58}$$

$$\times \left[\mu_c g^{0.25}/\left(\rho_c^{0.25} \sigma^{0.75}\right)\right]^{0.85} \left[U_d \rho_c/(g\sigma)\right]^{0.22} \times (1 + U_c/U_d)^{0.35}$$

Slip velocity: The velocity in rotating disc columns is assumed to be a function of $\rho_c, \Delta\rho, \mu_c, \mu_d, \sigma, N, U_d, U_c + U_d, d_{co}, d_s, d_{disc}, l$ and g.

$$u_s \rho_c^{1/4}/\left(g^{1/4}\sigma^{1/4}\right) = \left[k_6 + k_7 \exp\left(-1.28N^2 d_{disc}/g\right)\right] \times (\Delta\rho/\rho_c)^{0.52}$$

$$\left[\mu_c g^{0.25}/\left(\rho_c^{0.25}\sigma^{0.75}\right)\right]^{-0.45} \times \left(d_{disc}^2 \rho_c g/\sigma\right)^{0.02} (l/d_{disc})^{1.03}$$

$$(d_{disc}/d_{co})^{0.51}\left[U_d \rho^{0.25}/\left(g^{0.25}\sigma^{0.25}\right)\right]^{0.22}$$

Where,

$$k_6 = 5.11\times10^{-2} \text{ and } k_7 = 0.20$$

Spray columns: In the loose dispersion region it is assumed that it is a function of $d_{32}, \Delta\rho, \rho_c, \mu_c, U_d, U_c + U_d$ and g.

Hold up

$$\phi = 3.78\left(d_{32}\rho_c^{2/3} g^{1/3}/\mu_c^{2/3}\right)^{-0.82}\left(\Delta\rho/\rho_c\right)^{-0.80}\times\left[U_d\rho_c^{0.33}/(g\mu_c)^{0.33}\right]^{0.47}$$

$$\left(1+U_c/U_d\right)^{0.27}$$

Slip velocity

$$V_s\rho_c^{1/3}/\left(g^{1/3}\mu_c^{1/3}\right) = 0.48\left(d_{32}\rho_c^{2/3} g^{1/3}/\mu_c^{2/3}\right)^{0.70}\left(\Delta\rho/\rho_c\right)^{0.78}$$

$$\times\left[U_d\rho_c^{0.25}/(g\mu_c)^{0.33}\right]^{0.8}\left(1+U_c/U_d\right)^{-0.3}$$

They have compared the values of u_s obtained from the present models and other correlations and found that the developed models hold reasonable consistency for most of the systems.

Dongaonkar *et al.* (1991) have given correlations of mass transfer coefficients, slip velocity and back-mixing coefficient in a kühni column. The given correlations apply to cases of axial dispersion for the system methyl isobutyl ketone-water-acetic acid. The study shows that backing mixing of the continuous phase is appreciable, while that of the dispersed phase is negligible.

Overall mass transfer coefficient

$$K_{od} = N_{od} d_{32} Q_d\, n/6\phi V_{ox}$$

Slip velocity

$$V_s = U_c/(1-\phi) + U_d/\phi$$

Back-mixing coefficient

$$\alpha_C = -0.346 + 0.063\left[\frac{Nd_{im}(1-\phi)}{U_c}\right]\left(\frac{h_{im}}{d_{im}}\right)^{0.067}\left(\frac{d_{im}}{d_{co}}\right)\varepsilon^{0.587}$$

Das et al **(1998)** have studied generalized transient back flow model to predict the transient tracer concentration in a multistage extraction column. The model does not assume any extra stage at the end of the contactor and is based on unified formulation. The solution can he obtained in a straight forward way by using the linear operator theoretic approach as opposed to Laplace transform. They assumed that Extractor is assumed to consist of N perfectly mixed stages of equal volume V with net volumetric flow rate F , back flow f, and carried out material balance for stage 1 to N then solved the tridiagonal matrix for different cases

$$V\frac{dc_1}{dt} = FC_0 - (F+f)C_1 + fC_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\frac{dC}{d\theta} = AC + B$$

Where A is tridiagonal matrix (jacobi matrix) B is the column matrix.

Godfrey *et al* **(1991)** have studied a wide variety of equations exists for relating the superficial flow velocities and dispersed phase hold-up in liquid—liquid extraction equipment. Such equations are helpful in estimating maximum throughputs and for correlating hold-up conditions at lower throughputs. Many of the equations proposed are similar in nature to one based on Richardson and Zaki's equation for fluidized systems of monosize rigid particles. It is shown that all common types of extraction equipment demonstrate hydrodynamic behavior which can be correlated by the equation:

$$V_{slip} = V_k(1-x)^m$$

for $x < 0.3$ typically (a normal condition) and where $0 < m < 4$ approximately.

Values of m are correlated for the packed, RDC, pulsed sieve plate, and reciprocating plate columns as:

$$m = k(\rho_c d V_k / \mu_c)^n$$

And it is considered that m depends on uniformity of flow distribution and on the nature of dependence of a drop drag coefficient on Re_K. Empirical correlations of the characteristic velocity V_K are proposed.

Baudot *et al.* (2001) have introduced extraction of aroma compounds from aqueous feeds in a membrane based hollow fiber contactor. They have presented concentration profiles of aroma compounds with respect to time assuming that the feed streams are perfectly mixed. The relative concentration, that is, the ratio between the concentration at a certain time t and the initial concentration of aroma compound in the aqueous feed is given by

$$\frac{C_W(t)}{C_{0,W}} = \frac{1}{1+V_f}\left[V_f + \exp\left\{-\frac{1-\exp(-N_0(1-q))}{1-Q_c\exp(-N_0(1-q))}\right\}\times(1+V_f)\frac{Q_W}{V_W}t\right]$$

Where,

$$N_0 = \frac{K_O A_{OV}}{Q_W} = NTU$$

$$q = \frac{Q_W}{Q_O P}$$

$$V_f = \frac{V_W}{V_O P}$$

P = oil/water partition coefficient

C_w = concentration of aroma compounds in aqueous feed, $kg \cdot m^{-3}$

V_w = aqueous feed volume, m^3

Q_0 = volumetric flow rate of sunflower oil feed, $m^3 \cdot s^{-1}$

A_{0V} = contact area between two phases, m^2

From the experimental results three conclusions are drawn.

1. The relative concentration of the aroma compounds in the aqueous feed first decreases exponentially and eventually reached a plateau when the equilibrium between the two phases was reached.
2. A higher oil/water partition coefficient led to a faster concentration decrease as a function of time.
3. The higher aqueous the feed flow, the faster the mass transfer between the two phases.

2.4 MODEL DEVELOPMENT

The different mathematical models developed by research workers which describe the steady state and unsteady state behavior of extraction column, are summarized below.

Baird and Shen (1984) have modeled for flooding conditions in a reciprocating plate extraction column. They have noticed that when mass transfer occurs from $c \rightarrow d$, the model appears to give a reasonably close prediction of flooding conditions. When mass transfer direction is reversed $(d \rightarrow c)$ enhanced droplet coalescence leads to larger drops, lower holdups and higher flooding velocities than expected from our model. If plates are preferentially wet by the dispersed phase, holdups are reduced relative to the model predictions. The present model can form a partial basis of column design provided the system properties are known.

Assumptions

1. Uniform hydrodynamic conditions throughout the column.
2. The model considers Sauter mean drop diameter.

RPC holdup model

$$d_{32} = 0.36\frac{\sigma^{0.6}}{\Psi^{0.4}\bar{\rho}^{0.2}}$$

$$\Psi = \frac{2\pi^2}{3}\left(\frac{1-\varepsilon^2}{l C_0{}^2\varepsilon^2}\right)\bar{\rho}(Af)^3$$

$$U_s = \frac{1-\phi}{K^{2/3}\phi^{1/3}}d_{32}\left[\frac{g^2\Delta\rho^2}{\rho_c\mu_c}\right]^{1/3}$$

RPC flooding model

$$U_c = \frac{(1-\phi)^2 V^*}{\phi^{1/3}(1-L)+L\phi^{-2/3}}$$

$$\phi_F = \frac{(9L^2+54L+1)^{1/2}-7L-1}{10(1-L)}$$

The model can form a partial basis of column design provided the system properties are known.

Khani *et al.* (1988) have described a drop population balance model, taking into account the basic mechanisms to which the drops are subject: transport, breakage, coalescence, and mass transfer that is applied to the simulation of a disks and rings pulsed column. The simulation results are compared with steady state holdup profiles and profiles of concentrations of solute in both phases. Hydrodynamics and mass transfer are described from the bottom to the top of the column. The model relies on a drop population balance that leads to the size distributions at every level in the column.

Assumptions

1. The model takes into account the basic mechanisms to which the drops are subject: transport, breakage, coalescence, and mass transfer.
2. Every drop breaks to give three equal sized drops.
3. The mass transfer coefficient depends only on drop diameter.

Characteristic velocity

$$V_K(d) = K_V(\rho_c/\mu_c)^{1/3}(g\Delta\rho/\rho_c)^{2/3}(1 - E_0/6)d/4.2$$

Drop generation

$$P(h,d) = P_{gb}(h,d) + P_{gc}(h,d)$$

Average concentration in drops

$$\frac{\partial}{\partial t}\left[X^*(h,d)P(h,d)\right] = -\frac{\partial}{\partial h}\left[X^*(h,d)P(h,d)V_d(h,d)\right] + \frac{\partial}{\partial h}\left[D_d\frac{\partial}{\partial h}\left\{X^*(h,d)P(h,d)\right\}\right] + S' + \int_0^\infty T_x\delta x$$

Concentration in continuous phase

$$\frac{\partial}{\partial t}\left[(1-\phi)y(h)\right] = -\frac{\partial}{\partial h}\left[(1-\phi)V_c y(h)\right] + \frac{\partial}{\partial h}\left[D_c(h)\frac{\partial}{\partial h}\left\{(1-\phi)y(h)\right\}\right] - S$$

Dispersion coefficient

$$D_c = 2.36\times10^{-2}Af$$

Mean concentration in dispersed phase

$$X^{**}(h) = \frac{1}{\phi(h)}\int_0^{d_{max}} X^*(h,d)P(h,d)\delta d$$

The mathematical model describes the behavior of a disks and rings pulsed column. The simulated results give satisfactorily the gradients of holdup and concentrations of solute in both phases.

Dongaonkar *et al.* (1991) have determined concentration profiles in both phases for the system methyl isobutyl ketone-water-acetic acid in a kühni extraction column. They estimated mass transfer and back mixing parameters from the concentration profiles in backflow model. They considered axial dispersion to occur in one or both phases. They collected samples for concentration profile measurement and photographs of the droplets were taken during steady state to determine drop size. The dispersed phase holdup was determined using drainage method.

Assumptions

1. The model assumes axial dispersion in both phases.
2. Back mixing occurs in continuous phase.

Solute concentration

$$X_{eq} = \left(1.7428 - 0.0701Y + 0.0027Y^2\right)Y$$

In steady state tracer injection the tracer concentration C_n at any upstream stage n related to that at the injection C_0 is given by

Tracer concentration at stage n

$$C_n = C_0\left(\frac{\alpha_c}{1+\alpha_c}\right)^n$$

Where,

C_n = Solute concentration at stage n

C_0 = Solute concentration in feed

Result indicates that dispersed phase back mixing is negligible. The correlation predicted the experimental backing parameter values to within ±20%.

Baudot *et al.* **(2001)** have tested the extraction of aroma compounds from model aqueous feeds to sunflower oil in a hollow-fiber contactor. The mass transfer between the two phases was modeled based on the resistances in series approach. A correlation describing the mass transfer with a transverse flow in the shell is proposed. Aroma concentrates are widely used in food industry to improve the flavor of formulated foods. Natural-labeled aroma compounds are generally found at very low concentration in natural raw materials. Therefore, a cost-effective and efficient extraction step constitutes a major challenge for the productions of such additives by the flavour industry. The physico-chemical properties are mainly concerned in order to recover odor-active organic substitutes.

Assumptions

1. The mass loss due to flavor sorption on the membrane material is negligible when carrying out oil-water stripping experiments.
2. The oil-water partition coefficient of each individual aroma compound is not influenced by the presence of the other compounds.
3. The fluid streams are perfectly mined between the two chambers.

Overall mass transfer coefficient

$$K_O = \frac{Q_W}{(1-q)A_{OV}} \ln \frac{1-\beta q}{1-\beta}$$

Where,

$$\beta = -\ln\left[\frac{C_W(t)}{C_W{}^0}(1-V_f)-V_f\right]\times\left(\frac{V_W}{(1+V_f)Q_W \times t}\right)$$

C_W = Concentration of aroma compounds in aqueous feed, $kg \cdot m^{-3}$

Modeling of mass transport between two phases

$$Sh_F = \frac{K_F \cdot d_F}{D_F} = 1.62\left(\frac{d_F}{L} \cdot Re_F \cdot Sc_F\right)^{1/3}$$

Where,

$$Re_F = \frac{4Q_F}{\eta_F n \pi d_F}$$

$$Sc_F = \frac{\eta_F}{D_F}$$

$$U_s = \frac{Q_s}{\pi L} \frac{2\ln(d_a/d_i)}{d_a - d_i}$$

Where, subscript F refers to fluid flowing in lumen side of fibers

n = number of hollow fibers

L = length of hollow fibers, m

It is shown that the stripping of the aroma compounds is more efficient when flowing the aqueous feed phase in the shell side than inside the fibers.

Tudose and Apreotesei (2001) have used a ternary system (water-acetone-CCl_4) to determine specific fluxes, the driving forces and individual and overall mass transfer coefficients by measuring the inflow and outflow acetone concentrations in the two phases. They performed experiments in an improved Lewis cell in continuous and batch operation modes. The Lewis cell provides mixing of the liquids apart in its two compartments. Some devices which are mounted inside the compartments of the cell, moderate the interfacial turbulence. The advantage of Lewis cell consists in the possibility to be applied for any system containing an initial solvent and a solute, from which the solute is extracted with another solvent. The statistical analysis of the experimental data allowed for the development of several criterial equations, which can be used to calculate the individual and overall mass transfer coefficients. The criterial equations have the following general form.

$$Sh = b\,Re_{ag}^{\ P}\,Sc^{1/3}$$

Where,

$$Sh = dk/D$$

$$Re_{ag} = Nd^2\rho/\mu$$

$$Sc = \eta/D$$

They have found that for $Re_{ag} > 11000$ the value of the individual mass transfer coefficients remains constant. The flux of the transferred solute is higher if the transfer occurs from the organic to the aqueous phase.

Brodkorb *et al.* (2003) have obtained single drop mass transfer data for the ternary and quaternary systems: toluene-acetone-water and toluene-acetone-phenol-water. The results obtained from experiments were assumed using a single solute mass transfer model and a non equilibrium model based on Maxwell-Stefan equations. In both cases empirical correlations of mass transfer coefficients that include contamination effects were used. It is considered that the phenol is sufficiently interficially-active to behave like a surfactant and this has major impact on mass transfer coefficients and hydrodynamic assumptions made for the non-equilibrium model.

<u>Assumptions</u>

1. The continuous phase is considered to be a semi-infinite continuum.
2. The total molar flux across the interface and the component fluxes are considered to be quasi steady-state for a defined finite time interval.

3. The molar flows across the interface, as well as the concentrations at the interface and, therefore, the phase equilibrium relationships are also considered in quasi steady-state fashion as the component fluxes.

4. System pressure and temperature are considered to be constant and equal through the system.

Sherwood correlation

$$\mathrm{Sh}_c = \frac{2}{\sqrt{\pi}}\sqrt{\alpha}\sqrt{\mathrm{Pe}_c}$$

Where,

$$\alpha = \left[1 + \frac{2 + 3(\mu_d/\mu_c) + m}{1 + (\rho_d\mu_d/\rho_c\mu_c)^{0.5}}\frac{1.45}{\mathrm{Re}^{0.5}}\right]^{-1}$$

α Represents the ratio of drop interfacial and terminal velocities which results in

$$\mathrm{Sh}_c = \left(\frac{2}{\sqrt{\pi}}\right)\left[1 + \frac{2 + 3(\mu_d/\mu_c) + m}{1 + (\rho_c\mu_d/\rho_c\mu_c)^{0.5}}\frac{1.45}{\mathrm{Re}^{0.5}}\right]^{-0.5} \mathrm{Re}^{0.5}\,\mathrm{Sc}_c{}^{0.5}$$

For rigid drops

$$\mathrm{Sh}_{\mathrm{ccrit}} = 2.43 + 0.773\,\mathrm{Re}^{0.5}\,\mathrm{Sc}_c{}^{0.33} + 0.0103\,\mathrm{Re}\,\mathrm{Sc}_c{}^{0.33}$$

Mass transfer coefficient

$$k_d = -\left(\frac{d}{6t}\right)\ln\left[\left(\frac{6}{\pi^2}\right)\cdot\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{4n^2\pi^2 D_o t}{d^2}\right)\right]$$

Effective diffusivity

$$D_{ef} = \frac{d\alpha V_T}{2048\left(1 + \dfrac{\mu_d}{\mu_c}\right)}$$

The use of the multicomponent single drop mass transfer non-equilibrium model to simulate the experimental data for single and multiple solute mass transfer showed that the surface active nature of solutes must be accounted for and the contamination factor model for mass transfer coefficients can be used for this purpose.

2.5 OBJECTIVE OF STUDY

On the basis of the above literature review, we have aimed the following objectives.

1. To develop the simple mathematical model for a kühni column,
2. To solve the mathematical model by using MATLAB 6.5 software.
3. To validate the model with the available experiment results in the literature,
4. To study the effect of various parameters on the performance of the column.

CHAPTER-3

MODEL DEVELOPMENT

3.1 INTRODUCTION

This chapter describes the development of a mathematical model for a counter current Kühni liquid-liquid extraction column applicable to remove acetone from water by toluene. The model takes into account the hydrodynamics as well as mass transfer aspects. The hydrodynamic model assumes that the dispersed phase drops behave as spheres of uniform diameter under prevailing conditions of agitation. The model assumes a uniform drop diameter and thus, the number of equations that need to be solved is much smaller than that for drop population models. Many important aspects of extraction-column dynamics may be investigated with sufficient accuracy using a simpler approach, based on a hydrodynamic model relying on the Sauter mean diameter, which is an accepted measure of the average diameter of a dispersed phase drop. The model is intended to be applied to simulate conditions for a Kühni extraction column, in which the perforated plate between each stage can control the droplet holdup by the percentage of open area in the plate The droplet size can be controlled by the speed and diameter of the impeller, while the circulation rate can be controlled by the design of the width of the impeller.

3.2 DYNAMIC MODEL

This section describes the formulation of mathematical model equations for a Kühni column based on the Law of conservation of mass.

3.2.1 Assumptions

The mathematical model for a Kühni column depends on the following simplifying assumptions.

a) The radial variations of the mean velocity and the concentrations of each phase are negligible.

b) The phase volume flow rates are independent of mass transfer and solute concentration.

c) The dispersed phase drops behave as spheres of a uniform diameter.

d) The model describes the process occurring in the dispersion layer of an extraction column. The length of this dispersion layer is fixed.

3.2.2 Choice of Control Volume

The control volume of the extraction column is taken to be a small section of the column where dispersion prevails. The dispersion is assumed to occur only in between $h = 0^+$ and $h = L^-$ of the extraction column.

3.2.3 Modeling of Hydrodynamics

Since the dispersed phase is assumed to consist of spherical drops of uniform diameter, the mean drop size in dispersion is expressed as the Sauter mean drop diameter.

$$d_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$$

Where,

d_i = Individual drop diameter

n_i = Number of drops with this diameter

The direction of movement of the dispersed phase coincides with the positive vertical direction. The mass flow rate consists of two terms: due to convective transport and due to dispersive transport.

$$\dot{m} = \rho VS - D\frac{\partial(S\rho)}{\partial h} \tag{3.1}$$

$$\Rightarrow Q\rho = \rho VS - D\frac{\partial(S\rho)}{\partial h} \tag{3.2}$$

For dispersed phase (assuming incompressible fluid) equation (3.2) can be written as

$$Q_d\rho_d = \rho_d V_d S\varepsilon - D_d\frac{\partial(S\varepsilon\rho_d)}{\partial h}$$

$$\Rightarrow Q_d = V_d S\varepsilon - D_d S\frac{\partial\varepsilon}{\partial h} \tag{3.3}$$

At any level h in the column

$$Q_d(h) = S\varepsilon(h)V_d(h) - SD_d(h)\frac{\partial\varepsilon(h)}{\partial h} \tag{3.4}$$

The flow rate of continuous phase can be obtained by assuming incompressible flow in the material balance between cross sections $h = 0$ and $h = L$.

$$Q_c - Q_d = Q_{c,in} - Q_{d,out} = Q_{c,out} - Q_{d,in} = \Delta Q \tag{3.5}$$

Volumetric flow rate of continuous phase:

$$Q_c = S(1-\varepsilon)V_c$$

$$\Rightarrow V_c = \frac{Q_c}{S(1-\varepsilon)} \tag{3.6}$$

The slip velocity is given by:

$$V_d + V_c = V_s(\varepsilon) \tag{3.7}$$

Since the cross sectional area is constant, it is possible to introduce new variables.

$$U_i = Q_i / S$$

Where i =phase i.e. continuous or dispersed

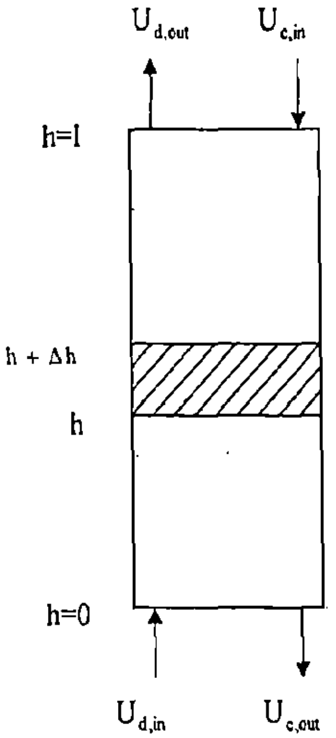

Fig. 3.1 Simplified Diagram with Input and Output Velocities

Thus, equation (3.4) reduces to

$$U_d(h) \cdot S = S\varepsilon(h) \cdot V_d(h) - SD_d(h) \cdot \frac{\partial \varepsilon(h)}{\partial h}$$

$$\Rightarrow U_d(h) = \varepsilon(h) V_d(h) - D_d(h) \frac{\partial \varepsilon(h)}{\partial h} \qquad (3.8)$$

Equation (3.5) reduces to

$$SU_c - SU_d = SU_{c,in} - SU_{d,out} = SU_{c,out} - SU_{d,in} = \Delta(SU)$$

$$\Rightarrow U_c - U_d = U_{c,in} - U_{d,out} = U_{c,out} - U_{d,in} = \Delta U \tag{3.9}$$

Equation (3.6) reduces to

$$V_c = \frac{Q_c}{S(1-\varepsilon)} = \frac{SU_c}{S(1-\varepsilon)} = \frac{U_c}{1-\varepsilon}$$

$$\Rightarrow V_c = \frac{U_c}{1-\varepsilon} \tag{3.10}$$

Consider a small elemental volume of cross sectional area S and height Δh (Fig. 3.1).

Conservation of mass:

$$\left[VS\rho - DS\frac{\Delta\rho}{\Delta h}\right]_h - \left[VS\rho - DS\frac{\Delta\rho}{\Delta h}\right]_{h+\Delta h} = S(\Delta h)\frac{\Delta\rho}{\Delta t}$$

For dispersed phase, the above equation reduces to

$$\left[V_d S\rho_d\varepsilon - D_d S\frac{\Delta(\rho_d)}{\Delta h}\right]_h - \left[V_d S\rho_d\varepsilon - D_d S\frac{\Delta(\rho_d\varepsilon)}{\Delta h}\right]_{h+\Delta h} = S(\Delta h)\frac{\Delta(\rho_d\varepsilon)}{\Delta t}$$

Since the fluid is incompressible,

$$\left[V_d\varepsilon - D_d\frac{\Delta\varepsilon}{\Delta h}\right]_h - \left[V_d\varepsilon - D_d\frac{\Delta\varepsilon}{\Delta h}\right]_{h+\Delta h} = (\Delta h)\frac{\Delta\varepsilon}{\Delta t}$$

$$\Rightarrow \frac{\Delta\varepsilon}{\Delta t} = \frac{1}{\Delta h}D_d\left[\left.\frac{\Delta\varepsilon}{\Delta h}\right|_{h+\Delta h} - \left.\frac{\Delta\varepsilon}{\Delta h}\right|_h\right] - \frac{1}{\Delta h}\left[V_d\varepsilon|_{h+\Delta h} - V_d\varepsilon|_h\right]$$

On taking the limits as $\Delta t \to 0$ and $\Delta h \to 0$, we get

$$\frac{\partial\varepsilon}{\partial t} = -\frac{\partial(V_d\varepsilon)}{\partial h} + \frac{\partial}{\partial h}\left(D_d\frac{\partial\varepsilon}{\partial h}\right) \tag{3.11}$$

Substitution of equation (3.8) into equation (3.9) gives

$$U_c = \Delta U + U_d = \Delta U + \varepsilon V_d - D_d\frac{\partial\varepsilon}{\partial h} \tag{3.12}$$

From equation (3.7), (3.10), (3.12)

$$V_d = (1-\varepsilon)V_s(\varepsilon) - \Delta U + D_d \frac{\partial \varepsilon}{\partial h} \tag{3.13}$$

Dispersion is assumed to occur between $h = 0^+$ and $h = L^-$.

$$\left[\begin{array}{l}\text{Mass flow rate of dispersed phase} \\ \text{due to Convectional at } h = 0^-\end{array}\right] = \left[\begin{array}{l}\text{Mass flow rate of dispersed phase due to} \\ \text{Convectional and dispersion at } h = 0^+\end{array}\right]$$

$$[SV_d\varepsilon\rho_d]_{h=0^-} = [SV_d\varepsilon\rho_d]_{h=0^+} + \left[-D_d S\frac{\partial(\varepsilon\rho_d)}{\partial h}\right]_{h=0^+}$$

$$\Rightarrow [U_d]_{h=0^-} = [\varepsilon V_d]_{h=0^+} + \left[-D_d\frac{\partial \varepsilon}{\partial h}\right]_{h=0^+}$$

$$\Rightarrow U_{d,in} = \varepsilon V_d - D_d\frac{\partial \varepsilon}{\partial h} \tag{3.14}$$

<u>Boundary conditions:</u>

At $h = L$,

$$\frac{\partial \varepsilon}{\partial h} = 0 \tag{3.15}$$

Equation (3.8) can be written as

$$U_{d,out} = \varepsilon V_d \quad \text{(Applying equation (3.15))}$$

$$= \varepsilon(V_s - V_c) \quad \text{(From equation (3.7))}$$

$$= \varepsilon\left(V_s - \frac{U_{c,in}}{1-\varepsilon}\right) \quad \text{(Applying equation (3.10))} \tag{3.16}$$

From equation (3.9)

$$U_{c,out} = U_{c,in} + U_{d,in} - U_{d,out} \tag{3.17}$$

3.2.4 Modeling of Mass Transfer

Molar flow rate of solute is due to convective and dispersive contribution.

$$\text{Molar flow rate of solute} = SVC - DS\frac{\partial C}{\partial h}$$

Where,

C =solute concentration (kg mol/m^3)

For continuous phase:

$$Q_Y = SV_cY(1-\varepsilon) + SD_c\frac{\partial[(1-\varepsilon)Y]}{\partial h} \tag{3.18}$$

For dispersed phase:

$$Q_X = SV_dX\varepsilon + SD_d\frac{\partial[\varepsilon X]}{\partial h} \tag{3.19}$$

The mass transfer in an arbitrary elemental volume of column of cross sectional area S and height Δh can be expressed as;

In dispersed phase: $S\Delta haK_X(X^* - X)$

In continuous phase: $S\Delta haK_Y(Y - Y^*)$ (3.20)

Consider a small elemental volume of the column of cross sectional area S and height Δh in the interval $0 < h < L$ as shown in Fig. 3.1.

Conservation of mass:

For dispersed phase:

$$S(\Delta h)\frac{\Delta(\varepsilon X)}{\Delta t}=\left[V_dS\varepsilon X-D_dS\frac{\partial(\varepsilon X)}{\partial h}\right]_h-\left[V_dS\varepsilon X-D_dS\frac{\partial(\varepsilon X)}{\partial h}\right]_{h+\Delta h}-S(\Delta h)aK_X\left(X^*-X\right)$$

$$\Rightarrow\frac{\Delta(\varepsilon X)}{\Delta t}=-\frac{\left[V_d\varepsilon X\big|_{h+\Delta h}-V_d\varepsilon X\big|_h\right]}{\Delta h}+\frac{\left[D_d\frac{\partial(\varepsilon X)}{\partial h}\Big|_{h+\Delta h}-D_d\frac{\partial(\varepsilon X)}{\partial h}\Big|_h\right]}{\Delta h}-aK_X\left(X^*-X\right)$$

On taking limits as $\Delta t\rightarrow 0$ and $\Delta h\rightarrow 0$, we get

$$\frac{\partial[\varepsilon X]}{\partial t}=-\frac{\partial}{\partial h}[V_d\varepsilon X]+\frac{\partial}{\partial h}\left(D_d\frac{\partial[\varepsilon X]}{\partial h}\right)+aK_X\left(X^*-X\right) \tag{3.21}$$

Similarly for continuous phase

$$S(\Delta h)\frac{\Delta(Y(1-\varepsilon))}{\Delta t}=\left[-V_cS(1-\varepsilon)Y-D_cS\frac{\partial(Y(1-\varepsilon))}{\partial h}\right]_h-\left[-V_cS(1-\varepsilon)Y-D_cS\frac{\partial(Y(1-\varepsilon))}{\partial h}\right]_{h+\Delta h}$$

$$-S(\Delta h)aK_X\left(X^*-X\right)$$

$$\Rightarrow\frac{\Delta((1-\varepsilon)Y)}{\Delta t}=\frac{\left[V_c(1-\varepsilon)Y\big|_{h+\Delta h}-V_c(1-\varepsilon)Y\big|_h\right]}{\Delta h}+\frac{\left[D_c\frac{\partial((1-\varepsilon)Y)}{\partial h}\Big|_{h+\Delta h}-D_c\frac{\partial((1-\varepsilon)Y)}{\partial h}\Big|_h\right]}{\Delta h}$$

$$-aK_X\left(X^*-X\right)$$

On taking limits as $\Delta t\rightarrow 0$ and $\Delta h\rightarrow 0$, we get

$$\frac{\partial[(1-\varepsilon)Y]}{\partial t}=\frac{\partial}{\partial h}[V_c(1-\varepsilon)Y]+\frac{\partial}{\partial h}\left(D_c\frac{\partial[(1-\varepsilon)Y]}{\partial h}\right)-aK_X\left(X^*-X\right) \tag{3.22}$$

At $h = 0$,

$$\left[\begin{array}{l}\text{Molar flux of dispersed phase}\\ \text{due to plug flow at } h = 0^{-}\end{array}\right] = \left[\begin{array}{l}\text{Molar flux of dispersed phase}\\ \text{due to plug flow and dispersion}\\ h = 0^{=}\end{array}\right]$$

$$\left[\varepsilon X V_d\right]_{h=0^-} = \left[\varepsilon X V_d - D_d \frac{\partial(\varepsilon X)}{\partial h}\right]_{h=0^+}$$

$$\Rightarrow X_{in} U_{d,in} = \varepsilon V_d X - D_d \frac{\partial(\varepsilon X)}{\partial h}$$

At $h = 0$,

$$X_{in} U_{d,in} = \varepsilon V_d X - D_d \frac{\partial(\varepsilon X)}{\partial h}$$

$$\frac{\partial[(1-\varepsilon)Y]}{\partial h} = 0 \tag{3.23}$$

At $h = L$,

[Molar flux of continuous phase at $h = L^{+}$] = [Molar flux of continuous phase at $h = L^{-}$]

$$\left[(1-\varepsilon)YV_c\right]_{h=l^+} = \left[(1-\varepsilon)YV_c - (-)D_c \frac{\partial((1-\varepsilon)Y)}{\partial h}\right]_{h=l^-}$$

$$\Rightarrow Y_{in} U_{c,in} = (1-\varepsilon)V_c Y + D_c \frac{\partial((1-\varepsilon)Y)}{\partial h}$$

<u>Boundary Conditions:</u>

At $h = L$,

$$Y_{in} U_{c,in} = (1-\varepsilon)V_c Y + D_c \frac{\partial((1-\varepsilon)Y)}{\partial h}$$

$$\frac{\partial[\varepsilon X]}{\partial h} = 0 \tag{3.24}$$

Table 3.1 summarizes the Model Equations as given below.

Table 3.1 Non linear Partial differential Equations for Dynamic Model

$$\frac{\partial \varepsilon}{\partial t} = -\frac{\partial (V_d \varepsilon)}{\partial h} + \frac{\partial}{\partial h}\left(D_d \frac{\partial \varepsilon}{\partial h}\right)$$

$$V_d = (1-\varepsilon)V_s(\varepsilon) - \Delta U + D_d \frac{\partial \varepsilon}{\partial h}$$

$$V_c = V_s - V_d$$

$$\frac{\partial[\varepsilon X]}{\partial t} = -\frac{\partial}{\partial h}[V_d \varepsilon X] + \frac{\partial}{\partial h}\left(D_d \frac{\partial[\varepsilon X]}{\partial h}\right) + aK_X (X^{*} - X)$$

$$\frac{\partial[(1-\varepsilon)Y]}{\partial t} = \frac{\partial}{\partial h}[V_c (1-\varepsilon)Y] + \frac{\partial}{\partial h}\left(D_c \frac{\partial[(1-\varepsilon)Y]}{\partial h}\right) - aK_X (X^{*} - X)$$

Boundary Conditions	
At h = 0	At $h = L$
$U_{d,in} = \varepsilon V_d - D_d \frac{\partial \varepsilon}{\partial h}$ $V_{d,in} = \frac{U_{c,in}}{\varepsilon}$ $X_{in} U_{d,in} = \varepsilon V_d X - D_d \frac{\partial(\varepsilon X)}{\partial h}$ $\frac{\partial[(1-\varepsilon)Y]}{\partial h} = 0$	$\frac{\partial \varepsilon}{\partial h} = 0$ $V_{d,out} = \left(V_s - \frac{U_{c,in}}{1-\varepsilon}\right)$ $Y_{in} U_{c,in} = (1-\varepsilon)V_c Y + D_c \frac{\partial((1-\varepsilon)Y)}{\partial h}$ $\frac{\partial[\varepsilon X]}{\partial h} = 0$

Above Non linear Partial differential Equations reduced to linear system by assuming holdup and phase velocities as constant with respect to column height and time. Table 3.2 summarizes the linear Partial differential Equations as given below.

Table 3.2 Linear Partial differential Equations for Dynamic Model

$\varepsilon\frac{\partial X}{\partial t}=-V_d\varepsilon\frac{\partial X}{\partial h}+\varepsilon\frac{\partial}{\partial h}(D_d\frac{\partial X}{\partial h})+aK_x(X^*-X)$ $(1-\varepsilon)\frac{\partial Y}{\partial t}=V_c(1-\varepsilon)\frac{\partial Y}{\partial h}+(1-\varepsilon)\frac{\partial}{\partial h}(D_c\frac{\partial Y}{\partial h})-aK_x(mY-X)$	
Boundary Conditions	
At $h=0$	At $h=L$
$X_{in}U_{d,in}=\varepsilon V_d X-D_d\frac{\partial(\varepsilon X)}{\partial h}$ $\frac{\partial[(1-\varepsilon)Y]}{\partial h}=0$	$Y_{in}U_{c,in}=(1-\varepsilon)V_c Y+D_c\frac{\partial((1-\varepsilon)Y)}{\partial h}$ $\frac{\partial[\varepsilon X]}{\partial h}=0$

3.3 STEADY STATE MODEL

Model equations are simplified for steady state conditions to study effect of parameters along the length at steady state. In steady state we consider velocity and holdup are constant along the column. Thus above Model equations reduced as follows.

For steady state $\frac{\partial[\varepsilon X]}{\partial t}=0$, $\frac{\partial[(1-\varepsilon)]y}{\partial t}=0$

From equation (3.21)

$$-\frac{d}{dh}[V_d\varepsilon X]+\frac{d}{dh}\left(D_d\frac{d[\varepsilon X]}{dh}\right)+aK_X\left(X^{*}-X\right)=0$$

$$\Rightarrow D_d\varepsilon\frac{d^2X}{dh}-V_d\varepsilon\frac{dX}{dh}+aK_X\left(X^{*}-X\right)=0$$

$$D_d\varepsilon\frac{d^2X}{dh}=V_d\varepsilon\frac{dX}{dh}-aK_X\left(X^{*}-X\right) \tag{3.25}$$

From equation (3.22) and steady state condition

$$\frac{d}{dh}\left[V_c(1-\varepsilon)Y\right]+\frac{d}{dh}\left(D_c\frac{d\left[(1-\varepsilon)Y\right]}{dh}\right)-aK_X\left(X^{*}-X\right)=0$$

$$\Rightarrow V_c(1-\varepsilon)\frac{dY}{dh}+D_c(1-\varepsilon)\frac{d^2Y}{dh}-aK_X\left(X^{*}-X\right)=0$$

$$D_c(1-\varepsilon)\frac{d^2Y}{dh}=-V_c(1-\varepsilon)\frac{dY}{dh}+aK_X\left(X^{*}-X\right)=0 \tag{3.26}$$

Table 3.3 given below provides all necessary boundary conditions.

Table 3.3 Mathematical Equations for Steady State Model

<table>
<tr><td colspan="2">$D_d\varepsilon\frac{d^2X}{dh}=V_d\varepsilon\frac{dX}{dh}-aK_X\left(X^{*}-X\right)$
$D_c(1-\varepsilon)\frac{d^2Y}{dh}=-V_c(1-\varepsilon)\frac{dY}{dh}+aK_X\left(X^{*}-X\right)=0$</td></tr>
<tr><td>Boundary Conditions</td><td></td></tr>
<tr><td>At $h=0$</td><td>At $h=L$</td></tr>
<tr><td>$X_{in}U_{d,in}=\varepsilon V_dX-D_d\frac{\partial(\varepsilon X)}{\partial h}$
$\frac{\partial[(1-\varepsilon)Y]}{\partial h}=0$</td><td>$Y_{in}U_{c,in}=(1-\varepsilon)V_cY+D_c\frac{\partial((1-\varepsilon)Y)}{\partial h}$
$\frac{\partial[\varepsilon X]}{\partial h}=0$</td></tr>
</table>

3.4 MODEL PARAMETERS

The following correlations are used for solving the model equations

Holdup of dispersed phase:

Holdup of dispersed phase refers to the volume fraction of dispersed phase in extraction column. Holdup is found to depend upon many factors, like phase velocities, physical properties of phases, operating conditions etc. **Kumar A.** ***et al.*** **(1988)** holdup correlation is used for solving Equations in Table3.2 and Table 3.3

$$\varepsilon = 2.10x10^{6}\exp[44.53|Af-(Af_m)|]V_d^{0.86}x(V_c+V_d)^{0.28}\Delta\rho^{-0.30}\rho_d^{-0.93}\mu_d^{0.77}\alpha^{-0.56}h^{-0.56} \qquad (3.27)$$

Where

$$(Af)_m = 9.69x10^{-3}(\sigma\Delta\rho^{0.25}\frac{\alpha}{\mu_d^{3/4}})^{0.33}$$

Sauter mean diameter:

Sauter mean diameter is calculated from an equation given of fisher as repor

Hufnagl ***et al.*** **(1991)**

$$d_{32} = 0.19W\varepsilon_R^{-0,61}d_R(1+\frac{11}{n_Z^{1.22}\sqrt{We_R}})(1+2.8\varepsilon) \qquad (3.28$$

Slip velocity:

Slip velocity is the net linear velocity between the contacted phases. In many liquid systems, slip velocity is found to depend upon the physical properties of the system. The Slip velocity is given by the empirical equation of Kumar **A.** ***et al.*** **(1986)**

$$V_s = 1.18x10^{-3}\frac{\varphi\sigma g}{\eta_c d_R n_Z^2} \qquad (3.29)$$

Film mass transfer coefficients:

Mass transfer outside the drops is determined using the film coefficient equation of **Heertjes** *et al.* **(1954).**

$$k_c = 0.83\sqrt{\frac{V_s D_{m,c}}{d_s}} \tag{3.30}$$

Mass transfer inside the drops is determined by an equation of **Hufnagl** *et al.* **(1991)**

$$k_d = 0.00375 V_s \left(\frac{\mu_c}{\mu_c + \mu_d}\right) \tag{3.31}$$

Overall mass transfer coefficient:

$$\frac{1}{K_x} = \frac{1}{k_c} + \frac{1}{m k_d} \tag{3.34}$$

Velocity of dispersed phase:

$$V_d = \frac{U_d}{\varepsilon} \tag{3.35}$$

Velocity of continuous phase:

$$V_c = \frac{U_c}{1-\varepsilon} \tag{3.36}$$

Density difference:

$$\Delta\rho = \rho_c - \rho_d \tag{3.37}$$

Mean density:

$$\bar{\rho} = \rho_d \varepsilon + \rho_c (1-\varepsilon) \tag{3.38}$$

Interfacial area:

$$a = \frac{6\varepsilon}{d_s} \tag{3.39}$$

Equilibrium relation ship:

$$y = 0.835x \tag{3.40}$$

Where,

y = Weight fraction of acetone in continuous phase

x = Weight fraction of acetone in dispersed phase

Consider the following variables.

C_d = Solute concentration in dispersed phase, kg mol/(m^3 of column)

C_c = Solute concentration in continuous phase, kg mol/(m^3 of column)

X = Solute concentration in dispersed phase, kg mol/(m^3 of dispersed phase)

Y = Solute concentration in continuous phase, kg mol/(m^3 of continuous phase)

Therefore,

$$X = \frac{C_d}{\varepsilon}$$

$$Y = \frac{C_c}{1-\varepsilon}$$

The equilibrium relationship in terms of C_c and C_d can be written as

$$\frac{C_c M_{solute}}{(1-\varepsilon)\rho_c} = 0.835\frac{C_d M_{solute}}{\varepsilon\rho_d}$$

$$\Rightarrow C_d^{\bullet} = \frac{C_c\varepsilon\rho_d}{0.835(1-\varepsilon)\rho_c}$$

$$\Rightarrow \varepsilon X^{\bullet} = \frac{Y(1-\varepsilon)\varepsilon\rho_d}{0.835(1-\varepsilon)\rho_c}$$

$$\Rightarrow X^{\bullet} = \frac{\rho_d}{0.835\rho_c}Y \tag{3.41}$$

3.5 Concluding remarks

In this chapter, the model equations are developed by applying conservation principles into the control volume. Prior knowledge of convective transport and diffusion mass transfer has been utilized for developing the model equations. In Dynamic model one system consists of four nonlinear partial differential equations and other consists of two linear partial differential equations. In Steady state model two ordinary differential equations, which form a boundary value problem. These model equations are solved using MATLAB 6.5. software to predict the model behavior of Kühni column. The solution of model equations can be had from the author or from the supervisor concerned on request. Results of model behavior are discussed in the next chapter.

CHAPTER-4

SOLUTION OF MODEL, RESULTS AND DISCUSSION

4.1 SOLUTION

The mathematical model for liquid-liquid extraction column has been developed in chapter 3.This model consists of partial differential equations which are non linear in nature. Under appropriate boundary conditions and constitutive properties model have been solved by using MATLAB 6.5 tool "PDEPE" (partial differential equation solver). The model equations are reduced to linear partial differential equations by setting hold up and velocities of phases as constant. Again reduced model has been solved and results are compared. Further, again the model equations are reduced to linear ordinary differential equations by setting accumulation equal to zero. There are two ordinary differential equations of order two. These model equations have been solved by using MATLAB 6.5 Tool "BVP4C" (Boundary value ode solver). In the present study Kühni column for extraction has been considered. The operating and design conditions to solve model equations are mentioned in table 4.1.

4.1 VALIDATION OF THE MODEL

The mathematical model, which consists of non linear partial differential equations, has been solved for the same operating conditions as mentioned by **Weinstein *et al.* (1998)** in their studies. They mentioned the experimental values of variation in concentrations of dispersed phase with time corresponding to 10% step input in concentration of continuous phase. In order to compare the model results with available data. The difference in concentration with steady state condition ΔX has been plotted vs. time in Fig 4.1. From this Fig 4.1 it is clear that all model results are quite close to experimental results and are within permissible limit of error of $\pm 10\%$. Thus model is validated.

4.2 RESULTS AND DISCUSSIONS

4.2.1 Variation in holdup

The model equations are solved for hold up variation with time and height of the column. At all heights, the hold up is found to be constant at approximately 0.035. This value is same at one location for all times. This is clear from Fig 4.2. This implies that hold up is constant through out the column. **Kumar and Hartland (1988 b)** have given a correlation for hold up in terms of velocities and of as mentioned in chapter 3. This equation is plotted in Fig 4.3. for holdup against the product of amplitude and frequency for different velocities. For Af equal to 0.02, at all velocities the hold up is 0.035. These results lead to the conclusion that there is no need to consider the variation in holdup along the height with time. Instead, the correlation given by Kumar and Hartland for holdup can be successfully used in the model.

4.2.2 Comparison between Two models

Non linear partial differential equations are reduced to linear partial differential equations by considering correlation for holdup given by Kumar & Hartland. Again model equations are solved the results of linear partial differential

Table 4.1 Operating conditions for simulation of Kühni Column

Name	Parameter Specification/Value	Units
Equipment Specification		
Column Height (L)	2.52	m
Column diameter (d_k)	0.15	m
Rotor diameter (d_R)	0.085	m
Section height (h_z)	0.07	m
Free fractional area late (α)	0.27	
Discharge coefficient (C_0)	0.6	
Physical Properties		
Water phase density (ρ_c)	998.2	$kg \cdot m^{-3}$
Toluene phase Density (ρ_d)	866.7	$kg \cdot m^{-3}$
Water phase viscosity (μ_c)	1.10×10^{-3}	$kg \cdot m^{-1}.s^{-1}$
Toluene phase viscosity (μ_d)	0.58×10^{-3}	$kg \cdot m^{-1}.s^{-1}$
Interfacial tension (σ)	34.3×10^{-3}	$N \cdot m^{-1}$
Molecular diffusion ($D_{m,c}$)	10^{-12}	$m^2 \cdot s^{-1}$
Operating Conditions		
U_d	0.0024	$m \cdot s^{-1}$
U_c	0.0024	$m \cdot s^{-1}$
Y_{in}	11	$Kmol \cdot m^{-3}$
X_{in}	0	$Kmol \cdot m^{-3}$
ε_{in}	0.1	
Constants		
Distribution coefficient (m)	0.835	
Gravitational Constant(g)	9.81	
π	3.1416	

equations and non linear partial differential equations are plotted in Fig 4.4 it is evident that results of linear partial differential equations are quite close to non - linear partial differential equations. From this figure it is concluded that linear partial differential equations with Kumar & Hartland hold up correlation can be successfully used as model equations to study the performance of the column.

4.2.3 Concentration profile at steady state

In kühni Column with Water–Acetone–Toluene system, water acetone mixture is in continuous phase and solvent Toluene is in dispersed phase. Therefore transfer of solute Acetone is formed continuous to dispersed phase (c ⟶ d). Both phases move counter currently in the column. Therefore along the lengths of the concentration of continuous phase decrease from Top to bottom and concentration of solute is dispersed phase increase from Bottom to top. In order to study the concentration profiles at Steady state Conditions model equations are changed. Fig 4.5. shows the concentration profile of both the phases along the height of the column.

At steady state accumulation of the property becomes zero. Therefore at steady state conditions non-linear partial differential equations in model are reduced linear ODE of order 2. Those equations are solved for concentration profiles.

4.2.4 Concentration profile at unsteady state

In order to study the concentration profile at unsteady state condition 10 % step input is the concentration of solute in continuous phase has been given.Non-linear partial diffential equations of the model have been solved Fig 4.6.to Fig 4.9Shows the concentrations profiles at unsteady state conditions. In Fig 4.6& Fig 4.7 deviation in concentration with the steady state condition ΔY & ΔX are plotted against height of the column at time 1000s. Fig 4.8 & 4.9 show the concentration profile y & x various at height 1m at various times. Fig 4.10 & Fig 4.11 Show the concentration profile y & x at various heights at time 1000s. Fig 4.12 & Fig 4.13 Shows the concentration Profile y & x at various times at height 1m. From these plots it is evident that at time1500 s. the S.S conditions have been attaining since there is no appropriate change is concentration beyond time1500 s.

4.25 Velocity profiles at unsteady state

Velocities of dispersed and continuous phases have been studied at 10% step input in solute concentration in continuous phase, Fig 4.14 &. Fig 4.15 shows the concentration profiles of continuous and dispersed phase respectively at various height of the column for time 500 sec and 1000sec. At lower time the fluctuation in velocities are large as the time pass system approaches steady state condition and so consequently the fluctuation get reduced this behavior is clearly visible in Fig 4.14 &. Fig 4.15.

4.3 CONCLUDING REMARKS

On the basis of solution of the both dynamic and steady state model equations, the results are obtained and are presented graphically in this chapter. The behavior concentration of solute in dispersed and continuous phase has been studied. In addition to this effect on behavior of velocity, holdup is also presented. In view of the above mentioned results and discussion, it may be concluded that the developed model is suitable for studying the behavior of system under prevailing operating conditions.

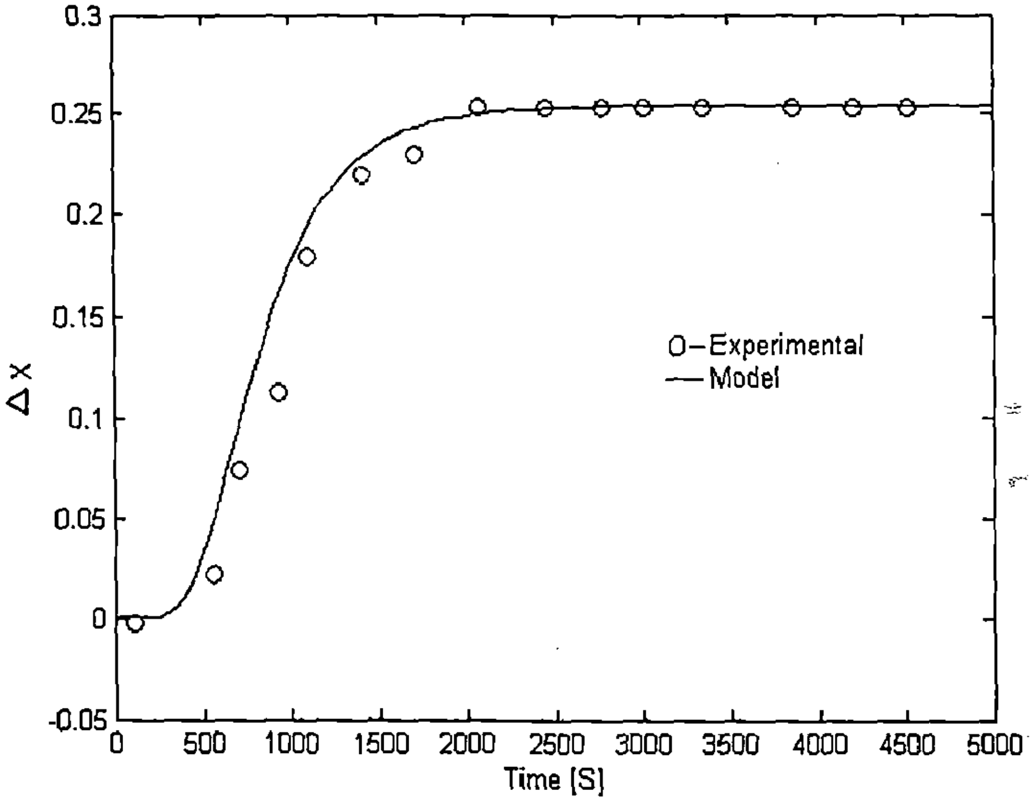

Fig 4.1 Comparison of ΔX calculated with the Experimental data for 10%step input in solute concentration in the continuous phase at h=1m.

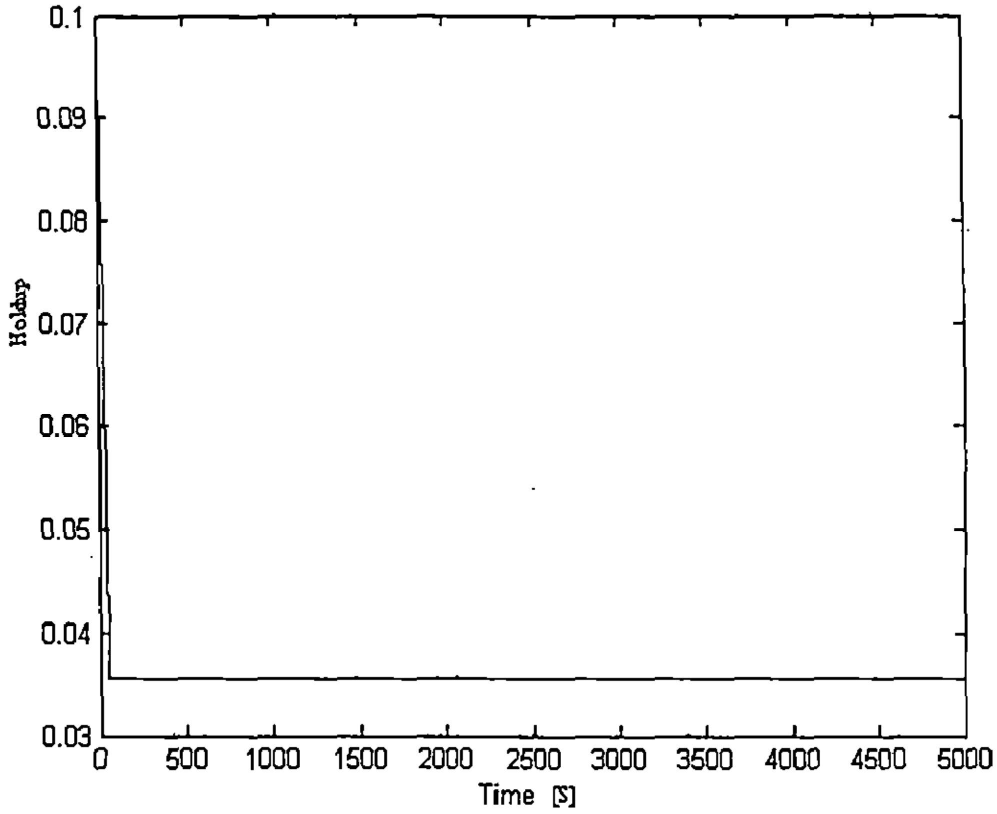

Fig 4.2.Variation of holdup with time at 1m height

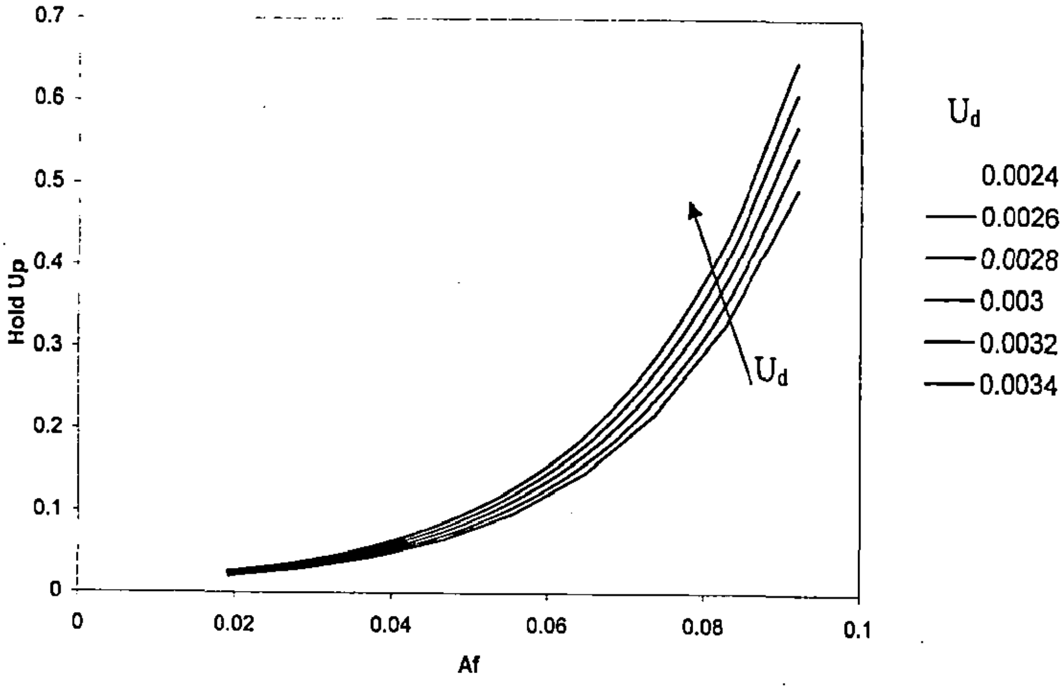

Fig 4.3 Variation of hold up with Af for Different values of U_d

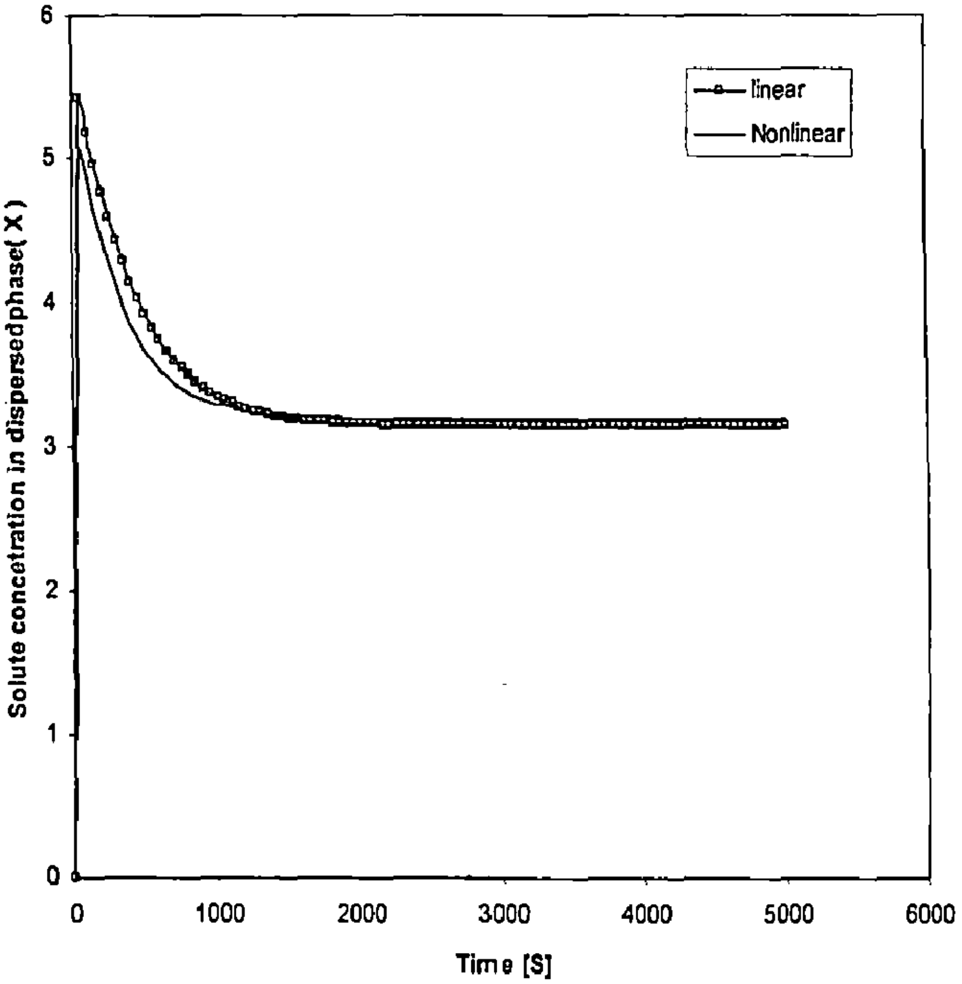

Fig 4.4. Comparison of linear pde model with Non linear pde model Solution

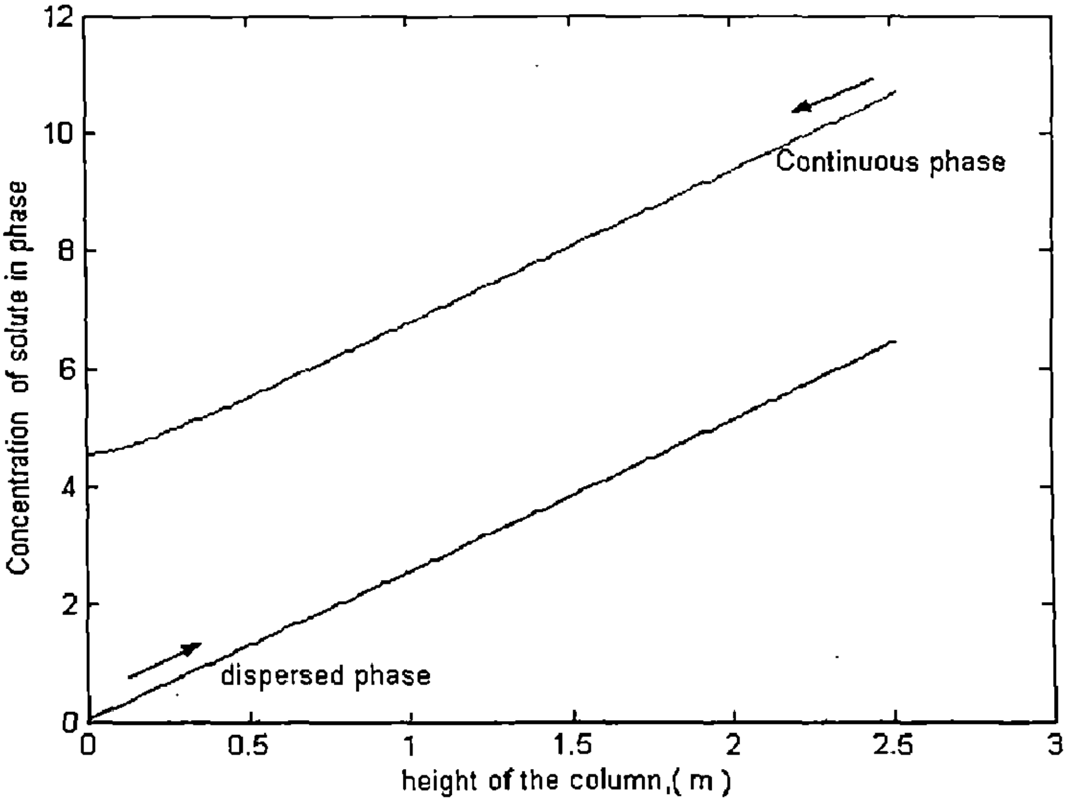

Fig 4.5 Variation of Concentration of solute in both phases along the height at steady state

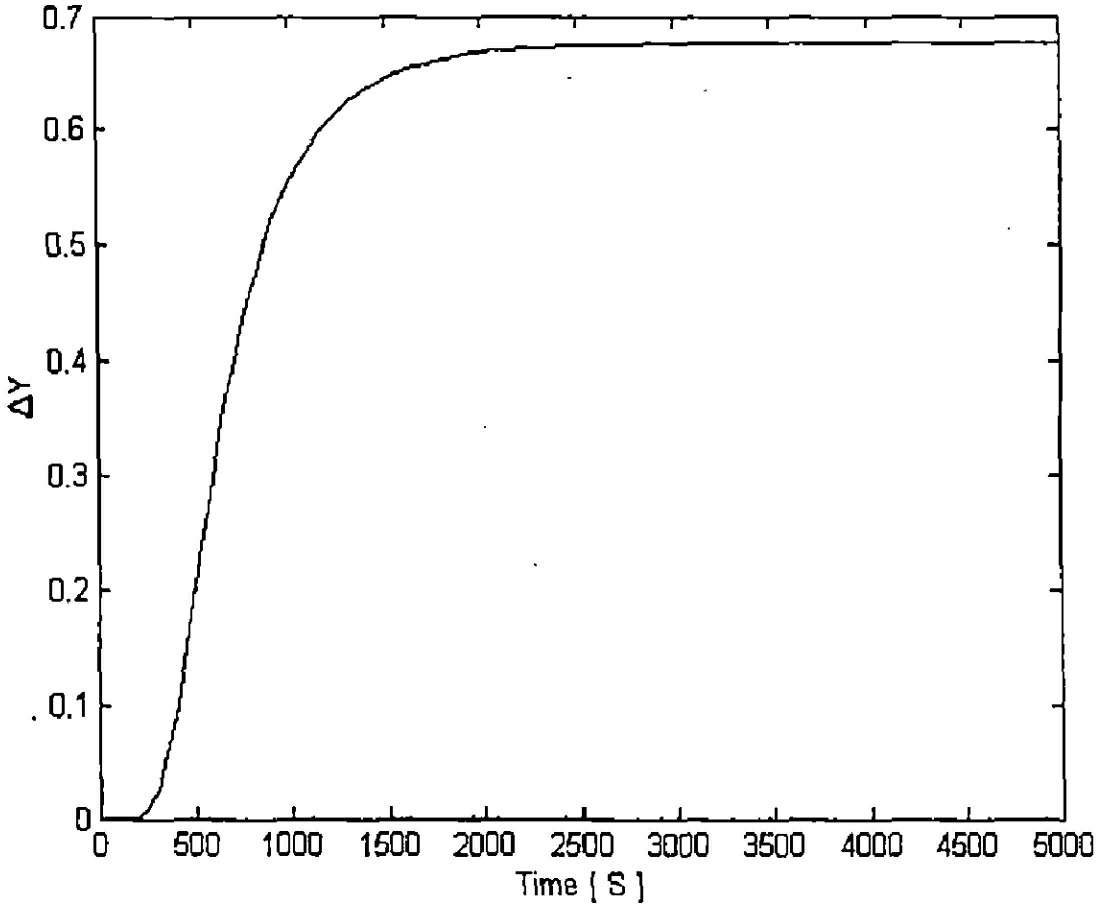

Fig 4.6 Transient behavior of solute concentration in Raffinate to 10% step change in solute concentration in the continuous phase at 1m height

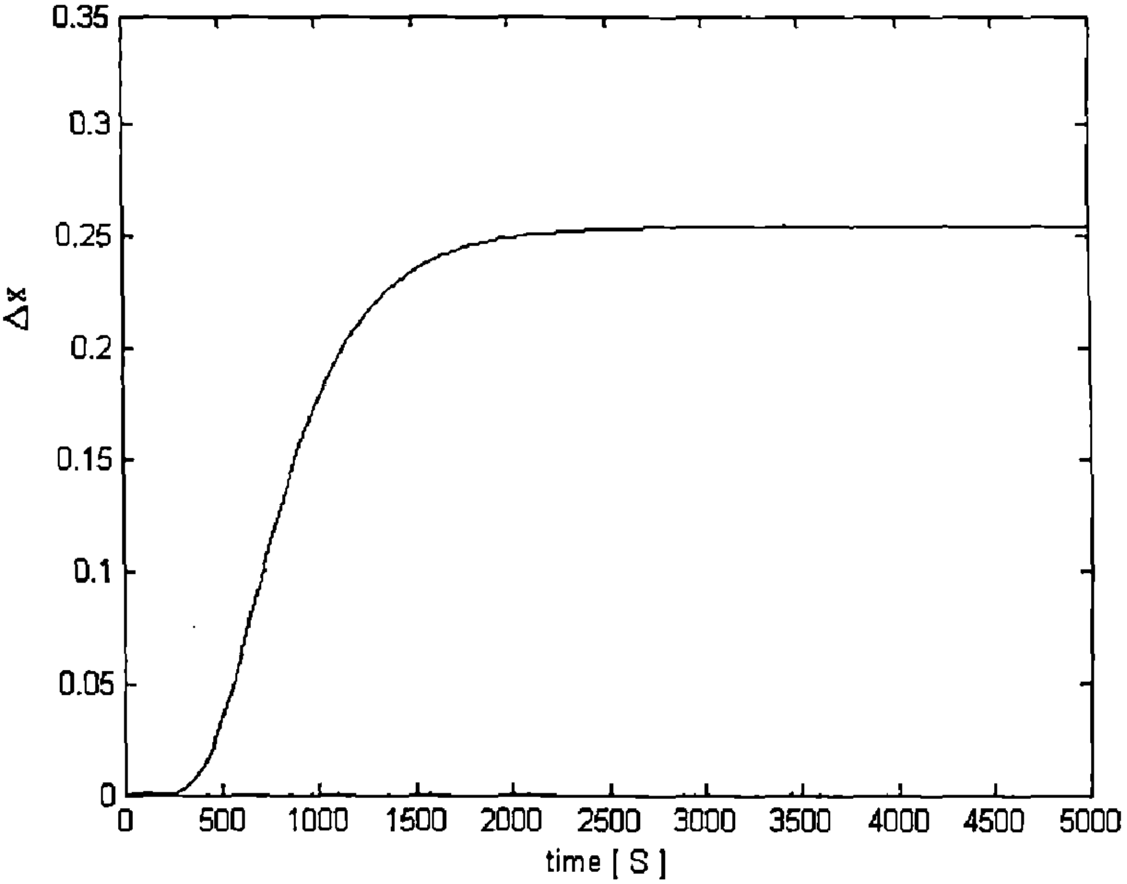

Fig 4.7 Transient behavior of solute concentration in Extract phase to 10% step change in solute concentration in the continuous phase at 1m height

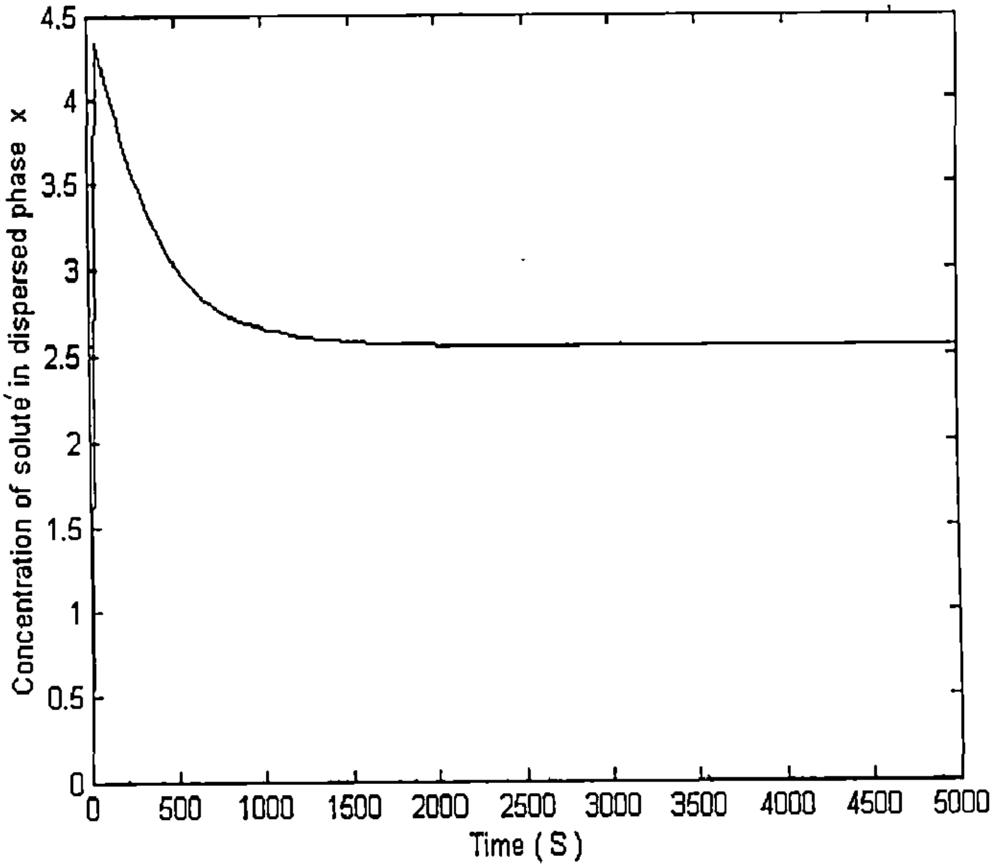

Fig 4.9 Variation of solute concentration in the dispersed phase with time at 1m height.

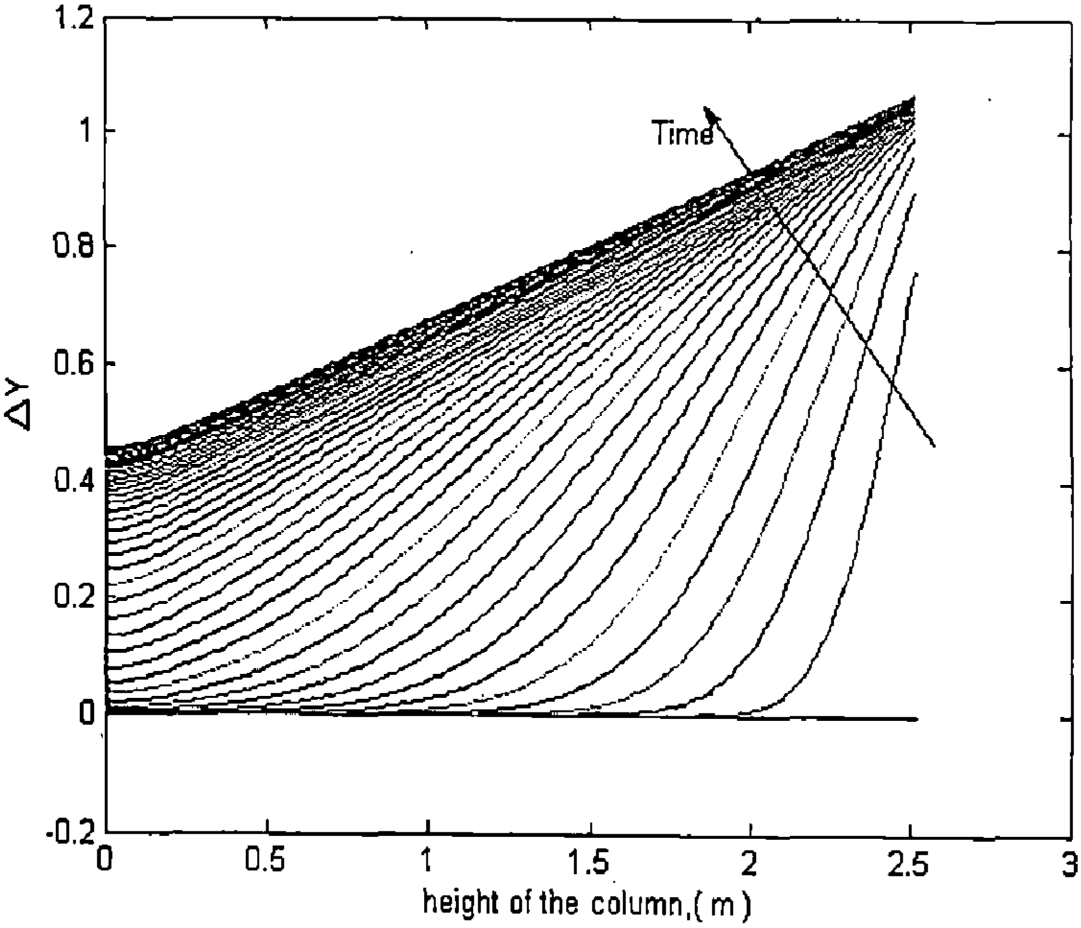

Fig 4.10 Variation of solute concentration in the continuous phase along the height at different time for 10% step input in the solute concentration of continuous phase

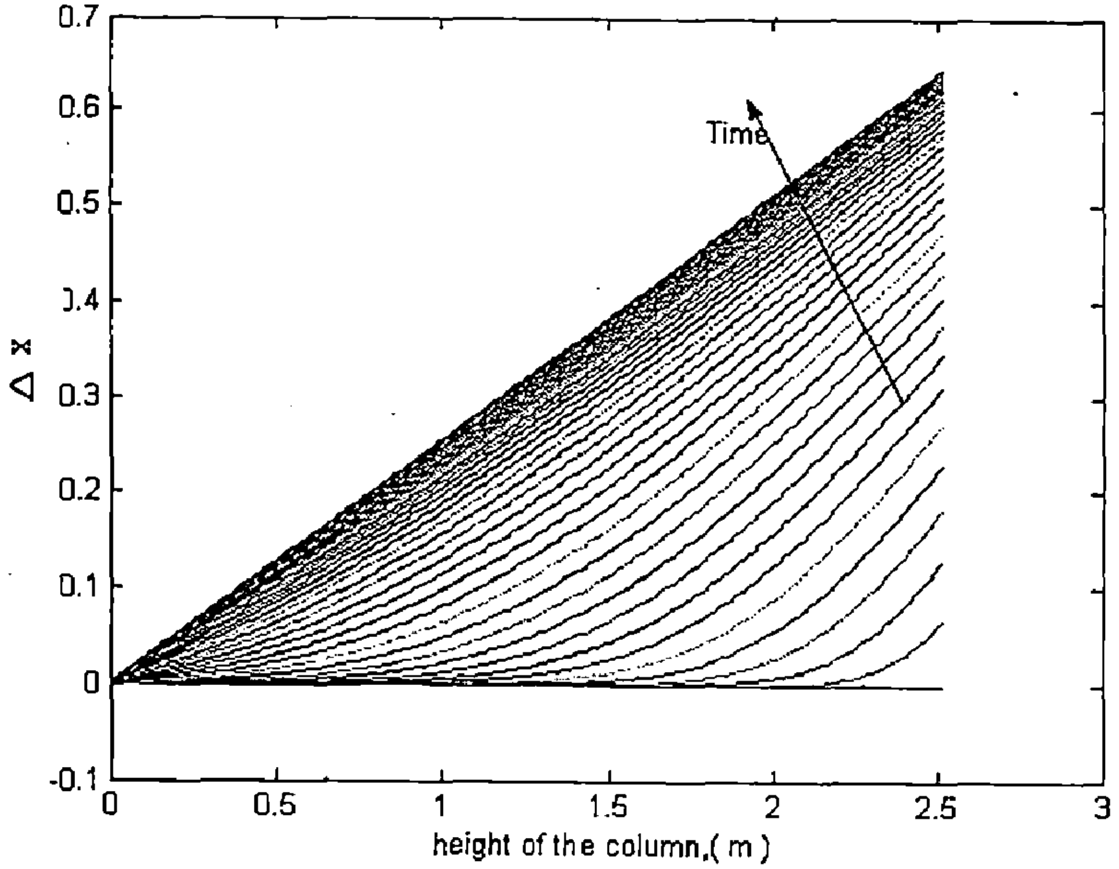

Fig 4.11 Variation of solute concentration in the dispersed phase along the height at different time for 10% step input in the solute concentration of continuous phase

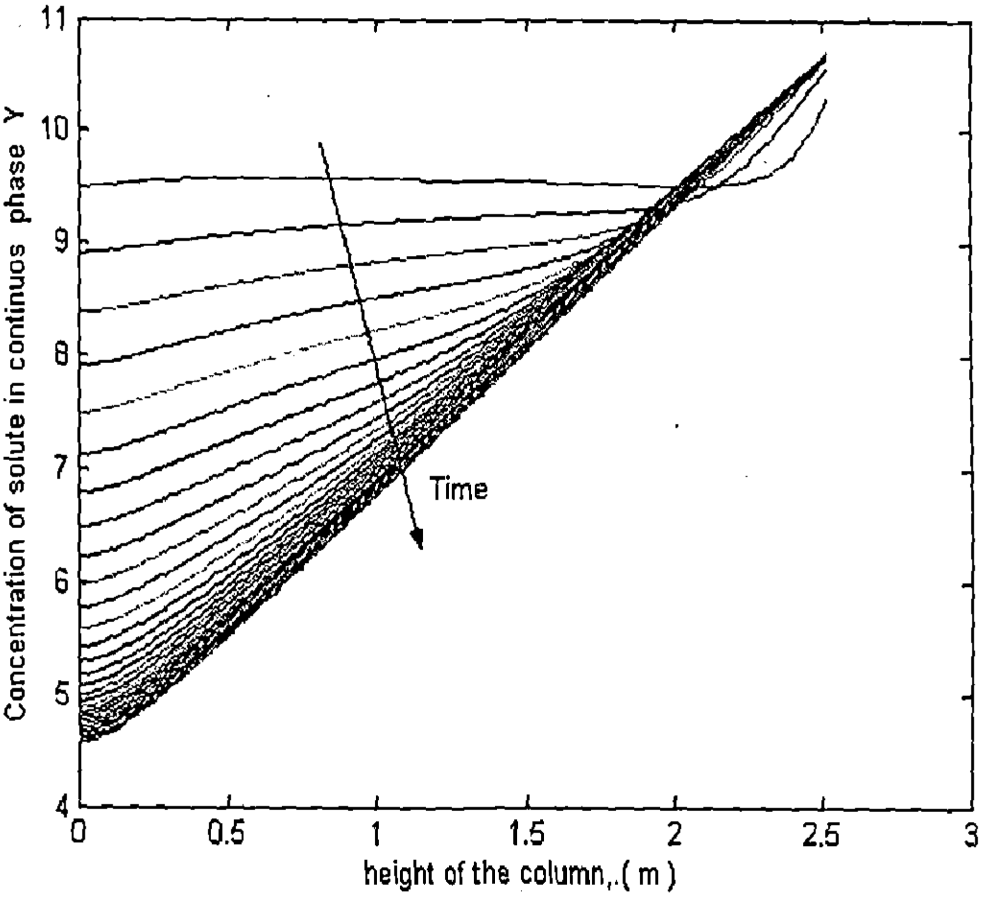

Fig 4.12 Variation of solute concentration in the continuous phase along the height at different time

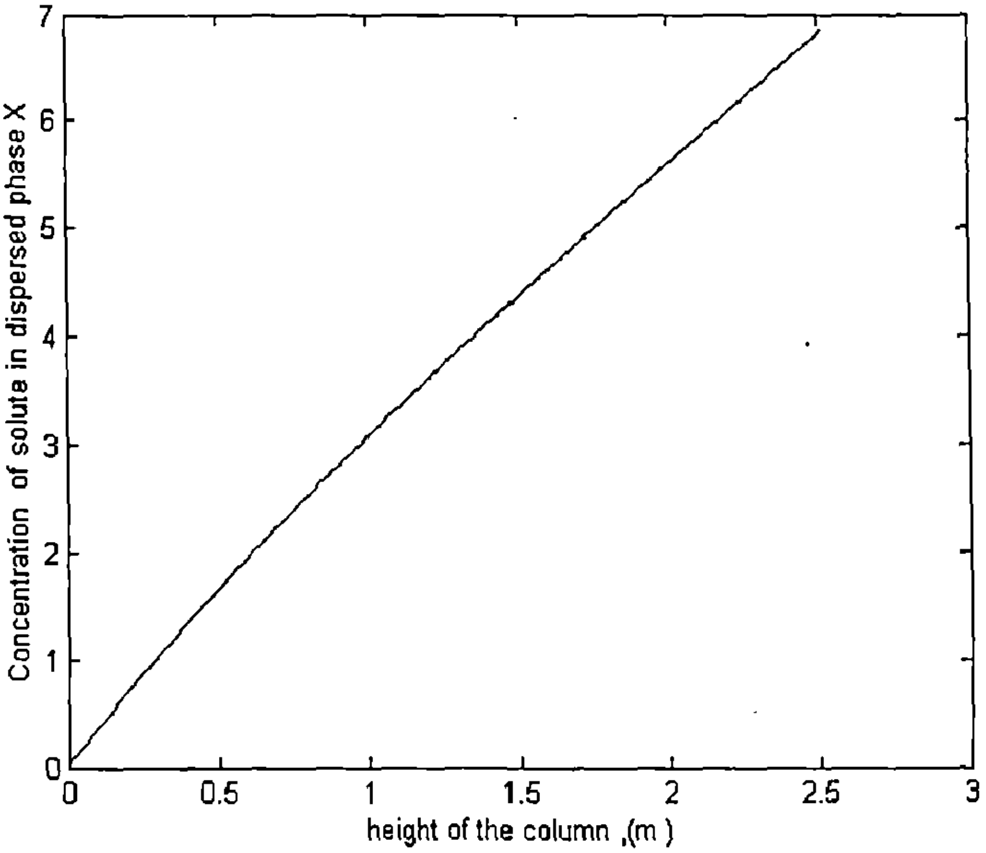

Fig 4.13 Variation of solute concentration in the dispersed phase along the height at different time 500sec

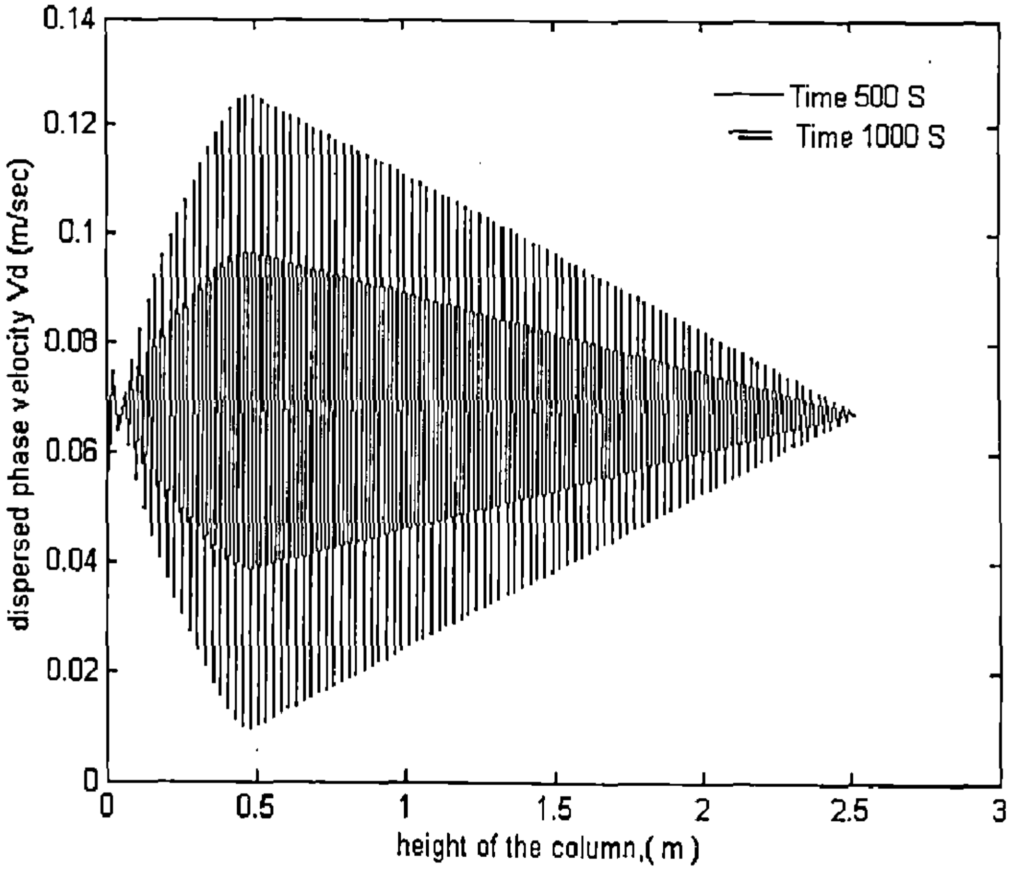

Fig 4.14 Variation of he dispersed phase velocity along the height at 500 sec and 1000 sec

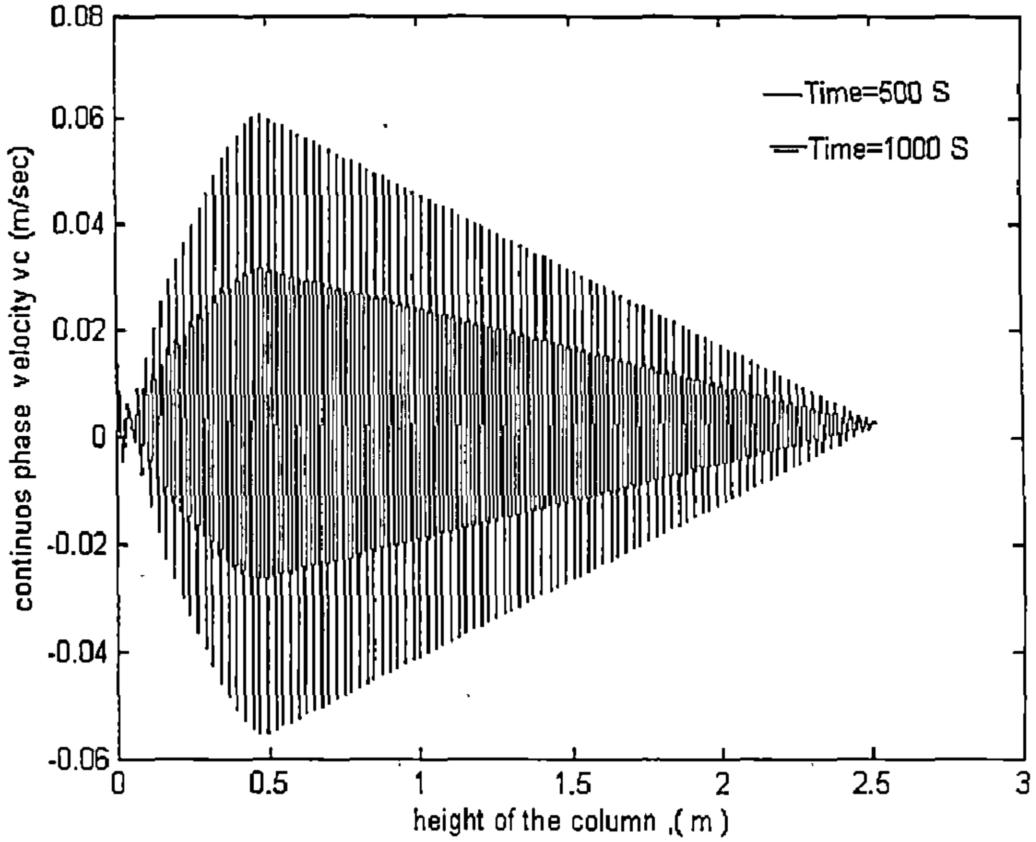

Fig 4.15 Variation of the continuous phase velocity along the height at 500 sec and 1000 sec

CHAPTER-5

CONCLUSIONS AND RECOMMENDATIONS

5.1 INTRODUCTION

In this chapter we have discussed concluding remarks and recommendations briefly.

5.2 CONCLUSIONS

- Mathematical models for countercurrent Kühni extraction column have been developed.
- Each mathematical model consists of set of non linear partial differential equations; linear partial differential equations, ordinary differential equations with boundary value problem respectively.
- The model equations are solved using MATLAB 6.5 software.
- Step response, dynamic and steady state simulations have been carried out for the detailed analysis of countercurrent extraction column.
- The effect of superficial velocity on the performance of extraction column has also studied.
- One can use Linear Partial differential Equations with Kumar & Hartland holdup correlation instead of Non linear partial differential equations

5.3 RECOMMENDATIONS FOR FUTURE WORK

- The results obtained from the work in the laboratory are sometimes quite different from those obtained at the industrial scale. It is, therefore, recommended that the model developed here be tested for the data from the industries. This will enhance the applicability of the model.

- Correlation for slip velocity, sauter mean diameter, mass transfer coefficient and distribution coefficient play important role in predicting the performance of the extraction column .so these correlations should studied at different conditions before applying in mathematical model.
- We have used the values of physical properties at room temperature. It is recommended that for better accuracy, the physical properties and other data which are functions of temperature should be chosen properly.

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