Minimum Solvent Flow Rate for Counter-Current Liquid-Liquid Extraction Columns

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A simple scheme to determine the minimum solvent flow rate for counter-current extraction columns is obtained and its validity is verified using two case studies. An infinite number of equilibrium stages are simplified to a single equilibrium stage. The first case study considers the extraction of a solute using a system made of only three compounds and a non-reactive extraction column to verify the results by rigorous simulation, i.e. aqueous acetic acid. The second case study is focused on biodiesel synthesis in a hybrid reactive extraction column.

1. Introduction

Liquid–liquid extraction is a unit operation that separates compounds based on their solubility in two immiscible liquids. The degree of extraction increases using several equilibrium stages in a column where the immiscible liquids flow in counter-current. Calculating reliable mass transfer coefficients is not easy (Outili et al., 2009). Combining droplet population balance models and computational fluid dynamics, a useful model is obtained for industrial scale column design. Computer fluid dynamics predicts the hydrodynamics, while turbulence and population balance models take into account the droplet coalescence and break up, thus predicting the size distribution of the dispersed phase. There is a strong interdependency between droplet interactions and fluid dynamics. The Population Balance Equation can be solved using the Differential Maximum Entropy Method (Attarakih and Bart, 2014). Such models are not only computationally expensive, but they also require complete specification of the unit and are therefore not well-suited for a rapid evaluation of process alternatives in the early design phase. A first choice of suitable solvents sometimes is based on distribution ratios and separation factors in a liquid-liquid equilibrium stage (Garcia et al., 2011). However, a further analysis is required to check if the solvent can be recovered by distillation or it forms a new azeotropic mixture, to determine the minimum solvent flowrate required and energy necessary for solvent recovery.

Simple models, based only on thermodynamic data, without the need of detailed unit specifications, are very useful in the early process design steps. A plausible strategy is to fix the unknown unit specifications to infinite or to its minimum value instead of using an arbitrary value. Therefore, the model gets important simplification and the limit conditions are calculated, e.g. infinite/infinite analysis for distillation columns (Plesu et al., 2008). The minimum solvent flow rate is an important parameter useful to compare the suitability of different alternative solvents and as input parameter to calculations. The methods reported in literature for minimum solvent flow rate calculations are based on methods used for distillation, e.g. Ponchon-Savarit, tray-to tray calculations, Rectification Body Method, a.s.o. (Redepenning et al., 2013). They are based on determining the solvent flow rate that produces a null driving force in some point of the column profile. In the present paper, the use of infinite number of stages (NTU) assumption is applied to liquid-liquid extraction columns. Thus, the recovery of acetic acid from water is used as illustrative example for solvent choosing, while biodiesel synthesis in a hybrid extractive reactive column is used as case study

to illustrate the influence of the raw material on the required solvent flow rate. The validity of the method proposed is checked by rigorous simulation with Aspen Plus® v8.2.

2. Method

The assumption of infinite number of transfer units in a distillation column implies that the column profile contains a singular point, where liquid and vapour are in equilibrium. By analogy, in an extraction column operated in counter-current, the assumption of infinite number of transfer units also implies that equilibrium between both liquid phases is attained. The equilibrium between the feed containing the solute and the extract occurs at one column extremity where most of the solute is recovered (Figure 1). Therefore, in a computer simulation software, an extraction column with an infinite number of stages can be assimilated to a single decanter, where feed and extract are in equilibrium and therefore as output streams. The decanter proposed does not represent a "real" process unit but an artifice allowing easy calculation of a column with infinite number of stages. The flow rate of raffinate without solute becomes the calculation basis for decanter input. Solute input stream fed to the decanter is specified to satisfy the solute mass balance in the decanter. This must be in agreement with the solute mass balance calculated for the extraction column (the solute concentration in column input streams and solvent recovery are known). Therefore, the solvent stream feed to the column corresponds also to a solvent stream feed to the decanter. The flow rate of this stream is calculated using a design specification that provides the solute concentration in the feed solution. This becomes an output stream from the decanter.

The minimum solvent flow rate and quantity of solvent lost in the raffinate are calculated using the above described simplified scheme and compared to the results of rigorous model for a 50-equilibrium stages extraction column. The simulations are performed using the NRTL thermodynamic model. The decanter with a single equilibrium stage converges faster and without the convergence problems that can be encountered for the extraction column, where several equilibrium stages must be calculated. A very large number of stages lead to convergence problems. The use of an extraction column with an arbitrary number of stages, not higher than the minimum number of stages, cannot lead to the most suitable solvent according to its flow rate requirement. As a compromise, although 50 stages are not infinite, it is a quite large number that allows approaching the infinite stages result, considering that larger columns presented convergence problems. The extraction column is fed with solute fraction and the solvent flow rate is calculated using a design specification according to the solute recovery at the extract, in agreement with the mass balance used for the decanter. All the streams and units are at the same temperature and pressure (20 °C and 1 bar).
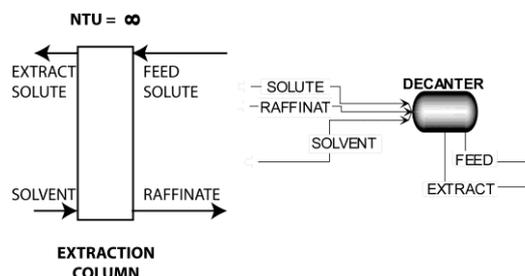

Figure 1: Process scheme and simplified scheme

3. Results

3.1 Case study I: acetic acid recovery from water

Water and acetic acid form a mixture difficult to separate by distillation due to the presence of an azeotrope. An option to separate the mixture is the acetic acid extraction with a solvent that can be further separated easier from acetic acid than from water. Table 1 list some solvent alternatives that do not form any azeotrope with acetic acid.

The solute feed has a flow rate of 10 kg/s, with a 0.1 acetic acid mass fraction (9 kg/s water and rest acetic acid). The operating conditions for the extraction column are fixed to 20 ºC and 1 bar, and the recovery of acetic acid is fixed to 99.9 %. The three compounds of the mixture are introduced separately by three input streams to the decanter: water (RAFFINAT), acetic acid (SOLUTE) and SOLVENT. The flow rate of water in the solute feed to the extraction column is 9 kg/s (FEED SOLUTE) and therefore, in the simulation, the same amount is introduced to the decanter (RAFFINAT). The solvent flow rate (SOLVENT) is calculated

using a design specification to fulfil that the acetic acid feed flow rate is 1 kg/s (FEED). As in the extract is just recovered 99.9 % of the fed acetic acid (EXTRACT SOLUTE), its acetic acid flow rate is 0.999 kg/s (EXTRACT). In order to fullfill the acetic acid mass balance, the decanter must be fed with a virtual stream of 1.999 kg/s acetic acid (SOLUTE).

For the selection of the appropriate solvent, the compounds analysed are ordered from the lowest solvent flow rate required to the highest (Table 1). High solvent flow rate determines the use of extraction columns with higher diameter and additional pumping costs. However, any of the alternatives should not be disregarded until the energy requirements for its recovery are evaluated. Around half of the compounds of Table 1 reduce the dilution of the solute and the other half increases it. The values range from 7 kg/s of furfural until 72.3 kg/s of chloroform. Taking into account environmental aspects, the chloroform could be disregarded as it is a chlorinate compound and its minimum flowrate requirements are too high. On the other hand, an appreciable amount of furfural is lost in the raffinate stream. Therefore, based only on these two aspects, n-hexanoic acid and 2-ethyl-butyric acid seem good candidates. This result is contrary to the belief that acetate should be the best option due to chemical similarity with the acetate group of the acetic acid. Figure 2 illustrates that, using only a decanter, a value directly proportional to the minimum solvent requirement, calculated using a large 50 stages extraction column, can be obtained. An increase of the number of stages is expected that would provide a result closer to the decanter, but as the number of stages increases, the convergence issues appear due to the complexity of mathematical operations. Hence, it can be concluded that the minimum solvent flowrate can be calculated using only one liquid-liquid equilibrium stage.

Table 1: List of compounds without forming an azeotropic mixture with acetic acid

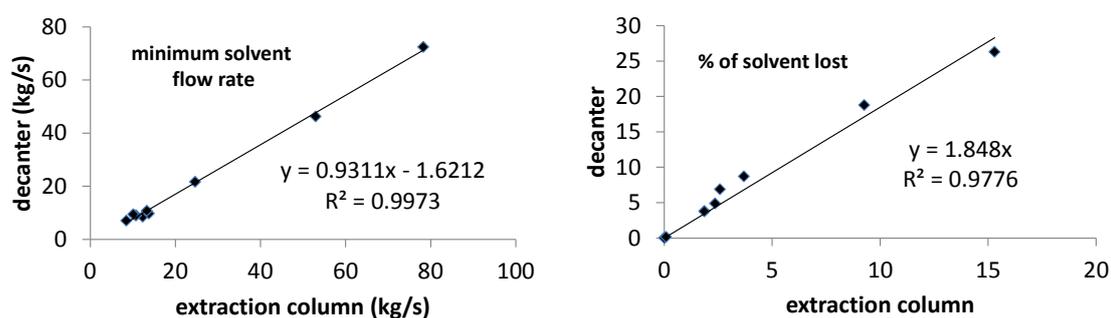| Compound	Minimum solvent (kg/s)		% of solvent lost in raffinate	
	Decanter	Extraction column	Decanter	Extraction column
Furfural	7.0	8.5	18.8	9.3
Ethylidene diacetate	8.4	12.3	6.9	2.6
N-hexanoic acid	8.9	10.8	3.8	1.9
2-ethyl-butyric acid	8.9	10.8	3.8	1.9
Methyl acetate	9.4	10.1	26.3	15.3
Ethyl acetate	9.6	13.8	8.7	3.7
Vinyl acetate	10.7	13.3	4.9	2.4
5-nonanone	21.6	24.7	0.0	0.0
N-octyl acetate	46.2	53.0	0.0	0.0
Chloroform	72.3	78.3	0.2	0.1

Figure 2: The results of the rigorous and simplified model are directly proportional

An alternative minimum solvent calculation method based on a separator unit (SEP) instead of a decanter has been also tested. In this case the feed and solvent are input streams and raffinate and extract are the output. The total split of the two immiscible liquids in the two output streams is defined, the split of solute between the output streams is defined according its recovery and the minimum input solvent flow rate is

determined with a design specification that produces a zero Gibbs energy variation between input and output streams. However, this method does not take into account the solubility of the two immiscible liquids and the solvent lost cannot be calculated. On the other hand, as the solvent lost is not taken into account, the calculated minimum flow rate becomes higher than the one calculated using the 50-stages extraction column. This other method is useful when there is no solubility between both immiscible phases.

3.2 Case study II: purification of biodiesel from methanol using glycerol as solvent

Biodiesel can be produced in a hybrid reactive extraction column using a stoichiometric mixture of vegetable oil and methanol, generating glycerol and biodiesel. The column consists of a reactive section where the biodiesel is produced and a non-reactive section, where biodiesel is purified. Methanol is fed at the top of the reactive section. A part of glycerol is recycled and used as solvent in the non-reactive section. Otherwise, the biodiesel collected would contain an unacceptable high amount of methanol due to the partial miscibility of methanol in biodiesel. To promote the kinetics of the reactive section, the temperature is set at 60 ºC and the pressure at 1 bar. Garcia et al (2013) provides a detailed discussion of the hybrid reactive extraction unit.

One of the main challenges using vegetable oil as raw material to produce biodiesel is the oil composition. Garcia et al (2013) assumed a fixed oil composition of pure trioleine and pure methyl oleate was produced. In this paper, the influence of the vegetable oil composition on the solvent requirement (glycerol recirculated) is evaluated.

Glycerol is required as solvent to recover methanol and to avoid its presence in final biodiesel composition. Both column ends are mainly glycerol/biodiesel and oil/glycerol. The methanol present in the collected biodiesel must not exceed 0.2 % (weight percent), according to the nowadays regulations. The presence of methanol is very small in the output streams, but it reaches maximum concentrations inside the column. Therefore, the entire column cannot be assimilated to a single decanter, but only to an extraction column section (Figure 3). The case described in Figure 3 is an application of the method presented in Figure 1, illustrating the steps involved in simplifying the simulation of a hybrid reactive extraction column. However, a column section between the output glycerol/biodiesel and the maximum mass fraction of methanol in biodiesel can be assumed to have infinite number of stages and can be assimilated to a decanter, as described previously. This allows to calculate the minimum solvent flow rate. The implementation procedure is detailed in the following paragraph.

The biodiesel production flow rate is used as calculation basis, e.g. 100 kg/s. The stoichiometric methanol required is calculated according to the biodiesel flow rate used as calculation basis, for each mole of biodiesel produced, one mole of methanol must be fed. The minimum solvent flow rate is represented versus maximum mass fraction of methanol in the biodiesel+methanol stream. The stream of methanol solute is used as variable for a sensitivity analysis. The solvent glycerol flow rate is calculated using a design specification that considers the methanol flow rate mass balance in the biodiesel+methanol or glycerol+methanol streams and respecting the maximum allowed methanol mass fraction (0.002) in the final biodiesel product. For instance, 11.8 kg/s of methanol must be feed to the system in order to produce 100 kg/s of methyl palmitate (component of biodiesel). As the biodiesel product contains 0.2 % of methanol, then the methanol feed to the system becomes 11.6 kg/s (it must be substracted as it is does not exit by the streams biodiesel+methanol or glycerol+methanol). The methanol feed to the column section in the stream biodiesel+methanol is collected in the stream glycerol+methanol (together with the stoichiometric methanol). As in the previous case study, when using a decanter, both become output streams, therefore the flowrate of methanol solute stream must be two times the methanol flow rate in the stream biodiesel+methanol. This condition is used as target to calculate the glycerol solvent flow rate: two times the methanol flow rate in the stream biodiesel+methanol divided by the methanol solute flow rate must be equal to one. The rigorous simulation of the hybrid reactive extraction column presents convergence problems, but the proposed scheme allows fast calculations without convergence problems.

The methanol concentration in biodiesel phase is much lower than in glycerol phase (Figure 4). The square point representing the result obtained by Garcia et al (2013) for a column with 14 stages and 7 reactive stages is in good agreement with the calculated curves in the present paper. The process with a low number of stages (8 stages) does not adjust to the calculated curve because the quantity of triolein is not negligible when methanol reaches maximum concentration in the column profile. Although it is only a point and more experiments should be performed, it seems that the curves adjust well for extraction columns with a high enough number of equilibrium stages.
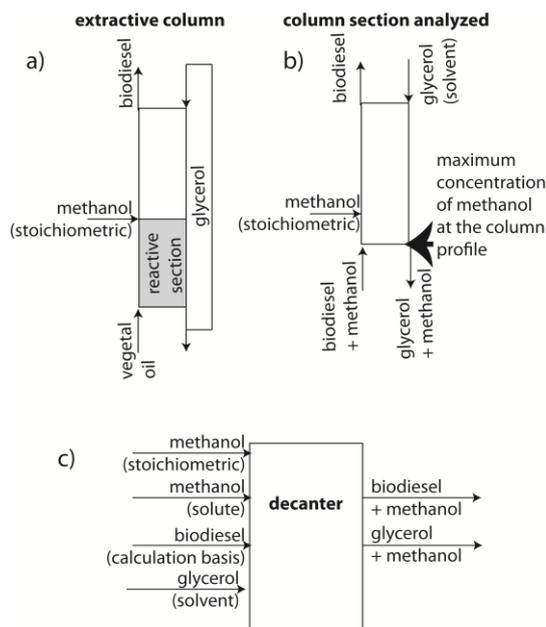
Figure 3: Hybrid reactive extraction column with infinite number of stages assimilated to a decanter; a) hybrid reactive extraction column; b) non-reactive section of the extraction column; c) simplified scheme proposed

The variation of the vegetable oil composition in the fatty acid distribution will not affect much the minimum mass flow rate of solvent (Figure 5 and 6). The methyl myristate is the only chemical compound that increases the glycerol solvent requirement. For low minimum glycerol solvent flow rate, a small variation leads to high changes in methanol mass fraction, and this affects the convergence of the system. Therefore, it is recommended to work in the zone where the curves flatten.
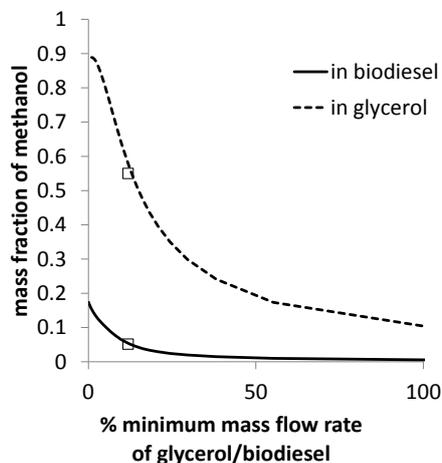

Figure 4: Minimum solvent flow rate and maximum mass fraction of methanol in column profile for both phases (methyl oleate) and point obtained by rigorous simulation by Garcia et al. (2013)

Therefore, the results obtained by the proposed method are useful to perform a first selection of suitable solvents for a certain solute extraction problem (case I) or to check the influence of solvent flow rate on the recovery of a solute from several feed media (case II). The method is robust and fast without the convergence problems encountered in rigorous simulations, providing the minimum solvent flow rate value.
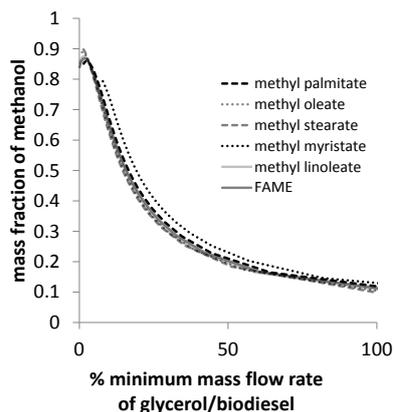
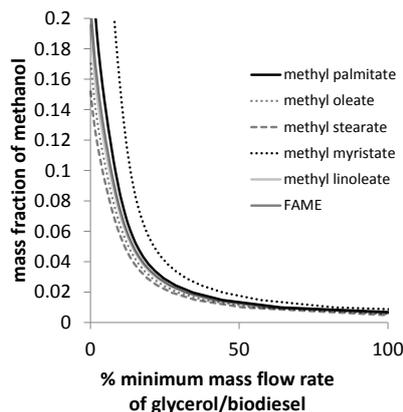Figure 5: Maximum mass fraction of methanol in the composition column profile of the glycerol phase

Figure 6: Maximum mass fraction of methanol in the composition column profile of the biodiesel phase

4. Conclusions

The liquid-liquid extraction column is one of the main alternatives to distillation, e.g. separation of acetic acid from water, and provides competitive processes with low energy requirements, e.g. biodiesel synthesis. In this paper, a simplified scheme is proposed to determine the minimum required solvent flowrate, based on the assumption of infinite number of stages. The simplified scheme converges fast and without problems of convergence. Two case studies are analyzed: the recovery of acetic acid from water is used as illustrative example for solvent choosing, while biodiesel synthesis in a hybrid extractive reactive column is used as case study to illustrate the influence of the raw material on the required solvent flow rate. The obtained solutions are compared to the results of rigorous simulations using AspenPlus[®] v8.2 and the suitability of the method is verified.

Acknowledgements

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