EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Extractive Distillation

TECHNOLOGY CODE: 2.1.3

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1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Extractive distillation is commonly applied in industry, and is becoming an increasingly important separation method in petrochemical engineering. The production scale in industrial equipment is diverse, from several kilotons (column diameter about 2.5 m) per year. It is mainly used in the following cases: one application is separating hydrocarbons with close boiling point, such as C4, C5, C6 mixtures and so on; the other is the separation of mixtures which exhibit an azeotrope, such as alcohol/water, acetic acid/water, acetone/methanol, methanol/methyl acetate, ethanol/ethyl acetate, acetone/ethyl ether and so on.

In extractive distillation, an additional solvent, i.e. separating agent or entrainer, is used to alter the relative volatility of the components to be separated. In this way, it is possible to obtain one pure component at the top of one column and the other, together with the solvent at the bottom, which may be separated easily in a secondary distillation column, due to a high boiling point of the solvent. The solvent doesn't need to be vaporized in the extractive distillation process. However, in azeotropic distillation, which is also often used for the separation of close boiling point or azeotropic mixtures, both the solvent and components must be vaporized into the top of an azeotropic distillation column. Moreover, the amount of azeotropic solvent is usually large, which leads to large energy consumption compared to extractive distillation. For this reason, extractive distillation is more attractive than azeotropic distillation.

Besides altering the relative volatility, the solvent should also be easily separated from the distillation products, that is, a high boiling point difference between the solvent and the components to be separated is desirable. Other criteria, e.g. corrosion, prices, sources, etc. should also be taken into account. However, the relative volatility (which is consistent with selectivity) is the most important index. When solvents are ranked in the order of relative volatility (or selectivity), the solvent with the highest relative volatility is always considered to be the most promising solvent for a given separation task. This may indicate that, from the viewpoint of economic consideration, the use of the solvent with the highest relative volatility (or selectivity) will always give the lowest total annual cost (TAC) of the extractive distillation process.

1.2 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

The solvent is the core of extractive distillation, and thus selection of the most suitable solvent plays an important role in the economical design of extractive distillation. Excellent solvents should at least decrease the solvent ratio and the liquid load of the extractive distillation column, and make the operation easily implemented. Up to date, there are five types of solvents used in extractive distillation, i.e. solid salt, liquid solvent, the combination of liquid solvent and solid salt, hyperbranched polymer, and ionic liquid.

<u>Extractive distillation with solid salt</u>

In certain systems where solubility permits, it is feasible to use a solid salt dissolved into the liquid phase, rather than a liquid additive, as the separating agent for extractive distillation.

Extractive distillation with liquid solvent

Like extractive distillation with solid salt, in certain systems where solubility permits, it is feasible to use a liquid solvent with small molecular weight dissolved into the liquid phase as the separating agent for extractive distillation.

Extractive distillation with the combination of liquid solvent and solid salt

Like extractive distillation with solid salt or liquid solvent, in certain systems where solubility permits, it is feasible to use a combination of liquid solvent and solid salt dissolved into the liquid phase, rather than only salt or liquid solvent, as the separating agent for extractive distillation.

Extractive distillation with hyperbranched polymers

Hyperbranched polymers represent highly branched, polydisperse macromolecules with a treelike topology and a large number of functional groups. In certain systems where solubility permits, it is feasible to use a hyperbranched polymer dissolved into the liquid phase as the separating agent for extractive distillation.

Extractive distillation with ionic liquid

Ionic liquids are salts consisting entirely of ions, which exist in the liquid state at ambient temperature, i.e. they are salts that don't normally need to be melted by means of an external heat source. In certain systems where solubility permits, it is feasible to use an ionic liquid dissolved into the liquid phase as the separating agent for extractive distillation.

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	For the isopropanol-water separation, an energy requirement of only 45% of those with azeotropic distillation; for the ethanol-water separation, the maximum saving in overall heat duty up to 19% using hyperbranched polymer as the entrainer and 24% using ionic liquid as the entrainer	Extractive distillation with the combination of liquid solvent and solid salt as the entrainer combines the advantages of liquid solvent (easy operation) and solid salt (high separation ability). That is why it is widely used in industry. Extractive distillation with hyperbranched polymer and with ionic liquid are new promising methods having the following unique advantages: ● The entrainer cannot pollute the product at the top of the column; ● No main column separation section and internals are needed for the separation of entrainer from high volatile product; ● A variety of entrainer regeneration options are feasible.
CO_2 emission	No data available	This problem is not involved.
Cost savings	No industrial data so far	Cost savings can result from: ● Low solvent ratio and liquid load, which lead to small size of equipment; ● No main column separation section and internals are needed for the separation of nonvolatile entrainer from high volatile product; ● Better product quality (for nonvolatile entrainer); ● Less loss (for nonvolatile entrainer).

1.4 Stage of development

Extractive distillation with solid salt, liquid solvent, or the combination of liquid solvent and solid salt as the entrainer has already been widely used in industry. But extractive distillation with hyperbranched polymer or ionic liquid as the entrainer are new development. The BASF company in Germany has set up a pilot plant for extractive distillation with ionic liquid. It was found that the color of ionic liquid was changed after several runs. However, it was said "we sell property, not sell color". One disadvantage of using hyperbranched polymer or ionic liquid as the entrainer is that it often takes much time to prepare hyperbranched polymer or ionic liquid and the prices of the materials used for synthesizing them are somewhat expensive.

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

For the separation of the components with close boiling point or forming azeotropes, both azeotropic distillation and extractive distillation are often used. In azeotropic distillation the azeotropic entrainer and the components to be separated must be vaporized into the top of distillation column. Moreover, the amount of azeotropic entrainer is usually large, which leads to a high energy consumption compared with extractive distillation. For this reason, extractive distillation is applied more often than azeotropic distillation.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

Extractive distillation with solid salt or liquid solvent as the entrainer is widely applied in industry in the following cases: one application is separating hydrocarbons with close boiling point, such as C4, C5, C6 mixtures and so on; the other is the separation of mixtures which exhibit an azeotrope, such as alcohol/water, acetic acid/water, acetone/methanol, methanol/methyl acetate, ethanol/ethyl acetate, acetone/ethyl ether and so on.

Extractive distillation with the combination of liquid solvent and solid salt as the entrainer has been used for the separation of aqueous alcohol solutions in more than 100 industrial towers in China.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity /Plant size	Year of application	Reported effects
Fine Chemicals and Pharma	Extractive distillation with the combination of liquid solvent and solid salt /anhydrous	Double-column process in continuous operation	3000 ton/y / column diameter	since 1980s	• Yield of ethanol >95.0% • Purity of ethanol >99.5%

	ethanol		700mm		• Concentration of water in ethanol <0.2%

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

No demonstration projects on extractive distillation with hyperbranched polymer or ionic liquid as the entrainer are known since the prices of hyperbranched polymer or ionic liquid are expensive in relation to solid salt and liquid solvent with small molecular weight that are easily available.

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
				•

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

Extractive distillation can be suitable either for the separation of polar systems or for the separation of non-polar systems with close boiling point or forming azeotropes. A number of products can be manufactured with this technology. The separation systems reported in the literatures include, but not restricted to,

- separation of ethanol and water
- separation of isopropanol and water
- separation of nitric acid and water
- separation of acetic acid and water
- separating C4 mixture with ACN, DMF, NMP
- separation of cyclopentane and 2,2-dimethylbutane
- separation of n-pentane and 1-pentene
- separation of aromatics and non-aromatics
- separation of tetrahydrofuran and water
- separation of 1-hexene and n-hexane
- separation of cyclohexane and toluene

The more detailed information is described in Lei et al. (2003, 2005).

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Engineering & design concepts for commercial-scale devices	It is required to synthesize the entrainers in a cheap way on the industrial scale. The loss of entrainers due to decomposition, leakage, etc. after several runs should be considered. Also, material issues are important here (entrainers not corrosive to the column wall and pipes).	R & D projects carried at the universities, in collaboration with chemical manufactures of industrial-scale amount
Modeling and scale-up methodologies	The predictive molecular thermodynamic models are used for describing phase equilibrium. The equilibrium (EQ) stage model is commonly used for modeling extractive distillation process. The robust and reliable non-equilibrium (NEQ) stage model has to be developed.	R & D projects carried at the universities, in collaboration with chemical manufactures of industrial-scale amount
Control systems for commercial-scale extractive distillation process	Proper control of extractive distillation process is of crucial importance for the reliability and safety of the operation. The quality of products can be controlled by adjusting operation parameters (e.g. temperature, pressure, the mole ratio of entrainer to feeding mixture, etc.).	R & D projects carried at the universities, in collaboration with extractive distillation equipment vendors

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Identify the relation between molecular structure of the entrainer and separation performance	It is tiresome to choose the best entrainer from thousands of different substances for a given separation task through experiment. In this case predictive molecular thermodynamic models are used as a screening tool to find out the best suited entrainer rapidly. Only on this basis is the best suited entrainer synthesized so as to largely reduce the amount of experimental work.	This challenge should be addressed in the R & D projects on engineering & design concepts for commercial-scale extractive distillation process.
Stability of entrainer	Some entrainers are easy to be decomposed gradually at distillation temperature, and thus the separation performance may decreases little by little. This also brings a change of entrainers' color.	Feasibility studies at the end-user for each specific case.
Safety	Operations of extractive distillation require certain safety precautions as many entrainers are harmful to the human health.	Process development has to enable a fully safe use of entrainers and devices.
Control	Proper control of extractive distillation process is of crucial importance not only to the safety of operation, but also to the quality of products.	Reliable models, control policies and devices have to be developed for the on-line control of extractive distillation process in continuous operation.

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Berg, L., 1969, Selecting the agent for distillation processes, Chem Eng Prog, 65 (9), 52-57.	Research paper	A early paper introducing how to select the suitable entrainer
Momoh, S. O., 1991, Assessing the accuracy of selectivity as a basis for solvent screening in extractive distillation processes, Sep Sci Technol, 26, 729-742.	Research paper	Selectivity (or relative volatility) is the most important index for evaluating the potential entrainer
Furter, W. F., 1992, Extractive distillation by salt effect, Chem Eng Commun, 116, 35-40.	Research paper	The first paper on extractive distillation with solid salt
Lei, Z. G., Wang, H. Y., Zhou, R. Q. and Duan, Z. T., 2002, Influence of salt added to solvent on extractive distillation, Chem Eng J, 87 (2), 149-156.	Research paper	The first paper on extractive distillation with the combination of liquid solvent and solid salt
Lei, Z. G., Li, C. Y. and Chen, B. H., 2003, Extractive distillation: a review, Sep Purif Rev, 32, 121-213.	Review paper	A comprehensive and critical review on extractive distillation
Seiler, M., Kohler, D. and Arlt, W., 2003, Hyperbranched polymers: new selective solvents for extractive distillation and solvent extraction, Sep Purif Technol, 30, 179-197.	Research paper	The first paper on extractive distillation with hyperbranched polymer
Lei, Z. G., Arlt, W. and Wasserscheid, P., 2006, Separation of 1-hexene and n-hexane with ionic liquids, Fluid Phase Equilib, 241, 290-299.	Research paper	The first paper on extractive distillation with ionic liquid
Lei, Z. G., Chen, B. H. and Ding, Z. W., 2005, Special Distillation Processes, (Elsevier, Amsterdam)	Book	Provide a detailed introduction on extractive distillation

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

There are too many patents on extractive distillation. Herein, only some typical patents are listed.

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
DE patent No. 10160518.8 (2001)	TU Berlin	
DE patent No. 10114734 (2001)	TU Berlin	
DE patent No. 10136614 (2001)	TU Berlin	
WO patent No. 02/074718 A2 (2002)	TU Berlin	
CN patent No. ZL 01141847.8: Separation of acetic acid and water by reactive extractive distillation	Beijing University of Chemical Technology	
CN patent No. ZL 200310115075.6: A method of separating tert-butyl alcohol and water by extractive distillation	Beijing University of Chemical Technology	

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Chair of Separation Science and Tehcnology, Universitat Erlangen - Nurnberg	Germany	Focus primarily on extractive distillation with hyperbranched polymer or ionic liquid
School of Chemical, Environmental and Mining Engineering, The University of Nottingham	UK	Focus primarily on simulation and optimization of extractive distillation
State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology	China	Broad range of research activities, including scale-up issues

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

Table 9. Supplier and developers

Institute/Company	Country	Remarks
BASF	Germany	Manufacture and design of commercial extractive distillation process
Sulzer Chemtech Ltd	Switzerland	Manufacture and design of commercial extractive distillation process
The Dow Chemical Company	U.S.A.	Manufacture and design of commercial extractive distillation process
Total Petrochemicals	France	Manufacture and design of commercial extractive distillation process
SINOPEC Corp.	China	Manufacture and design of commercial extractive distillation process
CNPC Corp.	China	Manufacture and design of commercial extractive distillation process
TianDa BeiYang Equipment Corp.	China	Supply commercial extractive distillation equipment
State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology	China	Supply the entrainer for extractive distillation

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Potential group of end users includes companies operating in the fine chemical & pharmaceutical sector.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Material science has a strong influence on the development of extractive distillation. For instance, new entrainers recently proposed such as hyperbranched polymer and ionic liquid come from interdisciplinary material science. However, the most important is that we should identify the relation between molecular structure of the entrainer and separation performance. Only on this basis the best suited entrainer synthesized so as to largely reduce the amount of experimental work. By means of predictive molecular thermodynamic models, the materials including solid slat, liquid solvent with small molecular weight, polymer and ionic liquid can be regarded as "designer solvents" in extractive distillation.