

EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:

Adsorptive Distillation

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1. Technology

1.1 Description of technology / working principle

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

Adsorptive distillation means adsorption and distillation take place simultaneously and is coupled in a same column. By far there are two types called adsorptive distillation. One has been proposed by Abu Al-Rub et al. (1999) and Banat et al. (2000). It involves replacement of the inert packing material in packed-bed distillation column by an active packing material such as 3 Å or 4 Å molecular sieves, ion-exchange resins and so on. The active packing materials would increase the relative volatility of the components to be separated.

Another type of adsorptive distillation has been proposed by Cheng et al. (1999). It doesn't involve replacement of internals of distillation. Tiny solid particles are used as the adsorptive agent and blended with liquid phase in the column. The enhancement of gas-liquid mass transfer has been proved, and the mechanism model is proposed.

Adsorptive distillation is a completely environment-friendly process because no extra organic solvent is introduced except the components to be separated, and thus there doesn't exist entrainer loss which, on the contrary, often occurs in extractive distillation and azeotropic distillation.

Adsorptive distillation is especially suitable for the separation of aqueous organic solutions including the mixtures with close boiling point or forming azeotropes. The separation mechanism is based on the different interactions between the active solid material and the components to be separated.

1.2 Types and “versions”

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

Two basic types of adsorptive distillation can be distinguished:

Fixed-bed adsorptive distillation (FAD)

It involves replacement of the inert packing material in packed-bed distillation column by an active packing material. The relative volatility of the components to be separated would be increased by the double actions of adsorption and distillation.

Suspension adsorptive distillation (SAD)

It doesn't involve replacement of internals of distillation. Tiny solid particles are used as the adsorptive agent and blended with liquid phase in the column. However, when adding solid particles to liquid phase, the distillation column is prone to be jammed. From this viewpoint, the tray column is more suitable for SAD. Moreover, it is difficult to run the distillation column again while the solid particles are deposited after a long time. This should be noted in the operation.

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; CO₂ 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	No industrial	The active packing materials would increase

	data so far	the relative volatility of the components to be separated. It is generally believed that from the viewpoint of economic consideration, the use of the entrainer with the highest relative volatility (or selectivity) will always give the lowest total annual cost (TAC) of the distillation process. Therefore, overall energy savings should be expected by decreasing reflux ratio. Moreover, adsorptive distillation as a new promising method has the following unique advantages: no entraining into the top product of distillation column, no entrainer recovery, no vapor pressure, no decomposition, etc., which, however, doesn't occur in extractive distillation and azeotropic distillation.
CO ₂ emission	No available data	This problem is not involved.
Cost savings	No industrial data so far	Cost savings can result from: <ul style="list-style-type: none"> ● Small size of equipment due to the increase of relative volatility; ● No main column separation section and internals are needed for the recovery of active packing materials; ● Better product quality (no entraining into the top product of distillation column); ● no loss of active packing materials (especially for FAD)

1.4 Stage of development

Adsorptive distillation is a very new separation method, and the stage of development is still in the laboratory scale. Contrary to other separation methods like extractive distillation and azeotropic distillation, no organic entrainer is introduced for the separation of the mixtures with close boiling point or forming azeotropes. So it is a completely environment-friendly process. Unfortunately, so far there is no commercial adsorptive distillation process announced, although adsorptive distillation is easy to be carried out in practice. For example, for FAD, only the packing material is required to be replaced while others remain constant in the distillation column. The study on adsorptive distillation should be strengthened in the field of process intensification (PI)!

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 where organic entrainer is introduced are often used.

On the other hand, for the separation of aqueous organic solutions, ordinary distillation sometimes is used.

However, adsorptive distillation as a completely environment-friendly separation method can replace azeotropic distillation, extractive distillation and ordinary distillation in practice.

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)

So far, no commercial application of adsorptive distillation has been reported.

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
					•

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 adsorptive distillation are known.

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)

Unlike azeotropic distillation and extractive distillation, the literatures concerning adsorptive distillation are very few. The separation systems reported in the literatures include

- separation of ethanol and water
- separation of isopropanol and water
- separation of methanol and acetone

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	Adsorptive distillation has been developed on the laboratory scale so far. New design concepts are needed for commercial-scale adsorptive distillation columns, which should address the issues of the type and loading amount of adsorbents, loading mode, phase equilibrium, etc.	R & D projects carried at the universities, in collaboration with equipment manufactures
Modeling and scale-up methodologies	The process mathematical models including the equilibrium (EQ) stage and non-equilibrium (NEQ) stage models have to be developed in order to find the optimum operation condition.	R & D projects carried at the universities, in collaboration with equipment manufactures
Control systems for commercial-scale adsorptive distillation process	Proper control of adsorptive 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 type and loading amount of adsorbents, etc.).	R & D projects carried at the universities, in collaboration with 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 type of adsorbents and separation performance	It is better to find out the best suited adsorbents (e.g. molecular sieve, ion-exchange resin, silica gel) for a given separation task so as to reduce the amount of experimental work.	This challenge should be addressed in the R & D projects on engineering & design concepts for commercial-scale adsorptive distillation process.
Loading mode of adsorbents	For a given separation task it is needed to determine which kind of adsorptive distillation (FAD or SAD) is selected and how adsorbent is loaded in distillation column. Other special distillation processes (e.g. catalytic distillation) may be referred to for possible solutions to this problem.	This challenge should be addressed in the R & D projects on engineering & design concepts for commercial-scale adsorptive distillation process.
Safety	Operations of SAD require certain safety	Process development

	precautions as the distillation column is prone to be jammed when adding solid particles to liquid phase. Also, SAD and FAD should be operated within the feasible range of loads of vapor and liquid phases.	has to enable a fully safe use of devices.
Control	Proper control of adsorptive 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 adsorptive 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
Cheng, H., Zhou, M., Xu, C. J. and Yu, G. C., 1999, Enhancement of fine adsorbent particles on gas-liquid mass transfer (I) mechanism, J Chem Ind Eng (China), 50, 766-771.	Research paper	Explain the enhancement of gas-liquid mass transfer in SAD
Cheng, H., Zhou, M., Zhang, Y. and Xu, C. J., 1999, Enhancement of fine adsorbent particles on gas-liquid mass transfer (II) experiment, J Chem Ind Eng (China), 50, 772-777.	Research paper	Verify the enhancement by experiment in SAD
Abu Al-Rub, F. A., Banat, F. A. and Jumah, R., 1999, Vapor-Liquid equilibrium of ethanol-water system in the presence of molecular sieves, Sep Sci Technol, 34, 2355-2368.	Research paper	Study on separation mechanism
Banat, F. A., Abu Al-Rub, F. A. and Simandl, J., 2000, Analysis of vapor-liquid equilibrium of ethanol-water system via headspace gas chromatography: effect of molecular sieves, Sep Purif Technol, 18, 111-118.	Research paper	Measurement of vapor-liquid equilibrium of ethanol - water in the presence of 3 and 4 Å molecular sieves
Lei, Z. G., Li, C. Y. and Chen, B. H., 2003, Extractive distillation: a review, Sep Purif Rev, 32, 121-213.	Review paper	Comparison of adsorptive distillation with extractive distillation for the separation of ethanol and water
Mujiburohman, M., Sediawan, W. B. and Sulisty, H., 2006, A preliminary study: distillation of isopropanol - water mixture using fixed adsorptive distillation method, Sep Purif Technol, 48, 85-92.	Research paper	Process experiments on the separation of isopropanol - water using FAD
Lei, Z. G., Chen, B. H. and Ding, Z. W., 2005, Special Distillation Processes, (Elsevier, Amsterdam)	Book	Provide a detailed introduction on adsorptive 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.)

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
JP patent No. 7163869 (1995): Packing with catalytic agent or adsorbent	Sulzer Chemtech AG	Loading mode of adsorbents in FAD
CN patent No. 200710062948 X (2007): A kind of structure of distillation packing	Beijing University of Chemical Technology	Loading mode of adsorbents in FAD

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
Department of Chemical Engineering, Jordan University of Science and Technology	Jordan	Focus primarily on VLE and separation mechanism
Chemical Engineering Department of Muhammadiyah University of Surakarta (UMS)	Indonesia	A preliminary study on adsorptive distillation process
Chemical Engineering Research Center, Tianjin University	China	Focus on gas-liquid mass transfer in SAD
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)

No suppliers of commercial-scale adsorptive distillation columns are known. Manufactures of large-scale distillation equipments can be seen as potential stakeholders. Some of these manufacturers are listed in Table 9.

Table 9. Supplier and developers

Institute/Company	Country	Remarks
BASF	Germany	Manufacturer of commercial adsorptive distillation column
Sulzer Chemtech Ltd	Switzerland	Manufacturer of commercial adsorptive distillation column
The Dow Chemical Company	U.S.A.	Manufacturer of commercial adsorptive distillation column
Total Petrochemicals	France	Manufacturer of commercial adsorptive distillation column
SINOPEC Corp.	China	Manufacturer of commercial adsorptive distillation column
CNPC Corp.	China	Manufacturer of commercial adsorptive distillation column
TianDa BeiYang Equipment Corp.	China	Manufacturer of commercial adsorptive distillation column
State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology	China	Process design

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)

Since there are not so many types of adsorbents to choose, the key of adsorptive distillation is the loading mode of adsorbents in the distillation column, not the selection of adsorbents. In principle, the loading mode of catalysts in catalytic distillation column also can be applied to adsorptive distillation, which, however, would greatly promote the development of adsorptive distillation. In addition, adsorptive distillation is a completely environment-friendly process and thus the study on it should be strengthened in the field of process intensification (PI)!