EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Reactive Absorption

TECHNOLOGY CODE: 2.2.6

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1. Technology

1.1 Description of technology / working principle

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

The main purposes of *absorption processes* are the removal of one or more components from the gas phase, the production of particular substances in the liquid phase and the separation of gas mixture. *Reactive absorption* represents a process in which the solution of gaseous species in a liquid solvent phase is combined with chemical reactions. As compared to purely physical absorption, reactive absorption does not necessarily require elevated pressure and a high solubility of the absorbed components since the chemical reaction in the liquid phase results in the transfer of a molecular dissolved component to a different chemical state and thus enhances the solution capacity. Most of the reactive absorption processes involve only reactions in the liquid phase, but in some of them reactions occur in both phases. Reactive absorption processes are predominantly used for the production of basic chemicals, e.g. sulphuric or nitric acids, and for the removal of harmful substances like H_2S from gas streams. This can be either the clean up of process gas streams or the removal of toxic or harmful substances in flue gases and liquids.

1.2 Types and "versions"

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

Industrial absorption operations are usually realised by combining *absorption* and *desorption* units (See Figure 1). In an absorber, one or more gas components are absorbed by a lean solvent, either physically or chemically. A rich solvent, after preheating in heat exchangers H_1 and H_3, is transported to the top of a desorption unit. A part of the absorbed gas is removed due to flashing and heating. The other part has to be desorbed in the stripper via counter-current contact of liquid with the inert gas or steam. The lean solvent then flows through the heat exchanger H_1 to recover heat necessary for heating the reach solvent, pass the heat exchanger H_2 to cool down to a desired temperature and finally enters the absorber. Reactive absorption can be realised in a variety of equipment types. The process is characterised by independent flow of both phases and permits both co-current (down-flow and up-flow) and counter-current regimes. Chemical absorption usually has a much more favorable equilibrium relationship than physical absorption (solubility of most gases is very low).

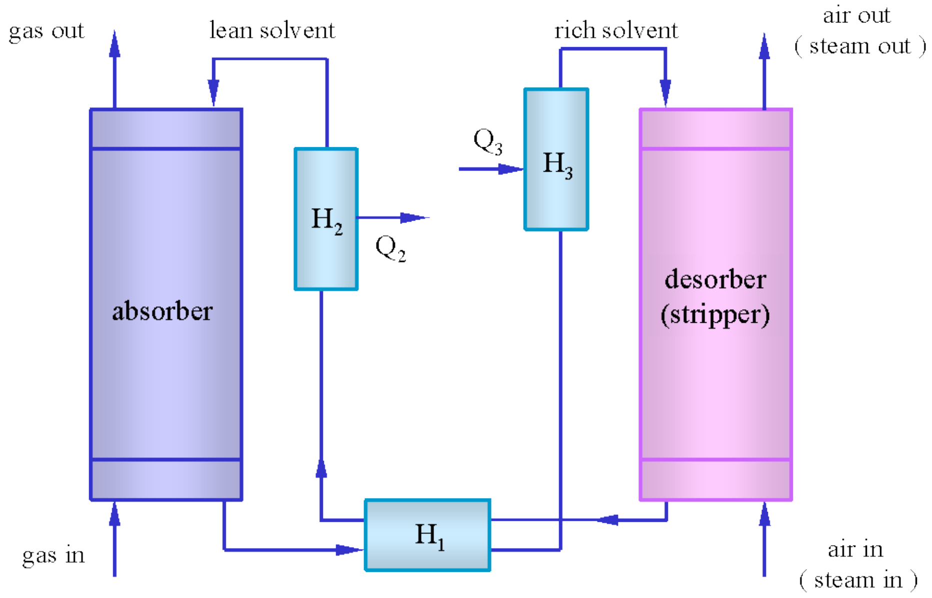

Figure 1: Combined absorption and desoprtion process with heat integration

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**
Reduction of CO_2 emission	Up to 20% of the outlet streams in the chemical industry; Up to 30% of the waste gases in energy generation	The separation of CO2 from other components is very important for syngas and fertilizer production, and in natural gas processing. The effective CO_2 removal from flue gases in power generation is a key issue in a zero emission plant projects
Energy saving in desorption	Case dependent, but up to 37% possible	Thermal desorption usually requires about 80% of the whole energy consumption of the absorption/desoprtion process.
Investment cost saving	Up to 15% of the investment costs	Operating conditions for reactive absorption are often up to 40 bar in a corrosive environment. The intensified unit become smaller, thus reducing the capital costs substantially
Increasing of waste gas purity	Down to several ppm of absorptive	Less environmental pollution; increased gas purity allows for preventing of the undesired reactions in the subsequent production steps
Less corrosion problems	Can not be quantified at the moment	The additives may prevent the corrosion without diminishing of the chemical reaction enhancement

1.4 Stage of development

Reactive absorption is essentially an old process known since the foundation of modern industry. This is a very important process, too, being the basic operation in many technological chains. More recently, the role of reactive absorption as a key environmental protection process has grown up significantly. Today reactive absorption appears to be the most widely applied reactive separation operation. Despite the clear importance of reactive absorption, its behaviour is still not properly understood. This can be attributed to a very complex combination of process thermodynamics and kinetics, with intricate reaction schemes including ionic species, reaction rates varying over a wide range, and complex mass transfer–reaction coupling. As compared to distillation, reactive absorption is a fully rate-controlled process and it occurs definitely far from the equilibrium state.

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)

Physical absorption is the most obvious method to wash the gases. It is mostly carried out in the same apparatus as reactive absorption but no chemicals are necessary. Physical absorption is advantageous only if the plant capacity is high at high absorptive concentration or if the solubility of absorptive is high (e.g. ammonia in water).

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)

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

Sector	**Company - Process/ Product name/type**	**Short charac-teristic of applica-tion**	**Production capacity/ Plant size**	**Year of applic ation**	**Reported effects**
Chemistry, refineries, natural gas processing	**BASF**/Amine treating/syn-gas	Selective absorption of CO2 and sour comp-onents using amines	at least 240 amine treating plants worldwide	From 1980 till now	High purity of the exhaust gases Separation of the components for the further synthesis steps (syngas)
Steel production /environ-mental protection	**Thyssen Krupp**/ desulphuri-sation (e.g. VACASULF process)	Coke oven gas purification	At least 80 integrated plants for absorption/ desorption; capacity: from 30 Nm^3/h up to 190 Nm^3/h	From 1990	High purity of the recovered sulfur Sulfur concent-ration less than 800 mg/ Nm^3 H_2S concentration less than 500 mg/ Nm^3.
Energy generation	**RWE**	Desulphuri zation of flue gases	At least 37 scrubbers	From 1980 till now	Reduction of the CO2 emission under the limits required by law
Chemistry	**Lurgi**/ Syngas processing/ Methanol (e.g. Rectisol)	Selective gas absorption	75 % of the syngas produced world wide by coal, oil and waste gasification is purified in Rectisol units (About 120)	From 1960	1- 50 ppm H_2S 10 – 50 ppm CO_2
Fine Chemisry	Proctle & Gamble/polyol polyesters	Combina-tion of absorption and transeste-rification	Not known	1995	

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.)

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 applica-tion	Reported effects
Energy generation	RWE/Germany (CASTOR project)	The aim is to have available CO_2 scrubbing for new and recently built hard coal and lignite power stations	2009	Increasing of scrubbing efficiency up to 10%
Energy generation/ hydrogen production	FutureGen Allance/USA	commercial-scale plant for the technical and economic feasibility of producing low-cost electricity and hydrogen from coal while nearly eliminating emissions	2012	Up to 90% pf the SO_2removal
Environ-mental protection	Environmental Protection Agency/ USA	Acid Rain NOX Emission Reduction Program	2020	Meeting the legislative standards
Environ-mental protection	Environmental Protection Agency/ USA	Acid Rain SO2 Emission Reduction Program	2020	Meeting the legislative standards

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)

Aim of the process	Examples	Application area
Removal of harmful substances	• Coke oven gas purification • Carbon dioxide removal by amines/ amine blends/ hot potassium carbonate solutions • NO_x removal	Gas purification
Retrieval/regeneration of valuable substances or non-reacted reactants	• Solvent regeneration	Gas separation
Production/preparation of particular products	• Sulphuric and nitric acid manufacturing • Formaldehyde preparation	Chemical synthesis
Water removal	• Water removal from natural gas • Air drying	Gas drying
Conditioning of gas streams	• Synthesis gas conditioning	Gas separation/ gas purification
Separation of substances	• Olefin/paraffin separation	Separation of organic components

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?
Methods for design of the processes	Modelling of the reaction kinetics and mass transfer in multireaction and multicomponent systems	Collaboration between academia and end users
Optimal process configuration	The optimal connection of absorption and regeneration allows for energy savings	Better process models developed in R&D entities; improvement of flexibility through better control
Broad technology applications, combined with other technologies	Hybrid processes, combination of wet and dry separation technologies, implementation for flue gas purification	Joint projects between universities and energy providers

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?
Toxity and bio-degrability of solvents	Several solvents (e.g. additives, activators, ionic liquids) are either toxic or not bio-degradable. The storage and/or recycling is a barrier in the further technology development at the moment	New, green solvents to be developed by academia and technology providers
Increasing purity of exhaust gases and process selectivity	The selective recovery of pure gases would increase the efficiency of the process efficiency in the chemical production, reduce the number of synthesis steps and decrease the energy consumption	Better design and operation methods to be developed by R&D departments
Smaller equipment and reduced pressure	The reduction both in volume and pressure causes significant savings in capital expenditure	Better design and operation methods to be developed by R&D departments
Non-corrosive materials for innovative equipment applications	The application of structured column internals is prohibited because of the corrosion of the metal in an aggressive sour gas environment	New metals used for known internals or new internal constructions should be provided by internal suppliers

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
Kenig, E. Y. & Górak, A. (2005). Reactive absorption, in: Sundmacher, K., Kienle, A., Seidel-Morgenstern, A. (Eds.), Integrated Chemical Processes, Wiley, Weinheim.	Chapter in the book	Most recent overview on the reactive absorption modeling and applications
K. Hölemann und A. Górak: „Absorption“ in: „Fluidverfahrenstechnik“ – Grundlagen, Methodik, Technik, Praxis. Weinheim: Wiley-VCH, 2006	Chapter in the handbook	In German; the most com-prehensive overview on (reactive) absorption
van Loo, S., van Elk, E.P., Versteeg, G.F. The removal of carbon dioxide with activated solutions of methyl-diethanol-amine (2007) Journal of Petroleum Science and Engineering, 55 (1-2), pp. 135-145.	Paper	Solvent activation in gas treating
Faber, R., Li, B., Li, P., Wozny, G. Data reconciliation for real-time optimization of an industrial coke-oven-gas purification process (2006) Simulation Modelling Practice and Theory, 14 (8), pp. 1121-1134.	Paper	Process optimization, data reconciliation
Algusane, T.Y., Proios, P., Georgiadis, M.C., Pistikopoulos, E.N. A framework for the synthesis of reactive absorption columns (2006) Chemical Engineering and Processing, 45 (4), pp. 276-290.	Paper	Conceptual process design
Hüpen, B., Kenig, E.Y. Rigorous modelling of NOx absorption in tray and packed columns (2005) Chemical Engineering Science, 60 (22), pp. 6462-6471	Paper	Process modeling
Reine, T.A., Eldridge, R.B. Absorption equilibrium and kinetics for ethylene-ethane separation with a novel solvent (2005) Industrial and Engineering Chemistry Research, 44 (19), pp. 7505-7510.	Paper	Data for process design
Srivastava RK, Jozewicz W. Flue gas desulfurization: the state of the art. J Air Waste Manag Assoc. 2001 Dec;51(12):1676-88.	Review	The most recent overview over the de-sulfurization
Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R. Kinetics of the reactive absorption of carbon dioxide in high CO2-loaded, concentrated aqueous	Paper	Reaction kinetics for gas treating

monoethanolamine solutions (2003) Chemical Engineering Science, 58 (23-24), pp. 5195-5210.		
Kenig, E.Y., Kucka, L., Górak, A. Rigorous modeling of reactive absorption processes (2003) Chemical Engineering and Technology, 26 (6), pp. 631-646.	Review	The most comprehensive review on modeling
Safarik, D.J., Eldridge, R.B. Olefin/paraffin separations by reactive absorption: a review (1998) Industrial and Engineering Chemistry Research, 37 (7), pp. 2571-2581	Review	The most comprehensive review on olefin-parafin separation

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
Continuous transesterification method for preparing polyol polyesters	The Procter & Gamble Company	polyesters
Process for the condensation of an aldehyde with hydrogen cyanide	Rhone-Poulenc Nutrition Animale	condensation reaction process
Method and reactor for producing ethylene oxide	Linde Aktiengesellschaft	production of ethylene oxide from a gaseous feedstock
Method of separating carbon dioxide from a gas mixture	Battelle Memorial Institute	separating a non-aqueous component from a gas mixture
Method for removing mercaptans from fluid fluxes	BASF Aktiengesellschaft	removing mercaptans from CO2 and H2S
Process for generating heat to reduce the emission of oxides of sulphur	Institut Francais du Petrole	reduced emissions of sulfur oxides
Method and apparatus for wet type flue-gas desulfurization	Mitsubishi Heavy Industries, Ltd.	desulfurizing device
Multi-component removal in flue gas by aqua ammonia	United States of America Department of Energy	removing acid anhydrides precursors
System and method for purifying exhaust gases	Johnson Matthey Public Limited Company	treating exhaust gases including NO, nitrogen and particulate matter

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
BASF AG	Germany	Amine producer; gas treating technology provider
UOP	USA	Amine gas washing
The University of Texas at Austin, Department of Chemical Engineering	USA	Patent holder of several commercialized applications
Dortmund University, Chair of Fluid Separations	Germany	The most sophisticated simulation tool for design of absorption processes
RWE	Germany	Zero emission IGCC with CCS
International Energy Agency	USA	Stakeholder; coordination activities
ASPENTECH	USA	Commercial simulation software (RateSep)
Procede Group BV	NL	Activators of reactive solvents
Department of Chemical and Materials Engineering, Tamkang University, Taipei	Taiwan	Process simulation

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	Amines and activators
UOP	USA	Absorption technologies
Sulzer	Switzerland	Equipment
Koch-Glitsch	USA	Equipment
RWE	Germany	Gas treating
Shanxi jiaocheng hongxing chemical Co.	China	Nitric acid production
ALSTOM	France	Desulphurization
Lurgi	Germany	Gas treating technologies
DOW	USA	Gas treating technologies

5.2 End users

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

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Reactive absorption undergoes its revival in the recent 5 years because of the increased legislation restrictions, reduced energy demand and CO2 sequestration. The main challenge in the technology application is the lacking tailored absorption solvents, not sufficient demonstration projects in flue gas purification and little experience in process design. The technology offers great potential within next 10 years.