

Inaugural lecture
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18 April 2008



/ Department of Chemical Engineering and Chemistry

TU / **e**

Technische Universiteit
Eindhoven
University of Technology

Value generating separation systems

Where innovation starts

Inaugural lecture prof.dr.ir. André de Haan

Value generating separation systems

Presented on 18 April 2008
at the Eindhoven University of Technology

Introduction

When starting the preparation of this inaugural lecture, I decided to hold it in English. The reason is not only to maximize the understanding by all of you present today. In the current, highly international academic environment, I believe English should be the standard official communication language to ensure optimal dissemination.

As you have been able to read in the invitation I have now been working at Eindhoven University of Technology for almost two years. During the past two years I was asked many times about my reasons for changing universities and whether this was the result of a strategic decision within the 3TU cooperation. Let me assure you that the 3TU cooperation has made absolutely no contribution to the reallocation process. The main reason for deciding that my future career would probably prosper better in a different environment is most clearly reflected in a press release dating from November 2007:

UT wants to get rid of purely technical image (Tubantia, 14-11-2007).

According to its mission, Eindhoven University of Technology (TU/e) intends to be a research driven, design oriented **university of technology** at an international level, with the primary objective of providing young people with an academic education within the '**engineering science & technology**' domain. With this focus on technology and engineering I hope to have found an environment that better fits my personal strengths and ambitions.

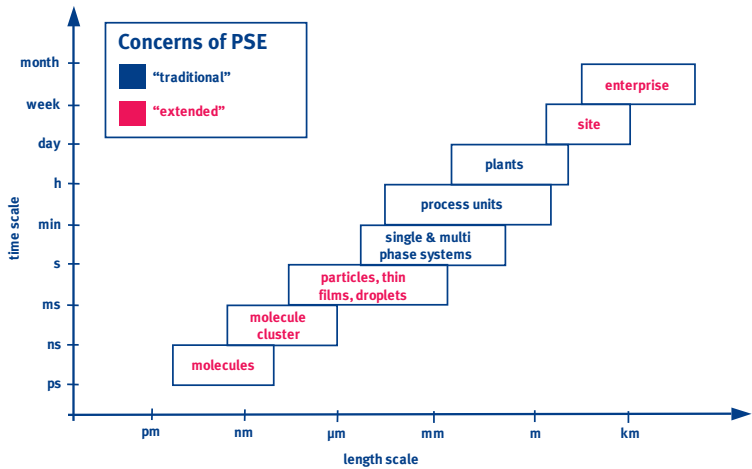
My appointment in Eindhoven concerns a chair in the field of Process Systems Engineering. As many of you know, Process Systems Engineering (PSE) is an extremely broad research area covering nearly all technical and non-technical disciplines at all scales. For this reason I will start this lecture with an overview of recent developments and current trends in PSE, focusing on their importance to the field of chemical engineering. Based on this overview it will become clear that process systems for value generating separations is a challenging research area with tremendous future scientific and innovation potential. After that, I will explain my view on the main research challenges in this area and outline how I intend to address these challenges within the research program of my chair. Finally I will conclude the lecture with some personal views on education.

From Value Preservation to Value Generation

Let us start by reviewing and analyzing the latest trends in Process Systems Engineering.

The origin of systems engineering goes back to the 1940s in the efforts to exploit the possibilities of the newly-invented electronic digital computers (Sargent, 2005). During the subsequent decades, Process Systems Engineering (PSE) has become an established discipline in chemical engineering, its progress closely linked to developments in computing. Traditionally, the scope of PSE in chemical engineering has comprised the development of concepts, problem formulations and algorithms to deal with systems problems on the scale of a unit operation and of the plant (Sargent, 2004; Ponton 1995; Takamatsu, 1983). Novel representations and models that capture non-trivial features, as well as computationally efficient solution methods and software tools, are considered the main contributions of PSE during the last century.

figure 1
Chemical supply chain



While this traditional scope has been adequate for many decades, it is currently being extended to the length and time scales of the complete chemical supply chain, as illustrated in figure 1 (Charpentier and McKenna, 2004; Grossmann and Westerberg, 2000; Klatt and Marquardt, 2007). This chain starts with chemicals and other products that industry must synthesize and characterize at the molecular level. The molecules are then aggregated into clusters, particles or thin films. These single or multiphase systems finally take the form of macroscopic mixtures as solid, paste-like or emulsion products. Transitioning from chemistry and biology to engineering involves the design of the production units, which are integrated into a chemical process that in turn becomes part of a multi-product industrial site. Finally, this site is part of a commercial enterprise driven by business considerations and product quality in the framework of sustainability. Taking into account these considerations, Grossmann (2000) redefined the field as:

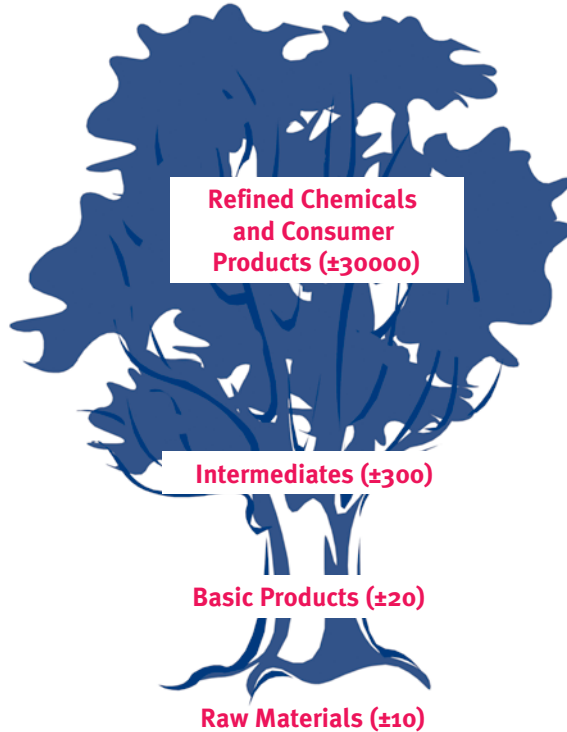
Process Systems Engineering is concerned with the improvement of decision-making processes for the creation and operation of the chemical supply chain. It deals with the discovery, design, manufacture, and distribution of chemical products in the context of many conflicting goals (Grossmann and Westerberg, 2000).

This definition ties fundamental scientific discoveries at the molecular or microscopic level to strategies and logistics for manufacturing and production planning. An important implication of this definition for PSE is to provide knowledge and tools to support both the 'value preservation' (e.g. large-scale commodity chemicals) and the 'value generation' (e.g. specialty chemicals, biotechnology and pharmaceuticals) industries for systematic decision making. Objectives for the 'value preservation' industry are cost reduction, efficient operation and continuous improvement of product quality. These are the traditional concerns of PSE, which largely lie in the middle and upper part of figure 1. The 'value generating' industry must discover new products and be agile and fast to market, concerns which PSE is only now beginning to address. These concerns are typically found both in the lower and higher ends of figure 1.

The past strong focus of Process Systems Engineering on value preservation is also illustrated by the 'chemical product tree' in figure 2, which shows that thousands of products can be obtained from a basic set of starting materials. At present most data, models and PSE methodologies have been established for products and processes in the lower ends of the tree, while hardly any predictive models exist for the products and processes in the top 'value generating' section of the

figure 2

Chemical product
tree



tree (Gani, 2004). The main reason for this situation is the complexity of the ‘top section’ molecular systems and the lack of adequate models to describe them. This short analysis makes clear that the transition to ‘value generating’ complex molecular systems will be an important challenge for Process Systems Engineering research in the coming decades.

During the past ten years various colleagues have identified future challenges for Process Systems Engineering (Bakshi and Fiksel, 2003; Gani, 2004; Grossmann, 2000; Klatt and Marquardt, 2007). The overall picture originating from their contributions is that these challenges range from design at the molecular level, through process design for new products to enterprise-wide optimization and global life cycle assessment, all within the context of sustainability and economics. For process and product engineering the generally accepted major challenges for the coming decades are extension to complex molecular systems, process intensification and sustainability. In process intensification significant

contributions have already been made (Moulijn et al., 2008). Plant miniaturization and integration of reaction and separation are widely recognized achievements. Moving towards the Holy Grail in establishing sustainable and environmentally benign processes implies the design of chemistry in which the target molecule is made of renewable readily available starting materials in one simple, safe, environmentally friendly and resource-effective operation with 100% yield (Garcia-Serna et al., 2007).

Although to some extent understandable, it is interesting to note that most of the attention for process intensification and sustainability has been devoted to the chemical reaction part of the processes. This focus is especially interesting when one considers that 50-100% of the current process operations concern separations, which in turn also consume the major part of the energy and solvents used. Furthermore, by the very nature of chemistry, there will always be contaminants in the raw materials, incompletely converted raw materials, unavoidable byproducts or spent catalysts and solvents that produce waste.

This lack of recognition of the importance of separation technology for the future competitive position of the Dutch process industry was also identified in 1998 during the Technology Radar of the Dutch ministry of economic affairs (Technologie radar, 1998). I got involved in this process in 1999, the same year I was appointed in Twente. Nevertheless it took until 2003 before sufficient commitment was gathered within the Dutch process industry to start the development of a Separation Technology roadmap (PA Consulting Group, 2004), which in turn provided the basis for establishing a first outline for a research program during the famous Lunteren Workshops in October 2005. Many of the people present today attended those workshops. For me there were two important outcomes of the Lunteren meetings. First that all participants, industry, institutes and universities, clearly confirmed that affinity separations is one of the key technology areas to provide the required future breakthroughs with respect to process intensification and the recovery of value generating products from complex mixtures. A second important conclusion was that industry as well as institutes indicated that systematic methods for the design and implementation of affinity separation systems are largely lacking, which is one of the major hurdles to be taken to achieve industry-wide application.

In other words, affinity separations is an important area in which Process Systems Engineering can make major contributions to establish the intensified, sustainable processes required for the 'value generating' products of the future.

Affinity Separation Systems

Now, before jumping directly into research plans, let us pay a little attention to what distinguishes affinity separation systems from most current separation systems.

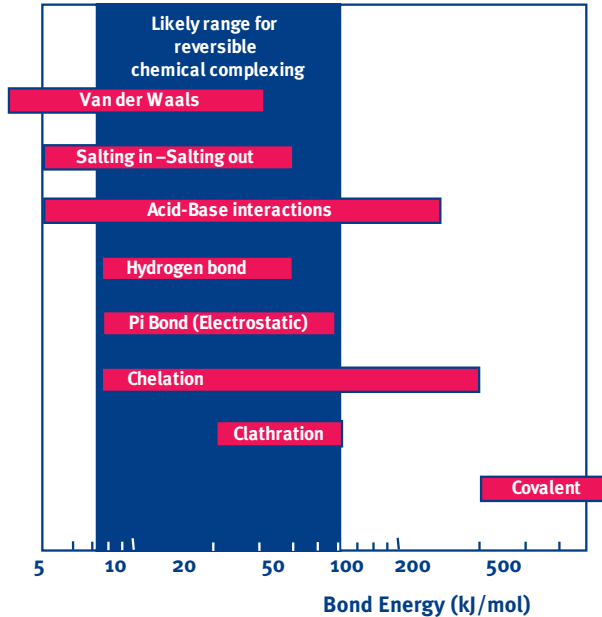
Traditionally, separation systems are subdivided into mechanical and molecular separations. Molecular separations require the addition of a separating agent to create a second phase and enforce a separation between the targeted components. Most current industrial separations employ separating agents with non-specific, non-directed interactions utilizing regular solvents or non-functionalized adsorbents. The main limitation of these separation systems is that they only perform adequately for relatively simple mixtures in which significant differences between the molecular properties of the components to be separated can be exploited.

The main challenge with complex molecular systems is that such significant differences do not exist and that often a large number of largely identical molecules are present. Typical examples are encountered in pharmaceuticals, specialty chemicals, natural feedstocks, fermentation, biorefineries, Fisher Tropsch synthesis and even naphtha crackers. In all these examples breakthroughs can only be established by using much more advanced separation principles that are able to recognize either specific molecules or specific molecular classes. This is only possible by applying highly specific, directed molecular interactions, which is the domain of affinity separation systems.

Affinity separations rely on the specific recognition between an affinity ligand and a solute, also referred to as host-guest interactions. As this interaction is much more specific, the use of affinity separations reduces non-specific interactions, increases operational yields, intensifies the separation system and facilitates the elimination of undesirable contaminants. It is essential that affinity materials can provide strong, specific, directed but reversible interactions with the solutes of interest. In order for an interaction to be reversible in an economically attractive process, it must have a relatively low bond energy. Such interactions are known as complexation or association reactions. Figure 3 shows some important examples of such reactions with the bond energies typically involved. Generally interactions

figure 3

Bond energies most suited for affinity extractants (King, 1987).



with bond energies less than 10 kJ/mol are too weak to be of interest, while interactions with bond energies above 50 kJ/mol tend to be too difficult to reverse. In many cases, multiple types of interactions can be incorporated into affinity materials to obtain the desired properties with respect to capacity, selectivity and reversibility. From this it is clear that an indefinite number of options exist to design and develop affinity materials. One of the main challenges is therefore to structure this affinity material design process in such a way that systems are established that can be applied with sufficient confidence on industrial scale.

Affinity separation systems are not a complete novelty but are already successfully employed in some parts of the process industry. Well-known examples are:

- metal ion extraction and refining in hydrometallurgy (Rydberg et al., 2004)
- acid gas removal by absorption with primary amines in the bulk chemical and oil&gas industry (Kohl and Nielsen, 1997)
- enantiomer resolution by diastereomeric crystallization in the pharmaceutical industry (Sheldon, 1993)
- extractive recovery of primary and secondary metabolites by reactive extraction from fermentation broths (Schügerl, 1994)

Nevertheless, the process industry is, in my opinion, currently only exploiting a fraction of the tremendous potential of affinity separation systems. This situation is rather interesting because in the field of chemistry an extensive amount of high-quality research is being performed on the discovery, understanding and improvement of host-guest interaction systems. Unfortunately most of this research only ends up in scientific journals and never reaches the chemical process industry. When applied, typical areas concern analytical chemistry, sensors, diagnostics, lab-on-chip etc. Apparently a tremendous gap exists between both worlds, inhibiting the exploitation of molecular scale discoveries in macro-scale process applications. Bridging this gap is only possible by establishing a paradigm shift in the research methodologies used, to enable the connection of macro-scale performance in process systems with the design of affinity separating agents at the molecular level.

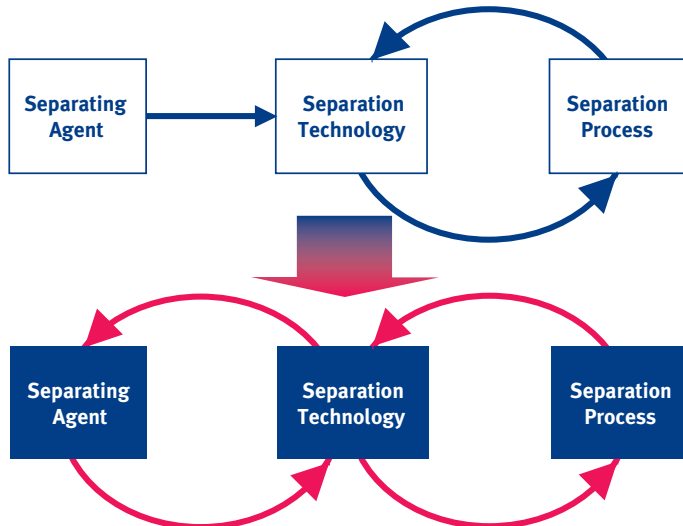
A Paradigm Shift in Affinity Separation System Engineering

The obvious question now becomes what kind of paradigm shift would be needed.

To answer this question we should start by considering the traditional process development cycle as illustrated schematically by the top picture of figure 4. This traditional development cycle is based on a sequential approach with mostly a unidirectional interface between separating agent and process. Optimization typically takes place at the level of the selected technology and the integration of this technology in the process system. The achievable results in process development will therefore largely be restricted by the available separating agents on the market and depend on the performance of these materials within the process. A feedback to separating agent design will then provide information about the potential for future process improvement. However, the overall progress in both material and process performance will be incremental, and will require considerable efforts because the improved materials have to be implemented into the process for each iteration.

figure 4

Required paradigm shift



Making step changes with respect to process intensification and sustainability therefore requires that the existing paradigm – having separating agents determine the process performance – is exchanged for a process-driven approach, as illustrated by the bottom picture in figure 4. Here, the selection of optimum process performance parameters will determine the criteria for separating agent design, which then will be accomplished by providing materials optimized for maximum process performance. This paradigm shift in material and process performance can only be achieved if material design, process development, and model-based process integration are pursued in one joint design approach. However, at this moment such integrated model-based design approaches that are able to integrate the molecular level design with process performance are almost non-existent for affinity separation systems. For instance, even the recently established systematic engineering methodologies for reactive separations (Almeida et al., 2004; Bart et al., 2008; Moulijn et al., 2008; Schembecker, 2003) still start with a preselected (affinity) separating agent and focus on optimization of technology and/or process system performance.

Affinity Separation System Research

The subsequent question to be answered is how this need to establish a paradigm shift in affinity separation system engineering will be addressed by my research plans.

From the preceding it is clear that research in affinity separation systems should be directed towards connecting the molecular level of the separating agent with the macro level of the process system. Two of my main research lines address this challenge:

- Affinity Solvent Separation Systems
- Affinity Solid Separation Systems

In both topics my goal is to define the desired performance of the separating agent at a molecular level from a conceptual analysis of process systems. Based on the defined performance, the separating agent can be designed and subsequently characterized to evaluate its actual performance in the conceptual separation process system. All this research is typically focused on establishing technology breakthroughs by designing affinity solvents and solids that enable a step change compared with the existing separation systems. Since this research remains to a large extent at the proof of concept level, a second cycle will be needed to actually implement the established affinity separation systems into industrial processes. Everyone knows that in the last decades the process industry has largely shifted its research focus from research to development. Furthermore industrial applicability involves much more than a proof of concept. For these reasons one can no longer expect that a promising finding at a university will be taken up by industry just like that. To support valorization of new affinity separation systems by the process industry, I have incorporated a third line in our research program:

- System Integration and Equipment Intensification

The main aim of this research line is to investigate issues associated with the design and operation of affinity-based separation systems and their integration into complete process systems.

Affinity Solvent Separation Systems

The next part of this inaugural lecture will be devoted to describing these three research lines in more detail. I will start with affinity solvent separation systems.

Two important questions arise. What can we achieve using affinity solvents, instead of regular solvents and how can we design affinity solvent separation systems in a systematic manner? As all engineers know it is no use developing systematic methodologies when no clear advantage can be achieved. Let us therefore start with addressing the first question by looking at some examples from our own work during the last five years.

For the separation of olefin isomers by distillation, which is one of the most complex separations in the Fisher Tropsch downstream processing, we have developed a technology concept called Reactive Extractive Distillation (Wentink et al., 2007). Instead of using regular solvents we have introduced affinity solvents that are capable of π -complexation. As a result, we have been able to increase the relative volatility, which is very close to unity for C6 olefins, to a value of around 1.4. The direct implication of this relative volatility increase is a tenfold reduction in the number of trays of a distillation column from over 500 to less than 50. Simultaneously the amount of energy required is also reduced by a factor of 10 due to a significantly lower reflux ratio.

A second example concerns the utilization of ionic liquids for extracting aromatics at low concentrations from aliphatics (Meindersma et al., 2007). At present there is no economically feasible technology to do so. With ionic liquids up to a factor 5 higher solvent capacities for aromatics can be achieved. Furthermore the non-volatility of ionic liquids allows the use of simpler solvent recovery techniques. As a result the investment costs can be reduced by a factor 4 and the energy requirements by 70-80% compared with the current bench-mark technologies.

The final example concerns the extractive separation of optical isomers (Steensma et al., 2006). For these separations the main driver is to obtain the right product with the desired quality with a minimum of development activities. For this reason preparative chromatography has rapidly become a very popular technology.

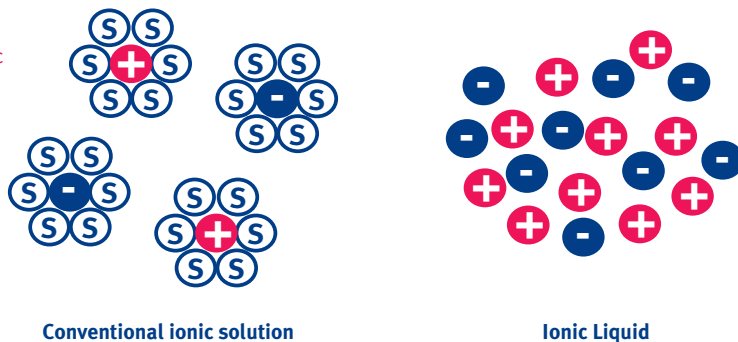
Consequently, most researchers are developing new chiral stationary phases without considering the effectiveness of their selectors in a liquid phase. In our case the crown ether used immobilized on a stationary phase displayed a typical selectivity between amino alcohol enantiomers in the range of 1.05-1.1, while using the same selector dissolved in a solvent provided selectivities ranging between 3 and 10. Furthermore, application of enantioselective selectors in solvent systems provides the potential of achieving at least 10 times higher volumetric capacities, and can therefore result in a factor 4 reduction in investment costs and up to a factor 10 reduction in eluent consumption.

It is clear that all these three examples have in common that the application of affinity solvents can provide significant step changes with respect to size of installations (process intensification), energy consumption, waste production (both sustainability) and the ability to produce new and existing products in a cost-effective way.

The ability to achieve tremendous step changes is the reason that we have already started research projects on affinity solvent systems for various potential application areas. A running project is the removal of low concentration aromatics from various petrochemical streams by extraction with ionic liquids. In this case the ionic liquid enables the production of low aromatic content fuels as a new value generating product, which is not feasible with current technologies. In relation to this project, we have just started to investigate the applicability of ionic liquids in extractive distillation for the separation of hydrocarbon mixtures. For this application the demands on the ionic liquid are exactly opposite to those in extraction. The solvent in extractive distillation should be able to increase the selectivity and be highly miscible while for extraction a high immiscibility is desired. This implies directly that for both application areas totally different affinity solvent systems need to be designed. For such applications ionic liquids are of tremendous interest as affinity solvent due to their designer character. As illustrated by figure 5 ionic liquids differ from regular ionic solutions by the fact that they consist solely of ions, without any solvent. Ionic liquids are also known as designer solvents since their properties can be tailored by designing and combining the right anion and cation.

figure 5

Schematic of ionic liquids



Other recently started projects include designer solvents for water removal, multi-functional extractants for organic acids and bases recovery from fermentation broths and affinity solvent-based technologies for the removal of trace components. Especially this last project is a clear example of how affinity solvent systems can be utilized to improve product quality and thereby generate added value compared with the current technologies. In addition to ionic liquids a variety of other promising affinity solvents such as:

- hyperbranched polymers
- supramolecular systems (crown ethers, calixarenes or cyclodextrins)
- systems with multiple synergistic functionalities
- self assembling solvent systems

will be explored within the mentioned projects to provide the breakthroughs aimed for.

Affinity Solvent System Design

From these examples it is clear that the first and most important step in these projects is the identification and design of an adequate affinity solvent (De Haan, 2006).

The initial selection criteria for affinity solvent systems are more or less similar to the criteria for regular solvent extraction. Most important is a combination of a high **Distribution Coefficient** with a high **Selectivity**. The main difference between affinity solvents and regular solvents is that, by applying reversible solute-specific reactive interactions, it is possible to combine high selectivities with high capacities, while with regular solvents high selectivity is nearly always obtained at the expense of low capacity and vice versa.

Other important criteria that must be met by the affinity solvent are related to the design of the affinity separation system in which the **Recovery and Recycling** of the affinity solvent is a major issue. In most cases the affinity solvent will be considerably more expensive than regular solvents, thereby increasing the required efficiency of its recovery. It is therefore extremely important to already incorporate the ease of solute recovery from the loaded affinity solvent during the identification/design stage. Furthermore, care should be taken to reduce potential affinity solvent losses to the absolute minimum.

For the design of affinity solvent-based processes the common selection criteria such as sufficient density difference, not too high viscosity and favorable interfacial tensions apply. Furthermore standard issues such as availability, cost, toxicity, compatibility, flammability, stability and environmental impact should be taken into account. The main difference with regular solvents is the selectivity providing reversible complexation and association reaction in addition to mass transfer. For economically feasible processes, the applied affinity interactions should have sufficiently fast kinetics in order to avoid the need for excessive residence times.

This overview clearly illustrates that developing suitable affinity solvent systems involves the fulfillment of many different, often conflicting goals. Within the field of Process Systems Engineering this challenge has been addressed by establishing

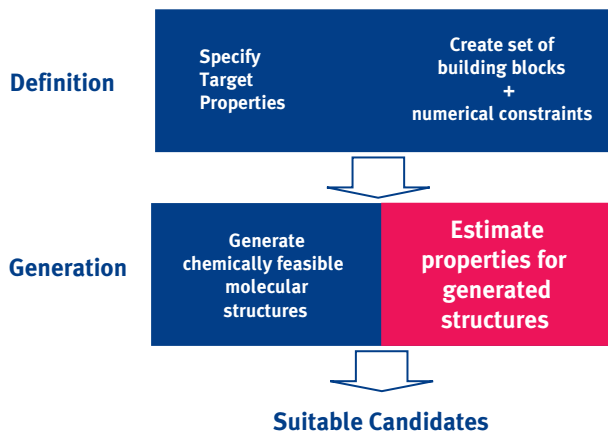
computer-aided molecular design (CAMD) methodologies. (Folic, 2007; Gani, 2004; Giovanoglou et al., 2003; Papadopoulos and Linke, 2006). Computer-aided molecular design (CAMD) problems are defined as:

Given a set of building blocks and a specified set of target properties; determine the molecule or molecular structure that matches these properties.

The main steps of any CAMD method are to generate chemically feasible molecular structures, to estimate target properties for the generated structures and to screen/select those that satisfy the specified property constraints. Most currently used CAMD methods and tools work at the macroscopic level where the molecular structure is represented by groups. Figure 6 illustrates a typical group-contribution-based CAMD method, where first the basic needs are defined, then the feasible candidates are determined and tested for desired properties and finally a selection of suitable candidates is made.

figure 6

Basic scheme of CAMD



The application range of any CAMD method is directly related to the limitations in the application range of the property model used. The major difficulty is always associated with unavailable model parameters, which may eliminate a large portion of potential candidates. CAMD methods based on macroscopic properties are typically suitable for the design of relatively small and simple molecules. For the design of more complex and larger molecules, distinction between isomers and/or different molecular structures of the same chemical type becomes more important. Such complex molecular systems require molecular modeling-based property

estimation methods to include microscopic and/or mesoscopic scales for a reliable molecular design. To connect these multiple property models at different scales or levels of molecular structural variables, interfaces between lower-level and higher level modeling tools need to be established.

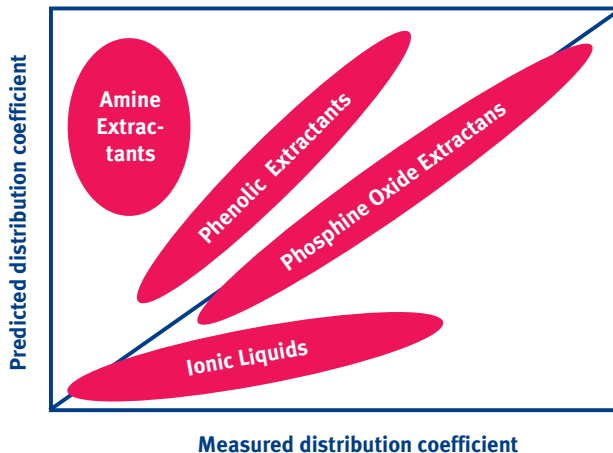
Affinity solvent systems are a typical example for which macroscopic property prediction using standard group contribution methods is insufficient for reliable design and feasibility evaluation. The main reason being the combination of strong directed interactions with generally complex molecular structures. At the same time molecular modeling-based methods are far too complex and time-consuming to be used for the design and optimization of large numbers of affinity solvent structures taking into account all selection criteria and accounting for effects such as solvent environment.

For this reason we have made several attempts to establish methodologies and interfaces that connect the molecular design level with process performance during the past years. An interesting way forward in this aspect appears to be the use of a COSMO-RS-based approach (Klamt, 2005). COSMO-RS stands for Conductor-like-Screening-Model for Real Solvents. This model is based on unimolecular quantum chemical calculations that are used to determine the charge profile distribution across a single molecule. After these unimolecular calculations, higher-level models are used to combine the molecules in mixtures and predict chemical potentials, activity coefficients and recently even physical properties (Klamt, 2005; Palomar, 2007). The main advantage of this approach is that the time-consuming quantum chemical charge profile calculation is only needed once for each molecule. Thereafter subsequent property calculations require only minimal computational effort, making this approach well suited for affinity solvent performance evaluation in complex mixtures.

Some of our experiences are collected in figure 7, which shows a schematic comparison between COSMO-RS predicted and measured distribution coefficients of various solutes with different affinity solvent classes. Although not always quantitatively correct, it is directly evident that for most affinity solvent classes the general sequence of performance can be predicted with reasonable reliability. Amine extractants are a well-known exception, which is mainly caused by deficiencies in the molecular scale models used to generate the charge distribution profiles.

figure 7

Schematic comparison between COSMO-RS predicted and experimental distribution coefficients



In the coming years one of my personal aims is to continue and strengthen the development of systematic methodologies for the design and performance evaluation of affinity solvent systems. This science-driven activity is a crucial foundation to support our more application-driven industrial and institute-funded projects. Our main focus will be on establishing methodologies for the utilization of recent advances in property modeling to design new affinity solvent separation systems. For this reason these activities offer excellent opportunities for cooperation within my network of national and international colleagues that focus on establishing improved molecular modeling-based property estimation methodologies.

Affinity Solid Separation Systems

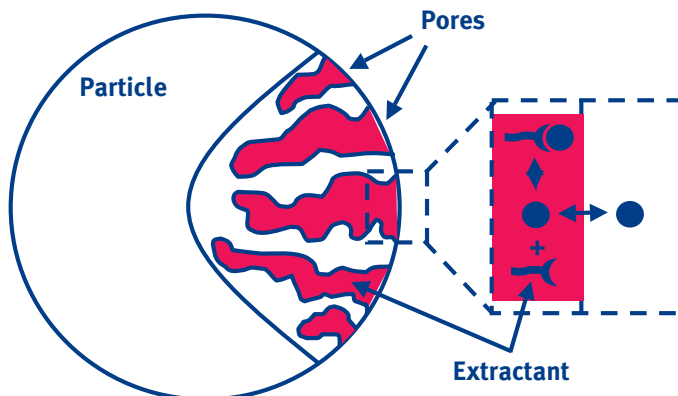
Besides solvents, affinity interactions can also be fruitfully applied in affinity solids.

Affinity solids have already been employed for several decades in various applications. Most established is the use of chelating ion exchangers for the recovery of metal ions (Zagorodni, 2007). Nevertheless most ion exchange applications still use sulfonic acid ion exchange resins because of their much lower costs. In the pharmaceutical and biotechnological area, affinity chromatography has become one of the major technologies for product recovery and purification. For pharmaceuticals, chiral stationary phases are used to separate optical isomers (Davankov, 2003; Schulte and Strube, 2001). Biotechnology employs affinity adsorbents such as Protein-A or Cibachrome resins to capture therapeutic proteins such as monoclonal antibodies (Roque et al., 2007). At present many groups around the world are working on these generally resin-based affinity solids.

This short analysis illustrates that, although affinity adsorbents have found their way into the very high value generating industry, their advantages are not yet exploited in most other industry sectors such as bulk chemicals, food and drink or specialty chemicals. The main reason being that for larger-scale applications the current affinity adsorbents are generally too expensive and do not have sufficiently high capacity. In my opinion the current resin-based affinity solids will not be able to address this challenge of combining molecular affinity with high capacity and low costs. I have therefore decided to focus my research on separation systems based on novel classes of affinity solids. Over the past years we have already made considerable progress in two areas: Extractant Impregnated Resins (EIRs) and low cost affinity adsorbents.

Figure 8 illustrates the concept of EIRs. Porous particles are used to immobilize an affinity solvent by simple impregnation. The main advantage over regular adsorbents is the utilization of the whole pore volume instead of only the pore surface. For this reason impregnated particles can contain considerably higher functional group loadings and thereby attain significantly higher capacities. Furthermore impregnation is considerably easier to perform than covalent anchoring. In several projects we have established EIRs for the selective recovery of polar solutes such

figure 8
Schematic of an
Extractant
Impregnated Resin
(EIR)



as aldehydes (Babic, 2006), phenols (Burghoff, 2008), ethers and even chiral EIRs for the separation of amino alcohol isomers (Babic, 2007).

Most of the low-cost adsorbent research worldwide is focused on relatively low-added-value applications such as the removal of heavy metals (Babel, 2003) and dyes (Crini, 2006) from waste water. Noteworthy is that most authors typically take a natural or waste material from their back yard and evaluate its adsorption properties without paying attention to the material design aspects from the application point of view. In our research projects we have typically approached the adsorbent selection and design problem from the reverse side by first establishing the functional groups in a solute we can target to achieve selective recovery. Following this approach we have demonstrated that for peptide separations simple affinity zeolites can outperform resin-based affinity adsorbents by orders of magnitude (Wijntje, 2005) and that tailored clay adsorbents can achieve anionic surfactant loadings that are one order of magnitude higher than those of regular materials (Schouten, 2007).

These examples clearly illustrate the interesting potential that affinity solids offer for process intensification throughout the process industry, which is why affinity solid separation systems are a key area in my research program. In addition to the examples I have already referred to, I see many more opportunities for developing separation process systems utilizing high capacity low-cost affinity solid materials such as functionalized textiles, functionalized foams and multifunctional materials that for instance combine affinity interactions with molecular sieving.

Rational design of affinity solid separation systems requires the establishment of systematic methods to guide decision making. As for affinity solvent separation systems there is currently no integrated methodology that connects the design of an affinity solid at the molecular and material level with its process performance. An important additional challenge compared with affinity solvent separation systems is the incorporation of the solid matrix, which has a strong influence on the affinity solid performance but is at the same time difficult to include in predictive modeling. A clear example is undesired interactions between the ligand and solid matrix that often reduce ligand availability.

Also on the topic of systematic affinity solid design we have made some first attempts to integrate the desired material design with required process performance. For the chromatographic separation of oligosaccharides a short-cut model has been developed that relates the effect of changes in adsorbent functionality directly to overall volumetric process efficiency (Vente, 2004). This model was subsequently used to guide adsorbent design in terms of material selection and optimization. For functionalized silica adsorbents, an adsorbent design model was developed in which the adsorbent properties for optimal process performance were combined with the attainable properties from a material perspective to derive the best-performing affinity adsorption materials (Djekic, 2008). For the coming years it is my aim to expand this affinity solid design methodology toolbox in order to move towards an integrated design methodology. Due to the complexity of affinity solid systems over affinity solvent systems, these methodologies will most probably contain a hybrid experimental/computational structure, as has already been successfully applied for other complex material design problems (Folic, 2007).

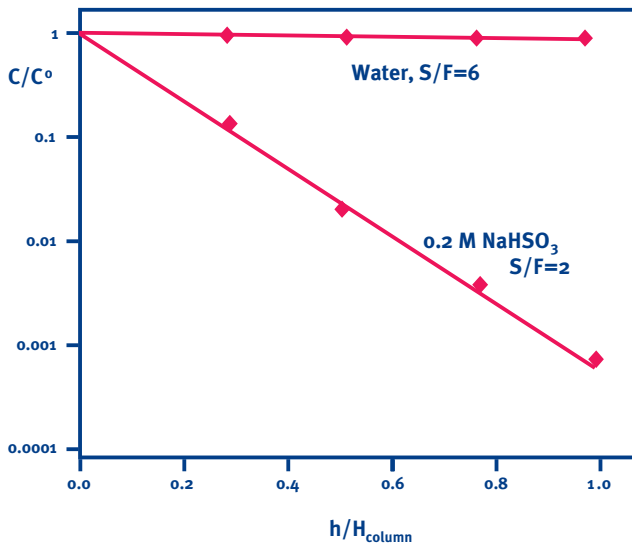
System Integration and Equipment Intensification

Once an affinity separating agent has been established, there is still a tremendous gap between concept and implementation. Actually this gap is a major hurdle for valorization and I therefore see it as one of my tasks to establish research activities that contribute to the elimination of these initial hurdles.

As a start it is interesting to illustrate once again the contribution that affinity solvents can make to increased process efficiency. This is shown in figure 9, where the extraction of 5% benzaldehyde from toluene with water in a pulsed disc and donut column is depicted. As one can clearly see pure water is a very unsuitable solvent. However, by adding only a small amount of sodium bisulfite the benzaldehyde is nearly quantitatively extracted with a considerably smaller solvent-to-feed ratio. The overall intensification is about 1000 times, mainly due to the increased distribution coefficient resulting from the reversible reaction.

figure 9

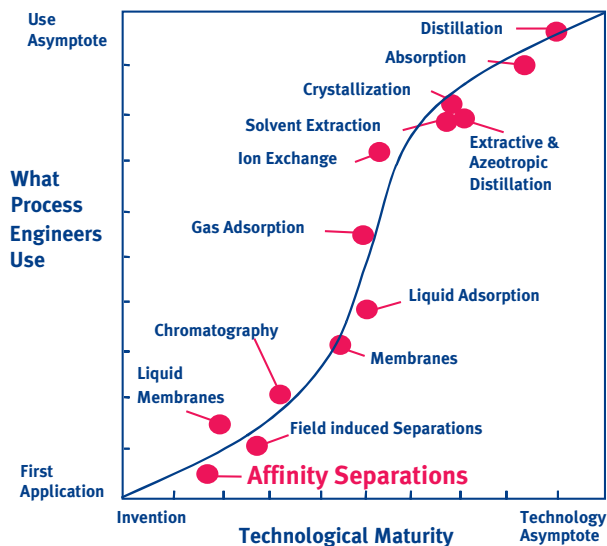
Concentration profile of benzaldehyde in a PDDC



Adding bisulfite to water for selective aldehyde recovery is a well-known procedure in organic chemistry, but is not used in industrial processes. As already indicated, many more such examples exist, where potentially interesting affinity materials and new separation concepts never reach the process industry. The technological and use maturity plot in figure 10 illustrates that the main reason for not considering new affinity materials by process engineers is the tremendous lack of knowledge of their behavior in process systems at the meso and macro scale. As mentioned earlier, the main distinction between affinity and regular materials is the utilization of reversible reactive interactions. For most affinity systems it is simply unknown how this reversible reaction affects the design, scale-up and operation of process equipment and whether new or improved designs can be established that allow equipment intensification.

figure 10

Technological and use maturities of separation technologies (De Haan and Bosch, 2007; Humphrey and Keller, 1997)



To reduce this knowledge hurdle, we are currently establishing a pilot plant in which the implementation aspects of affinity solvent systems can be investigated. A picture of this plant is shown in figure 11. At the front you can see the feed and product vessels and right behind them two of the planned four extraction columns. At this moment a considerable part of the affinity solvent research activities concern extraction with ionic liquids. Our group was the first to evaluate ionic liquids as extraction solvents in pilot scale contactors, which has resulted in worldwide recognition and a series of invitations for plenary lectures. The first

activities have been directed at the evaluation of early-day ionic liquid performance in existing contactors such as a rotating disc column. We are currently taking the next step by investigating a new generation of ionic liquids of which the physical properties have been designed for improved equipment performance.

At the back of the picture you can see the distillation part of the pilot. This part will contain various columns for evaluating the performance of affinity solvents such as ionic liquids in extractive distillation systems. In addition a reactive distillation column is being constructed. Reactive distillation is the industrial example of process intensification by system integration. In the past decades reactive distillation has become a relatively mature technology for single-product large-scale applications (Harmsen, 2006). Interestingly, reactive distillation is hardly applied for producing value generating products in the specialty chemicals sector. One of the main reasons for this is that most specialty chemicals are produced in multi-product plants. This immediately implies that to enter this value generating segment reactive distillation concepts for multi-product applications that can efficiently deal with product transitions need to be established. We currently have two projects running on this topic.

figure 11

SPS pilot installation
in the Matrix building



Education

The previous part of the lecture has provided an outline of my research plans. However, the primary task of an university is to provide excellent education to the young people that will become the foundation of our future society, our students.

At this moment my chair is already making a significant contribution to the curriculum of the Chemical Engineering and Chemistry department. The subjects we teach include separation technology, multi-phase systems and applied thermodynamics. From the research activity overview it is clear that these subjects fit excellently with our core expertise.

When we look at our department, the main challenge for the coming years will in my opinion not be further quality improvement of the current educational program. Due to retirement and acceptance of positions outside the university a large number of vacancies will need to be filled, especially in the area of process technology. For this reason the main issue will be to maintain educational quality by attracting highly motivated assistant, associate and full professors who are qualified to teach the process technology part of the curriculum. It is clear that part of this gap can be filled by attracting part-time senior lecturers from industry. Nevertheless, the teaching of a core area like process technology should retain its base in the permanent scientific staff of the department.

This challenge of finding sufficient highly educated people is currently also one of the key issues for the chemical process industry. Some years ago several companies indicated that this problem could easily be solved by attracting employees from outside the Netherlands and even from outside Europe. However, the same companies have experienced that it is not that straightforward to attract a new employee from outside Western Europe and have him or her perform well within a Dutch organization. The cultural differences are simply too large. What we do see, however, is that after completing the PhD or TOIO program, most students have adapted perfectly to the local culture and perform excellently. It is therefore not surprising that over 90% of the foreign PhD and TOIO students find their way to starting positions in Dutch companies. The university environment is apparently a perfect place to enable international students to adapt.

Efforts have also been made at the universities to attract international Master's students. For our department we managed to attract ten international MSc students in 2006. However, in 2007 this number has dropped to only one because of the high costs and the lack of available scholarships. To me this implies that if the Dutch process industry is really serious about attracting sufficient highly educated employees, the companies should follow the example of ASML and Océ, both of which have initiated a strategic five-year cooperation with the Eindhoven University of Technology by providing scholarships for excellent Master's students from the Far East.

Acknowledgements

With this inaugural lecture I hope I have given you an impression of the challenges that I plan to address in the field of Affinity Separation Process Systems Engineering. I would like to conclude my lecture by expressing my gratitude and addressing some people.

Of course I want to thank the board of the Eindhoven University of Technology and my colleagues from the department of Chemical Engineering and Chemistry for putting their trust in me and providing me with the facilities to initiate and execute my research program and construct the pilot installation. It is not common that after starting, over twenty people are already working in a new chair within two years. This has put quite some pressure on the department organization to create the necessary space. For this reason I want to express my special thanks to some of my colleague professors for providing the office and laboratory space, as well as the department board and the department management support staff for their support in making things happen.

As may of you know I did not move to Eindhoven alone. Antje, Bernd, Ferdy, Lara, Mariette, Meritxell and Tanja, I know that moving in the middle of your PhD is challenging and I want to pay you all a great compliment for your decision to follow me to Eindhoven and your determination in making the move a success. I know things were a bit rocky every now and then but overall you have really done a great job. This is most clearly reflected by the fact that Tanja already successfully defended her thesis and Meritxell has completed her draft thesis, both without any delay.

Moving PhD students from one university to another is only possible when you receive support from both sides to find constructive solutions in transferring projects and equipment. For this reason I would also like to express my appreciation to the University of Twente for their support in achieving a smooth transition.

Changing positions not only effects the working environment but also has a considerable impact on one's private situation. For my family it meant moving from Losser to Best, starting at a new school and establishing a new social life.

All this turned out very positive but making my switch the same success would not have been possible without the love, understanding and support from the three of you.

Preceding this inaugural lecture we have organized a mini-symposium on 'Engineering Separation Process Systems'. For their efforts in preparing lectures and their contribution to this special occasion I would like to express my great appreciation to my colleagues Prof. Gani, Prof. Gorak, Prof. Bongers and Prof. Zuilhof.

Finally I would like to conclude by expressing my gratitude to all of you for having taken the effort to be present today.

Ik heb gezegd.

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Curriculum Vitae

André de Haan (1964) studied at Delft University of Technology, graduating in chemical engineering in 1987. At the Laboratory of Process Equipment of the TU Delft he completed his PhD in 1991, studying the unique properties of supercritical fluids in separation processes. In 1991, he joined DSM Research as head of the Applied Thermodynamics and High Pressure Technology group. From 1996 to 1998, he continued at DSM as Technology Manager Styrenics within the business unit Performance Polymers. In his latest position with DSM he established a long-term technology research program to support DSM's emerging life science business as senior scientist Life Science Technology. He was appointed full-time professor for Separation Technology at the University of Twente in 1999, where his research activities focused on affinity separations and their industrial utilization.

Prof. de Haan is Scientific Program Manager at the Dutch Separation Technology Institute, chairman of the NWO program committee Separation Technology and the TU/e representative in the board of the OSPT. Since 2002 he has acted as editor for the journal Separation and Purification Technology. Furthermore he is board member of the Dechema working group Extraction and the European Federation of Chemical Engineers working party on Fluid Separations and section Separation Technology.

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