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Comparison and limitation of different evaluation methods for novel PCC solvents

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Abstract

As part of a cooperation finalized between BASF, RWE Power and Linde to develop optimized post combustion capture technology for power plants, BASF developed a screening and selection procedure for identifying potential solvent candidates to be tested in pilot plant and demonstration facilities. The lab screening procedure characterizes a solvent with a number of variables derived from measurements of phase equilibrium, reaction kinetics, and stability. A method based on statistical data analysis known as the principal component analysis was developed to find the best suited solvent. Several potential solvent candidates were identified with this method, tested in a mini plant, and benchmarked against MEA. The tests showed that the screening procedure not only successfully identified solvents which perform better than the MEA benchmark but also correctly predicted the order of suitability. Furthermore, a tool was established using the modified Kremser method to predict the energy demand of a solvent system with reasonable accuracy using, as the only inputs, the phase equilibrium and the heat of absorption of CO₂ in the solvent.

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1. Introduction

Post Combustion Capture Technology (PCC) is one of the worldwide discussed options to mitigate the green house gas emission caused by the power production based on fossil fuels. The removal of CO₂ from flue gases by absorption with a reactive solvent is a well-known process for the production of pure CO₂. In 2007 RWE Power, BASF and Linde entered into a cooperation to develop an optimized post combustion capture technology for power plants. The objectives of the cooperation between to develop an optimized post combustion capture technology for power plants can be condensed in two major goals: The loss of efficiency caused by the integration of the PCC technology should be less than 10%-points (including CO₂ compression for pipeline transport to the storage site) and the CO₂ avoidance costs should be less than 30 €/t CO₂.

BASF is responsible for the development, selection and pre-qualification of the new, optimized solvents and the design of the improved capture process. Linde has taken over the task to construct the pilot plant and to optimize the PCC plant. RWE Power operates the pilot plant under the real boundary conditions of a power plant and optimizes the integration concept for the full scale PCC plant. The process of identifying and selecting promising candidates for testing in a pilot plant involves the screening of numerous variables and properties and analyzing thousands of data points, which represent the list of requirements in capturing CO₂ from flue gases. In this paper a method is described that statistically analyzes the experimental data and delivers a ranking of solvent candidates. Furthermore we suggest a new method of estimating the energy demand of a chosen solvent with little effort of experiments. Because of the huge dimensions in CCS applications it is necessary to further screen the candidates from the lab phase in a mini-plant, before they are tested in a pilot plant.

2. Screening procedure

Within the cooperation project, BASF started an extensive solvent screening program to develop an optimized post-combustion technology with the goal of reducing the disadvantages of the currently available technologies, e.g. monoethanolamine (MEA) based solvents. The main criteria are as following:

- Low regeneration duty to fit the goal of less than 10 % point efficiency losses
- High stability against oxygen and thermal stress
- Low vapor pressure to reduce solvent losses
- High reactivity to CO₂, i.e. fast reaction kinetics
- Non-hazardous (e.g. non-toxic, high flash and ignition point)
- Good availability
- Low cost

In addition to the demand of low solvent losses, caused by losses due to the vapor-pressure of the solvent, and by degradation of the solvent due to oxygen and thermal stress, the main challenge for every PCC technology is the reduction of the power plant efficiency losses. Consequently, one of the main questions to be answered by the research is how to estimate the reboiler duty of a PCC-process. Focused on these needs, the screening procedure was divided in three steps:

1. Pre-selection of substances based on easily available data, such as material safety data sheets, vapor pressure, molecular mass, and alkalinity data. About 400 substances were tested. About 70 candidates were selected for step two.
2. Lab screening experiments, including phase vapor-liquid equilibrium, reaction kinetics, and stability measurements, about 160 systems were investigated at total and the top candidates were selected for step 3
3. Performance tests of the top solvent candidates were conducted in BASF's mini-plant to verify the lab experiments completely.

A detailed description of the different laboratory screening tests can be found in [1]. The following section describes the procedure of analyzing the experimental data and finding a number of optimal candidates for testing in a mini plant.

3. Analysis of lab screening experiments and identifying candidates for mini-plant testing

After lab experiments each system is described by the variables cyclic capacity, energy demand, reaction kinetics, and stability. Hence, the set of experimental data forms a 160x4 Matrix. To analyze this amount of data and find the optimal solvents for the application, a method based on the Principal Component Analysis (PCA) has been developed [2]. The basic idea of the method is to reduce the complexity by transforming a number of - possibly correlated - variables into a smaller number of uncorrelated variables (principal components). In other words, a multivariate set of experimental data will be changed into set of data with reduced dimensions to analyze them visually and identify the internal structure. In

the case, PCA shows a strong correlation between two or more experimental variables, one of them might be obsolete. The loss of information is comparably small and can be calculated with the method. In our investigation the value for stability is not a continuous variable and hence not considered in the PCA, but applied after it. From the results of the PCA firstly the structure of the data set can be discussed. As one result the PCA delivers the covariance matrix containing the covariances and the correlation coefficients. From that, the following can be derived:

- Energy demand and cyclic capacity are correlated inversely since the covariance shows negative values.
- Reaction kinetics correlate directly with energy demand, and cyclic capacity.

As a second result PCA delivers the correlation matrix which shows that

- Reaction kinetics correlate weaker with energy demand than with cyclic capacity, but both directly, i.e. in the same direction.

As a main result the PCA delivers the principal components, the new variables. In our case it delivers two new variables denoted as comp1 and comp2. Comp1, here carries mainly the information of energy demand and cyclic capacity and comp2 the information of the kinetics. In a so called biplot, all the information gained by the PCA can be displayed.

- The cosine of the angle between two original variables, represented by the red arrows in Figure 1, corresponds to the correlation of those two variables, the larger the angle, the less is the correlation
- The length of the red arrows (original variables) correlates with the quality of representation, i.e. the longer they are, the better is the representation

Figure 1 shows the biplot of the screening phase results for 40 systems exemplarily. The axes are formed by the new variables comp1 and comp2, the original variables can be found as red arrows. Additionally, areas of potential interest are marked: red = high capacity, blue = low energy demand, yellow = fast kinetics. From the length of the red arrows one can see, that the representation of the variables is equal to each other. The value of a variable increases in the direction each arrow points. By just ranking kinetics the following order results: 152, 168, 166, 117, 165. By just ranking energy demand 63, 147, 111, 135, 13 and by cyclic capacity 166, 168, 147, 145, 63. The candidates which have been identified after PCA and after applying the stability criteria, can be found in table 2. As mentioned earlier, one of the most important requirements is the low energy demand of the whole process. The results discussed here are based on an energy estimation evaluated from vapor liquid equilibrium measurements. The reboiler duty has been estimated on the assumption that the operating line in the desorber can be approximated by the equilibrium curve. The gradient of the equilibrium curve and the operating line, respectively, are inversely proportional to the needed strip stream rate [1]. This information is sufficient to compare the different solvents and to identify the top solvents candidates concerning the heat duty. But, by this simple screening procedure the value of the required regeneration duty cannot be determined exactly. To improve the prediction of the energy demand a new method – modified Kremser method - was introduced and validated during BASF's lab screening phase.

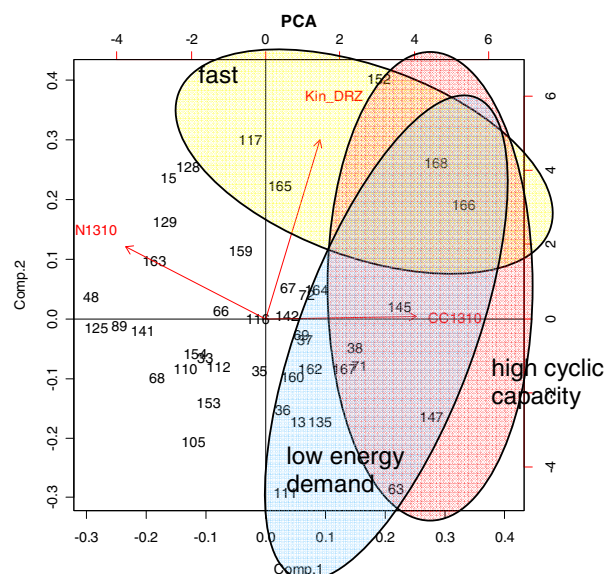


Figure 1 Biplot of the data matrix after lab screening results (Kin_DRZ: reaction kinetics; CC1310: cyclic capacity; N1310: energy demand)

4. Modified Kremser method

The energy balance shows that the reboiler heat duty consists of four contributions:

1. desorption enthalpy,
2. stripping steam,
3. heating the solvent,
4. heating the condensate reflux.

The enthalpy of desorption depends on the type of the solvent, the temperature and the CO₂ loading. The energy required for heating up the solvent can be calculated when the solvent flow rate and heat capacities are known. To calculate the energy required for the stripping steam and the heating of the condensate reflux, the vapor flow rate in the desorber must be known. This value itself depends on the equilibrium lines both at absorber and at desorber temperature. For the absorptions/desorption process of CO₂ removal from flue gases, the desorption enthalpy and the stripping steam requirement are the two dominant contributors to the regeneration energy.

Here the so called Kremser method is applied to calculate the four contributions to the regeneration energy. This simplified equilibrium stage model can be used to estimate the minimum energy requirement based on the assumption that equilibrium is reached in the absorber and desorber. The main advantage of this short-cut method is that it allows an estimation of the vapor flow rate in the desorber in dependence of the solvent flow rate. Only a limited number of physical properties is required (see Table 1). The method is briefly explained here, a detailed explanation including all relevant equations is given in [3].

The Kremser equation for absorber and desorber respectively gives a relationship between an operating line, a linearized equilibrium line and the number of stages (N_{Stages}). For this equation the gas flow rate, the vapor flow rate and the CO₂-free solvent flow rate are assumed to be constant in each column. In order to apply the Kremser equation, also the equilibrium curve needs to be linear. Therefore, the equilibrium isotherms are discretized here into three linear segments. After solving the Kremser equations, the results are used to calculate the four contributions to the regeneration energy requirement based on a simplified energy balance.

The input variables and their value used in this study are summarized in Table 1. The main input data are the equilibrium isotherms for typical absorber and desorber conditions (40 °C and 120 °C). In addition the temperature difference between desorber inlet and desorber outlet as well as the temperature difference between the condensate reflux and the solvent inlet at the desorber top needs to be specified. The caloric data needed for the energy balance of the desorber are determined at temperatures typical for the absorption/desorption process. As final result, the modified Kremser method gives the curve of the regeneration energy versus the solvent flow rate. Based on that result the optimum solvent flow rate and the lowest reboiler heat duty are determined. It should be mentioned that this value is the minimum energy requirement which can be reached without kinetic limitations.

In this paper the modified Kremser method is applied to compare different solvents under the flue gas conditions of a lignite fired power plant. The absorption enthalpy of the solvents was taken from published caloric data or alternatively estimated from the desorber energy balance from mini plant experiments. Results from the modified Kremser method are discussed in section 6 and 7.

Table 1: Input data for the application of the modified Kremser method under the flue gas conditions of lignite fired power plant for MEA.

P_{CO_2}	[mbar]	140
CO ₂ removal rate	[%]	90
T_{Absorber}	[°C]	40
T_{Desorber}	[°C]	120
P_{Absorber}	[bar]	1.013
P_{Desorber}	[bar]	2
$N_{\text{Stages, Absorber}}$	-	10
$N_{\text{Stages, Desorber}}$	-	15

$T_{\text{Desorber, solvent inlet}}$	[°C]	110
$T_{\text{Desorber, solvent outlet}}$	[°C]	120
$T_{\text{reflux, condensate}}$	[°C]	20
$\Delta H_{\text{vap, Water}}$	[kJ/kg]	2211
$\Delta H_{\text{absorption, CO}_2}$	[kJ/kg]	2291
$C_{p, \text{Solvent}}$	[kJ/kg K]	4.048
$C_{p, \text{Water}}$	[kJ/kg K]	4.197

5. Mini plant experiments

The solvent candidates selected during the lab screening phase were investigated in a mini plant under more realistic conditions than in the lab. The configuration of the mini plant is an absorber stripper design with all necessary pumps and heat exchangers. Additionally, the plant is equipped with an automated process control system enabling 24 h operation. At BASF site no coal based flue gas is available, so a synthetic mixture of nitrogen, carbon dioxide, water, and optional air is used. Due to the limitations of the plant with respect to the absorber column height and stripper in comparison with a technical plant, customized experiment conditions were chosen to allow a meaningful evaluation of the different solvent candidates. In addition, the mini plant does not allow determining the absolute performance data of all the solvents. This is caused by the typical disadvantages of mini plants like short columns, wall-effects in the columns due to small column diameters, and exaggerated heat losses. Nevertheless a relative comparison of the different solvents is feasible, regarding the regeneration duty. Additionally, valuable information is generated to rate aspects like solvent losses, foaming and degradation. With this approach, it took 10 operation days to characterize a new solvent. For solvent comparison in the mini plant the same feed gas conditions (flow rate, temperature and CO₂ content) were used for all solvents [4]. For a fixed CO₂ removal rate of 70 %, the circulation rate was varied and the energy consumption was adjusted accordingly. 30 wt% MEA solution was used as the benchmark. The solvent ranking as a result from mini plant investigations is discussed in section 6.



Figure 2 BASF's mini plant for solvent testing

6. Lab Screening results and mini plant test results

The main objective of solvent screening is to deliver candidates for further and more detailed testing in the mini plant and later in a pilot plant. The challenge is to perform as little and as less complex experiments as possible. The process described in section two delivers reasonable description of the kinetics, the cyclic capacity, and a rather simple estimation of the energy demand.

Table 2 shows the results of the PCA and the identified top candidates to be tested in the mini-plant and also their order of suitability, among them MEA as the chosen benchmark and Gustav 200, the later pilot testing candidate. The systems are marked by colors where same colors represent a similar result of the PCA. Table 2 shows also the results of the mini-plant experiments. Firstly one can see that system A which came out #1 in the lab screening is now #2 because Gustav 200 behaved superior in the mini plant. Particularly long-term stability and operability contributed to that result. Furthermore one can see that the groups of colors (same suitability after lab screening) are still close together, but mini-plant tests revealed some details regarding foaming, degradation, entrainment and other process parameters which are important for operability. This led to a changed order of systems.

Table 2 Results of PCA based on lab screening and mini-plant testing

PCA	Mini-plant
A	Gustav 200
Gustav 200	A
C	C
D	E
E	F
F	D
G	G
H	I
I	H
MEA 30	MEA 30

As result of the screening process the novel solvent, called Gustav 200, has been selected for further testing at the pilot plant in cooperation between RWE Power, BASF and Linde and comparison with MEA results from reference experiments in that plant [4].

As described above the energy demand can be determined much more precisely with the modified Kremser method from section 4. To investigate the influence on the result of candidates identified by lab experiments the PCA was applied to a limited number of systems, for which the energy demand, calculated with the Kremser method was available. Table 3 shows the order of systems.

Table 3 Results of PCA based on limited number of systems and Kremser results

A
E
Gustav 200
C
F
D
G
H
I
MEA 30

7. Pilot plant results – Comparison with screening results

The pilot plant tests at Niederaussem with MEA and Gustav 200 allow to validate and evaluate the whole screening process. With an absorber column sufficiently high, the energy demands of the pilot plant can be compared with the modified Kremser method and also with process simulation. Process simulations of the pilot plant have been performed with BASF's in-house tool CHEMASIM. This tool is suited for the description of heat and mass transfer problems, utilizing a non-equilibrium rate based model [5]. Since the method for estimating the energy demand based solely on equilibrium data and also the mini plant tests do not deliver actual - but representative - values, those data have been related to the benchmark solvent MEA (100%, see Table 4).

For the pilot plant and the corresponding simulation as well as for the modified Kremser method and the mini plant operation the regeneration energy is shown at the optimal solvent flow rate. For the lab based solvent screening, the assumption of vapor liquid equilibrium at the desorber sump is taken, so that the flow rate of the vapor phase can be estimated by the gradient of the isotherm in the desorber sump. The vapor flow rate is directly related to the energy requirement [1]. Since the CO₂ partial pressure in the evaporator is not known a priori and it changes with the solvent

flow rate, the evaluation is done at three specified values for the CO₂ partial pressure: 50 mbar, 100 mbar and 150 mbar. Table 4 summarizes the results.

Table 4: Comparison of the regeneration energy demand for an increasing depth of detail

Method for determination of the regeneration energy requirement		Regeneration energy requirement / GJ/tCO ₂	
		30 wt% MEA	Gustav 200
Pilot plant		3.5	2.8
Process simulation		3.4	2.8
Modified Kremser method		3.7	2.8
Mini plant		100%	-25%
Estimation from slope of equilibrium isotherm at 120 °C, evaluation at different p _{CO2}	p _{CO2} = 50 mbar	100%	-46%
	p _{CO2} = 100 mbar	100%	-48%
	p _{CO2} = 150 mbar	100%	-50%

It can be seen from the numbers, that the optimized solvent Gustav 200, developed during the screening phase and testing process, has a significantly lower energy demand than the benchmark solvent MEA. After long term testing in the pilot plant at Niederaussem it can be seen, that Gustav 200 requires 20% less reboiler heat duty. That is the same improvement which was calculated by the modified Kremser method. These promising results are discussed in detail in another GHGT 10 publication [6]. The pilot plant results for the benchmark solvent MEA showed a good agreement with other published results for MEA based PCC processes [7]. From the lab screening phase an improvement over MEA of about 50% was estimated. The mini plant tests showed that the new solvent is superior to MEA not only in terms of energy demand, but also in stability and operability. The energy demand compared to MEA is 25% less. Two main conclusions can be derived from these results: The screening as performed at BASF led to an improved solvent for the capture of CO₂ from flue gases in terms of energy demand and also stability. The quality of energy estimates during the lab screening phase can be improved significantly by the modified Kremser method. Test of further candidates at the pilot plant at Niederaussem site will finally show the quality of the screening process introduced here.

8. Conclusion

The lab screening procedure established by BASF [1] for identifying optimized solvents in Post Combustion Carbon Capture and Storage applications delivers an enormous amount of data and characterizes a potential solvent with numerous variables. To find the best suited solvent, a method based on statistical data analysis known as the principal component analysis was developed and applied. Several potential solvent candidates identified by that analysis were tested in a mini plant and benchmarked against MEA. These tests showed that the screening procedure identified solvents which all performed better than the benchmark solvent MEA. Moreover, the order of solvents after testing in the mini plant was very similar to that after lab screening. Detailed information could be gained during the mini plant tests which enabled the selection of two candidates to be further tested in a pilot plant. For a more realistic reproduction of the reboiler heat duty, the modified Kremser method was applied. As explained above, this method is a powerful tool to predict the energy demand of a solvent system.

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