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Aspects of long term Industry-University Cooperation Projects

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Increased demand on the global coke market led to a nearly eightfold price for coke. Building new plants with a modern competitive design for the gas section is therefore, also due to the overaged cookery plants in the world and increasingly stringent environmental regulations, imminent. In the industry design of gas purification plants was in the past often done using empirical methods and simple spreadsheet calculations. Thus, finding an efficient design for the units and optimal operating parameters for the entire process was the aim of the long term industrial-university cooperation project between Technische Universität Berlin and the ThyssenKrupp Uhde, Dortmund Company. In different joint research projects between an academic and an industrial partner, reactive absorption and desorption processes are investigated experimentally and theoretically. In a period of 15 years cooperation different problems like rigorously modelled Ammonia-Sulphur Absorption and Desorption Processes (AS-Kreislauf-wäsche®, CyclaSulf®-Process) using thermodynamic and chemical engineering fundamentals taking into account the complex reaction system and its effects on mass and heat transfer were investigated in detail. 10 PhD Theses and app. 20 Master Theses are treated during this time. For the design and the optimization of the VACASULF®-process, a selective absorption and desorption-process, a new model has been developed. The model was successfully validated by vapour-liquid equilibrium data and reaction kinetics from the literature as well as by own absorption and desorption experiments in the packed tower..

For the benzene separation as a part of the cookery a rate based model was developed and new washing fluid biodiesel was investigated theoretically and experimentally and compared with the traditional one.

Claus combustion is a significant process unit in coking plants. Its main purpose is the destruction of gaseous contaminants such as HS_2 combined with the recovery of sulphur. New aspects in direction of a direct sulphuric acid application are in progress.

As a result of these investigations the industrial process of the coke oven gas purification can be simulated in a more accurate manner and therefore turns out more efficiently in operation and process design. The operation of the plant is improved by

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introducing an advanced model based process treatment controller. The basic and detail engineering process is improved by using a modularization concept.

In the paper an overview about the industry-university cooperation is described. Different technical aspects like column designs, modelling and experimental validation, experimental design with application to absorption/desorption NH_2-H_2S-CO_2 and the catalytic H_2SO_4 process, optimizing the benzene recovery process are described. Moreover additional aspects concerning the project management, the cooperation between industry and university will also be highlighted.

Introduction

In the industry design of gas purification plants is still often done using empirical methods and simple spreadsheet calculations. Thus, finding an efficient design for the units and optimal operating parameters for the entire process is not possible. In a long term joint research project between an academic and an industrial partner, reactive absorption and desorption processes are rigorously modelled using thermodynamic and chemical engineering fundamentals taking into account the complex reaction system and its effects on mass and heat transfer (Thiele et al, 2003a; Thielert, 1997; Peters, 1997; Mayer, 2002). The main parts of the coke oven gas treatment process are shown in Fig. 1. Coke oven gas (e.g. 160.000 Nm^3/h with 7 $g/Nm^3/h$ NH_3 and 7.5 $g/Nm^3/h$ H_2S has to be treated (<0.2 $g/Nm^3/h$ H_2S). Coolers, filters absorption and desorption columns, BTX – columns and a Claus plant are parts of the whole plant.

Frequently installed processes like the ammonia-hydrogensulfide scrubbing process (CYCLASULF® process) and amine-based processes have already been modelled with great success (Peters, 1979; Thielert, 1979; Mayer, 2002; Brettschneider et al., 2004). These models are developed as user defined subroutines in ChemCad® and experimentally validated in pilot plants at TU Berlin and parallel to the real plant. The plant was designed built up and operated two years at University investigated the NH3-H2S Scrubbing Process in a scientific way with pure gases bought at Merck. The Absorption and Desorption Plant was built with stainless steel, 100mm diameter, and a height up to 6m. The column was fully atomised and operated with a digital control station from ABB, Freelance 2000. However, HCN and additionally components were neglected. Therefore, the plant was demounted, transported 600 km from Berlin to Duisburg City in Western Germany and build up. Additional imported experience was generated and the model was adapted and improved for real conditions. So the process design was modified and the newest research results were used for the new design procedure.

However, models for processes with potash like the VACASULF® process were not available in the beginning of this century at Uhde Company. During the start-up of an industrial VACASULF® plant built in that time, the experimental results showed a surprisingly large increase in efficiency for a specific alkaline concentration range, which was not predicted by the empirical methods in the design stage. Therefore, a rigorous rate-based non-equilibrium model for a more complex electrolyte system (NH_3-CO_2-H_2S-H_2O-KOH-NaOH) with chemical reactions taking into account the influence of chemical reactions in mass transfer using enhancement factors was developed at the Technical University of Berlin (Thiele, 2006).

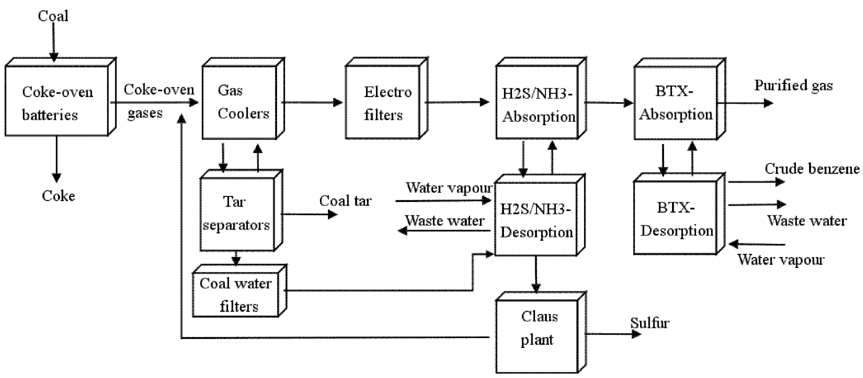

Fig. 1: Flow Diagram Coke oven treatment plant

Modelling Work

For simulating this absorption/desorption process, commercial simulators based on either equilibrium or non-equilibrium models (without reactions), fail to predict the selective absorption and desorption of H_2S and HCN over CO_2. CO_2-absorption is seriously overestimated by an equilibrium model due to the slow dissociation reactions of CO_2 in water and the also kinetically controlled reaction between NH_3 and CO_2. A selective absorption of H_2S compared to CO_2 during short contact times in packed towers could therefore not be predicted with the above mentioned models. Therefore, the development of a complex heat and mass transfer model taking the interactions of the different chemical species and their reactions into account was conducted using FORTRAN. An overview for one transfer unit of the model is shown in **Error! Reference source not found.**3 and will briefly be explained in the next subchapters. More details on the model can be found in Thiele, 2006.

A comparison of the simulation results of an equilibrium model and a rigorous rate-based model with the measurements of a pilot plant experiment is shown in Fig. .

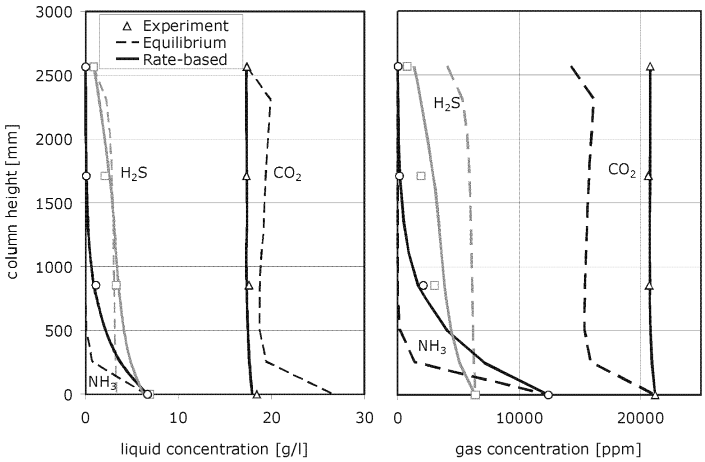

Fig. 2: Comparison experiment-model (rate-based & equilibrium), absorption in 32 g/l KOH, F = 1,8 Pa$^{1/2}$, B = 9 m³/m²h

Experimental Work

For the experimental validation of the simulation the pilot plant was transported back to the TU Berlin and adapted to the VACASULF® process condition. The columns have been designed for both absorption and desorption experiments under atmospheric pressure and vacuum conditions. It consists of a stainless steel column (∅ = 100 mm) equipped with three sections of packing's each of 856 mm height. The structured packing used is a SULZER Mellapak 350.Y. It is described in detail in Brettschneider et al., 2004 for the absorption mode. The entire experimental procedure including measurement errors is described in detail in Thiele, 2006. The flow diagram in Fig. 3 shows the pilot plant at TU Berlin for the absorption mode.

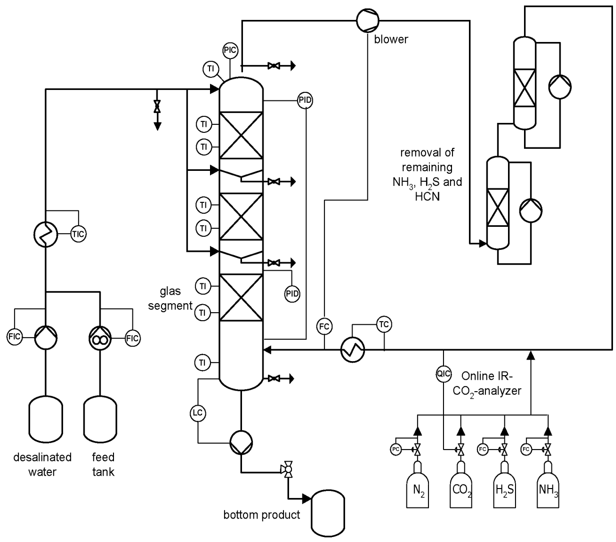

Fig. 3: Flowsheet of the pilot plant in absorption mode. Desorption equipment is hidden.

The results of the experimental and theoretical work for the absorption and desorption mode influenced directly the design of the world modernist cookery plant at Schwelgern, Germany.

Furthermore, the industrial process was systematically optimized regarding annual costs using an evolutionary strategy. This resulted in a decrease of 30% in operating costs still complying with the restrictions for the gas outlet concentration. For a new process the heights of the absorber and stripper were significantly reduced resulting also in a decrease in investment costs. The number of columns is reduced from 4 to 2 in the meantime.

The price of benzene increased the last few years. So the economic interest on an optimized benzene recovery process increased too (Fig 4). On the basis of experiments carried out in a pilot plant the concentration as well as temperature profiles are evaluated for the recovery of benzene and toluene in coal tar oil. Therefore, a pilot plant equipped with 2.6 m of structured packing Mellapak 350.Y with a diameter of 0.1 m was constructed at the laboratories of the Berlin Institute of Technology (TU Berlin). In order to minimize the effects of maldistribution liquid collector and distributor systems were placed each 0.85 m along the column height. Gas samples are taken at four different points along the column and the temperature profile is measured at eight points between the gas and the liquid outlets. The operation conditions were varied for liquid loads between 6.5 and 11.0 m³/m²h as well as gas loads between F = 1.3 and 1.6 in order to obtain different rates of recovery. Gas concentrations at the inlet of the column were varied between 2.0 and 15 g/m³ of benzene and 1.0 to 5 g/m³ of toluene. The evaluation of the applied models is carried out by the great number of measurements.

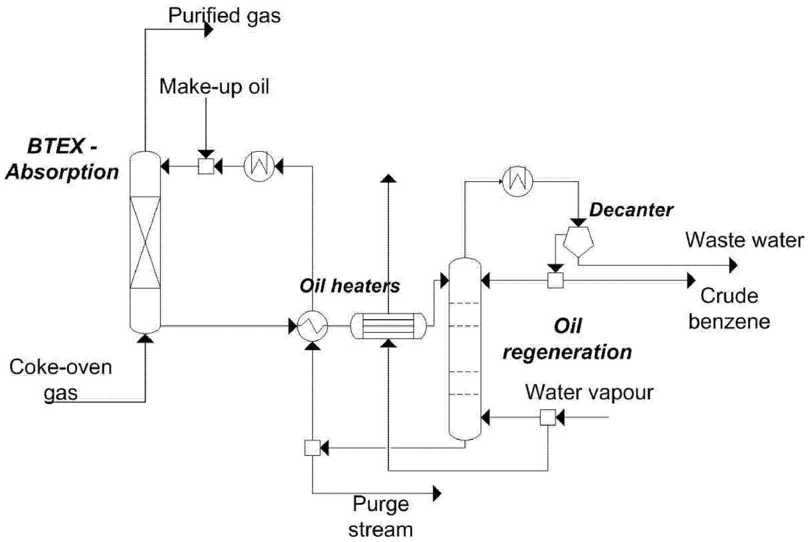

Fig. 4: Flow Diagram Benzene-Toluene recovery process

As a result of these investigations the industrial process BTX recovery process can be simulated in a more accurate manner and therefore turns out more efficiently in operation and process design. An overview of the pilot plant and the PID diagram shows Fig.5

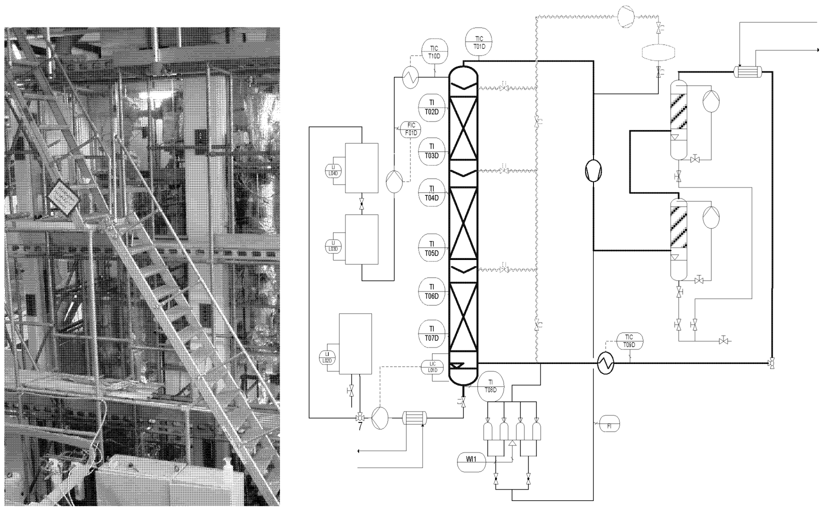

Fig.5: Pilot Plant BTX Absorption-Desorption Column System at TU Berlin

As shown, a Claus Plant is also a part of the whole coke oven purification plant. Cost aspects lead to new ideas a new solution. So a new process variant (KaltGasRecycle-Prozess®) was developed as shown in Fig. 6.

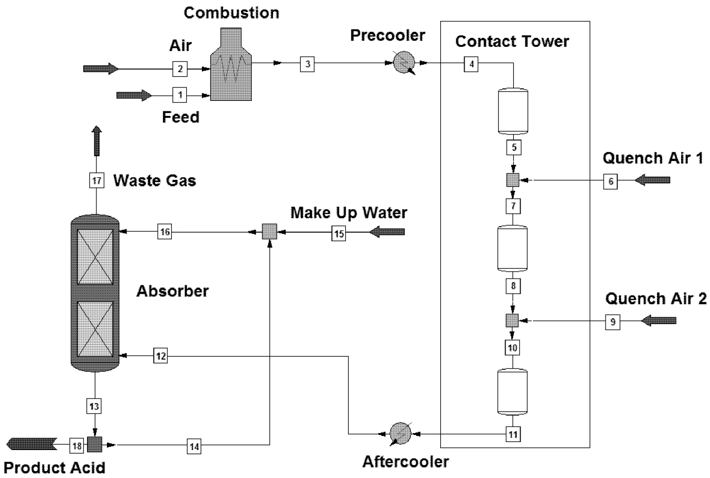

Fig. 6: Simplified sulfuric acid production process from sour gas (H_2S).

Beside the well known part of the sulfuric acid process the new reactor to convert flow 17 by hydrogenation has to be investigated and designed. A simplified flow chart and the 3D-Diagramm and the photo of the reactor of the mini-plant at TU Berlin are shown in Fig. 7.

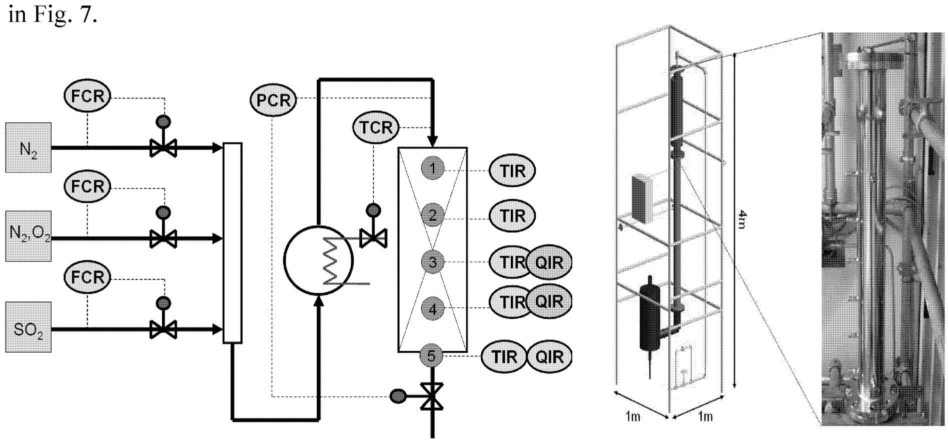

Fig. 7: Simplified flow sheet, 3D model and realization of the fixed bed reactor in the pilot plant at TU Berlin

New design options for the hydrogenation reactor and the whole process have to be investigated.

Conclusion

A 15 years' cooperation between industry and university is beneficially for both. University has beside others money for modern equipment, personal, realistic plant data and information about real world problems. Industries accept university research results and improve design methods and their processes.

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