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Emission Free Sulphur Recovery Process Development with Modular Mini-Plants in Industrial Plant Bypass

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The development of new processes or modifications of existing industrial processes often leads to acceptance issues, because not all real conditions can be reproduced in university facilities. The investigations under ideal conditions are mostly indispensable for scientific tasks, but lead to risks resulting from transferring university results to industry. With a tiered approach using preliminary scientific experiments without impurities from lab to miniplant scale followed by a bypass operation with the real industrial plant is a viable approach to solving this problem. In line with this approach intensive theoretical and experimental studies were carried out in the lab of the chair “Process Dynamics and Operation” of the “Technical University Berlin” for the development of a new emission free sulphuric acid process. In a further step a mobile, modular and fully automated experimental set-up was built and shipped to the industrial partner, where it was operated in bypass of the industrial plant. Main objectives were to gain important insights regarding long-term stability and interaction of secondary components. The application of this approach shows that a very fast and cost effective process development can be realized.

1. Introduction

In academic environment the development of new processes, process variants or modifications of existing industrial processes often leads to problems of acceptance. The main factor is the inability of university facilities to reproduce all real process conditions. For example, in academic scientific research most experiments are conducted with pure chemicals not containing any of the impurities inherent to industrial settings. Impurities are either ignored or fed to the system synthetically. If the experiments are carried out with original substances at the university, the time for the experiments is mostly restricted, because of the fact, that the substances have to be shipped and stored at the university. Furthermore, reproducing the entire process with all recycles is mostly not feasible because of financial reasons. This approach is mostly indispensable for scientific tasks, but leads to acceptance issues at interested plant employers, because of the possible risks resulting from transferring university results to industry. These risks are often not accepted by industry. In this paper a tiered methodology will be presented which represents a practical approach to reduce the time and costs necessary for the development of a new process. In a first step an intensive analysis of the process will be conducted, in which a selection of the critical unit operations will be carried out. Well known process steps, for which reliable models exist, will be omitted from the following experimental investigations. In a next step the approach contains lab work without the addition of impurities. This lab work will be conducted with the commercial equipment or chemicals, as for example in the analysed case study commercial catalyst pellets. That is in contrast to traditional lab work, which will be carried out under ideal conditions, like pulverized catalyst to neglect transport phenomena. This step represents the process development. The next step represents a process validation. In this step a mobile, modular miniplant will be constructed, and will be shipped directly to the target plant for example of a potential buyer. The conducted experiments will investigate the full compability and operability of the developed process. The construction is based on the knowledge gained from the further investigations and consequently reuses components from the plant in the lab. The modular design allows very cost- and time-effective experimental investigations. Besides reliable results, the high requirements of industry relating

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the critical component of time in successful product development can be achieved. Moreover plant extensions can be realized very easily, thus the plant could be reused almost completely in another application. In this work the approach will be applied in the process development of a new emission free sulphuric acid process.

2. Emission Free Sulphuric Acid Process

The sulphuric acid process in the context of coking plant conditions is in general a single catalytic wet sulphuric acid process which consists of three basic process steps. The hydrogensulfide containing feed gas stream is oxidized in a combustion unit to sulphurdioxide under excess air conditions to decrease temperature and minimize NOx formation. In a second step, the sulphurdioxide is oxidized to sulfurtrioxide over a vanadium pentoxide (V_2O_5) catalyst in a strongly exothermic reaction. The fixed bed reactor is divided into 4 or 5 beds and in each bed a defined temperature is set to maximize conversion. The temperature adjustment is realized with air quenches which, in addition to the temperature decrease, also lead to high oxygen concentrations in the process gas. The last bed typically has the lowest temperature of all reactor beds to shift the reaction equilibrium to the product side and minimize the sulphurdioxide content in the process gas stream. After the contact reactor, the gas passes through a sulfuric acid absorber, where the sulphurtrioxide is absorbed with water and converted to sulphuric acid. To prevent sulphuric acid mist, wire mesh filters are installed. After this last process step, the restgas is released through a stack to the environment.

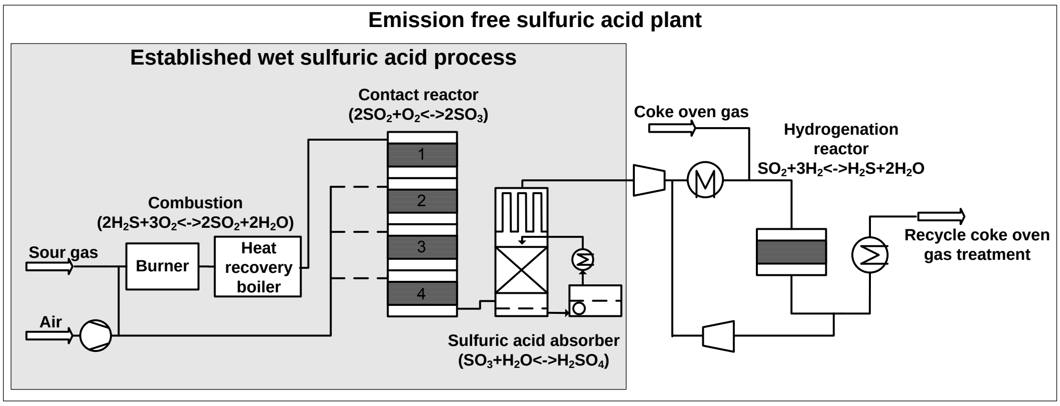

Figure 1: Established sulphuric acid process and extension to emission free sulphuric acid process with modified contact reactor and a recycle around the hydrogenation reactor. Graphic based on (Dittmeyer et al. (2006))

Due to the fact that the sulfurdioxide oxidation is an equilibrium reaction, there are always sulphurdioxide emissions. To prevent these emissions, a new process concept is recommended that recycles the sulfuric acid plant restgas back to the coking plant gas treatment. Thus, the sulphurdioxide emissions can be reduced down to zero, because of a completely closed process. A very low sulphurdioxide and oxygen content is required to feed a gas stream into the coking plant gas treatment. These requirements are only met if the sulfphurdioxide content is reduced, for example, by the hydrogenation of sulfurdioxide to hydrogensulphide ($3H_2+SO_2$<->H_2S+2H_2O) in an exothermal reaction with the equilibrium far to the product side. Therefore, a fixed bed with hydrogenation catalyst has to be installed behind the sulfuric acid absorber. To meet the requirements of the hydrogenation unit the oxygen content has to be less than a specific value. To realize these operation conditions there are four preferred possibilities, which are all related to plant modifications. First there is the possibility to install a catalytic combustion ahead of the hydrogenation reactor, second there is the possibility to recycle gas around the hydrogenation unit which is quite similar to the combustion concept, just that the oxidation takes place in the sulfurdioxide hydrogenation unit. The two other ways to realize the necessary process conditions are related to a modification of the contact reactor of the process. Thus for the third way there is the possibility to use an unsteady state contact reactor, which uses the transient behaviour of the vanadium pentoxide catalyst, witch is described in (Bunimovich et al. 1995). In this concept the oxygen is loaded shifted in time to the contact mass, so that at the sulphurdioxide oxidation no more oxygen is present down stream of the reactor. A detailed description of the process is given in Günther et al. (2012). The fourth possibility is to operate the contact reactor in steady state, but in a different configuration and operation point as in the established process (Schöneberger, 2010). In single catalytic wet gas processes the contact reaction is operated with a large oxygen excess to reach the necessary temperatures for a good conversion. In the emission free sulphuric acid process there is no need for these high conversions, because the sulphurdioxide containing rest gas will not be released into the environment. Because of the closed process the contact reactor is well designed not because of environmental regulations, but because of the whole process efficiency.

3. Process Development

The methodology for process development presented in this work is a tiered approach which combines theoretical studies, lab work and miniplant technology in bypass operations to industrial plants. The objective is the rigorous reduction of the expended effort in time and cost for the development of a new process, process variant or process modification. The main idea is a consequent analysis of the new process and a reduction of the traditional lab work to a minimum. In this chapter the required development steps will be presented. Figure 2 shows basic steps of the methodology in detail.

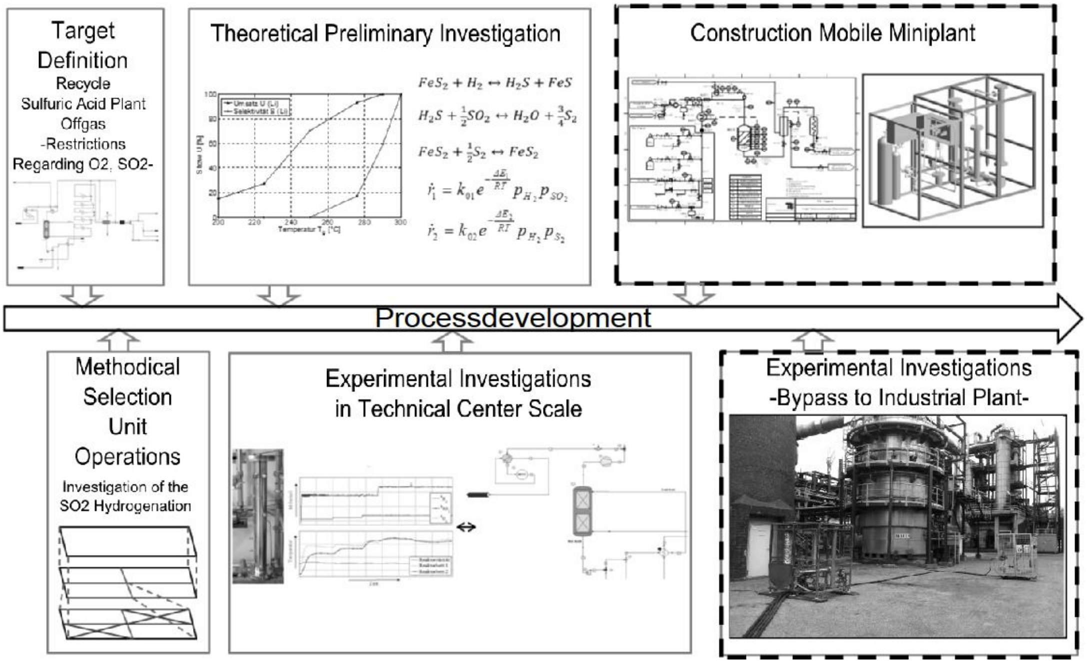

Figure 2: Approach for process development using the example of the emission free sulphuric acid process

At the first step, the target has to be defined, that has to be derived from the basic process idea. In that step first simple process simulations are carried out to check the feasibility of the concept and approximate required key data like energy and mass flows. A set of most promising concepts will be extracted out of the large variety of possible solutions. In case of the emission free sulphuric acid plant the target is to recycle the sulphuric acid plant offgas, to that belonges some specifications and restrictions regarding the SO_2 and O_2 concentrations. The resulting most promising process concepts, which were explained in the previous section, will be transferred to the next step of the process development. In this step a systematic identification of the unit operations that have to be investigated will be carried out. The aim is to select all unit operations from each process variant that aren‘t well investigated. The unit operations for which some very large experience and well based models exist, will be neglected during the next steps of the process development. The emission free sulphuric acid process contains the following four basic process steps:

1) Combustion of H_2S ($2H_2S+3O_2<->2SO_2+2H_2O$)
2) Oxidation of SO_2 ($2SO_2+O_2<->2SO_3$)
3) Absorption of SO_3 ($SO_3+H_2O->H_2SO_4$)
4) Hydrogenation of SO2 ($3H_2+SO_2<->H_2S+2H_2O$)

The combustion of hydrogensulphide and the absorption of the sulphurtrioxide are well investigated process steps that are present in nearly every wet sulphuric acid process. The oxidation is also very well

known as a basic step in the sulphuric acid production. In contrast, the catalytic step of the hydrogenation is the unit operation with the largest uncertainty. For that reason most of the effort in the process development will be put into the theoretical and experimental investigation of this step in particular.
Before the experimental investigations, extensive theoretical investigations should be carried out. For example the physical and chemical properties of the components have to be determined. In the case of a chemical reaction like in the case study, possible side reactions or side products and first estimates about the rate of the reaction should be identified. In the case study it was also an important step to determine a suitable catalyst for the packed bed reactor. Also a first mathematical model should be created. The modelling should be carried out in an environment which allows for an easy knowledge transfer. This is the case for example in commercial process simulators or in a very systematic and sustainable modelling environment like Mosaic (Kuntsche et al., 2011). With this knowledge the first experiments in the lab could be conducted. In this approach it is an important point to work from the beginning with process conditions that are very near the industrial conditions. Therefore, the investigation of the catalyst should be carried out with the commercial catalyst, and not with pulverized catalyst or lab reactors, for example to prevent transport limitations in the reaction (Schöneberger, 2010). The objective of this step is not to identify the exact mechanism and reaction rate of the catalyst, but to create data, that could be directly used for the design of the real process. In this step the feasibility of the proposed unit operation is determined. The kinetics and the mechanism of the reaction are to be identified. The obtained data will be used to gain experience with the system and specify the model for the simulation of the process. This step has a clear character of a process synthesis step. The next step is the step of the process validation and will be displayed in the next sections in detail. In this step a modular and mobile miniplant is built which will be shipped directly to the plant of an industrial partner. The construction of the miniplant consequently uses the gained information in the previous development steps. Furthermore it reuses as much as possible parts of the miniplant in the lab. The miniplant should be constructed from modular units as (Müller et al. 2010) shown for a BTX absorption process. That way the plant can be shipped very easily and cost effectively. Further modifications can also be realized very easily, because of the standardized geometry of the modules and the standardized process connections between each module. In Figure 3 the miniplant for the investigation of the emission free sulphuric acid process is shown.

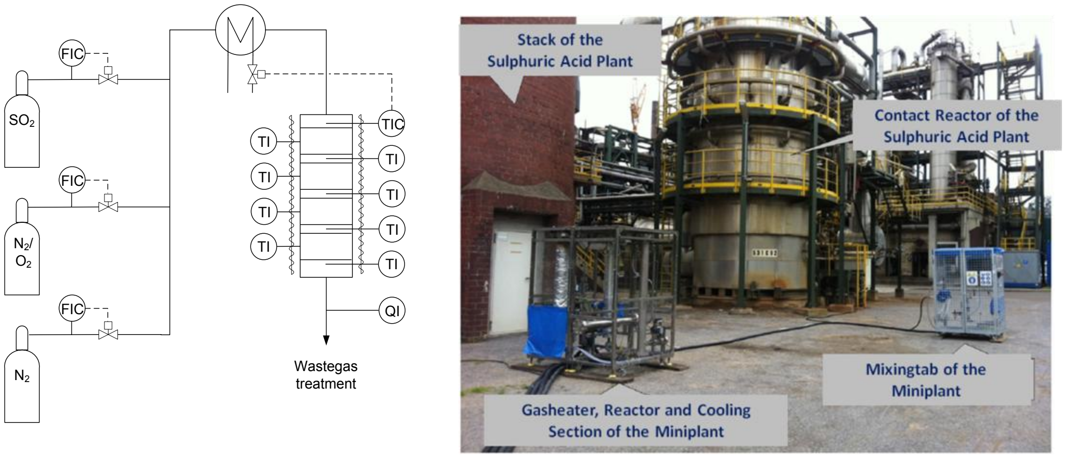

Figure 3: Simplified scheme and picture of the experimental set up at the industrial target plant

It consists of three modules. A gas mixing section, which is an explosion proof construction, a gas heating and reaction section, which heats the gas up to reaction temperature and feeds it to the reactor, and at least a gas treatment section which condenses specific components and cools down the gas for recycle in the industrial plant. The miniplant has to be designed to be able to adapt to a very broad range of operation conditions because of the uncertainties of the experimental work and because of the needed ability to investigate the operation points of the different process variants that have been defined in the previous step of the process development.

4. Experimental Results

The experimental results of the bypass operation are a very important step in the methodology of the process development. The gas streams delivered to the industrial plants contain a wide range of impurities. Because the impurities can form side products or have effects on the catalyst, they should not be neglected. In addition to the hydrogen necessary for hydrogenation, in this special case the provided coke oven gas stream contains large amounts of methane, carbon monoxide and a broad range of different organic components, which could form coke on the catalyst and decrease its activity. Furthermore the provided gas streams contain oxygen that can deactivate the catalyst. So, the main objective of the experimental investigations of the process in bypass to the real industrial plant is to gain information regarding the following points:

1) Conversion and selectivity in the industrial environment
2) Long-term stability of the catalyst
3) Tolerance of the catalyst against oxygen
4) Optimal operation strategy

The most critical point was the conversion of SO_2 at different operation points. A nearly complete SO_2 free gas stream out of the hydrogenation reactor is necessary, because the H_2S washers installed downstream are intolerant to it. So a specific concentration should not be exceeded at the reactor outlet. To prove that measurements were carried out with a FTIR spectroscope. The results are displayed in Figure 4.

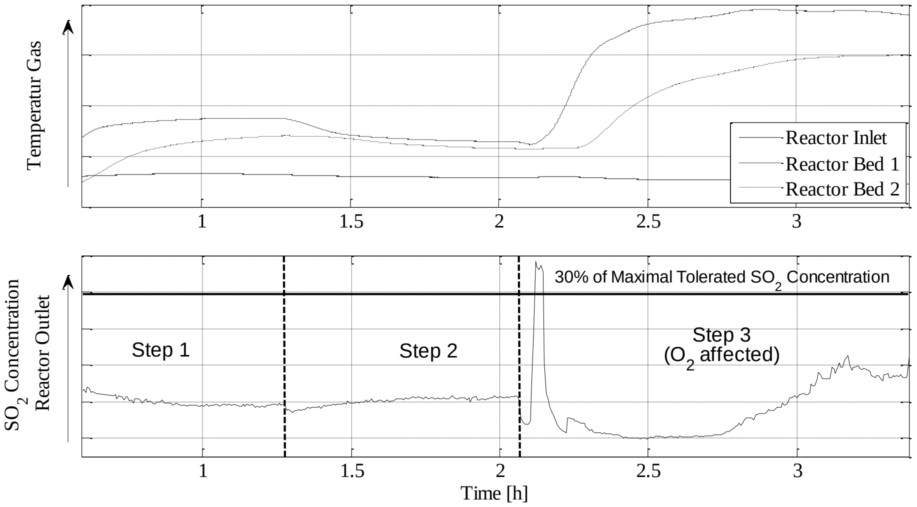

Figure 4: Axial temperatures in the reactor and SO_2 concentration at the reactor outlet

In a wide range of operation conditions, even in strongly dynamic behaviour with and without oxygen in the reactor feed of the system the outlet concentration of SO_2 did never exceed the maximal tolerated SO_2 concentration in a selective reaction. So it was proven, that the catalyst has a very strong capability to convert SO_2 to H_2S even under the influence of different concentrations of oxygen.

The quantification of the catalyst activity is a challenging task if the catalyst has such a high performance as the used one. If there is always a full conversion there is no efficient way to evaluate the activity from the base of investigations of for example the conversion. The SO_2 conversion would break down at a point where the catalyst is almost deactivated, which could result in long time periods of expensive experimental investigations. Because of that other parameters have to be identified, which are observable. In Figure 5 the used criteria are shown. In the experimental work a sensitive correlation between the activity and the temperature profiles in the reactor were observed. Especially the distance among the temperatures measured between the particular reactor beds are very good indicators for the activity of the catalyst for the observation of deactivation processes with a small time constant. If the activity of one catalyst bed decreases, the temperature decreases and the temperature of the following bed increases, because the bed compensates the loss of activity of the previous bed. A more direct indicator of the activity especially for slow deactivation processes was the reproduction of specific benchmark experiments. The temperature profile changed when a catalyst deactivation happened with a small time constant. As a third indicator the use of reference experiments was used. The catalyst also catalyses the water gas shift reaction ($CO+H_2O \leftrightarrow CO_2+H_2$). This reaction is much slower than the SO_2 hydrogenation. Because of that the reaction never reaches its equilibrium in the reactor. If a deactivation with a larger time constant takes place the conversion of the reference reaction is a quite good indicator.

With the information gained optimal operation strategies could be investigated. The most important point in the selection of a possible operation point for an industrial process was the ability of the catalyst to react at process disturbances in the frame of the safety requirements of the process. For that a conservative strategy with a focus on safety and long term stability was preferred. The investigation of the operation points is strongly coupled with the different process variants which have a completely different influence on the process characteristics and catalyst activity.

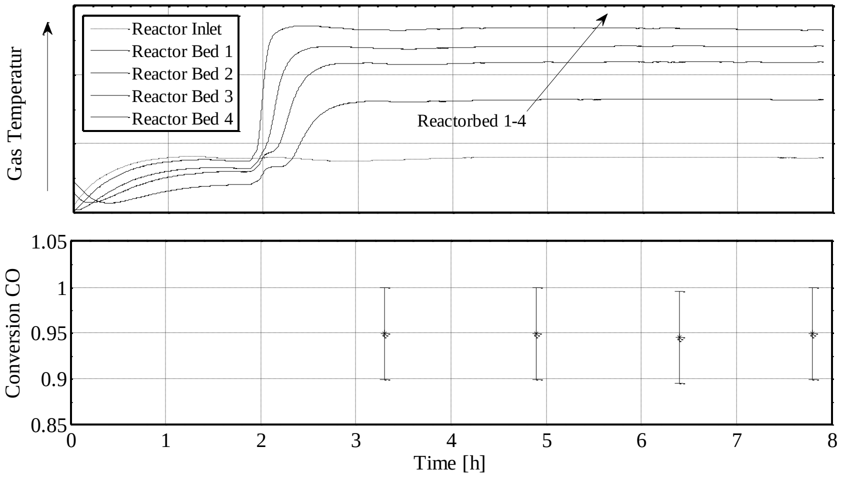

Figure 5: Axial temperatures in the reactor ant the CO conversion at the reactor outlet

5. Conclusions

An effective and practical methodology for the development of new processes was shown. The main objective was the reduction of the development time and costs. With a combination of investigations in the university and in a bypass of the real industrial target plant, very reliable results could be obtained. The methodology was shown using the example of an emission free sulphuric acid process, which was developed very successfully with this methodology. A process model for the investigation of an optimal process design was developed and integrated in the flowsheet simulator ChemCad. In this work the importance of the experimental work with real process gases was shown. Beside the work with the real process gases it is possible to prove the successful realization of the new process directly in the plant of a potential buyer. Because of the intensive cooperation with the staff of the target plant, exceptions and requests could be integrated in the process concept in a very early development stage.

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