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PREDICTION OF CATALYST ATTRITION IN AN INDUSTRIAL FLUIDIZED BED PLANT BASED ON LAB SCALE ATTRITION TESTS

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ABSTRACT

The concept that catalyst attrition in a fluidized bed process can be simulated based on the attrition characteristics of the catalyst determined on labscale is applied to DuPont's large scale process of maleic anhydride production from n-butane using a vanadium phosphorus oxide (VPO) catalyst. In the present cooperation effort the performance data and design parameters of the large scale plant are supplied by the École Polytechnique de Montréal and DuPont. At Hamburg University of Technology the catalyst's attrition characteristics were determined in labscale attrition tests. Furthermore the fate of the solids in the process was simulated. The results of the simulation are compared with the performance data of the industrial process.

INTRODUCTION

Coupled fluidized bed reactors are used in industries for many decades, eg. in the Fluid Catalytic Cracking (FCC) process. The focus of this work is Dupont's process for the production of maleic anhydride (MA) by partial oxidation of butane using a combination of a fluidized bed riser reactor and bubbling fluidized bed regenerator. The butane oxidation is catalyzed by a vanadium phosphorous oxide - $(VO)_2P_2O_7$ - (VPO) catalyst. The fact that the VPO catalyst itself is used as the source of the reactant oxygen improves the selectivity compared to the oxidation reaction with gaseous oxygen (1) (2). In the oxidizing environment established in the regenerator a fraction of the VPO catalyst changes its oxidation state from V^{4+} to V^{5+} (3). The oxygen-laden VPO catalyst is transferred to the reducing environment in the riser reactor where the catalyst supplies the oxygen for the partial butane oxidation and catalyses the reaction. The reduced catalyst is then separated from the product gas stream and recycled to the regenerator reactor.
The fluidization of the catalyst in and the transport between the two reactors together with the gas solid separation in the solids recovery system (eg. cyclones)

means a considerable mechanical stress for the catalyst material. This mechanical stress leads to particle attrition. The primary consequence of attrition is the production of fine particles which can not be kept in the process by the solid recovery system. Thus attrition leads to a loss of valuable catalyst material (4). Catalyst attrition is therefore a major issue and efforts have to be made to produce sufficiently attrition resistant catalyst in order to reduce the costs for make up catalyst (5).

Over the last decade attrition mechanisms have been investigated at the Hamburg University of Technology (e.g. (6)) Test procedures were established to characterize the material's attrition propensity under well defined mechanical stress conditions.
In the present work, based on the VPO catalyst's attrition characteristics determined on the labscale (7) together with the detailed information about the process, the catalyst's attrition and the loss rate in the large scale DuPont process is predicted. For the simulation of the coupled fluidized bed process the commercial flow-sheet simulation software SolidSim (8), which provides an appropriate environment for the steady-state simulation of solids processes, is used. The simulation takes account of the fluid-mechanics inside fluidized beds, solid-gas separation and attrition phenomena.
The results of the simulation are compared with the loss rates measured in the industrial process.

THEORY

The system to be modelled is shown in Fig. 1 (after (9)). The reactant gas enters the fast bed via the gas distributor grid and fluidizes the VPO catalyst. In the fast bed and riser the butane is partially oxidized. The reaction is catalyzed by the VPO catalyst, which also supplies the oxygen for the oxidation of butane. Additional gaseous oxygen can be fed into the lower part of the fast bed via spargers. Together with the gas stream the catalyst material is entrained from the fast bed and is then transported upwards through the riser into the Stripper. In the stripper an inert gas is injected to avoid gas leakages between the reactors. Fine particles elutriated from the stripper are separated from the gas in the reactor cyclone and are recycled to the bottom zone of the stripper. According to the cyclone's separation efficiency curve some catalyst particles will leave the reactor cyclone with the gas. Downstream of the reactor cyclone a filter collects the elutriated fines and the collected fines are transported to the

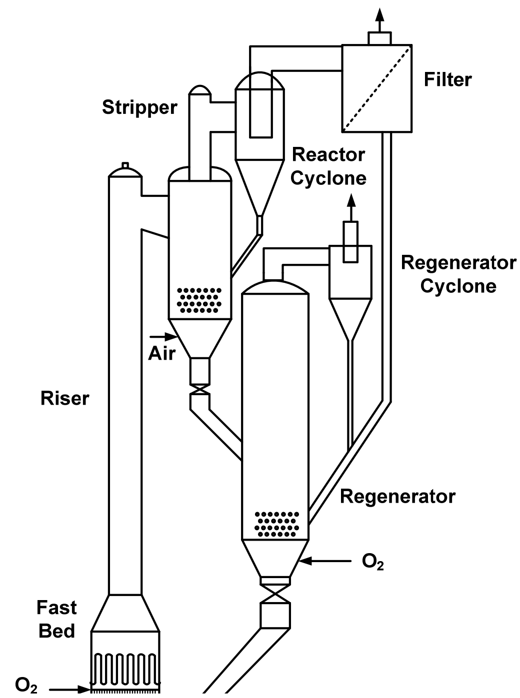

Figure 1 Process flowsheet

regenerator. From the bottom zone of the stripper the solid material is discharged and fed into the regenerator. The regenerator is fluidized with oxidizing gas introduced via spargers. Inside the regenerator a cyclone is installed. Particles elutriated from the bottom fluidized bed zone are separated from the gas in the regenerator cyclone. According to the cyclone's separation efficiency curve fine particles will leave the regenerator together with the gas. The entrained catalyst is collected in so called "totes" and is not fed to the process again. However, most of the solid material is oxidized in the regenerator and is then transported back into the fast bed.

Catalyst Attrition in Fluidized Bed Systems

In the fluidized bed process the VPO catalyst is subjected to various mechanical stress conditions. In general, the attrition in a fluidized bed process occurs as surface abrasion, which means that asperities and edges are removed from the surface of mother particles (10). According to Werther and Reppenhagen (4) the most relevant attrition sources in a fluidized bed process are the cyclones, gas jets issuing from the gas distributor into the fluidized bed and bubble motion in the fluidized bed. The attrition of catalyst particles is simulated according to the models given in (7).

Modeling of the Fluidized Bed System

The complex fluidized bed process is simulated using the commercial flowsheet software SolidSim. The calculation mode in SolidSim is sequential-modular: The individual unit models are calculated separately with an automated information transfer between them using streams. The simulation loops are solved iteratively. The fluidized beds are simulated with a fluidized bed module developed by Püttmann (11). The model takes the hydrodynamic as well as attrition processes in the mode of pure abrasion into account. Since we focus on the attrition process and the change in volumetric flow rate due to reactions is negligible, the reactions are not modeled. Based on the population balance modelling approach developed by Werther and Hartge (e.g. ((12)) the effect of attrition on the particle size distribution (PSD) in the system is calculated. The attrition process produces fine particles, which are added to the smallest size class. Moreover mother particles shrink due to surface abrasion, which leads to a mass transfer from the size class i to i-1. The simulation considers the attrition in the bubbling fluidized bed, attrition due to jets issuing from the gas distributor in the fluidized bed and attrition occurring in the cyclone.

RESULTS AND DISCUSSION

The SolidSim flowsheet used to simulate the process is presented in Fig 2.

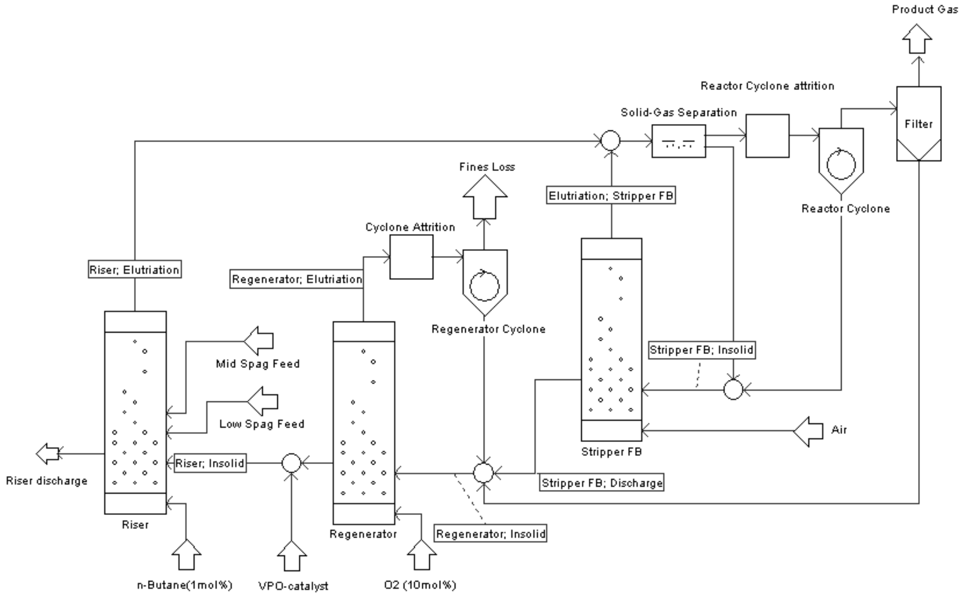

Figure 2 Flowsheet as modeled in SolidSim

The riser in the simulation flowsheet represents both the fast bed and riser in the process flowsheet (Fig. 1). The gas stream together with the catalyst leaves the riser and enters the stripper at the top. In this region of the stripper most of the solids are separated from the gas (Solid-Gas Separation unit in Fig. 2) and are directly transported to the fluidized bed module (designated as Stripper FB). Some particles are entrained with the gas stream and pass the reactor cyclone. The fines which are not separated from the gas stream in the reactor cyclone are collected on a filter and then transported to the regenerator. The solids entrained from the regenerator are separated from the gas by an internal cyclone (Regenerator Cyclone in Fig. 2). The fine particles which can not be separated from the gas leave the process (Fines Loss in Fig. 2). In the commercial process the solids entrained from the regenerator cyclone were collected in a "tote". The dimensions of the components and the operating conditions used in the simulation can be found elsewhere ((13).
Furthermore material specific attrition rate constants determined previously (7) are used in the simulation. The attrition constants of used VPO catalyst ("u" VPO), which was already used in the process, are $C_c = 0.72x10^{-3}$ [s²/m³], $C_b = 3,31x10^{-8}$ [1/m] and $C_j = 2.5x10^{-5}$ [s²/m³] The attrition constants used for the simulation with fresh VPO catalyst are $C_c = 3.91x10^{-3}$ [s²/m³], $C_b = 18x10^{-8}$ [1/m] and $C_j = 13.6x10^{-5}$ [s²/m³]. The attrition constants C_b and C_j of fresh VPO are calculated from the respective values measured for used VPO by multiplication with the factor 5.43, which was calculated based on the attrition constants measured for used and fresh VPO in the cyclone.

Particle size distributions of the solid material

During 80 days of operation the particle size distribution of the VPO catalyst used in the industrial process was measured. The mass fractions of particles in the process loop smaller than 15, 20 and 44 µm versus the operating time is shown in Figure 3.

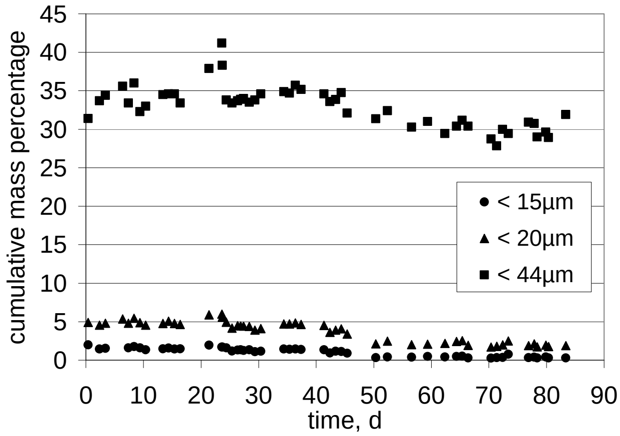

Figure 3 Cumulative mass percentage of solids smaller than 15, 20 and 44 µm, respectively measured in the industrial process for the riser versus the operating time

It can be seen, that the cumulative mass percentage is almost constant from day 1 to 40. After day 40 the cumulative mass percentage drops down and is then almost constant again (day 50-80). This change is related to the removal of fines between day 40 and 50 of plant operation. The constant mass fractions before and after the removal of fines indicate, that the solid recovery system is able to keep most of the small particles with diameter less then 15 µm inside the system. However, a slight decrease in cumulative mass percentage of particles smaller than 15 and 20 µm can be seen. This might be explained by the attrition process, which on the one hand side produces very fine particles which can not be kept inside the system and furthermore leads to a shrinking of the mother particles.
Figure 4 displays measurements and simulations relating to the development of the PSD with operating time. Both, measurement and simulation indicate that the PSD is getting slightly coarser with operating time. However, the effect of operating time is small. Compared to the simulation the PSD's measured in the process are significantly finer which indicates the capability of the technical solids recovery system to keep the fines inside the loop with a better efficiency as is predicted by the simulation. A possible reason of the deviation could be that the precise geometry of the regenerator cyclone was not available and a guess has therefore to be made.

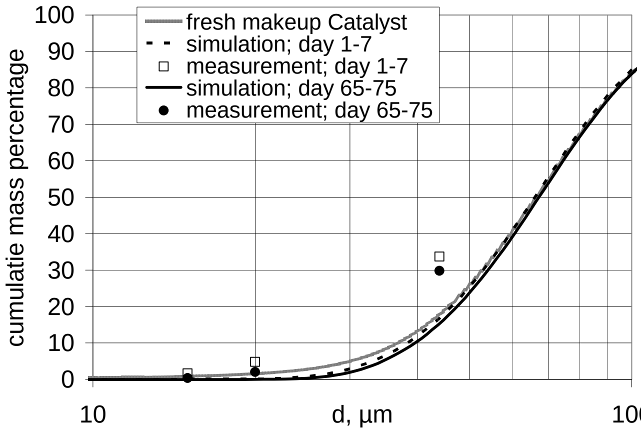

Figure 4 Simulated PSD's compared with values measured in the industrial process

Material streams

In Figure 5 the measured mass loss of VPO catalyst versus the time is shown.

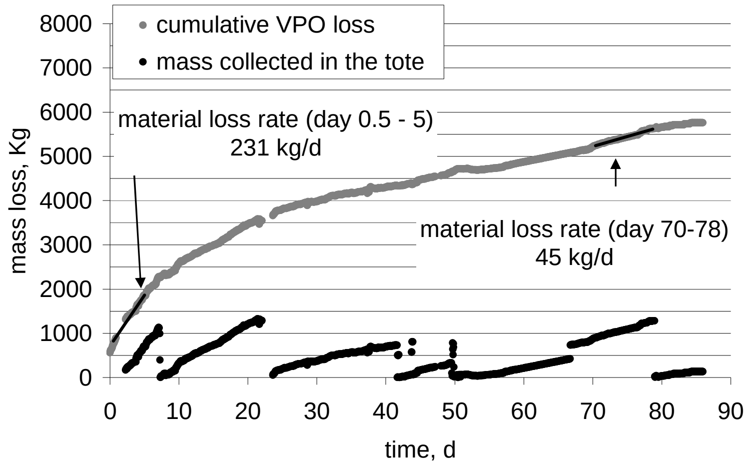

Figure 5 Mass loss of VPO catalyst measured in the industrial plant

The slope of the cumulative mass loss curve represents the material loss rate in mass per time. It can be seen that the material loss rate decreases with operation time. The average mass loss rate measured in the industrial process between day 70 and 78 is only 19.5% of the value measured during the start-up phase (day 0.5-5). This can be explained by fines present in the fresh VPO catalyst being elutriated during the first days of operation. Furthermore the fresh VPO catalyst has a lower attrition resistance (7), hence more fines are produced by attrition.

In Table 1 the measured and simulated material loss rates are shown.

Table 1 Measured and simulated material loss rates

	measurement (large scale process) [kg/d]	simulation [kg/d]
start-up phase (day 0.5-5)	245	902
steady-state operation (day 70-78)	45	189

The absolute values of the material loss rates measured in the large scale process deviate from the simulated values. Nevertheless the relative change in material loss rate between start-up phase and steady-state operation (large scale process: 19.5% of initial rate and simulation: 21%) is predicted without significant deviations.

The material loss rate and the PSD of the solids in the loop are influenced by the separation efficiency of the solid recovery system. As mentioned above the precise geometry of the regenerator cyclone is not available; hence the separation inside the cyclone might be a source of inaccuracy. In the simulation of the attrition process the particles are assumed to be of homogenous structure. This is not correct for the VPO catalyst considering its special structure (hard shell and friable core). Moreover the hydrodynamics and the attrition model in the riser are extrapolated from data obtained under bubbling bed conditions. If the attrition in the fluidized beds is neglected and only the mass of fines produced by attrition occurring in cyclones per unit time is considered, the material loss rate under steady-state operation and during the start-up phase is 39 kg/d and 165 kg/d, respectively, which is much closer to the plant values. Ongoing work is focused on the improvement of attrition models for the simulation of circulating fluidized bed risers.

CONCLUSION

The catalyst attrition in DuPont's process of making maleic anhydride from n-butane was simulated based attrition characteristics determined on labscale at the Hamburg University of Technology. Plant data of the industrial process were supplied by the École Polytechnique de Montréal and DuPont.
The simulation results are compared with performance data of the industrial process. The material loss rates simulated are higher than those measured in the industrial process, however, the relative change of the mass loss rate with operating time is well described.

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KEY WORDS

Attrition, Coupled Fluidized Beds, Fluidized Bed