



Process Safety

TÜV SÜD Process Safety· Mattenstrasse 24, CH-4002 Basel

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Safety Aspects of Hydrogenation Processes

Hydrogenation reactions are critical processes. First because they involve hydrogen and pyrophoric catalyst, but also because of the high potential of the reactions (desired and secondary reactions). Therefore, the different process steps should be studied in order to define a protection strategy allowing for a safe process.

Hydrogen is particularly dangerous due to its broad explosive range (4–77% in air) and its very low minimum ignition energy: 17 μ J. Moreover, because of its small size, hydrogen molecules can easily diffuse and leakages might be expected. Additionally, hydrogenation processes often involve flammable solvents and pyrophoric catalyst.

In general, hydrogenation reactions take place as heterogeneous systems (slurry reactor): reactants are in a liquid phase, catalyst is solid and hydrogen is gaseous. Therefore, the reaction kinetics are often limited by mass transfer (hydrogen solubilisation, transfer of hydrogen and reactant to the catalyst). This feature allows to implement strategies in case of deviations, such as stopping stirring and reactor decompression. However, such safety measures should be used in combination with knowledge of reaction mechanism. Essential questions are: are intermediates formed? Are they stable? Measurement in reaction calorimeter under hydrogen pressure allows measuring the reaction power and energy as well as determining the reaction regime (kinetic or mass transfer control). The stirrer used for the measurement should be chosen with care and mimic the industrial reactor, so as to facilitate scale-up. It is also possible to test the efficiency of stopping the stirrer as a safety measure. Measurement of hydrogen consumption permits the determination of

the thermal accumulation and the identification of a change of mechanism or reactant accumulation. Measurement with Differential Scanning Calorimetry or Calvet calorimetry allows to assess reaction mixture stability at different process steps (initial and final reaction masses but also intermediates). A screening of common process deviations can also be performed, such as the effect of catalyst settling which can lead to locally higher catalyst concentration and destabilize the reaction mixture, reactants or products.

At the end of the reaction, the reactor should be decompressed in a safe way. Indeed, formation of an explosive atmosphere should be prevented.



Contaminations from hydrogen in other parts of the plant or from catalyst carry over should be avoided. If the decompression is too fast, the gas may carry liquid and suspended catalyst to the vent system. The catalyst might dry in the vent line and then present a potential ignition source. Different strategies allow preventing this phenomenon. Conception of the vent line and safe decompression procedure require special care.

Catalyst filtration for reuse presents another danger. Indeed, the catalyst soaked with reaction mixture can lead to self-heating.

Hydrogenation processes present some technical challenges for safety. They involve two important aspects of process safety: ATEX and thermal safety. However, these processes can be performed safely thanks to a range of reliable safety measures.

Our laboratory and expertise are there to help you design and run safe hydrogenation processes. Do not hesitate to contact us for further information on our services.

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