SCI LECTURE PAPERS SERIES

REACTOR DESIGN AND SAFETY

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ISSN 1353-114X
LPS 0094/98

Key words *hydrogenation, reactor, safety*

Introduction

The subject of reactor design is too large to be covered in 20 minutes; I will therefore concentrate on some safety aspects of reactor design.

The modern approach to process safety emphasises

- inherent safe design & operation, where possible
- preventive & contingency measures, in all cases
- containment rather than relief of overpressure

In reactor design (Figure 1) the main concerns are the avoidance of

- explosive mixtures of Air + H_2, and of course ignition sources
- overpressure i.e. pressure > design pressure
- and therefore the necessity of pressure relief

The relief of a mixture of Oil + H_2 + Ni-catalyst to atmosphere at, say 200°C and 10bar should obviously be avoided at all costs.

Where possible, overpressure should be avoided by preventing or restricting the causes i.e.

- uncontrolled input of oil, hydrogen or steam
- water ingress at high temperatures

This implies that we know what pressures, temperatures and flows are required for normal operation, before we can define what is “too much”.

Absorption and reaction

Hydrogenation involves absorption of H_2 in the oil followed by (an exothermic) reaction at the Ni-catalyst surface. The overall reaction rate (Figure 2) depends on, and is limited by, the potential rates of these two steps, which are both proportional to the (absolute) H_2 pressure:

- a certain amount of catalyst will be poisoned in most cases
- thereafter the rate initially increases linearly with increasing catalyst concentration
- at higher catalyst concentrations the rate approaches, and is limited by, the maximum $_{H2}$ absorption capacity of the reactor.

The optimal rate and catalyst dosage for normal operation are chosen such that they are not unduly affected by variations in poisoning on the one hand, or suffer from decreasing marginal returns on the other. Since the chemical reaction is also dependent on temperature and IV (the reactant concentration), the overall rate will increase with temperature and will be lower at lower IVs.

The heat of reaction is removed by the cooling system. The maximum controllable rate depends on the heat removal (transfer) capacity of the reactor. The heat transfer characteristics also determine the heating rate if the same system is for heating.

Both the maximum rates of H_2 absorption and the heat transfer capacity are characteristics of the reactor design, and should be defined or measured in practice. They determine the maximum operating limits of the reactor, and hence affect the choice of input restrictions we can apply to prevent overpressure.

Supply restrictions to avoid overpressure

The simplest way of preventing overpressure in the reactor is to limit the normal supply pressure to less than design pressure and relieve any (single-phase) overpressure in the supply system itself. This avoids the necessity and problems of (multi-phase) relief from the reactor.

Oil

The oil input pressure is preferably restricted by appropriate specification of the maximum head of the pump.

Steam

The steam supply to batch systems is normally restricted by an orifice to limit peak demand. By accepting slightly longer heating times, the supply pressure can also be limited to less than design pressure; for example

Steam supply		**Heating time for**	
Maximum (kg/h per ton)		75 --> 125°C	50 -->150°C
Unrestricted			
14 barg	360	17 min	38 min
Restricted			
14 barg	200	21 min	44 min
8 barg	200	24 min	56 min

Hydrogen

The H_2 supply has to be controlled over a wide range of conditions (Figure 3):

- at fairly high initial rates with an optimal catalyst dosage
- at rates approaching the maximum absorption rate with an (accidental) overdose of catalyst, whereby the reactor headspace pressure must not be allowed to fall below 1 bara (risk of air ingress)
- and at much lower rates at low IVs

In addition
- the maximum H_2 supply rate should not exceed the maximum controllable rate allowed by the cooling system, which is dependent on reaction temperature
- and, of course, the H_2 supply pressure should not exceed the reactor design pressure.

These conditions and requirements can usually be satisfied by
- choosing a (controlled) H_2 supply pressure less than the reactor design pressure
- installing a suitably sized reactor pressure control valve and/or orifice plate to limit the maximum flow.

Temperature
By limiting the maximum H_2 flow, the reactor temperature is also "limited" (i.e. controllable) under normal conditions. In an emergency, for example due to failure of the cooling system, the simplest solution is to cut off the source of heat (i.e. the reaction) by stopping the agitator; no H_2 dispersion, no reaction!

Ingress of water
The pressure caused by any ingress of water should preferably not exceed the reactor design pressure: at 200°C the vapour pressure of water is about 15 barg and the resulting reactor pressure will be even higher.

It is just as important to prevent any accidental water ingress, for example by regular inspection and if necessary replacement of cooling coils. The life-time of coils is finite and, with increased utilisation and shorter cycle times, coils which may have been expected to last more than 20 years in the past may only have a safe life of less than 10 years under present operating conditions.

Summarising
Overpressure in – and relief from – the reactor should be avoided by ensuring that
a) The maximum supply rates of H_2 and steam are limited to what is required and controllable
b) The normal supply pressure of oil, H_2 and steam is less than the reactor design pressure
c) Any overpressure is relieved in the supply systems themselves and not from the reactor
d) Overpressure due to water ingress at high temperatures is avoided – and preferably cannot exceed the reactor design pressure

Vacuum requirements for evacuated reactors
With evacuated reactors safe operation is ensured by evacuating the reactor
- prior to reaction, to remove air before letting in any H_2
- after reaction, to remove H_2 before breaking vacuum

but, since complete removal of air or H_2 is impracticable, what is a safe final evacuation pressure?

Assuming adiabatic combustion of a perfect gas mixture, the potential explosion pressure of an H_2 + Air mixture can be estimated. The explosion isobars in Figure 4 illustrate the effect of the initial pressure and composition. A stiochiometric mixture (~ 29 vol% H_2) gives the highest potential

 ISSN 1353-114X

explosion pressure; with air- or H_2-rich mixtures part of the heat of combustion is absorbed by the "excess" gas.

This "explosion pressure chart" can be used to plot operating lines indicating the potential explosion pressure

- when filling with H_2, after evacuating air
- when breaking vacuum with air, after evacuating H_2

for any chosen final evacuation pressure, in this case 100mbar.

The results show that the worst situation occurs when breaking vacuum with air after evacuating H_2 after reaction, and evacuation to less than 50 - 100mbar is advisable in most situations. Breaking vacuum with N_2 is inherently safer and therefore the prefered method - but use of N_2 also has safety implications!

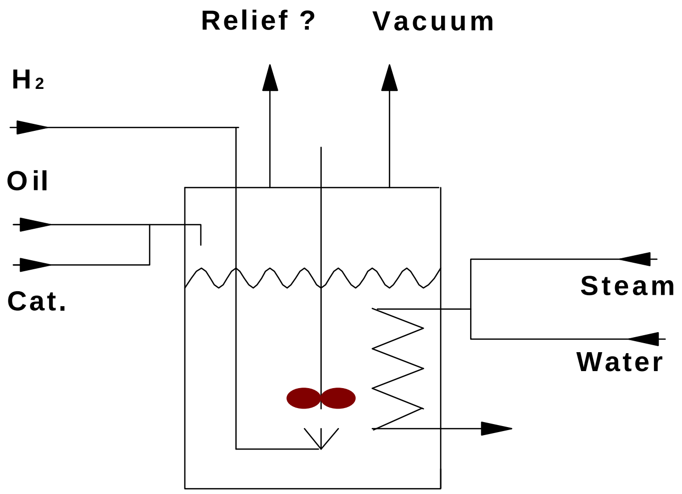

Figure 1. The reactor

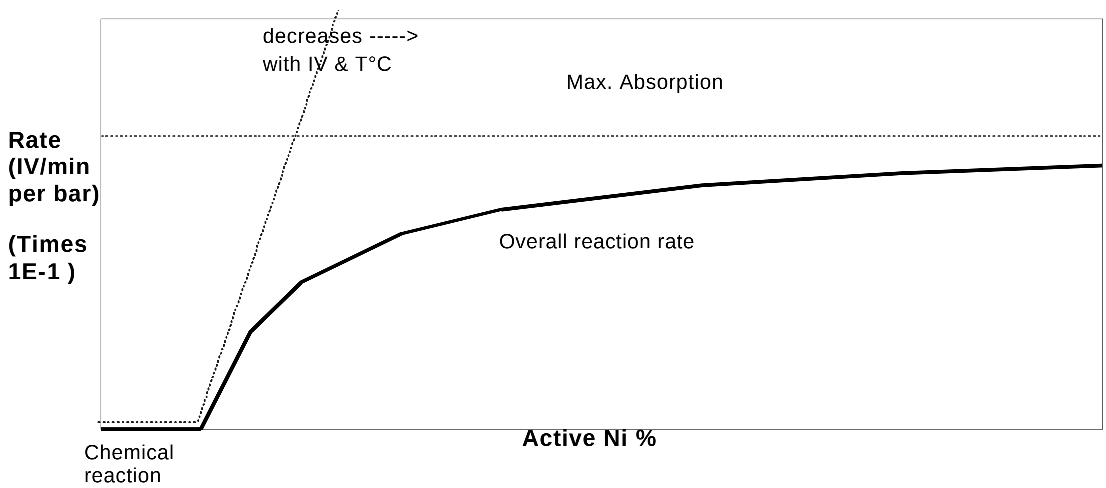

Figure 2. Hydrogenation rate

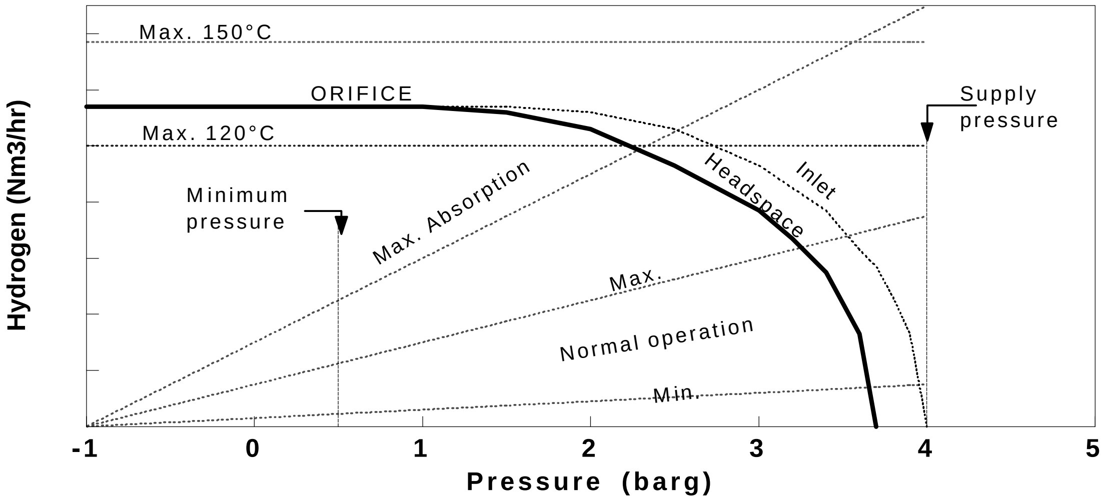

Figure 3. Hydrogen Supply & Control

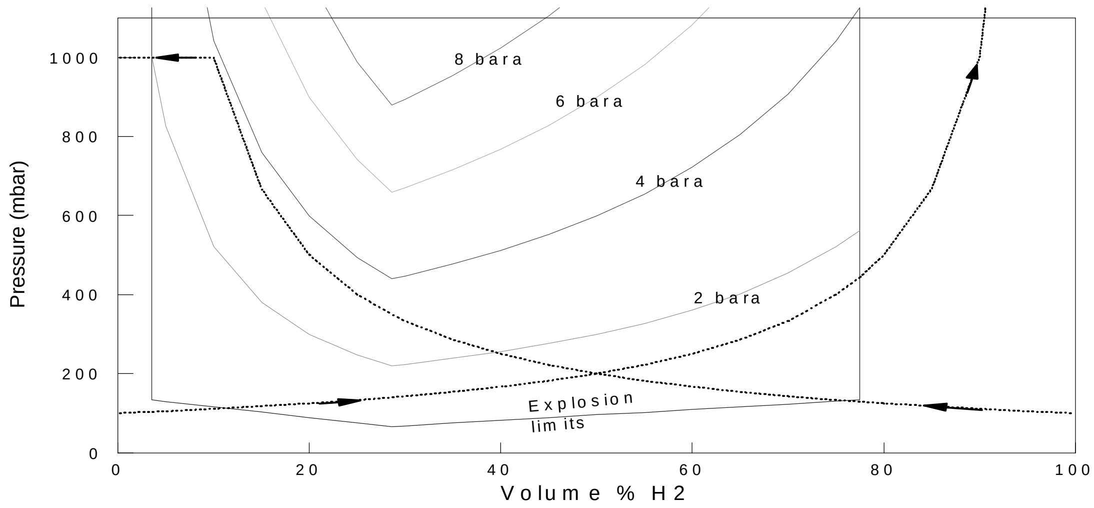

Figure 4. H_2-Air explosion chart

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