CATALYST HANDLING AND REACTOR PERFORMANCE

Many of the 700+ refineries in the world were designed years ago to process light, low-sulphur crudes. As a result, there is currently a shortage of capacity for processing the increasingly heavier crudes – with higher levels of sulphur and other contaminants compared to traditional feedstocks – while meeting the market requirement for lighter products that are required to meet ever more stringent fuel specifications. In addition, over the last 35 years, refiners have had to meet new fuel specifications ranging from unleaded gasoline, to oxygenates as a gasoline blending component, to ultra-low sulphur diesel (ULSD) products, to biofuels, with regulations varying from region to region. The balance of demand for gasoline versus diesel has also changed over time in different regions. Given the refining industry's cyclical margin, today's refiner are looking into ways of maintaining reasonable margins to recover the investments they have made to date and to justify additional investment to cope with a changing market.

Increasingly stringent fuel regulations, heavier crudes and feedstocks, and soaring energy demand have created complex – and sometimes conflicting – challenges for refiners operating hydroprocessing units. In response, many refiners are building new licensed units or revamping their existing facilities. An important part of the process is not only to implement the most optimised hydroprocessing solution, but also to select the best catalysts for an application. Catalysts are critical to many industrial reactions. Refineries and chemical plants rely on them to help boost product yields and reduce the proportions of unwanted by-products and contaminants. Over time, however, the effectiveness of a catalyst declines. The loss of catalytic activity and/or selectivity is known as catalyst deactivation, and it can be caused by chemical, thermal or mechanical problems. For refinery operators, maximising the effective catalyst life, or cycle length, is vital for efficient and profitable operation.

Catalyst is of vital importance for the operation of a unit and should be handled with care. It seems so logical, but in reality catalyst is often handled as non-important material. It would perhaps be beneficial to inform persons involved of the amount of money they are dealing with and what is to be expected from catalyst.

INCREASE CATALYST UTILIZATION

(SOCK LOADING)

Although it starts to be common to load reactors by means of dense loading, the largest number of reactors is still loaded by sock. If applied well, sock loading can be done safely and efficiently. Discussions are continuously going on how sock loading should be done in order to minimize breakage and still obtain a good distribution. Telescopic pipes have been used in order to avoid having men walking over the catalyst and crushing it, but the disadvantage is that the catalyst is loaded from the centre and slides to the side by gravity, which can result in dust and fines building up in the center and bigger parts rolling to the side. The above could result in channelling, sometimes already recognizable during presulphiding, if unsulphided catalyst is used. If this is the case, think twice before you continue.
One can also learn a lot by studying the reactor history.

In case a reactor is loaded by means of sock loading, there are a few disciplines you should follow.
- Personnel in the reactor must wear breathing protection, also in normal atmosphere, as dust protection.
- Personnel must wear so-called "snow-shoes" at all times, when standing or walking on the catalyst bed in order to prevent catalyst from crushing.
- Use anti-static loading sock to prevent static electricity building-up and creating dust explosion.
- Minimize dust during loading;
- Remove loading sock cut offs from reactor immediately;
- Keep sock full with catalyst at all times during loading;
- Do not allow catalyst to drop more than 30 cm.

As mentioned before, there is an alternative.

(DENSE LOADING)

With conventional sock loading techniques, the particles of catalyst fall to a repose angle and roll on each other to fill up the catalyst bed. The result is that the obtained density does not correspond with that of optimum compaction and the void fraction is not homogeneous. The principle of dense loading consists of simultaneously covering the entire cross section of the bed with a "rain" of granulated solids.
This "rain" is formed by an appropriate rotation. The parameters of the rotating device are easy to adapt to all geometrical configurations of the catalyst bed of reactors to be loaded. The loading rate can vary between 2 and 15 tons per hour, depending upon configurations.

The advantage of dense loading is not only that the catalyst bed is uniform loaded; there is also a considerable increase in density. The increase in density could be as much as 22% compared with ABD.
For exact registration it should not be compared with previous obtained densities because they could vary according to circumstances.An average increase:
- Bead catalyst 9 - 14 %
- Pellet catalyst 16 - 18 %
- Extrudate catalyst 16 - 20 %
- Quadrilobe catalyst 16 - 22 %

This gain in density enables industrial units:
- to increase the conversion rate without changing the operating conditions,
  or;
- to improve the operating conditions for the same performances.

For instance, a dense loaded gasoil hydrodesulfurization unit can possibly drop the reaction temperature by 5 degrees centigrade and provide an appreciable fuel saving.

<u>Catalyst homogenity</u>
A loading operation with dense loading allows a full and more efficient use of the catalyst in the reactor, the catalyst bed being quite homogeneous, the severity of the reaction can be increased without any hot spots, the flowpath is better and the mass transfer between phases is improved. For instance, the monitoring of the pressure drop of a Naphtha hydrodesulfurization reactor indicates that the pressure drop change is much slower with dense loading than what is usually obtained by conventional sock loading techniques, this increases the cycle length.

<u>Catalyst bed stability</u>
The bed settlings usually encountered with conventional loading techniques may decrease by 10 to 15 % the height of the bed and consequences may be:
- tilting or turning over the scale traps on the bed.
- damage to internal components (thermometric rods, center
  pipe, etc.)
- feed by-passing catalyst bed in radial flow units.

Optimum compaction stability of the bed obtained with dense loading eliminates all catalyst bed settlings and such related consequences.

<u>CONCLUSION:</u>
The higher costs of dense loading over sock loading could be easily recouped in cycle-life and better performance.

REDUCE DOWNTIME

Research backed by years of refinery experience has established that reducing void fraction and controlling catalyst particle orientation helps to prevent reactor flow maldistribution. Catalyst dense loading systems increases catalyst bed density and uniformity by means of the unique way in which the catalyst bed is loaded. As a result of this increased density and uniformity, producers operating a fixed bed catalytic process unit gain the ability to increase operating severity, run longer cycles and/or process more fresh charge stock in their process units.

A proper catalyst loading accounts for the majority of the activity and stability of your hydroprocessing Catalyst. A proper liquid distribution throughout the catalyst bed and maximum catalyst wetting is essential to get the best out of your hydroprocessing catalyst. How to detect maldistribution?
• Radial ΔT greater than 5°C (9° F);
• Slow response to temperature changes in some parts of the reactor;
• Radioactive tracer studies;
• Flow rate test, calculating the Δk_{HDS} at two space velocities;
• Reactor loading records review;
• Distributor design/installation review.

Distribution tray:
It is essential to start with good liquid distribution (distribution usually only gets worse with penetration into the bed)
• All trickle flow reactors should have one;
•Works well within the design flow range;
• Must be leak tight; must be clean;
• Must be perfectly horizontal -- 1 mm variation in liquid level can cause 1-2% variation in flow rate.

EFFICIENT MAINTENANCE SERVICES

Before any activity on a reactor starts, history of the unit should be investigated. It is surprising to find out how little is known of the "modification" applied to a reactor during previous change-outs. It is not always necessary to keep record of the modifications yourself, because a catalyst handling contractor could do this for you, but do not be afraid of the truth and be realistic. Over the years we have seen the most unexpected results from so-called "modifications" varying from missing scale traps to a 5 inch difference in reactor diameter between drawing and reality. It speaks for itself that small things like these could have a dramatic effect on final results. The 5 inch difference in diameter for example resulted in an "almost" claim towards the catalyst manufacturer who was blamed to have delivered an insufficient amount of catalyst.

It does happen that there is a shortage of catalyst, for whatever reasons, thus the indicated height of catalyst is not correct when loading is finished. If it is decided to close the reactor on this "modified" level, make sure it is recorded, because the next time, some-one might open all piping to search for the missing catalyst, not knowing that it has not been loaded in the first place.
It happens quite often that scale traps are damaged while no spares are available; so the drawing tells you for example 150, but only 145 are present ! If not recorded properly one will try to recover all (150) scale traps before opening the unloading nozzle because one scale trap in front of the nozzle could delay the operation by hours. Well searching for 5 scale traps that never have been installed is also time consuming.

Fore-mentioned examples are only a few in a wide variety, but to prevent almost all of them, the only option is: take good record of the changes and do not be afraid to admit mistakes. They happen to all of us.Good advice:
- Inspect the condition of distributor plates;
- Measure the level of catalyst before unloading;
- Count the number of scale traps present;

- Inspect the bed for distortion;
- Check the reactor I.D. (a lining might have been removed);
- Inspect the condition of the outlet collector;
- Double check the loading schedule for the correct amount of catalyst and amount and size of inert support.

If, due to inert conditions, inspection is not possible, have the contractor do it for you and witness it by video or ask for polaroids. It does cost money but it saves guessing in darkness.

Technology is a must
For refiners to sustain their profit margins, access to state-of-the-art technology is a must. Accessing new technology allows refiners to increase their refinery complexity, enabling them to process heavier feedstock while producing higher-margin product, at the same time reducing energy consumption and increasing operational reliability. Maintenance is a most of the time underestimated part of this. Mourik offers high-tech maintenance technologies for catalyst handling services to help achieve this. Indeed, technology is the backbone of Mourik's worldwide operations – state-of-the-art solutions evolving through the application of lessons learned from operating refineries all over the world.

HSE-Q

It is, we believe, now fully accepted by catalyst manufacturers, process licensors and plant operators that the unloading of catalyst under inert conditions is effective both in terms of minimum off-stream days and a maximum catalyst performance which is to the direct advantage of all concerned. The cost of employing an experienced, reputable contractor to perform the unloading is easily recouped from the increased performance over the life of a catalyst.

Additionally, few companies would now consider a total catalyst unloading preceded by an in-situ regeneration in order to overcome a pressure drop problem caused by scale built-up within the top 0.5 metre of catalyst. It is normal to "skim" this waste material under nitrogen. Even though this "skimming" operation has become common practice, it is still necessary to be fully aware of the problems if it is to be kept as safe as possible. Specialised vacuum equipment may be required which is normally only obtainable from a skilled contractor, who is familiar with its proper use. More details of this will be given later.

Having established and agreed that inert entry is an economically viable proposition, it is our view that only contractors who can satisfactorily show effective training of personnel with safe, modern equipment and a full awareness of the risks involved, should be considered suitable. Normally inert entry is performed under a nitrogen atmosphere - occasionally this may be carbon dioxide or gas from an inert gas generator, although this latter case is fortunately becoming increasingly rare. Nobody should be under any illusions as to the dangers of operating or working under nitrogen. It is, of course, not toxic by normal definition but a man in a nitrogen atmosphere, even with, say, three percent oxygen present, will suffocate within ten seconds if breath is drawn. There are still examples every year of the untrained or misinformed person believing that if he takes a good deep breath before he puts his head into a manway, there will be no problem - There is. Not all survive this brutal induction course for inert entry.

It is now also possible to utilise specialised techniques for enhanced reactor cooling, inert vacuuming, pre-sulphiding etc., all of which, if properly applied, are totally safe for the catalyst, the reactor and the process. If not properly applied by experienced technicians, the results can be and have been disastrous.
We have tried to incorporate safe working parameters for these techniques in this brief paper, together with an outline of personnel training and our views on the pros and cons of soft mask respirators and hard, so-called "spacesuit" helmets.

All inert operations, whether for a simple skimming, inspection, total unload or even sampling must be treated in the same way. The techniques and precautions used are essentially the same although obviously exposure periods vary. In order to perform a safe inert entry, detailed information concerning in particular the bed levels and position of distributor trays and internals is required. This will normally be obtained prior to arrival of the specialist team. It is also desirable to agree an outline shutdown procedure. The catalyst handling company cannot dictate to the refinery the method of shutdown but he should be made aware of any unusual conditions that may be expected, for example, the possibility of bed collapse.

Before the removal of the top elbow or cover, a nitrogen purge of approximately fifty cubic metres per hour should be established through the catalyst bed from an inlet at the reactor base. In addition, a spare nitrogen hose should be available for immediate use at the top platform for emergency use inside the reactor, should oxygen contents be for any reason excessive. Following removal of the top cover the contractor should immediately initiate atmosphere and temperature monitoring. We would, as a matter of course, monitor oxygen that should be less than three percent for normal operations. Explosivity, hydrocarbon content, is any, and temperature will also be measured. We like to see a maximum temperature of 35°C. before an entry. At higher temperatures exposure of personnel must be limited to ensure both medically safe conditions and efficiency. With respect to hydrocarbon content, we take the view that from the standpoint of personnel safety, if measurements are obtained at above T.L.V. value of for example benzene, the entry must be performed in gas-tight suits. Whilst benzene is the real "bad actor" due to skin contact, it is very difficult to identify as a single component without sophisticated equipment not normally available at the top of a reactor. We therefore advise the worst option principle. The need for gas-tight suits is one of the factors which influences our choice of breathing masks and will be referred to later. Presence of benzene of course, is just an example.

Continuous monitoring is, in our opinion, vital, particularly for oxygen. An increase in oxygen concentration above 3% should be audibly alarmed so that any personnel within the reactor can be evacuated and the work stopped. After additional nitrogen is established from the base and at the top, and the top manway is covered until the oxygen level is back below the established safe upper limit th work can again be continued. This could of course be significantly less than three percent on occasion, if, for example, welding or cutting is to take place within the reactor or the catalyst is particularly pyrophoric. Ammonia synthesis and high nickel hydrogenation catalysts are examples.

It is also worth mentioning that taking precautions outside the reactor is equally important. It is a matter of some discussion as to whether anybody, without full B.A., should be allowed on or around the reactor during an inert operation. Our guidelines require a rescue man in full breathing apparatus to be present at the entry point at all times, if there is a man inside. A second man may be present as well who may or may not wear a respirator but he must always have one immediately available.

We believe it is advisable to measure for gas concentrations on the platform. If possible, a wind direction indicator, even a small wind sock, should be used sothat any personnel on the platform can stand upwind of the reactor outlet.

Controversially perhaps, it is our preference that once the reactor is open and permits granted for entry, plant personnel enter the roped off area only after reporting to the inert entry supervisor, who is, obviously, the contractors' employee. The supervisor is in constant radio contact with both the rescue man and the inside man and is probably the only person totally aware of conditions on or around the platform. Clearly the customer needs to have great confidence in the contractor and his personnel if he is to be excluded during nitrogen operations.

Occasionally we do not find what we expect, when we eventually get inside. For example, we have seen badly distorted or damaged internals, badly deformed catalyst beds and, from time to time, fused areas of catalyst. Bearing in mind that discovering unexpected problems may significantly change the extent and time-frame of a contract, there will be a need for the client to be informed and consulted on what has been found. This is rather difficult if, for safety reasons, you have agreed to exclude him from the reactor. Use

of photography or video cameras is normally sufficient or decisions to be made, but under some circumstances a little flexibility is needed to satisfy all concerned. However, this flexibility can only be agreed after discussions and the establishment of guidelines with and by the inert entry supervisor and refinery safety personnel. A typical compromise would be, for example, an inspection from the platform only with the refiner's own self-contained
breathing apparatus.

We do not, as a general rule, allow anybody other than our own trained personnel to use our equipment. We believe this to be the safest option. Only on a few occasions we have contravened this general rule and that was after the client, expecting a problem, agreed to nominate an employee to undertake our in-house training program ahead of the contract execution. Even then the nominated person had to pass the training program which is a pre-requisite before issue of an inert operators' certificate. However, there are failures, even amongst personnel with refinery experience.

This brings us to an outline of what we consider to be a satisfactory training program, which is mandatory for all our employees engaged for inert entry operations. Clearly other reputable catalyst handling contractors will have their own ideas on training. What follows is our approach. At first, all employees presented for training are volunteers. That said, we do impose requirements on the volunteers, which must be met. Briefly, these criteria relate to age, weight, height, lung capacity and general health. Working inside any vessel under inert atmosphere with life support and, possibly in a gas-tight suit requires a high level of physical fitness. Climbing a rope ladder for, in extreme cases, twenty meters or more can be exhausting.

It is also unfortunately true that skilled tailors do not make gas suits to individual sizes and it is doubtful whether a person of 1,5 meters height and 170 kilos would be able to get into a gas suit, even if he wants to. The object of a training program is to assess the ability and performance of an individual to
a) undertake defined tasks in a hostile environment;
b) determine his physical abilities within parameters such as breathing rate and;
c) probably most important of all, to expose him to emergency procedures requiring escape.

A typical programm of full training would last up to 5 days of which approximately thirty percent is spent on theory of breathing apparatus, general principles of physics and chemistry applied to explosions, fire etc., toxicology, industrial hygiene and respiration metabolism. Refresher courses and re-assessment programs of up to three days duration regularly supplement this.Examples of defined tasks would be removal and replacement of bolted manways, removal and replacement of tray sections and the installation and fixing of baskets in defined patterns such as may be encountered in any normal reactor.

These tasks are expected to be performed with reasonable speed in varying degrees of light and temperature in and out of a gas suit. Our main method of determining physical fitness is to use a continuous vertical ladder on which the trainee must exercise for extended periods during which his breathing rate may be monitored. This latter test is one that we consider extremely important. Using a sophisticated life support module equipped with endless quantities of breathing air supplied either from bottles or a compressor, breathing rate is relatively unimportant. However, in an emergency situation, if all external air is lost, the technician must use an emergency egress bottle for escape. This, by definition, has a limited volume of air normally sized to give about ten minutes supply at twenty-five percent above normal breathing rates. Any significant uncontrollable increase in rate can substantially reduce the escape time. Again, this physical test is carried out both in and out of a gas suit.

However, clearly the most important aspect of training is the last to be discussed - what to do in an emergency? It can be agreed that you cannot create a realistic emergency but this of itself is no reason to ignore it or not attempt to train for it. Very simply we warn trainees at the start of the course that at some stage or stages of the "hands on" part of the program their breathing air supply will be deliberately cut.

They are instructed on the correct action to be taken and are expected to follow it. This action is either automatic or manual transfer to the egress bottle followed by immediate exit. In addition, since we prefer soft mask equipment, removal of the mask followed by use of a carried spare and bottle is also part of the training. To simulate situations where two men are working under nitrogen we create an emergency for one man and expect and train the second man to assist in escape and rescue.

As mentioned previously, individuals do sometimes fail this training program which obviously means they do not undertake life support operations with our company. The training program and refresher courses are conducted under our supervision by an independent company within our organisation in co-operation with the Dutch Industrial Cleanning Association , who also make use of the same training facilities. It is our opinion that this removes to a large extent, the temptation of allowing unsuitable employees to be certified for inert entry or allowing "old hands" to continue because they are known to us to the detriment of both the employee and the company and therefore the client. Additional, less arduous training is also provided in the use and theory of gas filter masks, fresh air hoods, demand regulators, communication equipment and gas and oxygen detection apparatus. All supervisors receive a standard first aid (red cross) course which has to be renewed every year. Finally, having received his inert entry specialists' certificate, a raw recruit is not expected to perform the most arduous and difficult tasks. He is slowly assimilated into the team until he has gained experience. His supervisor constantly monitors his performance. Having dealt with the safety and health of personnel and the high cost of providing and continuously updating good training, we can now consider additional services that can be supplied. Special emphasis will be made on the safety and integrity of the reactor, process circuit and catalyst.